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Modelling of chemical conversion processes in multicomponent reciprocal salt systems

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Abstract. The review surveys geometric and algebraic models of chemical conversion (exchange) processes occurring in multicomponent salt systems in the molten state. Thermochemical and matrix methods for the construction of conversion figures are described in detail. The practical applications of matrices and graphs in studies of complex systems are illustrated. There are good prospects for using multicomponent salt systems in thermal power sources and high-temperature processes, such as electrolytic aluminising of niobium and silver plating. The bibliography includes 62 references.

I. Introduction

Multicomponent reciprocal salt systems are involved as major components in many natural (rocks, minerals, glasses, salt lakes) and artificial (fertilisers, materials of construction) materials. Technologies for the production of salts, heat technology, manufacturing engineering (salt melts are used for chemical thermal treatment of metal and alloy products), metallurgy and foundry practice are the most important areas of applications of multicomponent systems. In the last quarter of the 20th century, salt systems found increasing application due to considerable growth in the production of semiconducting materials and progress in the nuclear industry, rocket technology with the use of autonomous power supply sources and other branches.

Investigation of reciprocal systems containing four or more components (unlike binary and ternary systems) requires a special approach. Prior to the experiment, it is necessary to carry out a theoretical examination of the composition diagram,[1–5] *viz*., to partition the diagram of an *n*-dimensional polytope, derive non-equilibrium and singular stars and reveal conversion elements.†

Geometric, matrix and algebraic models are widely used in analysis of reciprocal systems. Below we describe models of conversion (exchange) processes occurring in reciprocal systems. These models are based on interchange reactions in systems consisting of inorganic salts. Composition figures (polytopes) are generally partitioned without considering the formation of binary and triple salts. However, as will be demonstrated in the present review, phase diagrams of compositions corresponding to conversion elements, which were determined experimentally by differential thermal analysis (DTA), provide sufficient information also on complexation processes in multicomponent systems.

Non-equilibrium and singular stars, which are graphical models of reciprocal systems, reflect the compositions of simplex cells resulting from the partition of polytopes. Radishchev [2] considered a singular star as a stable complex of a system and defined it as a combination of geometric models of the system derived by partitioning the composition figures into simplexes. Therefore, a singular star consists of stable simplexes and is represented as a graph. Alekseeva and Dombrovskaya [5] characterised a singular star as an equilibrium chemical diagram. The latter is a geometric figure that represents a combination of components, which do not react with each other on mixing.

The partition of composition diagrams and location of the compositions of simplex cells in reciprocal systems are determined by exchange reactions occurring in these systems. According to the criterion proposed by Voskresenskaya,[2,3] the exchange reactions are shifted toward the formation of a salt pair, which is derived from another salt pair with heat evolution ($\Delta_f H_{298} < 0$). The validity of this criterion was confirmed by numerous experiments.[2,3]

The partition can be carried out in various ways, *e.g*., using geometric, matrix and combined (matrices + graphs) approaches. Methods were developed for partitioning polytopes into multidimensional figures consisting of any number of components with the use of tables of vertex indices in the absence of connections between salts [3] and taking into account the complex formation in terms of the graph theory.[4]

An intersection of non-equilibrium and equilibrium complexes of a system gives geometric elements, which model interchange reactions (the so-called conversion elements).

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† In physicochemical analysis of multicomponent salt systems, the term 'conversion' is used to describe transformations of two salts into two other salts, both pairs having the same ion composition and different molecular compositions. The conversions of basic and secant elements are distinguished.

In systems containing no less than 9 salts, the basic elements are salt compositions corresponding to geometric figures, which serve as the basis of simplexes of a cyclic fragment of a star (triangles for quinary reciprocal systems consisting of nine salts, tetrahedra for senary reciprocal systems consisting of 12 salts, *etc.*).

The secant elements are geometric figures corresponding to metastable pairs of the starting salts, which react to form reaction products (a non-equilibrium partition), or stable salt pairs formed by exchange reactions (an equilibrium partition). The diagonals of a composition square of a system serve as secant elements for ternary reciprocal systems, two triangles serve as secant elements for quaternary reciprocal systems consisting of six salts, *etc.*

Non-equilibrium and equilibrium partitions can be represented in a matrix form as tables of vertex indices and matrices of reciprocal salt pairs. In matrices used in physicochemical analysis, both composition figures and exchange reactions occurring in the system as well as the reaction products and particular thermochemical relations are encoded. For example, a matrix referred to as a table of vertex indices [2,3] contains information on how many times each salt is formed in the system under consideration by exchange reactions. The composition of a system is expressed by ions rather by the formulas of salts, and the compositions of the salts are seen at the intersection of a row and a column of the matrix. For example, the table of vertex indices for the A,B//X,Y,Z,T system (A and B are cations; X, Y, Z and T are anions) is as follows:

	X	Y	Z	T
A	0	1	2	3
B	3	2	1	0

In this matrix, the AY salt is a product of one exchange reaction (1), and the BT salt is metastable (0), *i.e.*, the latter is the starting compound rather than a product of any reaction.

In a matrix of reciprocal salt pairs,[3] the numbers 1 and 0 signify stability and instability, respectively, of a salt pair. Compounds produced in an exchange reaction are denoted by unity. The number of unities is equal to the number of exchange reactions in the system. For example, the matrix for a quaternary reciprocal system A,B//X,Y,Z consisting of four salts is as follows:

	BX	BY	BZ
AX	0	1	1
AY	0	0	1
AZ	0	0	0

Radishchev [2] introduced the concepts of a point of complete conversion and a point of incomplete conversion for ternary reciprocal systems and the concept of a conversion line for quaternary reciprocal systems. These concepts are used in physicochemical analysis. Radishchev derived components of conversion figures of secant elements for reciprocal systems consisting of eight salts and considered the conversion of axial (basic) triangles and secant elements of quinary reciprocal systems consisting of nine salts. The further development of these concepts involved three lines.

1. The construction of conversion figures of basic elements.[3] Presently, this line of investigation has no practical application.

2. The construction and investigation of conversion figures of secant elements.[6] These figures reflect the main thermochemical relations and the energetics of exchange reactions.

3. The construction of conversion figures taking into account the formation of binary and ternary compounds involving salts. These figures are very complicated, and calculations for these systems can be carried out only on a computer. The energy characteristics of particular compositions can be estimated by calculation methods (these characteristics can also be estimated using conversion figures of secant elements, the procedure being more simple). This line of investigation has not been developed in detail.

The second line served as the basis for devising a conversion method for studying reciprocal multicomponent systems.[6] This method was used for solving a number of theoretical problems and practical tasks.[7,8] For example, this method made it possible to choose salt compositions characterised by the optimal heat-accumulation properties [8–10] and determine the final target products in complex mixtures.[11]

The first review on the conversion method was given in the monograph,[3] where the essence of this method was presented, procedures for deriving conversion elements were considered, examples of conversion figures and the prediction of phases, which crystallise from melts modelled by these figures, were offered, and a proximate method for studying multicomponent reciprocal systems was briefly described.

Phase complexes of systems were extensively studied by the conversion method in the late 1970s/early 1980s. Selected results were given in the monograph;[11] however, a systematic review was lacking. The practical application of the conversion method to the solution of applied problems (in particular, for heat accumulation) was described in the monograph.[8] More recent reviews on the modelling of conversion processes are lacking. This method was only briefly mentioned (a few references were given) in the monograph,[4] because the latter was devoted to an alternative methodology for studying complex salt systems.

Up to the mid-1990s, experimental data on conversion elements and their practical applications were accumulated.[11–18] Theoretical studies were devoted primarily to a combination of the conversion and matrix methods and examination of energy transfer processes in exchange reactions.[19–31] In this period, a method was devised for the construction of singular stars of tetrahedra from conversion elements; matrices of conversion figures and conversion graphs were derived; the structures of conversion figures of quinary reciprocal systems of the 3//3 series were refined; the fine energy structure of axial triangles of quinary reciprocal systems consisting of nine salts was revealed; the mechanism of transformation of a system from a non-equilibrium state to an equilibrium state was studied and intermediate stars of pentatopes and tetrahedra of reciprocal systems of the 3//3 series were derived; energy diagrams for the transformation from a non-equilibrium combination of three salts (a non-equilibrium triangle) to an equilibrium state (a stable axial triangle) were constructed; relationships between various models of conversion processes were revealed. Based on the conversion method, heat-accumulation compositions were developed, and studies of the behaviour of ionic liquids in multicomponent melts at various temperatures were started.

The concept of rational investigation of multicomponent reciprocal salt systems in melts was elaborated. This concept is based on thermochemical (energy) criteria and Kurnakov's correspondence principle.

The aim of the present review is to summarise data on the modelling of conversion processes in salt melts. Theoretical and experimental studies, which were performed in the last 20 years, were surveyed. The relationship between models used in studies of exchange equilibria was demonstrated. The conversion method of investigation of reciprocal systems was shown to be of importance in solving technological problems and developing fundamental sciences.

II. Conversion figures, conversion graphs and matrices

1. Ternary reciprocal systems

A stable secant complex of ternary reciprocal systems consisting of four salts is represented by one stable diagonal, which divides the composition square of a system into two ternary systems (Fig. 1). The stable AX – BY diagonal intersects the metastable AY – BX diagonal (a metastable secant complex) in the centre of

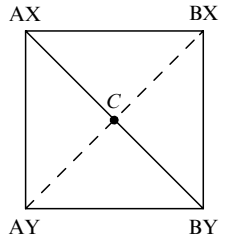


Figure 1. Composition square of the ternary reciprocal system A,B//X,Y with the full conversion point *C*.

the square, *viz*., at the point *C* (a point of complete conversion). At this point, salts of a metastable pair are completely transformed into a stable pair (complete conversion):

$$AY + BX = AX + BY.$$

An incomplete transformation of salts, *i.e*., incomplete conversion, corresponds to an arbitrary point of the composition figure, for example, on the metastable diagonal, but off the conversion point.

2. Quaternary reciprocal systems consisting of six salts

The conversion figure of a quaternary reciprocal system A,B,C//X,Y consisting of six salts of the 2//*n* (*n*//2) series contains two conversion lines denoted in the Fig. 2 as *EF* and *FT*. The points of complete conversion are *E*, *T* and *F*. The following exchange reactions correspond to these points:

for the point *E*: $CX + AY = AX + CY$, the first-stage reaction,

for the point *T*: $AX + BY = AY + BX$, the first-stage reaction,

for the point *F*: $CX + BY = BX + CY$, the second-stage reaction.

By summing these equations, we obtain

$$2\,CX + AY + 2\,BY + AX = AX + 2\,CY + 2\,BX + AY$$

or

$$CX + BY = CY + BX.$$

Hence, two first-stage reactions in the A,B,C//X,Y system are independent, whereas the reaction corresponding to the point of complete conversion *F* depends on the first-stage reactions.

The full conversion figure includes three points of complete conversion denoted as *E*, *F* and *T* (in accordance with the number of interchange reactions occurring in the system) and two conversion lines (see Fig. 2) converging to a common point corresponding to the second-stage reaction.

Since the conversion figure is a part of a composition figure, one can construct the phase diagram of the system under study using the lines of the conversion figures as the composition axis. The conversion figure is a polythermal section, which reflects the dependence of the melting point on the combination of salt pairs. This diagram displays salts, which initially crystallise from melts, secondary, tertiary, *etc*. crystallisation products and temperatures corresponding to invariant points.

If only vertices and edges of a conversion figure are displayed, one obtains a conversion graph. The vertices of this graph correspond to salt pairs or thermal effects of exchange reactions giving rise to these salts. In the latter case, the graph is referred to as an energy graph. This graph can be used for thermochemical calculations.

Each vertex of a conversion figure or a conversion graph corresponds to a reaction of a particular stage, and the degree of this vertex (*i.e*., the number of edges incident to this vertex) depends on the stage of the corresponding reaction. As a rule, the higher the stage, the larger the number of edges incident to the vertex of the graph corresponding to this reaction. Therefore, the number of reactions of a particular stage can directly be determined from the graph. The number of edges incident from vertices of conversion graphs for systems containing different numbers of salts are given in Table 1.

Rapid progress in computer technology made it possible to use matrix methods for displaying composition figures and physicochemical interactions in systems,[3] and, consequently, the use of the conversion method [6] for solving various applied problems on a computer caused a need to go from geometric objects, *viz*., graphs of conversion figures, to matrices of these figures.[32, 33]

It is known that each graph has its own adjacency matrix $A = (a_{ij})$ with dimensions $n \times n$, in which the element a_{ij} is equal to the number of edges of the graph connecting the vertices V_i and V_j. The distinguishing feature of the graphs of conversion figures is that they have no multiple edges. Hence, elements of rows and columns of the matrix can be only 1 or 0. The number of rows and columns in the matrix is determined by the number of vertices of the graph, *i.e*., the number of points of complete conversion of ternary reciprocal systems involved in the figure. For example, the graph of a conversion figure of any quaternary reciprocal system consisting of 6 salts can be expressed by a matrix, in which the points *A* and *C* correspond to first-stage reactions, and the point *B* corresponds to a second-stage reaction.

	A	*B*	*C*
A	0	1	0
B	1	0	1
C	0	1	0

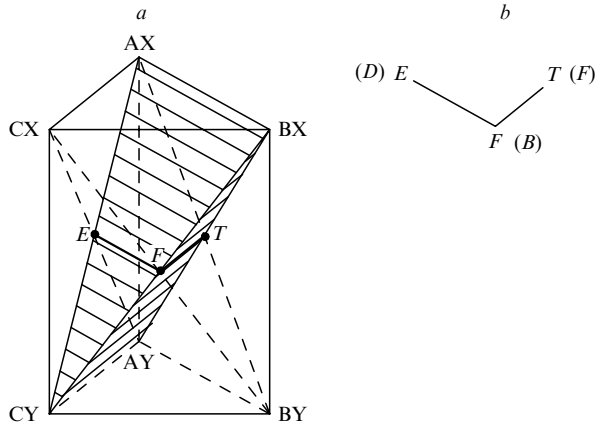


Figure 2. Arrangement of the conversion lines in the composition prism (*a*) and the conversion figure (*b*) of the quaternary reciprocal system A,B,C//X,Y (letters in parentheses correspond to a special case, *viz*., the Na,K,Ba//F,WO_4 system).

Table 1. Number of edges of conversion graphs incident to the points corresponding to reactions of particular stages for systems consisting of 4 – 12 salts.

Number of salts	Number of edges for the reaction of stage				
	I	II	III	IV	V
4	1	0	0	0	0
6	1	2	0	0	0
8	2	3	4	0	0
9 of the type					
A ⇄ B	2	5	5	8	0
C	3	3	0	8	0
D ⇄ E	2	6	0	0	0
10 (2//*n* series)	3	4	5	6	0
12 (2//*n* series)	4	5	6	7	8

The matrix of a conversion graph has the following properties.

1. The sum of the numbers in each row and each column is equal to the degree of the corresponding vertex of the graph (in the above matrix, the point *B* has two connections, and the points *A* and *C* each have one connection).

2. The matrix is symmetric with respect to the diagonal, whose elements are zero.

3. The matrix unambiguously defines the graph with an accuracy of up to isomorphous; hence, the corresponding graph can be constructed based on any matrix.

For practical use of a conversion figure, it is not necessary to construct the corresponding graph from the adjacency matrix. Geometric objects can completely be excluded, because the matrix of a conversion figure contains all necessary information. For example, the degree of a vertex of a graph defines not only the number of edges connecting this vertex to other vertices (*i.e.*, the number of conversion lines) but also the number of chemical reactions giving rise to the corresponding salt pair, as well as the reaction stage (the diagonal), on which the conversion point is located, and the compositions of simplexes of a singular star.

3. Quinary reciprocal systems consisting of eight salts of the 2//*n* (*n*//2) series

A conversion figure of a quinary reciprocal system consisting of eight salts (Fig. 3) contains six vertices (in accordance with the number of exchange reactions), eight conversion lines, two conversion triangles (*4–1–6* and *2–6–5*) and one conversion square (*3–5–6–4*). The third-stage reaction corresponds to the vertex 6, which has the largest number of connections to other vertices. The second-stage reactions correspond to the points *4* and *5*. The vertices *1*, *2* and *3* are the points of complete conversion of ternary reciprocal systems, in which first-stage reactions proceed.

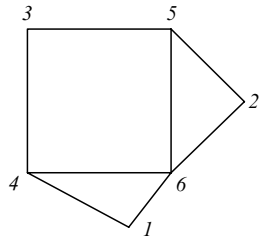


Figure 3. Conversion figure of a quaternary reciprocal system consisting of eight salts.

A conversion figure is a geometric model of chemical processes occurring in a system. This figure forms as the intersection of stable and metastable complexes or singular or non-equilibrium stars. Each element of the conversion figure (a point, a line, a plane, *etc.*) models exchange reactions taking place in the system. The point reflects a reaction of one salt pair (*i.e.*, one reaction), the line reflects an interaction between two salt pairs (two reactions), the plane reflects an interaction between three salt pairs (three reactions), *etc*. For systems including no less than 5 components, a fragment of the conversion figure enclosed by four conversion lines, which is commonly referred to as a conversion square, can be divided by the diagonal into two triangles.

Conversion triangles and squares have central points, which are points of complete conversion for a particular number of reactions. For each point of the conversion figure, a chemical reaction can be constructed. The number of salts involved in this reaction is equal to the number of these salts located at the vertices, which enclose this fragment of the conversion figure. The reaction equations include salts in stoichiometric amounts.

As an example we refer to the quinary reciprocal system Li,Na//Br,Cl,NO_3,SO_4 consisting of 8 salts. The thermochemical characteristics of this system are given in Table 2.

The matrix of the conversion graph for this system takes the form

	1	*2*	*3*	*4*	*5*	*6*
1	0	0	0	1	0	1
2	0	0	0	0	1	1
3	0	0	0	1	1	0
4	1	0	1	0	0	1
5	0	1	1	0	0	1
6	1	1	0	1	1	0

Table 2. Points of complete conversion and thermochemical relations for the quinary reciprocal system Li,Na//Br,Cl,NO_3,SO_4 .

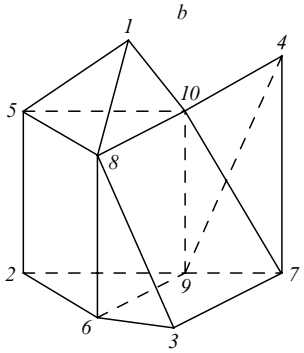
Point	Ternary reciprocal system	Stable salt pair	Reaction	
			stage	*Q*
1	Li,Na//Cl,Br	LiCl + NaBr	I	Q_1
2	Li,Na//NO_3,SO_4	Li_2SO_4 + $NaNO_3$	I	Q_2
3	Li,Na//Cl,NO_3	$LiNO_3$ + NaCl	I	Q_3
4	Li,Na//Br,NO_3	$LiNO_3$ + NaBr	II	$Q_4 = Q_1 + Q_3$
5	Li,Na//Cl,SO_4	Li_2SO_4 + NaCl	II	$Q_5 = Q_2 + Q_3$
6	Li,Na//Br,SO_4	Li_2SO_4 + NaBr	III	$Q_6 = Q_1 + Q_2 + Q_3$

4. Senary reciprocal systems consisting of ten salts of the 2//*n* (*n*//2) series

The conversion figure of a senary reciprocal system shown in Fig. 4 *a*,*b* contains conversion points, lines, triangles and squares along with bulk elements, such as conversion tetrahedra

a

	Na_2SO_4	$NaNO_3$	NaCl	NaBr	NaI
Li_2SO_4	0	1	1	1	1
$LiNO_3$	0	0	1	1	1
LiCl	0	0	0	1	1
LiBr	0	0	0	0	1
LiI	0	0	0	0	0



c

	I^-	Br^-	Cl^-	NO_3^-	SO_4^{2-}
Li^+	0	1	2	3	4
Na^+	4	3	2	1	0

Figure 4. Conversion graph inscribed in the matrix of mutual salt pairs (*a*), the conversion figure of secant tetrahedra (*b*) and the table of vertex indices (*c*) of the senary reciprocal system Li,Na//Cl,Br,I,NO_3,SO_4 consisting of ten salts.

(*1–5–10–8* and *4–7–9–10*) and triangular prisms (*4–7–10–8–6–3* and *5–8–10–9–6–2*). The point *10*, from which six conversion lines emerge, corresponds to a fourth-stage reaction. The points *8* and *9* (five lines) correspond to third-stage reactions. The points of complete conversion, from which four conversion lines emerge (the points *7*, *6* and *5* in Fig. 4 *b*), correspond to second-stage reactions.

Other vertices are points of complete conversion modelling first-stage reactions. The matrix table of vertex indices of the senary reciprocal system Li,Na//Br,Cl,I,NO_3,SO_4 is presented in Fig. 4 *c*.

5. Quinary reciprocal salt systems consisting of nine salts of the 3//3 series

Three thermochemical (five topological A, B, C, D, E) types of reciprocal quinary systems, *viz*., 9A ⇄ 9B, 9C ⇄ 9C′ and 9D ⇄ 9E, are known.[2] These pairs are characterised by the same set of reactions of particular stages (Table 3). However, their singular stars have different geometry (different topology) and, correspondingly, different notations.

Table 3. Number of reactions of particular stages for reciprocal systems of the 3//3 series.

Type of system	Number of reactions of a given stage			
	I	II	III	IV
9A ⇄ 9B	4	2	2	1
9C ⇄ 9C′	4	4	0	1
9D ⇄ 9E	6	3	0	0

The conversion figure of a reciprocal system of any thermochemical type of the 3//3 series is a graph, whose vertices correspond to points of complete conversion of ternary reciprocal systems involved in a more complex system (Figs 5–7). The lines of complete conversion of quaternary reciprocal systems serve as edges of the graph. For systems of the 2//*n* (*n*//2) series, the conversion figures contain no other conversion elements. Hence, the thermochemical type of the conversion figure coincides with the topological type. The structures of the conversion figures of quinary reciprocal systems of the 3//3 series are complicated,

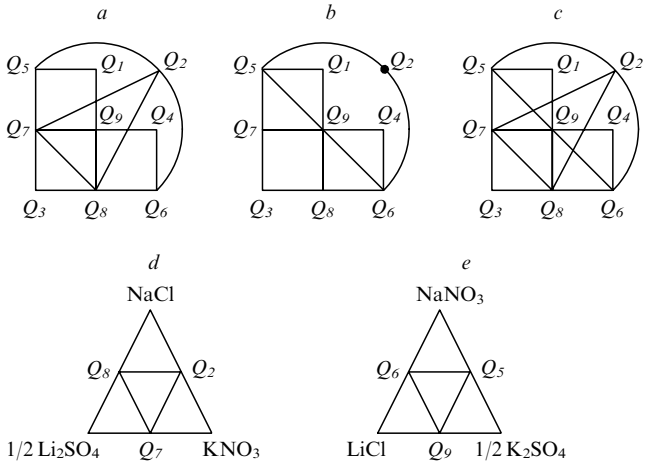


Figure 5. Conversion figures of quinary reciprocal systems consisting of nine salts of different topological types.
(*a*) 9A type; (*b*) 9B type; (*c*) 9A ⇄ 9B type; (*d*) the conversion lines $Q_9–Q_2–Q_7$ intersecting the axial stable triangle of the 9A ⇄ 9B-type Li,Na,K//Cl,NO_3,SO_4 system; (*e*) the conversion lines $Q_9–Q_5–Q_6$ intersecting the axial metastable triangle of the 9A ⇄ 9B-type Li,Na,K// Cl,NO_3,SO_4 system.

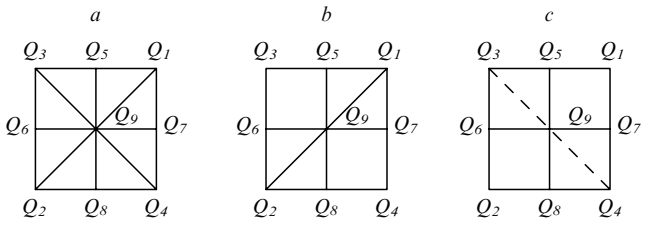


Figure 6. Conversion figures of the 9C-type quinary reciprocal system.
(*a*) The common conversion figure for the 9C ⇄ 9C′ equilibrium; (*b*) the conversion figure with the conversion lines $Q_1–Q_9–Q_2$ intersecting the axial stable triangle; (*c*) the conversion figure with the conversion lines $Q_3–Q_9–Q_4$ intersecting the axial metastable triangle.

because each topological type of these systems is characterised by its own conversion figure. It should be noted that the conversion figures of the same thermochemical type (9A ⇄ 9B, 9C ⇄ 9C′, 9D ⇄ 9E)[6,8] differ in the position of additional lines resulting from the intersection of axial (basic) triangles with conversion planes. Therefore, there are various topological types of conversion figures, which have a common thermochemical framework.

The number of edges incident to a vertex of a graph depends on the stage of the reaction, which is modelled by a particular conversion point. Systems of the 3//3 series differ in the characteristic features from 2//*n* (*n*//2) systems. For example, the points corresponding to second-stage reactions in 9B-type systems (see Fig. 5 *b*, the points Q_5 and Q_6) can have a larger number of connections than the points corresponding to third-stage reactions (the points Q_7 and Q_8 in Fig. 5 *b*).

The points of intersection of the first-stage diagonals in 9C-type systems also have different numbers of connections (Fig. 6, the points Q_1, Q_2, Q_3 and Q_4), which indicates that systems of the 3//3 series are more complicated than systems of the 2//*n* series.

From the thermochemical point of view, the conversion squares of 9C-, 9D- and 9E-type quinary reciprocal systems consisting of nine salts are equivalent, because they have diagonals corresponding to reactions of the same stages: I, II, II, IV (9C type); I, I, II, II (9D and 9E types). In 9A- and 9B-type systems, the conversion squares are thermochemically non-equivalent. For example, the conversion squares for 9A-type systems ($Q_1–Q_5–Q_7–Q_9$ and $Q_4–Q_6–Q_8–Q_9$) have the same sets of stages of the diagonals (I, II, III, IV), whereas the $Q_3–Q_7–Q_8–Q_9$ square differs from these squares (a set of stages of the I, III, III and IV diagonals). The same is true for 9B-type systems: the $Q_1–Q_5–Q_7–Q_9$ and $Q_4–Q_6–Q_8–Q_9$ squares are equivalent,

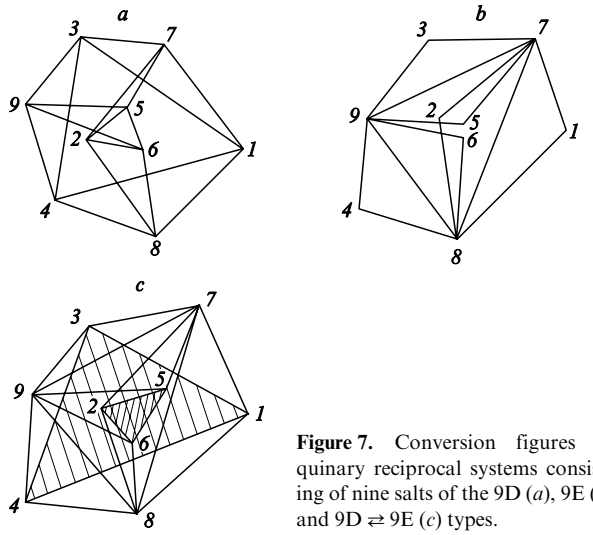


Figure 7. Conversion figures of quinary reciprocal systems consisting of nine salts of the 9D (*a*), 9E (*b*) and 9D ⇄ 9E (*c*) types.

whereas the $Q_3-Q_7-Q_9-Q_8$ square differs from the above two squares. This fact indicates that salts (or salt pairs) in the $Q_3-Q_7-Q_9-Q_8$ (9A type) and $Q_8-Q_9-Q_7-Q_3$ (9B type) squares are less reactive, and this region of the model (a conversion square) is characterised by a smaller number of reactions between salts, which are involved in pairs located at the vertices of this conversion square. The latter can be considered as the most stable square. The nature of the thermochemical non-equivalence of the conversion squares in 9A- and 9B-type systems (see Fig. 5 *a*,*b*) calls for a more detailed study.

Comparative investigation of conversion figures of systems belonging to different topological and thermochemical types may be useful in constructing mixtures of reciprocal salt systems possessing desired properties. Changes in the reactivity of a salt mixture upon the addition of a new component or the replacement of one component with another one can be predicted on the basis of conversion figures.

For example, the replacement of a component in a 9A-type system giving rise to a 9C-type system can lead to an increase in the reactivity of the salt system, because the conversion squares for 9A-type systems contain sets of higher-stage diagonals compared to the set of diagonals of the conversion squares for 9C-type systems. The reactivity of the mixtures can be further increased on going to 9D- or 9E-type systems (see Fig. 7).

Let us consider this relationship using real systems as examples.

a. Type 9A ⇄ 9B

Systems of the 9A ⇄ 9B thermochemical type are characterised by the occurrence of nine reactions (four first-stage reactions, two second-stage reactions, two third-stage reactions and one fourth-stage reaction). Topological conversion graphs for 9A- and 9B-type systems contain nine points corresponding to the number of exchange reactions (see Fig. 5 *a*,*b*), squares and triangles located on different planes of the three-dimensional space resulting from the intersection of secant tetrahedra of singular and non-equilibrium stars.[8]

The main framework of these figures is composed of lines corresponding to conversion figures of quaternary systems consisting of six salts. These lines connect nine vertices of the conversion figure. For example, these are the $Q_5-Q_7-Q_3$, $Q_6-Q_8-Q_3$, $Q_1-Q_9-Q_8$, $Q_4-Q_9-Q_7$, $Q_1-Q_5-Q_2$ and $Q_2-Q_6-Q_4$ lines in 9A-type systems (see Fig. 5 *a*). The inner lines, *viz*., Q_7-Q_8, Q_2-Q_8 and Q_2-Q_7 in 9A-type systems and Q_5-Q_6, Q_5-Q_9 and Q_6-Q_9 in 9B-type systems (see Fig. 5 *b*), are a special case. These lines intersect the planes of axial (stable and metastable) triangles (see Fig. 5 *d*,*e*). In Fig. 5 *c*, three conversion squares ($Q_1-Q_5-Q_7-Q_9$, $Q_3-Q_7-Q_9-Q_8$ and $Q_4-Q_6-Q_8-Q_9$) reflect chemical interactions in the quinary reciprocal system consisting of nine salts.

b. Type 9C ⇄ 9C′

The conversion figure of quinary systems of the 9C ⇄ 9C′ thermochemical type (see Fig. 6) contains nine vertices (in accordance with the number of points of complete conversion of ternary reciprocal systems involved in a quinary reciprocal system consisting of nine salts) and 16 lines, twelve of which are fragments of the conversion figures of all six reciprocal systems consisting of six salts involved in the quinary system.[8] Four lines emerging from the central point of the square (the point of intersection of the stable highest-stage diagonal with the corresponding metastable diagonal) are special lines. Both the stable and metastable axial triangles are divided into four triangles by these lines together with the conversion line of basic elements of a 9C ⇄ 9C′-type quinary reciprocal system consisting of nine salts.

c. Type 9D ⇄ 9E

The conversion figure of reciprocal systems of the 9D ⇄ 9E thermochemical type is a graph (see Fig. 7), whose vertices correspond to nine points of complete conversion of nine ternary reciprocal systems and edges correspond to 12 conversion lines of quaternary reciprocal systems consisting of six salts. The inner lines corresponding to interactions between all salts of the system are the *7–8*, *8–9*, *7–9* (E type); *5–6*, *5–2*, *2–6* (D type); *1–4*, *4–3*, *1–3* (common) lines, which intersect the planes of two stable axial triangles and one metastable triangle.

Nine diagonals (six first-stage diagonals and three second-stage diagonals) serve as thermochemical characteristics of 9D ⇄ 9E-type systems.

The thermal effects of the second-stage reactions can be expressed in a dual fashion as the sums of the thermal effects of first-stage reactions.

$$Q_2 + Q_3 = Q_1 + Q_5 = Q_7,$$

$$Q_1 + Q_6 = Q_2 + Q_4 = Q_8,$$

$$Q_4 + Q_5 = Q_3 + Q_6 = Q_9.$$

From these equations it follows that

$$Q_2-Q_1 = Q_5-Q_3 = Q_6-Q_4.$$

These relations can be used for solving problems associated with the construction of systems possessing the desired thermochemical characteristics of salt compositions.

III. Methods of construction of conversion figures

Several methods were developed for the construction of conversion figures, the so-called, geometric, thermochemical and matrix methods.

As mentioned above, the geometric method[2] is very complicated, because it requires the use of multidimensional geometry. According to this method, the conversion figures are constructed by intersecting stable and metastable complexes.

The thermochemical method[8] is based on thermochemical relations, which are used for the construction of an energy graph. Generally, the centre of this graph is occupied by a conversion point corresponding to the highest thermal effect, which is the sum of several thermal effects. This point has the largest number of thermochemical connections. For example, the point Q_9 for 9C ⇄ 9C′-type systems consisting of nine salts (see Fig. 6 *c*) has six connections and is connected to all points corresponding to reactions with independent thermal effects (first-stage reactions). The latter points have a minimum number of connections (three) and are connected to points corresponding to reactions with dependent thermal effects (as summands) and the point corresponding to the reaction with the highest thermal effect. The points corresponding to the thermal effects of second-stage reactions are connected to the points corresponding to first-stage reactions and the point corresponding to the reaction with the highest thermal effect. Three lines emerge from each of these points.

The conversion figure for systems of the 2//*n* type can be constructed from conversion figures of lower dimensionality. For example, the conversion figure of secant tetrahedra for systems of the 2//4 series can be constructed from the conversion figures of systems of the 2//3 series.

The matrix metod[8,33] will be discussed below.

1. The thermochemical method for the construction of conversion figures of systems of the 2//*n* (*n*//2) series

Conversion figures of systems of the 2//*n* (*n*//2) series are shown in Figs 1; 2 *a*,*b*; 3; 4 *a*,*b*.

Let us consider the method for the construction of conversion figures of a quaternary reciprocal system consisting of six salts using the Li,Na//Cl,NO_3,SO_4 system as an example. The conversion figure of reciprocal systems of the 2//3 (3//2) series is constructed based on thermochemical relations. The point of complete conversion corresponding to a second-stage reaction is connected by conversion lines to the points corresponding to first-stage reactions. The thermochemical relations for the Li,Na//

Table 4. Thermochemical relations for the Li,Na//Cl,NO_3,SO_4 system.

Ternary reciprocal system	Stable salt pair	Reaction [a]	
		stage	Q /kJ (mol equiv)$^{-1}$
Li,Na//Cl,SO_4	Li_2SO_4 + NaCl	II	$Q_3 = Q_1 + Q_2 = 26.78$
Li,Na//NO_3,SO_4	Li_2SO_4 + $NaNO_3$	I	$Q_1 = 7.95$
Li,Na//Cl,NO_3	$LiNO_3$ + NaCl	I	$Q_2 = 18.83$

[a] Hereinafter, the thermal effects of the reactions are given in kJ per mole of equivalents.

Cl,NO_3,SO_4 system are given in Table 4. The elements of the conversion figure of this system are listed in Table 5.

Three points of complete conversion correspond to the following chemical reactions:

point *B*: $2\,LiCl + Na_2SO_4 = Li_2SO_4 + 2\,NaCl - Q_3$,

point *C*: $2\,LiNO_3 + Na_2SO_4 = Li_2SO_4 + 2\,NaNO_3 - Q_1$,

point *A*: $2\,LiCl + 2\,NaNO_3 = 2\,LiNO_3 + 2\,NaCl - Q_2$.

The composition figures of systems of the 2//4 (4//2) series have three first-stage diagonals, two second-stage diagonals and one third-stage diagonal. The conversion figure of these systems consists of two triangles and one quadrangle connected in a particular manner.

Table 5. Conversion elements for the Li, Na//Cl,NO_3,SO_4 system.

Conversion element	Salt composition
Point *A*	$LiNO_3$, NaCl
Point *B*	Li_2SO_4, NaCl
Point *C*	Li_2SO_4, $NaNO_3$
Line *A* – *B*	Li_2SO_4, $LiNO_3$, NaCl
Line *B* – *C*	Li_2SO_4, NaCl, $NaNO_3$

The thermochemical relations in the quinary system Li,Na// Br,Cl,NO_3,SO_4 consisting of eight salts are given in Table 6. The elements of the conversion figure are shown in Fig. 8.

Table 6. Thermochemical relations for the Li,Na//Br,Cl,NO_3,SO_4 system.

Ternary reciprocal system	Metastable pair	Stable pair	Reaction	
			stage	Q
Li,Na//Cl,Br	LiBr + NaCl	LiCl + NaBr	I	Q_1
Li,Na// NO_3,SO_4	$LiNO_3$ + + Na_2SO_4	Li_2SO_4 + + $NaNO_3$	I	Q_2
Li,Na//Cl,NO_3	LiCl + $NaNO_3$	$LiNO_3$ + NaCl	I	Q_3
Li,Na//Br,NO_3	LiBr + $NaNO_3$	$LiNO_3$ + NaBr	II	$Q_4 = Q_1 + Q_3$
Li,Na//Cl,SO_4	LiCl + Na_2SO_4	Li_2SO_4 + NaCl	II	$Q_5 = Q_2 + Q_3$
Li,Na//Br,SO_4	LiBr + Na_2SO_4	Li_2SO_4 + NaBr	III	$Q_6 = Q_1 + Q_2 + Q_3$

The conversion figure for the Li,Na//Br,Cl,NO_3,SO_4 system is constructed based on the thermochemical relations taking into account the following facts. The centre of the conversion figure should be occupied by a point corresponding to the maximum thermal effect. This is the point *B* in Fig. 8 corresponding to intersection of the stable Li_2SO_4 – NaBr diagonal (a third-stage diagonal) and the metastable LiBr – Na_2SO_4 diagonal. The point *B* has the maximum number of connections to points of intersection of the lowest-stage diagonals (four connections).

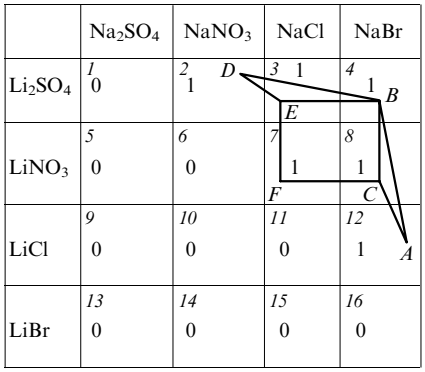


Figure 8. Conversion graph of the quaternary reciprocal system Li,Na// Cl,Br,NO_3,SO_4 inscribed in the matrix of mutual salt pairs.

These are the points *A* (a point of intersection of the first-stage diagonals LiCl – NaBr and LiBr – NaCl), *D* (a point of intersection of the first-stage diagonals Li_2SO_4 – $NaNO_3$ and $LiNO_3$ – Na_2SO_4), *E* (a point of intersection of the second-stage diagonals Li_2SO_4 – NaCl and LiCl – Na_2SO_4) and *C* (a point of intersection of the second-stage diagonals $LiNO_3$ – NaBr and LiBr – $NaNO_3$).

The points of intersection of second-stage diagonals (*E* and *C*) each have three connections to the points of intersection of first-stage diagonals (*A*, *D* and *F*) and the point of intersection of fourth-stage diagonals (*B*). Finally, the points of intersection of first-stage diagonals *A*, *D* and *F* each have two connections (see Fig. 8).

The conversion elements for the Li,Na//Br,Cl,NO_3,SO_4 system are given in Table 7.

The following reactions occur in the system:

point *A*: $2\,LiBr + 2\,NaCl =$ (1)

$= 2\,LiCl + 2\,NaBr - 6.69$ kJ (mol equiv)$^{-1}$,

point *B*: $2\,LiBr + Na_2SO_4 =$ (2)

$= Li_2SO_4 + 2\,NaBr - 33.47$ kJ (mol equiv)$^{-1}$,

point *C*: $2\,LiBr + 2\,NaNO_3 =$ (3)

$= 2\,LiNO_3 + 2\,NaBr - 25.52$ kJ (mol equiv)$^{-1}$,

point *D*: $2\,LiNO_3 + Na_2SO_4 =$ (4)

$= Li_2SO_4 + 2\,NaNO_3 - 7.95$ kJ (mol equiv)$^{-1}$,

Table 7. Conversion elements for the Li,Na//Br,Cl,NO_3,SO_4 system.

Conversion element	Salt composition
Point *A*	LiCl, NaBr
Point *B*	Li_2SO_4, NaBr
Point *C*	$LiNO_3$, NaBr
Point *D*	Li_2SO_4, $NaNO_3$
Point *E*	Li_2SO_4, NaCl
Point *F*	$LiNO_3$, NaCl
Line *A* – *B*	Li_2SO_4, NaBr, LiCl
Line *A* – *C*	$LiNO_3$, NaBr, LiCl
Line *B* – *C*	Li_2SO_4, $LiNO_3$, NaBr
Line *B* – *E*	Li_2SO_4, NaBr, NaCl
Line *B* – *D*	Li_2SO_4, $NaNO_3$, NaBr
Line *C* – *F*	$LiNO_3$, NaBr, NaCl
Line *D* – *E*	Li_2SO_4, $NaNO_3$, NaCl
Line *E* – *F*	Li_2SO_4, $LiNO_3$, NaCl
Triangle *A* – *B* – *C*	Li_2SO_4, $LiNO_3$, LiCl, NaBr
Triangle *B* – *E* – *D*	Li_2SO_4, $NaNO_3$, NaCl, NaBr
Plane *B* – *C* – *F* – *E*	Li_2SO_4, $LiNO_3$, NaCl, NaBr

point E: $2\,LiCl + Na_2SO_4 =$ (5)

$= Li_2SO_4 + 2\,NaCl - 26.78$ kJ (mol equiv)$^{-1}$,

point F: $2\,LiCl + 2\,NaNO_3 =$ (6)

$= 2\,LiNO_3 + 2\,NaCl - 18.83$ kJ (mol equiv)$^{-1}$.

By summing the reactions (1)–(6), we obtain the overall equation for the chemical reactions proceeding in a reciprocal system consisting of eight salts

$$6\,LiBr + 2\,LiCl + 3\,Na_2SO_4 + 2\,NaNO_3 = 3\,Li_2SO_4 + 2\,LiNO_3 + 2\,NaCl + 6\,NaBr.$$

The right-hand side of the equation represents the most stable salt composition. In the diagram of this system, this composition is modelled by a four-vertex sphenoid, which can include stable eutectic mixtures characterised by the highest thermal capacity.[8]

2. The thermochemical method for the construction of conversion figures of the 3//3 series

The principle for the construction of conversion figures of secant tetrahedra for reciprocal systems consisting of nine salts of various thermochemical types is analogous to that used for systems of the 2//n (n//2) series. Let us consider selected systems.

a. System Li,Cd,Na//Cl,NO$_3$,SO$_4$ (9A type)

The centre of the conversion graph (see Fig. 5 *a*) is occupied by the point Q_9 corresponding to intersection of fourth-stage diagonals (the $LiNO_3 + CdCl_2$ salt pair). This point has four thermochemical connections to the points Q_1, Q_4 (points of intersection of first-stage diagonals) and Q_7, Q_8 (points of intersection of third-stage diagonals). Data on the salt compositions corresponding to these points, the reaction stages and constituent thermal effects are given in Table 8. The points of intersection of third-stage diagonals Q_7 and Q_8 each have 5 connections: one connection between these points (Q_7-Q_8 lines), one connection to the point Q_9, one connection to the point Q_2, one connection to the point Q_3 (the latter three points correspond to first-stage reactions; the Q_3-Q_8, Q_3-Q_7 and Q_2-Q_7, Q_2-Q_8 lines) and connections to the points of intersections of second-stage diagonals (the Q_6-Q_8 and Q_5-Q_7 lines).

The following three connections correspond to the points of intersection of second-stage diagonals Q_5 and Q_6: two connections to the points of intersection of first-stage diagonals (the Q_1-Q_5, Q_2-Q_5, Q_2-Q_6 and Q_4-Q_6 lines) and connections to the points of intersection of third-stage diagonals (the Q_5-Q_7 and Q_6-Q_8 lines). The points of intersection of first-stage diagonals have the minimum number of connections (2) (except for the point Q_2). These points form the Q_1-Q_5, Q_2-Q_5, Q_1-Q_9, Q_2-Q_6, Q_2-Q_7, Q_2-Q_8, Q_3-Q_7, Q_3-Q_8 and Q_4-Q_6, Q_4-Q_9 lines.

Each of three conversion squares and the conversion triangle (see Fig. 5 *a*) are characterised by a particular set of stages of stable diagonals. These three conversion squares are thermochemically non-equivalent. The conversion square $Q_9-Q_8-Q_3-Q_7$ includes a point of intersection of fourth-stage diagonals, two points of intersection of third-stage diagonals and one point of intersection of first-stage diagonals. Consequently, these points correspond to the most stable salts of the system.

The relationships between the geometric elements of conversion and the chemical composition of the quinary reciprocal system Li,Cd,Na//Cl,NO$_3$,SO$_4$ are given in Table 9. The conversion figure of this system is characterised by the following features: the point of complete conversion of ternary reciprocal systems corresponds to crystallisation of two salts with different cations and anions; the conversion line of quaternary reciprocal systems corresponds to crystallisation of four salts with either three different cations and two different anions or with two different cations and three different anions; the planes, which characterise interactions in the quinary reciprocal system, correspond to crystallisation of four or five salts. (The conversion figure of the thermochemical type 9A ⇄ 9B is shown in Fig. 5 *c*.)

Table 8. Points of complete conversion and thermochemical relations for the Li,Cd,Na//Cl,NO$_3$,SO$_4$ system.

Point	Ternary reciprocal system	Stable salt pair	Reaction	
			stage	Q /kJ (mol equiv)$^{-1}$
1	Li,Cd//SO$_4$,NO$_3$	$LiNO_3 + CdSO_4$	I	$Q_1 = 2.51$
2	Li,Na//SO$_4$,NO$_3$	$NaNO_3 + Li_2SO_4$	I	$Q_2 = 7.95$
3	Na,Cd//Cl,SO$_4$	$Na_2SO_4 + CdCl_2$	I	$Q_3 = 12.55$
4	Li,Na//Cl,NO$_3$	$LiNO_3 + NaCl$	I	$Q_4 = 18.41$
5	Na,Cd//SO$_4$,NO$_3$	$NaNO_3 + CdSO_4$	II	$Q_5 = Q_1 + Q_2 = 10.46$
6	Li,Na//Cl,SO$_4$	$Li_2SO_4 + NaCl$	II	$Q_6 = Q_2 + Q_4 = 26.36$
7	Na,Cd//Cl,NO$_3$	$NaNO_3 + CdCl_2$	III	$Q_7 = Q_1 + Q_2 + Q_3 = 23.01$
8	Li,Cd//Cl,SO$_4$	$Li_2SO_4 + CdCl_2$	III	$Q_8 = Q_2 + Q_3 + Q_4 = 38.91$
9	Li,Cd//Cl,NO$_3$	$LiNO_3 + CdCl_2$	IV	$Q_9 = Q_1 + Q_2 + Q_3 + Q_4 = 41.42$

Table 9. Conversion elements for the Li,Cd,Na//Cl,NO$_3$,SO$_4$ system.

Reciprocal system	Conversion element	Salt composition
Li,Cd//NO$_3$,SO$_4$	point Q_1	$LiNO_3$, $CdSO_4$
Li,Na//NO$_3$,SO$_4$	point Q_2	Li_2SO_4, $NaNO_3$
Na,Cd//Cl,SO$_4$	point Q_3	Na_2SO_4, $CdCl_2$
Li,Na//Cl,NO$_3$	point Q_4	$LiNO_3$, NaCl
Cd,Na//NO$_3$,SO$_4$	point Q_5	$NaNO_3$, $CdSO_4$
Li,Na//Cl,SO$_4$	point Q_6	Li_2SO_4, NaCl
Na,Cd//Cl,NO$_3$	point Q_7	$NaNO_3$, $CdCl_2$
Li,Cd//Cl,SO$_4$	point Q_8	Li_2SO_4, $CdCl_2$
Li,Cd//Cl,NO$_3$	point Q_9	$LiNO_3$, $CdCl_2$
Li,Cd,Na//NO$_3$,SO$_4$	pair of lines $Q_1-Q_5-Q_2$	$LiNO_3$, Li_2SO_4, $NaNO_3$, $CdSO_4$
Na,Cd//Cl,NO$_3$,SO$_4$	pair of lines $Q_5-Q_7-Q_3$	$NaNO_3$, Na_2SO_4, $CdCl_2$, $CdSO_4$
Li,Na//Cl,NO$_3$,SO$_4$	pair of lines $Q_2-Q_6-Q_4$	$LiNO_3$, Li_2SO_4, NaCl, $NaNO_3$
Li,Na,Cd//Cl,SO$_4$	pair of lines $Q_6-Q_8-Q_3$	Li_2SO_4, NaCl, Na_2SO_4, $CdCl_2$
Li,Cd//Cl,NO$_3$,SO$_4$	pair of lines $Q_1-Q_9-Q_8$	$LiNO_3$, Li_2SO_4, $CdCl_2$, $CdSO_4$
Li,Na,Cd//Cl,NO$_3$	pair of lines $Q_4-Q_9-Q_7$	$LiNO_3$, NaCl, $NaNO_3$, $CdCl_2$
Li,Na,Cd//Cl,NO$_3$,SO$_4$	triangle $Q_8-Q_9-Q_7$	$LiNO_3$, Li_2SO_4, $NaNO_3$, $CdCl_2$
	triangle $Q_7-Q_3-Q_8$	Li_2SO_4, $NaNO_3$, Na_2SO_4, $CdCl_2$
	square $Q_4-Q_9-Q_8-Q_6$	$LiNO_3$, Li_2SO_4, NaCl, $CdCl_2$
	square $Q_1-Q_9-Q_7-Q_5$	$LiNO_3$, $NaNO_3$, $CdCl_2$, $CdSO_4$
	square $Q_7-Q_9-Q_8-Q_3$	Li_2SO_4, $NaNO_3$, $LiNO_3$, Na_2SO_4, $CdCl_2$

b. System K,Ba,Na//F,MoO$_4$,WO$_4$ (9B type)

For 9B-type systems (unlike 9A-type systems), the conversion figure of secant tetrahedra contains one conversion square

Table 10. Points of complete conversion and thermochemical relations for the K,Ba,Na//F,MoO_4,WO_4 system.

Point	Ternary reciprocal system	Stable salt pair	Reaction	
			stage	Q /kJ (mol equiv)$^{-1}$
1	Ba,Na// MoO_4,WO_4	Na_2WO_4 + + $BaMoO_4$	I	$Q_1 = 1.67$
2	K,Ba//F,MoO_4	$BaF_2 + K_2MoO_4$	I	$Q_2 = 2.51$
3	Na,K// MoO_4,WO_4	K_2WO_4 + + Na_2MoO_4	I	$Q_3 = 12.34$
4	Ba,Na//F,WO_4	$BaWO_4 + (NaF)_2$	I	$Q_4 = 19.04$
5	K,Ba// MoO_4,WO_4	K_2WO_4 + + $BaMoO_4$	II	$Q_5 = Q_1 + Q_3 = 14.01$
6	Ba,Na//F,MoO_4	$(NaF)_2 + BaMoO_4$	II	$Q_6 = Q_1 + Q_4 = 20.71$
7	K,Na//F,MoO_4	$(NaF)_2 + K_2MoO_4$	III	$Q_7 = Q_1 + Q_2 + + Q_4 = 23.22$
8	K,Ba//F,WO_4	$BaF_2 + K_2WO_4$	III	$Q_8 = Q_1 + Q_2 + + Q_3 = 16.52$
9	K,Na//F,WO_4	$(NaF)_2 + K_2WO_4$	IV	$Q_9 = Q_1 + Q_2 + + Q_3 + Q_4 = 35.56$

$Q_3-Q_7-Q_9-Q_8$ and five conversion triangles, $Q_1-Q_9-Q_5$, $Q_5-Q_7-Q_9$, $Q_4-Q_9-Q_6$, $Q_6-Q_8-Q_9$ and $Q_5-Q_6-Q_9$ (a degenerate triangle, see Fig. 5 *b*,*c*). The thermochemical relations for the K,Ba,Na//F,MoO_4,WO_4 system are given in Table 10.

The framework of the conversion graph for this system is constructed analogously to the conversion graph for 9A-type systems. The difference is that the former contains the additional Q_5-Q_6, Q_5-Q_9 and Q_6-Q_9 lines resulting from the intersection of the conversion figure with the axial triangle of the $(NaF)_2-K_2WO_4-BaMoO_4$ system. The point of intersection of fourth-stage diagonals Q_9 has the largest number of thermochemical connections (six connections) (see Fig. 5 *b*). The points Q_5 and Q_6, which correspond to second-stage reactions, each have four thermochemical connections. The points Q_7 and Q_8 corresponding to third-stage reactions each have three connections, and the points Q_1, Q_2, Q_3 and Q_4 corresponding to first-stage reactions each have two connections.

A chemical conversion reaction of the salts, which are located at the vertices of metastable figures, into salts located at the vertices of stable figures can be written for each point of the conversion figure. To follow the conversion in quinary reciprocal systems consisting of nine salts, one can use special diagrams put forward by Radishchev.[2] These diagrams can be constructed as follows: three-dimensional figures, which intersect each other (a pyramid and a sphenoid), are projected onto the plane of intersection of both spaces ‡ (giving rise to a conversion square, Fig. 9). The metastable and stable diagonals in this planar figure are indicated by dashed and solid lines, respectively.

For the K,Ba,Na//F,MoO_4,WO_4 system, this method gave one of conversion squares $B-Z-T-F$ of secant tetrahedra (see Fig. 9) resulting from the intersection of the metastable sphenoid $(KF)_2-Na_2WO_4-K_2MoO_4-BaWO_4$ and the stable pyramid $(NaF)_2-Na_2MoO_4-BaMoO_4-BaF_2-K_2WO_4$.

The equation for the central point of the conversion square $B-Z-T-F$ has the form

$$2\,(KF)_2 + 2\,Na_2WO_4 + 2\,K_2MoO_4 + 2\,BaWO_4 = \quad (7)$$
$$= (NaF)_2 + BaF_2 + BaMoO_4 + Na_2MoO_4 + 4\,K_2WO_4.$$

‡ The figures are located in different three-dimensional spaces involved in this four-dimensional space.

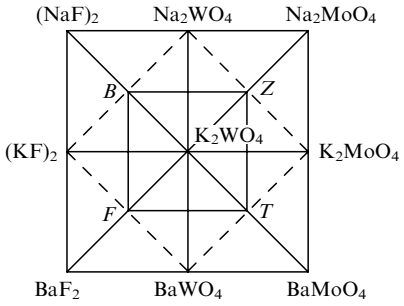


Figure 9. Conversion square $B-Z-T-F$ (a fragment of the conversion figure) of the 9B-type quinary reciprocal system Na,K,Ba//F,MoO_4,WO_4.

The right-hand side of the equation includes a metastable pair of salts, which react according to the equation

$$BaF_2 + Na_2MoO_4 = (NaF)_2 + BaMoO_4. \quad (8)$$

By summing the equations (7) and (8), we obtain

$$2\,(KF)_2 + 2\,Na_2WO_4 + 2\,K_2MoO_4 + 2\,BaWO_4 = \quad (9)$$
$$= 2\,(NaF)_2 + 4\,K_2WO_4 + BaMoO_4.$$

The exchange reactions afford salts, which form a stable axial triangle.

c. System Li,Na,K//Cl,Br,SO_4 (9C type)

Let us consider a procedure for the construction of a conversion figure based on stages of stable diagonals using the Li,Na,K// Cl,Br,SO_4 system as an example (see Fig. 6).

The thermal effects of the second-stage reactions giving rise to the stable $Na_2SO_4 + (KBr)_2$ (Q_5), $(LiCl)_2 + (KBr)_2$ (Q_6), $Li_2SO_4 + (KCl)_2$ (Q_7) and $Li_2SO_4 + (NaBr)_2$ (Q_8) pairs are the sums of two effects, and the thermal effect of the fourth-stage reaction [the stable $Li_2SO_4 + (KBr)_2$ pair (Q_9)] is the sum of four effects (Table 11). Hence, the conversion point corresponding to the second-stage reaction should have the following three connections: two connections to conversion points corresponding to first-stage reactions and one connection to the Q_9 point. Below are given the thermochemical connections for four points of complete conversion.

Table 11. Points of complete conversion and thermochemical relations for the Li,Na,K//Cl,Br,SO_4 system.

Point	Ternary reciprocal system	Stable salt pair	Reaction	
			stage	Q /kJ (mol equiv)$^{-1}$
1	K,Na//Cl,SO_4	$Na_2SO_4 + (KCl)_2$	I	$Q_1 = 3.56$
2	Li,Na//Cl,Br	$(LiCl)_2 + (NaBr)_2$	I	$Q_2 = 6.69$
3	Na,K//Cl,Br	$(KBr)_2 + (NaCl)_2$	I	$Q_3 = 7.53$
4	Li,Na//Cl,SO_4	$Li_2SO_4 + (NaCl)_2$	I	$Q_4 = 26.78$
5	K,Na//Br,SO_4	$Na_2SO_4 + (KBr)_2$	II	$Q_5 = Q_1 + Q_3 = 11.09$
6	Li,K//Cl,Br	$(LiCl)_2 + (KBr)_2$	II	$Q_6 = Q_2 + Q_3 = 14.22$
7	Li,K//Cl,SO_4	$Li_2SO_4 + (KCl)_2$	II	$Q_7 = Q_1 + Q_4 = 30.34$
8	Li,Na//Br,SO_4	$Li_2SO_4 + (NaBr)_2$	II	$Q_8 = Q_2 + Q_4 = 33.47$
9	Li,K//Br,SO_4	$Li_2SO_4 + (KBr)_2$	IV	$Q_9 = Q_1 + Q_2 + + Q_3 + Q_4 = 44.56$

Point of complete conversion	Thermochemical connections
Q_5	Q_1-Q_5, Q_3-Q_5, Q_5-Q_9
Q_6	Q_2-Q_6, Q_3-Q_6, Q_6-Q_9
Q_7	Q_1-Q_7, Q_4-Q_7, Q_7-Q_9
Q_8	Q_2-Q_8, Q_4-Q_8, Q_8-Q_9

The conversion graph presented in Fig. 6 *b*,*c* is constructed based on thermochemical relations in such a way that the central conversion point Q_9 is connected to the points of intersection of second-stage diagonals (the points Q_5, Q_6, Q_7 and Q_8) and the conversion points corresponding to first-stage reactions (Q_1, Q_2, Q_3 and Q_4) along the diagonal of the conversion square.

The main thermochemical framework of the conversion figure of secant tetrahedra for systems consisting of nine salts of any type can also be constructed from the conversion figures of quaternary reciprocal systems consisting of six salts, which are involved in this quinary system of the 3//3 series. The conversion lines of the quaternary reciprocal systems involved in the Li,Na,K//Cl,Br,SO_4 system are as follows:

System	Conversion line
Na,K//Cl,Br,SO_4	$Q_1-Q_5-Q_3$
Li,K//Cl,Br,SO_4	$Q_6-Q_9-Q_7$
Li,Na//Cl,Br,SO_4	$Q_2-Q_8-Q_4$
Li,Na,K//Cl,Br	$Q_3-Q_6-Q_2$
Li,Na,K//Cl,SO_4	$Q_4-Q_7-Q_1$
Li,Na,K//Br,SO_4	$Q_8-Q_9-Q_5$

The above-listed lines serve as the outer edges of the graphs and the inner lines dividing the figure into four smaller squares.

The conversion figure of a 9C-type quinary system (see Fig. 6 *b*,*c*) contains nine vertices (in accordance with the number of ternary reciprocal systems involved in the quinary system) and 14 lines, twelve of which are elements of the conversion figures of all six reciprocal systems consisting of six salts, which are involved in this quinary system. Two lines emerging from the central point of the square (the point of intersection of the most stable fourth-stage diagonal with the corresponding metastable diagonal) are special lines (Q_9-Q_1 and Q_9-Q_2, Fig. 6 *b*; Q_3-Q_9 and Q_4-Q_9, Fig. 6 *c*). These lines together with the conversion line of the basic elements of the 9C-type quinary reciprocal system consisting of nine salts divide the stable and metastable axial triangles into four triangles.

d. System Na,K,Ca//F,Cl,WO_4 (9D type)

Let us consider the construction of a conversion figure of the topological type D using the Na,K,Ca//F,Cl,WO_4 system as an example. The thermochemical characteristics of this system and the salt compositions for the conversion elements are given in Tables 12 and 13, respectively. The conversion figure of secant tetrahedra is shown in Fig. 7 *a*. The conversion graph of this system consists of three conversion planes and two conversion triangles: *9–6–8–4*, *2–7–1–8*, *9–3–7–5*, *3–4–1*, *2–6–5*. Each conversion square necessarily includes two points of intersection of second-stage diagonals and two points of intersection of first-stage diagonals [9D-type systems are characterised by the presence of six first-stage diagonals and three second-stage diagonals (see Table 12)]. The vertices of the conversion triangles *3–4–1* and *2–6–5* are the points of intersection of first-stage diagonals. The conversion squares (the main framework of the conversion figure) of this system are identical to the conversion squares of 9E-type systems. There are the following special six inner lines in the conversion figure of the Na,K,Ca//F,Cl,WO_4 system: *3–4*, *3–1*, *4–1*, *2–5*, *2–6* and *5–6*. These lines correspond to exchange reactions proceeding in the quinary reciprocal system consisting of nine salts and intersect the planes of the stable basic triangles $CaWO_4-(NaF)_2-(KCl)_2$ and $CaF_2-K_2WO_4-(NaCl)_2$.

Table 12. Thermochemical relations for the 9D-type quinary reciprocal system Na,K, Ca//F,Cl,WO_4 consisting of nine salts.

Metastable salt pair	Stable salt pair	Reaction	
		stage	Q /kJ (mol equiv)$^{-1}$
$CaF_2+Na_2WO_4$	$CaWO_4+(NaF)_2$	I	$Q_1=12.636$
$Na_2WO_4+(KCl)_2$	$K_2WO_4+(NaCl)_2$	I	$Q_2=22.720$
$(KF)_2+(NaCl)_2$	$(NaF)_2+(KCl)_2$	I	$Q_3=32.342$
$K_2WO_4+CaCl_2$	$CaWO_4+(KCl)_2$	I	$Q_4=40.710$
$CaWO_4+(KF)_2$	$K_2WO_4+CaF_2$	I	$Q_5=42.426$
$(NaF)_2+CaCl_2$	$CaF_2+(NaCl)_2$	I	$Q_6=50.794$
$Na_2WO_4+(KF)_2$	$K_2WO_4+(NaF)_2$	II	$Q_7=Q_2+Q_3=$ $=Q_1+Q_5=55.062$
$Na_2WO_4+CaCl_2$	$CaWO_4+(NaCl)_2$	II	$Q_8=Q_2+Q_4=$ $=Q_1+Q_6=63.430$
$(KF)_2+CaCl_2$	$CaF_2+(KCl)_2$	II	$Q_9=Q_4+Q_5=$ $=Q_3+Q_6=83.136$

Table 13. Salt compositions for conversion elements of the 9D-type Na,K,Ca//F,Cl,WO_4 system.

System	Conversion element	Salt composition
Na,Ca,K//F,WO_4	*1–7*	NaF, K_2WO_4, $CaWO_4$
Na,Ca//F,Cl,WO_4	*1–8*	NaF, NaCl, $CaWO_4$
Na,K//F,Cl,WO_4	*2–7*	NaF, NaCl, K_2WO_4
Na,Ca,K//Cl,WO_4	*2–8*	NaCl, K_2WO_4, $CaWO_4$
Na,Ca,K//F,Cl	*3–9*	NaF, KCl, CaF_2
Ca,K//F,Cl,WO_4	*4–9*	CaF_2, KCl, $CaWO_4$
Ca,K//F,Cl,WO_4	*5–9*	KCl, K_2WO_4, CaF_2
Na,Ca,K//F,Cl	*6–9*	NaCl, KCl, CaF_2
Na,K//F,Cl,WO_4	*3–7*	NaF, KCl, K_2WO_4
Na,Ca,K//F,WO_4	*5–7*	NaF, K_2WO_4, CaF_2
Na,Ca,K//Cl,WO_4	*4–8*	NaCl, KCl, $CaWO_4$
Na,Ca//F,Cl,WO_4	*6–8*	CaF_2, NaCl, $CaWO_4$

The points of intersection of second-stage diagonals each have four thermochemical connections. The points of intersection of first-stage diagonals *1–7*, *2–7*, *3–7*, *5–7*, *1–8*, *2–8*, *4–8*, *6–8*, *3–9*, *4–9*, *5–9*, *6–9* have the same number of connections (see Fig. 7 *a*). These 12 lines form the 9D ⇄ 9E-type framework of the conversion figure common to the two types. The salt compositions involved in the thermochemical 9D ⇄ 9E-type framework of the conversion figure belong to quaternary reciprocal systems.

The special conversion lines *2–5–6* and *1–3–4* correspond to the NaCl, K_2WO_4, CaF_2 and NaCl, KCl, $CaWO_4$ salt compositions, respectively in the Na,Ca,K//F,Cl,WO_4 system.

Hence, the conversion figure of secant tetrahedra for 9D-type quinary reciprocal systems consisting of nine salts is a graph containing nine points of complete conversion of ternary reciprocal systems, 12 lines (edges) corresponding to salt compositions of six salts and six special inner lines, which model an interaction in a system composed of nine salts.

e. System Na,Ba,Fe//Cl,S,SO_4 (9E type)

The conversion figure of reciprocal systems of the 3//3 series of the 9E topological type is a nine-point graph (see Fig. 7 *b*).

Nine points of complete conversion of ternary reciprocal systems serve as vertices of the graph, and 12 conversion lines of quaternary reciprocal systems consisting of six salts, which are constituents of the main thermochemical framework of the figure, serve as edges. Six triangular planes are sections of the composition prism for a quinary reciprocal system consisting of nine salts. The *8–7*, *9–8* and *7–9* diagonals intersecting the plane of the axial stable triangle are special inner lines of three conversion squares.

Nine diagonals (six first-stage diagonals and three second-stage diagonals) serve as the thermochemical characteristics of 9E-type systems. The thermal effects of a second-stage reaction can be expressed as the sums of the thermal effects of first-stage reactions:

$$Q_1 + Q_3 = Q_2 + Q_4,$$

$$Q_1 + Q_6 = Q_5 + Q_4,$$

$$Q_2 + Q_6 = Q_3 + Q_5.$$

From these equations it follows that

$$Q_6 - Q_5 = Q_4 - Q_1 = Q_3 - Q_2,$$

i.e., the thermal effects for six diagonals are related by the following condition: the differences for three pairs of thermal effects should be equal to each other. For example, these differences for the Na,Ba,Fe//Cl, S,SO_4 system are as follows:

$$Q_6 - Q_5 = 89.12 - 85.56 = 3.56 \text{ kJ (mol equiv)}^{-1},$$

$$Q_4 - Q_1 = 10.04 - 6.48 = 3.56 \text{ kJ (mol equiv)}^{-1},$$

$$Q_3 - Q_2 = 11.72 - 8.16 = 3.56 \text{ kJ (mol equiv)}^{-1}.$$

The main thermochemical characteristics of the Na,Ba,Fe//Cl,S,SO_4 system (9E type) are given in Table 14. The conversion graph of the 9E-type system consists of three conversion squares, which are divided by diagonals into six triangles. The diagonals of the conversion squares are the *7–8*, *8–9* and *7–9* lines, which correspond to the FeS + $(NaCl)_2$, FeS + $BaSO_4$ and $(NaCl)_2$ + $BaSO_4$ salt pairs, respectively. These lines intersect the stable axial triangle $(NaCl)_2$–FeS–$BaSO_4$ and characterise the chemical interaction in the quinary reciprocal system Na,Ba,Fe//Cl,S,SO_4. The conversion points *1*, *2*, *3*, *4*, *5* and *6* corresponding to first-stage reactions are involved in conversion squares (two points per square) and each have two thermochemical connections to conversion points corresponding to second-stage reactions. For example, the conversion square *4–9–6–8* includes the conversion points *4* and *6* (first-stage reactions) connected to the points *8* and *9* (second-stage reactions).

The points *7*, *8* and *9* each have six thermochemical connections (four connections to the points corresponding to first-stage reactions and two connections to each other). The points corresponding to second-stage reactions should be connected to other points, *viz*., the conversion points of first-stage reactions. For example, the point *9* is connected to the points *3* and *5* [the points of intersection of the first-stage diagonals $BaCl_2$ + FeS (Q_5) and $BaSO_4$ + $FeCl_2$ (Q_3)], and the point *8* is connected to the points *1* and *4* [the points of intersection of the first-stage diagonals $FeSO_4$ + $(NaCl)_2$ (Q_1) and $(NaCl)_2$ + BaS (Q_4)]. Finally, the point *7* corresponding to the second-stage reaction giving rise to the $(NaCl)_2$ + $BaSO_4$ pair (Q_7) is connected to the points *1* and *2* of the conversion square *2–7–1–8* and the points *3* and *5* of the conversion square *9–3–7–5*. All these constructions are determined by the thermochemical dependences of the second-stage reactions on the first-stage reactions. For example, the thermal effect of the second-stage reaction giving rise to the $BaSO_4$ + FeS pair is equal to the sum of the thermal effects of the first-stage reactions (see Table 14) Q_5 (the stable $BaCl_2$ + FeS pair) and Q_3 (the stable $BaSO_4$ + $FeCl_2$ pair)

$$Q_9 = Q_5 + Q_3 = 85.56 + 11.72 = 97.28 \text{ kJ (mol equiv)}^{-1}.$$

At the same time, this thermal effect is related to the thermal effects of the first-stage reactions yielding the $BaSO_4$ + Na_2S (Q_2) and Na_2SO_4 + FeS (Q_6) pairs

$$Q_9 = Q_2 + Q_6 = 8.16 + 89.12 = 97.28 \text{ kJ (mol equiv)}^{-1}.$$

Analogously, the thermal effect of the second-stage reaction giving rise to the $(NaCl)_2$ + FeS pair (Q_8) is equal to the sum of the thermal effects of the following first-stage reactions: $(NaCl)_2$ + BaS (Q_4) and $BaCl_2$ + FeS (Q_5) as well as $(NaCl)_2$ + $FeSO_4$ (Q_1) and Na_2SO_4 + FeS (Q_6)

$$Q_8 = Q_4 + Q_5 = Q_1 + Q_6 = 10.04 + 85.56 = \\ = 6.48 + 89.12 = 95.60 \text{ kJ (mol equiv)}^{-1}.$$

Analogously, the following equation can be written for Q_7:

$$Q_7 = Q_2 + Q_4 = Q_1 + Q_3 = 8.16 + 10.04 = \\ = 6.48 + 11.72 = 18.20 \text{ kJ (mol equiv)}^{-1}.$$

The above-considered methods for the construction of conversion figures of secant elements for quinary reciprocal systems consisting of nine salts of various thermochemical types are simple, convenient and do not require complicated tools of multidimensional geometry.

The general algorithm for the construction of conversion figures of secant tetrahedra for quinary reciprocal systems consisting of nine salts of various thermochemical types can be stated as follows:[8]

(1) the determination of stable diagonals in ternary reciprocal systems based on the thermal effects of exchange reactions;

(2) the determination of reaction stages and the constituent thermal effects;

(3) the determination of the thermochemical type of the system;

(4) the determination of the number of thermochemical connections for each point of complete conversion corresponding to the diagonal of the corresponding stage from the thermochemical relations in the system;

(5) the connection of nine points of complete conversion of ternary reciprocal systems, which correspond to intersections of diagonals of the stable and metastable complexes of the system, in accordance with the number of thermochemical functional connections revealed for each conversion point.

Table 14. Points of complete conversion and thermochemical relations for the Na,Ba,Fe//Cl,S,SO_4 system.

Point	Ternary reciprocal system	Stable salt pair	Reaction	
			stage	Q /kJ (mol equiv)$^{-1}$
1	Na,Fe//Cl,SO_4	$(NaCl)_2$ + $FeSO_4$	I	$Q_1 = 6.48$
2	Ba,Na//S,SO_4	Na_2S + $BaSO_4$	I	$Q_2 = 8.16$
3	Ba,Fe//Cl,SO_4	$BaSO_4$ + $FeCl_2$	I	$Q_3 = 11.72$
4	Na,Ba//Cl,S	$(NaCl)_2$ + BaS	I	$Q_4 = 10.04$
5	Ba,Fe//Cl,S	$BaCl_2$ + FeS	I	$Q_5 = 85.56$
6	Na,Fe//S,SO_4	Na_2SO_4 + FeS	I	$Q_6 = 89.12$
7	Na,Ba//Cl,SO_4	$(NaCl)_2$ + $BaSO_4$	II	$Q_7 = Q_2 + Q_4 = Q_1 + Q_3 = 18.20$
8	Na,Fe//Cl,S	$(NaCl)_2$ + FeS	II	$Q_8 = Q_5 + Q_4 = Q_1 + Q_6 = 95.60$
9	Ba,Fe//S,SO_4	$BaSO_4$ + FeS	II	$Q_9 = Q_2 + Q_6 = Q_3 + Q_5 = 97.28$

3. The matrix method for the construction of conversion figures

The thermochemical method is simple and convenient but requires the determination of the stages of stable diagonals, which is not always possible because of the lack of reliable data on the enthalpies of formation of salts. This gave impetus to the development of a procedure without this drawback. The matrix method is the most descriptive way of constructing conversion figures of secant elements.[8,32,33] This method does not require numerical values of the thermal effects of exchange reactions. To construct a conversion figure for reciprocal systems of the 2//n (n//2) series using matrices of reciprocal salt pairs, it is only necessary to know which salt pair is more stable. The presence (or the absence) of unities in cells of matrices of reciprocal salt pairs determines the sought-for thermochemical relations.

In the ternary reciprocal system A,B//X,Y, a stable diagonal in a four-cell matrix is denoted by unity. The conversion point of this system results from the intersection of the AX – BY and AY – BX diagonals, which occupy the cells 2 and 3, respectively. Since the conversion point belongs both to stable and metastable diagonals, it can be placed either in the cell 2 or in the cell 3. For convenience, let us display the point of complete conversion of the ternary reciprocal system in the cell occupied by the stable diagonal, *i.e.*, in the cell with unity.

	BX	BY
AX	1) 0	2) 0
AY	3) 1	4) 0

In the matrix of reciprocal salt pairs of a quaternary reciprocal system consisting of six salts, three cells are occupied by unities. A stable salt pair, *i.e.*, the unity located at the intersection of a row and column with two unities, forms a stable second-stage diagonal. The other two salt pairs denoted by unities correspond to first-stage diagonals.

	BX	BY	BZ
AX	0	0	1
AY	1	0	1
AZ	0	0	0

A conversion figure is constructed as follows: points corresponding to points of complete conversion of ternary reciprocal systems are placed in cells with unities. Then the points are connected by straight lines emerging from the point corresponding to the second-stage diagonal.

Let us consider the construction of a conversion figure of secant elements for more complex systems of the 2//*n* series, for example, for a quinary reciprocal system consisting of eight salts. This system is represented by a matrix consisting of 16 cells, six of which have unities and correspond to stable diagonals of ternary reciprocal systems. The matrix of reciprocal salt pairs for the Li,Na//Cl,Br,NO_3,SO_4 system is presented in Fig. 8.

For convenience, the conversion figure of the salt is placed in the matrix in such a way that the first row contains three unities, the second row has two unities, and the third row contains one unity, *i.e.*, in accordance with an increase in the stability of salts of the upper row and a decrease in the stability of salts of the left column. The unity in the fourth cell corresponds to a third-stage diagonal, unities in the third and eighth cells correspond to second-stage diagonals, and all other unities correspond to first-stage diagonals (see Fig. 8).

Conversion figures are constructed by connecting successively the points placed in cells with unities. The conversion point corresponding to the intersection of a stable third-stage diagonal and its metastable pair is connected by straight lines to the points in cells occupied by second-stage diagonals. The latter points, in turn, are connected to the point in the cell occupied by a first-stage diagonal. Therefore, the connection of four points located in the cells of the upper right part of the matrix by lines gives rise to a fragment of the conversion figure forming a quadrangle. Triangles result from the connection of points located in the first row and the last column of the matrix, respectively. The order in which the points are connected can be represented by the following scheme. The quadrilateral fragment of the conversion figure is $3 \to 4 \to 8 \to 7 \to 3$; the first triangle is $2 \to 3$ and $2 \to 4$; the second triangle is $8 \to 12$ and $4 \to 12$. In the case of this arrangement of unities and zeros in the matrix, the conversion figure always has the form shown in Fig. 8.

A conversion figure can be constructed in an alternative way. Let us consider this procedure with the use of the same Li,Na//Cl,Br,NO_3,SO_4 system consisting of eight salts as an example.

1. First, we write matrices of reciprocal salt pairs, which are constituents of quaternary reciprocal systems consisting of six salts.

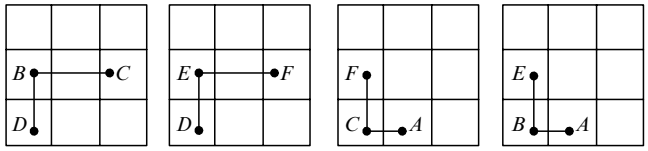
	NaBr	Na_2SO_4	NaCl
LiBr	0	0	0
Li_2SO_4	1	0	1
LiCl	1	1	0

	NaBr	$NaNO_3$	NaCl
LiBr	0	0	0
$LiNO_3$	1	0	1
LiCl	1	1	0

	NaCl	$NaNO_3$	Na_2SO_4
LiCl	0	0	0
$LiNO_3$	1	0	1
Li_2SO_4	1	1	0

	NaBr	$NaNO_3$	Na_2SO_4
LiBr	0	0	0
$LiNO_3$	1	0	1
Li_2SO_4	1	1	0

2. Then we inscribe conversion figures for all quaternary reciprocal systems into the matrices by connecting the points corresponding to unities in rows and columns.



3. Finally, the conversion figures are transferred to a matrix of a quinary reciprocal system consisting of eight salts. The conversion figure for the Li,Na//Cl,Br,NO_3,SO_4 system is obtained automatically.

This procedure is particularly convenient for the construction of conversion figures for senary and more complex systems of the 2//*n* (*n*//2) series, because it substantially simplifies the determination of thermochemical relations.

The proposed algorithm is applicable only to systems of one thermochemical type, *viz.*, to systems of the 2//*n* (*n*//2) series. For systems consisting of nine salts of the 3//3 series, three matrices of the 2//3 (3//2) series involved in this quinary system should be considered.[32]

Conversion figures for various thermochemical types of quinary reciprocal systems are different. Hence, the algorithms for the construction of these figures are also different.

Let us consider the procedure for the construction using the Ba,K,Na//F,MoO_4,WO_4 system (the $B \rightleftarrows A$ thermochemical type) as an example. The thermochemical relations for this system are given in Table 15.

Table 15. Points of complete conversion and thermochemical relations for the Na,K,Ba//F,MoO_4,WO_4 system.

Point	Ternary reciprocal system	Stable salt pair	Reaction	
			stage	Q /kJ (mol equiv)$^{-1}$
1	Na,Ba//F,WO_4	$(NaF)_2 + BaWO_4$	I	$Q_4 = 19.04$
2	K,Ba//F,MoO_4	$K_2MoO_4 + BaF_2$	I	$Q_2 = 2.51$
3	Na,Ba// MoO_4,WO_4	$Na_2WO_4 +$ $+ BaMoO_4$	I	$Q_1 = 1.67$
4	Na,K// MoO_4,WO_4	$Na_2MoO_4 +$ $+ K_2WO_4$	I	$Q_3 = 12.34$
5	Na,Ba//F,MoO_4	$(NaF)_2 + BaMoO_4$	II	$Q_5 = Q_1 + Q_4 =$ $= 20.71$
6	K,Ba// MoO_4,WO_4	$K_2WO_4 +$ $+ BaMoO_4$	II	$Q_6 = Q_1 + Q_3 =$ $= 14.01$
7	K,Ba//F,WO_4	$BaF_2 + K_2WO_4$	III	$Q_7 = Q_1 + Q_2 + Q_3 =$ $= 16.52$
8	K,Na//F,MoO_4	$(NaF)_2 + K_2MoO_4$	III	$Q_8 = Q_1 + Q_2 + Q_4 =$ $= 23.22$
9	K,Na//F,WO_4	$(NaF)_2 + K_2WO_4$	IV	$Q_9 = Q_1 + Q_2 +$ $+ Q_3 + Q_4 = 35.56$

This system includes three quaternary reciprocal systems of the 3//2 series (Na,K,Ba//F,WO_4; Na,K,Ba//F,MoO_4; Na,K,Ba//MoO_4,WO_4) and three systems of the 2//3 series (Na,Ba//F,MoO_4,WO_4; K,Ba//F,MoO_4,WO_4; Na,K//F,MoO_4,WO_4). The matrices of reciprocal salt pairs and the matrices of conversion figures for these systems are given below (in the matrices of reciprocal salt pairs, the point numbers from the matrices of the conversion figures are given in parentheses).[11]

Let us write the matrix table consisting of 9 columns and 9 rows and then place unities from the matrices of the conversion figures in rows and columns. The conversion graph corresponding to this matrix belongs to the 9B topological type (Fig. 10).

	Z	*K*	*E*	*D*	*T*	*C*	*F*	*A*	*B*
Z(*1*)	0	0	0	0	1	0	0	0	1
K(*2*)	0	0	0	0	0	0	1	1	0
E(*3*)	0	0	0	0	1	1	0	0	0
D(*4*)	0	0	0	0	0	1	0	0	1
T(*5*)	1	0	1	0	0	1	1	0	1
C(*6*)	0	0	1	1	0	0	0	1	1
F(*7*)	0	1	0	0	1	0	0	1	1
A(*8*)	0	0	0	0	0	1	1	0	1
B(*9*)	1	0	0	1	1	1	1	1	0

Matrices of reciprocal salt pairs

	Na_2WO_4	K_2WO_4	$BaWO_4$
NaF	0	1(9)	1(1)
KF	0	0	0
BaF_2	0	1(7)	0

	Na_2MoO_4	K_2MoO_4	$BaMoO_4$
NaF	0	1(8)	1(5)
KF	0	0	0
BaF_2	0	1(2)	0

	Na_2WO_4	K_2WO_4	$BaWO_4$
Na_2MoO_4	0	1(4)	0
K_2MoO_4	0	0	0
$BaMoO_4$	1(3)	1(6)	0

	BaF_2	$BaMoO_4$	$BaWO_4$
NaF	0	1(5)	1(1)
Na_2MoO_4	0	0	0
Na_2WO_4	0	1(3)	0

	BaF_2	$BaMoO_4$	$BaWO_4$
KF	0	0	0
K_2MoO_4	1(2)	0	0
K_2WO_4	1(7)	1(6)	0

	KF	K_2MoO_4	K_2WO_4
NaF	0	1(8)	1(9)
Na_2MoO_4	0	0	1(4)
Na_2WO_4	0	0	0

Matrices of conversion figures

	1	7	9
1	0	0	1
7	0	0	1
9	1	1	0

	2	5	7
2	0	0	1
5	0	0	1
7	1	1	0

	3	4	6
3	0	0	1
4	0	0	1
6	1	1	0

	1	3	5
1	0	0	1
3	0	0	1
5	1	1	0

	2	6	8
2	0	0	1
6	0	0	1
8	1	1	0

	4	8	9
4	0	0	1
8	0	0	1
9	1	1	0

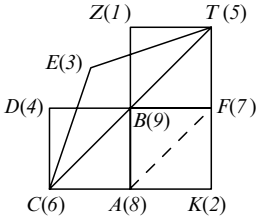


Figure 10. Conversion figure of the 9B-type quinary reciprocal system Na,K,Ba//F,MoO_4,WO_4.

A conversion graph can be constructed by the matrix method using an alternative procedure. In this case, stable salt pairs, which are determined from the melting diagram (if data on the enthalpies of formation of the salts are lacking) of ternary reciprocal systems, serve as the starting data. Let us consider the construction of a conversion graph using the quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4 of the $9C \rightleftarrows 9C'$ type as an example. The thermochemical data for this system are given in Table 16. This system includes nine ternary reciprocal systems. Stable salt pairs for these systems are determined from experimental data.

Table 16. Thermochemical characteristics of the 9C-type quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4.

Ternary reciprocal system	Stable salt pair	Reaction	
		stage	*Q*
Ag,Li//Cl,SO_4	AgCl + Li_2SO_4	IV	$Q_9 = Q_1 + Q_2 + Q_3 + Q_4 = Q_8 + Q_7 = Q_5 + Q_6$
Ag,Na//Cl,SO_4	AgCl + Na_2SO_4	II	$Q_8 = Q_3 + Q_4$
Li,Na//Cl,SO_4	NaCl + Li_2SO_4	II	$Q_7 = Q_1 + Q_2$
Ag,Li//Cl,NO_3	AgCl + $LiNO_3$	II	$Q_6 = Q_2 + Q_4$
Ag,Na//Cl,NO_3	AgCl + $NaNO_3$	I	Q_4
Li,Na//Cl,NO_3	NaCl + $LiNO_3$	I	Q_2
Ag,Li//NO_3,SO_4	$AgNO_3$ + Li_2SO_4	II	$Q_5 = Q_1 + Q_3$
Ag,Na//NO_3,SO_4	$AgNO_3$ + Na_2SO_4	I	Q_3
Li,Na//NO_3,SO_4	$NaNO_3$ + Li_2SO_4	I	Q_1

Two adjacency matrices (Fig. 11) are constructed from the matrices of reciprocal salt pairs of six reciprocal quaternary systems involved in the Ag,Li,Na//Cl,NO_3,SO_4 system.[33] In one matrix, the salts are arranged according to common cations (the cation matrix I), whereas the salts in another matrix are arranged according to common anions (the anion matrix II). As a result, the thermochemical characteristics of all six quaternary reciprocal systems, which are involved in the quinary reciprocal system of nine salts, are determined.

From the matrices I and II, it is evident that the AgCl and Li_2SO_4 salts each have four unities; the $AgNO_3$, $LiNO_3$, NaCl, $NaNO_3$ and Na_2SO_4 salts each have two unities; and the Ag_2SO_4 and LiCl salts have no unities.

Then the table of vertex indices is compiled (Table 17).

Table 17. Table of vertex indices for the 9C-type quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4.

Metal	Cl	NO_3	SO_4	$\sum$
Ag	4	2	0	6
Li	0	2	4	6
Na	2[a]	2[b]	2[c]	6
$\sum$	6	6	6	18

Note. Here and in the figures presented below, the indices of different salts of the same metals are labelled a, b, c.

It is known that this type of system is characterised by one fourth-stage reaction, four first-stage reactions, and four second-stage reactions. The pair of salts, both of which are characterised by the presence of four unities in the corresponding adjacency matrices, AgCl – Li_2SO_4 (the thermal effect of the reaction is Q_9), corresponds to a fourth-stage reaction. The salt pairs produced in second-stage reactions are located at the intersection of rows and columns with two unities in the adjacency matrices I and II: AgCl – Na_2SO_4 (Q_8), NaCl – Li_2SO_4 (Q_7), AgCl – $NaNO_3$ (Q_6) and $AgNO_3$ – Li_2SO_4 (Q_5).

Other salt pairs are formed by first-stage reactions (Q_1, Q_2, Q_3 and Q_4). To determine the constituents of the thermal effects of the

I

	AgCl	$AgNO_3$	Ag_2SO_4	LiCl	$LiNO_3$	Li_2SO_4	NaCl	$NaNO_3$	Na_2SO_4
AgCl	0	0	0	0	1	1	0	1	1
$AgNO_3$	0	0	0	0	0	1	0	0	1
Ag_2SO_4	0	0	0	0	0	0	0	0	0
LiCl	0	0	0	0	0	0	0	0	0
$LiNO_3$	1	0	0	0	0	0	1	0	0
Li_2SO_4	1	1	0	0	0	0	1	1	0
NaCl	0	0	0	0	1	1	0	0	0
$NaNO_3$	1	0	0	0	0	1	0	0	0
Na_2SO_4	1	1	0	0	0	0	0	0	0

II

	AgCl	LiCl	NaCl	$AgNO_3$	$LiNO_3$	$NaNO_3$	Ag_2SO_4	Li_2SO_4	Na_2SO_4
AgCl	0	0	0	0	1	1	0	1	1
LiCl	0	0	0	0	0	0	0	0	0
NaCl	0	0	0	0	1	0	0	1	0
$AgNO_3$	0	0	0	0	0	0	0	1	1
$LiNO_3$	1	0	1	0	0	0	0	0	0
$NaNO_3$	1	0	0	0	0	0	0	0	1
Ag_2SO_4	0	0	0	0	0	0	0	0	0
Li_2SO_4	1	0	1	1	1	0	0	0	0
Na_2SO_4	1	0	0	1	0	0	0	0	0

Figure 11. Cation (I) and anion (II) adjacency matrices of the quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4.

reactions, submatrices of quaternary reciprocal systems extracted from the adjacency matrices I and II should be considered. For the Ag,Li//Cl,NO_3,SO_4 system (in the upper right part of the cation matrix), the following reactions can be written:

$$AgNO_3 + LiCl = AgCl + LiNO_3 - Q_6$$

$$1/2\,Ag_2SO_4 + LiNO_3 = 1/2\,Li_2SO_4 + AgNO_3 - Q_5$$

$$1/2\,Ag_2SO_4 + LiCl = 1/2\,Li_2SO_4 + AgCl - Q_9$$

Hence, $Q_9 = Q_6 + Q_5$.

A consideration of the Ag,Li,Na//Cl,SO_4 system (the upper right semimatrix in the anion matrix) shows that $Q_9 = Q_7 + Q_8$. Other relations given in Table 16 are obtained in the same way.

Then the matrix of the conversion figure of the Ag,Li,Na//Cl,NO_3,SO_4 system is compiled (Fig. 12 *a*). This matrix includes unities from the matrices I and II along with two connections, *viz*., *1*–9 and *9*–*4*, resulting from the intersection of the stable (AgCl–Li_2SO_4–$NaNO_3$) and metastable (Ag_2SO_4–LiCl–$NaNO_3$) axial triangles of singular and non-equilibrium stars.

Once all necessary connections have been determined from the matrix of the conversion figure, one can construct the conversion graph of the quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4 of the 9C type (Fig. 12 *b*).

Using the matrix of the conversion figure, one can find the salt compositions of secant tetrahedra and determine the total thermal effect for each tetrahedron.[8] For this purpose, it is necessary to perform a summation over the corresponding rows of the matrix. For example, the rows *5*, *3*, *8* and *9* should be summed for the

a

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1	0	0	0	0	1	0	1	0	1
2	0	0	0	0	0	1	1	0	0
3	0	0	0	0	1	0	0	1	0
4	0	0	0	0	0	1	0	1	1
5	1	0	1	0	0	0	0	0	1
6	0	1	0	1	0	0	0	0	1
7	1	1	0	0	0	0	0	0	1
8	0	0	1	1	0	0	0	0	1
9	1	0	0	1	1	1	1	1	0

b

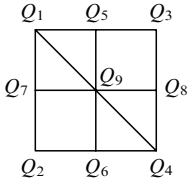


Figure 12. The matrix of the conversion figure (*a*) and the conversion figure (*b*) of the quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4. (*1*) AgCl, (*2*) LiCl, (*3*) NaCl, (*4*) $AgNO_3$, (*5*) $LiNO_3$, (*6*) $NaNO_3$, (*7*) Ag_2SO_4, (*8*) Li_2SO_4, (*9*) Na_2SO_4; unity and zero in the cells of the matrix signify respectively the presence and the absence of a connection between stable salt pairs from the cation and anion matrices.

$Q_5 - Q_3 - Q_8 - Q_9$ square: $AgNO_3 - Li_2SO_4$ (Q_5), $AgNO_3 - Na_2SO_4$ (Q_3), $AgCl - Na_2SO_4$ (Q_8) and $AgCl - Li_2SO_4$ (Q_9). The salt composition of the tetrahedron is $AgNO_3 - Li_2SO_4 - AgCl - Na_2SO_4$, the total thermal effect of the reaction is $Q_9 + Q_8 + Q_5 + Q_3$. The results of summation are given in Table 18.

Table 18. Salt compositions of the secant tetrahedra for the quinary reciprocal system Ag,Li,Na//Cl,NO_3,SO_4.

Fragment of conversion figure	Salt composition of tetrahedron	Overall thermal effect of salts of tetrahedron
Square $Q_5 - Q_3 - Q_8 - Q_9$	$AgNO_3 - Li_2SO_4 - Na_2SO_4 - AgCl$	$Q_9 + Q_8 + Q_5 + Q_3$
Square $Q_2 - Q_7 - Q_9 - Q_6$	$LiNO_3 - Li_2SO_4 - NaCl - AgCl$	$Q_9 + Q_7 + Q_6 + Q_2$
Triangle $Q_1 - Q_9 - Q_7$	$NaNO_3 - Li_2SO_4 - NaCl - AgCl$	$Q_9 + Q_7 + Q_1$
Triangle $Q_1 - Q_5 - Q_9$	$AgNO_3 - Li_2SO_4 - NaNO_3 - AgCl$	$Q_9 + Q_5 + Q_1$
Triangle $Q_4 - Q_6 - Q_9$	$LiNO_3 - Li_2SO_4 - NaNO_3 - AgCl$	$Q_9 + Q_6 + Q_4$
Triangle $Q_4 - Q_8 - Q_9$	$NaNO_3 - Li_2SO_4 - Na_2SO_4 - AgCl$	$Q_9 + Q_8 + Q_4$

For the practical application of conversion figures, the corresponding graphs need not be constructed from the adjacency matrices. Geometric images can completely be omitted, because the matrix of the conversion figure contains all necessary information. For example, the degree of a vertex of a graph not only defines the number of connections of this vertex to other vertices (*i.e.*, the number of conversion lines) but also indicates the number of chemical reactions giving rise to a salt pair, the stage of diagonals, the intersection of which is occupied by a particular conversion point; the compositions of simplexes of a singular star, and the heat capacities of mixtures corresponding to secant elements of the singular star.

IV. Practical applications of matrices and graphs in studies of complex systems

Matrices of reciprocal salt pairs with inscribed conversion figures can be used for searching for salt mixtures, which are characterised by the highest energy capacity and are constituents of simplexes for systems of the 2//*n* (*n*//2) series.[8]

The thermochemical relations in a system can be judged from a matrix of reciprocal salt pairs with an inscribed conversion figure of secant elements, *i.e.*, such matrices allow one to determine the reaction stages yielding the corresponding salt pairs. It can easily be found out which simplex has a higher energy capacity. The larger the number of unities in the matrix that contains elements of a conversion figure (from which a simplex is obtained), the higher the total heat content of the salt mixture and, consequently, the higher all other energy characteristics.

All simplexes of a singular star of a system can be determined from the conversion figure inscribed into a matrix of reciprocal salt pairs, *i.e.*, triangulation can be performed without the use of tools of multidimensional geometry.

1. Construction of singular stars of secant tetrahedra of systems of the 2//*n* (*n*//2) series

Let us consider the determination of simplexes from a conversion figure inscribed into a canonical matrix b_0 of reciprocal salt pairs [11] for a system consisting of sodium, potassium and barium fluorides and tungstates (Fig. 13). In the Na,K,Ba//F,WO_4 system, $BaF_2 + K_2WO_4$, $(NaF)_2 + BaWO_4$ and $K_2WO_4 + (NaF)_2$ are stable pairs. The former two pairs are generated by first-stage

a

b_0	$(NaF)_2$	$(KF)_2$	BaF_2
Na_2WO_4	0	0	0
K_2WO_4	1	0	1
$BaWO_4$	1	0	0

b

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

Figure 13. Conversion graph inscribed in the matrix of mutual salt pairs of the quaternary reciprocal system Na,K,Ba//F,WO_4 (*a*), and the general form of the matrix (*b*).

reactions, whereas the third pair is formed by a second-stage reaction. These pairs correspond to unities in cells of the matrix. Points are placed in cells with unities, and then the points are connected by solid lines to form the conversion figure of this system inscribed in the matrix (Fig. 13 *a*). The analysis of the conversion figure of the system starts with the determination of secant simplexes (triangles).

The vertices of the first triangle are determined from the row, which includes one of the lines a_{21} or a_{23}. This line corresponds to potassium tungstate, which forms stable pairs with sodium and barium fluorides.

Therefore, $K_2WO_4 - (NaF)_2 - BaF_2$ is one of the stable triangles. The vertices of the corresponding metastable triangle represent salts located in cells with zeros, which are symmetric to cells with unities relative to the zero diagonal. The cell a_{21} with unity is symmetric to the cell a_{12} with zero, and the cell a_{23} is symmetric to the cell a_{32}. Hence it follows that the $K_2WO_4 + (NaF)_2$ pair corresponds to the metastable $Na_2WO_4 + (KF)_2$ pair, and the stable $K_2WO_4 + BaF_2$ pair corresponds to the $BaWO_4 + (KF)_2$ pair. This gives rise to the metastable $Na_2WO_4 - (KF)_2 - BaWO_4$ triangle. The compositions of the stable $K_2WO_4 - (NaF)_2 - BaWO_4$ triangle and the metastable $(KF)_2 - Na_2WO_4 - BaF_2$ triangle are determined analogously from the conversion line in the column of the matrix.

The next stage involves the determination of tetrahedra of singular and non-equilibrium stars of the system. A stable sphenoid (irregular tetrahedron) is determined by salts corresponding simultaneously to all unities of the matrix (the overall conversion figure). In the case under consideration, this is the $K_2WO_4 - (NaF)_2 - BaWO_4 - BaF_2$ tetrahedron. The metastable sphenoid is formed by salts, which determine the row and column with three or two zeros [$BaWO_4 - BaF_2 - Na_2WO_4 - (KF)_2$]. Salts corresponding to the shared edge of the stable and metastable sphenoids are determined by the row and column with two zeros ($BaWO_4 - BaF_2$).

Stable tetrahedra correspond to salts, which occupy the cells of an entire row or column, through which conversion lines pass. For the system under consideration, these are the stable $K_2WO_4 - (KF)_2 - (NaF)_2 - BaF_2$ (row) and $(NaF)_2 - K_2WO_4 - Na_2WO_4 - BaWO_4$ (column) tetrahedra. Metastable tetrahedra are formed from columns and rows containing salts, which are located in cells with zeros, the cells being symmetric to cells with unities relative to the zero diagonal. The a_{21}, a_{22}, a_{23} row is symmetric to the a_{12}, a_{22}, a_{32} column, and the a_{11}, a_{21}, a_{31} column is symmetric to the a_{11}, a_{12}, a_{13} row. Hence, $K_2WO_4 - (KF)_2 - Na_2WO_4 - BaWO_4$ and $Na_2WO_4 - (NaF)_2 - (KF)_2 - BaF_2$ are metastable tetrahedra.

All elements of the stable and metastable complexes of the system are given in Table 19. The results obtained for the Na,K,Ba//F,WO_4 system according to the above-described procedure correlate well with the experimental data.[11]

Therefore, this method provides a simple and convenient way to determine secant elements of singular and non-equilibrium stars for reciprocal systems of the 2//*n* (*n*//2) series without the use

Table 19. Compositions of simplexes of the singular and non-equilibrium stars for the Na,K,Ba//F,WO_4 system.

Secant elements		Stable cells of singular star	Metastable cells of non-equilibrium star
stable	metastable		
$(NaF)_2-K_2WO_4-BaWO_4$	$(KF)_2-BaF_2-Na_2WO_4$	$(NaF)_2-K_2WO_4-BaWO_4-BaF_2$ $(NaF)_2-Na_2WO_4-BaWO_4-K_2WO_4$	$(KF)_2-Na_2WO_4-BaWO_4-BaF_2$ $(KF)_2-Na_2WO_4-BaF_2-(NaF)_2$
$(NaF)_2-K_2WO_4-BaF_2$	$Na_2WO_4-(KF_2)-BaWO_4$	$(KF)_2-NaF-BaF_2-K_2WO_4$	$(KF)_2-K_2WO_4-Na_2WO_4-BaWO_4$

of complicated geometric constructions. This method is rapid and allows one to study multicomponent systems (for example, systems containing 8, 10 or 12 salts).

The simultaneous determination of the energy characteristics of simplexes makes it possible (after the transformation of a conversion figure to an energy graph) to obtain a rapid semi-quantitative estimate of the energy capacities of salt compositions within one system. The estimation is performed as follows: the heats of melting of the salts involved in tetrahedra are added to the heats of exchange reactions occurring between the salts (taking into account whether the reaction is endothermic or exothermic, which is established by calculations or determined experimentally from DTA data). If the heats of melting of salts have similar values, the main difference in the energy capacity of salt mixtures is associated with the heats of reactions. Therefore, the energy capacity of a mixture depends on the number of exchange reactions that can occur between the salts. This value can easily be determined from the energy models (graphs).

For reciprocal systems containing six salts, the singular star consists of three tetrahedra divided by two secant triangles. Salt mixtures with the highest energy capacity are generally modelled by sphenoids, because they are intersected by two conversion lines, and, consequently, the salts belonging to the sphenoids are involved in three exchange reactions [in the case under consideration, the $(NaF)_2-BaWO_4-BaF_2-K_2WO_4$ sphenoid]. Other tetrahedra correspond to two exchange reactions. Hence, the overall thermal effect of the reaction of salts involved in a sphenoid is equal to twice the sum of the thermal effects of first-stage reactions.

It was experimentally established that a eutectic present in a sphenoid has the highest energy capacity.[8] Eutectics in systems consisting of six salts were found according to this procedure. The energy capacities of such eutectics are twice as high as those of foreign standards.[9,10] These eutectics were used as heat-accumulation mixtures in thermal chemical power sources.

2. Construction of systems with the desired direction of interchange reactions

Analysis of matrices of reciprocal salt pairs represents the basis for the rational choice of salts for the preparation of systems with the desired direction of exchange reactions. To prepare a quaternary reciprocal system consisting of six salts with the desired direction of interchange reactions, salts can be chosen using summary matrix tables of reciprocal salt pairs composed for particular groups of cations and anions.[3]

If the aim is to prepare a system characterised by the highest stability of a particular salt, the ions should be chosen using a matrix, in which this salt has two unities. In this case, the desired salt (for example, AX) is formed in the system according to the following reactions:

$$AY + BX = AX + BY,$$

$$AZ + BX = AX + BZ.$$

To construct a quinary reciprocal system consisting of nine salts, in which the desired salt is the most stable, one should be guided by the following principle. The chosen composition should be such that the desired salt has two unities in two of the three matrices compiled for the starting quaternary reciprocal systems or at least has two unities in one matrix and one unity in another matrix. For instance, the aim is to choose a salt composition of nine salts involving alkali metal halides and sulfates such that the exchange reactions are shifted toward the formation of lithium sulfate.

To solve this problem, cations, whose halides form stable pairs with lithium sulfate, are found from the matrix tables. All cations of Group I elements satisfy this requirement. If the choice is limited to lithium, sodium and potassium salts, a salt composition with the desired direction of exchange reactions can be constructed using a mixture of lithium, sodium and potassium chlorides, bromides and sulfates or a mixture of chlorides, iodides and sulfates of these alkali metals. In these cases, the following quinary reciprocal systems of nine salts are formed: Li,Na,K//Cl,Br,SO_4; Li,Na,K//Cl,I,SO_4; Li,Na,K//Br,I,SO_4.

In addition to lithium sulfate, the basic triangle for such systems involves a pair of sodium and potassium halides, which has unity in the third starting matrix. For the Li,Na,K//Cl,Br,SO_4 system, this is the KBr – NaCl pair, *i.e.*, the basic triangle has the composition $Li_2SO_4-KBr-NaCl$. This fact was confirmed by experimental data.[8] Lithium sulfate is formed according to the following equation:

$$2\,LiBr + K_2SO_4 + NaCl = Li_2SO_4 + 2\,KBr + NaCl.$$

The NaCl salt has crystallisation fields both in the non-equilibrium and basic triangles (Fig. 14).

For particular pairs of cations, reciprocal quaternary and quinary systems are conveniently constructed by setting up series of chemical reactivity (stability) of salts with these cations. For example, there are the following series of stability for systems involving lithium and sodium (stability increases from left to right):

LiI, LiBr, LiCl, $LiNO_3$, Li_2SO_4;

Na_2SO_4, $NaNO_3$, NaCl, NaBr, NaI.

To construct a quaternary reciprocal system of six salts characterised by the highest stability of a particular salt (for

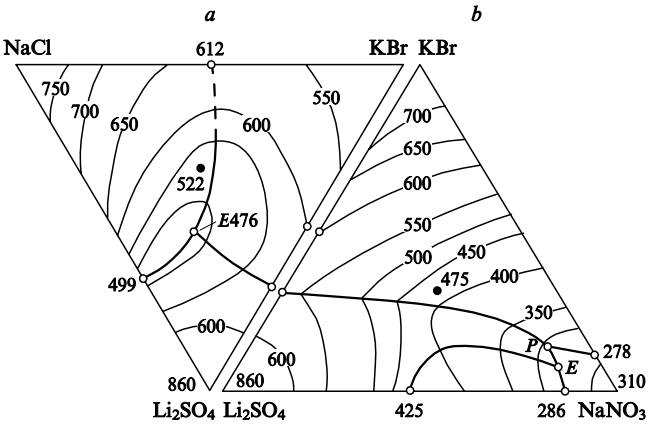


Figure 14. Axial stable triangles of the quinary reciprocal systems Li,Na,K//Cl,Br,SO_4 (*a*) and Li,Na,K//Br,NO_3,SO_4 (*b*).
E and *P* are quasiternary eutectic and peritectic points, respectively; the temperatures are given in degrees Centigrade.

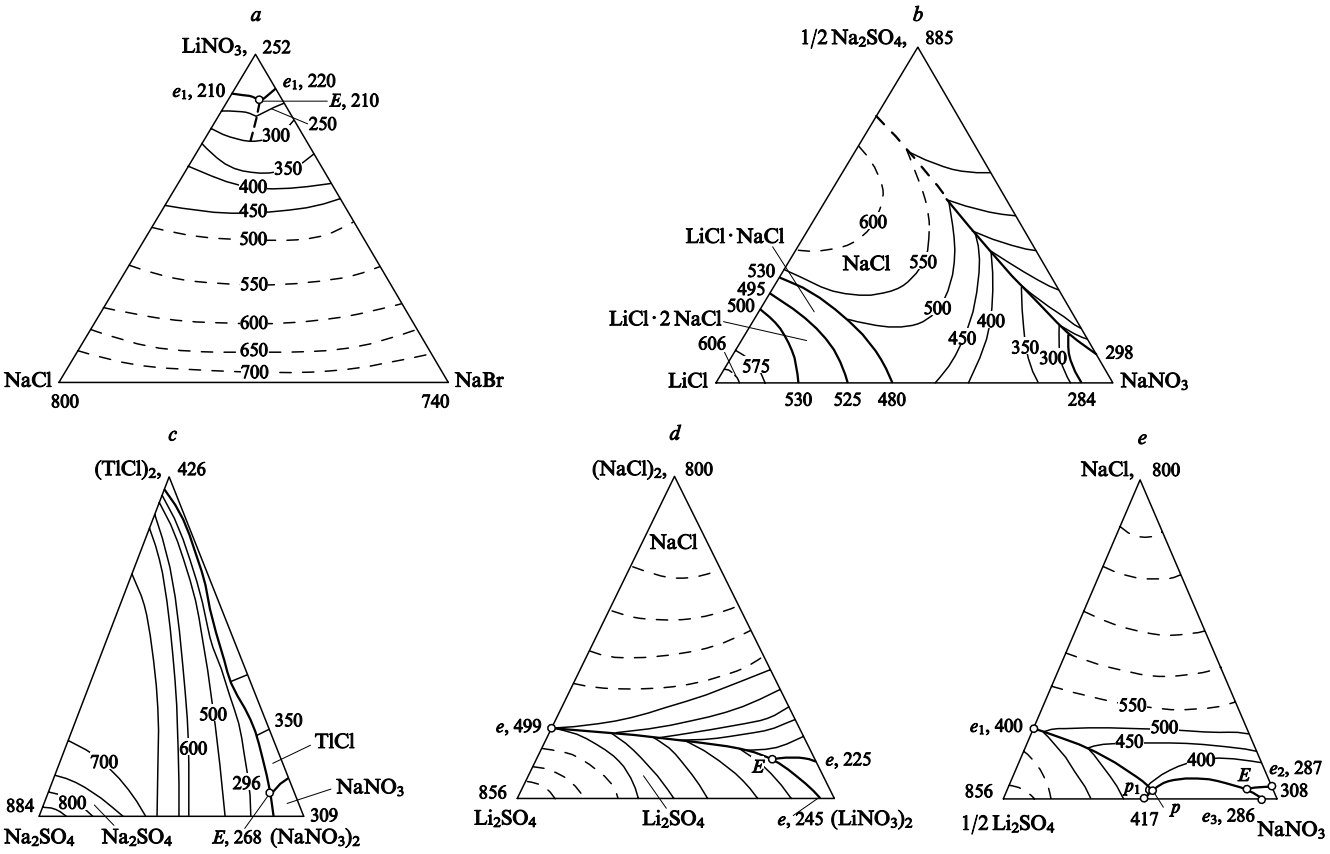


Figure 15. Sections of the quaternary reciprocal systems Li,Na//Cl,Br,NO_3 (*a*), Li,Na//Cl,NO_3,SO_4 (*b*), Na,Tl//Cl,NO_3,SO_4 (*c*) and Li,Na//Cl,NO_3,SO_4 (*d*, *e*); *e* and *p* are the saddle eutectic and peritectic points, respectively; the temperatures are given in degrees Centigrade.

example, lithium nitrate), a composition of salts, which are located in the left side of the series of stability (*i.e.*, lithium chlorides and bromides, chlorides and iodides, bromides and iodides), should be chosen. Actually, investigation of the quaternary reciprocal system Li,Na//Cl,Br,NO_3 demonstrated that $LiNO_3$ is the most stable salt in this system even in the presence of stable sodium salts (Fig. 15 *a*).

Let us consider another situation, where the aim is to change the direction of the exchange reaction in the reciprocal system Li,Na//Cl,NO_3,SO_4 consisting of six salts toward the formation of sodium sulfate.

The matrix of reciprocal salt pairs for this system has the form

		I		
		Na^+		
	c_0	Cl^-	NO_3^-	SO_4^{2-}
	Cl^-	0	0	0
Li^+	NO_3^-	1	0	0
	SO_4^{2-}	1	1	0

The main reaction

$$2\,LiCl + Na_2SO_4 = Li_2SO_4 + 2\,NaCl,$$

proceeding in this system can be shifted in the required direction by replacing one of the ions. In deciding on a cation to be replaced, one should choose an ion characterised by a reciprocal matrix. In the case under consideration, this is the type *c*, because the starting system has the matrix c_0. The thallium ion satisfies this requirement.

		II		
		Na^+		
	c	Cl^-	NO_3^-	SO_4^{2-}
	Cl^-	0	1	1
Tl^+	NO_3^-	0	0	1
	SO_4^{2-}	0	0	0

The main reaction in the Na,Tl//Cl,NO_3,SO_4 system is

$$2\,NaCl + Tl_2SO_4 = Na_2SO_4 + 2\,TlCl.$$

This fact can be confirmed by comparing the corresponding sections of the Li,Na//Cl,NO_3,SO_4 (Fig. 15 *b*) and Na,Tl//Cl,NO_3,SO_4 systems (Fig. 15 *c*).

In the former system, sodium sulfate is involved in the metastable $LiCl-Na_2SO_4-NaNO_3$ section. The liquidus surface of the section is shown in Fig. 15 *b*. It can be seen that the section is metastable, because it involves NaCl as the exchange product. After the replacement of the lithium ion with thallium, the section becomes stable.

The direction of the exchange reactions in quinary reciprocal systems consisting of 8 or 9 salts can be changed in the same manner as for reactions in quaternary reciprocal systems, except for the fact that one or two reciprocal matrices should be used.

Analysis of matrices of reciprocal salt pairs gives an idea of how one can influence the complexation processes. Let us consider the situation where complex compounds are formed by a stable salt produced by an exchange reaction. The complexation leads to a decrease in stability of the salt, and the yield of the salt in the reaction also decreases. To prevent complexation, it is necessary

to replace one component. For example, stability of lithium sulfate in the quaternary reciprocal system Li,Na//Cl,NO_3,SO_4 is low due to formation of $Li_2SO_4 \cdot Na_2SO_4$.

It is necessary to choose a salt composition, in which the $Li_2SO_4 \cdot Na_2SO_4$ compound has no effect on stability of the salt under consideration. It appeared that the stability of the desired salt can be increased within the same system by introducing an excess of lithium ions. For example, Li_2SO_4 is more stable in the presence of lithium nitrate (Fig. 15*d*). If it is required to replace a particular ion in a system with another ion, one should use an ion, the replacement of which leaves the main exchange reaction unaffected. In the Li,Na//Cl,NO_3,SO_4 system, the nitrate ion satisfies this requirement. This ion can be replaced with an anion or cation provided that the type of the matrix of reciprocal salt pairs remains unchanged. As can be seen from the series of chemical interactions of the cations, any cation to the left of lithium can be used for the replacement. Let us use potassium. In this case, the quaternary reciprocal system Li,K,Na//Cl,SO_4 is formed. The elementary matrix of this system is as follows:

	c_0	SO_4^{2-} Li^+	Na^+	K^+
	Li^+	0	0	0
Cl^-	Na^+	1	0	0
	K^+	1	1	0

In this matrix, lithium sulfate has two unities. This compound is formed by the reaction

$$K_2SO_4 + 2\,LiCl = Li_2SO_4 + 2\,KCl.$$

The $Li_2SO_4 \cdot Na_2SO_4$ compound in the Li,K,Na//Cl,SO_4 system occupies a small volume and is not manifested in the phase diagrams of stable sections.

The choice of salts, which promote immiscibility with retention of the direction of the exchange reaction toward the formation of the desired salt, is of practical interest. For instance, immiscibility in reciprocal systems can be used for extraction of salts from melts.

Suppose that there is a need to choose a salt composition, which consists of nine salts involving the Li^+ and Na^+ cations and is suitable for extraction of lithium sulfate from melts. Initially, information on which salts (in combination with lithium sulfate) lead to immiscibility can be extracted from the analysis of the data on ternary reciprocal systems. These salts are silver, cadmium and thallium chlorides. Then we choose cations, which have no effect on the stability of Li_2SO_4, based on series of chemical interactions for the halide – sulfate exchange.

For these cations, other anions can be included in the consideration (for example, nitrate ions, which do not decrease the stability of the salt of interest, in whatever combination desired). The procedure gives the following systems: Ag,Li,Na//Cl,NO_3,SO_4; Ag,Li,Na//Cl,Br,SO_4; Cd,Li,Na//Cl,NO_3,SO_4; Cd,Li,Na//Cl,Br,SO_4; Li,Na,Tl//Cl,NO_3,SO_4; Li,Na,Tl//Cl,Br,SO_4. Some of these systems were studied experimentally. For the Li,Na,Cd//Cl,NO_3,SO_4 system, the immiscibility region in the phase diagram of the axial stable triangle comprises 54.5% of the diagram.

3. Construction of singular stars of secant tetrahedra for systems consisting of nine salts

To construct singular stars, it is necessary to determine the salt compositions of secant tetrahedra. This can be done by interpreting elements of the graph (the conversion figure of this system).[8, 34, 35]

Let us consider the procedure for the determination of salt compositions of secant tetrahedra using the quinary reciprocal system Li,Na,K//Cl,Br,NO_3 consisting of nine salts as an example. This system belongs to the 9B topological type.[8, 23, 36] The conversion graph of this system is shown in Fig. 16. The stable salt pairs and elements of singular and non-equilibrium stars are given in Table 20.

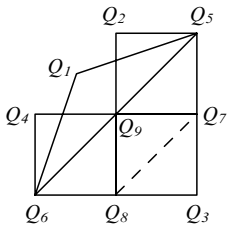


Figure 16. Conversion figure of the 9B-type quinary reciprocal system Li,Na,K//Cl,Br,NO_3.

Table 20. Elements of the conversion graph and salt compositions of secant tetrahedra for the quinary reciprocal system Li,Na,K//Cl,Br,NO_3.

Element of conversion graph	Stable salt pair	Element of singular star
Square	$LiNO_3 + KCl$ (Q_4)	pyramid
$Q_4 - Q_6 - Q_8 - Q_9$	$LiNO_3 + NaCl$ (Q_6)	$LiNO_3 - KCl - NaCl - NaBr - KBr$
	$LiNO_3 + NaBr$ (Q_8)	tetrahedra
	$LiNO_3 + KBr$ (Q_9)	$LiNO_3 - KCl - NaCl - KBr$
		$LiNO_3 - NaCl - NaBr - KBr$
Square	$KBr + NaNO_3$ (Q_2)	pyramid
$Q_2 - Q_5 - Q_7 - Q_9$	$KBr + NaCl$ (Q_5)	$KBr - LiNO_3 - LiCl - NaCl - NaNO_3$
	$KBr + LiCl$ (Q_7)	tetrahedra
	$KBr + LiNO_3$ (Q_9)	$KBr - LiNO_3 - LiCl - NaCl$
		$KBr - LiNO_3 - NaNO_3 - NaCl$
Square	$LiCl + NaBr$ (Q_3)	sphenoid
$Q_3 - Q_8 - Q_9 - Q_7$	$LiNO_3 + NaBr$ (Q_8)	$NaBr - KBr - LiNO_3 - LiCl$
	$LiNO_3 + KBr$ (Q_9)	
	$LiCl + KBr$ (Q_7)	
Triangle	$NaCl + KNO_3$ (Q_1)	tetrahedron-hemipyramid
$Q_1 - Q_5 - Q_6$	$KBr + NaCl$ (Q_5)	$LiNO_3 - KBr - NaCl - KNO_3$
	$NaCl + LiNO_3$ (Q_6)	

The salt compositions of the tetrahedra can be determined according to three procedures.

1. The procedure based on the thermochemical relations in a system. Individual squares and triangles of the conversion figure are considered. For each point of complete conversion, stable pairs and the corresponding stages of stable diagonals are written. For example, the point Q_4 for the conversion square $Q_4 - Q_6 - Q_8 - Q_9$ corresponds to the first-stage diagonal $LiNO_3 - KCl$, the point Q_6 corresponds to the second-stage diagonal $LiNO_3 - NaCl$, the point Q_8 corresponds to the third-stage diagonal $LiNO_3 - NaBr$, and the point Q_9 corresponds to the fourth-stage diagonal $LiNO_3 - KBr$. The $LiNO_3$ salt is repeated four times and, consequently, serves as the vertex of the pyramid, whose base is formed by the ternary reciprocal system Na,K//Cl,Br. The pyramid is composed of two tetrahedra, *viz.*, $LiNO_3 - KCl - NaCl - KBr$ and $LiNO_3 - NaCl - NaBr - KBr$, sharing the axial triangle $LiNO_3 - NaCl - KBr$. Analogously, the $LiNO_3 - NaNO_3 - NaCl - KBr$ and $LiNO_3 - LiCl - NaCl - KBr$ tetrahedra are determined from the conversion square $Q_2 - Q_5 - Q_7 - Q_9$.

2. The procedure based on chemical reactions described by conversion figures. By summing the reactions for points of complete conversion of ternary reciprocal systems, we obtain the reaction equation for the central point of the conversion square. For example, for the $Q_2 - Q_5 - Q_7 - Q_9$ square (see Fig. 16),

$$LiBr + KCl + NaBr + KCl + NaBr + KNO_3 + LiBr + KNO_3 =$$
$$= LiNO_3 + LiCl + 4\,KBr + NaCl + NaNO_3.$$

The salts formed in the reactions are placed at the vertices of the $KBr - LiNO_3 - LiCl - NaCl - NaNO_3$ pyramid, with the ternary reciprocal system Li,Na//Cl,NO_3 lying on its base. The salt

compositions of the tetrahedra involved in the pyramid can be derived from the reaction equations for the conversion triangles:

for the $Q_2-Q_5-Q_9$ triangle,

$$2\ KNO_3 + NaBr + NaBr + KCl + LiBr = \\ = 3\ KBr + LiNO_3 + NaCl + NaNO_3;$$

for the $Q_5-Q_7-Q_9$ triangle,

$$NaBr + LiBr + 2\ KCl + KNO_3 = \\ = 3\ KBr + LiNO_3 + NaCl + LiCl.$$

3. The geometric procedure.[8, 34] A fragment of the conversion figure, *viz*., a square or triangle, is displayed on the plane, and points of complete conversion are indicated. The conversion square is inscribed in a quadrangle (Fig. 17). The notations of salts common to each pair of points are placed at the vertices of the tetrahedron. For example, the NaBr salt is common to the points Q_3 and Q_8, $LiNO_3$ is common to the points Q_8 and Q_9, *etc*. The conversion triangle is inscribed in a tetrahedron parallel to one of its faces. A salt common to three points of complete conversion serves as a vertex of the resulting tetrahedron.

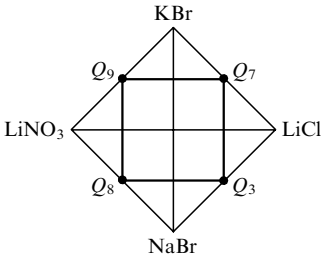


Figure 17. Geometric procedure for the determination of the salt compositions of the tetrahedra for the reciprocal system Li,Na,K// Cl,Br,NO_3 consisting of nine salts.

Once the salt compositions of the tetrahedra have been determined, the scheme of a singular star is constructed taking into account the reaction stages and constituents of the thermal effects.

The tetrahedra in the singular star are connected to each other in a particular manner. Schemes of singular stars of tetrahedra can be derived by analogy with singular stars of pentatopes.[8] Systems belonging to different topological types are characterised by different schemes (Fig. 18). In Fig. 18, the points correspond to the tetrahedron, and the line characterises the presence of three common salts involved in the tetrahedron. Hence, the triangle formed by stable diagonals serves as a connection unit between the tetrahedra.

Each topological type of a singular star of tetrahedra is characterised by a particular set of reaction stages.

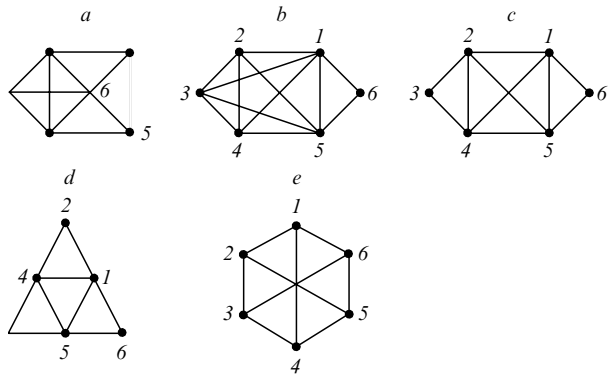


Figure 18. Schemes of singular stars of secant tetrahedra for quinary reciprocal systems of the topological types 9A (*a*), 9B (*b*), 9C (*c*), 9D (*d*) and 9E (*e*).

Schemes of connections between tetrahedra represent graphs with different arrangements of vertices corresponding to the topological type of the system. Analysis of such graphs allows one to reveal the reactivity of salts, which compose any tetrahedron of a singular star. The advantage of this procedure for the construction of graphs of singular stars of tetrahedra for systems of various topological types is that it clearly shows the relationships between the thermochemical relations, chemical reactions in the system as a whole and its constituents and the geometric elements of singular stars.

4. Proximate method for studying phase complexes of reciprocal salt systems in melts

According to Kurnakov's theory, the composition – property diagram of a system is formed at the intersection of the coordinate frame (the phase diagram of the system) with the phase complex. Triangulation methods allow one to construct a phase complex of a system after the construction and partitioning of the composition diagram.

The conversion method[6] enables one to study and construct phase diagrams of multicomponent reciprocal systems without preliminary investigation of the composition diagram, because conversion figures of secant elements can be constructed and analysed with the use of matrices of reciprocal salt pairs, sometimes without deducing singular and non-equilibrium stars.[8, 32, 33]

This method of studying phase complexes of reciprocal condensed systems reduces substantially the time of experimentation and, hence, is a proximate method, which allows one to solve a number of problems in serial technological investigations.[7] The essence of the method is that the minimum number of points in phase diagrams are studied experimentally. Differential thermal analysis (DTA) is used as the main method, which should be supplemented with methods for the determination of compositions of invariant points (zone melting, chemical analysis) and methods for the identification of phase compositions (powder X-ray diffraction analysis, microstructural analysis).

Investigation of a phase diagram is simplified due to a decrease in the amount of required data. With information only on binary systems and polymorphism of salts in hand, it is sufficient to study one point of complete conversion for a ternary reciprocal system. For quaternary reciprocal systems, two lines of complete conversion should be studied if experimental data on points of complete conversion of ternary reciprocal systems are available, and so forth.[11, 36]

The procedure for studying systems is as follows. Investigation of a ternary reciprocal system starts with the measurement of a thermogram of the point of complete conversion, *i.e*., the point corresponding to the equivalent ratio of a pair of salts, which have no ions in common. The thermogram is interpreted using data on the phase complex of binary systems.[36, 37] The first thermal effect corresponds to the onset of crystallisation of the phase, which crystallises at the point of complete conversion. The phase can be identified by microstructural analysis or otherwise. The second peak in the thermogram is assigned to co-crystallisation of the phases that form by the exchange reaction or complex formation. Data on binary systems give an indication of the irreversibly reciprocal character of a ternary reciprocal system, and the presence of two thermal effects in the thermogram confirms this suggestion. In this case, the temperatures of invariant points can be determined by thermographic analysis.[37]

In addition to the temperatures of invariant points, it is necessary to determine their compositions by zone melting followed by chemical analysis. Therefore, to reveal the phase complex of irreversibly reciprocal ternary systems, one needs to study several concentration points. Methods were developed for the calculation of crystallisation surfaces of ternary reciprocal systems and their sections.[38–42] Combinations of calculation and experimental methods were also used.[43–45]

The question about complexation in a ternary reciprocal system can also be solved using a thermogram for the point of

complete conversion, in which the thermal effects are observed. These effects accompany the following processes: the onset of crystallisation; co-crystallisation of a salt pair formed by an exchange reaction; co-crystallisation of a stable salt pair with a compound resulting from complexation.[37]

Thermograms of the points of complete conversion[11] are shown in Fig. 19. The Na,Ba//F,WO_4 system is irreversibly reciprocal, which was confirmed experimentally (Fig. 19 *a*). The Na,K//F,WO_4 system is complicated by the complexation process. The thermogram of the point of complete conversion of this system (Fig. 19 *b*) shows that the following competitive reactions proceed in the system

$$2\,KF + Na_2WO_4 = 2\,NaF + K_2WO_4,$$

$$3\,KF + Na_2WO_4 = 2\,NaF + KF\cdot K_2WO_4.$$

The compound is formed in the secondary reaction, which does not take place at the point of complete conversion. The overall phase complex of this system can be revealed by also studying points of incomplete conversion.[8, 11]

The conversion figure becomes more complicated as the number of components increases. Investigation of two lines of complete conversion, which include points of complete conversion of ternary reciprocal systems, is sufficient to obtain phase complexes of systems consisting of six salts.[46] The phase diagram of the Na,K,Ba//F,WO_4 system is shown in Fig. 20. The conversion lines *B*, *D* and *F* serve as the composition axis of this diagram. Based on analysis of the diagram, one can draw conclusions regarding the crystallisation volumes in the system under consideration, exchange and complexation reactions and invariant points.

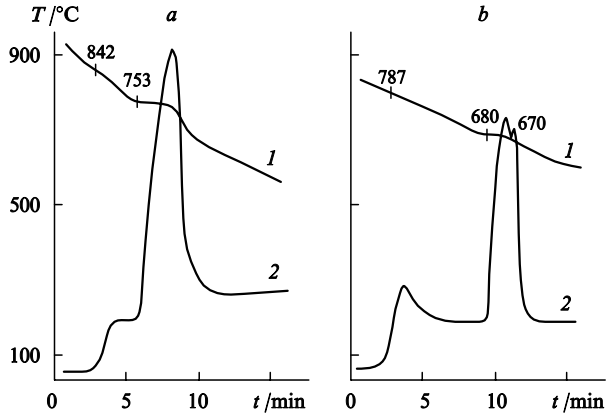


Figure 19. Thermograms of the points of complete conversions of the Na,Ba//F,WO_4 (*a*) and K,Ba//F,WO_4 (*b*) systems.
(*1*) Thermal analysis, (*2*) DTA.

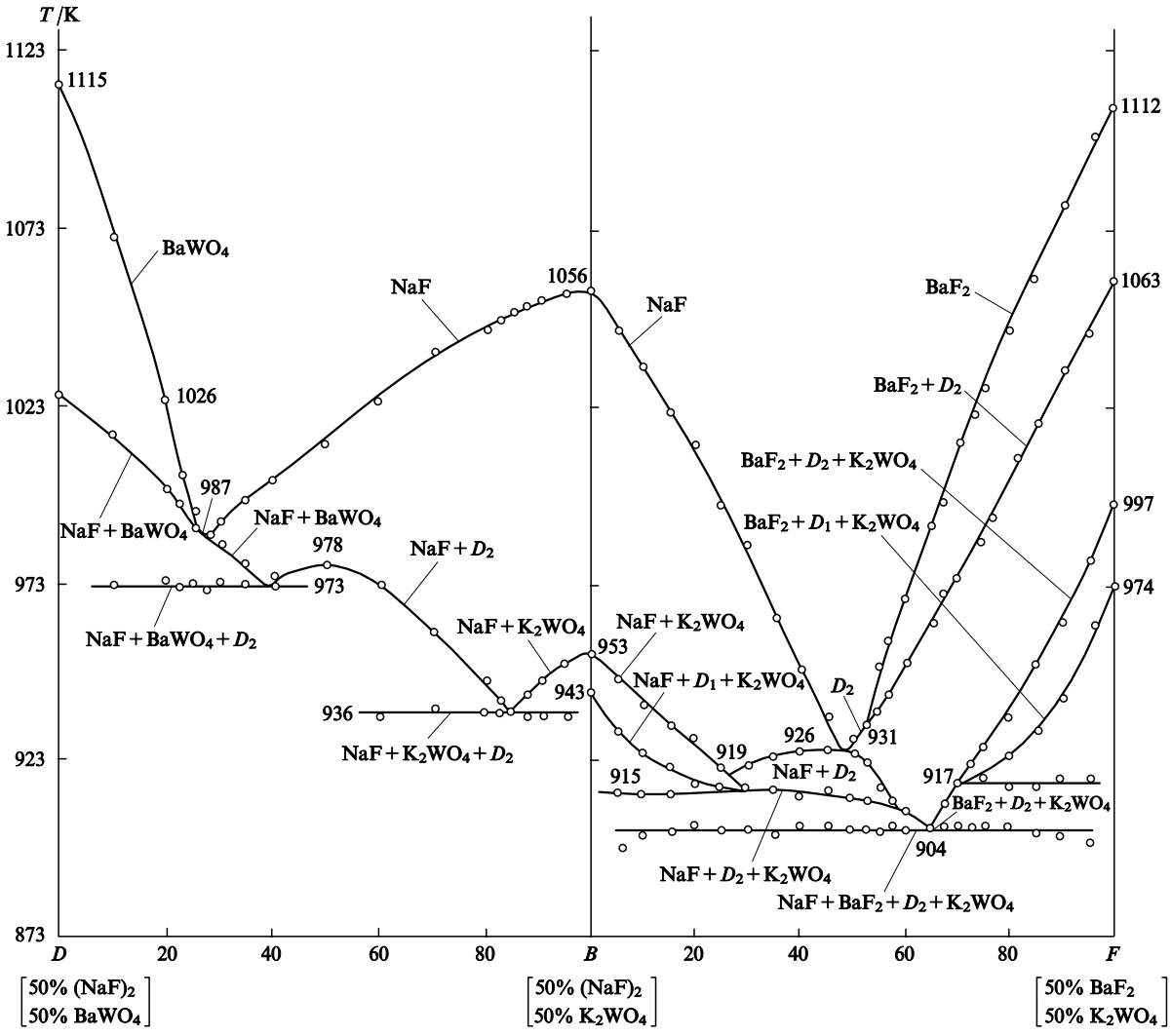


Figure 20. Temperature–composition diagram for the quaternary reciprocal system Na,K,Ba//F,WO_4.[11]
The composition axis represents the conversion lines *B*–*D* and *B*–*F* (see Fig. 2 *b*), $D_1 = KF\cdot K_2WO_4$, $D_2 = K_2WO_4\cdot BaWO_4$.

For example, the BaF_2, $BaWO_4$ and NaF salts are characterised by the largest volumes in the Na,K,Ba//F,WO_4 system. Experimental study of the conversion lines demonstrated that the following reactions occur in the system containing metastable salts in a stoichiometric ratio:

$$2\,KF + BaWO_4 = BaF_2 + K_2WO_4,$$

$$2\,KF + Na_2WO_4 = 2\,NaF + K_2WO_4,$$

$$BaF_2 + Na_2WO_4 = 2\,NaF + BaWO_4,$$

$$2\,KF + 2\,BaWO_4 = BaF_2 + K_2WO_4 \cdot BaWO_4,$$

$$3\,KF + Na_2WO_4 = 2\,NaF + KF \cdot K_2WO_4.$$

The $B-D$ line in Fig. 20 intersects the crystallisation fields of sodium fluoride, as evidenced by two branches of primary crystallisation intersecting at the point with coordinates 987 K and 27.5% of B. This point lies on the curve, which separates the crystallisation fields of NaF and $BaWO_4$ (Fig. 21). The curves of secondary crystallisation ($NaF + BaWO_4$), ($NaF + K_2WO_4 \cdot BaWO_4$) and ($NaF + K_2WO_4$) intersect at two points with the following coordinates: 973 K, 38.5% of B; and 936 K, 84% of B. These points correspond to quasiternary eutectics in the plane of the $(NaF)_2 - BaWO_4 - K_2WO_4$ triangle.

At 50% of B, a minimum is observed at 978 K in the curve of secondary crystallisation, and only two phases, *viz*., sodium fluoride and $K_2WO_4 \cdot BaWO_4$, are observable (see Fig. 20).

The results of powder X-ray diffraction analysis of the points of co-crystallisation of three phases on the $B-D$ line with $B > 50\%$ demonstrated that the following phases occur on this line: NaF, $K_2WO_4 \cdot BaWO_4$ and K_2WO_4. For melts with $B < 50\%$, the NaF, $K_2WO_4 \cdot BaWO_4$ and $BaWO_4$ phases were detected. The central point of the conversion line is characterised by crystallisation of two phases, *viz*., NaF and $K_2WO_4 \cdot BaWO_4$.

On the whole, the conversion lines and, consequently, the $(NaF)_2 - K_2WO_4 - BaWO_4$ triangle correspond to four phases, *viz*., NaF, K_2WO_4, $K_2WO_4 \cdot BaWO_4$ and $BaWO_4$ (see Figs 20, 21).

The $B-D$ line of complete conversion lies in the plane of the diagonal triangle $(NaF)_2 - K_2WO_4 - BaWO_4$, whose vertices correspond to salts formed by exchange reactions in the Na,K,Ba//F,WO_4 system. By summing the equations of the exchange reactions for the points B and D, we obtain the equation for the conversion line $B-D$.

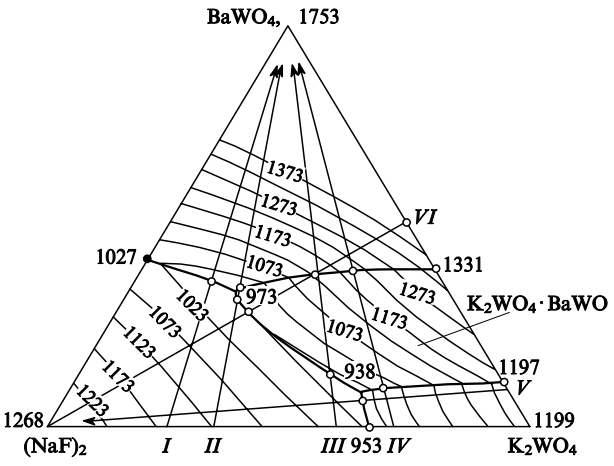


Figure 21. Phase diagram of the secant triangle $(NaF)_2 - BaWO_4 - K_2WO_4$ of the Na,K,Ba//F,WO_4 system.
Here and in Fig. 22, the temperatures are given in Kelvin (K); $I-VI$ denote the sections studied.

For the point B:

$$2\,KF + Na_2WO_4 = 2\,NaF + K_2WO_4,$$

for the point D:

$$BaF_2 + Na_2WO_4 = 2NaF + BaWO_4.$$

The following reaction corresponds to the central point of the $B-D$ line:

$$2\,KF + BaF_2 + 2\,Na_2WO_4 = 4\,NaF + K_2WO_4 + BaWO_4. \quad (10)$$

The data on the boundary elements show that K_2WO_4 and $BaWO_4$ taken in a ratio of 1:1 form the highly stable $K_2WO_4 \cdot BaWO_4$ compound

$$K_2WO_4 + BaWO_4 = K_2WO_4 \cdot BaWO_4. \quad (11)$$

By summing the latter two equations, we obtain

$$2\,KF + BaF_2 + 2\,Na_2WO_4 = 4\,NaF + K_2WO_4 \cdot BaWO_4. \quad (12)$$

Therefore, the following two phases should correspond to the central point of the conversion line $B-D$: NaF and $K_2WO_4 \cdot BaWO_4$. These compounds are stable products of exchange and complexation reactions.

The following equation is true for any other point of the conversion line $B-D$:

$$x(KF)_2 + (1-x)\,BaF_2 + Na_2WO_4 = (NaF)_2 + x\,K_2WO_4 + (1-x)\,BaWO_4. \quad (13)$$

Let us consider two cases: $x > 0.5$ and $x < 0.5$. Let $x = 0.6$. By summing the equations, we obtain

$$0.6(KF)_2 + 0.4BaF_2 + Na_2WO_4 = (NaF)_2 + 0.6K_2WO_4 + 0.4BaWO_4$$

$$0.4K_2WO_4 + 0.4BaWO_4 = 0.4(K_2WO_4 \cdot BaWO_4)$$

$$0.6(KF)_2 + 0.4BaF_2 + Na_2WO_4 = (NaF)_2 + 0.2K_2WO_4 + 0.4(K_2WO_4 \cdot BaWO_4).$$

Therefore, three phases, *viz*., NaF, K_2WO_4 and $K_2WO_4 \cdot BaWO_4$, should be observed at points on the conversion line $B-D$ with $B > 50\%$. This is consistent with the experimental data.

Let $x = 0.4$. Then

$$0.4(KF)_2 + 0.6BaF_2 + Na_2WO_4 = (NaF)_2 + 0.4K_2WO_4 + 0.6BaWO_4$$

$$0.4K_2WO_4 + 0.4BaWO_4 = 0.4(K_2WO_4 \cdot BaWO_4)$$

$$0.4(KF)_2 + 0.6BaF_2 + Na_2WO_4 = (NaF)_2 + 0.2BaWO_4 + 0.4(K_2WO_4 \cdot BaWO_4).$$

Hence, the NaF, $BaWO_4$ and $K_2WO_4 \cdot BaWO_4$ phases should be detected at the points on the conversion line $B-D$ with $B < 50\%$.

In addition to exchange reactions, the complexation reactions giving rise to the $KF \cdot K_2WO_4$ compound correspond to the conversion points B and F (see Fig. 20).

For the point B:

$$3\,(KF)_2 + 2\,Na_2WO_4 = 2\,(NaF)_2 + 2\,(KF \cdot K_2WO_4),$$

for the point F:

$$3\,(KF)_2 + 2\,BaWO_4 = 2\,BaF_2 + 2\,(KF \cdot K_2WO_4).$$

The following reaction corresponds to the central point of the conversion line $B-F$:

$$6\,(KF)_2 + 2\,BaWO_4 + 2\,Na_2WO_4 = \\ = 2\,(NaF)_2 + 2\,BaF_2 + 4\,(KF\cdot K_2WO_4)$$

or

$$3\,(KF)_2 + BaWO_4 + Na_2WO_4 = \\ = (NaF)_2 + BaF_2 + 2\,(KF\cdot K_2WO_4).$$

For any point on the $B-F$ line, the complex formation is described by the equation

$$3\,(KF)_2 + 2(1-x)\,BaWO_4 + 2x\,Na_2WO_4 = \\ = 2x\,(NaF)_2 + 2\,(KF\cdot K_2WO_4) + 2(1-x)\,BaF_2\,.$$

The reaction affords sodium fluoride, barium fluoride and $KF\cdot K_2WO_4$ for all x varying from 0 to 1.

However, the field of the $KF\cdot K_2WO_4$ compound is not observed in the plane of the diagonal triangle $(NaF)_2-BaF_2-K_2WO_4$ (Fig. 22), which is intersected by the conversion line $B-F$. From this it follows that a stable diagonal section with the $BaF_2-(NaF)_2$ edge and the third vertex $KF\cdot K_2WO_4$ should be present in the composition prism. This triangle was examined by the visual polythermal method.[46] The liquidus surface of this triangle consists of three crystallisation fields, *viz*., $(NaF)_2$, BaF_2 and $KF\cdot K_2\,WO_4$, intersecting at the point of crystallisation of three phases (a quasiternary eutectic point).

As can be seen from the phase diagrams of the conversion lines of the Na,K,Ba//F,WO_4 system, the central part of the composition prism includes the crystallisation volumes of stable components, which are products of exchange and complexation reactions: NaF, BaF_2, $BaWO_4$, K_2WO_4, $KF\cdot K_2WO_4$ and $K_2WO_4\cdot BaWO_4$.

The starting KF and Na_2WO_4 salts are absent in the phase diagrams, because they are metastable components and are consumed in the reaction.

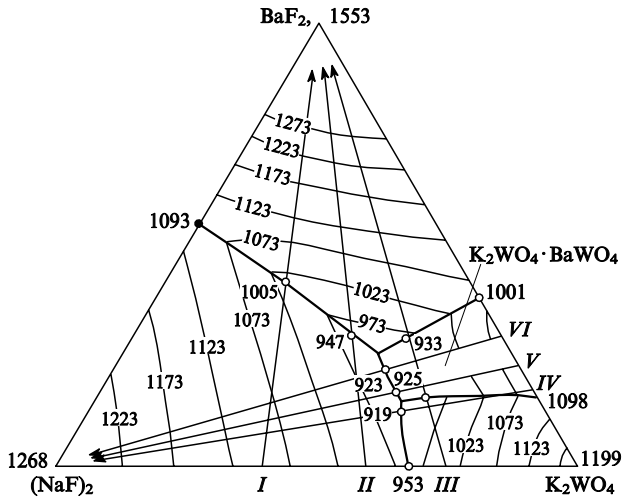


Figure 22. Phase diagram of the secant triangle $(NaF)_2-BaF_2-K_2WO_4$ of the Na,K,Ba//F,WO_4 system.

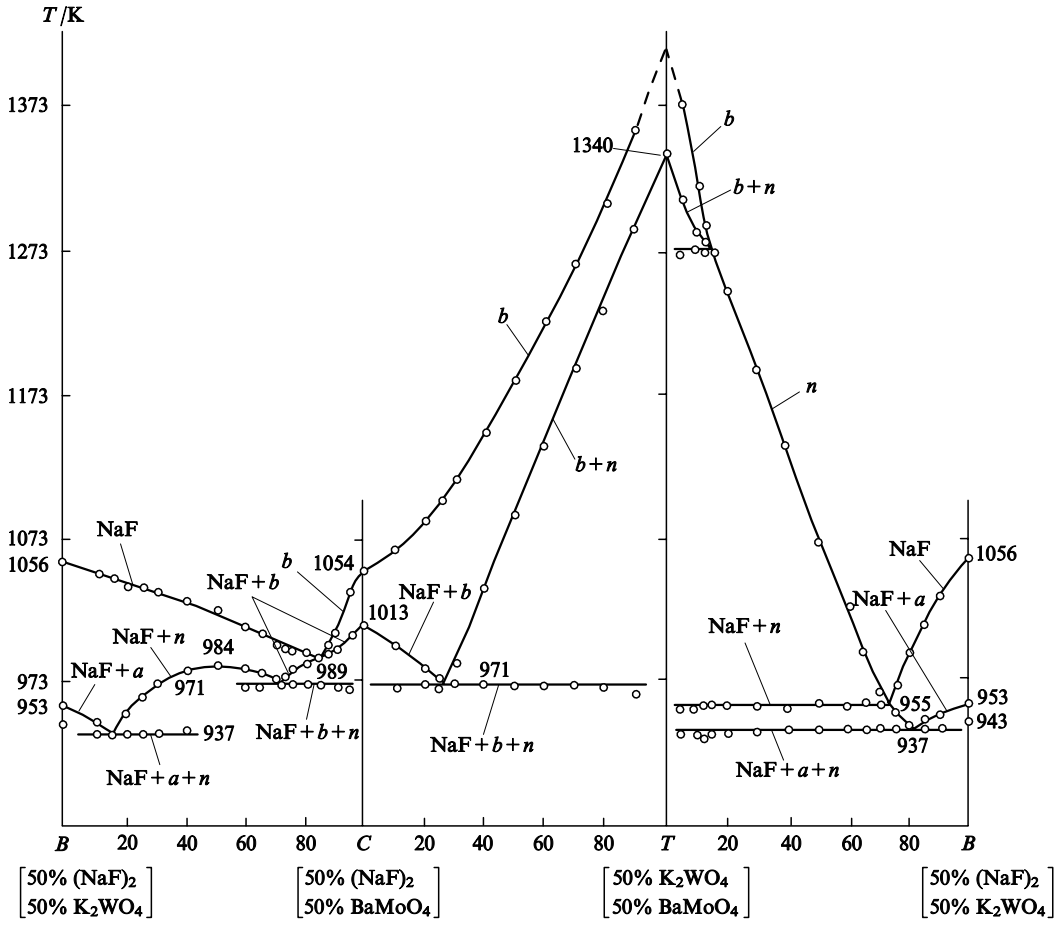


Figure 23. Temeprature–composition diagram for the quinary reciprocal system Na,K,Ba//F,MoO_4,WO_4.[11]
The composition axis represents the conversion lines $B-C$, $B-T$ and $C-T$ (see Fig. 10).

It should be noted that, in addition to two ternary invariant points, a quaternary eutectic point is present in the conversion lines.

The conversion figure of secant tetrahedra of quinary reciprocal systems consisting of nine salts represents a polythermal section and, consequently, the phase diagram of the system.

The conversion figure of the 9B ⇄ 9A-type quinary reciprocal system Na,K,Ba//F,MoO_4,WO_4 consisting of nine salts is shown in Fig. 10. The inner lines $C-T$, $B-T$ and $F-A$, $B-C$ of the conversion graph differ from other lines [46] in that the lines making up the conversion graph belong to none of the six prisms of the quaternary reciprocal systems, which bound the composition polytope of the quinary reciprocal system, and lie in the planes of the stable and non-equilibrium axial triangles.

The $B-C$, $B-T$ and $C-T$ lines intersect the stable axial triangle of the quinary reciprocal system Na,K,Ba//F,MoO_4,WO_4, and the $F-A$ line intersects the non-equilibrium triangle of this system.[46] Consequently, the crystallising phases involving all six ions correspond to these four lines. Hence, the lines were assigned to the quinary reciprocal system.

The $B-C$ line in Fig. 23 intersects the crystallisation volumes of NaF and the phase b (the $BaMoO_4-BaWO_4$ solid solution), as evidenced by two branches of primary crystallisation intersecting at the point with coordinates 989 K and 15.5% of B [the composition: 50% $(NaF)_2$, 43% $BaMoO_4$ and 7% K_2WO_4]. The curve of secondary crystallisation consists of the following three branches: NaF + a, NaF + b and NaF + n (a, the $K_2MoO_4-K_2WO_4$ solid solutions; b, the $BaMoO_4-BaWO_4$ solid solutions; n, the $K_2MoO_4\cdot BaMoO_4-K_2WO_4\cdot BaWO_4$ solid solutions). These branches intersect at the eutectic points of three phases: at 937 K and 28.5% B [33% $(NaF)_2$, 10% $BaMoO_4$ and 57% K_2WO_4], the solid phases NaF, a and n; at 971 K and 85% B [44% $(NaF)_2$, 39.5% $BaMoO_4$ and 16.5% K_2WO_4], the solid phases NaF, b and n.

The curve of secondary crystallisation has a maximum at 984 K and 50% B [44% $(NaF)_2$, 28% $BaMoO_4$ and 28% K_2WO_4], the solid phases NaF and n.[46] In Fig. 23, the conversion line $C-T$ intersects the crystallisation volume of the phase b, as evidenced by the curve of primary crystallisation (without extremes). Secondary crystallisation is represented by two branches, *viz.*, NaF – phase b and $n + b$, intersecting at the eutectic point of crystallisation of three phases, *viz.*, NaF, b and n (at 971 K and 27% T). The conversion line $B-T$ intersects the crystallisation volumes of NaF and the phases b and n. The branches of primary crystallisation intersect at two points with coordinates 1271 K and 15% B [7.5% $(NaF)_2$, 42.5% $BaMoO_4$ and 50% K_2WO_4], the solid phases b and n; and 955 K and 63% B [37% of $(NaF)_2$, 13% $BaMoO_4$ and 50% K_2WO_4], the solid phases NaF and n.

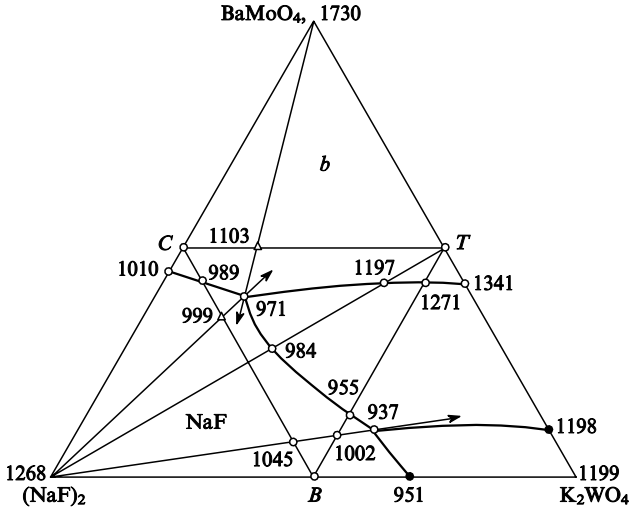


Figure 24. Phase diagram of the stable axial triangle $(NaF)_2-BaMoO_4-K_2WO_4$ of the Na,K,Ba//F,MoO_4,WO_4 system. Temperatures are given in Kelvin (K).

The phase diagram of the overall stable axial triangle can be constructed based on the data corresponding to the conversion lines $B-T$, $C-T$ and $B-C$ (Fig. 24).[11]

5. Stable tetrahedra of quinary reciprocal systems consisting of nine salts

The salt compositions of all tetrahedra of a singular star can be determined from a conversion figure of secant tetrahedra for quinary reciprocal systems of nine salts belonging to any topological type. Each point of the conversion figure of this system corresponds to an exchange reaction between stable and metastable salt pairs located at the vertices of the conversion graph.

The chemical interaction in the system under consideration can be described by reaction equations for the points lying in the planes of the conversion figure. Based on these equations, the crystallising phases in stable secant tetrahedra can be predicted.

The $A-B-C-D$ square of the conversion figure for the Na,K,Ba//F,MoO_4,WO_4 system is shown in Fig. 25. The equation for the central point of this square has the form

$$2(KF)_2 + 2Na_2MoO_4 + 2Na_2WO_4 + 2BaF_2 = 4(NaF)_2 + K_2MoO_4 + K_2WO_4 + BaMoO_4 + BaWO_4. \quad (14)$$

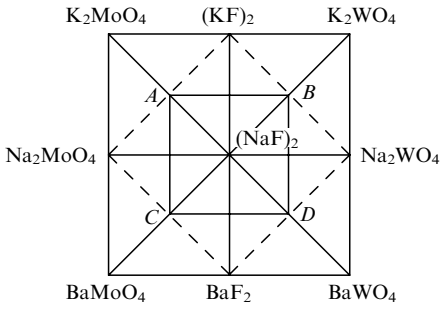


Figure 25. Conversion square $A-B-D-C$ (a fragment of the conversion figure) for the quinary reciprocal system Na,K,Ba//F,MoO_4,WO_4.

The right-hand side of this equation includes a metastable pair of salts, which react according to the equation

$$BaWO_4 + K_2MoO_4 = BaMoO_4 + K_2WO_4. \quad (15)$$

By summing Eqns (14) and (15), we obtain

$$2(KF)_2 + 2Na_2MoO_4 + 2Na_2WO_4 + 2BaF_2 = 4(NaF)_2 + 2BaMoO_4 + 2K_2WO_4. \quad (16)$$

Analysis of the data on the boundary elements demonstrated that crystallisation of $BaMoO_4$ and K_2WO_4 (taken in equivalent amounts) affords the phase n, *viz.*, the solid solutions of the $K_2MoO_4\cdot BaMoO_4-K_2WO_4\cdot BaWO_4$ compounds. Consequently, the latter reaction produces the phases NaF and n.

The central point of the conversion square $A-B-D-C$ coincides with the central point of the conversion line $B-C$ (see the diagrams of the conversion lines $B-T$, $C-T$ and $C-B$, Fig. 23). For this point, crystallisation of the phases NaF and n (the $K_2MoO_4-BaMoO_4$ and $K_2WO_4-BaWO_4$ solid solutions) was established experimentally. This fact is in complete agreement with the prediction of phases formed according to the above-given equation taking into account the data on the boundary elements.

The conversion square $A-B-D-C$ is divided by the $B-C$ line (the diagonal of the conversion square) into two triangles, $A-B-C$ and $B-D-C$. Each triangle is characterised by its own equation of the exchange reaction (Fig. 26).

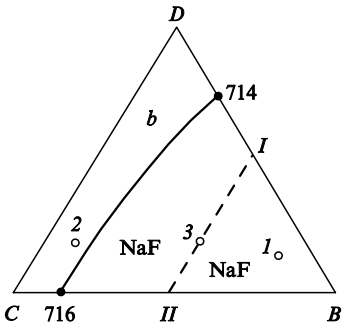


Figure 26. Phase diagram of a system represented by the conversion triangle $B-C-D$.

The composition of each point of the $B-C-D$ triangle can be expressed by the ratio between the B, C and D components, which reflect the transformation of a metastable salt pair into a stable pair. On the whole, the equation of exchange reactions for each point of the $B-C-D$ triangle can be written as follows:

$$x(Na_2MoO_4 + BaF_2) + y[(KF)_2 + Na_2WO_4] +$$
$$+ (1-x-y)(BaF_2 + Na_2WO_4) = x[BaMoO_4 + (NaF)_2] +$$
$$+ y[(NaF)_2 + K_2WO_4] + (1-x-y)[(NaF)_2 + BaWO_4].$$

After simple algebraic transformations, we obtain

$$x\,Na_2MoO_4 + (1-y)\,BaF_2 + y\,(KF)_2 + (1-x)Na_2WO_4 = \quad (17)$$
$$= (NaF)_2 + x\,BaMoO_4 + y\,K_2WO_4 + (1-x-y)\,BaWO_4.$$

Therefore, the exchange reactions afford stable salts located at the vertices of the secant tetrahedron, which is intersected by the conversion triangle $B-C-D$ (see Fig. 26). Let us analyse the possible reaction products for points on this triangle. Experimental studies demonstrated that the crystallisation surface of this triangle is represented by the fields of sodium fluoride and the phase b.

The triangle can be divided by the $I-II$ line, which connects the saddle points of the conversion lines $B-C$ and $B-D$, into two regions, $B-II-I$ and $I-II-C-D$. Particular stable phases correspond to both regions of the conversion triangle and the $I-II$ line. These phases are formed in the course of crystallisation of the products of the exchange reaction described by Eqn (17).

For each point of the $B-II-I$ region ($y > 0.5$, $x < 0.5$), the composition can be expressed as follows: y is the amount of the component B, x is the amount of the component C, the amount of the component D is $1-x-y$. Let us consider the arbitrarily chosen point 1, for which $x = 0.1$ and y = 0.7. The equation for this point has the form

$$0.1\,Na_2MoO_4 + 0.3\,BaF_2 + 0.7\,(KF)_2 + 0.9\,Na_2WO_4 = \quad (18)$$
$$= (NaF)_2 + 0.1\,BaMoO_4 + 0.2\,BaWO_4 + 0.7\,K_2WO_4.$$

If the $BaMoO_4 + BaWO_4$ and K_2WO_4 products are present in a ratio corresponding to the right-hand side of this equation, complete crystallisation affords the phases n (the $K_2MoO_4-BaMoO_4$ and $K_2WO_4-BaWO_4$ solid solutions) and a (the $K_2MoO_4-K_2WO_4$ solid solutions), as is obvious from the data on the boundary elements. Therefore, the following final reaction products correspond to the points in the $B-II-I$ region: NaF, the $K_2MoO_4-BaMoO_4$ and $K_2WO_4-BaWO_4$ solid solutions and the $K_2MoO_4-K_2WO_4$ solid solutions. For the point *2* in the $I-II-C-D$ region ($y < 0.5$) at $x = 0.7$ and $y = 0.1$, the equation has the form

$$0.7\,Na_2MoO_4 + 0.9\,BaF_2 + 0.1\,(KF)_2 + 0.3\,Na_2WO_4 = \quad (19)$$
$$= (NaF)_2 + 0.7\,BaMoO_4 + 0.2\,BaWO_4 + 0.1\,K_2WO_4.$$

At the above-mentioned ratio between the $BaMoO_4 + BaWO_4$ and K_2WO_4 products, crystallisation affords the phases NaF, b and n, as indicated by the data on the boundary elements. For the point *3* on the $I-II$ line ($y = 0.5$, $x = 0.5$) at $y = 0.5$, $x = 0.3$, the equation has the form

$$0.3\,Na_2MoO_4 + 0.5\,BaF_2 + 0.5\,(KF)_2 + 0.7\,Na_2WO_4 = \quad (20)$$
$$= (NaF)_2 + 0.3\,BaMoO_4 + BaWO_4 + 0.5\,K_2WO_4.$$

If $BaMoO_4 + BaWO_4$ and K_2WO_4 are present in equivalent amounts, crystallisation yields only the phase n. Consequently, the reaction affords NaF and n for all points on the $I-II$ line.

On the whole, the conversion triangle $B-C-D$ corresponds to products of the chemical reaction, *viz*., the phases NaF, b and n. This fact was confirmed experimentally.[46] Hence, the secant tetrahedron $(NaF)_2-BaMoO_4-BaWO_4-K_2WO_4$ corresponds to the crystallisation volumes of NaF, a, b and n (Fig. 27) intersecting along univariant curves. Quaternary invariant points are lacking.

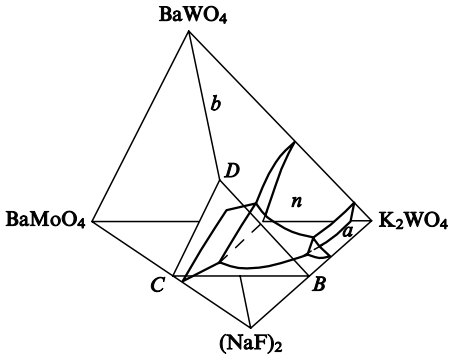


Figure 27. Crystallisation volumes of the $(NaF)_2-BaWO_4-K_2WO_4-BaMoO_4$ tetrahedron of the Na,K,Ba//F,MoO_4,WO_4 system.

The above-considered procedure can be used for determining the salt compositions and crystallisation volumes of all six secant tetrahedra of any quinary reciprocal system.[16,46]

V. Practical applications of multicomponent salt melts

The use of melts in various technological processes has attracted increasing attention in recent years. Considerable interest in molten salt systems as reaction media is associated with their specific properties, among which are their ability to dissolve many organic and inorganic compounds. Besides, these systems can intensify processes due to high heat- and mass-transfer coefficients, thermal conductivity and heat transfer; reacting compounds in these systems can occur in oxidation states, which are inaccessible in typical solutions; the density and viscosity of such reaction media are relatively low; the reaction products can easily be separated from the reaction mixtures; water as a solvent can completely be excluded from the technological scheme. (The growing problem of water deficiency needs urgent attention; hence, the above-mentioned possibilities are not only of scientific interest but are also sometimes technologically and economically advantageous.)

Electrochemistry, metallurgy and electrometallurgy are traditional areas of application of molten salt media. They also have promising applications in fuel cells and high-temperature information transformers, in single-crystal growth of optical materials and ferroelectric materials, in nuclear technology, as nuclear fuel, and as claddings for thermonuclear reactors. Inorganic synthesis in molten salts is yet another promising area of application of salt melts.[12] In many cases, reactions in molten salts proceed faster

and afford the target products in higher yields because of the highest possible concentrations of the reagents, one of which is the melt.[12]

The diversity of inorganic salts, all the more their mixtures, makes it possible to prepare a wide range of molten salt systems and, consequently, to carry out various syntheses in these media.[4,16–18,47] Actually, all main types of chemical reactions, *viz*., exchange, acid–base, redox and complexation reactions, have been performed in these media.

Systems containing eutectic composites, which are characterised by the constant melting points and compositions, are of great scientific interest. The melting points of the starting components of such systems decrease substantially already in binary systems.[48] In ternary systems, the melting points continue to decrease, the rate of decrease in the melting point being lower in quaternary systems. Nevertheless, even a slight decrease in the temperature of a eutectic composite (by 15–20 °C) may be of considerable practical importance for technological purposes.

Among salt melts, multicomponent reciprocal systems are of special interest. Reciprocal systems consisting of 4, 5, 6 or 7 components are the most difficult to study by methods of physicochemical analysis. These systems can be used for preparing materials possessing the desired combinations of properties, which is an important problem of applied chemistry. Hence, the rational choice of salt compositions is of considerable importance in improving conditions for the preparation of substances possessing the required characteristics.

1. Thermal chemical power sources

Ionic melts have found wide application in high-temperature power sources.[12]

Aqueous electrolytes are unsuitable for the construction of thermal chemical power sources, because certain electrode materials (alkali and alkaline-earth metals, halides) react with water. Salt melts serve as convenient electrolytes in high-temperature power sources.[13]

A molten electrolyte satisfying these requirements was designed on the basis of the quaternary reciprocal system Li,K,Ni//Cl,SO_4. The challenge was to find a low-melting electrolyte consisting of stable phases and exhibiting the required properties to use in chemical power sources.[13–15]

A procedure for revealing stable salt mixtures, which are modelled by tetrahedral simplexes in the composition diagram of a multicomponent system, and a procedure for the estimation of stability of such mixtures were described.[49]

A salt mixture is assumed to be stable, if the phase diagram obtained after heating the mixture above the melting point followed by crystallisation, includes crystallisation fields of salts produced by exchange reactions and crystallisation fields of double compounds formed by these salts, which are stable in the temperature range under consideration. A mixture is assumed to be metastable if the phase diagram has fields of the starting reactive salts involved in exchange reactions with each other and crystallisation fields of metastable double compounds, which decompose in the temperature range under consideration to yield reactive salts.

The procedure involves the following steps.

1. A composition figure of a multicomponent system is partitioned using one of the simplest procedures[11] with the aim of revealing tetrahedral simplexes, *i.e*., determining their salt compositions.

2. The possibilities of exchange reactions and complex formation for salts of each salt mixture are examined and estimated from the thermodynamical standpoint. It is most reasonable to study the regions of the conversion figure involved in this simplex.

3. If experimental data on the boundary subsystems are available, stability of the subsystems is estimated. Mixtures of three salts, which are modelled by triangles of ternary reciprocal systems, triangulating sections of quaternary reciprocal systems, *etc*., can serve as boundary subsystems of tetrahedra in reciprocal multicomponent systems consisting of six salts.

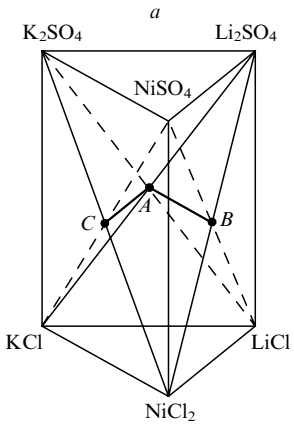
4. The stability of a salt mixture as a whole, which is modelled by a tetrahedron, is estimated from the data obtained in stages 2 and 3. If the mixture is estimated as metastable, further triangulation of the composition diagram is carried out and all of the procedure is repeated.

Let us apply this procedure to the quaternary reciprocal system Li,K,Ni//Cl,SO_4,[13] whose composition prism is divided into three tetrahedral simplexes by two triangular sections. The geometric partitioning is based on exchange reactions between the starting salts. The salt compositions of the tetrahedra can be determined from the matrix of reciprocal salt pairs with an inscribed conversion figure.[8] The composition prism of the quaternary reciprocal system Li,K,Ni//Cl,SO_4 along with the conversion figure $B-A-C$, the matrix of reciprocal salt pairs and the matrix of vertex indices is presented in Fig. 28. The stable tetrahedra of the singular star of the Li,K,Ni//Cl,SO_4 system are extracted from the matrix of reciprocal salt pairs:

$(LiCl)_2-(KCl)_2-NiCl_2-Li_2SO_4$,

$(KCl)_2-K_2SO_4-NiSO_4-Li_2SO_4$,

$NiCl_2-(KCl)_2-NiSO_4-Li_2SO_4$.



b

6	LiCl	KCl	$NiCl_2$
Li_2SO_4	0	1 *B*	1 *A*
K_2SO_4	0	0	0
$NiSO_4$	0	1 *C*	0

c

6	Cl	SO_4	∑
Li	0	2	2
K	2	0	2
Ni	1 [a]	1 [b]	2
∑	3	3	6

Figure 28. Models of the quaternary reciprocal system Li,Ni,K//Cl,SO_4. (*a*) The composition prism, (*b*) the matrix of reciprocal salt pairs with an inscribed conversion graph, (*c*) the matrix of vertex indices.

To predict stable phases crystallising from melts, the $(LiCl)_2-(KCl)_2-NiCl_2-Li_2SO_4$ tetrahedron with the conversion line $A-B$ was chosen (Fig. 29).[14]

The choice of the $(LiCl)_2-(KCl)_2-NiCl_2-Li_2SO_4$ tetrahedron was governed by the requirements imposed on chemical power sources. The stability of each boundary subsystem and the tetrahedron as a whole can be estimated from the morphological characteristics of the liquidus surface and the thermochemical relations in the quaternary reciprocal system Li,K,Ni//Cl,SO_4.

The $(KCl)_2-NiCl_2-Li_2SO_4$ face (Fig. 29). The conversion line $A-B$ intersecting the face reflects the exchange reactions in the Li,K,Ni//Cl,SO_4 system formed at the intersection of the stable triangle $(KCl)_2-NiCl_2-Li_2SO_4$ of a singular star with the corresponding metastable triangle $(LiCl)_2-NiSO_4-K_2SO_4$ of a non-equilibrium star.[14]

By summing the exchange reactions for the points of complete conversion A and B of the ternary reciprocal systems Li,K//Cl,SO_4 and Li,Ni//Cl,SO_4, we obtain

for the point A: $(LiCl)_2 + NiSO_4 = NiCl_2 + Li_2SO_4$

for the point B: $(LiCl)_2 + K_2SO_4 = (KCl)_2 + Li_2SO_4$

$$2\,(LiCl)_2 + NiSO_4 + K_2SO_4 = NiCl_2 + 2\,Li_2SO_4 + (KCl)_2\,. \quad (21)$$

This is the equation for the central point of the conversion line $A-B$. As can be seen from Eqn (21), the exchange equilibrium is shifted toward stable phases of the components of the face under consideration.

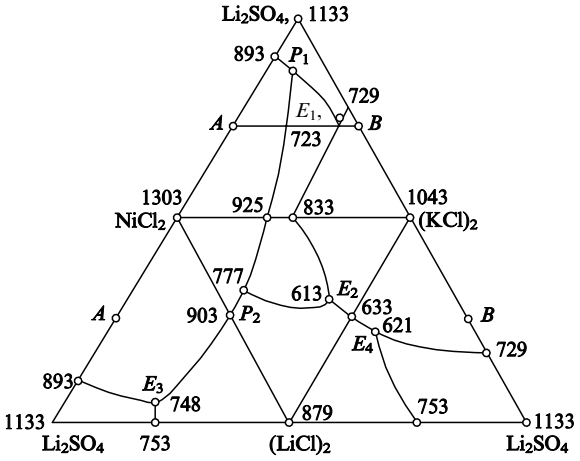


Figure 29. Development of the stable $(LiCl)_2-NiCl_2-Li_2SO_4-(KCl)_2$ tetrahedron of the quaternary reciprocal system Li,Ni,K//Cl,SO_4. The temperatures are given in Kelvin (K).

In addition to the exchange reaction, complex formation occurs in the Li,Ni//Cl,SO_4 system

$$(KCl)_2 + NiCl_2 = 2\,[KCl\cdot NiCl_2]. \quad (22)$$

By summing Eqns (21) and (22), we obtain

$$2\,(LiCl)_2 + NiSO_4 + K_2SO_4 + NiCl_2 = 2\,Li_2SO_4 + 2\,[KCl\cdot NiCl_2]. \quad (23)$$

The face of the $(KCl)_2-NiCl_2-Li_2SO_4$ tetrahedron is estimated as stable. Actually, the experiment gave the eutectic E_1 at 723 K and 51 mass% Li_2SO_4, 42 mass% KCl, 7 mass% $NiCl_2$ (see Fig. 29). The transition point P_1 has the following composition: 74 mass% Li_2SO_4, 13 mass% KCl and 13 mass% $NiCl_2$; the temperature is 833 K. The crystallisation surface of the $(KCl)_2-NiCl_2-Li_2SO_4$ system (the face of the tetrahedron) consists of the following four crystallisation fields: KCl, $NiCl_2$, Li_2SO_4 and $KCl\cdot NiCl_2$.[14]

The $(LiCl)_2-NiCl_2-Li_2SO_4$ face. As can be seen from Fig. 29, the point of complete conversion, which corresponds to the exchange reaction proceeding in the ternary reciprocal system Li,Ni//Cl,SO_4 [Eqns (21) and (23)], is located on the edge of the face. According to Eqn (21), $NiCl_2$ and Li_2SO_4 are stable phases. From the table of vertex indices, it follows that these salts are characterised by the highest indices. This prediction was confirmed experimentally. The crystallisation fields of the melting diagram converge at the eutectic point E_3 with coordinates 748 K, 45 mass% LiCl, 49.6 mass% Li_2SO_4 and 5.4 mass% $NiCl_2$. The LiCl, $NiCl_2$ and Li_2SO_4 compounds are solid phases.

The $(LiCl)_2-(KCl)_2-Li_2SO_4$ face. The exchange reaction giving rise to a stable pair of Li_2SO_4 and KCl salts [Eqn (21)], which are not involved in complex formation with the reactive K_2SO_4 and LiCl salts, occurs at the point of complete conversion B of the ternary reciprocal system Li,K//Cl,SO_4. The crystallisation surface of this system consists of crystallisation fields of the components; the eutectics occur at 621 K, 42 mass% LiCl, 50.5 mass% KCl and 7.5 mass% Li_2SO_4; LiCl, Li_2SO_4 and KCl are solid phases. Apparently, this section is stable (see Fig. 29).

The $(KCl)_2-NiCl_2-(LiCl)_2$ face. The melting diagram of the system was studied only partially because of decomposition of the mixtures containing large amounts of nickel chloride. The crystallisation surface of the $(KCl)_2-NiCl_2-(LiCl)_2$ system consists of four fields[14] belonging to the components and the incongruently melting $KCl\cdot NiCl_2$ compound (see Fig. 29).

Below are given the compositions, the equilibrium phases and the temperatures of invariant points of the $(KCl)_2-NiCl_2-(LiCl)_2$ system. This system is also stable.

Point	T/°C	Composition (mass%)			Equilibrium phases
		$NiCl_2$	LiCl	KCl	
E_2	340	3.5	42	54	LiCl, KCl, $KCl\cdot NiCl_2$
P_2	504	40	37.5	21.5	LiCl, $NiCl_2$, $KCl\cdot NiCl_2$

The $Li_2SO_4-(LiCl)_2-NiCl_2-(KCl)_2$ tetrahedron. Since the theoretical prediction of phases based on the boundary elements shows that all boundary systems of the tetrahedron are stable, the system, whose composition is represented by the $Li_2SO_4-(LiCl)_2-NiCl_2-(KCl)_2$ tetrahedron, should be stable. This assumption was confirmed experimentally.[15] The temperature and composition of the quaternary eutectic are 633 K, 39 mass% LiCl, 49.8 mass% KCl, 8 mass% Li_2SO_4, 3.2 mass% $NiCl_2$; the Li_2SO_4, LiCl, $NiCl_2$ and KCl solid phases.

2. High-temperature electrolytic aluminising of niobium

The quaternary reciprocal system Al,Ba,Na//F,Cl, *viz*., $BaCl_2$ (0.73%) – NaF (0.12%) – AlF_3 (0.15%), is used as a molten electrolyte for high-temperature electrolytic aluminising of niobium. The reaction of molten salts cannot be judged from the results of chemical analysis of a sample of the melt cooled and dissolved in water or acid. Chemical analysis provides only information on the concentrations of the ions dissolved in solution. Information on the true chemical reactions of molten salts in systems can be extracted from a phase complex, which is displayed in the melting diagram as crystallisation fields or volumes, lines of co-crystallisation and multiple points. This allows one to draw reliable conclusions about the reactions proceeding in systems at high temperatures. The quaternary reciprocal system Al,Ba,Na//F,Cl can be represented as a matrix of reciprocal salt pairs (Fig. 30 *a*), in which the conversion figure of secant triangles is inscribed. Using the conversion figure, the following secant triangles are extracted from the matrix: AlF_3-BaCl_2-NaCl and AlF_3-BaCl_2-NaF (elements of a singular star).

Data on the boundary elements are required to predict the crystallisation fields of these triangular sections. It is known that the NaF – AlF_3 subsystem contains two compounds, *viz*., Na_3AlF_6 and $5\,NaF\cdot 3\,AlF_3$, the $BaCl_2$ – NaF subsystem contains

a

6*b*	$AlCl_3$	$BaCl_2$	NaCl
AlF_3	0	1 *A*	1 *B*
BaF_2	0	0	0
NaF	0	1 *C*	0

b

	Cl^-	F^-	$\sum$
Al^{3+}	0	2	2
Ba^{2+}	2	0	2
Na^+	1 [a]	1 [b]	2
$\sum$	3	3	6

Figure 30. Models of the quaternary reciprocal system Al,Na,Ba//Cl,F. (*a*) The matrix of reciprocal salt pairs with an inscribed conversion graph, (*b*) the matrix of vertex indices.

the $BaCl_2 \cdot BaF_2$ compound, and the $AlF_3 - BaCl_2$ subsystem is characterised by a eutectic point (all data refer to the $AlF_3 - BaCl_2 - NaF$ system).

The required electrolyte can be chosen with the use of the phase diagrams of the triangular section of the Al,Ba,Na//F,Cl system. It was experimentally demonstrated that the liquidus surface of this stable triangular section consists of seven crystallisation fields: $BaCl_2$, NaF, AlF_3, BaF_2, Na_3AlF_6, $5\,NaF \cdot 3\,AlF_3$ and $BaCl_2 \cdot BaF_2$. Hence, the experimental results confirmed the predicted existence of three compounds in the $AlF_3 - BaCl_2 - NaF$ triangle of the singular star.

At the point of complete conversion *A*, the salt pairs undergo interchange according to the reaction

$$3\,BaF_2 + AlCl_3 = 2\,AlF_3 + 3\,BaCl_2.$$

The Na_3AlF_6 compound is formed at the point of complete conversion by the secondary reaction

$$2\,AlCl_3 + 12\,NaF = 2\,Na_3AlF_6 + 6\,NaCl.$$

At the point of complete conversion *C*, an exchange reaction and complex formation take place

$$BaF_2 + 2\,NaCl = 2\,NaF + BaCl_2,$$

$$4\,BaF_2 + 4\,NaCl = 2\,(BaF_2 \cdot BaCl_2) + 4\,NaF.$$

The conditions of the process are as follows: at a carbon anode, electrolysis is carried out at 900 °C; the thickness of an aluminium coating is 40 – 50 μm, the coating consists of Al, $NbAl_3$ and Nb_2Al.[12]

As can be seen from the matrix table of vertex indices (see Fig. 30 *b*), the $AlCl_3$ salt is most reactive and is completely consumed in the exchange reaction and the reaction giving rise to the compound, *i.e.*, this salt is absent in the melt (the index is 0). The system contains AlF_3 formed by the exchange reaction (the index of AlF_3 is 2). Barium chloride is consumed in the synthesis of the $BaF_2 \cdot BaCl_2$ compound and the exchange reaction yielding $BaCl_2$. The BaF_2 salt is most reactive (its index is 0). The $BaCl_2$ salt is stable and has the highest index (2). The latter salt is an exchange reaction product. The NaCl and NaF salts have the index 1. They are intermediate between the most reactive and stable salts.

From the above, it can be concluded that the composition of the electrolyte for high-temperature aluminising was chosen correctly.

3. Silver plating

Nitrate and halide – nitrate molten systems are used for electrolytic silver plating.[12] For example, the molten $AgI - NaNO_3 - KNO_3$ system is used for electrolytic silver plating. This system corresponds to a diagonal section of the composition prism of the quaternary reciprocal system Ag,K,Na//I,NO_3 consisting of six salts. The process occurs at 300 °C and at a current density of 50 A m^{-2}.

Electrolytic silver plating can be carried out with the use of a molten electrolyte developed on the basis of the quinary reciprocal system Ag,K,Na//Cl,Br,NO_3 consisting of nine salts, which belongs to the A ⇄ B thermochemical type.[21]

Let us construct the matrix table of vertex indices using the thermochemical relations for the salt pairs of the system. The stable axial triangle of a singular star with the highest indices in each row of the matrix can be determined from this matrix table.

9A	Br^-	Cl^-	NO_3^-	$\sum$
Ag^+	4	2	0	6
K^+	2	1	3	6
Na^+	0	3 [a]	3 [b]	6
$\sum$	6	6	6	18

This is the $AgBr - KNO_3 - NaCl$ triangle. The most stable salts formed by exchange (conversion) reactions are AgBr (the index is 4), KNO_3 (the index is 3) and NaCl (the index is 3 [a]). The $AgNO_3$ (the index is 0), NaBr (the index is 0) and KCl (the index is 1) salts are most reactive and are consumed in the interchange reaction

$$2\,AgNO_3 + 2\,KCl + 2\,NaBr = \\ = AgCl + KNO_3 + AgBr + NaNO_3 + KBr + NaCl.$$

The metastable salt pairs react further

$$AgCl + KBr = AgBr + KCl,$$

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Hence,

$$AgNO_3 + KCl + NaBr = AgBr + KNO_3 + NaCl.$$

As a result, stable salts forming a eutectic mixture should appear in the melt for electrolysis. It was experimentally demonstrated that a low-melting eutectic is formed in the $AgBr - KNO_3 - NaCl$ system at 513 K and 21.5% AgBr, 12% NaCl, 66.5% KNO_3.

A procedure for studying multicomponent reciprocal systems, which involves the experimental investigation of conversion elements, including elements of incomplete conversion, was also successfully used for solving some other problems, in particular, for preparing bronzes, rare-metal compounds, phase-transition materials, *etc.*[4, 50 – 53]

VI. Conclusion

Nowadays, the methodology of investigation of multicomponent systems involves the theoretical study of models of multicomponent systems followed by experimental examination of particular regions of phase diagrams and their construction as the necessary stages. This methodology can also serve as the basis for the development of important technological processes (construction of heat accumulators, heat carriers, galvanised coatings, *etc.*).

Modelling of multicomponent reciprocal salt systems provides a rational approach to solving numerous theoretical and practical problems. A conversion figure of secant elements plays a unique role, because it is common to non-equilibrium and equilibrium complexes and ensures spatial and physicochemical relationships between these complexes.

Conversion figures can be used in the analysis of the mechanisms of transformation from a non-equilibrium state of the system to equilibrium. These figures allow one to follow the sequence of transformations of the starting compounds into the final reaction products. In models, this is manifested as a spatial transformation from a non-equilibrium star through intermediate stars (containing partially non-equilibrium and partially equilibrium elements) to a singular (equilibrium) star. Conversion elements can be used for studying the structures of phase diagrams in more detail (determination of remarkable points and analysis of their metrics in various systems of coordinates, the polarity and symmetry in various multidimensional spaces).

The proximate analysis developed on the basis of the conversion method enables one to solve practical problems, such as the construction of a phase complex of a system with a minimum of experimental studies (investigation of a small number of compositions) as well as the construction of reciprocal systems with the desired direction of exchange reactions.

The practical value of the conversion method became evident after the development of media for electrolytic coatings and the preparation of low-melting composites, *viz.*, heat carriers and heat-accumulation composites, which are used to prolong the life of batteries with high energy characteristics. In particular, the composites, whose enthalpies of melting are almost twice as high as those of foreign standards, were constructed.

There are several directions of development of the conversion method for investigating reciprocal salt systems: construction and improvement of models; development of new methodological concepts; exploration of new areas of practical application of this methodology; integration of conversion models into scientific foundations of chemical disciplines.

The following theoretical problems are yet to be solved.

1. The thermodynamical description of conversion models taking into account the available data on the algebraic models of processes occurring in salt melts.[54, 55]

2. More detailed investigation of the energetics of exchange reactions using alternative models of multicomponent reciprocal salt systems, *viz*., energy diagrams and non-equilibrium, intermediate and singular stars.

3. Thermodynamical calculations of conversion processes at different temperatures.

4. The construction of models for the description of the behaviour of ionic liquids at different temperatures and the energy transfer performed by these liquids.

5. Study of the topology of the distribution of conversion elements over subspaces of the multidimensional space of the phase diagram of a multicomponent reciprocal system.

6. The development of models of conversion processes, involving complexation reactions.

The prospects of the development of the conversion method are tightly related to the worldwide scientific trends associated with investigations and applications of salt melts, which are reflected in papers presented at scientific conferences and symposia on molten salts.[56–62] Among these problems are investigations of the dynamic, structural, electrochemical and other properties of melts, thermodynamical modelling and calculations of phase diagrams, construction of models of ionic liquids and the energetics of melts, *etc*. The conversion method can be used for solving many of these problems.

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