Chemistry

1961

SovietRxiv

Abstract

Full Text

Chemistry

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Decomposition of the Composition Diagram and Exchange Reactions of a Quinary Reciprocal System of Nine Salts: Chlorides, Bromides, and Sulfates of Lithium, Sodium, and Thallium

(Presented by Academician I. V. Tananaev, 16 XI 1960)

Developing the ideas of N. S. Kurnakov in the field of multicomponent equilibria, V. P. Radishchev theoretically derived five types of decomposition of quinary reciprocal systems of nine salts: A, B, C, D, and E ([1]). Determination of the type of decomposition and finding the singular and nonequilibrium stars make it possible to evaluate exchange reactions and to reduce experimental studies of reciprocal systems ([2]). Type A has been described using as an example the systems Na, K, Ag Cl, Br, NO_3 ([3]). In the present work, type C has been experimentally confirmed for the first time. The composition diagram

Table 1

Indices of vertices, cutting elements, and stable cells of the composition diagram in the quinary reciprocal system of 9 salts:
Li, Na, Tl Cl, Br, SO_4

Cations	Singular star	Singular star	Singular star	Nonequilibrium star	Nonequilibrium star	Nonequilibrium star
Cations	Anions	Anions	Anions	Anions	Anions	Anions
Cations	Br	Cl	SO_4	SO_4	Cl	Br
Li	0	2	4	0	2	4
Na	2	2	2	2	2	2
Tl	4	2	0	4	2	0

Base triangle: 4–2 –4
Cutting tetrahedra:
1) 24–2 –4; 2) 4–2 –42; 3) 24–2 –4; 4) 4–2 2 –4;
5) 4–2 2 –4; 6) 4–2 –42.

Stable cells:
1) 024–2 –4 }
2) 4–2 –420 } Sprouts

Fig. 1. Ternary system LiBr–NaCl–1/2 Tl2SO4

Figure 1: Fig. 1. Ternary system LiBr–NaCl–1/2 Tl2SO4

Pentatopes of the cyclic part of the star:
3) 24–2 2 –4; 4) 24–2 –2 –42; 5) 4–2 2 2 –4;
6) 4–2 2 –42

of the quinary reciprocal system of 9 salts is represented in the form of a four-dimensional nine-vertex polytope (a prism of the second kind). The determination of the cutting and stable elements of the composition diagram was carried out with the aid of a table of vertex indices* ([4]).

* The index of a vertex indicates the number of stable diagonals incident to the given vertex of the polytope.

Table 1 gives the indices of the vertices of the singular and nonequilibrium stars. In type C both stars are identical, as a result of which the sets of vertex indices are the same. The arrangement of the cations in the nonequilibrium star is the same, while the arrangement of the anions is reversed.

Fig. 1. Ternary system LiBr—NaCl—$\frac{1}{2}Tl_2SO_4$

As can be seen from Table 1, the secant tetrahedra 3, 4, 5, and 6 have a common base–the basic triangle 4—2^B—4. For the nonequilibrium star it corresponds to the salts LiBr—NaCl—$\frac{Tl_2SO_4}{2}$, and for the singular star to $\frac{Li_2SO_4}{2}$—NaCl—TlBr. The ternary systems corresponding to these triangles were checked experimentally. The nonequilibrium triangle LiBr—NaCl—$\frac{Tl_2SO_4}{2}$ is characterized by the presence of six crystallization fields (Fig. 1): three fields of the components LiBr, NaCl, Tl_2SO_4, two fields of the exchange products Li_2SO_4, Na_2SO_4, and a small field of phase X. In the quinary reciprocal system $Li, Na, Tl \parallel Cl, Br, SO_4$, the salt combination corresponding to the components of the nonequilibrium star is the least stable.

The basic triangle (Fig. 2) of the singular star $\frac{Li_2SO_4}{2}$—NaCl—TlBr is a simple ternary system with three fields of the initial components and a ternary eutectic point at 424° and composition $2\%\ \frac{Li_2SO_4}{2} + 7\%\ NaCl + 91\%\ TlBr$. Thus, the stability of the basic triangle is confirmed. Both triangles–the nonequilibrium and the stable–possess considerable regions of immiscibility. In type C, the intersection of the nonequilibrium and basic triangles is effected along the conversion line (1), which indicates that both triangles are located in one hyperplane of the four-dimensional diagram. The conversion line is determined by points of the composition diagram corresponding to

$$50\%\ \frac{Li_2SO_4}{2} + 50\%\ TlBr \rightarrow NaCl$$

or

$$50\%\ LiBr + 50\%\ \frac{Tl_2SO_4}{2} \rightarrow NaCl.$$

Fig. 2. Ternary system TlBr–NaCl–1/2 Li2SO4

Figure 2: Fig. 2. Ternary system TlBr–NaCl–1/2 Li2SO4

As can be seen, the component NaCl enters into both triangles, so that the exchange decomposition reduces to the reaction of a pair of salts:

$\mathrm{LiBr} + \frac{\mathrm{Tl_2SO_4}}{2} \rightarrow \frac{\mathrm{Li_2SO_4}}{2} + \mathrm{TlBr},$

while the component NaCl remains unchanged.

Fig. 2. Ternary system TlBr $-$NaCl $-\frac{1}{2}\mathrm{Li_2SO_4}$

Thus, the exchange reactions in the quinary reciprocal system Li, Na, Tl ‖ Cl, Br, SO_4 are expressed in the form of the following equations:

Nonequilibrium star:

$$\mathrm{LiBr} + \tfrac{1}{2}\mathrm{Tl_2SO_4} \rightarrow \tfrac{1}{2}\mathrm{Li_2SO_4} + \mathrm{TlBr},$$

$$\mathrm{LiBr} + \mathrm{NaCl} \rightarrow \mathrm{LiCl} + \mathrm{NaBr},$$

$$\mathrm{NaCl} + \tfrac{1}{2}\mathrm{Tl_2SO_4} \rightarrow \tfrac{1}{2}\mathrm{Na_2SO_4} + \mathrm{TlCl}.$$

Singular star:

$$\tfrac{1}{2}\mathrm{Tl_2SO_4} + \mathrm{LiBr} \rightarrow \mathrm{TlBr} + \tfrac{1}{2}\mathrm{Li_2SO_4},$$

$$\tfrac{1}{2}\mathrm{Na_2SO_4} + \mathrm{LiCl} \rightarrow \tfrac{1}{2}\mathrm{Li_2SO_4} + \mathrm{NaCl},$$

$$\mathrm{NaBr} + \mathrm{TlCl} \rightarrow \mathrm{NaCl} + \mathrm{TlBr}.$$

Summing and canceling, we obtain:

$$\mathrm{LiBr} + \frac{\mathrm{Tl_2SO_4}}{2} \rightarrow \frac{\mathrm{Li_2SO_4}}{2} + \mathrm{TlBr}.$$

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of Chemical Machine Building

Received
14 XI 1960

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Note: Figure translations are in progress. See original paper for figures.