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Abstract

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THE BASIC TETRAHEDRON $\frac{1}{2}Li_2SO_4$–NaCl–$RbNO_3$–TlBr IN THE SEVEN-COMPONENT RECIPROCAL SYSTEM Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4

(Presented by Academician I. I. Chernyaev, 15 X 1959)

In a previous communication a singular star of the reciprocal system of 16 salts Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4 ([1]), determining the direction of exchange reactions, was described. At the center of the cube orienting the singular star, from the table of vertex indices, the position of the most stable basic tetrahedron $\frac{1}{2}Li_2SO_4$–NaCl–$RbNO_3$–TlBr was determined; its vertices represent salts formed by four different cations and four different anions.

An experimental study of fusibility made it possible to determine the configuration of the principal crystallization volumes in the tetrahedron. The edges of the tetrahedron are the more stable diagonals of six ternary reciprocal systems $A, B \parallel x, y$. However, only four diagonals are completely stable: TlBr–$RbNO_3$; TlBr–$\frac{1}{2}Li_2SO_4$; $RbNO_3$–NaCl; and NaCl–$\frac{1}{2}Li_2SO_4$. The stability of the diagonal TlBr–NaCl is less definite, since in the system Na, Tl ‖ Br, Cl solid solutions Tl(Br, Cl) and Na(Br, Cl) are observed. For the salts of lithium and rubidium, M. N. Zakhvalinskii ([2]) established on the diagonal $RbNO_3$–$\frac{1}{2}Li_2SO_4$ the presence of two complex compounds of the presumed compositions $Li_2SO_4 \cdot Rb_2SO_2$ (1 : 1) and $4Li_2SO_4 \cdot Rb_2SO_4$ (4 : 1).

At the base of the tetrahedron lies the ternary system $\frac{1}{2}Li_2SO_4$–NaCl–$RbNO_3$, in which, in addition to the three crystallization fields of the components, two additional fields are observed, corresponding to the above-mentioned double compounds.

In the ternary system $\frac{1}{2}Li_2SO_4$–$RbNO_3$–TlBr these two complex compounds also appeared; separate fields correspond to them. For this system a very characteristic feature is an extensive region of stratification, occupying 78% of the area of the triangle. In the ternary system NaCl–$RbNO_3$–TlBr there are three crystallization fields of the components. A considerable region of stratification adjoins the side $RbNO_3$–TlBr and covers almost completely the TlBr field and part of the NaCl field (30% of the area). In the ternary system $\frac{1}{2}Li_2SO_4$–NaCl–TlBr there are three crystallization fields of the components and a considerable

region of stratification extending along the edge $\frac{1}{2}Li_2SO_4$–TlBr and covering almost completely the Li_2SO_4 field and a large part of the NaCl field (60% of the area). The tetrahedron $\frac{1}{2}Li_2SO_4$–NaCl–$RbNO_3$–TlBr was investigated in the part adjacent to the "lithium" corner only up to a temperature of 500°, since rubidium nitrate decomposes at this temperature.

In the investigated part of the tetrahedron there are, in addition to the four crystallization volumes of the components, two more comparatively small volumes of the complex compounds of lithium and rubidium sulfates (1 : 1 and 4 : 1). Rubidium sulfate is the product of exchange between Li_2SO_4 and $RbNO_3$. The six crystallization volumes meet four at a time at two quaternary points, eutectic and transition, lying in the "rubidium" corner of the diagram. Table 1 gives the temperatures and compositions of the multiple points of the ternary systems and quater-

Table 1

Composition and temperature of invariant points

System	Invariant points	T, °C	Composition of invariant points, mol.%
$\frac{1}{2}Li_2SO_4$–NaCl –$RbNO_3$	Transitional	200	1% $\frac{Li_2SO_4}{2}$ + 14% NaCl + 85% $RbNO_3$
$\frac{1}{2}Li_2SO_4$–NaCl –$RbNO_3$	Eutectic	145	2% $\frac{Li_2SO_4}{2}$ + 19% NaCl + 79% $RbNO_3$
$\frac{1}{2}Li_2SO_4$– $RbNO_3$–TlBr	Transitional	440	2% $\frac{Li_2SO_4}{2}$ + 11% $RbNO_3$ + 87% TlBr
$\frac{1}{2}Li_2SO_4$– $RbNO_3$–TlBr	Eutectic	270	1% $\frac{Li_2SO_4}{2}$ + 6% TlBr + 93% $RbNO_3$
NaCl–$RbNO_3$– TlBr	Eutectic	135	4% TlBr + 17% NaCl + 79% $RbNO_3$
$\frac{1}{2}Li_2SO_4$–NaCl –TlBr	Eutectic	424	2% $\frac{Li_2SO_4}{2}$ + 7% NaCl + 91% TlBr

Fig. 1. Development of the tetrahedron Li2SO4–NaCl–RbNO3–TlBr

Figure 1: Fig. 1. Development of the tetrahedron Li2SO4–NaCl–RbNO3–TlBr

Fig. 2. Perspective representation of the tetrahedron Li_2SO_4—NaCl—$RbNO_3$—TlBr

Figure 2: Fig. 2. Perspective representation of the tetrahedron Li_2SO_4—NaCl—$RbNO_3$—TlBr

System	Invariant points	T, °C	Composition of invariant points, mol.%
$\frac{1}{2}Li_2SO_4$–NaCl –$RbNO_3$–TlBr	Transitional	145	$1\%\,\frac{Li_2SO_4}{2} + 13\%\,NaCl + 9\%\,TlBr + 77\%\,RbNO_3$
$\frac{1}{2}Li_2SO_4$–NaCl –$RbNO_3$–TlBr	Eutectic	107	$2\%\,\frac{Li_2SO_4}{2} + 17\%\,NaCl + 72\%\,RbNO_3 + 9\%\,TlBr$

of the reciprocal system. In Fig. 1 the development is given, and in Fig. 2 the perspective representation of the tetrahedron.

The compositions of the ternary and quaternary eutectic and transitional points were determined by graphical constructions; the temperatures were determined by recording heating and cooling curves on an N. S. Kurnakov recording pyrometer.

Fig. 1. Development of the tetrahedron Li_2SO_4–NaCl–$RbNO_3$–TlBr

As a result of the investigation carried out, a conclusion may be drawn regarding the type of the seven-component reciprocal system of 16 salts, since the tetrahedron studied determines the direction of reactions, similarly to the "basic" triangle for the five-component reciprocal system of 9 salts (*), and also po-

similar to the stable diagonal triangles in the quaternary reciprocal system of 6 salts (4) and, finally, to the stable diagonal of the square of the ternary reciprocal system of 4 salts. On the basis of an experimental determination–

Fig. 2. Perspective representation of the tetrahedron Li_2SO_4—NaCl—$RbNO_3$—TlBr

–of the fusibility of the system $\frac{1}{2}Li_2SO_4$—NaCl—$RbNO_3$—TlBr, it has been established that the septenary reciprocal system $Li, Na, Rb, Tl \parallel Br, Cl, NO_3, SO_4$

can be assigned to the class of reversibly reciprocal systems (5).

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