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Abstract

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INTERSECTION OF STABLE AND NONEQUILIBRIUM TETRAHEDRA IN THE QUINARY RECIPROCAL SYSTEM Li, Na, Rb, Tl Br, Cl, NO_3, SO_4

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

Exchange reactions in reciprocal systems are represented on the composition diagram by the intersection of nonequilibrium elements with stable cutting elements (1).

The composition diagram of a quinary reciprocal system of 16 salts is a six-dimensional polytope (2). In the singular star of the system Li, Na, Rb, Tl Br, Cl, NO_3, SO_4, at the center of the cube orienting the star, there is the basic tetrahedron Li_2SO_4–NaCl–$RbNO_3$–TlBr, which is the most stable (3). The nonequilibrium tetrahedron of this system represents the most reactive salts, which, as a result of reaction with one another, form the components of the system represented by the stable tetrahedron. Both tetrahedra lie in the six-dimensional space of the composition diagram of the quinary system and intersect along a conversion line. Exchange reactions in the quinary reciprocal system Li, Na, Rb, Tl Br, Cl, NO_3, SO_4 may be represented by equations for the nonequilibrium tetrahedron:

$$\mathrm{RbCl} + \mathrm{NaNO_3} = \mathrm{RbNO_3} + \mathrm{NaCl} \qquad \mathrm{RbCl} + \mathrm{LiBr} = \mathrm{RbBr} + \mathrm{LiCl}$$

$$\mathrm{LiBr} + \frac{1}{2}\mathrm{Tl_2SO_4} = \frac{1}{2}\mathrm{Li_2SO_4} + \mathrm{TlBr} \qquad \mathrm{LiBr} + \mathrm{NaNO_3} = \mathrm{LiNO_3} + \mathrm{NaBr}$$

$$\mathrm{RbCl} + \frac{1}{2}\mathrm{Tl_2SO_4} = \frac{1}{2}\mathrm{Rb_2SO_4} + \mathrm{TlCl} \qquad \mathrm{NaNO_3} + \frac{1}{2}\mathrm{Tl_2SO_4} = \frac{1}{2}\mathrm{Na_2SO_4} + \mathrm{TlNO_3}.$$

for the equilibrium tetrahedron:

$$\mathrm{NaNO_3 + RbCl = NaCl + RbNO_3} \qquad \mathrm{LiNO_3 + \frac{1}{2}Rb_2SO_4 = \frac{1}{2}Li_2NO_4 + RbNO_3}$$

$$\mathrm{LiBr + \frac{1}{2}Tl_2SO_4 = \frac{1}{2}Li_2SO_4 + TlBr} \qquad \mathrm{LiCl + \frac{1}{2}Na_2SO_4 = \frac{1}{2}Li_2SO_4 + NaCl}$$

$$\mathrm{TlNO_3 + RbBr = TlBr + RbNO_3} \qquad \mathrm{NaBr + TlCl = NaCl + TlBr}$$

Summing all the equations and dividing by 4, we obtain the equation of the exchange reaction:

$$\mathrm{LiBr + NaNO_3 + RbCl + \frac{1}{2}Tl_2SO_4 = \frac{1}{2}Li_2SO_4 + NaCl + RbNO_3 + TlBr.}$$

In addition to exchange reactions, complex-formation reactions occur in the system, as a result of which the appearance of a number of double complex salts is observed: $\mathrm{Li_2SO_4 \cdot Rb_2SO_4}$, $\mathrm{4Li_2SO_4 \cdot Rb_2SO_4}$, $\mathrm{RbCl \cdot 2Li_2SO_4}$, and possibly others.

The stable tetrahedron of the system has been investigated experimentally (^{4}). Of considerable interest is the experimental study of the line of intersection of the stable and nonequilibrium tetrahedra, proceeding from the components of both tetrahedra. Figure 1 gives a diagram in which the circles show the data of the visual-polythermal method obtained from the salts of the stable tetrahedron $\mathrm{(0.5NaCl + 0.5RbNO_3)}$—$\mathrm{(0.5\frac{Li_2SO_4}{2} + 0.5TlBr)}$,
and the crosses those of the nonequilibrium tetrahedron
$\mathrm{(0.5NaNO_3 + 0.5RbCl)}$—$\mathrm{(0.5LiBr + 0.5\frac{Tl_2SO_4}{2})}$. The liquidus line consists of two crystallization branches: NaCl and $\mathrm{Li_2SO_4}$. On the $\mathrm{Li_2SO_4}$ curve there is a region of immiscibility, which begins at 35 mol.% of the mixture $\mathrm{(0.5\frac{Li_2SO_4}{2} + 0.5\ TlBr)}$ or $\mathrm{(0.5LiBr+0.5\frac{Tl_2SO_4}{2})}$ and extends to 100% of the mixture. On the crystallization branch of lithium sulfate, beneath the immiscibility region, there is a smooth bend, after which the melting temperatures of the mixtures begin to rise rapidly. However, a more detailed investigation of this region is not possible because of the decomposition of nitrates and the sublimation of thallium salts at temperatures above 500°. Thermograms were recorded for melts corresponding to the compositions of the central points of the line of intersection, prepared from salts corresponding to the vertices of the stable and nonequilibrium tetrahedra (Fig. 2). Table 1 gives the temperatures of arrests and the corresponding phases.

[Fig. 1 and Fig. 2]

Fig. 1. Melting diagram for the conversion line of intersection of two tetrahedra

Fig. 2. Cooling curves of the central points of the conversion line of intersection of the stable and nonequilibrium tetrahedra

Fig. 3. Microstructure of alloys corresponding to the central point of the line of intersection of the stable (a) and nonequilibrium (b) tetrahedra

Figure 1: Fig. 3. Microstructure of alloys corresponding to the central point of the line of intersection of the stable (a) and nonequilibrium (b) tetrahedra

As is evident from the data of Table 1, the thermograms are completely identical. On cooling of the melts, four arrests are observed: the first arrest at 453° corresponds to the separation of the first crystals of Li_2SO_4; the second, at 409°, to the simultaneous separation of Li_2SO_4 and NaCl; the third arrest, at 391°—the simultaneous separation of Li_2SO_4, NaCl, and TlBr, and, finally, at 107° a significant effect is observed, corresponding to a quaternary eutectic, where $RbNO_3$ joins the first three phases.

Table 1

Tetrahedron	1st arrest: temp., °C	1st arrest: phases	2nd arrest: temp., °C	2nd arrest: phases	3rd arrest: temp., °C	3rd arrest: phases	4th arrest: temp., °C	4th arrest: phases
Stable	453	Li_2SO_4	409	Li_2SO_4NaCl	398	Li_2SO_4TlBrNaCl	107	Li_2SO_4TlBrNaCl$RbNO_3$
Nonequilibrium	458	Li_2SO_4	410	Li_2SO_4NaCl	399	Li_2SO_4TlBrNaCl	107	Li_2SO_4TlBrNaCl$RbNO_3$

Fig. 3. Microstructure of alloys corresponding to the central point of the line of intersection of the stable (*a*) and nonequilibrium (*b*) tetrahedra

Figure 3*a* and *b* shows the microstructure of alloys having the composition of the central points of the stable and nonequilibrium tetrahedra. As can be seen, the microstructures are completely identical.

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