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Abstract

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CHEMISTRY

O. S. SOBOLEVA

POLYTHERM OF EQUILIBRIA OF THE SYSTEM $MgSO_4$—$NiSO_4$—H_2O

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For the system under consideration, the literature contains indications of the existence of a continuous series of mixed crystals for the heptahydrates (1) and data on the study of equilibria in the corresponding binary systems: $MgSO_4$—H_2O (2) and $NiSO_4$—H_2O (3,4). We have carried out a study of equilibria in the system $MgSO_4$—$NiSO_4$—H_2O by the method of isothermal evaporation at 50, 45, 40, 25, and partly at 38°, and have constructed the isotherms (5). In addition, the equilibrium at 35° was investigated by the method of isothermal crystallization from supersaturated solutions. In all, 83 points were studied; for each point an analysis was made of the solution and of the crystals in equilibrium with it. The composition of the solid phase was determined by Schreinemakers' residue method (6); in order to establish precisely the character of the crystals separating out, optical control was used: they were examined under a microscope, and their refractive indices were determined by the immersion method (7,8). A thermal investigation of the heptahydrate mixed crystals was carried out (9). To reveal the equilibrium conditions in the system, on the basis of the data obtained we constructed two plane polythermal diagrams, which are presented in the present article.

The first diagram (Fig. 1) is a concentration triangle with isotherms plotted on it; the polytherm is drawn in heavier type. In the second diagram (Fig. 2), the abscissa gives the ratio of $MgSO_4$ and $NiSO_4$ both in the salt mass of the solution and in the crystals, while the ordinate gives the temperature. This diagram is a projection of the spatial diagram onto one of the faces of the prism $MgSO_4$—$NiSO_4$—t. The projection is made by rays drawn from the edge H_2O—t parallel to the base of the prism. The curves corresponding to the composition of the salt mass of the solution are plotted in heavy type on the diagram; the curves corresponding to the composition of the corresponding crystals are plotted with thinner lines.

On both diagrams there are three regions of two-phase equilibrium: the field

Fig. 1

Figure 1: Fig. 1

of separation of monoclinic hexahydrate crystals ($RSO_4 \cdot 6H_2O_{mon}$), a small closed field of tetragonal hexahydrate crystals ($RSO_4 \cdot 6H_2O_{tetr}$), and the field of separation of rhombic heptahydrate crystals ($RSO_4 \cdot 7H_2O_{rhomb}$).

Although investigations above 50° were not carried out, there is no doubt that at temperatures above 53.8° and up to the beginning of monohydrate formation there will be a continuous series of mixed crystals of monoclinic hexahydrates. We obtained an almost complete distribution curve (^{10}) for this series in the interval from 0 to 96 mole % $NiSO_4$. The crystals, in comparison with the salt mass of the corresponding solutions, are enriched in the nickel component, and the maximum difference between its content in the crystals and in the salt mass of the solution reaches 12%. This field wedges out toward lower temperatures, i.e., in the ternary system the crystals will separate from solution down to a temperature of 38.2° (the quaternary point).

The field of separation of tetragonal crystals is represented by a small closed region in the area rich in the nickel component. As in

in the case of monoclinic crystals, the solid phase, compared with the salt mass of the solution, is enriched in the nickel component; moreover (judging from the monovariant-equilibrium curves in Fig. 2), the accumulation of the nickel component in these crystals is greatest. Addition of the magnesium component to the solution somewhat lowers the transition point of tetragonal crystals into monoclinic ones and raises the transition point of rhombic crystals into tetragonal ones. Thus, tetragonal crystals in the three-component

Fig. 1

system exist in equilibrium with the solution between the transition points for the pure nickel salts, and the temperature interval of stability narrows upon addition of the magnesium component.

The field of separation of heptahydrate crystals belongs to lower temperatures. A continuous series of mixed crystals will occur at temperatures below 30.7°. The distribution curve of this series was studied by us for 25°; here too the solid phase is always enriched in the nickel component compared with the salt mass of the corresponding solution, but the difference between its content is smaller than for monoclinic crystals (the maximum difference is 8%).

Thus, for all three fields the solid phase is enriched in the nickel component compared with the salt mass of the solution and, consequently, during isothermal evaporation the change in the composition of the solution will proceed in the direction of enrichment of its salt mass in the magnesium component.

The fields considered are separated by three monovariant-equilibrium curves—

Fig. 2

Figure 2: Fig. 2

AL, BL, and CL. In three-phase equilibrium, the curves determining the composition of the solid phases (Fig. 2) everywhere lie on one side of the curve determining the composition of the salt mass of the solution; consequently, during isothermal evaporation the characteristic feature will be not the simultaneous crystallization of two solid phases, but a reaction between the solution and one of the solid phases with the formation of another.

The nature of the crystallization process upon cooling in a closed system is determined for this case on the first diagram (Fig. 1) by the position of the tangents to the monovariant-equilibrium curve relative to

corresponding triangle of phases. For illustration, we have shown the triangle of phases for the temperature 45° ($L'S_1'S_2'$). It is seen that if a tangent is drawn to the curve AL at the point L', it will lie outside the triangle of phases; this will be characteristic of all the curves at all points and indicates that the process will have a peritectic character.

The curves of monovariant equilibrium determine the position of the quadruple point L, at which they all meet. By extending the curves AL and BL

Fig. 2

(Fig. 2), by drawing secant straight lines through two adjacent experimentally found points (i.e., by replacing the convex curves in this portion by straight lines) on a special diagram of larger scale, we obtained an intersection point at 38.4°, which determines the upper temperature limit for the quadruple point. Investigation of the equilibrium at 38° showed that this isotherm passes below the quadruple point, since it intersects only the fields of separation of rhombic and tetragonal crystals. Thus, for the quadruple point a temperature of $38.2° \pm 0.2°$ has been established. The composition of the phases (crosses in Fig. 1 and Fig. 2) for this point was determined graphically.

Phase	Composition
Salt mass of the solution	85.1 mol. % (on an anhydrous-salt basis)
$RSO_4 \cdot 6H_2O_{\text{tetr}}$	92.0 mol. % » » »
$RSO_4 \cdot 6H_2O_{\text{mon}}$	90.8 mol. % » » »
$RSO_4 \cdot 7H_2O_{\text{rhomb}}$	89.3 mol. % » » »

The solution contains 29.2 wt. % $NiSO_4$ and 4 wt. % $MgSO_4$. In Fig. 1, for the quadruple point a quadrilateral of phases ($LS_1S_2S_3$) has been constructed; since the quadrilateral is convex and the composition of the liquid phase lies inside the triangle of solid phases, for the invariant point the process has a peritectic character with the reaction according to the scheme:

$$\text{solution} + RSO_4 \cdot 6H_2O_{\text{mon}} = RSO_4 \cdot 6H_2O_{\text{tetr}} + RSO_4 \cdot 7H_2O_{\text{rhomb}}$$

Lviv State University
named after I. Franko

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