ON THE SOLUBILITY POLYTHERM OF THE SYSTEM

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Abstract

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ON THE SOLUBILITY POLYTHERM OF THE SYSTEM

K, Na, Mg‖Cl, SO_4–H_2O

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The five-component reciprocal system named in the title was, as is known, the subject of a partial investigation by J. H. van ' t Hoff and N. S. Kurnakov with collaborators. We have carried out a complete study of it at temperatures from 0 to 100°.

The equilibria were investigated by the isothermal method (^{1,2}). The isothermal region of crystallization of each salt in the quinary system at constant pressure is represented in the form of a volume (^{3}). In Fig. 1A, B a photograph is given of a model of the volumes of the salts of the system studied by us at 0, 25, 55, and 100°; the composition prism is shown from the side of the faces corresponding to the systems:
$K_2SO_4 + 2NaCl \rightleftarrows 2KCl + Na_2SO_4$ (Fig. 1A) and
$K_2SO_4 + MgCl_2 \rightleftarrows 2KCl + MgSO_4$ (Fig. 1B); the list of salts crystallizing in the system is given in Table 1, where crosses mark the compounds belonging to each isotherm. A characteristic feature of the system is that chlorides over the entire temperature interval (0-100°) sharply displace sulfates from the solutions; only under very limited conditions (temperature and concentration) do they interact with one another, forming chemical compounds of the type: $KCl{\cdot}MgSO_4{\cdot}3H_2O$ and $MgSO_4{\cdot}3NaCl{\cdot}9Na_2SO_4$. The ratios of the volumes of the salting-out sulfates, the phase composition of the latter, and also the parageneses of the solid phases of the system change substantially under the influence of temperature; in general outline this can be traced in Fig. 1. Among the numerous compounds of the system, double sulfuric-acid compounds of potassium with sodium and magnesium—glaserite, schoenite, leonhardite, langbeinite (Nos. 2, 3, 4, 5 in Table 1 and in Fig. 1)—are of considerable practical interest, being effective (chlorine-free) mineral fertilizers. The regions of existence of these compounds in the composition prism are outlined by us, for convenience of consideration, with thicker lines. Glaserite ($3K_2SO_4 \cdot Na_2SO_4$) and its solid solutions at 0° have a small closed volume, which gradually expands with increasing temperature, reaches maximum dimensions at approximately about 55°, and then begins to decrease again (Fig. 1A); the largest region in the prism at 0° (designated by the numeral one) belongs to pure potassium

Figure 1. Model of the crystallization volumes of salts in the system $\mathrm{K, Na, Mg} \parallel \mathrm{Cl, SO_4}$—$H_2O$ at temperatures of 0, 25, 55, and 100°. 1—$K_2SO_4 \cdot H_2O$; 2—$3K_2SO_4 \cdot Na_2SO_4$; 3—$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; 4—$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$; 5—$K_2SO_4 \cdot 2MgSO_4$; u—inversion point.

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sulfate monohydrate.

The region of schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) at 0 and 25° is comparatively small; at 55° this salt exists in a somewhat dehydrated state, in the form of leonhardite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), and partially passes into the anhydrous compound—langbeinite ($K_2SO_4 \cdot 2MgSO_4$), the volume of the latter at 100° exceeds in magnitude the volumes of all other salts of the system, occupying the central place in the composition prism (Fig. 1B). In other words, the maximum amounts of anhydrous sulfuric-acid compounds—glaserite and langbeinite —separate from solutions of the system at temperatures between 55 and 100°; upon cooling the same solutions to 0° (and below), pure hydrated sulfates and schoenite can be separated. It should be noted, however, that in the process of crystallization of schoenite at 0° and of langbeinite at 100° the content

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Table 1

Solid phases of the system $K, Na, Mg \parallel Cl, SO_4$—$H_2O$ at temperatures 0—100°

No.	Compounds	0°	25°	55°	100°
1	$KCl \cdot MgCl_2 \cdot 6H_2O$ (carnallite)	+	+	+	+
2	$3K_2SO_4 \cdot Na_2SO_4$ (glaserite)	+	+	+	+

No.	Compounds	0°	25°	55°	100°
3	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (schoenite)	+	+		
4	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (leonite)		+	+	
5	$K_2SO_4 \cdot 2MgSO_4$ (langbeinite)			+	+
6	$KCl \cdot MgSO_4 \cdot 3H_2O$ (kainite)		+	+	
7	$MgSO_4 \cdot 3NaCl \cdot 9Na_2SO_4$			+	+
8	$3Na_2SO_4 \cdot MgSO_4$ (vanthoffite)			+	+
9	$Na_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ (loeweite)			+	+
10	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (astrakhanite)		+	+	
11	$MgSO_4 \cdot 7H_2O$ (epsomite)	+	+		

No.	Compounds	0°	25°	55°	100°
12	$MgSO_4\cdot 6H_2O$ (hexahydrite)		+	+	
13	$MgSO_4\cdot H_2O$ (kieserite)		+	+	+
14	$Na_2SO_4\cdot 10H_2O$ (mirabilite)		+	+	
15	Na_2SO_4 (thenardite)	+	+		+
16	$K_2SO_4\cdot H_2O$ (monohydrate)	+			
17	K_2SO_4 (arcanite)		+	+	+
18	KCl (sylvite)	+	+	+	+
19	$NaCl$ (halite)	+	+	+	+
20	$MgCl_2\cdot 6H_2O$ (bischofite)	+	+	+	+
		9	15	16	12

potassium in the terminal solutions is almost identical and corresponds to 4.74—4.99% KCl.

The temperature projection of the polythermic equilibrium diagram (0—100°) has a complex structure owing to the presence in the system of many compounds (ten chemical compounds, apart from the initial components and their hydrates; see Table 1); the number of coexisting solid phases on the diagram varies from two to five. An example of the paragenesis of the maximum number of solid phases is point u in Fig. 1b, for a temperature of 55°. At this inversion point the crystallization regions of five salts converge simultaneously:
$KCl\cdot MgSO_4\cdot 3H_2O + K_2SO_4\cdot 2MgSO_4 + Na_2SO_4\cdot MgSO_4\cdot 2H_2O + NaCl + KCl$; similar salt parageneses correspond to nonvariant equilibrium in this system.

The results of the study of the solubility polytherm, distinguished by exceptional complexity among the few systems of this type that have been studied, are of importance for questions of seawater evaporation, crystallization of brines in marine gulfs and basins, the genesis of potassium deposits, and the technology of salts in the exploitation of the latter.

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

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