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ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ K,Ca//SO₄,CO₃,F-H₂O ПРИ 25 °C

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PHASE-EQUILIBRIUM IN THE SYSTEM K, Ca // SO₄, CO₃, F-H₂O AT 25 °C

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Рассматриваются результаты определения фазовых равновесий на геометрических образах приведенной системы с последующим построением ее фазовой диаграммы методом трансляции. Метод перевода следует из принципа совместности структурных элементов n и $n+1$ компонентных систем на одной диаграмме. Это позволяет прогнозировать фазовые равновесия в $n+1$ -компонентной системе на основе данных о фазовых равновесиях в n -компонентных системах и строить их фазовую диаграмму. Установлено, что исследуемая система при 25 °C характеризуется наличием 5 невариантных точек, 16 моновариантных кривых и 18 дивариантных полей.

Key words: дивариантное поле; метод трансляции; моновариантная кривая; невариантная точка; фазовая диаграмма; фазовые равновесия.

Realization of technological processes of obtaining inorganic salts from natural mineral raw materials or purification of industrial effluents from salts is associated with the implementation of physical and chemical processes in multicomponent systems¹.

The analysis of existing methods of research of multicomponent systems and their comparison with the translation method shows that the translation method is the most optimal for these purposes. The translation method follows from the principle of compatibility of structural elements n and $n+1$ of component systems in one diagram. This makes it possible to predict phase equilibria in the $n+1$ component system on the basis of data on phase equilibria in the n component systems and to plot their phase diagram. It is found that the system under study at 25 °C is characterized by the presence of 5 nonvariant points, 16 monovariant curves and 18 divariant fields.

Key words: constitutional diagram; divariant fields; monovariant curve; multicomponent system; nonvariant point, phase composition; phase identification; solids, translation method.

As a rule, in such systems, the influence of salts on mutual solubility is possible, phase equilibria become diverse, the composition of the precipitating solid phase changes.

The most frequently experimentally studied three-component systems containing a solvent and different salt. The research of systems with the number of components more than three of

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them meet with additional difficulties (identification of equilibrium solid phases, construction of diagrams of the state, high material costs and time resources) of the experiment.

The work ²⁻⁴ describes in more detail the difficulties of visualization of phase equilibria in multicomponent systems, the component content of which is higher than three. Therefore, most researchers study systems with no more than four components.

In this paper, using the translation method ⁵⁻⁸ for the first time studied this particular five-component system, which is a necessary step for further study of six-component systems. Like this work has peculiarity and scientific novelty, as it serves as a theoretical basis for the technology of processing of multicomponent real objects in the form of sulfates, carbonates and fluorides of potassium and calcium.

Research methods

In this article firstly research dealt a five-component system $K, Ca // SO_4, CO_3, F-H_2O$ at 25 °C. For the theoretical study of this system, the method of translation is applied, the essence of which is as follows:

The studied five-component system is presented as a combination of such four-component systems as $K_2SO_4-K_2CO_3-KF-H_2O$; $CaSO_4-CaCO_3-CaF_2-H_2O$; $K, Ca // SO_4, F-H_2O$; $K, Ca // SO_4, CO_3-H_2O$ and $K, Ca // CO_3, F-H_2O$, which are described in articles ⁹.

In turn, the description of these four-component systems is based on the experimental data of the corresponding three-component systems ^{10,11}. During the use of translation method, the principle of compatibility of structural elements of n and $n+1$ -component systems in one diagram [8.9] is realized. Than on the base predicting phase equilibria in $n+1$ component system and plotting its phase diagram basis of data on phase equilibria in n component systems. The translation method was used as an effective method in ^{12,13}.

Results and its discussion

Physico-chemical properties of the studied five component system $K, Ca // SO_4, CO_3, F-H_2O$ are obtained by the corresponding translation of data on phase equilibria at non-invariant points of the following four component systems: $K_2SO_4-K_2CO_3-KF-H_2O$; $CaSO_4-CaCO_3-CaF_2-$

H_2O ; $K, Ca // SO_4, F-H_2O$; $K, Ca // SO_4, CO_3-H_2O$ and $K, Ca // CO_3, F-H_2O$ ⁹.

Figure 1 shows the «Disclosure» of the salt part of the phase equilibrium diagram of the five-component system $K, Ca // SO_4, CO_3, F-H_2O$ at 25 °C at the level of the four-component composition. In the fig. 1 positions of geometrical images of the diagram (points, curves, fields) are schematically plotted ^{14,15}, without linking them to the coordinate skeleton. However, at the same time, sufficient information content of the constructed diagram is preserved: the total number of geometric images and their mutual arrangement, according to the basic principles of physical and chemical analysis and the Gibbs phase rule.

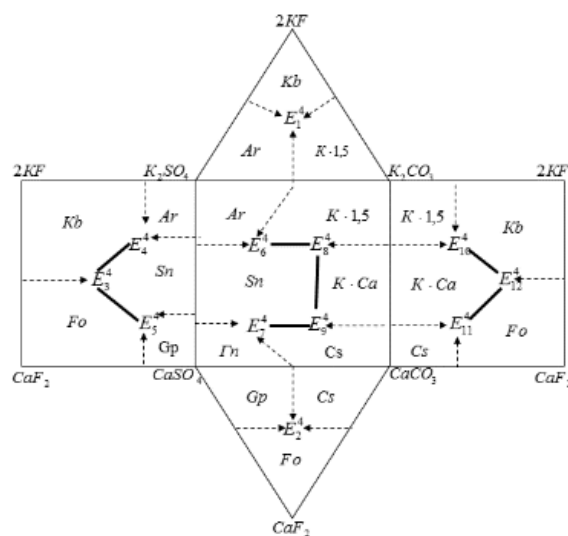


Fig. 1. Schematic diagram of the phase equilibrium of the system $K, Ca // SO_4, CO_3, F-H_2O$ at 25 °C at the level of the four-component composition as a «Disclosure» of the prism, built by translation.

In figure 1, and below in the text are taken following meaningful symbols ^{10, 11}:

- Ar – Arcanite K_2SO_4 ;
- Kb – carobititis KF ; $K \cdot 1.5-K_2CO_3 \cdot 1.5H_2O$;
- Cs – Calcite $CaCO_3$;
- Fo – Fluorite CaF_2 ; $K-Ca-K_2CO_3-CaCO_3$;
- Sn – syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$;
- Gp – gypsum $CaSO_4 \cdot 2H_2O$.

The letter E denotes a non-invariant point, the upper index of which denotes the multiplicity (component) of the system, and the lower index the ordinal number of the point.

In order to use the constructed diagram as a basis (matrix) for drawing on it the elements of the structure of the system under study at the level of five-component composition (according to the principle of compatibility ⁸), which are formed during the translation of geometric

images of the level of four-component composition, it is necessary to combine identical crystallization fields. After completion of this operation, we obtain a schematic diagram^{14, 15} of the isotherm at 25 °C for the system K,Ca//SO₄,CO₃,F-H₂O, which is shown in fig. 2.

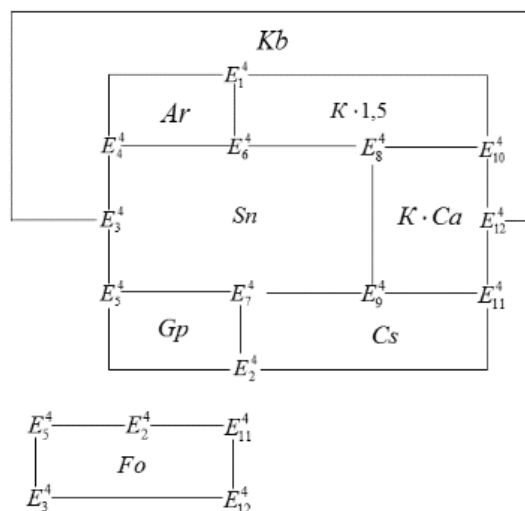
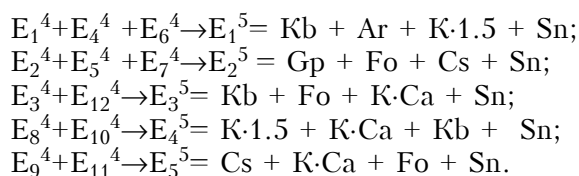


Fig. 2. The salt part of the schematic diagram of phase equilibria in the system K,Ca//SO₄, CO₃, F-H₂O at 25 °C at the level of four-component composition.

This schematic diagram shows that the translation of non-invariant points from the level of three-component composition to the level of four-component composition produces 12 non-invariant points, 22 monovariant curves, 8 divariant fields, which differ in the chemical nature of the components and phases involved in equilibrium processes (specific compounds are shown in fig. 2).

Stream nonvariant points-level four-part composition on the level pathcomponents composition gives the following nonvariant point of this level component with the set of equilibrium solid phases:



As you can see, of the five nonvariant points level pathcomponents composition of two (E_3^5 - E_5^5) formed by a triangular cross-cutting and three (E_1^5 - E_2^5) as a result of bilateral pass-through broadcast¹⁴. On the basis of the data obtained, in compliance with the basic principles of physical and chemical analysis and the Gibbs phase rule, a schematic¹⁵ phase diagram of the

system K,Ca//SO₄,CO₃,F-H₂O at 25 °C, which is shown in fig. 3.

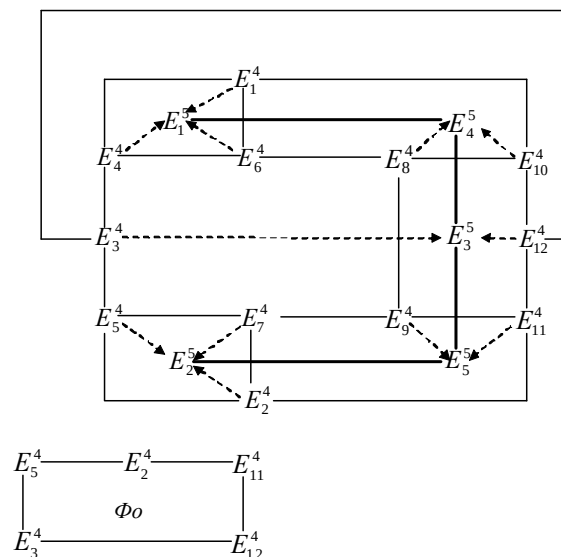
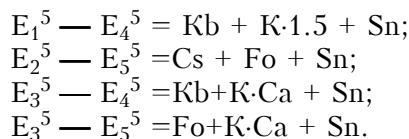


Fig. 3. The salt part of the schematic diagram of phase equilibria in the K,Ca//SO₄,CO₃,F-H₂O at 25 °C at the level of a five-component composition.

The analysis of the constructed diagram shows that the system under study at 25 °C is characterized by the presence of 5 non-invariant points (equilibrium of three phases), 16 monovariant curves (equilibrium of two phases) and 18 divariant fields (one phase). From 16-and monovariant curves 12 are formed as a result of translation of nonvariant points of level of five-component structure (on the diagram they are designated by dashed lines, and directions of translation-point lines). The phase composition of precipitation characteristic of these monovariant curves is identical to the phase composition of the corresponding translatable Quad nonvariant points (tab.1).

Four monovariant curves are between nonvariant points level pathcomponents composition. They are marked by thick solid lines and are characterized by the following phase composition of precipitation:



Divariant fields are formed as a result of translation of monovariant curves of the level of four-component composition. Their list and contours on the diagram are given in the tab. 2.

Table 1

Phase composition of the nonvariant points of the system $K, Ca // SO_4, CO_3, F-H_2O$ at 25 °C at the level of the four-component composition

Nonvariant points	Phase composition of precipitation	Nonvariant points	Phase composition of precipitation
System $K_2SO_4 - K_2CO_3 - KF - H_2O$		System $K, Ca // SO_4, CO_3 - H_2O$	
E_1^4	$Kb + Ar + K \cdot 1.5$	E_6^4	$Ar + K \cdot 1.5 + Sn$
System $CaSO_4 - CaCO_3 - CaF_2 - H_2O$		E_7^4	$Gp + Cs + Sn$
E_2^4	$Gp + Cs + Fo$	E_8^4	$K \cdot 1.5 + K \cdot Ca + Sn$
System $K, Ca // SO_4, F - H_2O$		E_9^4	$K \cdot Ca + Cs + Sn$
E_3^4	$Kb + Fo + Sn$	System $K, Ca // CO_3, F - H_2O$	
E_4^4	$Kb + Ar + Sn$	E_{10}^4	$K \cdot 1.5 + Kb + K \cdot Ca$
E_5^4	$Fo + Gp + Sn$	E_{11}^4	$K \cdot Cs + Fo + K \cdot Ca$
		E_{12}^4	$Kb + Fo + K \cdot Ca$

Table 2

The list and contours of the divariant fields of the system $K, Ca // SO_4, CO_3, F - H_2O$ at 25 °C, found by the translation method

Solid phases of divariant fields	The contours of the fields in the diagram (Fig.3)	Solid phases of divariant fields	The contours of the fields in the diagram (Fig.3)
Ar+Kb		$K \cdot 1.5 + Sn$	
Ar+K·1.5		Sn+Cs	
$K \cdot 1.5 + Kb$		$K \cdot 1.5 + K \cdot Ca$	
Gp+Fo		$K \cdot Ca + Sn$	
Gp+Cs		$K \cdot Ca + Cs$	
Fo+Cs		$K \cdot Ca + Kb$	
Sn+Fo		$K \cdot Ca + Fo$	
Fo+Sn		Ar+Sn	

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Geometric sort	The functionality of the system	
	A	B
Divariant fields	8	18
Monovariant curves	18	16
Non-invariant points	12	5

On the base of given, we can concluded that the above factors should be taken into account in the development of modern technologies for the production of individual salts from minerals, as well as in the treatment of multi-component industrial salt-con.

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