Phase Equilibria in the Na, K//SO₄, CO₃, HCO₃ – H₂O System at 50°C

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Phase equilibria in Na,K//SO₄,CO₃,HCO₃–H₂O system at 50°C are studied by the translation method. 32 divariant fields, 36 univariant curves, and 13 invariant points are determined in the system. The first closed phase diagram (phase complex) of the investigated quinary system is constructed. The constructed phase diagram is fragmented into divariant fields of co-crystallization of the two phases at the quinary level.

Keywords: multicomponent phase equilibria; quinary phase diagram, translation method; compatibility principle; Gibb's phase rule

1. Introduction

The study of multicomponent systems, including water-salt systems, is one of the urgent tasks in chemistry. It is necessary not only to determine the laws governing the state of the phase equilibria and solubility in them, but it is essential to establish the optimal concentration and temperature processing conditions of poly-mineral natural and complex technical material. At the same time, the study of multicomponent systems holds many challenges, the most important of which are; high material costs and time for experimentation, difficulties in the identification of the equilibrium solid phases and inability to display the discovered patterns using geometric shapes of the real three-dimensional space, etc. In this regard, there is an urgent need to search for new methods of investigation of multicomponent systems to get as much information as possible about the patterns of phase equilibria in multicomponent systems with the minimal use of material resources and time.

2. Method

In the present paper we consider the results of prediction of phase equilibria in the quinary Na, K//SO₄, CO₃, HCO₃–H₂O system at 50°C by means of translation method. The translation method originates from the compatibility principle of structural elements of n-component subsystems and global (n+1)-component system in a single diagram [1]. Translation method allows us to predict the phase equilibria in global (n+1)-component system on the basis of data on phase equilibria in n-component subsystems. Whereby taking into account both results of this prediction and Gibbs phase rule [2] enables us to construct closed phase equilibria diagram for global (n+1)-component system which is under consideration. Thus constructed closed phase diagram for the multicomponent system can more accurately identify its equilibrium phases, significantly reducing its time and cost of its experimental study. The prediction of multicomponent phase equilibria and construction of multicomponent phase diagrams by means of translation method are comprehensively considered in the literature [3-5]. This method has been earlier employed to study the phase equilibria at 0 and 25°C in the investigated system [6, 7].

3. The quinary Na, K//SO₄, CO₃, HCO₃–H₂O system at 50°C

The studied quinary system comprises the following quaternary subsystems: Na₂SO₄-Na₂CO₃-NaHCO₃-H₂O, K₂SO₄-K₂CO₃-KHCO₃-H₂O, Na, K//SO₄, HCO₃–H₂O, Na, K//CO₃, HCO₃–H₂O and Na, K//SO₄, CO₂–H₂O. Phase equilibria characterizing the invariant points of listed quaternary systems which are taken from available literature [8] and partially complemented by the translation method presented in Table 1. In Table 1 and thereafter, E denotes an invariant point, whose superscript indicates the point multiplicity (system complexity) and subscript indicates the point number. For the equilibrium solid phases the following conventional notations are used throughout the study: Nh-Nahkolite NaHCO₃; Te-Thenardite Na₂SO₄; Tr-Trona NaHCO₃–NaCO₃–2H₂O; Br-Burkeite-2Na₂SO₄,Na₂CO₃; Ar-Arkanite K₂SO₄; Gs-Glasersite 3K₂SO₄,Na₂SO₄; Ke-Kalicinite KHCO₃; C.1-Na₂CO₃–H₂O; K.1,5-K₂CO₃,1,5H₂O; S-2KHCO₃,K₂CO₃,1,5H₂O; N- NaHCO₃,K₂CO₃,2H₂O and Na,K-Na₂CO₃-K₂CO₃.

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3.1 Phase equilibria diagram of Na, K//SO$_4$, CO$_3$, HCO$_3$-H$_2$O system on quaternary level

Figure 1 shows the phase equilibria diagram constructed on the basis of data given in Table 1 by the translation method at the quaternary level (development of salt part of the systems).

Table 1. Phase equilibria in invariant points in the Na, K//SO$_4$, CO$_3$, HCO$_3$-H$_2$O system at 50°C at the quaternary level

| Point | Composition |
|-------|-------------|
| E$_1$ | Nh + Te + Tr |
| E$_2$ | Br + Te + Tr |
| E$_3$ | Br + Tr + C.1 |
| Na, K//SO$_4$, CO$_3$, HCO$_3$-H$_2$O | Na$_2$SO$_4$–Na$_2$CO$_3$–NaHCO$_3$–H$_2$O |
| E$_4$ | Na.K + Tr + C.1 |
| E$_5$ | Kc + Nh + Tr |
| E$_6$ | Na.K + N + K.1.5 |
| Na, K//SO$_4$, HCO$_3$–H$_2$O | Na, K//CO$_3$, HCO$_3$–H$_2$O |
| E$_7$ | Ar + Gs + K.1.5 |
| E$_8$ | Gs + Na.K + K.1.5 |
| E$_9$ | Br + Na.K + C.1 |
| E$_10$ | N + S + K.1.5 |
| E$_11$ | Br + Na.K + Gs |
| E$_12$ | Ar + Gs + Kc |
| E$_13$ | Gs + Nh + Kc |
| E$_14$ | Na.K + Tr + C.1 |
| E$_15$ | Ar + S + K.1.5 |
| E$_16$ | K$_2$SO$_4$–K$_2$CO$_3$–KHCO$_3$–H$_2$O |
| E$_17$ | Ar + S + Kc |
| E$_18$ | K$_2$SO$_4$–K$_2$CO$_3$–KHCO$_3$–H$_2$O |
| E$_19$ | N + Tr + Na.K |
| E$_20$ | N + Tr + Kc |

Fig. 1. Development of the salt part of the phase diagram of Na, K//SO$_4$, CO$_3$, HCO$_3$–H$_2$O system at 50°C at the quaternary level.
After unification of the constructed diagrams (association of identical crystallization fields of different quaternary subsystems) we obtain schematic [9] phase equilibria diagram of the studied quinary system at the quaternary level, which is presented in Figure 2.

![Figure 2](image-url)

**Figure 2.** Schematic phase equilibria diagram constructed by the translation method for the system Na,K//SO₄,CO₃,HCO₃,H₂O at 50°C at the quaternary level

**3.2. Translation of quaternary points into quinary level**

The "through translation" [3, 5] of quaternary invariant points of quaternary subsystems to the quinary level gives the following quinary invariant points with characterized equilibrium solid phases:

- \( E_1 + E_{11} \rightarrow E_1 = \text{Nh+Te+Tr+Gs} \)
- \( E_2 + E_6 \rightarrow E_2 = \text{Br+Te+Tr+Gs} \)
- \( E_5 + E_{17} \rightarrow E_5 = \text{Ar+S+Kc+N} \)
- \( E_3 + E_9 + E_{14} \rightarrow E_3 = \text{Br+Tr+C.1+Na.K} \)
- \( E_4 + E_{18} \rightarrow E_4 = \text{Ar+S+N+K.1,5} \)
- \( E_7 + E_{12} \rightarrow E_6 = \text{Ar+Gs+K.1,5+Kc} \)
- \( E_8 + E_{16} \rightarrow E_7 = \text{Gs+Na.K+K.1,5+N} \)
- \( E_{13} + E_{15} \rightarrow E_8 = \text{Gs+Nh+Kc+Tr} \)

As a result of "single-direction translation" [3, 5] of quaternary \( E_{10}^4, E_{19}^4 \) and \( E_{20}^4 \) invariant points to the quinary level, the following quinary invariant points with characterized equilibrium solid phases are determined:

- \( E_{10} + \text{Tr} \rightarrow E_9 = \text{Br+Gs+Na.K+Tr} \)
- \( E_{19} + \text{Gs} \rightarrow E_{10} = \text{Tr+N+Na.K+Gs} \)
- \( E_{20} + \text{Gs} \rightarrow E_{11} = \text{Tr+N+Kc+Gs} \)

For the unification of all geometric figures of the Na, K//SO₄, CO₃, HCO₃,H₂O system at 50°C, the presence of two more quinary invariant points, which are characterized by the following phase composition of precipitates, determined by "intermediate translation" [3, 5]:

- \( E_{12}^5 = \text{Ar+K.1,5+N+Kc} \)
- \( E_{13}^5 = \text{Gs+K.1,5+Kc+N} \)
3.3. Phase equilibria diagram of Na, K//SO₄, CO₃, HCO₃-H₂O system at the quinary level

The unified phase equilibria diagram constructed by translation method for the quinary Na, K//SO₄, CO₃, HCO₃-H₂O system at 50°C at the quinary level, is shown in Figure 3.

In Figure 3, thin solid lines represent univariant curves of the quaternary level whose phase composition of precipitation are given above. The dashed lines are also the univariant curves. They are formed as a result of translation of quaternary invariant points. Their phase composition is identical to the phase composition of the quaternary invariant points translated (Table 1) and the direction of translation of these points are indicated by arrows. Thick solid lines are univariant curves extending between the quinary invariant points and characterized by the following phase composition of precipitates:

\[
\begin{align*}
E_1 & = Gs + Tr + Tc; \\
E_2 & = Gs + Tr + S + N; \\
E_9 & = Br + Gs + Tr; \\
E_5 & = Br + Tr + Na. K; \\
E_4 & = Ar + S + N; \\
E_10 & = Gs + Tr + Na.K; \\
E_11 & = Gs + Tr + N; \\
E_12 & = Ar + N + K.1.5; \\
E_13 & = Gs + N + Kc;
\end{align*}
\]
whose outlines and equilibrium solid phases are presented in Table 2.

Conclusions
The quinary Na,K/\(\text{SO}_4\),\(\text{CO}_3\),\(\text{HCO}_3\)-H\(_2\)O system at 50\(^\circ\)C is characterized by 32 divariant fields whose outlines and equilibrium solid phases are presented in Table 2.

Table 2. Listing and outlines of divariant crystallization fields in Na, K/\(\text{SO}_4\), \(\text{CO}_3\), \(\text{HCO}_3\)-H\(_2\)O system at 50\(^\circ\)C at the quinary level

| Solid Phases | Field Outlines (Fig. 3) | Solid Phases | Field Outlines (Fig. 3) | Solid Phases | Field Outlines (Fig. 3) |
|--------------|--------------------------|--------------|--------------------------|--------------|--------------------------|
| 1            | 2                        | 3            | 4                        | 5            | 6                        |
| Tr + Te      | \(E_1^4\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^5\) | Tr + Na.K    | \(E_1^4\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^3\) \(\rightarrow\) \(E_9^5\) | S + K.1.5    | \(E_4^5\) \(\rightarrow\) \(E_1^4\) \(\rightarrow\) \(E_3^4\) |
| Nh + Te      | \(E_1^1\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^1\) | Ar + N       | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Ar + Kc      | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
| Nh + Tr      | \(E_1^3\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^1\) | Kc + Nh      | \(E_1^3\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Kc + S       | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
| Br + Tr      | \(E_1^2\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^3\) | N+Tr         | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Br + Gs      | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
| Br + Te      | \(E_1^2\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^6\) | Gs + Tr      | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Gs + Te      | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
| Br + C.1     | \(E_1^3\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^6\) | Kc + N       | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Gs + K.1.5   | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
| Tr + C.1     | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^6\) | Gs + Kc      | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Ar + Gs      | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
| Ar + S       | \(E_1^4\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_2^1\) \(\rightarrow\) \(E_5^6\) | N + S        | \(E_1^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_5^4\) | Gs + Na.K    | \(E_4^5\) \(\rightarrow\) \(E_1^5\) \(\rightarrow\) \(E_3^4\) |
As seen in Table 2, 30 out of 32 divariant fields are formed as a result of translation of univariant curves of quaternary level to the quinary level and 2 more fields with the following equilibrium solid phases (Gs + Tr) and (Ar + N) are formed by delineation of the surface of system by quinary invariant points and curves extending between points.

As a whole, the quinary Na, K/\(\text{SO}_4\), \(\text{CO}_3\), HCO\(_3\)-H\(_2\)O system at 50°C is characterized by the following number of geometric figures for the quaternary(A) and quinary(B) levels:

| Level                  | A  | B  |
|------------------------|----|----|
| Invariant points       | 20 | 13 |
| Univariant curves      | 30 | 36 |
| Divariant fields       | 12 | 32 |

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