Elucidation of phase equilibria in quinary system composed of lithium, sodium, and potassium cations along with sulfate and tetraborate anions at 0°C

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Abstract
The results of determination of phase equilibria in quinary system which is composed of lithium, sodium, and potassium cations along with sulfate and tetraborate anions at 0°C by translation method were discussed. Six invariant points, eighteen monovariant curves, nineteen divariant fields and eight trivariant volumes were observed in this system. The total phase equilibria diagram of the system was fragmented into divariant co-crystallization fields of two solid phases and trivariant crystallization volumes of individual solid phases. The extracted crystallization volumes from total diagram reflect the structures of projected Janecke diagrams of the system saturated with the solid phases. The obtained results agree well with available experimental results and comprehensively clarify the reciprocal relations of phases in the system.

Keywords: translation method, phase equilibria, trivariant crystallization volume, divariant field, total phase equilibria diagram.

1. Introduction
The phase equilibria in the Li, Na, K // SO4, B4O7 - H2O quinary system at the isotherm of 0°C have recently been studied by Zeng et al [1]. The authors experimentally measured the solubilities and the densities of the equilibrated solutions in the system and have presented a stereodiagram along with two more projected diagrams of the system saturated with Na2B4O7 and Li2B4O7 phases. Because reducing the dimension of total phase diagrams inevitably leads to a loss of information [2], the study of the parts saturated with the latter two Na2B4O7 and Li2B4O7 phases has generated only partial data on this complex system. Unless the parts saturated with other phases are observed a thorough knowledge on the corresponding phase equilibria in the system is not obtained.

Much more detailed phase equilibria data can be obtained by means of translation method [3] for conditions where saturation of the Li, Na, K // SO4, B4O7 - H2O system with Na2B4O7 and Li2B4O7 phases is not under consideration at 0°C. This work presents the results of comprehensive investigation of phase equilibria in Li, Na, K // SO4, B4O7 - H2O quinary system at 0°C using translation method. A brief discussion of phase equilibria along with crystallization and dissolution processes in the system were considered in the previous study of the systems by means of translation method [4]. The method which has already demonstrated its advantages was used in investigation of phase equilibria in several complicated water –salt systems so far [5-10]. Translation method provides comprehensive phase equilibria knowledge at the geometrical figures and produces total phase equilibria diagram which reveals reciprocal relation among points, curved, fields and volumes of the system. It derives from the third principle of physicochemical analysis [11] and complies with Gibbs’ phase rule. The phase equilibria data in n-component subsystems are used to predict the phase equilibria in higher (n+1) - component...
overall system by means of translation method. This method outlines the transformation and respective extension of geometrical figures of n-component subsystems into overall composition of system that contains \((n+1)\) - components. While the geometrical figures increase their dimension by one unit the points, curves and fields of n-component subsystems transform into curves, fields and volumes of the overall \((n+1)\) - component system respectively.

The primary step of this method is determination of invariant points in \((n+1)\) - component system which leads to the extension of other geometrical figures (curves and fields) of subsystems into the overall composition. This extension facilitates consecutive generation of geometrical figures of the overall system.

The invariant points of the overall system generate by simultaneous extension of two or three invariant points or by independent extension of points of subsystems. The formation of points by independent extension of points of subsystems into overall composition requires a complementary solid phase from adjacent subsystems. Intermediate points of overall composition are not required in this study.

The obtained results from the experimental investigation by Zeng et al lead to more comprehensive and conclusive theoretical elucidations of phase equilibria in the Li, Na, K // SO₄, B₂O₇ - H₂O system when the system is investigated using translation method.

There are 8 solid phases in equilibrium in Li, Na, K // SO₄, B₂O₇ - H₂O quinary system at 0°C. The following notations were acquired for the solid phases: mirabilite - Na₂SO₄·10H₂O (Mb); arcanite- K₂SO₄ (Ar); borax - Na₂B₄O₇·10H₂O (NB10); LiBO₂·8H₂O (LB8); KLiSO₄ (KLS); 3Na₂SO₄·Li₂SO₄·12H₂O (NL12); Li₂SO₄·H₂O (LS1); K₂B₄O₇·4H₂O (KB4).

2. Determination of phase equilibria using translation method

2.1 Phase equilibria in quaternary subsystems

The quinary system which is composed of lithium, sodium, and potassium cations along with sulfate and tetraborate anions involves five quaternary Li, Na, K // SO₄, B₂O₇ –H₂O; Na, K // SO₄, B₂O₇ –H₂O; Li, K // SO₄, B₂O₇ –H₂O; Li, Na // SO₄, B₂O₇ –H₂O; Li, Na // SO₄, B₂O₇ –H₂O subsystems. The equilibrium solid phase compositions of these quaternary subsystems are given in Table 1 [1]. The invariant points in Table 1 enable the construction of quaternary schematic phase equilibria diagrams where the monovariant co-crystallization curves extending from the relevant ternary points and the curves that link the latter quaternary points are reflected. The direction of the arrows that represent the quaternary curves extending from ternary points show the translation of the points as monovariant curves of the quaternary composition.

In Table 1 and thereafter the invariant points are represented by capital letter “E” whose subscript and superscript denote the point serial number and the complexity of the system relevant to the point respectively.

| Invariant Point | Equilibrium Solid Phases | Invariant Point | Equilibrium Solid Phases | Invariant Point | Equilibrium Solid Phases |
|-----------------|--------------------------|-----------------|--------------------------|-----------------|--------------------------|
| Quaternary Na, K // SO₄, B₂O₇ – H₂O | Quaternary Li, Na // SO₄, B₂O₇ – H₂O | Quaternary Li, K // SO₄, B₂O₇ – H₂O |

Table 1. The list of quaternary invariant points and relevant equilibrium solid phases in Li, Na, K // SO₄, B₂O₇ – H₂O quinary system at 0°C. (Also solid phase composition of the quinary curves that generate from the relevant quaternary invariant points)
The quaternary schematic phase equilibria diagrams arranged on an unfolded prism in Figure 1 which reflects the composition of quinary Li, Na, K // SO₄, B₄O₇ - H₂O system on quaternary level are constructed according to the data in Table 1. The curves on the sides belong to the n-component subsystems whereas the internal curves belong to the relevant (n+1)-component overall systems in phase equilibria diagrams. Similarly, the external thin curves in Figure 1 belong to the ternary subsystems while the thick curves along with dotted arrows inside the diagrams belong to the quaternary subsystems.
Combining common crystallization fields of quaternary diagrams in Figure 1 produces a transition diagram from quaternary to quinary composition of the system in Figure 2. The obtained diagram in Figure 2 will be used as a matrix where the quinary geometrical figures are superimposed. A separate segment for arcanite in diagram in Figure 2 completes the external parts of the prism which reflects the solid phase composition of system on quaternary level. The reason for being called transition diagram is that it reflects the composition of the quinary system in terms of the quaternary points, curves and fields of the system.

2.2 Determination of quinary invariant points

Equations 1-4 list the four of the quinary points of the systems; the quinary $E^5_1$ point in eq 1 is generated by triple translation while the three $E^5_2$, $E^5_3$ and $E^5_4$ points in eqs 2-4 are generated by double translation of relevant quaternary points into the quinary composition. Each of the participating points in generation of the latter four quinary points is found in different quaternary subsystems and vary by one solid phase generating the same quinary point.

$$E^4_1 + E^4_9 + E^4_{12} \rightarrow E^5_1 = \text{Ar} + \text{KB4} + \text{NB10} + \text{LB8} \quad (1)$$

$$E^4_8 + E^4_{10} \rightarrow E^5_2 = \text{LB8} + \text{NB10} + \text{LS1} + \text{KLS} \quad (2)$$

The solid composition quinary

$$E^4_5 + E^4_6 \rightarrow E^5_3 = \text{LS1} + \text{NL12} + \text{NB10} + \text{KLS} \quad (3)$$

$$E^4_3 + E^4_7 \rightarrow E^5_4 = \text{KLS} + \text{Mb} + \text{NB10} + \text{NL12} \quad (4)$$

The solid composition quinary

of the points in eqs 1-4 does not have any other alternative choices on the overall composition. These are the four points in the system that can easily be determined based on the location of the quaternary points. Except the nine quaternary points that participate in generation of the quinary points in equations
1-4; there are three more quaternary $E_2^4$, $E_4^4$ and $E_{11}^4$ points among which one must extend independently and two others simultaneously into the overall composition of the system. This case involves two options; if the two $E_2^4$ and $E_4^4$ points extend simultaneously and generate a quinary point then the quaternary $E_{11}^4$ point extends independently, if the $E_4^4$ and $E_{11}^4$ points extend simultaneously then the $E_2^4$ point extends independently.

In the latter case of determination of quinary points from the extension of three $E_2^4$, $E_4^4$ and $E_{11}^4$ points the results obtained by Zeng et al were taken into consideration. Each of the 6 quinary points determined by Zeng et al contains NB10 phase, hence; the presence of the latter phase in generating quinary points must be ensured. Because none of the quaternary $E_{11}^4$ and $E_4^4$ points contains the required NB10 phase; the concurrent translation of two $E_{11}^4$ and $E_4^4$ points does not meet this requirement. As a result of concurrent extension of two $E_{11}^4$ and $E_4^4$ quaternary points and independent translation of the remaining $E_2^4$ point along with NB10 phase which occurs in adjacent subsystem the invariant points of quinary composition in eqs 5, 6 are obtained.

\[
\begin{align*}
E_2^4 + E_4^4 & \rightarrow E_5^5 = \text{NB10 + KLS + Ar + Mb} \quad (5) \\
E_1^4 + \text{NB10} & \rightarrow E_6^5 = \text{Ar + KLS + NB10 + LB8} \quad (6)
\end{align*}
\]

2.3 Quinary monovariant curves

Translation method, which has undoubtedly achieved a well degree of maturity classifies the monovariant curves of overall (n+1) - component systems into two main types; the curves that generate as a result of transformation and extension of invariant points of n-component subsystems and the curves that link the invariant points of overall (n+1) - component systems. Although these two types of curves meet the requirements of the Gibbs’ phase rule for overall compositions of systems, they have different nature of formation and hence must be considered separately in investigation of multicomponent water-salt systems.

There are 12 quaternary invariant points in Table 1 that extend as monovariant curves of the quinary composition as the relevant subsystems enter into the composition of quinary Li, Na, K // SO$_4$, B$_4$O$_7$ - H$_2$O system. The equilibrium solid phase compositions of this type of curves are identical with the equilibrium solid phase compositions of relevant quaternary invariant points at the origin of the curves.

The second type of monovariant curves includes the ones that link the determined quinary invariant points in eqs 1-6. Each of these curves extends between two different quinary points that vary from each other by one equilibrium solid phase. There are six curves of this type in the Li, Na, K // SO$_4$, B$_4$O$_7$ - H$_2$O system, which are shown in Table 2.
Table 2. The equilibrium solid phases at the quinary curves that link the quinary points of the Li, Na, K // SO₄, B₄O₇ - H₂O system at 0°C.

| Quinary points and linking curves | Solid phases saturating the curves | Quinary points and linking curves | Solid phases saturating the curves | Quinary points and linking curves | Solid phases saturating the curves |
|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| E₁ → E₆ = LB₈, NB₁₀, Ar;         | E₄ → E₅ = Mb, NB₁₀, KLS;         | E₃ → E₄ = NL₁₂, NB₁₀, KLS;       |                                  |                                  |                                  |
| E₂ → E₃ = KLS, NB₁₀, LS₁;        | E₂ → E₆ = KLS, NB₁₀, LB₈.        |                                  | E₅ → E₆ = Ar, NB₁₀, KLS.         |                                  |                                  |

The extension of quaternary points as monovariant curves, the determined quinary points at their intersection points and also the curves that link the quinary points are shown schematically in Figure 3. The whole set of determined quinary geometrical figures by means of translation method and reciprocal relationship among them are reflected in the scheme in Figure 3. It settles inside the triangular prism that represents the phase equilibria in investigated quinary system.

There are three and four solid phases along with relevant liquid phases in equilibrium at each of the curves and points of the quinary composition. The points that are generated as a result of translation of three, two and one quaternary points into the overall composition link to one, two and three other points through the monovariant curves respectively. The first quinary E₅₁ invariant point is generated from extension of three quaternary points hence links through only one quinary monovariant curve to the adjacent quinary E₅₆ point. While the E₅₆ point links to three adjacent points through the monovariant curves due to its independent formation. Each of the rest of the quinary points, which are generated from extension of two quaternary points into the overall composition, links to two other quinary points through the monovariant curves. The superimposition of set of quinary geometrical figures in Figure 3 on transition diagram in Figure 2 produces the total phase equilibria diagram of the system in Figure 4.

![Figure 3](image-url)  
*Figure 3. Reciprocal relationship between quinary geometrical figures in Li, Na, K // SO₄, B₄O₇–H₂O system at 0°C.*

![Figure 4](image-url)  
*Figure 4. Total diagram of the quinary Li, Na, K // SO₄, B₄O₇–H₂O system at 0°C [4].*
3. Results

The diagram in Figure 4 is considered as a total phase equilibria diagram due to its possession of every geometrical figure relevant to equilibrium solid phases in the system. The quinary invariant points saturated with four solid phases and monovariant curves saturated with solid phases along with their relevant equilibrium liquid phases in the system have been considered in the previous sections. In the two forthcoming sections; the divariant fields saturated with two solid phases and trivariant volumes saturated with one solid phases along with equilibrium liquid phases will be discussed through the fragmentation of obtained diagram in Figure 4 into segments.

3.1 Extraction of divariant co-crystallization fields from total diagram

There are two solid phases and relevant liquid phase in equilibrium in quinary divariant fields. The fields which were extracted from the total diagram in Figure 4 along with their relevant equilibrium solid phases are shown in Table 3. While the nineteenth divariant field in the table forms on the overall quinary composition. The extraction which follows the quinary monovariant curves and invariant points at their linkage includes every curve in Figure 2.

| # | Equilibrium solid phases and outlines of divariant fields | # | Equilibrium solid phases and outlines of divariant fields | # | Equilibrium solid phases and outlines of divariant fields | # | Equilibrium solid phases and outlines of divariant fields |
|---|---|---|---|---|---|---|---|
| 1 | E<sub>4</sub> - E<sub>5</sub> | 4 | E<sub>5</sub> - E<sub>6</sub> | 5 | E<sub>6</sub> - E<sub>5</sub> | 1 | E<sub>4</sub> - E<sub>5</sub> |
| 2 | E<sub>9</sub> - E<sub>10</sub> | 5 | E<sub>10</sub> - E<sub>9</sub> | 6 | E<sub>10</sub> - E<sub>9</sub> | 7 | E<sub>9</sub> - E<sub>10</sub> |
| 3 | E<sub>12</sub> - E<sub>13</sub> | 8 | E<sub>13</sub> - E<sub>12</sub> | 9 | E<sub>12</sub> - E<sub>13</sub> | 10 | E<sub>12</sub> - E<sub>13</sub> |
| 4 | E<sub>14</sub> - E<sub>15</sub> | 11 | E<sub>15</sub> - E<sub>14</sub> | 12 | E<sub>15</sub> - E<sub>14</sub> | 13 | E<sub>15</sub> - E<sub>14</sub> |
| 5 | E<sub>16</sub> - E<sub>17</sub> | 14 | E<sub>17</sub> - E<sub>16</sub> | 15 | E<sub>17</sub> - E<sub>16</sub> | 16 | E<sub>17</sub> - E<sub>16</sub> |

Each pair of solid phases in divariant fields in Table 3 saturates every relevant geometrical figure.
at the outlines of fields. The quaternary and quinary invariant points and monovariant curves that link them are saturated with the phases namely. The number of involvement of each of the equilibrium solid phases in relevant divariant fields is: K₂B₄O₇·4H₂O in 3 fields; each of Li₂SO₄·H₂O, Na₂SO₄·10H₂O and 3Na₂SO₄·Li₂SO₄·12H₂O in 4 fields; each of K₂SO₄ and LiBO₂·8H₂O in 5 fields; KLiSO₄ in 6 fields and Na₂B₄O₇·10H₂O in 7 fields. Sets of relevant divariant fields to the equilibrium solid phases are arranged in each of the volumes obtained in the next section.

3.2 Extraction of trivariant crystallization volumes from the total diagram

In individual crystallization volumes in Figure 5 that were extracted from the diagram in Figure 4 every point, curve and field is saturated with the relevant solid phase. The volumes which are saturated with the related solid phases throughout occupy the interior of the total phase equilibria diagram.
The Table 4 compiles the total number of quaternary and quinary geometrical figures in the quinary Li, Na, K // SO₄, B₂O₇ - H₂O system at 0°C. As the quinary trivariant volumes form when the quaternary divariant fields extend into the composition of overall system the number of volumes is equal to the number of quaternary divariant fields. While the quinary divariant fields involves the translated 18 quaternary monovariant curves and the field formed on the quinary level making the total number of 19 which is one more than the number of quaternary monovariant curves. Whereas, the quinary monovariant curves includes the 12 curves generated from translation of quaternary invariant points into overall composition and the 6 curves extending between determined quinary points.

### Table 4. Number of geometrical figures at the quinary and quaternary compositions of Li, Na, K // SO₄, B₂O₇ - H₂O system at 0°C.

| Level             | Quaternary | Quinary |
|-------------------|------------|---------|
| Invariant points  | 12         | 6       |
| Monovariant curves| 18         | 18      |
| Divariant fields  | 8          | 19      |
| Trivariant volumes| –          | 8       |

4. Discussions

The number of divariant fields in recent experimental study was misinterpreted as eight, which is equivalent to the number of trivariant volumes of the respective equilibrium solid phases in the system, due to complexity of the system. Table 3 gives 19 divariant fields of the system which are extracted from total phase equilibria diagram in Figure 4. Eighteen of the fields are generated as a result of extension of available quaternary monovariant curves to the quinary composition while the last field where the pair of NB10 and KLS solid phases are in equilibrium is formed on the quinary level in involvement of the quinary geometrical figures hence possesses a different nature.

The total phase equilibria diagram in Figure 4, which is constructed without elimination of any of the phases in the system, involves the whole content of the system. What is widely used today; is the parts of the multicomponent systems saturated with a solid phase, which is due to dimensionality of the space and complicated compositions of the systems. Although the Gibbs’ diagrams obtained for halite saturated oceanic systems are used widely [12]; there is no guarantee of such kind of saturation in every multicomponent water-salt system. The obtained diagram in Figure 4 which was simplified by fragmentation into segments in Figure 5 responses to most of
the questions about the system; the individually saturated parts by each of the available solid phases, nearby crystallization fields, the crystallization pathways and genetic formation of solid phases from contents of system etc.

The reciprocal arrangement of geometrical figures in latter volumes in Figure 5 gives the structures of projected diagrams of system saturated with relevant equilibrium solid phases in the quinary Li, Na, K // SO₄, B₄O₇ - H₂O system at 0°C. The parts of the system which were experimentally observed and investigated by Zeng et al are shown in Figure 5e and 5h. The volume in Figure 5e involves the 3 quinary points, 7 monovariant curves and 5 divariant fields saturated with the LiBO₄·8H₂O while the volume in Figure 5h involves the 6 quinary points, 12 monovariant curves and 7 divariant fields saturated with the Na₂B₄O₇·10H₂O. The respective projected diagrams presented by Zeng et al involves the same number of geometrical figures and identical equilibrium solid phases shown in Figure 5e and 5h. The reciprocal locations of nearby crystallization phases in Figure 5e and 5h are in well agreement with the results of Zeng et al [1].

Likewise this quinary Li,Na,K //SO₄,B₄O₇ - H₂O system the oceanic quinary Na,K,Mg//Cl,SO₄ - H₂O system which has thoroughly been studied thermodynamically [13,14] and experimentally can also be investigated with respect to saturated parts with each of the equilibrium solid phases by means of translation method.

The simplified diagrams which do not give quantitative relations but show common crystallizing phases along with their crystallization sequences are preferred particularly in physicochemical mineralogy of multicomponent systems. These simplified or as sometimes called qualitative diagrams have great importance in paragenetic investigation of minerals; e.g. observation of laws of their coexistence in rocks [15].

The diagrams in Figure 6 show simplified forms of the volumes in Figure 5. The $E_2^a$ invariant notations and the arrows that represented the quinary curves generated from the quaternary points are given as the intersections points of the curves and mere solid curves respectively in Figure 6. The diagrams in Figure 6 which are obtained from the diagrams in Figure 5 for each of the equilibrium solid phases have the same importance and usage as qualitative diagrams in physicochemical analysis of relevant minerals.
5. Conclusions

This study reveals a comprehensive phase equilibria knowledge in the quinary Li, Na, K // SO₄, B₄O₇ – H₂O system at 0°C and broaden the relevant phase equilibria data. The obtained results can be used as guides in comprehensive utilization and exploitation of the quinary Li, Na, K // SO₄, B₄O₇ – H₂O system. They can also be used as reference data to understand the physical chemistry as well as crystallization-dissolution pathways of salts in this complicated system. The total phase equilibria diagram of the system involves structures of the available diagrams of the system saturated with Na₂B₄O₇ and Li₂B₄O₇ phases along with the diagrams of the system saturated with rest of the solid phases in the system. The relevant structures of the Jancecke dry-salt diagrams were obtained volumes from total phase equilibria diagram which includes all sections of the system saturated with the equilibrium solid phases.

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Figures 6 (a-h). Simplified forms of trivariant volumes in the quinary Li, Na, K // SO₄, B₄O₇ – H₂O system at 0°C.

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