Prediction of phase equilibria in multicomponent water-salt systems by means of translation method

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Abstract. The translation method which can produce all the geometrical figures and closed phase equilibria diagram for multicomponent water-salt systems was described. The phase equilibria in quinary NaCl - KCl - MgCl₂ - CaCl₂ - H₂O (25°C) system which is an important part of the more complex oceanic Na, K, Mg, Ca // Cl, SO₄, H₂O system were determined using translation method. Three invariant points of quadruple saturation, ten monovariant curves of triple saturation and twelve divariant fields of double saturation salts were identified in the system. Two of the curves extend between the quinary invariant points while the other eight are generated from extension of the relevant quaternary invariant points into the quinary composition. A total phase equilibria diagram for the quinary NaCl - KCl - MgCl₂ - CaCl₂ - H₂O system at 25°C was constructed on the basis of obtained results. The diagram was fragmented into divariant fields of common crystallization of two salts. A good agreement was observed between the results obtained in this work and the available data in literature.

1. Introduction

The investigation of multicomponent systems, especially water-salt systems, is one of the primary tasks of relevant chemical scientists and chemical engineers. Not only the phase equilibria and solubility in systems are needed, but also the optimal parameters like concentration and temperature ranges of processing conditions of natural minerals and complex industrial wastes are required today. On the other hand, the study of multicomponent systems is not exempted from challenges. High amounts of experimental material resources and time, hardships in identification of the equilibrium solid phases, and human inability to display the discovered patterns using three-dimensional geometrical shapes of the space can be regarded as some of the difficulties in this field. In this regard, there is an urgent need to seek for new methods and methodologies of investigation of multicomponent systems to get as much information as possible about the patterns of phase equilibria with the minimal use of material resources and required time.

One of the main methods of studying multicomponent systems is the physicochemical analysis, which allows establishing the relation between constituent parts (components) of the homogeneous and heterogeneous systems. The founder of the theory of equilibrium multicomponent systems in its analytical expression was Josiah Wiliard Gibbs, who formulated the equilibrium conditions and the phase rule for the first time [1]. The exceptional value of the theory in phase equilibria of multicomponent systems was emphasized by Tamman [2] who emphasized that "the greater the number of substances in the mixture, the higher the demands on the experimenter to avoid unnecessary tests. In this case, the theory shows how with a minimum number of experiments one can achieve the desired results". The founder of
physicochemical analysis—Nikolai Semenovich Kurnakov who had formulated the subject and tasks along with the twofundamental principles of physicochemical analysis; consistency and continuity principles, had played very significant role in the development of experimental and theoretical research methods of multicomponent water-salt systems [3]. Most importantly, a valuable observation was made by him in the study of structure of phase diagrams of the chemical systems, based on which he deduced that the geometrical figures of subsystems extend into the overall composition of the system by the addition of new component or by changing any affecting parameter.

By making a proposal on the third fundamental principle of physicochemical analysis, which is called compatibility principle, Goroshchenko[4] theoretically justified the latter observation made by Kurnakov. According to compatibility principle, the phase diagram of the overall system must contain all of the geometrical figures of the diagrams of n-component subsystems along with the ones of the (n+1)-component overall system. The recognition of this principle as the third fundamental principle of physicochemical analysis enables one to predict the phase composition of the overall system and construct its relevant diagram on the basis of the data along with the structure of diagrams of its subsystems.

2. Translation method

In the present study we examined the results of prediction of phase equilibria in multicomponent systems by the translation method, which is based on both the compatibility principle of geometrical figures of “n” and (n+1)-component water-salt systems in the same diagram and the Gibbs’ phase rule.

2.1 "Through translation" technique

Application of the translation method for prediction of phase equilibria leads to the determination of invariant points of the overall (n+1)-component system by the use of its three different techniques. The first of the latter techniques determines the invariant points of overall systems by the unification of invariant points of relevant subsystems. This unification takes place by the extension of invariant points of n-component subsystems whose equilibrium solid phases correspond to the Gibbs’ phase rule and those are different from each other by one solid phase into the overall composition of the system. In multicomponent phase equilibria diagram it is implemented by the intersection of monovariant curves formed by the transformation of the invariant points which are translated to the (n+1)-component overall composition. This translation which is conventionally called "through-translation" [5, 6] is based on the fact that the monovariant curves generated by the extension of invariant points of n-component subsystems permeate the considered system through the aisles of its composition.

2.2. "Unilateral translation" technique

Invariant points of n-component subsystems which are not translated by the latter "through-translation" technique to the (n+1)-component composition are translated by the "unilateral-translation" [5, 6]. It is implemented by the intersection of the monovariant curve which is formed by the translation of latter invariant point to the (n+1)-component composition with the monovariant curve extending between the invariant points of overall (n+1)-component composition in phase equilibria diagram. Mathematically, this boils down to the determination of the phase composition of the invariant point at (n+1)-component level by the addition of missing solid phase to the composition of translated invariant point of n-component subsystem in consistence with the Gibbs’ phase rule.
2.3. **“Intermediate translation” technique**

The third and the complementary technique of determination of invariant points of \((n+1)\)-component overall systems is required at times. This type of prediction is conventionally called the "intermediate-translation" \([5, 6]\) and is used for the determination of the invariant points required to enclose the divariant fields generated by translation of monovariant curves of \(n\) - component subsystems to the \((n+1)\)-component composition. In phase equilibriadiagrams such invariant point is generated by the intersection of the monovariant curves that extend between the invariant points formed by "through" and/or "unilateral" translations.

2.4 Criteria of reliability of results obtained by translation method

The closure of all geometrical figures of phase equilibria (complex of phases) diagram of the investigated water-salt system in accordance with the Gibbs’ phase rule is considered as the primary criterion of the reliability of the data obtained by the translation method. The prediction of phase equilibria and construction of phase equilibriadiagrams for multicomponent systems by means of translation method is a versatile and promising method \([7]\) which functions in consistent with the fundamental concepts and main principles of physicochemical analysis as well as the Gibbs’ phase rule \([8]\). The amount of time and material resources of experimental studies of complicated systems are considerably reduced by the prediction of phase equilibria and construction of phase diagrams for the multicomponent salt-water systems by the translation method.

2.5 Thermodynamic predictions

Another relatively common method of prediction of the stable phase associates at the invariant points of multicomponent water-salt systems is the method based on the determination of thermodynamic potentials \([9-11]\). In this method, a solid phase is added to the composition of invariant points of the subsystems so a new component occurs in the system. The stability of the resulting combinations of solid and liquid phases is estimated by the value of the Gibbs’ free energy. However, as it is noted even by the authors of the method, the effectiveness of this method depends on the probability of calculating the change in Gibbs’ free energy to the extent of required accuracy, which decreases by increasing the number of components in the system. In addition, the construction of a closed phase equilibriadiagram for the quinary system and above is not enabled by this method.

3. **Prediction of phase equilibria in the quinary NaCl - KCl - MgCl₂ - CaCl₂ - H₂O system at 25°C by means of translation method**

Consider the application of the method for the calculation of phase diagram in quinary system NaCl - KCl - MgCl₂ - CaCl₂ - H₂O at 25°C which is considerably well investigated by the solubility method \([12]\) and thus enables us to compare the results obtained by the translation method. Quinary system NaCl - KCl - MgCl₂ - CaCl₂ - H₂O consists of the following four quaternary subsystems: NaCl - KCl-MgCl₂ - H₂O; NaCl - KCl - CaCl₂ - H₂O; NaCl - MgCl₂ - CaCl₂ - H₂O and KCl - MgCl₂ - CaCl₂ - H₂O. They are characterized by the quaternary invariant points of equilibrium solid phases presented in Table 1. In Table 1 and thereafter, \(E\) denotes the invariant point with superscript indicating the multiplicity of the point and subscript indicating its number. The following notations are adopted for the equilibrium solid phases: Bis - bischofite MgCl₂ · 6H₂O; Hal - halite, NaCl; Carn - carnallite KCl · MgCl₂ · 6H₂O; Syl - sylvite KCl; Tah - tachhydrite 2 MgCl₂ · CaCl₂ · 12H₂O and Ca · 6 - CaCl₂ · 6H₂O.
Table 1. Phase equilibria at invariant points of the system NaCl – KCl – MgCl2 – CaCl2 – H2O at 25°C at the quaternary level.

| Invariant points | Equilibrium solid phases | Invariant points | Equilibrium solid phases |
|------------------|--------------------------|------------------|--------------------------|
| System NaCl – KCl – MgCl2 – H2O | System NaCl – MgCl2 – CaCl2 – H2O |
| E1 | Bis + Hal + Carn | E4 | Bis + Hal + Tah |
| E2 | Hal + Carn + Syl | E5 | Hal + Tah + Ca6 |
| System NaCl – CaCl2 – H2O | System KCl - MgCl2 – CaCl2 – H2O |
| E3 | Hal + Syl + Ca6 | E6 | Carn + Syl + Ca6 |
| E7 | Carn + Syl + Ca6 | E8 | Carn + Tah + Ca6 |
| | Bis + Carn + Tah |}

A phase equilibria diagram for the quinary system NaCl - KCl - MgCl2 - CaCl2 - H2O at 25°C which reflects the salt part of its quaternary composition and which was constructed using the data in Table 1 is presented in Figure 1.

Figure 1. Development of salt part of the phase equilibrium diagram of the system NaCl – KCl – MgCl2 – CaCl2 – H2O at 25°C at the quaternary level.

The quaternary subsystems of the quinary NaCl – KCl – MgCl2 – CaCl2 – H2O system share common crystallization fields and following unification of identical crystallization fields of different quaternary subsystems, the quaternary level schematic [13] phase equilibria (complex of phases) diagram of the system Figure 2 is obtained.
The resulting schematic phase equilibria diagram serves as a matrix for superimposition of the geometrical figures of the overall (n+1)-component composition determined by the translation method.

All the possible phase equilibria; in the divariant fields (crystallization fields of individual solid phases), univariant curves (crystallization curves of two phases) and invariant points (crystallization points of the three phases in the system NaCl - KCl - MgCl₂ - CaCl₂ - H₂O at the four-component level) are reflected on the constructed schematic diagram (Figure 2). The equilibrium solid phase divariant fields are indicated in the figure. The equilibrium solid phase invariant points are shown in Table 1. The equilibrium solid phase composition of the monovariant curves that pass between the quaternary invariant points are given in Table 2.

The equilibrium solid phases at the quaternary monovariant curves of NaCl – KCl – MgCl₂ – CaCl₂ – H₂O system at 25°C.

| Quaternary point | Quaternary curve | Quaternary point | Equilibrium phases | Quaternary point | Quaternary curve | Equilibrium phases |
|------------------|------------------|------------------|--------------------|------------------|------------------|--------------------|
| E₁⁴            | ——               | E₄⁴             | Bis + Hal;         | E₁⁴            | ——               | Hal + Carn;       |
| E₂⁴            | ——               | E₄⁴             | Bis + Carn;        | E₂⁴            | ——               | Hal + Syl;        |
| E₃⁴            | ——               | E₄⁴             | Carn + Syl;        | E₃⁴            | ——               | Hal + Ca ∙ 6;     |
| E₄⁴            | ——               | E₄⁴             | Bis + Ca ∙ 6       | E₄⁴            | ——               | Tah + Tah;        |
| E₅⁴            | ——               | E₄⁴             | Carn + Ca ∙ 6     | E₅⁴            | ——               | Carn + Tah.       |

Translation of the quaternary invariant points to composition of quinary systems leads to the quinary invariant points with equilibrium solid phases given in Table 3.
Table 3. Generation and equilibrium solid phases at the quinary invariant points generated from the extension of quaternary points in the NaCl – KCl – MgCl₂ – CaCl₂ – H₂O system at 25°C.

| Quaternary points | Translation | Quinary points |
|-------------------|-------------|---------------|
| E₁⁴ + E₄⁴ + E₈⁴   | - - - ➔      | E₅⁵ = Bis + Hal + Carn + Tah; |
| E₂⁴ + E₃⁴ + E₆⁴   | - - - ➔      | E₅⁵ = Hal + Carn + Syl + Ca₆; |
| E₅⁴ + E₇⁴          | - - - ➔      | E₅⁵ = Hal + Carn + Tah + Ca₆. |

4. Results and discussion

The combined schematic phase equilibria (complex of phases) diagram [13] at the quinary level of the investigated system which is constructed based on the obtained data is presented in Figure 3.

As it can be seen in Figure 3 all three quinary invariant points are produced by the “through translation” technique which is associated with a small number of equilibrium solid phases in the system.

As the application example of the translation method in this work shows, in the prediction and construction of multicomponent phase equilibria diagrams of systems with a larger number of equilibrium solid phases, besides the "through" translation there can also be realized the "unilateral" and "intermediate" types of translations [14, 15].

Thin solid lines shown in Figure 3 represent the quaternary monovariant curves whose equilibrium solid phase compositions are given in Table 2, while the dotted arrows indicate the monovariant curves of five-component composition which are formed as a result of translation of quaternary invariant points to the quinary level. The solid phase compositions of the curves are identical to the phase composition of translated quaternary invariant points in Table 1 and the arrows indicate the direction of translation.
Thick solid lines shown in Figure 3 represent monovariant curves of the system at the five-component composition. They extend between the quinary invariant points of the system and are characterized with the equilibrium solid phases presented in Table 4.

| Quinary points and the curves extending between them | Equilibrium solid phases at the curves |
|------------------------------------------------------|---------------------------------------|
| \( E_3 \) | Hal + Carn + Tah                        |
| \( E_2 \) | Hal + Carn + Ca-6                      |

As the comparison of our data obtained by the translation method and the data obtained by the solubility method [12] shows, the phase composition of precipitates of quinary invariant points is identical to the experimental data. This proves the reliability of the data obtained by the translation method.

To read the diagrams constructed by translation method, fragmentation of the divariant fields of diagrams is needed. Table 5 presents the equilibrium solid phases and the contours of divariant fields saturated with two salts of the system \( \text{NaCl - KCl - MgCl}_2 - \text{CaCl}_2 - \text{H}_2\text{O} \) at 25°C, whose phase equilibria diagram is predicted and constructed by the translation method.

| Equilibrium solid phases of fields | Field outlines in the diagram(Fig.3) | Equilibrium solid phases of fields | Field outlines in the diagram(Fig.3) |
|-----------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|
| Hal + Carn | \( E_2 \rightarrow E_5 \rightarrow E_1 \) | Carn + Syl | \( E_2 \rightarrow E_5 \rightarrow E_1 \) |
| Bis + Hal | \( E_4 \rightarrow E_5 \rightarrow E_1 \) | Hal + Ca-6 | \( E_6 \rightarrow E_5 \rightarrow E_3 \) |
| Bis + Carn | \( E_4 \rightarrow E_5 \rightarrow E_1 \) | Carn + Ca-6 | \( E_4 \rightarrow E_5 \rightarrow E_3 \) |
| Hal + Syl | \( E_2 \rightarrow E_5 \rightarrow E_1 \) | Carn + Tah | \( E_4 \rightarrow E_5 \rightarrow E_1 \) |
5. Conclusions

We can conclude based on our results that the translation method is the most promising method for prediction and construction of phase equilibriadiagrams of multicomponent water-salt systems. It is based on the fundamentals of physico-chemical analysis, its fundamental principles, the Gibbs’ phase rule and topological properties of geometrical figures of chemical systems. The method enable determination of the quantity of characteristic geometrical figures of the system, their solid phase compositions and their relative arrangement on the diagram which greatly facilitates the subsequent experimental studies while reducing its time and material uses.

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