

GENERAL RESEARCH

A Generalized Method for the Solid–Liquid Equilibrium Stage and Its Application in Process Simulation

Xiaoyan Ji, Xin Feng, Xiaohua Lu,* Luzheng Zhang, Yanru Wang, and Jun Shi

Nanjing University of Chemical Technology, Nanjing 210009, China

Yunda Liu

ChemSim, 163 Summer Street, Maynard, Massachusetts 01754

For the important need of simulations of the crystallization process in aqueous electrolyte solutions, a generalized method is proposed in this paper for predicting the solid–liquid equilibrium stage by identifying the number of phases and their identities automatically. The proposed method is also used to generate phase diagrams and crystallization paths and to provide an example of the software that can be used to design, simulate, and optimize the related process. Several cases are studied to demonstrate the capability of the proposed method for systems with hydrate, multi-ion, and complex salts.

1. Introduction

Processes related to aqueous electrolyte solutions and solid phases represent an important aspect of modern chemical engineering, in areas such as inorganic chemicals, materials science, biochemistry, and environmental protection. For these processes, crystallization is often performed at a constant temperature, and in the related systems, electrolytes dissociate completely or partly into cations and anions, solid phases are immiscible, and compounds are often formed in the solid phase. The number of phases and their identities are too complicated to predict, which causes difficulties in the design of such processes.

At present, the number of phases and their identities are determined in advance using phase diagrams^{1–6} or the enumerative method^{7–9} during process design. The former method is unsuitable for complicated systems and infeasible to calculate continuously. In the latter method, all combinations should be tried, and good initial values are often required to calculate the activity coefficients of liquid components reliably. The difficulty of estimating initial values limits the use of this method in practice.

Another method based on free energy minimization is also used, especially in the field of metallurgy.¹⁰ The number of phases and their identities must be determined in advance for the free energy to be calculated. Presently, this is done by the enumerative method. Furthermore, the calculation of the free energy is also related to activity coefficients. For aqueous electrolyte solutions, a large number of models have been proposed, and the parameters of all of the models have been correlated with experimental data for up to saturated solutions. In other words, the reliability of each model

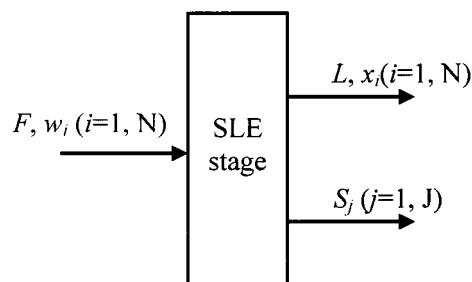


Figure 1. Schematic diagram of a SLE stage.

for calculating activity coefficients extends up to saturated solutions. To calculate activity coefficients reliably and to obtain a reliable free energy, a good initial estimate is required to ensure that the composition in the liquid phase is within or near saturated conditions.

For process simulation, one must also predict whether a given feed will be split into multiple phases, the number of phases and their identities at equilibrium, and the distribution of components within these phases (named the solid–liquid equilibrium stage). Moreover, the applied method should be generalized, reliable, and computationally efficient. To satisfy these requirements, a new method for the solid–liquid equilibrium (SLE) stage is proposed in this paper in which the number of phases and their identities are determined automatically in advance.

2. Solid–Liquid Equilibrium Stage

A schematic diagram of a SLE stage is shown in Figure 1. In practice, the feed can be more than one stream. Because the material balance and the phase equilibrium are independent of the stream number, one total feed stream was assumed in this paper.

Two key problems should be solved in the SLE stage. One is the determination of the number of phases and

* To whom correspondence should be addressed. E-mail: xhlu@njuct.edu.cn.

Table 1. Stoichiometric Coefficients λ_{ij} between the Components (Na^+ , K^+ , Cl^- , and H_2O) and the Precipitated Solid Phase (halite) for the $\text{NaCl-KCl-H}_2\text{O}$ System

<i>j</i>	<i>i</i>			
	1 (Na^+)	2 (K^+)	3 (Cl^-)	4 (H_2O)
1 (halite)	1	0	1	0

their identities at equilibrium; the other is the calculation of the distribution of components within these phases.

2.1. Distribution of Components. When the number of phases and their identities at equilibrium are determined, the distribution of components within these phases can be calculated by solving the material balance and phase equilibrium simultaneously. For the SLE stage shown in Figure 1, the material balance can be written as

$$F = \sum_{j=1}^J S_j + L \quad (1)$$

$$FW_i = \sum_{j=1}^J (\lambda_{ij} S_j) + Lx_i \quad (i = 1, \dots, N) \quad (2)$$

where F , L , and S are the flow rates of the feed, liquid, and solid phases, respectively (kg h^{-1}). w_i and x_i are the mass fractions of component i in the feed and in the liquid phase, respectively. As electrolytes can be dissociated into ions completely or partly, component (species) in this paper refers to ions, neutral compounds, and the solvent (organic solvent or water). λ_{ij} is the stoichiometric coefficient between the component i and the precipitated solid j . For example, for the $\text{NaCl-KCl-H}_2\text{O}$ system, if the precipitated solid phase is halite at equilibrium, the values of λ_{ij} between components and the precipitated solid phase are those listed in Table 1.

Let

$$A_{\text{sp}j} = \prod_{i=1}^N (x_i \gamma_i)^{\lambda_{ij}} \quad (j = 1, \dots, J) \quad (3)$$

where $A_{\text{sp}j}$ is the activity product of solid j and γ_i is the activity coefficient of component i in the liquid phase. Generally, the activity coefficient is a function of the liquid composition and temperature,^{11,12} and it can be calculated with a suitable thermodynamic model.^{11,12}

The condition for phase equilibrium is therefore

$$K_{\text{sp}j} = A_{\text{sp}j} = \prod_{i=1}^N (x_i \gamma_i)^{\lambda_{ij}} \quad (j = 1, \dots, J) \quad (4)$$

where $K_{\text{sp}j}$ is the thermodynamic solubility product constant of solid j , which is a function of temperature under normal conditions. The value of K_{sp} can be correlated with SLE experimental data^{13,14} or calculated from standard thermodynamic data.¹⁵

Equations 1, 2, and 4 constitute $J + N + 1$ equations with $J + N + 1$ unknowns (S_j , $j = 1, \dots, J$; x_i , $i = 1, \dots, N$; L). All variables can be solved directly, but the formation contains a large number of variables, and the possibility of the failure of convergence is very high. In this paper, an algorithm is proposed to improve convergence by rearranging equations, and it is similar to

that developed by Prausnitz¹⁶ for the calculation of flash vaporization.

Rearranging eqs 1, 2, and 4 yields

$$K_{\text{sp}j} = \prod_{i=1}^N \left(\frac{w_i - \sum_{j=1}^J (\lambda_{ij} \beta_j)}{1 - \sum_{j=1}^J \beta_j} \gamma_i \right)^{\lambda_{ij}} \quad (j = 1, \dots, J) \quad (5)$$

where

$$\beta_j = \frac{S_j}{F} \quad (j = 1, \dots, J) \quad (6)$$

As a result of this arrangement, the iteration variables are changed to β_j ($j = 1, \dots, J$), and the other variables (L , S_j , x_i) can be calculated from β_j easily by solving the linear equations. Furthermore, the corresponding Jacobian matrix is changed from $(J + N + 1) \times (J + N + 1)$ dimensions to $J \times J$. This change, in itself, constitutes a considerable potential savings in computational effort.

It is important to observe that, for aqueous electrolyte solutions, the composition of ionic components in the liquid phase should also satisfy charge balance. Before rearrangement, the iteration equations are eqs 1, 2, and 4, and the number of the iteration variables is $N + J + 1$. Subsequently, $N + J + 1$ independent equations should be given. However, in the material balance for ions (eq 2), only $N - 1$ equations are independent if the number of ions is N . It is necessary to choose $N - 1$ equations from the original N equations, and the composition of the last ion should be calculated from the charge balance equation. For the same studied system, different combinations for $N - 1$ equations can be chosen, and the corresponding equation for charge balance will be different. However, after rearrangement, the iteration equation is eq 5. The number of iteration variables is J , which is the number of precipitated solid phases. For the studied system, if the number and identities of the solid phases are determined, the number and corresponding phase equilibrium (solid-liquid equilibrium) equations are determined. In this case, it is unnecessary to choose $N - 1$ equations.

The enthalpy balance for the system is governed by

$$Q + Fh^F = Lh^L + \sum_{j=1}^J (S_j h^{S_j}) \quad (7)$$

where Q is the heat exchanged with environment. In an adiabatic process, Q is equal to 0. h^F , h^L , and h^{S_j} are the enthalpies of the feed, output liquid, and solid phases, respectively. An iteration is done to calculate the flow rate of each phase, h^L , and h^{S_j} ($j = 1, \dots, J$) at a certain temperature until eq 7 is satisfied.

2.2. Number of Phases and Their Identities.

Because the solid phase is immiscible and compounds can be formed, the determination of the number of phases and their identities is quite difficult. Meanwhile, crystallization in aqueous electrolyte solutions is often performed at constant temperature. On the basis of these characteristics, a method is proposed in this paper to determine the number of phases and their identities automatically.

The principle of the proposed method is similar to that used for an evaporation process at fixed temperature, which is to remove the solvent from a given unsaturated solution at a given temperature. With decreasing solvent content, solid phases will be precipitated in turn. In this procedure, the absolute quantity of solvent in solution is different when each solid phase is just saturated, so the quantity of solvent can be split into different intervals. Comparing the real quantity of solvent in the feed with that in each interval, the number of phases and their identities at equilibrium can be determined.

Using this principle, the detailed steps of the proposed method are described as follows. Recall that, throughout the procedure, the temperature is fixed. (1) Calculate the initial quantity of solvent (section 2.2.1) and the degree of freedom f . (2) Remove increments of solvent from the solution, and calculate A_{sp} from eq 3 for the solid phases that might precipitate after each increment. In the calculations, γ_i is calculated with a thermodynamic model. The increment is calculated with the proposed method described in section 2.2.2 (3) Determine the identity of the first precipitated solid phase (section 2.2.3) (4) Determine the quantity of solvent when the first solid phase is just saturated with liquid (section 2.2.4). Decrease the degree of freedom by 1 ($f = f - 1$). (5) Remove increments of solvent from the solution, determine the quantities of the precipitated solid phases (section 2.2.5), and calculate A_{sp} of the solid phases that might precipitate after each increment. (6) Determine the identity of the next precipitated solid phase (section 2.2.3). (7) Determine the quantity of solvent when the next solid phase is just saturated with liquid (section 2.2.4). Decrease the degree of freedom by 1 ($f = f - 1$). (8) Repeat steps 5–7 until the degree of freedom is equal to 0. (9) Remove a small amount of solvent (10%), and calculate the quantities of the precipitated solid phases. (10) Determine whether the quantity of a precipitated solid phase is decreased with decreasing amount of solvent. If not, go to step 13. (11) Calculate the quantity of solvent when a solid phase is just dissolved completely (section 2.2.4). Increase the degree of freedom by 1 ($f = f + 1$). (12) Repeat the steps 5–11 until the solvent is completely evaporated. (13) Determine the intervals based on the quantities of the solvent. (14) Determine the number of phases and their identities at equilibrium based on the quantity of the solvent in the feed.

When the process is a cooling crystallization, an outer loop should be added, and the proposed SLE stage should be used as an inner loop. The details are to calculate the SLE stage at a certain temperature. If more than one solid phase is present, change the temperature, and determine the number of the solid phases. When the number of solid phases is just one, the identity of the first solid phase is determined, and the temperature is calculated when the solid phase is just saturated. Using the same method, the next precipitated solid phases are determined in turn. By comparing the temperature of the feed with the temperatures when one solid phase is just saturated, the number of phases and their identities can be determined.

It is important to realize that, in the proposed method, the first step is similar to that proposed by Kusik et al.¹⁷ However, in this paper, methods are also given to estimate initial solvent and increments. Furthermore,

the method proposed by Kusik et al.¹⁷ cannot calculate the quantity of precipitated solid phase, but the value of A_{sp} is related to the quantity of the precipitated solid phases. Therefore, using the method of Kusik et al.,¹⁷ the value of A_{sp} cannot be calculated when the solid phases are precipitated from the liquid phase. In other words, the method of Kusik et al.¹⁷ cannot be used to determine the number of phases and their identities at equilibrium.

2.2.1. Initial Quantity of Solvent. The initial quantity of solvent is very important in the proposed method. If the value is very small, the initial distribution of components in the liquid might be far higher than would be found in a saturated solution. In this case, it is difficult to ensure a reliable estimation of A_{sp} because of the deviation of activity coefficients. If the value is very large, the initial distribution of components in the liquid is much lower than would be found in a saturated solution, which increases the number of calculations.

On the other hand, it is impossible to determine a definite value for the initial amount of solvent because, for different systems, the quantity of solvent needed to dissolve 1 mol of solid phase is very different. In this paper, an automatic generalized method is proposed to determine the initial quantity of solvent. The proposed method begins from an original set of values based on the almost-pure components. That is

$$n^0 = \frac{\prod_{i=1}^K G_i + \prod_{i=2}^K G_i + \dots + 1}{\prod_{i=1}^K G_i M_1 + \prod_{i=2}^K G_i M_2 + \dots + M_K} \quad (8)$$

where K is the number of electrolytes and G_i is the mole ratio of electrolyte i to electrolyte $i - 1$ on a solvent-free basis. M_i is the saturated molality in a single-electrolyte solution.

2.2.2. Increment. The increment also affects the iteration speed. In this paper, it was estimated by a combination of the methods of Newton and Dichotomy. For the studied case, $F(n) = A_{sp}/K_{sp} - 1$, where n is the quantity of solvent. Because $F(n)$ is an implicit function, the method of differences was used to substitute the differential equation of $F(n)$. Using the method of Newton, the quantity of solvent for the next step can be calculated as

$$n_{k+1} = \max \left[n_k - \frac{\left(\frac{A_{sp}}{K_{sp}} \right)_{k,j} - 1.0}{\left(\frac{A_{sp}}{K_{sp}} \right)_{k,j} - \left(\frac{A_{sp}}{K_{sp}} \right)_{k-1,j}} (n_k - n_{k-1}) \right] \quad (j = 1, \dots, J) \quad (9)$$

where

$$n_2 = 0.9n^0 \quad (10)$$

When the initial quantity of solvent is far from the ultimate value, n_{k+1} might be less than 0. In this case, the method of Dichotomy is used to calculate the quantity of solvent for the next step. That is

$$n_{k+1} = 0.5n_k \quad (11)$$

2.2.3. Determination of the Identity of the Next Precipitated Solid Phase. If the solution is super-saturated, A_{sp} is larger than K_{sp} . In this paper, the following criteria were used to determine the identity of the next precipitated solid phase.

$$\text{If } \begin{cases} A_{sp,K} > K_{sp,K}, & S_K = 0 \\ A_{sp,j} < K_{sp,j}, & S_j = 0 \quad (j \neq K; j = 1, \dots, L) \end{cases} \quad (12)$$

at equilibrium, solid K will be precipitated.

$$\text{If } \begin{cases} A_{sp,j} = K_{sp,j}, & S_j > 0 \quad (j = 1, \dots, K) \\ A_{sp,K+1} > K_{sp,K+1}, & S_{K+1} = 0 \\ A_{sp,j} < K_{sp,j}, & S_j = 0 \quad (j = K + 2, \dots, L) \end{cases} \quad (13)$$

at equilibrium, solid K + 1 will be precipitated.

2.2.4. Quantity of Solvent when One Solid Phase Is Just Saturated or Dissolved Completely. The calculation of the quantity of the solvent when one solid phase (J) is just saturated or dissolved completely is similar to that for the SLE stage in which the feed composition w_i' (mass fraction) and the feed flow rate F' are calculated by

$$\begin{cases} w_i'' = \frac{w_i'}{F' + n} \\ w_N'' = \frac{n}{F' + n} \end{cases} \quad (i = 1, \dots, N - 1) \quad (14)$$

$$F' = F(1.0 - w_N) + n \quad (15)$$

where w_i' and F' are the mass fraction and flow rate of feed, respectively, on a solvent-free basis. They are calculated according to

$$w_i' = \frac{w_i}{1.0 - w_N} \quad (i = 1, \dots, N - 1) \quad (16)$$

$$F' = F(1.0 - w_N) \quad (17)$$

The iteration function is

$$K_{sp,j} = \prod_{i=1}^N \left(\frac{w_i'' - \sum_{j=1}^{J-1} \left(\lambda_{ij} \frac{S_j}{F'} \right)}{1 - \sum_{j=1}^{J-1} \frac{S_j}{F'}} \right)^{\lambda_{ij}} \gamma_i \quad (j = 1, \dots, J) \quad (18)$$

and the iteration variables are S_j ($j = 1, \dots, J - 1$) and n .

2.2.5. Quantities of Precipitated Solid Phases. The quantities of precipitated solid phases should be calculated to calculate A_{sp} . The determination of S_j can be considered as a calculation of the SLE stage. In this case, the mass fraction w_i'' and flow rate F' of feed are also calculated by eqs 14 and 15, respectively, and the iteration function is the same as eq 18, but the iteration variables are S_j ($j = 1, \dots, J$).

3. Case Study and Discussion

The proposed method is suitable for a system containing one solvent. The following examples show the calculation results for aqueous electrolyte solutions.

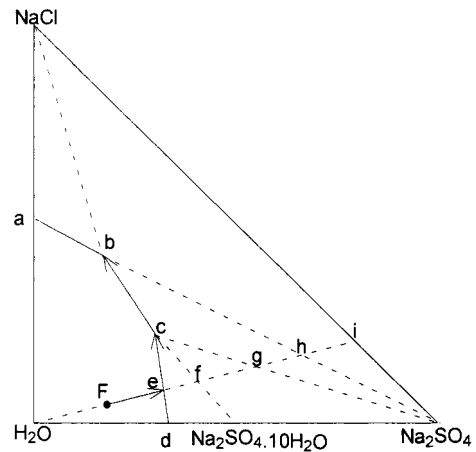


Figure 2. Phase diagram for the ternary system $\text{Na}^+\text{--Cl}^-\text{--SO}_4^{2-}\text{--H}_2\text{O}$ at 298.15 K.

Table 2. the Evaporation Process of Point of F in Figure 2 for the $\text{Na}^+\text{--Cl}^-\text{--SO}_4^{2-}\text{--H}_2\text{O}$ System at 298.15 K

interval in Figure 2	saturated solution	significance
e	e	solid 3 is not precipitated
e → f	e → c	solid 3 is precipitated
f	c	solid 3 is precipitated, solid 2 is not precipitated
f → g	c	solid 3 is dissolved, solid 2 is precipitated
g	c	solid 3 is dissolved completely, solid 2 is precipitated
g → h	c → b	solid 2 is precipitated
h	b	solid 2 is precipitated, solid 1 is not precipitated
h → i	b	solid 2 and solid 1 are precipitated

3.1. Prediction of the Crystallization Path. One of the laboratory experimental approaches for determining the crystallization path is the evaporation method. In this method, solvent is evaporated from solution. Solids will be precipitated in turn with decreasing solvent. At a certain quantity of solvent, the number of phases and their identities are determined by analyzing the composition of the solid phases. The proposed method for determining the number of phases and their identities is similar to that used in experiments, and it can also be used to predict the crystallization path.

3.1.1. The $\text{Na}^+\text{--Cl}^-\text{--SO}_4^{2-}\text{--H}_2\text{O}$ System. For a given feed ($T = 298.15$ K, $F = 1$ kg h^{-1} , 0.00758 kg of NaCl, 0.02761 kg of Na_2SO_4 , 0.96482 kg of H_2O), a strange phenomenon occurs. With decreasing solvent, mirabilite is dissolved, whereas thenardite is precipitated. Using the proposed method, the crystallization paths were predicted as shown in Table 2 and Figure 2. The prediction results are the same as those determined from experimental data.

In the calculations, the required information is the possible precipitated solid phases, the value of K_{sp} , and the activity coefficients for the liquid components. In this case, the possible precipitated solid phases are halite (solid 1), thenardite (solid 2), and mirabilite (solid 3). Their values of K_{sp} were taken from Pabalan and Pitzer.¹⁵ Activity coefficients were calculated using the Pitzer equation.¹¹

3.1.2. The $\text{Na}^+\text{--K}^+\text{--Cl}^-\text{--NO}_3^-\text{--H}_2\text{O}$ System. For the more complicated system of $\text{Na}^+\text{--K}^+\text{--Cl}^-\text{--NO}_3^-\text{--H}_2\text{O}$, the crystallization paths of the feed (point F in Figure 3; $T = 323.15$ K, $F = 1$ kg h^{-1} , 0.198 kg of KNO_3 , 0.033 kg of NaNO_3 , 0.115 kg of NaCl) were predicted. The prediction results are shown in Figure 3. The

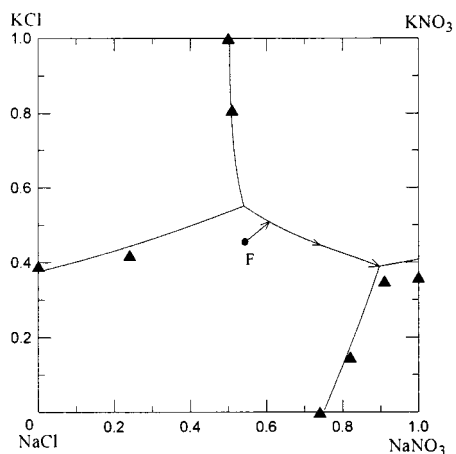


Figure 3. Phase diagram for the system $\text{Na}^+-\text{K}^+-\text{Cl}^--\text{NO}_3^--\text{H}_2\text{O}$ at 323.15 K: \blacktriangle , experimental data;¹⁸ —, predicted in this work.

activity coefficients for this system were calculated with the model of Lu and Maurer,¹² and the values of K_{sp} for halite, sylvite, soda niter, and salt peter were taken from Lu et al.¹³

3.2. Generation of Phase Diagrams. In the procedure of determining the intervals, the distribution of components in the liquid is determined simultaneously when one solid phase is just saturated. Therefore, the proposed method can be used to generate the phase diagrams by calculating different proportions of feed on a solvent-free basis.

For a ternary system, such as $\text{Na}^+-\text{Cl}^--\text{SO}_4^{2-}-\text{H}_2\text{O}$, a point in the line of SLE in phase diagrams represents the solution saturated with one solid phase, and the degree of the freedom is 1. The phase diagram can be generated by calculating different proportions of feeds on a solvent-free basis, with each point being calculated until the first solid phase is just saturated. In the present work, the different mole proportions of feed on a solvent-free basis were derived using a linear relationship.

For a quaternary conjugate system, such as $\text{Na}^+-\text{K}^+-\text{Cl}^--\text{NO}_3^--\text{H}_2\text{O}$, a point in the line of SLE in phase diagrams represents the solution saturated with two solid phases, and the degree of the freedom is also 1. The phase diagram can be generated by calculating different mole proportions of feeds on a solvent-free basis until the second solid phase is just saturated. The predicted phase diagram for the system $\text{Na}^+-\text{K}^+-\text{Cl}^--\text{NO}_3^--\text{H}_2\text{O}$ at 323.15 K is shown in Figure 3.

For more complicated systems, the phase diagram can be generated by calculating the points until the degree of freedom is 1.

3.3. Calculation of SLE Stage and Discussion. Two feeds (points F in Figures 2 and 3) were calculated to verify the method of SLE stage calculations proposed in this paper and compared with the results of previous methods.

The calculation results in this paper show that all of these feeds were within the saturated solutions and that no solid phase precipitated from the liquid phase, which is consistent with experiment.

In the calculation of the SLE stage, the determination of the number of phases and their identities can also be performed on the basis of phase diagrams. For the simple system $\text{Na}^+-\text{Cl}^--\text{SO}_4^{2-}-\text{H}_2\text{O}$, it is easy to determine the number of phases and their identities

Table 3. Combinations in the Enumerative Method and Comparison with Those in the Method Proposed in This Work

	N_p^a	M_p^b	S_p^c	enumerative		this work	
				N_c^d	T_c^e	N_c^d	T_c^e
$\text{Na}^+-\text{K}^+-\text{Cl}^--\text{H}_2\text{O}$	2	2	1	2	3	1	2
$\text{Na}^+-\text{Cl}^--\text{SO}_4^{2-}-\text{H}_2\text{O}$	3	2	1	3	6	1	2
$\text{Na}^+-\text{K}^+-\text{Cl}^--\text{NO}_3^--\text{H}_2\text{O}$	4	3	1	4	18	1	3
$\text{Na}^+-\text{K}^+-\text{Cl}^--\text{SO}_4^{2-}-\text{H}_2\text{O}$	5	3	1	5	35	1	3
			2	10		1	
			3	20		1	

^a N_p = number of possible precipitated solid phases. ^b M_p = maximum number of solid phases coexisting as determined by the phase rule. ^c S_p = postulated number of solid phases at equilibrium. ^d N_c = number of possible cases or combinations that should be calculated. ^e T_c = number of calculations required to determine the number of phases and their identities.

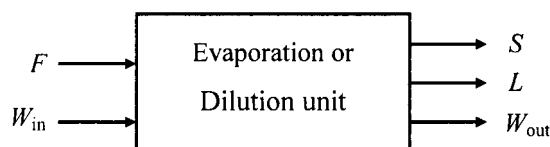


Figure 4. Schematic diagram of evaporation or dilution unit.

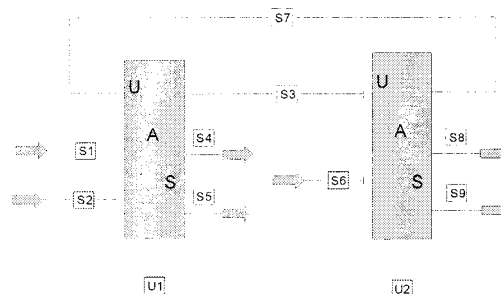


Figure 5. Schematic diagram of potash production from sylvinite.

using phase diagrams. However, for the complicated $\text{Na}^+-\text{K}^+-\text{Cl}^--\text{NO}_3^--\text{H}_2\text{O}$ system, the number of phases in the feed F in Figure 3 might be zero or one based on the phase diagram. That means that the number of phases cannot be determined by means of the phase diagram only for complicated systems.

The enumerative method is suitable for determining the number of phases and their identities for simple and complicated systems. However, all combinations should be tried. A comparison of the enumerative method with the proposed method is shown in Table 3. From Table 3, it is clear that, with the enumerative method, the greater the number of possible precipitated solid phases, the greater the number of possible cases and combinations that should be calculated. However, in the proposed method of this paper, it is unnecessary to examine all of the combinations. Furthermore, when the identities of the precipitated solid phases are determined, the identity of the next precipitated solid phase is among the remainder. Meanwhile, the number of possible precipitated solid phases hardly affects the calculation.

In another method based on free energy minimization, the number of phases and their identities are also determined by the enumerative method. It is unnecessary to compare the number of calculations with that in the proposed method.

Table 4. Comparison of the Simulation Results with the Literature Data of Cisternas and Rudd³ for the System Na⁺-K⁺-Cl⁻-H₂O^a

	U_1 (U1)	U_2 (U2)	W_{in1} (kg) (S2)	W_{out2} (kg) (S9)	S_1 (kg) (S4)	S_2 (kg) (S8)	L_2 (kg) (S7)
this work	dilution	evaporation	1.76	1.76	KCl, 427	NaCl, 566	2.62
lit data	dilution	evaporation	1.68	1.68	KCl, 427	NaCl, 566	2.51

^a $T_1 = 303.15$ K, $T_2 = 373.15$ K.

It should be mentioned that, in the enumerative method and in the method based on free energy minimization, good initial estimates are all required to obtain reliable activity coefficients for the liquid components. Unfortunately, no generalized approach for doing this was proposed in those methods. In the proposed method of this paper, both initial estimates and increments are considered carefully, which ensures that the solution is always within or near the saturated range.

3.4. Fractional Crystallization. It is well-known that the flash evaporation equilibrium calculation is the basis of VLE process simulation. The SLE stage calculation established in this paper can be used as a basis in SLE process simulation. For fractional crystallization processes, one must know the quantity of solvent evaporated or diluted to obtain the maximum quantity of product. The value of the solvent alone is one of the terminal vertex values of the intervals. Therefore, a special unit for fractional crystallization process was designed, as shown in Figure 4, where F is the mixed feed, W_{in} is the quantity of dilution solvent, S is the output of the solid phases, L is the output of the liquid phase, W_{out} is the quantity of evaporation solvent. If the unit is an evaporation unit, W_{in} is equal to 0; if the unit is a dilution unit, W_{out} is equal to 0.

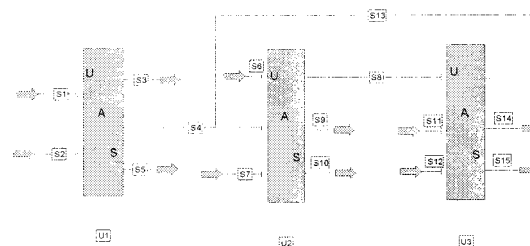
Commercial process simulators such as Pro/II¹⁹ and Aspen²⁰ are quite attractive, and their user-added units make it very convenient for a user to add his own units into simulations. If the SLE stage unit is added into the software, processes involving solid phases can be simulated successfully. In this paper, the program Pro/II was chosen as an example to illustrate the simulation results obtained when a SLE stage is added to this software through a user-added unit.

3.4.1. Production of Potash. A typical process involving solid phases is the production process of potash from sylvinites (42.7% KCl, 56.6% NaCl) shown in Figure 5. It can be simulated by the enumerative method. In the enumerative method, initial estimates are necessary. If the initial conditions are such that no solid phase exists, the initial concentration of the liquid phase is very high ($m_{KCl} = 818.786$ mol kg⁻¹, $m_{NaCl} = 1382.17$ mol kg⁻¹). For this high concentration, no thermodynamic model can be used to calculate activity coefficients, and the simulation will be interrupted.

The simulation results of this work are listed in Table 4. Activity coefficients for this system were calculated by the Pitzer equation,¹¹ and the values of K_{sp} were taken from Pabalan and Pitzer.¹⁵

Cisternas and Rudd³ have simulated this process on the basis of the phase diagram, and their results are also listed in Table 4. Their calculation results are close to those of this paper. In the work of Cisternas and Rudd,³ the number of phases and their identities were determined in advance from the phase diagram, whereas they were determined automatically in this paper.

3.4.2. Arcanite Production Process. Generally, the simulation and optimization of the arcanite production

**Figure 6.** Schematic diagram of arcanite production process.**Table 5. Simulation Results for the System Na⁺-K⁺-Cl⁻-SO₄²⁻-H₂O^a**

	feed (mol)		product (g)
F_1 (S1)	sylvite 1.1013	S_1 (S4) (glasserite)	165.32
	thenardite 0.7472	S_2 (S9) (arcanite)	150.04
F_2 (S6)	sylvite 1.0621	S_3 (S13) (glasserite)	68.16
F_3 (S11)	thenardite 0.4275	Recover fraction of K ⁺	79.6%

^a $T = 298.15$ K.

process are patented or depends on phase diagrams. In this system, there are reactions, and the solid phases can be hydrates or compounds. Furthermore, the field of two solid phases coexisting is a surface that is difficult to describe with an analytical formula. Therefore, it is difficult to determine the number of phases and their identities using the phase diagram.

For this system, with four ions and five possible precipitated solid phases, the combinations are numerous. Good initial estimates and a large number of calculations are required to determine the number of phases and their identities by the enumerative method.

Using the method proposed in this paper, the process was simulated easily. One case shown in Figure 6 was calculated as an example. The simulation results are listed in Table 5. Activity coefficients were calculated by the Pitzer equation,¹¹ and the values of K_{sp} were taken from Greenberg and Møller.¹⁴

4. Conclusions

For the important need of crystallization process simulations, a generalized method for the SLE stage was proposed. In the proposed method, the number of phases and their identities are determined automatically on the basis of the quantity of solvent in the feed and the calculated intervals. The proposed method is much simpler and more computationally efficient than the enumerative method because the solvent was considered as a single and independent variable. Furthermore, good initial estimates and increments in the calculations are considered carefully to ensure that the solution is within or near the saturated range.

Meanwhile, the proposed method for the SLE stage was used to predict crystallization paths and to generate phase diagrams of SLE. It was added to the commercial software Pro/II to simulate a process involving solid phases. Several study cases were examined to demon-

strate the capability of this method for use with systems with hydrate, multi-ion, and complex salts.

Acknowledgment

The authors are grateful for the financial support received from the National Natural Science Foundation of P. R. China (29376244), Natural Science Foundation of Jiangsu Province of P. R. China (BK 97124), the Outstanding Young Teacher Foundation of Education Ministry of P. R. China, and the Outstanding Youth of National Natural Science Foundation (29925616).

Nomenclature

A_{sp} = activity product
 F = mass flow rate of feed
 G = mole ratio of solutes for binary system
 ΔG = Gibbs free energy
 ΔG° = Gibbs free energy at standard state
 h = enthalpy
 J = number of solid phases
 K_{sp} = solubility product
 L = mass flow rate of liquid
 M = saturation solution in binary system
 M_p = maximum number of the solid phases coexisting based on the phase rule
 N = number of species
 N_c = number possible cases or combinations that should be calculated
 N_p = number of possible precipitated solid phases
 n = quantity of solvent
 Q = heat exchanged with the environment
 R = gas constant
 S = mass flow rate of solid
 S_p = postulated number of solid phases at equilibrium
 T = temperature
 T_c = number of calculations required to determine the number of phases and their identities
 U = evaporation or dilution unit
 W = dilution and evaporation mass flow rates
 w = mass fraction of feed
 x = mass fraction of output liquid

Greek Letters

β = ratio of solid to feed
 γ = activity coefficient
 λ = stoichiometric coefficient between components and solid phases

Subscripts

i = liquid component
 j = solid phase

Superscript

0 = initial estimate

Literature Cited

- (1) Fitch, B. How to Design Fractional Crystallization Process. *Ind. Eng. Chem. Res.* **1970**, *62*, 6.
- (2) Rajagopal, S.; Ng, K. M.; Douglas, J. M. Design of Solids Processes: Production of Potash. *Ind. Eng. Chem. Res.* **1988**, *27*, 2071.
- (3) Cisternas, L. A.; Rudd, D. F. Process Design for Fractional Crystallization from Solution. *Ind. Eng. Chem. Res.* **1993**, *32*, 1993.
- (4) Dye, S. R.; Ng, K. M. Fractional Crystallization: Design Alternatives and Tradeoffs. *AIChE J.* **1995**, *41*, 2427.
- (5) Berry, D. A.; Ng, K. M. Separation of Quaternary Conjugate Salt Systems by Fractional Crystallization. *AIChE J.* **1996**, *42*, 2162.
- (6) Cisternas, L. A.; Swaney, R. E. Separation System Synthesis for Fractional Crystallization from Solution Using a Network Flow Model. *Ind. Eng. Chem. Res.* **1998**, *37*, 2761.
- (7) Rafal, M.; Berthold, J. W.; Scrivner, N. C.; Grise, S. L. *Models for Electrolyte Solutions*; Marcel Dekker: New York, 1994.
- (8) Berry, D. A.; Ng, K. M. Synthesis of Reactive Crystallization Process. *AIChE J.* **1997**, *43*, 1737.
- (9) Thomsen, K.; Rasmussen, P.; Gani, R. Simulation and Optimization of Fractional Crystallization Process. *Chem. Eng. Sci.* **1998**, *53*, 1551.
- (10) Nano, N.; Lu, W. K.; Riboud, P. *Advanced Physical Chemistry for Process Metallurgy*; North-Holland: Amsterdam, 1997.
- (11) Pitzer, K. S. *Activity Coefficients in Electrolyte Solution*, 2nd ed.; CRC Press: Boca Raton, FL, , 1991; Chapter 3.
- (12) Lu, X.; Maurer, G. Model for Describing Activity Coefficients in Mixed Electrolyte Aqueous Solutions. *AIChE J.* **1993**, *39*, 1527.
- (13) Lu, X.; Zhang, L.; Wang, Y.; Shi, J. Prediction of Activity Coefficients of Electrolytes in Aqueous Solutions at High Temperatures. *Ind. Eng. Chem. Res.* **1996**, *35*, 1777.
- (14) Pabalan, R. T.; Pitzer, K. S. *Activity Coefficients in Electrolyte Solution*, 2nd ed.; Boca Raton, FL, , 1991; Chapter 7.
- (15) Greenberg, J. P.; Möller, N. The Prediction of Mineral Solubilities in Natural Waters: A Chemical Equilibrium Model for the Na–K–Ca–Cl–SO₄–H₂O System to High Concentration from 0 to 250 °C. *Geochim. Cosmochim. Acta* **1989**, *53*, 2503.
- (16) Prausnitz, J. M. *Computer Calculation for Multicomponent of Vapor–Liquid Equilibria*; Prentice Hall: Upper Saddle River, NJ, 1980.
- (17) Kusik, C. L.; Meissner, H. P.; Field, E. L. Estimation of Phase Diagrams and Solubilities for Aqueous Multi-ion Systems. *AIChE J.* **1979**, *25*, 759.
- (18) Silcock, H. L. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1979.
- (19) *PRO/II Manual*, version 3.02; Simulation Sciences: Brea, CA, 1991.
- (20) *Aspen User's Manuals*; Aspen Technology: Cambridge, MA, 1999.

Received for review May 4, 2000

Revised manuscript received November 27, 2001

Accepted January 25, 2002

IE0004545