



## Predictive Phase Equilibria for Aqueous Quaternary System Containing Sodium, Potassium, Chloride and Sulfate Ions from 273.15 to 473.15 K

YUANHUI LIU, YAFEI GUO, SHIQIANG WANG, XUEKUI WANG and TIANLONG DENG\*

Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering, Tianjin University of Science and Technology, Tianjin 300457, P.R. China

\*Corresponding author: Tel/Fax: +86 22 60602963; E-mail: [tl Deng@tust.edu.cn](mailto:tl Deng@tust.edu.cn)

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Pitzer ion-interaction model is widely used to calculate the solubilities of salt-water systems. In paper, the solubilities of the aqueous reciprocal quaternary system ( $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  -  $\text{H}_2\text{O}$ ) from 273.15 to 473.15 K were calculated using the extended chemical equilibrium Harvie-Weare model (HW model) and high temperature chemical model. The dry-salt phase diagrams were plotted based on the Jänecke indexes. In the temperature range from 273.15 to 473.15 K, the mineral crystallization regions in the phase diagrams of the quaternary system change regularly with the changing of temperature. The calculated phase diagrams agree well with the experimental phase diagrams totally from 273.15 to 473.15 K except for the phase region of double salt glasserite ( $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$ ) at 273.15 K.

**Keywords:** Chemical model, Pitzer parameters, Solubility prediction.

### INTRODUCTION

The calculation of solubilities of multicomponent salt-water systems is of great importance in the fields of chemistry, chemical engineering and especially in the field of saline chemistry, such as the prediction of the evaporative path and the separation of minerals from brines by solar pond techniques. Among the numerous theories of the electrolyte solution, Pitzer theory characterizing thermodynamics properties of electrolyte solution in brief and terse form is widely used either in geochemical behaviours of natural waters and mineral deposits or in the predictions of solubility of salt-water systems. Wear and Harvie *et al.*<sup>1-6</sup> showed that Pitzer's specific interaction of electrolyte solutions could be extended as Harvie-Weare (HW) model to construct accurate models of solubilities in complex multicomponent natural system ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2\text{-H}_2\text{O}$ ) with high ionic strength (20 mol/kg  $\text{H}_2\text{O}$ ) at 298.15 K and the HW model was successfully applied to predict the borate mineral equilibrium in Searles lake. Song *et al.*<sup>7,8</sup> have applied the HW model to the calculation of metastable phase equilibria of the salt-water systems ( $\text{Na}^+$ ,  $\text{Mg}^{2+}//\text{Cl}^-$ ,  $\text{SO}_4^{2-}\text{-H}_2\text{O}$ ) and ( $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}\text{-H}_2\text{O}$ ) at 298.15 K.

While a large database for the modeling of aqueous salt systems exists at 298.15 K and many applications have been found for the 298.15 K models, variable temperature chemical models would have much wider uses. Spencer *et al.*<sup>9</sup> cons-

tructed a low temperature chemical model in eqn. (1) to predict mineral solubility in the natural waters ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}//\text{Cl}^-$ ,  $\text{SO}_4^{2-}\text{-H}_2\text{O}$ ) to high concentration in the temperature range below 298.15 K (to near 213.15 K). Møller *et al.*<sup>10,11,13</sup> used an expanded high temperature chemical model in eqn. (2) to calculate mineral solubility in natural waters ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}//\text{Cl}^-$ ,  $\text{SO}_4^{2-}\text{-H}_2\text{O}$ ) and ( $\text{Na}^+$ ,  $\text{Mg}^{2+}//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-\text{-H}_2\text{O}$ ) and calcium acid-base system ( $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}//\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}\text{-H}_2\text{O}$ ) from low to high solution concentration within 273.15-473.15 K. Holmes and Mesmer<sup>14</sup> calculated the thermodynamic properties such as osmotic and activity coefficients and apparent molal heat capacity on aqueous solution of the alkali metal sulfates with variable-temperature chemical model in eqn. (3).

$$P(T) = a_1 + a_2T + a_6T^2 + a_9T^3 + a_3/T + a_4\ln T \quad (1)$$

$$P(T) = a_1 + a_2T + a_3/T + a_4\ln T + a_5/(T-263) + a_6T^2 + a_7/(680-T) + a_8/(T-227) \quad (2)$$

$$P(T) = p_1 + p_2(T_R - T_R^2/T) + p_3(T^2 + 2T_R^3/T - 3T_R^2) + p_4(T + T_R^2/T - 2T_R) + p_5(\ln(T/T_R) + T_R/T - 1) + p_6(1/(T - 263) + (263T - T_R^2)/T(T_R - 263)^2) + p_7(1/(680 - T) + (T_R^2 - 680T)/T(680 - T_R)^2) \quad (3)$$

where  $T_R$  in eqn. (3) is 298.15 K.

The chemical model of salt-water system containing lithium at 298.15 K has been constructed and successfully applied to the prediction of solubility in some systems such as ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}//\text{Cl}^-$ ,  $\text{SO}_4^{2-}\text{-H}_2\text{O}$ )<sup>15</sup> and ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{B}_4\text{O}_7^{2-}\text{-H}_2\text{O}$ )<sup>16</sup>. However the variable temperature chemical

model of salt-water system containing lithium is less reported and so far, only that of  $\text{Li}_2\text{SO}_4$  single salt at 273.15-498.15 K<sup>14</sup> and that of  $\text{LiCl}$  single salt 273.15-373.15 K were developed<sup>17,18</sup>. Additionally mixing Pitzer parameters of common ion systems ( $\text{Li}^+$ ,  $\text{Na}^+//\text{Cl}^-$ - $\text{H}_2\text{O}$ )<sup>19</sup> and ( $\text{Li}^+$ ,  $\text{Mg}^{2+}//\text{Cl}^-$ - $\text{H}_2\text{O}$ )<sup>18</sup> at several temperatures were reported. With regard to the reciprocal quaternary system ( $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$ ), the variable temperature chemical model in eqn. (2) provides all Pitzer parameters and therefore in the paper the solubilities of the quaternary system were calculated in higher temperature ranges.

### Ion interaction model (HW equations)

Pitzer standard ion interaction and its extended HW model were used to calculate osmotic and activity coefficients<sup>1</sup>. These equations are as in following.

$$\sum_i m_i(\phi - 1) = 2(-A^\phi I^{3/2} / (1 + 1.2I^{1/2})) + \sum_{c=1}^{Nc} \sum_{a=1}^{Na} m_c m_a (B_{ca}^\phi + ZC_{ca}) + \sum_{c=1}^{Nc-1} \sum_{c'=c+1}^{Nc} m_c m_{c'} (\Phi_{cc'}^\phi + \sum_{a=1}^{Na} m_a \Psi_{cc'a}) + \sum_{a=1}^{Na-1} \sum_{a'=a+1}^{Na} m_a m_{a'} (\Phi_{aa'}^\phi + \sum_{c=1}^{Nc} m_c \Psi_{aa'c}) \quad (4)$$

$$\ln \gamma_M = z_M^2 F + \sum_{a=1}^{Na} m_a (2B_{Ma} + ZC_{Ma}) + \sum_{c=1}^{Nc} m_c (2\Phi_{Mc} + \sum_{a=1}^{Na} m_a \Psi_{Mca}) + \sum_{a=1}^{Na-1} \sum_{a'=a+1}^{Na} m_a m_{a'} \Psi_{aa'M} + |z_M| \sum_{c=1}^{Nc} \sum_{a=1}^{Na} m_c m_a C_{ca} \quad (5)$$

$$\ln \gamma_X = z_X^2 F + \sum_{c=1}^{Nc} m_c (2B_{cX} + ZC_{cX}) + \sum_{a=1}^{Na} m_a (2\Phi_{Xa} + \sum_{c=1}^{Nc} m_c \Psi_{Xac}) + \sum_{c=1}^{Nc-1} \sum_{c'=c+1}^{Nc} m_c m_{c'} \Psi_{cc'X} + |z_X| \sum_{c=1}^{Nc} \sum_{a=1}^{Na} m_c m_a C_{ca} \quad (6)$$

In the above equations, the subscripts M, c, c' and X, a, a' express the different cations and anions. The symbols of  $m_c$  and  $Z_c$  are the mass molality and the charge of cation c.  $Nc$  is the total number of cations. Similar definitions apply for anions (a). For use of the equations, the terms of F, C, Z, B and  $\Phi$  are defined<sup>1</sup>.

$$F = -A^\phi [I^{1/2} / (1 + 1.2I^{1/2}) + 2 / 1.2 \ln(1 + 1.2I^{1/2})] + \sum_{c=1}^{Nc} \sum_{a=1}^{Na} m_c m_a B_{ca}^\phi + \sum_{c=1}^{Nc-1} \sum_{c'=c+1}^{Nc} m_c m_{c'} \Phi_{cc'}^\phi + \sum_{a=1}^{Na-1} \sum_{a'=a+1}^{Na} m_a m_{a'} \Phi_{aa'}^\phi \quad (7)$$

$$C_{MX}^\phi = C_{MX}^\phi / (2|z_M z_X|^{1/2}) \quad (8)$$

$$Z = \sum_i |z_i| m_i \quad (9)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_{MX} \sqrt{I}} + \beta_{MX}^{(2)} e^{-12\sqrt{I}} \quad (10)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_{MX} \sqrt{I}) + \beta_{MX}^{(2)} g(12\sqrt{I}) \quad (11)$$

$$B_{MX}^i = \beta_{MX}^{(1)} g'(\alpha_{MX} \sqrt{I}) / I + \beta_{MX}^{(2)} g'(12\sqrt{I}) / I \quad (12)$$

$$g(x) = 2[1 - (1+x)e^{-x}] / x^2 \quad (13)$$

$$g'(x) = -2[1 - (1+x+x^2/2)e^{-x}] / x^2 \quad (x = \alpha_{MX} \sqrt{I} \text{ or } 12\sqrt{I}) \quad (14)$$

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij}(I) + I {}^E\theta_{ij}'(I) \quad (15)$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (16)$$

$$\Phi_{ij}' = {}^E\theta_{ij}'(I) \quad (17)$$

$${}^E\theta_{ij}(I) = (Z_i Z_j / 4I) [J(x_{ij}) - J(x_{ii}) / 2 - J(x_{jj}) / 2] \quad (18)$$

$${}^E\theta_{ij}'(I) = -({}^E\theta_{ij}(I) / I) + (Z_i Z_j / 8I^2) [x_{ij} J'(x_{ij}) - x_{ii} J'(x_{ii}) / 2 - x_{jj} J'(x_{jj}) / 2] \quad (19)$$

$$x_{ij} = 6Z_i Z_j A^\phi I^{1/2} \quad (20)$$

$$J(x) = x(4 + C_1 x^{-C_2} e^{-C_3 x^{C_4}})^{-1} \quad (21)$$

$$J'(x) = (4 + C_1 x^{-C_2} e^{-C_3 x^{C_4}})^{-1} + (4 + C_1 x^{-C_2} e^{-C_3 x^{C_4}})^{-2} \cdot C_1 x e^{-C_3 x^{C_4}} \cdot (C_2 x^{-C_2-1} + C_3 C_4 x^{C_4-1} x^{-C_2}) \quad (22)$$

In the functions  $J(x)$  and  $J'(x)$ ,  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  equal to 4.581, 0.7237, 0.0120 and 0.528, respectively.

In above terms,  $C_{MX}^\phi$ ,  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$  and  $\beta_{MX}^{(2)}$  are Pitzer interaction parameters of single salts in which  $\beta_{MX}^{(2)}$  is important to 2-2 or higher valence electrolytes and nevertheless may be neglected in this system.  $\theta_{ij}$  and  $\Psi_{ijk}$  represent Pitzer interaction parameters of mix ions:  $\theta_{ij}$  for each cation-cation and anion-anion pair;  $\Psi_{ijk}$  for each cation-cation-anion and anion-anion-cation triplet.  $\alpha_{MX}$  equals to 2.0 because electrolytes in this reciprocal quaternary system include one single valence ion at least.

### THEORETICAL CALCULATION

According to the extended variable-temperature chemical model in eqn. (2) and the constants listed in Tables 1 to 3<sup>11</sup>, the Pitzer parameters for single electrolytes, pairwise ions and triple ions, the Debye-Hückel limiting slope and the standard chemical potentials of solid phases are available for the reciprocal quaternary system ( $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$ ) at 273.15-473.15 K. Then activity coefficient of ions and activity of water in the quaternary system may be calculated on the basis of Pitzer ion-interaction model and its extended HW model. Through solving the nonlinear coupled equations on equilibrium relation between solid and liquid phases with quasi-newton method, ionic molalities are obtained and afterward translated into Jänecke indexes of  $2\text{K}^+$  and  $\text{SO}_4^{2-}$  in order to plot the dry-salt phase diagram.

Then the stable phase equilibria of the reciprocal quaternary system ( $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$ ) at different temperatures in the temperature ranges 273.15-473.15 K were achieved. The results are showed in Fig. 1 and the solubilities of co-saturated points are listed in Table-4. However the equilibrium solubilities of the reciprocal quaternary system weren't predicted above 473.15 K and below 273.15 K because of lack of the standard chemical potential of glasserite solid phase.

### RESULTS AND DISCUSSION

There are five crystallization regions corresponding to thenardite ( $\text{Na}_2\text{SO}_4$ , Th), glasserite ( $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$ , Gla), arcanite ( $\text{K}_2\text{SO}_4$ , Arc), halite ( $\text{NaCl}$ , Hal) and sylvite ( $\text{KCl}$ , Syl) and seven univariant curves consisting of these crystallization regions in the quaternary system ( $\text{Na}^+$ ,  $\text{K}^+//\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$ ) in the temperature range 308.15-473.15 K as illustrated in Fig. 1. As increase of temperature,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  crystallization regions increase and  $\text{K}_2\text{SO}_4$  and  $\text{KCl}$  crystallization

regions decrease, nevertheless Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub> crystallization region has slight change about its area and moves to K<sub>2</sub>SO<sub>4</sub> crystallization region. The movement remains unchanged nearly in 373.15-423.15 K range and above 423.15 K Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub> crystallization region obviously moves again. In the temperature range 273.15-308.15 K, mirabilite (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, Mir) crystallization region appears in the equilibrium phase diagram, which increases significantly with decrease of temperature and adjoins K<sub>2</sub>SO<sub>4</sub> and KCl phase regions at 273.15 K. With decrease of temperature at 273.15-308.15 K, K<sub>2</sub>SO<sub>4</sub> and KCl phase regions gradually increase and however Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub> and NaCl phase regions decrease. Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub> phase area forms a close triangle at 273.15 K and Na<sub>2</sub>SO<sub>4</sub> phase region disappears below 288.15 K. Na<sub>2</sub>SO<sub>4</sub> field also disappears below 288.15 K in the experimental phase diagram of the ternary system (NaCl-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O), which indicates that addition of K<sup>+</sup> doesn't influence existing temperature range of Na<sub>2</sub>SO<sub>4</sub> solid phase in

complex system. The relative position of equilibrium curve of K<sub>2</sub>SO<sub>4</sub> and KCl and that of Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub> and KCl in the system nearly don't change with variable temperature in the whole temperature range, so concentrations of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> on the two equilibrium curves are slightly affected by temperature.

The stable phase equilibria of the reciprocal quaternary system (Na<sup>+</sup>, K<sup>+</sup>//Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O) at higher temperature range from 273.15 to 373.15 K were determined experimentally<sup>20</sup> and then the calculated and experimental phase equilibria are compared as shown in Fig. 2. In Fig. 2, the predictive phase diagrams using HW model agree well with experimental phase diagrams of this system as a whole from 273.15 to 373.15 K except for glasserite field at 273.15 K and univariant curve of arcanite and glasserite at 298.15 to 373.15 K. The better agreement between calculated and experimental solubility above 273.15 K shows that Pitzer parameters are reliable from the temperature-dependent equations and the high temperature

TABLE-1  
CONSTANTS IN THE TEMPERATURE EQN (2) FOR ELECTROLYTE  
PARAMETERS IN THE AQUEOUS QUATERNARY SYSTEM Na<sup>+</sup>, K<sup>+</sup>//Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O

Species	Parameters	a1	a2	a3	a4	a5	a6	a7	a8
NaCl	β <sup>0</sup>	1.43783204D1	5.60767406D-3	-4.22185236D2	-2.51226677D0	0.0D0	-2.61718135D-6	4.43854508D0	-1.70502337D0
NaCl	β <sup>1</sup>	-4.83060685D-1	1.40677479D-3	1.19311989D2	0.0D0	0.0D0	0.0D0	0.0D0	-4.23433299D0
NaCl	C <sup>Φ</sup>	-1.00588714D-1	-1.80529413D-5	8.61185543D0	1.24880954D-2	0.0D0	3.41172108D-8	6.83040995D-2	2.93922611D-1
KCl	β <sup>0</sup>	2.67375563D1	1.00721050D-2	-7.58485453D2	-4.70624175D0	0.0D0	-3.75994338D-6	0.0D0	0.0D0
KCl	β <sup>1</sup>	-7.41559626D0	0.0D0	3.22892989D2	1.16438557D0	0.0D0	0.0D0	0.0D0	-5.94578140D0
KCl	C <sup>Φ</sup>	-3.30531334D0	-1.29807848D-3	9.12712100D1	5.86450181D-1	0.0D0	4.95713573D-7	0.0D0	0.0D0
Na <sub>2</sub> SO <sub>4</sub>	β <sup>0</sup>	8.16920027D1	3.01104957D-2	-2.32193726D3	-1.43780207D1	-6.66496111D-1	-1.03923656D-5	0.0D0	0.0D0
Na <sub>2</sub> SO <sub>4</sub>	β <sup>1</sup>	1.00463018D3	5.77453682D-1	-2.18434467D4	-1.89110656D2	-2.03550488D-1	-3.23949532D-4	1.46772243D3	0.0D0
Na <sub>2</sub> SO <sub>4</sub>	C <sup>Φ</sup>	-8.07816886D1	-3.54521126D-2	2.02438830D3	1.46197730D1	-9.16974740D-2	1.43946005D-5	-2.42272049D0	0.0D0
K <sub>2</sub> SO <sub>4</sub>	β <sup>0</sup>	4.07908797D1	8.26906675D-3	-1.41842998D3	-6.74728848D0	0.0D0	0.0D0	0.0D0	0.0D0
K <sub>2</sub> SO <sub>4</sub>	β <sup>1</sup>	-1.31669651D1	2.35793239D-2	2.06712594D3	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
K <sub>2</sub> SO <sub>4</sub>	C <sup>Φ</sup>	-1.88D-2	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0

TABLE-2  
THE CONSTANTS IN THE TEMPERATURE EQN (2) FOR MIX PARAMETERS IN THE AQUEOUS QUATERNARY SYSTEM Na<sup>+</sup>, K<sup>+</sup>//Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O

Species	Parameters	a1	a2	a3	a4	a5	a6	a7	a8
Na,K	θ	-5.02312111D-2	0.0D0	1.40213141D1	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Cl,SO <sub>4</sub> (273.15-423.15K)	θ	7.0D-2	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Cl,SO <sub>4</sub> (423.15-523.15K)	θ	5.67983244D1	-1.63021206D-1	-1.87479820D4	5.70511185D0	8.90099309D2	9.21443436D-5	0.0D0	0.0D0
Na,K,Cl (273.15-523.15K)	Ψ	1.34211308D-2	0.0D0	-5.10212917D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Na,K,SO <sub>4</sub> (273.15-423.15K)	Ψ	3.48115174D-2	0.0D0	-8.21656777D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Na,K,SO <sub>4</sub> (423.15-523.15K)	Ψ	6.56482122D-2	0.0D0	-2.12651122D1	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Cl,SO <sub>4</sub> ,Na (273.15-423.15K)	Ψ	-9.0D-3	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Cl,SO <sub>4</sub> ,Na (423.15- 523.15K)	Ψ	-3.29811409D2	-4.42410302D-2	1.62957351D4	5.16258079D1	-3.53341751D2	0.0D0	0.0D0	0.0D0
Cl,SO <sub>4</sub> ,K (273.15-523.15K)	Ψ	-2.12481475D-1	2.84698333D-4	3.75619614D1	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0

TABLE-3  
THE CONSTANTS IN THE TEMPERATURE EQN (2) FOR THE STANDARD CHEMICAL POTENTIALS (μ<sup>0</sup>/R<sub>T</sub>)  
OF SOLID PHASES AND A<sup>Φ</sup> IN THE AQUEOUS QUATERNARY SYSTEM Na<sup>+</sup>, K<sup>+</sup>//Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O

Parameters <sup>a</sup>	a1	a2	a3	a4	a5	a6	a7	a8
A <sup>Φ</sup>	3.36901532D-1	-6.32100430D-4	9.14252359D0	-1.35143986D-2	2.26089488D-3	1.92118597D-6	4.52586464D1	0.0D0
H <sub>2</sub> O(aq)	1.04031130D3	4.86092851D-1	-3.26224352D4	-1.90877133D2	-5.35204850D-1	-2.32009393D-4	5.20549183D1	0.0D0
Hal	4.93249179D2	2.37823586D-1	-1.20440669D4	-8.93349441D1	-8.59061145D-1	-1.13740605D-4	-3.73924867D2	0.0D0
Th	-5.12155332D3	-2.61751950D0	1.14225946D5	9.50777893D2	-2.88441000D0	1.19461496D-3	-1.90759987D3	0.0D0
Syl	6.34353871D2	2.70625625D-1	-1.82938538D4	-1.12304199D2	0.0D0	-1.25228517D-4	-2.21701937D2	0.0D0
Arc	3.27583167D1	-4.82092643D-2	-6.71134677D3	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Gla (273.15- 423.15 K)	1.06315565D2	-1.64763994D-1	-2.21379535D4	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Gla (423.15- 473.15 K)	-5.62101726D1	0.0D0	1.71328432D4	0.0D0	0.0D0	0.0D0	0.0D0	0.0D0
Mir	6.54118884D4	1.93357359D1	-1.78625843D6	-1.14979542D4	0.0D0	0.0D0	0.0D0	0.0D0

<sup>a</sup>Hal, NaCl; Th, Na<sub>2</sub>SO<sub>4</sub>; Syl, KCl; Arc, K<sub>2</sub>SO<sub>4</sub>; Gla, Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub>; Mir, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O

TABLE-4  
CALCULATED SOLUBILITY OF CO-SATURATED POINTS IN THE SYSTEM (Na<sup>+</sup>, K<sup>+</sup>//Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O) at 273.15-473.15 K

T/K	Composition of liquid phase, /(mol/kgH <sub>2</sub> O)				Jänecke index, J[mol/100mol dry-salt]			Equilibrium solid phases <sup>a</sup>
	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	J(2K <sup>+</sup> )	J(SO <sub>4</sub> <sup>2-</sup> )	J(H <sub>2</sub> O)	
273.15	5.6722	1.3561	6.6241	0.2021	19.29	5.75	1579.6	Hal+Syl+Mir
	3.5509	2.2207	5.2464	0.2626	38.48	9.10	1923.5	Mir+Syl+Gla
	1.6175	1.6895	2.4918	0.4076	51.09	24.65	3357.0	Mir+Gla+Arc
	2.2402	2.7954	4.6470	0.1943	55.51	7.72	2204.7	Gla+Syl+Arc
278.15	5.4729	1.6222	6.4503	0.3224	22.86	9.09	1564.7	Mir+Syl+Gla
	5.7201	1.5306	6.6146	0.3181	21.11	8.77	1531.1	Hal+Syl+Mir
	2.1574	3.0032	4.8215	0.1695	58.19	6.57	2151.2	Arc+Syl+Gla
283.15	6.0306	1.2392	6.3283	0.4707	17.05	12.95	1527.1	Mir+Hal+Gla
	5.6144	1.6950	6.7396	0.2849	23.19	7.79	1518.8	Hal+Syl+Gla
	2.1005	3.2151	4.9955	0.1601	60.48	6.02	2088.5	Arc+Syl+Gla
288.15	6.4333	0.9893	5.9881	0.7172	13.33	19.33	1495.7	Mir+Hal+Gla
	5.5137	1.8643	6.8678	0.2551	25.27	6.92	1504.7	Hal+Syl+Gla
	2.0551	3.4269	5.1697	0.1562	62.51	5.70	2025.1	Arc+Syl+Gla
293.15	6.4305	0.8552	5.0598	1.1129	11.74	30.55	1523.8	Mir+Th+Gla
	6.5981	0.9536	5.8906	0.8306	12.63	22.00	1470.1	Th+Hal+Gla
	5.4261	2.0402	6.9914	0.2374	27.33	6.36	1486.9	Hal+Syl+Gla
	2.0170	3.6369	5.3439	0.1550	64.33	5.48	1963.5	Arc+Gla+Syl
298.15	6.2618	0.7948	3.2333	1.9117	11.26	54.18	1573.2	Mir+Th+Gla
	6.4958	1.0562	6.0293	0.7613	13.99	20.16	1470.0	Th+Hal+Gla
	5.3466	2.2209	7.1152	0.2261	29.35	5.98	1467.0	Hal+Syl+Gla
	1.9846	3.8445	5.5179	0.1556	65.95	5.34	1904.5	Arc+Gla+Syl
308.15	6.3534	1.2664	6.2647	0.6775	16.62	17.78	1457.0	Th+Hal+Gla
	5.2061	2.5925	7.3699	0.2144	33.24	5.50	1423.5	Hal+Syl+Gla
	1.9337	4.2511	5.8648	0.1600	68.73	5.17	1795.0	Arc+Syl+Gla
323.15	6.2311	1.5879	6.5759	0.6216	20.31	15.90	1419.8	Th+Hal+Gla
	5.0358	3.1650	7.7768	0.2120	38.59	5.17	1353.7	Hal+Syl+Gla
	1.8878	4.8385	6.3823	0.1720	71.93	5.12	1650.5	Arc+Syl+Gla
333.15	6.1890	1.8068	6.7786	0.6086	22.60	15.22	1388.4	Th+Hal+Gla
	4.9488	3.5514	8.0660	0.2171	41.78	5.11	1306.0	Hal+Syl+Gla
	1.8759	5.2161	6.7265	0.1827	73.55	5.15	1565.4	Arc+Syl+Gla
348.15	6.1683	2.1483	7.0964	0.6101	25.83	14.67	1334.9	Th+Hal+Gla
	4.8600	4.1335	8.5275	0.2330	45.96	5.18	1234.4	Hal+Syl+Gla
	1.8850	5.7648	7.2452	0.2023	75.36	5.29	1451.2	Arc+Syl+Gla
373.15	6.2283	2.7828	7.7077	0.6517	30.88	14.46	1232.0	Th+Hal+Gla
	4.8311	5.1123	9.3787	0.2823	51.41	5.68	1116.5	Hal+Syl+Gla
	1.9737	6.6446	8.1301	0.2441	77.10	5.67	1288.1	Arc+Syl+Gla
398.15	6.4314	3.5540	8.4847	0.7503	35.59	15.03	1111.8	Th+Hal+Gla
	4.9796	6.1342	10.3687	0.3726	55.19	6.70	998.9	Hal+Syl+Gla
	2.1645	7.5004	9.0682	0.2983	77.60	6.17	1148.7	Arc+Syl+Gla
423.15	7.0122	4.5750	9.5652	1.0110	39.48	17.45	958.1	Th+Hal+Gla
	5.4286	7.3367	11.6431	0.5611	57.47	8.79	869.7	Hal+Syl+Gla
	2.4837	8.3519	10.0997	0.3680	77.08	6.79	1024.6	Arc+Syl+Gla
448.15	6.9587	4.7546	10.0759	0.8187	40.59	13.98	947.8	Th+Hal+Gla
	5.5722	8.3182	12.8742	0.5081	59.88	7.32	799.2	Hal+Syl+Gla
	1.8574	9.8212	10.8057	0.4365	84.10	7.48	950.6	Arc+Syl+Gla
473.15	7.2050	5.3136	10.9507	0.7840	42.45	12.53	886.8	Th+Hal+Gla
	5.9502	9.3222	14.3248	0.4738	61.04	6.20	726.9	Hal+Syl+Gla
	1.7604	10.7945	11.6820	0.4364	85.98	6.95	884.3	Arc+Syl+Gla

<sup>a</sup>Hal, NaCl; Th, Na<sub>2</sub>SO<sub>4</sub>; Syl, KCl; Arc, K<sub>2</sub>SO<sub>4</sub>; Gla, Na<sub>2</sub>SO<sub>4</sub>·3K<sub>2</sub>SO<sub>4</sub>; Mir, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O

model can be used to predict the solubility of complex brine and make up the lack of experimental solubility data at higher and broader temperature ranges.

As shown in Fig. 2, the predictive glasserite phase area is evidently less than experimental measurements at 273.15 K and relatively large discrepancy exists between the calculated and experimental values, which illustrates that the equilibrium constant of glasserite from the higher temperature model is greater and the high temperature chemical model is difficult to extrapolate and accurately express the standard chemical

potential of glasserite at and below 273.15 K. However, there is no low temperature model on the standard chemical potential of glasserite in the literature<sup>9</sup>. The main reason is that less solubility data of the ternary system (Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O) at and below 273.15 K are insufficient to fit the standard chemical potential of glasserite and so better model is needed to calculate phase equilibrium containing glasserite solid phase at and below 273.15 K.

The standard chemical potential of glasserite at 273.15 K from the high temperature chemical model is calculated as

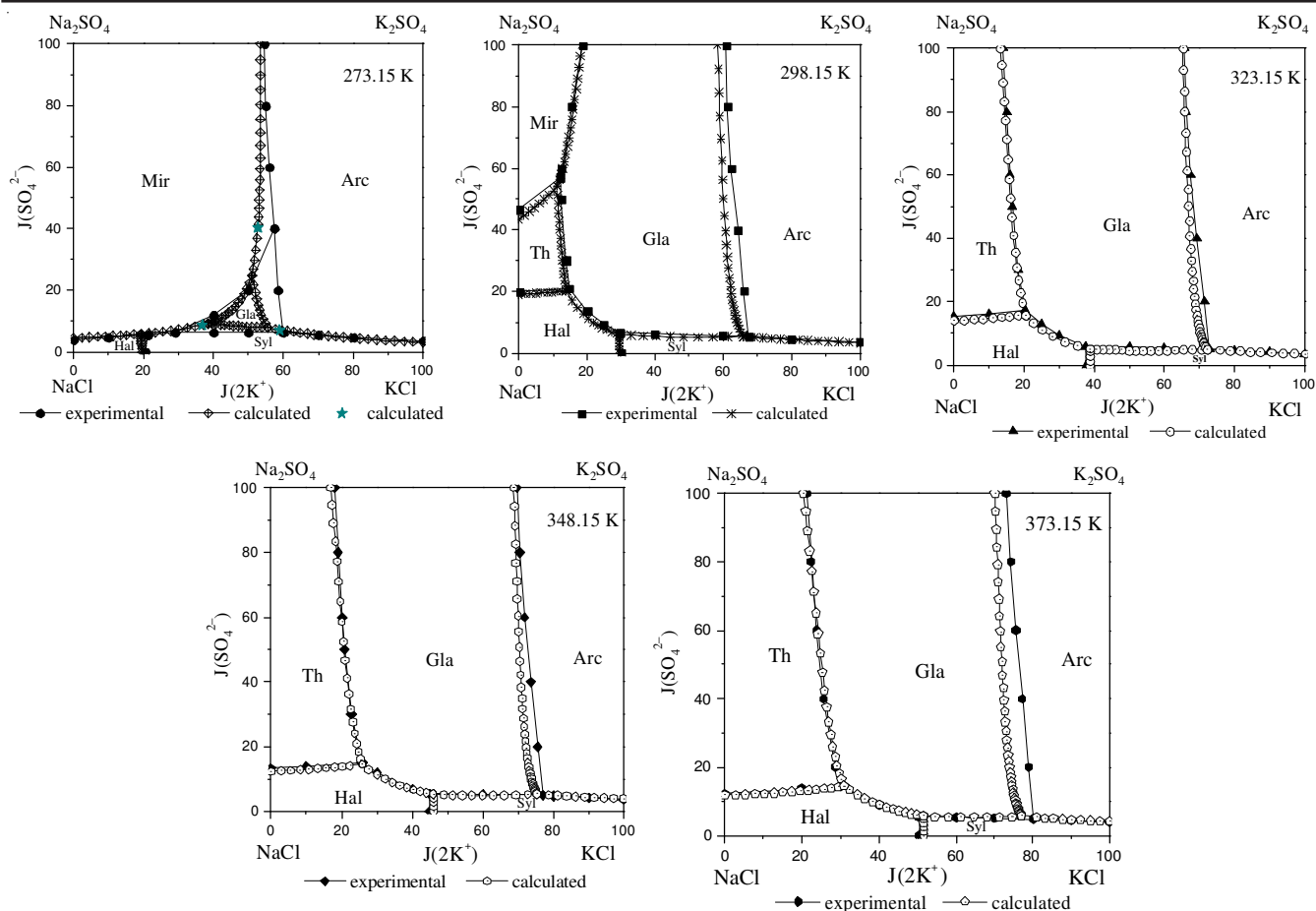


Fig. 2. Calculated and experimental phase diagram of the system  $\text{Na}^+$ ,  $\text{K}^+/\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$  at 273.15, 298.15, 323.15, 348.15, 373.15 K. Hal, NaCl; Th,  $\text{Na}_2\text{SO}_4$ ; Syl, KCl; Arc,  $\text{K}_2\text{SO}_4$ ; Gla,  $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$ ; Mir,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

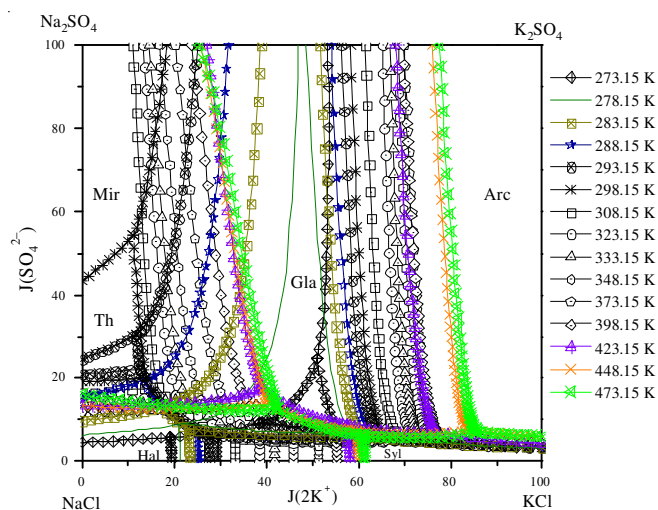


Fig. 1. Predicted phase diagram of the system ( $\text{Na}^+$ ,  $\text{K}^+/\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$ ) from 273.15 to 473.15 K

-19.736593 where ionic chemical potentials are set equal to zero. If we take its value as -20.038192, the co-saturated point on Gla + Mir + Arc assembly will significantly move up along the Mir + Arc univariant curve and extremely approach experimental value as shown in Fig. 2. The other two co-saturated points containing glaserite slightly move and therein Gla + Arc + Syl invariant point almost coincides with determined value. The minor change of chemical potential of glaserite

causes larger change of co-saturated point position, which resembles that the position of co-saturated point on  $\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$  is very sensitive to chemical potential of double salt  $\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$  in the reciprocal quaternary system ( $\text{Li}^+$ ,  $\text{Na}^+/\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$ )<sup>15</sup>. Then it may be inferred that co-saturated point consisting of sulphate double salt and other sulphate assembly is sensitive to chemical potential of sulphate double salt especially when sulphate double salt forms a close pattern in salt-water system containing chlorine ion.

## Conclusion

The high temperature chemical model can be used to obtain reliable Pitzer parameters and the equilibrium solubility of complex brine can be accurately predicted by using Pitzer ion-interaction model and its extended HW model. But the chemical model at the lower temperature should continue to be developed to gain perfect Pitzer parameters and chemical potentials of solid phases. Furthermore the chemical model for the stable and metastable solubilities of complex brine systems containing lithium ion need be constructed to calculate distinct phase equilibrium in broader temperature range.

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