RICE UNIVERSITY

**Improvement of thermodynamic modeling of calcium
carbonate and calcium sulfates at high temperature and high
pressure in mixed electrolytes**

by

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Abstract

Improvement of thermodynamic modeling of calcium carbonate and calcium sulfates at
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Pitzer theory is used to predict the solubility of gypsum, anhydrite and calcite over wide ranges of temperature, pressure, and ionic strength with mixed electrolytes, which usually occurs in deep water oil and gas production. Gypsum solubility was measured from 0 to 40 °C, from 14.7 to 20000 psi, with 0 to 4 mol NaCl/kg H₂O. Anhydrite solubility in literature was confirmed and adopted in this study. The equilibrium constants of gypsum and anhydrite were incorporated by temperature and pressure dependent parts from different researches. Along with other virial coefficients, virial coefficients for Ca²⁺-SO₄²⁻ interactions were fitted and used to precisely predict solubility of gypsum/anhydrite. They are also applied to accurately predict calcite solubility with mixed electrolytes from 0 to 250 °C (except for 100 °C) up to 21000 psi. The K_{assoc} for CaSO₄⁽⁰⁾ derived from $\beta_{CaSO_4}^{(2)}$ in this study matches well with other experimental data at 1 atm 25 °C.

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Chapter 1. Introduction

1.1. Problem statement

As an important sector of global energy support, deep water oil and gas production are getting more attention today (Miller and Newman 2011; Fan et al. 2012; Kan and Tomson 2012). Increasing water depth in the oil and gas production process not only indicates increasing financial rewards due to the larger amounts of oil and gas reserves, but also means increasing risks due to extreme operation conditions with high temperature (150 to 200 °C, or 302 to 392 °F), high pressure (1,000 to 1,500 bar, about 14,500 to 22000 psi), and high concentration of total dissolved solids (TDS more than 300,000 mg/L) (Chawathe et al. 2009; Kan and Tomson 2012). Scaling is one of the most serious problems costing millions of dollars a year in the oil and gas production industry. Scaling will more likely occur when undergoing larger temperature and pressure changes from down hole to surface under such extreme operation conditions.

Scale prediction and control need good understanding of the thermodynamic and kinetic properties of common minerals over such temperature, pressure, and TDS ranges (Kan and Tomson 2012; Shi et al. 2012). However, Figure 1 shows that the typical temperature, pressure and TDS ranges of existing thermodynamic data (i.e. about 250 °C, 12000 psi, and 200,000 mg/L TDS) can hardly cover typically observed conditions in current deep, and ultra-deep water oil and gas productions. Thus it is both financially profitable and technically required to pay close attention to thermodynamic and kinetic properties of common minerals under such extreme conditions.

Figure 1. Plot of temperature, pressure, and TDS ranges of literature solubility data, and that of current and future deep water oil and gas production conditions (Fan et al. 2011)

Scale prediction and control are closely related to mineral solubility prediction which strongly relies on accurate equilibrium constants (including solubility product of the minerals, K_{sp} , and other association constants for complexes, if applicable, as a function of T and P) and activity coefficients (as a function of T , P) of different species. However, the equilibrium constants are sparse and uncertain especially at extended temperatures and pressures (Helgeson and Kirkham 1974; Djamali et al. 2012). The same equilibrium constants reported in different researches might vary a lot. In addition, accurate prediction of activity coefficients under HTHP in the presence of mixed electrolytes has also been of great challenge in the past. Pitzer theory is usually applied as

one of the most popular approaches to predict the activity coefficients for mixed electrolytes and neutral compounds under high ionic strength (*IS*) greater than 5 mol/kg H₂O (He 1992; Voigt 2011). The activity coefficients are composed of Debye Huckel long range interactions and short range ion-specific interactions which can be represented by virial coefficients as a function of temperature and pressure. But the virial coefficients are difficult to be determined accurately in complex mixed electrolyte solutions especially under high temperature and high pressure, which always occurs in realistic oil and gas production process. For example, inaccurate equilibrium constants or inaccurate solubility data in a mineral dissolution system will result in theoretically incorrect virial coefficients. Though they are mathematically right, able to fit the experimental data in the certain system well, the fitted virial coefficients might be wrong in other systems under different conditions. Such inaccuracies of ion-specific virial coefficients will be big limitations for their inter-system applications, which is one of the most important ways Pitzer theory is made use of and strengthened.

Shi et al. (2013) found that the discrepancies in calcite solubility predictions with mixed electrolytes can be mainly attributed to the inaccurate virial coefficients of Ca²⁺ and SO₄²⁻ interactions (Shi et al. 2013). In addition, since Ca²⁺ and SO₄²⁻ are important components in various solutions, especially in brine water produced during oil and gas production, accurate determination of virial coefficient for Ca²⁺ and SO₄²⁻ interactions is not only important for calcite system with mixed electrolytes, but also for gypsum and anhydrite systems, which are all important scale minerals in oil and gas production field.

1.2. Purpose of the study

This study is to identify the virial coefficients for Ca^{2+} and SO_4^{2-} interactions based on Pitzer theory and reliable sources of equilibrium constants, accurate solubility measurement of gypsum and anhydrite under high temperature high pressure (HTHP) and high ionic strength conditions. The virial coefficients for Ca^{2+} and SO_4^{2-} interactions will be fitted as a function of temperature and pressure over wide ranges in gypsum and anhydrite system. The fitted virial coefficients will be applied to calcite systems in the presence of mixed electrolytes to predict calcite solubility. This study will be a good example of identification and application of certain ion-specific virial coefficients based on Pitzer theory.

In Chapter 2, study background and literature review on activity coefficient estimation, equilibrium constants calculation, calcium sulfate system studies, and calcite system researches will be discussed in detail. Details of solubility measurement and data selection are included in Chapter 3. Based on the solubility data, a thermodynamic model based on Pitzer theory is established in Chapter 4. The thermodynamic model will generate improved virial coefficients for Ca^{2+} - SO_4^{2-} interactions. These virial coefficients will be applied to calcium sulfate and calcite systems and the details are also discussed in Chapter 4. Conclusions are given in Chapter 5 and suggestions for future studies will be given in Chapter 6.

Chapter 2. Background and literature review

2.1. The scaling problem under HTHP conditions

Oil and gas will be in increasing demand at least in medium term as is shown in Figure 2 (Miller and Newman 2011; Kan and Tomson 2012). The offshore production is predicted to become more important and will take account of 35% of total oil and gas production by 2025, among which offshore deepwater oil and gas production is believed to be the only sector continuing to grow after 2015 (Miller and Newman 2011). During the processes of deepwater oil and gas production, produced water will undergo mixture from different sources and great temperature and pressure changes when elevated from downhole to surface. Such brine water mixture and temperature and pressure changes will lead to a great potential for scale formation which will cost millions of dollars per year. In the past, in order to solve the scale problem, many researchers have focused on properties of common minerals including barite (BaSO_4), calcite (CaCO_3), calcium sulfates ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$, anhydrite ($n = 0$), hemihydrate ($n = 0.5$), or gypsum ($n = 2$)), celestite (SrSO_4), halite (NaCl), silica or silicate, siderite (FeCO_3), sulfides (FeS , FeS_2 , PbS , CaS , and ZnS), and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Blount and Dickson 1969; Blount and Dickson 1973; Pitzer et al. 1984; Johnson and Tomson 1991; Kaasa 1998; Duan and Li 2008; Lu et al. 2010; Okocha and Sorbie 2010; Kan and Tomson 2012; Shi et al. 2012; Shi et al. 2013). However, the thermodynamic properties of most minerals, especially at HTHP in complex electrolytes solutions, have not been thoroughly analyzed. This study is to fill the gap for calcium sulfates and calcite at high temperature and high pressure starting from virial coefficient identifications for Ca^{2+} - SO_4^{2-} interactions.

Figure 2. Records and predictions of global oil supply from 1930 to 2025 (Miller and Newman 2011)

2.2. Osmotic and activity coefficients

2.2.1. Basic definitions

In infinitely dilute solutions, solute ions or molecules will act as if they are in ideal solutions, where individual solute ions or molecules will only interact with solvent molecules (e.g. water) but will not interact with other solute species. When solute concentration increases, there are more chances for individual solute species to get together and interact with each other, and thus deviate from ideality. Moreover, the interactions between solute and solvent species (e.g. solvation) will also contribute to deviation from ideality when the solute concentration increases. In realistic aqueous systems, the activities of solvents, solutes (electrolytes or neutral compounds) will be affected by temperature, pressure, and the compositions of the solution. In order to describe the non-ideality referred to as standard state, which is in hypothetically one

molal infinitely dilute solutions, activity coefficient (γ) for solutes is introduced with the equation

$$\mu_i = \mu_i^\phi + RT \ln(a_i) = \mu_i^\phi + RT \ln(m_i) + RT \ln(\gamma_i), \quad (1)$$

where μ_i stands for the chemical potential of species i , and superscript ϕ is for standard state; a_i is effective activities of species i ; m_i is molality of species i ; T is in Kelvin scale and R is the gas constant (8.315 J/(K mol)).

For pure liquid solvent (e.g. water), the activity is defined as

$$a_i = \frac{f_i}{f_i^0} = \frac{P_i}{P_i^0}, \quad (2)$$

where superscript 0 denotes pure solvent; P is the partial pressure of solvent which equals the solvent fugacity (f) assuming solvent vapor behaves as a perfect gas. Specifically, the activity of water can be calculated with

$$\ln a_w = - \frac{\sum_i m_i}{1000 / Mr} \phi, \quad (3)$$

$$\Pi = \phi \left(\frac{RT \sum_i (m_i Mr)}{1000 V_w} \right), \quad (4)$$

where a_w is the water activity; m_i is the solute molalities in the solution; ϕ stands for the osmotic coefficients as defined in Equation 3 to represent the non-ideality of solvent (e.g. water) (Harned et al. 1959); where Π is the osmotic pressure (bar); Mr is the molecular

weight of the solvent (for H₂O it's 18.01534 g/mol); $\overline{V}_w$ is the partial molar volume of water (cm³/mol).

The activity coefficient is a bridge between equilibrium constants and realistic solute molalities and solvent activities. Saturation index (*SI*) is introduced as the indication of scale potential for certain minerals in realistic conditions. For example, for mineral $M_{v+}X_{v-} \cdot nH_2O$, the dissolution equation is

The *SI* for mineral $M_{v+}X_{v-} \cdot nH_2O$ is related to equilibrium constants, solutes molality, and activity coefficients (Kan and Tomson 2012):

$$SI = \log_{10} \frac{(\gamma_M [M])^{v_+} (\gamma_X [X])^{v_-} (a_w)^n}{K_{sp}}, \quad (6)$$

where $[\cdot]$, γ , and v stands for the molality, activity coefficient, and stoichiometric coefficient of certain species, respectively; a_w is the activity of water; K_{sp} is solubility product. Theoretically, *SI* should be zero when solids are at equilibrium with the solution. If *SI* is larger than zero, it means the solution is oversaturated for this mineral and it has a potential to precipitate.

Thus it is theoretically possible to predict the scale potential of minerals as long as the equilibrium constants and activity constants of each species are known accurately. The solubility of certain minerals can be predicted accurately under different conditions. In the past, numerous models have been developed to predict the activity coefficient of aqueous species under different conditions. In this part, starting from Debye Huckel

limiting law, several of the most important equations will be introduced in detail. As an example, the activity coefficient of Ca^{2+} in pure CaCl_2 solutions will be calculated using different methods and plotted in Figure 4.

Figure 3. The applicability and formula of different activity coefficient equations for divalent cation (Langmuir 1997)

Figure 4. Activity of Ca^{2+} in pure $CaCl_2$ solutions in function of Ionic strength at 25 °C and 1 atm (revised based on Langmuir 1997).

2.2.2. Debye Huckel law

In realistic solutions with electrolytes, the activities of individual ions depend on the solution compositions, temperature, and pressure. As for solution compositions, different species will have different charges, different ion size, different electron shell structures, and different interactions with other ions or molecules. For simplicity, in dilute solutions, only the interactions between two individual solute ions with relatively long ranges will be considered. Such long range interactions between ions are largely due to Coulombic forces which are proportional to the charges of the two ions. In order to

indicate the impacts of the solution compositions on individual ion interactions, ionic strength (IS) is defined and is expressed as follows (Langmuir 1997):

$$IS = \frac{1}{2} \sum (m_i z_i^2), \quad (7)$$

where m_i is the molality of ion i ; z_i is the charge of ion i . IS includes the charge-specific impacts of all the charged species in the solutions. When the solution is very dilute (i.e. $IS < 0.01$ m), IS can represent the impacts due to solute-solute interactions on activity coefficients accurately and included in Debye-Huckel (DH) limiting law,

$$\log \gamma_i = -A z_i^2 \sqrt{IS}, \quad (8)$$

where z_i is the ion charge of interest; A is the Debye-Huckel limiting law slope for the activity coefficient and can be calculated as

$$A = \frac{1}{\ln 10} \left[\frac{2\pi N_{av} \rho_w}{1000} \right]^{1/2} \left[\frac{e^2}{DkT} \right]^{3/2}, \quad (9)$$

in which N_{av} stands for Avogadro's number; ρ_w is the water density; e is the electron charges; D is the dielectric constant of solvent (e.g. H₂O) as a function of temperature and pressure; k is the Boltzman's constant; T is in Kelvin temperature scale; the dominator $\ln 10$ is for transition between Napierian logarithm (i.e., natural logarithm, base e) and Briggsian logarithm (i.e. scientific logarithm, base 10). At 25 °C and 1 atm for water, A is about 0.509.

Along with density and dielectric constant of water in A term, the Debye-Huckel limiting law successfully incorporates the temperature and pressure impacts on water as

the medium of long range solute-solute interactions which are important at low ionic strength. In detail, water density and dielectric constant can be calculated with the functions below (Millero 2001):

$$D = u_1 \cdot e^{u_2 TK + u_3 TK^2} + \left(u_4 + \frac{u_5}{u_6 + TK} \right) \cdot \ln \left(\frac{u_7 + u_8 / TK + u_9 TK + P_{atm}}{u_7 + u_8 / TK + u_9 TK + 1000} \right), \quad (10)$$

$$\rho_w = \rho_{1atm} + (a_7 + a_8 TC + a_9 TC^2 + a_{10} TC^3) \times (P_{atm} - 1), \quad (11)$$

$$\rho_{1atm} = \frac{(\rho_0 + a_1 TC + a_2 TC^2 + a_3 TC^3 + a_4 TC^4 + a_5 TC^5)}{1 + a_6 TC}, \quad (12)$$

where the constants in the equations are $u_1 = 342.79$, $u_2 = -0.0050866$, $u_3 = 0.0000009469$, $u_4 = -2.0525$, $u_5 = 3115.9$, $u_6 = -182.89$, $u_7 = -8032.5$, $u_8 = 4214200$, $u_9 = 2.1417$; $\rho_0 = 999.83952$, $a_1 = 16.945176$, $a_2 = -0.0079870401$, $a_3 = -0.000046170461$, $a_4 = 0.00000010556302$, $a_5 = -2.8054253E-10$, $a_6 = 0.01687985$, $a_7 = 0.043922$, $a_8 = -0.000076$, $a_9 = 0.000000126$, $a_{10} = 0.00000000319$.

The Debye-Huckel limiting law is successfully applied in very dilute solutions ($IS < 0.01$ m) assuming: (1) ions are treated as point charges and ion size has no impact on activity coefficients; (2) the solvent is treated as a dielectric continuum; (3) ion interactions are all Coulombic; (4) ions with the same sign charge will not interact with each other.

When solute concentration and IS increase, ions will get closer to each other and thus ions cannot be simply treated as point charges. The extended Debye-Huckel equation which includes the ion size impacts is needed:

$$\log \gamma_i = -Az_i^2 \frac{IS^{1/2}}{1+Ba_i \cdot IS^{1/2}}, \quad (13)$$

where a_i is the empirical parameter representing the distance of closest approach between two interacting ions taking into account of ion size and ranges from 3 to 9 Å; B is dependent on solvent dielectric constant and temperature, and can be calculated by

$$B = \left(\frac{8\pi N_{av} e^2}{1000k} \right)^{1/2} \frac{1}{(DT)^{1/2}} = \frac{50.29 \times 10^8}{(DT)^{1/2}}. \quad (14)$$

The extended DH equation was a breakthrough in electrolyte activity coefficient prediction. It can work quite well compared with experimental results at IS lower than 0.1 m. It is also based on the assumptions (2-4) listed above, and the assumption that a_i term which represents ion size impacts will not change with IS . The physical meaning of a_i is not accurate and inadequate to represent a physically meaningful distance, and it also contains other short-range effects (Robinson and Stokes 2002). The incorporation of a_i in the equation starts to consider the ion-specific properties in the activity coefficient prediction. It is needed to consider such ion-specific properties when short-range interactions are more important in more concentrated solutions, in which solute ions cannot be treated as point charges.

However, the activity coefficient predicted by extended DH equation is reflecting the hydrated ions behavior without considering the ion-solvent solvation impacts (Robinson and Stokes 2002). When the solution is more concentrated (> 0.1 m), more solvent molecules will interact with or be captured by ions (e.g. solvation) and thus, fewer free solvent molecules will be available in the solution. Ostensibly, there will be

more active solutes in the solution and thus have more chances to react with other solute species (i.e. solutes have larger activities). As a result, there will be deviation of activity coefficients from continued decreasing as the extended DH equation describes. It indicates the requirement to adjust the extended DH model through various ways, for instance, including the ion-solvent interactions into the prediction model.

2.2.3. Davis equation and TJ equation

Starting from the extended DH equation, many models were developed to account for such deviations. For example, the Davis equation adjusted and added an empirical term into the extended DH equation as follows (Harned and Owen 1958; Davies 1962):

$$\log \gamma_i = -Az_i^2 \left(\frac{IS^{1/2}}{1+IS^{1/2}} - b^* IS \right), \quad (15)$$

where b is empirical parameter and is set to be 0.3. It can work well up to 0.5 m, but it sacrifices the accuracy of Extended DH equation at low IS , since it omits the ion size parameter. There is no physical meaning for the b value which is only empirical to account for the deviation at high IS .

The Truesdell-Jones (TJ) equation is also developed from Extended DH equation by simply adding an ion-specific b^*IS term as follows:

$$\log \gamma_i = -Az_i^2 \frac{IS^{1/2}}{1+Ba_i \cdot IS^{1/2}} + b_i^* IS, \quad (16)$$

where a_i , b_i are both empirical ion size parameters. The a_i values for each ion are different from that in the extended DH equation, though the formula is the same. For example, in the extended DH equation, a_i for H^+ is 9 Å, but in TJ model is 4.78 Å. These

ion-specific ion size parameters improve the TJ model able to predict activity coefficients accurately up to 2.0 m.

2.2.4. Robinson-Stokes equation

However, these models do not theoretically incorporate the ion-solvent interactions accurately but simply add on empirical terms. Robinson and Stokes (1955) considered the Gibbs free energy change in the solvation process that happens in the solution. They assumed that a total of h moles of solvent will combine with v moles of electrolytes in the solution and ignored “non-electrolyte” contributions such as mixing heat of solvated species with solvent. In the derivation process, the authors only assume that the value of h is unchanged even when proceeding to infinite dilution, which means the interactions of solvent and solutes considered in the model are treated at least as near saturated state. By combining extended DH model, they derived the Robinson-Stokes (RS) equation for mean ion activity coefficient of electrolyte $M_{v+}X_{v-}$ as below:

$$\log \gamma_{\pm} = -A |z_+ z_-| \frac{IS^{1/2}}{1 + Ba \cdot IS^{1/2}} - \frac{h}{v} \log a_w - \log [1 + 10^{-3} M_w (v - h) m], \quad (17)$$

$$\gamma_{\pm} = (\gamma_M^{\nu_+} \gamma_X^{\nu_-})^{1/(\nu_+ + \nu_-)}, \quad (18)$$

$$z_+ \nu_+ + z_- \nu_- = 0, \quad (19)$$

where a_w is water activity; M_w is water molecular weight. The RS model has two to be fitted parameters which are a and h . The a values are obviously not identical to those in the previous models though they are all derived from the extended DH model. h values represent the solvation state of the electrolytes, which means if h is larger, more water molecules will be captured by the electrolytes, and vice versa. Based on the fitted values

of a and h , R-S equation can be used to accurately predict the activity coefficient of 1-1 electrolyte up to 4-5 M, and of 2-1 electrolyte up to 1.5 to 1.8 M. According to the fitted results, cations with larger crystallographic radii will hold fewer water molecules (i.e. smaller h), which is consistent with other experimental results. For example, in NaCl and KCl solutions, h for sodium (3.5) is larger than for potassium (1.9) while the sodium ion has smaller radii of bare ions. However, it also shows inconsistency for anion species which are in reverse order. Moreover, it is not additive for separate ions, which means the h values are only meaningful for electrolytes but not for single ions. It is a limitation for RS model to be applied to solutions with mixed electrolytes in which it is hard to tell which electrolyte a separate ion belongs to. In addition, it is still not theoretically adequate since it ignores the “non-electrolyte” effects, and the h values will not be consistent with experiments to represent the number of hydrated water molecules especially when IS changes a lot. For solutions with mixed electrolytes, an ion-specific rather than an electrolyte-specific model might be needed.

2.2.5. Meissner model

Different from these models adjusted with extended DH equation, Kusik and Meissner (1978) developed a thoroughly different way to predict activity coefficients for electrolyte $M_{v+}X_{v-}$ which gets rid of the inaccuracies of extended DH equation at high concentrations. In their model, the reduced activity coefficient γ_r^0 is defined as follows:

$$\gamma_r^0 = \gamma_{\pm}^{1/v_+v_-} = [1 + B(1 + 0.1IS)^q - B]\gamma^*, \quad (20)$$

where:

$$B = 0.75 - 0.065q, \quad (21)$$

$$\log \gamma^* = \frac{-0.5107\sqrt{IS}}{1 + C\sqrt{IS}}, \quad (22)$$

$$C = 1 + 0.055qe^{-0.023IS^3}. \quad (23)$$

In the model, at a certain temperature, only one empirical electrolyte-specific parameter q is to be defined. Thus this model is easy to apply and needs only one accurate data point at a certain temperature to fit the q value. The temperature dependence of activity coefficient is also incorporated in q values based on the function below:

$$\frac{q_t - q_{25}}{TC - 25} = aq_{25} + b^*, \quad (24)$$

where temperature TC is Celsius. It is reported that a , b^* are the same for most electrolytes with $a = -0.005$ and $b^* = 0.0085$, except for sulfuric acid with a , b^* values of -0.0079 and -0.0029 , respectively. However, this temperature equation cannot work over wide ranges of temperature (less than 120 °C). The replacement of constant 0.5107 in Equation 22 with the A term in Equation 9 with temperature and pressure dependence can make the function much more accurate up to 300 °C (Cohen 1989).

For solutions with mixed electrolytes, the reduced activity coefficient for a specific electrolyte (i.e. M_iX_j) is calculated by a weighted function,

$$\begin{aligned} \log \gamma_{r,MX} = & \frac{z_M}{z_M + z_X} \sum_{a=1}^{N_a} \left(\frac{(z_M + z_a)^2}{2z_M z_a} \cdot \frac{m_a z_a^2}{2} \log \gamma_{r,Ma}^0 \right) / IS \\ & + \frac{z_X}{z_M + z_X} \sum_{c=1}^{N_c} \left(\frac{(z_X + z_c)^2}{2z_X z_c} \cdot \frac{m_c z_c^2}{2} \log \gamma_{r,cX}^0 \right) / IS, \end{aligned} \quad (25)$$

where z_i is the charge of ion i ; m_i is the molality of ion i ; a denotes for anions and c denotes for cations; N_a and N_c stand for the number of total anions and cations, respectively.

The advantage of this model is that it is easy to apply to different systems over wide ranges of ionic strength based on more readily available necessary data and relatively few parameters. This model also overcomes the disadvantage of the RS model which is hard to apply to mixed electrolytes solutions by simple weighting equations. However, on the other hand, it does have about a 20% error for various mixed electrolytes. The error might even be larger if it is applied to a system with large temperature ranges since the temperature dependent function is incorporated only in the parameter q . In addition, the authors pointed out that there will be significant deviations for some electrolytes such as zinc and cadmium chlorides, bromides, and iodides, sulfuric acid, and thorium nitrate. Thus this model is effective for relatively rough (20% error) activity coefficient prediction at high ionic strength for certain electrolytes. Moreover, for mixed electrolytes, the weighting equations cannot accurately represent the complex ion interactions in mixed electrolytes solutions in which the chemical environment is totally different from that in single electrolyte solutions, especially at higher temperatures.

2.2.6. *Specific ion interaction (SIT) theory*

When solute concentration increases even higher with mixed electrolytes, ion-ion interactions will be more significant, and more importantly, the ion-ion specific interaction will be more related to ion specific properties rather than be dependent on ion charges or hypothetical sizes. The Bronsted-Guggenheim-Scatchard specific ion

interaction model is developed based on extended DH model considering the ion-specific interactions as follows:

$$\ln \gamma_{MX} = -\frac{A_\gamma |z_M z_X| IS^{1/2}}{1 + IS^{1/2}} + \frac{2\nu_M}{\nu_M + \nu_X} \sum_a m_a \beta_{Ma} + \frac{2\nu_X}{\nu_M + \nu_X} \sum_c m_c \beta_{cX} \quad (26)$$

where in the extended DH part, B^*a_i term is arbitrarily chosen to make it equal to 1.

In the SIT model, the weighted function similar to that used in the Meissner model is also applied. A big breakthrough in the SIT model is the incorporation of the specific ion interaction term β . It is thus much more accurate than extended DH and Davis equation at high IS when ion interactions become much more important. However, it assumes that only unlikely charged ions have non-zero β values which means it ignores the interaction between likely charged ions and with neutral species. In addition, the β term is assumed to be independent of IS in the SIT model which means the specific ion interactions are irrelevant with surrounding conditions. Such assumptions are reasonable in activity coefficients predictions when IS is under 3.5 m, but when IS is larger, they will lead to large deviations especially for solutions with mixed electrolytes.

2.2.7. Pitzer theory

Considering the shortcomings of the SIT model, Pitzer and his associate researchers expanded the SIT model by incorporating not only binary interactions, but also ternary interactions, even including neutral species. The Pitzer model is one of the most popular models applied to predict the activities of aqueous species. The general formula is selected at first as follows:

$$\frac{G^{ex}}{RT} = \frac{G - G^\phi}{RT} = w_w f(IS) + \frac{1}{w_w} \sum_{ij} \lambda_{ij}(IS) n_i n_j + \frac{1}{w_w^2} \sum_{ijk} \mu_{ijk} n_i n_j n_k \quad (27)$$

where G is the Gibbs free energy of the study system with certain compositions at certain conditions, and G^ϕ is the Gibbs free energy of the ideal system with the same compositions under the same temperature and pressure; G^{ex} is defined as the excess Gibbs free energy of the real system; $f(IS)$ is to represent long range interactions with an extended DH equation form; w_w is the mass (kg) of solute in solvent; the second virial coefficient $\lambda_{ij}(IS)$ is the short range binary interactions as a function of IS ; the third virial coefficient μ_{ijk} stands for short range ternary interactions and is assumed to be independent of IS which might be significant at high IS ; ternary interactions will be set as 0 when i, j, k are all in the like charges since the repulsion effects among them will lead to small ternary interactions. At IS over 3.5 m, or even higher, not only the binary interactions between anion and cation pairs, but also binary interactions between pairs of ions in the same charge, and the ternary interactions among three ions among which two have the same sign charge, will all be significant. Thus the Pitzer model will be much more accurate especially for brines with high ionic strength (Langmuir et al. 1997; Benjamin 2002).

Based on the general formula, more exact forms of certain interactions are chosen with reasonable physical meanings according to experimental data. In solutions with mixed electrolytes with cations, anions, and neutral species (denoted as c , a and n in equations, respectively), the Pitzer equations for the osmotic coefficients and activity coefficients of cations, anions and neutral species (denoted as M , X and N , respectively) are listed as follows:

$$\phi = 1 + \frac{2}{\sum_i m_i} \left\{ -\frac{A^\phi}{1+b\sqrt{IS}} IS^{3/2} + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\ \left. + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} (\Phi_{cc'}^\phi + \sum_{a=1}^{N_a} m_a \psi_{cc'a}) + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} (\Phi_{aa'}^\phi + \sum_{c=1}^{N_c} m_c \psi_{aa'c}) \right. \\ \left. + \sum_{n=1}^{N_n} \sum_{c=1}^{N_c} m_n m_c \lambda_{nc} + \sum_{n=1}^{N_n} \sum_{a=1}^{N_a} m_n m_a \lambda_{na} + \sum_{n=1}^{N_n} \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_n m_c m_a \xi_{nca} \right\}, \quad (28)$$

$$\ln \gamma_M = z_M^2 F + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{Ma}) + \sum_{c=1}^{N_c} m_c (2\Phi_{Mc} + \sum_{a=1}^{N_a} m_a \psi_{Mca}) + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \psi_{aa'M} \\ + |z_M| \left\{ \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_n (2\lambda_{nM}) + \sum_{n=1}^{N_n} \sum_{a=1}^{N_a} m_n m_a \xi_{nMa} \right\}, \quad (29)$$

$$\ln \gamma_X = z_X^2 F + \sum_{c=1}^{N_c} m_c (2B_{cX} + ZC_{cX}) + \sum_{a=1}^{N_a} m_a (2\Phi_{aX} + \sum_{c=1}^{N_c} m_c \psi_{caX}) + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \psi_{cc'X} \\ + |z_X| \left\{ \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_n (2\lambda_{nX}) + \sum_{n=1}^{N_n} \sum_{c=1}^{N_c} m_n m_c \xi_{ncX} \right\}, \quad (30)$$

where Z is the total molality of charges in the system, and z denotes the charge of an individual species; F terms includes two parts. The first part is the extended Debye-Huckel terms representing long-term interactions, and the second part are the terms with derivatives of virial coefficients in respect to ionic strength:

$$F = -A^\phi \left\{ \frac{\sqrt{IS}}{1+b\sqrt{IS}} + \frac{2}{b} \ln(1+b\sqrt{IS}) \right\} \\ + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B_{ca}' + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \Phi_{cc'}' + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \Phi_{aa'}', \quad (31)$$

where b value is arbitrarily chosen as 1.2 (kg/mol)^{0.5} for all electrolytes; A^ϕ is the Debye-Huckel limiting law slope for the osmotic coefficient and can be calculated as follows:

$$A^\phi = \frac{\ln 10}{3} A = \frac{1}{3} \left[\frac{2\pi N_{av} \rho_w}{1000} \right]^{1/2} \left[\frac{e^2}{DkT} \right]^{3/2}. \quad (32)$$

In Equations (28 - 30), B , Φ , and λ terms are components of the second virial coefficients in Equation 27 which stand for binary interactions. Among them, B term is for binary interactions of unlikely charged ions; Φ term stands for likely charged electrolytes binary interactions; λ (in Equations 28 - 30) represents the binary interaction between neutral species and ions. These terms are as a function of IS theoretically, but for simplicity λ is set to be constant which is of little impacts. B terms are in the formula below with IS dependence:

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_{MX} \sqrt{IS}) + \beta_{MX}^{(2)} g(12\sqrt{IS}), \quad (33)$$

$$B'_{MX} = \frac{1}{IS} [\beta_{MX}^{(1)} g'(\alpha_{MX} \sqrt{IS}) + \beta_{MX}^{(2)} g'(12\sqrt{IS})], \quad (34)$$

$$B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_{MX} \sqrt{IS}) + \beta_{MX}^{(2)} \exp(-12\sqrt{IS}), \quad (35)$$

where the function $g(x)$ equals $2[1 - (1+x)e^{-x}]/x^2$ which is the IS dependent function; α_{MX} equals to 2.0 for 1-1, 1-2, or 2-1 electrolytes interactions, and equals to 1.4 for 2-2 or higher valence pairs. When there are 2-2 electrolytes in the solution, possible significant deviations due to ion pair associations especially in relatively low IS (< 0.1 m) should be considered. $\beta^{(2)}$ term is thus included for 2-2 electrolytes to account for such ion pair association interactions with $\beta^{(2)} = -K_{assoc} / 2$. The discussion about ion pairs will be included in section 2.3 in more details.

In the B term, only $\beta^{(0)}$ is not incorporated with IS dependence, while the impacts expressed in $\beta^{(1)}$ and $\beta^{(2)}$ are both controlled by IS through function $g(\alpha\sqrt{IS})$.

In Figure 5 is plotted the values of $g(\alpha\sqrt{IS})$ in terms of IS . The $g(\alpha\sqrt{IS})$ values for both $\beta^{(1)}$ and $\beta^{(2)}$ will decrease with IS but with different rates, indicating that the impacts expressed by them to the activity coefficients will decrease with IS . For example, about 75% of the individual impact of $\beta^{(1)}$ ($\alpha = 1.4$) and only 12% of $\beta^{(2)}$ ($\alpha = 1.4$) for 2-2 binary ion interactions will be included in B term when IS is larger than 0.1 m.

Figure 5. Values of $g(\alpha(IS)^{1/2})$ changing with IS

The Φ term contains two contributions and can be represented as follows:

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}, \quad (36)$$

$$\Phi'_{ij} = {}^E\theta'_{ij}, \quad (37)$$

$$\Phi_{ij}^{\phi} = \theta_{ij} + {}^E\theta_{ij} + IS {}^E\theta'_{ij}, \quad (38)$$

where θ_{ij} is IS independent, and ion specific contribution; $^E\theta_{ij}$ is theoretically derived from the higher order ($> 1/2$) part in terms of IS in DH equations which is negligible in diluted solutions but significant in concentrated solutions. It has charge specific terms but not ion specific.

C , ψ , ξ and ζ terms are components of the third virial coefficients in Equation 27 which stand for ternary interactions. Among them, the C term is for the interactions between opposite charged ions in single electrolyte solutions; ψ represents the ternary ion interactions with mixed electrolytes; while ξ and ζ stand for interactions among one neutral species, one cation and one anion. ψ , ξ and ζ are usually set as constants, while C term is assumed to be independent of IS and can be expressed as follows:

$$C_{MX} = \frac{C_{MX}^{\phi}}{2\sqrt{|z_M z_X|}}. \quad (39)$$

In B and C terms, $\beta^{(0)}$, $\beta^{(2)}$, and C^{ϕ} are suggested to be only as a function of both temperature and pressure, while $\beta^{(1)}$ is only as a function of temperature. Empirically, the temperature and pressure dependence of these virial coefficients are described by 12 or more parameters with T in K and P in atm:

$$\begin{aligned} PZ(T, P) = z_1 + \frac{z_2}{T} + z_3 T + z_4 \ln T + \left(z_5 + \frac{z_6}{T} + z_7 T + z_8 \ln T \right) P \\ + \left(z_9 + \frac{z_{10}}{T} + z_{11} T + z_{12} \ln T \right) P^2 \end{aligned} \quad (40)$$

Temperature and pressure dependences are also incorporated in extended DH part through dielectric constants (D) as a function of both temperature and pressure. It means

in Pitzer theory, both the long range interactions and the short range ion specific interactions are temperature and pressure dependent. Thus, theoretically the activity coefficient of a certain ion can be predicted using the Pitzer theory over wide ranges of temperature and pressures, as long as the solution compositions are known. Previously, Pitzer theory has been widely applied to solutions especially with high *IS* (Harvie et al. 1984; Pitzer et al. 1984; He and Morse 1993; Kaasa 1998; Christov and Moller 2004). For example, Pitzer et al. (1984) have used measured osmotic and activity coefficients, the enthalpy, and the heat capacity to model the ion-specific interaction coefficients for Na and Cl in the ranges of temperature from 0 to 300 °C, pressure from saturation pressure to 1 kbar, and NaCl concentration from 0 to 6.0 m (Pitzer et al. 1984); He and Morese (1993) predicted the solubility of minerals in Na-K-H-Ca-Mg-Cl-OH-SO₄-H₂O solutions at temperature from 0 to 200 °C and pressure from 1 to 1000 bar (14.7 to 14,500 psi), based on Pitzer theory and the virial coefficients from other literature (He and Morse 1993); Christov and Moller (2004) improved the Ca-Cl interaction coefficients using the solubility data and then apply these virial coefficients to predict the solubility of calcium chloride minerals (Christov and Moller 2004).

In this study, the Pitzer theory is to be applied to predict the activity coefficients of various aqueous species under HTHP conditions. However, the parameters for specific ion interactions have only been fitted for major ions, and are usually unknown for ions in low concentrations (Langmuir et al. 1997). Moreover, the Pitzer theory uses semi-empirical equations (e.g Equation 40) to represent the temperature and pressure dependence of virial coefficients without theoretical derivations (Pitzer et al. 1984; Voigt 2011). Thus the values of virial coefficients cannot be extrapolated out of the ranges of

temperature and pressure within which they are fitted. Most virial coefficients are fitted within a relatively narrow temperature range, and the pressure dependence is usually not considered. Such shortages will limit the application of the Pitzer theory to realistic conditions similar to that in the deepwater oil and gas production process, where multiple ion interactions, high temperature and high pressure conditions should all be taken into consideration.

The Pitzer theory is a powerful approach to derive virial coefficients based on experimental data with tens of adjusted parameters. However, on one side, the fitted results are only one of the possible mathematically right solution sets. It means the fitted virial coefficients may not have exact theoretical meanings. On the other side, a set of mathematically right solutions to the model will also be derived even if inaccurate stability constants, inaccurate solubility data, or other inaccurate virial coefficients are used. In order to eliminate such possible inaccuracies, it is needed to fit the ion interactions of interest from simple systems with less uncertain virial coefficients based on reliable data source over wide ranges of temperature, pressure and ionic strength. Virial coefficients fitted through this way can be more trusted and applied to other complex systems over corresponding ranges of temperatures and pressures. The fitted virial coefficient sets can be used to predict mineral solubility in complex solutions at HTHP conditions with mixed electrolytes.

2.2.8. *Simplified estimation equation*

In some realistic applications, some simplified equations can be used for simplicity. For example, (1) DH equation can be used when IS is very low (< 0.1 m); (2) the Meissner model is a good estimation especially for simple solution at very high IS (up

to 10 m) with only one parameter q ; (3) simplified Pitzer equation or kind of SIT model can also be applied in relatively lower IS by setting likely charged binary interaction coefficient θ , and ternary coefficient ψ , ξ and ζ to be zero.

Another estimation method can be applied based on the DH equation and Pitzer theory. According to the DH model, the ion activity coefficient is only a function of temperature, pressure, IS , and ion charges (i.e. z^2). Previously, NaCl solutions have been thoroughly analyzed over wide ranges of temperature, pressure and IS (Pitzer et al. 1984). Thus based on the knowledge of NaCl as the reference electrolytes, the activity coefficient of an ion with z charge can be estimated with the function below (Cohen 1989):

$$\log \gamma_{|z|} = z^2 \log \gamma_{\pm NaCl}, \quad (41)$$

where the mean activity coefficient $\gamma_{\pm}$ follows the equation below for electrolyte $M_{v+}X_{v-}$:

$$\gamma_{\pm} = (\gamma_M^{v+} \gamma_X^{v-})^{1/(v_+ + v_-)}, \quad (42)$$

$$z_+ v_+ + z_- v_- = 0. \quad (43)$$

However, this estimation can only work at low IS range where DH can fit well with experimental data. In more concentrated solutions with more than one electrolyte, the ionic strength will also be sensitive to the solution composition. For example, Figure 6 shows the mean activity coefficient of HCl under different IS in HCl-H₂O system ($\gamma_{HCl}^{\pm 0}$), in KCl-H₂O system ($\gamma_{HCl}^{\pm tr}$), and mean activity coefficient of KCl in KCl-H₂O system ($\gamma_{KCl}^{\pm 0}$) with totally different values especially at high IS , though from the

simplified estimation equation above, these three activity coefficients should be the same under the same IS . To deal with such composition dependence, the simplified Pitzer theory can be applied here (Harvie et al. 1984):

$$\begin{aligned}\ln \gamma_{HCl}^{\pm} &= \ln \gamma_{DH}(IS) + B_{HCl}(IS)m_H + B_{KCl}(IS)m_K + B_{HCl}(IS)m_{Cl}, \\ \ln \gamma_{KCl}^{\pm} &= \ln \gamma_{DH}(IS) + B_{HCl}(IS)m_H + B_{KCl}(IS)m_K + B_{KCl}(IS)m_{Cl},\end{aligned}\quad (44)$$

where the γ_{DH} term stands for the DH part. B terms are the IS dependent second virial coefficients which can be analyzed in the single electrolyte solutions HCl-H₂O or KCl-H₂O system. Assuming that in the single electrolyte solutions (denoted with 0) when the molality of HCl or KCl is m_0 , the ionic strength will be IS_0 (for single 1-1 electrolyte solution, $IS_0 = m_0$). Thus we have

$$\begin{aligned}\ln \gamma_{HCl}^{\pm 0} &= \ln \gamma_{DH}(IS_0) + B_{HCl}(IS_0)m_H + B_{KCl}(IS_0)m_K + B_{HCl}(IS_0)m_{Cl} \\ &\approx \ln \gamma_{DH}(IS_0) + B_{HCl}(IS_0)m_0 + B_{HCl}(IS_0)m_0 \\ &= \ln \gamma_{DH}(IS_0) + 2B_{HCl}(IS_0)m_0 \\ \ln \gamma_{KCl}^{\pm 0} &= \ln \gamma_{DH}(IS_0) + B_{HCl}(IS_0)m_H + B_{KCl}(IS_0)m_K + B_{KCl}(IS_0)m_{Cl} \\ &\approx \ln \gamma_{DH}(IS_0) + B_{KCl}(IS_0)m_0 + B_{KCl}(IS_0)m_0 \\ &= \ln \gamma_{DH}(IS_0) + 2B_{KCl}(IS_0)m_0 \\ \ln \gamma_{HCl \text{ in } KCl}^{\pm tr} &= \ln \gamma_{DH}(IS_0) + B_{HCl}(IS_0)m_H + B_{KCl}(IS_0)m_K + B_{HCl}(IS_0)m_{Cl} \\ &\approx \ln \gamma_{DH}(IS_0) + B_{KCl}(IS_0)m_0 + B_{HCl}(IS_0)m_0 \\ &= \frac{1}{2}(\ln \gamma_{HCl}^{\pm 0} + \ln \gamma_{KCl}^{\pm 0})\end{aligned}\quad (45)$$

Figure 6 shows that this estimation in Equation 45 (dashed line) is in good agreement with other literature (Harvie et al. 1984). This estimation provides the way to predict the activity coefficient of trace amount electrolyte in solutions dominated by other electrolytes sharing the same cation or anion based on the available activity coefficients of single electrolyte solutions.

Figure 6. Mean activity coefficients of HCl and KCl in single electrolyte solutions, and of trace HCl in KCl dominated solutions (Harvie et al. 1984).

2.3. Equilibrium constants

In thermodynamic models, equilibrium constants are one of the most important data needed. Reliable equilibrium constants are critical to the accuracies of virial coefficients derived through Pitzer theory. Many methods can be applied to get accurate equilibrium constants based on different experimental data. If mineral solubility is measured at equilibrium ($SI = 0$), based on Equation 6, the equilibrium constants can be

derived if accurate activity coefficients of each species can be estimated. For example, Langmuir and Melchior (1985) derived the stability constant for Ca, Sr, Ba and Ra sulfates according to solubility data and Pitzer theory (Langmuir and Melchior 1985). The derivation is based on the assumption that the temperature derivatives up to 100 °C for virial coefficients and the pressure dependence of ion activities are negligible. Thus, though it is a good estimation when temperature and pressure ranges are not high, the derived stability constants can neither be applied up to much higher temperature and pressure, nor be used to fit for accurate virial coefficients similar to this study.

As another approach, the equilibrium constants are related to the Gibbs free energy change, enthalpy change, and entropy change of the reaction which can be written as:

$$\ln K_{T,P}^{\phi} = \frac{-\Delta G_{T,P}^{\phi}}{RT} = -\frac{\Delta H_{T,P}^{\phi} - T\Delta S_{T,P}^{\phi}}{RT} \quad (46)$$

The thermodynamic properties can be measured by other solubility independent methods including calorimetric measurement, vapor pressure measurement and so on. These thermodynamic properties are as a function of both temperature and pressure. Generally, the equilibrium constants can be expressed as the combination of the temperature dependent part (as a function of temperature) and the pressure dependent part (as a function of pressure and temperature) as follows:

$$\log_{10} K = \log_{10} K_T(T) + \log_{10} K_P(P,T) \quad (47)$$

For a certain pressure, the temperature dependence of equilibrium constants can be related to the heat capacity change for the reaction:

$$\begin{aligned}\Delta H_{T,P}^{\phi} &= \Delta H_{T_0,P}^{\phi} + \int_{T_0}^T \Delta C_p dT \\ \Delta S_{T,P}^{\phi} &= \Delta S_{T_0,P}^{\phi} + \int_{T_0}^T \frac{\Delta C_p}{T} dT\end{aligned}\quad (48)$$

where ΔC_p is the heat capacity change for the reaction which is also as a function of temperature. The temperature dependence of solids heat capacity can be given for the Maier-Kelley heat capacity function (Kelley and King 1937):

$$C_p = A + BT + \frac{C}{T^2} \quad (49)$$

While for aqueous species, the heat capacities can be estimated by the equation below (Helgeson et al. 1981):

$$C_p = C_{li} + \frac{C_{2i}T}{T - \theta_i} - w_i T x \quad (50)$$

where C_{li} , C_{2i} , θ_i , and w_i are all species specific empirical constants; x is the derivative of dielectric constant of water (D) in terms of temperature. Based on these estimations, equilibrium constants are achieved from 0 to 350 °C and listed in SOLMINEQ. 88 (Kharaka et al. 1989). In the estimation process, the main errors result from the estimation of C_p with the simplified function forms in Equations 49 and 50.

The pressure dependence of equilibrium constants can be related to partial molar volume change ($\Delta \bar{V}_r^{\phi}$) of the reaction as follows:

$$\left(\frac{\partial G_r^{\phi}}{\partial P} \right)_T = -RT \left(\frac{\partial \ln K^{\phi}}{\partial P} \right)_T = \Delta \bar{V}_r^{\phi} \quad (51)$$

However, $\Delta\bar{V}_r^\phi$ is mainly composed of partial molar volume of solvent (water), aqueous species, and mineral. Among them, the partial molar volumes of minerals are assumed to be ignorable, partial molar volume of water can be obtained from literature, but partial molar volumes of most aqueous species are usually unavailable (Helgeson and Kirkham 1974). As an estimation, Helgeson et al. (1981) proposed the equation below to calculate the partial molar volume of aqueous species (Helgeson et al. 1981):

$$\bar{V}_i = a_{1i} + a_{2i}P + a_{3i}T + \frac{a_{4i}PT}{T - \theta_i} - w_iQ \quad (52)$$

$$Q = \frac{1}{D} \left(\frac{\partial \ln D}{\partial P} \right)_T \quad (53)$$

where Q is the electrostatic Born function defined by the function above.

Based on these equations, $\Delta\bar{V}_r^\phi$ can be calculated for mineral dissolution reactions and integrated back into Equation 51 to represent the pressure dependence of the equilibrium constants. However, there will be errors in the estimation of $\bar{V}_i$ for each species and the errors will be propagated to the final pressure dependent function. As a more direct way, Atkinson and Mecik (1996) directly fit the $\Delta\bar{V}_r^\phi$ through solution thermodynamics of the ion and density of the solid which are not just from the solubility. In this way, the error propagation from different sources and the systematic error of using solubility data can be minimized. In detail, it is assumed that, in infinite dilute solution, the first order differentiation of partial molar volume $\Delta\bar{V}_r^\phi$ in respect of pressure (called compressibility, $\Delta\bar{\kappa}_r^\phi$), is independent of pressure (Atkinson and Mecik 1997; Kaasa

1998). Thus the pressure dependent part of K_{sp} can be described by the pressure dependence of $\Delta \bar{V}_r^\phi$ and $\Delta \bar{\kappa}_r^\phi$ at infinite dilution solutions:

$$\ln K_{T,P} = \ln K_{T,P_0} - \frac{\Delta \bar{V}_{r,T,P_0}^\phi}{RT} (P - P_0) + \frac{\Delta \bar{\kappa}_r^\phi}{2RT} (P - P_0)^2 \quad (54)$$

where for both $\Delta \bar{V}_{r,T,P_0}^\phi$ and $\Delta \bar{\kappa}_r^\phi$ are only a function of temperature and can be formulated by the following empirical equation:

$$f(TC) = q_0 + q_1 TC + q_2 TC^2 + q_3 TC^3 + q_4 TC^4 \quad (55)$$

where $TC (^{\circ}\text{C}) = TK (\text{K}) - 273.15$. The theoretical derivation of $K_{T,P}$ with $\Delta \bar{V}_r^\phi$ and $\Delta \bar{\kappa}_r^\phi$ can help clarify the pressure dependent part of stability constants.

2.4. Calcium sulfate system

Calcium sulfate is a precious resource and is widely applied to different disciplines including plaster ingredients, fertilizer and soil conditioner, sculpture material, tofu coagulant, building material, and so on. For example, in agriculture, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can help improve soil structure to get rid of compactions; it can decrease the soil pH and thus decrease the evaporation of fertilizer nitrogen; the calcium in gypsum can assist the nutrients absorption process by roots and also protect plants from absorbing an excess amount of Na (offset the soil sodium adsorption ratio), which is toxic (Shainberg et al. 1989; Akhavan-Kharazian et al. 1991). Moreover, calcium sulfate is one of the most common scale minerals in oil and gas production process and usually occurs as evaporate minerals precipitated from evaporating water (Rolnick 1954; Kan and Tomson 2012; Lu et al. 2012). Thus the researches on the properties of calcium sulfate

are very important for the applications of calcium sulfate and the solutions for calcium sulfate scaling problems.

2.4.1. Phase stability

Under different conditions, calcium sulfate will be hydrated to different extents and thus have different phases, among which the three most common phases are anhydrite (CaSO_4), hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). These three phases will transit between each other depending on the supersaturation state, temperature, pressure, and water activity (Rolnick 1954; Lu et al. 2012). A lot of researchers have focused on the transition temperature between different phases. But in experiments it is hard to determine the transition temperature accurately due to the long equilibrium time. In Figure 7 is plotted the solubility of the three phases at 1 atm from 0 to 220 °C in pure water which is summarized by Partridge and White according to many researchers (Partridge and White 1929). The less soluble phase should always be the more stable one indicating that hemihydrate is not a stable phase within this temperature range. In the $\text{Ca-SO}_4\text{-H}_2\text{O}$ system, gypsum and anhydrite are believed to be the only two stable phases that can occur as geologic deposits, while hemihydrate will occur as the transition phase between these two (Partridge and White 1929; Rolnick 1954). At 1 atm in pure water, the transition temperature analyzed previously varies between 38 to 66 °C, either from experiments or from thermodynamic derivation (Van't Hoff et al. 1903; Hill 1937; Posnjak 1938; Dickson et al. 1963; Hardie 1967; Blount and Dickson 1973). It is well accepted that the transition temperature between gypsum and anhydrite at 1 atm in pure water is between 40 to 42 °C with confidence from experimental data. It is also believed that under 40 °C gypsum will be the dominant phase and over 100 °C anhydrite

will be dominant and stable (Partridge and White 1929; Hill 1937; Posnjak 1938; Rolnick 1954).

Figure 7. Equilibrium diagram of the calcium sulfate-water system at temperatures from 0-220 °C (Partridge and White 1929)

The pressure dependence of transition temperature has also been analyzed, however, due to not enough accurate data, results from different sources varied a lot. For example, Marsal (1952) calculated the pressure effect is 83 bars/°C (1204 psi/°C) based on thermodynamic derivation and experimental results; Mac Donald (1953) proposed that the transition temperature will increase by 1 °C if the pressure increases by 85.4 bars

(1239 psi) (MacDonald 1953); Blount and Dickson (1973) claimed that 1 °C increase is about 78 bars (1131 psi) increase correspondingly (Blount and Dickson 1973); while Zen (1965) derived that the pressure dependence of transition temperature is about 71 bars/°C (1030 psi/°C) (Zen 1965).

Since water molecules are also incorporated in the mineral lattice of calcium sulfates to different extent, water activity changes will also impact the stabilities of different phases. Water activity will be impacted by temperature and pressure, and more importantly, it will also be impacted by the solutes and cosolvents. For example, Lu et al. (2012) found that a high concentration of salts and MEG (monoethylene glycol, kind of hydrate inhibitors) will promote the transition of gypsum to anhydrite as is shown in Figure 8 (Lu et al. 2012).

Figure 8. Phase transition temperature between anhydrite and gypsum under different NaCl and MEG concentration (Lu et al. 2012)

However, from the view of kinetics, the transition process might be too long to tell if there will be other unstable phases present in the solution. In this study, gypsum solubility under 40 °C and anhydrite solubility over 130 °C are selected to minimize the phase interference.

2.4.2. Solubility data

Solubility of gypsum under different temperatures and pressures has been measured by many researchers in the past years and summarized in Figure 9 (Hulett and Allen 1902; Posnjak 1938; Marshall and Slusher 1966; Blount and Dickson 1973). Most measurements are only done at 1 atm under various conditions. Blount and Dickson (1973) measured gypsum solubility at pressure up to 14,500 psi, but no measurement is done below 40 °C under which gypsum is trusted as stable phase. Thus a systematic

measurement of gypsum solubility is needed to cover the high pressure range at reliable temperature ranges with less phase interference under different ionic strength.

Figure 9. Solubility of gypsum and anhydrite from literature (Blount and Dickson 1973)

Solubility of anhydrite has been measured systematically by Dickson et al. (1963) in pure water from 100 to 250 °C and from 14.7 to 14,500 psi, and by Blount and Dickson (1969) in 0.15 to 6.2 m NaCl solutions from 100 to 450 °C and 14.7 to 14,500 psi (Dickson et al. 1963; Blount and Dickson 1969). They designed a novel hydrothermal

solution equipment (shown in Figure 10) to measure the solubility of anhydrite at HTHP in the presence of NaCl. These solids and solutions approach equilibrium in a deformable Teflon sample cell under different temperature and pressure. The constant pressure and temperature are controlled by the solution outside the sample cell which is pumped in and out at the same rate with constant pressure and temperature. The sample cell will change its shape to make sure the pressure in the cell equals to the outside pressure. They ascertained the equilibrium if the concentration changes very little.

Figure 10. Hydrothermal solution pressure vessel (Dickson et al. 1963).

2.4.3. Ca^{2+} - SO_4^{2-} ion pairs

For 2-2 or higher valence type of electrolytes, a distinct species of inner-shell ion pairs has been detected by spectroscopic or ultrasonic data and such ion pairs show big impacts to the system especially from very low ionic strength (about 0.0001 M) to about 0.1 M (Pitzer and Mayorga 1974). Such an ion pair interaction is weaker than that between precipitated crystals, but is also much stronger than that between free aqueous ions. More importantly, at higher temperature, the ion pair interaction will become much stronger due to the decrease of dielectric constant of water, and thus will lead to smaller activity coefficients and relatively larger solubility (He 1992; Morel and Hering 1993).

In general, there are two different ways to deal with such 2-2 type ion pairs in the solution. The first way is to treat the ion pairs as a distinct species and the stability constants are expressed explicitly (Harvie et al. 1984; Monnin 1999). A charge specific equation for the stability constants of ion pairs with different charges theoretically derived from statistical thermodynamics is shown below (Margerum et al. 1978; Morel and Hering 1993; Israelachvili 2011):

$$K_{assoc} = \frac{4000\pi N_{av} a^3}{3} \exp\left[\frac{-z_M z_L e^2}{4\pi\epsilon_0 DkTa}\right] \exp\left[\frac{z_M z_L e^2 \kappa}{4\pi\epsilon_0 DkT(1+\kappa a)}\right] \quad (56)$$

$$\kappa^2 = \frac{2000e^2 N_{av} IS}{\epsilon_0 DkT} \quad (57)$$

where a is the distance of closest approach of the ions (usually set as 5×10^{-10} m); N_{av} is Avogadro constant; κ is the Debye-Huckel ion atmosphere parameter; e is elementary charge; k stands for Boltzmann constant; ϵ_0 is the dielectric constant of vacuum; D is the dielectric constant of solvent (water). This equation is an approximation of charge

specific ion pair association constants, but is not accurate enough for ion specific ion interactions. For example, the association constants for $\text{CaSO}_4^{(0)}$ ion pairs at 25 °C 1 atm is $10^{2.36}$ based on the database of software Visual MINTEQ. However, using the model above, the association constant for 2-2 ion pairs is 95 which is smaller.

In such an explicit treatment, the portion of ions forming ion pairs is not treated as free ions. Thus the effective ionic strength (IS_e) is used in which only free ions are included instead of total ionic strength (IS_t). Or in other words, the ion pairs are treated similarly with the precipitation solids which are separate from aqueous system.

As an example, in the solution in equilibrium with solid gypsum at 25 °C and 1 atm, the calcium and sulfate ions are composed of two parts, which are free ions and the associated ions. Assume the K_{sp} of gypsum is $10^{-4.61}$ and K_{assoc} of $\text{CaSO}_4^{(0)}$ ion pairs is $10^{2.36}$ (229) which are the same with those used in software Visual MINTEQ. Water activity is assumed to be 1 since the IS is low, and the ion pair activity is also assumed to be 1 just like solids. The Davis equation is applied to calculate the activity coefficients of calcium and sulfate ions using IS_e rather than IS_t . Thus we have the equations below for this system:

$$\begin{aligned}
 IS_e &= \frac{1}{2} \sum_i (m_{i,free} z_i^2) \\
 \log \gamma_i &= -0.51 * z_i^2 \left(\frac{IS_e^{1/2}}{1 + IS_e^{1/2}} - 0.3 * IS_e \right) \\
 a_{\text{CaSO}_4^{(0)}} &= \gamma_{\text{CaSO}_4^{(0)}} m_{\text{CaSO}_4^{(0)}} \approx m_{\text{CaSO}_4^{(0)}} = K_{assoc} (\gamma_{\text{Ca}} m_{\text{Ca},free}) (\gamma_{\text{SO}_4} m_{\text{SO}_4,free}) \\
 K_{sp, \text{gyp}} &= (\gamma_{\text{Ca}} m_{\text{Ca},free}) (\gamma_{\text{SO}_4} m_{\text{SO}_4,free}) (a_{\text{H}_2\text{O}})^2 \\
 Tot(m_i) &= m_{i,free} + m_{\text{CaSO}_4^{(0)}}
 \end{aligned} \tag{58}$$

where i represents calcium or sulfate ion. According to the Davis equation, the activity coefficient for calcium and sulfate ion is about 0.479. The calculated total calcium concentration $\text{Tot}(\text{Ca}) = \text{Tot}(\text{SO}_4) = 15.96 \text{ mm}$, which is very close to the value 15.95 mm calculated from using the software Visual MINTEQ. The molality of free calcium ion is 10.34 mm taking account of 64.8% of total calcium concentration, and the rest 35.2% is in the form of $\text{CaSO}_4^{(0)}$. This result also indicates that $\text{CaSO}_4^{(0)}$ ion pair cannot be ignored under such conditions.

The second way to deal with an ion pair is to implicitly treat them as kind of ion interactions, but not explicit ion pairs. In Pitzer theory, Pitzer and Mayorga (1974) found the ambiguity of quantitatively setting a standard (e.g. the distance between the two ions) to differentiate ion pairs, other weak ion interactions in Pitzer theory (i.e. binary interactions), and strong forces in crystals. Thus they incorporated the ion pairs association implicitly into the ion specific $\beta^{(2)}$ term with $\beta^{(2)} = -K_{\text{assoc}} / 2$ (Pitzer and Mayorga 1974). The IS dependence of the stability constants is controlled by the multiplier $g(12\sqrt{IS})$ of $\beta^{(2)}$ in Pitzer equations (e.g. Equation 33). Using such an implicit method, the ion pairs are treated as free ions; however, the ion pair will lead to the decrease of their activity coefficient between which they have stronger interactions than typical binary ion interactions. As an example of using the implicit method to deal with ion pair association, the software ScaleSoftPitzer (SSP) is used to calculate the equilibrium concentration of Ca in the pure gypsum solutions. SSP uses Pitzer theory to predict ion activity coefficients based on the virial coefficients from different sources. The activity coefficient for calcium ion is calculated as 0.348 which is smaller than that in the explicit method when considering the ion pair association as a kind of ion

interaction. However, the calculated equilibrium concentration of Ca^{2+} (i.e. $\text{Tot}(\text{Ca})$ corresponding to the explicit method) is 13.87 mM, which is smaller than that from the explicit method, though the same K_{sp} is used. The deviation might be due to the inaccurate virial coefficients used in SSP leading to underestimation of the ion interactions, and thus larger activity coefficients. $\beta_{\text{CaSO}_4}^{(2)}$ used in SSP at 1 atm and 25 °C is -54.24 which is much larger than $-K_{\text{assoc}}/2$ (-114.5) indicating an underestimation of ion pair interactions. Such deviation is also a motivation of this study to derive more accurate equations for virial coefficients between Ca^{2+} and SO_4^{2-} ions.

Although the relation of $\beta^{(2)} = -K_{\text{assoc}}/2$ is theoretically right, it is hard to evaluate the correlation between $\beta^{(2)}$ and K_{assoc} . First, it is because the K_{assoc} available usually cannot accurately cover wide ranges of temperature, pressure and IS . Second, large uncertainties of $\beta^{(2)}$ will exist when fitting Pitzer theory due to the reasons listed above. $\beta^{(2)}$ values can only be evaluated together with other virial coefficients which are fitted together with $\beta^{(2)}$. Third, considering the IS dependent multiplier of $\beta^{(2)}$ in Pitzer function, $g(12\sqrt{IS})$ will decrease with IS quickly, as shown in Figure 5. Thus at relatively higher IS (e.g. 0.1 m), only 10% of $\beta^{(2)}$ term (or ion pair interaction term) will contribute to the B term. There will be large deviations if data collected at high IS are used to fit $\beta^{(2)}$ values. On the other hand, if the IS is too low, the IS will be sensitive to the measured concentration of trace ions, which are also incorporated with large errors. Such errors in IS will finally result in inaccurate $\beta^{(2)}$ values. Thus it is useful to compare the stability constants from different sources and the derived virial coefficients from Pitzer theory.

2.5. Calcite system

Calcite is the most common scale type found in oil and gas production (Kan and Tomson 2012). In reality, it is in close relation with carbonic acid system and controlled by many processes, including CO₂ dissolution in water, dissociations of carbonic acid, dissolution and precipitation of calcite, as well as the formation of complex species in the system (Shi et al. 2013). In the past years, many researches have been done on solubility measurement of calcite at different conditions both in pure water and in NaCl solutions with/out separate vapor phase (Sharp 1964; Malinin and Kanukov 1971; Caciagli and Manning 2003; Duan and Li 2008). But, literature data for calcite solubility from different sources can differ substantially sometimes. Many models have also been developed able to predict calcite solubility including PHREEQC, PHRQPITZ, WATEQ4F and MINTEQ. However, these models incorporate different sources of equilibrium constants and activity coefficients models and cannot provide reliable temperature and pressure dependence over wide ranges. Duan and Li (2008) summarized some of the literature measurements and proposed a model of coupled phase and aqueous species equilibrium in the H₂O-CO₂-NaCl-CaCO₃ system from 0 to 250 °C, 14.7 to 14,500 psi up to halite saturation (Duan and Li 2008). Nevertheless, it cannot deal with a calcite system with mixed electrolytes due to unavailability of experimental data and virial coefficients, a situation which usually occurs in realistic conditions. Shi et al. (2013) reexamined the equilibrium constants involved in calcite system from different sources first at low ionic strength under which the activity coefficients can be calculated with confidence. Then he confirmed the effectiveness of a set of virial coefficients from different sources under elevated *IS*. But when he applied these confirmed equilibrium

constants and activity coefficients into a calcite system with mixed electrolytes, deviations are observed and they claimed that such deviations result from inaccurate $\text{Ca}^{2+}\text{-SO}_4^{2-}$ interactions. As one possible method, they adjusted the $\beta_{\text{CaSO}_4}^{(2)}$ value as a function of temperature and pressure to eliminate the deviations, and finally extended the prediction ranges to temperature up to 250 °C and pressure to 21,000 psi in the presence of mixed electrolytes (Shi et al. 2013). However, such adjustment is not theoretically correct since they didn't consider possible errors in virial coefficients for $\text{Ca}^{2+}\text{-SO}_4^{2-}$. In addition, in such complex calcite system with mixed electrolytes, virial coefficients adjustment for Ca^{2+} and SO_4^{2-} interactions might possibly be impacted by other ion interactions. Thus a thorough re-examination is needed to derive accurate virial coefficients for Ca^{2+} and SO_4^{2-} interactions in simple systems with less interference. In this case, solubility measurement of gypsum or anhydrite in simple solutions can also contribute to the implementation of calcite solubility prediction model proposed by Shi et al. (2013).

Chapter 3. Solubility measurement at high temperature and high pressure

3.1. Apparatus and chemicals

Shi et al. (2012, 2013) have designed a novel apparatus for solubility measurement of minerals at high temperature (up to 250 °C) and pressure (up to 24000 psi), and measured the solubility of barite and calcite (Shi et al. 2012; Shi et al. 2013). As is shown in Figure 11 and Figure 12, the solids (gypsum, 99.998% trace metals basis, Sigma-Aldrich; anhydrite, 99%, Acros Organics) were packed in a stainless steel column (SS316, High Pressure Equipment Company, packed porosity is 50%; for gypsum, the total volume is 9 mL, and for anhydrite, the total volume is 24 mL) with 0.2 µm filter at the end of it, and it is enclosed in the oven within which the temperature can be kept stable up to 300 °C. The feeding solution is at undersaturated state under operating conditions prepared with pure CaSO₄ solids and 0 to 4 m NaCl (> 99.0%, Sigma-Aldrich, ACS reagent). The feeding solution is pumped in under desired pressure by a high pressure syringe pump (ISCO Teledyne 65 HP) at constant pressure through tubings with 1/8 inch OD (outside diameter) made of Hastelloy C. EDTA solution (0.2 m, pH = 10) is also pumped in by another syringe pump (ISCO Teledyne 65 HP) at the end of column to prevent the precipitation of minerals when temperature and pressure changes (especially when pressure drops quickly after the needle valve). The EDTA solution is prepared with EDTA disodium salt (> 99%, Sigma-Aldrich, ACS reagent) and then adjust pH to about 10 with sodium hydroxide (> 99%, pellets, EMD chemicals) and potassium hydroxide (KOH > 86.9%, Ca < 0.005%, SO₄ < 0.003%, pellets, Fisher Scientific). The high pressure is kept by the high pressure syringe pump and a needle valve (High Pressure

Equipment Company). In Figure 11, the red parts are under high pressure in the experiments, and the parts in the oven will be kept at constant temperature. The solution will be cooled down to room temperature outside the oven and pressure will drop to 1 atm pressure after the needle valve. The solution is collected for ion concentration measurement using ICP (induced coupled plasma) and all the results in this study are reported in molality units. The mixing ratio of EDTA and equilibrated solution can be calculated based on the potassium concentration in the collected sample and that in the EDTA solution:

$$\frac{V_{EDTA}}{V_{sample}} = \frac{m_{K,sample}}{m_{K,EDTA}} \quad (59)$$

where V_{EDTA} is the volume of original EDTA solution mixed into the collected sample (V_{sample}); m_K is the concentration of K in the collected sample or in the original EDTA solution. Using potassium as an internal standard can help handle the fluctuation of the mixing ratio due to pressure and flow rate vibration especially at high pressure.

Figure 11. Sketch of solubility measurement apparatus

Figure 12. Apparatus used for solubility measurement at HTHP

Compared with the apparatus designed by Dickson et al. (1963), this novel apparatus has several advantages. Firstly, the column experiment can substantially increase the reaction surface area and thus decrease the equilibrium time; secondly, it's easier to control the pressure with high pressure syringe pump and control temperature with oven in a more accurate way; thirdly, in the continuous plug flow system, the sampling process has no impacts on the equilibrium, however, in the previous apparatus, new solution is needed to be pumped into the bulk solution which might bring in fluctuation.

3.2. Solubility measurement experiments

Solubility measurement of gypsum is done at temperatures of 0, 25, and 40 °C, at pressures of 15, 600, 7000, 16000, and 20000 psi, with 0, 1, 2, 4 mol NaCl/kg H₂O. It is

found that if retention time (RT) at 1 atm and 25 °C is more than 30 minutes, the final concentration will not change as is shown in Figure 13. It indicates that the RT should be more than 30 minutes to make sure the samples collected are in equilibrium with the packed solids. At tested pressure, the flow rate is adjusted with the needle valve to about 0.06 mL/min with RT about 75 min ($4.5\text{ mL}/(0.06\text{ mL/min})$) in the column. The EDTA is pumped in at flow rate of 0.02 mL/min and the mixing ratio is calculated according to the potassium concentration. Total calcium and total sulfate are measured for some experiments showing the difference is within 5%. Thus it is assumed that Ca^{2+} concentration equals SO_4^{2-} concentration in the collected sample and only Ca^{2+} is measured in the experiments.

Figure 13. Effluent concentration of gypsum changing with retention time

Anhydrite solubility is measured at 3 different conditions identical to those measured by Blount and Dickson (1969), which are 150 °C and 19400 psi, 200 °C and 19000 psi, and 250 °C and 17900 psi, respectively, all in 1.9 mol NaCl/kg H₂O

background. At tested pressure, the flow rate is adjusted to about 0.2 mL/min with RT about 60 min ($12\text{mL}/(0.2\text{ mL/min})$) in the column. The EDTA is pumped in at flow rate of 0.04 mL/min and the mixing ratio is calculated according to the potassium concentration. Only Ca^{2+} is measured in the experiments to represent the concentration of Ca^{2+} and SO_4^{2-} .

3.3. Measured solubility data and analysis

Solubility of gypsum under relatively low temperature (0 to 40 °C), over a wide range of pressure (14.7 to 20,000 psi) in the presence of different concentration of NaCl (0 to 4.0 m) are measured and presented in Table 1 and Figure 14. The experiments are conducted to include temperature of 4 °C which is the deep sea water temperature that will occur in deep water oil and gas production. Marshall and Slusher's results at corresponding conditions are also plotted in Figure 14 (a) and (b) and match quite well with our measurements (Marshall and Slusher 1966). Within 0 to 40 °C, the impacts of temperature on the solubility measurement are not significant. For most cases especially at relatively high pressure, the solubility will decrease with temperature in this temperature range. While the pressure impacts are huge under the same temperature and NaCl concentration. When pressure increases from 14.7 psi to 20000 psi, the solubility of gypsum will increase substantially. For example, in 0 m NaCl under 0 °C, the solubility at 20000 psi (69.66 mmol/kg H_2O , 11981.89 mg/kg H_2O) will be 5 times larger than that at 14.7 psi (13.60 mmol/kg H_2O , 2339.72 mg/kg H_2O). Thus when pressure decreases suddenly, the SI will increase a lot. Assuming a solution is in equilibrium with solid gypsum at 20000 psi and 25 °C in the presence of 1 m NaCl, if the pressure drops to 15 psi, the SI will increase with about 0.55 units. Solubility is sensitive to NaCl

concentration when IS is low (i.e. lower than 1 m), but at relatively high IS , the solubility will change little with IS . For instance, as is shown in Figure 15, at 16000 psi and 0 °C, the solubility increases a lot from 49.45 mmol/kgH₂O in 0 m NaCl to 92.89 mmol/kg H₂O in 1 m NaCl, and then slightly increases to 95.85 mmol/kgH₂O in 2 m NaCl and decreases to 80.77 mmol/kgH₂O in 4 m NaCl.

Table 1. Solubility of gypsum under different conditions and the SI values calculated with the virial coefficients derived in this study

Sample ID	T (°C)	P (psi)	NaCl (mol/kg H ₂ O)	Gypsum (mmol/kg H ₂ O)	SI - fitted
1	0	15	0	13.603	-0.0906
2	0	600	0	14.247	-0.0851
3	0	7000	0	22.771	-0.0629
4	0	16000	0	49.453	-0.0374
5	0	20000	0	69.662	-0.024
6	25	15	0	16.624	-0.0518
7	25	600	0	16.964	-0.0564
8	25	7000	0	24.377	-0.0381
9	25	16000	0	45.428	0.0033
10	25	20000	0	58.135	-0.0149
11	40	15	0	17.453	-0.0121
12	40	600	0	16.493	-0.0574
13	40	7000	0	26.144	0.0324
14	40	16000	0	45.756	0.0716
15	40	20000	0	58.686	0.057
16	0	15	1	45.012	-0.0678
17	0	600	1	44.985	-0.0888
18	0	7000	1	60.336	-0.0906
19	0	16000	1	92.886	-0.0418

20	0	20000	1	109.067	-0.011
21	25	15	1	45.620	0.0262
22	25	600	1	49.120	0.0617
23	25	7000	1	62.957	0.0419
24	25	16000	1	89.909	0.0311
25	25	20000	1	102.323	0.0028
26	40	15	1	45.212	0.0635
27	40	600	1	46.178	0.0616
28	40	7000	1	61.678	0.0919
29	40	16000	1	87.568	0.0784
30	40	20000	1	98.898	0.0253
31	0	15	2	50.238	-0.2296
32	0	600	2	53.380	-0.1933
33	0	7000	2	73.807	-0.0771
34	0	16000	2	95.849	-0.0687
35	0	20000	2	110.153	-0.0309
36	25	15	2	54.980	0.0397
37	25	600	2	59.021	0.0783
38	25	7000	2	68.048	0.0035
39	25	16000	2	89.607	-0.0204
40	25	20000	2	104.917	0.0023
41	40	15	2	55.464	0.105
42	40	600	2	58.148	0.1253
43	40	7000	2	67.972	0.0665
44	40	16000	2	89.045	0.0315
45	40	20000	2	105.615	0.0448
46	0	15	4	55.308	-0.3005
47	0	600	4	55.678	-0.2901
48	0	7000	4	63.343	-0.1823

49	0	16000	4	80.766	-0.1245
50	0	20000	4	97.757	-0.0557
51	25	15	4	58.867	0.1186
52	25	600	4	58.416	0.0942
53	25	7000	4	66.945	0.0315
54	25	16000	4	86.858	0.0641
55	25	20000	4	93.489	0.0646
56	40	15	4	57.800	0.1523
57	40	600	4	58.108	0.1366
58	40	7000	4	70.515	0.1078
59	40	16000	4	83.430	0.0552
60	40	20000	4	88.855	0.0468

(a) NaCl = 0m

(b) NaCl = 1m

(c) NaCl = 2m

Figure 14. Solubility of gypsum under 0, 25, and 40 °C, at pressure of 15, 600, 7000, 16000, and 20000 psi, with NaCl concentration of 0, 1, 2, 4 mol/kg H₂O

Figure 15. Solubility of gypsum at 0 °C changing with NaCl concentration

Blount and Dickson (1963 and 1969) measured solubility of anhydrite in NaCl solution systematically from 94.5 to 450 °C and from 14.7 to 14,500 psi (Dickson et al. 1963; Blount and Dickson 1969). Anhydrite solubility is measured at conditions mentioned above from undersaturation and the results are listed in Table 2. The results match well with Blount and Dickson's data indicating the data acquired from the novel apparatus and Blount and Dickson's experiment are consistent with each other. In the literature, the authors took several measurements of anhydrite solubility under nearly the same conditions. The average solubility is calculated to represent the multi-duplicated measurements under similar conditions to get rid of the situation that the more duplicated conditions will have larger impacts on the final results. The average temperature, pressure and NaCl concentrations are calculated as the temperature, pressure and NaCl concentrations for the average solubility (shown in Table 3).

Table 2. Solubility of anhydrite under certain conditions

T (°C)	P (psi)	Measured anhydrite solubility (mmol/kg H ₂ O)	Blount and Dickson's data (mmol/kg H ₂ O)
150	19400	31.42	31.10
200	19000	21.28	19.97
250	17900	14.61	13.77

Table 3. Anhydrite solubility data under different conditions and the SI values calculated with the virial coefficients derived in this study (modified from (Dickson et al. 1963; Blount and Dickson 1969))

Sample ID	T (°C)	P (psi)	NaCl (mol/kg H ₂ O)	Anhydrite (mmol/kg H ₂ O)	SI
61	146.5	14047.12	6.08	29.25	-0.0063
62	148.75	14591.02	4.20	32.09	0.0333

63	149.5	14351.71	1.21	22.32	-0.0239
64	151.433 3	19517.55	1.91	31.20	-0.0871
65	198.5	15272.71	3.70	23.65	-0.076
66	199.333 3	18777.85	1.91	19.89	-0.1449
67	199.5	14699.8	6.23	28.02	-0.0367
68	200.5	15026.14	1.55	15.57	-0.0422
69	200.5	15118	2.87	21.03	-0.0663
70	231.25	14627.28	6.13	27.61	-0.01
71	248.5	17926.94	1.90	13.77	-0.1355
72	130	1450.4	0.00	3.12	0.053
73	131	14504	0.00	7.65	-0.0522
74	131	72.52	0.00	2.63	0.0509
75	156	14504	0.00	4.78	-0.0413
76	157	7397.04	0.00	2.64	0.0203
77	157	1334.368	0.00	1.62	0.1144
78	157	217.56	0.00	1.48	0.1341
79	183	6961.92	0.00	1.38	0.116
80	184	1450.4	0.00	0.86	0.2439
81	221	14286.44	0.00	1.10	0.083
82	263	14504	0.00	0.50	0.0862
83	145.5	1160.32	6.08	22.15	-0.0678
84	148	1513.251	4.20	22.62	0.0104
85	148.5	87.024	1.91	15.54	-0.0408
86	148.666 7	1445.565	1.22	13.00	-0.0426
87	150.5	5753.253	1.91	19.31	0.0125
88	150.5	11936.79	1.91	24.36	0.0154
89	152.5	348.096	1.91	15.29	-0.0294
90	198.75	1617.196	1.90	10.15	0.0216
91	199.75	2197.356	1.54	9.06	0.0405

92	200	9123.016	1.90	13.98	0.0424
93	200	1783.992	3.69	15.56	0.0231
94	200	391.608	3.69	14.85	0.0084
95	200.25	1827.504	2.86	13.31	0.0249
96	200.25	7585.592	6.23	24.05	0.0196
97	247	1696.968	1.88	6.89	0.0757
98	264.25	14496.75	6.07	27.33	0.0376
99	132	7339.024	0.00	4.50	-0.0237
100	183	14504	0.00	2.40	-0.0541

Chapter 4. Thermodynamic model improvements

4.1. Equilibrium constants

In the experiments, it is required that in the $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$ system, $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ solids approach equilibrium with the solution. Thus we have:

At pressure of 1 atm, the temperature dependent part of K_{sp} can be determined by the equation fitted from the equilibrium constants of dissolution from 0 to 350 °C listed in SOLMINEQ. 88 (Helgeson et al. 1981; Kharaka et al. 1989). Since gypsum is only to be analyzed under 40 °C and anhydrite is to be analyzed over 100 °C, thus more accurate semi-empirical equations which can accurately fit the stability constants of gypsum from 0 to 75 °C and that of anhydrite from 75 to 250 °C are developed and shown in Equation 61. The results of fitted function and the original data are both plotted in Figure 16.

$$\begin{aligned} \log_{10} K_{sp, \text{gypsum}} &= 110.504 - 5040.336 / TK - 39.689 \log_{10}(TK) \\ \log_{10} K_{sp, \text{anhydrite}} &= -762806 / TK + 11600.95 - 1763.68 \log_{10}(TK) \\ &\quad + 1.321TK + 5.42 \times 10^7 / TK^2 \end{aligned} \quad (61)$$

Figure 16. Temperature dependent part of the stability constants of (a) gypsum, and (b) anhydrite

As comparison, the stability constants of gypsum and anhydrite adopted by Kaasa and PhreeQC are also plotted in Figure 16 (Haarberg et al. 1992; Kaasa 1998). Stability constants of anhydrite from these sources deviate from each other to a large amount. In this study, for both gypsum and anhydrite, the temperature dependent part of stability constants are selected from that listed in SOLMINEQ. 88.

The pressure dependent part of equilibrium constant is usually hard to be obtained due to little experimental data especially at high temperature and high pressure conditions for gypsum and anhydrite. The pressure effect on the stability constants for minerals were estimated at 500 and 1000 bars (7,252 psi and 14,500 psi) at 100, 150, 200, 300 and 350 °C by Helgeson et al. based on the estimation of partial molar volume of each species in the reactions (Helgeson et al. 1981). The values are then fitted to the formula below to get the coefficients:

$$\log K_{T,p} = \begin{cases} \log K_T + \frac{\Delta \log K_{500} P}{500} & (P \leq 500 \text{ bar}) \\ \log K_T + \Delta \log K_{500} + \frac{(\Delta \log K_{1000} - \Delta \log K_{500})(P - 500)}{500} & (P > 500 \text{ bar}) \end{cases} \quad (62)$$

where $\Delta \log K = A + Bt + Ct^6$ and two different sets of A, B, C are fitted for pressure under 500 bars (7252 psi) and over 500 bars, respectively. In Table 4 are the parameters fitted and listed in SOLMINEQ. 88 (Kharaka et al. 1989):

Table 4. Parameters for the pressure dependent part of stability constants for anhydrite and gypsum (Kharaka et al. 1989)

Minerals	$\Delta \log K_{500}$			$\Delta \log K_{1000}$		
	A	B	C	A	B	C

Gypsum	0.328	5.89×10^{-5}	1.612×10^{-15}	0.553	4.785×10^{-4}	2.018×10^{-15}
Anhydrite	0.423	1.00×10^{-4}	1.6176×10^{-15}	0.729	1.576×10^{-4}	2.302×10^{-15}

In a more direct way, Atkinson and Mecik (1997) directly fitted $\Delta V_{r,T,p_0}^\phi$ and $\Delta \kappa_r^\phi$ for the two reactions which are all as a function of temperature (Equation 55) (Atkinson and Mecik 1997; Kaasa 1998). The values of q sets are listed in Table 5. However, it still deserves notice that the temperature dependence of $\Delta V_{r,T,p_0}^\phi$ and $\Delta \kappa_r^\phi$ are not theoretically derived indicating the extrapolation should be careful.

Table 5. Parameters for the temperature dependence of $\Delta V_{r,T,p_0}^\phi$ and $\Delta \kappa_r^\phi$ for gypsum and anhydrite (Kaasa 1998)

Minerals		q ₀	q ₁	q ₂	q ₃	q ₄
Gypsum	$\Delta V_{r,T,p_0}^\phi$	-47.722	0.22247	-1.8252×10^{-3}	-2.1242×10^{-6}	0
	$\Delta \kappa_r^\phi$	-17.83	1.543×10^{-2}	1.601×10^{-3}	-1.684×10^{-5}	0
Anhydrite	$\Delta V_{r,T,p_0}^\phi$	-55.379	0.22423	-1.9922×10^{-3}	-2.0301×10^{-6}	0
	$\Delta \kappa_r^\phi$	-15.89	6.0247×10^{-3}	-1.673×10^{-5}	0	0

$\Delta V_{r,T,p_0}^\phi$ in unit of cm³/mole, $\Delta \kappa_r^\phi$ in unit of 10³ cm³/(mole bar).

In this study, the temperature dependent part provided by Helgeson (listed in SOLMINEQ. 88) and pressure dependent part provided by Atkinson and Mecik will be incorporated together to represent the stability constants for dissolution of gypsum and anhydrite.

4.2. Virial coefficients

It is always a big challenge to apply Pitzer theory to concentrated solutions with mixed electrolytes at HTHP conditions since it is hard to get accurate ion interaction

coefficients especially with temperature and pressure dependence. In oil field brine, Ca^{2+} and SO_4^{2-} concentrations are both high. Thus large deviations will occur if the interactions between Ca^{2+} and SO_4^{2-} are not accurate (Shi et al. 2013). Based on the solubility of gypsum and anhydrite at HTHP in the presence of high NaCl concentrations, the Ca^{2+} and SO_4^{2-} interactions can be determined more accurately in such simple solutions based on accurate equilibrium constants and other accurate ion interactions that may occur. However, it is also hard to validate the virial coefficients for different ion interactions in complex systems, especially with ion-pairs. Shi et al. (2013) systematically studied the calcite system and evaluated the effectiveness of stability constants and virial coefficients. Based on his own independent measurement of calcite solubility under low *IS* (0.1 m) over a wide range of temperature (i.e. 0 to 250 °C) and pressure (i.e. 500 to 21,000 psi), the equilibrium constants provided by Li and Duan (2007) and Kharaka et al. (1989) are selected among various different sources (Kharaka et al. 1989; Li and Duan 2007; Shi et al. 2013). Under high ionic strength (4.0 m), the solubility data can be fitted very well with the virial coefficients selected from literature listed in Table 6 and the equilibrium constants verified under low ionic strength. Good fitting results shows the accuracies of these virial coefficients over the temperature and pressure range with similar chemical compositions. According to sequential experiments of calcite solubility measurement in complex brine, Shi et al. find the ineffectiveness of Ca^{2+} - SO_4^{2-} virial coefficients, especially in high concentrations under high pressure, which usually occurs in realistic conditions. Among the B and C terms of Ca^{2+} and SO_4^{2-} interaction, since $\beta_{\text{CaSO}_4}^{(1)}$ values are independent of pressure, it can be accurately determined with experiments under low pressure. Thus all the coefficients verified by Shi

et al. including $\beta_{CaSO_4}^{(1)}$ will be adopted in this study except other coefficients related to Ca^{2+} and SO_4^{2-} interaction (i.e. $\beta_{CaSO_4}^{(0)}, \beta_{CaSO_4}^{(2)}, C_{CaSO_4}^\phi$). These virial coefficients will be modeled with Equation 40 incorporating temperature and pressure dependence in this study.

Table 6. Sources of virial coefficients used in Shi et al.'s paper and this study (Shi et al. 2013)

Virial coefficients	Sources
$\beta_{CaCl}^{(0)}, \beta_{CaCl}^{(1)}, C_{CaCl}^\phi, \theta_{HCl}$	(Christov and Moller 2004)
$\beta_{NaHCO_3}^{(0)}, \beta_{NaHCO_3}^{(1)}, C_{NaHCO_3}^\phi, \lambda_{CO_2Na}, \lambda_{CO_2Cl}$	(He and Morse 1993)
$\beta_{NaCl}^{(0)}, \beta_{NaCl}^{(1)}, C_{NaCl}^\phi$	(Pitzer et al. 1984)
$\theta_{NaCl}, \theta_{ClHCO_3}, \psi_{HCl}, \psi_{NaClHCO_3}$	(Harvie et al. 1984)
$\theta_{HNa}, \psi_{NaCl}$	(He and Morse 1993)
$\beta_{CaSO_4}^{(0)}, \beta_{CaSO_4}^{(1)}, \beta_{CaSO_4}^{(2)}$	(Kaasa 1998)
$\beta_{NaSO_4}^{(1)}$	(He 1992)
$\beta_{NaSO_4}^{(0)}, \beta_{NaSO_4}^{(2)}, C_{NaSO_4}^\phi$	(Shi et al. 2012)

4.3. Model construction and results analysis

4.3.1. Fitted results

A MATLAB model is constructed to simulate the thermodynamic properties of all species present in the calcium sulfates system. The input is the solubility of gypsum or anhydrite at various temperatures and pressures under different concentrations of NaCl. The fitting process is aiming at reducing the total square deviations of SI values in respect of zero which is the theoretical SI value (i.e. $\sum SI^2$) by changing the parameters which

represent the temperature and pressure dependence of the three virial coefficients (i.e. $\beta_{CaSO_4}^{(0)}, \beta_{CaSO_4}^{(2)}, C_{CaSO_4}^\phi$). The same temperature and pressure dependent function for the same virial coefficients are applied in both gypsum and anhydrite systems (under two different temperature ranges). Based on the fitted function, values of virial coefficients at the temperature gap (40 °C to 130 °C) can be interpolated with confidence.

In total, 100 data points with temperatures ranging from 0 to 264.25 °C and pressures ranging from 14.7 to 20000 psi are input into this model to derive 36 parameters (i.e. 12 parameters for each virial coefficient). In Table 7 are listed the corresponding parameters in Equation 40 for the three virial coefficients. With these parameters these three virial coefficients can be calculated under any temperature and pressure within the temperature and pressure range of the solubility. The values of virial coefficients under certain temperatures and pressures are listed in Table 8. Based on Pitzer theory and the virial coefficients from literature and model fitting, *SI* values are plotted in Figure 17 and also listed in Table 1 and Table 3 with corresponding sample ID. Figure 17 shows that most *SI* values are located within [-0.1, 0.1] range, though few data points are bigger than 0.2 or smaller than -0.2. The average of the *SI* values is -0.001 and standard deviation is 0.088, indicating that the current model achieves a good fit to the experimental data measured over a wide range of temperature, pressure and NaCl concentrations.

Table 7. Parameters fitted for $\beta_{CaSO_4}^{(0)}, \beta_{CaSO_4}^{(2)}, C_{CaSO_4}^\phi$

	$\beta_{CaSO_4}^{(0)}$	$\beta_{CaSO_4}^{(2)}$	$C_{CaSO_4}^\phi$
z ₁	8.91101078650966E-02	-1.83275129405988E-02	2.10093614166613E-03

z_2	3.39492639397076E-03	4.51823266916082E-04	-3.61313314012244E-04
z_3	-2.79604525244827E-03	-2.12801005961393E-01	8.99731413307297E-04
z_4	2.07321718332405E-01	-6.20761679394803E-02	-4.06330406536896E-03
z_5	-6.11317986149408E-04	5.80923145892471E-02	-6.41837518040533E-05
z_6	7.17699685698741E-02	1.63195932000453E-03	4.03284213128895E-02
z_7	5.10327928945625E-05	-1.07306949233810E-03	2.04586931550914E-05
z_8	-2.69214976543139E-03	3.90502496615939E-02	-1.55398709918255E-03
z_9	-9.24097833071662E-07	-1.00399177362503E-03	4.07413099845437E-06
z_{10}	1.43950302911880E-03	-3.55775949443628E-02	1.76810206927376E-03
z_{11}	-2.95831022082558E-08	-3.67933346294581E-07	9.75056448662670E-09
z_{12}	8.64468785073341E-07	2.23364999776374E-04	-1.81128874462945E-06

Table 8. Values of $\beta_{CaSO_4}^{(0)}$, $\beta_{CaSO_4}^{(2)}$, $C_{CaSO_4}^\phi$ under certain temperatures and pressures

T	P	$\beta_{CaSO_4}^{(0)}$	$\beta_{CaSO_4}^{(2)}$	$C_{CaSO_4}^\phi$
0	15	0.48692	-89.7219	0.233513
0	600	0.428606	-84.1202	0.27759
0	7000	0.021301	-41.8489	0.700786
0	16000	0.163673	-41.3508	1.11294
0	20000	0.495258	-63.2447	1.227475
25	15	0.436212	-97.9615	0.169139
25	600	0.41657	-93.5678	0.195347
25	7000	0.203587	-58.1947	0.484186
25	16000	-0.09001	-47.81	0.896957
25	20000	-0.21828	-57.9611	1.082883
40	15	0.405081	-102.905	0.129886
40	600	0.409132	-99.2513	0.145765
40	7000	0.324483	-68.544	0.365509
40	16000	-0.19438	-54.1004	0.81723

40	20000	-0.575	-58.4632	1.071535
75	15	0.330691	-114.442	0.036734
75	600	0.391214	-112.549	0.029463
75	7000	0.633526	-93.9803	0.115054
75	16000	-0.32732	-74.4767	0.74739
75	20000	-1.2427	-68.288	1.220511
100	600	0.377986	-122.075	-0.05408
100	7000	0.87313	-113.064	-0.04529
100	16000	-0.34577	-93.0519	0.778507
100	20000	-1.60604	-81.4032	1.449074
150	600	0.350614	-141.18	-0.22215
150	7000	1.388314	-153.015	-0.33047
150	16000	-0.23899	-137.961	0.99447
150	20000	-2.12025	-119.378	2.137575
200	600	0.322208	-160.343	-0.39133
200	7000	1.939986	-194.814	-0.57952
200	16000	0.011035	-190.834	1.365515
200	20000	-2.42352	-169.385	3.059003
250	600	0.292946	-179.552	-0.56144
250	7000	2.518737	-238.017	-0.80165
250	16000	0.365274	-249.698	1.850947
250	20000	-2.57408	-228.427	4.151815

Figure 17. SI values of gypsum and anhydrite data points based on fitted virial coefficients

However, it is found that the *SI* values of the data points collected at 0 °C (red points in Figure 17) are all less than zero. Such systematic deviations might be due to inaccurate temperature control at 0 °C when measuring solubility, or inaccurate stability constants and virial coefficients at 0 °C. The model is fitted again without 0 °C data and the *SI* values are calculated and listed in Figure 18. Without these 0 °C data, only two *SI* values are out of [-0.1, 0.1] range indicating very good fitting results. Considering the uncertainties of solubility data, stability constants, virial coefficients, and the possible inaccuracies of the semi-empirical temperature and pressure dependent function, it is hard to tell which uncertain factor is incorporated errors and leads to such imperfect fitting. Thus this modeling process requires more confidential data and more theoretically accurate temperature and pressure dependent functions. Before figuring out the inaccurate factor, the analysis below will be based on all the data points including those at 0 °C to cover larger ranges of temperature from 0 to 250 °C.

Figure 18. SI values of gypsum and anhydrite data points based on fitted virial coefficients without 0 °C data

4.3.2. Ion pairs of $\text{CaSO}_4^{(0)}$

In the solutions with Ca^{2+} and SO_4^{2-} ions, including gypsum and anhydrite system, there will be $\text{CaSO}_4^{(0)}$ pairs with strong interactions. Such interaction is incorporated into different models either explicitly through stability constants, or implicitly by $\beta^{(2)}$ terms in Pitzer theory. As distinct ion pairs in solution, the stability constant for infinitely dilute solutions has been studied a lot and has slightly different values from different sources. Bell and George (1953) provided the thermodynamic data for $\text{CaSO}_4^{(0)}$ at 25 °C from which the stability constant is calculated as $10^{2.30}$ (Bell and George 1953). Kharaka et al. (1989) listed the association constants for $\text{CaSO}_4^{(0)}$ at different temperatures from 0 to 350 °C based on the researches done by Kalyanaraman et al. in SOLMINEQ. 88 (Kalyanaraman et al. 1973; Kharaka et al. 1989). The estimated stability constant at 25 °C and 1 atm is $10^{2.30}$ which matches well with Bell and George's data. The database used in

Visual MINTEQ gives $10^{2.36}$ as the stability constant of $\text{CaSO}_4^{(0)}$ which is close to Bell and George's data, and that used in SOLMINEQ. 88.

In this study, based on Pitzer assumptions and the fitted virial coefficients at 25 °C and 1 atm (14.7 psi), $K_{assoc} = -2\beta_{\text{CaSO}_4}^{(2)} = 195.923 = 10^{2.29}$ which is identical with Bell and George's data and that used in SOLMINEQ. 88. Such good match indicates the accuracy of Pitzer theory and the fitting process in this study at this condition.

However, stability constants over wide ranges of temperature and pressure are not available from experimental results. For comparisons with Pitzer theory based on the virial coefficients fitted in this study, the charge specific ion pair association equations are applied to calculate K_{assoc} for $\text{CaSO}_4^{(0)}$ within the temperature and pressure ranges under *IS* of 0, 0.01 M and 4.0 M. The stability constants derived from these two theories are listed in Table 9. Since the charge specific ion pair association equation is only charge specific but not ion specific, it cannot show exactly accurate stability constants for $\text{CaSO}_4^{(0)}$. However, it still gives us a rough view over the impacts of temperature, pressure and *IS* on ion pair stability constants.

These two sets of data both show huge dependence on *IS*. When *IS* increases from 0 to 4.0 M, the stability constants decrease by several magnitudes indicating that the ion pair interactions diminish a lot with *IS*. The stability constants derived from charge specific ion pair association equation tend to increase with temperature and decrease with pressure. The stability constants based on Pitzer theory and the fitted virial coefficients also show similar trends, but with some erratic values. In detail, within low temperature ranges (i.e. lower than or equal to 100 °C), it shows similar temperature and pressure

dependence with charge specific ion pair association equation, except that at 20000 psi which increase with pressure instead. Within high temperature range (over 100 °C), K_{assoc} values from charge specific equation increase much faster with temperature than that from this study. In addition, K_{assoc} values from this study will increase with pressure first, and then decrease with pressure at very high pressures. For instance, at 250 °C and 0 M ionic strength, stability constant from this study increases from 359.10 at 600 psi to 499.40 at 16,000 psi, and decreases to 456.85 at 20,000 psi; while stability constant from charge specific equation decreases from 4326.13 at 600 psi to 893.92 at 20,000 psi, which are all much bigger than that from this study.

Lack of experimental data, it is hard to evaluate the accuracy of the stability constants based on Pitzer theory and the virial coefficients derived in this study. However, even though Pitzer equation is theoretically right, when applying Pitzer equation into realistic modeling process, many uncertainties will lead to the inaccuracies of the ion pair stability constants (i.e. $\beta^{(2)}$) even in simple systems. Firstly, the solubility data might be not accurate enough. Secondly, the model fitting process might undergo over-fitting problem due to not enough solubility data but too many parameters to be fitted. Thirdly, the temperature and pressure dependent functions might not be accurate.

Table 9. Stability constants of $\text{CaSO}_4^{(0)}$ based on charge specific ion pair association equation (Equation 56) and Pitzer theory

T (°C)	P (psi)	Charge specific equation			Pitzer Theory $K_{assoc} = -2\beta_{\text{CaSO}_4}^{(2)} g(12\sqrt{IS})$		
		IS = 0.00 M	IS = 0.01 M	IS = 4.00 M	IS = 0.00 M	IS = 0.01 M	IS = 4.00 M
0	15	82.79	38.03	1.17	179.44	84.08	0.62

0	600	81.94	37.72	1.17	168.24	78.83	0.58
0	7000	73.69	34.64	1.15	83.70	39.22	0.29
0	16000	64.40	31.10	1.13	82.70	38.75	0.29
0	20000	60.97	29.75	1.12	126.49	59.27	0.44
25	15	96.14	42.86	1.20	195.92	91.80	0.68
25	600	95.13	42.49	1.19	187.14	87.69	0.65
25	7000	85.15	38.90	1.18	116.39	54.54	0.40
25	16000	74.11	34.80	1.15	95.62	44.80	0.33
25	20000	70.06	33.27	1.14	115.92	54.32	0.40
100	600	198.20	76.07	1.32	244.15	114.40	0.85
100	7000	168.34	66.87	1.29	226.13	105.96	0.79
100	16000	138.71	57.37	1.26	186.10	87.20	0.65
100	20000	128.65	54.04	1.25	162.81	76.29	0.57
150	600	410.58	134.59	1.46	282.36	132.31	0.98
150	7000	322.26	111.40	1.41	306.03	143.40	1.06
150	16000	245.81	90.12	1.36	275.92	129.29	0.96
150	20000	222.18	83.21	1.34	238.76	111.87	0.83
250	600	4326.13	816.02	1.94	359.10	168.27	1.25
250	7000	2085.93	469.89	1.78	476.03	223.06	1.65
250	16000	1100.02	288.27	1.65	499.40	234.00	1.73
250	20000	893.92	245.81	1.61	456.85	214.07	1.59

4.3.3. Calcite system

One of the advantages of Pitzer theory is that the virial coefficients derived from simple systems can be applied to other complex systems with mixed electrolytes. Shi et al. (2013) conducted calcite solubility measurements in synthetic brine to represent the typical composition of realist brine, and found that Ca^{2+} and SO_4^{2-} interaction is one of the biggest interference (Shi et al. 2013). As a possible mathematically right solution, the

authors adjusted $\beta_{CaSO_4}^{(2)}$ in this system and fixed the *SI* deviations as is listed in Table 11. However, such adjustments didn't consider other virial coefficients for Ca^{2+} and SO_4^{2-} interactions at the same time, especially under such low Ca^{2+} concentrations and high *IS*, under which conditions the $CaSO_4^{(0)}$ ion pair interactions represented by $\beta_{CaSO_4}^{(2)}$ only account for little portion of total Ca-SO₄ interactions. Thus the adjusted $\beta_{CaSO_4}^{(2)}$ don't have any physical meanings and cannot be applied to other systems with different chemical compositions and different conditions.

In this study, all three uncertain virial coefficients for Ca^{2+} and SO_4^{2-} interactions are fitted over wide ranges of temperature, pressure and *IS* in simple calcium sulfate system. The fitted virial coefficients for Ca^{2+} and SO_4^{2-} interactions are applied to systems under corresponding temperature and pressure ranges. In Shi's researches, they measured solubility of calcite in mixed electrolytes (Table 10). The *SI* values of calcite using virial coefficients fitted in this study are listed in the last column of Table 11. Except for that at 100 °C, most *SI* values of calcite for this mixed electrolyte system are close to 0. However, at 100 °C, the *SI* values of calcite under most conditions deviate a lot from 0. In addition, the average of all the *SI* values is -0.0955 indicating the underestimations of certain ion interactions in the system. Such discrepancies can be ascribed to several possible problems. First, the solubility measurement of calcite in such complex system and calcium sulfates might not be accurate enough. The *SI* values are sensitive to Ca^{2+} concentration which means small error of effluent concentration might lead to big errors on *SI* values of calcite. The Ca-SO₄ interaction coefficients also strongly depend on calcium sulfates solubility measurements. Second, other virial

coefficients involved in this mixed electrolyte solutions and stability constants of minerals involved might be inaccurate. For example, some ion interactions (e.g. Ca-HCO₃) might also have big impacts in the system but are not adjusted with temperature and pressure dependence in the study. Therefore, in order to improve the prediction for calcite system with mixed electrolytes, more ion interactions should be taken into account, more accurate solubility data and stability constants are needed, and more accurate temperature and pressure dependent function are required.

Table 10. Composition of the synthetic brine for calcite dissolution tests (Shi et al. 2013)

Constituents	Concentration	Concentration
Total	(mg/L)	(mol/L)
Na	102000	4.44
HCO ₃	3000	0.0492
B	150	0.0136
Br	3500	0.0438
SO ₄	4500	0.0469
Si	30	0.001
Cl	150000	4.23
TDS	~262000	—

Table 11. SI values of calcite in synthetic solution before and after virial coefficients revision under various conditions (Shi et al. 2013)

T (°C)	P (psi)	Effluent concentrations (mmol/kg-H ₂ O)			SI w/o $\beta_{CaSO_4}^{(2)}$ adjustment	SI w/ $\beta_{CaSO_4}^{(2)}$ adjustment	This research
		Ca ²⁺	HCO ₃ ⁻	CO ₂ (aq)			
0	500	4.07	61.72	11.67	-0.06	-0.03	-0.03

Chapter 5. Summary

This research focuses on the improvement of Pitzer virial coefficients for Ca^{2+} and SO_4^{2-} interactions and applying them to calcite system at HTHP with mixed electrolytes. With these virial coefficients, solubility of gypsum, anhydrite and calcite can be predicted accurately at HTHP in the presence of high NaCl concentrations based on Pitzer theory. In this study, solubility of gypsum was measured at temperature from 0 to 40 °C, pressure from 14.7 to 20000 psi, and in the presence of 0 to 4m NaCl. Solubility of anhydrite was measured at certain conditions identical to that conducted in literature. The measured solubility matches well with literature data and thus the literature data was adopted in this research. The stability constants of gypsum and anhydrite from different sources were analyzed and the temperature dependent part from Helgeson and pressure dependent part from Atkinson and Mecik are incorporated together to represent stability constants for gypsum and anhydrite in this research. Virial coefficients for different ions interactions were re-examined and selected for the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ system. Three important virial coefficients for Ca^{2+} and SO_4^{2-} interactions dependent on pressure (i.e. $\beta_{\text{CaSO}_4}^{(0)}, \beta_{\text{CaSO}_4}^{(2)}, C_{\text{CaSO}_4}^\phi$) were fitted based on solubility of gypsum and anhydrite under different conditions.

Since 2-2 ion pairs will be present in aqueous system taking account for a portion that cannot be ignored, Pitzer theory incorporates it into $\beta_{\text{CaSO}_4}^{(2)}$ term with $\beta_{\text{CaSO}_4}^{(2)} = -K_{\text{assoc}} / 2$. At 25 °C and 1 atm, stability constants according to the fitted $\beta_{\text{CaSO}_4}^{(2)}$ values matches well with those reported in literature. However, at relatively high temperature and high pressures, the stability constants calculated from $\beta_{\text{CaSO}_4}^{(2)}$ show

inconsistency with charge specific equations. Such inconsistency might be due to inaccurate experimental data especially at high temperatures or inaccurate temperature and pressure dependent functions.

The fitted virial coefficients were applied to calcite system with mixed electrolytes which is typical in realistic brine. Under most conditions except for that under 100 °C, the SI values of calcite are close to zero indicating a successful application of Pitzer theory in both gypsum/anhydrite system and calcite system. The discrepancies at 100 °C might be due to inaccurate measurement for calcite system and calcium sulfates systems, inaccurate stability constants applied, or inaccurate virial coefficients for certain ion interactions.

This study gives much attention to the accuracies of source data (including equilibrium constants, virial coefficients, and solubility data) which are critical to the inter-system application of Pitzer theory. It is a good example of data selection, model fitting, and inter-system application of Pitzer theory over wide ranges of temperature, pressure and IS in the presence of mixed electrolytes.

Chapter 6. Future research

The virial coefficients for Ca^{2+} and SO_4^{2-} interactions (i.e. $\beta_{\text{CaSO}_4}^{(0)}, \beta_{\text{CaSO}_4}^{(2)}, C_{\text{CaSO}_4}^\phi$) are fitted in gypsum and anhydrite system simultaneously over wide ranges of temperature, pressure and ionic strength. The derived coefficients are also applied to calcite system with mixed electrolytes. The results show good modeling process in respect of SI values. However, more can be done to overcome the imperfect fitting in this study and help accurately apply Pitzer theory to complex systems:

- (1) More accurate solubility data of gypsum and anhydrite over wider ranges of temperature and pressure are needed. More data points will help eliminate the fitting problems in Pitzer theory which is incorporated with dozens of parameters.
- (2) More data is needed at relatively low IS under which the ion pair impacts will be more significant. Thus the $\beta_{\text{CaSO}_4}^{(2)}$ values will be more accurately fitted.
- (3) Accurate equilibrium constants from solubility-independent methods such as vapor pressure measurement and calorimetric measurement, are needed especially at high temperature and high pressure.
- (4) The temperature and pressure dependent function for virial coefficients should be improved with theoretical derivation or more accurate form.
- (5) The virial coefficients for other ion interactions should also be carefully analyzed for their pressure dependence just as what this study has done. Or in another way, the uncertain virial coefficients can be modeled together among different systems simultaneously.

Curriculum Vitae

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□ Education

- Aug. 2012 – present   PhD candidate, Environmental Engineering, **Rice University**, USA
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- Aug. 2012 – present   Thermodynamic modeling of calcite, barite, and calcium sulfates at high temperature and high pressure in mixed electrolytes
- Sep. 2011 – Jul. 2012   Bactericidal activities of nano-Ag₂O/TNBs
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- **Dai, Zhaoyi**, Wei Shi, Amy T. Kan, Nan Zhang, and Mason B. Tomson. "Thermodynamic model improvements for common minerals at high temperature, high pressure and high TDS with mixed salts." In *2013 SPE International Symposium on Oilfield Chemistry*. 2013.
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