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Thermodynamic Modeling of CO₂-N₂-O₂-Brine-Carbonates in Conditions from Surface to High Temperature and Pressure

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Abstract: Nitrogen (N₂) and oxygen (O₂) are important impurities obtained from carbon dioxide (CO₂) capture procedures. Thermodynamic modeling of CO₂-N₂-O₂-brine-minerals is important work for understanding the geochemical change of CO₂ geologic storage with impurities. In this work, a thermodynamic model of the CO₂-N₂-O₂-brine-carbonate system is established using the “fugacity-activity” method, i.e., gas fugacity coefficients are calculated using a cubic model and activity coefficients are calculated using the Pitzer model. The model can calculate the properties at an equilibrium state of the CO₂-N₂-O₂-brine-carbonate system in terms of gas solubilities, mineral solubilities, H₂O solubility in gas-rich phase, species concentrations in each phase, pH and alkalinity. The experimental data of this system can be well reproduced by the presented model, as validated by careful comparisons in conditions from surface to high temperature and pressure. The model established in this work is suitable for CO₂ geologic storage simulation with N₂ or O₂ present as impurities.

Keywords: thermodynamic modeling; CO₂ geologic storage; CO₂-N₂-O₂-brine-carbonates; fugacity; activity

1. Introduction

Carbon emission reduction is becoming a more and more important topic for the sustainable development of human beings. Carbon capture and storage (CCS) has been validated as a useful method for reducing carbon emission and the clean use of fossil energy. High cost is one of the main barriers for commercial use of CCS. In the whole chain of CCS, more than half of the cost is consumed by carbon dioxide (CO₂) capture, because a high purity of CO₂ is usually used for real CO₂ storage projects [1]. Lowering the CO₂ purity could be a way to reduce the CO₂ capture cost.

According to an International Energy Agency Greenhouse Gas R&D Programme (IEAGHG) report [2], even though there are various impurities obtained from CO₂ capture techniques, the main impurities are nitrogen (N₂) and oxygen (O₂). When CO₂ is injected with impurities, fluid properties such as gas density, viscosity and gas-water-mineral interactions could be different [3,4] compared to the injection of pure CO₂. The presence of impurities decreases CO₂ solubility in brine and also affects H₂O contents in non-aqueous phase. A change in fluid property also affects fluid migration and CO₂ storage capacity in subsurface porous media. When O₂ is injected with CO₂ into the subsurface reservoir, the oxidation-reduction environment is changed, which triggers related water-mineral interactions. In this case, water properties (such as composition, pH and alkalinity), porosity and permeability vary consequently [5,6].

Thermodynamic modeling of CO₂-impurities-brine systems is essential work for understanding subsurface fluid transport. It mainly consists of the modeling of phase partitioning, density and viscosity. Soreide and Whitson [7] constructed mutual solubility of multi-gases (including CO₂, CH₄, H₂S and N₂) and brine systems. The model shows good accuracy at low temperature and pressure with a salinity less than 2 (molal). Li et al. [3] made modifications and achieved good accuracy at wider ranges of temperature, pressure and salinity for CO₂-CH₄-H₂S-brine systems. Gas solubility modeling of CO₂, N₂ and O₂ in water and brine has been performed by Duan and Sun [8], Mao and Duan [9] and Geng and Duan [10] based on comprehensive reviews of experimental data. These models can reproduce most of the experimental data over wide ranges of temperature, pressure and salinity. However, they can only consider single gas component cases, and cannot calculate multi-gas and brine system equilibria. Tan et al. [11] developed a model for CO₂, SO₂ and brine system equilibria using a “cubic plus association” (CPA) method. Sun and co-workers developed an improved “Statistical Associating Fluid Theory” (SAFT) model for CO₂-brine and water-hydrocarbon systems by introducing a Lennard-Jones (LJ) term (SAFT-LJ models, [12–14]). CPA and SAFT type models usually have high computation accuracy, but are time-consuming and are not practical for reservoir simulation implementations.

Carbonates (including calcite, magnesite and dolomite) are important minerals for CO₂ geologic storage. When CO₂ is injected into porous media with carbonate minerals, dissolution of carbonates into aqueous phase is enhanced. Water property (such as pH, ion concentration, density and viscosity), porosity and permeability are affected consequently. Thermodynamic modeling work for CO₂-brine-mineral systems began in the 1980s. Harvie and Weare [15] and Harvie et al. [16] used the Pitzer model to predict mineral solubility in the system Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O. Moller [17], Greenberg and Moller [18], and Christov and Moller [19] further consider the temperature effects for model parameters of the system. The pressure effects are not considered in these models. Duan and Li [20] proposed a thermodynamic model for the quaternary system CO₂-H₂O-NaCl-CaCO₃ which predicts the solubility of calcite, CO₂ and other properties over wide ranges of temperature and pressure. Li and Duan [21] extended the model to a quinary system with CaSO₄ included. Gypsum and anhydrite dissolution, precipitation and interactions with CO₂ and H₂O can be considered in the model.

This work discusses the phase partitioning modeling of the CO₂-N₂-O₂-brine system based on careful review and validation with experimental data at high temperature, pressure and salinity. The model is then extended to CO₂-N₂-O₂-brine-carbonates phase equilibria. Calcite, magnesite and dolomite are considered to be carbonate minerals of this system. The calculation results given by the model are compared with existing experimental data such as mineral solubilities with CO₂ contained, CO₂ solubility in brine saturated with minerals, water pH, and ion concentrations at various pressures and temperatures.

2. Thermodynamic Modeling of CO₂-N₂-O₂-Brine Equilibria

When gas components (CO₂, N₂ and O₂) are dissolved in brine, chemical potentials approach equality, and the whole system approaches an equilibrium state. The Henry constant [21] is defined as:

$$K_H = \frac{f_i}{a_i} \quad (1)$$

where K_H is the Henry constant; f_i is the gas fugacity of component i ; a_i is activity of component i in water phase. This equation is valid only when the system is at equilibrium state.

Furthermore, $f_i = Py_i\phi_i$, where y_i is the mole fraction of component i in gas phase and ϕ_i is fugacity coefficient of component i in gas phase. For activity $a_i = m_i\gamma_i$, where m_i is the molality of component i in aqueous phase, and γ_i is the activity coefficient of component i in aqueous phase. From Duan and Li [20], K_H is the function of temperature and pressure:

$$K_H(T, P) = K_H(T, P_{ref}) \times \exp(PF) \quad (2)$$

where P_{ref} is pressure at reference state and is usually set as 1 atm. PF is Poynting factor, which is defined as,

$$PF = \int_{P_{ref}}^P \frac{V_m}{RT} dP = \frac{\bar{V}_m}{RT} (P - P_{ref}) \quad (3)$$

R is gas constant and V_m is partial molar volume. $\bar{V}_m$ is average partial molar volume. From Equations (1) to (3), solubility of component i can be calculated as,

$$m_i = \frac{Py_i\phi_i}{\gamma_i K_H(T, P_{ref}) \exp\left(\frac{\bar{V}_{m,i}(P - P_{ref})}{RT}\right)} \quad (4)$$

In this work, fugacity coefficients are calculated based on the Peng-Robinson (PR) [22] equation. The related parameters for CO₂, N₂, O₂, and H₂O can be found in Tables 1 and 2. Activity coefficients are calculated by the Pitzer [23] model. The model parameters, as well as K_H and V_m , are discussed in Section 2. The related experimental work of the concerned fluid system is used for the parameterization of the model.

2.1. Fugacity Coefficients

The two-parameter cubic form equation of state has been widely used in the oil and gas industry for phase properties and flash calculations [22,24,25], and has shown good accuracy for non-polar molecules. In this work, fugacity coefficients of gaseous species are calculated using the Peng-Robinson [22] model of the form as follows:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \quad (5)$$

where $a(T) = a(T_c)\alpha(T_r, \omega)$; $a(T_c)$ is the Van der Waals' attraction factor at a critical temperature defined as $a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c}$, where P_c is critical pressure; $b = 0.07780 \frac{RT_c}{P_c}$; T_r is reduced temperature $T_r = \frac{T}{T_c}$; T_c is critical temperature; ω is acentric factor; $\alpha(T_r, \omega)$ is a dimensionless function of relative temperature and acentric factor.

When gaseous phase has more than one component, the mixing rule is considered for parameters "a" and "b".

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (6)$$

$$b = \sum_i b_i y_i \quad (7)$$

where $a_{ij} = \sqrt{a_i a_j} (1 - \delta_{ij})$ and δ_{ij} is binary interaction coefficient of species i and j ; y_i is mole fraction of species i in gaseous phase.

The parameters (critical temperature T_c , critical pressure P_c , and acentric factor ω) used in PR [22] EOS for each individual component are listed in Table 1.

Table 1. Parameters of each component for PR EOS.

	T_c (K)	P_c (bar)	ω
CO ₂	304.2 ^a	73.83 ^a	0.2236 ^a
N ₂	126.2 ^b	34.0 ^b	0.0377 ^b
O ₂	154.6 ^b	49.8 ^b	0.021 ^b
H ₂ O	647.3 ^a	221.2 ^a	0.3434 ^a

^a: from Soreide and Whitson [7]; ^b: from PHREEQC database [26].

The binary interaction parameters (δ_{ij}) used PR EOS are listed in Table 2.

Table 2. Binary interaction parameters for PR EOS.

δ_{ij}	H ₂ O	CO ₂	N ₂	O ₂
H ₂ O	-	0.1896 ^a	0.32547 ^b	0.20863 ^c
CO ₂	0.1896 ^a	-	-0.007 ^d	0.1140 ^d
N ₂	0.32547 ^b	-0.007 ^d	-	-0.0119 ^c
O ₂	0.20863 ^c	0.1140 ^d	-0.0119 ^c	-

^a: from Soreide and Whitson [7]; ^b: from Ziabakhsh-Ganji and Kooi [27]; ^c: from Wang et al. [28]; ^d: from Li and Yan [29].

2.2. Equilibrium Constant

From Equations (2) and (3), equilibrium constant can be expressed as,

$$K_i = K_H(T, P_{ref}) \exp\left(\frac{\overline{V}_{m,i}(P - P_{ref})}{RT}\right) \quad (8)$$

where i denotes a component (i = H₂O, CO₂, N₂, and O₂).

For H₂O, the equation from previous work [3,4] is used,

$$K_{H_2O} = (a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \exp\left(\frac{(P - 1)(a_6 + a_7T)}{RT}\right) \quad (9)$$

where $a_1 - a_7$ are the parameters found in Li et al. [3].

For CO₂, N₂ and O₂, Equation (8) is used for the equilibrium constant. $K_H(T, P_{ref})$ is calculated following Appelo [30]:

$$\log(K_H(T, P_{ref})) = A_0 + A_1T + \frac{A_2}{T} + A_3 \log(T) + \frac{A_4}{T^2} + A_5T^2 \quad (10)$$

where $A_0 - A_5$ are the parameters found in Appelo [30], listed in Table 3. Also, $\overline{V}_{m,i}$ is calculated as follows:

$$\overline{V}_{m,i} = 41.84 \left(0.1a_{1,i} + \frac{100a_{2,i}}{2600 + P} + \frac{a_{3,i}}{(T - 288)} + \frac{10^4a_{4,i}}{(2600 + P)(T - 288)} - \omega_i \times QBrn \right) \quad (11)$$

where $a_{1,i} - a_{4,i}$ and ω_i are the parameters found in Appelo [30], listed in Table 3, and $QBrn$ is the Born function, which can be found in Helgson et al. [31].

Table 3. Parameters for equilibrium constants of CO₂, N₂ and O₂.

	A_0	A_1	A_2	A_3	A_4	A_5	a_1	a_2	a_3	a_4	ω
CO ₂	-10.52624	2.3547×10^{-2}	3972.8	0	-5.8746×10^5	-1.9194×10^{-5}	7.29	0.92	2.07	-1.23	-1.6
N ₂	58.453	-1.818×10^{-3}	-3199	-17.909	27,460	0	7	0	0	0	0
O ₂	7.5001	-7.8981×10^{-3}	0	0	-2.0027×10^5	0	5.7889	6.3536	3.2528	-3.0417	-0.3943

2.3. Activity Model

Activity or activity coefficient is an important parameter to describe the deviation of solvent and aqueous species from ideal solution at a given temperature and pressure. The Pitzer [23,32,33] model is an accurate model for calculating the activity of water and various aqueous species especially to high salinity of brine. This activity model has wide application to water-salt-mineral system computation and modeling at different temperatures and pressures [16–21,34]. These applications have shown the success of the Pitzer [23] model. In this work, the Pitzer [23] model is used to calculate aqueous species activity coefficients. The details of Pitzer [23] equations have been discussed in previous research

papers [20,21]. When gas components are dissolved in water, it is assumed that they are in the form of neutral species in aqueous phase. The Pitzer [23] equation of neutral species is as follows [8]:

$$\ln \gamma_i = \sum_c 2m_c \lambda_{i-c} + \sum_a 2m_a \lambda_{i-a} + \sum_c \sum_a m_c m_a \zeta_{i-a-c} \quad (12)$$

where γ_i is the activity coefficient of component i ; $i = \text{CO}_2$, N_2 , or O_2 ; λ_{i-c} , λ_{i-a} and ζ_{i-a-c} are the Pitzer interaction parameters; m_c and m_a are the aqueous species molality; “c” denotes cation species and “a” denotes anion species. In this work, λ_{i-c} , λ_{i-a} and ζ_{i-a-c} are parameterized from the gas solubility experimental data.

The fitting equation of Pitzer interaction parameters follows Appelo [30]:

$$Param = b_0 + b_1 \times \left(\frac{1}{T} - \frac{1}{T_R} \right) + b_2 \times \ln \left(\frac{T}{T_R} \right) + b_3 \times (T - T_R) + b_4 \times (T^2 - T_R^2) + b_5 \times \left(\frac{1}{T^2} - \frac{1}{T_R^2} \right) \quad (13)$$

where $b_0 - b_5$ are fitting parameters; T is temperature in (K); $T_R = 298.15$ (K). The parameters are listed in Table 4.

Table 4. Parameters of Pitzer interaction equations for gas components and main ion species.

.	b_0	b_1	b_2	b_3	b_4	b_5
$\lambda_{\text{CO}_2-\text{Na}^+}^a$	0.085					
$\lambda_{\text{CO}_2-\text{Mg}^{+2}}^a$	0.183					
$\lambda_{\text{CO}_2-\text{Ca}^{+2}}^a$	0.183					
$\lambda_{\text{CO}_2-\text{SO}_4^{-2}}^a$	0.075					
$\lambda_{\text{CO}_2-\text{K}^+}^a$	0.051					
$\lambda_{\text{N}_2-\text{Na}^+}^b$	0.1402	−595	−4.025	0.01044	-2.131×10^{-6}	49,970
$\lambda_{\text{N}_2-\text{Mg}^{+2}}^b$	0.2804	−1190	−8.05	0.02088	-4.262×10^{-6}	99,940
$\lambda_{\text{N}_2-\text{Ca}^{+2}}^b$	0.2804	−1190	−8.05	0.02088	-4.262×10^{-6}	99,940
$\lambda_{\text{N}_2-\text{K}^+}^b$	0.1402	−595	−4.025	0.01044	-2.131×10^{-6}	49,970
$\lambda_{\text{N}_2-\text{SO}_4^{-2}}^b$	0.0371					
$\lambda_{\text{O}_2-\text{Na}^+}^c$	0.19997					
$\lambda_{\text{O}_2-\text{Mg}^{+2}}^c$	0.31715					
$\lambda_{\text{O}_2-\text{Ca}^{+2}}^c$	0.35135					
$\lambda_{\text{O}_2-\text{K}^+}^c$	0.15022					
$\lambda_{\text{O}_2-\text{SO}_4^{-2}}^c$	0.14383					
$\zeta_{\text{CO}_2-\text{Na}^+-\text{SO}_4^{-2}}^b$	−0.015					
$\zeta_{\text{N}_2-\text{Na}^+-\text{SO}_4^{-2}}^b$	-1.16×10^{-2}					
$\zeta_{\text{N}_2-\text{Na}^+-\text{Cl}^-}^b$	-0.58×10^{-2}					
$\zeta_{\text{N}_2-\text{K}^+-\text{Cl}^-}^b$	-0.58×10^{-2}					
$\zeta_{\text{N}_2-\text{K}^+-\text{SO}_4^{-2}}^b$	-1.16×10^{-2}					
$\zeta_{\text{N}_2-\text{Ca}^{+2}-\text{Cl}^-}^b$	-1.16×10^{-2}					
$\zeta_{\text{N}_2-\text{Ca}^{+2}-\text{SO}_4^{-2}}^b$	-2.32×10^{-2}					
$\zeta_{\text{N}_2-\text{Mg}^{+2}-\text{Cl}^-}^b$	-1.16×10^{-2}					
$\zeta_{\text{N}_2-\text{Mg}^{+2}-\text{SO}_4^{-2}}^b$	-2.32×10^{-2}					

^a: from Appelo [30]; ^b: this work; ^c: from Geng and Duan [10].

2.4. Gas-Brine Mutual Solubility Reproduction

To validate the above thermodynamic model, comparisons are made between the gas-brine mutual solubility calculated from this model and existing experimental data including CO_2 -brine, N_2 -brine, O_2 -brine and multi-gas-brine systems.

The experimental work for CO_2 -brine system is extensive and substantial, with a wide range of temperatures, pressures and water salinities. A comparison of the CO_2 -brine system mutual solubility obtained from the experimental data and the model proposed in this work is shown in Figure 1. The experimental data for validation was mainly obtained from Todheide and Franck [35], Takenochi and Kennedy [36], Malinin and Savelyeva [37], Malinin and Kurorskaya [38],

Tabasinejad et al. [39]. As shown in the comparison, the model can well reproduce CO_2 solubility in aqueous phase with pressure ranging from 1 to more than 1000 (bar), temperature range from 0 to more than 250 ($^{\circ}\text{C}$), NaCl molality range from 0 to more than 6 (molal). The H_2O solubility in CO_2 -rich phase can also be well reproduced by this model.

Figure 1. CO_2 -brine system mutual solubility from experimental data [35–39] (dots) and results calculated by this model (lines) at various temperatures, pressures and salinities. (a) CO_2 solubility in pure water. (b) CO_2 solubility in NaCl solutions varying with pressure at different temperature and NaCl molality. (c) CO_2 solubility in NaCl solutions varying with NaCl molality at different temperatures and pressures. (d) H_2O solubility in CO_2 -rich phase at different pressures and temperatures.

A comparison of the mutual solubility of N_2 -brine obtained from the experimental data and the results calculated by this work, is shown in Figure 2. The experimental data of N_2 solubility in water or NaCl solutions are from Weibe et al. [40] and Mishnima et al. [41]. The experimental data of H_2O in N_2 -rich phase is from Althaus [42] and Namiot and Bondareva [43]. It is shown that the model of this work can well reproduce the experimental work at a wide range of temperatures, pressures and salinities.

Figure 2. N₂-brine mutual solubility obtained from experimental data [40–43] (dots) and the results calculated by the model at various values of temperature, pressure and salinity. (a) N₂ solubility in water. (b) N₂ solubility in NaCl solutions varying with pressure. (c) N₂ solubility in NaCl solutions varying with NaCl molality at 1 atm. (d) H₂O solubility in N₂-rich phase.

The experimental work on the O₂-brine system is not as comprehensive as on the CO₂-brine and N₂-brine systems. The temperature is lower than 100 (°C), and pressure is below 200 (bar). A comparison of the model results and experimental data obtained from Stephen et al. [44], Pray and Stephen [45], and Yasunishi [46] is shown in Figure 3. The model can well reproduce the existing experimental data.

Figure 3. O₂-brine mutual solubility obtained from experimental data [44–46] (dots) and the results calculated by the model (lines) at various values of temperature, pressure and salinity. (a) O₂ solubility in water. (b) O₂ solubility in NaCl solutions.

For multi-component gas mixture and brine systems, the experimental work is rare. Liu et al. [47] proposed CO₂-N₂-H₂O equilibrium experiments at two temperatures and three pressures with different CO₂-N₂ gas mixture compositions. As shown in Figure 4, the experimental results can accurately be predicted by this model.

Figure 4. CO₂-N₂-H₂O equilibria (i.e., CO₂ and N₂ mole fractions in brine varying with N₂ mole fractions in gas) obtained from experimental work (Liu et al. [47], dots) and the calculated results (lines) by the model in this work at various values of temperature and pressure. (a) at P=80 bar and T=308.15 K; (b) at P=120 bar and 308.15 K; (c) at P=160 bar and T=308.15 K; (d) at P=80 bar and T=318.15 K; (e) at P=120 bar and T=318.15 K; (f) P=160 bar and T=318.15 K.

3. Gas-Brine-Mineral Equilibria

In this section, the modeling and validation of gas-brine-mineral equilibria are discussed. When CO₂ is injected into a saline aquifer in industrial CO₂ geologic storage projects, CO₂ existence significantly influences the water-carbonate mineral equilibrium. The commonly found carbonate minerals in sedimentary environments are calcite (CaCO₃), magnesite (MgCO₃), and dolomite (CaMg(CO₃)₂). The above three minerals are considered in this work even though there are many other kinds of carbonate minerals in natural environments. The gas-brine equilibrium model was explained in detail in Section 2. This section will focus on brine-mineral equilibrium modeling and its

coupling with the gas-brine model. When the above carbonate minerals reach an equilibrium state with water/brine at a given temperature and pressure, the following chemical reactions are observed.:

where superscript ⁽⁰⁾ denotes neutral aqueous species.

Similar to Equation (1), when an equilibrium state is reached, the following equation for each of the above chemical reactions is applicable [30]:

$$K_r = \prod_i a_i^{v_i} \quad (24)$$

where K_r is the equilibrium constant of a chemical reaction “ r ”; v_i is the stoichiometric coefficient of species i of a chemical reaction “ r ”; a_i is the activity of species i of a chemical reaction “ r ”. For aqueous species i , $a_i = m_i \gamma_i$, where m_i is the molality of species i , and γ_i is the activity coefficient of species i . Activity of minerals is 1.

To solve the speciation of the brine-mineral system at equilibrium state at a given temperature and pressure, K or $\log K$ and the activity coefficients of all related reactions and species should be specified. The equilibrium constant is calculated by Equation (8) using the equilibrium constant (K_{ref}) at reference pressure (1 bar or water saturation pressure) and mole volume (V_m) of the related reaction. K_{ref} is a function of temperature and can be expressed by Equation (10). V_m is a function of temperature and pressure and can be expressed by Equation (11). For all the above reactions, the related parameters required for K_{ref} and V_m are obtained from PHREEQC database [30].

Activity coefficients (γ_i) of the aqueous species are calculated from the Pitzer [23] model. The expressions of the Pitzer [23] model can be found in Li and Duan [21]. The Pitzer parameters fall into three categories: (1) $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$ and C_{MX}^ϕ for each cation-anion pair of the species; (2) θ_{ij} for each cation-cation or anion-anion pair of the species; (3) ψ_{ijk} for each cation-cation-anion or anion-anion-cation triplet of the species, λ_{ni} for ion-neutral pairs of the species, and ζ_{nij} for cation-anion-neutral triplets of the species. The Pitzer parameters of various water-salt-mineral system have been studied since the 1980s via thermodynamic modeling in conjunction with experimental work. Table 5 lists the sources of the Pitzer parameters for the calculations of this work system.

Table 5. Literature sources of Pitzer parameters.

Pitzer Parameters	Literature Sources
$\beta_{Ca-CO_3}^{(0)}, \beta_{Ca-CO_3}^{(1)}, \beta_{Ca-CO_3}^{(2)}, C_{Ca-CO_3}^\phi$	Duan and Li [20]
$\beta_{Ca-HCO_3}^{(0)}, \beta_{Ca-HCO_3}^{(1)}$	Appelo [30]
$\beta_{Ca-Cl}^{(0)}, \beta_{Ca-Cl}^{(1)}, C_{Ca-Cl}^\phi$	Christov and Moller [19]
$\beta_{Mg-Cl}^{(0)}, \beta_{Mg-Cl}^{(1)}, C_{Mg-Cl}^\phi$	Christov and Moller [19]
$\beta_{Mg-HCO_3}^{(0)}, \beta_{Mg-HCO_3}^{(1)}, \beta_{Mg-HCO_3}^{(2)}$	Greenberg and Moller [18], Christov and Moller [19]
$\beta_{Ca-OH}^{(0)}, \beta_{Ca-OH}^{(1)}, \beta_{Ca-OH}^{(2)}$	Christov and Moller [19]
$\beta_{H-Cl}^{(0)}, \beta_{H-Cl}^{(1)}, C_{H-Cl}^\phi$	Christov and Moller [19]
$\beta_{Na-CO_3}^{(0)}, \beta_{Na-CO_3}^{(1)}, C_{Na-CO_3}^\phi$	Polya et al. [48]
$\beta_{Na-HCO_3}^{(0)}, \beta_{Na-HCO_3}^{(1)}, C_{Na-HCO_3}^\phi$	Polya et al. [48]
$\beta_{Na-OH}^{(0)}, \beta_{Na-OH}^{(1)}, C_{Na-OH}^\phi$	Pabalan and Pitzer [49]
$\beta_{Na-Cl}^{(0)}, \beta_{Na-Cl}^{(1)}, C_{Na-Cl}^\phi$	Pitzer [50]
$\theta_{H-Na}, \theta_{OH-Cl}, \theta_{OH-CO_3}, \theta_{Cl-CO_3},$ $\theta_{Cl-HCO_3}, \theta_{HCO_3-CO_3}$	Li and Duan [34]
$\theta_{Ca-H}, \theta_{Ca-Na}, \theta_{Ca-Mg}$	Christov and Moller [19]
$\psi_{OH-Cl-Na}, \psi_{OH-HCO_3-Na}, \psi_{CO_3-Cl-Na},$ $\psi_{CO_3-HCO_3-Na}, \psi_{CO_3-Cl-Ca}, \psi_{OH-Cl-Ca},$ $\psi_{CO_3-Na-OH}$	Pabalan and Pitzer [49]
$\psi_{Cl-Mg-Ca}, \psi_{Cl-Na-Ca}, \psi_{Cl-H-Ca}, \psi_{Cl-H-Mg}$	Li and Duan [34], Duan and Li [20]
	Appelo [30]

3.1. Mineral Solubility

With the thermodynamic model discussed above, the solubility of carbonate minerals (calcite, magnesite and dolomite) can be calculated in aqueous phase (with/without gases in equilibrium) at various temperatures and pressures. To validate the thermodynamic model, the existing experimental data of carbonate mineral-gas-water equilibria should be reproduced. Predictions of mineral solubilities are also made at various values of temperature, pressure and NaCl molality.

Calcite solubility experiments have usually been conducted with CO₂ in equilibrium. A comparison of the values of calcite solubility obtained from experimental data and those calculated by the proposed model at a CO₂ partial pressure of 12 (bar) at different temperatures and NaCl molalities is shown in Figure 5. This model can well reproduce the experimental data of calcite solubility, as shown in the comparison.

Figure 5. Calcite solubility in aqueous solution with CO₂ in equilibrium obtained from experimental data [51,52] and the calculated results using this model. (a) Calcite solubility varying with NaCl molality at different temperatures. (b) Calcite solubility varying with temperature at different NaCl molalities.

Calcite solubility in pure water and in NaCl solutions at various values of pressure, temperature and NaCl salinity are shown in Figure 6. Calcite solubility in pure water increases with pressure and decreases with temperature. At a given temperature and pressure, within the lower NaCl molality range (0–1.5), calcite solubility increases with NaCl molality, but decreases in the higher NaCl molality range (1.5–6).

Experimental data for magnesite solubility is rare. Bénézeth et al. [53] conducted synthetic magnesite solubility product measurements at temperatures ranging from 50 to 200 (°C) with 0.1 (molal) NaCl solutions, and with CO₂ partial pressure under 30 (bars). A comparison of Mg²⁺ molality of the solution in equilibrium with magnesite between the experimental data and calculated results is shown in Figure 7. Generally, the calculated values and measurements are comparable with calculated values a little bit higher than the measurements. Magnesite solubility in pure water or NaCl solutions at various temperatures, pressures and NaCl molalities of the solutions are shown in Figure 8. The magnesite solubility in pure water increases with pressure and decreases with temperature. In NaCl solutions, magnesite solubility increases with NaCl molality in the lower salinity range (0–1.5) but decreases in the higher salinity range (1.5–6).

Figure 6. Calcite solubility in pure water or NaCl solutions calculated by this model at different temperature, pressure and NaCl molality. (a) Calcite solubility in pure water varying with pressure at different temperatures. (b) Calcite solubility in NaCl solutions varying with NaCl molality at 343.15 (K) and various pressures.

Figure 7. Magnesite solubility calculated by this model (lines) and obtained from the experimental work of Benezeth et al. [53] (dots).

Figure 8. Magnesite solubility in pure water or NaCl solutions calculated by this work at various values of pressure, temperature and NaCl molality of the solution. (a) Magnesite solubility in pure water varying with pressure at different temperature. (b) Magnesite solubility in NaCl solutions varying with NaCl molality at 343.15 (K) and various pressures.

To address the so-called “dolomite problem”, Bénézeth et al. [54] measured natural dolomite ($\text{CaMg}(\text{CO}_3)_2$) solubility with a temperature range of 50 to 253 ($^{\circ}\text{C}$) with 0.1 (molal) NaCl solutions using a hydrogen electrode concentration cell. The logarithmic concentrations of Mg^{2+} , Ca^{2+} and H^{+} in the solution at equilibrium with dolomite are provided in the literature [54]. A comparison between the experimental results from Bénézeth et al. [54] and the results calculated using this model is shown in Figure 9. The trends of the measurements varying with temperature are also obtained by this model.

Figure 9. Aqueous species concentration in equilibrium with dolomite obtained from experimental results [54] and the calculated results by this model at various temperatures.

The presented model is used for the calculation of dolomite solubility at various values of temperature, pressure and NaCl molality, as shown in Figure 10. From the figure, it is shown that dolomite solubility in water increases with pressure and decreases with temperature. In NaCl solutions, dolomite solubility increases with NaCl molality in the lower salinity range (0–1.5) but decreases in the higher salinity range (1.5–6).

Figure 10. Dolomite solubility in pure water or NaCl solution calculated by this work at various temperatures, pressures and NaCl molalities. (a) Dolomite solubility varying with pressure at different pressures. (b) Dolomite solubility varying with NaCl molality at 343.15 (K) and various pressures.

3.2. Mutual Effects of Dissolutions of Gases and Minerals

When CO_2 is injected into a carbonate aquifer, CO_2 and carbonate mineral solubility in water are affected by each other. It has been observed in subsurface hot water recovery projects that carbonate mineral deposition usually triggers a decrease in permeability, and the subsurface fluid can be blocked [2]. CO_2 injection into water can re-dissolve the carbonate minerals. The geochemical model constructed in the previous sections can be used to evaluate the solubility effects of CO_2 and carbonated minerals. The CO_2 solubility in pure water and carbonate mineral (calcite and magnesite) saturated solutions at various values of temperature and pressure is shown in Figure 11. The results show that the dissolved mineral effects on the CO_2 solubility in water are insignificant. This is because the solubility of carbonate minerals is not significant to change the solution properties.

Figure 11. CO_2 solubility in pure water or carbonate mineral saturated solutions at different temperatures and pressures. Solid lines are CO_2 solubility in pure water. Dashed lines represent calcite saturated solutions. Dash-dot lines represent magnesite saturated solutions.

To evaluate the effects of CO_2 on solubilities of carbonate mineral influenced by CO_2 , carbonate mineral (calcite, magnesite and dolomite) solubilities in pure water and CO_2 saturated solutions are calculated using the presented model at various values of temperature and pressure (Figure 12). It is evident from the comparison that the solubility of all three carbonate minerals in water with dissolved

CO₂ is significantly increased. The increase is higher at the lower temperature (25 °C) than at the higher temperature (150 °C).

Figure 12. Carbonate mineral solubility in pure water or in CO₂ saturated solutions. (a) Calcite solubility. (b) Magnesite solubility. (c) Dolomite solubility.

3.3. Impurity Effects on Gas-Water-Mineral Equilibria

In CO₂ geologic projects, the evaluation of the effects of impurities (such as N₂, O₂) in terms of water properties (density, viscosity, pH), gas-water-mineral equilibria, and reservoir property change (porosity and permeability) is an important topic, since decreasing CO₂ purity efficiently reduces the cost of CO₂ capture. Compared to CO₂-water-mineral systems, N₂ or O₂ affects the CO₂ dissolution and solute concentration in water. At the same temperature and pressure, the presence of N₂ or O₂ in gas phase changes the fugacity of CO₂, and the CO₂ solubility in water (Figure 13). The carbonate dissolution is significantly affected by CO₂ concentration in water as shown from the calculations in the previous section.

Figure 13. Phase equilibria of CO₂-brine-calcite and CO₂-N₂-brine-calcite at 100 (°C) and 300 (bar). (a) CO₂ molality varying with NaCl molality. (b) Ca²⁺ molality and pH varying with NaCl molality; solid lines are Ca²⁺ molality, and dashed lines are pH.

4. Conclusions

CO₂ geologic storage with impurities (such as N₂ and O₂) is an important choice for reducing the cost of the full chain of CCS. However, the phase behavior of CO₂-impurities-mineral systems is key to understanding the migration, storage capacity and safety when CO₂ and impurities are injected into subsurface porous media. Rodrigues et al. [55] analyzed the CO₂ utilization and storage mechanisms of different technologies (such as CO₂ enhanced coal seam recovery and shale gas recovery). From the analysis in their work, fluid-mineral interactions and CO₂ storage capacities are dramatically different in CO₂ utilization and storage projects with different technologies. Fluid equilibrium modeling is a basis for the analysis. In this work, a thermodynamic model of CO₂-N₂-O₂-brine system equilibria is established with a temperature range from 0–250 (°C), a pressure range from 1–1000 (bar) and a NaCl molality range from 0 to more than 6 (molal). The model is validated with existing experimental data from subsystems, such as CO₂-brine, N₂-brine, O₂-brine, and CO₂-N₂-brine, in terms of gas solubility in brine and H₂O solubility in gas phase. The comparison shows that the experimental data can be well reproduced by the presented model.

When CO₂ is dissolved in an aquifer, water properties are changed in terms of pH, alkalinity, cation and anion concentrations. Mineral dissolution and precipitation are affected by the water property change. In this work, the thermodynamic model of CO₂-N₂-O₂-brine system is extended to CO₂-N₂-O₂-brine-carbonate (mainly calcite, magnesite and dolomite) systems. With the new gas-water-mineral geochemical model, the following calculations can be performed:

The mineral solubility can be calculated with CO₂ and/or other impurity gas components (N₂ and O₂) dissolved. The comparisons with existing experimental data show that carbonate (calcite, magnesite and dolomite) solubility can be reproduced well by the presented model. It is also shown by the calculations at various values of temperature and pressure that carbonate solubilities raise considerably with CO₂ dissolved in brine.

Gas solubility in brine affected by carbonate dissolution in water is evaluated by the model. The effects of carbonate dissolution are not significant, because there is a lower level of mineral solubility in water.

Ion concentrations and pH can be calculated by the model at various temperatures, pressures and salinities. The effects of gas impurities on pH and Ca²⁺ concentration are evaluated in this work. When CO₂ is mixed with N₂ or O₂, less mineral dissolution, lower Ca²⁺ concentration and higher pH can be observed from the calculation. The change is mainly because of the CO₂ fugacity reduction in gas phase with the presence of N₂ or O₂, and the effect of N₂ or O₂ dissolution is not significant.

To address the validation of the model, future work should supply experimental measurements of phase behaviors of more complex systems at various temperatures and pressures, such as

phase equilibrium of CO₂-O₂-brine and CO₂-N₂-O₂-brine, and carbonate dissolved water properties (i.e., different ion concentrations, pH and/or alkalinity) with different levels of CO₂, N₂ and/or O₂ in the system. In real geologic systems, geochemical reactions are much more complicated. More work is still needed to assess the impurity effects on gas-water-mineral geochemical behaviors, especially when there are redox reactions in the systems. In future work, minerals with different chemical valences such as sulfides and sulfates will be considered to evaluate influences of oxygen.

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