

Research Article

A Geochemical Model of Fluids and Mineral Interactions for Deep Hydrocarbon Reservoirs

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Received 19 February 2017; Accepted 12 June 2017; Published 16 July 2017

Academic Editor: Keyu Liu

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A mutual solubility model for CO₂-CH₄-brine systems is constructed in this work as a fundamental research for applications of deep hydrocarbon exploration and production. The model is validated to be accurate for wide ranges of temperature (0–250°C), pressure (1–1500 bar), and salinity (NaCl molality from 0 to more than 6 mole/KgW). Combining this model with PHREEQC functionalities, CO₂-CH₄-brine-carbonate-sulfate equilibrium is calculated. From the calculations, we conclude that, for CO₂-CH₄-brine-carbonate systems, at deeper positions, magnesium is more likely to be dissolved in aqueous phase and calcite can be more stable than dolomite and, for CO₂-CH₄-brine-sulfate systems, with a presence of CH₄, sulfate ions are likely to be reduced to S²⁻ and H₂S in gas phase could be released after S²⁻ saturated in the solution. The hydrocarbon “souring” process could be reproduced from geochemical calculations in this work.

1. Introduction

With the exploration and production of middle-shallow oil and gas reservoirs, the main oil/gas fields have come to the late stages of production. More and more intensive exploration work has been done on middle-shallow fields and it is not easy to achieve more breakthroughs. So, researchers are devoting more efforts in deep reservoirs (with depth more than 5000 m). In China, the depositional environment is quite complex and special, so abundant hydrocarbon resources are possible. From the drilling evidence, an effective hydrocarbon reserve was found at more than 7000 m depth in China [1]. More and more research on deep layer hydrocarbon exploration has been carried out in recent years.

For deep hydrocarbon research, fluid-rock interaction is an important topic, as it will influence the fluid composition, physical and chemical properties, and transportation in porous media. The geochemical reactions are more active at locations with both gas and water, such as so-called gas-water transition zones [2, 3]. When gas and water contact, both gas components and mineral will be dissolved in water, and many

geochemical reactions could be triggered. In Sichuan basin, H₂S can usually be found from gas reservoirs. The existence of H₂S can be a result of geochemical reactions of dissolved hydrocarbon and sulfates. It is called “souring” process in some literature [2].

Numerical modeling of geochemistry is a useful tool to understand the mechanism of fluid-mineral interactions in deep reservoirs. PHREEQC is one of the most popular geochemistry software packages in hydrological applications [4]. The speciation in water associated with hundreds of chemical reactions can be dealt with. TOUGHREACT is a 3D reactive transportation simulator which is able to calculate geochemical reactions with similar database as PHREEQC [5]. This simulator has been widely used in CO₂ geological storage and geothermal recovery projects. Both of the software programs are powerful for geochemical reaction analysis in porous media. However, for fluid-mineral interactions in deep reservoir, gas-brine phase partitioning and speciation should be carefully considered due to high temperature and pressure. In gas reservoirs, CO₂ usually exists with quite a bit amount of hydrocarbons. So, in this work, we establish a

mutual solubility model for CO₂-CH₄-brine systems, which is accurate for a pressure range of 1 bar to 1500 bar, temperature range of 0°C to 250°C, and salinity range of 0 to 6 m. With the solubility calculated by the model, PHREEQC is used to calculate equilibrium of CO₂-CH₄-brine-minerals (carbonates and sulfates).

2. CO₂-CH₄-Brine Mutual Solubility Modeling

We assume that there are two fluid phases (i.e., aqueous phase and nonaqueous phase) existing at given temperature, pressure, and feed composition. CO₂ or CH₄ always dominates nonaqueous phase. Their solubilities in water and H₂O content in nonaqueous phase are desired to be accurately reproduced by a thermodynamic model. In equilibrium state, for each component in the system (e.g., component i), the chemical potential in each phase should be equal. Then we have,

$$\mu_i^{\text{NA}} = \mu_i^{\text{AQ}}. \quad (1)$$

For nonaqueous phase,

$$\begin{aligned} \mu_i^{\text{NA}}(T, P, y_i) &= \mu_i^{\text{NA}(0)}(T) + RT \ln f_i(T, P, y_i) \\ &= \mu_i^{\text{NA}(0)}(T) + RT \ln y_i P \\ &\quad + RT \ln \varphi_i(T, P, y_i), \end{aligned} \quad (2)$$

where $\mu_i^{\text{NA}(0)}(T)$ stands for standard chemical potential of component i , which is the ideal gas chemical potential at the pressure of 1 bar [6, 7]; y_i is mole fraction of component i in nonaqueous phase; f_i is fugacity and φ_i is fugacity coefficient; R is the gas constant (8.31446 J/K/mol); T is temperature in K; and P is pressure in bar hereafter.

For aqueous phase,

$$\begin{aligned} \mu_i^{\text{AQ}}(T, P, m_{\text{sol}}) &= \mu_i^{\text{AQ}(0)}(T, P) + RT \ln a_i(T, P, m_{\text{sol}}) \\ &= \mu_i^{\text{AQ}(0)}(T, P) + RT \ln (Nw \times x_i) \\ &\quad + RT \ln \gamma_i(T, P, m_{\text{sol}}), \end{aligned} \quad (3)$$

where $\mu_i^{\text{AQ}(0)}$ is the standard chemical potential of species i in an ideal aqueous solution with a hypothetical unit molality [8]; m_{sol} is the molality (in mole/Kg water, molal for short hereafter) of salt in the aqueous phase; Nw is the mole number of 1 kg water (55.508); x_i is the mole fraction of species i dissolved in the aqueous phase; a_i is activity of component i in aqueous phase; and γ_i is activity coefficient of component i .

With (1) to (3), we have

$$\frac{\mu_i^{\text{AQ}(0)} - \mu_i^{\text{NA}(0)}}{RT} = \ln \left(\frac{f_i}{a_i} \right). \quad (4)$$

Here, equilibrium constant is defined as $\ln(K_i) = (\mu_i^{\text{AQ}(0)} - \mu_i^{\text{NA}(0)})/RT$, so we have

$$y_i \varphi_i P = Nw K_i x_i \gamma_i. \quad (5)$$

TABLE 1: Parameters of H₂O equilibrium constant in (6).

Parameters	$T > 373.15 \text{ K}$	$T \leq 373.15 \text{ K}$
a_1	$-9.0283127E - 1$	$9.31063597E0$
a_2	$3.6492938E - 2$	$-1.892867005E - 1$
a_3	$4.3610019E - 4$	$1.307135652E - 3$
a_4	$-3.10936036E - 6$	$-3.800223763E - 6$
a_5	$4.5920530E - 9$	$4.0091369717E - 9$
a_6	$1.62996873E1$	$2.2769246863E1$
a_7	$2.81119409E - 2$	$-1.1291330188E - 2$

The mutual solubility model of CO₂-CH₄-brine system is established based on the above principle. Equilibrium constants (K_i), fugacity coefficients (φ_i), and activity coefficients (γ_i) should be properly carefully obtained.

2.1. Equilibrium Constants. For equilibrium constant of H₂O, we follow the work of Li et al. [7] with an empirical equation revised from Spycher et al. (2003):

$$\begin{aligned} K_{\text{H}_2\text{O}}(T, P) &= (a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \\ &\quad \cdot \exp \left(0.1 \frac{(P - 1)(a_6 + a_7 T)}{RT} \right). \end{aligned} \quad (6)$$

The parameters (a_1 to a_7) in (6) are all from Li et al. [7], listed in Table 1.

For equilibrium constants of CO₂ and CH₄, we follow the form of Mao et al. (2013):

$$\begin{aligned} \ln K_i &= b_1 + b_2 T + \frac{b_3}{T} + b_4 T^2 + \frac{b_5 P}{T^2} + b_6 P + b_7 P T \\ &\quad + \frac{b_8 P}{T} + b_9 P T^2 + b_{10} P^2 T + b_{11} P^3, \end{aligned} \quad (7)$$

where $i = \text{CO}_2, \text{CH}_4$. b_i ($i = 1, 2, \dots, 11$) are parameters. The parameters are determined from experimental data of gas solubility in aqueous phase. See Table 2 for more details.

2.2. Fugacity Coefficients. Peng-Robinson equation of state (PR-EOS for short [9]) is used from CO₂, CH₄, and H₂O fugacity coefficients in the nonaqueous phase. PR-EOS is a classic two-parameter equation of state of cubic form. The related parameters of pure component systems can be found from the original work of Peng and Robinson [9]. For gas mixtures, mixing rule is used for the two parameters.

$$\begin{aligned} a &= \sum_i \sum_j y_i y_j a_{ij} \\ b &= \sum_i b_i y_i, \end{aligned} \quad (8)$$

where $a_{ij} = \sqrt{a_i a_j} (1 - \delta_{ij})$ and δ_{ij} are binary interaction parameters of species i and j . Binary interaction parameters for CO₂, CH₄, and H₂O can be found in Table 3 according to Søreide and Whitson [10].

TABLE 2: Parameters of CO₂ and CH₄ equilibrium constants in (7).

	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}	b_{11}
CO ₂	2.302E-1	-3.654E-2	-1.8367E3	2.0331E-5	-3.9072E5	-5.8269E-2	1.5062E-2	7.8087E0	-1.3013E-7	1.1145E-9	-1.3074E-10
CH ₄	-1.6388E1	3.2371E-2	9.4682E3	-2.6573E-5	-1.4353E6	-1.3225E-2	3.1305E-5	2.2605E0	-2.9063E-8	3.4408E-9	-6.11809E-10

TABLE 3: Binary interaction parameter in PR-EOS.

δ_{ij}	H ₂ O	CO ₂	CH ₄
H ₂ O	—	0.19014	0.485
CO ₂	0.19014	—	0.1196
CH ₄	0.485	0.1196	—

2.3. Activity Coefficients. For activity coefficients, Pitzer model [11] was successfully used in gas-water-mineral modeling for high salinities in previous works [12–15]. Cations, anions, and interaction between particle pairs are considered to influence the component activity behaviors in aqueous phase. The activity coefficient equations are as follows:

$$\ln \gamma_i = \sum_c 2m_c \lambda_{i-c} + \sum_a 2m_a \lambda_{i-a} + \sum_c \sum_a m_a m_c \zeta_{i-a-c}, \quad (9)$$

where m_c is cation molality, m_a is anion molality, and λ_{i-c} , λ_{i-a} , and ζ_{i-a-c} are parameters that are functions of temperature and pressure. λ_{i-c} , λ_{i-a} , and ζ_{i-a-c} are known as Pitzer parameters and they are usually estimated from gas solubility data from aqueous solutions with dissolved salts. In this work, Pitzer parameters are usually calibrated from gas solubility from NaCl solutions. $\lambda_{i-\text{Cl}^-}$ is assumed to be 0. As the approximation in Duan and Sun [14] and Duan et al. [16], $\lambda_{i-\text{monovalent}}$ and $\lambda_{i-\text{bivalent}}$ are estimated as $\lambda_{i-\text{Na}^+}$ and $2\lambda_{i-\text{Na}^+}$. All ternary parameters are estimated as $\zeta_{i-\text{Na}-\text{Cl}}$. Pitzer parameters are listed in Table 4.

2.4. Model Validation. The model performance is evaluated from comparison of model results and related experimental data of CO₂-CH₄-brine systems (including the subsystems).

For CO₂-H₂O-NaCl systems, the experimental studies [17–19] are sufficient, which cover temperature from 0°C to more than 250°C and pressure from 1 bar to more than 1500 bar. From our comparison, the average absolute derivations for most of the data points are less than 10%. Figures 1(a) and 1(b) show a comparison of CO₂ solubilities in pure water and NaCl solutions calculated from this model and related experimental data. We can find that the model solutions agree with the experimental data in the wide ranges of temperature, pressure, and salinity. Figure 1(c) shows the H₂O solubility in nonaqueous (CO₂-rich) phase of the model solutions and experimental data. From the figure, the model can well reproduce H₂O solubility in nonaqueous phase.

Experimental data of CH₄-H₂O-NaCl system are also sufficient with temperature from 0 to more than 250°C and pressure from 1 bar to more than 1500 bar [20]. Figures 2(a) and 2(b) show the comparison of CH₄ solubilities in water and NaCl solutions of experimental data and this model. Figure 2(c) shows the experimental data of H₂O in nonaqueous (CH₄-rich) phase and the related model solutions. From the comparisons, the experimental data can be well reproduced by the model.

Compared with single gas (CO₂ or CH₄)-brine systems, gas mixture (CO₂ and CH₄ existing at the same time)-brine systems have less experimental data. The existing data are also not systematic. Qin et al. [21] have studied phase equilibria for CO₂-CH₄-H₂O system at 325 K and 376 K and with pressure

from 100 bar to 500 bar. 21 data points were generated in the work. We compared their results with our model. From the comparison (see Figure 3), we can conclude that the model can predict mutual solubilities for CO₂-CH₄-H₂O system.

In summary, the comparison of the model solutions with existing experimental data shows that the model can well reproduce and predict mutual solubility data of CO₂-CH₄-brine systems in wide ranges of temperature, pressure, and salinity. The model is reliable to be used in gas-water-mineral equilibrium analysis.

3. CO₂/CH₄-Water-Mineral Interactions in Deep Environments

In Sichuan basin, carbonates (such as dolomite or calcite) are the dominant minerals in some natural gas reservoirs; meanwhile sulfates (such as gypsum or anhydrite) and clay minerals are also commonly found [22, 23]. In Sichuan natural gas reservoirs, CH₄ is always accompanied with other components such as CO₂, N₂, or H₂S [24]. PHREEQC is a famous software package for water-mineral interaction calculations. Pressure effects can be considered using its third version [4]. With an accurate mutual solubility model of CO₂-CH₄-brine systems, geochemical reactions in CO₂-CH₄-water-mineral systems can be calculated by combining this model and the PHREEQC functionality. Through this research, we aim to find out

- (i) the influences on geochemical reactions in depth (i.e., temperature and pressure increase or decrease);
- (ii) sensitivity of gas components (i.e., CO₂ or CH₄) to water composition, mineral dissolution, or precipitation.

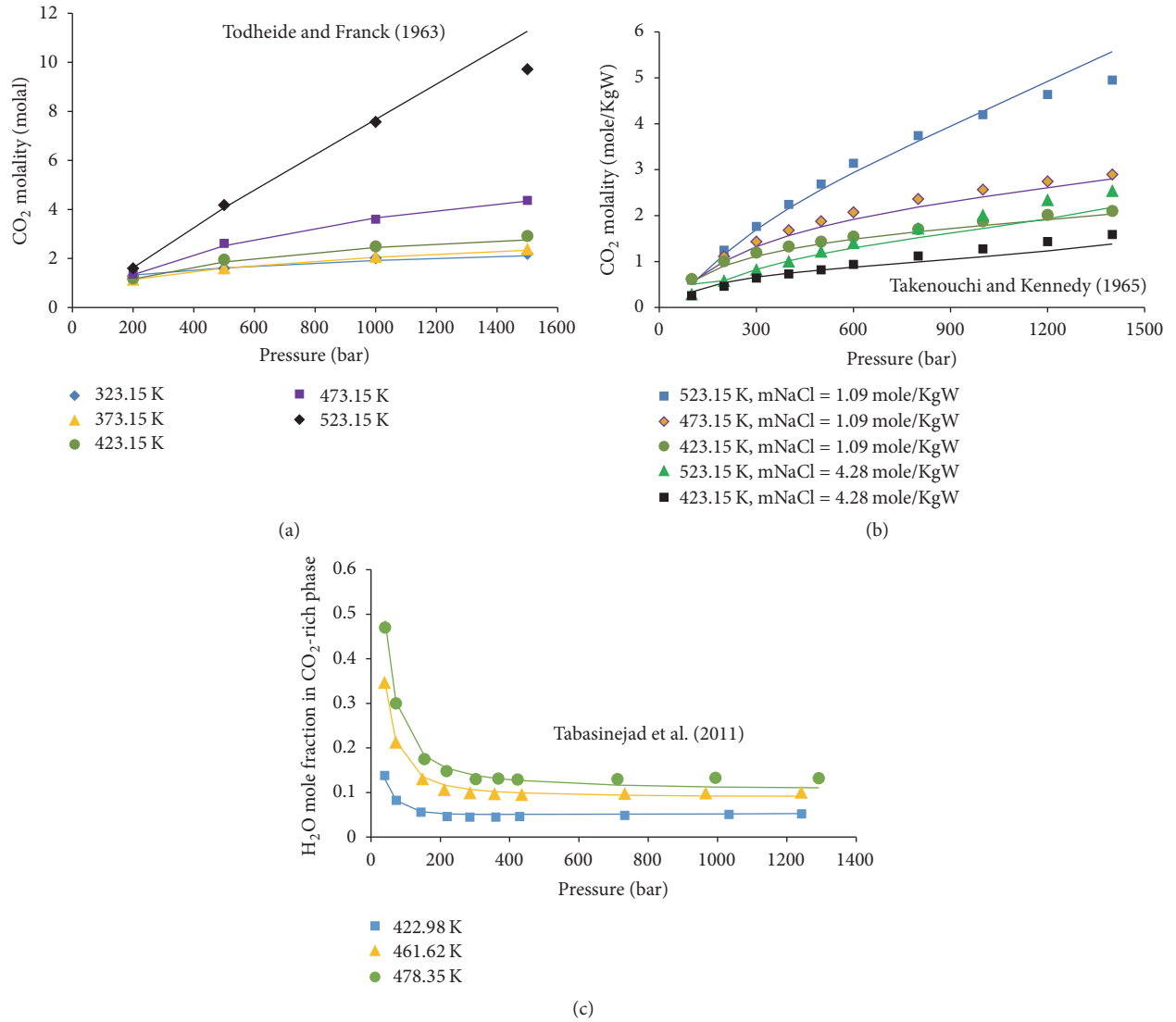
In this work, the calculations are based on Sichuan basin background. The hydrostatic pressure is assumed to be 100 bar/Km, and geothermal gradient is assumed as 25°C/Km according to a previous work [25] with surface temperature set as 25°C. The depth range of the research is from 3000 m to 6000 m. Relationships of depth, temperature, and pressure are shown in Figure 4. To clarify the influences from gas components, sodium chlorite is considered as the only salt that is dissolved in water as an initial solution. Geochemistry equilibrium of CO₂-CH₄-brine-dolomite, CO₂-CH₄-brine-calcite, and CO₂-CH₄-brine-gypsum/anhydrite systems is studied. Two gas compositions are considered, pure CH₄ or 10% CO₂ + 90% CH₄, to evaluate CO₂ influences.

Table 5 lists the species of ions, minerals, and gases which get involved in geochemical reactions in CO₂-CH₄-brine-carbonate systems and CO₂-CH₄-brine-sulfate systems.

3.1. CO₂-CH₄-Brine-Carbonate Systems. For CO₂-CH₄-brine-carbonate systems, cases of fluid equilibrium with calcite and dolomite are studied, respectively. Figure 5 shows the molality of carbon (including HCO₃⁻, CO₂, CaHCO₃⁺, CaCO₃, CO₃²⁻, MgHCO₃⁻, and MgCO₃) dissolved in aqueous phase with different depths, gas compositions, and salinities. Figure 6 shows the molality of calcium (including Ca²⁺, CaCO₃, CaHCO₃⁺, and CaOH⁺) and magnesium

TABLE 4: Pitzer parameters for activity coefficients.

Parameters	Equations
$\lambda_{\text{CO}_2\text{-Na}^+}$	$-3.1312239 \times 10^{-1} + 5.532647 \times 10^{-4}T + 7.5844401 \times 10^1/T - 1.8950519 \times 10^{-4}P + 7.1628762 \times 10^{-5}P/T - 1.458572 \times 10^{-8}P^2T$
$\lambda_{\text{CH}_4\text{-Na}^+}$	$-5.7066455 \times 10^{-1} + 7.2997588 \times 10^{-4}T + 1.5176903 \times 10^2/T + 3.1927112 \times 10^{-5}P - 1.642651 \times 10^{-5}P/T$
$\lambda_{\text{H}_2\text{S-Na}^+}$	$1.03658689 - 1.1784797 \times 10^{-3}T - 1.7754826 \times 10^2/T - 4.5313285 \times 10^{-4}P + 4.775165 \times 10^1P/T^2$
$\zeta_{\text{CO}_2\text{-Na}^+\text{-Cl}^-}$	$-1.14462 \times 10^{-2} + 2.8274958 \times 10^{-5}T + 1.3980876 \times 10^{-2}P/T - 1.4349005 \times 10^{-2}P/(630 - T)$
$\zeta_{\text{CH}_4\text{-Na}^+\text{-Cl}^-}$	$-2.9990084 \times 10^{-3}$
$\zeta_{\text{H}_2\text{S-Na}^+\text{-Cl}^-}$	$-1.0274152 \times 10^{-2}$

FIGURE 1: Mutual solubilities of CO₂-brine systems. Lines are calculated results from this model, and dots are from experimental data. (a) CO₂ solubility in pure water; (b) CO₂ solubility in NaCl solutions; (c) H₂O solubility in CO₂-rich phase.

(including Mg^{2+} , MgOH^+ , MgCO_3 , and MgHCO_3^+) that is dissolved in aqueous phase. From Figure 6, it is shown that CO₂ in the gas phase will promote calcite or dolomite dissolution. From the calculations, we find that, with CO₂ existing in the system, carbon concentration in aqueous

phase increases with depth. From 3000 m to 6000 m, the carbon molality is almost doubled in Figure 5 at different salinities. However, compared with calcium, magnesium is more solvable and increases with depth. From our calculation, in fluid-dolomite systems, with an increase in

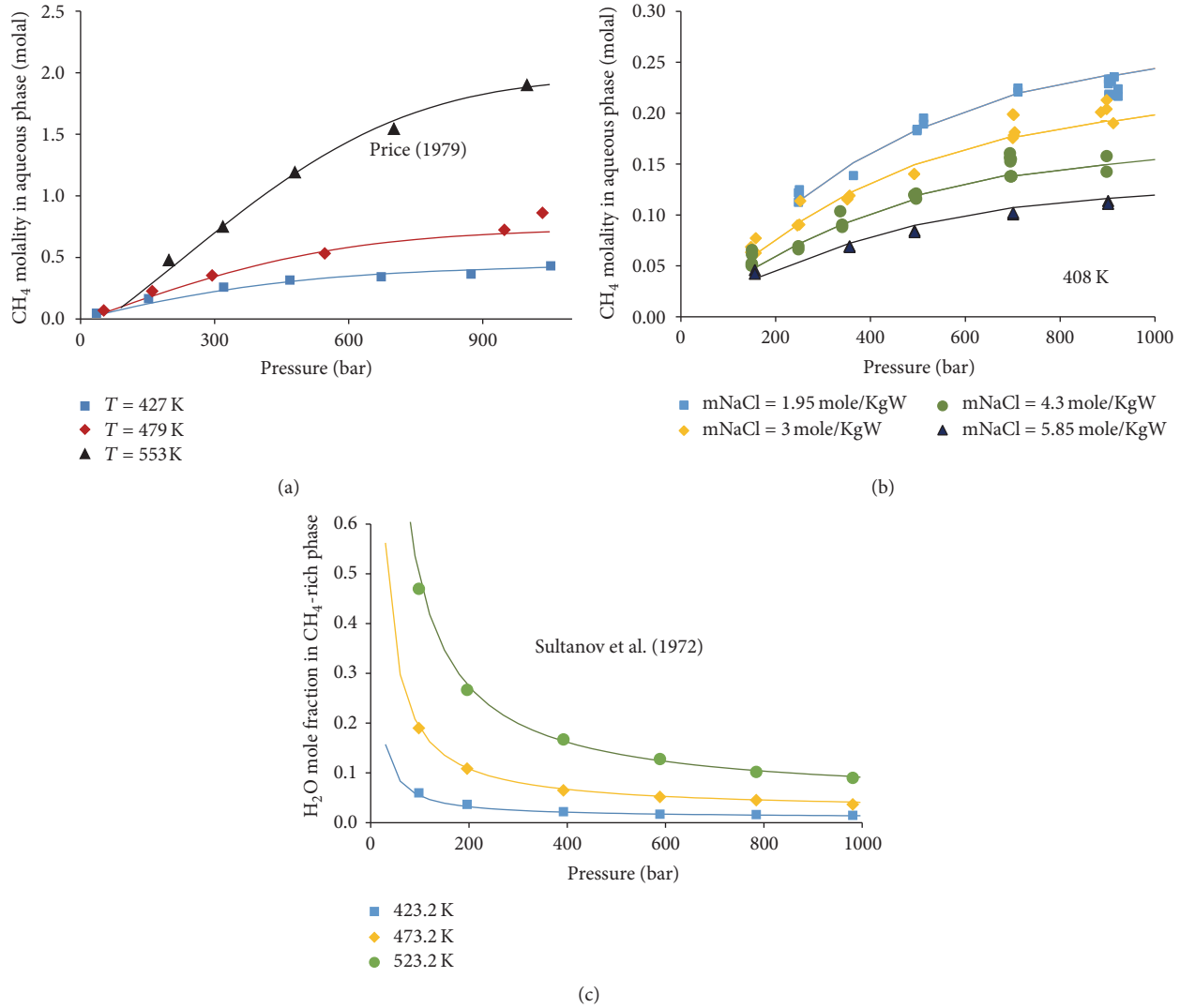


FIGURE 2: Mutual solubilities of CH₄-brine systems. Lines are calculated results from this model, and dots are from experimental data. (a) CH₄ solubility in pure water; (b) CH₄ solubility in NaCl solutions; (c) H₂O solubility in CH₄-rich phase.

temperature and pressure, more calcite precipitates. We can conclude that, in deep carbonate environments, calcium is more likely to precipitate and magnesium ion is more likely to be rich in aqueous phase and transport to shallower areas due to diffusion gradient. So, in general, calcite approaches being existing in deeper environments and dolomite is more likely to be existing in shallower environments.

3.2. CO₂-CH₄-Brine-Sulfate Systems. The element sulfur can have different chemical valences such as -2, 0, +4, and +6 in nature. When sulfates are dissolved in water, sulfur is usually in +6 valence state. It could be reduced to other valence states when reducer exists in the solution. In deep gas reservoirs in Sichuan basin, sulfates commonly exist. Different fluid compositions may trigger different redox geochemical reactions and lead to different forms of sulfur or even reservoir properties.

In this work, we perform several numerical experiments to evaluate the influence of gas composition and depth on fluid-mineral equilibrium. For gas composition, we considered three cases: pure CH₄, 10% CO₂ + 90% CH₄, and pure CO₂. The calculations covered depth from 3000 m to 6000 m. Figure 7 presents S(-2) (i.e., sulfur dissolved in water with chemical valence -2, which can be S²⁻, HS⁻, and H₂S as ions) and S(+6) (i.e., sulfur dissolved in water in chemical valence +6, which can be SO₄²⁻, HSO₄⁻, CaSO₄, and CaHSO₄⁺) concentration in equilibrium of gas-water-gypsum. From Figure 7, we can find the following:

- (1) With pure CO₂ in gas, S(-2) in water is extremely low, and more CH₄ is dissolved in water leading to higher S(-2) concentration.
- (2) Higher CO₂ mole fraction in gas phase will lead to higher S(+6) concentration in water phase.

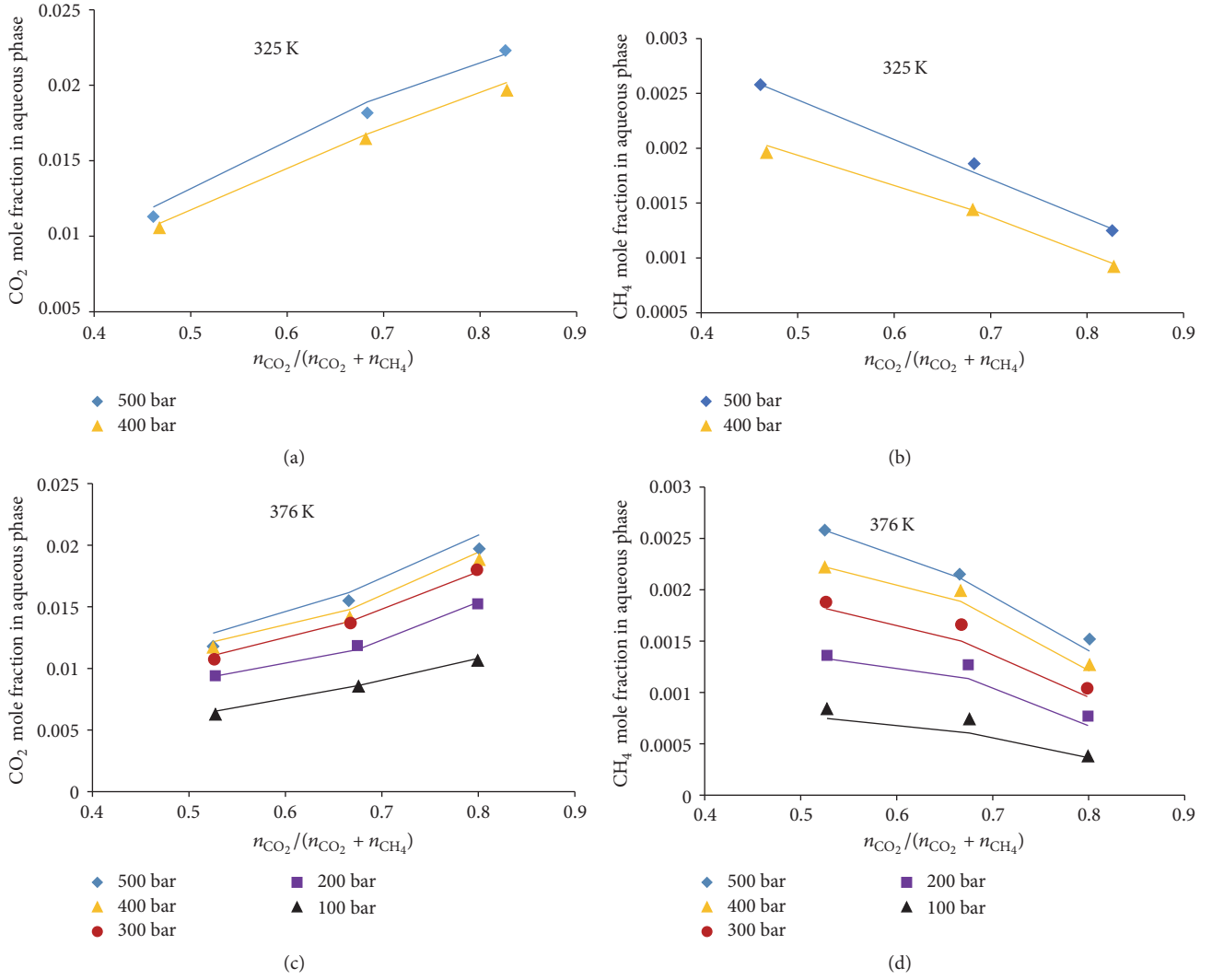


FIGURE 3: CO_2/CH_4 solubilities in water in $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O}$ systems at different temperature and pressure. Dots are from Qin et al.'s [21] experimental data, and lines are from this model.

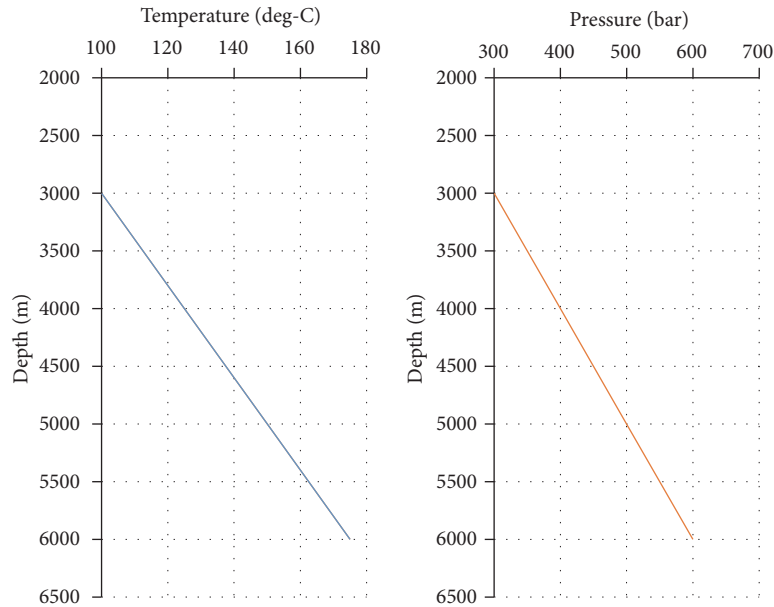


FIGURE 4: Temperature, pressure, and depth relationships.

TABLE 5

(a) Ions, minerals, and gases involved in CO₂-CH₄-brine-carbonate systems

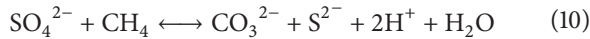
Cations	Anions	Neutral ions	Minerals and gases
H ⁺	OH ⁻	H ₂ O	Aragonite
Ca ²⁺	HCO ₃ ⁻	CH ₄	Calcite
CaHCO ₃ ⁺	CO ₃ ²⁻	CO ₂	Dolomite
CaOH ⁺	Cl ⁻	(CO ₂) ₂	Halite
Mg ²⁺	NaCO ₃ ⁻	CaCO ₃	CH ₄ (g)
MgHCO ₃ ⁺		H ₂	CO ₂ (g)
MgOH ⁺		MgCO ₃	H ₂ (g)
Na ⁺		NaHCO ₃	H ₂ O (g)
		NaOH	O ₂ (g)
		O ₂	

(b) Ions, minerals, and gases involved in CO₂-CH₄-brine-sulfate systems

Cations	Anions	Neutral ions	Minerals and gases
H ⁺	OH ⁻	H ₂ O	Anhydrite
Ba ²⁺	HCO ₃ ⁻	BaSO ₄	Aragonite
BaHCO ₃ ⁺	NaCO ₃ ⁻	BaCO ₃	Barite
BaOH ⁺	CO ₃ ²⁻	NaHCO ₃	Calcite
CaHCO ₃ ⁺	Cl ⁻	CaCO ₃	Dolomite
MgHCO ₃ ⁺	NaSO ₄ ⁻	(CO ₂) ₂	Gypsum
Ca ²⁺	HS ⁻	MgCO ₃	Halite
CaHSO ₄ ⁺	S ²⁻	CaSO ₄	Sulfur
CaOH ⁺	SO ₄ ²⁻	MgSO ₄	Witherite
Mg ²⁺	HSO ₄ ⁻	NaOH	H ₂ (g)
MgOH ⁺		O ₂	H ₂ O (g)
Na ⁺		H ₂ S	H ₂ S (g)
		H ₂	O ₂ (g)
		CH ₄	CH ₄ (g)
		CO ₂	CO ₂ (g)

(3) With higher depth, higher S(+6) concentration can be found, but depth influence on S(-2) concentration is not clear.

It is clear that CH₄ is the key component for S(+6) to be reduced to S(-2) species in water. The related redox geochemical reaction is



When CH₄ and SO₄²⁻ are dissolved in water, the above reaction is triggered, and CH₄ is oxidized from C(-4) to C(+4). In the meantime, SO₄²⁻ is reduced to S²⁻.

Figure 8(a) shows the amount of calcite precipitation for different cases of geochemical equilibrium. Referring to Figure 8(a), in case of pure CO₂ in gas phase, there is no calcite precipitation; with higher CH₄ mole fraction in gas phase, more calcite can be precipitated; in deeper environments, more calcite can be precipitated. This phenomenon is also connected with sulfur reduction. With CH₄ dissolved in water, more sulfate is consumed and more calcium ions are dissolved in water. In this process, carbanions are generated because of the redox reaction. With more and more calcium

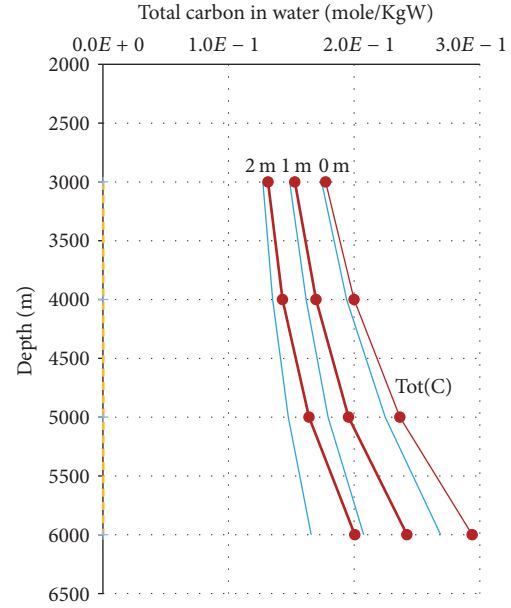


FIGURE 5: Molality of total carbon dissolved in water varying with depth at different salinities and gas compositions. Dashed yellow line represents the case of pure CH₄ of gas in the system. Blue lines represent results from fluid-calcite systems (with gas composition CO₂:CH₄ = 1:9 in mole). Red lines with dots represent the result from fluid-dolomite systems (with gas composition CO₂:CH₄ = 1:9 in mole).

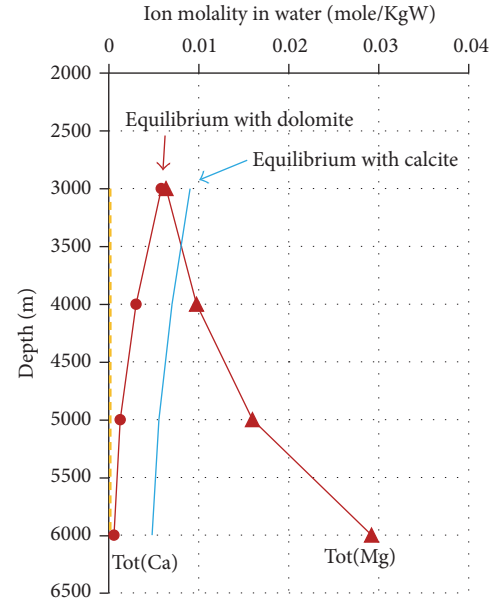


FIGURE 6: Molality of elements Ca and Mg dissolved in water varying with depth (with sodium chloride molality 0). Yellow line represents the case of pure CH₄ of gas in the system. Red lines with dots represent results from fluid-dolomite systems (with gas composition CO₂:CH₄ = 1:9 in mole). Blue line represents results from fluid-calcite systems (with gas composition CO₂:CH₄ = 1:9 in mole).

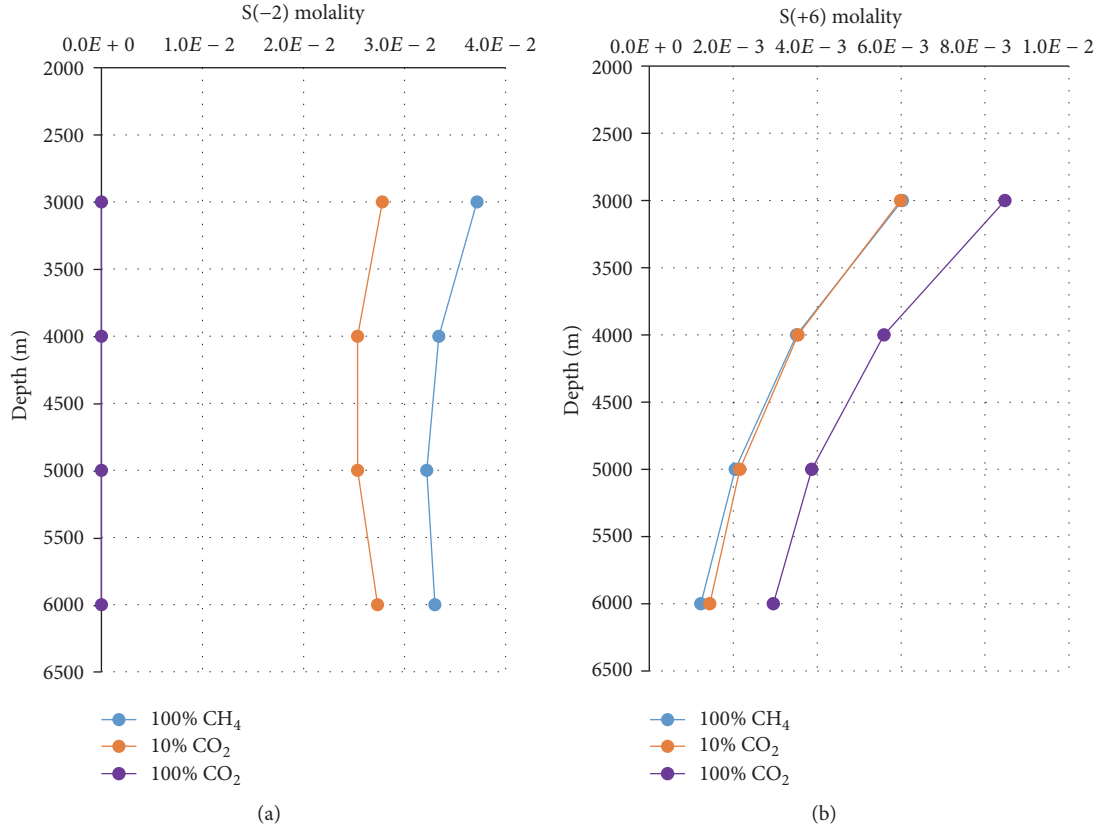


FIGURE 7: Concentration of S(+6) and S(-2) in aqueous phase varying with depth in equilibrium of gas (pure CH₄, 10% CO₂ + 90% CH₄, or pure CO₂), water, and gypsum.

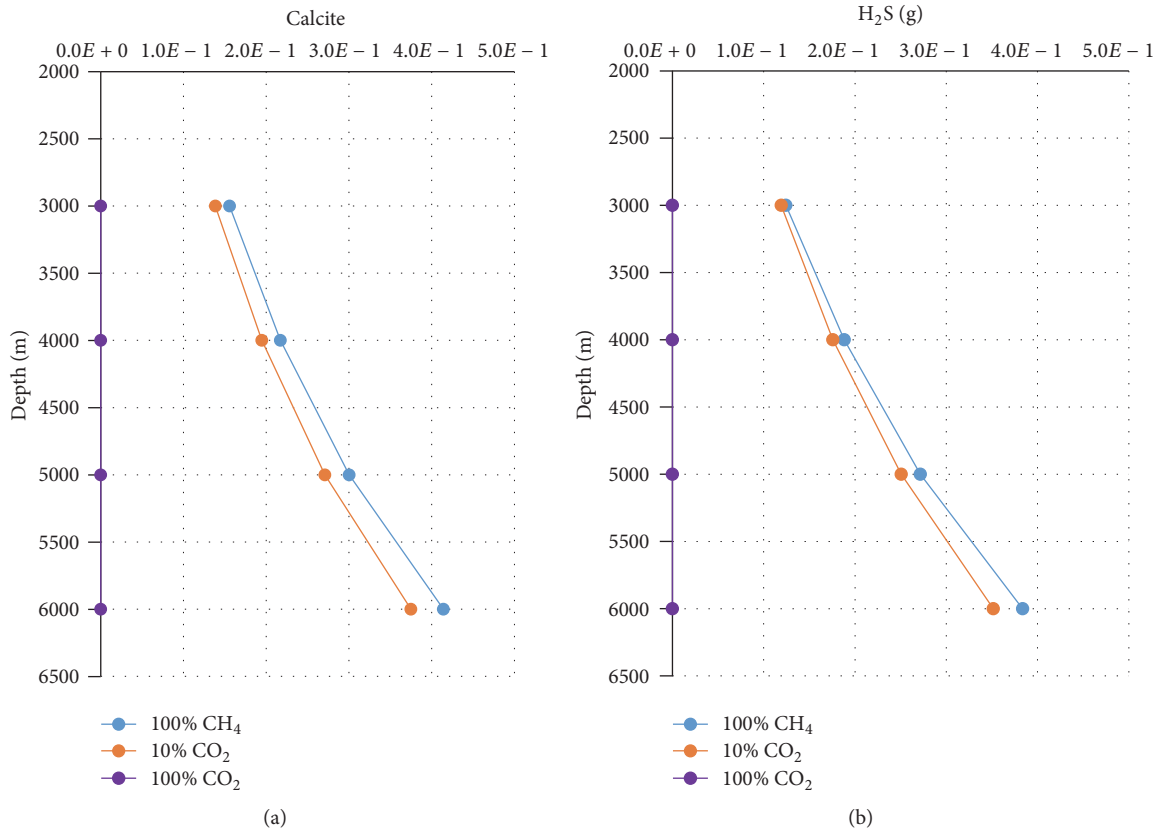


FIGURE 8: (a) Mole number of calcite precipitated and (b) mole number of H₂S released to gas with 1 KG water in equilibrium with gas (pure CH₄, 10% CO₂ + 90% CH₄, or pure CO₂) and gypsum at different depths.

and carbanion in the solution, calcite becomes saturated and precipitates. Another product is H_2S in gas phase. With more and more $\text{S}(-2)$ generated in water, S^{2-} and H^+ approach combining with one another, and H_2S becomes saturated and is released in gas phase. As shown in Figure 8(b), with more CH_4 in gas phase, more H_2S will be generated in gas phase at equilibrium states. From this study, we can find that CH_4 -water-sulfate redox reaction could be a mechanism of H_2S origin in gas reservoirs [2]. From the figure, we can also find that, at higher depth, more H_2S can be generated. This result agrees with the statement from Li et al. [2].

4. Conclusions

In this work, an accurate mutual solubility model is constructed with “fugacity-activity” method for CO_2 - CH_4 -brine systems. This model has a wide application range of pressure, temperature, and salinity, which can be used for fluid phase equilibrium in deep hydrocarbon reservoirs.

Combined with the mutual solubility model and PHREEQC, the equilibrium CO_2 - CH_4 -brine-mineral systems under deep reservoir conditions can be calculated. The mutual solubility model can be used to calculate the mole numbers of CO_2/CH_4 dissolved in brine at given temperature, pressure, and salinity. With the dissolved mole numbers of CO_2/CH_4 , PHREEQC is used to calculate the speciation between aqueous phase and mineral.

CO_2/CH_4 -brine-carbonate (i.e., dolomite or calcite) and CO_2/CH_4 -brine-sulfate (i.e., gypsum or anhydrite) equilibria were studied with the above methodology. From the study, we find the following:

- (1) For CO_2/CH_4 -brine-carbonate (calcite or dolomite) systems, with an increase in depth, calcium is more likely to precipitate as calcite and magnesium is more likely dissolved in aqueous phase. In other words, dolomite could be rich in shallower position and calcite may approach being existing at deeper locations.
- (2) With CH_4 present in the CO_2/CH_4 -brine-sulfate (gypsum or anhydrite) systems, redox reaction is triggered and $\text{S}(+6)$ is reduced to $\text{S}(-2)$. H_2S will be released when $\text{S}(-2)$ becomes saturated in aqueous phase. This process could be one of the origins for H_2S in gas reservoirs in Sichuan basin, China.

This work is an attempt to do preliminary fluid-mineral interaction calculations with a new established accurate mutual solubility model of CO_2 - CH_4 -brine systems combined with PHREEQC, version 3. The geochemical reaction parameters are still needed to be validated for high temperature and pressure. Also, more systematic research work of gas-water-minerals is still required in the future according to real depositional environments.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This work is supported by National Natural Science Foundation of China (Grant no. 41502246). Dimue Tech. Ltd. Co. provided technical support during the research. The authors also acknowledge the sponsorship from National Key R&D Program of China (2016YFE0102500).

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