Research Article

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

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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,

\[
\mu_i^{\text{NA}} = \mu_i^{\text{AQ}}. \tag{1}
\]

For nonaqueous phase,

\[
\mu_i^{\text{NA}}(T, P, y_i) = \mu_i^{\text{NA}(0)}(T) + RT \ln f_i(T, P, y_i) = \mu_i^{\text{NA}(0)}(T) + RT \ln y_i P + RT \ln \varphi_i(T, P, y_i), \tag{2}
\]

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 \(\varphi_i\) 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,

\[
\mu_i^{\text{AQ}}(T, P, m_{\text{sol}}) = \mu_i^{\text{AQ}(0)}(T, P) + RT \ln a_i(T, P, m_{\text{sol}}) = \mu_i^{\text{AQ}(0)}(T, P) + RT \ln (Nw \times x_i) + RT \ln y_i(T, P, m_{\text{sol}}), \tag{3}
\]

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]; \(m_{\text{sol}}\) 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 \(y_i\) is activity coefficient of component \(i\).

With (1) to (3), we have

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

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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>(T &gt; 373.15) K</th>
<th>(T \leq 373.15) K</th>
</tr>
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<tbody>
<tr>
<td>(a_1)</td>
<td>-9.0283127 E - 1</td>
<td>9.31063597 E 0</td>
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<tr>
<td>(a_2)</td>
<td>3.6492938 E - 2</td>
<td>-1.892876005 E - 1</td>
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<td>(a_3)</td>
<td>4.3610019 E - 4</td>
<td>1.307135652 E - 3</td>
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<tr>
<td>(a_4)</td>
<td>-3.1093603 E - 6</td>
<td>-3.800223763 E - 6</td>
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<tr>
<td>(a_5)</td>
<td>4.5920530 E - 9</td>
<td>4.009136971 E - 9</td>
</tr>
<tr>
<td>(a_6)</td>
<td>1.6299687 E 1</td>
<td>2.276924686 E 3</td>
</tr>
<tr>
<td>(a_7)</td>
<td>2.8111940 E - 2</td>
<td>-1.129133018 E - 2</td>
</tr>
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</table>

The mutual solubility model of CO2–CH4–brine system is established based on the above principle. Equilibrium constants (\(K_i\)), fugacity coefficients (\(\varphi_i\)), and activity coefficients (\(\gamma_i\)) 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):

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

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):

\[
\ln K_i = b_1 + b_2 T + b_3 \frac{P}{T} + b_4 P + b_5 P + b_6 PT + b_7 P^2 T + b_8 P^3, \tag{7}
\]

where \(i = \text{CO}_2, \text{CH}_4\), \(b_i (i = 1, 2, \ldots, 11)\) 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.

\[
a = \sum_i \sum_j y_i y_j a_{ij} \tag{8}
\]

\[
b = \sum_i b_i y_i,
\]

where \(a_{ij} = \sqrt{a_i a_j (1 - \delta_{ij})}\) and \(\delta_{ij}\) 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 CO\(_2\) and CH\(_4\) equilibrium constants in (7).

<table>
<thead>
<tr>
<th></th>
<th>(b_1)</th>
<th>(b_2)</th>
<th>(b_3)</th>
<th>(b_4)</th>
<th>(b_5)</th>
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<th>(b_8)</th>
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<td>CO(_2)</td>
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<td>-1.8367E3</td>
<td>2.0331E-5</td>
<td>-3.9072E5</td>
<td>-5.8269E2</td>
<td>1.5062E-4</td>
<td>7.8087E0</td>
<td>-1.3013E-7</td>
<td>1.1145E-9</td>
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</table>


Table 3: Binary interaction parameter in PR-EOS.

<table>
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<tr>
<th>$\delta_{ij}$</th>
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<th>$CO_2$</th>
<th>$CH_4$</th>
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<td>$H_2O$</td>
<td>—</td>
<td>0.19014</td>
<td>0.485</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.19014</td>
<td>—</td>
<td>0.1196</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>0.485</td>
<td>0.1196</td>
<td>—</td>
</tr>
</tbody>
</table>

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:

$$\ln y_i = \sum_c 2m_c \lambda_{i,c} + \sum_a 2m_a \lambda_{i,a} + \sum_c \sum_a m_a m_c \xi_{i,a,c},$$

where $m_c$ is cation molality, $m_a$ is anion molality, and $\lambda_{i,c}$, $\lambda_{i,a}$, and $\xi_{i,a,c}$ 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. $\lambda_{i,Cl^-}$ 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 $\lambda_{i,Na^+}$ and $2\lambda_{i,Na^+}$. All ternary parameters are estimated as $\xi_{i,NaCl}$. 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 $CO_2$-$CH_4$-brine systems (including the subsystems).

For $CO_2$-$H_2O$-$NaCl$ 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 $CO_2$ 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 $H_2O$ solubility in nonaqueous ($CO_2$-rich) phase of the model solutions and experimental data. From the figure, the model can well reproduce $H_2O$ solubility in nonaqueous phase.

Experimental data of $CH_4$-$H_2O$-$NaCl$ 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 $CH_4$ solubilities in water and NaCl solutions of experimental data and this model. Figure 2(c) shows the experimental data of $H_2O$ in nonaqueous ($CH_4$-rich) phase and the related model solutions. From the comparisons, the experimental data can be well reproduced by the model.

Compared with single gas ($CO_2$ or $CH_4$)-brine systems, gas mixture ($CO_2$ and $CH_4$ 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 $CO_2$-$CH_4$-$H_2O$ 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 $CO_2$-$CH_4$-$H_2O$ 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 $CO_2$-$CH_4$-brine systems in wide ranges of temperature, pressure, and salinity. The model is reliable to be used in gas-water-mineral equilibrium analysis.

3. $CO_2$/$CH_4$-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, $CH_4$ is always accompanied with other components such as $CO_2$, $N_2$, or $H_2S$ [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 $CO_2$-$CH_4$-brine systems, geochemical reactions in $CO_2$-$CH_4$-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., $CO_2$ or $CH_4$) 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 chloride is considered as the only salt that is dissolved in water as an initial solution. Geochemistry equilibrium of $CO_2$-$CH_4$-brine-dolomite, $CO_2$-$CH_4$-brine-calcite, and $CO_2$-$CH_4$-brine-gypsum/anhydrite systems is studied. Two gas compositions are considered, pure $CH_4$ or 10% $CO_2 + 90% CH_4$, to evaluate $CO_2$ influences.

Table 5 lists the species of ions, minerals, and gases which get involved in geochemical reactions in $CO_2$-$CH_4$-brine-carbonate systems and $CO_2$-$CH_4$-brine-sulfate systems.

3.1. $CO_2$-$CH_4$-Brine-Carbonate Systems. For $CO_2$-$CH_4$-brine-carbonate systems, cases of fluid equilibrium with calcite and dolomite are studied, respectively. Figure 5 shows the molality of carbon (including $HCO_3^-$, $CO_2$, $CaHCO_3^{2-}$, $CaCO_3$, $CO_3^{2-}$, $MgHCO_3^-$, and $MgCO_3$) dissolved in aqueous phase with different depths, gas compositions, and salinities. Figure 6 shows the molality of calcium (including $Ca^{2+}$, $CaCO_3$, $CaHCO_3^{2-}$, and $CaOH^+$) and magnesium

...
Table 4: Pitzer parameters for activity coefficients.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{CO}_2-\text{Na}^+}$</td>
<td>$-3.1312239 \times 10^{-1} + 5.532647 \times 10^{-4}T + 7.5844401 \times 10^{-7}P - 1.8950519 \times 10^{-8}P^2/$ $T - 1.458572 \times 10^{-7}P/$ $T$</td>
</tr>
<tr>
<td>$\lambda_{\text{CH}_4-\text{Na}^+}$</td>
<td>$-5.706455 \times 10^{-1} + 7.2997588 \times 10^{-4}T + 1.5176903 \times 10^{-7}P - 1.642651 \times 10^{-8}P/$ $T^2$</td>
</tr>
<tr>
<td>$\lambda_{\text{H}_2\text{S}-\text{Na}^+}$</td>
<td>$1.03658689 - 1.1784797 \times 10^{-3}T - 1.7754826 \times 10^{-2}T^2 - 4.5313285 \times 10^{-5}P + 4.775165 \times 10^{-6}P/$ $T^2$</td>
</tr>
<tr>
<td>$\zeta_{\text{CO}_2-\text{Na}^+}$</td>
<td>$-1.14462 \times 10^{-2} + 2.8274958 \times 10^{-5}T + 1.3980876 \times 10^{-2}P - 1.4349005 \times 10^{-2}P/(630 - T)$</td>
</tr>
<tr>
<td>$\zeta_{\text{CH}_4-\text{Na}^+}$</td>
<td>$-2.9990084 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\zeta_{\text{H}_2\text{S}-\text{Na}^+}$</td>
<td>$-1.0274152 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Figure 1: Mutual solubilities of CO$_2$-brine systems. Lines are calculated results from this model, and dots are from experimental data. (a) CO$_2$ solubility in pure water; (b) CO$_2$ solubility in NaCl solutions; (c) H$_2$O solubility in CO$_2$-rich phase.

(including Mg$^{2+}$, MgOH$^+$, MgCO$_3$, and MgHCO$_3^+$) that is dissolved in aqueous phase. From Figure 6, it is shown that CO$_2$ in the gas phase will promote calcite or dolomite dissolution. From the calculations, we find that, with CO$_2$ 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
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. CO\textsubscript{2}-CH\textsubscript{4}-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 CH\textsubscript{4}, 10% CO\textsubscript{2} + 90% CH\textsubscript{4}, and pure CO\textsubscript{2}. 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 S\textsuperscript{2-}, HS\textsuperscript{-}, and H\textsubscript{2}S as ions) and S($+6$) (i.e., sulfur dissolved in water in chemical valence $+6$, which can be SO\textsubscript{4}\textsuperscript{2-}, HSO\textsubscript{4}\textsuperscript{-}, CaSO\textsubscript{4}, and CaHSO\textsubscript{4}$^+$) concentration in equilibrium of gas-water-gypsum. From Figure 7, we can find the following:

1) With pure CO\textsubscript{2} in gas, S($-2$) in water is extremely low, and more CH\textsubscript{4} is dissolved in water leading to higher S($-2$) concentration.

2) Higher CO\textsubscript{2} mole fraction in gas phase will lead to higher S($+6$) concentration in water phase.
Figure 3: CO₂/CH₄ solubilities in water in CO₂-CH₄-H₂O 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 CO$_2$-CH$_4$-brine-carbonate systems

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
<th>Neutral ions</th>
<th>Minerals and gases</th>
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<tbody>
<tr>
<td>H$^+$</td>
<td>OH$^-$</td>
<td>H$_2$O</td>
<td>Aragonite</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>HCO$_3^-$</td>
<td>CH$_4$</td>
<td>Calcite</td>
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<tr>
<td>CaHCO$_3^+$</td>
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(b) Ions, minerals, and gases involved in CO$_2$-CH$_4$-brine-sulfate systems

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</table>

(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 CH$_4$ is the key component for S(+6) to be reduced to S(−2) species in water. The related redox geochemical reaction is

$$\text{SO}_4^{2-} + \text{CH}_4 \rightleftharpoons \text{CO}_3^{2-} + \text{S}^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \quad (10)$$

When CH$_4$ and SO$_4^{2-}$ are dissolved in water, the above reaction is triggered, and CH$_4$ is oxidized from C(−4) to C(+4). In the meantime, SO$_4^{2-}$ is reduced to S$^{2-}$.

Figure 8(a) shows the amount of calcite precipitation for different cases of geochemical equilibrium. Referring to Figure 8(a), in case of pure CO$_2$ in gas phase, there is no calcite precipitation; with higher CH$_4$ 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 CH$_4$ 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 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$_2$S in gas phase. With more and more S(−2) generated in water, S$^2$ and H$^+$ approach combining with one another, and H$_2$S becomes saturated and is released in gas phase. As shown in Figure 8(b), with more CH$_4$ in gas phase, more H$_2$S 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$_2$S origin in gas reservoirs [2]. From the figure, we can also find that, at higher depth, more H$_2$S 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 S(+6) is reduced to S(−2). H$_2$S will be released when S(−2) becomes saturated in aqueous phase. This process could be one of the origins for H$_2$S 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.

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