



Original research paper

Solubility models of CH₄, CO₂, and noble gases and their geological applications[☆]

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Abstract

Solubility models for CH₄, CO₂, and noble gases are widely used in Earth Sciences, playing pivotal roles in the study of homogenization pressure of inclusions, paleoclimate variation, gas migration and accumulation, formation of helium-rich gas plays, and the volumetric ratio of gas to water in reservoirs. This paper reviews solubility models of CH₄, CO₂, and noble gases in pure water and aqueous NaCl solutions. Specifically, the models with high accuracy and wide applicability are introduced in detail: (1) CH₄ solubility model in aqueous solutions within the range of 0–250 °C, 0.1–200 MPa, and 0–6.0 mol/kg NaCl; (2) CO₂ solubility model in aqueous solutions within the range of 0–450 °C, 0.1–150 MPa, and 0–4.5 mol/kg NaCl; (3) Models for calculating the solubility and Henry's constant of atmospheric noble gases within 0–80 °C range; (4) Models for calculating the Henry's constant of noble gases in pure water; (5) Solubility models of noble gases in aqueous solutions within the range of 0–65 °C, 0.1 MPa, and 0–5.8 mol/kg NaCl. The paper also presents some calculated results obtained using these models. The solubility models of CH₄ and CO₂ are complex yet highly accurate, with a broad range of applications. In contrast, the solubility models of noble gases exhibit relatively lower accuracy and a narrower application range, necessitating corrections. In the noble gases-CO₂-H₂O system, low-density CO₂ has little effect on the solubility of noble gases, whereas high-density CO₂ significantly influences their solubilities. Currently, accurately evaluating the solubility of CH₄, CO₂, and noble gases in their mixtures proves challenging, warranting further research into solubility models for gas mixtures.

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Keywords: CH₄ and CO₂; Noble gases; Aqueous NaCl solution; Henry's constant; Solubility model

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1. Introduction

Methane (CH₄) and carbon dioxide (CO₂) are dominant components of geological fluids and potent greenhouse gas sources. Noble gases (He-Ne-Ar-Kr-Xe) are chemically stable and serve as important tracers for subsurface fluid migrations and accumulations. The study of solubility for CH₄, CO₂, and noble gases has garnered significant attention in Physical Chemistry [1] and Earth Sciences [1–4]. Their solubility models play crucial roles in understanding the molecular structure of liquid water [5,6], the coupling relationship of gas and water [3,7,8], homogenization pressures of fluid inclusions [9], migration and accumulation of natural gas [3], volumetric gas-to-water ratios in reservoirs [10], geological reserve and storage mechanism of CO₂ [3,9], formation mechanism of gas hydrate [7], paleoclimate change [11], and the reliability of experimental solubility data [7–9]. Thus, developing solubility models for CH₄, CO₂, and/or noble gases holds immense value and significance.

The foundation of gas solubility models lies in the balance of chemical potential balance (i.e., the chemical potentials of gas in the liquid phase and vapor phase are equal) and Henry's Law. Over the 20th century, thousands of experimental solubility data for noble gases [5,12–14], CH₄ [1,2,7], and CO₂ [2,15,16] have been published, forming the basis for solubility modeling. However, most solubility models for CH₄, CO₂, and noble gases are semi-empirical theoretical models or fitted formulas. While they can estimate solubility within specific temperature and pressure ranges, they often struggle to strike the right balance between accuracy and generalizability. At present, no models exist that can accurately calculate the solubility of CH₄, CO₂, and/or noble gases across a wide range of temperature, pressure, and salinity.

Given the strategic importance of helium gas and other noble gases as valuable and scarce strategic resources, the geochemical study, exploration, and development of helium-rich natural gas have become a focus in China. The gas solubility model plays a key role in understanding the formation mechanisms of helium-rich gas plays [3,10]. To disseminate the latest research progress on solubility models of CH₄, CO₂, and noble gases, we aim to summarize the advantages and disadvantages of typical solubility models for these gases, with an emphasis on models with higher accuracy and wider applicability. Additionally, we present some calculated results from these typical models.

2. Theory formulas of gas solubility in aqueous solutions

The solubility of a gas in aqueous solutions depends on phase equilibrium. At solubility equilibrium, the chemical potential of the gas in the vapor phase is equal to that in the liquid phase,

$$\mu_i^v(T, P, y_i) = \mu_i^l(T, P, m_i) \tag{1}$$

Since,

$$\begin{cases} \mu_i^v(T, P, y_i) = \mu_i^{v(0)}(T) + RT \ln(y_i P) + RT \ln \varphi_i(T, P, y_i) \\ \mu_i^l(T, P, m_i) = \mu_i^{l(0)}(T, P) + RT \ln m_i + RT \ln \varphi_i(T, P, m_i) \end{cases} \tag{2}$$

Therefore,

$$\ln m_i = \ln(y_i P) + \frac{\mu_i^{v(0)}(T) - \mu_i^{l(0)}(T, P)}{RT} + \ln \varphi_i(T, P, y_i) - \ln \varphi_i(T, P, m_i) \tag{3}$$

$$\ln k_i = \ln \frac{y_i P \varphi_i(T, P, y_i)}{m_i \varphi_i(T, P, m_i)} = \frac{\mu_i^{l(0)}(T, P) - \mu_i^{v(0)}(T)}{RT} \tag{4}$$

where, y_i is the mole fraction of component i in the vapor phase; m_i is the solubility of i in the liquid phase, mol/kg; $\mu_i^{v(0)}$ and $\mu_i^{l(0)}$ are the standard chemical potentials of the vapor and liquid phases, respectively; $\varphi_i(T, P, y_i)$ and $\varphi_i(T, P, m_i)$ are the fugacity and activity coefficients, respectively; k_i is Henry's constant; T is temperature, K; P is pressure, MPa; and R is the universal gas constant, $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Based on formulas (1), (3) and (4), researchers developed different kinds of equations to calculate the solubility and Henry's constant of gas in solutions. Obviously, when gas is an ideal gas and the solution is an ideal solution, the formulas (3) and (4) have the simplest forms.

3. CH₄ solubility models

3.1. Review of CH₄ solubility models

Most of the solubility models for CH₄ are semi-empirical theoretical models. Table 1 lists some typical models. Zuo et al. [17] extended the Patel-Teja equation to estimate CH₄ solubility in pure water and aqueous NaCl solutions within the T - P - m range of 51–125 °C, 10.1–60.8 MPa, and 0–4.4 mol/kg. The average deviation is up to 18% compared to experimental data from O'Sullivan et al. [18]. Søreide et al. [19] developed a highly accurate model to calculate CH₄ solubility in low-concentration NaCl solutions within the range of 25–171 °C

Table 1
Typical models for calculating CH₄ solubility in pure water and in NaCl solutions.

$T/^\circ\text{C}$	P/MPa	$m_{\text{NaCl}}/(\text{mol}/\text{kg})$	Refs.
51–125	10.1–60.8	0–4.4	[17]
25–171	1.4–69	0–5.0	[19]
0–250	0–160	0–6.0	[2]
25–170	4–61.6	0	[21]
10–125	0.1–61.6	0.25–4.35	[21]
2–40	<20	0	[22]
20–350	0.9–200	0–6.0	[23]
0–250	0.1–200	0–6.0	[7]

and 1.4–69 MPa. Based on Pitzer phenomenology, Duan et al. [2] developed a model to calculate CH₄ solubility in NaCl solutions within the range of 0–250 °C, 0–160 MPa, and 0–6.0 mol/kg. In most cases, the model can predict CH₄ solubility in pure water within the experimental uncertainty. However, the deviation can be up to 20% at some temperatures in NaCl solutions. Using a cubic equation of state and the mixing rule of Huron et al. [20], Sørensen et al. [21] provided models to calculate CH₄ solubility in pure water (25–170 °C and 4–61.6 MPa) and in NaCl solutions (10–125 °C, 0.1–61.6 MPa, and 0.25–4.35 mol/kg). The average deviation is up to 26% in the CH₄–H₂O system and up to 25% in the CH₄–H₂O–NaCl system. Chapoy et al. [22] developed a model to calculate CH₄ solubility in pure water. The *T*–*P* range is small (*T* = 2–40 °C, *P* < 20 MPa), but the calculated value is in good agreement with experimental data. Spivey et al. [23] presented a model to calculate CH₄ solubility in aqueous solutions within the range of 20–350 °C, 0.9–200 MPa, and 0–6.0 mol/kg NaCl. However, the model is not precise [7]. Duan et al. [7] developed a model to calculate CH₄ solubility in aqueous solutions within the range of 0–250 °C, 0.1–200 MPa, and 0–6.0 mol/kg NaCl. The model is highly accurate with an average deviation generally <8% compared to experimental data.

Based on reliable theories, the CH₄ solubility model developed by Duan et al. [7] has high accuracy and covers a wider range of temperature, pressure, and salinity. The model has been widely used in Earth Sciences. We will introduce in detail the modeling and the calculation of parameters in the model equation.

3.2. CH₄ solubility model from Duan et al.

According to formula (3), CH₄ solubility can be calculated using formula (5):

$$\left\{ \begin{array}{l} P_c(X) = 22.064 + q_5X + q_6X^2 + q_7X^3 + q_8X^4 + q_9X^5 + q_{10}X^6 \\ g(T) = h^{-1}(1-h) \left[-7.85951783 + 1084408259(1-h)^{0.5} - 11.7866497(1-h)^2 \right. \\ \quad \left. + 22.6807411(1-h)^{2.5} - 15.9618719(1-h)^3 + 1.80122502(1-h)^{6.5} \right] \\ h(X) = \begin{cases} \frac{a_2X}{X+a_1} + a_3X^2 & 0 \leq X \leq u \\ (X-u) \left[\frac{a_1^2 a_2}{(u+a_1)^2} + 2a_3u + b_1(X-u) + b_2(X^2-u^2) \right] + \frac{a_2u}{u+a_1} + a_3u^2 & u < X \leq L \end{cases} \end{array} \right.$$

$$\text{Ln } m = \text{Ln}(yP) + \text{Ln } \varphi_{\text{CH}_4}(T, P, y) + \frac{\mu_{\text{CH}_4}^{(0)}(T) - \mu_{\text{CH}_4}^{(0)}(T, P)}{RT} - \text{Ln } \varphi_{\text{CH}_4}(T, P, m) \quad (5)$$

where, *m* is the solubility of CH₄, mol/kg; *y* is the mole fraction of CH₄ in the vapor phase; $\mu_{\text{CH}_4}^{(0)}$ and $\mu_{\text{CH}_4}^{(0)}$ are the standard

chemical potentials of CH₄ in the vapor phase and the liquid phase, respectively; $\varphi_{\text{CH}_4}(T, P, y)$ and $\varphi_{\text{CH}_4}(T, P, m)$ are the fugacity and the activity coefficients, respectively. The calculation of the parameters in the formula (5) is as follows.

3.2.1. Calculation of CH₄ mole fraction in the vapor phase

The mole fraction of CH₄ in the vapor phase is calculated from

$$y = 1 - y_{\text{H}_2\text{O}}^v = 1 - \frac{x_{\text{H}_2\text{O}}^l P_{\text{H}_2\text{O}}^S}{\varphi_{\text{H}_2\text{O}} P} \exp\left(\frac{V_{\text{H}_2\text{O}}^l (P - P_{\text{H}_2\text{O}}^S)}{RT}\right) \quad (6)$$

where, $x_{\text{H}_2\text{O}}^l$ is the mole fraction of H₂O in the liquid, $x_{\text{H}_2\text{O}}^l = 1 - 2x_{\text{NaCl}}$.

The fugacity coefficient of water, $\varphi_{\text{H}_2\text{O}}$, can be calculated

$$\varphi_{\text{H}_2\text{O}} = \exp\left(a_1 + a_2P + a_3P^2 + a_4PT + \frac{a_5P}{T} + \frac{a_6P^2}{T}\right) \quad (7)$$

where, the value of *a_i* can be seen in literature [7].

Molar volume of liquid water, $V_{\text{H}_2\text{O}}^l$ (cm³/mole), can be calculated by using the formula [24]

$$\frac{\rho}{\rho_c} = 1 + b_1\tau^{1/3} + b_2\tau^{2/3} + b_3\tau^{5/3} + b_4\tau^{16/3} + b_5\tau^{43/3} + b_6\tau^{110/3} \quad (8)$$

where, $\rho_c = 322\text{kg/m}^3$, $\tau = 1 - T/647.096$, the values of *b_i* can be found in Ref. [24].

The saturation pressure of water, $P_{\text{H}_2\text{O}}^S$, can be calculated,

$$\text{Ln } P_{\text{H}_2\text{O}}^S = \text{Ln } P_c(X) + g(T) + h(X) \quad (9)$$

where, *X* is the mole fraction of NaCl in solutions, *h* = 647.096⁻¹*T*, *u* = 0.024, *L* = 0.117, the values of other parameters can be seen in Ref. [25].

3.2.2. Calculation to CH₄ fugacity coefficient

CH₄ fugacity coefficient, φ , can be approximated from the formula

$$\ln \varphi = Z - 1 - \ln Z + \frac{B}{V_r} + \frac{C}{2V_r^2} + \frac{D}{4V_r^4} + \frac{E}{5V_r^5} + G \quad (10)$$

where,

$$\left\{ \begin{aligned} Z &= \frac{P_r V_r}{T_r} P_r = \frac{P}{P_c}, T_r = \frac{T}{T_c}, \\ B &= a_1 + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3} \\ C &= a_4 + \frac{a_5}{T_r^2} + \frac{a_6}{T_r^3} \\ D &= a_7 + \frac{a_8}{T_r^2} + \frac{a_9}{T_r^3} \\ E &= a_{10} + \frac{a_{11}}{T_r^2} + \frac{a_{12}}{T_r^3} \\ G &= \frac{\alpha}{2\gamma T_r^3} \left[\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2} \right) \exp\left(-\frac{\gamma}{V_r^2}\right) \right] \end{aligned} \right.$$

P_c and T_c are the critical pressure and the critical temperature of gas, respectively. V_r can be calculated from the formula

$$\frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^4} + \frac{E}{V_r^5} + \frac{\alpha}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp\left(-\frac{\gamma}{V_r^2}\right). \quad (11)$$

Formulas (10) and (11) developed by Duan et al. [26] are complex but accurate. The fugacity coefficient of pure CH₄ can be calculated by an iterative method. Assuming that the fugacity coefficient of pure CH₄ is equal to that of CH₄ in the mixed gas, the fugacity coefficient of CH₄ in the mixed gas (CH₄+H₂O) can be calculated using formulas (10) and (11).

3.2.3. Calculation of standard chemical potential and activity coefficient of CH₄

$\mu_{CH_4}^{(0)}(T)$ is set to 0 because only the $\frac{\mu_{CH_4}^{(0)}(T) - \mu_{CH_4}^{(0)}(T,P)}{RT}$ value is important in formula (5). $\mu_{CH_4}^{(0)}(T,P)$ can be fitted using the experimental solubility data of CH₄ in pure water, where the activity coefficient of CH₄ is set to 1.

In aqueous NaCl solutions, the CH₄ activity coefficient can be expressed as a virial expansion of excess Gibbs energy [27].

$$\ln \varphi_{CH_4} = 2\lambda_{CH_4-Na} m_{Na} + 2\lambda_{CH_4-Cl} m_{Cl} + \xi_{CH_4-Na-Cl} m_{Na} m_{Cl}. \quad (12)$$

Set $\lambda_{CH_4-Cl} m_{Cl} = 0$, substituting formula (12) into formula (5) yields

$$\ln \frac{yP}{m_{CH_4}} = \frac{\mu_{CH_4}^{(0)}(T,P)}{RT} - \ln \varphi_{CH_4}(T,P,y) + 2\lambda_{CH_4-Na} m_{Na} + \xi_{CH_4-Na-Cl} m_{Na} m_{Cl}. \quad (13)$$

λ_{CH_4-Na} and $\xi_{CH_4-Na-Cl}$ can be fitted by using the experimental solubility data of CH₄ in aqueous NaCl solutions.

Duan et al. [7] used the formula (14) from Pitzer et al. [28].

$$\begin{aligned} Par(T, P) = & c_1 + c_2 T + \frac{c_3}{T} + c_4 T^2 + \frac{c_5}{T^2} + c_6 P + c_7 PT + \frac{c_8 P}{T} + \frac{c_9 P}{T^2} \\ & + c_{10} P^2 T \end{aligned} \quad (14)$$

to calculate $\mu_{CH_4}^{(0)}(T)$, λ_{CH_4-Na} and $\xi_{CH_4-Na-Cl}$. The values of c_i can be seen in Ref. [7].

In this paper, CH₄ solubility is calculated using formula (13). The variation characteristics of CH₄ solubility in pure water and in 1.0 mol/kg NaCl solutions are shown in Fig. 1. The solubility of CH₄ in pure water is greater than that in NaCl solutions. The solubility of CH₄ increases with an increase in pressure, but it does not monotonically increase or decrease with an increase in temperature. Formula (13) is more accurate but complex, as it includes more parameters. To calculate CH₄ solubility using formula (13), specific calculation software is often required. Duan et al. [7] provided a computer code for this model on the website: www.geochem-model.org/programs.htm. However, this website is inaccessible at present. We expect that readers can design codes to calculate CH₄ solubility according to formula (13), so that relevant researchers can use it easily.

4. CO₂ solubility models

4.1. Review of CO₂ solubility models

There are various solubility models of CO₂ in aqueous solutions. Akinfiev et al. [8] and Shi et al. [15] have reviewed most of these models. Here, a brief overview of the advantages and disadvantages of typical solubility models of CO₂ in pure water and NaCl solutions is presented (Table 2).

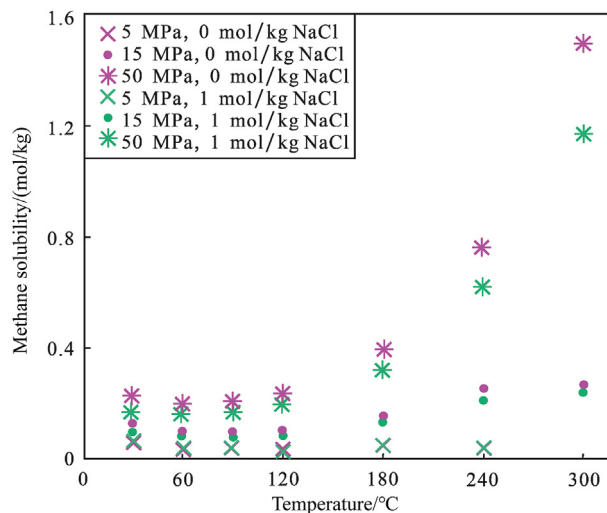


Fig. 1. Comparison of CH₄ solubility in pure water and 1.0 mol/kg NaCl solutions under different temperature and pressure.

Table 2
Typical models for calculating CO₂ solubility in pure water and in NaCl solutions.

T/°C	P/MPa	m _{NaCl} /(mol/kg)	Refs.
75–350	1.6–142	0	[21]
25–250	0.1–140	0.46–5.70	[21]
0–260	0–200	0–4.5	[29]
27–227	5–200	1–4.0	[30]
–1.5–100	0.1–100	0	[31]
–22–100	0.1–100	0–6.0	[8]
0–450	0.1–150	0–4.5	[9]
0–300	0.1–200	0–6.0	[16]

Harvey et al. [32] developed a model to predict CO₂ solubility in NaCl solutions; however, it overestimates CO₂ solubility by up to 20%. Sørensen et al. [21] modeled CO₂ solubility in pure water (75–350 °C and 1.6–142 MPa) and NaCl solutions (25–250 °C, 0.1–140 MPa, and 0.46–5.70 mol/kg). However, the average deviation of CO₂ solubility is up to 37% in pure water and up to 20% in solutions. Duan et al. [29] developed a model to calculate CO₂ solubility in mixed-salt (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, and SO₄²⁻) solutions in the range of 0–260 °C, 0–200 MPa, and 0–4.5 mol/kg. The model has been widely used in Earth Sciences, but the deviation is large in aqueous K⁺ and SO₄²⁻ solutions [15]. Darwish et al. [30] developed a model to calculate CO₂ solubility in NaCl solutions within the range of 27–227 °C, 5–200 MPa, and 1–4 mol/kg. Diamond et al. [31] collected 520 experimental data of CO₂ solubility in pure water from the literature and selected 70% of the data. Based on Henry's Law, they developed a CO₂ solubility model in water within the range of –1.5–100 °C and 0.1–100 MPa. The model is accurate, but the range of temperature and pressure is smaller. Using the same method, Akinfiev et al. [8] collected 508 experimental data of CO₂ solubility in NaCl solutions, selected 67% of the data, and gave the solubility model of CO₂ within the range of –22–100 °C and 0.1–100 MPa. The model is more accurate in the 0–100 °C range. However, discarding many experimental solubility data [8,31] may be unreasonable. Mao et al. [9] developed a model to calculate CO₂ solubility in NaCl solutions within the *T-P-m* range of 0–450 °C, 0.1–150 MPa, and 0–4.5 mol/kg. The model is highly accurate, with an average deviation generally <5% compared to experimental data. Subsequent studies [15,16] have shown that the model is more reliable. The model is widely used in Earth Sciences. We will introduce in detail how to calculate the parameters in the model equation of Mao et al. [9].

4.2. CO₂ solubility model from Mao et al.

According to formulas (1) and (2), CO₂ solubility can be calculated as followed

$$\ln \frac{yP}{m} = \frac{\mu_{\text{CO}_2}^{(0)}(T, P) - \mu_{\text{CO}_2}^{(0)}(T)}{RT} + \ln \phi_{\text{CO}_2}(T, P, m) - \ln \phi_{\text{CO}_2}^p(T, P) - \ln \gamma_{\text{CO}_2}^v(T, P) \quad (15)$$

where, *m* is the solubility of CO₂, mol/kg; *y* is the mole fraction of CO₂ in the vapor phase; $\mu_{\text{CO}_2}^{(0)}$ and $\mu_{\text{CO}_2}^{(0)}$ are the standard chemical potentials of CO₂ in vapor and liquid phases, respectively; $\phi_{\text{CO}_2}^p$ is the fugacity coefficient of pure CO₂; $\phi_{\text{CO}_2}(T, P, m)$ and $\gamma_{\text{CO}_2}^v(T, P)$ are the activity coefficients of CO₂ in the liquid phase and vapor phase, respectively. The calculation to these parameters in formula (15) is as follows.

4.2.1. Calculation of the mole fraction and fugacity coefficient of CO₂

The mole fraction of CO₂ in the vapor phase is calculated as follows:

$$y = \frac{P - P_{\text{H}_2\text{O}}}{P} \approx \frac{P - P_{\text{H}_2\text{O}}^S}{P} \quad (16)$$

where, $P_{\text{H}_2\text{O}}^S$ is the saturated pressure of H₂O in NaCl solutions. It can be calculated using the formula from Ref. [33].

The method to calculate the fugacity coefficient, $\phi_{\text{CO}_2}^p$, is the same as the method used to calculate the fugacity coefficient of CH₄. Based on formulas (10) and (11), the iterative method is used to calculate $\phi_{\text{CO}_2}^p$. The parameter values in formulas (10) and (11) can be found in Ref. [26].

4.2.2. Calculation of the standard chemical potential and activity coefficient of CO₂

$\frac{\mu_{\text{CO}_2}^{(0)}(T, P) - \mu_{\text{CO}_2}^{(0)}(T)}{RT} - \ln \gamma_{\text{CO}_2}^v(T, P)$ can be fitted using the experimental data of CO₂ solubility in pure water, where the activity coefficient of CO₂ is set to 1.

In NaCl solutions, the calculation of the activity coefficient of CO₂ is the same as that of CH₄. Setting $\lambda_{\text{CO}-\text{Cl}}m_{\text{Cl}} = 0$, then formula (15) becomes:

$$\ln \frac{yP}{m_{\text{CO}_2}} = \frac{\mu_{\text{CO}_2}^{(0)}(T, P) - \mu_{\text{CO}_2}^{(0)}(T)}{RT} - \ln \gamma_{\text{CO}_2}^v(T, P) - \ln \phi_{\text{CO}_2}^p(T, P) + 2\lambda_{\text{CO}_2-\text{Na}}m_{\text{Na}} + \xi_{\text{CO}_2-\text{Na}-\text{Cl}}m_{\text{Na}}m_{\text{Cl}} \quad (17)$$

$\lambda_{\text{CO}_2-\text{Na}}$ and $\xi_{\text{CO}_2-\text{Na}-\text{Cl}}$ can be fitted using the experimental data of CO₂ solubility in NaCl solutions.

Mao et al. [9] used the formula (18) from Pitzer et al. [28].

$$\text{Par}(T, P) = c_1 + c_2T + \frac{c_3}{T} + c_4T^2 + \frac{c_5}{T^2} + c_6P + c_7PT + \frac{c_8P}{T} + \frac{c_9P}{T^2} + c_{10}P^2T \quad (18)$$

to calculate $\frac{\mu_{\text{CO}_2}^{(0)}(T, P) - \mu_{\text{CO}_2}^{(0)}(T)}{RT} - \ln \gamma_{\text{CO}_2}^v(T, P)$, $\lambda_{\text{CO}_2-\text{Na}}$ and $\xi_{\text{CO}_2-\text{Na}-\text{Cl}}$.

Mao et al. [9] provided a computer code to calculate CO₂ solubility in aqueous NaCl solutions. In the paper, some solubility data of CO₂ are calculated according to formula (17). The variation characteristics of CO₂ solubility in pure water and in 1.0 mol/kg NaCl solutions are shown in Fig. 2. The solubility of CO₂ in pure water is greater than that in NaCl

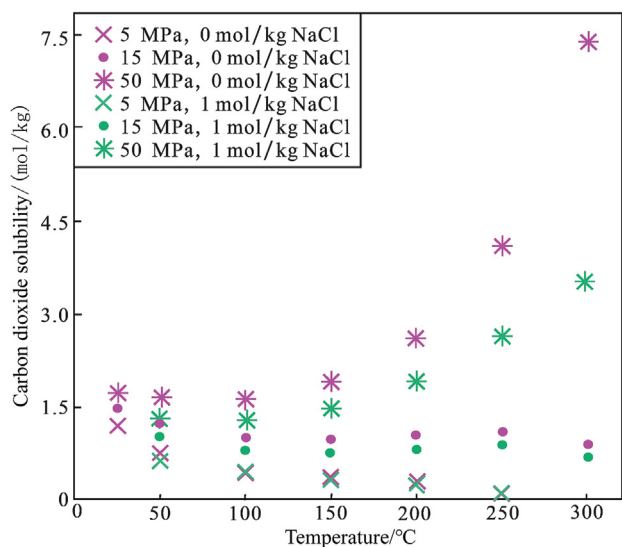


Fig. 2. Comparison of CO₂ solubility in pure water and in 1.0 mol/kg NaCl solutions under different temperature and pressure.

solutions. The solubility of CO₂ increases with an increase in pressure, but it does not monotonically increase or decrease with an increase in temperature. Figs. 1 and 2 show that the solubility of CO₂ is significantly greater than that of CH₄ under the same conditions.

5. Solubility models of noble gases

Compared with CO₂ and CH₄, there are fewer theoretical and experimental studies on the solubility of noble gases (He-Ne-Ar-Kr-Xe). Preliminary discussions on the theoretical models of noble gas solubility have been done in Refs. [1,6]. Semi-empirical theoretical models for estimating the solubility and Henry's constant of noble gases are presented below.

5.1. Solubility models of atmospheric noble gases

Studying the solubility of atmospheric noble gases holds great significance, as the distributions of noble gases in Earth's atmosphere remain extremely homogeneous over extended

periods [4,16]. Henry's Law enables us to estimate the recharge temperature of groundwater and changes in paleotemperature by measuring the concentration of atmospheric noble gases in (paleo) surface water [4,11,34].

Jenkins et al. [14] measured the concentrations of atmospheric noble gas in distilled water and seawater within the temperature range of 0–35 °C. Based on their experimental data, a fitting formula for estimating the solubility of atmospheric noble gases is derived as follows:

$$\begin{aligned} \ln C = & A_1 + A_2 \frac{100}{T} + A_3 \ln\left(\frac{T}{100}\right) + A_4 \frac{T}{100} + S \left(B_1 + B_2 \left(\frac{T}{100}\right) \right. \\ & \left. + B_3 \left(\frac{T}{100}\right)^2 \right) + 10^{-6} C_1 S^2 \end{aligned} \tag{19}$$

where, *C* is the concentration of noble gas (He, Ne, Ar, Kr, Xe) in water, mol/kg; *S* is salinity, PSS78; *T* is temperature, K [14]. The coefficients for each noble gas in formula (19) are provided in Table 3. Overall, the systematic uncertainty is approximately 0.15% for all gases.

Schwenk et al. [4] measured the solubility of atmospheric noble gases in deionized water within the 25–80 °C range. Using the obtained solubility data and the data from Ref. [14], they fitted a formula to calculate the Henry's constant of noble gas within the 0–80 °C range,

$$L(T) = \exp\left(A + B \frac{100}{T} + C \ln\left(\frac{T}{100}\right) + D \frac{T}{100} \right) \tag{20}$$

where, *L* is the inverse of the Henry's constant for atmospheric noble gas, measured in mol/(kg·bar). Table 3 provides the coefficients for each noble gas in formula (20).

The formulas (19) and (20) are highly accurate in estimating the solubility and Henry's constant of atmospheric noble gases. However, it is important to note that the experimental measurements involved equilibration with pure noble gas, which necessitates extrapolating partial pressures over several orders of magnitude. Additionally, the absence of other gases can introduce co-solvency-induced biases, leading to larger errors in the results.

Table 3
Coefficients of formulas (19) and (20) for calculating solubility and Henry's constant of atmospheric noble gases.

Formula	Coefficients	He	Ne	Ar	Kr	Xe
19	<i>A</i> ₁	−178.142 4	−274.132 9	−227.460 7	−122.469 4	−224.510 0
	<i>A</i> ₂	217.599 1	352.620 1	305.434 7	153.565 4	292.823 4
	<i>A</i> ₃	140.750 6	226.967 6	180.527 8	70.196 9	157.612 7
	<i>A</i> ₄	−23.019 54	−37.133 93	−27.994 50	−8.525 24	−22.668 95
	<i>B</i> ₁	−0.038 129	−0.063 860	−0.066 942	−0.049 522	−0.084 915
	<i>B</i> ₂	0.019 190	0.035 326	0.037 201	0.024 434	0.047 996
	<i>B</i> ₃	−0.002 689 8	−0.005 325 8	−0.005 636 4	−0.003 396 8	−0.007 359 5
20	<i>C</i> ₁	−2.55	12.8	−5.30	4.19	6.69
	<i>A</i>	−83.696 8	−180.580 3	−88.646 2	−36.036 9	−142.030 3
	<i>B</i>	106.020 0	240.622 2	122.887 1	54.195 9	202.744 8
	<i>C</i>	51.762 4	137.872 1	48.639 6	1.529 9	88.909 6
	<i>D</i>	−5.466 4	−19.601 2	−4.120 8	3.417 6	−9.567 7

5.2. Solubility models of noble gases in pure water

Experimental determination of the solubility of noble gases is difficult, and the error is often large. Refs. [4,12,14,35,41] have reported experimental solubility data of noble gases in water in the range of 0–300 °C. However, there are certain differences among these data, and some data are considered unreliable. For example, Wilhelm et al. [1] pointed out that the accuracy of the solubility data of noble gases reported in Ref. [35] was low. Benson et al. [38] measured the solubility of noble gases in pure water in the 0–50 °C range and provided the Bunsen coefficient of noble gases. They found that the Bunsen coefficients of noble gases reported in Refs. [35,37] are lower. The solubility data and the Henry's constants of noble gases measured by Potter et al. [39] have significant errors [12].

Wilhelm et al. [1] collected experimental solubility data of noble gases reported before 1977 and then screened out the data with high accuracy. Using these data (excluding the data in Ref. [38]), they fitted the formula

$$R\ln x = A + B/T + C\ln T + DT \tag{21}$$

to calculate the solubility (molar fraction) of noble gas at a partial pressure 0.1 MPa and in 0–100 °C range. Table 4 provided the coefficients of formula (21) for each noble gas. The authors neglected the non-ideality of noble gases; thus, the reliability of the formula needs to be further verified.

Combining theoretical formulas and experimental data, Crovetto et al. [12] and Krause et al. [5] provide model equations to calculate the solubility and Henry's constant of noble gases. Their models are generally highly accurate and have a wider application range.

Crovetto et al. [12] designed an experiment to measure the solubility data of the noble gases (Ne, Ar, Kr, Xe) in H₂O and D₂O in the range of 20–300 °C. With the assumption that the activity coefficient is 1, they used formulas

$$y = 1 - \frac{\gamma_1(1-x)P_1^*\varphi_1^*(P_1^*, T)}{P\varphi_1(P, T, y)}, \tag{22}$$

$$k_2 = \frac{yP\varphi_2(P, T, y)}{\gamma_2x_2} \tag{23}$$

to calculate the partial pressure y and the Henry's constant k_2 of noble gases. In the formulas (22) and (23), subscripts 1 and 2 represent water and noble gas, respectively. x_2 is the solubility of the noble gas; γ is the activity coefficient; P_1^* and φ_1^* are the effective vapor pressure and the fugacity coefficient of water, respectively. Finally, Crovetto et al. [12] provided a fitting formula to calculate the Henry's constant of noble gases (Ne, Ar, Kr, Xe)

$$\ln(k_j / \text{GPa}) = \sum_{i=0}^3 \frac{A_i}{(0.001T)^i} \tag{24}$$

Table 4 lists the coefficients of formula (24) for each noble gas.

The solubility of helium in water is at its minimum, and the corresponding temperature is 32 °C [1]. The solubilities of Ne, Ar, Kr, and Xe in water are at their minimum, and the corresponding temperatures calculated by formula (24) are 54, 91, 108, and 114 °C, respectively [12]. Therefore, within a certain range of temperature and pressure, the minimum solubility temperatures of noble gases (He, Ne, Ar, Kr, and Xe) increase with the increase of their relative molecular masses.

Table 4
Coefficients of formulas (21), (24), (26), (27) and (28) for calculating solubility and Henry's constant of noble gases in water.

Formula	Coefficients	He	Ne	Ar	Kr	Xe
21	A	-233.163	-310.827	-336.76	-270.967	-360.119
	B	8737.84	12 766.8	16 170.1	15 992.9	18 744.6
	C	32.265 2	43.618 5	46.211 7	33.289 2	49.033 2
	D	-0.011 972 6	-0.012 753 4	-0.006 087 9	0.026 048 5	-0.003 113 2
24	A ₀	-	-7.259	-9.52	-6.292	-3.902
	A ₁	-	6.95	8.83	5.612	2.439
	A ₂	-	-1.382 6	-1.895 9	-0.888 1	0.386 3
	A ₃	-	0.053 8	0.069 8	-0.045 8	-0.221 1
26	a ₀	4.827 122	4.612 54	3.718 433	3.095 855	1.984 034
	a ₁	6.586 451	7.218 989	8.545 065	9.212 515	10.405 394
	a ₂	-1.542 063	-1.819 817	-2.479 705	-2.779 465	-3.211 715
27	A ₀	5.424 148	5.196 67	4.289 125	3.648 42	2.560 135
	A ₁	15.355 998	16.677 833	19.225 988	20.615 112	23.220 466
	A ₂	-16.804 423	-18.403 594	-21.603 721	-23.292 806	-26.324 042
28	a ₋₂	-2.067 744	-1.992 174	-2.577 657	-2.680 26	-2.646 469
	a ₋₁	9.985 833	8.330 898	9.174 933	8.570 473	6.747 425
	a ₀	-2.486 081	2.226 299	2.371 603	4.4776 67	9.855 588
	a ₁	5.234 082	1.703 614	0.957 659	-0.988 997	-5.632 491

Benson et al. [38,42] have done a lot of work in theoretical and experimental studies on noble gas solubility and made great progress. They [5] provide a theoretical formula to estimate the Henry's constant of noble gases:

$$k_2 = k_2' \left[\left(1 + \frac{2B_{12}p_{\sigma 1}}{RT} \right) + \left(\frac{2B_{22} - \bar{v}_2^0}{RT} + \varepsilon p_{\sigma 1} \right) p_2 \right] \quad (25)$$

where, subscripts 1 and 2 denote water and noble gas; B is the virial coefficient; ε and \bar{v}_2^0 are constants. $k_2' = \frac{R}{M} \frac{p_u V_u}{p_d V_d} \frac{T_d Z_d}{T_u Z_u} \frac{V_s'}{V_b} \rho T$ can be measured. Subscripts d and u denote dissolved and gaseous noble gases, respectively; V_b is the total volume of the vapor phase; Z is the compression factor; M is the molar mass of water; and ρ is the density of water.

According to formula (25), Benson et al. [5] designed experiments to measure Henry's constants of noble gases in pure water in the 0–60 °C range. They derived three formulas:

$$\ln(k_2/P) = a_0 + a_1/T^* + a_2/T^{*2} \quad (26)$$

$$T^{*2} \ln(k_2/P) = A_0 T^{*2} + A_1(1 - T^*)^{1/3} + A_2(1 - T^*)^{2/3} \quad (27)$$

$$\ln(k_2/P) = a_{-2} T^{*-2} + a_{-1} T^{*-1} + a_0 + a_1 T^* \quad (28)$$

to calculate the Henry's constants of noble gases. In the formulas, $T^* = T/T_c$, $T_c = 647$ K, $P = 0.1$ MPa.

In theory, formula (27) can be used to calculate Henry's constants of noble gases in pure water from 0 to 374 °C [5]. Formula (28) is the most accurate within the 0–60 °C range. The coefficients of the three formulas (26), (27) and (28) are shown in Table 4.

Fig. 3 shows the variation characteristics of the Henry's constants of noble gases in water calculated by formulas (24),

(27) and (28). The calculated Henry's constants from Crovetto et al. [12] and Krause et al. [5] are consistent in the range of 0–330 °C (Fig. 3a). Within the 0–60 °C range, the Henry's constants calculated by the two methods are very close (Fig. 3b). This indicates that the two models are reliable. Additionally, Fig. 3a shows that within a certain range of temperature and pressure, the Henry's constant of each noble gas (He, Ne, Ar, Kr and Xe) reaches its maximum value, which corresponds to the minimum solubility of each noble gases.

5.3. Solubility models of noble gases in aqueous NaCl solutions

NaCl is the most important dissolved electrolyte in geological fluids. Studies on the solubility of noble gases in electrolyte solutions are mostly focused on aqueous NaCl solutions [13]. Before 1983, most studies only measured the solubility of some noble gases in NaCl solutions at certain temperature points within the 0–30 °C range. For example, Åkerlöf [43] measured the solubilities of He and Ar in NaCl solutions at 25 °C. Morrison et al. [44] measured the solubility of noble gases in 0.98 mol/L NaCl solutions at 25 °C. Clever et al. [45] measured Ar solubility in 0–2.0 mol/L NaCl solutions at 30 °C. Gardiner et al. [46] measured He solubility in 0–4.0 mol/kg NaCl solutions at 10.1–60.8 MPa and at 25, 50, and 100 °C. In 1983, Smith et al. [13] systematically studied the solubility of noble gases in NaCl solutions and developed a highly accurate model. The model is now commonly used in subsequent studies [3].

Smith et al. [13] measured the solubility of noble gases in 0–5.8 mol/kg NaCl solutions at 0.1 MPa and within the 0–65 °C range. They used the Setschenow formula:

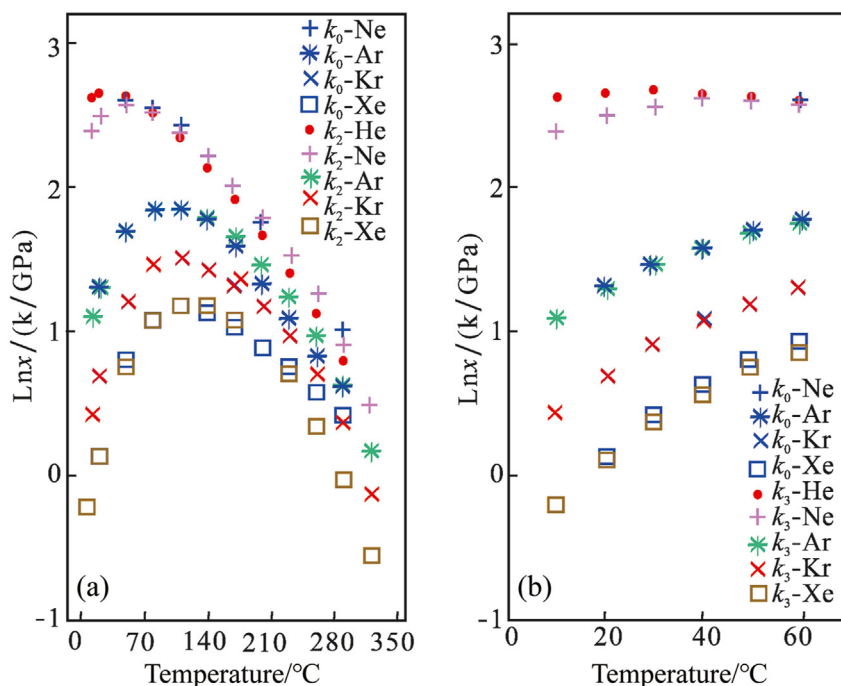


Fig. 3. Henry's constant k of noble gases in pure water (the k_0 , k_2 and k_3 are calculated by formulas (24), (27), and (28), respectively).

$$\ln \frac{x_0(T)}{x(T)} = MK_{M,x}(T) \tag{29}$$

to study the NaCl effect on the solubility of noble gases. In the formula (29), $x_0(T)$ and $x(T)$ are the molar fractions of noble gases in pure water and in NaCl solutions; T is the temperature, K; M is the concentration of NaCl in solutions; and $K_{M,x}$ is Setschenow coefficients.

Combining with previous experimental data, Smith et al. [13] provided fitting formulas to calculate the Setschenow coefficient and the molar fractions of noble gases in pure water and in 0–5.8 mol/kg NaCl solutions at 0.1 MPa partial pressure and within the 0–65 °C range:

$$K_{M,x}(Z) = A_1 + A_2/Z + A_3 \ln Z \tag{30}$$

$$\ln x_0(Z) = C_1 + C_2/Z + C_3 \ln Z \tag{31}$$

$$\ln x(Z) = D_1 + D_2/Z + D_3 \ln Z \tag{32}$$

where, $Z = \frac{T}{100}$, $D_i = C_i - MA_i$, $i = 1-3$; $x_0(T)$ and $x(T)$ are the molar fractions of noble gases in pure water and in NaCl solutions, respectively. Table 5 lists the coefficients for formulas (30) and (31).

At a partial pressure of 0.1 MPa and within the 0–65 °C range, the variation characteristics of noble gas solubility (He,

Table 5
Coefficients of formulas (30) and (31).

Gas	Formula (30)			Formula (31)		
	A_1	A_2	A_3	C_1	C_2	C_3
He	-10.081 0	15.106 8	4.812 7	-41.461 1	42.596 2	14.009 4
Ne	-11.955 6	18.406 2	5.546 4	-52.857 3	61.349 4	18.915 7
Ar	-10.695 1	16.751 3	4.955 1	-57.666 1	74.762 7	20.139 8
Kr	-9.970 7	15.161 9	4.618 1	-66.992 8	91.016 6	24.220 7
Xe	-14.552 4	22.525 5	6.751 3	-74.739 8	105.210 0	27.466 4

Ne, Ar, Kr, Xe) in 0, 0.01, 0.1, and 1.0 mol/kg NaCl solutions are shown in Fig. 4. The solubility of noble gases in pure water is significantly greater than that in 1.0 mol/kg NaCl solutions at the same temperature. Low concentration NaCl (<0.1 mol/kg) has little effect on the solubility of noble gases. The solubilities of He, Ne, Ar, Kr, and Xe increase with an increase in their relative molecular mass and decrease with an increase in temperature (except He).

6. Geological application of CH₄–CO₂-noble gas solubility models

The gas solubility model plays an important role in studying the formation and evolution of geological fluids. The solubility models of CH₄ and/or CO₂ can be used to determine the homogenization pressures and the molar fractions of different components in inclusions [7,9]. For example, the CO₂ solubility model has been used to estimate the total CO₂ yield in three-phase (liquid CO₂+vapor CO₂+liquid H₂O) CO₂-NaCl-H₂O inclusions [9].

CH₄, CO₂, and noble gases are the representative components of natural gas, and their solubility models are commonly used in the study of natural gas migration and accumulation [3,47–49]. The solubility model of CH₄ and CO₂ has been utilized to evaluate the resources and geological reserves of dissolved gas [48,49]. Atmospheric noble gas solubility models (noble gas thermometer) are employed to estimate paleoclimate change [4,11,34]. The argon solubility model is often used to estimate the volumetric ratio of gas/water in reservoirs [50]. The helium solubility model plays a vital role in studying helium-rich natural gas accumulation [51,52]. For example, Qin et al. [52] proposed that the helium gas in helium-rich reservoirs in the central and western basins of China mainly originates from the dissolved He in ancient formation water.

However, accurately estimating the solubility of each component in CH₄–CO₂-noble gases mixed gases poses

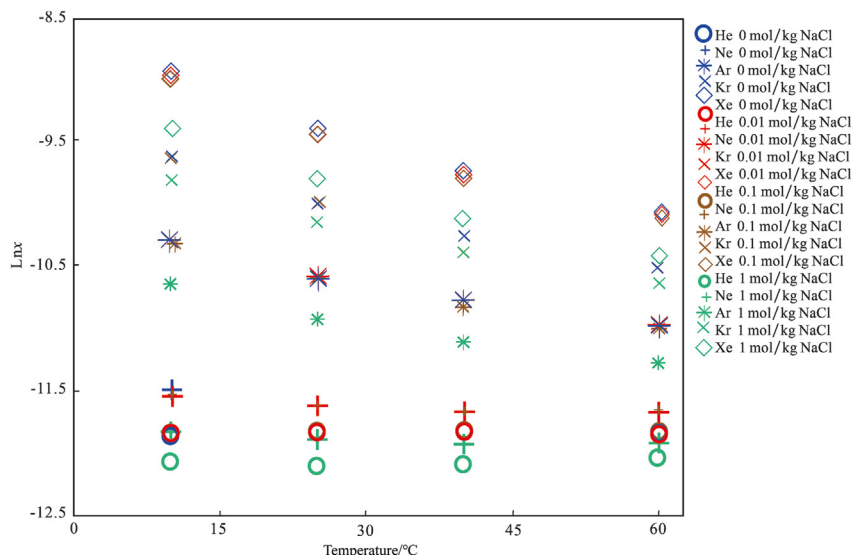


Fig. 4. Comparison of noble gas solubility in pure water and NaCl solutions at 0.1 MPa (x is the molar fraction of noble gas).

challenges. Due to the lack of experimental data, it is currently impossible to accurately evaluate the effects of mixed gas on the solubility of each component. In recent years, Warr et al. [41] designed experiments to study the effect of CO₂ density (169–656 kg/m³) on the solubility of noble gases within the range of 25–104 °C and 0.2–13.4 MPa. The results showed that low-density CO₂ had little effect on the solubility of noble gases, while high-density CO₂ had a significant impact on the solubility of noble gases. For example, compared with Henry's constant of noble gases in the noble gas-H₂O system, the deviations of Henry's constants for He, Ar, Kr, and Xe were –35, 74, 113, and 319%, respectively, in the noble gas-CO₂-H₂O system, where the density of CO₂ is 656 kg/m³. The study suggests that using the Henry's constant of noble gas from the noble gas-water system would result in larger errors in calculated values for CO₂-rich gas reservoirs. Therefore, it is necessary to strengthen theoretical and experimental research on the solubility model of CH₄-CO₂-noble gas mixed gases.

7. Conclusion

Most of the solubility models for CH₄-CO₂-noble gases are semi-empirical theoretical models or fitting formulas. In pure water and NaCl solutions, these five solubility models exhibit high accuracy and a wide application range. They include the CH₄ solubility model in 0–6.0 mol/kg NaCl solutions within the range of 0–250 °C and 0.1–200 MPa, the CO₂ solubility model in 0–4.5 mol/kg NaCl solutions within the range of 0–450 °C and 0.1–150 MPa, the models for calculating solubilities and Henry's constants of atmospheric noble gases in the range of 0–80 °C, the models for calculating Henry's constants of noble gases in pure water, and the solubility models of noble gases in 0–5.8 mol/kg NaCl solutions at 0.1 MPa and in the range of 0–65 °C. These models play important roles in studying the formation and evolution of geological fluids.

The results obtained from these model equations demonstrate that the following: under a certain range of temperature, pressure, and salinity, 1) the solubility of CH₄, CO₂, or noble gases decreases with an increase in NaCl concentration; 2) The solubilities of both CH₄ and CO₂ increase with rising pressure, but their solubilities do not monotonically increase or decrease with changes in temperature. Moreover, the solubility of CO₂ is significantly greater than that of CH₄ under similar conditions; 3) both the solubility and the minimum solubility temperature of He, Ne, Ar, Kr, and Xe increase with an increase in their relative molecular mass, and the Henry's constant of each noble gas can reach a maximum value in pure water.

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Declaration of competing interest

The authors declare no conflict of interest.

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