A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K and from 1 to 2000 bar

Zhenhao Duan *, Shide Mao

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

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Abstract

A thermodynamic model is presented to calculate methane solubility, liquid phase density and gas phase composition of the H₂O–CH₄ and H₂O–CH₄–NaCl systems from 273 to 523 K (possibly up to 573 K), from 1 to 2000 bar and from 0 to 6 mol kg⁻¹ of NaCl with experimental accuracy. By a more strict theoretical approach and using updated experimental data, this model made substantial improvements over previous models: (1) the accuracy of methane solubility in pure water in the temperature range between 273 and 283 K is increased from about 10% to about 5%, but confirms the accuracy of the Duan model [Duan Z., Moller N., Weare J.H., 1992a. Prediction of methane solubilities in natural waters to high ionic strength from 0 to 250 °C and from 0 to 1600 bar. Geochim. Cosmochim. Acta 56, 1451–1460] above 283 K up to 2000 bar; (2) the accuracy of methane solubility in the NaCl aqueous solutions is increased from >12% to about 6% on average from 273 K and 1 bar to 523 K and 2000 bar; (3) this model is able to calculate water content in the gas phase and liquid phase density, which cannot be calculated by previous models; and (4) it covers a wider range of temperature and pressure space. With a simple approach, this model is extended to predict CH₄ solubility in other aqueous salt solutions containing Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻, such as seawater and geothermal brines, with excellent accuracy. This model is also able to calculate homogenization pressure of fluid inclusions (CH₄–H₂O–NaCl) and CH₄ solubility in water at gas–liquid–hydrate phase equilibrium. A computer code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm.

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1. Introduction

CH₄, one of the most important gases in nature, has been found in gas hydrate, natural gases, coalbed gas and fluid inclusions. Accurate prediction of CH₄ solubility in pure water, NaCl solutions and other common aqueous salt solutions over a wide range of temperature, pressure and ionic strength, especially where data do not exist or where experimental data are of poor quality, is important for the above mentioned geochemical applications. There have been many experimental studies of the solubility of CH₄ in pure water and aqueous NaCl solutions. However, these data are very scattered and cover only a limited temperature–pressure space, and are inconvenient to use. Therefore, theorists have devoted extensive efforts to modeling of CH₄ solubility in aqueous solutions so as to interpolate between the data points or extrapolate beyond the data range [Duan et al., 1992a; Soreide and Whitson, 1992; Carroll and Mather, 1997; Li et al., 1997; Li et al., 2001; Spivey et al., 2004]. Among these models, the one by Duan et al. (1992a) has been widely cited for geochemical applications, including the analysis of fluid inclusions, the study of methane hydrates, calculating of the phase status and amount of methane in geothermal or geopressed-geothermal reservoirs. However, all of the published models, including the Duan model, are found to possess intolerable deficiencies, which lead to the motivation of this study.
Over the last two decades, about 10 models have been reported to calculate \( \text{CH}_4 \) solubility in aqueous solutions. \cite{Li1986} studied the phase equilibria of oil, gas and water/brine mixtures from a cubic equation of state and Henry’s Law, but the model is not reliable because they confused the molality with molarity of NaCl, which causes about 10% concentration deviation for a 4 M NaCl solution at 324.65 K and pressure between 100 and 600 bar. \cite{Harvey1989} used an equation of state to predict \( \text{CH}_4 \) solubility in aqueous salt solutions at high pressure, but the deviations are over 15% on average. Combining an EOS with a modified Debye-Hückel electrostatic term, \cite{Aasberg1991} tried to predict \( \text{CH}_4 \) solubility in aqueous mixtures of electrolytes. The predicted solubility is in agreement with experimental data \cite{O'Sullivan1970}. However, it cannot accurately predict \( \text{CH}_4 \) solubility in aqueous NaCl solutions for a large portion of temperature-pressure range, beyond which the deviations increase with temperatures and pressures. In addition, it is not accurate in aqueous NaCl solutions with \( m_{\text{NaCl}} \) above 2.5 mol kg\(^{-1}\). For instance, the average deviation is about 15% at 374 K and 5.7 mol kg\(^{-1}\) compared with experimental data \cite{Blount1982} for \( P < 700 \) bar. Using Henry’s law and Peng-Robinson EOS, \cite{Carroll1997} modeled the solubility of light hydrocarbons in water (C-M model). The valid temperature range for the \( \text{CH}_4-\text{H}_2\text{O} \) system is 298–444 K, but the pressure is limited below 300 bar. \cite{Li2001, Li2003} developed a model to predict the solubility and gas–liquid phase equilibrium in pure water and aqueous electrolyte systems using modified UNIFAC \cite{Weidlich1987} and Soave-Redlich-Kwong EOS \cite{Soave1972}, covering a valid range of 479–589 K and pressure up to 2000 bar for the \( \text{CH}_4-\text{H}_2\text{O} \) system, and the range of 303–398 K, 14–616 bar and 0.5–4.0 mol kg\(^{-1}\) for \( \text{CH}_4-\text{H}_2\text{O}-\text{NaCl} \) system. However, this model cannot calculate \( \text{CH}_4 \) solubility at low temperature, e.g., the average solubility deviation in pure water is up to 20% at 324.65 K compared with experimental measurements \cite{O'Sullivan1970}. \cite{Wu1998} developed a model to predict phase equilibria for systems containing hydrocarbons, water and salt by using an extended Peng-Robinson equation of state, and the calculated \( \text{CH}_4 \) solubility results are no better than those of \cite{Zuo1991}. \cite{Vanderbeken1999} used MVH2 mixing rule to predict \( \text{CH}_4 \) solubility in brines at high temperature and high pressure. The fitted data are mainly calculated from the \cite{Duan1992} model, therefore the prediction accuracy is not better than Duan model.
With a cubic equation of state and the mixing rule of Huron and Vidal (1979), Sorensen et al. (2002) predicted gas solubility in brine. They tried to model CH4 solubility in pure water (298.15–444.15 K and 40–608 atm) and aqueous NaCl solutions (283.15–398.15 K, 1–608 atm and 0.25–4.35 mol kg\(^{-1}\)). However, the average deviation of the calculated CH4 solubility from experimental measurements is up to 26.4% in the CH4–H2O system and up to 25.4% in the CH4–H2O–NaCl system. Chapoy et al. (2004) used the Valderrama modification of the Patel-Teja equation (Valderrama, 1990) and non-density dependent mixing rules (Avlonitis et al., 1994) to model CH4 solubility in water. The \(T–P\) range is very small (275–313 K and 2–200 bar) but the modeling results are in good agreement with experimental measurements. Spivey et al. (2004) presented an empirical model (S-M-N model) to model CH4 solubility in aqueous NaCl solutions, and claimed that the model is valid in the range of 293–623 K, 9–2000 bar and 0–6 molality of NaCl. However, comparison with their fitting data (Sultanov et al., 1972) indicates that the calculated average absolute deviation from data is about 20% between 423 and 623 K. In the important low \(T–P\) regions (273–293 K and 1–9 bar), calculated solubilities are lower than experimental values by about 40% on average.

Trying to overcome the deficiencies of the previous models, in this article we present an improved model to calculate methane solubility, liquid phase density and gas phase composition of the H2O–CH4–NaCl system (273–523 K, 1–2000 bar and 0–6 molality of NaCl) by improving the theoretical approach and using updated experimental data including the corrected data of Blount and Price (1982) instead of their data published in 1979. The framework of the model is presented in Section 2 and the experimental data are reviewed in Section 3. Parameterization and comparison with experimental data are shown in Section 4. Then in Section 5, the model is extended to predict CH4 solubility in other complicated systems like seawater and geothermal brines containing Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Cl\(^-\), and SO\(_4^{2-}\), to calculate homogenization pressure of fluid inclusions; to predicate CH4 solubility in water at gas–liquid–hydrate equilibrium; and to calculate liquid phase density of CH4–H2O–NaCl system at equilibrium.

### 2. Phenomenological description of gas solubility as a function of pressure, temperature and composition

CH4 solubility in aqueous solutions depends on the balance between the chemical potential of CH4 in the liquid phase \(\mu_{CH4}^L\) and that in the vapor phase \(\mu_{CH4}^v\). The potential can be written in terms of fugacity in vapor phase and activity in the liquid phase:

\[
\mu_{CH4}(T, P, y) = \mu_{CH4}^{(0)}(T) + RT \ln f_{CH4}(T, P, y) = \mu_{CH4}^{(0)}(T) + RT \ln y_{CH4}P + RT \ln \varphi_{CH4}(T, P, y_{CH4})
\]

\[
\mu_{CH4}^{(0)}(T) = \frac{\mu_{CH4}(T, P, m) - \mu_{CH4}(T, P)}{m_{CH4}} + RT \ln m_{CH4} + RT \ln \gamma_{CH4}(T, P, m)
\]

where \(\mu_{CH4}^{(0)}\), the standard chemical potential of CH4 in liquid, is defined as the chemical potential in hypothetically ideal solution of unit molality (Denbigh, 1971) and \(\mu_{CH4}^{(0)}\), the standard chemical potential in vapor, is the hypothetical ideal gas chemical potential when the pressure is set to 1 bar.

At phase equilibrium \(\mu_{CH4}^L = \mu_{CH4}^v\), and we obtain

\[
\ln \frac{\gamma_{CH4}P}{m_{CH4}} = \frac{\mu_{CH4}^{(0)}(T, P) - \mu_{CH4}^{(0)}(T)}{RT} - \ln \varphi_{CH4}(T, P, y) + \ln \gamma_{CH4}(T, P, m).
\]

In the parameterization, the reference value \(\mu_{CH4}^{(0)}\) can be set to 0 for convenience, because only the difference between \(\mu_{CH4}^{(0)}\) and \(\mu_{CH4}^{(0)}\) is important. Since there is little water in the vapor phase, the fugacity coefficient of CH4 in gaseous mixtures differs little from that of pure CH4 at 273–565 K. Therefore, \(\ln \varphi_{CH4}\) can be approximated from the EOS for pure CH4 (Duan et al., 1992b) (see Appendix A). \(y_{CH4}\), the mole fraction of CH4 in the gas, is calculated from

\[
y_{CH4} = 1 - y_{H2O} = \frac{P - P_{H2O}}{P},
\]

where the partial pressure of water in vapor, \(P_{H2O}\), is approximated as the saturated pressure of pure water in our previous studies (Duan et al., 1992a; Duan and Sun, 2003; Mao et al., 2005), which will lead to errors (up to 5%) for \(\mu_{CH4}/RT\) and \(\ln \gamma_{CH4}\). However, these errors can be cancelled to a large extent in the parameterization. In this study, the mole fraction of water, \(y_{H2O}\) in the gas phase is estimated using the following semi-empirical equation:

\[
y_{H2O} = \frac{x_{H2O}P_{H2O}^{S} \exp \left( \frac{v_{H2O}^m \left( P - P_{H2O}^S \right) }{RT} \right) }{\varphi_{H2O}P},
\]

where \(x_{H2O}\) is the mole fraction of H2O in the liquid, and is approximated as 1 for CH4–H2O system and \(1 - 2x_{NaCl}\) for CH4–H2O–NaCl system; \(P_{H2O}^S\), the saturation pressure (bar) of water, is calculated from the recent correlation of Shibue (2003); \(v_{H2O}^m\), molar volume of liquid water (cm\(^3\)/mole), approximates saturated liquid phase volume of water and is calculated from the equation of Wagner and Pruss (1993).

The only remaining parameter of Eq. (5) for the calculation of water content in the gas phase, \(y_{H2O}\), is the fugacity coefficient of water (\(\varphi_{H2O}\)) in the gas phase, which can be calculated from the following equation:

\[
\varphi_{H2O} = \exp \left( a_1 + a_2P + a_3P^2 + a_4PT + \frac{a_5P}{T} + \frac{a_6P^2}{T} \right),
\]

where \(a_1 - a_6\) (Table 1) are obtained by regressing the water content data in the gas phase for the CH4–H2O sys-
tem (Olds et al., 1942; Rigby and Prausnitz, 1968; Sultanov et al., 1972; Yarym-Agaev et al., 1985; Yokoyama et al., 1988; Chapoy et al., 2005a,b; Mohammadi et al., 2004a,b). The water content in the gas phase can be accurately calculated by Eqs. (5 and 6), as shown by Fig. 1.

$\ln c_{CH_4}$ is expressed as a virial expansion of excess Gibbs energy (Pitzer, 1973).

$$\ln c_{CH_4} = \sum c_{C}^{2} k_{CH_4}/C_{0}^{m_{C}} + \sum a_{a}^{2} k_{CH_4}/C_{0}^{m_{a}} + \sum c_{a} n_{CH_4}/C_{0}^{m_{C}/C_{0}^{m_{a}}};$$

where $\lambda$ and $\xi$ are second-order and third-order interaction parameters, respectively; $c$ and $a$ refer to cation and anion, respectively. Substituting Eq. (7) into Eq. (3) yields

$$\ln \frac{y_{CH_4}P}{m_{CH_4}} = \frac{\mu_{CH_4}}{RT} - \ln \phi_{CH_4} + \sum c_{C}^{2} \lambda_{C}^{m_{C}} + \sum a_{a}^{2} \lambda_{a}^{m_{a}} + \sum c_{a} n \lambda_{C-a}^{m_{C}} m_{a} m_{a}.$$  

### Table 1

<table>
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<th>Parameters</th>
<th>Values</th>
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<td>$a_1$</td>
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<td>$a_6$</td>
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Fig. 1. The prediction of water content in the gas phase from this model (a–d is for CH$_4$–H$_2$O system and e–f is for CH$_4$–H$_2$O–NaCl system).
<table>
<thead>
<tr>
<th>References</th>
<th>Solution</th>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$N^a$</th>
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(continued on next page)
Following Pitzer et al. (1984), we choose the following equation for the $P-T$ dependence of the solubility parameters, $\mu_{\text{CH}_4}/RT$:

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

Eqs. (8) and (9) form the basis of our model parameterization.

### 3. Review of the CH₄ solubility data

The solubility of CH₄ in pure water and aqueous NaCl solutions has been measured over a wide $P-T-m$ range (Table 2). The measurements of CH₄ solubility in water are extensive. We find that most of the data sets are consistent with each other except for those reported by Michels et al. (1936), Song et al. (1997) and Winkler (1901), whose solubility data deviate from other data sets. Some data points of Duffy et al. (1961) are very scattered. The experimental data of Sultanov et al. (1972) below 523 K are compatible with data of Price (1979) below 523 K, but not above 523 K. Therefore, except for these small number of inconsistent data points (Winkler, 1901; Michels et al., 1936; Duffy et al., 1961; Song et al., 1997), the data points of Sultanov et al. (1972) above 523 K and those of Price (1979) above 565 K, most of experimental solubility measurements in water mentioned in Table 2 are used in the parameterization. The optimal $T-P$ range of this model for CH₄-H₂O system is 273–565 K and 1–2000 bar.

Experimental CH₄ solubility data in aqueous NaCl solutions are not as extensive as in water. The data of Duffy et al. (1961) and Michels et al. (1936) are not accurate due to an inaccurate pressure decline technique as pointed out by O'Sullivan and Smith (1970). Experimental data of Cramer (1984) are not only internally inconsistent, but also inconsistent with other data sets. Therefore, all data points but those of Cramer (1984), Duffy et al. (1961) and Michels et al. (1936) are included in the parameterization which cover a wide $T-P-m$ range (273–513 K, 1–1600 bar and 0–6 mol kg⁻¹) for the CH₄-H₂O-NaCl system.

CH₄ solubility data in aqueous solutions with salts other than NaCl are limited. Blanco and Smith (1978), Duffy et al. (1961) and Michels et al. (1936) measured the CH₄ solubility in aqueous CaCl₂ solutions and Stoessell and Byrne (1982b) measured CH₄ solubility in different aqueous salt solutions at 298 K and pressure below 52 bar. Kiepe et al. (2003) measured the CH₄ solubility in KCl solutions below 100 bar. Experimental data for CH₄ in aqueous CaCl₂ solutions from Duffy et al. (1961) and Michels et al. (1936) are unreliable, as are those in NaCl solutions, due to adopting the inaccurate pressure decline technique.

### 4. Parameterization and comparison with experimental data

Since measurements can only be made in electronically neutral solutions, one of the parameters in Eq. (8) must be assigned arbitrarily (Duan et al., 1992a). $\lambda_{\text{CH}_4-\text{NaCl}}$ is set to zero and then the remaining parameters are fit to the experimental solubility data selected above, where $\mu_{\text{CH}_4}/RT$ is evaluated from the CH₄ solubility data in pure water with a standard deviation of 3.35%; $\chi_{\text{CH}_4-\text{Na}}$ and $\tilde{\chi}_{\text{CH}_4-\text{NaCl}}$ are then evaluated simultaneously to the solubility measurements in aqueous NaCl solutions with a standard deviation of 5.83%. Table 3 lists the optimized parameters.

With these parameters, the CH₄ solubility in pure water (Table 4) and aqueous NaCl solutions (Tables 5–8) can be calculated. It should be noted that the lower left blank region of Tables 4–8 is the CH₄-hydrate region where this model cannot be applied. Table 9 shows the deviation of our model from each data set for the CH₄ solubility in water and aqueous NaCl solutions. Other competitive models (C-M, S-M-N and Duan model) are also compared with experimental data. Figs. 2 and 3 show the comparisons between the experimental results and model predictions. As can be seen from the figures, the experimental

### Table 2 (continued)

<table>
<thead>
<tr>
<th>References</th>
<th>Solution</th>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$N^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duan et al. (1998)</td>
<td>Water</td>
<td>344</td>
<td>200–1000</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0.99–3.99 m KCl</td>
<td>313.51–373.19</td>
<td>4.2–97.9</td>
<td>86</td>
</tr>
<tr>
<td>Wang et al. (2003)</td>
<td>Water</td>
<td>283.2–303.2</td>
<td>20–400.3</td>
<td>17</td>
</tr>
</tbody>
</table>

Note. $^a$ denotes that partial pressure of methane is 1 atm.
data are accurately reproduced by this model and represent improvements over previous models.

Fig. 2 (a–f) shows the experimental CH₄ solubility in water compared with the competitive models. It can be seen that this model and Duan model are apparently better than other models. S-M-N model cannot be applied in low-pressure and low-temperature regions (Fig. 2 a and f). C-M model is only applicable in a small T–P range (<444 K and <300 bar) within experimental uncertainty. This model improves the prediction accuracy between 273 and 283 K over
the Duan model. Note that the less competitive models discussed in the introduction are not compared here.

From Fig. 3 (a–f) we can see that the present model is much more accurate than other models in aqueous NaCl solutions. S-W-N model cannot predict CH₄ solubility in both low and high T–P regions (Fig. 3a, b and f). Duan model deviates substantially from data in the low T–P regions (Fig. 3a, b and d).

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>303.15</td>
</tr>
<tr>
<td>273.15</td>
<td>303.15</td>
</tr>
<tr>
<td>1</td>
<td>0.00127</td>
</tr>
<tr>
<td>50</td>
<td>0.03320</td>
</tr>
<tr>
<td>100</td>
<td>0.05670</td>
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<tr>
<td>150</td>
<td>0.07337</td>
</tr>
<tr>
<td>200</td>
<td>0.08566</td>
</tr>
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<td>0.10308</td>
</tr>
<tr>
<td>400</td>
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<td>500</td>
<td>0.12533</td>
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<tr>
<td>600</td>
<td>0.13342</td>
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<tr>
<td>700</td>
<td>0.14028</td>
</tr>
<tr>
<td>800</td>
<td>0.14621</td>
</tr>
<tr>
<td>900</td>
<td>0.15139</td>
</tr>
<tr>
<td>1000</td>
<td>0.15596</td>
</tr>
<tr>
<td>1100</td>
<td>0.16001</td>
</tr>
<tr>
<td>1200</td>
<td>0.16362</td>
</tr>
<tr>
<td>1300</td>
<td>0.16685</td>
</tr>
<tr>
<td>1400</td>
<td>0.16975</td>
</tr>
<tr>
<td>1500</td>
<td>0.18859</td>
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<tr>
<td>1600</td>
<td>0.19299</td>
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<tr>
<td>1700</td>
<td>0.19723</td>
</tr>
<tr>
<td>1800</td>
<td>0.20133</td>
</tr>
<tr>
<td>1900</td>
<td>0.20532</td>
</tr>
<tr>
<td>2000</td>
<td>0.20922</td>
</tr>
</tbody>
</table>

Table 6
Calculated CH₄ solubility (mol kg⁻¹) in 2 mol kg⁻¹ NaCl solutions

Table 7
Calculated CH₄ solubility (mol kg⁻¹) in 4 mol kg⁻¹ NaCl solutions
solutions can also be derived from the above solubility model:

\[
\frac{\partial \chi_{CH4,H2O}}{\partial P} = \frac{\partial}{\partial P} \left( \frac{\mu^{(0)}(P,T)}{RT} \right)_{m} + \left( \frac{\partial \ln \chi_{CH4}}{\partial P} \right)_{m} + \sum_{a} 2m_{a} \left( \frac{\partial \chi_{CH4-a}}{\partial P} \right)_{T,m} + \sum_{a} \sum_{b} m_{a}m_{b} \left( \frac{\partial \chi_{CH4-a-b}}{\partial P} \right)_{T,m}
\]

(10)

\[
k_{H2}(T) = y_{CH4} \chi_{CH4} \frac{P}{\chi_{H2}} - c_{m}P \exp \left( -\frac{T_{\chi_{H2}}(P-P_{H2,O})}{RT} \right)
\]

(11)

\[
-\frac{\Delta H^'}{RT^2} = \frac{\partial}{\partial T} \left( \frac{\mu^{(0)}(P,T)}{RT} \right)_{P,m} + \left( \frac{\partial \ln \chi_{CH4}}{\partial T} \right)_{P,m} + \sum_{a} 2m_{a} \left( \frac{\partial \chi_{CH4-a}}{\partial T} \right)_{P,m} + \sum_{a} \sum_{b} m_{a}m_{b} \left( \frac{\partial \chi_{CH4-a-b}}{\partial T} \right)_{P,m}
\]

(12)

\[
\left( \frac{\partial Par(T,P)}{\partial P} \right)_{T,m} = c_{6} + c_{7}T + c_{8}P + c_{9}T^{2} + 2c_{10}PT
\]

(13)

The predicted molar heat of solution (Table 10) and Henry’s constant of CH4 in water (Table 11) are compared with some experimental or calculated results, which exhibit a good agreement. These, from another respective, prove the reliability of this model.

5. Applications of this model

5.1. Calculating CH4 solubility in aqueous solutions with salts other than NaCl, such as seawater and geothermal brines

This model can be extrapolated to more complex aqueous solutions containing Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, and SO₄²⁻. Because of the data limitations for aqueous solutions with salts other than NaCl, it is impossible to fit directly to experimental measurements as is possible with CH₄–H₂O–NaCl system. We therefore take a theoretically predictive approach to this problem. According to Duan et al. (1992a), CH₄–monovalent–cation interaction parameters have roughly the same value, and CH₄–bivalent cation interaction parameters are about twice as much as the CH₄–monovalent interaction parameters at various temperatures and pressures. The CH₄–anion interaction parameters are relatively small
and contribute little to the calculation. Using the same approach, we approximate all CH$_4$–monovalent cation and CH$_4$–bivalent cation interaction parameters as $k_{\text{CH}_4-Na^+}$ and $2k_{\text{CH}_4-Na^{2+}}$, respectively. The same treatment applies to the ternary parameters. With this simplification, Eq. (8) becomes

$$\ln m_{\text{CH}_4} = \ln \left( \frac{y_{\text{CH}_4}}{u_{\text{CH}_4} P} \right) - \frac{1}{RT} \left( \frac{m_{\text{Na}^+}}{\lambda_{\text{CH}_4-Na^+}} + \frac{m_{\text{K}^+}}{\lambda_{\text{CH}_4-Na^{2+}}} + 2m_{\text{Ca}^{2+}} + 2m_{\text{Mg}^{2+}} \right)$$

$$- \frac{m_{\text{Cl}^-}}{\xi_{\text{CH}_4-Na^{2+}+\text{Cl}^-}} \left( \frac{m_{\text{Na}^+}}{\lambda_{\text{CH}_4-Na^{2+}+\text{Cl}^-}} + \frac{m_{\text{K}^+}}{\lambda_{\text{CH}_4-Na^{2+}+\text{Cl}^-}} + 2m_{\text{Ca}^{2+}} + 2m_{\text{Mg}^{2+}} \right)$$

$$\times \left( \frac{m_{\text{Cl}^-}}{\lambda_{\text{CH}_4-\text{Cl}^-}} - 4\lambda_{\text{CH}_4-\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}} \right),$$

(15)

where $\lambda_{\text{CH}_4-\text{SO}_4^{2-}} = 0.0332$. In order to test this approximation, we compare the calculated results from Eq. (15) with experimental data of CH$_4$ solubility in aqueous CaCl$_2$, KCl, and K$_2$SO$_4$ solutions (Fig. 4), seawater and brines (Table 12). It can be seen that the agreement between this approach and the experimental measurements is excellent.

5.2. Calculating homogenization pressure of fluid inclusions with CH$_4$–H$_2$O–NaCl

Fluid inclusions provide the most direct information on the formation conditions (such as temperature, pressure, and composition) of geological bodies. Phase relations in the CH$_4$–H$_2$O–NaCl system at high temperatures have been carefully studied by Lamb et al. (2002, 1996). Dubessy et al. (2001) and Théry (2006) have studied the methane-bearing aqueous fluid

<table>
<thead>
<tr>
<th>References</th>
<th>System</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>Na AAD (%)</th>
<th>MAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bunsen (1855)</td>
<td>Water</td>
<td>279.35–298.75</td>
<td>1$^\dagger$</td>
<td>5</td>
<td>1.18</td>
</tr>
<tr>
<td>Winkler (1901)</td>
<td>Water</td>
<td>273.38–353.17</td>
<td>1$^\dagger$</td>
<td>9</td>
<td>7.93</td>
</tr>
<tr>
<td>Culberson et al. (1950)</td>
<td>Water</td>
<td>298.15</td>
<td>36.2–667.4</td>
<td>10</td>
<td>6.94</td>
</tr>
<tr>
<td>Eucken and Hertzberg (1950)</td>
<td>0–2.77 m NaCl</td>
<td>273.15–293.15</td>
<td>1$^\dagger$</td>
<td>7</td>
<td>5.55</td>
</tr>
<tr>
<td>Culberson and Mcketta (1951)</td>
<td>Water</td>
<td>298.2–444.3</td>
<td>22.3–689.1</td>
<td>71</td>
<td>2.12</td>
</tr>
<tr>
<td>Morris and Billiet (1952)</td>
<td>Water</td>
<td>285.1–346.4</td>
<td>1$^\dagger$</td>
<td>11</td>
<td>5.00</td>
</tr>
<tr>
<td>Clausen and Polglase (1952)</td>
<td>Water</td>
<td>274.8–312.8</td>
<td>1$^\dagger$</td>
<td>6</td>
<td>1.13</td>
</tr>
<tr>
<td>Lannung and Gjaldbaek (1960)</td>
<td>Water</td>
<td>291.15–310.15</td>
<td>1$^\dagger$</td>
<td>6</td>
<td>1.83</td>
</tr>
<tr>
<td>Namjot (1961)</td>
<td>Water</td>
<td>273.15–303.15</td>
<td>1$^\dagger$</td>
<td>2</td>
<td>0.75</td>
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<tr>
<td>Mishinina et al. (1962)</td>
<td>0–6.24 m NaCl</td>
<td>277.15–363.15</td>
<td>1$^\dagger$</td>
<td>45</td>
<td>4.73</td>
</tr>
<tr>
<td>Wen and Hung (1970)</td>
<td>Water</td>
<td>278.15–308.15</td>
<td>1$^\dagger$</td>
<td>4</td>
<td>1.63</td>
</tr>
<tr>
<td>Amirijafari and Campbell (1972)</td>
<td>Water</td>
<td>310.93–344.26</td>
<td>41.4–344.7</td>
<td>8</td>
<td>2.22</td>
</tr>
<tr>
<td>Ben-Naim et al. (1973)</td>
<td>Water</td>
<td>278.15–298.15</td>
<td>1$^\dagger$</td>
<td>5</td>
<td>0.78</td>
</tr>
<tr>
<td>Ben-Naim and Yaacobi (1974)</td>
<td>Water</td>
<td>283.15–303.15</td>
<td>1$^\dagger$</td>
<td>5</td>
<td>0.83</td>
</tr>
<tr>
<td>Moudgil et al. (1974)</td>
<td>Water</td>
<td>298.15</td>
<td>1$^\dagger$</td>
<td>1</td>
<td>0.48</td>
</tr>
<tr>
<td>Yano et al. (1974)</td>
<td>0–1.55 m NaCl</td>
<td>298.15</td>
<td>1$^\dagger$</td>
<td>4</td>
<td>12.20</td>
</tr>
<tr>
<td>Yamamoto et al. (1976)</td>
<td>Water</td>
<td>273.91–302.70</td>
<td>1$^\dagger$</td>
<td>35</td>
<td>1.23</td>
</tr>
<tr>
<td>Namjot et al. (1979)</td>
<td>Water</td>
<td>1.01–4.41 m NaCl</td>
<td>324.65–398.15</td>
<td>101.3–616.1</td>
<td>22</td>
</tr>
<tr>
<td>Price (1979)</td>
<td>Water</td>
<td>427.5–589</td>
<td>35.4–1924.7</td>
<td>53</td>
<td>5.53</td>
</tr>
<tr>
<td>Muccitelli and Wen (1980)</td>
<td>Water</td>
<td>278.15–298.15</td>
<td>1$^\dagger$</td>
<td>5</td>
<td>1.33</td>
</tr>
<tr>
<td>Cosgrove and Walkley (1981)</td>
<td>Water</td>
<td>278.15–318.15</td>
<td>1$^\dagger$</td>
<td>9</td>
<td>3.16</td>
</tr>
<tr>
<td>Reitich et al. (1981)</td>
<td>Water</td>
<td>275.46–328.15</td>
<td>1$^\dagger$</td>
<td>16</td>
<td>0.88</td>
</tr>
<tr>
<td>Crovetto et al. (1982)</td>
<td>Water</td>
<td>297.5–518.3</td>
<td>13.27–64.51</td>
<td>7</td>
<td>3.31</td>
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<tr>
<td>Stoessel and Byrne (1982b)</td>
<td>Water</td>
<td>298.15</td>
<td>24.1–51.7</td>
<td>3</td>
<td>0.83</td>
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<tr>
<td>Stolz et al. (2000)</td>
<td>Water</td>
<td>298.15</td>
<td>24.1–51.7</td>
<td>3</td>
<td>0.83</td>
</tr>
<tr>
<td>Yarym-Agaev et al. (1985)</td>
<td>Water</td>
<td>298.2–338.2</td>
<td>25–125</td>
<td>15</td>
<td>2.63</td>
</tr>
<tr>
<td>Lekvam and Bishnoi (1997)</td>
<td>Water</td>
<td>274.19–285.68</td>
<td>5.67–90.82</td>
<td>18</td>
<td>5.05</td>
</tr>
<tr>
<td>Dhima et al. (1998)</td>
<td>Water</td>
<td>344</td>
<td>200–1000</td>
<td>4</td>
<td>2.88</td>
</tr>
<tr>
<td>Kiepe et al. (2003)</td>
<td>Water</td>
<td>313–473</td>
<td>3.4–93</td>
<td>15</td>
<td>2.08</td>
</tr>
<tr>
<td>Wang et al. (2003)</td>
<td>Water</td>
<td>283.2–303.2</td>
<td>20–400.3</td>
<td>17</td>
<td>6.11</td>
</tr>
</tbody>
</table>
inclusions. If the homogenization temperature and compositions of the fluid inclusions are known from microthermometric and spectroscopic techniques, the homogenization pressure of inclusions and the density at the homogenization can be determined from solubility models. Taking advantage of this approach, we calculate the trapping pressure of the quartz crystal from central alpine clefts (Table 13), using the fluid compositions in the H₂O–CH₄–NaCl system and homogenization temperatures of Mullis (1979). Mullis (1979) also calculated the trapping pressure using an alternative approach and the results are also shown in Table 13. They generally fall within the range of pressure calculated from our model. At a given temperature, the uncertainty of pressure increases with molality of CH₄ and NaCl (Fig. 5) and the average uncertainty of pressure in the studied region is about 9.5%.

5.3. Calculating CH₄ solubility in liquid phase at gas–liquid–hydrate three phase equilibrium

CH₄ can form hydrate in pure water and aqueous NaCl solutions in the low-temperature and high-pressure region. Once the pressure of CH₄ at gas–liquid–hydrate
equilibrium is determined for a given temperature, the CH$_4$ solubility in pure water and aqueous NaCl solutions can be calculated from this model. Recently, Sun and Duan (2005) developed a model that can predict the CH$_4$–hydrate and CO$_2$–hydrate formation pressure for a given temperature. With the temperature and pressure from the Sun and Duan (2005) model, we calculate the CH$_4$ solubility in pure water at gas–liquid–hydrate equilibrium (273.15–314.15 K and 26–2185 bar) (see Table 14).

5.4. Calculating liquid phase density of CH$_4$–H$_2$O–NaCl system at equilibrium

Liquid phase density of CH$_4$–H$_2$O–NaCl system at equilibrium can also be calculated from this model. In order to calculate the density of liquids in the CH$_4$–H$_2$O–NaCl system, an accurate density model for H$_2$O–NaCl system is required. There are two good density models for the H$_2$O–NaCl system covering a large T–P–m range. One was developed by Spivey et al. (2004) with valid T–P–m
Here, we present a simple but reliable approach to calculate the liquid phase density of CH$_4$–H$_2$O–NaCl system at phase equilibrium:

\[
m_{\text{sol}} = 1000 + m_{\text{NaCl}}M_{\text{NaCl}} + m_{\text{CH}_4}M_{\text{CH}_4},
\]

\[
V_{\text{sol}} = \frac{1000 + m_{\text{NaCl}}M_{\text{NaCl}} + m_{\text{CH}_4}V_{\text{CH}_4}}{\rho_{\text{H}_2\text{O}-\text{NaCl}}},
\]

\[
\rho_{\text{sol}} = \frac{m_{\text{sol}}}{V_{\text{sol}}},
\]

where the partial molar volume of CH$_4$, $V_{\text{CH}_4}$, can be obtained from Eqs. (10) and (13), the molar mass of NaCl $M_{\text{NaCl}} = 58.4428$ g mol$^{-1}$ and the molar mass of CH$_4$ $M_{\text{CH}_4} = 16.042$ g mol$^{-1}$. $\rho_{\text{H}_2\text{O}-\text{NaCl}}$ is the liquid phase density of the H$_2$O–NaCl system, either calculated from the Spivey model or from Roger-Pitzer model. The calculated liquid phase density of CH$_4$–H$_2$O–NaCl system at phase equilibrium based on Roger-Pitzer model and the Spivey model is compiled in Table 15. It can be seen that the calculated results by using two different density models of the H$_2$O–NaCl system are very close in the $T$–$P$–$m$ region where the studies overlap.

Table 10
Molar heat of solution of CH$_4$ in water

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$-\Delta H^m_s$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>288.15</td>
<td>1</td>
<td>15.45</td>
</tr>
<tr>
<td>298.15</td>
<td>1</td>
<td>13.18</td>
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<tr>
<td>308.15</td>
<td>1</td>
<td>11.09</td>
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<td>9.75</td>
</tr>
<tr>
<td>323.15</td>
<td>1</td>
<td>7.59</td>
</tr>
<tr>
<td>333.15</td>
<td>1</td>
<td>5.54</td>
</tr>
</tbody>
</table>

a. Dec and Gill (1984, 1985); b. Olofsson et al. (1984); c. Rettich et al. (1981); d. This study.

Table 11
Henry’s constants ($k_H$) of CH$_4$ in water

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k_{H1}$ (bar)</th>
<th>$k_{H2}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>22110</td>
<td>22804</td>
</tr>
<tr>
<td>298</td>
<td>38741</td>
<td>39381</td>
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<td>40064</td>
<td>40690</td>
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<td>350</td>
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<td>42390</td>
<td>44294</td>
</tr>
<tr>
<td>500</td>
<td>24824</td>
<td>28128</td>
</tr>
</tbody>
</table>

$k_{H1}$, calculated from this model; $k_{H2}$, from Fernandez-Prini et al. (2003).

Fig. 4. CH$_4$ solubility predictions in aqueous CaCl$_2$, KCl and K$_2$SO$_4$ solutions (a–b is for CaCl$_2$(aq) solution, c is for KCl(aq) solution and d is for K$_2$SO$_4$(aq) solution).
Based on a simple fugacity coefficient equation used to predict gas phase water content, and a highly accurate EOS (Duan et al., 1992b) for gas phase, and the electrolyte solution theory of Pitzer (1973) for liquid phase, an accurate model is presented here to calculate CH$_4$ solubility in pure water and aqueous NaCl solutions, gas phase compositions and liquid phase density with experimental accuracy from 273 to 523 K (possibly to 573 K), from 1 to 2000 bar and up to high salt concentrations (0–6 mol kg$^{-1}$ of NaCl). With a simple approach, this model is extrapolated to predict the CH$_4$ solubility in other aqueous solutions containing Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, and SO$_4^{2-}$ like seawater and geothermal brines with remarkable accuracy. In addition, this model can be used to calculate the homogenization pressure of fluid

**Table 12**
Solubility of CH$_4$ in seawater and Salton Sea geothermal brine

<table>
<thead>
<tr>
<th>Solutions</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>$m_{\text{CH}_4}$(exp) (mol kg$^{-1}$)</th>
<th>$m_{\text{CH}_4}$(cal) (mol kg$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>Seawater (Stoessell and Byrne, 1982b)</td>
<td>298.15</td>
<td>24.1</td>
<td>0.0263</td>
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<td>298.15</td>
<td>51.7</td>
<td>0.0514</td>
<td>0.05228</td>
</tr>
<tr>
<td>Salton Sea geothermal brine (Cramer, 1984)</td>
<td>277.65</td>
<td>26</td>
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<td>0.01047</td>
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<td></td>
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*Note. $m_{\text{CH}_4}$(exp) and $m_{\text{CH}_4}$(cal) denote experimental and calculated CH$_4$ solubility data from this model, respectively.*

**Table 13**
The formation pressure of the ‘Fadenquartz’ in Central Alps

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<tr>
<th>Locality</th>
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<th>$x_{\text{CH}_4}$</th>
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<td></td>
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<td>Val d’Iliez</td>
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<td>0.022–0.030</td>
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<td>Chexx</td>
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<td>Les Monte</td>
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<td>0.016–0.022</td>
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<tr>
<td>Metholz</td>
<td>503.15</td>
<td>0.014–0.020</td>
<td>621–1223</td>
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<tr>
<td>Jour De Duin</td>
<td>517.15</td>
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**Table 14**
CH$_4$ solubility in pure water at CH$_4$ hydrate–liquid water–gas equilibrium

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$P_{\text{eq}}$ (bar)</th>
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<tr>
<td>275.15</td>
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<tr>
<td>276.15</td>
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<td>278.15</td>
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</table>

$P_{\text{eq}}$, equilibrium pressure for the CH$_4$ hydrate–liquid water–gas assemblage.

Fig. 5. The uncertainty of pressure vs. molality of CH$_4$ at a given temperature.

**6. Conclusions**

Based on a simple fugacity coefficient equation used to predict gas phase water content, and a highly accurate EOS (Duan et al., 1992b) for gas phase, and the electrolyte solution theory of Pitzer (1973) for liquid phase, an accurate model is presented here to calculate CH$_4$ solubility in pure water and aqueous NaCl solutions, gas phase compositions and liquid phase density with experimental accuracy from 273 to 523 K (possibly to 573 K), from 1 to 2000 bar and up to high salt concentrations (0–6 mol kg$^{-1}$ of NaCl). With a simple approach, this model is extrapolated to predict the CH$_4$ solubility in other aqueous solutions containing Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, and SO$_4^{2-}$ like seawater and geothermal brines with remarkable accuracy. In addition, this model can be used to calculate the homogenization pressure of fluid
Table 15
Calculated liquid phase density of CH$_4$–H$_2$O–NaCl system from this model at equilibrium

<table>
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<tr>
<th>$T$ (K)</th>
<th>P (bar)</th>
<th>$m_{NaCl}$ (mol kg$^{-1}$)</th>
<th>$m_{CH_4}$ mol kg$^{-1}$</th>
<th>Method 1 $\rho_{H_2O,NaCl}$ (g cm$^{-3}$)</th>
<th>$\rho_{CH_4,H_2O,NaCl}$ (g cm$^{-3}$)</th>
<th>Method 2 $\rho_{H_2O,NaCl}$ (g cm$^{-3}$)</th>
<th>$\rho_{CH_4,H_2O,NaCl}$ (g cm$^{-3}$)</th>
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Note. $m_{CH_4}$ is the calculated solubility data from this model; Method 1, $\rho_{H_2O,NaCl}$ from Spivey et al. (2004) (273–548 K and 1–2000 bar); Method 2, $\rho_{CH_4,NaCl}$ calculated from Duan et al. (1992b) and $\rho_{H_2O,NaCl}$ from Rogers and Pitzer (1982) (273–573 K and saturation pressure $\leq P \leq 1000$ bar); $\rho_{CH_4,H_2O,NaCl}$ denotes liquid phase density of CH$_4$–H$_2$O–NaCl system at equilibrium.

inclusions (CH$_4$–H$_2$O–NaCl), to predict CH$_4$ solubility in liquid phase at gas–liquid–hydrate equilibria and the liquid phase density of CH$_4$–H$_2$O–NaCl system at phase equilibria. A FORTRAN code is developed for this model and can be downloaded from the website: www.chem-model.org/programs.htm.

Acknowledgments

We thank Drs. Jean Dubessy, Robert J. Bodnar, David J. Wesolowski, and an anonymous reviewer for their constructive suggestions. This work is supported by Zhenhao Duan’s “key Project” funds (40537032) and his outstanding young scientist funds (#40225008) awarded by National Natural Science Foundation of China.

Associate editor: David J. Wesolowski

Appendix A

The equation of state for CH$_4$

$$Z = \frac{P_r V_r}{T_r} = 1 + a_1 + a_2/T_r + a_3/T_r^2 + a_4 + a_5/T_r^2 + a_6/T_r^3$$

$$+ a_7 + a_8/T_r^2 + a_9/T_r^3 + a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3$$

$$+ a_{13} \frac{P_r}{T_r^2} \exp \left( -a_{15} \frac{V_r}{T_r^2} \right)$$

(A1)

$$P_r = \frac{P}{P_c}; \quad T_r = \frac{T}{T_c};$$

$$V_r = \frac{V}{V_c}; \quad V_c = \frac{RT_c}{P_c}$$

(A2)

(A3)
where $P_c$ and $T_c$ are critical pressure and critical temperature, respectively; $R$ is universal gas constant (83.14472 bar cm$^3$ K$^{-1}$ mol$^{-1}$); $V$ is molar volume. Note that $V_c$ is not the real critical volume. The parameters of the EOS are referred to Duan et al. (1992b). The critical properties of CH$_4$ are: $T_c = 190.6$ K; $P_c = 46.41$ bar. The fugacity coefficient of CH$_4$ can be derived from Eq. (A1):

$$
\ln \varphi(T, P) = Z - 1 - \ln Z + \frac{a_1 + a_2/T_r^2 + a_3/T_2^2}{V_t} + \frac{a_4 + a_5/T_r^2 + a_6/T_2^2}{2V_r^2} + \frac{a_7 + a_8/T_r^2 + a_9/T_2^2}{4V_r^4} + \frac{a_{10} + a_1/T_r^2 + a_{12}/T_2^2 + a_{13}}{5V_r^2} + \frac{a_{14}}{2T_r^2 a_{15}} \times \left[a_{14} + 1 - \left(a_{14} + 1 + \frac{a_{15}}{V_r^2}\right) \exp \left(-\frac{a_{15}}{V_r^2}\right)\right].
\] (A4)

### References


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