

# An improved model for the calculation of CO<sub>2</sub> solubility in aqueous solutions containing Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>−</sup>, and SO<sub>4</sub><sup>2−</sup>

Zhenhao Duan<sup>a,\*</sup>, Rui Sun<sup>a</sup>, Chen Zhu<sup>b</sup>, I-Ming Chou<sup>c</sup>

<sup>a</sup> State Key Laboratory of Lithospheric Evolution, Chinese Academy of Sciences, Institute of Geology and Geophysics, Beijing, 100029, China

<sup>b</sup> Department of Geological Sciences, Indiana University, Bloomington, IN 47401, USA

<sup>c</sup> MS 954, U.S. Geological Survey, Reston, VA 20192, USA

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## Abstract

An improved model is presented for the calculation of the solubility of carbon dioxide in aqueous solutions containing Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>−</sup>, and SO<sub>4</sub><sup>2−</sup> in a wide temperature–pressure–ionic strength range (from 273 to 533 K, from 0 to 2000 bar, and from 0 to 4.5 molality of salts) with experimental accuracy. The improvements over the previous model [Duan, Z. and Sun, R., 2003. An improved model calculating CO<sub>2</sub> solubility in pure water and aqueous NaCl solutions from 273 to 533K and from 0 to 2000 bar. *Chemical Geology*, 193: 257–271] include: (1) By developing a non-iterative equation to replace the original equation of state in the calculation of CO<sub>2</sub> fugacity coefficients, the new model is at least twenty times computationally faster and can be easily adapted to numerical reaction-flow simulator for such applications as CO<sub>2</sub> sequestration and (2) By fitting to the new solubility data, the new model improved the accuracy below 288 K from 6% to about 3% of uncertainty but still retains the high accuracy of the original model above 288 K. We comprehensively evaluate all experimental CO<sub>2</sub> solubility data. Compared with these data, this model not only reproduces all the reliable data used for the parameterization but also predicts the data that were not used in the parameterization. In order to facilitate the application to CO<sub>2</sub> sequestration, we also predicted CO<sub>2</sub> solubility in seawater at two-phase coexistence (vapor–liquid or liquid–liquid) and at three-phase coexistence (CO<sub>2</sub> hydrate–liquid water–vapor CO<sub>2</sub> [or liquid CO<sub>2</sub>]). The improved model is programmed and can be downloaded from the website <http://www.geochem-model.org/programs.htm>.

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**Keywords:** CO<sub>2</sub>; Solubility; Aqueous solution; CO<sub>2</sub> sequestration; Fluid flow simulation

## 1. Introduction

Accurate prediction of CO<sub>2</sub> solubility over a wide range of temperature, pressure and ionic strength is important to the studies of geological CO<sub>2</sub> sequestration, carbonate precipitation, the global carbon cycle, and fluid inclusions (Kaszuba et al., 2003; Spycher et

al., 2003; Xu et al., 2004; Cipolli et al., 2004; Wolf et al., 2004). A thermodynamic model was developed previously to predict CO<sub>2</sub> solubility in aqueous NaCl solutions and other aqueous electrolyte solutions (Duan and Sun, 2003). The relatively high accuracy and wide temperature–pressure–composition range (from 0 to 260 °C, 0 to 2000 bar, and 0 to 4.5 m NaCl) of that model permit its applications in numerical simulation programs. However, that model uses an accurate fifth-order virial equation of state (EOS) to calculate the

\* Corresponding author. Tel.: +1 8588220281.

E-mail address: [duanzhenhao@yahoo.com](mailto:duanzhenhao@yahoo.com) (Z. Duan).

fugacity coefficients iteratively, which is computationally expensive for numerical simulations of large-scale geological sequestration processes that require calculation of CO<sub>2</sub> solubility at each grid and at each time step (Spycher et al., 2003).

Considering the demand for efficient calculations of CO<sub>2</sub> solubility, this study has developed a non-iterative equation to calculate the fugacity coefficient of CO<sub>2</sub> and provided a computer program to calculate CO<sub>2</sub> solubility in aqueous solutions at given temperature, pressure and concentrations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>−</sup>, and SO<sub>4</sub><sup>2−</sup>. The non-iterative equation will be described in the next section. Since the submittal of the article of Duan and Sun (2003), quite a few new experimental data sets have become available, e.g., the work of Anderson (2002), Servio and Englezos (2001), Chapoy et al. (2004), Valtz et al. (2004), and Robert Rosenbauer (personal communication). Most of the new data are consistent with our model (Duan and Sun, 2003), but there is an average deviation of 5–10% below 288 K. Therefore, we re-fitted our model to the data between 273 and 288 K by adjusting the modeling parameters. This modification will also be introduced in Section 2. In Section 3, we comprehensively evaluate all the CO<sub>2</sub> solubility data and compared our model with both the data used for the parameterization and the data not used for the parameterization. We also predicted CO<sub>2</sub> solubilities in seawater under two-phase coexistence (vapor–liquid or liquid–liquid) and three-phase coexistence conditions (CO<sub>2</sub> hydrate–liquid solution–vapor or liquid CO<sub>2</sub>) in order to facilitate applications.

## 2. The improvements of the previous CO<sub>2</sub> solubility model

According to Eq. (9) of Duan and Sun (2003), the solubility of CO<sub>2</sub> can be calculated by

$$\begin{aligned} \ln m_{\text{CO}_2} = & \ln y_{\text{CO}_2} \phi_{\text{CO}_2} P - \mu_{\text{CO}_2}^{(0)} / RT \\ & - 2\lambda_{\text{CO}_2-\text{Na}} (m_{\text{Na}} + m_{\text{K}} + 2m_{\text{Ca}} + 2m_{\text{Mg}}) \\ & - \zeta_{\text{CO}_2-\text{Na}-\text{Cl}} m_{\text{Cl}} (m_{\text{Na}} + m_{\text{K}} + m_{\text{Mg}} + m_{\text{Ca}}) \\ & + 0.07m_{\text{SO}_4} \end{aligned} \quad (1)$$

where  $T$  is absolute temperature in Kelvin,  $P$  represents the total pressure of the system in bar,  $R$  is universal gas constant,  $m$  means the molality of components dissolved in water,  $y_{\text{CO}_2}$  is the mole fraction of CO<sub>2</sub> in vapor phase,  $\phi_{\text{CO}_2}$  is the fugacity coefficient of CO<sub>2</sub>,  $\mu_{\text{CO}_2}^{(0)}$  is the standard chemical potential

of CO<sub>2</sub> in liquid phase,  $\lambda_{\text{CO}_2-\text{Na}}$  is the interaction parameter between CO<sub>2</sub> and Na<sup>+</sup>,  $\zeta_{\text{CO}_2-\text{Na}-\text{Cl}}$  is the interaction parameter between CO<sub>2</sub> and Na<sup>+</sup>, Cl<sup>−</sup>. All parameters presented in Eq. (1) can be calculated directly without any iteration, except the fugacity coefficient of CO<sub>2</sub>,  $\phi_{\text{CO}_2}$ , which is calculated from the fifth-order virial EOS developed by Duan et al. (1992), and a time-consuming iterative procedure was needed to solve the EOS. This study proposes a non-iterative equation to calculate  $\phi_{\text{CO}_2}$  as a function of temperature and pressure,

$$\begin{aligned} \phi_{\text{CO}_2} = & c_1 + [c_2 + c_3T + c_4/T + c_5/(T - 150)]P \\ & + [c_6 + c_7T + c_8/T]P^2 \\ & + [c_9 + c_{10}T + c_{11}/T] \ln P + [c_{12} + c_{13}T]/P \\ & + c_{14}/T + c_{15}T^2, \end{aligned} \quad (2)$$

where  $T$  is in K and  $P$  in bar. The parameters  $c_1, c_2, c_3, \dots, c_{14}, c_{15}$  were fitted to  $\phi_{\text{CO}_2}$  calculated from the EOS of Duan et al. (1992) at the  $T$ – $P$  range where our CO<sub>2</sub> solubility model is valid. We found that it is difficult to reproduce  $\phi_{\text{CO}_2}$  over a wide  $T$ – $P$  range with a single set of parameters. Thus, we divided the  $T$ – $P$  range into six sections and fit a set of parameters for each section. Table 1 lists the parameters for Eq. (2). The absolute average deviation between  $\phi_{\text{CO}_2}$  calculated from Eq. (2) and  $\phi_{\text{CO}_2}$  calculated from the EOS of Duan et al. (1992) is less than 0.4%. The maximum deviation is 1%. The consequent deviation in CO<sub>2</sub> solubility is less than 0.4% from those calculated with Eq. (1). This deviation is small, considering the average experimental error is in the order of about 5%.

Since the manuscript of Duan and Sun (2003) was submitted, a few experimental solubility data sets in the  $T$ – $P$  range from 273 to 298 K and from 2 to 50 bar have become available (Anderson, 2002; Chapoy et al., 2004; Servio and Englezos, 2001; Valtz et al., 2004). The accuracy of the data of Anderson (2002) was confirmed by Diamond and Akinfiev (2003). The data of Chapoy et al. (2004) are consistent with that of Anderson (2002). The solubility data measured by Servio and Englezos (2001) are smaller than that of Anderson (2002) by 4–9%. The measurements of Valtz et al. (2004) are greater than that of Anderson (2002) by 3–6%. The predictions of our solubility model for CO<sub>2</sub> solubility in pure water at temperatures below 288 K are lower than the measurements of Anderson (2002) by 3–8%. Although this deviation is not large, when compared with the average experimental uncertainty of about 5%, we re-evaluat-

Table 1  
The parameters of Eq. (2)

Par	<i>T</i> – <i>P</i> range					
	1	2	3	4	5	6
<i>c</i> <sub>1</sub>	1.0	−7.1734882E−1	−6.5129019E−2	5.0383896	−16.063152	−1.5693490E−1
<i>c</i> <sub>2</sub>	4.7586835E−3	1.5985379E−4	−2.1429977E−4	−4.4257744E−3	−2.7057990E−3	4.4621407E−4
<i>c</i> <sub>3</sub>	−3.3569963E−6	−4.9286471E−7	−1.1444930E−6	0.0	0.0	−9.1080591E−7
<i>c</i> <sub>4</sub>	0.0	0.0	0.0	1.9572733	1.4119239E−1	0.0
<i>c</i> <sub>5</sub>	−1.3179396	0.0	0.0	0.0	0.0	0.0
<i>c</i> <sub>6</sub>	−3.8389101E−6	−2.7855285E−7	−1.1558081E−7	2.4223436E−6	8.1132965E−7	1.0647399E−7
<i>c</i> <sub>7</sub>	0.0	1.1877015E−9	1.1952370E−9	0.0	0.0	2.4273357E−10
<i>c</i> <sub>8</sub>	2.2815104E−3	0.0	0.0	−9.3796135E−4	−1.1453082E−4	0.0
<i>c</i> <sub>9</sub>	0.0	0.0	0.0	−1.5026030	2.3895671	3.5874255E−1
<i>c</i> <sub>10</sub>	0.0	0.0	0.0	3.0272240E−3	5.0527457E−4	6.3319710E−5
<i>c</i> <sub>11</sub>	0.0	0.0	0.0	−31.377342	−17.763460	−249.89661
<i>c</i> <sub>12</sub>		−96.539512	−221.34306	−12.847063	985.92232	0.0
<i>c</i> <sub>13</sub>		4.4774938E−1	0.0	0.0	0.0	0.0
<i>c</i> <sub>14</sub>		101.81078	71.820393	0.0	0.0	888.76800
<i>c</i> <sub>15</sub>		5.3783879E−6	6.6089246E−6	−1.5056648E−5	−5.4965256E−7	−6.6348003E−7

1: 273 K < *T* < 573 K, *P* < *P*<sub>1</sub> (when *T* < 305 K, *P*<sub>1</sub> equals to the saturation pressure of CO<sub>2</sub>; when 305 K < *T* < 405 K, *P*<sub>1</sub> = 75 + (*T* − 305) × 1.25; when *T* > 405 K, *P*<sub>1</sub> = 200 bar); 2: 273 K < *T* < 340 K, *P*<sub>1</sub> < *P* < 1000 bar; 3: 273 K < *T* < 340 K, *P* > 1000 bar; 4: 340 K < *T* < 435 K, *P*<sub>1</sub> < *P* < 1000 bar; 5: 340 K < *T* < 435 K, *P* > 1000 bar; and 6: *T* > 435 K, *P* > *P*<sub>1</sub>.

Par=parameters.

ed the parameters of the solubility model at temperatures below 288 K. As shown by Fig. 1, the resulting model has an average error of about 3.5% for temperatures below 288 K. At temperatures higher than 288 K, the parameters presented in Duan and Sun (2003) is still valid.

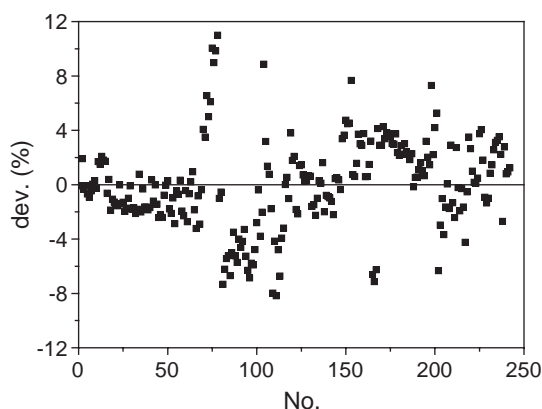


Fig. 1. The deviation of this model from the experimental data at *T* < 300 K and *P* < 600 bar. The abscissa is the number of data points and the deviation is defined as  $100\% \times (m_{\text{CO}_2}^{\text{model}} - m_{\text{CO}_2}^{\text{exp}}) / m_{\text{CO}_2}^{\text{exp}}$ . The sources of the experimental data are Anderson (2002), Bartholomé and Friz (1956), Chapoy et al. (2004), Gillespie and Wilson (1982), Harned and Davis (1943), King et al. (1992), Kritschewsky et al. (1935), Malinin and Savelyeva (1972), Markham and Kobe (1941), Morrison and Billett (1952), Oleinik (1986), Rosenbauer et al. (2001), Servio and Englezos (2001), Teng et al. (1997), Teng and Yamasaki (2002), Valtz et al. (2004), Wiebe and Gaddy (1940), Yang et al. (2000), Zel'vinskii (1937), and Zheng et al. (1997).

### 3. Evaluation of CO<sub>2</sub> solubility data and prediction of the model

Besides the new measurements for CO<sub>2</sub> solubility in water below 298 K discussed in the last section, some new experimental data above 298 K have been published by recent studies, e.g. the work of Dhima et al. (1999), Kiepe et al. (2002), Teng and Yamasaki (2002), Bando et al. (2003), Chapoy et al. (2004), Li et al. (2004), and Valtz et al. (2004). Our previous work (Duan and Sun, 2003) has compared the prediction of our solubility model with many of the data available at that time, but not the new data or the data we did not locate then. Here we tried to compare the model with as many data sets as possible (both the data used for parameterization and the data not used for the parameterization in the *T*–*P* range from 273 to 533 K, from 0 to 2000 bar). We also tried to give an evaluation on the quality of all the experimental data based on our analysis and the evaluation made by Diamond and Akinfiev (2003), and Spycher et al. (2003).

Tables 2 and 3 listed all the reliable experimental data sets for CO<sub>2</sub> solubility in pure water at temperatures from 273 to 533 K and at pressures up to 2000 bar. The data presented in Table 2 are those used by Duan and Sun (2003) and also in this study to evaluate the parameters of CO<sub>2</sub> solubility model while the data presented in Table 3 are those not used but predicted by our model. Column 5 of Tables

Table 2

The reliable experimental data of CO<sub>2</sub> solubility in pure water at 273–533 K and 1–2000 bar

Authors	<i>T</i> (K)	<i>P</i> (bar)	<i>N</i> <sup>a</sup>	AAD (%) <sup>b</sup>	Quality <sup>c</sup>
Wiebe and Gaddy (1939)	323–373	25–710	29	1.41	h
Wiebe and Gaddy (1940)	285–313	25–507	42	1.77	h
Markham and Kobe (1941)	273–313	1.01–1.09	3	2.07	h
Hamed and Davis (1943)	273–323	1.01–1.14	18	0.94	h
Prutton and Savage (1945)	374–393	23–703	26	3.27	h
Morrison and Billett (1952)	286–348	1.02–1.40	19	3.07	h
Malinin (1959)	473–523	98–490	10	3.24	h
Todheide and Franck (1963)	323–533	200–2000	30	5.16	h
Takenouchi and Kennedy (1964)	383–533	100–1500	76	3.86	h
Takenouchi and Kennedy (1965)	423–523	100–1400	30	3.93	h
Malinin and Savelyeva (1972)	298–348	47.9	11	4.18	m
Malinin and Kurorskaya (1975)	298–423	47.9	9	4.08	m
Drummond (1981)	303–523	40–126	41	5.12	m
Zawisza and Malesinska (1981)	323–473	1–54	33	5.61	m
Müller et al. (1988)	373–473	3–80	49	2.81	h
Nighswander et al. (1989)	353–471	20–102	33	6.50	m
King et al. (1992)	288–298	60–250	27	1.85	h
Servio and Englezos (2001)	277–283	20–42	9	7.23	m
Anderson (2002)	274–288	1–22	54	1.33	h
Chapoy et al. (2004)	274–351	2–93	27	2.97	h
Valtz et al. (2004)	278–318	5–80	47	4.70	m

These data were used by Duan and Sun (2003) to evaluate the parameters of CO<sub>2</sub> solubility model or used in this study to improve the accuracy below 288 K.

<sup>a</sup> Number of measurements, <sup>b</sup> the average absolute deviation of the data set from the model, and <sup>c</sup> h=high quality and m=moderate quality.

2 and 3 gives the average absolute deviation of each data set from the solubility model. The average absolute deviation of all the data listed in Tables 2 and 3 from the solubility model is 3.3%, which confirms the high accuracy of our solubility model. Fig. 2 compares the prediction of our model with the ex-

perimental data not used in parameterization. From Fig. 2 and Tables 2 and 3, we can find that our solubility model not only can reproduce the experimental data used to parameterize model's parameters but also can predict the experimental data not used in parameterization.

Table 3

The reliable experimental data of CO<sub>2</sub> solubility in pure water at 273–533 K and 1–2000 bar

Authors	<i>T</i> (K)	<i>P</i> (bar)	<i>N</i> <sup>a</sup>	AAD (%) <sup>b</sup>	Quality <sup>c</sup>
Kritschewsky et al. (1935)	293–303	5–30	10	4.44	m
Zel'vinskii (1937)	273–373	11–94	80	2.59	m
Bartholomé and Friz (1956)	283–303	1–20	15	1.52	h
Matous et al. (1969)	303–353	10–39	13	2.51	h
Shagiakhmetov and Tarzimanov (1981)	323–373	100–800	9	3.23	m
Gillespie and Wilson (1982)	288–366	7–203	24	4.87	m
Oleinik (1986)	283–343	10–160	23	1.95	h
Briones et al. (1987)	323	68–177	7	2.61	h
D'Souza et al. (1988)	323–348	101–152	4	2.53	h
Dohrn et al. (1993)	323	101–301	3	1.28	h
Teng et al. (1997)	278–293	64–295	24	1.55	m
Zheng et al. (1997)	278–338	0.49–0.84	10	1.18	h
Dhima et al. (1999)	344	100–1000	7	1.90	h
Bamberger et al. (2000)	323–353	40–141	29	2.62	h
Yang et al. (2000)	298	21–77	9	5.67	m
Rosenbauer et al. (2001)	294	100–600	3	1.76	h
Teng and Yamasaki (2002)	298	75–300	6	1.87	h
Bando et al. (2003)	303–333	100–200	12	2.25	h

These data were not used to evaluate the parameters of the CO<sub>2</sub> solubility model of this study.

<sup>a</sup> Number of measurements, <sup>b</sup> the average absolute deviation of the data set from this model, and <sup>c</sup> h=high quality and m=moderate quality.

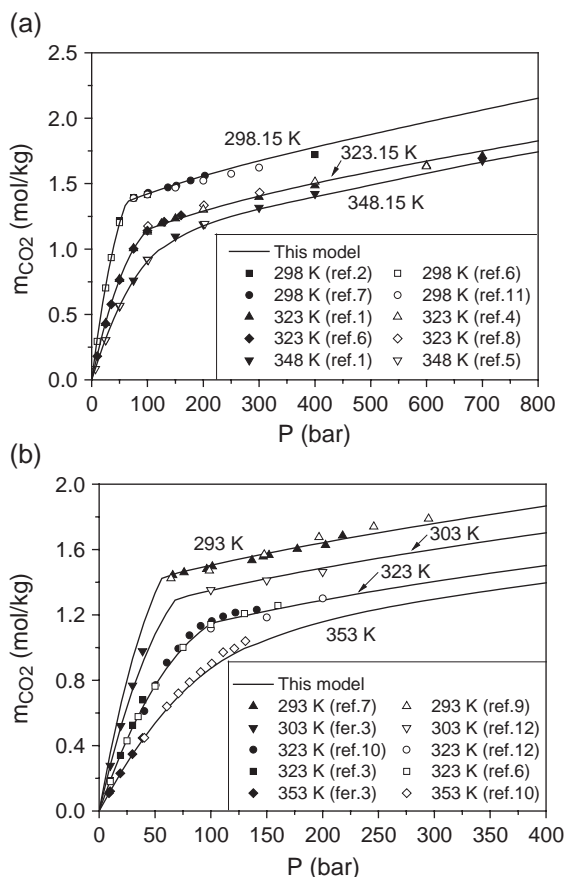


Fig. 2. CO<sub>2</sub> solubility in pure water—the prediction of this model vs. experimental data which were not used in the parameterization. The experimental data presented in the figure are from—ref. 1: Wiebe and Gaddy (1939), ref. 2: Wiebe and Gaddy (1940), ref. 3: Matous et al. (1969), ref. 4: Shagiakhmetov and Tarzimanov (1981), ref. 5: Gillespie and Wilson (1982), ref. 6: Oleinik (1986), ref. 7: King et al. (1992), ref. 8: Dohm et al. (1993), ref. 9: Teng et al. (1997), ref. 10: Bamberger et al. (2000), ref. 11: Teng and Yamasaki (2002), and ref. 12: Bando et al. (2003).

Column 6 of Tables 2 and 3 lists the quality of the solubility data set determined by this study. We used the character h to represent high quality and the letter m to represent moderate quality. We agreed with the evaluation of Diamond and Akinfiev (2003) that the measurements of Wiebe and Gaddy (1939), Wiebe and Gaddy (1940), Bartholomé and Friz (1956), Matous et al. (1969), Müller et al. (1988), King et al. (1992), Bamberger et al. (2000), and Anderson (2002) are of high quality. The high quality of the experimental data of Prutton and Savage (1945), Malinin (1959), Todheide and Franck (1963), Takenouchi and Kennedy (1964), and Takenouchi and Kennedy (1965) in the  $T$ – $P$  range of our model was demonstrated by Duan and Sun (2003). This study con-

firmed the high quality of the data of Oleinik (1986), Briones et al. (1987), D'Souza et al. (1988), Dohrn et al. (1993), Zheng et al. (1997), Dhima et al. (1999), Rosenbauer et al. (2001), Teng and Yamasaki (2002), Bando et al. (2003), and Chapoy et al. (2004).

The data of Kritschewsky et al. (1935) at 303 K are higher than the prediction of our model by 7–13%. The data of Malinin and Savelyeva (1972) and Malinin and Kurorskaya (1975) at 298 K are higher than the model by 7–8%. Some data of Zawisza and Malinska (1981) and Nighswander et al. (1989) above 373 K deviate from the measurements of Müller et al. (1988) and the prediction of our solubility model by 7–20%. The data of Yang et al. (2000), Servio and Englezos (2001), and Valtz et al. (2004) have a systematic deviation from our solubility model by 5–10%. A few data of Zel'vinskii (1937), Shagiakhmetov and Tarzimanov (1981), and Gillespie and Wilson (1982) deviate from our solubility model by more than 7%. A few data of Drummond (1981) measured during the pressure increasing process are not consistent with those measured in the pressure decreasing process. The deviation between them is 7–10%. Thus this study concluded that these data sets are of moderate quality. The measurements of Teng et al. (1997) at 278 and 283 K are not in the region of vapor–liquid equilibrium but in the metastable equilibrium absence of CO<sub>2</sub> hydrate (Ohmura and Mori, 1999). However, the measurements of Teng et al. (1997) at 288 and 293 K are in the region of vapor–liquid equilibrium and are consistent with the data published by other studies. So we concluded that the data of Teng et al. (1997) are of moderate quality.

Table 4 lists CO<sub>2</sub> solubility data with poor quality. Some data of Wroblewski (1883), Hahnel (1920), and Stewart and Munjal (1970) are in the metastable equilibrium of CO<sub>2</sub> hydrate. Many data of these studies deviate from our solubility model by 10–25%. Many data of Sander (1912) and Vilcu and Gainar (1967) are

Table 4  
The unreliable experimental data for CO<sub>2</sub> solubility in water

Authors	$T$ (K)	$P$ (bar)	$N^a$
Wroblewski (1883)	273–285	1–30	12
Sander (1912)	293–333	24–120	34
Hahnel (1920)	273–288	5–53	18
Vilcu and Gainar (1967)	293–308	25–75	20
Stewart and Munjal (1970)	273–298	10–46	12
Sako et al. (1991)	348–421	100–200	7
Kiepe et al. (2002)	313–393	1–93	39
Li et al. (2004)	332	33–200	6

<sup>a</sup> Number of measurements.



far away from the solubility model. The average deviations of the two data sets are more than 20%. More than half of the data of [Sako et al. \(1991\)](#) deviate from those predicted from our model by more than 10%. Many data of [Kiepe et al. \(2002\)](#) deviate from those predicted from our model by 7–20%. The data of [Li et al. \(2004\)](#) are greater than the prediction of our model by 7–13%.

Injecting carbon dioxide into deep saline aquifers is one of the more promising carbon dioxide sequestration options for the long term ([Spycher et al., 2003](#); [Gale, 2004](#)). This method is technically feasible now ([Bando et al., 2003](#)). Predicting CO<sub>2</sub> solubility in brines is important for estimating the total amount of CO<sub>2</sub> stored. We have extrapolated our model to predicting CO<sub>2</sub> solubility in aqueous CaCl<sub>2</sub>, MgCl<sub>2</sub> solutions and in seawater-type brines in the paper of [Duan and Sun \(2003\)](#). Here we developed a computer program to predict CO<sub>2</sub> solubility in pure water, in aqueous NaCl solution, and in seawater-type brines. The program, named CO2SOLUBILITY, was written in FORTRAN 77 and can be downloaded from our website, [www.geochem-model.org/programs.htm](http://www.geochem-model.org/programs.htm). Table 5 listed CO<sub>2</sub> solubility calculated from our model in seawater at *P*–*T* conditions from 273 to 393 K and from 1 to 500 bar.

The idea of sequestering carbon dioxide on the ocean floor in the form of CO<sub>2</sub> hydrate has also drawn much attention from the scientific community ([Brewer et al., 1999](#)). Predicting the stability of CO<sub>2</sub> hydrate in seawater and predicting CO<sub>2</sub> solubility at CO<sub>2</sub> hydrate–seawater–gas (or liquid CO<sub>2</sub>) equilibrium is essential for sequestration of CO<sub>2</sub> in the ocean. Tables 6 and 7 give the equilibrium pressure of CO<sub>2</sub> hydrate and CO<sub>2</sub> solubility in pure water and seawater, respectively. The pressure of CO<sub>2</sub> hydrate–seawater–gas or liquid CO<sub>2</sub> equilibrium was calculated from the hydrate model developed recently by [Sun and Duan \(2005\)](#) and CO<sub>2</sub> solubility is calculated from our improved solubility model in this study.

#### 4. Conclusion

This study improved the previous model of [Duan and Sun \(2003\)](#) by developing a non-iterative equation to calculate the fugacity coefficient of CO<sub>2</sub> so that it can be efficiently used in the fluid-flow computer models for such applications as CO<sub>2</sub> sequestration. Another improvement of the new model was achieved by re-fitting the model to the recent experimental data below 288 K so that it reduces the uncertainty from about 6% to about 3% below 288

Table 5  
CO<sub>2</sub> solubility (mol/kg H<sub>2</sub>O) in 35‰ seawater

<i>P</i> (bar)	<i>T</i> (K)							
	273.15	283.15	293.15	313.15	333.15	353.15	373.15	393.15
1.0	.0655	.0458	.0330	.0200	.0124	.0063	.0000	.0000
5.0	.3159	.2228	.1624	.1030	.0719	.0532	.0396	.0268
10.0	.6042	.4282	.3136	.2011	.1429	.1093	.0873	.0701
25.0		.9478	.7034	.4610	.3346	.2632	.2200	.1914
50.0		1.4647	1.1607	.7911	.5914	.4773	.4098	.3688
75.0		1.4983	1.2729	1.0078	.7792	.6448	.5652	.5190
100.0		1.5309	1.3063	1.0814	.9074	.7720	.6909	.6457
125.0		1.5622	1.3382	1.1140	.9925	.8644	.7908	.7517
150.0		1.5925	1.3688	1.1448	1.0249	.9239	.8686	.8400
175.0		1.6218	1.3983	1.1741	1.0555	.9768	.9257	.9131
200.0			1.4266	1.2020	1.0844	1.0201	.9789	.9709
225.0			1.4541	1.2286	1.1119	1.0566	1.0249	1.0260
250.0			1.4808	1.2542	1.1381	1.0881	1.0652	1.0751
275.0			1.5068	1.2788	1.1631	1.1159	1.1012	1.1192
300.0			1.5322	1.3025	1.1871	1.1410	1.1337	1.1593
325.0			1.5571	1.3255	1.2102	1.1644	1.1635	1.1960
350.0			1.5816	1.3478	1.2324	1.1864	1.1911	1.2299
375.0			1.6058	1.3695	1.2539	1.2076	1.2170	1.2614
400.0			1.6297	1.3908	1.2747	1.2282	1.2415	1.2910
425.0			1.6534	1.4117	1.2950	1.2484	1.2649	1.3190
450.0			1.6770	1.4321	1.3148	1.2684	1.2874	1.3456
475.0			1.7004	1.4523	1.3342	1.2883	1.3092	1.3711
500.0			1.7237	1.4723	1.3532	1.3081	1.3304	1.3955

The chemical composition of seawater is from [Holland \(1978\)](#).

K but confirms the accuracy of the original model above 288 K. The high accuracy of this model is confirmed by both the data used in the parameterization and the many data sets not used in the parameterization. In order to facilitate the application in CO<sub>2</sub> sequestration, we predicted CO<sub>2</sub> solubility in seawater under two-phase coexistence (vapor–liquid or liquid–liquid) and at three-phase coexistence (CO<sub>2</sub> hydrate–liquid solution–vapor or liquid CO<sub>2</sub>). A simple computer program was developed to calculate the solubility of CO<sub>2</sub> in aqueous solutions. The program, named CO2SOLUBILITY, was written in FORTRAN 77 and is valid from 273 to 533 K, from 0 to 2000 bar, and from 0 to 4.5 molality of

Table 6

CO<sub>2</sub> solubility in pure water at CO<sub>2</sub> hydrate–liquid water–gas or liquid CO<sub>2</sub> equilibrium

<i>T</i> (K)	<i>P</i> <sub>eq</sub> (bar) <sup>a</sup>	<i>m</i> <sub>CO<sub>2</sub></sub> (mol/kg)
272.65	11.52	.8113
273.15	12.20	.8378
273.65	12.92	.8653
274.15	13.68	.8938
274.65	14.50	.9233
275.15	15.37	.9540
275.65	16.31	.9858
276.15	17.31	1.019
276.65	18.37	1.053
277.15	19.52	1.089
277.65	20.75	1.126
278.15	22.08	1.164
278.65	23.51	1.204
279.15	25.06	1.246
279.65	26.74	1.289
280.15	28.57	1.334
280.65	30.58	1.380
281.15	32.78	1.429
281.65	35.22	1.480
282.15	37.94	1.533
282.65	41.01	1.588
283.15	44.54	1.645
283.65	67.04	1.703
284.15	115.9	1.760
284.65	171.5	1.819
285.15	231.7	1.878
285.65	296.3	1.939
286.15	365.2	2.001
286.65	438.3	2.064
287.15	515.8	2.128
287.65	597.7	2.194
288.15	684.2	2.260
288.65	775.7	2.328
289.15	872.3	2.397
289.65	974.6	2.468
290.15	1083.	2.539

<sup>a</sup> *P*<sub>eq</sub>=equilibrium pressure for the assemblage CO<sub>2</sub> hydrate–liquid water–gas or liquid CO<sub>2</sub>.

Table 7

CO<sub>2</sub> solubility in 35‰ seawater at CO<sub>2</sub> hydrate–seawater–gas or liquid CO<sub>2</sub> equilibrium

<i>T</i> (K)	<i>P</i> <sub>eq</sub> (bar)	<i>m</i> <sub>CO<sub>2</sub></sub> (mol/kg)
270.15	10.04	.6804
270.65	10.62	.7024
271.15	11.25	.7252
271.65	11.91	.7489
272.15	12.62	.7734
272.65	13.37	.7989
273.15	14.18	.8252
273.65	15.03	.8526
274.15	15.95	.8811
274.65	16.93	.9106
275.15	17.98	.9412
275.65	19.11	.9731
276.15	20.33	1.006
276.65	21.64	1.041
277.15	23.05	1.076
277.65	24.58	1.114
278.15	26.24	1.152
278.65	28.05	1.193
279.15	30.04	1.235
279.65	32.22	1.279
280.15	34.64	1.324
280.65	37.34	1.372
281.15	40.40	1.423
281.65	43.93	1.494
282.15	78.24	1.527
282.65	132.4	1.584
283.15	192.4	1.642
283.65	258.2	1.701
284.15	330.0	1.763
284.65	408.3	1.827
285.15	493.7	1.896
285.65	587.0	1.971
286.15	689.8	2.053
286.65	803.9	2.142
287.15	932.3	2.238
287.65	1080.	2.352
288.15	1256.	2.476
288.65	1478.	2.623

The chemical composition of seawater is from Holland (1978).

<sup>a</sup> *P*<sub>eq</sub>=equilibrium pressure for the assemblage CO<sub>2</sub> hydrate–liquid water–gas or liquid CO<sub>2</sub>.

NaCl or other salts. The program is available to the public and may be downloaded from our website, [www.geochem-model.org/programs.htm](http://www.geochem-model.org/programs.htm).

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## References

- Anderson, G.K., 2002. Solubility of carbon dioxide in water under incipient clathrate formation conditions. *J. Chem. Eng. Data* 47, 219–222.
- Bamberger, A., Sieder, G., Maurer, G., 2000. High-pressure (vapor plus liquid) equilibrium in binary mixtures of (carbon dioxide plus water or acetic acid) at temperatures from 313 to 353 K. *J. Supercrit. Fluids* 17, 97–100.
- Bando, S., Takemura, F., Nishio, M., Hihara, E., Akai, M., 2003. Solubility of CO<sub>2</sub> in aqueous solutions of NaCl at (30 to 60) °C and (10 to 20) MPa. *J. Chem. Eng. Data* 48, 576–579.
- Bartholomé, E., Friz, H., 1956. Solubility of CO<sub>2</sub> in water. *Chem. Ing. Tech.* 28, 706–708.
- Brewer, P.G., Friederich, G., Peltzer, E.T., Orr, F.M.J., 1999. Direct experiments on the ocean disposal of fossil fuel CO<sub>2</sub>. *Science* 284, 943–945.
- Briones, J.A., Mullins, J.C., Thies, M.C., Kim, B.U., 1987. Ternary phase equilibria for acetic acid–water mixtures with supercritical carbon dioxide. *Fluid Phase Equilib.* 36, 235–246.
- Chapoy, A., Mohammadi, A.H., Chareton, A., Tohidi, B., Richon, D., 2004. Measurement and modeling of gas solubility and literature review of the properties for the carbon dioxide–water system. *Ind. Eng. Chem. Res.* 43, 1794–1802.
- Cipolli, F., Gambardella, B., Marini, L., Ottonello, G., Zuccolini, M.V., 2004. Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO<sub>2</sub> sequestration in serpentinite aquifers. *Appl. Geochem.* 19, 787–802.
- Dhima, A., de Hemptinne, J.C., Jose, J., 1999. Solubility of hydrocarbons and CO<sub>2</sub> mixtures in water under high pressure. *Ind. Eng. Chem. Res.* 38, 3144–3161.
- Diamond, L.W., Akinfiev, N.N., 2003. Solubility of CO<sub>2</sub> in water from –1.5 to 100 °C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modelling. *Fluid Phase Equilib.* 208, 265–290.
- Dohrn, R., Bunz, A.P., Devlieghere, F., Thelen, D., 1993. Experimental measurements of phase-equilibria for ternary and quaternary systems of glucose, water, CO<sub>2</sub> and ethanol with a novel apparatus. *Fluid Phase Equilib.* 83, 149–158.
- Drummond, S.E., 1981. Boiling and mixing of hydrothermal fluids: chemical effects on mineral precipitation, PhD Thesis, Penn. State Univ.
- D'Souza, R., Patrick, J.R., Teja, A.S., 1988. High pressure phase equilibria in the carbon dioxide–*n*-hexadecane and carbon dioxide–water systems. *Can. J. Chem. Eng.* 66, 319–323.
- Duan, Z., Moller, N., Weare, J.H., 1992. An equation of state for the CH<sub>4</sub>–CO<sub>2</sub>–H<sub>2</sub>O system: I. Pure systems from 0 to 1000 °C and 0 to 8000 bar. *Geochim. Cosmochim. Acta* 56, 2605–2617.
- Duan, Z., Sun, R., 2003. An improved model calculating CO<sub>2</sub> solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chem. Geol.* 193, 257–271.
- Gale, J., 2004. Geological storage of CO<sub>2</sub>: what do we know, where are the gaps and what more needs to be done? *Energy* 29, 1329–1338.
- Gillespie, P.C., Wilson, G.M., 1982. Vapor–liquid and liquid–liquid equilibria: water–methane, water–carbon dioxide, water–hydrogen sulfide, water–*n*-pentane, water–methane–*n*-pentane, Research report RR-48, Gas Processors Association, Tulsa.
- Hahnel, O., 1920. Solubility of carbon dioxide in water. *Centr. Min. Geol.* 25, 25–32.
- Harned, H.S., Davis, R., 1943. The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50 °C. *J. Am. Chem. Soc.* 65, 2030–2037.
- Holland, H.D., 1978. *The Chemistry of the Atmosphere and Oceans*. Wiley-Interscience, New York.
- Kaszuba, J.P., Janecky, D.R., Snow, M.G., 2003. Carbon dioxide reaction processes in a model brine aquifer at 200 °C and 200 bars: implications for geologic sequestration of carbon. *Appl. Geochem.* 18, 1065–1080.
- Kiepe, J., S.H., S., Fischer, K., Gmehling, J., 2002. Experimental determination and prediction of gas solubility data for CO<sub>2</sub>+H<sub>2</sub>O mixtures containing NaCl or KCl at temperatures between 313 and 393 K and pressures up to 10 Mpa. *Ind. Eng. Chem. Res.* 41, 4393–4398.
- King, M.B., Mubarak, A., Kim, J.D., Bott, T.R., 1992. The mutual solubilities of water with supercritical and liquid carbon dioxide. *J. Supercrit. Fluids* 5, 296–302.
- Kritschewsky, I.R., Shaworonkoff, N.M., Aepelbaum, V.A., 1935. Combined solubility of gases in liquids under pressure: I. Solubility of carbon dioxide in water from its mixtures with hydrogen of 20 and 30 °C and total pressure of 30 kg/cm<sup>2</sup>. *Z. Phys. Chem.*, A 175, 232–238.
- Li, Z., Dong, M., Li, S., Dai, L., 2004. Densities and solubilities for binary systems of carbon dioxide plus water and carbon dioxide plus brine at 59 °C and pressures to 29 MPa. *J. Chem. Eng. Data* 49, 1026–1031.
- Malinin, S.D., 1959. The system water–carbon dioxide at high temperatures and pressures. *Geokhimiya* 3, 292–306.
- Malinin, S.D., Kurorskaya, N.A., 1975. Investigation of CO<sub>2</sub> solubility in a solution of chlorides at elevated temperatures and pressures of CO<sub>2</sub>. *Geokhimiya* 4, 547–551.
- Malinin, S.D., Savelyeva, N.I., 1972. The solubility of CO<sub>2</sub> in NaCl and CaCl<sub>2</sub> solutions at 25, 50, and 75 °C under elevated CO<sub>2</sub> pressures. *Geokhimiya* 6, 643–653.
- Markham, A.E., Kobe, K.A., 1941. The solubility of carbon dioxide and nitrous oxide in aqueous salt solutions. *J. Am. Chem. Soc.* 63, 449–454.
- Matous, J., Sobr, J., Novak, J.P., Pick, J., 1969. Solubility of carbon dioxide in water at pressures up to 40 atm. *Collect. Czechoslov. Chem. Commun.* 34, 3982–3985.
- Morrison, T.J., Billett, F., 1952. The salting-out of non-electrolytes: Part I. The effect of variation in non-electrolyte. *J. Chem. Soc.*, 3819–3822.
- Müller, G., Bender, E., Maurer, G., 1988. Das Dampf-Flüssigkeitsgleichgewicht des ternären Systems Ammoniak–Kohlendioxid–Wasser bei hohen Wassergehalten im Bereich zwischen 373 und 473 Kelvin. *Ber. Bunsenges. Phys. Chem.* 92, 148–160.
- Nighswander, J.A., Kalogerakis, N., Mehrotra, A.K., 1989. Solubilities of carbon dioxide in water and 1 wt% NaCl solution at



- pressures up to 10 MPa and temperatures from 80 to 200 °C. *J. Chem. Eng. Data* 34, 355–360.
- Ohmura, R. and Mori, Y.H., 1999. Comments on “Solubility of liquid CO<sub>2</sub> in synthetic seawater at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa, and densities of the corresponding aqueous solutions” (Teng, H.; Yamasaki, A. *J. Chem. Eng. Data* 1998, 43, 2–5). *J. Chem. Eng. Data*, 44: 1432–1433.
- Oleinik, P.M., 1986. Method of Evaluating Gases in Liquids and Volumetric Properties of Solutions Under Pressure. Neft. Promst., Ser. “Neftepromysl. Delo”.
- Prutton, C.F., Savage, R.L., 1945. The solubility of carbon dioxide in calcium chloride–water solutions at 75, 100, 120 °C and high pressures. *J. Am. Chem. Soc.* 67, 1550–1554.
- Rosenbauer, R.J., Bischoff, J.L., Koksalan, T., 2001. An experimental approach to CO<sub>2</sub> sequestration in saline aquifers: application to Paradox Valley, CO. EOS: Trans. Am. Geophys. Union, 82(47, Fall Meet. Suppl., Abstract V32B-0974).
- Sako, T., et al., 1991. Phase-equilibrium study of extraction and concentration of furfural produced in reactor using supercritical carbon-dioxide. *J. Chem. Eng. Jpn.* 24, 449–454.
- Sander, W., 1912. The solubility of carbon dioxide in water. *Z. Phys. Chem., Stochiom. Verwandtsch.* 78, 513–549.
- Servio, P., Englezos, P., 2001. Effect of temperature and pressure on the solubility of carbon dioxide in water in the presence of gas hydrate. *Fluid Phase Equilib.* 190, 127–134.
- Shagiakhmetov, R.A. and Tarzimanov, A.A., 1981. Measurements of CO<sub>2</sub> solubility in water up to 60 MPa. Deposited Document SPSTL 200khp-D81-1982.
- Spycher, N., Pruess, K., Ennis-King, J., 2003. CO<sub>2</sub>–H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>: I. Assessment and calculation of mutual solubilities from 12 to 100 °C and up to 600 bar. *Geochim. Cosmochim. Acta* 67, 3015–3031.
- Stewart, P.B., Munjal, P., 1970. Solubility of carbon dioxide in pure water, synthetic seawater, and synthetic seawater concentrates at –5 to 25 °C and 10 to 45 atm pressure. *J. Chem. Eng. Data* 15, 67–71.
- Sun, R., Duan, Z., 2005. Prediction of CH<sub>4</sub> and CO<sub>2</sub> hydrate phase equilibrium and cage occupancy from ab initio intermolecular potentials. *Geochim. Cosmochim. Acta* accepted.
- Takenouchi, S., Kennedy, G.C., 1964. The binary system H<sub>2</sub>O–CO<sub>2</sub> at high temperatures and pressures. *Am. J. Sci.* 262, 1055–1074.
- Takenouchi, S., Kennedy, G.C., 1965. The solubility of carbon dioxide in NaCl solutions at high temperatures and pressures. *Am. J. Sci.* 263, 445–454.
- Teng, H., Yamasaki, A., 2002. Pressure–mole fraction phase diagrams for CO<sub>2</sub>–pure water system under temperatures and pressures corresponding to ocean waters at depth to 3000 m. *Chem. Eng. Commun.* 189, 1485–1497.
- Teng, H., Yamasaki, A., Chun, M.-K., Lee, H., 1997. Solubility of liquid CO<sub>2</sub> in water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa, and densities of the corresponding aqueous solutions. *J. Chem. Thermodyn.* 29, 1301–1310.
- Todheide, K., Franck, E.U., 1963. Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxid–Wasser bis zu Drucken von 3500 bar. *Z. Phys. Chem.* 37, 387–401.
- Valtz, A., Chapoy, A., Coquelet, C., Paricaud, P., Richon, D., 2004. Vapour–liquid equilibria in the carbon dioxide–water system, measurement and modelling from 278.2 to 318.2 K. *Fluid Phase Equilib.* 226, 333–344.
- Vilcu, R., Gainar, I., 1967. Löslichkeit der Gase Unter Druck in Flüssigkeiten .i. das System Kohlendioxid–Wasser. *Rev. Roum. Chim.* 12, 181–189.
- Wiebe, R., Gaddy, V.L., 1939. The solubility in water of carbon dioxide at 50 °C, 75 °C, and 100 °C at pressures to 700 atm. *J. Am. Chem. Soc.* 61, 315–318.
- Wiebe, R., Gaddy, V.L., 1940. The solubility of carbon dioxide in water at various temperatures from 12 to 40 °C and at pressures to 500 atm. *J. Am. Chem. Soc.* 62, 815–817.
- Wolf, G.H., Chizmeshya, A.V.G., Diefenbacher, J., Mckelvy, M.J., 2004. In situ observation of CO<sub>2</sub> sequestration reactions using a novel microreaction system. *Environ. Sci. Technol.* 38, 932–936.
- Wroblewski, S.V., 1883. The solubility of carbon dioxide in water. *Ann. Phys. Chem.* 18, 290–308.
- Xu, T., Apps, J.A., Pruess, K., 2004. Numerical simulation of CO<sub>2</sub> disposal by mineral trapping in deep aquifers. *Appl. Geochem.* 19, 917–936.
- Yang, S.O., Yang, I.M., Kim, Y.S., Lee, C.S., 2000. Measurement and prediction of phase equilibria for water+CO<sub>2</sub> in hydrate forming conditions. *Fluid Phase Equilib.* 175, 75–89.
- Zawisza, A., Malesinska, B., 1981. Solubility of carbon dioxide in liquid water and of water in gaseous carbon dioxide in the range 0.2–5 MPa and at temperatures up to 473 K. *J. Chem. Eng. Data* 26, 388–391.
- Zel’vinskii, Y.D., 1937. Measurements of carbon dioxide solubility in water. *Zhurn. Khim. Prom.* 14, 1250–1257 (in Russian).
- Zheng, D., Guo, T., Kanpp, H., 1997. Experimental and modeling studies on the solubility of CO<sub>2</sub>, CHClF<sub>2</sub>, CHF<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>F<sub>2</sub> in water and aqueous NaCl solutions under low pressures. *Fluid Phase Equilib.* 129, 197–209.