

An improved model for the calculation of CO₂ solubility in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl[−], and SO₄^{2−}

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Abstract

An improved model is presented for the calculation of the solubility of carbon dioxide in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl[−], and SO₄^{2−} 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ sequestration, we also predicted CO₂ solubility in seawater at two-phase coexistence (vapor–liquid or liquid–liquid) and at three-phase coexistence (CO₂ hydrate–liquid water–vapor CO₂ [or liquid CO₂]). The improved model is programmed and can be downloaded from the website <http://www.geochem-model.org/programs.htm>.

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1. Introduction

Accurate prediction of CO₂ solubility over a wide range of temperature, pressure and ionic strength is important to the studies of geological CO₂ 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 CO₂ 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

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fugacity coefficients iteratively, which is computationally expensive for numerical simulations of large-scale geological sequestration processes that require calculation of CO₂ solubility at each grid and at each time step (Spycher et al., 2003).

Considering the demand for efficient calculations of CO₂ solubility, this study has developed a non-iterative equation to calculate the fugacity coefficient of CO₂ and provided a computer program to calculate CO₂ solubility in aqueous solutions at given temperature, pressure and concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl[−], and SO₄^{2−}. 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 CO₂ 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 CO₂ solubilities in seawater under two-phase coexistence (vapor–liquid or liquid–liquid) and three-phase coexistence conditions (CO₂ hydrate–liquid solution–vapor or liquid CO₂) in order to facilitate applications.

2. The improvements of the previous CO₂ solubility model

According to Eq. (9) of Duan and Sun (2003), the solubility of CO₂ 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_{CO_2} is the mole fraction of CO₂ in vapor phase, ϕ_{CO_2} is the fugacity coefficient of CO₂, $\mu_{\text{CO}_2}^{(0)}$ is the standard chemical potential

of CO₂ in liquid phase, $\lambda_{\text{CO}_2-\text{Na}}$ is the interaction parameter between CO₂ and Na⁺, $\zeta_{\text{CO}_2-\text{Na}-\text{Cl}}$ is the interaction parameter between CO₂ and Na⁺, Cl[−]. All parameters presented in Eq. (1) can be calculated directly without any iteration, except the fugacity coefficient of CO₂, ϕ_{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 ϕ_{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 ϕ_{CO_2} calculated from the EOS of Duan et al. (1992) at the T – P range where our CO₂ solubility model is valid. We found that it is difficult to reproduce ϕ_{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 ϕ_{CO_2} calculated from Eq. (2) and ϕ_{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 CO₂ 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 CO₂ 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	T–P range					
	1	2	3	4	5	6
c_1	1.0	$-7.1734882\text{E}-1$	$-6.5129019\text{E}-2$	5.0383896	-16.063152	$-1.5693490\text{E}-1$
c_2	$4.7586835\text{E}-3$	$1.5985379\text{E}-4$	$-2.1429977\text{E}-4$	$-4.4257744\text{E}-3$	$-2.7057990\text{E}-3$	$4.4621407\text{E}-4$
c_3	$-3.3569963\text{E}-6$	$-4.9286471\text{E}-7$	$-1.1444930\text{E}-6$	0.0	0.0	$-9.1080591\text{E}-7$
c_4	0.0	0.0	0.0	1.9572733	$1.4119239\text{E}-1$	0.0
c_5	-1.3179396	0.0	0.0	0.0	0.0	0.0
c_6	$-3.8389101\text{E}-6$	$-2.7855285\text{E}-7$	$-1.1558081\text{E}-7$	$2.4223436\text{E}-6$	$8.1132965\text{E}-7$	$1.0647399\text{E}-7$
c_7	0.0	$1.1877015\text{E}-9$	$1.1952370\text{E}-9$	0.0	0.0	$2.4273357\text{E}-10$
c_8	$2.2815104\text{E}-3$	0.0	0.0	$-9.3796135\text{E}-4$	$-1.1453082\text{E}-4$	0.0
c_9	0.0	0.0	0.0	-1.5026030	2.3895671	$3.5874255\text{E}-1$
c_{10}	0.0	0.0	0.0	$3.0272240\text{E}-3$	$5.0527457\text{E}-4$	$6.3319710\text{E}-5$
c_{11}	0.0	0.0	0.0	-31.377342	-17.763460	-249.89661
c_{12}		-96.539512	-221.34306	-12.847063	985.92232	0.0
c_{13}		$4.4774938\text{E}-1$	0.0	0.0	0.0	0.0
c_{14}		101.81078	71.820393	0.0	0.0	888.76800
c_{15}		$5.3783879\text{E}-6$	$6.6089246\text{E}-6$	$-1.5056648\text{E}-5$	$-5.4965256\text{E}-7$	$-6.6348003\text{E}-7$

1: $273\text{ K} < T < 573\text{ K}$, $P < P_1$ (when $T < 305\text{ K}$, P_1 equals to the saturation pressure of CO_2 ; when $305\text{ K} < T < 405\text{ K}$, $P_1 = 75 + (T - 305) \times 1.25$; when $T > 405\text{ K}$, $P_1 = 200\text{ bar}$); 2: $273\text{ K} < T < 340\text{ K}$, $P_1 < P < 1000\text{ bar}$; 3: $273\text{ K} < T < 340\text{ K}$, $P > 1000\text{ bar}$; 4: $340\text{ K} < T < 435\text{ K}$, $P_1 < P < 1000\text{ bar}$; 5: $340\text{ K} < T < 435\text{ K}$, $P > 1000\text{ bar}$; and 6: $T > 435\text{ K}$, $P > P_1$.

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.

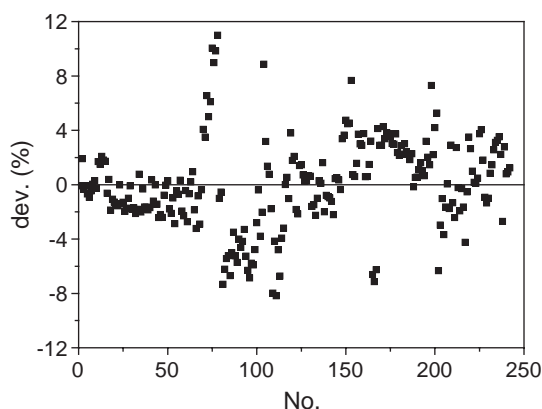


Fig. 1. The deviation of this model from the experimental data at $T < 300\text{ K}$ and $P < 600\text{ bar}$. The abscissa is the number of data points and the deviation is defined as $100\% \times (m_{\text{CO}_2}^{\text{model}} - m_{\text{CO}_2}^{\text{exp}}) / m_{\text{CO}_2}^{\text{exp}}$. The sources 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_2 solubility data and prediction of the model

Besides the new measurements for CO_2 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_2 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_2 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 CO₂ solubility in pure water at 273–533 K and 1–2000 bar

Authors	<i>T</i> (K)	<i>P</i> (bar)	<i>N</i> ^a	AAD (%) ^b	Quality ^c
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 CO₂ solubility model or used in this study to improve the accuracy below 288 K.

^a Number of measurements, ^b the average absolute deviation of the data set from the model, and ^c 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 CO₂ solubility in pure water at 273–533 K and 1–2000 bar

Authors	<i>T</i> (K)	<i>P</i> (bar)	<i>N</i> ^a	AAD (%) ^b	Quality ^c
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 CO₂ solubility model of this study.

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

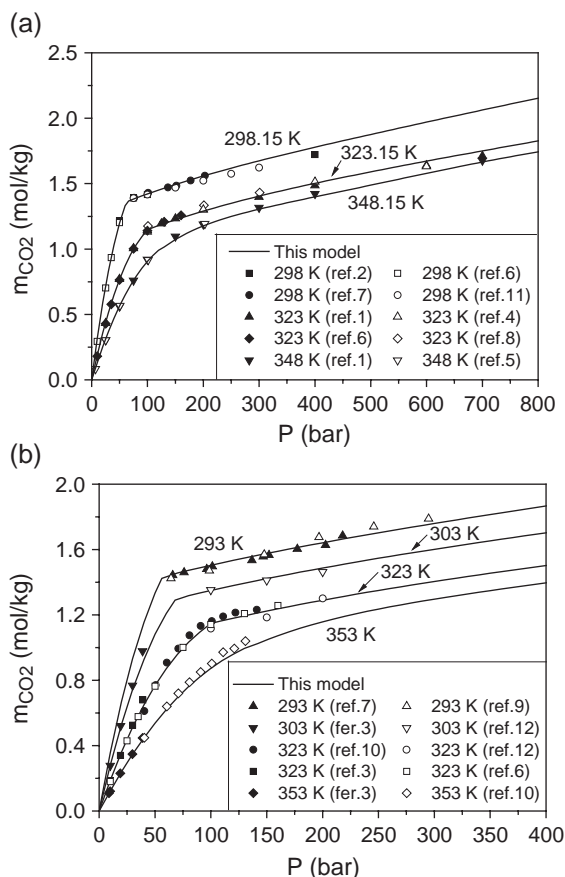


Fig. 2. CO₂ solubility in pure water—the prediction of this model vs. experimental data which were not used in the parameterization. The experimental data presented in the figure are from—ref. 1: Wiebe and Gaddy (1939), ref. 2: Wiebe and Gaddy (1940), ref. 3: Matous et al. (1969), ref. 4: Shagiakhmetov 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 CO₂ 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 CO₂ solubility data with poor quality. Some data of Wroblewski (1883), Hahnel (1920), and Stewart and Munjal (1970) are in the metastable equilibrium of CO₂ 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 CO₂ 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

^a 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 CO₂ solubility in brines is important for estimating the total amount of CO₂ stored. We have extrapolated our model to predicting CO₂ solubility in aqueous CaCl₂, MgCl₂ solutions and in seawater-type brines in the paper of [Duan and Sun \(2003\)](#). Here we developed a computer program to predict CO₂ 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. Table 5 listed CO₂ 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 CO₂ hydrate has also drawn much attention from the scientific community ([Brewer et al., 1999](#)). Predicting the stability of CO₂ hydrate in seawater and predicting CO₂ solubility at CO₂ hydrate–seawater–gas (or liquid CO₂) equilibrium is essential for sequestration of CO₂ in the ocean. Tables 6 and 7 give the equilibrium pressure of CO₂ hydrate and CO₂ solubility in pure water and seawater, respectively. The pressure of CO₂ hydrate–seawater–gas or liquid CO₂ equilibrium was calculated from the hydrate model developed recently by [Sun and Duan \(2005\)](#) and CO₂ 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 CO₂ so that it can be efficiently used in the fluid-flow computer models for such applications as CO₂ 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
CO₂ solubility (mol/kg H₂O) 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 CO₂ sequestration, we predicted CO₂ solubility in seawater under two-phase coexistence (vapor–liquid or liquid–liquid) and at three-phase coexistence (CO₂ hydrate–liquid solution–vapor or liquid CO₂). A simple computer program was developed to calculate the solubility of CO₂ 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

CO₂ solubility in pure water at CO₂ hydrate–liquid water–gas or liquid CO₂ equilibrium

<i>T</i> (K)	<i>P</i> _{eq} (bar) ^a	<i>m</i> _{CO₂} (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

^a *P*_{eq}=equilibrium pressure for the assemblage CO₂ hydrate–liquid water–gas or liquid CO₂.

Table 7

CO₂ solubility in 35‰ seawater at CO₂ hydrate–seawater–gas or liquid CO₂ equilibrium

<i>T</i> (K)	<i>P</i> _{eq} (bar)	<i>m</i> _{CO₂} (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).

^a *P*_{eq}=equilibrium pressure for the assemblage CO₂ hydrate–liquid water–gas or liquid CO₂.

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

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