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Geochimica et Cosmochimica Acta 74 (2010) 5631–5640

Geochimica et Cosmochimica Acta

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Prediction of oxygen solubility in pure water and brines up to high temperatures and pressures

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Received 11 January 2010; accepted in revised form 28 June 2010; available online 7 July 2010

Abstract

A thermodynamic model is presented to calculate the oxygen solubility in pure water (273–600 K, 0–200 bar) and natural brines containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, over a wide range of temperature, pressure and ionic strength with or close to experimental accuracy. This model is based on an accurate equation of state to calculate vapor phase chemical potential and a specific particle interaction model for liquid phase chemical potential. With this approach, the model can not only reproduce the existing experimental data, but also extrapolate beyond the data range from simple aqueous salt system to complicated brine systems including seawater. Compared with previous models, this model covers much wider temperature and pressure space in variable composition brine systems. A program for this model can be downloaded from the website: http://www.geochem-model.org.

1. INTRODUCTION

Oxygen (O_2) is the second most abundant gas in Earth's atmosphere. Oxygen from the air dissolves in the oceans, natural waters and biological fluids. It is closely related to the evolution of the whole eco-system on the earth. The knowledge of oxygen concentrations in natural waters is necessary to describe and model some important geochemical processes. Oxygen solubility in water is of great interest to geochemists, oceanographers, limnologists and physical chemists. For example, the oxygen in the ground water and geological brines will cause various reactions in the rock. Siever and Woodford (1979) investigated the effect of oxygen on the rate of weathering of hypersthenes and other iron-containing minerals. They concluded that the dissolution rate of hypersthenes at pH 4.5 decrease in the presence of oxygen. White and Yee (1985) investigated oxidation and dissolution reactions of augite and hornblende at ambient temperature in aqueous solution, which concluded that the presence of oxygen might enhance the weathering rates of iron-containing silicates. Due to its importance, there have been many experimental studies of O_2 solubility in different kinds of solutions. However, these data cover only a limited pressure-temperature range. Many researchers devoted great efforts to the modeling of oxygen in order to interpolate between data or extrapolate beyond the data space. However, few models reported can be used for the calculation of the solubility of oxygen in brines except for seawater, which was given by Battino (1981).

$$\ln x = A_1 + A_2/(T/100\ \mathrm{K}) + A_3 \ln(T/100\ \mathrm{K}) \qquad (1)$$

Battino (1981) fitted the data he reviewed to Eq. (1) to smooth the experimental data at 101.325 kPa partial pressure of oxygen and claimed that the mole fraction deviation is 0.36% in the temperature range of 273 K to 348 K. Benson and Krause (1976) also reported a smoothing equation which fits $\ln k$ to a power series in $1/T$. Both of the above models are in forms independent of oxygen partial pressure. We think this will cause great deviations if it is used for high pressures. As the Fig. 2 shows, the Broden and Simonson (1978) model, based on their experimental data, is believed to be incorrect because the model obviously deviates from the experimental data. Tromans (1998a,b, 2000a,b) did a

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doi:10.1016/j.gca.2010.06.034

Notations

T	absolute temperature in Kelvin
P	total pressure in bar
m_i	molality (mol/kg) of component
R	universal constant
x_i	mole fraction of component in liquid phase
y_i	mole fraction of component in vapor phase
a	activity
f	fugacity
φ	fugacity coefficient
γ	activity coefficient
μ	chemical potential
ρ	density
Par	parameter
λ_{O_2-ion}	interaction parameter
$\xi_{O_2-\text{cation}-\text{anion}}$	interaction parameter

Superscripts

a	anion
c	cation

Superscripts

l	liquid
v	vapor
sol	solution

series of theoretical studies on oxygen concentration in aqueous solutions as a function of temperature and partial pressure of O_2. His models might be the simplest with an average deviation of 10%, but as pressure increases, his models have large errors.

Solubility of oxygen in salt solutions has often been described using the Setschenow (1889) equation. Millero and Huang (2003), Millero et al. (2002a,b) and Cramer (1980) proposed different models to describe the oxygen solubility in salt solutions. Garcia and Gordon (1992) fitted the experimental measurements of Benson and Krause (1984). Among these models, Millero and Huang (2003), Millero et al. (2002a,b) models do not calculate the absolute concentrations of O_2 in the salt solution but the activity coefficient of O_2, so his model can only calculate the solubility difference between pure water and salt solutions, which can be useful only if the model for pure water solubility model is correct.

In this study, we have developed a thermodynamic model which can not only reproduce the existing experimental data, but also predict O_2 solubility well beyond the data range. With this approach, the solubility of O_2 in pure water and in complicated brine systems including seawater can be predicted without parameterization from these systems.

2. PHENOMENOLOGICAL DESCRIPTION OF GAS SOLUBILITY

Oxygen solubility in aqueous solutions is determined by the balance between its chemical potential in the liquid phase and that in the gas phase. The potential can be written in terms of fugacity in the vapor phase and activity in the liquid phase as Eqs. (2) and (3).

$$\begin{aligned}\mu^{\mathrm{v}}_{O_2}(T,P,y) &= \mu^{\mathrm{v}_0}_{O_2}(T) + RT\ln f_{O_2}(T,P,y)\\ &= \mu^{\mathrm{v}_0}_{O_2}(T) + RT\ln y_{O_2}P\\ &\quad + RT\ln\varphi_{O_2}(T,P,y_{O_2}) \end{aligned} \tag{2}$$

$$\begin{aligned}\mu^{\mathrm{l}}_{O_2}(T,P,m) &= \mu^{\mathrm{l}k_0}_{O_2}(T,P) + RT\ln a_{O_2}(T,P,m)\\ &= \mu^{\mathrm{l}_0}_{O_2}(T,P) + RT\ln m_{O_2}\\ &\quad + RT\ln\gamma_{O_2}(T,P,m) \end{aligned} \tag{3}$$

where $\mu^{\mathrm{l}_0}_{O_2}$, the standard chemical potential of O_2 in liquid, is defined as the chemical potential in hypothetically ideal solution of unit molality and $\mu^{\mathrm{v}_0}_{O_2}$, the standard chemical potential in vapor, is the hypothetical ideal gas chemical potential when the pressure is set to 1 bar.

At phase equilibrium $\mu^{\mathrm{l}}_{O_2} = \mu^{\mathrm{v}}_{O_2}$ and we can obtain Eq. (4)

$$\begin{aligned}\ln\frac{y_{O_2}P}{m_{O_2}} &= \frac{\mu^{\mathrm{l}_0}_{O_2}(T,P) - \mu^{\mathrm{v}_0}_{O_2}(T)}{RT} - \ln\varphi_{O_2}(T,P,y)\\ &\quad + \ln\gamma_{O_2}(T,P,m) \end{aligned} \tag{4}$$

In the parameterization, the reference value $\mu^{\mathrm{v}_0}_{O_2}$ can be set to 0 for convenience, because only the difference between $\mu^{\mathrm{v}_0}_{O_2}$ and $\mu^{\mathrm{l}_0}_{O_2}$ is important. Since there is little water in the vapor phase, the fugacity coefficient of O_2 in gaseous mixtures differs little from that of pure O_2 in the studied region. Therefore, $\ln\varphi_{O_2}$ can be approximated from the EOS of pure O_2 (Schmidt and Wagner, 1985). y_{O_2}, the mole fraction of oxygen in the gas phase, and the $y_{O_2}P$ can be approximately calculated from $y_{O_2}P = P - P^{\mathrm{Sat}}_{H_2O}$ in vapor phase with Raoult's Law. $P^{\mathrm{Sat}}_{H_2O}$ is the saturation pressure of pure water in the system, which can be calculated by IAPWS-IF97 (Wagner et al., 2008). These assumptions may lead to errors up to about 5%. However, these errors approximately cancel each other in the parameterization so the subsequent error in the calculation of O_2 solubility is negligible.

$\ln\gamma_{O_2}$ is expressed as a virial expansion of excess Gibbs energy (Pitzer 1973) as Eq. (5).

$$\begin{aligned}\ln\gamma_{O_2} &= \sum_{\mathrm{c}} 2\lambda_{O_2-c}m_{\mathrm{c}} + \sum_{\mathrm{a}} 2\lambda_{O_2-a}m_{\mathrm{a}}\\ &\quad + \sum_{\mathrm{c}}\sum_{\mathrm{a}} \xi_{O_2-a-c}m_{\mathrm{a}}m_{\mathrm{c}} \end{aligned} \tag{5}$$

Where λ and ξ are second-order and third order interaction parameters, respectively. Substituting Eq. (5) into Eq. (4) yields Eq. (6).

$$\begin{aligned}\ln\frac{P - P^{\mathrm{Sat}}_{H_2O}}{m_{O_2}} &= \frac{\mu^{\mathrm{l}_0}_{O_2}}{RT} - \ln\varphi_{O_2} + \sum_{\mathrm{c}} 2\lambda_{O_2-c}m_{\mathrm{c}}\\ &\quad + \sum_{\mathrm{a}} 2\lambda_{O_2-a}m_{\mathrm{a}} + \sum_{\mathrm{c}}\sum_{\mathrm{a}} \xi_{O_2-c-a}m_{\mathrm{c}}m_{\mathrm{a}} \end{aligned} \tag{6}$$

Table 1
Interaction parameters for Eq. (8).

T-P coefficient	$\mu^{l0}_{O_2}/RT$	$\lambda_{O_2-Na^+}$	$\lambda_{O_2-K^+}$	$\xi_{O_2-Na-Cl}$	$\lambda_{O_2-Mg^{2+}}$	$\lambda_{O_2-Ca^{2+}}$	$\lambda_{O_2-SO_4^{2-}}$
C1	3.2832E + 01	1.9997E-01	1.5022E-01	-1.2793E-02	3.1715E-01	3.5135E-01	1.4383E-01
C2	−4.2731E-02						
C3	−4.4074E + 03						
C4	1.5253E-05						
C5							
C6	1.0279E-03						
C7	−2.9945E-03						
C8							
C9	2.6179E-03						
C10							
C11	−5.6660E-05						

Table 2
Experimental data for O_2 solubility in aqueous solutions.

References	Solution	T(K)	P_{O2}(bar)	Na
Geffcken (1904)*	Water	288–298	1	2
Muller (1912)	Water	288–289	1	2
Fox (1909)*	Water	273–323	1	40
Adeney and Becker (1919)	Water	275–308	1	7
Morgan and Richardson (1930)*	Water	298	1	1
Morrison and Billett (1952)	Water	285.85–248.05	1	11
Steen (1958)	Water	279.15–297.15	1	4
Elmore and Hayes (1960)*	Water	274.96–302.45	1	54
Morris et al. (1961)	Water	278.29–303.11	1	25
Klots and Benson (1963)*	Water	275.44–299.42	1	16
Douglas (1964)	Water	281.15-302.3	1	15
Carpenter (1966)*	Water	273.63–307.97	1	26
Shchukarev and Tolmacheva (1968)	Water	277.15–323.15	1	4
Murray et al. (1969)	Water	286.75–301.46	1	3
Murray and Riley (1969)	Water	273.89–301.46	1	15
Wise and Houghton (1969)	Water	283.2–333.2	1	6
Novak and Conway (1973)	Water	298.15	1	1
Benson and Krause (1976)*	Water	273.63–308.10	1	21
Pray et al. (1952)*	Water	435.5–616.5	6.89–27.6	18
Pray and Stephan (1953)*	Water	373–436	13.4–99.3	35
Stenphan et al. (1956)*	Water	373.15–560.93	13.4–201.7	116
Power (1968)*	Water	310.15	0.48–0.93	10
Japas and Frank (1985)	Water	523–623	230–2000	44
MacArthur (1916)	NaCl	298.15	0.212	8
Cramer (1980)	NaCl	274.65–569.35	43–52	85
Millero et al. (2002a)*	NaCl	298.15	0.212	13
Millero et al. (2002b)*	NaCl	273.19–318.54	0.212	153
Eucken and Hertzberg (1950)	NaCl	273.15–298.15	1	13
Mishnina et al. (1961)	NaCl	273.15–303.15	1	84
Geffcken (1904)	NaCl	288.15–298.15	1	13
MacArthur (1916)	KCl	298.15	0.212	8
Eucken and Hertzberg (1950)*	KCl	273.15–293.15	1	8
Yasunishi (1978)*	KCl	288–308	1	33
Millero and Huang (2003)*	KCl	278.15–318.15	0.212	42
MacArthur (1916)	$MgCl_2$	298.15	0.212	8
Eucken and Hertzberg (1950)	$MgCl_2$	273.15–293.15	1	8
Yasunishi (1978)*	$MgCl_2$	298.15	1	9
Millero et al. (2002b)*	$MgCl_2$	278.15–318.15	0.212	59
MacArthur (1916)*	$CaCl_2$	298.15	0.212	4
Yasunishi (1978)*	$CaCl_2$	298.15	1	14
MacArthur (1916)	Na_2SO_4	298.15	0.212	8
Eucken and Hertzberg (1950)	Na_2SO_4	273.15–293.15	1	8
Yasunishi (1978)*	Na_2SO_4	298.15	1	9
Millero et al. (2002b)*	Na_2SO_4	278.28–318.54	0.212	53

* used for parameterization.

Following Pitzer et al. (1984), we choose Eq. (7) for the P-T dependence of λ, ξ and $\mu^{l0}_{O_2}/RT$:

$$Par(T,P) = c_1 + c_2T + \frac{c_3}{T} + c_4T^2 + \frac{c_5}{630-T} + c_6P + c_7\log(T) + \frac{c_8P}{T} + \frac{c_9P}{630-T} + \frac{c_{10}P^2}{(630-T)^2} + c_{11}T\log \quad (7)$$

Eqs. (6) and (7) form the basis of our model parameterization.

3. REVIEW OF SOLUBILITY DATA OF OXYGEN

The solubility of oxygen in pure water and aqueous salts solutions has been measured at various temperatures, pressures and salinity. Battino (1981) has reviewed over 40 arti-

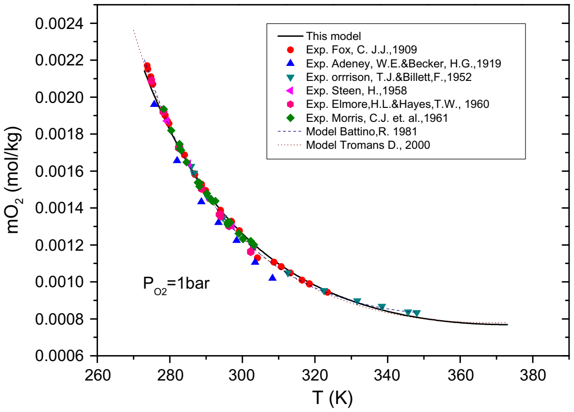

Fig. 1. Oxygen solubility in water at 1 bar.

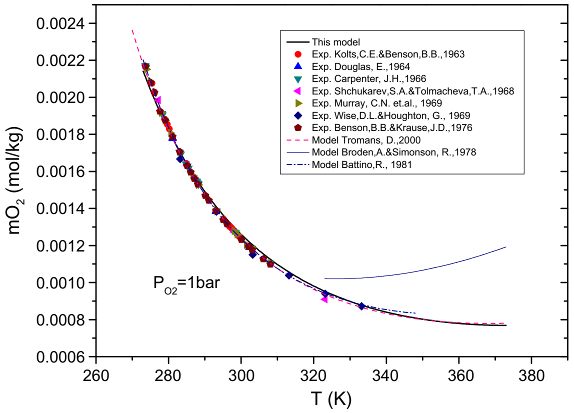

Fig. 2. Oxygen solubility in water at 1 bar.

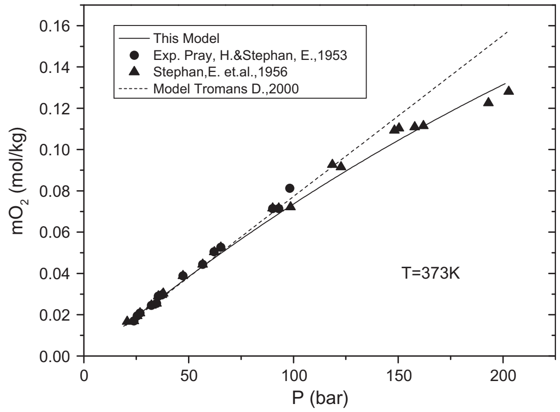

Fig. 3. Oxygen solubility in water at 373 K.

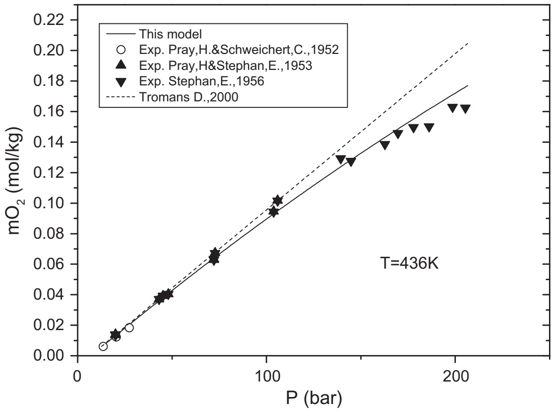

Fig. 4. Oxygen solubility in water at 436 K.

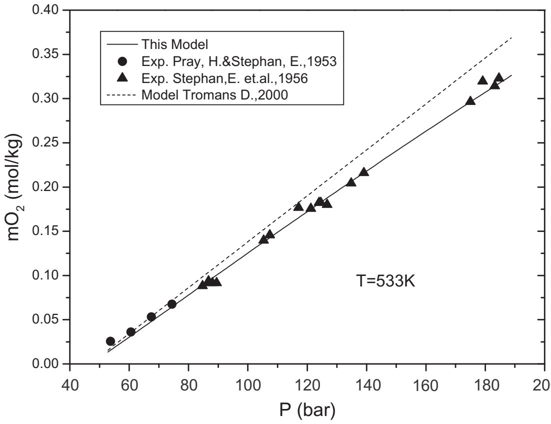

Fig. 5. Oxygen solubility in water at 533 K.

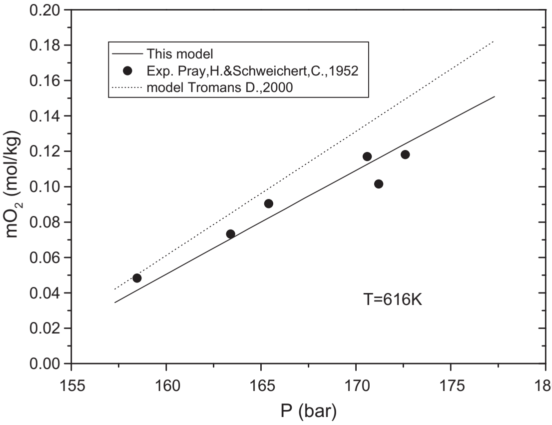

Fig. 6. Oxygen solubility in water at 616 K.

cles about the solubility of oxygen and ozone in liquids. Most datasets published before 1980 can be found in their work. The measurements are all listed in Table 2.

Most measurements in pure water are in similar arrangement at pressures near 1 bar and temperatures below 350 K. Pray et al. (1952), Pray and Stephan (1953), Stephan et al. (1956), Broden and Simonson (1978), Zoss (1954) provide data in the high pressure and high temperature range (from 373.15 to 560.93 K with the partial pressure of oxygen up to 201.7 bar), which are the only

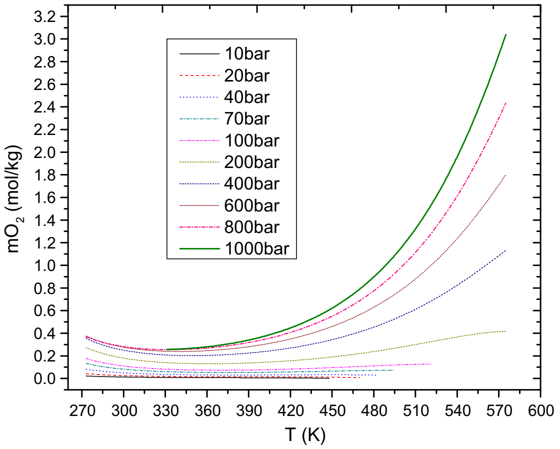

Fig. 7. The calculated isobaric solubility of O_2 in pure water.

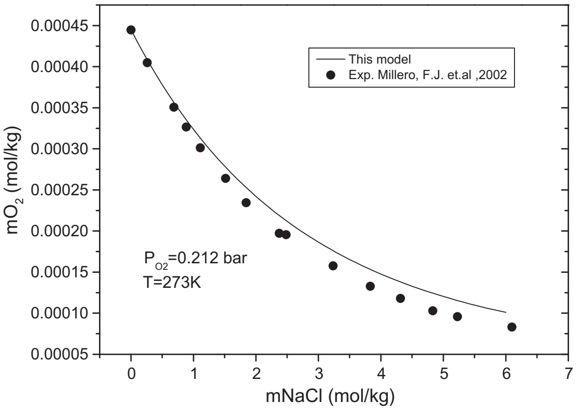

Fig. 10. Oxygen solubility in NaCl solution at 273 K.

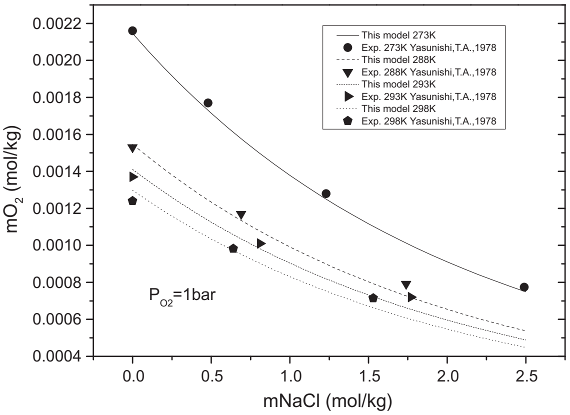

Fig. 8. Oxygen solubility in NaCl solution with $P_{O_2} = 1$ bar.

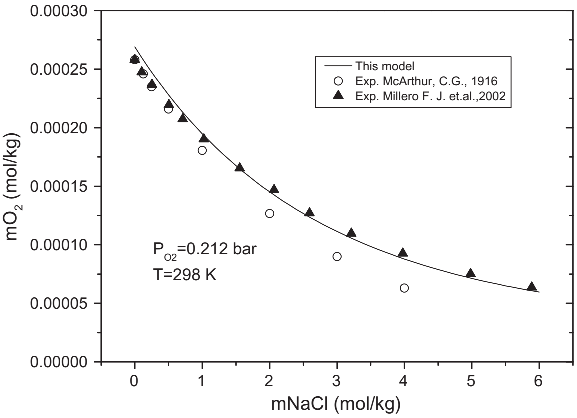

Fig. 11. Oxygen solubility in NaCl solution at 298.15 K.

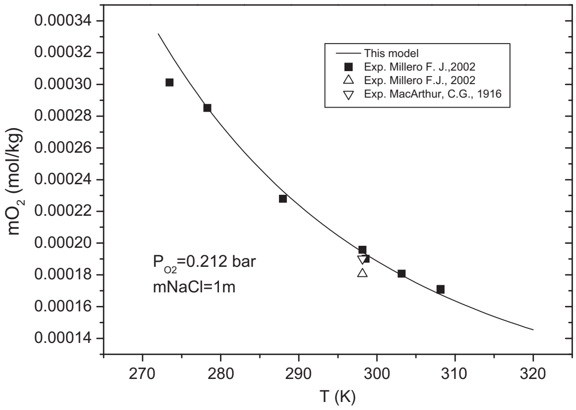

Fig. 9. Oxygen solubility in NaCl solution with mNaCl is 1 mol/kg.

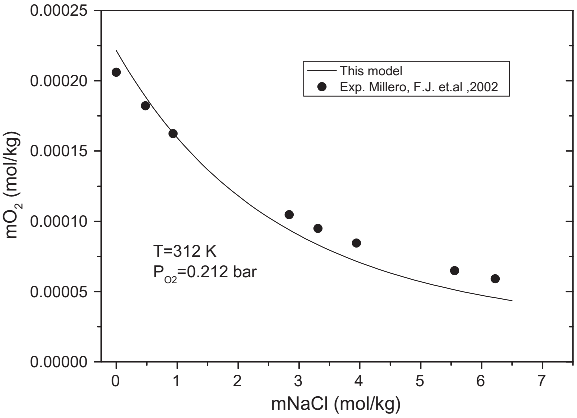

Fig. 12. Oxygen solubility in NaCl solution at 312 K.

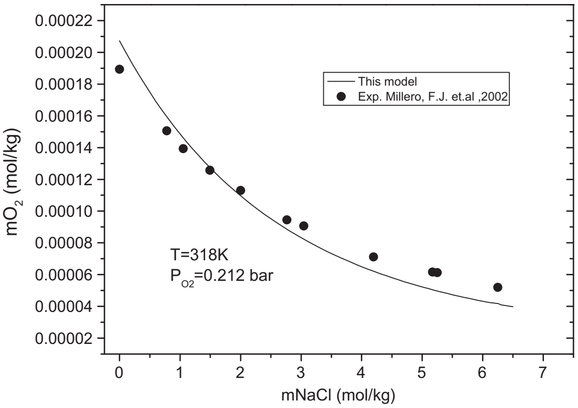

Fig. 13. Oxygen solubility in NaCl solution at 318 K.

datasets covering the widest temperature and pressure range by now. Japas and Frank (1985) reported phase equilibrium data of oxygen and water near the critical point of water which correspond to the highest pressure and temperature investigated.

O_2 solubility in aqueous salt solutions has not been studied extensively. Very few data are found at high pressures, due to the simple reason that under these conditions the dissolution vessel may become a bomb calorimeter or reaction vessel because of the high reactivity of compounds with oxygen. Most researchers interested in this system are focused on Marine sciences and Limnology. So their measurements are limited to a relative low temperature range. Geffcken (1904) reported oxygen solubility in aqueous solution in 1904. MacArthur (1916) reported oxygen solubility in different salt solutions at 25 °C for solutions at equilibrium with the oxygen in atmosphere. Eucken and Hertzberg (1950) also reported solubility of oxygen in different solutions in 1950. The data of Millero and Huang (2003), Millero et al. (2002a,b) cover the major sea salts at 277–318 K. The only high pressure data we found is from Cramer (1980) which covers 43–52 bar. He reported his measurements in Henry's Law Constant without specification of pressures.

4. PARAMETERIZATION AND COMPARISON WITH EXPERIMENTAL DATA

In order to calculate the solubility of oxygen as a function of temperature, pressure and salt concentration, we need to determine the parameters for ions in liquid as well as the standard chemical potential in Eq. (6). Since the measurements can be made only in electrically neutral solutions, one parameter must be assigned arbitrarily. We set λ_{O_2-Cl} to zero and fit the remaining parameters. We converted the different units of the O_2 solubility to mol/kg for fitting the equation. $\mu^{l0}_{O_2}/RT$ was evaluated using the O_2 solubility data in pure water with the average standard deviation of 3.89%. The extrapolation ability of our model to high pressure was gauged using Japas and Frank's (1985) data with analytical method. As shown by the result listed in Table 5 our model can predict accurate solubility of O_2 in liquid phase at high pressure. Parameters $\lambda_{O_2-Na^+}$ and $\xi_{O_2-Na^+-Cl^-}$ were then evaluated simultaneously by least squares fitting of solubility data for aqueous NaCl solutions listed in Table 2 with the average standard deviation of 13.5%. The optimized parameters are listed in Table 1.

With these parameters, the O_2 solubility in pure water and aqueous NaCl solutions can be calculated. As we stated above, Battino's (1981) model has great precision at 1 atm from 273 to 348 K, and the Tromans (1998a,b, 2000a,b) models can be easily applied to high pressure and temperature range. Therefore, we choose Battino (1981) model and Tromans (1998a,b, 2000a,b) model for comparison.

Figs. 1 and 2 shows the experimental O_2 solubility in water compared with our model and the other models. It can be seen that our model has a similar precision with the models of Battino's (1981), Tromans (1998a,b, 2000a,b) at 1 bar, but Battino's (1981) model cannot apply to pressures >1 bar where our model can, and Tromans (1998a,b, 2000a,b) model gradually deviate from experimental data as pressure increases. It can be seen from the Fig. 3 that the solubility of O_2 keeps a linear relationship with the partial pressure if the pressure is below 100 bar at 373 K. So it can be estimated that Henry's Law applies to roughly 100 bar for predicting the solubility of O_2 in

Table 3
Calculated O_2 solubility (mol/kg) in pure water.

P	*T*(K)											
(bar)	273	303	333	363	393	423	453	483	513	543	573	603
1	2.133E-03	1.152E-03	7.009E-04	2.319E-04								
5	1.090E-02	6.089E-03	4.303E-03	3.397E-03	2.417E-03	2.319E-04						
10	2.183E-02	1.228E-02	8.838E-03	7.406E-03	6.481E-03	4.779E-03	9.054E-06					
50	0.10355	0.059419	0.043869	0.038712	0.038542	0.041114	0.044388	0.044416	0.032077			
100	0.19063	0.11151	0.083517	0.074741	0.07591	0.08391	0.097198	0.11333	0.12579	0.11818	0.052973	
200	0.32599	0.19674	0.15054	0.137	0.14148	0.15986	0.19173	0.23757	0.2959	0.3582	0.3989	0.35486
300	0.4296	0.26456	0.20535	0.1889	0.19687	0.22461	0.27287	0.34475	0.4432	0.56668	0.69992	0.79183
400	0.51699	0.32184	0.25191	0.23323	0.2444	0.28035	0.34284	0.43726	0.57039	0.74664	0.9593	1.165
500	0.59565	0.37253	0.29277	0.27196	0.28581	0.32879	0.40354	0.51735	0.68025	0.90166	1.1819	1.4815
600	0.66911	0.41879	0.32948	0.30639	0.32232	0.37125	0.45645	0.58683	0.77514	1.035	1.3721	1.7482
700	0.73916	0.46182	0.36299	0.33737	0.3548	0.40867	0.50272	0.64717	0.85702	1.1493	1.5341	1.9713
800	0.80677	0.50235	0.39391	0.36548	0.38387	0.44177	0.54323	0.69953	0.92751	1.2469	1.6711	2.1564
900	0.87254	0.54082	0.42265	0.39112	0.40998	0.4711	0.57869	0.74486	0.98792	1.3298	1.7862	2.3081
1000	0.93685	0.57753	0.44948	0.41461	0.43348	0.49707	0.60965	0.78394	1.0394	1.3996	1.8818	2.4306

water at 373 K. Figs. 4–6 show that this limit pressure decreases as the temperature increases. As can be seen from the figures that the previous models cannot calculate the solubility precisely in the high PT region, and our model shows good agreement with the experimental data in the region of temperature 273–600 K and oxygen partial pressure at least up to 200 bar. We believe that our model can be extrapolated to higher pressure–temperature region, because we used an accurate equation of state for the calculation of the chemical potential in vapor phase and specific interaction approach in the liquid phase, which was previously demonstrated for the prediction of other gas solubility (Duan and Sun, 2003). Fig. 7 shows oxygen solubility under different temperatures and pressures, showing a minimum solubility around 350 K.

We have not found experimental solubility data in NaCl solutions at the temperature other than room temperature; we can only fit our equation with data near 1 atm and room temperature. Figs. 8–13 demonstrate that our model also accurately reproduced the experimental data for NaCl solutions with high accuracy. Since the salting-out parameter in our model is independent of temperature and pressure, we believe that the model should be able to predict O_2 solubility in the aqueous salt solutions in the T-P range of 273–600 K and 0–200 bar. Millero et al. (2002a,b) claimed that O_2 solubility calculated with their model agree with the measured values at the μmol/kg level, which means our model has a similar accuracy with their model. However, as we mentioned before, Millero et al. (2002a,b) model is focused on the relative part of the solubility not the absolute value. So his model cannot calculate the absolute value of oxygen solubility in NaCl without an accurate oxygen solubility in pure water as our model can Tables 3 and 4 show the solubility of O_2 in pure water and NaCl solution calculated from our model.

5. OXYGEN SOLUBILITY IN OTHER SALT SOLUTIONS: EXTRAPOLATION OF THE MODEL

The advantage of the specific interaction approach is that the model can be applied to more complex systems. Natural waters often contain NaCl, KCl, $MgCl_2$, $CaCl_2$, and sulfate and carbonate salts, although NaCl is often the major component. Because of data limits, a direct fit to experimental measurements is possible only for the O_2–NaCl–H_2O system. We take a predictive approach used by Duan et al.(1992) for methane solubility to include K^+, Mg^{2+}, Ca^{2+}, $SO_4{}^{2-}$. According to Duan et al.(1992), the interaction parameters for ions of same charge have roughly the same value, and the CH_4 bivalent cation inter-

Table 4
Calculated O_2 solubility (mol/kg) in NaCl Solutions.

T(K)	*P* (bar)									
	1	3	5	10	15	25	50	100	200	400
mNaCl = 1 mol/kg										
273	0.001448	0.004420	0.007402	0.014824	0.022160	0.036506	0.070308	0.129435	0.221341	0.351027
303	0.000782	0.002453	0.004134	0.008335	0.012507	0.020718	0.040345	0.075715	0.133581	0.218523
333	0.000476	0.001693	0.002922	0.006001	0.009070	0.015138	0.029787	0.056707	0.102212	0.171043
363		0.001224	0.002307	0.005029	0.007750	0.013152	0.026285	0.050749	0.093022	0.158362
393			0.001641	0.004401	0.007169	0.012684	0.026170	0.051542	0.096065	0.165945
423				0.003245	0.006361	0.012592	0.027916	0.056974	0.108540	0.190352
453						0.011364	0.030139	0.065996	0.130180	0.232785
483							0.030158	0.076947	0.161307	0.296896
513							0.021780	0.085407	0.200909	0.387290
mNaCl = 2 mol/kg										
273	0.001009	0.003079	0.005156	0.010326	0.015436	0.025430	0.048975	0.090163	0.154183	0.244520
303	0.000545	0.001709	0.002880	0.005806	0.008712	0.014432	0.028103	0.052742	0.093051	0.152220
333	0.000332	0.001179	0.002035	0.004180	0.006318	0.010545	0.020749	0.039501	0.071200	0.119146
363		0.000853	0.001607	0.003503	0.005399	0.009161	0.018310	0.035351	0.064798	0.110312
393			0.001143	0.003065	0.004994	0.008835	0.018229	0.035903	0.066918	0.115595
423				0.002260	0.004431	0.008771	0.019446	0.039687	0.075608	0.132596
453						0.007916	0.020994	0.045972	0.090682	0.162154
483							0.021008	0.053600	0.112364	0.206813
513							0.015172	0.059493	0.139950	0.269780
mNaCl = 4 mol/kg										
273	0.000529	0.001613	0.002701	0.005410	0.008088	0.013324	0.025660	0.047240	0.080783	0.128115
303	0.000285	0.000895	0.001509	0.003042	0.004565	0.007562	0.014725	0.027634	0.048753	0.079754
333	0.000174	0.000618	0.001066	0.002190	0.003310	0.005525	0.010871	0.020696	0.037304	0.062426
363		0.000447	0.000842	0.001835	0.002829	0.004800	0.009593	0.018522	0.033950	0.057797
393			0.000599	0.001606	0.002617	0.004629	0.009551	0.018811	0.035061	0.060565
423				0.001184	0.002322	0.004596	0.010188	0.020794	0.039614	0.069473
453						0.004147	0.011000	0.024087	0.047512	0.084960
483							0.011007	0.028083	0.058872	0.108358
513							0.007949	0.031171	0.073326	0.141349

Table 5
Prediction of the model as compared with high pressure measurements.

Temperature (K)	Pressure (bar)	Mole fraction of O_2 (Japas and Frank,1985)	Mole fraction of O_2 (This Work)	Deviation (%)	Temperature (K)	Pressure (bar)	Mole fraction of O_2 (Japas and Frank,1985)	Mole fraction of O_2 (This Work)	Deviation (%)
593	230	0.99	0.991	0.101	613	590	0.95	0.9685	1.947
613	230	0.99	0.9919	0.191	573	640	0.97	0.9748	0.495
623	230	0.99	0.9933	0.333	623	670	0.93	0.9673	4.011
573	240	0.99	0.9907	0.070	593	680	0.96	0.9688	0.917
548	280	0.99	0.9903	0.030	603	710	0.95	0.9654	1.621
613	300	0.98	0.986	0.612	563	760	0.97	0.9742	0.433
623	300	0.98	0.987	0.714	523	820	0.98	0.9817	0.173
603	310	0.98	0.9853	0.540	583	840	0.96	0.9672	0.750
523	330	0.99	0.9906	0.061	613	880	0.93	0.9588	3.097
593	340	0.98	0.9839	0.398	593	920	0.95	0.9625	1.316
623	360	0.97	0.9824	1.278	553	930	0.97	0.9738	0.392
583	370	0.98	0.9832	0.327	573	1040	0.96	0.9667	0.698
613	390	0.97	0.9795	0.979	543	1160	0.97	0.9739	0.402
573	410	0.98	0.9826	0.265	583	1260	0.95	0.961	1.158
623	430	0.96	0.9779	1.865	563	1320	0.96	0.9671	0.740
603	440	0.97	0.9772	0.742	533	1470	0.97	0.9747	0.485
613	480	0.96	0.974	1.458	578.5	1500	0.95	0.9612	1.179
593	500	0.97	0.9757	0.588	603	1500	0.93	0.9535	2.527
623	500	0.95	0.974	2.526	523	1900	0.97	0.9746	0.474
583	560	0.97	0.9751	0.526	559	2000	0.96	0.9673	0.760
603	560	0.96	0.9712	1.167	573	2000	0.95	0.9628	1.347
548	590	0.98	0.9811	0.112	600	2000	0.93	0.9551	2.699

action parameters are about twice as large as CH_4 monovalent interaction parameter, within the accuracy of experiment, which is true at different temperatures and pressures. The CH_4 anion interaction parameters are relatively small and therefore contribute little to the calculations. Hence, Duan et al. (1992) approximated all CH_4 monovalent cation and CH_4 bivalent cation interaction as $\lambda_{CH_4-Na^+}$ and $2\lambda_{CH_4-Na^+}$, respectively, and neglected all ternary parameters, but $\xi_{CH_4-Na-Cl}$. Using the similar approach, we approximate all O_2-monovalent-cation and O_2-bivalent-cation interaction parameters as $\lambda_{O_2-Na^+}$ and $2\lambda_{O_2-Na^+}$, respectively. The ternary parameters approximate as $\xi_{O_2-Na-Cl}$. In this study this simplification leads to a deviation of the model from data of about 20%. We made adjustments of the parameters $\lambda_{O_2-K^+}$, $\lambda_{O_2-Mg^{2+}}$, $\lambda_{O_2-Ca^{2+}}$ and $\lambda_{O_2-SO_4^{2-}}$ to reduce the deviation. With the simplification and correction, Eq. (6) becomes Eq. (8).

$$\ln m_{O_2} = \ln\left[(P - P^{\mathrm{Sat}}_{H_2O})\varphi_{O_2}\right] - \frac{\mu^{l_0}_{O_2}}{RT} - 2\sum_{i=1}^{n}\lambda_{O_2-i}m_{i\,(i=Na^+,K^+,Ca^{2+},Mg^{2+},SO_4^{2-})}$$
$$-\xi_{O_2-Na^+-Cl^-}(m_{Na^+} + m_{K^+} + 2m_{Ca^{2+}} + 2m_{Mg^{2+}})(m_{Cl^-} + 2m_{SO_4^{2-}}) \tag{8}$$

With these parameters (Table 1), the O_2 solubility in different kinds of aqueous solutions can be calculated from the model. Figs. 14–17 shows the experimental data compared with our model. The average standard deviation of our model from experiments in KCl, Na_2SO_4, $CaCl_2$ and $MgCl_2$ solution is 5.66%, 5.52%, 7.39% and 6.11%, respectively. With this model, the oxygen solubility in brines such as sea-

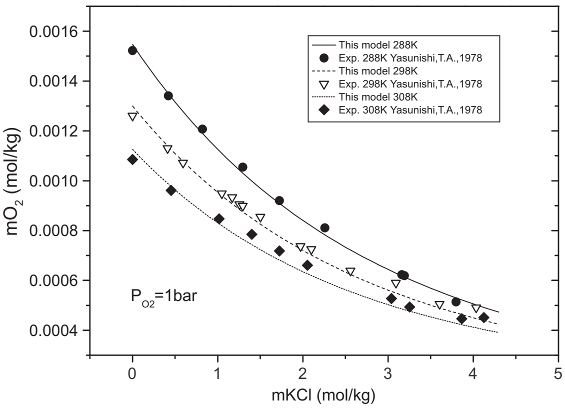

Fig. 14. Oxygen solubility in KCl solution.

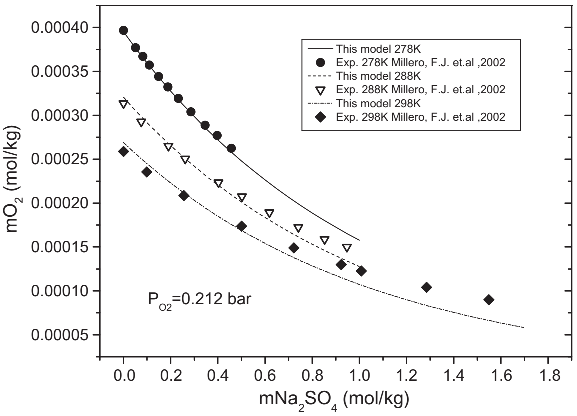

Fig. 15. Oxygen solubility in Na_2SO_4 solution.

water or concentrated brines can be predicted, as shown by Fig. 18. Considering that only one constant is used as a parameter for each salt, the accurate prediction under different temperatures, pressures and salinity range is remarkable.

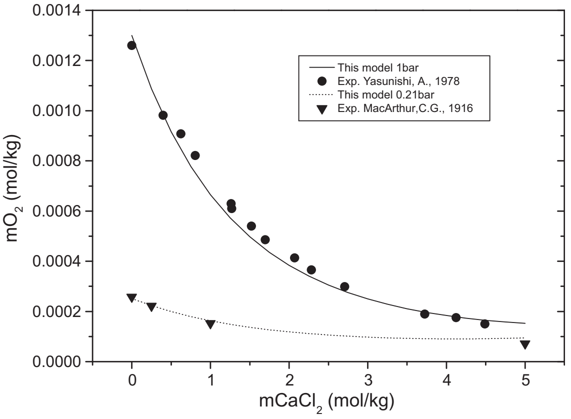

Fig. 16. Oxygen solubility in $CaCl_2$ solution.

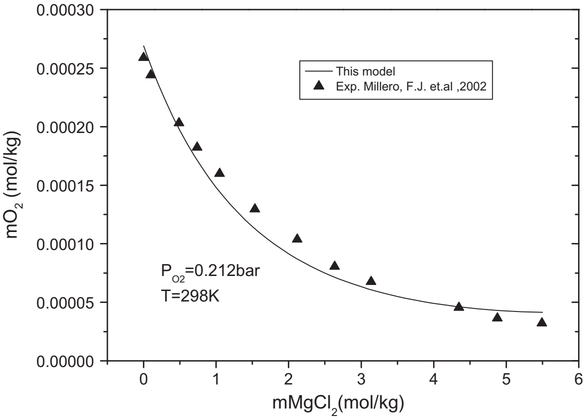

Fig. 17. Oxygen solubility in $MgCl_2$ solution.

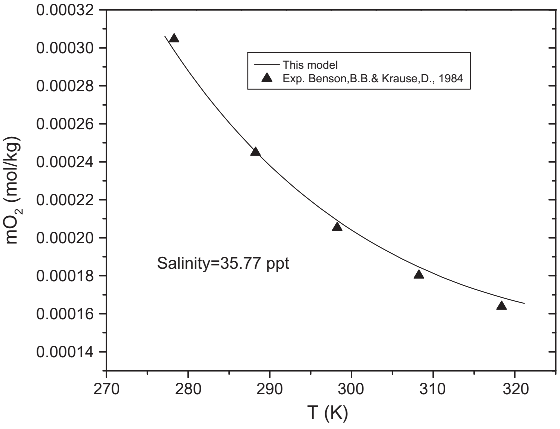

Fig. 18. Oxygen solubility in seawater.

6. CONCLUSION

Based on a highly accurate equation of state for gas phase, and the electrolyte solution theory of Pitzer et al. (1984) for Liquid phase, an accurate model is presented to predict O_2 solubility in pure water and brines over a wide temperature, pressure and salinity range (273–600 K, 0–200 bar). Comparison with experimental data demonstrates that this model can give results with or close to the experimental accuracy. Groundwater and hydrothermal brines with oxygen dissolved in may cause the oxidation and dissolution of sulfide minerals, like pyrite, which is common in the coal and metal ore deposits. The concentration of oxygen in the water plays critical part in the pyrite oxidation (Williamson and Rimstidt, 1994). This model provides a quantitative model for the calculation of oxygen in brines, hydrothermal fluids and shallow and deep ocean waters.

ACKNOWLEDGMENT

This research is supported by the National Science Foundation of China (Grants #90914010 and #40873050) and "Major development Funds" (#:kzcx2-yw-124) by Chinese Academy of Sciences. Thanks to the three anonymous reviewers and Dr. Jacques Schott for their constructive suggestions for improving the paper.

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Associate editor: Jacques Schott