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## Abstract

### **Exploratory Research on Simulation of CO<sub>2</sub>-Brine-Mineral Interactions**

Application of many carbon sequestration strategies requires knowledge of thermodynamic properties for the extremely complex chemical system of CO<sub>2</sub>-SO<sub>2</sub>-H<sub>2</sub>O-NaCl-CaCl<sub>2</sub>-MgCl<sub>2</sub>. This University Coal Research Phase I program has been successful and highly productive in exploring an approach to develop an equation of state (EOS) to describe thermodynamic properties in the above chemical system. We have compiled available laboratory experimental data and thermodynamic models, and evaluated their appropriateness for the carbon sequestration process. Based on this literature review, we provided an improved CO<sub>2</sub> solubility model for the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system, which incorporates newly available experimental measurements funded by DOE, and is valid in temperature range from 273 to 533 K, pressure from 0 to 2000 bar, and salinity from 0 to 4.5 molality of NaCl equivalent. The improved model also greatly improves the computational efficiency of CO<sub>2</sub> solubility calculations and thus is better suited to be incorporated into large computer simulation models (e.g., reservoir simulation models). The literature review and model development provided insights of the data needs and directions for future work. Synergetic collaboration with DOE scientists has resulted in simulations of injected CO<sub>2</sub> fate in sandstone aquifer with a one-dimensional numerical coupled reactive transport model. We evaluated over 100 references on CO<sub>2</sub> solubility and submitted two manuscripts to peer-reviewed journals. One paper has been accepted for publication in *Environmental Geosciences*.

## Table of Contents

Introduction.....	1
Executive Summary .....	4
EXPERIMENTAL .....	6
RESULTS AND DISCUSSIONS.....	7
1. <i>PVTx</i> Properties of the CO <sub>2</sub> -H <sub>2</sub> O and CO <sub>2</sub> -H <sub>2</sub> O-NaCl Systems: Assessment of experimental data and thermodynamic models .....	7
1.1. Experimental <i>PVTx</i> properties of the CO <sub>2</sub> -H <sub>2</sub> O system .....	8
1.1.1 <i>The data distribution in the P-T space and phase fields</i> .....	10
1.1.2 <i>The precision of the data</i> .....	13
1.1.3 <i>The agreement among data sets</i> .....	14
1.2. Experimental <i>PVTx</i> properties of the CO <sub>2</sub> -H <sub>2</sub> O-NaCl system .....	16
1.2.1 <i>The data distribution in the T-P space and phase fields</i> .....	17
1.2.2 <i>Precision estimate and agreement among data sets</i> .....	19
1.3. Thermodynamic Modeling of the Mixture <i>PVTx</i> properties.....	20
1.3.1 <i>The CO<sub>2</sub>-H<sub>2</sub>O system</i> .....	21
1.3.2 <i>The CO<sub>2</sub>-H<sub>2</sub>O-NaCl system</i> .....	29
2. An Improved CO <sub>2</sub> Solubility Model.....	31
2.1. Description of the CO <sub>2</sub> solubility model.....	32
2.2 Evaluation of CO <sub>2</sub> solubility data and prediction of the model .....	35
Conclusions.....	44
References.....	47
Fig. 1 The distribution of experimental <i>PVTx</i> data of the CO <sub>2</sub> -H <sub>2</sub> O system in <i>P-T</i> space.	
Fig. 2 The distribution of experimental <i>PVTx</i> data of the CO <sub>2</sub> -H <sub>2</sub> O-NaCl system in <i>P-T</i> space.	
Fig. 3. CO <sub>2</sub> solubility in pure water—the prediction of this model vs. experimental data.	

# **Final Report**

## **Introduction**

The carbon sequestration program critically and urgently needs upgrading for modeling capabilities:

- For geological carbon sequestration, -- the injection of CO<sub>2</sub> into deep saline formations--, the injected CO<sub>2</sub> can be trapped by either hydrodynamics (CO<sub>2</sub> dissolved in slow moving brine or remains to be in a separate liquid phase) or mineral trapping (precipitation of carbonates). In both mechanisms, accurate model predictions of solubility and volumetric properties of CO<sub>2</sub> for a wide range of temperature, pressure, and compositions (e.g., CO<sub>2</sub> and salts) are essential for evaluation of the effectiveness and viability of this sequestration strategy;
- For mineral carbonation, -- the reactions of CO<sub>2</sub> with serpentines and olivines at hydrothermal conditions (e.g., 155 °C and 50 bars of CO<sub>2</sub>) --, the solubility of CO<sub>2</sub> in these systems is critical to evaluation of the reaction mechanisms and efficiency of the laboratory experiments. Moreover, a geochemical simulator can help to optimize the experimental and operating conditions to achieve the highest efficiency;
- For brine sequestration, -- the reactions of CO<sub>2</sub> with brines brought up on the ground surface in laboratory and precipitation of carbonate minerals --, again accurate calculations of CO<sub>2</sub> solubility are necessary to achieve the highest efficiency; and
- For some innovative but as yet untested ideas, such as co-sequestration of CO<sub>2</sub> and SO<sub>2</sub>, which may result in major cost reduction for carbon capture, the thermodynamic properties of H<sub>2</sub>O-CO<sub>2</sub>-SO<sub>2</sub>-salt systems are critical for evaluation of feasibility.

The challenge posed by carbon sequestration programs is that the chemical system ( $\text{CO}_2\text{-H}_2\text{O-SO}_2\text{-NaCl-CaCl}_2\text{-MgCl}_2$ ) is extremely complex. Under field conditions, the temperature ( $T$ ) ranges from 25 ° to 200 °C and the pressure ( $P$ ) up to 500 atmospheres. These conditions indicate that ionic complexation is significant. The thermodynamic properties of gas-liquid-salt systems are typically described by an **Equation of State** (EOS), which calculates the quantitative relationships between intensive parameters of systems (e.g.,  $T, P$ ) and extensive parameters (e.g., volume, mass, composition of different phases). Although significant progress has been made regarding development of EOS for geological applications, the suitability of existing EOS for the PTX range needed for carbon sequestration is unknown. All geochemical simulators currently used for carbon sequestration (PHREEQC, USGS; EQ3/6, Lawrence Livermore; Geochemist's Workbench, University of Illinois, Urbana-Champaign) use a Henry's law approach to estimate  $\text{CO}_2$  solubility in the brines. This results in unacceptable uncertainties, and this significantly hampers the progress of carbon sequestration efforts.

Although an EOS describes the quantitative relationship between intensive parameters of a system (e.g.,  $T, P$ ) and extensive parameters (e.g., volume, mass), an accurate EOS can also be used to derive almost all-important thermodynamic properties, including gas-liquid phase distribution, activities and volumetric properties. These properties are essential in the quantitative understanding of  $\text{CO}_2$  sequestration processes. A number of attempts have been made to develop an equation of state for geological applications. However, it is clear that these EOS and models were developed without carbon sequestration in mind. The particular challenge to geological carbon sequestration is the wide compositional range and a low  $T, P$  regime where dissociation of  $\text{CO}_2$  and NaCl is significant. This makes the development of an EOS difficult without explicitly accounting for aqueous dissociation.

Meanwhile, as building blocks for the unified model, the CO<sub>2</sub> solubility model and volumetric model need to be recalibrated and developed. A modified model for CO<sub>2</sub> solubility that incorporates newly available experimental data from NETL partners (e.g., Rosenbaure and Koksalan, 2002, GSA, v.34, no.6, p.304) will greatly benefit many research programs currently undergoing at NETL and other national labs. Although there have been extensive experimental and theoretical studies of the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system, no model is available for the accurate calculation of volumetric properties below 573 K because of the complexity of speciation and ionization properties.

## **Executive Summary**

### **Exploratory Research on Simulation of CO<sub>2</sub>-Brine-Mineral Interactions**

Application of many carbon sequestration strategies requires knowledge of thermodynamic properties for the extremely complex chemical system of CO<sub>2</sub>-SO<sub>2</sub>-H<sub>2</sub>O-NaCl-CaCl<sub>2</sub>-MgCl<sub>2</sub>. This University Coal Research Phase I program has been successful and highly productive in exploring an approach to develop an equation of state (EOS) to describe thermodynamic properties in the above chemical system. We have compiled available laboratory experimental data and thermodynamic models, and evaluated their appropriateness for the carbon sequestration process. Based on this literature review, we provided an improved CO<sub>2</sub> solubility model for the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system, which incorporates newly available experimental measurements funded by DOE, and is valid in temperature range from 273 to 533 K, pressure from 0 to 2000 bar, and salinity from 0 to 4.5 molality of NaCl equivalent. The improved model also greatly improves the computational efficiency of CO<sub>2</sub> solubility calculations and thus is better suited to be incorporated into large computer simulation models (e.g., reservoir simulation models). The literature review and model development provided insights of the data needs and directions for future work. Synergetic collaboration with DOE scientists has resulted in simulations of injected CO<sub>2</sub> fate in sandstone aquifer with a one-dimensional numerical coupled reactive transport model. We evaluated over 100 references on CO<sub>2</sub> solubility and submitted two manuscripts to peer-reviewed journals. One paper has been accepted for publication in *Environmental Geosciences*.

The principal investigator for this project is Professor Chen Zhu at Indiana University. Professor Shiao-hung Chiang is the substitute principal investigator at University of Pittsburgh when Zhu moved to Indiana. Dr. Zhenhao Duan of University of California – San Diego worked

as a consultant for the project. Collaborating scientists at National Energy Technology Laboratory are Drs. Sheila Hedges and Brian Strasizar. Professor Zhu can be contacted at Department of Geological Sciences, Indiana University, IN 47405. Phone: (812) 856-1884, FAX: (812) 856 - 2223, e-mail: [czhu@indiana.edu](mailto:czhu@indiana.edu).

## **EXPERIMENTAL**

This University Coal Research (UCR) Phase I project is literature search and theoretical modeling. No experimental data were produced. In RESULTS and DISCUSSIONS below, we will discuss and evaluate experimental data in the literature.

## RESULTS AND DISCUSSION

### 1. *PVTx* Properties of the CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl Systems: Assessment of experimental data and thermodynamic models

Per Task 1 in the STATEMENT OF PROJECT OBJECTIVES, we made a comprehensive survey and evaluation of the experimental *PVTx* properties and thermodynamic modeling of the systems CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl. The distribution of data in *P-T* space and in different phase fields, the data precision and the consistencies between data sets are systematically evaluated, and the thermodynamic modeling of the *PVTx* properties is also critically reviewed. We conclude that: (1) The existing data for the binary range from 276.15 to 1673.15K and from 0.855 to 19400 bar, roughly covering the temperature-pressure (*T-P*) conditions of sedimentary basins, medium to low pressure metamorphism and they are mostly below the melting *T-P* conditions of rocks. The data in the ternary range from 276.15 to 1213.15K and from 2.4 to 7458 bar, and they cover a smaller *T-P* space than those in the binary. However, in these *T-P* spaces, there are many barren regions without any data. For the binary, there is a lack of *PVTx* data in the region of  $T < 493\text{K}$  and  $P > 350$  bar and the region of  $T > 1073\text{K}$  and  $P < 9500$  bar; For the ternary, there is no *PVTx* data for  $T < 400\text{K}$  and  $P > 300$  bar; (2) In most cases, the errors below 647K are within 2% in volume and within 5% at higher temperatures; (3) There is a shortage of volumetric measurements for coexistent liquid-vapor phases, near-critical regions, and bulk liquid at low temperatures; (4) There are obvious inconsistencies among some important data sets for the ternary at high pressures and temperatures; (5) The existing models are only partially successful in the calculation of the binary and ternary *PVTx* properties for both systems in the single-phase regions away from phase boundaries, but there are no good models to calculate the *PVTx* properties of both binary and ternary systems in and near critical regions and

those of the ternary below 573K; (6) There is no good model in predicting vapor  $PVT_x$  properties in the ternary system; (7) There is no good model to calculate the densities of both the binary and the ternary in liquid below 573K.

### **1.1. Experimental $PVT_x$ properties of the CO<sub>2</sub>-H<sub>2</sub>O system**

The existing experimental  $PVT_x$  data of the CO<sub>2</sub>-H<sub>2</sub>O system in literature are summarized in Table 1 below, and the  $P$ - $T$  conditions for these scattered measurements are projected on Fig.1. We present only data below the critical temperature of water [ $T_c(\text{H}_2\text{O})$ , 647.21K] here.

Table 1. The experimental PVTx properties of the CO<sub>2</sub>-H<sub>2</sub>O system

Authors	T/K	P/bar	Concentration	N <sub>d</sub>
Ohsumi et al. (1992)	276.15	347.54	x(CO <sub>2</sub> ) %=0.1798-0.6294	5
Teng et al. (1997)	278-293	64.4-294.9	x(CO <sub>2</sub> ) %=2.50-3.49	24
Parkinson & De Nevers (1969)	278.1-313.7	10.342-344.744	x <sub>CO2</sub> %(mol)=0.1-2.2	28
Hebach et al. (2004)	283.80-333.19	10.9-306.6	x(CO <sub>2</sub> )=saturated values	201
King et al. (1992)	288.15-298.15	60.8-243.2	x(CO <sub>2</sub> ) %=2.445-3.070	27
Hnědkovský et al. (1996)	298.15-705.38	10-350	m(CO <sub>2</sub> )=0.155-0.185	32
Zhang et al. (2002)	308.15	77.52-124.84	x(CO <sub>2</sub> ) %=0.3	16
Patel et al. (1987)	323.15-498.15	0-100	x(CO <sub>2</sub> )=0.5-0.98	457
Patel & Eubank (1988)	323.15-498.15	0.855-10.237	x(CO <sub>2</sub> )=0.02-0.5	297
Nighswander et al. (1989)	352.85-471.25	20.4-102.1	x(CO <sub>2</sub> ) %=0.22-1.66	33
Zawisza & Malesińska (1981)	373.15-473.15	3.85-33.5	y(H <sub>2</sub> O)=0.1210-0.9347	145
Ellis (1959)	387.15-621.15	5-164	y(CO <sub>2</sub> ) %=3.90-6.27-84.02	36
Fenghour et al. (1996)	415.36-699.30	58.84-345.77	x(CO <sub>2</sub> )=0.0612-0.7913	164
Wormald et al. (1986)	437.2-773.2	10-120	x(CO <sub>2</sub> )=0.5	115
Sterner & Bodnar (1991)	494.15-608.15	487-3100	x(CO <sub>2</sub> )=0.1234-0.7473	84
Franck & Tödheide (1959)	673.15-973.15	1000-6000	x(CO <sub>2</sub> )=0.1234-0.8736	107
Ellis (1963)	504.15-643.15	47.91-254.43	**	9
Zarikov (1984)	573.15-673.15	50-1800	x(CO <sub>2</sub> )=0.2-0.805	149
Zhang & Frantz (1992)	519.95-634.45	*	x(CO <sub>2</sub> ) %=5.5-16.5	29
Crovetto & Wood (1992)	622.75-642.70	196.4-281.3	x(CO <sub>2</sub> ) %=0.48-0.8745	72
Crovetto et al. (1990)	651.10-725.51	279.8-380.5	x(CO <sub>2</sub> ) %=0.130-1387	94
Seitz & Blencoe (1999)	673.15	99.4-999.3	x(CO <sub>2</sub> )=0.1-0.9	95
Gehrig (1980)	673.15-773.15	100-600	x(CO <sub>2</sub> )=0.1-0.9	198
Shmulovich et al. (1980)	673.15-773.15	1000-4500	x(CO <sub>2</sub> )=0.087-0.6232	33
Franck & Tödheide (1959)	673.15-1023.15	300-2000	x(CO <sub>2</sub> )=0.2-0.8	303
Greenwood (1969)	723.15-1073.15	50-500	x(CO <sub>2</sub> )=0.1-0.9	711
Sterner (1992)	973.15	3000	x(CO <sub>2</sub> )=0.375-0.775	5
Frost & Wood (1997)	1473.15-1673.15	9500-19400	x(CO <sub>2</sub> )=0.108-0.787	19

Note: N<sub>d</sub>= number of data points, x,y=mole fraction, m=molality, \* pressures are not reported, but can be calculated from their empirical formulations, \*\* concentrations are not directly reported, but can be calculated from the report.

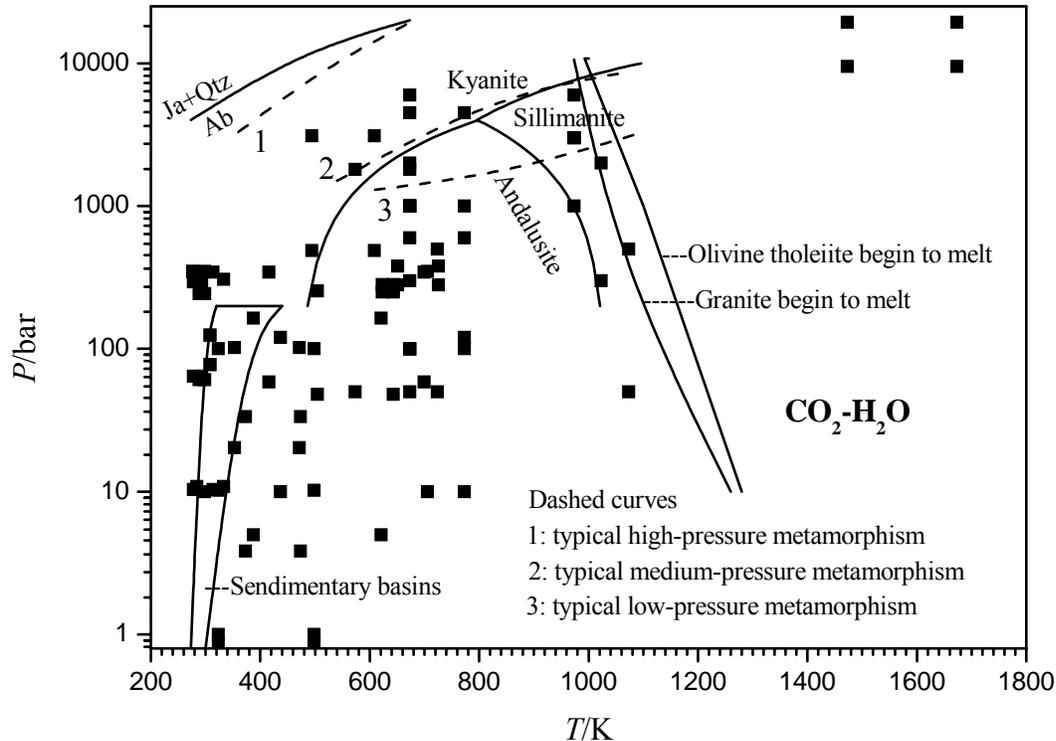


Fig.1 The distribution of experimental  $PVTx$  data of the  $\text{CO}_2\text{-H}_2\text{O}$  system in  $P\text{-}T$  space. Shown for reference are the phase boundary between albite (Ab) and jadeite (Jad) + quartz (Qtz), and those for  $\text{Al}_2\text{SiO}_5$  phases. Also shown are the minimum melting curves for granite and olivine tholeiite and the region for sedimentary basins. Note the lack of data for some of geologically important regions, i.e., between 800 and 950 K, along the high-pressure metamorphism trend, and parts of sedimentary basins.

### 1.1.1 The data distribution in the $P\text{-}T$ space and phase fields

In this temperature range, most data are in the low pressure range of  $P < 350$  bar (Ellis (1959), Ellis and Golding (1963), Parkinson and De Nevers (1969), Zawisza and Malesińska (1981), Wormald et al. (1986), Patel et al. (1987), Patel and Eubank (1988), Nighswander et al. (1989), Crovetto and Wood (1992), King et al. (1992), Ohsumi et al. (1992), Fenghour et al. (1996), Hnědkovský et al. (1996), Teng et al. (1997), Zhang et al. (2002), and Hebach et al. (2004)). These data sets cover a temperature range from 276.15 to 644.78K. Among these data sets, Parkinson and De Nevers (1969) reported partial molar volumes of  $\text{CO}_2$  in aqueous

solutions, but did not give the corresponding pressure information. Hebach et al. (2004) gave densities of aqueous solutions, but did not provide the corresponding composition information for the liquids, thus their density data can only be used through a reliable solubility model. Zarikov (1984) and Sterner and Bodnar (1991) are the only ones who reported high-pressure data up to 3100 bar in the temperature range between 494.15 and 608.15K.

A large portion of data stated above are density or volume measurements for the single saturated liquid or vapor phase, such as those of Zawisza and Malesińska (1981), Sterner and Bodnar (1991), King et al. (1992), Teng et al. (1997) and Hebach et al. (2004) are either for saturated liquids or for saturated vapors. Only few data sets are for both coexistent phases, such as Ellis (1959) and Ellis and Golding (1963).

Zawisza and Malesińska (1981) measured the dew point densities in the range of 373.15 to 473.15 K and 3.85 to 33.5 bar. Sterner and Bodnar (1991) determined the molar volumes of the synthetic fluid inclusions in vapor or liquid state at homogenization conditions (from 494.15 to 608.15K and from 477 to 3100 bar). King et al. (1992) measured the densities of both water-rich liquids ( $L_{H_2O}$ ) and  $CO_2$ -rich liquids ( $L_{CO_2}$ ), but they did not find significant difference between the them. Teng et al. (1997) conducted density measurements for  $L_{H_2O}$  in equilibrium with  $L_{CO_2}$ . In some of their experiments ( $T \leq 283K$ ),  $CO_2$  clathrate hydrate formed at the  $L_{H_2O}$ - $L_{CO_2}$  interface, where the influence of hydrate on the measurements was considered to be negligible (Teng et al., 1997). However, we think that these measurements are not in the stable equilibrium state. According to the phase rule, there are at most two phases co-exist away from the three-phase coexistent line. For a given temperature, there is only one possible pressure at which three phase phases can coexist, so  $H+L_{CO_2}+L_{H_2O}$  cannot stably coexist in the hydrate region away from their three-phase coexistence line. This means that the experiments involving hydrate did not reach

stable equilibrium states. Hebach et al. (2004) measured the densities of the coexistent  $L_{H_2O}$  and  $L_{CO_2}$  phases in a wider  $P$ - $T$  range. They confirmed the results of King et al. (1992) for the  $L_{CO_2}$  phase, as can be expected because of the very low content of water. They also found hydrate in their experiments at  $T < 283K$  and  $P > 40$  bar. They claimed that their measurements were in the  $P$ - $T$  range up to the point of hydrate formation, but they did not point out which of their data points involve the hydrate.

Because of the importance of  $CO_2$  hydrate, numerous determinations have been made for the  $P$ - $T$  conditions of  $CO_2$  hydrate formation, but almost none of them were for the densities and compositions at the phase boundaries associated with hydrate. So far, no density data are available for the phase equilibria in the stable presence of hydrate.

Table 2. The precisions of the experimental PVTx properties of the CO<sub>2</sub>-H<sub>2</sub>O system

Authors	Precision of $T$	Precision of $P$	Precision of composition	Precision of $V$ , $Z$ or $d$
Ohsumi et al. (1992)				0.0004g·cm <sup>-3</sup> (d)
Teng et al. (1997)		0.1 bar		1.9% **
Parkinson & De Nevers (1969)	0.03K			2.4cm <sup>3</sup> ·mol <sup>-1</sup> (average, $V_{\phi}$ )
Hebach et al. (2004)	0.005K	0.5 bar		0.15%
King et al. (1992)			0.3%(H <sub>2</sub> O-rich)	~0.5%(d)
Hnědkovský et al. (1996)			0.5%(CO <sub>2</sub> molality)	<1%( $V_{\phi}$ , <625K) 4%( $V_{\phi}$ , ≥625K)
Zhang et al. (2002)	0.03K	0.1 bar		0.01cm <sup>3</sup> (V)
Patel et al. (1987)	1K	0.14 bar		0.05%(d, Z)
Patel & Eubank (1988)	0.01K	0.01%	0.0002-0.0023%	0.05%
Nighswander et al. (1989)	0.5%	0.35 bar	0.02mol%, 0.001g(wt)	0.006g/cm <sup>3</sup> , or 0.8%(d)
Zawisza & Malesińska (1981)	0.005K	0.03%		0.09%(V)
Ellis (1959)			not of high precision	
Fenghour et al. (1996)	0.01K	0.02%		0.08-0.14%(d, average)
Wormald et al. (1986)				
Sternier & Bodnar (1991)	1%(2 $\sigma$ ), ~6K(liq), 25K(vap)	1%(2 $\sigma$ )	0.0026( $x_{\text{CO}_2}$ )	6.8%(max, V) 0.8%(average, V)
Ellis (1963)				>5%(d, vap)
Zarikov (1984)	0.03%	0.06%	0.2%	0.09%
Crovetto & Wood (1992)	0.15-0.2K	0.5-1.0%	0.2%( $x$ )	0.05-3.0%(d)
Crovetto et al. (1990)	0.3K	0.4 bar	0.2%(molality)	0.5kg·m <sup>-3</sup> (d) 0.5%( $\Delta d$ )
Seitz & Blencoe (1999)	0.05K	0.2 bar		0.001g·cm <sup>-3</sup> (pure fluid, d), 0.001g·cm <sup>-3</sup> , or 0.15% (mixture, d)
Shmulovich et al. (1980)				1.6% for 1.5-2.0 kbar, 0.7% for 4.5-5.0 kbar
Franck & Tödheide (1959)				
Greenwood (1969)	1K	0.2%	<0.5% for $V_{\text{CO}_2}$ (<1.5% for $V_{\text{CO}_2}$ , when $P<50\text{bar}$ )	0.5%(Z)
Sternier (1992)				0.8%(average, V)
Frost & Wood (1997)	20K	450 bar	0.001( $x_{\text{CO}_2}$ )	0.83( $\sigma_V$ )

Note: \*\* uncertainty of densities given by Hebach et al. (2004), liq=liquid, vap=vapor,  $V$ =molar volume,  $Z$ =compressibility factor ( $PV/RT$ ),  $d$ = density,  $\Delta d$ =difference in density,  $V_{\phi}$ =apparent molar volume.

### 1.1.2 The precision of the data

The precisions for the data described above were estimated and presented in Table 2. The precisions here usually refer to the maximum values of the reported uncertainties or errors of the measured quantities in experiments, and sometimes refer to the average error of certain representative quantities as noted in Table 2. Details of the relevant discussions can be found in the original articles, but a few of them need more discussion here.

Ellis (1959) stated that their results are not of high precision (p.233), which resulted from at least two factors: i) the data do not truly represent the binary  $PVT_x$  properties, since the  $\text{CO}_2$ - $\text{H}_2\text{O}$  solutions contain both  $\text{NaCl}$  and  $\text{NaHCO}_3$ ; and (ii) the suggested approach for the computation of solution volumes is approximate. As pointed out by Ellis and Golding (1963), the Henry's Law coefficients ( $K$ ) of Ellis (1959) between 100 and 300 °C are too low to be used for the  $\text{CO}_2$  solubility calculation. In this case, the  $\text{CO}_2$  solubility calculation must resort to the distribution coefficients and vapor compositions.

Ellis and Golding (1963) pointed out that it is unlikely for their vapor densities to be more accurate than 5%, and that their distribution coefficients derived from the  $PVT$  method are different from those derived from the liquid analysis, which are much better in quality. In order to obtain more  $PVT_x$  data from Ellis and Golding (1963), it is better to replace the distribution coefficients in their Table 5 with those fitted from their Table 2.

On the same synthetic fluid inclusion samples, Sterner and Bodnar (1991) reported a relatively large variation in the total homogeneous temperatures ( $T_h$ ), about 6K for total homogenization to liquid, and up to about 25K for total homogenization to vapor. The influence of  $\text{CO}_2$  hydrate on the  $PVT_x$  measurements of Teng et al. (1997) cannot be negligible, as indicated by an uncertainty of 1.9% in their densities. Parkinson and De Nevers (1969) gave an average deviation of  $2.4 \text{ cm}^3 \cdot \text{mol}^{-1}$  from smoothed partial molar volumes ( $V_\phi$ ) of  $\text{CO}_2$ , which is not small as compared with their partial volumes of 37.6 to  $65.8 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

### ***1.1.3 The agreement among data sets***

There is an apparent inconsistency among the following data sets. Sterner and Bodnar (1991) found that their solvus temperatures are about 15 to 25 K higher than those of Tödheide

and Franck (1963) for CO<sub>2</sub>-rich and CO<sub>2</sub>-poor phases, and 2 to 10 K discrepancies were recorded for the phases with intermediate CO<sub>2</sub> contents. Their solvus temperatures for CO<sub>2</sub>-rich phases are 40 to 90 K higher than those of Takenouchi and Kennedy (1964), with a maximum disagreement at about 1500 bar. Blencoe et al. (2001) reported new vapor-liquid equilibrium data of the binary at 300°C, which are claimed to be highly precise and accurate and thus offer another test of the solvus data of Sterner and Bodnar (1991). According to these new data and other previous solvus data, they convincingly showed that the errors in the solvus data of Sterner and Bodnar (1991) are quite large, not due to the underestimated  $T_h$ 's of the fluid inclusions that homogenized to vapor, but rather from the calculated solvus pressures using the equation of Connolly and Bodnar (1983). The solvus pressures were overestimated up to about 300-700 bar for the 270°C isotherm, and up to about 50-110 bar for the 300°C isotherm (Blencoe et al., 2001). These results suggest that the solvus pressures of Sterner and Bodnar (1991) need to be corrected with a reliable equation of state. Except for a portion of the  $P$ - $T$  curve of the H<sub>2</sub>O-16.5mol%CO<sub>2</sub> mixture, the  $P$ - $T$  curves for the binary vapor-liquid equilibria obtained by Zhang and Frantz (1992) are significantly (about 20-70K or 100-500 bar) different from those of Takenouchi and Kennedy (1964), especially those of 5.5% and 11.0 % CO<sub>2</sub> samples. This suggests that the data of Zhang and Frantz (1992) have large errors. The apparent molar volumes of Hnědkovský et al. (1996) reasonably agree with those of Crovetto and Wood (1992) if the wrong sign used for the pressure correction is corrected. Fenghour et al. (1996) found their data agree with those of Patel and Eubank (1988) within a deviation of 1.5%. Teng et al. (1997) represent their experimental densities with a mixture density model, and one of their values agrees well (within 0.2 %) with a measurement of Aya et al. (1993). It is unknown whether the simple comparison is representative

for the two data sets. The liquid densities of Hebach et al. (2004) agree with those of King et al. (1992) and Yaginuma et al. (2000) within 0.25% in the range from 10 to 250bar.

## 1.2. Experimental PVTx properties of the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system

As shown in Table 3, the available experimental *PVTx* data for this system are much less than those for the system CO<sub>2</sub>-H<sub>2</sub>O. The data distribution, precision and the agreement among data sets are discussed below.

Table 3. The experimental PVTx properties of the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system

Researchers	<i>T</i> /K	<i>P</i> /bar	Concentration	<i>N<sub>d</sub></i>
Song et al. (2004)	276.15-283.15	40-130	<i>wt</i> (CO <sub>2</sub> )%=0-7.7 <i>Sr</i> %=3.5%	64 <sup>A</sup>
Teng & Yamasaki (1998)	278-293	64.4-294.9	<i>x</i> (CO <sub>2</sub> )%=1.96-3.27 <i>m</i> (NaCl)=0.99-4.99	24 <sup>B</sup>
Song et al. (2003)	303.15-323.15	100-200	<i>wt</i> (CO <sub>2</sub> )%=1-4 <i>Sr</i> =underground brine	99 <sup>B</sup>
Wang et al. (1996)	311	15.24-51.78	<i>x</i> (CO <sub>2</sub> )%=0.39-1.34 <i>Sr</i> %=0.25mol/L	5
Li et al. (2004)	332.15	2.4-289.3	<i>c</i> (CO <sub>2</sub> )= 0-0.958×10 <sup>-3</sup> mol·cm <sup>-3</sup> <i>Sr</i> %=Weyburn brine	37 <sup>C</sup>
Nighswander et al. (1989)	353.15-473.65	21.1-100.3	<i>x</i> (CO <sub>2</sub> )%=0.28-1.54 <i>wt</i> (NaCl)%=1.0	34
	408-793	30-2812	<i>x</i> (CO <sub>2</sub> )%=0.18-84.9 <i>Sr</i> %=6.0-20.0	114
Gehrig et al. (1986)	673-773	400-3000	<i>x</i> (CO <sub>2</sub> )%=0-100 <i>Sr</i> %=6.0, 10.0	279
Krüger & Diamond (2001a)	786.15-923.15	1670-4500	<i>x</i> (CO <sub>2</sub> )%=9.52-9.84 <i>Sr</i> %=6.0	14
Schmidt et al. (1995)	623.15-973.15	2000, 4000	<i>x</i> (CO <sub>2</sub> )%=5(relative to H <sub>2</sub> O) <i>Sr</i> %=40	14
Krüger & Diamond (2001b)	540-1123	650-3500	<i>x</i> (CO <sub>2</sub> )%=9.69-21.01 <i>x</i> (NaCl)%=1.52-1.74	Not given
Johnson (1992)	1197.15-1213.15	6600-7458	<i>x</i> (CO <sub>2</sub> )%=0.187-0.489 <i>S<sub>i</sub></i> NaCl)%=14.0-23.6	4

Note: A=a specific underground saline water within a Japanese city, B= artificial seawater, C=Weyburn brine, *Sr* =relative salinity, *wt*=weight, *m*=molality, *x*=mole fraction, *c*=concentration (mol·cm<sup>-3</sup>)

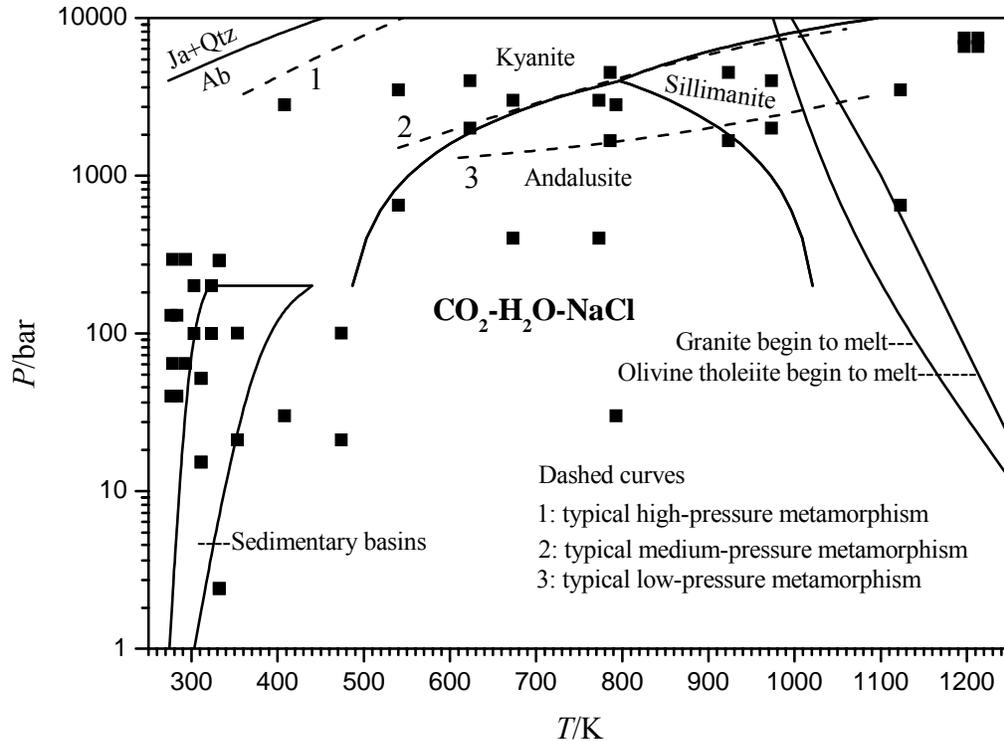


Fig.2 The distribution of experimental  $PVT_x$  data of the  $\text{CO}_2\text{-H}_2\text{O-NaCl}$  system in  $P$ - $T$  space. For phase boundaries, see Fig. 1. Note the lack of data in some of geologically important regions, i.e., along the high-pressure metamorphism trend and also parts of sedimentary basins.

### 1.2.1 The data distribution in the $T$ - $P$ space and phase fields

In this temperature range, the experimental data include those reported by Gehrig et al. (1986), Schmidt et al. (1995), Krüger and Diamond (2001b), Nighswander et al. (1989), Wang et al. (1996), Teng and Yamasaki (1998), Song et al. (2003, 2005) and Li et al. (2004). The first three report some data in the high-pressure region. Schmidt et al. (1995) has only one datum point in this temperature range at 4000 bar. The salinities of Gehrig et al. (1986) and Schmidt et al. (1995) are up to 20wt% and 40wt% (relative to  $\text{H}_2\text{O}$ ), respectively, and the  $\text{CO}_2$  contents of Gehrig et al. (1986) are up to 84.9 mol%. The other data sets are limited to low pressure (<300 bar), low  $\text{CO}_2$  content (<10mol%) and low salinity (<8%). Most of these data are in the range of 0-60°C, with an exception of the measurements of Nighswander et al. (1989) at 80-200.5°C. The data distribution are projected on Fig.2, showing no data for  $T < 400\text{K}$  and  $P > 300$  bar.

The  $PVT_x$  data for the homogeneous mixtures away from phase boundaries include Schmidt et al. (1995), Krüger and Diamond (2001b) and Song et al. (2003, 2005). The data of Krüger and Diamond (2001b) for the homogeneous mixtures were only given in the form of iso- $T_h$  lines (contours of total homogenization temperatures). The densities measured by Song et al. (2003) are for specific underground brine without reporting specific salt contents. Song et al. (2005) reported diagrams showing densities of artificial seawater varying from 40 to 130 bar at 3 and 10 °C. Here, it should be noted that the seawater composition given by Song et al. (2005) contains typographical errors, and thus should be corrected by referring to the usual seawater composition.

The data set on phase equilibria includes those reported by Gehrig et al. (1986), Krüger and Diamond (2001b), Nighswander et al. (1989), Wang et al. (1996), Teng and Yamasaki (1998), and Li et al. (2004), all reporting saturated liquid volumes or densities. Gehrig et al. (1986) is the only one that gives measurements on saturated vapor volumes for  $T \leq 647.21\text{K}$ .

Gehrig et al. (1986) presented the most extensive data on volumes of saturated liquid and vapor phases, covering a range of 408-793 K and 30-2812 bar. Krüger and Diamond (2001b) gave a graphical report of their experimental volumes on the bubble and dew curves and the relevant iso- $T_h$  lines. Besides, Schmidt et al. (1995) constructed a  $P$ - $T$  projection of the L+V→L phase boundary of the mixture containing 40wt%NaCl (relative to H<sub>2</sub>O) and 5%CO<sub>2</sub>. The diagram is drawn from their experimental synthetic fluid inclusion data, and partially falls within the range of  $T \leq T_C(\text{H}_2\text{O})$ .

Nighswander et al. (1989), Wang et al. (1996) and Li et al. (2004) measured the densities of saline water saturated with gaseous CO<sub>2</sub>, where the densities of Li et al. (2004) are for Weyburn formation brine. The experiments of Teng and Yamasaki (1998) for synthetic seawater

were conducted in the presence of liquid CO<sub>2</sub> at 278-293K, where a portion of their measurements falls within the CO<sub>2</sub> hydrate formation region, for which the influence of hydrate was considered to be negligible. Ohmura and Mori (1999) analyzed the temperature dependence of solubilities measured by Teng and Yamasaki (1998), Stewart and Munjal (1970), and Kimuro et al. (1994), and concluded that the data of Teng and Yamasaki (1998) represent the approximate *PVTx* properties of the system in the metastable absence of hydrate, not those of the seawater in equilibrium with hydrate. Using the same analysis for Teng and Yamasaki (1997), we conclude that the existence of hydrate stopped the mass transfer between aqueous solution and liquid CO<sub>2</sub>, so their experiments involving hydrate did not reach stable equilibrium states. So far, no volumetric data are available for the fluids in stable equilibrium with CO<sub>2</sub> hydrate, although there have been numerous measurements of CO<sub>2</sub> hydrate formation conditions for the ternary system.

Table 4. The precisions of the experimental *PVTx* properties of the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system

Researchers	<i>T</i>	<i>P</i>	Concentration	Density/volume
Song et al. (2004)				<1.5%(dΔρ/dW <sub>CO2</sub> )
Teng & Yamasaki (1998)	0.2K	0.1 bar	1.55%(mol)	1.87%( <i>d</i> )
Song et al. (2003)	0.1K		0.1wt%	0.005%( <i>d</i> )
Wang et al. (1996)	0.2K	0.007bar (0.025%)		<i>V</i> : 0.001cm <sup>3</sup>
Li et al. (2004)	0.2K	0.09 bar	<i>C</i> <sub>CO2</sub> : <2%, <i>W</i> <sub>H2O</sub> : 0.1%	<i>V</i> : 1cm <sup>3</sup> (0.7%), <i>d</i> : 10 <sup>-4</sup> gcm <sup>-3</sup>
Nighswander et al. (1989)	0.5%	0.35 bar	0.02%(mol), 0.001g(wt)	0.5cm <sup>3</sup> ( <i>V</i> )
	0.5K(~373K),	<0.2 bar	0.2mol%	~0.4%( <i>V</i> ),
Gehrig et al. (1986)	2K(773K), 5K ( <i>T</i> ≥673K, on phase boundary)			<1%( <i>V</i> , high <i>T</i> , <i>P</i> <15MPa)
Krüger & Diamond (2001a)	3K	20 bar	0.1%( <i>x</i> <sub>CO2</sub> )	0.5cm <sup>3</sup> ·mol <sup>-1</sup> ( <i>V</i> )
Schmidt et al. (1995)	0.5% (~5K when <i>T</i> >773K)	1%	~1%	~1%
Johnson (1992)	5-21K	50-70 bar		0.85-1.22cm <sup>3</sup> ·mol <sup>-1</sup> ( <i>V</i> )

Note: *V*=molar volume, *W*=mass fraction, wt=weight, *C*=concentration in mol·dm<sup>-3</sup>, *d*=density, dΔρ/dW<sub>CO2</sub>= partial derivative of density difference with respect to the mass fraction of CO<sub>2</sub>.

### 1.2.2 Precision estimate and agreement among data sets

The precisions of the experimental data mentioned above are listed in Table 4. Little evaluations or comments can be found in the literature for the precisions or consistencies of the ternary  $PVT_x$  data. Song et al. (2003) simply pointed out that the literature measurements, e.g., Parkinson and De Nevers (1969), Nighswander et al. (1989), Ohsumi et al. (1992), and his previous determinations, have respective shortcomings in their measurement principles and precisions, but without further comments. In order to find the inconsistencies in some literature  $PVT_x$  data, Krüger and Diamond (2001b) determined the immiscibility phase boundaries and the relevant iso- $T_h$  lines of two  $\text{CO}_2\text{-H}_2\text{O-NaCl}$  mixtures using the synthetic fluid inclusions. Their volumes along the bubble curve [below  $T_C(\text{H}_2\text{O})$ ] of the  $\text{H}_2\text{O}+9.69\text{mol\%CO}_2+1.74\text{mol\%NaCl}$  mixture are systematically higher than those of Gehrig (1980). Their bubble curve has higher pressures than that of Schmidt and Bodnar (2000), but it coincides perfectly with those of Gehrig (1980), and is very close to the points of Takenouchi and Kennedy (1965). Their slopes of the relevant iso- $T_h$  lines are close to the quasi-isochores of Gehrig (1980).

Overall, the principal error sources of the data sets in the temperature range below 647.21K are uncertainties in composition and volume (or density). The uncertainty in composition is usually within 2%, while the uncertainty in volume or density is within 1% for most data sets, except that of Teng and Yamasaki (1998), which has an uncertainty in density of about 2%.

### **13. Thermodynamic Modeling of the Mixture $PVT_x$ properties**

As can be seen from the assessment of experimental data above, laboratory experimental data exist only in a limited  $P$ - $T$  space as compared to the vast range of the Earth's interior. Therefore, thermodynamic modeling of  $PVT_x$  and phase equilibrium properties of fluids that

allows accurate extrapolation to a large  $P$ - $T$  range is extremely important for geochemists. The modeling needs to establish thermodynamic equations, mostly equations of state (EOS), to formulate the relationship among the pressures, temperatures, volumes and compositions ( $PVT_x$ ) of components, offering a theoretically rigorous way to calculate various thermodynamic properties, such as phase equilibrium and  $PVT$ . In these equations, there are empirical parameters to be evaluated from experimental data. Once these parameters are determined, the model is supposed to be able to predict properties beyond the experimental range. A well-established EOS may have extraordinary capabilities to predict the properties needed. For example, the EOS of Duan et al. (1996, 2000), which was only based on the  $PVT$  data of methane below 3000 bar, can predict (1)  $PVT$  properties of methane up to 100,000 bar; (2) the mixture  $PVT_x$  properties of salt-free fluids from above critical region up to 2000K and 100,000 bar; and (3) phase equilibria in the supercritical range. In this report, we give a review of the thermodynamic modeling of the systems  $\text{CO}_2$ - $\text{H}_2\text{O}$  and  $\text{CO}_2$ - $\text{H}_2\text{O}$ - $\text{NaCl}$ .

### ***1.3.1 The $\text{CO}_2$ - $\text{H}_2\text{O}$ system***

Different thermodynamic models have been reported to predict volumetric properties, including partial and apparent molar volumes, excess volumes, and densities of mass (or quantity of substance). They can be divided into the following three types:

#### *(1) Prediction of molar volumes or densities from classical equation of state*

The numerous cubic equations of state and virial equation of state truncated at second or third virial coefficient have been widely used in physical chemistry and chemical engineering for the prediction of low-pressure  $PVT_x$  properties and phase equilibria of mixtures including the

CO<sub>2</sub>-H<sub>2</sub>O system. However, these equations cannot be directly extended to the frequently encountered high-pressure fluids in natural systems. Since the 1970's, quite a few equations of state are developed for the CO<sub>2</sub>-H<sub>2</sub>O system at high pressures and temperatures, e.g., Holloway (1977), Flowers (1979), Kerrick and Jacobs (1981), Bowers and Helgeson (1983), Connolly and Bodnar (1983), Spycher and Reed (1988), Belonoshko and Saxena (1992), Duan et al. (1992b; 1995, 1996, 2000), Churakov and Gottschalk (2003b), etc. Ferry and Baumgartner (1987) summarize the equations of state for geological fluids before 1987, where the equations applicable for the binary include those of Holloway (1977), Flowers (1979), Kerrick and Jacobs (1981) and Spycher and Reed (1988). Mäder (1991) only briefly surveyed the equations before 1991 for geological fluids.

The equation of Holloway (1977) is one of the modified versions of the popular equation of Redlich and Kwong (1949), the so-called MRK type equations. Holloway (1977, 1981) used his equation to calculate the fugacities and activities of geological fluid mixtures at the  $P$ - $T$  conditions typical of crustal metamorphism, but no report on the applicable  $P$ - $T$  limits (Ferry and Baumgartner, 1987). Nevertheless, it is known that (1) the Holloway equation uses different temperature switching functions for the attractive term of H<sub>2</sub>O in three temperature intervals, so it is not continuous in temperature (Ferry and Baumgartner, 1987); (2) the attraction term is restricted to  $T > 400^\circ\text{C}$  for H<sub>2</sub>O, and consistent with that of De Santis et al. (1974) from 400 to 700 °C (Bowers and Helgeson, 1983). Kerrick and Jacobs (1981), Blencoe (2004) and our recent tests (Hu, 2002) clearly showed that the Holloway equation has relatively larger deviations in volumes than virial-type equations like Kerrick and Jacobs (1981) and Duan et al. (1992a,b; 1996), and that the equation cannot be used for temperatures below 673K and pressures above 10kbar for pure CO<sub>2</sub> and H<sub>2</sub>O.

The equation of Kerrick and Jacobs (1981) (**KJ**) is claimed to be valid from 300 to 1050°C, and may be extrapolated to higher temperatures for pure fluids, but the associated uncertainties are difficult to evaluate (Jacobs and Kerrick, 1981). The upper limit of the KJ EOS is 6 kbar for CO<sub>2</sub>, and at least 10 kbar for H<sub>2</sub>O (perhaps higher up to 20kbar). Kerrick and Jacobs (1981) did not advise their equation be used for H<sub>2</sub>O for  $P \leq 500$  bar and  $T = 400-500^\circ\text{C}$ . For the binary mixture, the KJ equation should not be used beyond the range 500-6000 bar. The comparisons made by Duan et al. (1992a) and Blencoe (2004) showed that the KJ equation is less accurate than Duan et al. (1992a,b) for both pure fluids and mixtures.

The MRK type equation of Connolly and Bodnar (1983) (**CB**) for the CO<sub>2</sub>-H<sub>2</sub>O system was used by Sterner and Bodnar (1991) to calculate the solvus pressures. Blencoe et al. (2001) found that the CB equation overestimates the binary solvus pressures at 300°C by about 50 to 110 bar. Bakker and Diamond (2000, Fig.2b) also showed that the binary equilibrium pressures at 270°C of Sterner and Bodnar (1991) calculated from the CB equation is 300-700 bar higher than those of Tödheide and Franck (1963) and Takenouchi and Kennedy (1964). So the CB equation should be inapplicable for the binary phase equilibrium calculation under the  $P$ - $T$  conditions described above.

Bakker (1999) concluded from his  $PVTx$  tests that the equation of Bowers and Helgeson (1983) can construct isochores for pure H<sub>2</sub>O up to 10 kbar and 1300K, and can be used to at least 973K and 6 kbar for the H<sub>2</sub>O-CO<sub>2</sub> system. Bowers and Helgeson (1983) used their equation to calculate the isobaric  $T$ - $x$  diagrams at 0.5 to 2 kbar, but there are significant systematic deviations from measurements of Tödheide and Franck (1963) and Takenouchi and Kennedy (1964) for the water-rich phases. Besides, the isobars predicted from their equation deviate

obviously from those of Takenouchi and Kennedy (1964) for saturated CO<sub>2</sub>-rich phases and thus their equations cannot be used to calculate phase boundaries.

The virial equation of Spycher and Reed (1988) is truncated at third virial coefficient, with  $P$  and  $T$  as variables, therefore, it is very convenient to use. However, it is valid only in two low-pressure ranges: 0-500 bar (50-350°C), and 0-1000 bar (450-1000°C).

Belonoshko and Saxena (1992) proposed a unified corresponding states equation for 13 supercritical fluids (including H<sub>2</sub>O and CO<sub>2</sub>) and their mixtures, which uses intermolecular potential parameters, and is claimed to be valid in the range 400(700 for H<sub>2</sub>O)-4000 K and 5-1000 kbar. Comparisons show that the equation can well predict the shock wave data at extremely high pressures and temperatures. However, it should be noted that the shock wave data at extreme conditions are usually inconsistent with the hydrostatic data at lower pressures and temperatures, and that the equation were fit to the molecular dynamics (MD) simulated data of Belonoshko and Saxena (1991a,b) for CO<sub>2</sub> and H<sub>2</sub>O, where the data for H<sub>2</sub>O are not consistent with some experimental data and our recent MD simulations (Zhang and Duan, 2005).

The equation of Duan et al. (1992b) can calculate both phase equilibria and volumetric properties of the CO<sub>2</sub> and H<sub>2</sub>O system with accuracy close to that of experiments at 50-1000°C and 0-1 kbar (or 3 kbar with less accuracy). For the pure end-members, it is valid for the range 0-1000°C and 0-8 kbar (or slightly above), but it cannot accurately predict the phase equilibria of pure end-members near the triple points. In addition, Seitz and Blencoe (1999), Bakker and Diamond (2000) and Blencoe (2004) showed that the equation of Duan et al. (1992b) cannot reproduce correct near-critical  $PVTx$  properties and phase behavior of the binary. Because of generally high accuracy, the equations of Duan et al. (1992a,b) were incorporated into a software package HCO-TERNARY written by Nieva and Barragán (2003) in FORTRAN language.

The equation of Duan et al. (1996, 2000) takes the form of corresponding states based on molecular potential parameter scaling. It uses a set of general constants, plus two specific constants for each pure fluid and two additional constants for each binary. It can be used from 1.35 times of critical temperatures to 2000K, and up to 100 kbar both pure end-members and mixtures. Furthermore, the equation is also capable of predicting supercritical phase equilibria (Duan et al., 2000; Sun et al., 2000; Costantino and Rice, 1991; Van Hinsburg et al., 1993), but the predicted locations of supercritical phase separation of the CO<sub>2</sub>-H<sub>2</sub>O system (Sun et al., 2000) need to be checked by future experiments. Nevertheless, Seitz and Blencoe (1999) showed that the equation has obvious negative deviations in the critical region (up to -40 cm<sup>3</sup>·mol<sup>-1</sup> or -24% at 400 °C).

Churakov and Gottschalk (2003a,b) proposed a perturbation theory based equation of state for both polar and non-polar molecular fluids and their mixtures. In the prediction of the phase boundaries of the CO<sub>2</sub>-H<sub>2</sub>O system, the equation deviates significantly from the experimental results of Takenouchi and Kennedy (1964) and Tödheide and Franck (1963), especially near and in the critical regions. In the binary *PVTx* prediction, the equation generally overestimates volumes, where the agreement between the predicted and experimental results ranges from good to poor. Overall, the equation can well reproduce the binary excess volumes of Gehrig (1980), Shmulovich et al. (1980), Sterner and Bodnar (1991), Frost and Wood (1997) and Seitz and Blencoe (1999), where the maximum deviations range from less than 2 cm<sup>3</sup>·mol<sup>-1</sup> to more than 10 cm<sup>3</sup>·mol<sup>-1</sup>. However, compared with the excess volume data of Greenwood (1969), the equation predicts reasonable values at higher pressures, but it yields much higher results at lower pressures, where the maximum deviation exceeds 50 cm<sup>3</sup>·mol<sup>-1</sup>.

Most of the equations of state above are developed for the  $PVT_x$  calculation of single phases, especially of the supercritical fluids and gaseous phases, not for the mixture phase equilibria. Only the equations of Duan et al. (1992b; 1995) are developed for both  $PVT_x$  and phase equilibrium calculation.

In the study of synthetic fluid inclusions, a special method is developed for the solvus  $PVT_x$  determination. In the systems Na-K-Ca-Cl-H<sub>2</sub>O and CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O, Zhang and Frantz (1987, 1992) found that the  $P$ - $T$  relations and total volumes along the iso- $T_h$  lines and isochores can be described with simple equations by using  $T_h$  as a variable, and the  $PVT_x$  relations along the phase boundaries can be readily determined from these  $P$ - $T$  relations. This approach is very convenient and thus widely used for the  $PVT_x$  correlation of synthetic fluid inclusions, e.g., Brown and Lamb (1989), Sterner and Bodnar (1991), Schmidt et al. (1995), and Schmidt and Bodnar (2000).

## *(2) The correlation and prediction of partial molar volumes and apparent molar volumes*

Present correlation and prediction of the partial molar volumes and apparent molar volumes of the aqueous non-electrolyte solutions are far less accurate than those for electrolyte solutions (Akinfiev and Diamond, 2003, 2004). For example, the revised equation of Helgeson, Kirkwood and Flowers (HKF) (Tanger and Helgeson, 1988; Shock and Helgeson, 1990; Shock et al, 1989, 1992) are designed to predict the thermodynamic properties of aqueous ions over a wide range (0-600°C and 1-5 kbar) (Akinfiev and Diamond, 2003). However, it does not correctly predict the behavior of the non-electrolyte solutes in the near-critical and supercritical regions of water (O'Connell et al., 1996; Plyasunov et al., 2000a; Plyasunov and Shock, 2001;

Akinfiev and Diamond, 2003). From this situation there arises a need to develop equations for aqueous non-electrolytes.

Plyasunov et al. (2000a,b) and Sedlbauer et al. (2000) briefly reviewed the previous equations for partial molar volumes of aqueous non-electrolytes and the associated theoretical details. Significant progresses have been made in improving the volumetric predictions, where one of the most important progresses is the models based on the fluctuation solution theory (Kirkwood and Buff, 1951; O'Connell, 1971, 1981, 1995), such as O'Connell et al. (1996), Plyasunov et al. (2000a,b), Sedlbauer et al. (2000), and Akinfiev and Diamond (2003, 2004). These models can predict well the partial molar volumes of aqueous CO<sub>2</sub> at infinite dilution over a wide  $P$ - $T$  range, including near-critical and supercritical regions. Besides, there are also models for the apparent molar volumes of aqueous CO<sub>2</sub>, e.g., García (2001), Crovetto et al. (1990), Teng et al. (1997). These models can be combined with appropriate NaCl-H<sub>2</sub>O volume model and ternary excess volume models to predict the total volumes or densities of the CO<sub>2</sub>-H<sub>2</sub>O solutions and the CO<sub>2</sub>-H<sub>2</sub>O-NaCl solutions.

### *(3) Correlation of excess volume equations*

Some excess volume models have been proposed for the CO<sub>2</sub>-H<sub>2</sub>O system at elevated pressures and temperatures, e.g., Shmulovich et al. (1980), Powell and Holland (1985), Sterner and Bodnar (1991), Destriqneville et al. (1996), Blencoe et al. (1999), etc., where the Margules type equations are the most popular formulations because of their simplicity. For example, Shmulovich et al. (1980) used two-constant (asymmetric) Margules equation for  $V^{\text{Ex}}$  modeling at a given  $P$  and  $T$ . Powell and Holland (1985) employed a two-parameter Margules model to derive the binary  $V^{\text{Ex}}$ , where the two parameters are simple linear functions of  $P$  and  $T$ , which

use two sets of parameters, where one set is for  $P=2-10$  kbar and  $T=400-800^{\circ}\text{C}$ , and the other is for  $P=0-1.5$  kbar. Sterner and Bodnar (1991) developed a three-parameter Margules equation for  $V^{\text{Ex}}$ , where the parameters are polynomials of  $P$  and  $T$  for 2-6 kbar and  $400-700^{\circ}\text{C}$ . This equation reproduces their  $V^{\text{Ex}}$  results with an average deviation of  $0.196\text{ cm}^3\cdot\text{mol}^{-1}$ . Destriqneville et al. (1996) proposed a new expression for the correlation of their  $V^{\text{Ex}}$  data from Monte Carlo simulation results from 0.2 to 3 kbar at 773.15 and 1073.15K, with a standard deviation of 0.4 and  $0.8\text{cm}^3\cdot\text{mol}^{-1}$ , respectively.

It is worthy to note that Blencoe et al. (1999) found that the Margules, Redlich-Kister, Wilson and Non-Random Two-Liquid (**NRTL**) formulations, as well as the expression of Destriqneville et al. (1996), cannot accurately represent the data of Seitz and Blencoe (1999) at  $400^{\circ}\text{C}$ , 100-1000 bar. So they developed an empirical  $V^{\text{Ex}}$  expression by adding two exponential terms to the two-parameter Margules equation, with 14 constants fit to the experiments. Besides this equation, they also gave a two-parameter Margules equation for two pressure ranges: 1-4 kbar and 0-100 bar, for which the parameters are different.

In addition to the methods described above, there are also many other ways for the *indirect* derivation of volumetric properties of geological fluids. For example, the volumetric properties can be derived from the equations of excess enthalpy ( $H^{\text{Ex}}$ ), excess free energy ( $F^{\text{Ex}}$ ,  $G^{\text{Ex}}$ ), activity ( $a$ ) or activity coefficient ( $\gamma_i$ ), fugacity ( $f$ ), or fugacity coefficient ( $\phi$ ), etc. Several applications of such approaches can be found for the  $\text{CO}_2\text{-H}_2\text{O}$  system at high pressures and temperatures, such as the two-fluid free energy model used by Gallagher et al. (1993) and Wormald et al. (1997), the excess enthalpy models of Wormald et al. (1983, 1986), Smith and Wormald (1984), Bottini and Saville (1985), the activity coefficient models of Saxena and Fei (1988), Joyce and Blencoe (1994), Anovitz et al. (1998), and Aranovich and Newton (1999) etc.

It is evident that only a few of the numerous excess function models in physical chemistry and chemical engineering were introduced into the modeling of the thermodynamic properties of geological fluids. Many recent, advanced or popular excess function models, such as the various theoretically and empirically based local composition equations in recent literature, have not been tested for geological fluids, and a lot of efforts are still needed in this regard.

### ***1.3.2 The CO<sub>2</sub>-H<sub>2</sub>O-NaCl system***

Only a few models on the *PVTx* and phase equilibrium calculation have been made for this system, e.g., Bowers and Helgeson (1983, 1985), Brown and Lamb (1989), Duan et al. (1995), Schmidt et al. (1995) and Schmidt and Bodnar (2000).

Bowers and Helgeson (1983) stated that their equation (**BH**) appears to generate reliable excess volumes for 350-500° C at 500-1500 bar and 0-35 wt% NaCl (relative to H<sub>2</sub>O). Bowers and Helgeson (1985) believe that their equation can generate reliable fluid volumes and fugacity coefficients of the components of the ternary at  $T=350-600^{\circ}\text{C}$ ,  $P>500$  bar and salinity=0-35 wt% NaCl (relative to H<sub>2</sub>O) in the single-phase fluid region. Nevertheless, the equation shows large deviations at the lower temperature and pressure limits (350°C, 500 bar). Bowers and Helgeson (1983) admitted that the predictions of their equation for the compositions of the ternary coexistent phases are only partially successful. The predicted solvus differs significantly from the experimental results for all but water-rich fluids. The poor solvus prediction of the equation at intermediate to high CO<sub>2</sub> content was attributed primarily to the limited salinity range of *PVT* data for parameter regression (Bowers and Helgeson, 1983).

Recently, Bakker (1999) re-examined the performance of the BH equation in the H<sub>2</sub>O-CO<sub>2</sub>-NaCl system, and extended it to the CH<sub>4</sub> and N<sub>2</sub> bearing fluids. He concluded that the

available experimental  $PVT_x$  data, and therefore isochores and fugacity coefficients of the H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub>-NaCl system can be accurately reproduced with the equation up to 10 kbar and 1300K, but cannot be used in and near the immiscibility regions and critical points. However, Bakker (1999) also showed that the equation has large deviations for NaCl-H<sub>2</sub>O below 773K at 3 kbar and 20.822 wt% NaCl, and for the ternary water-rich phases below 600 bar at 773K and 6 wt% NaCl. We believe that the equation generally fails in the range  $T < 673\text{K}$  (or higher to 773K for high salinity phases) and  $P < 600$  bar.

Based on the ideal geometrical mixing assumption, Brown and Lamb (1989) presented a formulation of volumetric properties by linear (ideal) interpolation between a CO<sub>2</sub> isochore predicted by the KJ equation and a NaCl-H<sub>2</sub>O isochore derived from an empirical regression equation. The approach is applicable for  $T > 350^\circ\text{C}$  and  $P = 2\text{-}10$  kbar, especially for high pressures and low to moderate temperatures (fluid densities  $\geq 1.0 \text{ cm}^3/\text{mol}^{-1}$ ). However, the simple mixing assumption is likely to introduce large errors because of the highly non-ideal features of the ternary. Furthermore, in addition to the uncertainties from the equations and the ideal assumption, the approach is also subject to the uncertainties of the necessary input parameters, such as the estimated volume percent. Large deviations have been found from experimental isochore locations of synthetic fluid inclusions (Johnson, 1992).

Duan et al. (1995) proposed a perturbation theory equation of state for the ternary, which is applicable for both  $PVT_x$  and phase equilibria in the range 300-1000°C, 0-6 kbar and 0-30wt%NaCl, with accuracy close to that of the experimental results. However, they also showed somewhat large deviations from experimental solvus compositions of water-rich fluids at the lower temperature limit (300° C) and temperatures near the critical point of water. Schmidt and Bodnar (2000) compared their experimental phase equilibria and isochores with the predictions

from the equation of Duan et al. (1995). There are significant inconsistencies between the predictions and experiments at lower temperatures (less than 400°C) and high CO<sub>2</sub> contents (or salinities), where the experimental data were not available for the equation parameterization, especially at the critical conditions. However, there is a close agreement between the equation and experiments at lower salinities or CO<sub>2</sub> contents, and the agreement becomes even better with increasing temperature. This is probably associated with the ion-pair assumption over the relevant *P-T-x* range of the equation (Schmidt and Bodnar, 2000). The inconsistency mentioned above results from at least two additional factors: the limited *P-T-x* range of the equation parameterization, and the use of Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> as CO<sub>2</sub> source. According to Krüger and Diamond (2001a), the *T<sub>h</sub>*'s of the Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-bearing mixtures are remarkably higher than the reasonable values, which will yield higher homogenization pressures (*P<sub>h</sub>*) and molar volumes. The higher molar volumes decrease slopes of isochores. These conclusions can be justified by the trend shown in the figures of Schmidt and Bodnar (2000), where the slopes of the experimental isochores are obviously smaller than those predicted from the equation of Duan et al. (1995), and the solvus pressures are systematically higher than those predicted from the equation. It can be expected that the consistency between the experiments and predictions will be improved to some extent if the errors caused by the use of Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in the experiments are properly corrected.

## 2. An Improved CO<sub>2</sub> Solubility Model

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 (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 (0-260 °C, 0-2000 bar, 0-4.5 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 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 refitted 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 tried to compare 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-vapor or liquid CO<sub>2</sub>) in order to facilitate applications.

### **2.1. Description of the 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

$$\ln m_{CO_2} = \ln y_{CO_2} \phi_{CO_2} P - \mu_{CO_2}^{(0)} / RT - 2\lambda_{CO_2-Na} (m_{Na} + m_K + 2m_{Ca} + 2m_{Mg}) - \zeta_{CO_2-Na-Cl} m_{Cl} (m_{Na} + m_K + m_{Mg} + m_{Ca}) + 0.07m_{SO_4} \quad (1)$$

The definitions and the values of all the parameters in the above equation are defined and listed in Duan and Sun (2003). All parameters can be calculated directly without any iteration, except the fugacity coefficient of CO<sub>2</sub>,  $\phi_{CO_2}$ , 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  $\phi_{CO_2}$  as a function of temperature and pressure,

$$\phi_{CO_2} = c_1 + [c_2 + c_3T + c_4/T + c_5/(T-150)]P + [c_6 + c_7T + c_8/T]P^2 + [c_9 + c_{10}T + c_{11}/T] \ln P + [c_{12} + c_{13}T]/P + c_{14}/T + c_{15}T^2, \quad (2)$$

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  $\phi_{CO_2}$  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  $\phi_{CO_2}$  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 5 lists the parameters for Eqn. (2). The absolute average deviation between  $\phi_{CO_2}$  calculated from Eqn. (2) and  $\phi_{CO_2}$  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 Eqn. (1). This deviation is small, considering the average experimental error is of the order of about 5%.

Table 5. The parameters of Eqn. (2)

Par	<i>T-P</i> range					
	1	2	3	4	5	6
$c_1$	1.0	-7.1734882E-1	-6.5129019E-2	5.0383896	-16.063152	-1.5693490E-1
$c_2$	4.7586835E-3	1.5985379E-4	-2.1429977E-4	-4.4257744E-3	-2.7057990E-3	4.4621407E-4
$c_3$	-3.3569963E-6	-4.9286471E-7	-1.1444930E-6	0.0	0.0	-9.1080591E-7
$c_4$	0.0	0.0	0.0	1.9572733	1.4119239E-1	0.0
$c_5$	-1.3179396	0.0	0.0	0.0	0.0	0.0
$c_6$	-3.8389101E-6	-2.7855285E-7	-1.1558081E-7	2.4223436E-6	8.1132965E-7	1.0647399E-7
$c_7$	0.0	1.1877015E-9	1.1952370E-9	0.0	0.0	2.4273357E-10
$c_8$	2.2815104E-3	0.0	0.0	-9.3796135E-4	-1.1453082E-4	0.0
$c_9$	0.0	0.0	0.0	-1.5026030	2.3895671	3.5874255E-1
$c_{10}$	0.0	0.0	0.0	3.0272240E-3	5.0527457E-4	6.3319710E-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
$c_{13}$		4.4774938E-1	0.0	0.0	0.0	0.0
$c_{14}$		101.81078	71.820393	0.0	0.0	888.76800
$c_{15}$		5.3783879E-6	6.6089246E-6	-1.5056648E-5	-5.4965256E-7	-6.6348003E-7

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

Par = Parameters

Since the manuscript of Duan and Sun (2003) was submitted, a few reliable 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; Servio and Englezos, 2001; Chapoy et al., 2004; 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 have re-evaluated the parameters of the solubility model at temperatures below 288 K. 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.

## **2.2 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 (1999), Kiepe et al. (2002), Teng and Yamasaki (2002), Bando et al. (2003), Chapoy et al. (2004), Li et al. (2004), 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 then, but not the new data or the data we did not locate then. Here we tried to compare the model with as many data 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 Akinfiyev (2003), and Spycher et al. (2003).

Table 6 and Table 7 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) or this study to evaluate the parameters of CO<sub>2</sub> solubility model while the data presented in Table 7 are those not used but predicted by our model. The column 5 of Tables 6 and 7 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. Figure 5 compares the prediction of our model with the experimental data not used in parameterization. From Figure 2 and Tables 6 and 7, 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.

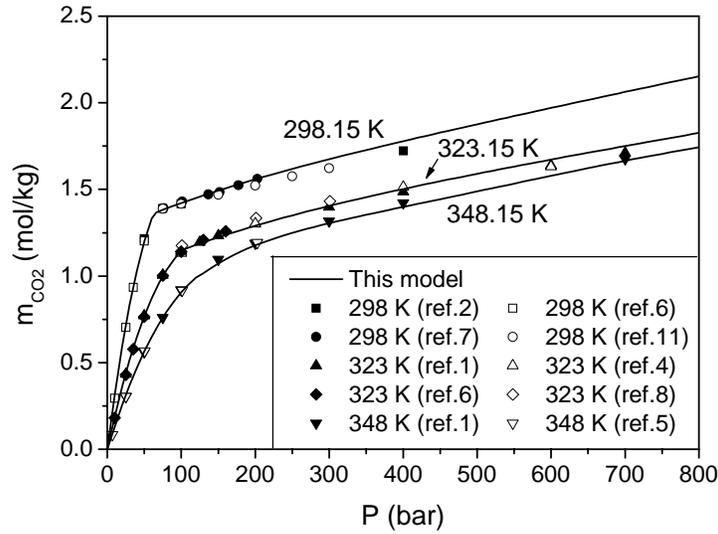


Figure 3. CO<sub>2</sub> solubility in pure water—the prediction of this model vs. experimental data which were not used in the parameterization. The experimental data presented in the figure are from—ref.1: Wiebe and Gaddy (1939), ref.2: Wiebe and Gaddy (1940), ref.3: Matous et al. (1969), ref.4: Shagiakhmetov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

Table 6. The reliable experimental data of CO<sub>2</sub> Solubility in pure water at 273-533 K and 1-2000 bar—the data 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.

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
Harned 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

a. Number of measurements

b. AAD% the average absolute deviation of the data from the model

c. 'h' means high quality and 'm' means moderate quality

Table 7. The reliable experimental data of CO<sub>2</sub> Solubility in pure water at 273-533 K and 1-2000 bar—the data not used to evaluate the parameters of the CO<sub>2</sub> solubility model.

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 (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

a. Number of measurements

b. AAD% the average absolute deviation of the data from the model

c. 'h' means high quality and 'm' means moderate quality

Column 6 of Tables 6 and 7 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 Akinfiyev (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), Takenouchi and Kennedy (1965) in the *T-P* range of our model were demonstrated by Duan and Sun (2003). This study confirmed 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 (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), Malinin and Kurorskaya (1975) at 298 K are higher than the model by 7-8%. Some data of Zawisza and Malesinska (1981), and Nighswander et al. (1989) above 373 K deviates 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 systematical deviation from our solubility model by 5-10%. A few data of Zel'vinskii (1937), Shagiakhmetov and Tarzimanov (1981), 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 8 lists CO<sub>2</sub> solubility data with poor quality. Some data of Wroblewski (1883), Hähnel (1920), Stewart and Munjal (1970) are in the metastable equilibrium of CO<sub>2</sub> hydrate. The data of these studies deviate from our solubility model by 10-25%. Many data of Sander (1912), Vilcu and Gainar (1967) are far away from the solubility model. The average absolute deviations of the two data sets are more than 20%. More than half of the data of Sako et al. (1991) deviate from our model by more than 10%. Many data of Kiepe et al. (2002) deviate from our model by 7-20%. The data of Li et al. (2004) are greater than the prediction of our model by 7-13%.

Table 8. 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
Hähnel (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

Table 9 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.

Table 9. CO<sub>2</sub> solubility in 35‰ seawater

P (bar)	T (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).

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 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. Table 10 and Table 11 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 is 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.

Table 10. CO<sub>2</sub> solubility in pure water at CO<sub>2</sub> hydrate-liquid water-gas or liquid CO<sub>2</sub> equilibrium

$T$ (K)	$P_{eq}$ (bar) <sup>a</sup>	$m_{CO_2}$ (m)	$T$ (K)	$P_{eq}$ (bar) <sup>a</sup>	$m_{CO_2}$ (m)
270.15	9.729	.7681	281.15	32.78	1.429
270.65	9.915	.7660	281.65	35.22	1.480
271.15	10.11	.7639	282.15	37.94	1.533
271.65	10.30	.7620	282.65	41.01	1.588
272.15	10.49	.7601	283.15	44.54	1.645
272.65	11.52	.8113	283.65	67.04	1.703
273.15	12.20	.8378	284.15	115.9	1.760
273.65	12.92	.8653	284.65	171.5	1.819
274.15	13.68	.8938	285.15	231.7	1.878
274.65	14.50	.9233	285.65	296.3	1.939
275.15	15.37	.9540	286.15	365.2	2.001
275.65	16.31	.9858	286.65	438.3	2.064
276.15	17.31	1.019	287.15	515.8	2.128
276.65	18.37	1.053	287.65	597.7	2.194
277.15	19.52	1.089	288.15	684.2	2.260
277.65	20.75	1.126	288.65	775.7	2.328
278.15	22.08	1.164	289.15	872.3	2.397
278.65	23.51	1.204	289.65	974.6	2.468
279.15	25.06	1.246	290.15	1083.	2.539
279.65	26.74	1.289	290.65	1198.	2.611
280.15	28.57	1.334	291.15	1321.	2.685
280.65	30.58	1.380	291.65	1452.	2.760

<sup>a</sup>  $P_{eq}$  means the pressure of CO<sub>2</sub> hydrate-liquid water-gas or liquid CO<sub>2</sub> phase equilibrium

Table 11. 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>CO2</sub> (m)	<i>T</i> (K)	<i>P</i> <sub>eq</sub> (bar)	<i>m</i> <sub>CO2</sub> (m)
270.15	10.04	.6804	279.65	32.22	1.279
270.65	10.62	.7024	280.15	34.64	1.324
271.15	11.25	.7252	280.65	37.34	1.372
271.65	11.91	.7489	281.15	40.40	1.423
272.15	12.62	.7734	281.65	43.93	1.494
272.65	13.37	.7989	282.15	78.24	1.527
273.15	14.18	.8252	282.65	132.4	1.584
273.65	15.03	.8526	283.15	192.4	1.642
274.15	15.95	.8811	283.65	258.2	1.701
274.65	16.93	.9106	284.15	330.0	1.763
275.15	17.98	.9412	284.65	408.3	1.827
275.65	19.11	.9731	285.15	493.7	1.896
276.15	20.33	1.006	285.65	587.0	1.971
276.65	21.64	1.041	286.15	689.8	2.053
277.15	23.05	1.076	286.65	803.9	2.142
277.65	24.58	1.114	287.15	932.3	2.238
278.15	26.24	1.152	287.65	1080.	2.352
278.65	28.05	1.193	288.15	1256.	2.476
279.15	30.04	1.235	288.65	1478.	2.623

*P*<sub>eq</sub> means the pressure of CO<sub>2</sub> hydrate-liquid water-gas or liquid CO<sub>2</sub> phase equilibrium

## Conclusions

This one-year exploratory Phase I UCR project has been highly successful and productive:

- (1) this project has resulted in an improved model that is presented for the calculation of the CO<sub>2</sub> solubility in brines for temperature from 273 to 533 K, pressure from 0 to 2000 bar, and ionic strength from 0 to 4.5 molality of NaCl equivalent. This is the PTx range for geological carbon sequestration. Newly available experimental data are included to improve the model, and the model used a non-iteration approach to increase computational efficiency. Thus, this project has made a significant contribution to the carbon sequestration program.
- (2) One paper in collaboration with NETL scientist on simulating CO<sub>2</sub>-brine-mineral Interactions is in press for publication at *Environmental Geosciences*.
- (3) One paper on improved CO<sub>2</sub> solubility model is in press for publication in *Marine Chemistry*. A manuscript on literature review of experimental data and thermodynamic models for the CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl systems was submitted for publication in *Applied Geochemistry*.

Based on the review and our conclusions above, we make the following suggestions:

- (1) Experimental work. Further experimental measurements of *PVTx* properties need to be made on: i) The blank areas in the *P-T* space in Figure 1; ii) the measurements of saturated vapor phases, or the simultaneous measurements of coexistent phases; iii) the critical regions, especially the regions near the critical point of water; iv) the two- and multi-phase equilibrium regions associated with CO<sub>2</sub> hydrate; and v) the large region containing supercritical phase equilibria.

(2) Thermodynamic modeling and molecular simulations.

i) Develop accurate models for the reproduction of volumetric properties along the phase boundaries, especially those at low temperatures. Since the large differences in the compositions and physicochemical properties of coexistent phases, it is difficult to simultaneously and accurately model the  $PVTx$  properties of coexistent phases. In these situations, mixed model may be a feasible option. For example, one can use an equation of state for the gaseous phase, and an activity coefficient model for liquid phases. Another feasible approach is to introduce local composition models into equations of state or excess thermodynamic functions. This approach has won wide successes in chemical engineering thermodynamic modeling.

ii) Develop appropriate models that are suitable for accurate prediction of the  $PVTx$  behaviors in the critical regions, for which it will be necessary and helpful to improve many existing approaches for critical phenomena. For example, the fluctuation solution theory can be used to resolve the diversity problem of the partial molar volumes of solutes in aqueous solutions.

iii) Establish an appropriate theoretical framework to overcome the difficulties in  $PVTx$  modeling that result from the speciation in the ternary system in the region including the critical point of water.

iv) Develop excess volume ( $V^{\text{Ex}}$ ) models. This is likely a good option for the modeling of volumetric properties of fluid mixtures, because a  $V^{\text{Ex}}$  model can take a new formulation that is completely different from those of the models for the relevant subsystems (including pure components), and thus can be combined with any forms of models for the relevant subsystems. Similar advantage also exists for excess partial molar volume models. Of course, other models for the excess thermodynamic functions (such as  $G^{\text{Ex}}$  and  $H^{\text{Ex}}$ ) are also convenient for the derivation of excess volumes.

v) Use the MC and MD simulation approaches to yield new  $PVT_x$  data in the regions without experimental data, or to check the data sets with large uncertainty or inconsistency with other data sets, especially those at high pressures and/or temperatures.

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