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PVTx properties of the CO_2–H_2O and CO_2–H_2O–NaCl systems below 647 K: Assessment of experimental data and thermodynamic models

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Abstract

Evaluation of CO_2 sequestration in formation brine or in seawater needs highly accurate experimental data or models of pressure–volume–temperature-composition (*PVTx*) properties for the CO_2–H_2O and CO_2–H_2O–NaCl systems. This paper presents a comprehensive review of the experimental *PVTx* properties and the thermodynamic models of these two systems. The following conclusions are drawn from the review: (1) About two-thirds of experimental data are consistent with each other, where the uncertainty in liquid volumes is within 0.5%, and that in gas volumes within 2%. However, this accuracy is not sufficient for assessing CO_2 sequestration. Among the data sets for liquids, only a few are available for accurate modeling of CO_2 sequestration. These data have an error of about 0.1% on average, roughly covering from 273 to 642 K and from 1 to 35 MPa; (2) There is a shortage of volumetric data of saturated vapor phase. (3) There are only a few data sets for the ternary liquids, and they are inconsistent with each other, where only a couple of data sets can be used to test a predictive density model for CO_2 sequestration; (4) Although there are a few models with accuracy close to that of experiments, none of them is accurate enough for CO_2 sequestration modeling, which normally needs an accuracy of density better than 0.1%. Some calculations are made available on www.geochem-model.org.

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Keywords: CO_2 sequestration; *PVTx* properties; Volume; Density; Thermodynamic modeling

1. Introduction

CO_2–H_2O and CO_2–H_2O–NaCl are the most commonly encountered fluids in various geological environments, such as the metamorphic rocks of almost all grades, igneous rocks, carbonates, geothermal brines, sedimentary basins, and a wide variety of hydrothermal deposits (Roedder, 1984; Labotka, 1991; Schmidt and Bodnar, 2000). Therefore, the pressure–volume–temperature-composition (*PVTx*) and phase equilibrium properties of these two systems play a very important role in understanding petrologic and geochemical processes. Furthermore, the knowledge of the *PVTx* and

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phase equilibrium properties of these systems is also required by many processes in industrial production, and chemical and environmental engineering, such as CO_2-related enhanced oil and gas recovery, supercritical fluid technology, seawater desalination and waste water treatment (Nighswander et al., 1989; Wang et al., 1996; Li et al., 2004; Ota et al., 2005; White et al., 2005). Today, with increasing interest in understanding the carbon cycle in Earth systems, and in storing CO_2 in geological formations and sea waters, the *PVTx* and phase equilibrium properties of the systems CO_2–H_2O and CO_2–H_2O–NaCl are becoming increasingly important (Haugan and Drange, 1992; Oldenburg and Benson, 2002; Kaszuba et al., 2003; Baines and Worden, 2004; Pruess et al., 2004; Talman et al., 2004; Xu et al., 2004; Kervevan et al., 2005; Portier and Rochelle, 2005; Fuller et al., 2006).

It is already known that density differences about 0.1 kg m^{-3} are sufficient to develop negatively buoyant plumes on kilometer scale in weakly stratified environments (Haugan and Drange, 1992), which is crucial for the natural transport of dissolved CO_2 to deeper water. Therefore, accurate prediction of liquid densities is very important. Under the P–T conditions of practical CO_2 sequestration, the total increase in solution density due to CO_2 dissolution are obviously larger than 0.1 kg m^{-3}, but usually within a few percents of water density. On the other hand, the liquid density data sets in existence usually have an accuracy better than 0.1% (about 1.0 kg m^{-3}). Considering these facts, an accuracy better than 0.1% seems to be necessary for a density model of CO_2-bearing solutions.

In this study, our interest focuses on the CO_2–H_2O and CO_2–H_2O–NaCl systems. We do not address the NaCl–H_2O system, because its experimental *PVTx* and phase equilibrium properties and thermodynamic modeling have been studied extensively (Haas, 1970; Helgeson and Kirkham, 1976; Rogers and Pitzer, 1982; Pitzer and Pabalan, 1986; Bischoff et al., 1986; Li and Pitzer, 1987a,b; Pitzer et al., 1987; Pitzer and Tanger, 1988; Gallagher and Levelt Sengers, 1988; Tanger and Pitzer, 1989; Harvey and Levelt Sengers, 1989; Bischoff and Pitzer, 1989; Bischoff, 1991; Archer, 1992; Anderko and Pitzer, 1993).

The thermodynamic properties of CO_2–H_2O and CO_2–H_2O–NaCl have been studied for more than a century. However, there is still a lack of experimental data, even in some geologically and industrially important P–T regions, and the most recent models still cannot accurately represent *PVTx* and phase equilibrium properties in some P–T ranges. With the perspective of geochemical, environmental, and industrial applications in mind, we have evaluated all available experimental *PVTx* data and the thermodynamic models for these two systems. Our goals were to identify the reliabilities of available data, to assess the strengths and weaknesses of the present thermodynamic models, and to identify important areas for future studies.

Comprehensive reviews on the CO_2 solubility or liquid-vapor equilibria have been published recently (Carroll et al., 1991; Crovetto, 1991; Duan et al., 1995; Diamond and Akinfiev, 2003; Duan et al., 2003; Duan and Sun, 2003; Spycher et al., 2003), and will not be repeated in this study. Tödheide (1982) reviewed the available *PVTx* data and some relevant thermodynamic models for the systems H_2O, CO_2–H_2O, NaCl–H_2O and CO_2–H_2O–NaCl, but at that time the data sets and thermodynamic models were limited. Ferry and Baumgartner (1987) summarized the equations of state for geological fluids before 1987, where the equations applicable for the binary include those of Holloway (1977), Kerrick and Jacobs (1981) and Spycher and Reed (1988). Mäder (1991) reviewed a few *PVTx* data sets for the CO_2–H_2O system relevant to mineral equilibria under high temperatures and pressures (Franck and Tödheide, 1959; Greenwood, 1969, 1973; Shmulovich et al., 1979, 1980; Gehrig, 1980; Sterner and Bodnar, 1991). In this study, we review the available experimental *PVTx* properties for both CO_2–H_2O and CO_2–H_2O–NaCl systems below the critical temperature of H_2O, $T_C(H_2O)$.

2. Experimental *PVTx* properties of the CO_2–H_2O system

Published experimental *PVTx* data for the CO_2–H_2O system are summarized in Table 1, and the P–T conditions for these measurements are plotted on Fig. 1.

2.1. The distribution of data in the P–T space and phase fields

Most data fall in the range of $P<35$ MPa (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; Hnedkovsky et al., 1996; Teng et al., 1997; Zhang et al., 2002; Song et al., 2003b; Hebach et al., 2004). These data sets cover a temperature range from 276.15 to 644.78 K. Parkinson and De Nevers (1969) reported partial molar volumes of CO_2 in aqueous solutions, but did not give the corresponding pressures. The data set of

Table 1
The experimental *PVTx* properties of the CO_2–H_2O system

Authors	*T*/K	*P*/MPa	Concentration	N_d
Ohsumi et al. (1992)	276.15	34.754	$x(CO_2)\%=0.1798–0.6294$	5
Song et al. (2003a,b)	273.25–284.15	5.0–12.5	$x(CO_2)\%=0–0.6.1$	33
Teng et al. (1997)	278–293	6.44–29.49	$x(CO_2)\%=2.50–3.49$	24
Parkinson and De Nevers (1969)	278.1–313.7	1.0342–34.4744	$x(CO_2)\%=0.1–2.2$	28
Hebach et al. (2004)	283.80–333.19	1.09–30.66	$x(CO_2)$ = saturated values	201
King et al. (1992)	288.15–298.15	6.08–24.32	$x(CO_2)\%=2.445–3.070$	27
Hnedkovsky et al. (1996)	298.15–633.41	1–35	$x(CO_2)\%=0.279–0.332$	18
Zhang et al. (2002)	308.15	7.752–12.484	$x(CO_2)\%=99.7$	16
Patel et al. (1987)	323.15–498.15	0.1–10	$x(CO_2)=0.5–0.98$	423
Patel and Eubank (1988)	323.15–498.15	0.0855–10.0237	$x(CO_2)=0.02–0.5$	297
Nighswander et al. (1989)	352.85–471.25	2.04–10.21	$x(CO_2)\%=0.22–1.66$	33
Zawisza and Malesińska (1981)	373.15–473.15	0.385–3.35	$y(H_2O)=0.1210–0.9347$	142
Ellis (1959)	387.15–621.15	0.5–16.4	$y(CO_2)\%=3.90–6.27–84.02$	36
Fenghour et al. (1996)	415.36–644.78	5.884–27.964	$x(CO_2)=0.0612–0.7913$	104
Wormald et al. (1986)	473.2–623.2	1–12	$x(CO_2)=0.5$	57
Sterner and Bodnar (1991)	494.15–608.15	48.7–310	$x(CO_2)=0.1234–0.7473$	84
Ellis and Golding (1963)	504.15–643.15	4.791–25.443	**	9
Singh et al. (2000)	573.15	7.44–99.93	$x(CO_2)=0.05–0.9$	58
Seitz and Blencoe (1997)	573.15–623.15	99.93	$x(CO_2)=0.1–0.9$	18
Blencoe et al. (2001b)	573.15	7.44–99.93	$x(CO_2)=0–0.9$	148
Zakirov (1984)	573.15	5–180	$x(CO_2)=0.3–0.77$	55
Zhang and Frantz (1992)	519.95–634.45	*	$x(CO_2)\%=5.5–16.5$	29
Crovetto and Wood (1992)	622.75–642.70	19.64–28.13	$x(CO_2)\%=0.48–0.8745$	72

Note: N_d = number of data points, *x*,*y* = mole fraction, * pressures are not reported, but can be calculated from their empirical formulations, ** concentrations are not directly reported, but can be calculated from the report.

Zhang et al. (2002) is the only one for the dilute solution of H_2O in supercritical CO_2 near the critical point of CO_2. Song et al. (2003b) published graphical representation of their experimental densities and a simple empirical correlation of the ratio of solution and pure water densities. Hebach et al. (2004) gave the densities of aqueous solutions, but did not provide the corresponding composition information for the liquids, so their data should be used with a reliable solubility model. There are a few high-pressure data sets (up to 310 MPa) in the temperature range 494.15–608.15 K (Zakirov, 1984; Sterner and Bodnar, 1991; Seitz and Blencoe, 1997; Singh et al., 2000; Blencoe et al., 2001a).

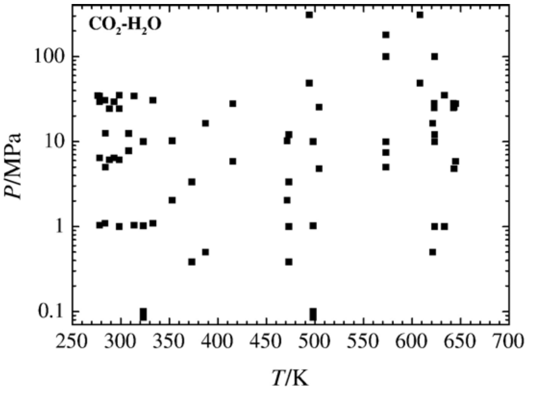

Fig. 1. The distribution of experimental *PVTx* data of the CO_2–H_2O system in *P*–*T* space.

A large portion of the data stated above were reported for a single saturated liquid or vapor phase (Parkinson and De Nevers, 1969; Zawisza and Malesińska, 1981; Nighswander et al., 1989; Sterner and Bodnar, 1991; King et al., 1992; Teng et al., 1997; Hebach et al., 2004). Few data sets are available for two coexistent phases (Ellis, 1959; Ellis and Golding, 1963).

Parkinson and De Nevers (1969) and Nighswander et al. (1989) presented CO_2-saturated liquid density data. Zawisza and Malesińska (1981) measured dew-point densities at 373.15–473.15 K and 0.385–3.35 MPa. Sterner and Bodnar (1991) determined the molar volumes of synthetic fluid inclusions in vapor or liquid state at homogenization conditions (494.15–608.15 K and 47.7–310 MPa). King et al. (1992) measured the densities of both water-rich (L_{H_2O}) and CO_2-rich liquids (L_{CO_2}) in equilibrium, but they did not find a significant difference between L_{CO_2} and pure CO_2 liquid. Hebach et al. (2004) measured the densities of 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 from the very low content of water in it. Their measurements were conducted up to the point of

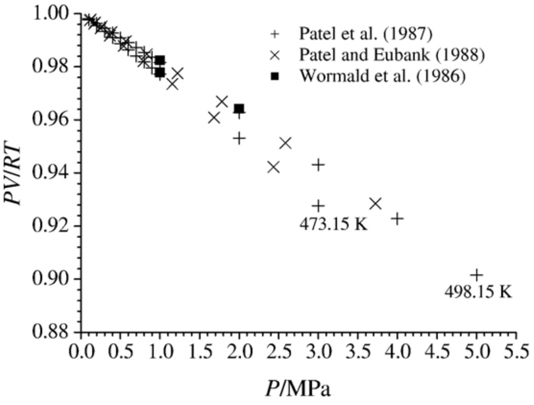

Fig. 2. Consistency between some gas *PVTx* data sets.

hydrate formation, but they did not report the equilibrium compositions. Teng et al. (1997) measured the densities of L_{H_2O} phases in equilibrium with L_{CO2}. In some of their experiments ($T \leq 283$ K), CO_2 clathrate hydrate (H) 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, as pointed out by Diamond and Akinfiev (2003) (p. 272), these measurements did not reach stable equilibrium. According to the phase rule, there are at most two phases co-existing away from the three-phase line, so $H + L_{H_2O} + L_{CO_2}$ cannot stably coexist inside the hydrate region. We believe that the existence of hydrate in the experiments stopped the mass transfer between aqueous solution and liquid CO_2. This is justified by the unusually sharp negative errors in CO_2 solubility found by Diamond and Akinfiev (2003) (p. 272).

There are numerous measurements of the formation conditions of CO_2 hydrate, but almost none of them determined the corresponding densities and compositions. So far, no density data are available for the phase equilibria in the stable presence of hydrate.

2.2. The precisions, consistency, and reliability of data

The *PVTx* data of Seitz and Blencoe (1997), Singh et al. (2000) (a part) and Blencoe et al. (2001a) (a part) below $T_C(H_2O)$ were obtained by the same technique as those of Seitz and Blencoe (1999). Seitz and Blencoe (1997) stated that their data are in excellent agreement with those of Fenghour et al. (1996) at 623.15 and 673.15 K. Additionally, Seitz and Blencoe (1999) have demonstrated that their data agree well with those of Shmulovich et al. (1980), Sterner and Bodnar (1991), and Fenghour et al. (1996). We found that the data of Seitz and Blencoe (1999) also agree well with the molecular dynamics simulation results based on *ab initio* potentials Duan and Zhang (2006), which also agree well with other *PVTx* data at high temperatures and pressures. Considering these points, we believe that the above-mentioned data below $T_C(H_2O)$ (Seitz and Blencoe, 1997; Singh et al., 2000; Blencoe et al., 2001a) are of good quality.

Fenghour et al. (1996) found that their data agree with those of Patel and Eubank (1988) within 1.5%, with an average deviation of about 0.4%. As mentioned just now, their data also agreement well with those of Seitz and Blencoe (1997).

Fig. 2 suggests that the gas phase *PVTx* data of Patel et al. (1987), Patel and Eubank (1988) and Wormald et al. (1986) agree very well with each other. This is remarkable considering the data of Wormald et al. (1986) were obtained from excess enthalpy measurements. On the other hand, if we extrapolate the data of Patel et al. (1987) to pure H_2O, the results will be in good agreement with those of Wagner and Pruss (2002).

Fig. 3 shows that the data of Ohsumi et al. (1992), Hnedkovsky et al. (1996), Song et al. (2003b) and Li et al. (2004) are consistent with each other within an uncertainty of about 0.25%, where the average deviation is less than 0.1%. The water densities derived from the experimental data of Hnedkovsky et al. (1996) agree with those of Wagner and Pruss (2002) within 0.23% in most cases, with an exceptional point caused by calibration error (up to 2.12%) at 523.15 K and 19.99 MPa. The apparent molar volumes of Hnedkovsky et al. (1996) agree reasonably well with those of Crovetto and Wood (1992) if, as pointed out by Hnedkovsky et al. (1996), the sign in Crovetto's pressure correction is corrected. The pure water densities of Li et al. (2004)

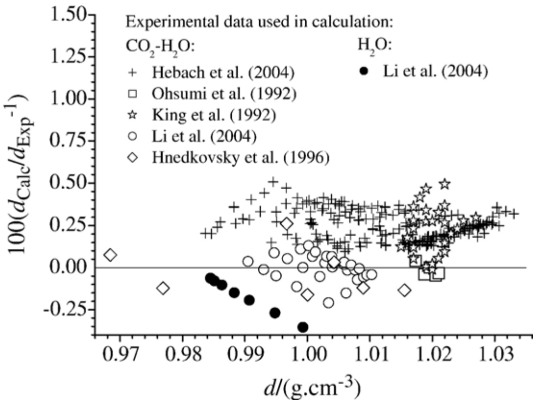

Fig. 3. Comparison of predicted and experimental densities of aqueous solutions of CO_2. The solution densities are calculated with Eq. (1) (an empirical model of Song et al. (2003b) correlated from their own experimental data), and the water density is calculated with Eq. (2).

Table 2
The experimental *PVTx* properties of the CO_2–H_2O–NaCl system

Researchers	*T*/K	*P*/MPa	Concentration	N_d
Song et al. (2005)	276.15–283.15	4–13	wt.(CO_2)%=0–7.7 *Sr*%=3.5%	64^A
Teng and Yamasaki (1998)	278–293	6.44–29.49	*x*(CO_2)%=1.96–3.27 *m*(NaCl)=0.99–4.99	24^B
Song et al. (2003a,b)	303.15–323.15	10–20	wt.(CO_2)%=1–4 Sr=underground brine	99^B
Li et al. (2004)	332.15	0.24–28.93	*c*(CO_2)=0–0.958×10^{-3}mol·cm^{-3} *Sr*%=Weyburn brine	37^C
Nighswander et al. (1989)	353.15–473.65	2.11–10.03	*x*(CO_2)%=0.28–1.54 wt.(NaCl)%=1.0	34
Gehrig et al. (1986)	408–647	3–281.2	*x*(CO_2)%=0.18–84.9 *Sr*%=6.0–20.0	52
Schmidt et al. (1995)	623.15	400	*x*(CO_2)%=5 (relative to H_2O) *Sr*%=40	1
Krüger and Diamond (2001b)	540–T_C(H_2O)	65–350	*x*(CO_2)%=9.69, *x*(NaCl)%=1.74	Not given

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.

have systematic deviations (up to 0.35%) from those of Wagner and Pruss (2002). The liquid densities of Hebach et al. (2004) agree with those of King et al. (1992) within 0.25%, with an average deviation of about 0.1%. Hebach et al. (2004) also reported that their data agree with those of Yaginuma et al. (2000) within 0.25% from 1 to 25 MPa, where the average deviation is less than 0.1%. However, if the data of Hebach et al. (2004) are extrapolated to the saturation pressures of pure water, the resulting densities will demonstrate systematic deviations (up to about 0.1–0.2%) from those of Wagner and Pruss (2002).

Ellis (1959) (p.233) stated that his results are not of high precision, where the vapor densities are unlikely to be more accurate than 5%. The sources of error include at least two factors: (1) the data do not truly represent the binary *PVTx* properties, because the CO_2–H_2O solutions contain both NaCl and $NaHCO_3$; and (2) the suggested approach for the computation of solution volumes is approximate. The derived Henry's Law coefficients (*K*) of Ellis (1959) between 373.15 and 573.15 K are too low to be used for the CO_2 solubility calculation (Ellis and Golding, 1963). In this case, the CO_2 solubility calculation must use the distribution coefficients and vapor compositions. Ellis and Golding (1963) pointed out that their distribution coefficients derived from the liquid analysis are much better than those derived from the *PVT* method. If one wants to obtain more *PVTx* data, it is better to replace the distribution coefficients in their Table 5 with those fitted from their Table 2.

The density data of Parkinson and De Nevers (1969) seem to be questionable. The pressure dependence of volume exhibited in their data at 278.1, 284.25, and 289.8 K are thermodynamically wrong. Their densities at 278.1 and 284.25 K decrease with increasing pressure (and CO_2 concentration) after reaching a maximum, while the densities at 289.8 K remain constant after $P>30$ MPa. These trends are inconsistent with the other experimental results (King et al., 1992; Ohsumi et al., 1992; Hnedkovsky et al., 1996; Song et al., 2003b; Hebach et al., 2004; Li et al., 2004), in which the solution density increases with increasing pressure and CO_2 concentration below 473.15 K. More importantly, the trends run against the rigorous theoretical

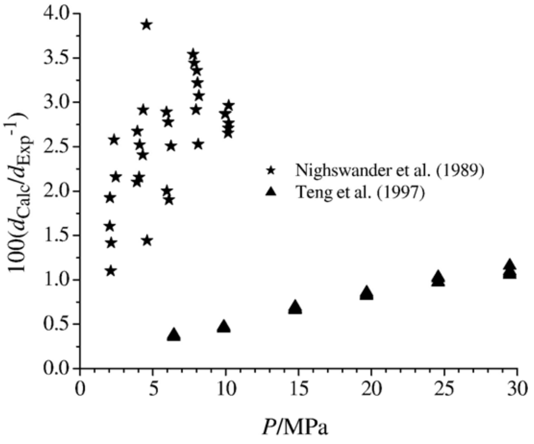

Fig. 4. Comparison of predicted and experimental densities of aqueous solutions saturated with CO_2. The solution densities are calculated with Eq. (1) (an empirical model of Song et al. (2003b) correlated from their own experimental data), where the water densities are calculated with Eq. (2).

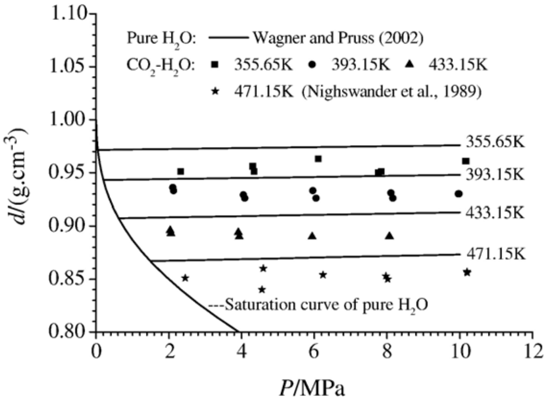

Fig. 5. Densities of saturated CO_2 solutions as a function of pressure at a given temperature. In principle, if the experimental densities at a given temperature are extrapolated to the saturated pressure of pure water at the same temperature, the resulting point should be on the saturation curve, but this is not the case for the data of Nighswander et al. (1989). That is, the experimental densities of Nighswander et al. (1989) have systematic deviations.

requirement of $[\partial V/\partial P]_{T,x}<0$ (which is also a common sense in thermodynamics).

The densities measured by Teng et al. (1997) are significantly lower than those of King et al. (1992) and Hebach et al. (2004) under the same conditions. They are also obviously inconsistent with other groups of low-temperature density data. A comparison of Figs. 3 and 4 indicates that the densities determined by Nighswander et al. (1989) have large uncertainties and large negative deviations. This is evident if we extrapolate every group of isothermal density data to the saturated pressure of pure water (Fig. 5). In addition, the CO_2-saturated densities determined by Nighswander et al. (1989) are almost constant as pressure (and CO_2 concentration) increases (Fig. 5). This is inconsistent with the accepted fact that the dissolution of CO_2 increases the liquid density, as demonstrated by the density measurements of Hnedkovsky et al. (1996) up to 473.35 K. Ji et al. (2005) also have similar findings. Therefore, the density data of Nighswander et al. (1989) and Teng et al. (1997) are unlikely to be of high precision.

Fig. 6 demonstrates that the gas *PVTx* data of Zawisza and Malesińska (1981) are inconsistent with those of Patel et al. (1987), and have larger deviations from predicted results of virial equation than those of Patel et al. (1987).

According to Zhang et al. (2002), their experimental pure CO_2 volumes can be derived from their mixture densities and partial molar volumes of H_2O. The results deviate about −1% from those of Span and Wagner (1996) in the region far from the critical condition of CO_2. The deviations become much larger (about −10%) near the critical conditions of CO_2.

Zakirov (1984) and Blencoe et al. (2001a) determined the excess volumes of CO_2–H_2O at 573.15 K, where the results of Zakirov (1984) are systematically higher than those of Blencoe et al. (2001a) under the same conditions. The deviations decrease with increasing pressure from about 8 $cm^3\ mol^{-1}$ to less than 1 $cm^3\ mol^{-1}$, which cause discrepancies of about 1–2% of the total volumes. As pressure increases, each isobaric excess volume-composition curve of Blencoe et al. (2001a) begins to show a negative minimum on the H_2O-rich side and a positive maximum on the CO_2-rich side. This variation is also followed by the spline fitting of Zakirov (1984) to his own experimental data, but his data at low $x(CO_2)$'s are scant (Fig. 7).

The solvus temperatures of CO_2-rich phases determined by Sterner and Bodnar (1991) are 40 to 90 K higher than those of Takenouchi and Kennedy (1964), where the maximum disagreement occurs at about 150 MPa. For the same samples, Sterner and Bodnar (1991) reported a relatively large uncertainty in the total homogeneous temperatures (T_h), which is about 6 K for total homogenization to liquid, and up to about 25 K for total homogenization to vapor. Blencoe et al. (2001b) reported new vapor-liquid equilibrium data for the binary at 573.15 K, which agree well with those of Takenouchi and Kennedy (1964), and are claimed to be highly accurate. These data can be used to examine the reliability of the solvus data of Sterner and Bodnar (1991). According to these new data and other previous solvus data, we think that the errors in the solvus data of Sterner and Bodnar (1991) are quite large. This is not due to the underestimated T_h's of the fluid inclusions that homogenized to vapor, but rather to the solvus pressures calculated from the equation of

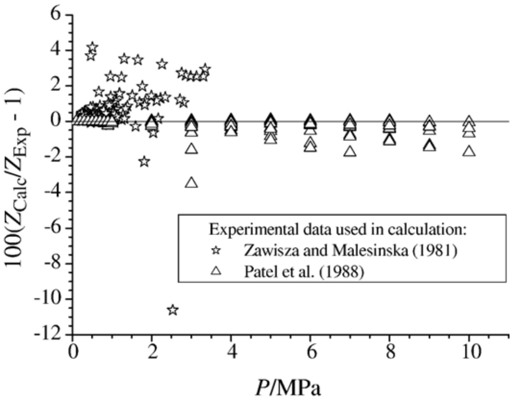

Fig. 6. Deviations of predicted compressibility factors of gaseous CO_2–H_2O mixtures. Compressibility factors are calculated with the cubic virial equation of state of Patel et al. (1987).

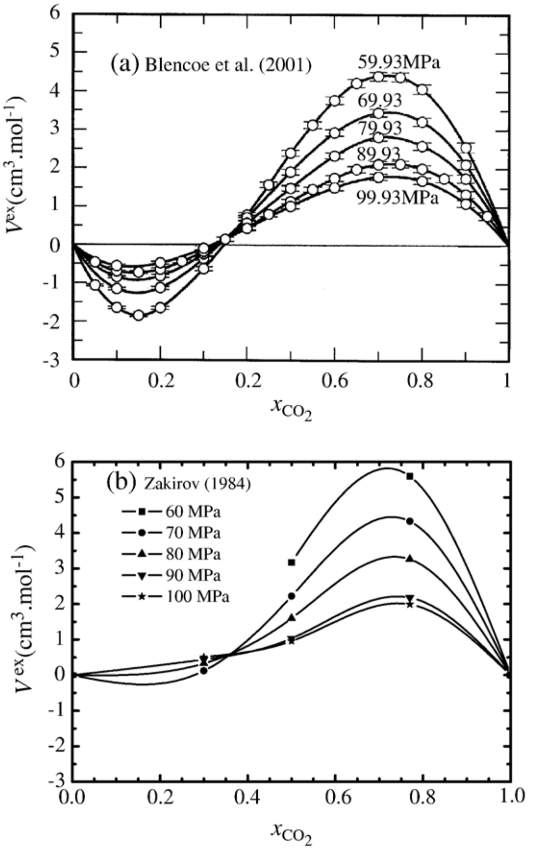

Fig. 7. Excess volumes of CO_2–H_2O mixtures at 573.15 K.

Connolly and Bodnar (1983). The solvus pressures were overestimated up to about 30–70 MPa for the 543.15 K isotherm, and up to about 5–11 MPa for the 573.15 K isotherm (Blencoe et al., 2001b). Therefore, the solvus pressures of Sterner and Bodnar (1991) should be corrected with a reliable equation of state or other approaches.

The P–T curves of the binary vapor-liquid equilibria obtained by Zhang and Frantz (1992) are significantly different (about 20–70 K or 10–50 MPa) from those of Takenouchi and Kennedy (1964). Similar differences also exist between the results of Zhang and Frantz (1992) and those of Tödheide and Franck (1963), Seitz and Blencoe (1997) and Blencoe et al. (2001a,b). The high accuracy of the data of Blencoe and co-workers suggests that the vapor-liquid equilibrium data of Zhang and Frantz (1992) may have systematic deviations.

3. Experimental *PVTx* properties of the CO_2–H_2O–NaCl system

As shown in Table 2, much less experimental *PVTx* data are available for this system than those for the CO_2–H_2O system. The data distribution, and precision, and the agreement among data sets are discussed below.

3.1. Distribution of data in P–T space and phase fields

Several experimental data sets are reported for this system (Gehrig, 1980; Gehrig et al., 1986; Nighswander et al., 1989; Schmidt et al., 1995; Teng and Yamasaki, 1998; Krüger and Diamond, 2001b; Song et al., 2003a; Li et al., 2004; Song et al., 2005). Some high-pressure data were reported by Gehrig (1980), Gehrig et al. (1986), Krüger and Diamond (2001b), and Schmidt et al. (1995), where the data of Gehrig et al. (1986) are revised from those of Gehrig (1980). Schmidt et al. (1995) have only one datum point below $T_C(H_2O)$. The reported salinities of Gehrig (1980), Gehrig et al. (1986), and Schmidt et al. (1995) are up to 20 and 40 wt.% (relative to H_2O), respectively, and the CO_2 contents are up to 84.9 mol.%. The other data sets are limited to low pressure (<30 MPa), low CO_2 content (<10 mol.%) and low salinity (<8 mol.%). Most of these data are in the range 273.15–333.15 K, where the measurements of Nighswander et al. (1989) from 355.15 K to 473.65 K are exceptional. The data distribution is plotted in Fig. 8. Apparently, there are no data for $T<400$ K and $P>30$ MPa.

The *PVTx* data for the homogeneous mixtures include those of Schmidt et al. (1995) and Song et al. (2003a, 2005). Song et al. (2003a) measured the densities of CO_2-bearing underground brine, but they did not mention the corresponding salt contents. Song et al. (2005) reported density diagrams of artificial seawater at 4–13 MPa, 276.15 and 283.15 K.

The data sets on phase equilibria include those of Gehrig (1980), Gehrig et al. (1986), Krüger and Diamond (2001b), Nighswander et al. (1989), Teng and

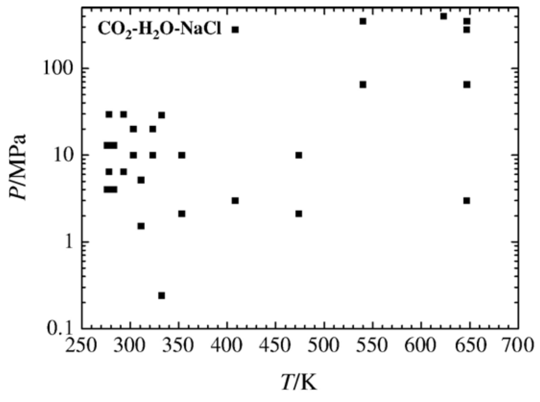

Fig. 8. Distribution of experimental *PVTx* data of the CO_2–H_2O–NaCl system in P–T space.

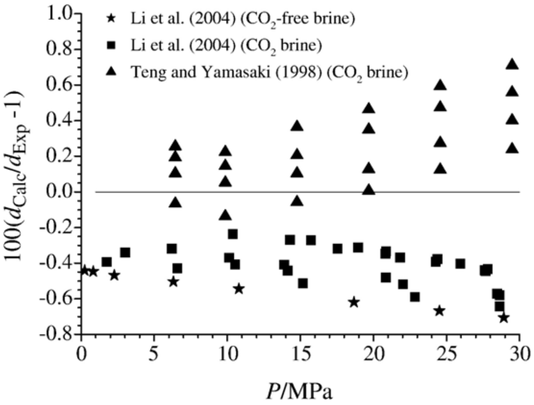

Fig. 9. Deviations of predicted densities of brines containing CO_2. The mixture densities are calculated with the model of Song et al. (2005), whereas the densities of the reference system NaCl–H_2O are calculated with the model of Rogers and Pitzer (1982), and the water densities are calculated with our Eq. (2).

Yamasaki (1998), and Li et al. (2004), all reporting saturated liquid volumes or densities. Gehrig and coworkers reported saturated vapor volumes for $T \leq T_C$ (H_2O) (Gehrig, 1980; Gehrig et al., 1986). It should be noted that at temperatures below 573K the solubility of NaCl in the vapor phase is very low, so it is a good approximation in practice to treat the vapor phase as a CO_2–H_2O mixture.

Gehrig and coworkers presented extensive data on volumes of saturated liquid and vapor phases, covering a range of 408–793 K and 3–281.2 MPa (Gehrig, 1980; Gehrig et al., 1986). Krüger and Diamond (2001b) presented a graphical report of their experimental volumes on the bubble and dew curves and the relevant iso-T_h lines (contours of total homogenization temperatures). According to experimental synthetic fluid inclusion data, Schmidt et al. (1995) constructed a P–T projection of the dew curve of the mixture containing 40 wt.% NaCl (relative to H_2O) and 5 wt.% CO_2. It partially falls within the range of $T \leq T_C(H_2O)$.

Nighswander et al. (1989) and Li et al. (2004) measured the densities of saline water saturated with gaseous CO_2, where the density data of Li et al. (2004) were determined for the Weyburn Formation brine. The experiments of Teng and Yamasaki (1998) were conducted for synthetic seawater in the presence of liquid CO_2 at 278–293 K, where some of their experimental conditions fall within the CO_2 hydrate formation region, for which the influence of hydrate was considered to be negligible. Ohmura and Mori (1999) analyzed the temperature dependence of solubility 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. As concluded by Diamond and Akinfiev (2003) for the data measured by Teng et al. (1997), the corresponding experiments did not reach stable equilibrium states. We believe that the existence of hydrate in the experiments of Teng and Yamasaki (1998) stopped the mass transfer between aqueous solution and liquid CO_2. It is important to point out that no volumetric data are available for the fluids in stable equilibrium with CO_2 hydrate, although there have been numerous measurements of CO_2 hydrate formation conditions for the ternary system.

3.2. Precision, consistency, and reliability of data

Few comments on the precision or consistency can be found for the ternary $PVTx$ data. Song et al. (2003a) noted that the measurements in literature, e.g., Nighswander et al. (1989), Ohsumi et al. (1992), and their previous determinations, have respective shortcomings in their measurement principles and precisions, but they failed to provide further comments.

Like the binary density data discussed earlier, the ternary density data of Nighswander et al. (1989) also have large negative deviations and large uncertainties. Fig. 9 suggests that the density data of Teng and Yamasaki (1998) and Li et al. (2004) are inconsistent with those of Song et al. (2005). It should be noted that the densities of NaCl–H_2O solutions of Li et al. (2004) deviate by about 0.4%–0.7% from the results of Rogers and Pitzer (1982) model. These deviations are greater than the error range of the model. In addition, Wong et al. (2005) found that the salting-out coefficients from

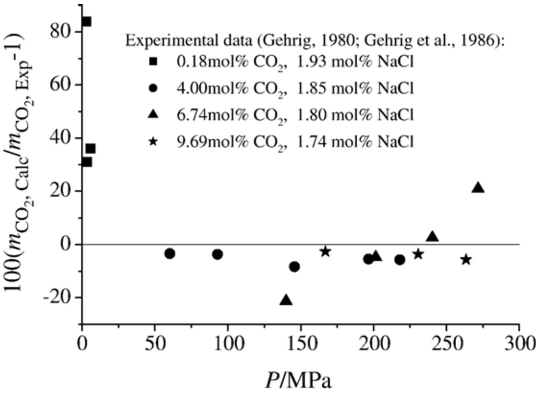

Fig. 10. Comparison of predicted CO_2 solubilities with experimental results. The solubilities (in molality) are calculated with the model of Duan et al. (2006).

the equation suggested by Teng and Yamasaki (1998) have two distinct features: (1) The coefficients decrease with increasing temperature; (2) They become positive close to 273 K. The first feature contradicts the salting-out coefficients of Weiss (1974), which were considered to be well-established (Wong et al., 2005). The second feature contradicts all the experimental data for CO_2 solubility in seawater (Wong et al., 2005).

In order to resolve the inconsistency problem in some *PVTx* data in literature, Krüger and Diamond (2001b) examined the immiscibility boundaries and the relevant iso-T_h lines of two CO_2–H_2O–NaCl mixtures (88.57 mol.% H_2O+9.69 mol.% CO_2+1.74 mol.% NaCl; 77.47 mol.% H_2O+21.01 mol.% CO_2 and 1.52 mol.% NaCl) using the synthetic fluid inclusion technique. Below $T_C(H_2O)$, their bubble curve of the first mixture 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). The bubble-point curve of the first mixture reported by Gehrig (1980) is also supported by the solubility model of Duan and Sun (2003) (Fig. 10). For the second mixture, however, the dew-point curve of Krüger and Diamond (2001b) is different from that of Gehrig (1980). The bubble-point compositions of the second mixture determined by Gehrig (1980) below $T_C(H_2O)$ also have large deviations from the predicted results of solubility model Duan and Sun (2003) (Fig. 10). The largest deviations are notably out of the error range of the model. These results suggest that some of the bubble-point and dew-point curves determined by Gehrig (1980) are unreasonable. As for bubble-point volumes, the results of the first mixture obtained by Gehrig (1980) are notably lower than those of Krüger and Diamond (2001b), where the maximum deviation is up to about 10% around the critical point. Much greater discrepancy is found between the dew-point volumes of the second mixture. In addition, the volumes of CO_2–H_2O obtained by Gehrig (1980) are also notably lower than those of Seitz and Blencoe (1999) (Fig. 11). Similarly, the volumes of NaCl–H_2O of Gehrig (1980) are also lower than the predicted results of Rogers and Pitzer (1982) model, where the differences is obviously out of the possible error range of the model. In summary, the volume data of Gehrig (1980) have large negative deviations.

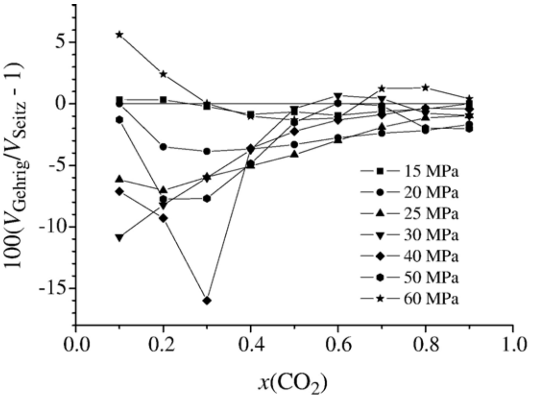

Fig. 11. Difference between the experimental volumes of CO_2–H_2O mixtures at 673.15 K determined by Gehrig (1980) and Seitz and Blencoe (1999). V_{Gehrig} and V_{Seitz} are the volumes determined by Gehrig (1980) and Seitz and Blencoe (1999), respectively.

4. Thermodynamic modeling of the mixture PVTx properties

As reviewed in the last section, the experimental *PVTx* data of the CO_2–H_2O and CO_2–H_2O–NaCl systems only occupy a very limited *P*–*T* range as compared to the vast *P*–*T* range encountered in the Earth's interior. Therefore, the modeling of *PVTx* and phase equilibrium properties of the two systems that allows accurate extrapolation over a wide *P*–*T* range is extremely important. Many thermodynamic models have been developed to predict volumetric properties of the two systems. They can be divided into five types according to the features of volumetric properties: (1) equations of state (EOS); (2) liquid density models; (3) partial molar volume models; (4) apparent molar volume models; and (5) excess volume models. All these models are assessed in this report.

4.1. The CO_2–H_2O system

4.1.1. Equations of state

At low to medium pressures, numerous cubic EOS and virial EOS truncated at the second or third virial coefficient are adequate to predict the *PVTx*, phase equilibria and other thermodynamic properties of fluids (including CO_2–H_2O). Thus, these two types of EOS are widely used in physical chemistry, chemical engineering and geochemistry (Shmulovich et al., 1980; Vanderzee and Haas, 1981; Patel et al., 1987; Wormald and Lloyd, 1994; Plyasunov and Shock, 2003). For the CO_2–H_2O system, there are many correlations of the second and third virial coefficients in literature (Tsonopouplos, 1974; Holste et al., 1987; Hendl et al., 1997; Abdulagatov et al., 2002; Plyasunov and Shock, 2003; Harvey and Lemmon, 2004). However, these equations cannot be directly extended to the high-pressure fluids that are frequently encountered in many natural systems. For example, Wormald and Lloyd (1994) used a cubic EOS for excess enthalpies of CO_2–H_2O gas mixtures up to 913 K and 20 MPa. The predicted enthalpies agree well with experimental results up to 10 MPa, but the deviations from experimental results increase rapidly with pressure. For the CO_2–H_2O system, cubic virial equation can be applied to about 10 MPa (Fig. 6), and the quadratic equation is only valid up to a few MPa. For these reasons, many EOS have been developed for the CO_2–H_2O mixtures in a wider P–T range (Kerrick and Jacobs, 1981; Connolly and Bodnar, 1983; Nitsche et al., 1984; Spycher and Reed, 1988; Duan et al., 1992b; Churakov and Gottschalk, 2003b; Ji et al., 2005).

Nitsche et al. (1984) used a lattice-gas model to represent the behavior of CO_2, H_2O, and their mixtures. This model correctly predicts the qualitative patterns of mixture phase behavior using two mixture parameters fitted to simple temperature functions over a small temperature range. They claimed that quantitative prediction of mixture phase behavior is possible over a not too wide temperature range.

The virial equation of Spycher and Reed (1988) is truncated at the third virial coefficient, with P and T as variables. It was claimed to be valid from 323.15 to 623.15 K, and from 0 to 50 MPa. However, this equation underestimates the volumes of gaseous mixtures. The deviations of predicted volumes from experimental results (Wormald et al., 1986; Patel et al., 1987; Fenghour et al., 1996) increase with increasing pressure, where the average deviation is about 4%, and the maximum deviation is nearly 10%.

The equation of Duan et al. (1992b) can calculate both phase equilibria and volumetric properties of the CO_2–H_2O system with accuracies close to those of experiments at 323–1273 K and 0–100 MPa (or 300 MPa with less accuracy). For the end-members, it is valid at 273–1273 K and 0–800 MPa (or slightly above), but it cannot accurately predict the phase equilibria of end-members near the triple points. For the binary, the equation cannot correctly reproduce near-critical $PVTx$ properties and phase behavior (Seitz and Blencoe, 1999; Bakker and Diamond, 2000; Blencoe, 2004). Because of the high overall accuracy, the equations of Duan et al. (1992a,b) were incorporated into a software package HCO-TERNARY written by Nieva and Barragán (2003). However, the accuracy of this equation cannot be better than 0.25% in volume, so it is still inadequate for the modeling of CO_2 sequestration.

Churakov and Gottschalk (2003a,b) proposed a perturbation theory-based EOS for both polar and non-polar molecular fluids and their mixtures. The CO_2–H_2O phase boundaries predicted with this equation deviate significantly from experimental results (Tödheide and Franck, 1963; Takenouchi and Kennedy, 1964), especially near and in the critical regions. Generally, the equation can reasonably reproduce experimental excess volumes (Gehrig, 1980; Shmulovich et al., 1980; Sterner and Bodnar, 1991; Frost and Wood, 1997; Seitz and Blencoe, 1999), where the maximum deviations range from less than 2 $cm^3 \cdot mol^{-1}$ to more than 10 $cm^3 \cdot mol^{-1}$. Churakov and Gottschalk (2003a,b) did not report the performance of the EOS in binary $PVTx$ prediction below $T_C(H_2O)$, which should not be better than the performance above $T_C(H_2O)$ because of the greater difficulty in $PVTx$ modeling below $T_C(H_2O)$. Considering the deviations in excess volume from experimental data, we believe that the error of this equation should be more than 0.5%, so it is not applicable for CO_2 sequestration.

Ji et al. (2005) used a semi-empirical statistical mechanics model (SAFT1-RPM) to model the densities and phase equilibria of the CO_2–H_2O system in the range 285–473 K, 0–60 MPa and the CO_2–H_2O–NaCl system in the range 298–373 K and 0–20 MPa. The model can reasonably reproduce both vapor and liquid density data of the binary (Patel and Eubank, 1988; King et al., 1992; Hebach et al., 2004; Li et al., 2004), where the average deviations of predicted liquid densities are about 0.35%. This model can also predict the solubilities of CO_2 in water and aqueous NaCl solutions, but its accuracy is generally inferior to the model of Duan et al. (2006). Because of the lack of reliable ternary density data, the accuracy of the model in ternary density prediction remains to be examined, even though it is not expected to be better than that of the binary.

4.1.2. Liquid density models

Some density models of aqueous CO_2 solutions can be regarded as another type of EOS of CO_2–H_2O (Teng et al., 1997; Garcia, 2001; Bachu and Adams, 2003; Song et al., 2003b). Teng et al. (1997) presented an approximate density difference model to correlate the densities of aqueous CO_2 solutions at low temperatures and low to medium pressures, where the parameters were taken as P–T independent. This kind of model is only valid in a small P–T range. The density model of Garcia (2001) was based on an approximate apparent molar volume expression regressed from experimental data in the range 278.15–573.15 K. It neglects the effects of pressure and CO_2 concentration on apparent molar volume. At low temperatures, the apparent molar volumes predicted with this model are inconsistent with other data (Ohsumi et al., 1992; Song et al., 2003b) due to the use of inaccurate density data of Teng et al. (1997) in the parameter regression. The CO_2–H_2O density model of Bachu and Adams (2003) consists of the water density model of Batzle and Wang (1992) and the apparent molar volume expression of Garcia (2001), where the water model deviates from the well-established results of Wagner and Pruss (2002) up to 0.2% below 373.15 K, and increases rapidly with increasing temperature and decreasing pressure. Song et al. (2003b) proposed a density model for the dilute solution of CO_2:

$$\rho_{aq} = \rho_w[1 + 0.275wt(CO_2)] \quad (1)$$

where ρ_{aq}, ρ_w and $wt(CO_2)$ are solution density, water density and mass fraction of CO_2, respectively. However, they did not give the corresponding ρ_w expression. In order to facilitate its application, we develop a formula for the molar volumes of liquid water:

$$\begin{aligned} &V_w = k_0 + k_1P + k_2P^2 + k_3P^3 \\ &k_i = k_{i1}T^3 + k_{i2}T^2 + k_{i3}T + k_{i4} + k_{i5}T^{-1} \quad (i = 0, 1) \\ &k_j = k_{j1}T^3 + k_{j2}T^2 + k_{j3} \quad (j = 2, 3) \end{aligned} \quad (2)$$

where the units of V_W, T and P are $cm^3 \cdot mol^{-1}$, K and bar, respectively, and the constants are given in Table 3. Eq. (2) reproduces the water volumes of Wagner and Pruss (2002) with an average deviation of 0.005% and a maximum deviation of 0.027% in the range 273.15–473.15 K and 0–200 MPa (Fig. 12).

4.1.3. Partial molar volume models

Current thermodynamic description of the aqueous non-electrolyte solutions is 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 et al., 1989; Shock and Helgeson, 1990; Shock et al., 1992) is designed to predict the thermodynamic properties of aqueous ions over a wide P–T range (273–1273 K and 0.1–500 MPa) (Akinfiev and Diamond, 2003). However, some deficiencies are found when it is extended to aqueous non-electrolytes. For example, it does not correctly predict the behavior of 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). Akinfiev and Zotov (1999) demonstrated that the HKF model cannot correctly predict the activity coefficients of aqueous CO_2 at infinite dilution below 573 K. This indicates that the corresponding excess partial volumes are also inaccurate. The infinite dilution partial molar volumes of CO_2 ($\overline{V}^{\infty}_{CO_2}$) predicted with the HKF model (Shock et al., 1989) have large deviations from the experimental results of dilute solutions of CO_2 (Crovetto and Wood, 1992; Hnedkovsky et al., 1996). Thus, we need to develop equations for the partial molar volumes of aqueous non-electrolytes.

Table 3
Constants in Eq. (2)

k_{01}	3.27225E−07	k_{14}	3.59860E−02
k_{02}	−4.20950E−04	k_{15}	−3.55071E+00
k_{03}	2.32594E−01	k_{21}	2.57241E−14
k_{04}	−4.16920E+01	k_{22}	−1.24336E−11
k_{05}	5.71292E+03	k_{23}	5.42707E−07
k_{11}	−2.32306E−10	k_{31}	−4.42028E−18
k_{12}	2.91138E−07	k_{32}	2.10007E−15
k_{13}	−1.49662E−04	k_{33}	−8.11491E−11

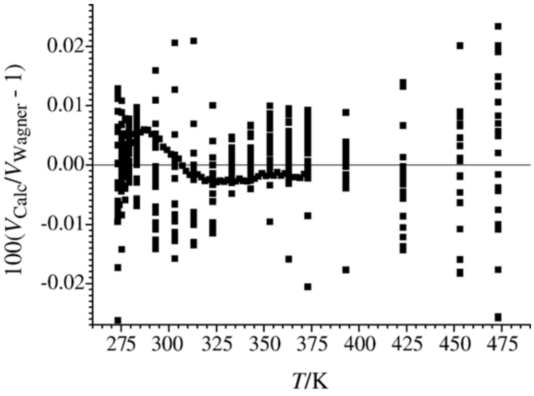

Fig. 12. Deviations of water volumes predicted with Eq. (2). V_{Wagner} is the molar volume predicted with the model of Wagner and Pruss (2002).

Akinfiev and Diamond (2003, 2004) proposed a three-parameter equation for the volumetric properties of aqueous non-electrolytes at infinite dilution, where the predicted ($\overline{V}^{\infty}_{CO_2}$)'s of CO_2 are in reasonable agreement with experimental results. Plyasunov et al. (2000a,b) and Sedlbauer et al. (2000) briefly reviewed the progress in the modeling of volumetric properties of aqueous non-electrolyte solutions, where one of the most important advances is the approach based on the fluctuation solution theory (Kirkwood and Buff, 1951; O'Connell, 1971; O'Connell, 1981; O'Connell, 1995; O'Connell et al., 1996; Harvey, 1998; Sedlbauer et al., 2000; Plyasunov et al., 2000a,b, 2006), which can be used to develop accurate $\overline{V}^{\infty}_{CO_2}$ models over a wide P–T range, including near-critical and supercritical regions (Harvey, 1998; Plyasunov et al., 2000b). However, if these $\overline{V}^{\infty}_{CO_2}$ models are used to predict the densities or total volumes of CO_2 solutions, they should be confined to the dilute solutions of CO_2, because the dependence of volume on composition is highly non-linear.

4.1.4. Apparent molar volume models

In principle, apparent molar volume (V_ϕ) models of aqueous CO_2 can be directly used to predict the total volumes (V_{aq}) or densities of CO_2–H_2O solutions:

$$V_{aq} = x_{H_2O} V_{H_2O} + x_{CO_2} V_{\phi,CO_2}$$
$$\rho_{aq} = (x_{H_2O} M_{H_2O} + x_{CO_2} M_{CO_2}) / (x_{H_2O} V_{H_2O} + x_{CO_2} V_{\phi,CO_2}) \qquad (3)$$

where M is relative molecular weight, x is mole fraction, and V is molar volume. If these V_ϕ models are combined with appropriate NaCl–H_2O volume (or density) models and ternary excess volume models, the total volumes (or densities) of CO_2–H_2O–NaCl solutions can also be predicted.

Presently, there are some empirical or semi-theoretical models for V_{ϕ,CO_2} (Crovetto et al., 1990; Andersen et al., 1992; Enick and Klara, 1992; Iglesias and Moya, 1992; Garcia, 2001). Except for the model of Crovetto et al. (1990), these models neglected the effects of pressure and composition on apparent molar volumes, so they cannot accurately reproduce experimental results (Fig. 13). The model of Crovetto et al. (1990) was proposed to correlate V_{ϕ,CO_2} in near-critical region of H_2O. Therefore, they employed the current near-critical theories of dilute solution that are believed to be successful in the treatment of critical singularity. This method is also applicable below $T_C(H_2O)$, but no analytical expression was given for its parameters, except for single parameter values under given P–T conditions.

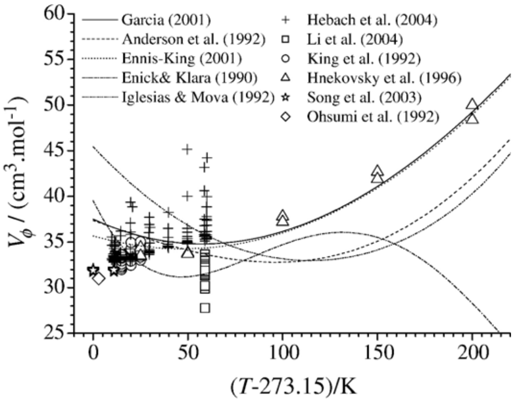

Fig. 13. Predicted apparent molar volumes of CO_2 in water compared with experimental results. The apparent molar volume model of Ennis-King (2001) was given by Garcia (2001) through his personal communication with Jonathan Ennis-King. The apparent molar volumes of Hnedkovsky et al. (1996) are directly given by the original authors. The other apparent molar volumes are calculated with experimental densities, where the water densities are calculated with Eq. (2). The CO_2 solubilities corresponding to the saturated density data of Li et al. (2004) and Hebach et al. (2004) are calculated with the model of Duan et al. (2006).

4.1.5. Excess volume models

Some excess volume models have been proposed for the CO_2–H_2O system, but most of them are developed for elevated pressures and temperatures (Shmulovich et al., 1980; Sterner and Bodnar, 1991; Destrigneville et al., 1996; Blencoe et al., 1999). Few models are developed for excess volumes of the binary below $T_C(H_2O)$.

In addition to the direct prediction of excess volumes, there are also many other ways for the *indirect* derivation of volumes. For example, excess volumes can be derived from equations of excess enthalpy, or excess free energy. These approaches have been used for the CO_2–H_2O system, such as the two-fluid free energy model (Gallagher et al., 1993; Wormald et al., 1997) and the excess enthalpy models (Wormald et al., 1983; Smith and Wormald, 1984; Bottini and Saville, 1985; Wormald et al., 1986). In fact, only a small part of the numerous excess function models in physical chemistry and chemical engineering have been introduced into the thermodynamic modeling of geological fluids, and most of them are old, such as Margules-type, Van Laar-type, Wilson-type (Wilson, 1964) and Non-Random Two-Liquid (Renon and Prausnitz, 1968) models. Better excess function models for geological fluids can be developed, if we use more advanced thermodynamic theories. Many theoretical or semi-empirical local composition and coordination number models can serve as a good base, such as those of Aranovich and Donohue (1996), Aranovich et al. (1997), Cao and Wang (2000), Guo et al. (1990), and Hu and Duan (2005).

4.2. The CO_2–H_2O–NaCl system

A few models on the *PVTx* and phase equilibria have been proposed for this system. Some of them are developed for temperatures above 573 K or 623 K (Bowers and Helgeson, 1983, 1985; Brown and Lamb, 1989; Duan et al., 1995), and are usually inadequate below $T_C(H_2O)$. The other models are developed to meet the needs of enhanced oil and gas recovery and CO_2 sequestration at low to medium P–T conditions (Teng and Yamasaki, 1998; Bachu and Adams, 2003; Bando et al., 2004; Ji et al., 2005; Song et al., 2005), and most of them are simple approximate density models. For example, Teng and Yamasaki (1998) and Song et al. (2005) used a density difference expression to correlate the densities of CO_2-bearing seawater. Bando et al. (2004) used the density difference expression of Teng et al. (1997) for CO_2–H_2O solutions and the density model of Pitzer et al. (1984) for NaCl–H_2O solutions to predict the densities of CO_2–NaCl–H_2O solutions. The three density difference expressions are all regressed from densities of dilute CO_2 solutions, and ignore the effects of pressure and temperature.

Different from these approaches, Bachu and Adams (2003) proposed an approximate model to predict the CO_2-bearing brine densities, where the apparent molar volumes of CO_2 in water is calculated from the approximate expression of Garcia (2001), the densities of water and NaCl solutions are calculated with the empirical models of Batzle and Wang (1992). We found that the NaCl solution densities predicted from the model of Batzle and Wang (1992) are systematically (0.45% on average) lower than those from the model of Rogers and Pitzer (1982). Because of the use of multiple approximations, the densities predicted with this model have significant negative deviations (−0.87% on average) from those predicted with the model of Song et al. (2005), where the latter model can accurately reproduce the experimental results of Song et al. (2005).

5. Conclusions

5.1. Experimental PVTx data for CO_2–H_2O and CO_2–H_2O–NaCl fluids

For CO_2–H_2O mixtures, the experimental *PVTx* data range from 276.15 to 644.78 K, and from 0.0855 to 310 MPa. New data are needed to fill the experimentally blank region of $T<493$ K and $P>35$ MPa. Below T_C (H_2O), a considerable portion of the binary volumetric data are measured for single saturated phases (liquid or vapor), and most of them are for saturated liquids. There is a shortage of saturated vapor volumes and the CO_2-rich liquid volumes at low temperatures. In the region close to $T_C(H_2O)$ and $P_C(H_2O)$, accurate or reliable *PVTx* data are scarce, especially for the compositions with high CO_2 contents.

About one-third of the reported data sets (Ellis, 1959; Ellis and Golding, 1963; Zawisza and Malesińska, 1981; Nighswander et al., 1989; Sterner and Bodnar, 1991; Zhang and Frantz, 1992; Teng et al., 1997; Zhang et al., 2002) have large systematic errors or uncertainties, or are significantly inconsistent with other data sets. Inconsistencies between these data and the others below $T_C(H_2O)$ can be very large, especially those between the *PVTx* data along phase boundaries. If we exclude the questionable data sets, the differences between the vapor volume data below $T_C(H_2O)$ are generally within 2%, and the liquid density data are within 0.5% for most cases. The phase boundary data usually have larger deviations. The discrepancies between data sets increase considerably with increasing temperature and pressure, indicating increasing uncertainties in *PVTx* measurements at higher temperatures and pressures.

For the CO_2–H_2O–NaCl system, the experimental *PVTx* data cover a temperature range from 276.15 to 647 K and a pressure range from 0.24 to 400 MPa. No *PVTx* data are available for $T<400$ K and $P>30$ MPa. Almost no accurate density measurements are made for the phase equilibria with CO_2 hydrate, although there are numerous studies of CO_2–H_2O–NaCl fluid inclusions at low temperatures.

Several *PVTx* data sets for CO_2–H_2O–NaCl or CO_2-bearing brines also have some quality or consistency problems. Some of the immiscibility boundaries determined by Gehrig coworkers (Gehrig, 1980; Gehrig et al., 1986) seem to have large deviations from other measurements or model predictions. The volumetric data of Gehrig (1980), Nighswander et al. (1989), Teng and Yamasaki (1998), and probably the CO_2 brine densities of Li et al. (2004) as well, are believed to have systematic deviations. Therefore, we still lack the sufficient and accurate volumetric data for the ternary to adequately model CO_2 sequestration.

5.2. Thermodynamic modeling of CO_2–H_2O and CO_2–H_2O–NaCl fluids

(i) Most models are developed for homogeneous fluids; very few are for phase equilibria. As mentioned in the introduction, an accuracy better than 0.1% is necessary for a density model in CO_2 sequestration modeling. However, none of the existing models is sufficient for this purpose, although there are a few models capable of predicting the liquid densities with accuracies close to those of experiments, such as the models of Duan et al. (1992b), Ji et al. (2005), Song et al. (2003b), O'Connell et al. (1996), Sedlbauer et al. (2000), and Plyasunov et al. (2000a,b).

Currently, establishing an accurate binary density model over a wide *PTx* range should be possible if the model is well constructed and its parameters are constrained with the best data sets in existence, such as those of Ohsumi et al. (1992), Song et al. (2005), Crovetto and Wood (1992), Hnedkovsky et al. (1996), Seitz and Blencoe (1997), Singh et al. (2000), Blencoe et al. (2001a), Li et al. (2004), and Hebach et al. (2004) (if the systematic deviations are corrected). As for the ternary, it is possible to develop a predictive density model using the existing ternary data plus the associated subsystem data if the model is based on a sound theory.

(ii) The existing equations of state are still inadequate for the *PVTx* prediction in and near critical regions. This failure results from the nonclassical (singular) behavior of fluids near their critical points, such as the diversity of $[\partial V/\partial P]_{T,x}$. This problem cannot be rigorously solved in the framework of the classical (analytical) EOS based on mean field theory, such as the numerous cubic, virial, SAFT and perturbation theory EOS, etc. A strict solution to this problem requires a nonclassical EOS, which must contain a non-analytical term to account for the singularity in the near-critical region. Now, many approaches have been developed for the accurate representation of near-critical behavior of fluids (Wilson, 1971; Chang and Doiron, 1983a; Wilson, 1983; Woolley, 1983; Sengers and Levelt Sengers, 1984; Anisimov et al., 1985; Albright et al., 1986; Sengers, 1986; Rainwater, 1989; White and Zhang, 1993; Anisimov et al., 1995; Kiselev, 1997; Edison et al., 1998; Lue and Prausnitz, 1998; Tang, 1998; Kiselev and Ely, 1999; Kiselev and Friend, 1999; White, 2000; van't Hof et al., 2001; Hu et al., 2003a,b; Kiselev and Ely, 2004). Almost all these approaches are based on the so-called renormalization group theory and crossover functions, which involve complicated knowledge of mathematics. Different from these approaches, the fluctuation solution theory is a very useful tool for us to solve the near-critical singularity problem. However, this theory is only valid for dilute solutions. Now, it is still an unsolved problem how to develop an equation that has a close form but can accurately describe both classical and nonclassical behaviors of fluids.

(iii) For the ternary system, only a few simple density models were proposed to correlate experimental data at low temperatures below 333.15 K, with accuracy close to that of experiments. At higher temperatures, there is no accurate model for the *PVTx* properties. Because of the great differences in compositions and physicochemical properties, accurate *PVTx* prediction of coexistent phases with a single model is very difficult. For the liquid *PVTx* modeling, the difficulty comes from the hydrogen bond, hydration, reaction, ionization and association phenomena of NaCl, CO_2, and H_2O. In this situation, a hybrid model may be an effective option. For example, one can use an equation of state for the gaseous phase, and an activity coefficient model for liquid phases, or use independent parameters for each of the coexistent phases. Using excess volume or apparent molar volume models is also a good option, because this approach has no constraint on the relevant subsystem models.

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References

Abdulagatov, A.I., Kaplun, A.B., Meshalkin, A.B., Abdulagatov, I.M., Stepanov, G.V., 2002. Second caloric virial coefficients for real gases and combined spherical symmetric potential for simple molecular interactions. J. Chem. Thermodyn. 34 (12), 2049–2072.

Akinfiev, N.N., Diamond, L.W., 2003. Thermodynamic description of aqueous nonelectrolytes at infinite dilution over a wide range of state parameters. Geochim. Cosmochim. Acta 67 (4), 613–629.

Akinfiev, N.N., Diamond, L.W., 2004. A three-parameter EOS to describe aqueous non-electrolytes at infinite dilution over a wide range of state parameters, with preliminary application to 1:1 electrolytes. Fluid Phase Equilib. 222–223, 31–37.

Akinfiev, N., Zotov, A., 1999. Thermodynamic description of equilibria in mixed fluids (H_2O-non-polar gas) over a wide range of temperature (25–700 °C) and pressure (1–5000 bars). Geochim. Cosmochim. Acta 63 (13–14), 2025–2041.

Albright, P.C., Sengers, J.V., Nicoll, J.F., Ley-Koo, M., 1986. A crossover description of thermodynamic properties of fluids in the critical region. Int. J. Thermophys. 7 (1), 75–85.

Anderko, A., Pitzer, K.S., 1993. Equation-of-state representation of phase equilibria and volumetric properties of the system NaCl–H_2O above 573 K. Geochim. Cosmochim. Acta 57 (8), 1657–1680.

Andersen, G., Probst, A., Murray, L., Butler, S., 1992. An accurate PVT model for geothermal fluids as represented by CO_2–H_2O–NaCl mixtures. The Seventeenth Workshop on Geothermal Reservoir Engineering. Stanford University, Stanford, California, pp. 239–248.

Anisimov, M.A., Kiselev, S.B., Kostukova, I.G., 1985. A scaled equation of state for real fluids in the critical region. Int. J. Thermophys. 6 (5), 465–481.

Anisimov, M.A., Gorodetskii, E.E., Kulikov, V.D., Povodyrev, A.A., Sengers, J.V., 1995. A general isomorphism approach to thermodynamic and transport properties of binary fluid mixtures near critical points. Physica A 220, 277–324.

Aranovich, G.L., Donohue, M.D., 1996. A new model for lattice systems. J. Chem. Phys. 105 (16), 7059–7063.

Aranovich, G.L., Hocker, T., Wu, D.W., Donohue, M.D., 1997. Nonrandom behavior in multicomponent lattice mixtures: effects of solute size and shape. J. Chem. Phys. 106 (24), 10282–10291.

Archer, D.G., 1992. Thermodynamic properties of the NaCl+H_2O System. II. Thermodynamic properties of NaCl(aq), $NaCl\cdot 2H_2O$ (cr), and phase equilibria. J. Phys. Chem. Ref. Data 21 (4), 793–829.

Bachu, S., Adams, J.J., 2003. Sequestration of CO_2 in geological media in response to climate change: capacity of deep saline aquifers to sequester CO_2 in solution. Energy Convers. Manag. 44 (20), 3151–3175.

Baines, S.J., Worden, R.H., 2004. Geological storage of carbon dioxide. GSL Special Publications. The Geology Society of London, vol. 233, 264 pp.

Bakker, R.J., Diamond, L.W., 2000. Determination of the composition and molar volume of H_2O–CO_2 fluid inclusions by microthermometry. Geochim. Cosmochim. Acta 64 (10), 1753–1764.

Bando, S., Takemura, F., Nishio, M., Hihara, E., Akai, M., 2004. Viscosity of aqueous NaCl solutions with dissolved CO_2 at (30 to 60) °C and (10 to 20) MPa. J. Chem. Eng. Data 49, 1328–1332.

Batzle, M., Wang, Z., 1992. Seismic properties of pore fluids. Geophysics 57 (11), 1396–1408.

Bischoff, J.L., 1991. Densities of liquids and vapors in boiling NaCl–H_2O solutions: a *PTVx* summary from 300° to 500 °C. Am. J. Sci. 291, 309–338.

Bischoff, J.L., Pitzer, K.S., 1989. Liquid-vapor relations for the system NaCl–H_2O: summary of the P–T–x surface from 300°to 500 °C. Am. J. Sci. 289, 217–248.

Bischoff, J.L., Rosenbauer, R.J., Pitzer, K.S., 1986. The system NaCl–H_2O: relations of vapor-liquid near the critical temperature of water and of vapor-liquid-halite from 300 °C to 500 °C. Geochim. Cosmochim. Acta 50 (7), 1437–1444.

Blencoe, J.G., 2004. The CO_2–H_2O system: IV. Empirical, isothermal equations for representing vapor-liquid equilibria at 110–350 °C, $P \leq 150$ MPa. Am. Mineral. 89, 1447–1455.

Blencoe, J.G., Seitz, J.C., Anovitz, L.M., 1999. The CO_2–H_2O system. II. Calculated thermodynamic mixing properties for 400 °C, 0–400 MPa. Geochim. Cosmochim. Acta 63 (16), 2393–2408.

Blencoe, J.G., Cole, D.R., Horita, J., Moline, G.R., 2001a. Experimental geochemical studies relevant to carbon sequestration. The First National Conference on Carbon Sequestration. U.S. National Energy Technology Laboratory, Washington, DC, p. 14.

Blencoe, J.G., Naney, M.T., Anovitz, L.M., 2001b. The CO_2–H_2O system: III. A new experimental method for determining liquid-vapor equilibria at high subcritical temperatures. Am. Mineral. 86, 1100–1111.

Bottini, S.B., Saville, G., 1985. Excess enthalpies for (water+nitrogen) (g) and (water+carbon dioxide) (g) at 520 to 620 K and up to 4.5 MPa. J. Chem. Thermodyn. 17 (1), 83–97.

Bowers, T.S., Helgeson, H.C., 1983. Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O–CO_2–NaCl on phase relations in geologic systems: equation of state for H_2O–CO_2–NaCl fluids at high pressures and temperatures. Geochim. Cosmochim. Acta 47, 1247–1275.

Bowers, T.S., Helgeson, H.C., 1985. FORTRAN programs for generating fluid inclusion isochores and fugacity coefficients for the system H_2O–CO_2–NaCl at high pressures and temperatures. Comput. Geosci. 11 (2), 203–213.

Brown, P.E., Lamb, W.M., 1989. P–V–T properties of fluids in the system $H_2O \pm CO_2 \pm$NaCl: new graphical presentations and implications for fluid inclusion studies. Geochim. Cosmochim. Acta 53 (6), 1209–1221.

Cao, D., Wang, W., 2000. Coordination number models and equations of state for square-well pure and mixture fluids, part I: coordination number models and Monte Carlo simulation at high density. Chem. Eng. Sci. 55 (11), 2099–2109.

Carroll, J.J., Slupsky, J.D., Mather, A.E., 1991. The solubility of carbon dioxide in water at low pressure. J. Phys. Chem. Ref. Data 20, 1201–1209.

Chang, R.F., Doiron, T., 1983a. Leung-Griffiths model for the thermodynamic properties of mixtures of CO_2 and C_2H_6 near the gas–liquid critical line. Int. J. Thermophys. 4 (4), 337–352.

Churakov, S.V., Gottschalk, M., 2003b. Perturbation theory based equation of state for polar molecular fluids: II. Fluid mixtures. Geochim. Cosmochim. Acta 67 (13), 2415–2425.

Connolly, J.A.D., Bodnar, R.J., 1983. A modified Redlich–Kwong equation of state for H_2O–CO_2 mixtures: application to fluid inclusion studies (abstract). Trans. Am. Geophys. Union (EOS) 64, 350.

Crovetto, R., 1991. Evaluation of solubility data of the system CO_2–H_2O from 273 K to the critical point of water. J. Phys. Chem. Ref. Data 20 (3), 575–589.

Crovetto, R., Wood, R.H., 1992. Solubility of CO_2 in water and density of aqueous CO_2 near the solvent critical temperature. Fluid Phase Equilib. 74, 271–288.

Crovetto, R., Wood, R.H., Majer, V., 1990. Densities of $\{xCO_2+(1-x)H_2O\}$ with $x<0.014$ at supercritical conditions. Molar volumes, partial molar volumes of CO_2 at infinite dilution, and excess molar volumes. Int. J. Thermophys. 22 (3), 231–243.

Destrigneville, C.M., Brodholt, J.P., Wood, B.J., 1996. Monte Carlo simulation of H_2O–CO_2 mixtures to 1073.15 K and 30 kbar. Chem. Geol. 133 (1–4), 53–65.

Diamond, L.W., Akinfiev, N.N., 2003. Solubility of CO_2 in water from −1.5 to 100 °C and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modeling. Fluid Phase Equilib. 208 (1–2), 265–290.

Duan, Z., Sun, R., 2003. An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem. Geol. 193, 253–271.

Duan, Z., Zhang, Z., 2006. Equation of state of the H_2O, CO_2, and H_2O–CO_2 systems up to 10 GPa and 2573.15 K: molecular dynamics simulations with ab initio potentials. Geochim. Cosmochim. Acta 70 (9), 2311–2324.

Duan, Z., MΦller, N., Weare, J.H., 1992a. An equation of state for CH_4–CO_2–H_2O: I. Pure systems from 0 to 1000 °C and 0 to 8000 bar. Geochim. Cosmochim. Acta 56, 2605–2617.

Duan, Z., MΦller, N., Weare, J.H., 1992b. An equation of state for CH_4–CO_2–H_2O: II. Mixtures from 0 to 1000 °C and 0 to 1000 bar. Geochim. Cosmochim. Acta 56, 2619–2631.

Duan, Z., MΦller, N., Weare, J.H., 1995. Equation of state for the NaCl–H_2O–CO_2 system: prediction of phase equilibria and volumetric properties. Geochim. Cosmochim. Acta 56, 2869–2882.

Duan, Z., MΦller, N., Weare, J.H., 2003. Equations of state for the NaCl–H_2O–CH_4 system and the NaCl–H_2O–CO_2–CH_4 system: phase equilibria and volumetric properties above 573 K. Geochim. Cosmochim. Acta 67, 671–680.

Duan, Z., Sun, R., Zhu, C., Chou, I.-M., 2006. An improved model for the calculation of CO_2 solubility in aqueous solutions containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}. Mar. Chem. 98, 131–139.

Edison, T.A., Anisimov, M.A., Sengers, J.V., 1998. Critical scaling laws and an excess Gibbs energy model. Fluid Phase Equilib. 150–151, 429–438.

Ellis, A.J., 1959. The solubility of carbon dioxide in water at high temperatures. Am. J. Sci. 257 (3), 217–234.

Ellis, A.J., Golding, R.M., 1963. The solubility of carbon dioxide above 100 °C in water and in sodium chloride solutions. Am. J. Sci. 261, 47–60.

Enick, R.M., Klara, S.M., 1992. CO_2 solubility in water and brine under reservoir conditions. Chem. Eng. Commun. 90, 23–33.

Fenghour, A., Wakeham, W.A., Watson, J.T.R., 1996. Densities of (water+carbon dioxide) in the temperature range 415 K to 700 K and pressures up to 35 MPa. J. Chem. Thermodyn. 28 (4), 433–446.

Ferry, J.M., Baumgartner, L., 1987. Thermodynamic models of molecular fluids at the elevated pressures and temperatures of crustal metamorphism. Rev. Miner. 17, 323–365 (Chapter 9).

Franck, E.U., Tödheide, K., 1959. Thermische Eigenschaften überkristischer Mischungen von Kohlendioxyd und Wasser bis zu 750 °C and 2000 atm. Z. Phys. Chem. (Neue Folge) 22, 232–245.

Frost, D.J., Wood, B.J., 1997. Experimental measurements of the properties of H_2O–CO_2 mixtures at high pressures and temperatures. Geochim. Cosmochim. Acta 61 (16), 3301–3309.

Fuller, R.C., Prevost, J.H., Piri, M., 2006. Three-phase equilibrium and partioning calculation for CO_2 sequestration in saline aquifers. J. Geophys. Res. 111, B06207 (11 pages).

Gallagher, J.S., Levelt Sengers, J.M.H., 1988. Modeling the thermodynamic properties of sodium chloride in steam through extended corresponding states. Int. J. Thermophys. 9 (5), 649–661.

Gallagher, J.S., Crovetto, R., Levelt Sengers, J.M.H., 1993. The thermodynamic behavior of the CO_2–H_2O system from 400 to 1000 K, up to 100 MPa, and 30% mole fraction of CO_2. J. Phys. Chem. Ref. Data 22 (2), 431–449.

Garcia, J.E., 2001. Density of aqueous solutions of CO_2. Lawrence Berkeley National Laboratory Paper LBNL-49023. University of California.

Gehrig, M., 1980. Phasengleichgewichte und pVT-daten ternärer mischungen aus wasser, kohlendioxid und natriumchlorid bis 3 kbar und 550 °C, Univ. Karlsrushe, Hochschul Verlag, Freiburg, 109 pp.

Gehrig, M., Lentz, H., Franck, E.U., 1986. The system water–carbon dioxide–sodium chloride to 773 K and 300 MPa. Ber. Bunsenges. Phys. Chem. 90, 525–533.

Greenwood, H.J., 1969. The compressibility of gaseous mixtures of carbon dioxide and water between 0 and 500 bars pressure and 450° and 800° centigrade. Am. J. Sci. 267-A, 191–208.

Greenwood, H.J., 1973. The thermodynamic properties of gaseous mixtures of H_2O and CO_2 between 450° and 800 °C and 0 to 500 bars. Am. J. Sci. 273, 561–571.

Guo, M., Wang, W., Lu, H., 1990. Equations of state for pure and mixture square-well fluids I: coordination number models. Fluid Phase Equilib. 60 (1–2), 37–45.

Haas, J.L.J., 1970. An equation for the density of vapor-saturated NaCl–H_2O solutions from 75° to 325 °C. Am. J. Sci. 269 (12), 489–493.

Harvey, A.H., 1998. Applications of near-critical dilute-solution thermodynamics. Ind. Eng. Chem. Res. 37 (8), 3080–3088.

Harvey, A.H., Lemmon, E.W., 2004. Correlation for the second virial coefficient of water. J. Phys. Chem. Ref. Data 33 (1), 369–376.

Harvey, A.H., Levelt Sengers, J.M.H., 1989. On the NaCl–H_2O coexistence curve near the critical temperature of H_2O. Chem. Phys. Lett. 56 (4), 415–417.

Haugan, P.M., Drange, H., 1992. Sequestration of CO_2 in the deep ocean by shallow injection. Nature 357, 318–320.

Hebach, A., Oberhof, A., Dahmen, N., 2004. Density of water + carbon dioxide at elevated pressures: measurements and correlation. J. Chem. Eng. Data 49 (4), 950–953.

Helgeson, H.C., Kirkham, D.H., 1976. Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high pressures and temperatures. III. Equation of state for aqueous species at infinite dilution. Am. J. Sci. 276, 97–240.

Hendl, H., Bich, E., Vogel, E., 1997. A new evaluation of (p, ρ, T) measurements on steam with corrections for the effects of physical and chemical adsorption. J. Chem. Thermodyn. 29, 765–784.

Hnedkovsky, L., Wood, R.H., Majer, V., 1996. Volumes of aqueous solutions of CH_4, CO_2, H_2S and NH_3 at temperatures from 298.15 K to 705 K and pressures to 35 MPa. J. Chem. Thermodyn. 28 (2), 125–142.

Holloway, J.R., 1977. Fugacity and activity of molecular species in supercritical fluids. In: Fraser, D.G. (Ed.), Thermodynamics in Geology. D Reidel Publishing Co., Holland, Dordrecht, pp. 161–181.

Holste, J.C., et al., 1987. Experimental (p, Vm, T) for pure CO_2 between 220 and 450 K. J. Chem. Thermodyn. 19 (12), 1233–1250.

Hu, J.W., Duan, Z.H., 2005. Theoretical prediction of the coordination number, local composition and pressure–volume–temperature properties of square-well and square-shoulder fluids. J. Chem. Phys. 123, 244505 (12 pages).

Hu, Z.-Q., Yang, J.-C., Li, Y.-G., 2003a. Crossover SAFT-BACK equation of state for pure CO_2 and H_2O. Fluid Phase Equilib. 205, 25–36.

Hu, Z.-Q., Yang, J.-C., Li, Y.-G., 2003b. Crossover SAFT equation of state for pure supercritical fluids. Fluid Phase Equilib. 205, 1–15.

Iglesias, E.R., Moya, S.L., 1992. An accurate formulation of the solubility of CO_2 in water for geothermal applications. The Seventeenth Workshop on Geothermal Reservoir Engineering. Stanford University, Standford, California, pp. 231–238.

Ji, X., Tan, S.P., Adidharma, H., Radosz, M., 2005. SAFT1-RPM approximation extended to phase equilibria and densities of CO_2–H_2O and CO_2–H_2O–NaCl systems. Ind. Eng. Chem. Res. 44, 8419–8427.

Kaszuba, J.P., Janecky, D.R., Snow, M.G., 2003. Carbon dioxide reaction processes in a model brine aquifer at 200 °C and 200 bars: implications for geologic sequestration of carbon. Appl. Geochem. 18, 1065–1080.

Kerrick, D.M., Jacobs, G.K., 1981. A modified Redlich–Kwong equation for H_2O, CO_2, and H_2O–CO_2 mixtures at elevated pressures and temperatures. Am. J. Sci. 281, 735–767.

Kervevan, C., Azaroual, M., Durst, P., 2005. Improvement of the calculation accuracy of acid gas solubility in deep reservoir brines: application to the geological storage of CO_2. Oil Gas Sci. Technol.-Rev. IFP 60 (2), 357–379.

Kimuro, H., Kusayanagi, T., Yamaguchi, F., Ohtsubo, K., Morishita, M., 1994. Basic experimental results of liquid CO_2 injection into the deep ocean. IEEE Trans. Energy Convers. 9 (4), 732–735.

King, M.B., Mubarak, A., D.K.J., Bott, T.R., 1992. The mutual solubilities of water with supercritical and liquid carbon dioxides. J. Supercrit. Fluids 5 (4), 296–302.

Kirkwood, J.G., Buff, F.P., 1951. The statistical mechanical theory of solutions, I. J. Chem. Phys. 19, 774–782.

Kiselev, S.B., 1997. Prediction of the thermodynamic properties and the phase behavior of binary mixtures in the extended critical region. Fluid Phase Equilib. 128 (1–2), 1–28.

Kiselev, S.B., Ely, J.F., 1999. Crossover SAFT equation of state: application for normal alkanes. Ind. Eng. Chem. Res. 38 (12), 4993–5004.

Kiselev, S.B., Ely, J.F., 2004. Generalized crossover description of the thermodynamic and transport properties in pure fluids. Fluid Phase Equilib. 222–223, 149–159.

Kiselev, S.B., Friend, D.G., 1999. Cubic crossover equation of state for mixtures. Fluid Phase Equilib. 162, 51–82.

Krüger, Y., Diamond, L.W., 2001b. P–V–T–X properties of two H_2O–CO_2–NaCl mixtures up to 850 °C and 500 MPa: a synthetic fluid inclusion study. In: Noronha, F., Dória, A., Guedes, A. (Eds.), XVI ECROFI European Current Research on Fluid Inclusions. Faculdade de Ciências do Porto, Departamento de Geologia, Porto, pp. 241–244.

Labotka, T.C., 1991. Chemical and physical properties of fluids. Rev. Miner. 26, 43–104.

Li, Y., Pitzer, K.S., 1987a. Thermodynamics of aqueous sodium chloride at high temperature and pressure (I) Thermodynamic properties over 373–573 K and 0.1–100 MPa. J. Chem. Ind. Eng., China (1), 40–50.

Li, Y., Pitzer, K.S., 1987b. Thermodynamics of aqueous sodium chloride at high temperature and pressure (II) Thermodynamic properties of aqueous NaCl to 823 K and 100 MPa. J. Chem. Ind. Eng., China (2), 249–255.

Li, Z., Dong, M., Li, S., Dai, L., 2004. Densities and solubilities for binary systems of carbon dioxide + water and carbon dioxide + brine at 59 °C and pressures to 29 MPa. J. Chem. Eng. Data 49 (4), 1026–1031.

Lue, L., Prausnitz, J.M., 1998. Renormalization-group corrections to an approximate free-energy model for simple fluids near to and far from the critical region. J. Chem. Phys. 108 (13), 5529–5536.

Mäder, U.K., 1991. H_2O–CO_2 mixtures: a review of P–V–T–X data and an assessment from a phase-equilibrium point of view. Can. Mineral. 29, 767–790.

Nieva, D., Barragán, R.M., 2003. HCO-TERNARY: a FORTRAN code for calculating P–V–T–X properties and liquid vapor equilibria of fluids in the system H_2O–CO_2–CH_4. Comput. Geosci. 29 (4), 469–485.

Nighswander, J.A., Kalogerakis, N., Mehrotra, A.K., 1989. Solubilities of carbon dioxide in water and 1 wt.% NaCl solution at pressures up to 10 MPa and temperatures from 80 to 200 °C. J. Chem. Eng. Data 34, 355–360.

Nitsche, J.M., Teletzke, G.F., E.S.L., Davis, H.T., 1984. Phase behavior of binary mixtures of water, carbon dioxide and decane predicted with a lattice-gas model. Fluid Phase Equilib. 17 (2), 243–264.

O'Connell, J.P., 1971. Thermodynamic properties of solutions based on correlation functions. Mol. Phys. 20, 27–36.

O'Connell, J.P., 1981. Thermodynamic properties of solutions and the theory of fluctuations. Fluid Phase Equilib. 6, 21–34.

O'Connell, J.P., 1995. Application of fluctuation solution theory to thermodynamic properties of solutions. Fluid Phase Equilib. 104, 21–39.

O'Connell, J.P., Sharygin, A.V., Wood, R.H., 1996. Infinite dilution partial volumes of aqueous solutes over wide ranges of conditions. Ind. Eng. Chem. Res. 35, 2808–2812.

Ohmura, R., Mori, Y.H., 1999. Comments on "Solubility of liquid CO_2 in synthetic sea water at temperatures from 278 K to 293 K and Pressures from 6.44 MPa to 29.49 MPa, and densities of the corresponding aqueous solutions" (Teng, H.; Yamasaki, A. J. Chem. Eng. Data 1998, 43, 2–5). J. Chem. Eng. Data 44 (6), 1432–1433.

Ohsumi, T., Nakashiki, N., Shitashima, K., Hirama, K., 1992. Density change of water due to dissolution of carbon dioxide and near-field behavior of CO_2 from a source on deep-sea floor. Energy Convers. Manag. 33 (5–8), 685–690.

Oldenburg, C.M., Benson, S.M., 2002. CO_2 injection for enhanced gas production and carbon sequestration. SPE (Society of Petroleum Engineers) 74367, 1–10.

Ota, M., Abe, Y., Watanabe, M., Smith, R.L.J., Inomata, H., 2005. Methane recovery from methane hydrate using pressurized CO_2. Fluid Phase Equilib. 228–229, 553–559.

Parkinson, W.J., De Nevers, N.J., 1969. Partial molal volume of carbon dioxide in water solutions. Ind. Eng. Chem. Fundam. 8 (4), 709–713.

Patel, M.R., Eubank, P.T., 1988. Experimental densities and derived thermodynamic properties for carbon dioxide–water mixtures. J. Chem. Eng. Data 33 (2), 185–193.

Patel, M.R., Holste, J.C., Hall, K.R., Eubank, P.T., 1987. Thermophysical properties of gaseous carbon dioxide–water mixtures. Fluid Phase Equilib. 36, 279–299.

Pitzer, K.S., Pabalan, R.T., 1986. Thermodynamics of NaCl in steam. Geochim. Cosmochim. Acta 50 (7), 1445–1454.

Pitzer, K.S., Tanger IV, J.C., 1988. Near-critical NaCl–H_2O: equation of state and discussion of anomalous properties. Int. J. Thermophys. 9 (5), 635–648.

Pitzer, K.S., Peiper, J.C., Busey, R.H., 1984. Thermodynamic properties of aqueous sodium chloride solutions. J. Phys. Chem. Ref. Data 13 (1), 1–102.

Pitzer, K.S., Bischoff, J.L., Rosenbauer, R.J., 1987. Critical behavior of dilute NaCl in H_2O. Chem. Phys. Lett. 134 (1), 60–63.

Plyasunov, A.V., Shock, E.L., 2001. Correlation strategy for determining the parameters of the revised Helgeson–Kirkham–Flowers model for aqueous nonelectrolytes. Geochim. Cosmochim. Acta 65 (21), 3879–3900.

Plyasunov, A.V., Shock, E.L., 2003. Second cross virial coefficients for interactions involving water. Critical data compilation. J. Chem. Eng. Data 48, 808–821.

Plyasunov, A.V., O'Connell, J.P., Wood, R.H., 2000a. Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes. I. Equations for partial molar volumes at infinite dilution and standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions. Geochim. Cosmochim. Acta 64 (3), 495–512.

Plyasunov, A.V., O'Connell, J.P., Wood, R.H., Shock, E.L., 2000b. Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes. II. Equations for the standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions including subcritical temperatures. Geochim. Cosmochim. Acta 64 (16), 2779–2795.

Plyasunov, A.V., Shock, E.L., O'Connell, J.P., 2006. Corresponding-states correlations for estimating partial molar volumes of nonelectrolytes at infinite dilution in water over extended temperature and pressure ranges. Fluid Phase Equilib. 247 (1–2), 18–31.

Portier, S., Rochelle, C., 2005. Modeling CO_2 solubility in pure water and NaCl-type waters from 0 to 300 °C and from 1 to 300 bar: application to the Utsira Formation at Sleipner. Chem. Geol. 217 (3–4), 187–199.

Pruess, K., et al., 2004. Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO_2. Energy 29 (9–10), 1431–1444.

Rainwater, J.C., 1989. Asymptotic expansions for constant-composition dew-bubble curves near the critical locus. Int. J. Thermophys. 10 (2), 357–368.

Renon, H., Prausnitz, J.M., 1968. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J. 14, 135–144.

Roedder, E., 1984. Fluid inclusions. Rev. Miner. 12, 1–644.

Rogers, P.S.Z., Pitzer, K.S., 1982. Volumetric properties of aqueous sodium chloride solutions. J. Phys. Chem. Ref. Data 11 (1), 15–81.

Schmidt, C., Bodnar, R.J., 2000. Synthetic fluid inclusions: XVI. PVTX properties in the system H_2O–NaCl–CO_2 at elevated temperatures, pressures, and salinities. Geochim. Cosmochim. Acta 64 (22), 3853–3869.

Schmidt, C., Rosso, K.M., Bodnar, R.J., 1995. Synthetic fluid inclusions: XIII. Experimental determination of PVT properties in the system H_2O + 40 wt.% NaCl + 5 mol.% CO_2 at elevated temperature and pressure. Geochim. Cosmochim. Acta 59 (19), 3953–3959.

Sedlbauer, J., O'Connell, J.P., Wood, R.H., 2000. A new equation of state for correlation and prediction of standard molal thermodynamic properties of aqueous species at high temperatures and pressures. Chem. Geol. 163 (1–4), 43–63.

Seitz, J.C., Blencoe, J.G., 1997. Experimental determination of the volumetric properties and solvus relations of H_2O–CO_2 mixtures at 300–400 °C and 75–1000 bars. The Fifth International Symposium on Hydrothermal Reactions. Oak Ridge National Laboratory, Oak Ridge, TN, pp. 109–112.

Seitz, J.C., Blencoe, J.G., 1999. The CO_2–H_2O system. I. Experimental determination of volumetric properties at 400 °C, 10–100 MPa. Geochim. Cosmochim. Acta 63 (10), 1559–1569.

Sengers, J.V., 1986. Thermodynamic behavior near the critical point. Ann. Res. Phys. Chem. 37, 189–222.

Sengers, J.V., Levelt Sengers, J.M.H., 1984. A universal representation of the thermodynamic properties of fluids in the critical region. Int. J. Thermophys. 5 (2), 195–208.

Shmulovich, K.I., Shmonov, V.M., Zharikov, I.V., 1979. P–V–T measurements in hydrous systems at high pressure and temperature. In: Godikov, A.A. (Ed.), Experimental Research Methods for Hydrothermal Solutions. Nauka, Novosibirsk, pp. 81–89 (in Russian).

Shmulovich, K.I., Shmonov, V.M., Mazur, V.A., Kalinichev, A.G., 1980. P–V–T and activity concentration relations in the H_2O–CO_2 system (homogeneous solutions). Geochem. Int. 17 (6), 123–139.

Shock, E.L., Helgeson, H.C., 1990. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of organic species. Geochim. Cosmochim. Acta 54, 915–945.

Shock, E.L., Helgeson, H.C., Sverjensky, D.A., 1989. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of inorganic neutral species. Geochim. Cosmochim. Acta 53 (9), 2157–2183.

Shock, E.L., Oelkers, E.H., Johnson, J.W., Sverjensky, D.A., Helgeson, H.C., 1992. Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: effective electrostatic radii, dissociation constants, and standard partial molal properties to 1000 °C and 5 kb. J. Chem. Soc., Faraday Trans. 88, 803–826.

Singh, J., Blencoe, J.G., Anovitz, L.M., 2000. Volumetric properties and phase relations of binary H_2O–CO_2–CH_4–N_2 mixtures at 300 °C and pressures to 1000 bars. In: Tremaine, P.R., et al. (Ed.), Steam, Water, and Hydrothermal Systems: Physics and Chemistry Meeting the Needs of Industry. NRC Research Press, Ottawa, Canada, pp. 134–143.

Smith, G.R., Wormald, C.J., 1984. The excess molar enthalpies of $\{xH_2O+(1-x)CO\}(g)$ and $\{xH_2O+(1-x)CO_2\}(g)$. J. Chem. Thermodyn. 16 (6), 543–550.

Song, Y.-C., Chen, B.-X., Shen, S.-Q., 2003a. Density and state function of CO_2 salt water solution in underground condition. J. Therm. Sci. Technol. (China) 2 (4), 358–364.

Song, Y., Nishio, M., Chen, B., Someya, S., Ohsumi, T., 2003b. Measurement on CO_2 solution density by optical technology. J. Vis. 6 (1), 41–51.

Song, Y., Chen, B., Nishio, M., Akai, M., 2005. The study on density change of carbon dioxide seawater solution at high pressure and low temperature. Energy 30, 2298–2307.

Span, R., Wagner, W., 1996. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. J. Phys. Chem. Ref. Data 25 (6), 1509–1596.

Spycher, N.F., Reed, M.H., 1988. Fugacity coefficients of H_2, CO_2, CH_4, H_2O and of H_2O–CO_2–CH_4 mixtures: a virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling. Geochim. Cosmochim. Acta 52 (3), 739–749.

Spycher, N., Pruess, K., Ennis-King, J., 2003. CO_2–H_2O mixtures in the geological sequestration of CO_2. I. Assessment and calculation of mutual solubilities from 12 to 100 °C and up to 600 bar. Geochim. Cosmochim. Acta 67 (16), 3015–3031.

Sterner, S.M., Bodnar, R.J., 1991. Synthetic fluid inclusions. X: Experimental determination of P–T–V–X properties in the CO_2–H_2O system to 6 kb and 700 °C. Am. J. Sci. 291, 1–54.

Stewart, P.B., Munjal, P., 1970. Solubility of carbon dioxide in pure water, synthetic sea water, and synthetic sea water concentrates at −5° to 25 °C. and 10- to 45-atm. pressure. J. Chem. Eng. Data 15 (1), 67–71.

Takenouchi, S., Kennedy, G.C., 1964. The binary system H_2O–CO_2 at high temperatures and pressures. Am. J. Sci. 262, 1055–1074.

Takenouchi, S., Kennedy, G.C., 1965. The solubility of carbon dioxide in NaCl solutions at high temperatures and pressures. Am. J. Sci. 263, 445–454.

Talman, S.J., Adams, J.J., Chalaturnyk, R.J., 2004. Adapting TOUGH2 for general equations of state with application to geological storage of CO_2. Comput. Geosci. 30 (5), 543–552.

Tang, Y.P., 1998. Outside and inside the critical region of the Lennard–Jones fluid. J. Chem. Phys. 109 (14), 5935–5944.

Tanger IV, J.C., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes. Am. J. Sci. 288, 19–98.

Tanger IV, J.C., Pitzer, K.S., 1989. Thermodynamics of NaCl–H_2O: a new equation of state for the near-critical region and comparisons with other equations for adjoining regions. Geochim. Cosmochim. Acta 53 (5), 973–987.

Teng, H., Yamasaki, A., 1998. Solubility of liquid CO_2 in synthetic sea water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa, and densities of the corresponding aqueous solutions. J. Chem. Eng. Data 43 (1), 2–5.

Teng, H., Yamasaki, A., Chun, M.-K., Lee, H., 1997. Solubility of liquid CO_2 in water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa and densities of the corresponding aqueous solutions. J. Chem. Thermodyn. 29 (11), 1301–1310.

Tödheide, K., Franck, E.U., 1963. Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxid–Wasser bis zu Drucken von 3500 bar. Z. Phys. Chem. (Neue Folge) 37, 387–401.

Tödheide, K., 1982. Hydrothermal solutions. Ber. Bunsenges. Phys. Chem. 86, 1005–1016.

Tsonopouplos, C., 1974. An empirical correlation of second virial coefficient. AIChE J. 20 (2), 263–272.

van't Hof, A., Laura Japas, M., Peters, C.J., 2001. Description of liquid–liquid equilibria including the critical region with the crossover-NRTL model. Fluid Phase Equilib. 192 (1–2), 27–48.

Vanderzee, C.E., Haas, N.C., 1981. Second cross virial coefficients B_{12} for gas mixture (carbon dioxide + water) from 300 to 1000 K. J. Chem. Thermodyn. 13 (3), 203–211.

Wagner, W., Pruss, A., 2002. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31 (2), 387–535.

Wang, L.-S., Lang, Z.-X., Guo, T.-M., 1996. Measurement and correlation of the diffusion coefficients of carbon dioxide in liquid hydrocarbons under elevated pressures. Fluid Phase Equilib. 117 (1–2), 364–372.

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of non-ideal gas. Mar. Chem. 2, 203–215.

White, J.A., 2000. Global renormalization calculation compared with simulations for Lennard–Jones fluid. J. Chem. Phys. 112 (7), 3236–3244.

White, J.A., Zhang, S., 1993. Renormalization group theory for fluids. J. Chem. Phys. 99 (3), 2012–2019.

White, C.M., et al., 2005. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery — a review. Energy Fuels 19 (3), 659–724.

Wilson, G.M., 1964. Vapor–liquid equilibrium. X. A new expression for the excess Gibbs free energy of mixing. J. Am. Chem. Soc. 86, 127–130.

Wilson, K.G., 1971. Renormalization group and critical phenomena. (I) Renormalization group and the Kadanoff scaling picture. Phys. Rev., B 4 (9), 3174–3183.

Wilson, K.G., 1983. The renormalization group and critical phenomena. Rev. Mod. Phys. 55 (3), 583–600.

Wong, C.S., Tishchenko, P.Y., Johnson, W.K., 2005. Effects of high CO_2 molality on the carbon dioxide equilibrium of seawater. J. Chem. Eng. Data 50 (3), 822–831.

Woolley, H.W., 1983. A switch function applied to the thermodynamic properties of steam near and not near the critical point. Int. J. Thermophys. 4 (1), 51–95.

Wormald, C.J., Lloyd, M.J., 1994. Excess molar enthalpies for ($0.5\ H_2O+0.5CO_2$) at temperatures from 598.2 K to 698.2 K and pressures up to 20 MPa. J. Chem. Thermodyn. 26 (1), 101–110.

Wormald, C.J., Colling, C.N., Smith, G., 1983. Thermodynamics of supercritical steam + carbon dioxide mixtures. Fluid Phase Equilib. 10 (2–3), 223–231.

Wormald, C.J., Lancaster, N.M., Sellars, A.J., 1986. The excess molar enthalpies of $\{xH_2O+(1-x)CO\}(g)$ and $\{xH_2O+(1-x)CO_2\}(g)$ at high temperatures and pressures. J. Chem. Thermodyn. 18, 135–147.

Wormald, C., Lloyd, M.J., Fenghour, A., 1997. The excess enthalpy of (steam + carbon dioxide) in the supercritical region up to $T = 698.2$ K and $p = 25.5$ MPa. J. Chem. Thermodyn. 29 (11), 1253–1260.

Xu, T., Apps, J.A., Pruess, K., 2004. Numerical simulation of CO_2 disposal by mineral trapping in deep aquifers. Appl. Geochem. 19 (6), 917–936.

Yaginuma, R., Sato, Y., Kodama, D., Tanaka, H., Kato, M., 2000. Saturated densities of carbon dioxide + water mixture at 304.1 K and pressures to 10 MPa. Nippon Enerugi Gakkaishi 79 (2), 144–146.

Zakirov, I.V., 1984. The P–V–T relations in the system H_2O–CO_2 at 300 and 400 °C up to 1000 bar. Geochem. Int. 21 (6), 13–20.

Zawisza, A., Malesińska, B., 1981. Solubility of carbon dioxide in liquid water and of water in gaseous carbon dioxide in the range 0.2–5 MPa and at temperatures up to 473 K. J. Chem. Eng. Data 26, 388–391.

Zhang, Y.-G., Frantz, J.D., 1992. Investigations of fluid properties in the CO_2–CH_4–H_2O system using synthetic fluid inclusions. Chem. Geol. 100 (1–2), 51–72.

Zhang, J., et al., 2002. Study on intermolecular interactions in supercritical fluids by partial molar volume and isothermal compressibility. J. Supercrit. Fluids 22 (1), 15–19.