

## **A MODEL FOR THERMOPHYSICAL PROPERTIES OF CO<sub>2</sub>-BRINE MIXTURES AT ELEVATED TEMPERATURES AND PRESSURES**

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### **ABSTRACT**

A mutual CO<sub>2</sub>-H<sub>2</sub>O solubility model was previously reported for application to CO<sub>2</sub>-enhanced geothermal systems. The ability of this model to predict PVT and caloric properties of the compressed gas phase is investigated. Compressibility factors of pure CO<sub>2</sub> and CO<sub>2</sub>-H<sub>2</sub>O mixtures can generally be predicted within a few percent of reference and experimental data. Caloric data are also reasonably well reproduced for CO<sub>2</sub>-H<sub>2</sub>O gas mixtures at moderate water content. At elevated water contents, more significant deviations are observed between model results and published experimental enthalpies of mixing. However, total enthalpies may still be predicted with reasonable accuracy for applications to CO<sub>2</sub>-enhanced geothermal systems. Experimental data in the temperature and pressure range of most interest to CO<sub>2</sub>-enhanced geothermal systems are scarce and would be needed for further model validation.

### **BACKGROUND AND OBJECTIVES**

Recent theoretical studies have stimulated interest in the potential of using CO<sub>2</sub> instead of water as heat transfer fluid in enhanced geothermal systems (EGS) (Brown, 2000; Fouillac et al., 2004; Pruess, 2006, 2008). Evaluating the development and operation of an EGS with CO<sub>2</sub> as a working fluid requires a capability to accurately represent the thermophysical properties of CO<sub>2</sub>-brine mixtures for the entire range of fluid compositions and thermodynamic conditions, from injection to production. Furthermore, in order to assess the behavior of CO<sub>2</sub> in natural subsurface environments, and to evaluate potential leakage scenarios, thermophysical properties need to be represented all the way to the land surface.

We have previously reported on the development of a phase partitioning model for CO<sub>2</sub>-brine mixtures that is based on thermodynamic equilibrium principles and a cubic equation of state (Spycher and Pruess, 2010). Our model represents the mutual solubilities

of CO<sub>2</sub> and NaCl brines largely within experimental uncertainties for temperatures of 12–300°C, pressures of 1–600 bar and salinities from 0 to 6 molal NaCl. Here, we investigate the application of this model to the calculation of pressure-volume-temperature (PVT) data and caloric properties, with the objective of applying this model to CO<sub>2</sub>-EGS studies.

### **MODELING APPROACH AND TESTING**

#### **Original Solubility Model**

The solubility model was described in detail by Spycher and Pruess (2010) and references therein. Aspects of the model relevant to the present study are described here. Mutual solubilities are computed using a modified Redlich-Kwong (RK) equation of state (EOS) to compute the fugacity coefficients of CO<sub>2</sub> and H<sub>2</sub>O in the compressed gas phase, coupled with equilibrium constants expressing the partitioning of CO<sub>2</sub> in water. The effect of salts on CO<sub>2</sub> solubility in saline solutions is also accounted for by a Pitzer activity coefficient model. The EOS parameters, equilibrium constants, and Pitzer interaction parameters were fitted to a large number of experimental mutual solubility data. Below 100°C, the amount of water partitioning into compressed CO<sub>2</sub> is very small, which allows neglecting H<sub>2</sub>O when computing properties of the gas mixture. At temperatures above 100°C, however, a significant amount of water can vaporize in compressed CO<sub>2</sub>, such that this amount can no longer be ignored when computing thermophysical properties and phase equilibrium. In the present study, focus is given to temperatures above 100°C, as it is most relevant to EGS with CO<sub>2</sub> as a working fluid. PVT and caloric properties predicted by the solubility model, without any modifications of its original EOS parameters, are presented below.

## PVT Properties

Compressibility factors ( $Z=PV/RT$ ) of pure CO<sub>2</sub> and H<sub>2</sub>O were fitted to reference data as part of the original solubility model. For CO<sub>2</sub>, compressibility factors from Span and Wagner (1996) could be reproduced with a root mean square error (RMSE) about 0.5 % and no absolute deviations > ~2%. For H<sub>2</sub>O, compressibility factors from Wagner and Pruß (2002) for the liquid phase could be reproduced with an RMSE < 0.5% and no absolute deviations > ~9%. However, as would be expected with any cubic EOS, the vapor phase data along the saturation curve and the saturation curve itself could not be accurately reproduced.

Few PVT data have been reported for CO<sub>2</sub>-H<sub>2</sub>O mixtures in the P-T range of interest to CO<sub>2</sub>-EGS (100–300°C and 100–600 bar). This is in part because, at these temperatures and pressures, CO<sub>2</sub>-H<sub>2</sub>O mixtures form two immiscible phases over most of the mixture compositional range. In addition, the water content at the dew-point of CO<sub>2</sub>-H<sub>2</sub>O mixtures below ~250°C and pressures above 100 bar is typically limited. As a result, experimental PVT properties are not only scarce, but also are mostly limited to pressures below 100 bar.

We previously reported a relatively good agreement of model results with the compressed gas phase density data of Fenghour et al. (1996). Comparisons of model results with experimental density values were since extended to include data from Patel et al. (1987), Patel and Eubank (1988) and Zawisza and Maleslnska (1981). Computed compressibility factors show deviations mostly within a few percent from these experimental data sets (Figure 1).

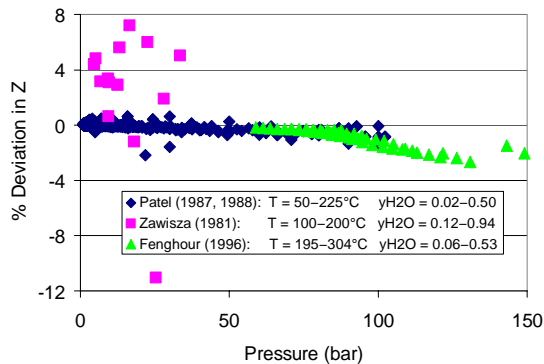


Figure 1. Percent deviation between computed compressibility factors ( $Z = PV/RT$ ) and experimental data from the literature for single-phase compressed CO<sub>2</sub>-H<sub>2</sub>O gas mixtures over a range of H<sub>2</sub>O mole fractions ( $y_{H_2O}$ ) as shown in the legend.

## Enthalpy

The total specific enthalpy ( $H_{tot}$ ) of a CO<sub>2</sub>-H<sub>2</sub>O mixture, or of its pure components, is calculated from the following relationship,

$$H_{tot} = y_{H_2O} H_{H_2O}^o + y_{CO_2} H_{CO_2}^o + \Delta H_{dep} \quad (1)$$

where  $y$  stands for mole fraction,  $H^o$  represents the specific molar enthalpy of the pure components at zero pressure (i.e., in the ideal gas state) and  $\Delta H_{dep}$  is the departure enthalpy, which represents the difference between the total enthalpy at a given temperature and pressure,  $H_{(T,P)}$ , and the total enthalpy at the same temperature and zero pressure,  $H_{(T,P=0)}$ .

Values of  $H^o$  are calculated from heat capacity Maier-Kelley power functions of temperature, which are easily integrated analytically to yield  $H^o$  as a function of temperature. Parameters for these functions were obtained by fitting reference heat capacity data ( $C_p^o$ ) from reference sources (Span and Wagner, 1996; Wagner and Pruß, 2002).

The enthalpy departure,  $\Delta H_{dep}$ , is computed with a departure function derived from the model EOS. The departure function includes derivatives of the EOS parameters as a function of temperature (e.g., Joffe and Zudkevitch, 1970; Rittman et al., 1982). These derivatives are calculated analytically from the relatively simple functions of temperature given for the parameters of the EOS and mixing rules (Spycher and Pruess, 2010). Numerical derivatives were also tested, yielding good results when centered, however highly inaccurate results when uncentered (i.e., when computationally more efficient forward numerical derivatives were used).

Note that for clarity and consistent data comparisons in this study, the specific enthalpies of both CO<sub>2</sub> and H<sub>2</sub>O are referred to zero for the pure gases at the triple point of water (at  $T = 0.01^\circ\text{C}$  and  $P = 0.00612 \approx 0$  bar).

For pure CO<sub>2</sub>, specific enthalpies computed following this approach yield values typically within a few percent or less of reference data (Figure 2, top), except near the critical point where larger deviations occur because the cubic EOS cannot accurately predict the point of the phase change. The average absolute deviation for points shown in Figure 2 above the critical temperature (~30.4°C) is about 1.7 kJ/kg, with the largest deviations occurring below 100°C.

For pure water, below 100°C, enthalpy predictions cannot be made because the mixing rules in the EOS assume infinite dilution of H<sub>2</sub>O in CO<sub>2</sub> (Spycher et al., 2010). Above 100°C, predicted liquid water enthalpies up to 300°C and 500 bar show average absolute deviations ~40 kJ/kg from reference data

(Figure 2, bottom). Because the EOS is not intended for pure water and cannot accurately predict the water saturation pressure curve, significant deviations from reference data are observed for enthalpies of pure gaseous H<sub>2</sub>O along the saturation curve (up to 170 kJ/kg deviations at 300°C).

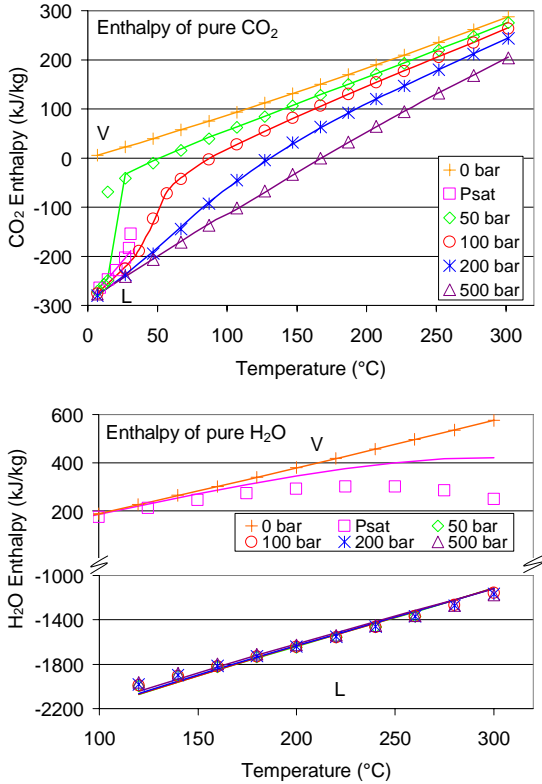


Figure 2. Comparison of computed specific enthalpies (lines) with reference data (symbols) from Span and Wagner (1996) for CO<sub>2</sub> (top), and from Wagner and Pruf (2002) for H<sub>2</sub>O (bottom). The same reference enthalpy is taken for CO<sub>2</sub> and H<sub>2</sub>O (zero for the pure vapors at 0.01°C and ~ 0 bar).

The only data found to evaluate model predictions with CO<sub>2</sub>-H<sub>2</sub>O mixtures in our P-T range of interest are total enthalpies reported by Patel and Eubank (1988) (Figure 3). These data are limited to pressures mostly below 100 bar and H<sub>2</sub>O mole fractions no larger than 0.5. The average absolute deviation of model predictions from these data was found to be reasonably small (1.9 kJ/kg), although larger deviations up to 13 kJ/kg occur at the higher end of investigated temperatures and H<sub>2</sub>O mole fractions (Figure 3).

Additional experimental caloric data were found in the literature for CO<sub>2</sub>-H<sub>2</sub>O mixtures at 100–300°C, although in the form of excess enthalpy. The excess

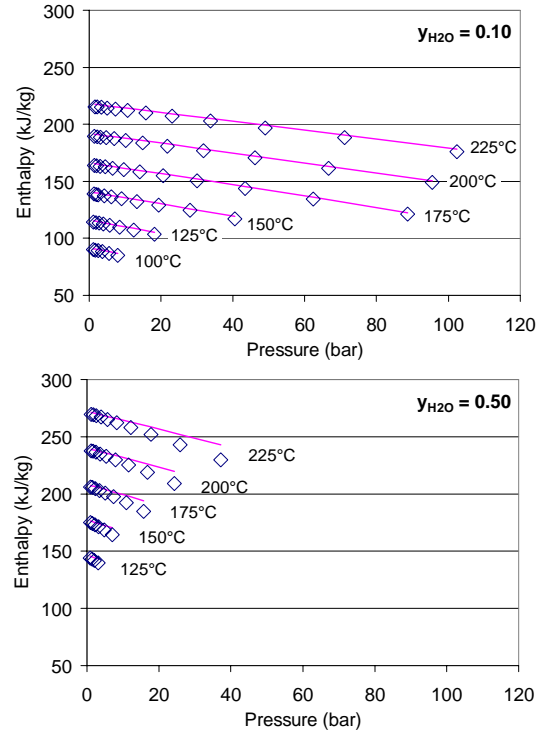


Figure 3. Computed total specific enthalpies (lines) for CO<sub>2</sub>-H<sub>2</sub>O mixtures at various H<sub>2</sub>O mole fractions ( $y_{H_2O}$ ) compared with data reported by Patel and Eubank (1988) (symbols). The same reference enthalpy is taken for CO<sub>2</sub> and H<sub>2</sub>O (zero for the pure vapors at 0.01°C and ~ 0 bar).

enthalpy ( $\Delta H_{mix}^E$ ) can be related to the departure enthalpy as follows (e.g., Ohta, 1993),

$$\Delta H_{mix}^E = \Delta H_{dep} - (y_{H_2O} \Delta H_{dep,H_2O}^o + y_{CO_2} \Delta H_{dep,CO_2}^o) \quad (2)$$

where  $\Delta H_{dep}$  is the departure enthalpy of the mixture and  $\Delta H_{dep}^o$  are the departure enthalpies of the pure components.

Enthalpies of mixing computed with Equation (2), using  $\Delta H_{dep}$  from the EOS and  $\Delta H_{dep}^o$  values from reference data, were compared with experimental data from the literature. The data of Bottini and Saville (1985), at 240–301°C and up to 45 bar, were reproduced fairly well, with an average absolute deviation of 2.4 kJ/kg, but deviations up to ~10 kJ/kg at H<sub>2</sub>O mole fraction above 0.5. The data of Wormald et al. (1986), at 175–300°C and up to 73 bar, are primarily at a 0.5 H<sub>2</sub>O mole fraction. Comparison of model results with these data show similar deviations. The data from both studies unfortunately cover a relatively low pressure range. At these moderate pressures, the enthalpy of mixing contributes to only a small fraction of the total

enthalpy (< ~6%), such that the error in total enthalpy remains less than a few percent (using the enthalpy reference point adopted here).

### ENTHALPY PREDICTIONS FOR CO<sub>2</sub>-EGS

The model was used to predict enthalpies of CO<sub>2</sub>-H<sub>2</sub>O mixtures at increasing H<sub>2</sub>O mole fractions, and temperatures and pressures fixed at values relevant to CO<sub>2</sub>-EGS applications (Figure 4). Results were then compared with enthalpies calculated by linear (ideal) mixing of the pure components according to the relationship

$$H_{tot} = y_{H_2O}H_{H_2O} + y_{CO_2}H_{CO_2} \quad (3)$$

where  $y$ , again, represents mole fraction and  $H$  is the specific molar enthalpy of the pure components (supercritical CO<sub>2</sub> and either liquid or gaseous H<sub>2</sub>O). As previously, these were taken from Span and Wagner (1996) and Wagner and Pruß (2002), and referred to zero enthalpy at the water triple point.

At moderate pressures, it would be expected that water in the compressed gas mixture behaves more like gaseous H<sub>2</sub>O, thus giving preference to using the enthalpy of gaseous H<sub>2</sub>O in Equation (3) (vaporization model). On a mass basis, the specific enthalpy of gaseous H<sub>2</sub>O (at saturation) exceeds that of CO<sub>2</sub> in the pressure range of interest (Figure 2). Accordingly, the mixture enthalpy predicted with Equation (3) using gaseous H<sub>2</sub>O increases with increasing H<sub>2</sub>O content (Figure 4). It should be noted that on a molar basis, the enthalpy change can be

either positive or negative, depending on pressure and temperature, because the specific molar enthalpies of gaseous H<sub>2</sub>O (at saturation) and CO<sub>2</sub> overlap (Figure 5).

Under increasing pressure, however, water in the mixture is expected to become more “liquid-like”. Because the specific enthalpy of liquid H<sub>2</sub>O is much lower than that of CO<sub>2</sub> (Figure 2), using this enthalpy in Equation (3) expectedly results in a strong total enthalpy decrease as the water content of the gas mixture increases (Figure 4). As would be expected, enthalpies predicted by the model mostly fall between the values given by Equation (3) with the specific enthalpy of either gaseous or liquid H<sub>2</sub>O, and thus with mostly negative deviations from the vaporization model (Figure 4). However, at pressures close to the water saturation pressure, slight positive deviations are predicted by the model (as the result of non-ideal mixing).

### DISCUSSION AND CONCLUSIONS

The mutual solubility model for CO<sub>2</sub>-H<sub>2</sub>O mixtures presented by Spycher and Pruess (2010) appears to predict PVT and caloric properties with a reasonable level accuracy, except for pure H<sub>2</sub>O vapor at saturation. The absence of experimental enthalpy data for CO<sub>2</sub>-H<sub>2</sub>O mixtures at pressures > 100 bar and temperatures < 300°C (mostly over the two-phase region), together with observed model deviations from available data at H<sub>2</sub>O mole fractions  $\geq 0.5$ ,

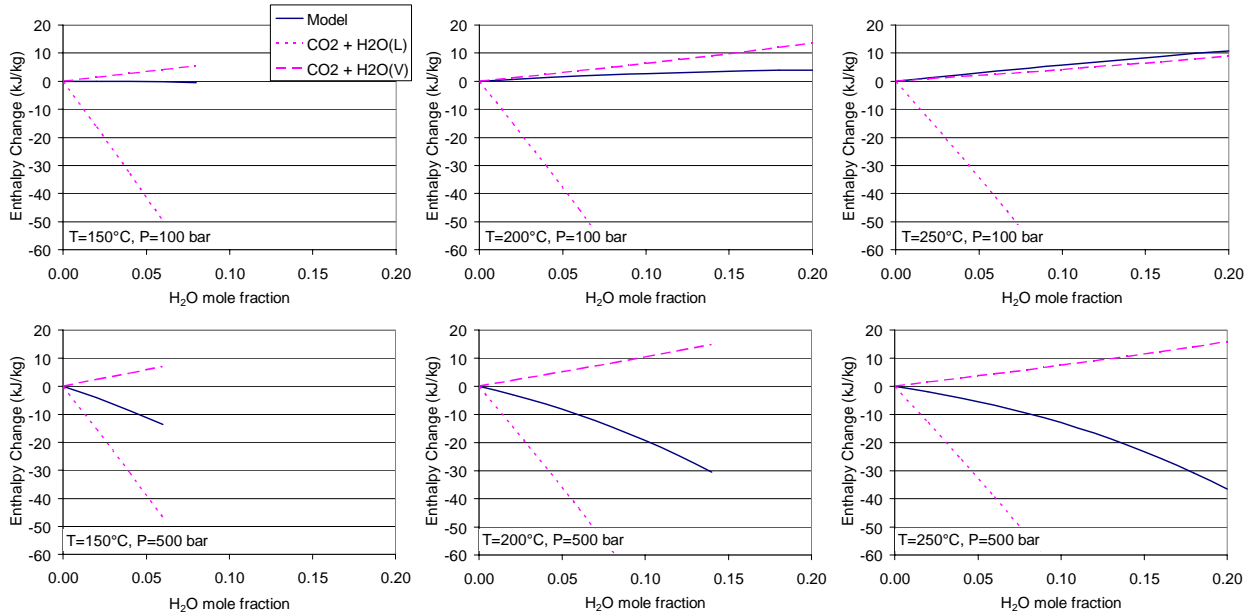


Figure 4. Computed enthalpy change with increasing water content in CO<sub>2</sub>-H<sub>2</sub>O mixtures at specified temperatures and pressures. Solid lines represent model predictions. The dashed and dotted lines represent approximations using Equation (3) and enthalpies of pure components, using either gaseous or liquid H<sub>2</sub>O (see text). At temperatures below 250°C the curves extend to H<sub>2</sub>O mole fractions corresponding approximately to the dew point of the compressed gas mixture.

renders the prediction of mixing enthalpies quite uncertain for P-T ranges typical of CO<sub>2</sub>-EGS. However, in terms of total enthalpy, model predictions may have an accuracy acceptable for most practical CO<sub>2</sub>-EGS applications. The model is also expected to provide more realistic enthalpies than values approximated assuming ideal mixing of pure CO<sub>2</sub> with either pure H<sub>2</sub>O vapor or pure H<sub>2</sub>O liquid. At fixed pressures around 100 bar and temperatures 150–250°C, addition of water to supercritical CO<sub>2</sub> is predicted (on a mass basis) to increase the mixture specific enthalpy (by ~ 0–6 kJ/kg per mole % added H<sub>2</sub>O). The reverse is predicted at 500 bar, with a computed drop in the mixture specific enthalpy (by ~ 1–2 kJ/kg per mole % added H<sub>2</sub>O). However, this would need to be validated with experimental data. The paucity of PVT and caloric data in the P-T range of most interest to CO<sub>2</sub>-EGS warrants making the collection of such data a priority.

### ACKNOWLEDGMENT

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Technology Development, Geothermal Technologies Program, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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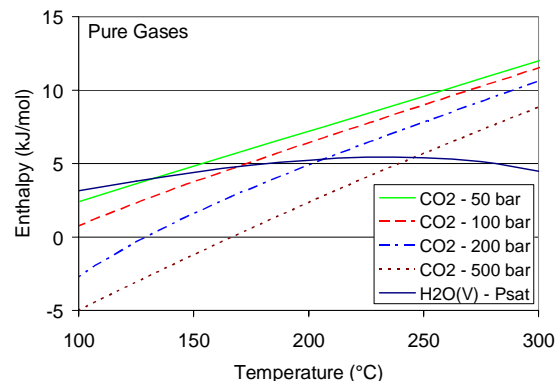


Figure 5. Reference specific molar enthalpies from Span and Wagner (1996) for CO<sub>2</sub> and from Wagner and Pruß (2002) for H<sub>2</sub>O. The same reference enthalpy is taken for CO<sub>2</sub> and H<sub>2</sub>O (zero for the pure vapors at 0.01°C and ~ 0 bar).

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