

AN ACCURATE FORMULATION OF THE SOLUBILITY OF CO₂ IN WATER, FOR GEOTHERMAL APPLICATIONS

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ABSTRACT

The solubility correlations for the H₂O-CO₂ system applied so far for numerical simulation of geothermal reservoir and well flows are crude. This is due, at least partly, to the significant disagreement existing between the solubility models and results published in the specialized literature. In this work we analyze the reasons underlying this disagreement. On this basis, we propose a thermodynamically correct, and numerically accurate model for the solubility of carbon dioxide in water. Its range of validity is up to 350 °C and 500 bar. Our main contributions are: (a) the adoption of an equation of state for the gas phase that realistically accounts for the non-ideal behavior of both components and that of the mixture, within the P-T range considered; and (b) to accurately include the effects of temperature and pressure on the solubility of carbon dioxide in the liquid phase. The proposed model fits the available phase equilibrium data for the H₂O-CO₂ system nicely. In particular, it does not present the severe conflict between the linearity of the model and the lack of linearity of the data, evident in earlier models. The tight fit obtained with our model indicates that the complexities of H₂O-CO₂ phase equilibrium are well represented by it.

INTRODUCTION

Numerical simulation of geothermal flows in reservoirs and wellbores requires knowledge of thermophysical properties of the fluids involved. In some cases the pure-water approximation is satisfactory. In others, the presence of noncondensable gases makes it inaccurate. Usually, carbon dioxide is, by far, the predominant gas in geothermal fluids. Thus, several models of the thermophysical properties of H₂O-CO₂ mixtures (e.g., Sutton 1976; O'Sullivan et al., 19; Pritchett et al., 1981) have been applied in the geothermal literature (e.g., Sutton 1976; Sutton and McNabb, 1977; Straus and Schubert, 1979; Iglesias and Schroeder, 1979; Pritchett et al., 1981; O'Sullivan et al., 1985; Mc Kibbin and Pruess, 1988).

The approximations to the solubility of CO₂ in water implemented in these models are not very accurate, as recognized by their authors. This is hardly surprising,

because the solubilities inferred by specialists (e.g., Ellis, 1959; Ellis and Golding, 1963; Takenouchi and Kennedy, 1964; Malinin, 1974; Zawisza and Malesińska, 1981; Nighswander et al., 1989), for temperature and pressure conditions of geothermal interest, disagree significantly (Fig.1). In this work we discuss the reasons underlying this disagreement, and propose an accurate formulation, suitable for geothermal applications.

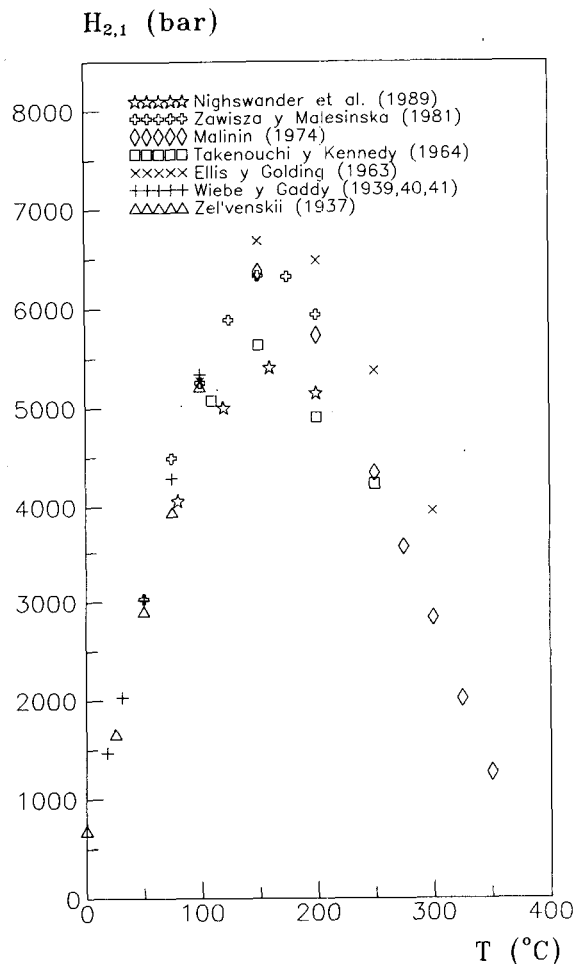


Fig. 1.

Values of Henry's law constant by different authors.

THERMODYNAMICS OF CO₂ SOLUBILITY

The solubility of a gas in a liquid is determined by the thermodynamic equations of phase equilibrium. If a gaseous phase (G) and a liquid phase (L) are in equilibrium, then for any component i the fugacities in both phases must be the same (e.g., Prausnitz, 1969):

$$f_i^G = f_i^L \quad (1)$$

For the CO₂ component ($i = 2$), equation (1) may be conveniently rewritten as (e.g., Prausnitz, 1969):

$$\phi_2 y_2 P = \gamma_2 x_2 H_{2,1} (P_1^s) \exp \int_{P_1^s}^P \frac{v_2^L - v_2^G}{RT} dP \quad (2)$$

where ϕ is the fugacity coefficient, P total pressure, x and y liquid- and gaseous-phase mole fractions respectively, γ the activity coefficient, $H_{2,1}$ the thermodynamic equivalent of Henry's law constant, P_1^s the saturation pressure of water, v_2^{∞} the partial molar volume of CO₂ in the liquid phase, T absolute temperature and R the gas constant. Note that, in general,

$$\phi_2 = \phi_2(T, P, Y_1, Y_2) \quad (3)$$

$$\gamma_2 = \gamma_2(T, P, Y_1, Y_2) \quad (4)$$

$$v_2^{\infty} = v_2^{\infty}(T, P) \quad (5)$$

DISCUSSION OF PREVIOUS WORK

As shown in Fig. 1, there is good agreement on the values of $H_{2,1}$ for $t \leq 100$ °C. Thus, we shall concentrate our discussion on the temperature range $100 < t \leq 350$ °C. The determinations of CO₂ solubility published in the specialized literature are based on different approximations to eq. (2). From this equation follows that the dispersion shown in Fig. 1 must arise from incompatibility of solubility data and/or from differences in the approximations adopted for variables appearing in (2).

The available experimental data cover a wide range of solubility. The experimental setups also differ, sometimes considerably. Some authors measured the compositions of both phases along isotherms, for different pressures (e.g., Malinin, 1959; Todheide and Franck, 1963; Takenouchi and Kennedy, 1964). Others simply measured the total pressure of the system and the liquid phase composition along isotherms and somehow estimated y_2 (e.g., Ellis, 1959; Ellis and Golding, 1963; Nighswander et al., 1989). Thus, there are several sets of (x_2, y_2, T, P) and (x_2, T, P) data available. Furthermore, the ranges of pressures and temperatures covered by different authors vary widely. Due to the experimental difficulties involved, some

serious disagreements exist between some of these data sets. For example, Ellis and Golding (1963) found significant disagreement with Ellis' (1959) results, in the range 100 °C $< t < 300$ °C; and Takenouchi and Kennedy (1964) showed that their solubility data agree reasonably with that of Malinin (1959) but are differ significantly from those of Todheide and Franck (1963) for some isotherms.

As to the approximations used in (2) by different workers to infer the thermodynamic equivalent of Henry's law constant, four parameters must be examined: P_2 the partial pressure of CO₂, ϕ_2 , γ_2 , and the integral in eq. (2), which is called the Poynting correction.

Ellis (1959) and Ellis and Golding (1963) approximated P_2 as $(P - P_1^s)$; Nighswander et al. (1989) seem to have done the same (they do not state explicitly how they computed the partial pressure of CO₂). This is a good approximation when $y_1 \ll y_2$. However, for the H₂O-CO₂ system, y_1 varies in a complex way, from about 0.04 to about 0.92, for $110 \leq t \leq 350$ °C and $100 \leq P \leq 500$ bar (e.g., Takenouchi and Kennedy, 1964). Most other workers cited in Fig. 1 adopted the correct thermodynamic definition: $P_2 = y_2 P$.

For the CO₂ fugacity coefficient, several authors (Ellis, 1959; Ellis and Golding, 1963; Takenouchi and Kennedy, 1964; Malinin, 1974) adopted the Lewis fugacity rule that estimates the fugacity coefficient of a component in a gas mixture as the fugacity coefficient of the pure component at the same temperature and pressure of the mixture. Although this is a good approximation for any gas mixture at any pressure when the component is present in large excess (say $y_2 > 0.9$, e.g., Prausnitz, 1969), the range of compositions found at the temperatures and pressures of geothermal interest (see preceding paragraph) preclude its utilization for H₂O-CO₂ mixtures. Moreover, for components of significantly different molecular properties, such as H₂O and CO₂, the error introduced by the Lewis rule is often extremely large (Prausnitz, 1969). Zawisza and Malesińska (1981) computed ϕ_2 from a virial equation of state truncated after the second term, and their own measurements of the molar volume of the gas mixture. Nighswander et al. derived their fugacity coefficients from a Peng-Robinson equation of state for the gaseous mixture.

The activity coefficient γ_2 was taken equal to unity by all the authors cited in Fig. 1, with the exception of Malinin (1974). This last author adopted $\gamma_2 = \exp[A(1 - x_2^2)/RT]$, a standard approximation first derived by Krichevsky and Illinskaya (1945), where A is an empirical constant determined by the intermolecular forces in the solution. Whether or not γ_2 can be taken equal to unity is a matter best resolved by comparing the model with the data. More discussion on this below.

The Poynting correction was assumed negligible by Ellis (1959) and Ellis and Golding (1963); Takenouchi and Kennedy (1964) adopted the Krichevsky-Kasarnovsky (1935) formulation, which implies that ν_2^∞ does not depend on pressure; Zawisza and Malesińska (1981) assumed ν_2^∞ to be independent of pressure and temperature. Malinin (1974) showed that ν_2^∞ varies significantly with temperature and pressure, and used a (different) mean value of ν_2^∞ for each isotherm to approximate the Poynting correction. Nighswander et al. (1989) assumed ν_2^∞ inversely proportional to their measured liquid density, which resulted a function of T but independent of P (i.e., $\nu_2^\infty(T)$) and adopted the Krichevsky-Kasarnovsky approximation. Within the P-t range considered in this work (up to 350 °C and 500 bar), Malinin's data for ν_2^∞ result in values of the Poynting correction varying from negligible to more than 0.7. Thus, the value of the exponential factor in eq. (2) may be as high as about 2, and cannot be ignored. Moreover, the variability of ν_2^∞ with T and P is not accurately represented by Malinin's approach to compute the Poynting correction.

PROPOSED MODEL

The preceding discussion indicates that a main source of error for the earlier solubility models is the choice of the Lewis fugacity rule to estimate ϕ_2 . Fortunately, Spycher and Reed (1988) recently provided a way to compute reliable fugacity coefficients for H₂O-CO₂ mixtures, at temperatures and pressures of geothermal interest. We adopted their method, which is based on a virial equation of state for gas mixtures, that includes up to the third virial coefficient. The virial equation of state is the only one known to have a thoroughly sound theoretical foundation for pure and mixed gases (Mason and Spurling, 1969). Unlike empirical or semi-empirical equations of state, it does not require the introduction of hard-to-justify mixing rules. The inclusion of the third virial coefficient was required to accurately fit the experimental data (Spycher and Reed, 1988).

To preserve accuracy, Spycher and Reed considered two P-t ranges: one up to 350 °C and 500 bar, and the other from 450 °C to 1000 °C and up to 1000 bar. As our present goal relates to subcritical geothermal systems, this work incorporates only the lower range.

Appendix 1 presents the formulae and the necessary coefficients to compute ϕ_2 with this model.

Another significant source of error indicated by the discussion of the preceding section is the Poynting correction. As mentioned, Malinin (1974) demonstrated the dependence of ν_2^∞ on temperature and pressure (Fig. 2). The 300 kg cm⁻² isobar represents also the behavior of ν_2^∞ at lower pressures. To facilitate accurate computation of the Poynting correction, we correlated Malinin's results as described in Appendix 2. The lines of Fig. 2 demonstrate the resulting fit. This fit

is applied to compute the Poynting correction in our solubility model.

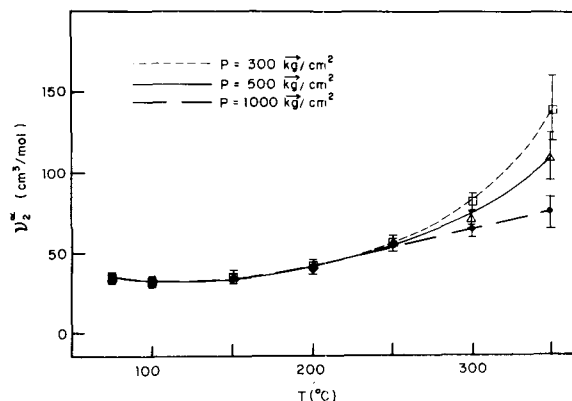


Fig. 2. Partial molar volume of CO₂ in liquid water, after Malinin (1974). The lines represent our fit.

The last important parameter in eq. (2) to be defined for our model is the activity coefficient. Our choice of more realistic fugacity coefficients and a more accurate way to account for the Poynting correction, promised significant improvements on earlier models of CO₂ solubility in water. Thus, we decided to first adopt the simplest approximation for the activity coefficient, i.e. $\gamma_2=1$, verify the consistency between the model and the data, and then decide whether a more involved approximation was necessary.

To complete the model, self-consistent values of $H_{2,1}(T)$ were needed. Replacing our fit for ν_2^∞ in eq. (2), integrating, taking logarithms and rearranging we obtained

$$\left[\log \left(\frac{\phi_2 Y_2 P}{X_2} \right) - AP^2 \right] - BP + C \quad (6)$$

where

$$A = \left[\frac{V_{300}(T)}{2 \cdot 2 \cdot 303 \cdot RT} \right] [\alpha T + \sigma] \quad (7)$$

$$B = \left[\frac{V_{300}(T)}{2 \cdot 303 \cdot RT} \right] [\alpha T + \sigma] \quad (8)$$

$$C = \log H_{2,1} - [AP_1^2 + B(P_1^2)^2] \quad (9)$$

Note that A , B and C depend only on temperature. Equation (6) is similar to that used by most authors to compute values of $H_{2,1}(T)$ from phase equilibrium data measured along isotherms. The left term is computable from experimental data and, in our case, Spycher and Reed's fugacity coefficients (Appendix 1). The right term is a linear function of pressure along isotherms. B , the slope, is a known quantity in our model. From C , the intercept, one infers the values of $H_{2,1}(T)$ for the available experimental isotherms.

We processed 11 isotherms from Malinin (1959), Todheide and Franck (1963) and Takenouchi and Kennedy (1964), that span the ranges $110 \leq t \leq 350$ °C and $P \leq 500$ bar. We selected isotherms for which there were at least 3 (x_2 , y_2 , P , T) data points. The intercepts were obtained from least square fits, constrained by our knowledge of B (eq. (8)). Our fits (Fig. 3) are satisfactory. In particular, they do not present the severe lack of linearity evidenced by Malinin's (1974) and Takenouchi and Kennedy's (1964) results in the lower pressure range. Moreover, the agreement between model and data indicates that the assumption of ideal solution (i.e., $\gamma_2=1$) was warranted. In all, the tight fit obtained with our model indicates that the complexities of H_2O - CO_2 phase equilibrium are well represented by it.

Figure 4 compares our results for $H_{2,1}(T)$ with those of previous work. Clearly, our values are significantly lower than the rest, for $110 < t \leq 325$ °C. Two main factors are responsible for this behavior. First, our fugacity coefficients differ significantly from the pure-gas coefficients of Majumdar and Roy (1956) adopted by Takenouchi and Kennedy and by Malinin (Figs. 5-6). Second, our values of the Poynting correction are significantly greater than those of Malinin (1974), for $t > 250$ °C and $P > 300$ bar, due to Malinin's averaging of the partial molar volumen to approximate the integral. The interplay between these two factors explains why our $H_{2,1}(T)$ results are lower. According to eq. (2), $H_{2,1}(T)$ is proportional to ϕ_2 and inversely proportional to the exponential of the Poynting integral. Thus, for $t < 250$ °C, our smaller values of ϕ_2 tend to result in lower values of $H_{2,1}$, while for $t > 250$ °C happens the opposite. On the other hand, our greater values of the Poynting correction have the effect of decreasing the values of $\log(f_2^G/x_2) - AP^2$ within the ranges of t and P just mentioned, which, in turn, tends to drag the values of the intercept C (and therefore, those of $H_{2,1}$) downwards in our model, due to the constraint imposed by the known values of the slope B . Thus, our results tend to be significantly smaller than Malinin's for $t \leq 250$ °C and grow closer to them for higher temperatures (Fig. 4).

To complete our formulation we wanted to fit our $H_{2,1}$ results with a convenient expression. As shown in Fig. 4, there is good agreement on the values of $H_{2,1}$ for $t \leq 100$ °C. Thus we fitted the low-temperature results of other workers and our own results for $t > 100$ °C by

$$H_{2,1}(t) = H_0 + H_1 t + H_2 t^2 + H_3 t^3 + H_4 t^4 + H_5 t^5 \quad (10)$$

where

$$H_0=666.128, \quad H_1=37.084, \quad H_2=0.325222 \\ H_3=-4.27297 \cdot 10^{-3}, \quad H_4=1.34383 \cdot 10^{-5}, \quad H_5=-1.3431 \cdot 10^{-8}$$

The resulting fit is presented in Fig. 7.

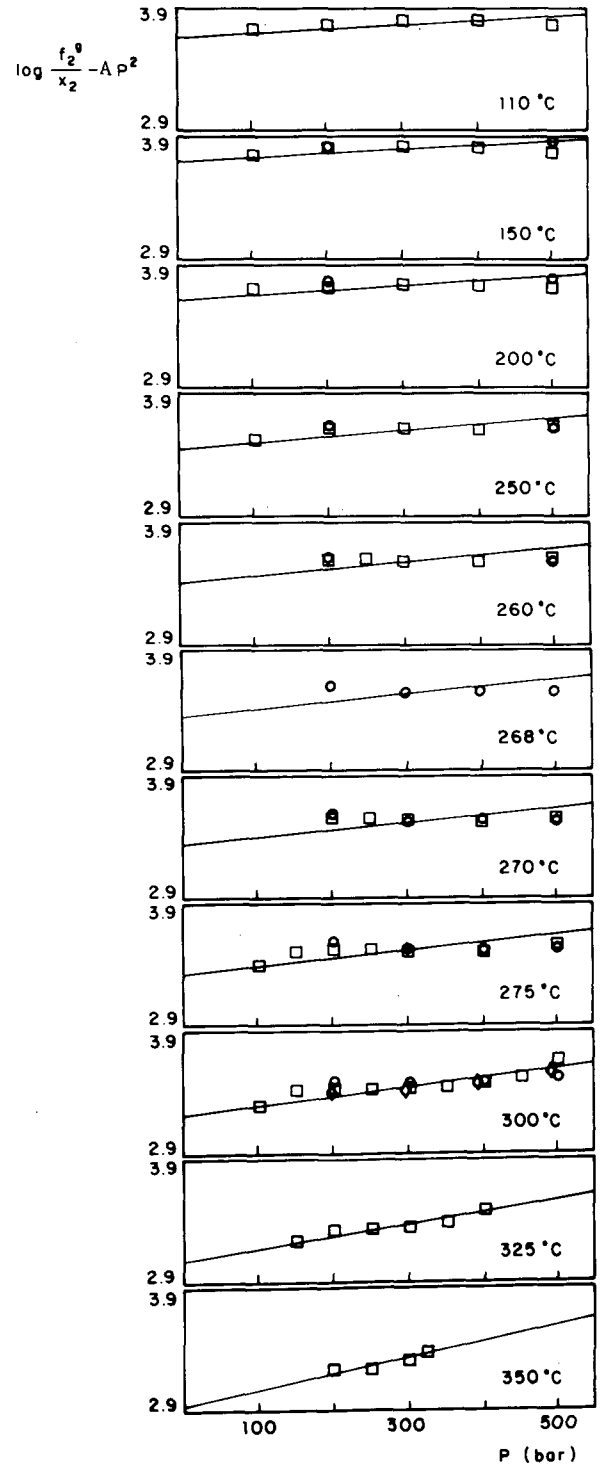


Fig. 3.

Our fits to phase equilibrium data for the H_2O - CO_2 system.

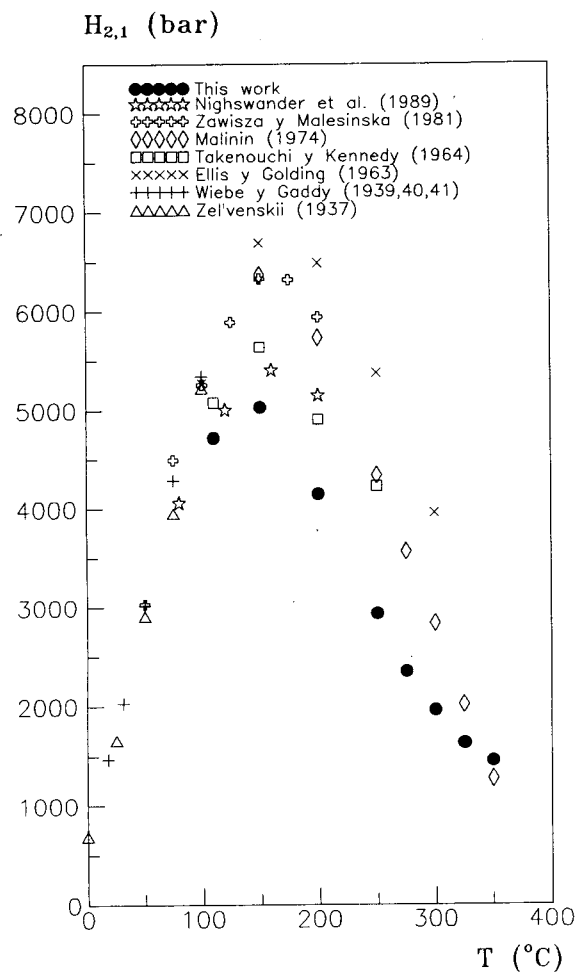


Fig. 4. Comparison of our results with previous ones.

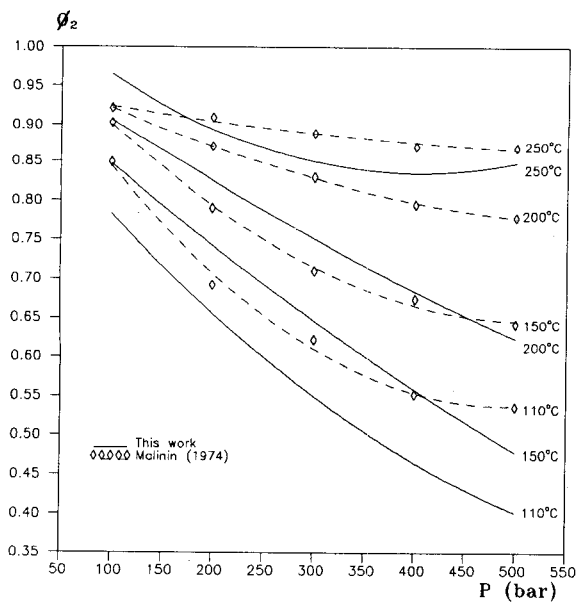


Fig. 5. Comparison of our fugacity coefficients with Majumdar and Roy's (1956) for pure CO₂, used in most previous work.

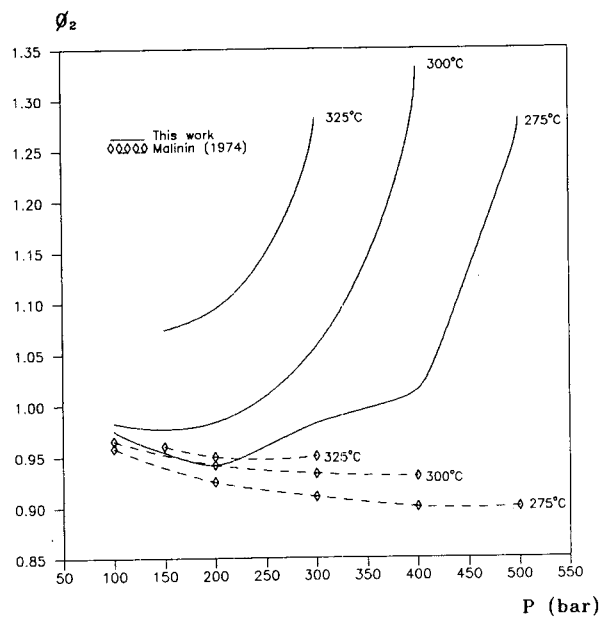


Fig. 6. Comparison of our fugacity coefficients with Majumdar and Roy's (1956) for pure CO₂, used in most previous work.

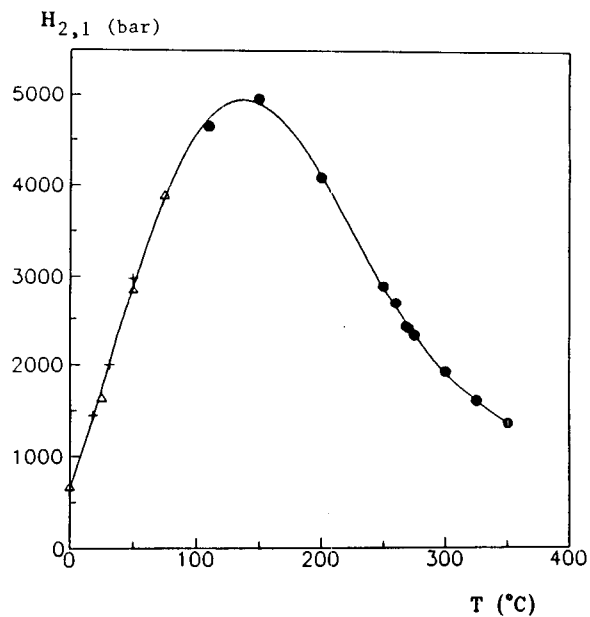


Fig. 7. Fit of expression (10) to our results for H_{2,1}.

SUMMARY AND CONCLUSIONS

We present a thermodynamically correct model for the solubility of carbon dioxide in water. Previous models rely on more-or-less crude approximations to represent the fugacity coefficient of CO₂ in the gas phase. Unlike them, we adopted a formulation that realistically accounts for the non-ideal behavior of both components and that of the mixture, within the P-T range considered. Furthermore, our model accounts accurately for the effects of temperature and pressure, in integral form, in the Poynting correction.

The proposed model fits the available phase equilibrium data for the H₂O-CO₂ system nicely. In particular, it does not present the severe conflict between the linearity of the model and the lack of linearity of the data, evident in earlier models. The tight fit obtained with our model indicates that the complexities of H₂O-CO₂ phase equilibrium are well represented by it.

Our model provides a thermodynamically correct, accurate and straightforward way to compute the effects of CO₂ in geothermal flows, for numerical reservoir and wellbore simulators.

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APPENDIX 1

Equations (11)-(18) allow accurate computation of the fugacity coefficient for carbon dioxide in H₂O-CO₂ gaseous mixtures, up to 350 °C and 500 bar (Spycher and Reed, 1988). T is in °K and P is in bar.

$$\ln \phi_2 = (2Y_1B_{21} + 2Y_2B_{22} - B_{mez})P + (3Y_1^2C_{211} + 6Y_1Y_2C_{221} + 3Y_2^2C_{222} - 2C_{mez})\frac{P^2}{2} \quad (11)$$

$$B_{11} - B_{22} = a/T^2 + b/T + c \quad (12)$$

$$C_{111} - C_{222} = d/T^2 + e/T + f \quad (13)$$

$$B_{12} - B_{21} = a_{12}/T^2 + B_{12}/T + c_{12} \quad (14)$$

$$C_{112} - C_{211} - C_{121} = d_{112}/T^2 + e_{112}/T + f_{112} \quad (15)$$

$$C_{122} - C_{221} - C_{212} = d_{122}/T^2 + e_{122}/T + f_{122} \quad (16)$$

$$B_{mez} = Y_1^2B_{11} + 2Y_1Y_2B_{12} + Y_2^2B_{22} \quad (17)$$

$$C_{mez} = Y_1^3C_{111} + 3Y_1^2Y_2C_{112} + 3Y_1Y_2^2C_{122} + Y_2^3C_{222} \quad (18)$$

Table 1 provides the values of the coefficients *a* through *f* required to compute *B_{ii}* and *C_{iii}*. Table 2 presents the values of the remaining coefficients.

Table 1. Constants for pure components (after Spycher and Reed, 1988)

Gas	Range of T (°C)	P _{max} (bar)	a	b	10 ⁵ c	10 ² d	10 ⁵ e	10 ⁸ f
H ₂ O	0-340	saturation	-6191.41	14.8528	-914.267	-6633.26	18277.00	-13274.00
CO ₂	50-350	500	-1430.87	3.5980	-227.376	347.64	-1042.47	846.27

Table 2. Constants for cross virial coefficients (after Spycher and Reed, 1988).

a ₁₂	b ₁₂	10 ² c ₁₂	d ₁₁₂	10 ² e ₁₁₂	10 ⁵ f ₁₁₂	d ₁₂₂	10 ² e ₁₂₂	10 ⁵ f ₁₂₂
-1954.7	7.74805	-1.02901	104.453	-38.4283	36.5858	-8.28426	1.19097	0.808886

APPENDIX 2

We fitted Malinin's (1974) partial molar volume results as follows:

$$v_{300}(T) = \exp(154.7881 - 3582.4521 T^{-1} - 26.775773 \ln T + 0.045234908 T) \quad (19)$$

where T is absolute temperature,

$$v_2^*(P, T) = v_{300}(T) \quad (20)$$

for $P \leq 300 \text{ Kg/cm}^2$ and $T \leq 523.15 \text{ K}$, and

$$v_2^*(P, T) = v_{300}(T)(a_P T + b_P) \quad (21)$$

for $P > 300 \text{ kg/cm}^2$ and $T > 523.15 \text{ K}$, with

$$a_P = \alpha P + \beta \quad b_P = \sigma P + \delta \quad (22)$$

where

$$\begin{aligned} \alpha &= -6.387005 \times 10^{-6}, & \beta &= 1.638605 \times 10^{-3} \\ \sigma &= 3.387074 \times 10^{-3}, & \delta &= 1.239184 \times 10^{-1} \end{aligned}$$