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Hydrogen Component Fugacities in Binary Mixtures with Carbon Dioxide: Pressure Dependence

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The fugacity coefficients of hydrogen in binary mixtures with carbon dioxide were measured isothermally using a physical equilibrium technique. This technique involves the use of an experimental chamber which is divided into two regions by a semipermeable membrane. Hydrogen can penetrate and pass through the membrane, while carbon dioxide cannot. During the approach to equilibrium, the pressure of pure hydrogen on one side of the membrane approaches the partial pressure of hydrogen in the mixture on the other side of the membrane. This allows a direct measurement of the hydrogen component fugacity at a given mixture mole fraction. In this study, results are reported for measurements made on the hydrogen + carbon dioxide binary at 130°C (403 K), with total mixture pressure of 3.45, 5.17, 8.62, 10.34, and 13.79 MPa. General trends in the experimental results are discussed, and comparisons are made with predictions from the Redlich–Kwong, Peng-Robinson, and extended corresponding-states models.

KEY WORDS: carbon dioxide; fugacity; high pressure; hydrogen; hydrogen + carbon dioxide binary system; mixtures.

1. INTRODUCTION

Fugacity is a very important thermodynamic function for the characterization of gaseous mixtures. This is especially true for industrially important mixtures for which a predictive capability is necessary for the engineering community. The fugacity of individual components of a mixture can, in principle, be calculated from an applicable equation of state (if the *PVT* surface of the gas is known in the region of interest) using, for example,

$$\ln f_i = \ln Px_i + \int_0^P (V_i/RT - 1/P)\, dP \tag{1}$$

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where f_i is the fugacity of component i, x_i is its mole fraction, V_i is its partial molar volume, P is the total pressure of the mixture, T is the temperature, and R is the gas constant. The need for a great deal of accurate *PVT* data for the mixture and limitations inherent in the application of many of the common equations of state to mixtures makes this approach time-consuming and difficult in many, if not most, cases. In the special case of gaseous mixtures containing hydrogen as one component, the physical equilibrium method provides a vast experimental simplification [1]. The problem of measuring the properties of a mixture is reduced to that of measuring the properties of a pure gas. A detailed description of the technique can be found elsewhere [2], so only a brief description is provided here.

An experimental chamber (usually a pressure vessel) is divided into two regions by a membrane which is permeable only to hydrogen. The membrane most often takes the form of a palladium–silver alloy [Pd, 75%; Ag, 25% (by weight)] fabricated into the form of a long section of tubing. If one side of the membrane is charged with a gaseous mixture (of which hydrogen is a component) and the other side is initially evacuated, an equilibrium will eventually be established between the two sides of the membrane, with hydrogen gradually entering the evacuated space. The approach to equilibrium is driven by the need to equalize the chemical potential of hydrogen on either side of the membrane. When equilibrium is actually reached in the system, the fugacity of hydrogen on both sides of the membrane must be equal [3–6].

Using appropriate instrumentation (which is described fully in the next section) the hydrogen partial pressure, P_{H_2}, and the mixture total pressure (outside the membrane), P_m, may be measured at a given temperature T and hydrogen mole fraction x_{H_2}. From these measurements, the component fugacity of hydrogen can be computed. At moderate pressures this can be determined using the pressure expansion of the virial equation of state (truncated after the third virial coefficient)

$$\ln \hat{\phi}_{H_2} = \left(\frac{B}{R}\right)\left(\frac{P_{H_2}}{T}\right) + \left(\frac{C - B^2}{2R^2}\right)\left(\frac{P_{H_2}^2}{T^2}\right) \tag{2}$$

where B and C are the second and third virial coefficients, respectively, and $\hat{\phi}_{H_2}$ is the fugacity coefficient of pure hydrogen inside the membrane. To determine the fugacity of (pure) hydrogen, $\hat{f}_{H_2}$, we apply the definition of the fugacity coefficient

$$\hat{f}_{H_2} = \hat{\phi}_{H_2} P_{H_2} \tag{3}$$

Recalling that pressure measurements are made when the system has reached equilibrium (that is, no net change in pressure with time on either side of the membrane), the fugacity of hydrogen must be the same on both sides of the membrane. Thus, the fugacity coefficient of hydrogen in the mixture follows from Eq. (3):

$$\hat{f}_{H_2} = f_{H_2} = x_{H_2} P_m \phi^m_{H_2} \tag{4}$$

where f_{H_2} and $\phi^m_{H_2}$ are the fugacity and fugacity coefficient, respectively, of hydrogen in the mixture.

In a previous study, fugacity coefficients of hydrogen in binary mixtures with carbon dioxide were measured (as a function of composition) at several temperatures [7]. In this paper, measurements (made at 130°C) of the fugacity coefficients of hydrogen in this system are reported at several pressures. This system was chosen for study because of the industrial importance of this mixture. The fugacity coefficient data obtained in this work were compared with several equation-of-state approaches, in order to assess the predictive capability of these equations. The equations of state considered were the simple, unmodified Redlich–Kwong equation, the Peng–Robinson equation, and an extended corresponding-states approach. These theoretical and computational methods have been described is detail elsewhere [6].

2. EXPERIMENTAL

The apparatus used in the present work is shown schematically in Fig. 1. It is similar to the instrument used earlier [2], except for a substantial modification to the pressure measurement system. The differential pressure transducer and deadweight pressure balance used previously have been replaced by an evacuable precision Boudon tube transducer. This modification was required since the differential pressure transducer causes a pressure disruption (in the pure hydrogen side of the membrane) at the beginning of a pressure measurement. This disruption is insignificant at pressures of up to approximately 5 MPa. At higher pressures, however, the disturbance to the physical equilibrium is quite serious and causes stable pressure readings to be unobtainable. The Bourdon tube causes no pressure disturbance during measurement and allows much faster measurements to be made. It should be noted that the use of the Bourdon tube (which was calibrated using the deadweight pressure balance) results in a slight sacrifice of accuracy in the pressure measurements. The Bourdon tube is accurate to within 0.05% in the pressure region of interest, while the deadweight instrument was accurate to 0.015%. The hydrogen and car-

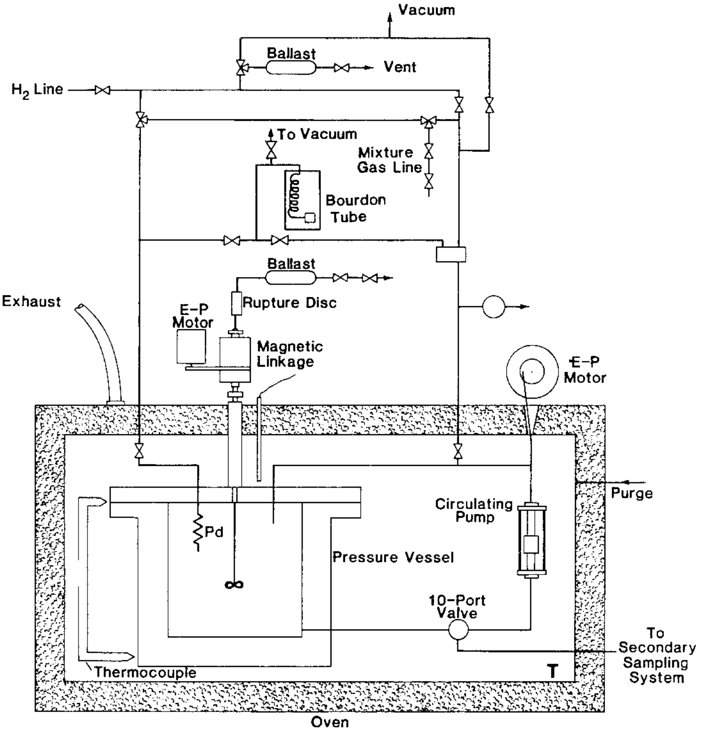

Fig. 1. Schematic diagram of the experimental apparatus.

bon dioxide used in this work were research grade (99.99% purity or better), and no impurities were detected (down to 1 ppm) using subambient-temperature gas chromatography.

Measurements of the hydrogen partial pressure, P_{H_2}, and the mixture total pressure, P_m, were accomplished using the same manifold system as in previous studies [2, 6–7]. Temperature measurements were made using a quartz crystal oscillator sensor accurate to ±0.009°C. Quantitation of the components of the mixture was done using a developmental gas chromatograph and sampling-injection system [8]. The thermal conductivity detector response of carbon dioxide was calibrated using the external standard method [9]. Carbon dioxide was chosen for analysis to allow the use of helium as the carrier gas. This is advantageous since the thermal conductivity detector is extremely sensitive to carbon dioxide in a helium carrier stream. Another advantage results from the compressibility of helium, since a minimal pressure pulse is observed upon sample injection. The hydrogen mole fraction was then obtained from that of carbon dioxide.

The chromatographic separations (for both the calibration and the actual fugacity measurements) were done using a packed column (2-m length, 0.32-cm o.d.) of Porapak-QS,[2] of 150 to 200 mesh. The column was maintained isothermally at $80.00 \pm 0.02°C$, with a carrier gas flow rate of $35\ \mathrm{ml \cdot min^{-1}}$. The separation under these conditions is very favorable to precise quantitation. Baseline resolved peaks of reasonable width, convenient retention time, and excellent symmetry are obtained easily.

3. THEORETICAL COMPARISONS

At high pressures such as those encountered in this work, equations of state provide the simplest avenue to obtaining predicted component fugacities. Given the equation of state as a function of volume, temperature, and composition, one must evaluate the integral of Eq. (1).

There are two common approaches to applying this equation, one involving cubic equations of state, which incorporate mixing rules on the equation-of-state parameters for the pure fluids, and the other being the extended corresponding-states theory (EXCST), which uses a reference-fluid equation of state and the conformal solution principle. In this study we have applied both of these methods, which have been described in detail previsously [6].

As an example of a cubic equation of state, we have used the popular Peng–Robinson [5] modification of the Redlich–Kwong equation. For comparative purposes, and as a matter of interest, fugacity coefficients were also calculated using the simple, unmodified Redlich–Kwong equation.

4. RESULTS AND DISCUSSION

Experimentally determined values of the component fugacity coefficients of hydrogen in carbon dioxide, $\phi^{\mathrm{m}}_{\mathrm{H_2}}$, at 130°C (403.15 K), at pressures of 3.45, 5.17, 8.62, 10.34, and 13.79 MPa are presented in Table I. A plot of the measured values of $\phi^{\mathrm{m}}_{\mathrm{H_2}}$ versus the hydrogen mole fraction $x_{\mathrm{H_2}}$ for each pressure is shown in Fig. 2. A typical error bar (in the box at the lower left) illustrates the uncertainty (1 SD) of a $\phi^{\mathrm{m}}_{\mathrm{H_2}} - x_{\mathrm{H_2}}$ pair for an equimolar mixture of hydrogen in carbon dioxide. Error bars for mixtures of lower hydrogen mole fraction are necessarily larger due to lower precision in the quantitation at lower hydrogen concentrations. The details

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[2] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table I. Hydrogen + Carbon Dioxide at 130°C (403 K)

x_{H_2}	$\phi^{m}_{H_2}$
$P_m = 3.45$ MPa	
0.309	1.123
0.487	1.054
0.607	1.034
0.754	1.022
0.800	1.019
0.927	1.020
$P_m = 5.17$ MPa	
0.366	1.082
0.593	1.047
0.697	1.038
0.787	1.031
0.858	1.027
0.898	1.027
$P_m = 8.62$ MPa	
0.323	1.193
0.518	1.120
0.602	1.092
0.680	1.075
0.738	1.055
0.787	1.053
0.831	1.049
$P_m = 10.34$ MPa	
0.570	1.121
0.761	1.065
0.825	1.058
0.859	1.055
0.888	1.052
0.909	1.051
$P_m = 13.79$ MPa	
0.547	1.151
0.644	1.121
0.709	1.105
0.822	1.082
0.859	1.076
0.889	1.073
0.919	1.070
0.936	1.067

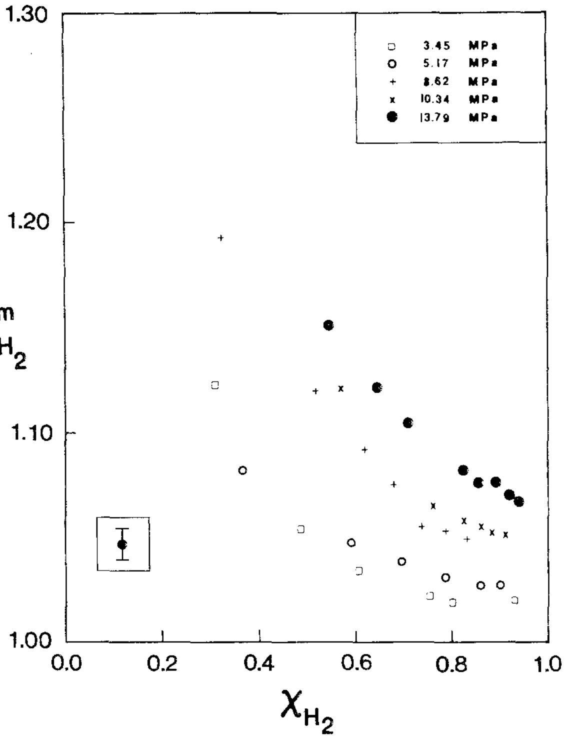

Fig. 2. Plot of hydrogen component fugacity coefficient, $\phi^m_{H_2}$, versus hydrogen mole fraction, x_{H_2}, for isobar studies.

of the error analysis have been provided elsewhere and are not reproduced here [2]. Plots of $\phi^m_{H_2}$ versus x_{H_2} for each isobar are provided in Figs. 3 through 7.

Before examining the agreement of the experimental values of the fugacity coefficient with those predicted using the equations of state, some general qualitative observations are in order. Examination of Fig. 2 shows that at constant temperature, an increase in pressure results in an increase in the component fugacity coefficients (for a given mixture mole fraction). This is expected since a higher degree of nonideality is expected in the mixture at the higher pressures. It should also be observed that the change in the value of $\phi^m_{H_2}$ with the mole fraction at a given pressure is more pronounced at lower values of the hydrogen mole fraction. This observation is consistent with equations-of-state predictions for a low molecular weight gas (at a relatively high reduced temperature) in a binary mixture with a heavier gas. This same general behavior has been observed in previous studies done with this apparatus on binary mixtures of hydrogen with propane, methane, and carbon dioxide [6, 7].

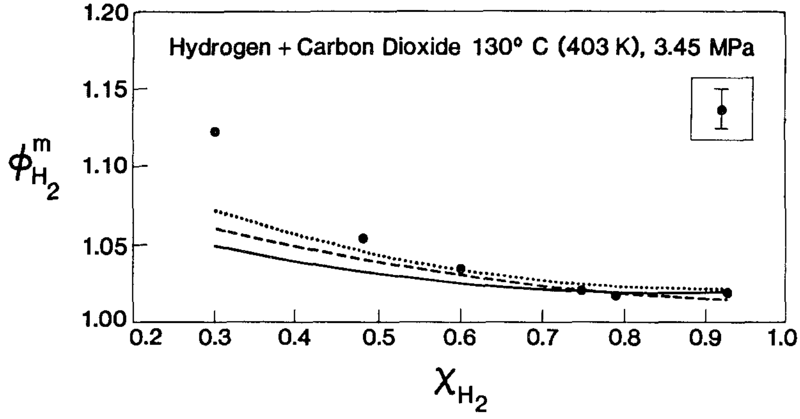

Fig. 3. Plot of $\phi_{H_2}^m$ versus x_{H_2} at a total mixture pressure of 3.45 MPa. Solid line, Redlich–Kwong equation; dashed line, Peng–Robinson equation; dotted line, extended corresponding-states approach.

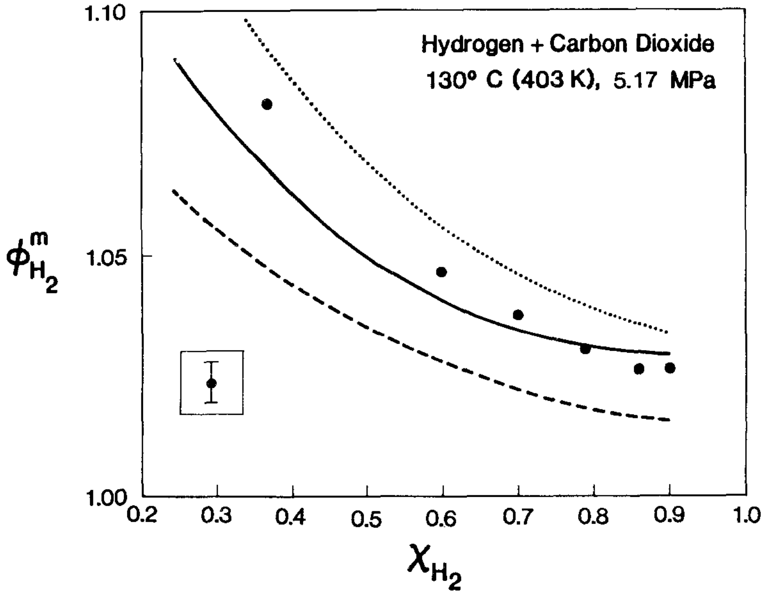

Fig. 4. Plot of $\phi_{H_2}^m$ versus x_{H_2} at a total mixture pressure of 5.17 MPa. Solid line, Redlich–Kwong equation; dashed line, Peng–Robinson equation; dotted line, extended corresponding-states approach.

In Figs. 3 through 7, the measurements made in this study are represented as filled circles. Values calculated using the simple Redlich–Kwong equation are represented by solid lines, values calculated using the Peng–Robinson equation are represented by dashed lines, and values predicted using the extended corresponding-states approach are represented by dotted lines. The value of the acentric factor for hydrogen was taken to be -0.22, which was determined by vapor–liquid equilibrium studies (vapor pressure measurements of the pure materials) [10]. It can be seen that all three of these theoretical approches can predict the measured fugacity coefficient values generally to within 3% over most of the mole fraction ranges of these studies (the error bars shown in the boxes are for equimolar mixtures of hydrogen–carbon dioxide). In each plot, the agreement seems to be worst in the low hydrogen mole fraction range. This is expected due to the greater uncertainty in mixture quantitation in the low mole fraction range. The higher error at low hydrogen concentrations has been a problem in all measurements of this type [6, 7].

Surprisingly, the best predictions at each pressure are obtained using the simple Redlich–Kwong equation and the extended corresponding-states

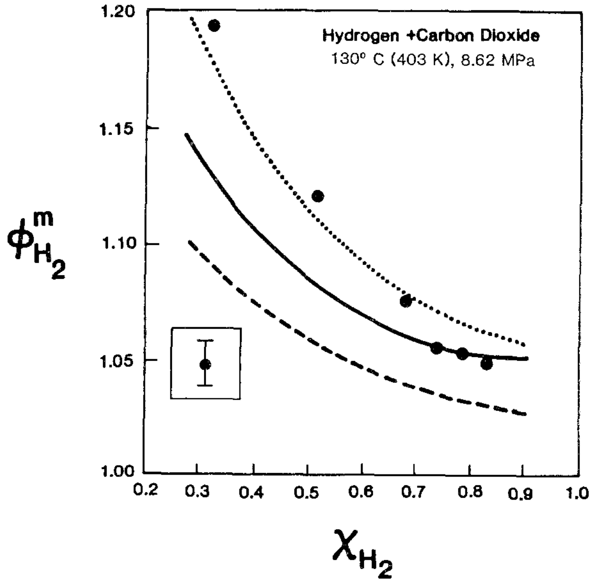

Fig. 5. Plot of $\phi^m_{H_2}$ versus x_{H_2} at a total mixture pressure of 8.62 MPa. Solid line, Redlich–Kwong equation; dashed line, Peng–Robinson equation; dotted line, extended coresponding-states approach.

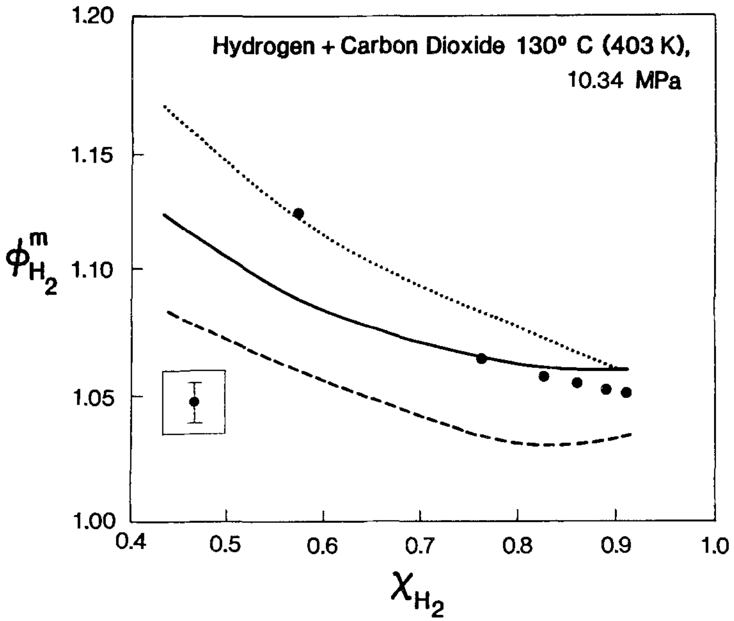

Fig. 6. Plot of $\phi^{\mathrm{m}}_{\mathrm{H}_2}$ versus x_{H_2} at a total mixture pressure of 10.34 MPa. Solid line, Redlich–Kwong equation; dashed line, Peng–Robinson equation; dotted lines, extended corresponding-states approach.

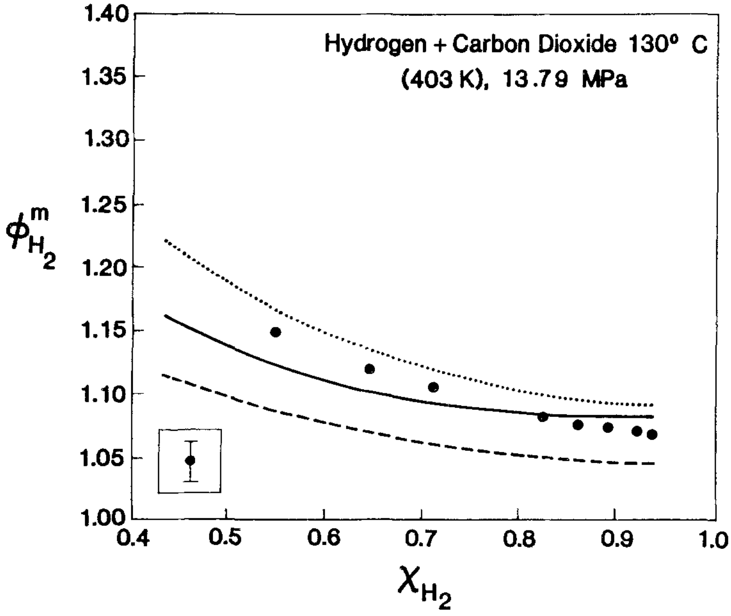

Fig. 7. Plot of $\phi^{\mathrm{m}}_{\mathrm{H}_2}$ versus x_{H_2} at a total mixture pressure of 13.79 MPa. Solid line, Redlich–Kwong equation; dashed line, Peng–Robinson equation; dotted line, extended corresponding-states approach.

approach. The Peng–Robinson equation consistently predicts values which are too low. In a previous study on the hydrogen + carbon dioxide system (in which data were collected at several temperatures with a constant mixture pressure of 3.45 MPa [7]), the Peng–Robinson equation gave a more accurate representation of the experimental data. In that study, the Redlich–Kwong equation provided the worst predictions. It is possible that the Peng–Robinson equation has some difficulty in accounting for the increased nonidealities at higher pressures. As in previous work on hydrogen mixtures with this type of equation, extensive parameter adjustment is often required in order to provide reasonable agreement [11].

5. CONCLUSIONS

Hydrogen component fugacity coefficients for the hydrogen + carbon dioxide gaseous binary system were measured as a function of mole fraction and total pressure at 130°C (403 K). The experimental data were used to evaluate the predictive capability of three equation of state approaches. The equations of state employed were the unmodified Redlich–Kwong equation, the Peng–Robinson equation, and the extended corresponding-states approach. All three of these equations predict fugacity coefficient values which are within or nearly within the experimental error of the measured data. The extended corresponding-states approach and the simple Redlich–Kwong equation appear to give the best predictions. At lower hydrogen concentrations, the deviations become larger, as expected.

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