International Journal of Thermophysics, Vol. 7, No. 5, 1986

Hydrogen Component Fugacities in Binary Mixtures with Carbon Dioxide

T. J. Bruno[1] **and G. L. Hume**[1]

Received October 9, 1985

The fugacity coefficients of hydrogen in binary mixtures with carbon dioxide were measured 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 the other component (in this case carbon dioxide) cannot. At equilibrium, pure hydrogen will permeate into one "compartment" of the chamber, while the binary mixture occupies the other compartment. Thus, 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 the 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 80°C (353 K), 130°C (403 K), 160°C (433 K), and 190°C (463 K), each at a total mixture pressure of 3.45 MPa. The experimental results are compared with predictions from the Redlich–Kwong, Peng–Robinson, and extended corresponding-states models.

KEY WORDS: carbon dioxide; fugacity coefficients; fugacity measurements; gas chromatograph; gas mixtures; hydrogen.

1. INTRODUCTION

Fugacity is an important thermodynamic function for the characterization of gas mixtures [1–3]. This is especially true for industrially important mixtures, for which a predictive capability is highly desirable. The fugacity of individual components of a mixture can, in principle, be calculated from an equation of state (if the P–V–T surface of the gas is known in the region of interest) using

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

---

[1] Thermophysics Division, National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

The need for a great deal of very accurate P–V–T data for the mixture and limitations inherent in the application of the equations of state to mixtures makes this approach less than favorable in many, if not most, cases. In the special case of gaseous mixtures containing hydrogen as a component, the physical equilibrium method provides a vast experimental simplification [4, 5]. The problem of measuring the properties of a mixture is reduced to that of measuring the properties of a pure gas. It is especially favorable in the case of a well-studied gas such as hydrogen. A detailed description of the technique is given elsewhere [5, 6], so only a brief outline is provided here.

An experimental chamber (such as a pressure vessel) is divided into two regions by a membrane which is permeable only to hydrogen. The membrane is invariably in the form of a metal (usually a palladium alloy) tube or thimble [7, 8]. If one side of the membrane (in the pressure vessel) 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. The approach to equilibrium is driven by the need to equalize the chemical potential of hydrogen on either side of the membrane. At equilibrium, the pressure of pure hydrogen on one side of the membrane will equal the partial pressure of hydrogen in the mixture on the other side of the membrane. At this point, the fugacity of hydrogen on both sides of the membrane must be equal [3].

Using appropriate instrumentation, the hydrogen partial pressure, P_{H_2}, and the mixture total pressure, P_M, may be measured at a given temperature T and a given mixture hydrogen mole fraction x_{H_2}. From these measurements, the component fugacity of hydrogen can be calculated. It is usually more convenient to deal with a dimensionless quantity called the fugacity coefficient, ϕ_i, defined by

$$\phi_i = f_i/(x_i P_i) \tag{2}$$

where $\hat{f}_i$ is the fugacity of component i, x_i is its mole fraction, and P_i is its ptressure. The fugacity coefficient of this individual pure substance (in the present case, hydrogen) can be determined using the virial equation truncated after the third virial coefficient:

$$\ln \phi_{H_2} = \frac{B}{R}\left(\frac{P_{H_2}}{T}\right) + \frac{C - B^2}{2R^2}\left(\frac{P_{H_2}^2}{T^2}\right) \tag{3}$$

where R is the gas constant, B and C are the second and third virial coefficients, and T is the temperature. The above quantity is for pure hydrogen only, at pressure P_{H_2}. Clearly, P_{H_2} is necessarily lower than P_M, due to the presence of the second component in the binary mixture. To determine the fugacity coefficient of hydrogen in the mixture, we apply the defining equation for the fugacity coefficient:

$$\phi^{m}_{H_2} = f_{H_2}/x_{H_2}P_M \tag{4}$$

to obtain

$$\hat{f}_{H_2} = f_{H_2} = X_{H_2}P_m\phi_{H_2} \tag{5}$$

where ϕ_{H_2} is given by Eq. (2).

In this paper, measurements of the fugacity coefficients of hydrogen in binary mixtures with carbon dioxide are reported. This series of mixtures was chosen for study because of the industrial importance of this system. Mixtures of this type are found in the effluent of hydrocracking and hydrotreating plants. They are also important as synthetic chemical feedstocks. Due to the presence of these mixtures in natural deposits, fugacity measurements are also of importance to the geologist [9].

The fugacity coefficient data obtained in this work were compared with several equation-of-state approaches, in order to assess their predictive capability. The equations of state considered were the simple, unmodified Redlich–Kwong equation, the Peng–Robinson equation, and an extended corresponding-states approach. These methods have been described in detail elsewhere [6].

2. EXPERIMENTAL

The apparatus used in the present work is the same as was used in previous studies [5, 6], with only minor modifications. The hydrogen and carbon dioxide used were research grade (99.99% purity or better), and no impurities were detected (down to 1 ppm) using gas chromatography.

Due to the elevated temperatures and pressures at which fugacity measurements were desired and the presence of the palladium alloy (Pd/Ag, 75/25) in the experimental chamber, the possibility of chemical reaction of the mixtures being studied was very real. This possibility was addressed before any fugacity measurements were attempted, using a high-temperature high-pressure reaction screening apparatus designed specifically for this purpose [10]. Representative samples of the hydrogen + carbon dioxide binary were maintained in contact with the palladium alloy at experimental conditions. These experimental conditions of pressure, temperature, and residence time were similar to the conditions under which the fugacity measurements were to be made. These residence times were between 200 and 250 h, which is typically the time required for the completion of an isotherm. The test mixtures, after being maintained under the appropriate conditions, were then analyzed using gas chromatography and combined gas chromatography and mass spectroscopy.

After 200 h at 220°C (493 K) and 3.45 MPa, an approximately equimolar mixture of hydrogen + carbon dioxide showed evidence of extensive reaction or decomposition. Water and carbon monoxide were detected in amounts of 0.5 and 1.0%, respectively. At 200°C (473 K), with approximately the same residence time, water was found at a mole percentage of 0.3, and carbon monoxide at 0.4%. Tests at lower temperatures revealed no evidence of appreciable reaction. Thus, a maximum temperature of 190°C (463 K) was chosen for these experiments. As an additional precaution, the residence time for the 190°C (463 K) isotherm was effectively reduced by venting and evacuating the pressure vessel after each run and recharging the vessel with new sample for the subsequent measurement. By observing these guidelines, no impurities could be detected down to 5 ppm in the chromatographic determinations of the mole fractions of hydrogen.

Measurements of the hydrogen partial pressure, P_{H_2}, the mixture total pressure, P_M, and the system temperature were done using the same methods as in previous studies [5, 6]. Quantitation of the components of the mixture was done using a developmental gas chromatograph and sampling/injection system [11]. The thermal conductivity detector response of carbon dioxide was calibrated using the external standard method [12, 13]. Carbon dioxide was chosen for analysis to allow the use of

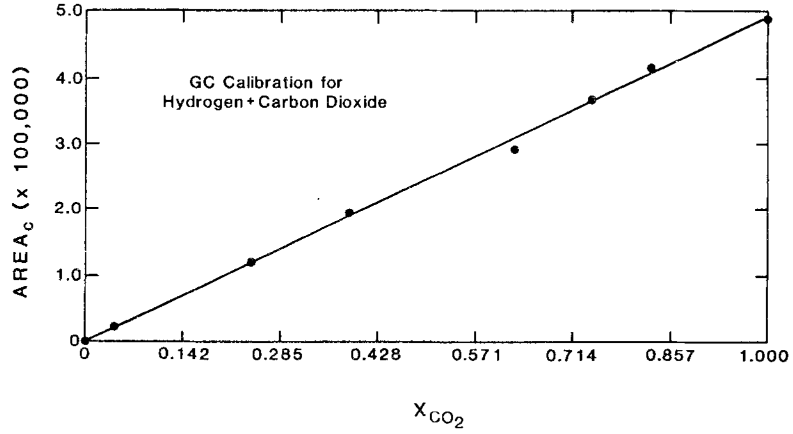

Fig. 1. Chromatographic calibration for hydrogen + carbon dioxide.

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 induced upon sample injection. To apply the external standard method, standard mixtures of hydrogen + carbon dioxide were prepared gravimetrically. The area response as logged by an electronic integrator was normalized by correcting for atmospheric pressure changes. The calibration curve obtained for this system is shown in Fig. 1. The data were fitted to a second-degree polynomial, with the resulting overall error being 0.2%. 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 in length, 0.3-cm o.d.) of Porapak-QS,[2] of 150 to 200 mesh. The column was maintained isothermally at 80.00 ± 0.02 K. The separation under these conditions is very favorable to precise quantitation. Baseline resolved peaks of reasonable width, convenient retention times, 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

$$RT\ln\left(\frac{f_i}{x_i p}\right)=\int_0^{\rho}\left[\left(\frac{\partial p}{\partial n_i}\right)_{T,\rho,n_j\neq 1}-\rho RT\right]\frac{d\rho}{\rho^2}-RT\ln Z \qquad (6)$$

In this equation R is the gas constant, T is the absolute temperature, f_i is the fugacity of component i in the mixture, x_i is the concentration of component i, ρ is the density, and Z is the compressibility factor $p/\rho RT$.

There are two common approaches to applying this relation, 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 a conformal solution principle. In this study we

---

[2] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify 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 80°C (353 K) and a Total Pressure of 3.45 MPa

Mole fraction, H_2	Fugacity coefficient, $\phi^m_{H_2}$
0.1670	1.203
0.4474	1.072
0.5806	1.045
0.6341	1.042
0.6907	1.035
0.7775	1.011
0.7824	1.024

have applied both of these methods, which have been described in detail previously [6].

As an example of a cubic equation of state we have used the popular Peng–Robinson [3] modification of the Redlich–Kwong equation. For comparative purposes, fugacity coefficients were also calculated using the simple, unmodified Redlich–Kwong equation.

4. RESULTS AND DISCUSSION

Component fugacity coefficients of hydrogen, in carbon dioxide, $\phi^m_{H_2}$, 80°C (353 K), 130°C (403 K), 160°C (433 K), and 190°C (463 K), are presented in Tables I through IV. Plots of $\phi^m_{H_2}$ versus the mole fraction of hydrogen, x_{H_2}, for each isotherm, are presented in Figs. 2 through 5. The error bars indicated in the figures represent the uncertainty of a $\phi^m_{H_2}$–x_{H_2} pair for an equimolar mixture. A detailed error analysis describing how the magnitude of the uncertainty was arrived at has been provided previously [5].

Table II. Hydrogen + Carbon Dioxide at 130°C (403 K) and a Total Pressure of 3.45 MPa

Mole fraction, H_2	Fugacity coefficient, $\phi^m_{H_2}$
0.3093	1.123
0.4867	1.054
0.6070	1.034
0.7535	1.022
0.7995	1.019
0.9273	1.020

Table III. Hydrogen + Carbon Dioxide at 160°C (433 K) and a Total Pressure of 3.45 MPa

Mole fraction, H_2	Fugacity coefficient, $\phi_{H_2}^{m}$
0.456	1.034
0.4813	1.027
0.6406	1.017
0.7358	1.015
0.819	1.01

Table IV. Hydrogen + Carbon Dioxide at 190°C (463 K) and a Total Pressure of 3.45 MPa

Mole fraction, H_2	Fugacity coefficient, $\phi_{H_2}^{m}$
0.6271	1.059
0.695	1.023
0.7343	1.019
0.7659	0.984

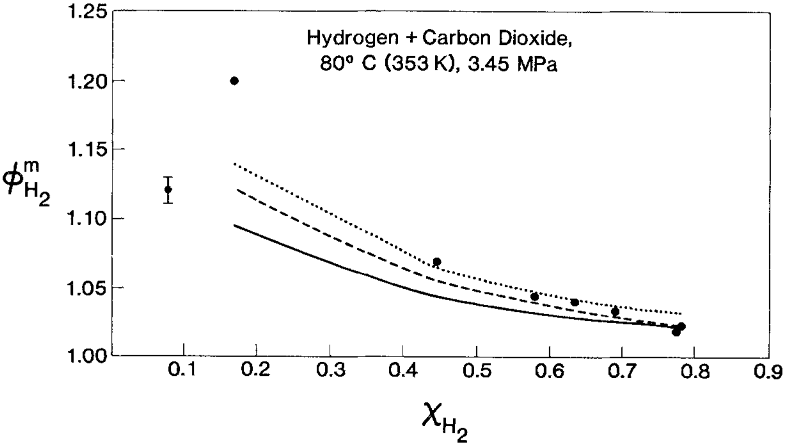

Fig. 2. Fugacity coefficients of hydrogen, $\phi_{H_2}^{m}$, versus the mole fraction of hydrogen for hydrogen + carbon dioxide at 80°C (353 K), with $P = 3.45$ MPa. ●, Experimental data; solid line, Redlich–Kwong; dashed line, Peng–Robinson; dotted line, EXCST. The error bar shown in the figure represents a typical uncertainty, and is not a data point.

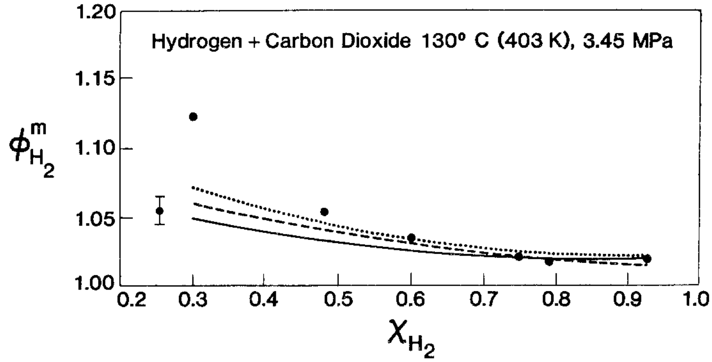

Fig. 3. Fugacity coefficients of hydrogen, $\phi^m_{H_2}$, versus the mole fraction of hydrogen for hydrogen + carbon dioxide at 130°C (403 K), with $P = 3.45$ MPa. ●, Experimental data; solid line, Redlich-Kwong; dashed line, Peng-Robinson; dotted line, EXCST. The error bar shown in the figure represents a typical uncertainty, and is not a data point.

Before examining the agreement of the experimental values with those predicted using the equations of state, some general qualitative observations can be made. In all plots, the change of $\phi^m_{H_2}$ is most pronounced at lower values of hydrogen mole fraction. This behavior is consistent for a low molecular weight gas (at a relatively high reduced temperature) in a binary mixture with a heavier gas. The same general trend was observed in previous studies done with this apparatus on binary mixtures of hydrogen + propane, [5, 6].

The behavior of each isotherm plot as a function of temperature is also of interest. At the higher temperatures, $\phi^m_{H_2}$ shows a more gentle increase in slope as x_{H_2} decreases. The total change in $\phi^m_{H_2}$ (over the entire mole frac-

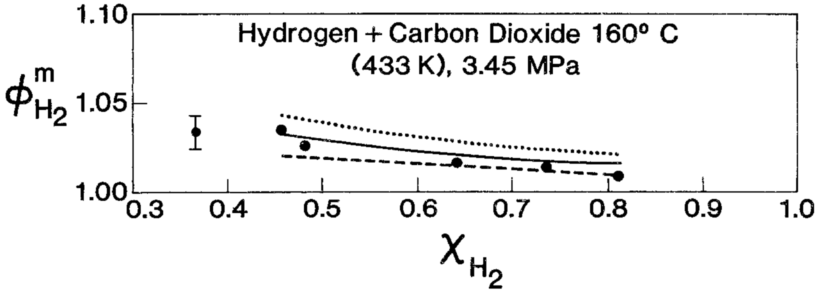

Fig. 4. Fugacity coefficients of hydrogen, $\phi^m_{H_2}$, versus the mole fraction of hydrogen for hydrogen + carbon dioxide at 160°C (433 K), with $P = 3.45$ MPa. ●, Experimental data; solid line, Redlich-Kwong; dashed line, Peng-Robinson; dotted line, EXCST. The error bar shown in the figure represents a typical uncertainty, and is not a data point.

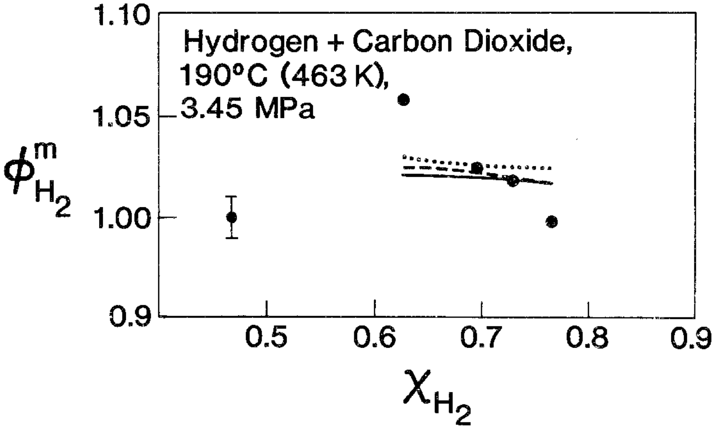

Fig. 5. Fugacity coefficients of hydrogen, $\phi^m_{H_2}$, versus the mole fraction of hydrogen for hydrogen + carbon dioxide at 190°C (463 K), with $P = 3.45$ MPa. ●, Experimental data; solid line, Redlich–Kwong; dashed line, Peng–Robinson; dotted line, EXCST. The error bar shown in the figure represents a typical uncertainty, and is not a data point.

tion range measured) is much less at higher temperatures than at lower temperatures. This observation is consistent with the expectation that $\phi^m_{H_2}$ be closer to unity at higher temperatures for a given gas composition.

In Figs. 2 through 5, the data measured in this study are represented as filled circles. The values as calculated using the unmodified, simple Redlich–Kwong equation are represented by the solid lines, values predicted by the Peng–Robinson equation are represented by the dashed lines, and values predicted using the extended corresponding-states approach are represented by the dotted lines. All of these equations of state predict fugacity coefficient values to within the experimental error of the measured values. In each case, the agreement is worst in the low hydrogen mole fraction region. This is expected due to the greater uncertainty in hydrogen quantitation in the low mole fraction range and has been a problem in all measurements of this type [14, 15]. The experimental error at a $x_{H_2} = 0.2$ is approximately double that of an equimolar mixture. In the high hydrogen mole fraction range, agreement with predicted values is much better (between 1.0 and 0.1%).

For the 80°C (353 K) isotherm, the extended corresponding-states model appears to give the best predictions at low hydrogen mole fractions. The Peng–Robinson equation and the Redlich–Kwong equation predict values with increasingly large deviations (rising to 10% in the case of the Redlich–Kwong equation). All three models give good predictions at higher hydrogen mole fractions (with deviations of between 1.0 and 0.1%).

For the 130°C (403 K) isotherm, the same trend is seen at the lowest values of x_{H_2}. The deviations are quite large, with the Redlich–Kwong equation giving the worst predictions (~7%), as expected from the simplicity of the model. The Peng–Robinson and the extended corresponding-states models predict slightly better values, with the EXCST approach giving the smallest deviations in this range. Again, in the high mole fraction range, all three models give predictions which agree with the experimental measurements to within 0.5% or better.

The data taken for the 160°C (433 K) isotherm do not extend very far below the equimolar mixture, thus assessment of low x_{H_2} performance of the equations of state is not possible. Of the mole fraction range considered, all three of the equations of state predict the experimental values to better than 1%. The experimental data of the 190°C (466 K) isotherm show a good deal of scatter, but the predictions are still acceptable. The deviations here range between 3 and 0.1%. It is possible that the scatter is caused by small amounts of sample decomposition on the semipermeable membrane surface, which may have introduced error into the measurement of p_{H_2}. The extent of decomposition would have to be quite small, since no impurities were observed during the chromatographic quantitation, which is done for each measurement.

5. CONCLUSIONS

Fugacity coefficients of the hydrogen + carbon dioxide binary system were measured as a function of the mole fraction of hydrogen along four isotherms, at a mixture pressure of 3.45 MPa. The experimental data were used to evaluate the predictive capability of three equations of state. At higher hydrogen mole fractions, all of the equations predict values which are quite close to the experimental values. At lower hydrogen concentrations, the deviations become large, as expected.

ACKNOWLEDGMENTS

The authors would like to thank Dr. James F. Ely for helpful discussions. The financial support of the Gas Research Institute is gratefully acknowledged.

REFERENCES

1. S. I. Sandler, *Chemical and Engineering Thermodynamics* (John Wiley and Sons, New York, 1977).
2. B. G. Kyle, *Chemical and Process Thermodynamics* (Prentice Hall, Englewood Cliffs, N.J., 1984).

3. J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria* (Prentice Hall, Englewood Cliffs, N.J., 1969).
4. H. Y. Cheh, *Proceedings of the 6th Symposium of Thermophysical Properties*, P. E. Liley, ed. (Am. Soc. Mech. Eng., New York, 1973), p. 256.
5. T. J. Bruno, *J. Res. Natl. Bur. Stds.* **90** (2):127 (1985).
6. T. J. Bruno, G. L. Hume, and J. F. Ely, *Int. J. Thermophys.* **7**:1033 (1986).
7. D. P. Smith, *Hydrogen in Metals* (University of Chicago Press, Chicago, 1948).
8. E. M. Wise, *Palladium* (Academic Press, New York, 1968).
9. B. Mason, *Principles of Geochemistry*, 3rd ed. (John Wiley and Sons, New York, 1958).
10. T. J. Bruno and G. L. Hume, *J. Res. Natl. Bur. Stds.* **90** (3):225 (1985).
11. T. J. Bruno, *J. Chromatogr. Sci.* **23**(7):325 (1985).
12. H. M. McNair and E. J. Bonnelli, *Basic Gas Chromatography* (Varian Aerograph, 1969).
13. E. Heftmann, *Chromatography, A Laboratory Handbook of Chromatographic and Electrophoretic Methods* (Van Nostrand Reinhold, New York, 1975).
14. F. Antezana and H. Y. Cheh, *Ind. Eng. Chem. Fund.* **14**:224 (1975).
15. F. Antezana and H. Y. Cheh, *Ind. Eng. Chem. Fund.* **15**:95 (1976).