

## Hydrogen Component Fugacity in Binary Mixtures with Carbon Monoxide: Temperature Dependence

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The fugacity coefficients of hydrogen in binary mixtures with carbon monoxide 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 through which hydrogen, but not carbon monoxide, can penetrate. Measurement of the gas pressures inside and outside of the membrane allows a direct measurement of the hydrogen component fugacity at a given temperature and binary mixture mole fraction. In this paper, results are reported at 130, 160, and 190°C. In each case, the total pressure of the mixture was maintained at a nominal value of 3.39 MPa. The general qualitative features of the data are discussed, and comparisons are made with predictions obtained from the Redlich-Kwong, Peng-Robinson-Soave, and extended corresponding-state models.

**KEY WORDS:** carbon monoxide; fugacity; hydrogen mixtures.

### 1. INTRODUCTION

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 mixture is known in the region of interest) along an isotherm using, for example,

$$\ln \left( \frac{f_i}{x_i P_m} \right) = \int_0^{P_m} (V_i/RT - 1/P_m) dP_m \quad (1)$$

where  $f_i$  is the fugacity of component  $i$ ,  $x_i$  is its mole fraction,  $V_i$  is its partial molar volume,  $P_m$  is the total pressure of the mixture,  $T$  is the tem-

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perature, and  $R$  is the gas constant. The need for a great deal of accurate  $PVT$  data for the mixture and the limitations inherent in the application of many of the common equations of state to mixtures make this approach time-consuming and difficult. 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 and its applications can be found elsewhere [2-6], 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 long section of thin-walled 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 gradual approach to equilibrium is driven by the need to equalize the chemical potential of hydrogen on both sides of the membrane. When equilibrium is actually reached in the system, the fugacity of hydrogen on both sides of the membrane must be equal [7-9].

Using appropriate instrumentation (which is described more fully in Section 2) 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 fugacity of pure hydrogen can be computed. We can begin the process (at moderate pressures) using the pressure expansion of the virial equation of state (truncated after the third virial coefficient):

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

where  $B$  and  $C$  are the second and third virial coefficients, respectively, and  $\hat{\phi}_{H_2}$  is the fugacity coefficient of pure hydrogen (which has permeated in from outside the membrane). The fugacity of (pure) hydrogen,  $\hat{f}_{H_2}$ , follows from

$$\hat{f}_{H_2} = \hat{\phi}_{H_2} P_{H_2} \quad (3)$$

Since pressure measurements are made when the system has reached equilibrium (that is, no net change in pressure or temperature 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 is determined from

$$\hat{f}_{H_2} = f_{H_2} = x_{H_2} P_m \phi_{H_2}^m \quad (4)$$

where  $f_{\text{H}_2}$  and  $\phi_{\text{H}_2}^m$  are the fugacity and fugacity coefficient, respectively, of hydrogen in the mixture. The mole fraction in Eq. (4) is that of hydrogen in the mixture after permeation through the membrane has occurred.

## 2. EXPERIMENTAL

The apparatus used in this work is essentially the same as that used in previous studies [2–6] except for slight modifications in the configuration of the membrane manifold. In the current apparatus, the palladium/silver tubing (three sections, 396 cm long, 0.025 cm in wall thickness) which comprises the membrane has been formed into a larger network which penetrates more of the internal volume of the pressure vessel. This modification allows for somewhat faster equilibration times while eliminating the need for the magnetic linkage stirrer which was required previously.

The pressures of the pure hydrogen,  $P_{\text{H}_2}$ , and of the mixture,  $P_m$ , were measured using a commercial precision Bourdon tube pressure transducer, as valved through the manifold system described elsewhere [2]. This pressure transducer was calibrated through the range of interest using an air deadweight pressure balance (a secondary standard traceable to the NIST primary standard). The Bourdon tube transducer thus calibrated is accurate to within  $\pm 0.04\%$  over the range of the measurements. Temperature measurements were made using a commercial quartz crystal oscillator sensor. This thermometer is accurate to within  $\pm 0.009^\circ\text{C}$  over the range of these measurements and shows negligible hysteresis effects in the present situation of isothermal operation. In addition to this main thermometer, opposed pairs of type J thermocouples are used to sense temperature gradients between key components of the apparatus. These gradients are then minimized using very low-power shimming heaters (under manual control) located on or near the major components.

The mole fractions of the mixtures studied were determined using a developmental gas chromatograph and sampling system [10, 11]. The thermal conductivity detector was calibrated using the external standard method [10] with five standard mixtures of hydrogen + carbon monoxide which were prepared gravimetrically. Nitrogen was chosen as the carrier gas to provide a high sensitivity to hydrogen [12, 13]. The chromatographic separations (for both the calibration and the actual fugacity measurements) were done using a packed column (2 m in length, 0.32 cm

<sup>3</sup> 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 Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

in o.d.) of Porapak-QS<sup>3</sup> of 150 to 200 mesh. The column was maintained isothermally at  $45.00 \pm 0.02^\circ\text{C}$ , with a carrier gas flow rate (volume, measured at the column exit) of  $35 \pm 0.05 \text{ ml} \cdot \text{min}^{-1}$ . The separation under these conditions is very favorable to precise quantitation. Baseline resolved peaks of reasonable width, convenient retention times, and excellent symmetry are easily obtained. The accuracy of the mole fraction thus obtained is approximately 0.5% for an equimolar mixture of hydrogen + carbon monoxide [2]. Somewhat lower precision and accuracy are obtained at lower hydrogen mole fractions.

The hydrogen and carbon monoxide used in this work were research grade (99.995% purity for hydrogen, 99.99% purity for carbon monoxide), and no impurities were detected down to 1 ppm using subambient-temperature gas chromatography [14].

Some relatively unusual experimental difficulties were encountered in the course of the measurements of this system. Carbon monoxide was found to be a potent irreversible poison to the palladium membrane, causing an abrupt halt to the diffusion process. The observation of this catastrophic failure of the membrane was unmistakable, since the measured values of the pure hydrogen pressure,  $P_{\text{H}_2}$ , would become constant regardless of hydrogen concentration in the mixture. The problem was more acute at higher carbon monoxide densities (i.e., higher pressures). Because of these problems, the study of this system was restricted to pressures no higher than approximately 3.4 MPa. This is in contrast to other systems studied with this apparatus, for which data were typically obtained for pressures up to approximately 14 MPa.

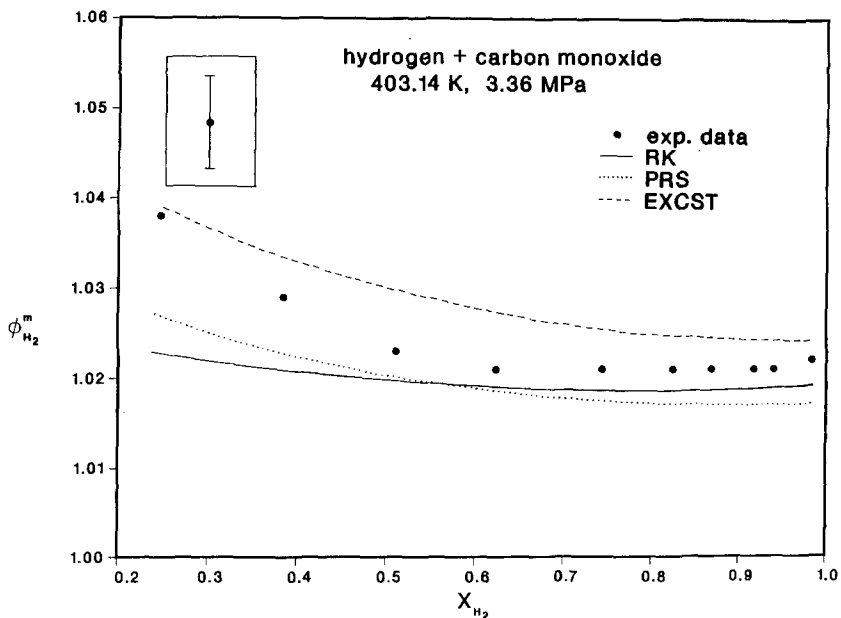
### 3. RESULTS AND DISCUSSION

Component fugacity coefficients,  $\phi_{\text{H}_2}^m$ , at nominal temperatures of 130, 160, and  $190^\circ\text{C}$  are presented in Table I, along with their measured hydrogen mole fractions. The total pressure of the mixture was, on average,  $3.39 \pm 0.02 \text{ MPa}$ . The actual measured values of temperature and pressure are presented in the table subheadings. Plots of  $\phi_{\text{H}_2}^m$  versus hydrogen mole fraction,  $x_{\text{H}_2}$ , are provided in Figs. 1 through 3. In each case, the experimental data are shown as filled circles. The error bars (enclosed in the boxes in each figure) represent the uncertainty of a  $\phi_{\text{H}_2}^m-x_{\text{H}_2}$  pair for an equimolar mixture of hydrogen + carbon monoxide. This error is typically of the order of 1.1%. A detailed error analysis describing how the magnitude of the error was arrived at has been presented previously [2].

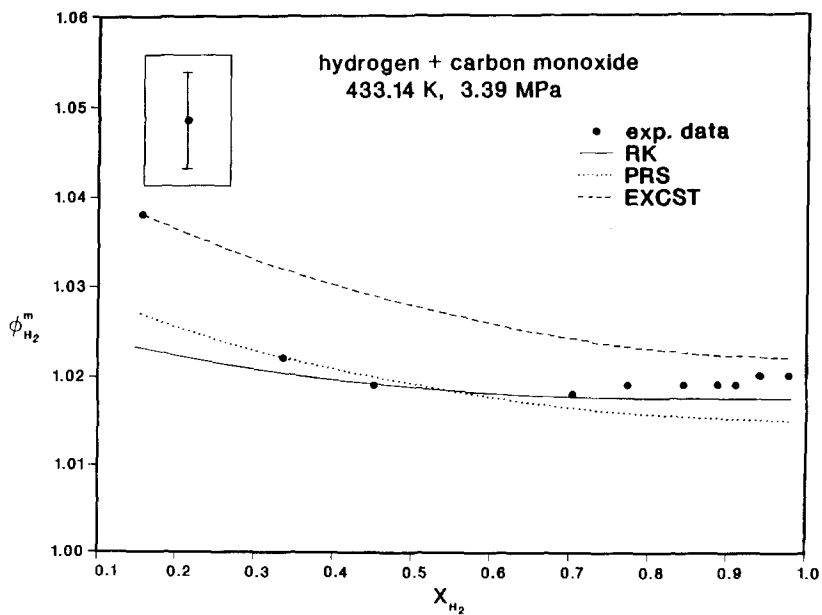
Before examining the agreement of the experimental data with predictions made using selected equations of state, some observations may be made about the qualitative features of the experimental data. The change in

**Table I.** Measured Values of Hydrogen Component Fugacity Coefficients,  $\phi_{\text{H}_2}^m$ , at Mole Fractions  $x_{\text{H}_2}$ , for the Hydrogen + Carbon Monoxide Binary System

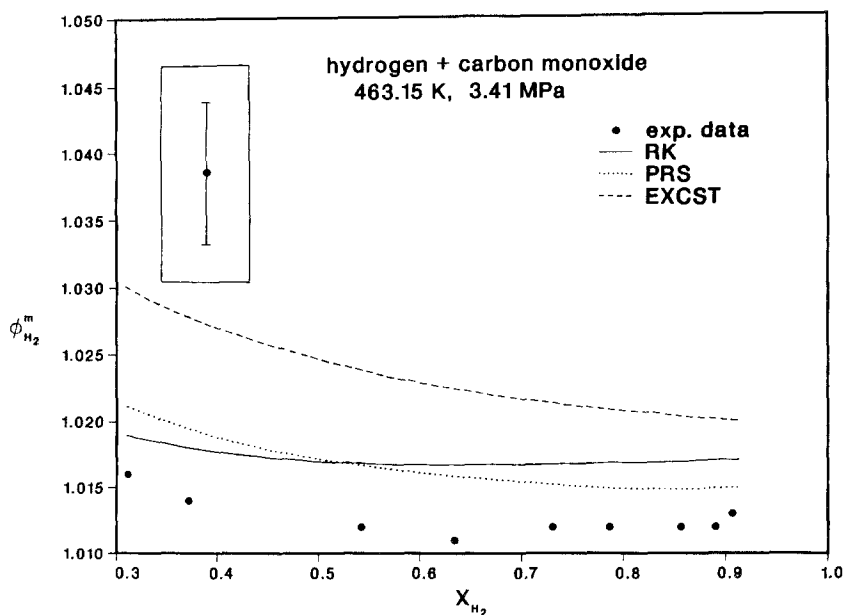
$x_{\text{H}_2}$	$\phi_{\text{H}_2}^m$
$T = 129.99 \pm 0.03^\circ\text{C}$ (403.14 K)	
$P_m = 3.36 \pm 0.03$ MPa	
0.247	1.038
0.384	1.029
0.510	1.023
0.623	1.021
0.743	1.021
0.824	1.021
0.868	1.021
0.917	1.021
0.940	1.021
0.983	1.020
$T = 159.99 \pm 0.03^\circ\text{C}$ (433.14 K)	
$P_m = 3.39 \pm 0.02$ MPa	
0.157	1.038
0.337	1.022
0.453	1.020
0.704	1.019
0.774	1.019
0.845	1.019
0.888	1.019
0.911	1.019
0.941	1.020
0.942	1.020
0.978	1.020
$T = 190.00 \pm 0.03^\circ\text{C}$ (463.15 K)	
$P_m = 3.41 \pm 0.03$ MPa	
0.311	1.016
0.372	1.014
0.542	1.012
0.634	1.011
0.730	1.012
0.786	1.012
0.856	1.012
0.890	1.012
0.907	1.013



**Fig. 1.** A plot of the fugacity coefficient for hydrogen (in the mixture),  $\phi_{H_2}^m$ , versus the hydrogen mole fraction,  $x_{H_2}$ , at 403.14 K and 3.36 MPa. The error bar in the box is typical for an equimolar mixture and is not a measured data point.



**Fig. 2.** A plot of the fugacity coefficient for hydrogen (in the mixture),  $\phi_{H_2}^m$ , versus the hydrogen mole fraction,  $x_{H_2}$ , at 433.14 K and 3.39 MPa. The error bar in the box is typical for an equimolar mixture and is not a measured data point.



**Fig. 3.** A plot of the fugacity coefficient for hydrogen (in the mixture),  $\phi_{H_2}^m$ , versus the hydrogen mole fraction,  $x_{H_2}$ , at 463.15 K and 3.41 MPa. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

$\phi_{H_2}^m$  with hydrogen mole fraction is more pronounced at the lower values of  $x_{H_2}$ , with a gradual leveling off at the higher values. This observation is consistent for a gas of low relative molecular mass in a mixture with a gas of a higher relative molecular mass. There is also a small but noticeable change in  $\phi_{H_2}^m$  as a function of temperature. As has been observed in previous work on other binary systems containing hydrogen, the effect of temperature is most pronounced in the region of lower hydrogen mole fractions. Thus, the present measurements show a decrease of approximately 1.5% upon a change in temperature from 130 to 190°C at a hydrogen mole fraction of 0.3; at a mole fraction of 0.9, the change is only of the order of 0.85%. Interpretation of the quantitative significance of these differences must be approached with care, however, since their magnitudes approach the experimental error.

The actual magnitudes of the measured fugacity coefficients are also worthy of mention. The total change of  $\phi_{H_2}^m$  over the mole fraction range is relatively small. We may consider, for example, the isotherm at 403 K (130°C). The hydrogen component fugacity coefficient changes by only 1.6% over the range of 0.247 to 0.983 in  $x^{H_2}$ . We may contrast this change with that observed for the hydrogen + carbon dioxide binary [4] at the

same temperature. In that system, a change in  $\phi_{\text{H}_2}^m$  of 9.2% was observed over a similar mole fraction range (0.309 to 0.927 in  $x_{\text{H}_2}$ ). The observation of such a small change in  $\phi_{\text{H}_2}^m$  in the present study is consistent with previous studies; a relatively small change is observed when the component with hydrogen is far above its critical temperature. A more detailed analysis of the dependence of  $\phi_{\text{H}_2}^m$  on the reduced temperature of the adcomponent will be reported on at a later time.

At the pressure encountered in this work, equations of state provide the simplest avenue for obtaining predictions of fugacity coefficients of gaseous mixtures. The common approaches involve either cubic equations of state or the extended corresponding-states approach (EXCST). In this study we have applied both methods. As an example of a cubic equation of state, we have used the popular Peng–Robinson–Soave (PRS) modification of the Redlich–Kwong (RK) equation [15]. For comparative purposes and as a matter of interest, we have also used the unmodified Redlich–Kwong equation of state, the simplest of the cubic equations [16] (with the exception of the original van der Waals equation). The extended corresponding-states model we have used employs propane (using a 32-term Benedict–Webb–Rubin equation) as the reference fluid [17].

In Figs. 1 through 3, the solid line represents the predictions of the simple Redlich–Kwong equation of state. The dotted lines were generated from the predictions of the Peng–Robinson–Soave equation, and the dashed line from the extended corresponding-states approach. Van der Waals mixing rules have been used throughout. As has been noted in previous studies [3–6], the acentric factor for hydrogen,  $\omega$ , is a variable in the Peng–Robinson–Soave and the extended corresponding-states models. The curves presented in Figs. 1 through 3 were determined using a value of  $\omega = 0$ . Binary interaction coefficients (for the EXCST and PRS models) were also assigned a value of zero, since there are none available which are based on measurements in the temperature range considered in this work.

In each of the three measured isotherms, it appears that the experimental data show more curvature in the low- $x_{\text{H}_2}$  area than any of the predictive approaches. While there is a somewhat higher uncertainty in the measured data at the lower hydrogen mole fractions, it is nevertheless possible that the predictive models chosen have some difficulty accounting for the mixture properties at lower hydrogen concentrations. A clear conclusion on this point is impossible, however, since the overall change in  $\phi_{\text{H}_2}^m$  is too close to the experimental error.

A comparison of the measured data with the calculated lines shows that all three equations of state are capable of providing acceptable predictions (within approximately 1 to 1.5%, i.e., close to experimental error). The best predictions are generally provided by the extended corresponding-



states equation and the simple Redlich–Kwong equation, especially at the higher values of  $x_{\text{H}_2}$ . This is despite the relatively low level of sophistication to the Redlich–Kwong equation. At lower values of  $x_{\text{H}_2}$  the predictions of the EXCST model approach the data more closely than those of either the PRS or the RK equation. Examination of the 463 K isotherm shows that all of the equations of state predict values which are higher than the experimental data. The 1% error bar and relatively magnified scale reveal that the predictions are still good, however. The agreement of the PRS model can be significantly improved (lowered by approximately 0.7% for this particular isotherm) by using the experimental value for the hydrogen acentric factor ( $-0.22$ ). This value of  $\omega$  has little effect on the EXCST predictions. We have chosen to present only the  $\omega = 0$  plots in this paper, for the sake of clarity.

#### 4. CONCLUSIONS

Hydrogen component fugacity coefficients for the hydrogen + carbon monoxide binary system were measured along three isotherms, at a total mixture nominal pressure of 3.39 MPa, using the physical equilibrium technique. The experimental data were examined for general trends and were used to evaluate the predictive capability of three equation-of-state approaches. These models were the extended corresponding-states approach, the Peng–Robinson (Soave modification) equation, and the unmodified Redlich–Kwong equation. The predictions were found to be generally good for both curve shape and actual numerical values. This was especially true in the hydrogen mole fraction region above 0.6. The EXCST and Redlich–Kwong methods were found to provide slightly better agreement with the experimental data than the PRS equation. The observed temperature dependence of the data, while very slight over the temperature range studied, was also qualitatively predicted by all three models.

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