

Hydrogen-Component Fugacity Coefficients in Binary Mixtures with Isobutane: Temperature Dependence¹

T. J. Bruno² and S. L. Outcalt²

The fugacity coefficients of hydrogen in binary mixtures with isobutane 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 isobutane, can penetrate. Measurement of the gas pressures inside and outside the membrane allow a direct measurement of the hydrogen component fugacity at a given temperature, binary mixture mole fraction, and mixture pressure. In this paper, results are reported at 120, 140, 160, and 180°C. In each case, the total pressure of the mixture was maintained at an average value of 3.40 MPa. The general qualitative features of the data are discussed, and comparisons are made with predictions obtained from the Redlich-Kwong and the Peng-Robinson equations of state.

KEY WORDS: fugacity; hydrogen mixtures; isobutane.

1. INTRODUCTION

The fugacity of individual components of a mixture can, in principle, be calculated from a applicable equation of state. In the special case of gaseous mixtures containing hydrogen as one component, however, the physical equilibrium method is preferable [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 [2-7], so only a brief description is provided here.

An experimental chamber (usually a pressure vessel) is divided into

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² Thermophysics Division, National Institute of Standards and Technology (formerly National Bureau of Standards), Boulder, Colorado 80303, U.S.A.

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 palladium/silver (75/25) 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 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.

Using appropriate instrumentation the pressure of the hydrogen which has permeated the membrane, 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 [2-7].

2. EXPERIMENTAL

The pressures of the pure hydrogen, P_{H_2} , and of the mixture, P_{m} , were measured using a commercial precision Bourdon tube pressure transducer. This pressure transducer was calibrated through the range of interest using an air deadweight pressure balance (a secondary standard traceable to NIST primary standard). The Bourdon tube transducer thus calibrated is accurate 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 shim heaters (under manual control) located on or near the major components.

The mole fractions of the mixtures studied were determined using a specially constructed gas chromatograph and sampling system [8, 9]. The thermal conductivity detector was optimized and calibrated using the external standard method [8, 10, 11]. The chromatographic separations were achieved using a packed column (2 m in length, 0.32 cm in o.d.) of Porapak-QS³ of 150 to 200 mesh. The column was maintained isothermally

³ 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.

Table I. Measured Values of Hydrogen Component Fugacity Coefficients, $\phi_{\text{H}_2}^m$, at Mole Fractions, x_{H_2} , for the Hydrogen + Isobutane Binary Systems

x_{H_2}	$\phi_{\text{H}_2}^m$
$T = 120.01 \pm 0.03^\circ\text{C}$ (393.16 K)	
$P_m = 3.38 \pm 0.02$ MPa	
0.530	1.130
0.613	1.077
0.686	1.046
0.744	1.031
0.783	1.024
0.828	1.020
0.858	1.019
0.905	1.019
$T = 140.00 \pm 0.04^\circ\text{C}$ (413.15 K)	
$P_m = 3.39 \pm 0.02$ MPa	
0.588	1.080
0.663	1.046
0.724	1.029
0.767	1.021
0.812	1.017
0.844	1.016
0.868	1.016
0.895	1.017
$T = 160.00 \pm 0.02^\circ\text{C}$ (433.15 K)	
$P_m = 3.41 \pm 0.02$ MPa	
0.439	1.215
0.553	1.101
0.637	1.055
0.713	1.030
0.770	1.020
0.819	1.015
0.850	1.015
0.886	1.015
0.918	1.017
$T = 180.02 \pm 0.01^\circ\text{C}$ (453.17 K)	
$P_m = 3.43 \pm 0.02$ MPa	
0.370	1.299
0.530	1.100
0.649	1.037
0.736	1.016
0.815	1.010
0.851	1.010
0.904	1.014
0.937	1.019

at $40.00 \pm 0.02^\circ\text{C}$, with a carrier gas flow rate (volume, measured at the column exit) of $35 \pm 0.05 \text{ ml} \cdot \text{min}^{-1}$. The accuracy of the mole fraction obtained is conservatively estimated at 0.5% for an equimolar mixture of hydrogen + isobutane. Somewhat lower precision and accuracy are obtained at lower hydrogen mole fractions.

The hydrogen and isobutane used in this work were research grade (99.995% purity for hydrogen, 99.99% purity for isobutane), and no impurities were detected down to 1 ppm (for hydrogen) and 100 ppm (for isobutane) using subambient-temperature gas chromatography [12].

3. RESULTS AND DISCUSSION

Hydrogen component fugacity coefficients, $\phi_{\text{H}_2}^m$, at nominal temperatures of 120, 140, 160, and 180°C for the isobutane binary mixtures are presented in Table I, along with their measured hydrogen mole fractions, x_{H_2} . The total pressure of the mixture was, on average, $3.40 \pm 0.02 \text{ MPa}$. The measured values of temperature and pressure are presented. A plot of $\phi_{\text{H}_2}^m$ versus x_{H_2} for each of the four isotherms is shown in Fig. 1. Figures 2 through 5 show plots of the individual isotherms, along with the equation of state predictions which are discussed later. The error bars (enclosed in the boxes in each figure), represent the uncertainty of a $\phi_{\text{H}_2}^m$, x_{H_2} pair for

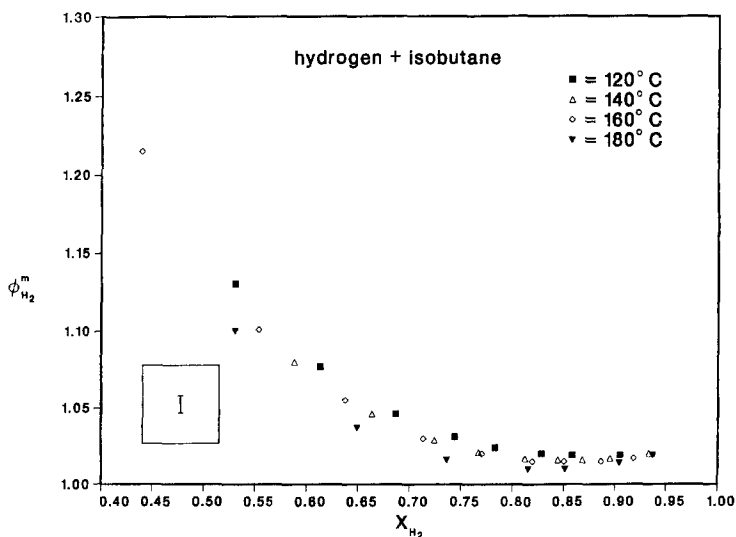


Fig. 1. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi_{\text{H}_2}^m$, versus the hydrogen mole fraction, x_{H_2} , for all measured isotherms. The error bar in the box is typical for an equimolar mixture.

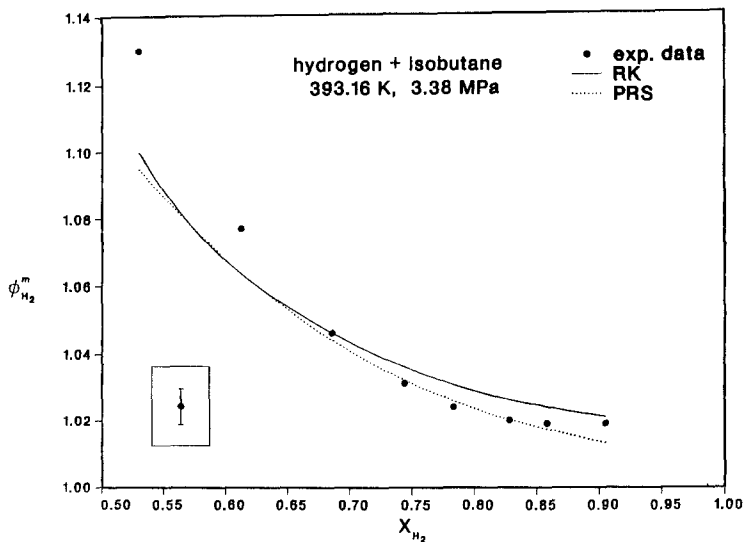


Fig. 2. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi_{H_2}^m$, versus the hydrogen mole fraction, x_{H_2} , at 393.16 K and 3.38 MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

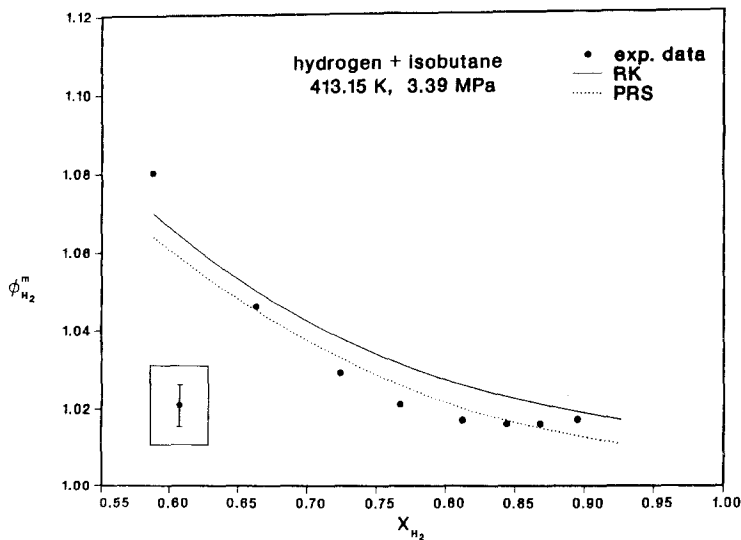


Fig. 3. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi_{H_2}^m$, versus the hydrogen mole fraction, x_{H_2} , at 413.15 K and 3.39 MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

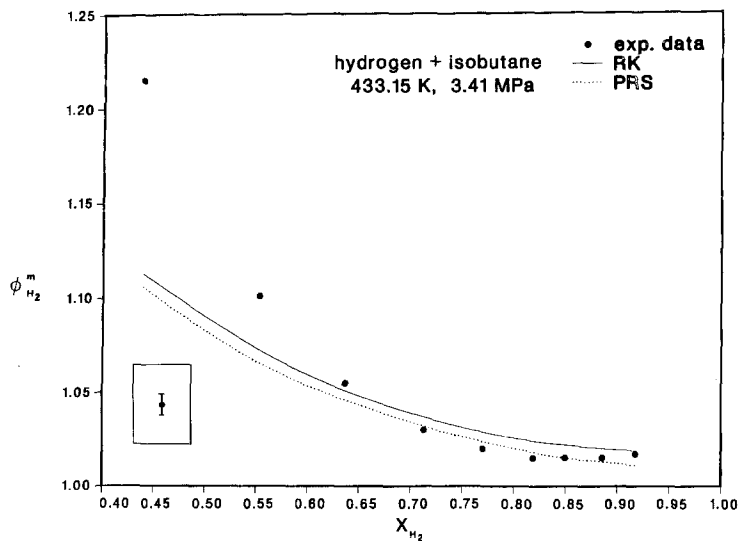


Fig. 4. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi_{H_2}^m$, versus the hydrogen mole fraction, x_{H_2} , at 433.15 K and 3.41 MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

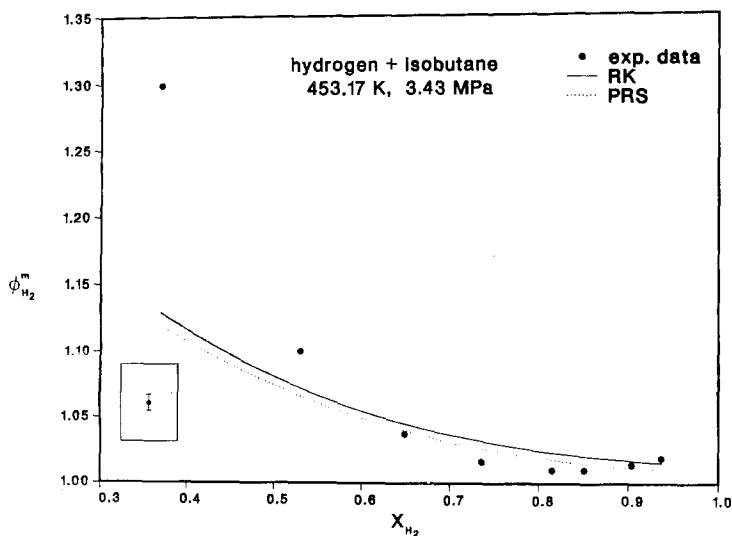


Fig. 5. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi_{H_2}^m$, versus the hydrogen mole fraction, x_{H_2} , at 453.17 K and 3.43 MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

an equimolar mixture of hydrogen + isobutane. This error is typically of the order of 1.1%. A detailed analysis describing how the magnitude of the error was estimated has been presented previously [2]. Errors due to lack of equilibration are minimized by design; the pure hydrogen pressure is measured during the approach to equilibrium and after a steady state has been obtained.

Before examining the agreement of the experimental data with equation-of-state predictions, some qualitative features may be described. The fugacity coefficient of hydrogen is observed to decrease with increasing temperature. This corresponds to the decrease in the nonideality of the system at the higher temperatures. As has been observed in all previous studies, the effect of temperature is most pronounced at lower values of x_{H_2} . In addition, the change of $\phi_{\text{H}_2}^m$ with x_{H_2} is more pronounced in the region of lower hydrogen mole fraction, leveling off to a constant value at x_{H_2} greater than 0.75. This mole fraction dependence is similar to that found in previous studies as well.

The actual magnitudes of the measured fugacity coefficients are also worthy of mention. The total change of $\phi_{\text{H}_2}^m$ over the mole fraction ranges considered is relatively large compared to other binary hydrogen mixtures. As an example, we may compare the 433.15 K isotherm in this work with that measured for the hydrogen + carbon monoxide system [7]. The total change of $\phi_{\text{H}_2}^m$ over the x_{H_2} range of 0.55 to 0.90 is approximately 7.8% for the hydrogen + isobutane system. There is no discernable change at all in the carbon monoxide system over the same mole fraction range. The observation of such a large relative change in the present study is consistent with previous studies [4–6], a large change in $\phi_{\text{H}_2}^m$ is observed when the adcomponent is at a low reduced temperature.

In Figs. 2 through 5, the filled circles represent the experimental data. The solid lines represent predictions from the simple Redlich–Kwong equation, and the dotted lines represent predictions from the Peng–Robinson equation. Van der Waals mixing rules have been used throughout. The acentric factor, ω (which is a parameter in the Peng–Robinson equation), was assigned the experimental value of -0.22 for hydrogen. Interaction coefficients were not applied since there are none available which are based on measurements in the temperature range of this work.

For each of the four isotherms considered here, the Peng–Robinson equation provides good predictions (within or nearly within experimental error) of the measured values at x_{H_2} values larger than 0.65. The Redlich–Kwong equation is found to predict values which are consistently a few percent too high in this mole fraction region. Predictions made using an extended corresponding-states model [2–7, 13] predicted even higher values (2 to 3% above the experimental data) and have not been included

in the figures. In the region of lower x_{H_2} , the Redlich–Kwong, Peng–Robinson, and extended corresponding-states approaches predict values which are too low. This has been consistently observed in systems in which the adcomponent is at a relatively low reduced temperature. Definitive observations cannot be made concerning this x_{H_2} range, however, since the data are not extensive enough. Performing more extensive measurements in this range is difficult due to very long equilibration times and less than favorable analytical conditions.

4. CONCLUSIONS

Hydrogen component fugacity coefficients for the hydrogen + isobutane system were measured along four isotherms (120, 140, 160, and 180°C), at an average total mixture pressure of 3.40 MPa using the physical equilibrium technique. The experimental data were examined for general trends and were compared with predictions obtained from two equations of state. These models were the Redlich–Kwong and Peng–Robinson equations; predictions from the extended corresponding states approach were calculated but not presented. The Peng–Robinson–Soave equation was found to predict the data to within experimental error in the higher hydrogen mole fraction range. Both of the equations of state examined were found to give poorer predictions in the low- x_{H_2} range. No clear conclusions can be made regarding this region, however, due to a lack of data in this area. Experimental modifications are currently being considered to allow more extensive measurement in this region.

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