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Hydrogen Component Fugacity Coefficients in Binary Mixtures with Ethane: Pressure Dependence

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The fugacity coefficients of hydrogen in binary mixtures with ethane were measured. Data were taken using an experimental chamber which is divided into two regions by a semipermeable membrane through which hydrogen, but not ethane, can penetrate. The measurement of the gas pressures inside and outside the membrane gives the hydrogen component fugacity at a given temperature, binary mixture mole fraction, and mixture pressure. In this paper, results are reported at mixture pressures of 5.25, 6.97, 10.21, and 13.47 MPa. In each case, the temperature of the mixture was maintained at an average value of 130°C (403.15 K). The general qualitative features of the data are discussed, and comparisons are made with predictions obtained from the Redlich–Kwong and Peng–Robinson equations of state.

KEY WORDS: binary mixtures; ethane; fugacity; hydrogen mixtures.

1. INTRODUCTION

This paper is part of a series of studies to determine the fugacity coefficient of hydrogen in binary mixtures. Systems studied to date include carbon monoxide, carbon dioxide, methane, ethane, propane, and isobutane [1–7]. A detailed description of the technique and its applications can be found elsewhere [1], so only a brief description is provided here.

The fugacity of individual components of a mixture can, in principle, be calculated from an applicable equation of state. In the special case of gaseous mixtures containing hydrogen as one component, however, the physical equilibrium method is preferable [8], since the problem of measuring the properties of a mixture is then reduced to that of measuring the properties of a pure fluid.

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

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two regions by a membrane [most often a long section of thin-walled (0.008-cm) palladium/silver (75/25%) tubing] that is permeable only to hydrogen. 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 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 hydrogen can be computed.

2. EXPERIMENTAL

The apparatus used in this work was essentially the same as that used in previous studies [1–7]. The pressures of the pure hydrogen P_{H_2} and 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 the NBS primary standard). The Bourdon tube transducer thus calibrated is accurate to within ±0.04% over the range of the measurements. Temperature measurements were made using a commercial quartz crystal oscillator sensor. This thermometer (which is regularly calibrated at the triple point of water) is accurate to within ±0.009°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 were used to sense temperature differences between key components of the apparatus. These differences 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 [9, 10]. The thermal conductivity detector was optimized and calibrated using the external standard method [9, 11, 12]. The chromatographic separations were done using a packed column (2 m in length, 0.32 cm in o.d.) of Porapak-QS[2]

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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 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 Coefficient, $\phi^{m}_{H_2}$, at Mole Fractions x_{H_2}

x_{H_2}	$\phi^{m}_{H_2}$
$T = 130.00 \pm 0.03$°C $P = 5.25 \pm 0.03$ MPa	
0.312	1.102
0.430	1.079
0.517	1.067
0.601	1.064
0.679	1.039
0.783	1.035
0.830	1.040
0.906	1.034
$T = 130.01 \pm 0.03$°C $P = 6.97 \pm 0.05$ MPa	
0.551	1.080
0.624	1.064
0.717	1.058
0.759	1.043
0.809	1.043
0.849	1.044
0.887	1.043
0.902	1.043
$T = 130.00 \pm 0.05$°C $P = 10.21 \pm 0.05$ MPa	
0.757	1.063
0.778	1.060
0.819	1.058
0.852	1.068
0.877	1.062
0.923	1.063
0.947	1.063
0.966	1.062
$T = 130.00 + 0.04$°C $P = 13.47 \pm 0.06$ MPa	
0.832	1.074
0.859	1.075
0.866	1.077
0.908	1.079
0.934	1.073
0.962	1.079
0.980	1.083

of 150 to 200 mesh. The column was maintained isothermally at 40.00 ± 0.02°C, with a carrier gas flow rate (volumetric, measured at the column exit) of 35 ± 0.05 ml · min^{-1}. The accuracy of the mole fraction obtained is approximately 0.5% for an equimolar mixture of hydrogen + ethane. Somewhat lower precision and accuracy are obtained at lower hydrogen mole fractions.

The hydrogen and ethane used in this work were research grade (99.995% purity for hydrogen, 99.99% purity for ethane), and no impurities were detected down to 1 ppm (for hydrogen) and 30 ppm (for ethane) using subambient-temperature gas chromatography [13].

3. RESULTS AND DISCUSSION

Hydrogen component fugacity coefficients, $\phi^{m}_{H_2}$, at mixture pressures of 5.25, 6.97, 10.21, and 13.47 MPa for the ethane binary system are presented in Table I, along with their measured hydrogen mole fractions, x_{H_2}. The average temperature of the mixture during the course of all measurements was 130.00 ± 0.02°C. The measured values of temperature and pressure (with their standard deviations) for each individual series of measurements are presented in the table subheadings. A plot of $\phi^{m}_{H_2}$ vs x_{H_2} for each of the pressures is shown in Fig. 1. The error bar (enclosed within the box)

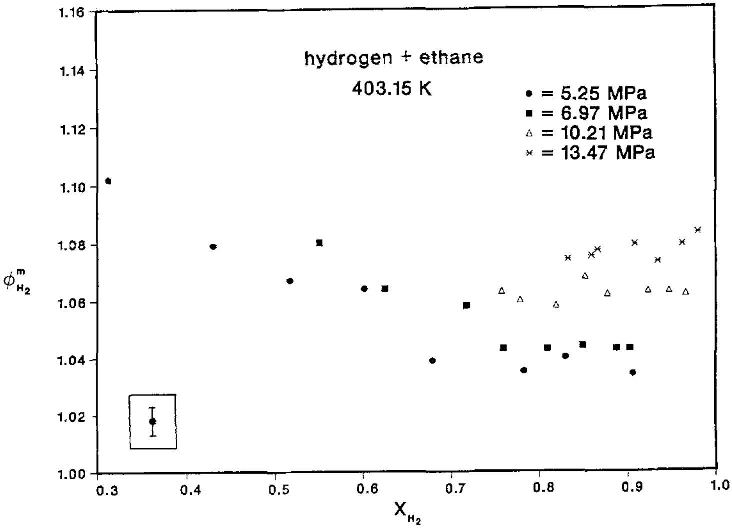

Fig. 1. A plot of the fugacity coefficient of hydrogen (in the mixture with ethane), $\phi^{m}_{H_2}$, versus hydrogen mole fraction, x_{H_2}, for all measured mixture pressures, at 403.15 K. The error bar in the box is typical for an equimolar mixture.

presents the uncertainty of a $\phi^m_{H_2}$, x_{H_2} pair for an equimolar mixture of hydrogen + ethane. This error is typically of the order of 1.1% for the fugacity coefficient. A detailed analysis describing how the magnitude of the error was estimated has been presented previously [1]. Errors due to the lack of adequate equilibration are minimized by design; the pure hydrogen pressure is measured during the approach to equilibrium and after a steady state has been obtained.

The fugacity coefficient of hydrogen in ethane is observed to increase with increasing pressure, as can be clearly seen from Fig. 1. This corresponds to the increase in nonideality of the system at the higher pressures (and corresponding higher densities). As has been observed in all previous studies, $\phi^m_{H_2}$ decreases with increasing hydrogen mole fraction. The change is most apparent in the region of low hydrogen concentration. The curves level off and approach a constant value as x_{H_2} increases beyond 0.75. Very little change with x_{H_2} is noted at the two higher pressures since the data are concentrated in the high hydrogen concentration range. The increase in $\phi^m_{H_2}$ with increasing pressure (which is the focus of the current study) is clear, however, if one fixes attention to a given mole fraction.

In Figs. 2 through 5, the filled circles represent the experimental data; the solid line represents the predictions of the Redlich–Kwong equation of state, and the dotted line represents the predictions of the Peng–Robinson

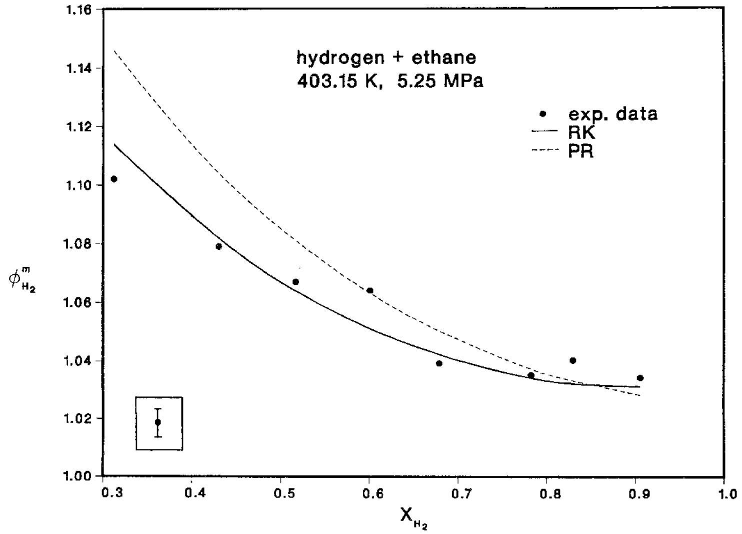

Fig. 2. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi^m_{H_2}$, versus hydrogen mole fraction, x_{H_2}, at 403.15 K and 5.25-MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

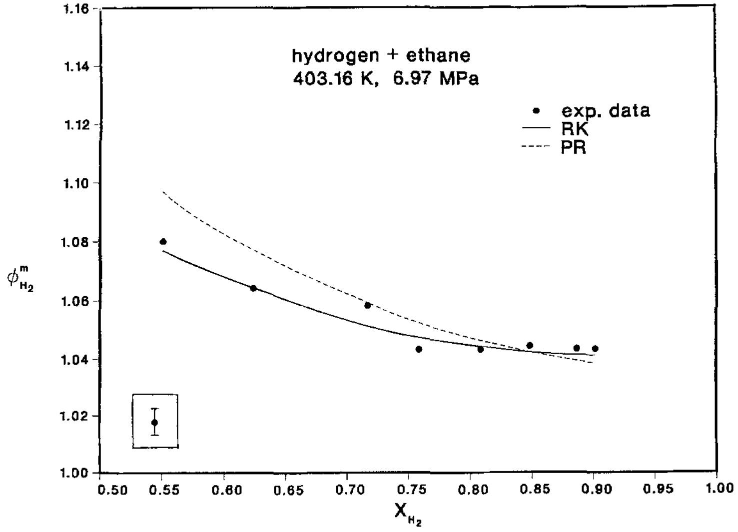

Fig. 3. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi^m_{H_2}$, versus hydrogen mole fraction, x_{H_2}, at 403.16 K and 6.97-MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

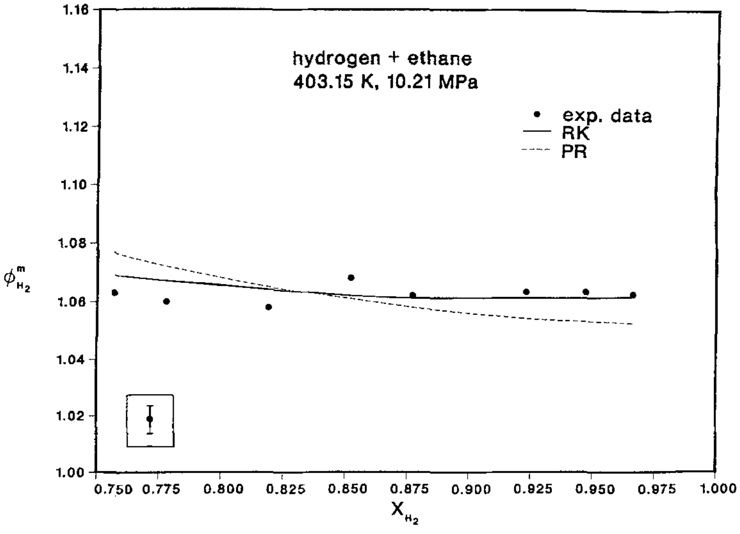

Fig. 4. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi^m_{H_2}$, versus hydrogen mole fraction, x_{H_2}, at 403.15 K and 10.21-MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

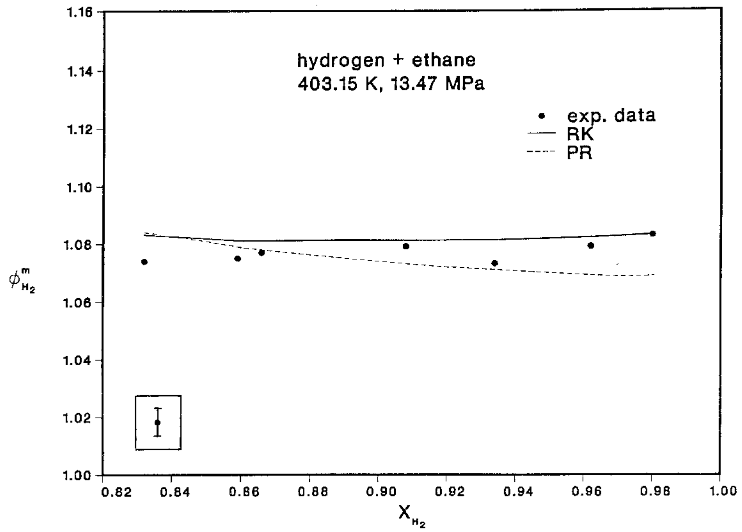

Fig. 5. A plot of the fugacity coefficient of hydrogen (in the mixture), $\phi^m_{H_2}$, versus hydrogen mole fraction, x_{H_2}, at 403.15 K and 13.47-MPa pressure. The error bar in the box is typical for an equimolar mixture and is not a measured data point.

equation. Van der Waals mixing rules have been used throughout. In the calculations using the Peng–Robinson equation, the acentric factor, α, was assigned a value of zero for hydrogen. It should be noted that the predictions of the fugacity coefficients from this equation are not very sensitive to the value of the acentric factor. The calculated values are usually within 1% as long as physically reasonable values (zero or the experimentally determined −0.22) are chosen. Binary interaction coefficients were assigned a value of zero for purposes of this comparison, since none are available which are based on measurements in the temperature range of this work.

Both the Redlich–Kwong and the Peng–Robinson equations provide good predictions (within 1 or 2%) of the experimental data measured in this study. The behavior of $\phi^m_{H_2}$ with increasing pressure is predicted well by both equations, although the Redlich–Kwong equation does a slightly better job despite its inherent simplicity. At the lower hydrogen mole fractions (as seen in Figs. 2 and 3), the Redlich–Kwong equation provides better predictions than does the Peng–Robinson. The relatively poorer agreement with equation-of-state predictions at lower hydrogen concentrations has been observed in all studies of this type. At least part of the reason for the larger deviations can be ascribed to the more difficult experimental conditions in this range (long times for pressure equilibration and less than favorable analytical conditions). For this reason, it is usual to concentrate data acquisition on the hydrogen mole fraction range above 0.6.

4. CONCLUSIONS

Hydrogen component fugacity coefficients for the hydrogen + ethane binary system were measured at 403.15 K (130°C) at pressures of 5.25, 6.97, 10.21, and 13.47 MPa using the physical equilibrium technique. The experimental data were examined for qualitative trends, and were compared with predictions obtained from two equations of state. These models were the Redlich–Kwong and Peng–Robinson equations, which were chosen because they have given good predicted values throughout the course of this work. While both equations give predictions within 1 to 2% of the experimental data, the simple Redlich–Kwong equation does a slightly better overall job. This is clearly the case in the region of low hydrogen mole fraction. No clear conclusion can be made regarding this region, however, due to a relative lack of data. Experimental modifications are currently being considered to allow more extensive measurement in this region.

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