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The Vapor-Liquid Equilibrium of the Hydrogen—n-Butane System at Elevated Pressures

The vapor-liquid equilibrium of the hydrogen–*n*–butane system was studied at temperatures between 54° and 121°C and at pressures up to 167 atm. The fugacity of hydrogen in the vapor phase was measured directly by using a palladium-silver semipermeable membrane, whereas p-T-x-y data were obtained in a conventional manner.

Henry's constants for hydrogen in *n*-butane were obtained from the experimental fugacity data without making any assumptions about the vapor phase. Constant-pressure, liquid-phase activity coefficients for both hydrogen and *n*-butane were calculated and correlated by using a modified van Laar equation.

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SCOPE

In chemical engineering practice, modern development in petroleum production and processing, such as the design of hydrocracking units and distillation equipment, have directed interest to the phase behavior of hydrogen-hydrocarbon systems at elevated pressures. Vaporization and condensation are unit operations of much importance in the fractional distillation process, where vapor-liquid equilibrium is approached on each stage of the process. Therefore, an accurate estimation on the vapor-liquid equilibrium is essential to the design of distillation and related equipment.

The purpose of this investigation is to obtain the vapor-liquid equilibrium data for the hydrogen–*n*-butane system at elevated pressures. In addition to the p-T-x-y data, the fugacity of hydrogen was measured directly using a palladium-silver semipermeable membrane. These data were used to calculate the Henry's constants for hydrogen in *n*-butane and liquid-phase activity coefficients for both hydrogen and *n*-butane. Both the fugacity and activity coefficients were then correlated by a number of equations of state.

CONCLUSIONS AND SIGNIFICANCE

In this investigation, new data were obtained on the phase equilibrium of hydrogen–*n*-butane at temperatures between 54° and 121°C and pressures up to 167 atm.

For the vapor phase at conditions only slightly removed from ideality (54° and 71°C), a modified Redlich-Kwong equation was most successful in correlating the fugacity coefficient data. With increasing deviations from ideality (88°, 104°, and 121°C), the data were correlated best by the B-W-R equation. The average deviations for the two cases are 0.48 and 0.56%, respectively.

Henry's constants of hydrogen in *n*-butane at the vapor pressure of *n*-butane were determined directly from the vapor-liquid equilibrium and fugacity data. They were shown to be a linear function of temperature, with a slope of −7.5 atm/°C.

Liquid-phase nonideality was expressed in terms of constant-pressure activity coefficients by using the unsymmetric convention. These coefficients for both hydrogen and *n*-butane were correlated by a modified van Laar equation with an average standard deviation of 0.018.

Finally, by using the equations of state described above, a bubble-pressure calculation was performed. Excellent agreement was obtained between the calculated and experimental values.

THERMODYNAMIC CONSIDERATIONS

For a two-phase system involving a vapor and a liquid, the condition for equilibrium is given by

$$f_i^V = f_i^L \tag{1}$$

where f_i^V is the fugacity of component i in the vapor phase at the temperature T and pressure p of the system, and f_i^L is the fugacity of component i in the liquid phase at the same system temperature and pressure.

For vapor-phase nonideality, f_i^V is usually expressed in terms of a fugacity coefficient given by

$$f_i^V = \phi_i y_i p_i \tag{2}$$

where ϕ_i is the fugacity coefficient, and y_i is the mole fraction of component i in the vapor phase. On the other hand, the liquid-phase nonideality is usually expressed in terms of an activity coefficient given by

$$f_i^L = \gamma_i x_i f_i^o, \tag{3}$$

where γ_i is the activity coefficient, and f_i^o is a standard state fugacity at the system temperature and an arbitrary but specified pressure, and x_i is the mole fraction of i in the liquid. It is therefore important to note that the value of γ_i depends on the value of the reference pressure.

Since the critical temperature of hydrogen is below the system temperature of this study, the logical choice of standard states for the present system is based on an unsymmetric convention recommended by Prausnitz (1968). According to this convention, the standard state for hydrogen which is based on an ideal dilute solution concept is the Henry's law constant $H_{2,1}$ for solute 2 (hydrogen) in solvent 1 (*n*-butane). On the other hand, the pure component fugacity, $f_{\text{pure } 1}$, is chosen as the standard state of the solvent. Based on these choices

$$\gamma_1 \rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \tag{4}$$

and

$$\gamma_2^* \rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 0 \tag{5}$$

In addition, for isothermal vapor-liquid equilibrium of a binary system such as hydrogen and *n*-butane, the system pressure varies with composition. In order to study the nonidealities of the liquid phase which are due only to composition effects, the activity coefficients and standard state fugacities should be adjusted from the experimental pressure to a constant reference pressure (Prausnitz and Chueh, 1968).

The fugacities of hydrogen and *n*-butane in the liquid phase at the system pressure are related to these constant-pressure activity coefficients and standard state fugacities by

$$f_1^L = \gamma_1^{(p^r)} x_1 f_1^{o(p^r)} \exp \int_{p^r}^{p} \frac{v_1^L}{RT} dp \tag{6}$$

and

$$f_2^L = \gamma_2^{*(p^r)} x_2 H_{2,1}^{(p^r)} \exp \int_{p^r}^{p} \frac{v_2^L}{RT} dp \tag{7}$$

where p^r is a fixed reference pressure, v_1^L and v_2^L are the partial molar volume of components 1 (*n*-butane) and 2 (hydrogen) in the liquid mixture at system temperature T, $f_1^{o(p^r)}$ is equal to $f_{\text{pure } 1}^{(p^r)}$, the fugacity of pure *n*-butane at p^r and T, and $H_{2,1}^{(p^r)}$ is Henry's constant for hydrogen in *n*-butane at p^r and T. Experimentally, Henry's constant is always found at p_1^s, the vapor pressure of the solvent at temperature T. However, these two Henry's constants are related by

$$H_{2,1}^{(p^r)} = H_{2,1}^{(p_1^s)} \exp \int_{p_1^s}^{p^r} \frac{v_2^\infty}{RT} dp \tag{8}$$

where v_2^∞ is the partial molar volume of hydrogen at infinite dilution in *n*-butane at system temperature T. The exponential term in Equations (6) to (8) is known as the Poynting correction which adjusts the standard state fugacities from the system pressure to a reference pressure.

In this investigation, the fugacity of hydrogen in the gas phase was determined experimentally by using a semipermeable membrane. In order to calculate component

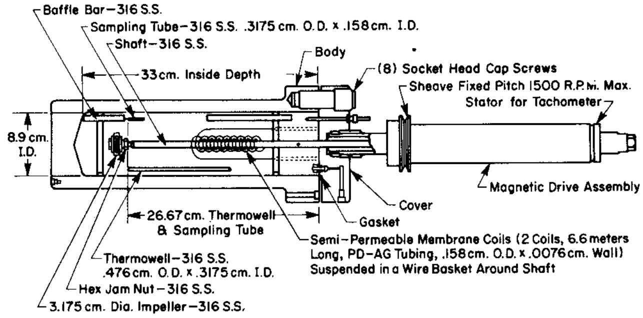

Fig. 1. Schematic diagram of the pressure vessel.

fugacities in the liquid from Equations (6) and (7), one must have the reference fugacities $f_1^{o(p^r)}$ and $H_{2,1}^{(p^r)}$, both activity coefficients $\gamma_1^{(p^r)}$ and $\gamma_2^{*(p^r)}$, and the partial molar volumes of the components v_1^L and v_2^L in the liquid. Following Chueh and Prausnitz (1968), the reference pressure was chosen as $p^r = 0$.

The Henry's constant $H_{2,1}^{(p_1^s)}$ was determined from the vapor-liquid equilibrium data by using the relation

$$H_{2,1}^{(p_1^s)} = \lim_{x_2 \to 0} \frac{f_2^L}{x_2} \qquad (9)$$

The Henry's constant $H_{2,1}^{(p^r)}$ was then calculated from Equation (8). The reference fugacity of *n*-butane, $f_1^{o(p^r)}$, was calculated from pure component data by following the method of Prausnitz et al. (1967). Although data on v_1^L are not available at each composition and pressure at a constant system temperature, it can usually be assumed that they can be replaced by corresponding values at infinite dilution of hydrogen. In the present work, this is justified, since the mole fraction of hydrogen in the liquid was always less than 0.2, so that the volumetric properties of the system do not deviate much from those at infinite dilution. The only remaining unknowns in Equations (6) and (7) are then $\gamma_1^{(p^r)}$ and $\gamma_2^{*(p^r)}$, and these can then be calculated by combining these two equations with Equation (1).

EXPERIMENTAL

The apparatus was designed for high-pressure, vapor-liquid equilibrium studies. The usual variables of temperature, pressure, vapor, and liquid compositions were measured. In addition, the fugacity of hydrogen was determined by measuring the temperature and pressure of the pure hydrogen on one side of the semipermeable membrane and by using the knowledge of its p-V-T behavior. The principle of the semipermeable membrane technique and its applications in fugacity measurements have been described in detail by Cheh (1973) and by Antezana and Cheh (1975).

Equipment

The same apparatus (including the palladium-silver semipermeable membrane) and analytical equipment used to determine the fugacity of hydrogen in mixtures with ammonia and propane (Antezana and Cheh, 1975) were used for the present investigation. Only a number of relatively minor modifications were made. A liquid sampling tube, baffles to promote liquid-phase mixing, and a stirring rod coupled to a magnetic drive assembly were included in the equilibrium vessel. In addition, a thermistor operated liquid level indicator probe (Model LD3, Conax) was positioned inside the vessel to indicate when the vessel contained 800 cm^3 of liquid. The stirrer was an impeller sparger on the bottom of a hollow shaft which had an opening in the vapor phase. This stirrer mixed the liquid and promoted vapor-liquid equilibrium by drawing gas out of the vapor phase and dispersing it in the liquid. A schematic diagram of the pressure vessel is shown in Figure 1.

For composition analysis, Squalane supported on Chromosorb-P was packed in the chromatographic column, and helium containing 8.5% hydrogen by volume was used as the carrier gas ultra pure (99.999%) hydrogen gas and instrument grade (99.5% purity minimum) n-butane gas were used in this work.

Experimental Procedure

Experiments were carried out along five isotherms ranging from 54° to 121°C. Pressures were measured on each isotherm up to 170 atm. The procedure used for composition analysis was the same as that reported by Antezana and Cheh (1975) in the analysis of hydrogen-propane mixtures. The gas chromatograph was calibrated by mixtures of hydrogen and *n*-butane at known compositions which were prepared by mixing known weights of the two gases.

The validity of temperature and pressure measurements was tested by measuring the vapor pressure of *n*-butane at the five experimental temperatures. The results are in excellent agreement with those reported by Kay (1940) with an average deviation of 0.3%.

At the start of the first mixture run for each isotherm, the pressure vessel was charged with liquid *n*-butane after several purgings. Then the temperature of the constant temperature air bath was adjusted and the vessel filled with hydrogen to a pressure of about 7 to 10 atm above the *n*-butane vapor pressure. The tube side was evacuated to allow only the hydrogen which had diffused through the membrane to enter the tube coil.

The system was then allowed to come to equilibrium, which took from 5 to 25 hr. depending on the temperature of the run and the concentration of hydrogen. At frequent intervals, pressures on both the hydrogen side and the mixture side of the membrane were measured with the dead weight piston gauge and the diaphragm differential pressure indicator until final constant pressures were indicated for at least 4 hr. After these final equilibrium pressures of both hydrogen and the mixture were measured, samples of the gas and liquid mixtures in the pressure vessel were withdrawn for analysis by gas chromatography.

For each succeeding run, hydrogen was added until the pressure had been incremented by about 14 atm. The above process was then repeated. Therefore, the shell pressure was always higher than the tube pressure, so that hydrogen diffused into the tubes. The highest pressure for a run at each isotherm was approximately 170 atm.

After the 14 atm increment of hydrogen, at the start of each run, a time study was made to ascertain the time required for the vapor liquid to come to equilibrium. This study consisted of following the system pressure and composition of the vapor and liquid phases, measuring these variables every hour for several hours. Previous investigators (Dean and Tooke, 1946) have estimated that hydrogen-hydrocarbon systems take about 10 min. to come to vapor-liquid equilibrium when reasonable stirring is used. In this case, no change in the measured variables was noted, indicating that the time for the vapor and liquid to come to equilibrium was less than 1 hr. Therefore, the time for the vapor liquid to come to equilibrium was very small compared to the time for the tube-side hydrogen to reach a steady pressure. The attainment of equilibrium was verified not only by constant pressure readings over 4 hr. but also by demonstrating that the readings could be attained from both directions, that is, by adding or releasing hydrogen gas. This demonstration was performed for the highest and lowest isotherms at the high pressure value of about 170 atm. After the final run was completed for each isotherm, system pressure was reduced to 136 atm, the system allowed to equilibrate, and samples taken. Within experimental error, analysis confirmed the composition values obtained at this pressure for the ascending pressure runs. The tube-side pressures agreed as well; this is reasonable since the hydrogen equilibrium should be the same whether the equilibrium is approached by hydrogen diffusing into the tube or out of it.

Several other precautions and measurements were made to ensure the precision of the experiments. At the end of the runs for each isotherm, the pure hydrogen inside the tube was analyzed to assure that no *n*-butane had leaked into the tube. For sampling, the agitator was shut off and the sample lines evacuated. The pressure was again measured to see if the agitator had any effect on it, but no difference was ever noted. The size of the samples taken were such that no change in pressure greater than 0.025% was ever observed, so that the effect on the equilibrium was negligible. Finally, duplicate samples of both liquid and vapor were taken, the lines being purged between samplings. Each vapor sample was analyzed several times. A deviation of no more than 0.1% was ever noted in the compositions. The liquid samples were expanded in the expansion chamber to a vapor and analyzed as such. Again, replicate composition determinations showed a deviation of no more than 0.1%.

The error in the measured quantities were estimated to be as follows: temperature, ±0.05°C; pressure, ±0.05 atm; mole fractions of vapor and liquid, ±0.04; and fugacity of hydrogen, ±0.3%.

RESULTS

The equilibrium data along with the fugacity of hydrogen in the vapor phase are presented in Tables 1 to 5. At equilibrium, the fugacity of hydrogen in the mixture is equal to that in the pure gas across the semipermeable membrane. The pure hydrogen fugacity was calculated from accurate p-v-T data in the literature (Woolley et al., 1948). Figure 2 is a hydrogen fugacity x-y plot at constant temperature. The results show that at low temperatures, the vapor phase is mostly hydrogen. As the temperature increases, more *n*-butane enters the vapor phase. Also, at all temperatures, the solubility of hydrogen is approximately linear with the fugacity of hydrogen in the vapor. Finally, as the temperature increases, the phase envelope becomes smaller.

A customary method of presenting high pressure vapor-liquid equilibrium data is in terms of a vapor-liquid equilibrium constant defined by the ratio of the mole fraction of a component in the vapor phase to that in the liquid phase. A plot of the hydrogen and *n*-butane vapor-liquid equilibrium constants vs. pressure at constant temperature is given in Figure 3. The equilibrium constants for hydrogen are quite large, as expected. It should also be noted that the points at an *n*-butane equilibrium constant of 1.0 are values of the *n*-butane vapor pressure as a function of temperature.

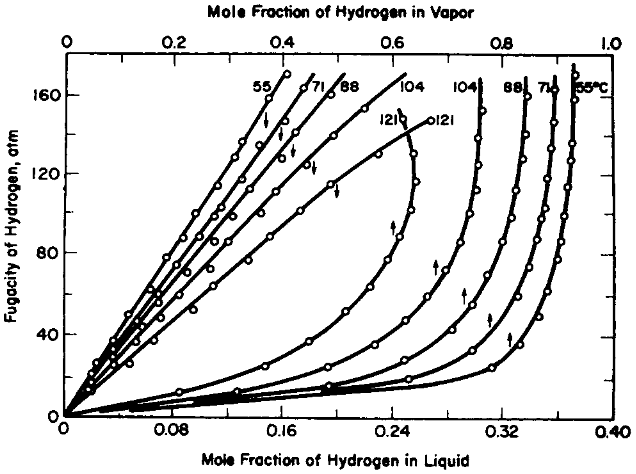

Fig. 2. Fugacity of hydrogen-composition diagram at constant temperature.

Finally, the Henry's constant of hydrogen at the system temperature and the *n*-butane vapor pressure were obtained from the experimental data and Equation (9). The results are presented in Figure 4 with an estimated error of the constants to be ±1%. The Henry's constant decreases with temperature at a slope of −7.5 atm/°C.

TABLE 1. FUGACITY AND CONSTANT-PRESSURE ACTIVITY COEFFICIENTS AT 54.5°C

Mole fraction of hydrogen in vapor	Mole fraction of hydrogen in liquid	Equilibrium pressure Hydrogen atm	Equilibrium pressure Mixture atm	Fugacity of hydrogen atm	Constant-pressure activity coefficient Hydrogen	Constant-pressure activity coefficient *n*-butane
0.777	0.025	24.80	30.86	25.16	0.927	1.019
0.828	0.036	35.68	41.98	36.42	0.898	1.014
0.863	0.047	48.64	55.12	49.89	0.903	1.000
0.879	0.063	60.74	67.79	62.79	0.814	1.025
0.896	0.074	75.20	82.66	78.41	0.824	1.009
0.903	0.086	83.56	91.27	87.53	0.770	1.009
0.910	0.094	94.85	102.95	99.97	0.774	1.004
0.916	0.110	107.33	115.88	113.92	0.723	1.007
0.922	0.123	119.69	128.61	127.91	0.696	0.995
0.924	0.128	127.02	136.23	136.30	0.696	0.995
0.925	0.129	127.25	136.40	136.56	0.691	0.987
0.930	0.147	145.88	155.71	158.17	0.660	0.982
0.932	0.160	156.02	166.27	170.12	0.630	0.985

TABLE 2. FUGACITY AND CONSTANT-PRESSURE ACTIVITY COEFFICIENTS AT 71.1°C

Mole fraction of hydrogen in vapor	Mole fraction of hydrogen in liquid	Equilibrium pressure Hydrogen atm	Equilibrium pressure Mixture atm	Fugacity of hydrogen atm	Constant-pressure activity coefficient Hydrogen	Constant-pressure activity coefficient *n*-butane
0.638	0.022	18.86	27.42	19.05	0.932	1.003
0.741	0.036	32.26	41.22	32.84	0.932	1.001
0.791	0.053	44.93	54.25	46.01	0.844	1.003
0.825	0.068	58.62	68.39	60.49	0.819	0.997
0.846	0.081	72.09	82.37	74.94	0.808	0.995
0.860	0.098	84.77	95.52	88.70	0.752	0.999
0.871	0.109	93.96	104.89	98.82	0.727	0.984
0.875	0.113	98.50	109.56	103.84	0.724	0.980
0.881	0.129	111.29	123.01	118.12	0.686	0.992
0.888	0.141	125.64	137.98	134.39	0.674	0.987
0.891	0.159	136.00	148.87	146.28	0.624	1.001
0.894	0.173	150.67	164.35	163.34	0.604	1.009

TABLE 3. FUGACITY AND CONSTANT-PRESSURE ACTIVITY COEFFICIENTS AT 87.8°C

Mole fraction of hydrogen in vapor	Mole fraction of hydrogen in liquid	Equilibrium pressure Hydrogen atm	Equilibrium pressure Mixture atm	Fugacity of hydrogen atm	Constant-pressure activity coefficient Hydrogen	Constant-pressure activity coefficient *n*-butane
0.483	0.021	15.42	27.56	15.53	0.937	0.995
0.619	0.037	28.05	40.63	28.48	0.919	1.006
0.706	0.058	42.60	55.44	43.56	0.838	1.008
0.743	0.069	53.85	67.20	55.39	0.849	1.018
0.772	0.090	68.01	82.10	70.45	0.774	1.045
0.799	0.108	82.83	97.39	86.46	0.738	1.049
0.814	0.122	94.41	109.40	99.14	0.710	1.055
0.825	0.134	106.41	121.94	112.43	0.692	1.062
0.835	0.158	120.47	136.66	128.21	0.626	1.084
0.839	0.166	131.18	148.01	140.37	0.619	1.093
0.843	0.193	147.80	165.68	159.52	0.559	1.126

TABLE 4. FUGACITY AND CONSTANT-PRESSURE ACTIVITY COEFFICIENTS AT 104.4°C

Mole fraction of hydrogen in vapor	Mole fraction of hydrogen in liquid	Equilibrium pressure Hydrogen atm	Equilibrium pressure Mixture atm	Fugacity of hydrogen atm	Constant-pressure activity coefficient Hydrogen	Constant-pressure activity coefficient *n*-butane
0.322	0.019	11.61	27.97	11.67	0.919	0.981
0.480	0.037	24.14	41.19	24.43	0.916	0.999
0.566	0.053	35.75	53.32	36.40	0.890	1.008
0.621	0.071	46.81	64.82	47.91	0.819	1.018
0.662	0.084	58.27	76.76	59.99	0.810	1.022
0.695	0.106	70.16	89.07	72.67	0.725	1.032
0.719	0.119	82.42	101.86	85.89	0.709	1.036
0.739	0.143	96.01	116.10	100.73	0.638	1.051
0.750	0.153	106.29	126.91	112.08	0.624	1.055
0.753	0.175	117.98	139.55	125.16	0.567	1.082
0.759	0.195	130.29	152.59	139.05	0.525	1.098
0.760	0.217	142.09	165.19	152.53	0.482	1.121

TABLE 5. FUGACITY AND CONSTANT-PRESSURE ACTIVITY COEFFICIENTS AT 121.1°C

Mole fraction of hydrogen in vapor	Mole fraction of hydrogen in liquid	Equilibrium pressure Hydrogen atm	Equilibrium pressure Mixture atm	Fugacity of hydrogen atm	Constant-pressure activity coefficient Hydrogen	Constant-pressure activity coefficient *n*-butane
0.213	0.021	11.08	33.86	11.14	0.970	0.992
0.367	0.049	24.74	47.98	25.05	0.839	1.003
0.444	0.066	36.68	60.66	37.35	0.841	1.011
0.514	0.095	51.59	76.16	52.90	0.734	1.023
0.555	0.109	62.58	87.49	64.50	0.715	1.021
0.588	0.135	74.80	100.17	77.54	0.629	1.034
0.609	0.149	85.52	111.39	89.14	0.601	1.035
0.632	0.172	97.45	123.69	102.16	0.543	1.044
0.637	0.193	110.12	137.09	116.12	0.496	1.057
0.638	0.194	110.17	137.17	116.22	0.493	1.057
0.633	0.228	123.14	150.89	130.69	0.424	1.088
0.615	0.266	138.41	166.55	147.97	0.365	1.120

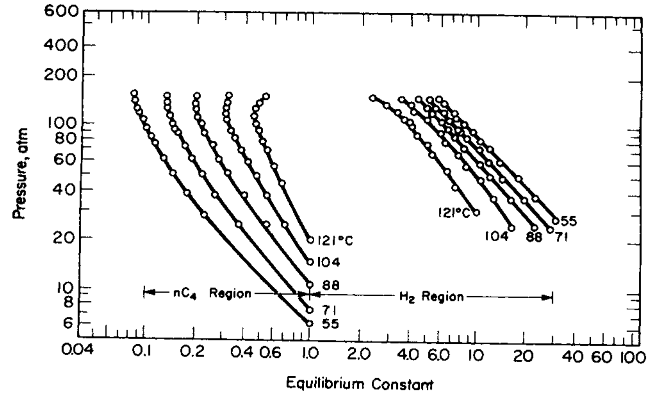

Fig. 3. Pressure-equilibrium constant diagram at constant temperature.

DISCUSSION

There are three previous investigations on the vapor-liquid equilibrium of the hydrogen-*n*-butane system. Frolich et al. (1931) reported three data points at 25°C and at pressures up to 95 atm, whereas Nelson and Bonnell (1943) reported data at three temperatures ranging from 24° to 116°C and pressures up to 106 atm. There is substantial disagreement between these two sets of data, the former being considerably higher than the latter. However, the comparison might not be rigorous, since the data of Frolich et al. were based on ambiguous units. Aroyan and Katz (1951) determined the vapor-liquid equilibrium of the system at temperatures between −129° and 24°C and pressures between 20 and 544 atm. There is general agreement between the results of Nelson and Bonnell and that of Aroyan and Katz at 24°C. An exact comparison on the results between the present investigation and the three reported studies is impossible because experiments were not carried out at identical temperatures. Only two of the temperatures, 82° and 116°C, studied by Nelson and Bonnell, fall in the same range of our work, and their results show apparent consistency with ours.

To test the consistency of vapor-liquid equilibrium data at high pressures, Kahre (1974) suggested that a plot of the partial pressure of the heavy component as a function of the total pressure of the system should be constructed. The intercept of this curve at zero total pressure is the vapor pressure of the heavy component, and for a supercritical system, the curve increases with pressure. Such a plot based on the present results at all five temperatures, and the measured vapor pressure of *n*-butane is shown in Figure 5. There is little question that extrapolations to the vapor pressures are valid. There is only one point at 104°C and two points at 121°C below the extrapolated curves. In view of the complexity of the experiments as well as the difficulty in accurate composition measurements, especially at low hydrogen compositions, it can be concluded that except for the three experimental points, the data appear to be of high accuracy.

For vapor-phase behavior, temperature has a more important effect on nonideality. This is due to the increasing amount of *n*-butane in the vapor phase at high temperatures, which contributes greatly to nonideality. The experimental fugacity coefficients of hydrogen were compared with values predicted by a number of equations of state. Details of the comparison were described in the dissertation by Klink (1973). Only two of the more succcessful equations are described here. These include a modified Redlich-Kwong equation by Chueh and Prausnitz (1967) and the B-W-R equation (Benedict et al., 1940).

For the modified Redlich-Kwong equation, the revised mixing rules and constants including the effective critical properties of hydrogen resulting from quantum effect as described by Chueh and Prausnitz (1967) were adopted in our calculation. For the B-W-R equation, conventional mixing rules as well as constants recommended by Motard and Organick (1960) were used.

At lower temperatures (54° and 71°C), where the system is relatively ideal, the modified Redlich-Kwong equation yields a value of the hydrogen fugacity coefficient in excellent agreement with the experimental data. The average and maximum deviations are 0.48 and 1.1%. The B-W-R equation predicts the fugacity coefficient with average and maximum deviations of 0.99 and 1.7%. On the other hand, at higher temperatures (88°, 104°, and 121°C), where the system is less ideal, the average and maximum deviations are 2.2 and 5.2% for the modified Redlich-Kwong equation, whereas the corresponding values are 0.56 and 1.6% for the B-W-R equation.

For liquid-phase nonideality, constant-pressure activity coefficients were calculated from experimental data by using Equations (6) to (8). In these equations, the fugacity of hydrogen and the liquid mole fractions of hydrogen and *n*-butane were measured experimentally. The fugacity of *n*-butane at the system temperature and pressure was calculated by using the modified Redlich-Kwong equation at the two lower temperatures and the B-W-R equation at the three higher temperatures. The reference fugacity for *n*-butane at zero pressure was calculated following the method of Prausnitz et al. (1967). The reference fugacity for hydrogen is Henry's constant; this was determined experimentally from the fugacity-composition data at the vapor pressure of *n*-butane. To obtain Henry's constant at zero pressure, Poynting correction was calculated. Values of the partial molar volume of hydrogen and *n*-butane at infinite dilution used in this calculation along with values of Henry's constant of hydrogen and the reference fugacity of *n*-butane are given in Table 6. Resulting values for the constant-pressure activity coefficients are included in Tables 1 to 5.

These activity coefficients were correlated by fitting the van Laar, Margules, and a modified van Laar equation by Chueh and Prausnitz (1968) to the experimental data. Details of the correlation were also presented in the dissertation by Klink (1973). Both the van Laar and Mar-

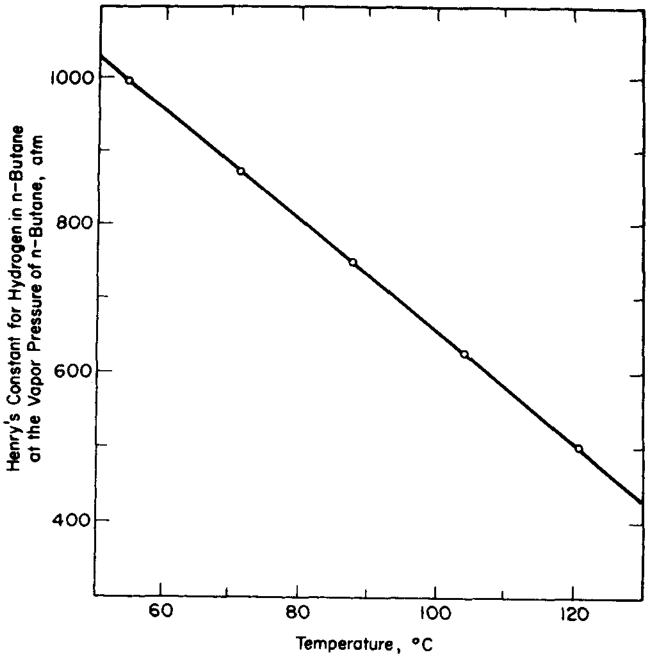

Fig. 4. Henry's constant vs. temperature.

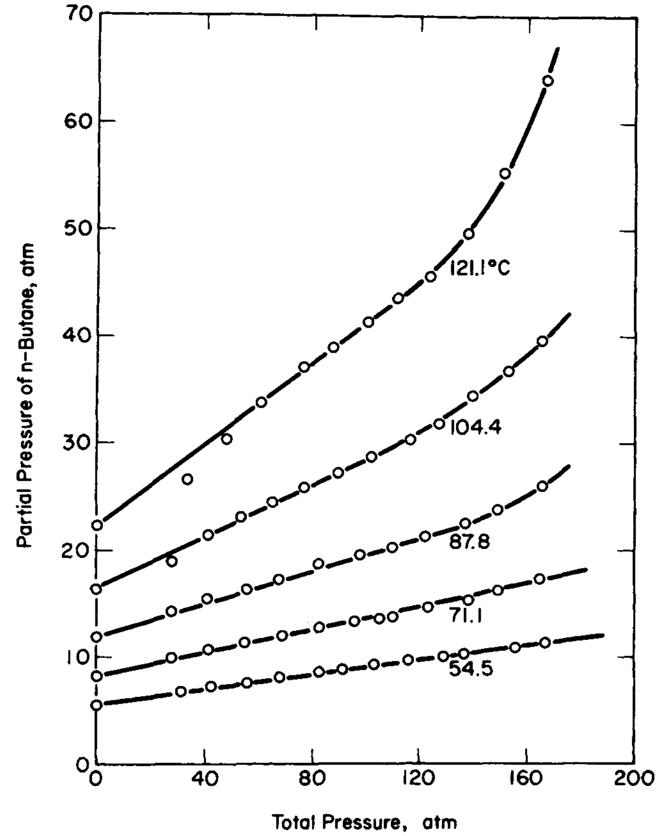

Fig. 5. Partial pressure of *n*-butane vs. total system pressure.

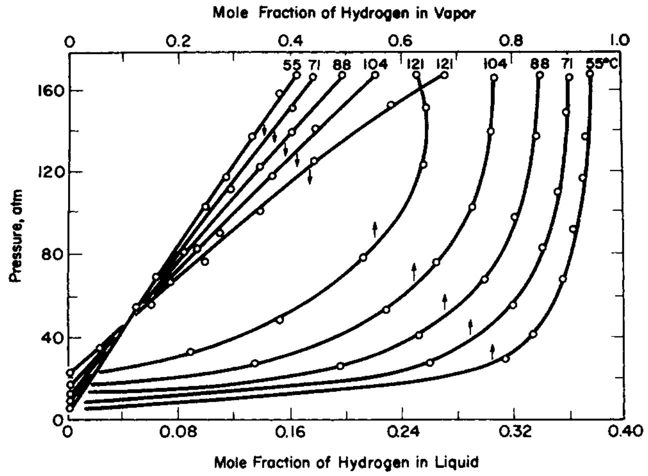

Fig. 6. Comparison of experimental data with bubble-pressure calculation.

gules equation follow the data reasonably well at lower temperatures and become poorer at higher temperatures. The average standard deviation was 0.024 for the van Laar equation and 0.048 for the Margules equation. However, the modified van Laar equation follows the data well at all temperatures, with an average standard deviation of 0.018. The characteristic constants A and B were found to be rather insensitive to temperature, and the results are presented in Table 7.

A bubble-pressure calculation was performed by using the modified Redlich-Kwong equation for the vapor phase at 54° and 71°C, the B-W-R equation at 88°, 104°, and 121°C, and the modified van Laar equation for the liquid at all five temperatures. The calculated results along with the experimental data are shown in Figure 6. Excellent agreement was obtained between the calculated and measured values.

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The authors wish to thank Dr. T. W. Schmidt for calling their attention to the paper by Kahre, which is the basis for Figure 5.

NOTATION

A = constant in modified van Laar equation
B = constant in modified van Laar equation
f_i = fugacity of component i
$H_{2,1}$ = Henry's constant of component 2 (solute) in component 1 (solvent)
p = pressure
R = universal gas constant
T = temperature
v_1, v_2 = partial molar volumes of component 1 and 2
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ_i = activity coefficient of component i
ϕ_i = fugacity coefficient of component i

Superscripts

L = liquid
o = standard state
p_1^s = saturation pressure of component 1
p^r = reference pressure
r = reference
s = saturation
V = vapor
$*$ = based on unsymmetric convention
∞ = infinite dilution

Subscripts

i = component i
1, 2 = components 1 and 2

TABLE 6. PARTIAL MOLAR VOLUMES AT INFINITE DILUTION AND REFERENCE FUGACITIES AT ZERO PRESSURE

Temperature, °C	Partial molar volume of hydrogen, cc/mole	Partial molar volume of *n*-butane, cc/mole	Henry's constant of hydrogen, atm	Reference fugacity of *n*-butane, atm
54.5	87.6	108.4	982.5	4.770
71.1	107.2	113.5	837.6	6.818
87.8	134.1	119.7	696.3	9.268
104.4	176.1	127.2	570.3	12.105
121.1	249.9	137.4	420.9	15.303

TABLE 7. CONSTANTS FOR THE MODIFIED VAN LAAR EQUATION

Temperature, °C	*A*	*B*
54.5	30.6	18.5
71.1	30.6	18.5
87.8	30.6	18.5
104.4	33.4	16.8
121.1	35.3	15.9

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