Vapor-Liquid Equilibrium of Hydrogen/Tetralin System at Elevated Temperatures and Pressures

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A flow type of apparatus is built to give equilibrium gas and liquid samples at elevated pressures and temperatures while minimizing thermal decomposition. Saturated vapor and liquid compositions and *K* values are determined with this apparatus for the binary system hydrogen/tetralin (1,2,3,4-tetrahydronaphthalene) at four temperatures from 189.6° to 389.1°C, and seven pressures from 20 to 250 atm. Vapor pressures of tetralin are determined with the same apparatus, and values are reported at the four temperatures of this work.

SCOPE

This work extends experimental investigation of phase equilibrium of hydrogen/heavy solvent systems to elevated pressures and temperatures of interest in hydro treating processes, particularly coal liquefaction processes. Information on the amount of dissolved hydrogen in the liquid phase is useful for analysis of reaction mechanism and for engineering design of blowdown and associated separation systems.

Previous studies of the phase equilibrium of hydrogen/solvent systems have been limited to relatively low temperatures. An exception is found in the work by Grayson and Streed (1963) in which a correlation of *K* values of hydrogen in heavy oils was presented for temperatures and pressures comparable to this work, but no detailed experimental data were given.

The system hydrogen/tetralin reported here is the first system studied in the new flow type of apparatus we have just built. The study is being continued with other hydrogen mixture systems. The data gathered with various types of solvents will contribute to the development of general quantitative description of the solubility of hydrogen in complex liquid mixtures.

CONCLUSIONS AND SIGNIFICANCE

Vapor-liquid equilibrium in hydrogen/solvent systems has been the subject of a great deal of investigation owing to their industrial importance and scientific interest. The development of hydro treating and coal liquefaction processes generated renewed interest focused on conditions of high temperature and pressure and on heavy solvents. In this work we built a new flow type of apparatus and showed that equilibrium data can be obtained from it with small residence times of the samples in the high temperature zone. Thermal decomposition is minimized as residence time is reduced, making possible determination of equilibrium data at high temperatures that would otherwise lead to excessive decomposition.

That equilibrium is attained in the apparatus at the conditions of operation is supported by the positive results obtained from three tests:

1. The sample compositions are independent of flow rates within the range of flow rates employed.
2. Data on hydrogen/benzene from our apparatus agree with results obtained by Connolly (1962) from a static apparatus.
3. The new data on hydrogen/tetralin satisfy the Gibbs-Duhem equation.

Equilibrium saturated liquid and gas compositions and *K* values are determined for the binary system hydrogen/tetralin at four temperatures (189.6°, 268.7°, 348.6°, 389.1°C) and seven pressures (20, 30, 50, 100, 150, 200, 250 am). Henry constant of hydrogen is determined from the data. The results are useful for modeling the phase behavior of hydro treating and coal liquefaction processes. Since tetralin is widely used as a hydrogen-donor solvent in coal liquefaction investigations, data on the present system should be particularly relevant.

Vapor-liquid equilibrium data in hydrogen/solvent systems are of interest to hydro treating and coal liquefaction processes. Information on the solubility of hydrogen in the liquid reaction mixture is useful for analysis of reaction kinetics and mechanism and for engineering design of the

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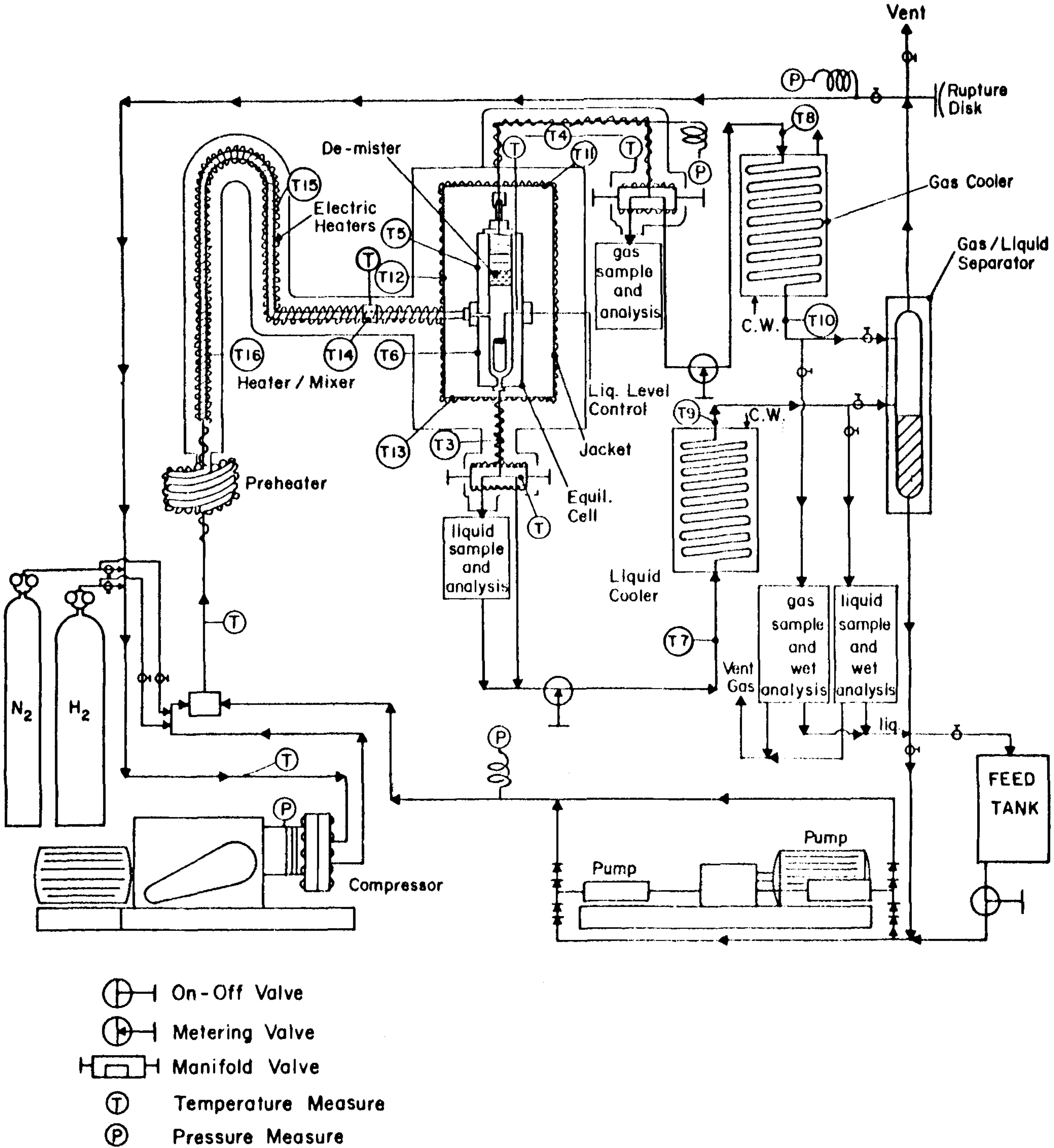

Fig. 1. Vapor-liquid equilibrium apparatus.

blowdown and recirculation systems. The needed information is, however, largely unavailable, particularly at elevated temperatures and pressures where the need is the greatest.

Solubility of hydrogen in several hydrocarbon solvents at low temperatures has been reported by Cook et al. (1957), Williams and Katz (1954), Benham and Katz (1957), and Sagara et al. (1972). Ipatiev et al. (1948) measured hydrogen/benzene up to 150°C and 200 atm. Nichols et al. (1957) reported data on hydrogen/*n*-hexane at 4° to 204°C and 120 to 680 atm. Studies of hydrogen/benzene and hydrogen/octane were made by Connolly (1962) and Connolly and Kandalic (1963) at temperatures up to 260°C and pressures to 175 atm. Low pressure solubilities were reported by Cukor and Prausnitz (1972) for hydrogen in hexadecane, bicyclohexyl, and diphenylmethane, and by Chappelow and Prausnitz (1974) for hydrogen in squalane and octamethylcyclotetrasiloxane. The temperature range was 25° to 200°C. The work which reached the highest temperature was by Grayson and Streed (1963) who presented *K* values of hydrogen in heavy oils at 320° to 480°C and pressures up to 200 atm, but no detailed data were given.

Clearly, there is a dearth of information on the behavior of hydrogen/solvent systems at hydro treating and coal liquefaction reaction conditions.

EXPERIMENTAL APPARATUS

We adopt a flow type of design for our equilibrium apparatus in order to reduce residence time of the sample in the high temperature zone and thereby to minimize thermal decomposition. Figure 1 shows the scheme of the apparatus. All parts exposed to high temperature and high pressure are made of stainless steel type 316.

Hydrogen is supplied to the system from a high pressure cylinder through a pressure regulator. The gas compressor shown in Figure 1 may be bypassed. The hydrogen cylinders are at a pressure of 140 atm as purchased, which is adequate for the experiments reported here at 120 atm and below. The compressor is used for higher pressures. Not shown in Figure 1 downstream from the compressor is a 500 ml pressure vessel equipped with a pressure regulator on the output line of the vessel. The presence of this vessel greatly reduces fluctuation of pressure caused by the compressor.

The liquid feed is delivered either from a Ruska pump (syringe type, single barrel, 1 000 ml contents) or a Hills-McCanna U type of metering pump at rates of 500 to 2 000 ml/hr. Flow from the Ruska pump is even and from the Hills-McCanna reciprocating type of pump not quite even. To reduce the fluctuations of flow, a cylindrical vessel of 75 ml (not shown in Figure 1) is installed in a vertical position in the liquid line. Flow of liquid is through the lower part of the vessel. The top of the vessel is connected to the hydrogen line through a valve, which permits the vessel to be filled with hydrogen gas to produce the damping action. A Teflon boat floats on the surface of the liquid to reduce depletion of the gas by absorption.

The gas and liquid streams are joined at a tee, and the two-phase mixture is heated initially in a tubing 2.1 m long, 6.35 mm OD, 2.11 mm ID, and finally in a larger tubing 1.2 m long, 9.54 mm OD, 5.15 mm ID. The larger tubing is fitted within with a notched twisted ribbon in its entire length to promote mixing of the flowing fluids. Heating is by means of electric heating tapes wound on the outside surface of the tubings. Variacs control the rate of heating so that the temperature of the stream leaving the heaters is within 1°C of the equilibrium cell temperature.

The function of the equilibrium cell is to separate the gas and liquid phases. Figure 2 shows the details of the cell. It is a pressure vessel approximately 90 ml in internal volume made by Autoclave Engineers. Two nozzles are welded on opposite sides at mid section of the vessel. One nozzle provides the opening for the gas/liquid feed and the other for an Aminco cone compression type of electrical connection to a liquid level detector. Insulation of the electrical wire from the cell body is by means of a soapstone cone which is rated for a temperature of 430°C, thus setting the upper limit of temperature that can be reached by this apparatus.

To avoid entrainment of gas in the liquid withdrawn from the cell, a pool of liquid is maintained in the cell. The liquid level is sensed by a capacitor in the cell and displayed on an oscilloscope screen as a horizontal line. The position of the line depends on the liquid level. By adjusting the metering valve at the bottom of the cell, we maintain the liquid level and keep the capacitor half immersed. The level detector is similar to that described by White and Brown (1942).

A demister pad in the equilibrium cell prevents entrained liquid droplets from escaping overhead.

To insure uniform temperature in the equilibrium cell, a copper jacket 32 mm thick encloses the entire cell. Adiabatic heating is supplied by heating wires insulated in fishspine ceramic beads placed in grooves cut on the outside surface of the copper jacket. Johns-Manville Thermo-12 insulation 0.17 W/(m-°K) in thermal conductivity and 76 mm thick surrounds the entire copper jacket to maintain high temperature and promote isothermal conditions within.

The liquid stream from the bottom of the equilibrium cell is reduced in pressure, cooled, and fed to a separator to separate the dissolved gas which is vented to the atmosphere. The separated liquid is recharged to the liquid pump after purification.

The gas stream from the top of the equilibrium cell is likewise reduced in pressure, cooled, and fed to the same separator as the liquid stream.

A Heise gauge that reads pressures up to 340 atm measures the pressure in the cell to ± 0.1% or 0.3 atm whichever is the greater.

The temperature of the equilibrium cell is measured by a calibrated type K chromel-alumel thermocouple inserted in the thermo well in the wall of the cell. The calibration of this couple is supplied by the Claude S. Gordon Company and is checked by us to be accurate to ± 0.05°C.

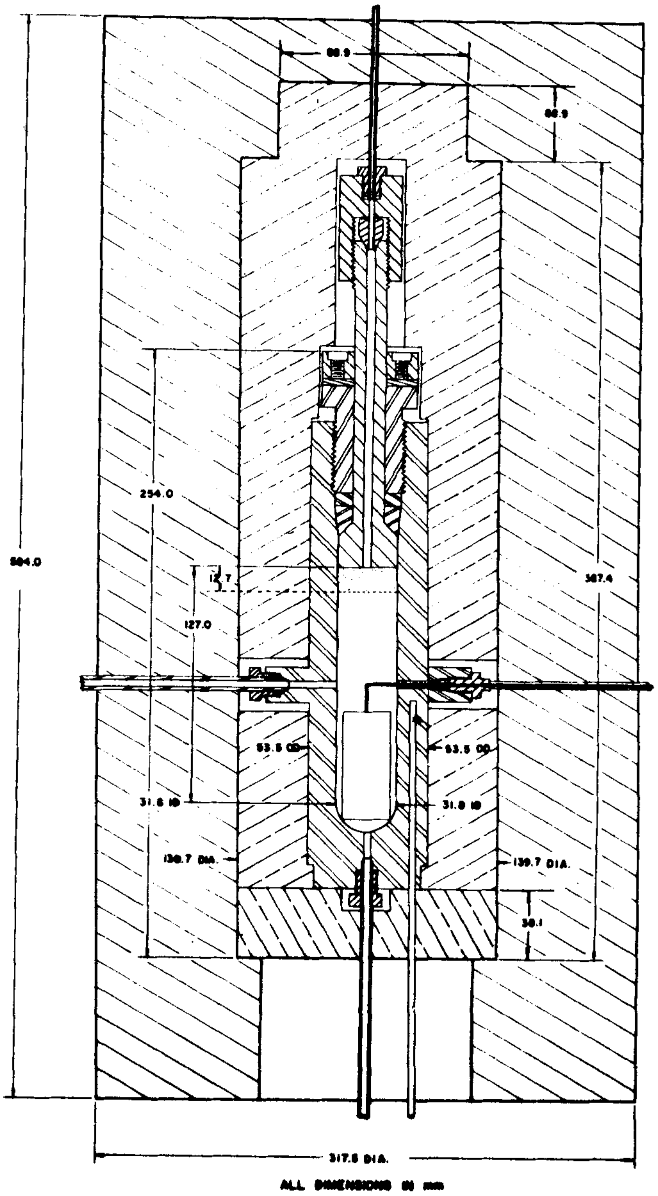

Fig. 2. Vapor-liquid equilibrium cell.

Two type K thermocouples are placed in between the equilibrium cell and the copper jacket at opposite sides and at different heights to sense the uniformity of temperature, or the lack of it. The couples have always given the same reading within their accuracy, that is, 0.75% above 260°C, indicating close approach to isothermal conditions in the cell jacket.

The temperature of the feed stream to the cell is measured with an Autoclave Engineers sheathed thermocouple housed in a valve bodylike block. The fluid flows through the block and around the sheath. The block is kept adiabatic by means of insulation and heating outside the insulation. A bare couple is attached to the outside surface of the block. The heater is adjusted until the bare couple and the sheathed couple give the same reading, indicating isothermal and adiabatic conditions for the thermocouple block.

The equilibrium apparatus is also useful for determining the vapor pressure of the solvent. In this mode of operation, the solvent alone is pumped into the equilibrium apparatus, and heating is adjusted to split the feed into equal parts of vapor and liquid. The temperature is measured in the same way as usual, but the pressure measurement is made differently because of the much lower pressures of interest. Two different pressure

TABLE 1. TEST DATA ON HYDROGEN/BENZENE

T, °C	p, atm	x_H		y_H	
		Ours	Connolly	Ours	Connolly
187	51.0	0.0307	0.0307	0.717	0.717
187	51.0	0.0303	0.0307	0.724	0.717
184	67.7	0.0421	0.0423	0.766	0.781
188	67.7	0.0455	0.0430	0.792	0.772
188	67.7	0.0432	0.0430	0.772	0.772

TABLE 2. VAPOR-LIQUID EQUILIBRIUM DATA FOR HYDROGEN/TETRALIN

p, atm	x_H	y_H	K_H	K_T
		189.6°C		
0.669*	0	0	—	1.000
20	0.0118	0.9652	81.8	0.0352
30	0.0176	0.9748	55.4	0.0256
50	0.0297	0.9828	33.1	0.01769
100	0.0571	0.9897	17.33	0.01093
150	0.0823	0.9927	12.06	0.00794
200	0.1051	0.990	9.46	0.00675
250	0.1289	0.9948	7.72	0.00597
		268.7°C		
3.49*	0	0	—	1.000
20	0.0143	0.8028	56.1	0.200
30	0.0221	0.8676	39.3	0.1353
50	0.0373	0.9155	24.6	0.0877
100	0.0732	0.9538	13.03	0.0499
150	0.1046	0.9657	9.23	0.0383
200	0.1373	0.9714	7.08	0.0332
250	0.1640	0.9748	5.94	0.0301
		348.6°C		
11.68*	0	0	—	1.000
50	0.0452	0.7066	15.63	0.307
100	0.0925	0.8346	9.02	0.1822
150	0.1390	0.8827	6.35	0.1362
200	0.1884	0.9038	4.80	0.1186
250	0.2314	0.9167	3.96	0.1084
		389.1°C		
18.98*	0	0	—	1.000
50	0.0482	0.4810	9.98	0.545
100	0.1170	0.7008	5.99	0.339
150	0.1760	0.7808	4.44	0.266
200	0.2303	0.8174	3.55	0.237
250	0.2824	0.8399	2.97	0.223

* Vapor pressure of tetralin.

gauges may be used depending on the pressure. A Texas Instrument fused quartz gauge is used for pressures up to 6.8 atm. This gauge is calibrated to an accuracy of 10^{-4} atm. A Wallace and Tiernan precision gauge with a stainless steel bourdon tube is used for higher pressures. The accuracy is 0.06% of the full scale which is 34 atm. The gauges are isolated from the vapor by means of a differential pressure indicator sensitive to about 10^{-4} atm. Argon gas is used to balance the differential pressure indicator, and the pressure of argon is measured by the gauges.

SAMPLING AND ANALYSIS

There are two sampling and analysis systems for the apparatus. In one system the cell effluents still at a high pressure and a high temperature are diverted by means of a manifold valve. The diverted streams are then sampled and the samples analyzed in a gas chromatograph. In the other system, the cell effluents are sampled after they are reduced in pressure and temperature. The latter system is used in the present study of hydrogen/tetralin mixtures. In this way the stream to be sampled is diverted before it enters the separator (see Fig. 1). The diverted stream enters a trap where the heavy component is retained as a liquid at ambient conditions and later weighed with an analytical balance. The quantity of hydrogen gas coming out of the trap is determined volumetrically. The gas liberated from the liquid phase samples is collected in a graduated cylinder over water. A wet test meter is used to measure the larger quantities of hydrogen in the gas phase samples. The volume determinations are accurate to 0.5%.

Owing to the enormous difference in volatilities of hydrogen and tetralin, quantitative separation is obtained at the liquid trap. Only small corrections need to be made to the directly observed liquid weights and gas volumes. Thus the quantity of tetralin in the sample is the sum of that in the weighed liquid and that vaporized into the gas volume, the latter being minute. The quantity of hydrogen in the sample is the sum of that in the gas volume and that dissolved in the liquid. The latter is calculated from Henry's law. The composition of the sample is calculated from the total moles of hydrogen and of tetralin.

Samples were taken and analyzed at various liquid flow rates while T and p were constant in order to detect any possible dependence of composition on flow rates. No appreciable effects were found within the range of flow rates employed. The liquid feed rate is 500 to 2 000 ml/hr. The gas flow rate at the vent is about 5.5 l/min.

MATERIALS

The hydrogen gas used in this study was supplied by Air Products Co. with a reported purity of 99.95%. The tetralin was originally obtained from Aldrich Chemical Co. with a purity of 99%. Both gas and liquid chromatographic analysis showed the main impurity in tetralin to be naphthalene. Samples of tetralin were collected from the cell effluent on both the liquid and the gas sides of all the runs and analyzed by liquid chromatography to determine the degree of thermal decomposition. Not more than 1% of impurity was found in the tetralin samples including those from runs at 390°C. A small quantity of yellow coloring material was observed to be formed in the cell liquid effluent. Tetralin recovered from the apparatus was therefore purified before reuse in a batch fractionating still operated at reduced pressure under a nitrogen blanket. The coloring material was removed, and the purified tetralin did not show any impurities other than naphthalene when examined in the liquid chromatograph.

RESULTS

Before the apparatus was used to collect data on the mixture system of interest, a test was made to determine if equilibrium was indeed attained in the apparatus. Saturated phase compositions were determined for the system hydrogen/benzene and compared with data obtained by Connolly (1962) from a static apparatus. Connolly's data were interpolated to our experimental conditions from large figures separately showing the x and y values. Table 1 presents the comparison. Agreement of our individual data points with Connolly's appears to be generally within 2%, with maximum differences of about 4%. Agreement is improved when duplicate sampels are used, which we did. The test was repeated after the completion of our experimental studies of the system of interest, and the results were comparable.

Table 2 shows the equilibrium saturated liquid and gas compositions and the K values of hydrogen and tetralin.

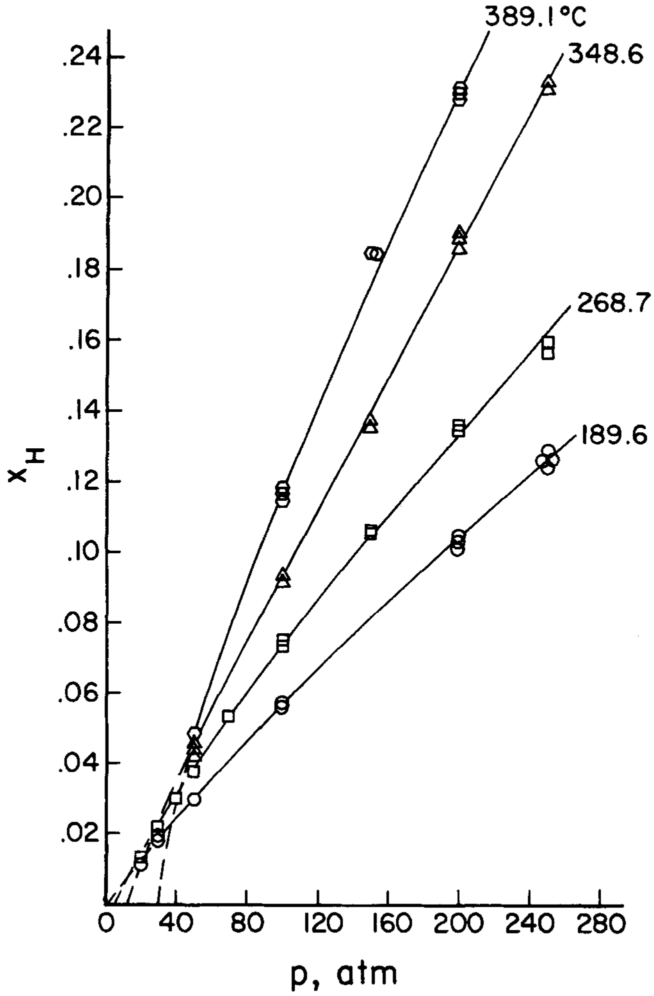

Fig. 3. Solubility of hydrogen in tetralin.

Entries in the table represent smoothed averaged values obtained from duplicate samples. The compositions of the duplicates generally do not deviate by more than 1%. The solubility of hydrogen in the liquid is also shown in Figure 3 as a function of pressure at different temperatures. Figure 4 shows the mole fraction of hydrogen in the gas phase. Individual sample compositions are shown in the figures. The highest value of observed x_H (at the highest T and p) in Table 2 and the lowest observed y_H (at the highest T and lowest p) are not included in the figures, as their inclusion would require appreciably enlarging the range of the figures.

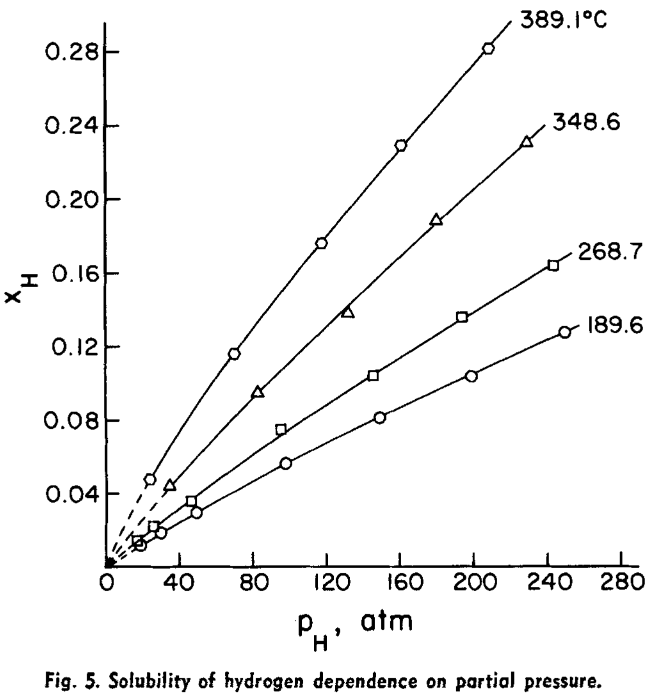

Fig. 5. Solubility of hydrogen dependence on partial pressure.

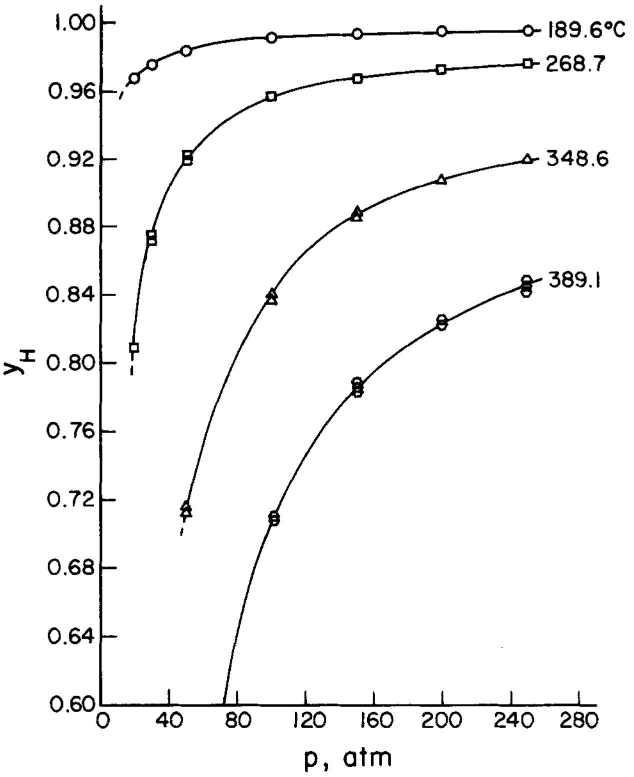

Fig. 4. Mole fraction of hydrogen in saturated gas.

The vapor pressure of the solvent defines the limit of the two phase region on the low pressure side of each isotherm. In Table 2 the vapor pressure is shown as the first entry at each temperature. The subatmospheric value at 189.6°C was obtained from the literature (Herz and Schuftan, 1922). The values at the other three temperatures of this work were interpolated from the data determined in the present apparatus. These values appear to be accurate to within 1%.

The solubility of hydrogen in Figure 3 appears to show three kinds of behavior. If the pressure is held constant, the solubility increases with increasing temperature at high pressures, decreases with increasing temperature at low pressures, and is insensitive to temperature at intermediate pressures. This apparent complexity is due to the variation of vapor pressure of tetralin with varying temperature. The partial pressure of hydrogen may be changed appreciably while the total pressure is held constant. The complex behavior disappears when the solubility of hydrogen is expressed as a function of its partial pressure, as shown in Figure 5. The solubility of hydrogen always increases with increasing temperature at fixed partial pressure of hydrogen in the entire range of this investigation.

The K values of hydrogen and tetralin are presented in Figures 6 and 7, respectively.

THERMODYNAMIC CONSISTENCY, HENRY CONSTANT, AND VAPOR PRESSURE

The equilibrium data of this work have been tested for thermodynamic consistency using the orthogonal colloca-

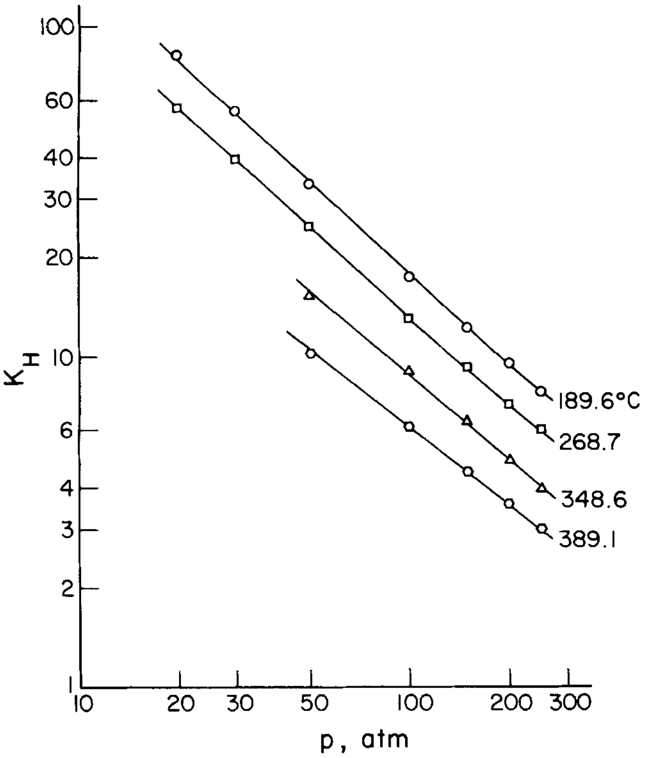

Fig. 6. Vaporization equilibrium ratio of hydrogen.

tion method (Christiansen and Fredenslund, 1975; and Fredenslund and Grausø, 1975). Gibbs-Duhem equation is integrated numerically for the prediction of y_H based on the experimental p-x data on an isotherm. Comparison of the predicted and experimental y_H values reveals the consistency of the data or the lack of it.

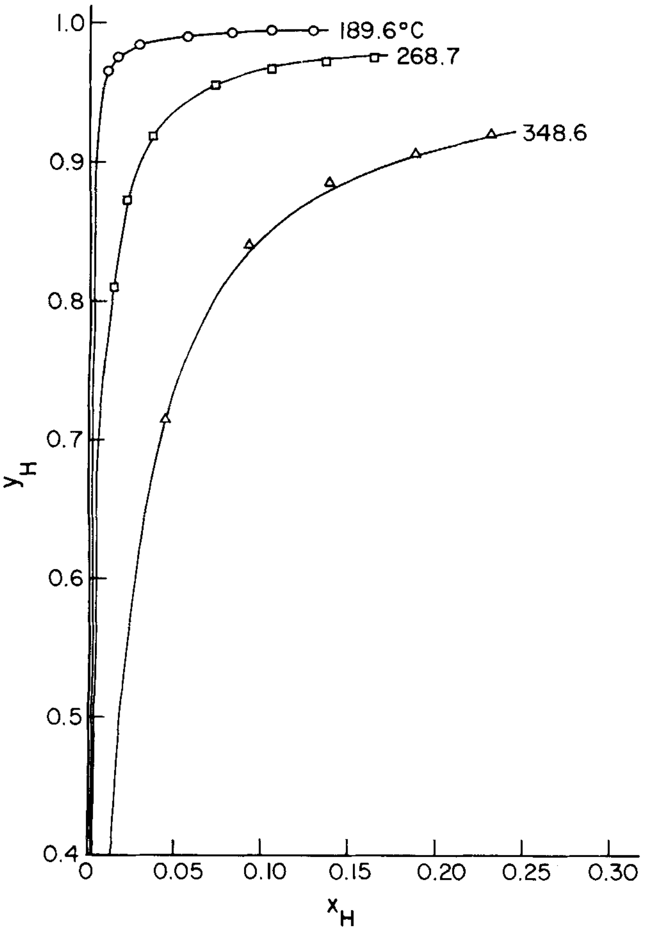

Fig. 8. Thermodynamic consistency test of data by orthogonal collocation calculation.

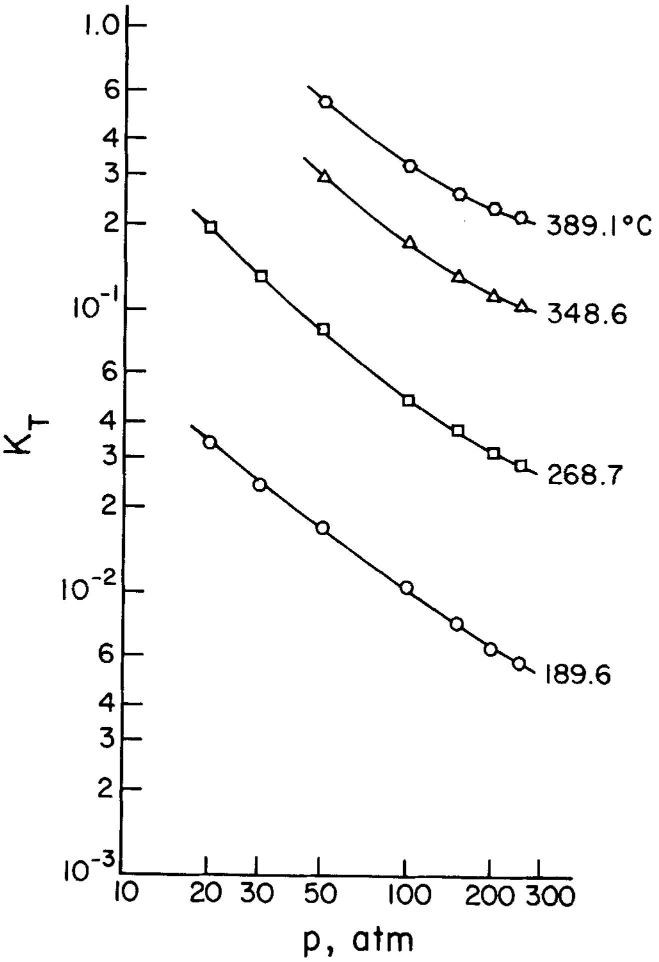

Fig. 7. Vaporization equilibrium ratio of tetralin.

Integration by the orthogonal collocation method is capable of good accuracy and flexibility. Very high accuracy of calculation is indeed required for the system studied here owing to the extremely rapid change of p with x_H. Successful application of the method in the past included systems containing carbon monoxide, carbon dioxide, and methane, each in solution in a light solvent, but not hydrogen in a heavy solvent. There was much less change in pressure.

In the orthogonal collocation method the following quantities are required to be known, in addition to the experimental isothermal p-x data: excess volume of the liquid solution V^E, fugacity coefficients of the components ϕ_i in the vapor mixture, partial volume of hydrogen for making the Poynting correction on Henry's constant, and vapor pressure of the solvent.

The excess volume and fugacity coefficients are estimated by the method of Prausnitz and Chueh (1968) based on the use of a modified Redlich and Kwong equation of state. The partial volume of hydrogen for making the Poynting correction is estimated according to Brelvi and O'Connell's correlation (1972). The vapor pressure of the solvent shown in Table 2 is used in the calculations.

The calculated y_H values do agree with the experimental values very well, as shown in Figure 8. The maximum deviation of 0.72% is found at 348.6°C and 150 atm. The deviations are all within the uncertainty of the experimental data. The calculated results are obtained and shown in Figure 8 for only three temperatures. The fourth

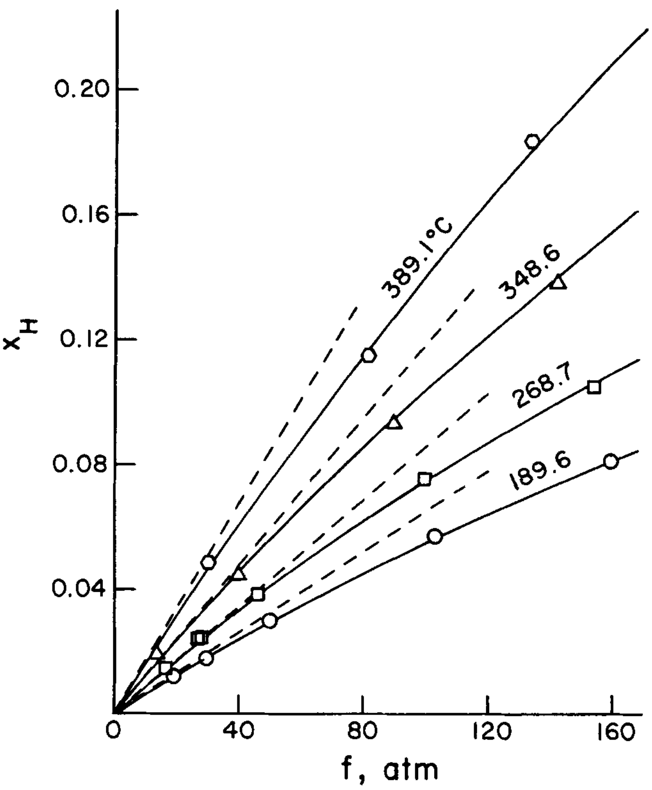

Fig. 9. Comparison of Henry's law and experimental solubility data.

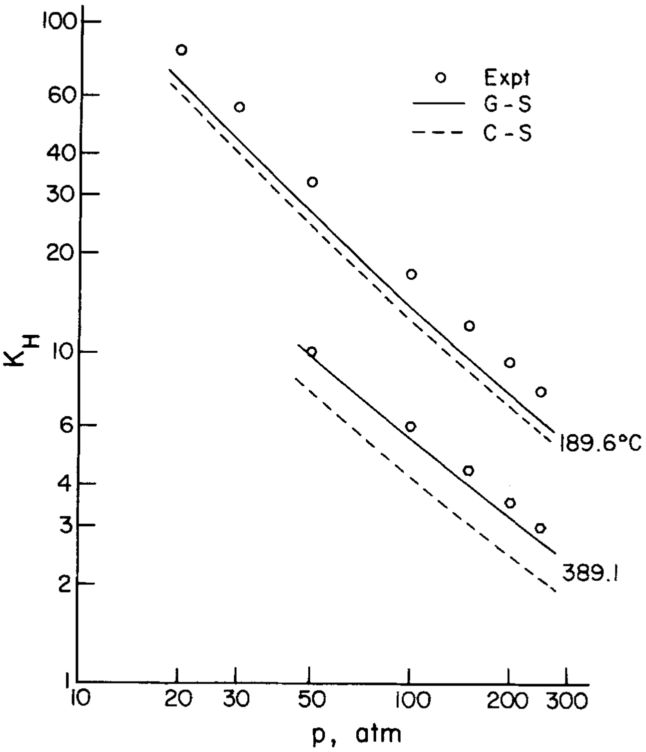

Fig. 10. Comparison of K_H data with correlations.

TABLE 3. HENRY CONSTANTS OF HYDROGEN IN TETRALIN

t, °C	H, atm
189.6	1 528
268.7	1 173
348.6	849
389.1	581

and highest temperature is beyond the range of Brelvi and O'Connell's correlation, as the reduced density of tetralin is less than 2.0. The agreement of the calculated and experimental y_H at the three temperatures clearly establishes the thermodynamic consistency of the data.

Henry constants of hydrogen in tetralin are given by the orthogonal collocation calculation as a bonus. In this way the values were obtained for the three lower temperatures of this work. The value at 389.1°C, where the method of orthogonal collocation was not applied, was obtained from a plot of f/x vs. x extrapolated to $x = 0$. Table 3 presents the results at all the temperatures of this work. The solubilities of hydrogen calculated from Henry's law using these values of Henry constant are shown in Figure 9 for comparison with experimentally observed values.

COMPARISON WITH CHAO-SEADER AND GRAYSON-STREED CORRELATIONS

TABLE 4. SOME PROPERTIES OF TETRALIN

Tc	716.5°K
Pc	33.05 atm
Vc	438.0 cm³/g-mole
ω	0.3155
δ	9.5 (cal/cm³)$^{1/2}$
$\tilde{V}$ (liq. at 25°C)	137.1 cm³/mol

The Chao-Seader correlation (1961) for vapor-liquid equilibrium in hydrocarbon systems has been in wide use. Their results for hydrogen have been found to agree with data up to pressures above the highest encountered in this study. But the applicable temperature is limited to a maximum of 260°C due to the lack of a data base at higher temperatures. In spite of this stated limitation, use of the correlation at higher temperatures has persisted. It is, therefore, of some interest to test the correlation with the present data to obtain indications as to the direction and magnitude of deviations.

Grayson and Streed (1963) extended the Chao-Seader correlation to higher temperatures by modifying the equations for pure liquid fugacity coefficient based on their own experimental data on hydrogen/heavy oil systems. No comparison of the Grayson-Streed correlation has ever been made with data other than their own at the temperatures of this work. It is, therefore, also of interest to test the correlation with the present data.

K values of hydrogen predicted by both correlations are sensitively dependent on the value of solubility parameter of the solvents. Heat of vaporization reported by Gould (1955) is used to calculate the solubility parameter of tetralin, which is in agreement with estimated values from Hildebrand's equation (Hildebrand and Scott, 1964) and modified Pitzer acentric-factor correlation (see Reid and Sherwood, 1966). The result is given in Table 4. K values of the solvent depend on its critical properties and acentric factor ω. For tetralin, values of T_c and p_c are estimated by the method of Forman and Thodos and V_c by that of Lydersen (see Reid and Sherwood, 1966). Acentric factor is then calculated from the vapor pressure at $Tr = 0.7$. Table 4 shows the estimated properties of tetralin.

Comparison of the correlations with the experimental K values is shown in Figures 10 and 11 for hydrogen and tetralin, respectively. Only the lowest and the highest isotherms are shown in Figure 10 to avoid overcrowding, as the intermediate isotherms are quite similar. K values of hydrogen from the Chao-Seader correlation appear consistently low by up to about 40%. The Grayson-Streed correlation also seems to be low by up to about 25%. The

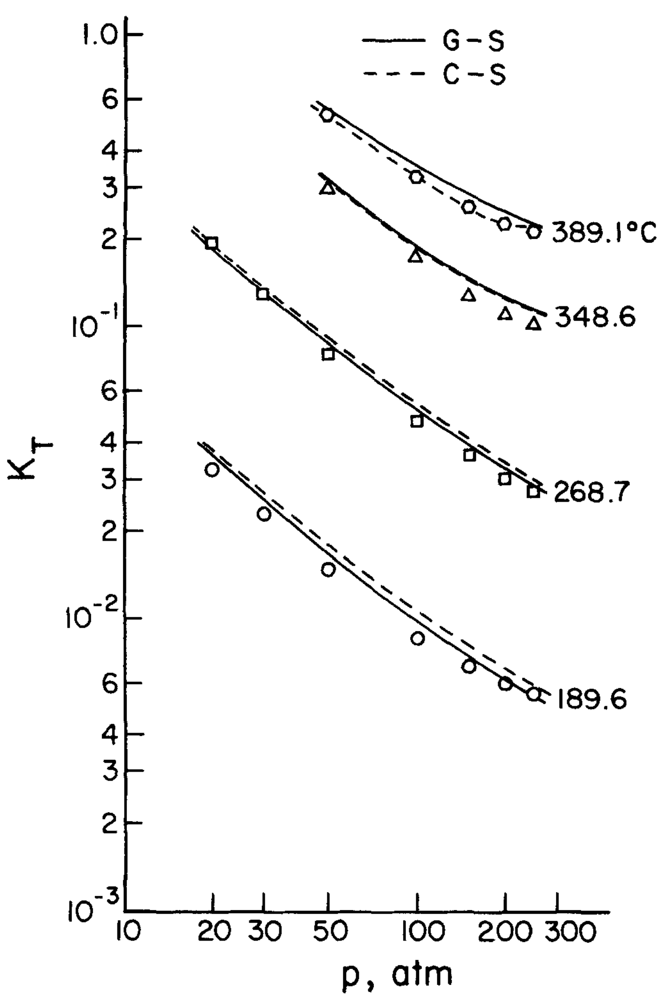

Fig. 11. Comparison of K_T data with correlations.

K values of tetralin appear to be well represented by both correlations up to the highest pressure studied.

Grayson-Streed differs from Chao-Seader only in the expression for fugacity coefficient of pure liquids, while the expressions for activity coefficients in liquid solution and fugacity coefficient in vapor mixture are kept unaltered. With this one modification, the Grayson-Streed appears to be improved over the Chao-Seader consistently in hydrogen K values at all conditions tested in this work. The tests indicate that potential still exists for further improvement of the Chao-Seader type correlations.

ACKNOWLEDGMENT

Financial support for this work is provided by the Electric Power Research Institute. H. W. Collins designed the liquid level detector and impedence bridge circuit. J. Yao carried out the calculations of orthogonal collocation, and with H. M. Sebastian, assisted in the operation of the apparatus. Professor G. M. Wilson made useful suggestions on sampling.

NOTATION

f = fugacity
H = Henry constant
K = vaporization equilibrium ratio = y/x
p = pressure
T = absolute temperature
V = volume
x = mole fraction, liquid phase
y = mole fraction, vapor phase
δ = solubility parameter
ω = acentric factor

Subscripts

c = critical constant
H = hydrogen
i = component i
T = tetralin

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