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Phase Equilibrium in Coal Liquefaction Processes

EPRI

[illegible]words:
Phase Equilibrium
Coal Liquefaction

EPRI AF-466
Project 367-1
Final Report
June 1977

Prepared by
Purdue University
Lafayette, Indiana

ELECTRIC POWER RESEARCH INSTITUTE

PHASE EQUILIBRIUM IN COAL LIQUEFACTION PROCESSES

EPRI AF - 466
(Research Project 367-1)

Final Report

January 1, 1975 - December 31, 1976

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ABSTRACT

Gas-liquid equilibria in mixtures of hydrogen and heavy hydrocarbons were determined experimentally in simulation of coal liquefaction process conditions. A flow apparatus was built to produce the saturated equilibrium liquid and gas samples at temperatures up to 430°C and pressures to 250 atm. Equilibrium data were obtained on four binary mixture systems of hydrogen with tetralin, diphenylmethane, 1-methylnaphthalene, and bicyclohexyl respectively. Comparison of the new data on the vapor-liquid ratio K of hydrogen was made with the correlations of Chao and Seader, and Grayson and Streed. Substantial deviations of the data from the correlations were indicated up to 37% from the Chao-Seader, and 30% from the Grayson-Streed. However the new data show a regular orderly behavior with respect to the solubility parameter of the solvent, indicating that improved correlation can be developed based on the Chao-Seader scheme. Additional new data are needed on hydrogen solubility in other solvents and in mixtures including coal liquids to revise the existing correlations for improved results or for developing new correlations.

ACKNOWLEDGEMENT

Valuable suggestions were derived from technical discussions with Grant M. Wilson of Brigham Young University, and with the Advisory Committee of this project. Members of the committee are:

Linda F. Atherton, EPRI
James F. Ely, Shell Development Co.
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H. W. Collins designed the liquid level detector and impedence bridge circuit. The Central Machine Shop at Purdue fabricated the apparatus.

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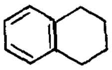
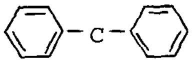
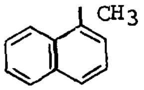
Section 1.0

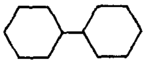
INTRODUCTION

Vapor-liquid equilibrium data in H_2/solvent systems are needed for the reliable and accurate design of coal liquefaction processes. For various operating conditions of temperature and pressure it is necessary to know when and where in the liquefaction plant multiphases can be expected to coexist and the quantities and compositions of the phases. This information is vital for the accurate sizing of plant equipment including the vessels, piping, and compressors. The information should also be useful for the analysis of reaction kinetic data of coal liquefaction. The needed information is, however, largely unavailable, particularly at elevated temperatures and pressures where the need is the greatest.

This work extends experimental investigation of phase equilibrium of H_2/heavy solvent systems to 250 atm in pressure and 430°C in temperature. The experimental conditions simulate those in the liquefaction reactors and in the reactor effluent treatment sections of the liquefaction plant. Four solvents have been used to simulate coal liquids, and these are:

- tetralin 
- diphenylmethane 

- 1-methylnaphthalene 

- bicyclohexyl 

It is known that 1 and 2 ring aromatics are found in abundant quantities in coal liquids, and 1 and 2 ring naphthenes are also present in significant amounts. The four compounds of this work are reasonably representative of the important components of coal liquids, but the representation is not complete. The investigation is being continued with additional solvents including three-ring compounds, and hetero-atom-containing hydrocarbons, and finally with liquid mixtures including coal liquids.

New data have been obtained to test existing correlations such as the Chao-Seader, and the Grayson-Streed; both correlations are in wide use. The new data can be used to modify the existing correlations for improved results, and for developing new correlations.

Previous studies of the phase equilibrium of hydrogen/solvent systems have been mostly limited to relatively low temperatures. 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 H_2/benzene up to 150°C and 200 atm. Nichols et al. (1957) reported data on H_2/n-hexane at 4 - 204°C and 120 - 680 atm. Studies of H_2/benzene and H_2/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 - 200°C. The work which reached the highest temperature was by Grayson and Streed (1963) who presented a correlation of K-value of hydrogen in heavy oils at temperatures up to 430°C and pressures up to 200 atm, but no detailed data were given.

Clearly there is a dearth of information on the phase behavior of H_2/solvent systems at coal liquefaction and hydro-treating reaction conditions.

Section 2.0

EXPERIMENTAL APPROACH

2.1 INTRODUCTION

In this work a flow apparatus has been built for the determination of vapor-liquid equilibrium at temperatures from the ambient to 430°C and pressures from the ambient to 300 atm. The apparatus has been checked out to give reliable results, and phase equilibrium data have been obtained for four binary mixture systems:

- H_2/tetralin
- H_2/diphenylmethane
- H_2/1-methylnaphthalene
- H_2/bicyclohexyl

For each binary system data have been taken at the grid points of four temperatures and seven pressures as follows:

- temperatures at 190°, 270°, 350° and 430°C
- pressures at 20, 30, 50, 100, 150, 200, 250 atm

The use of the same T-p grid facilitates interpolation and extrapolation with respect to solvent properties in the use of the data, e.g. the development of correlations.

Several tests have been applied to check out the apparatus, and the data:

(1) Variation of flow rate. The gas and liquid compositions were found to be independent of flow rates within the range of flow rates employed in this study, as long as the temperature and pressure in the equilibrium cell were kept constant.

(2) Comparison of data on a test system. Data on H_2/benzene determined in the present apparatus were found to agree with results obtained by Connolly (1962) from a static apparatus.

(3) Thermodynamic consistency test. The new data were found to agree with the Gibbs-Duhem equation when integrated along the isothermal saturation locus of the binary systems.

The results of these tests show that reliable equilibrium data have been obtained.

2.2 APPARATUS

A flow-type design was adopted for the 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 down stream 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, 1000 ml contents) or a Hills-McCanna U-type metering pump at rates of 500 - 2000 ml/hr. Flow from the Ruska pump is even; but from the Hills-McCanna reciprocating type pump the flow is 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. Rheostats control the rate of heating so that the temperature of the stream leaving the heaters is within 1°C of the equilibrium cell temperature.

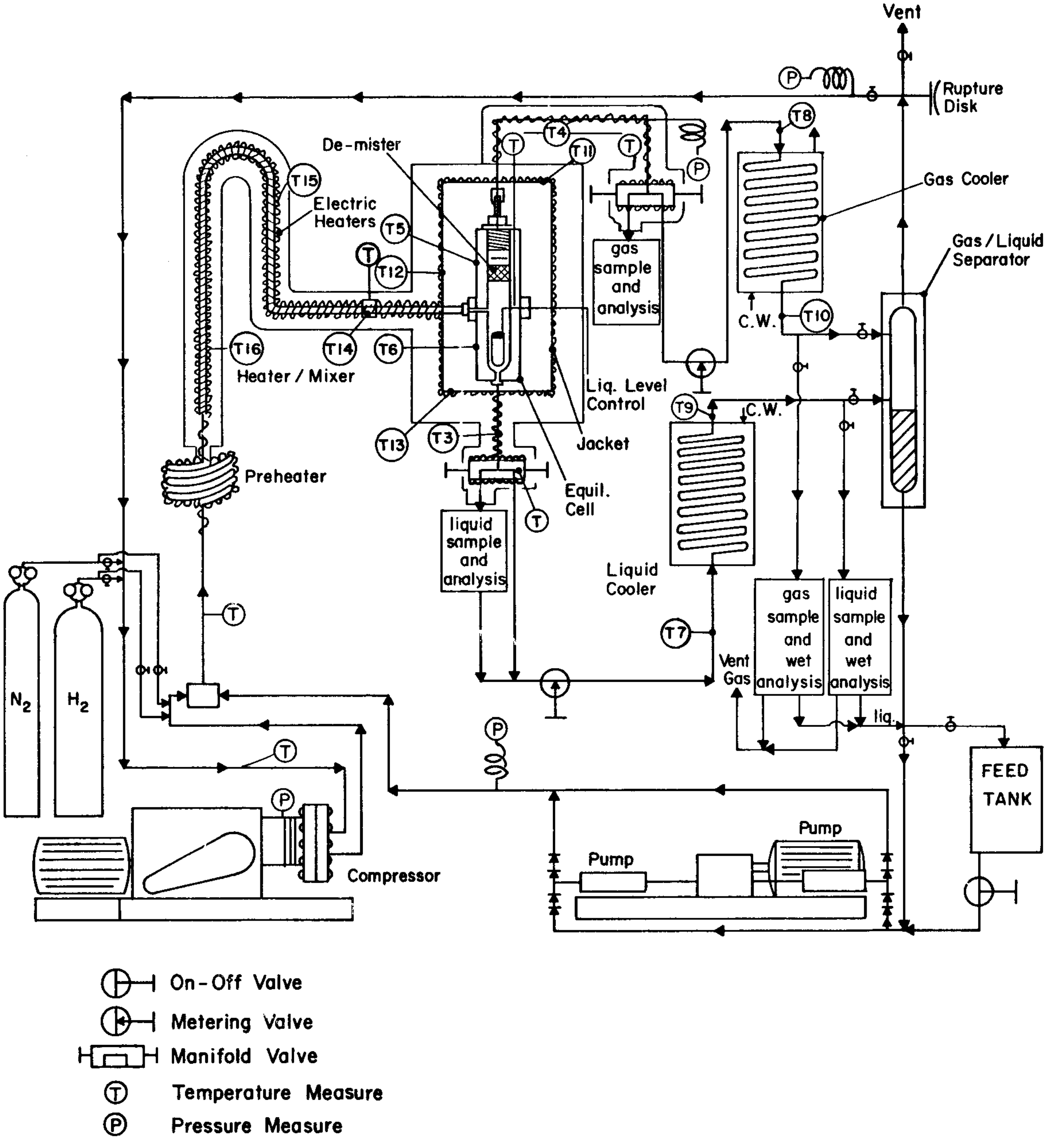


Figure 1. Vapor-liquid Equilibrium Apparatus.

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; the other for an Aminco cone compression-type 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.

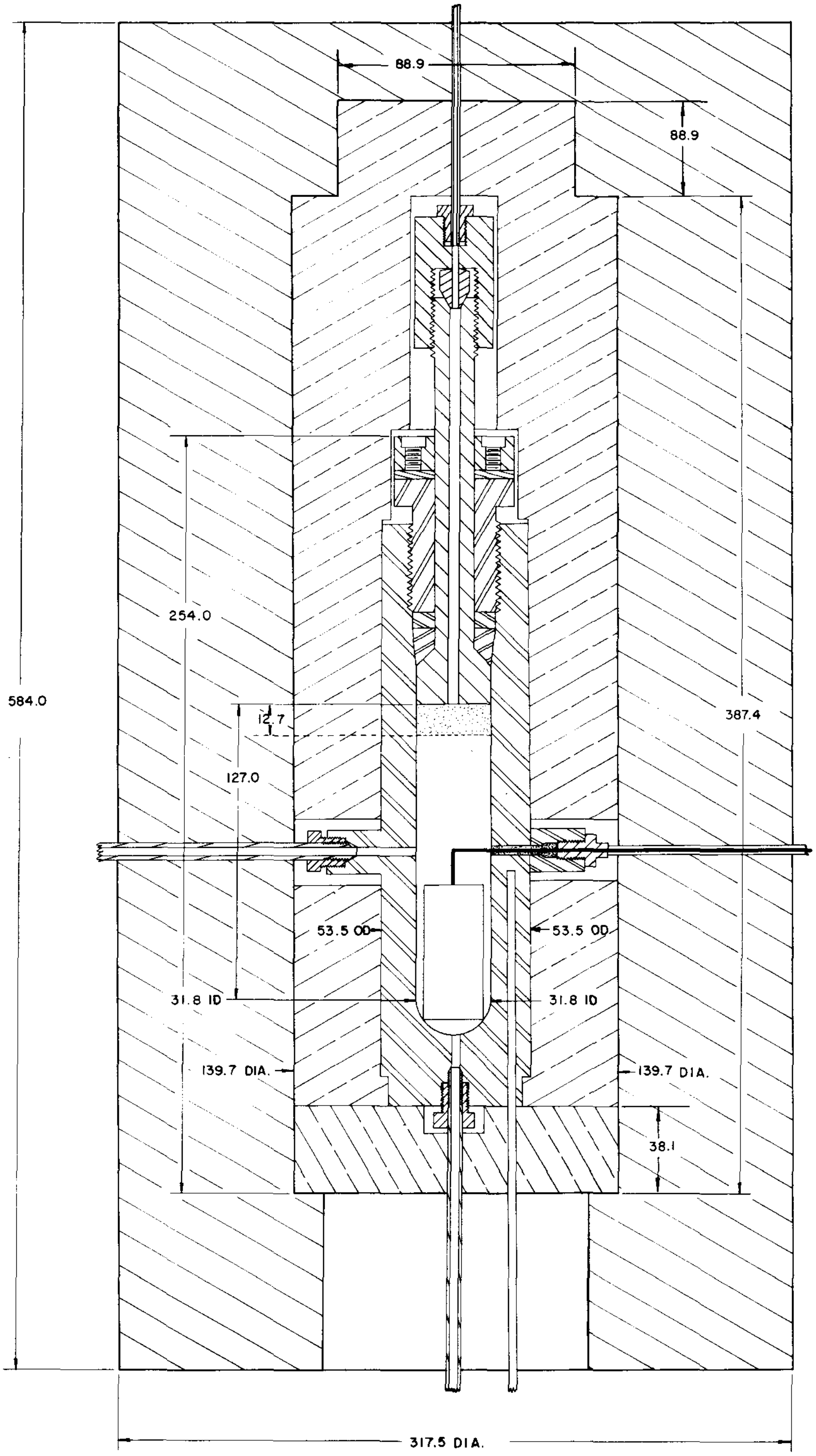
To avoid entrainment of gas in the liquid withdrawn from the cell, a pool of liquid is maintained in the cell. The liquid level is sensed by a capacitor in the cell and displayed on an oscilloscope screen as a horizontal line. The position of the line depends on the liquid level. By adjusting the metering valve at the bottom of the cell the liquid level is maintained and the capacitor is kept half immersed. The level detector capacitor is shown in Figure 3, and the detector circuit is shown in Figure 4. The design is similar to that described by White and Brown (1942).

A demister pad made of 40 mesh stainless steel wire gauze and placed at the gas exit port of 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 fishspine heating wires insulated in ceramic beads placed in grooves cut on the outside surface of the copper jacket. Johns-Manville Thermo-12 insulation 0.17 watts/(m-°K) in thermal conductivity and 76 mm thick surrounds the entire copper jacket to maintain high temperature and promote isothermal condition 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 (see Materials).

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.



ALL DIMENSIONS IN mm

Figure 2. Vapor-liquid Equilibrium Cell.

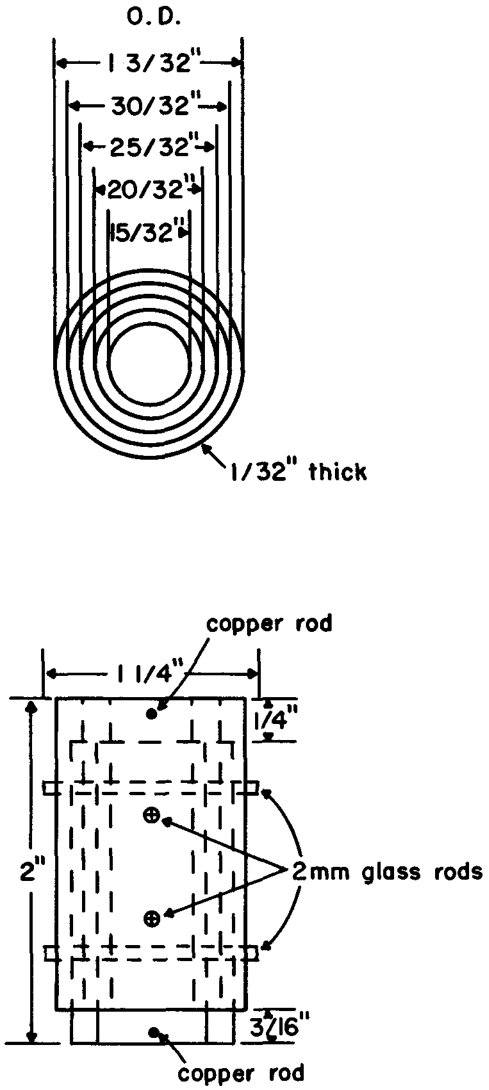


Figure 3. Electric Capacitor.

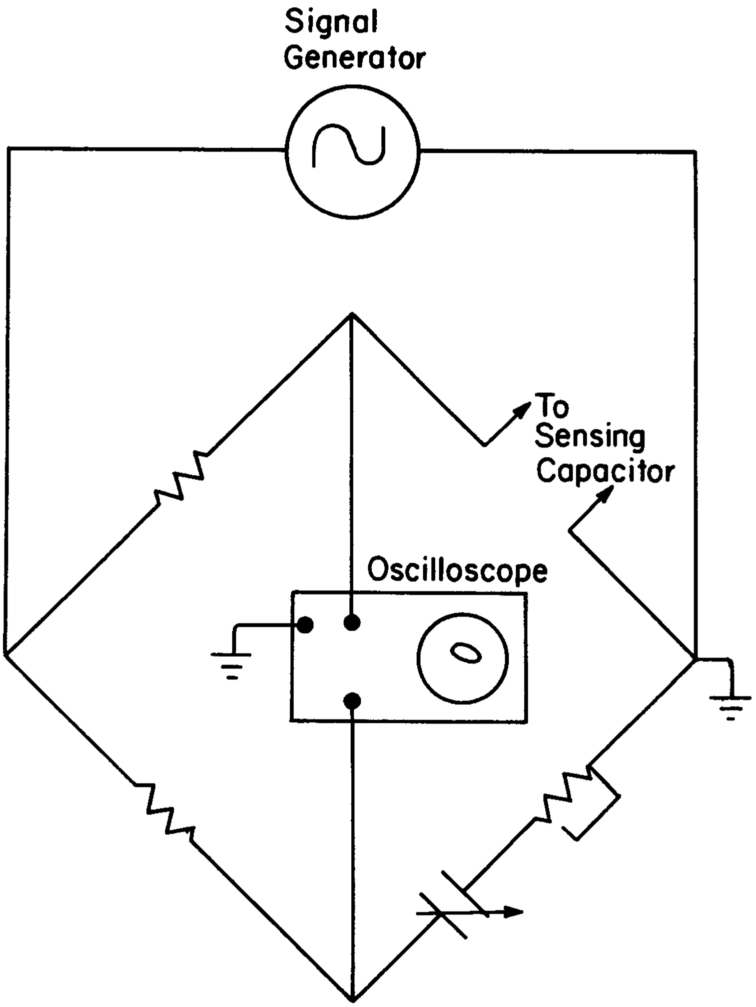


Figure 4. Liquid Level Detector Circuit.

A Heise gauge measures the pressure in the cell to ± 0.1% or 0.2 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 accurate to ± 0.05°C.

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, i.e., 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 body-like 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 condition for the thermocouple block.

2.3 SAMPLING AND ANALYSIS

The cell effluents are diverted for sampling after they are reduced in pressure and temperature and before they enter the separator (see Figure 1). The diverted stream enters a trap (see Figure 5) 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%.

Due to the enormous difference in volatilities of hydrogen and the solvent 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 solvent in the sample is the sum of that in the weighed liquid

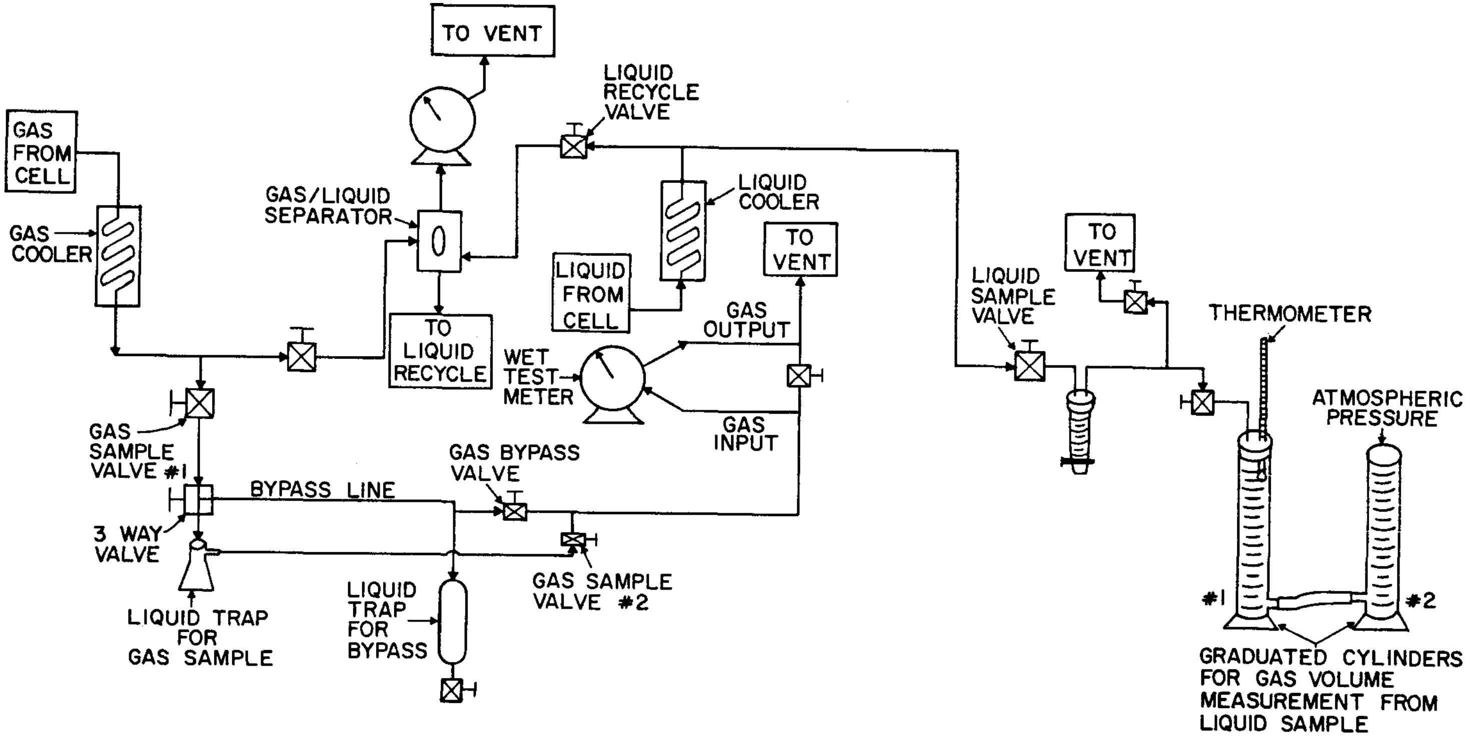


Figure 5. Volumetric Sampling System

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 which states that the mole fraction of the dissolved gas in the liquid is proportional to the partial pressure of the gas. The composition of the sample is calculated from the total moles of hydrogen and of solvent.

Samples were taken and analyzed at various liquid flow rates while keeping T and p 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 from 500 to 2000 ml/hr for the liquid. The gas flow rate at the vent was about 5.5 l/min. at ambient conditions.

The plug-flow residence time of the fluids in the heaters amounts to about 3 - 30 seconds. The lower figure applies to the lowest pressure (20 atm) and highest temperature (430°C) conditions; and the upper figure to the highest pressure (250 atm) and lowest temperature (190°C). The real residence time of the liquid should be substantially longer than these figures due to departure from plug-flow conditions.

Not all the residence time is spent at the final temperature attained in the heater.

The plug-flow residence time of the liquid in the equilibrium cell depends directly on the volume of liquid maintained in the cell. Ordinarily with the capacitor kept half immersed the cell contents amount to about 20 ml, corresponding to about 33 seconds of residence time. When the liquid level is kept low as in the high temperature runs, the cell contents may be reduced to about 10 ml, and the residence time correspondingly reduced to about 12 seconds. These residence times are based on a liquid flow rate of 0.6 ml/sec. which was used in the majority of the runs.

2.4 MATERIALS

The hydrogen gas used in this study was supplied by Air Products Co. with a reported purity of 99.95%.

The tetralin was obtained from Aldrich Chemical Co. with a purity of 99%. Both gas and liquid chromatographic analyses 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 with a Perkin-Elmer Model 601 liquid chromatograph 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.

The diphenylmethane was obtained from Aldrich Chemical Co. with a purity of 99%. Liquid chromatograph analysis showed the main impurities to be benzene and toluene. Samples collected from the cell effluent on both the gas and liquid sides were analyzed on the liquid chromatograph for purity. To within the accuracy of the chromatogram peak height method of analysis which is ± 2%, the samples were all found to be pure diphenylmethane. Nevertheless liquid samples from the high temperature runs were yellowish in color. The cell effluents were therefore all vacuum fractionated under a nitrogen blanket and the distillate which was colorless was reused. The residue was quite red and was discarded. Johns and co-workers (1962) reported that diphenylmethane decomposed 1 mole % per hour at 454°C.

The 1-methylnaphthalene was also obtained from Aldrich Chemical Co. with a purity of 97%. The main impurity is probably 2-methylnaphthalene. Liquid samples from the high temperature runs appeared slightly yellow in color. The coloring material was removed through distillation. Chromatograph analysis showed the impurity in the distillate to be not more than 2%.

The bicyclohexyl was obtained from Fischer Chemical Co. with a grade of "highest purity" (actual m.p. range = 3-4°C). The samples collected from the cell effluent were colorless. Vacuum distillation at constant temperature overhead yielded no residue indicating no impurities.

Section 3.0

EXPERIMENTAL RESULTS

3.1 VALIDATION OF EQUILIBRIUM

That the experimental results obtained in this work do represent equilibrium conditions is of fundamental importance. Equilibrium conditions are completely described by a relatively few variables, and for the binary mixtures of interest here the variables are: temperature T, pressure p, mole fraction of H_2 in the saturated liquid mixture x_H, and mole fraction of H_2 in the saturated gas mixture y_H. An alternate set of variables is T, p, equilibrium vaporization ratio of hydrogen $K_H(\equiv y_H/x_H)$ and equilibrium vaporization ratio of the solvent $K_S(\equiv y_S/x_S)$. Neither set would be sufficient for the meaningful representation of the experimental results if equilibrium conditions were not obtained in the experiments and many more variables would be required to be known, e.g., degree of approach to equilibrium, mass transfer coefficients, number of mass transfer units, etc.

The attainment of equilibrium 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 (refer to § 2.3).

(2) The new data satisfy the Gibbs-Duhem equation when integrated along the isothermal saturation locus (see § 3.3).

(3) Data on H_2/benzene from our apparatus agree with results obtained by Connolly from a static apparatus.

Table 1 presents the comparison of the saturated phase compositions of H_2/benzene mixtures obtained at the beginning of this work with those reported by Connolly. Graphical interpolation is made of Connolly's table values to the experimental conditions shown in Table 1.

Agreement of the individual data points of this work with Connolly's appears to be generally within 2%, with maximum differences of about 4%. Agreement is

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

improved when duplicate samples are used. The test with H_2/benzene mixtures was repeated at the completion of the experimental study of each binary mixture system and the results were comparable to those shown in Table 1.

The results from the three tests show that the data reported here are truly representative of equilibrium states to within the accuracy of the experiments.

3.2 RESULTS

Table 2 shows the saturated liquid and gas compositions at equilibrium and the K-values of hydrogen and tetralin in the hydrogen/tetralin system. The compositions are expressed in mole fractions denoted by x for the liquid and by y for the gas. The K-value of a component expresses its vaporization equilibrium ratio defined by $K \equiv y/x$.

Entries in Table 2 represent average values obtained from duplicate samples. The compositions of the duplicated data generally do not deviate by more than 1%. The solubility of hydrogen in the liquid is also shown in Figure 6 as a function of pressure at different temperatures. Figure 7 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 shown in the Figures but can similarly be plotted.

The solubility of hydrogen, in Figure 6, appears to show three kinds of behavior. Holding the pressure 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 (See Table 6). 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 8. 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 9 and 10 respectively.

Table 2

VAPOR-LIQUID EQUILIBRIUM DATA FOR H_2/TETRALIN

p atm	x_H	y_H	K_H	K_T
189.6°C				
20	.0118	.9652	81.8	.0352
30	.0176	.9748	55.4	.0256
50	.0297	.9828	33.1	.01769
100	.0571	.9897	17.33	.01093
150	.0823	.9927	12.06	.00794
200	.1051	.9940	9.46	.00675
250	.1289	.9948	7.72	.00597
268.7°C				
20	.0143	.8028	56.1	.200
30	.0221	.8676	39.3	.1353
50	.0373	.9155	24.6	.0877
100	.0732	.9538	13.03	.0499
150	.1046	.9657	9.23	.0383
200	.1373	.9714	7.08	.0332
250	.1640	.9748	5.94	.0301
348.6°C				
50	.0452	.7066	15.63	.307
100	.0925	.8346	9.02	.1822
150	.1390	.8827	6.35	.1362
200	.1884	.9038	4.80	.1186
250	.2314	.9167	3.96	.1084
389.1°C				
50	.0482	.4810	9.98	.545
100	.1170	.7008	5.99	.339
150	.1760	.7808	4.44	.266
200	.2303	.8174	3.55	.237
250	.2824	.8399	2.97	.223

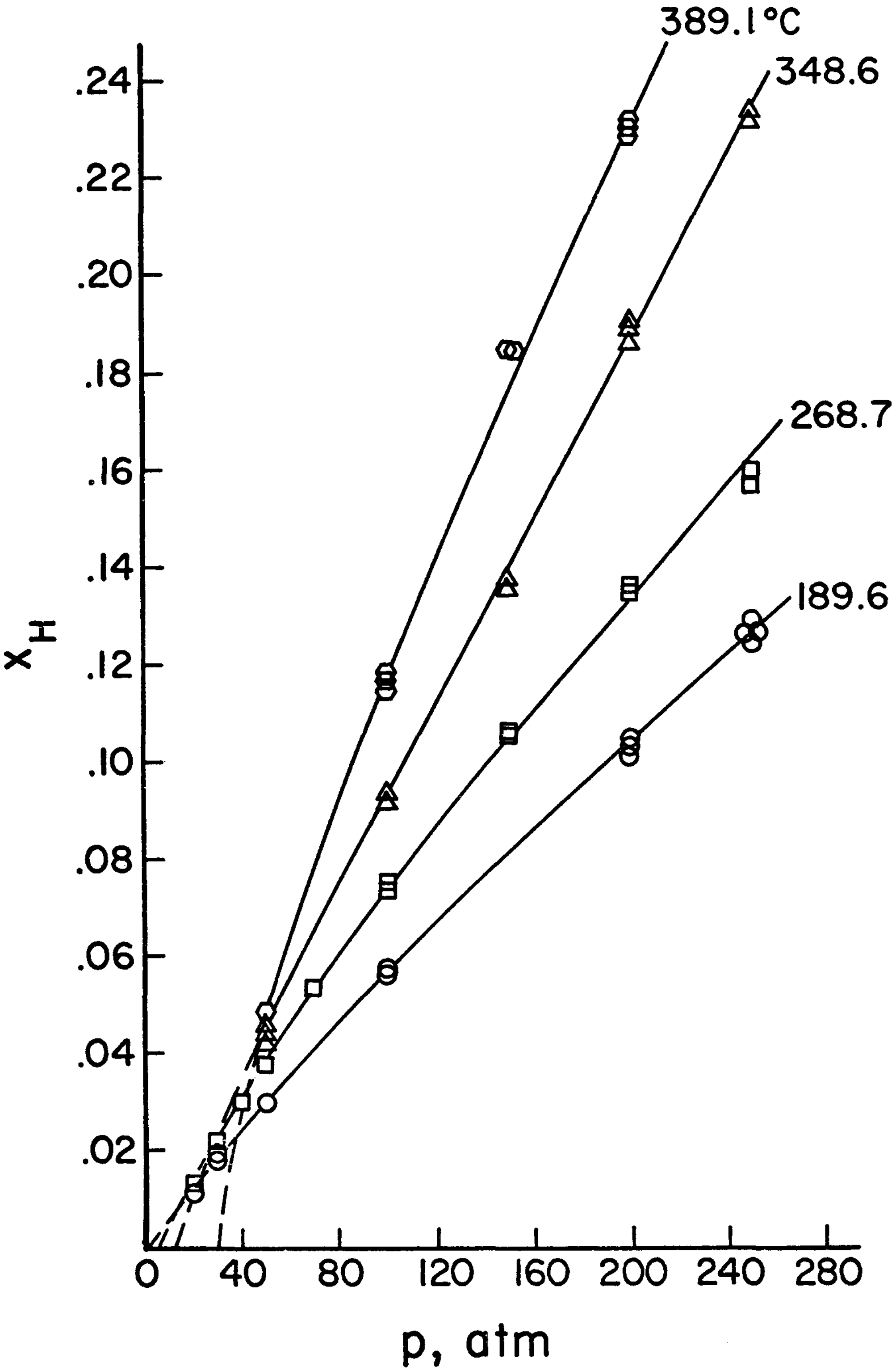


Figure 6. Solubility of Hydrogen in Tetralin.

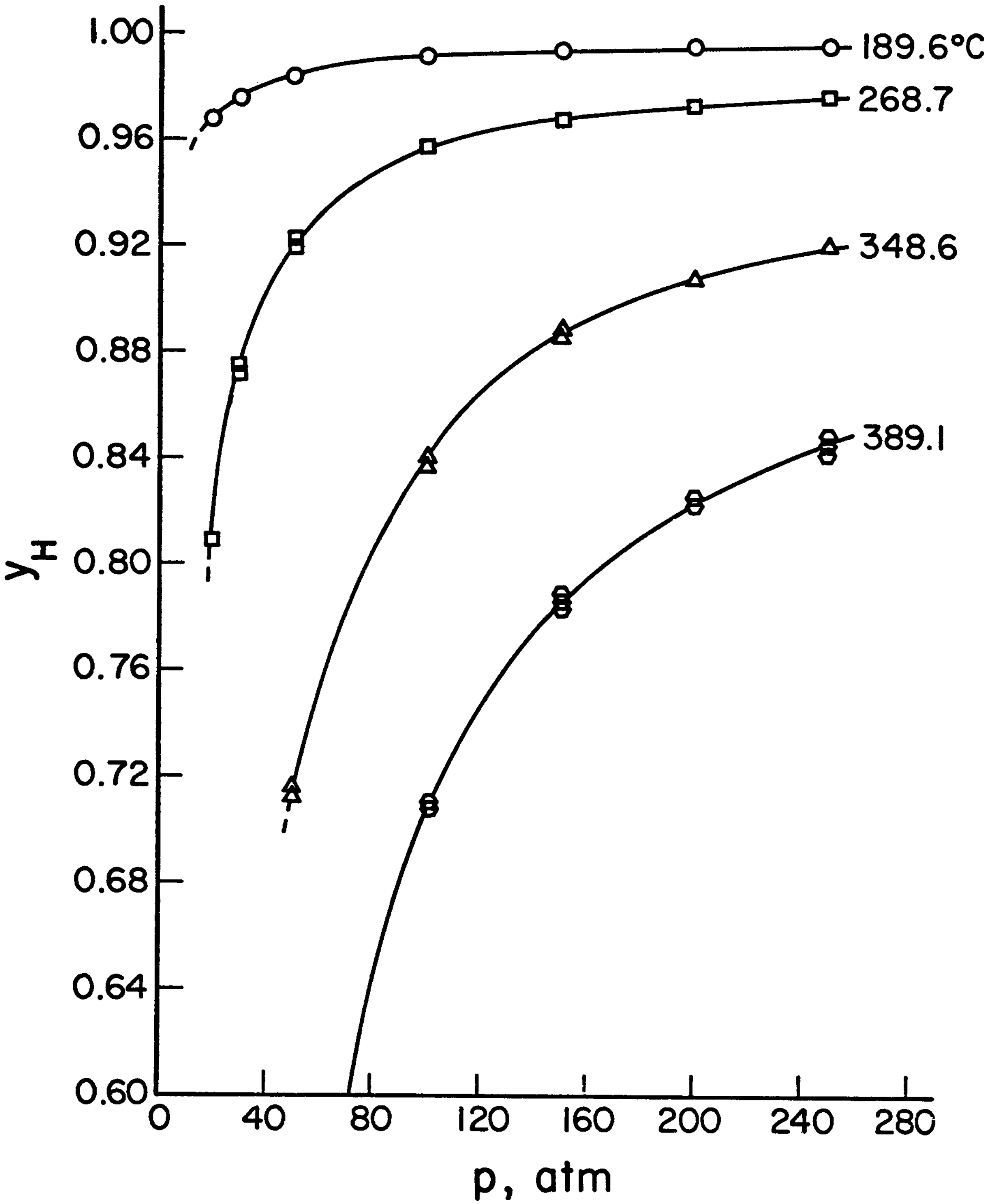


Figure 7. Mole Fraction of Hydrogen in Saturated H_2/tetralin Gas Mixtures.

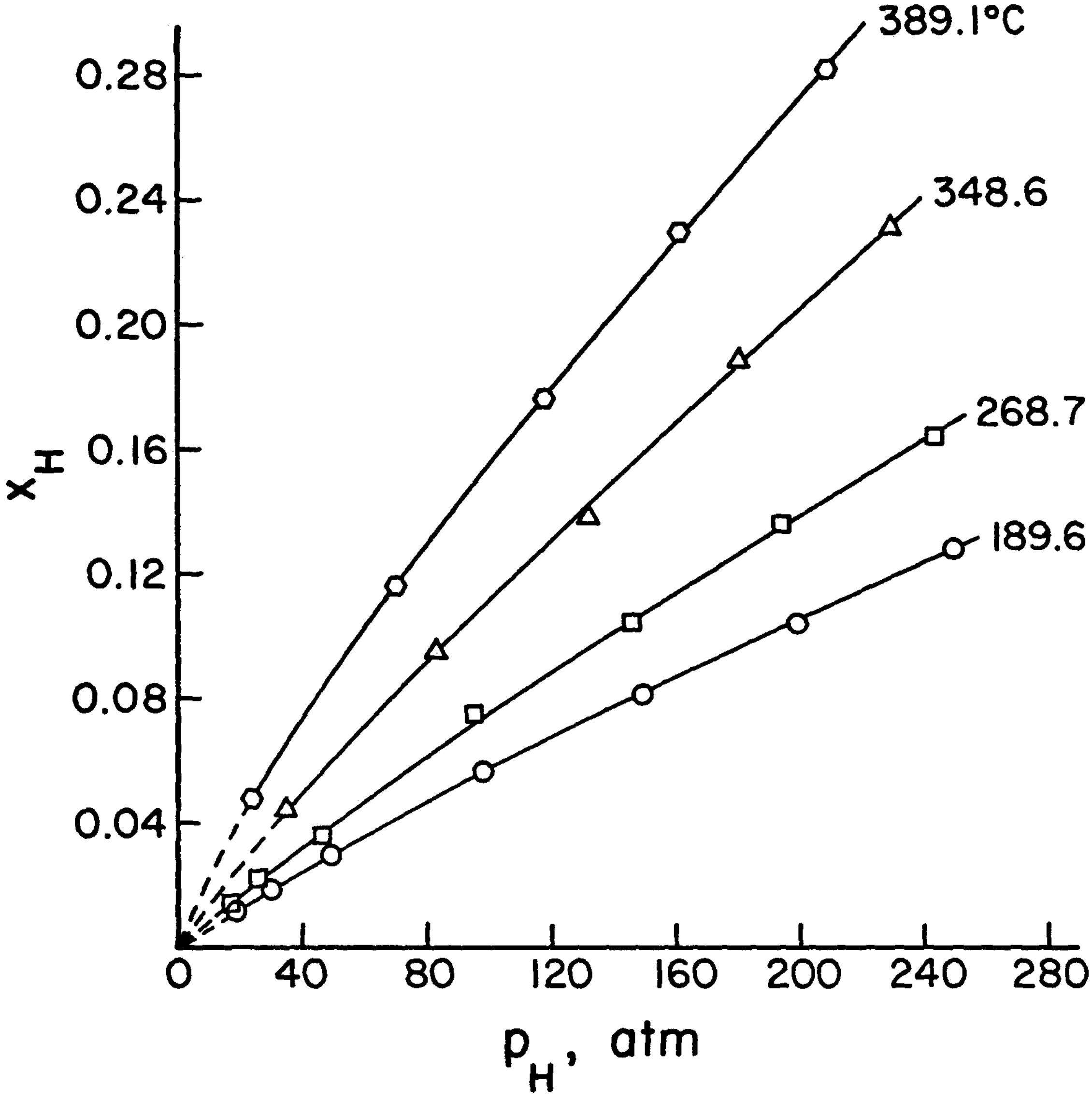


Figure 8. Solubility of Hydrogen in Tetralin Showing Dependence on Partial Pressure.

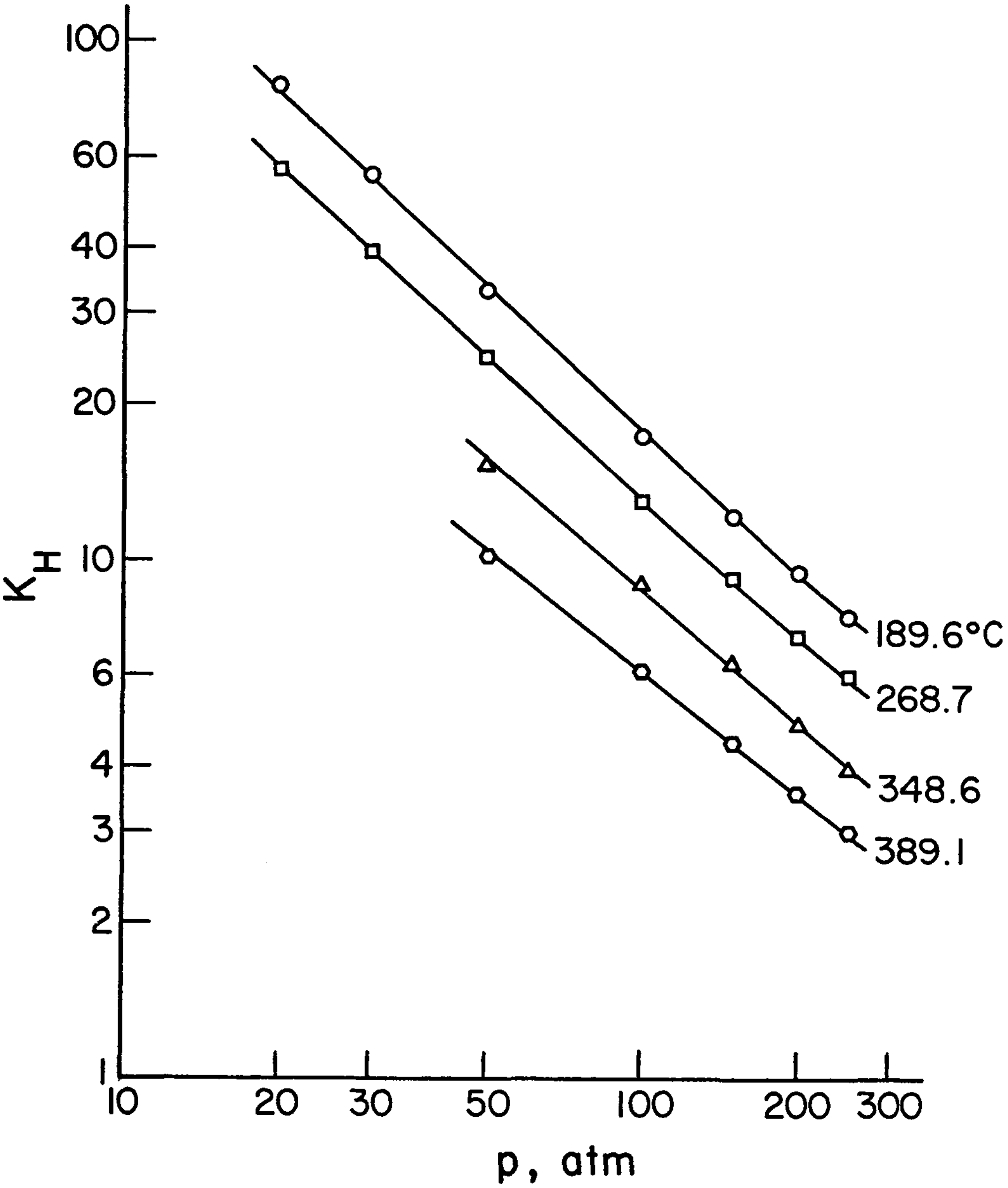


Figure 9. Vaporization Equilibrium Ratio of Hydrogen in H_2/tetralin.

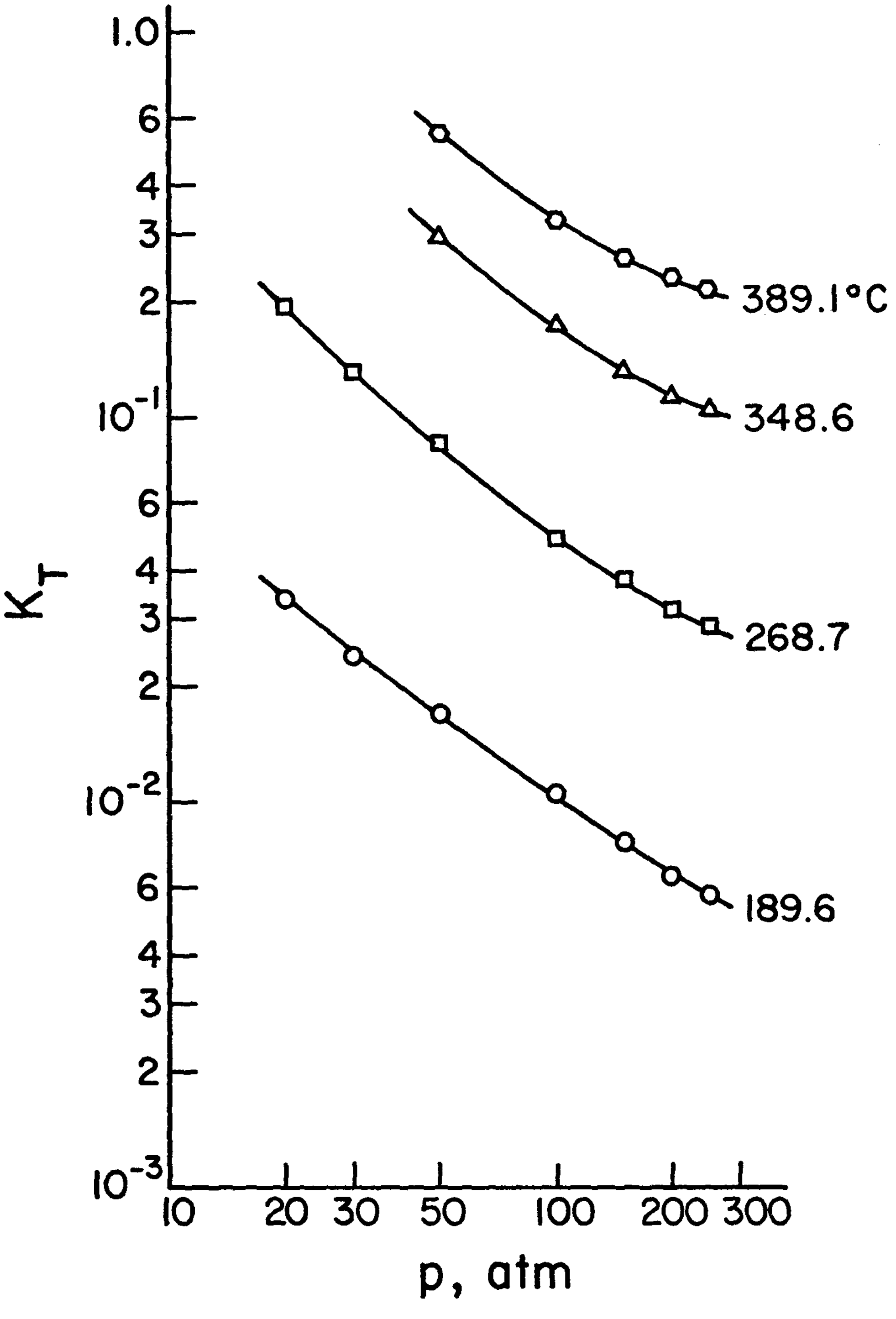


Figure 10. Vaporization Equilibrium Ratio of Tetralin in H_2/tetralin.

Saturated gas and liquid compositions at equilibrium and K-values are presented in Table 3 for H_2/diphenylmethane, in Table 4 for H_2/1-methylnaphthalene, and in Table 5 for H_2/bicyclohexyl.

The same information is shown in Figures 11 to 14 for H_2/diphenylmethane, in Figures 15 - 18 for H_2/1-methylnaphthalene, and in Figures 19 - 22 for H_2/bicyclohexyl.

3.3 THERMODYNAMIC CONSISTENCY

The compositions of the saturated phases in heterogeneous equilibrium are interrelated by the Gibbs-Duhem equation. For a binary mixture system in vapor-liquid equilibrium at a constant temperature the Gibbs-Duhem equation can be integrated to calculate the equilibrium vapor composition y from the total pressure p if known as a function of the liquid composition x. The calculated y should in principle be the same as the experimentally determined y if equilibrium is indeed obtained at the experimental conditions. In practice the uncertainty of the experimental data and the uncertainty of the calculations must be taken into consideration. Thus, a comparison of the calculated and the experimental y values can be used as a criterion to determine the achievement of equilibrium in the experiments. The experimental conditions are said to be at equilibrium and the data are thermodynamically consistent if the comparison gives satisfactory results, considering the uncertainties in the y values.

The method of orthogonal collocation (Christiansen and Fredenslund, 1975; and Fredenslund and Grausø, 1975) is used in this work to integrate the Gibbs-Duhem equation for the calculation of y. The rapid variation of p with x in the gas/liquid systems of interest makes the integration difficult, and orthogonal collocation is the only method that has been found successful to deal with this type of system. Details of the calculations are described in Appendix A.

In addition to the experimental isothermal p-x data, the following quantities are also required to be known in the integration of the Gibbs-Duhem equation:

1. vapor pressure of the solvent
2. excess volume of the liquid solution $\tilde{V}^E$
3. fugacity coefficients of the components in the vapor mixture ϕ_i

Vapor pressure is important in defining the initial condition of the integration. Vapor pressure data are found in the literature for tetralin and

Table 3

VAPOR-LIQUID EQUILIBRIUM DATA FOR H_2/DIPHENYLMETHANE

p atm	x_H	y_H	K_H	K_D
		189.6°C		
20	.0123	.9903	80.5	.00980
30	.0183	.9935	54.3	.00657
50	.0300	.9963	33.2	.00381
100	.0591	.9980	16.88	.00213
150	.0830	.9985	12.03	.00159
200	.1055	.9988	9.47	.00140
250	.1240	.9989	8.06	.00131
		268.7°C		
20	.0159	.9390	59.1	.0620
30	.0244	.9580	39.3	.0427
50	.0408	.9741	23.9	.0270
100	.0785	.9861	12.56	.01513
150	.1105	.9895	8.95	.01182
200	.1416	.9912	7.00	.01025
250	.1724	.9921	5.75	.00956
		348.6°C		
20	.0184	.7362	40.0	.269
30	.0296	.8144	27.5	.1913
50	.0516	.8825	17.10	.1239
100	.0985	.9362	9.50	.0708
150	.1450	.9533	6.57	.0546
200	.1880	.9615	5.11	.0474
250	.2272	.9675	4.26	.0421
		428.5°C		
30	.0306	.4497	14.70	.568
50	.0630	.6360	10.10	.388
100	.1380	.7881	5.71	.246
150	.2030	.8469	4.17	.1922
200	.2577	.8799	3.41	.1618
250	.3056	.8964	2.93	.1492

Table 4

VAPOR-LIQUID EQUILIBRIUM DATA FOR H_2/1-METHYLNAPHTHALENE

p atm	x_H	y_H	K_H	K_M
189.0°C				
20	.0103	.9863	95.8	.01388
30	.0153	.9906	64.8	.00951
50	.0250	.9939	39.8	.00626
100	.0479	.9965	20.8	.00372
150	.0692	.9974	14.41	.00280
200	.0887	.9978	11.25	.00241
250	.1060	.9980	9.42	.00221
268.7°C				
20	.0127	.9007	70.9	.1006
30	.0202	.9360	46.3	.0653
50	.0342	.9596	28.1	.0419
100	.0641	.9778	15.25	.0237
150	.0931	.9838	10.57	.01790
200	.1191	.9867	8.28	.01510
250	.1452	.9883	6.81	.01363
348.6°C				
20	.0132	.6153	46.6	.390
30	.0225	.7384	32.8	.268
50	.0406	.8368	20.6	.1701
100	.0814	.9113	11.20	.0966
150	.1180	.9350	7.92	.0737
200	.1564	.9481	6.06	.0616
250	.1923	.9541	4.96	.0569
428.5°C				
30	.0184	.3084	16.76	.706
50	.0459	.5169	11.26	.506
100	.1051	.7111	6.77	.323
150	.1615	.7881	4.88	.253
200	.2129	.8263	3.89	.221
250	.2950	.8500	2.88	.213

Table 5

VAPOR-LIQUID EQUILIBRIUM DATA FOR H_2/BICYCLOHEXYL

p atm	x_H	y_H	K_H	K_B
		189.0°C		
20	.0181	.9842	54.4	.01611
30	.0262	.9889	37.7	.01143
50	.0443	.9929	22.4	.00743
100	.0810	.9958	12.29	.00453
150	.1158	.9969	8.61	.00351
200	.1418	.9974	7.03	.00303
250	.1718	.9977	5.81	.00277
		268.7°C		
20	.0212	.8988	42.4	.1034
30	.0329	.9312	28.3	.0712
50	.0543	.9558	17.60	.0467
100	.1031	.9748	9.45	.0281
150	.1480	.9813	6.63	.0220
200	.1899	.9845	5.18	.0191
250	.2268	.9866	4.35	.0174
		348.6°C		
20	.0211	.6117	29.0	.397
30	.0382	.7322	19.16	.278
50	.0686	.8296	12.09	.1829
100	.1398	.9060	6.48	.1093
150	.1975	.9298	4.71	.0875
200	.2578	.9445	3.66	.0747
250	.3112	.9533	3.06	.0677
		428.5°C		
20	.0054	.0655	12.13	.940
30	.0289	.2554	8.89	.767
50	.0793	.4885	6.16	.555
100	.1818	.6720	3.70	.400
150	.2680	.7467	2.79	.346
200	.3494	.7857	2.25	.330
250	.4239	.8050	1.90	.339

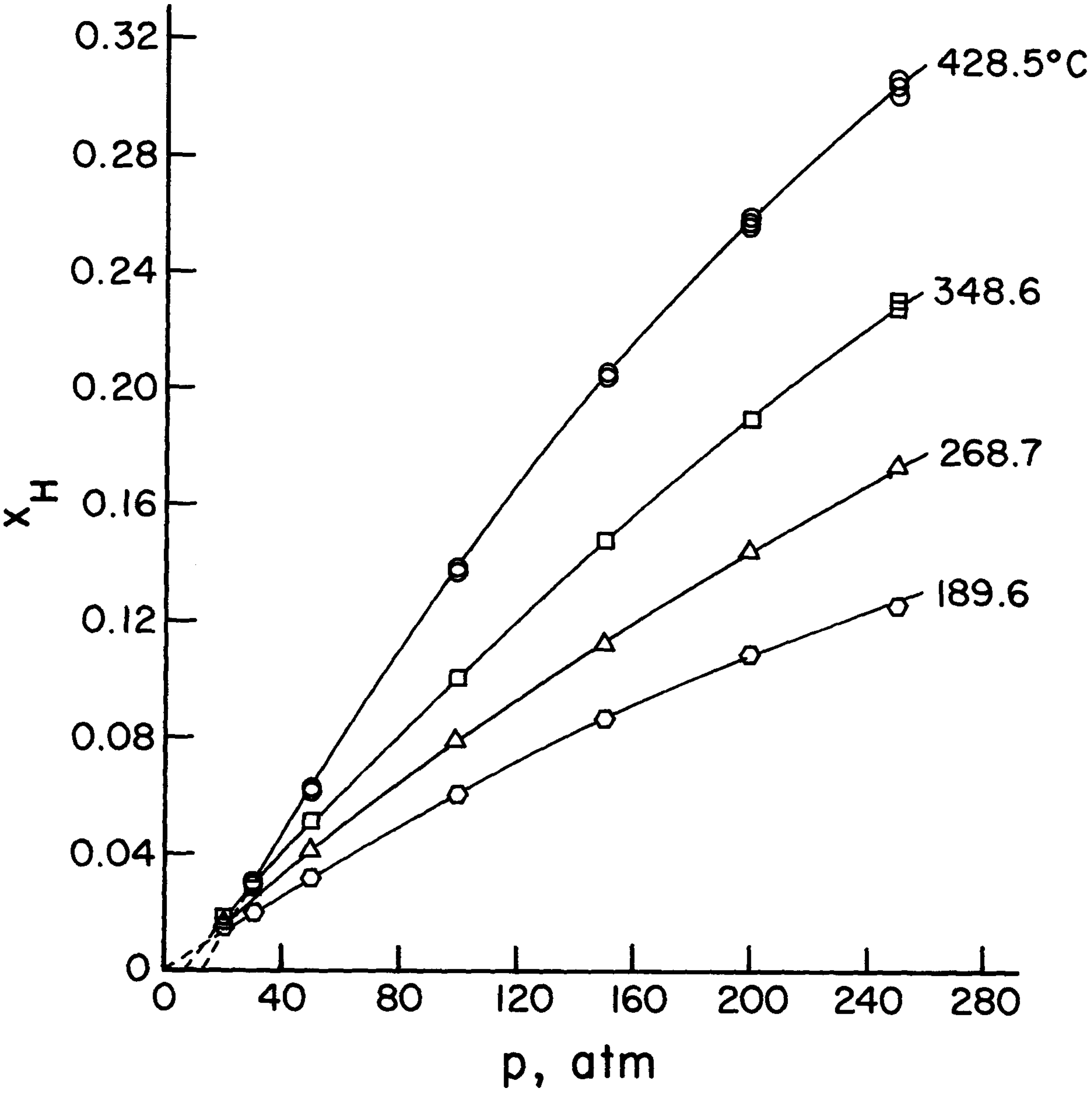


Figure 11. Solubility of Hydrogen in Diphenylmethane.

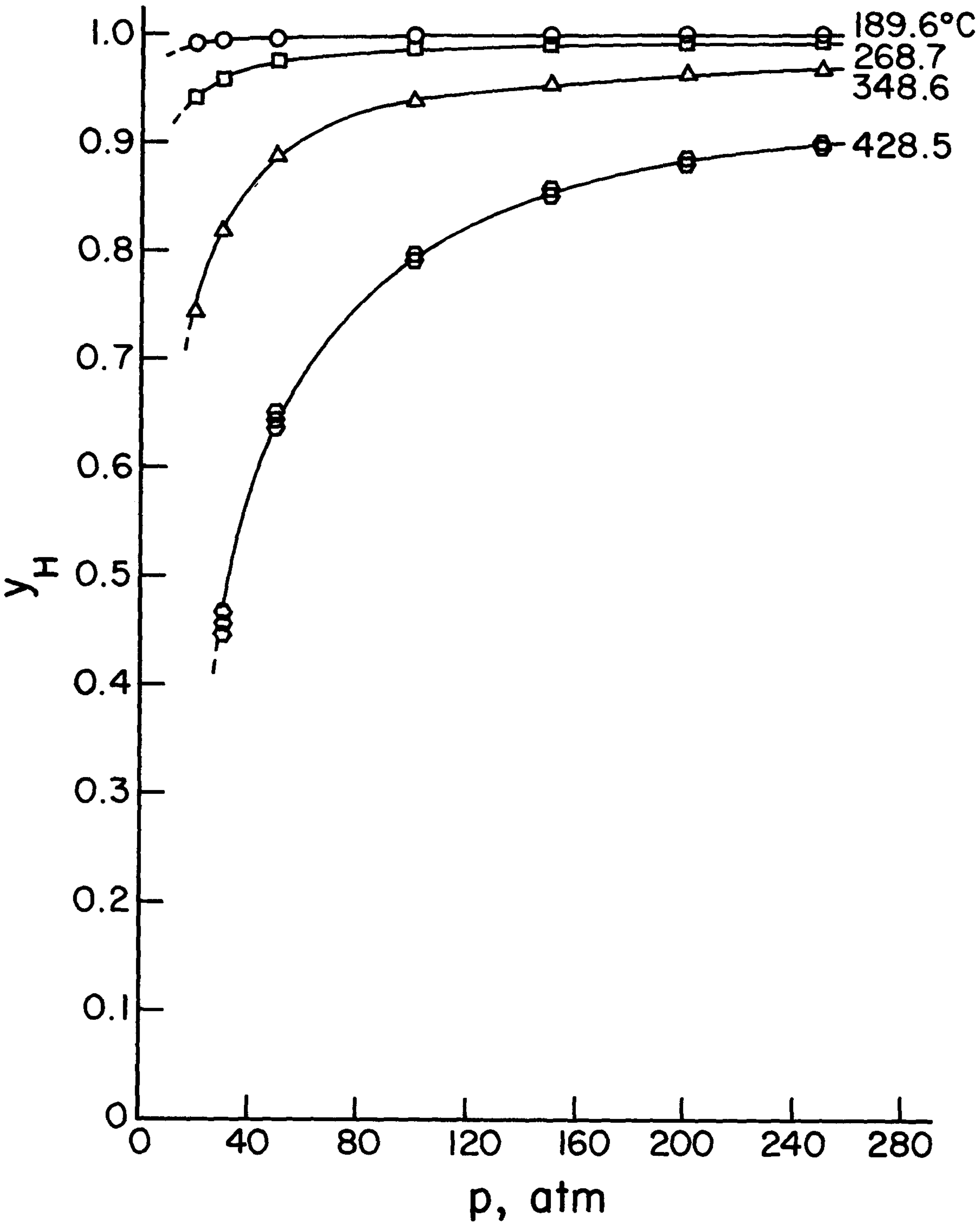


Figure 12. Mole Fraction of Hydrogen in Saturated H_2/diphenylmethane Gas Mixtures.

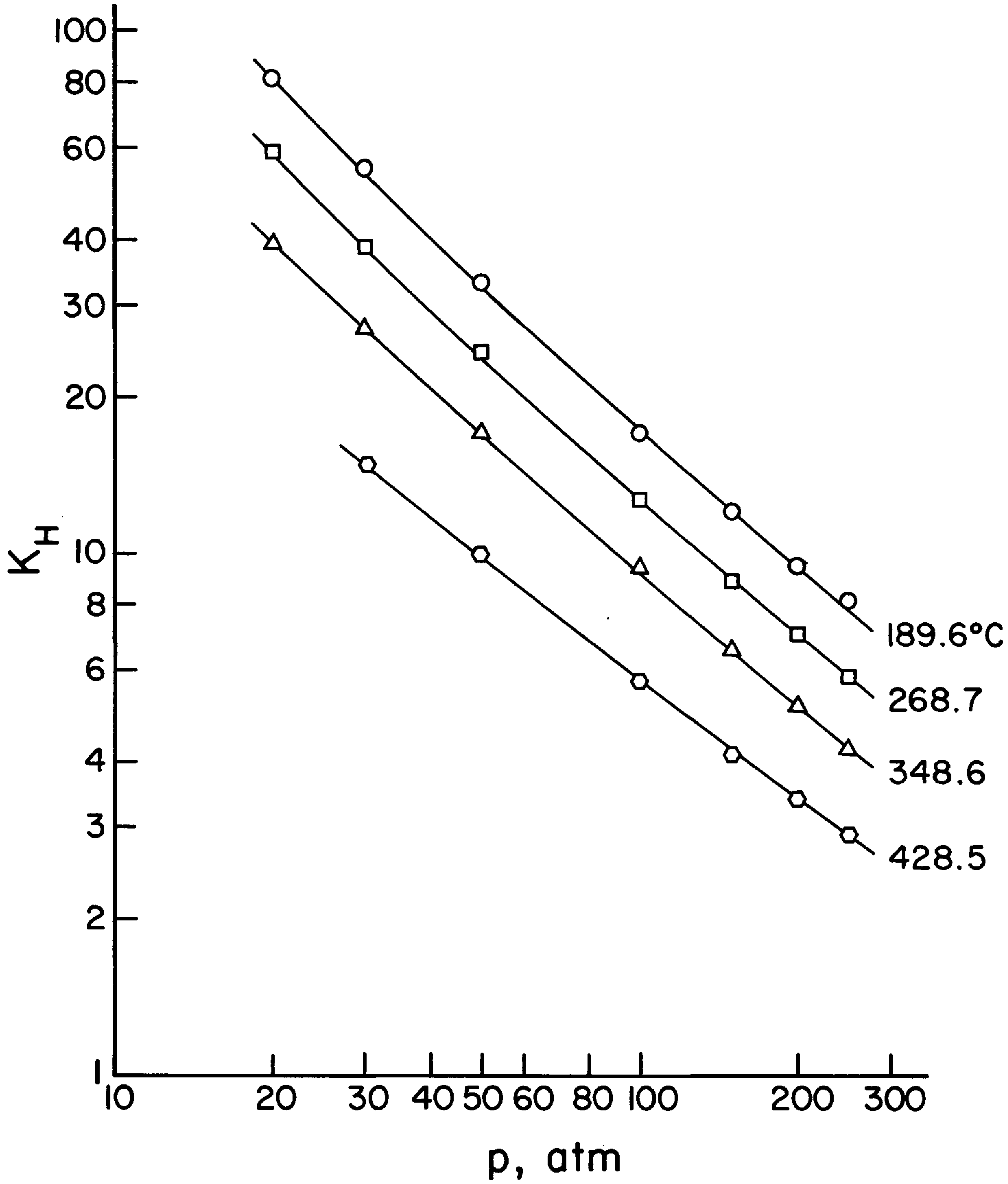


Figure 13. Vaporization Equilibrium Ratio of Hydrogen in H_2/diphenylmethane.

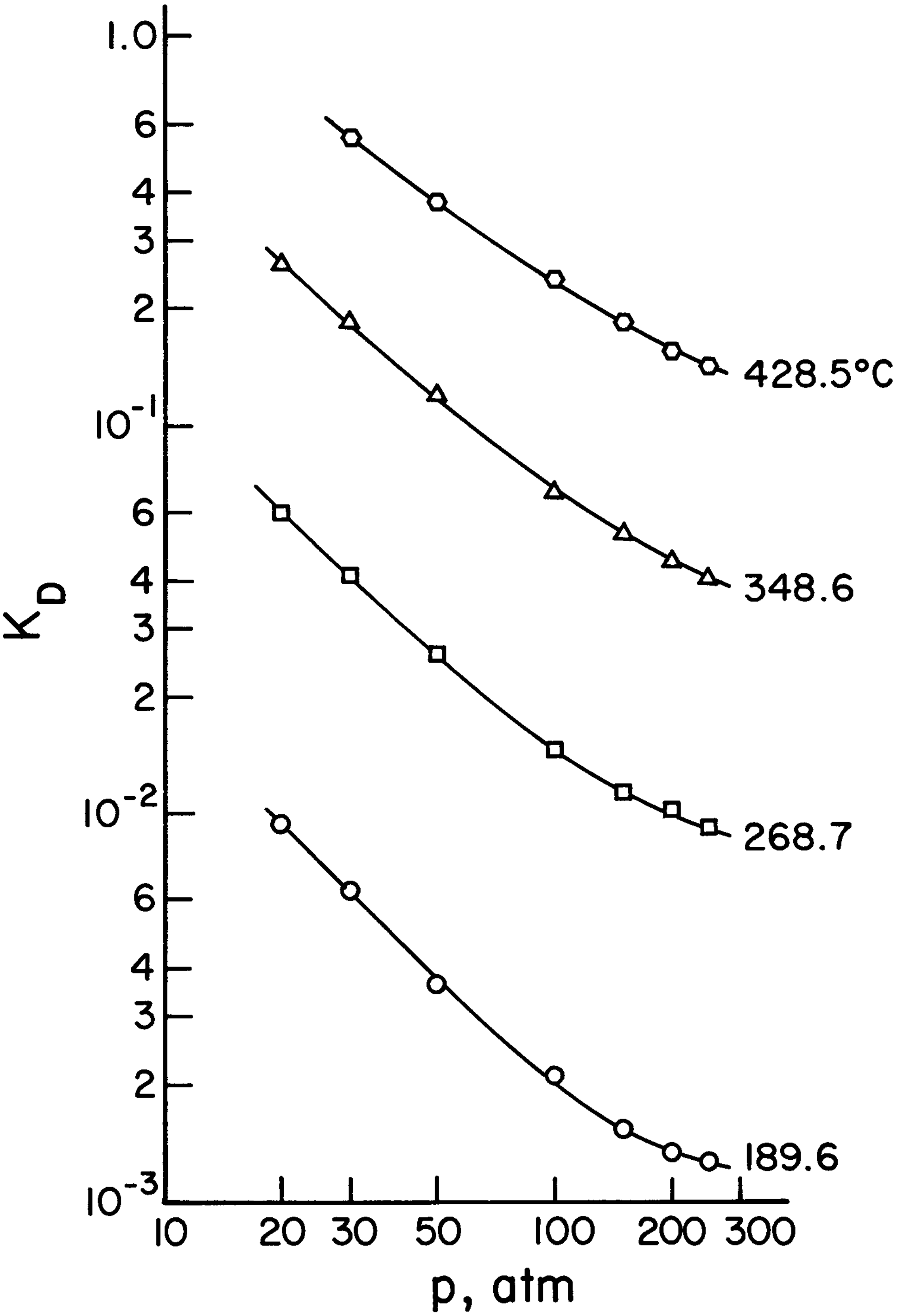


Figure 14. Vaporization Equilibrium Ratio of Diphenylmethane in H_2/diphenylmethane.

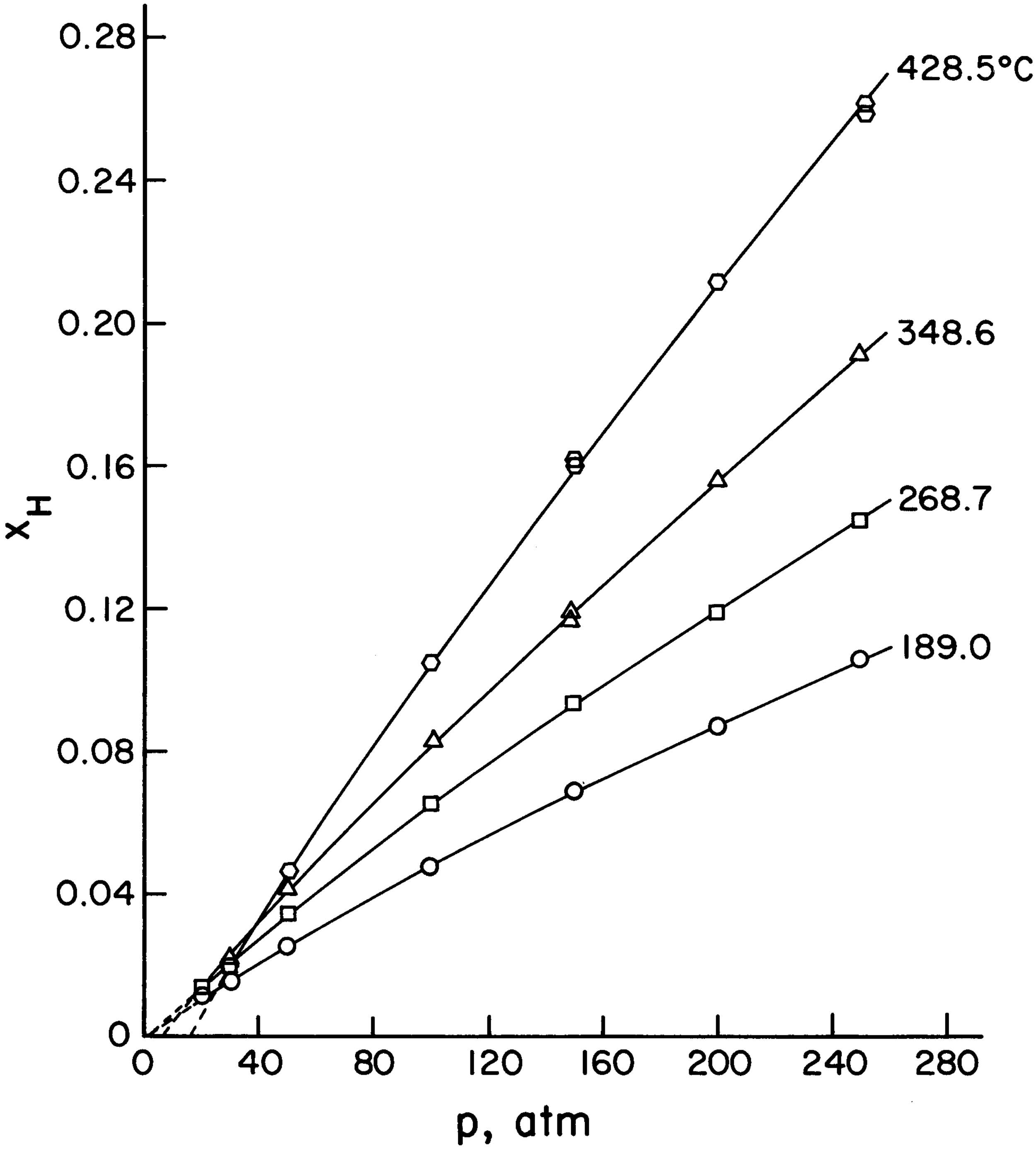


Figure 15. Solubility of Hydrogen in 1-methylnaphthalene.

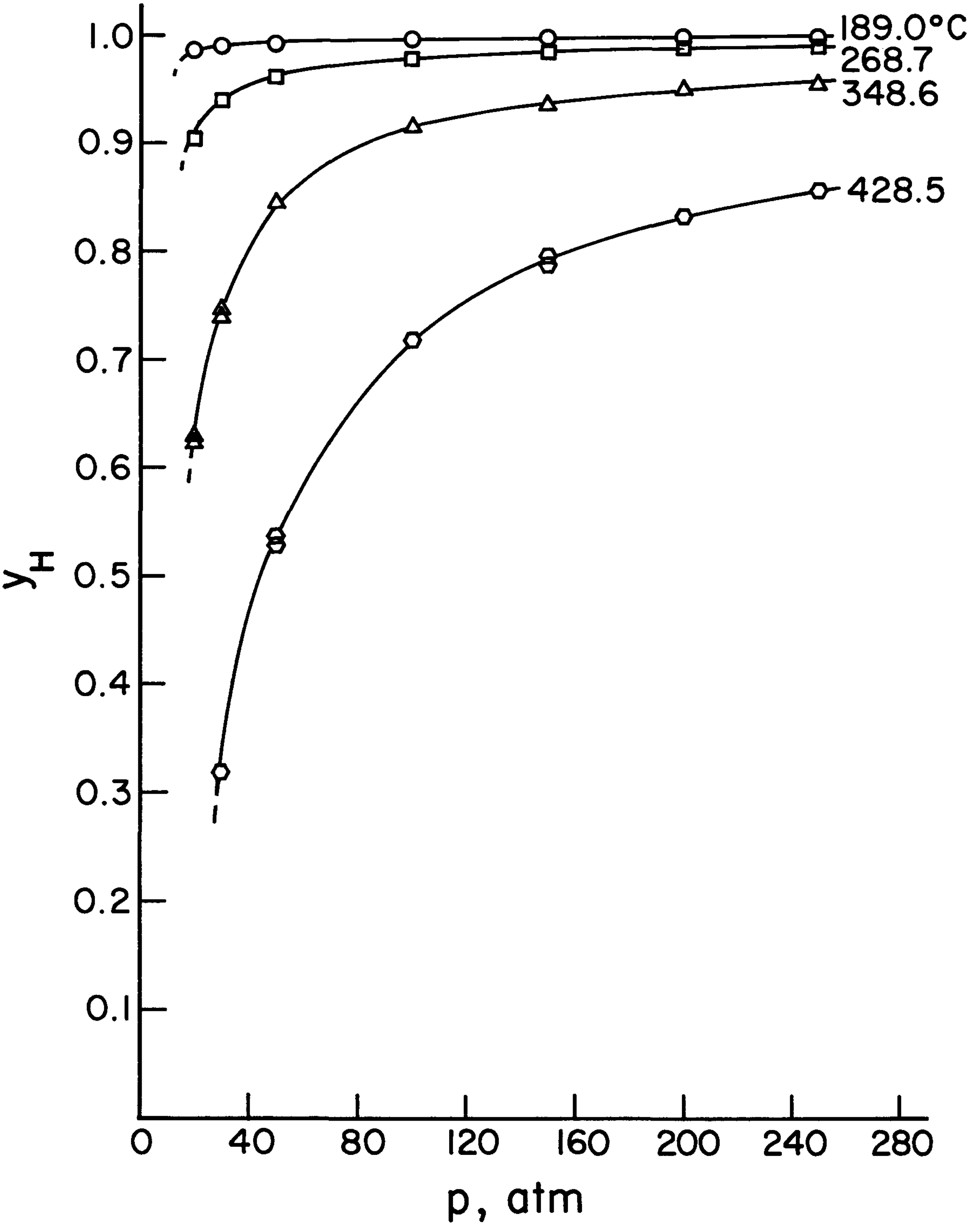


Figure 16. Mole Fraction of Hydrogen in Saturated H_2/1-methylnaphthalene Gas Mixtures.

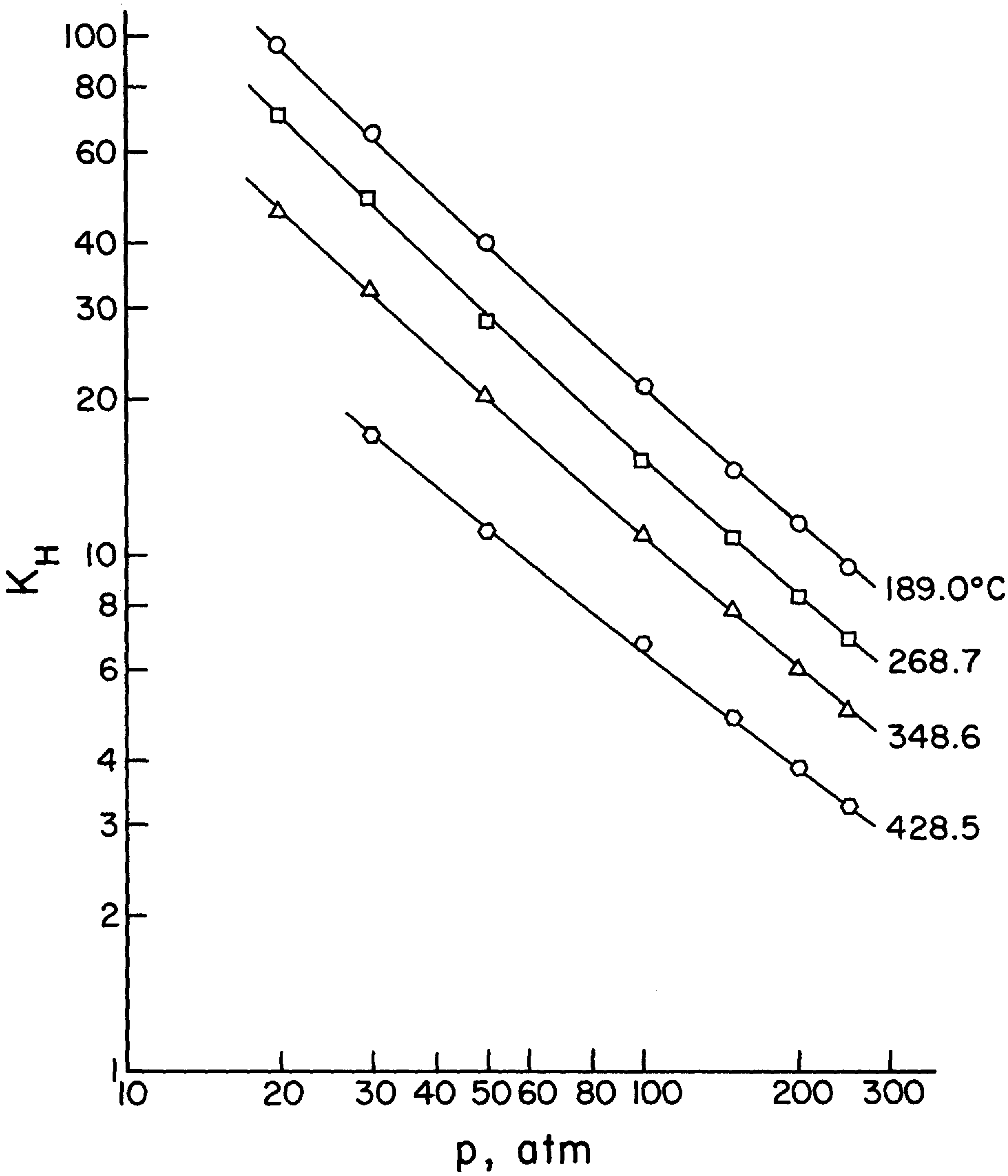


Figure 17. Vaporization Equilibrium Ratio of Hydrogen in H_2/1-methylnaphthalene.

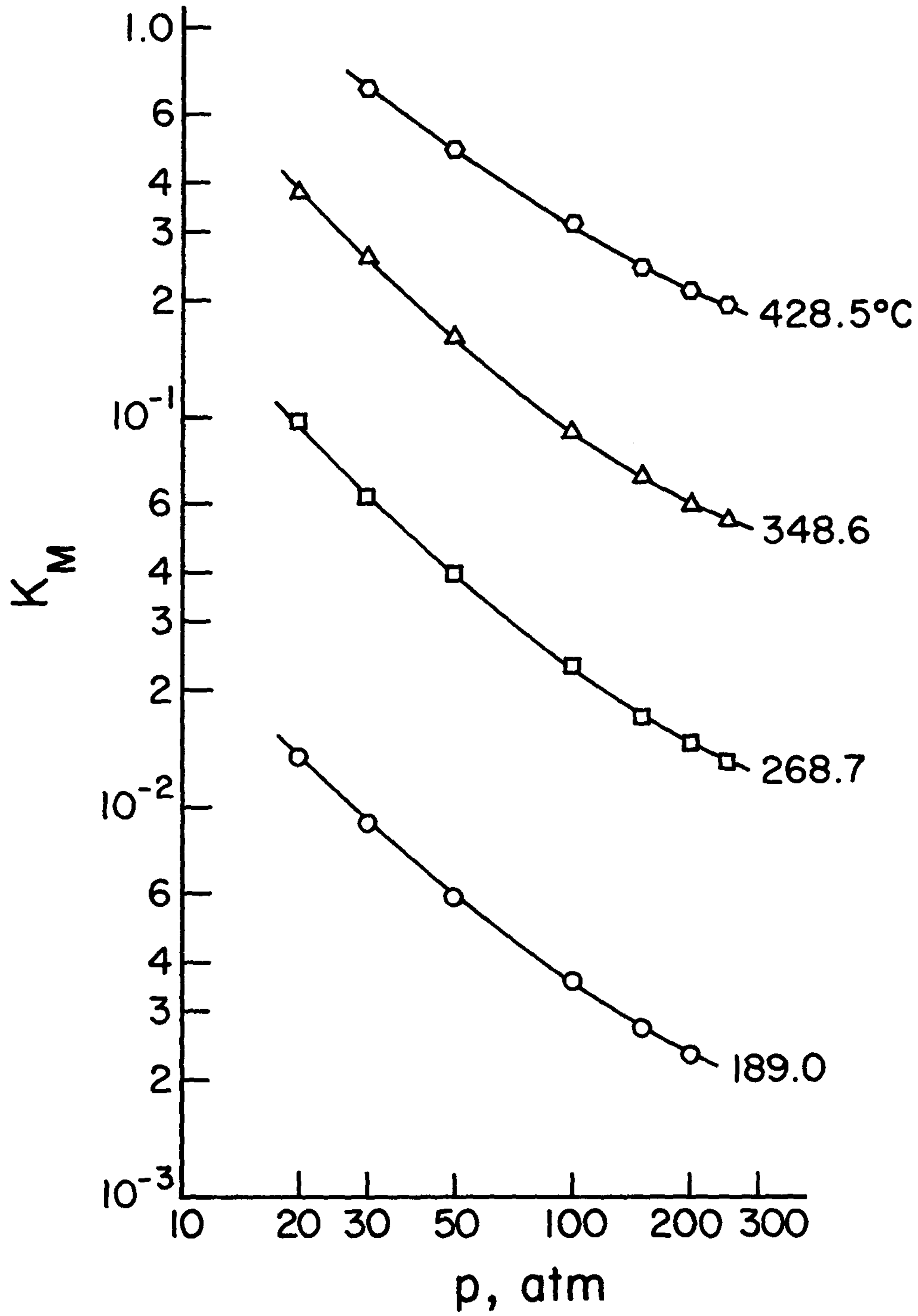


Figure 18. Vaporization Equilibrium Ratio of 1-methylnaphthalene in H_2/1-methylnaphthalene.

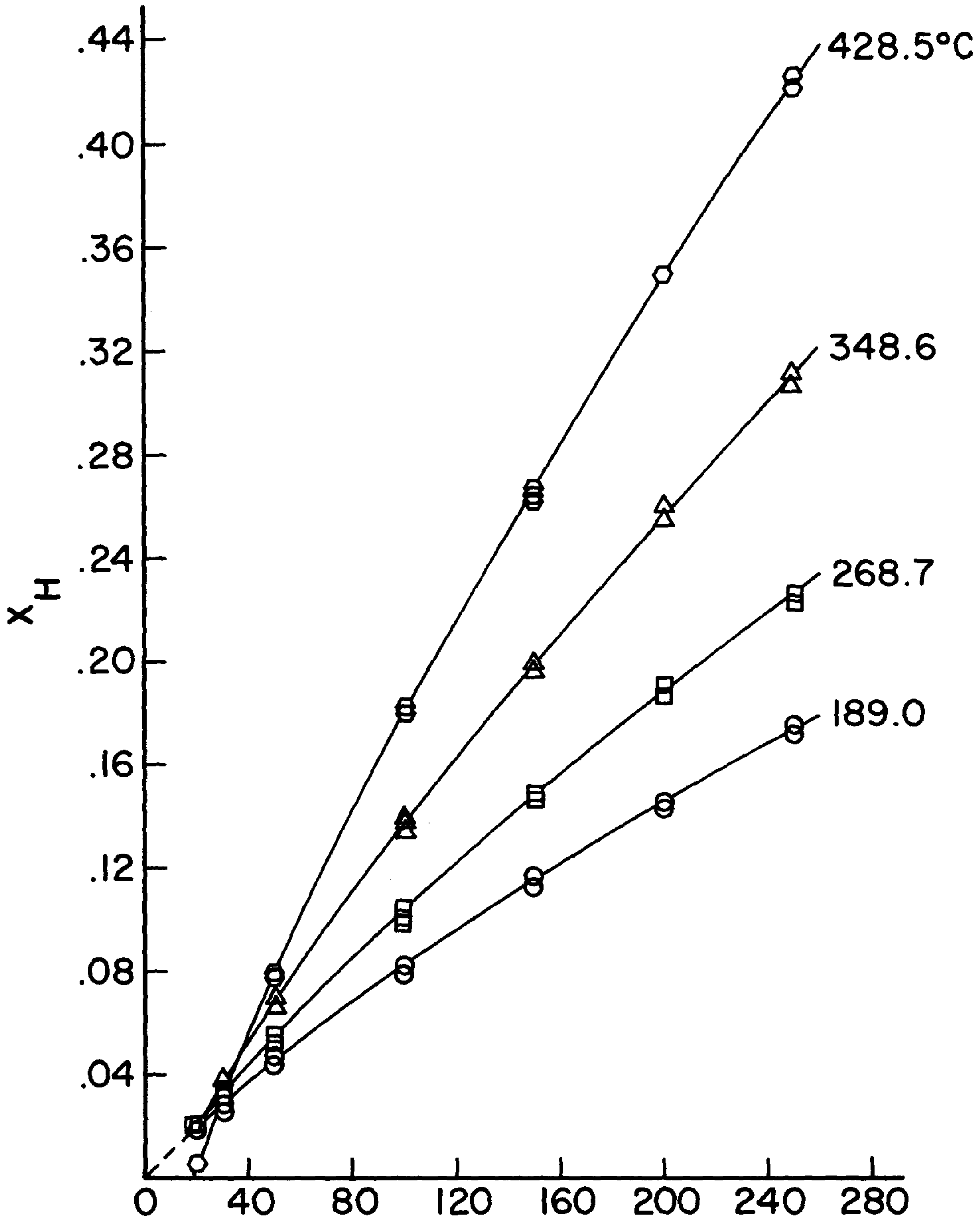


Figure 19. Solubility of Hydrogen in Bicyclohexyl.

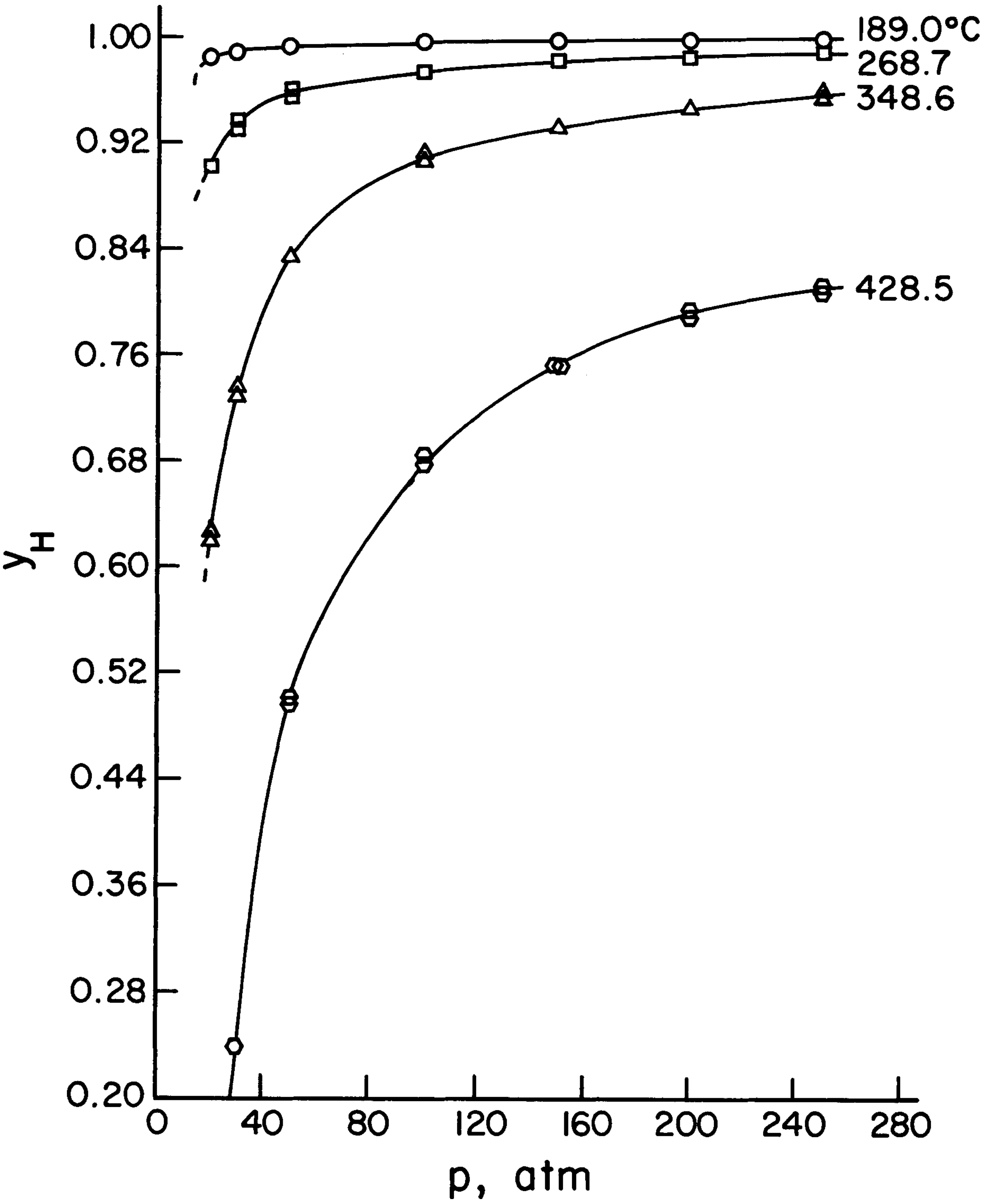


Figure 20. Mole Fraction of Hydrogen in Saturated H_2/bicyclohexyl.

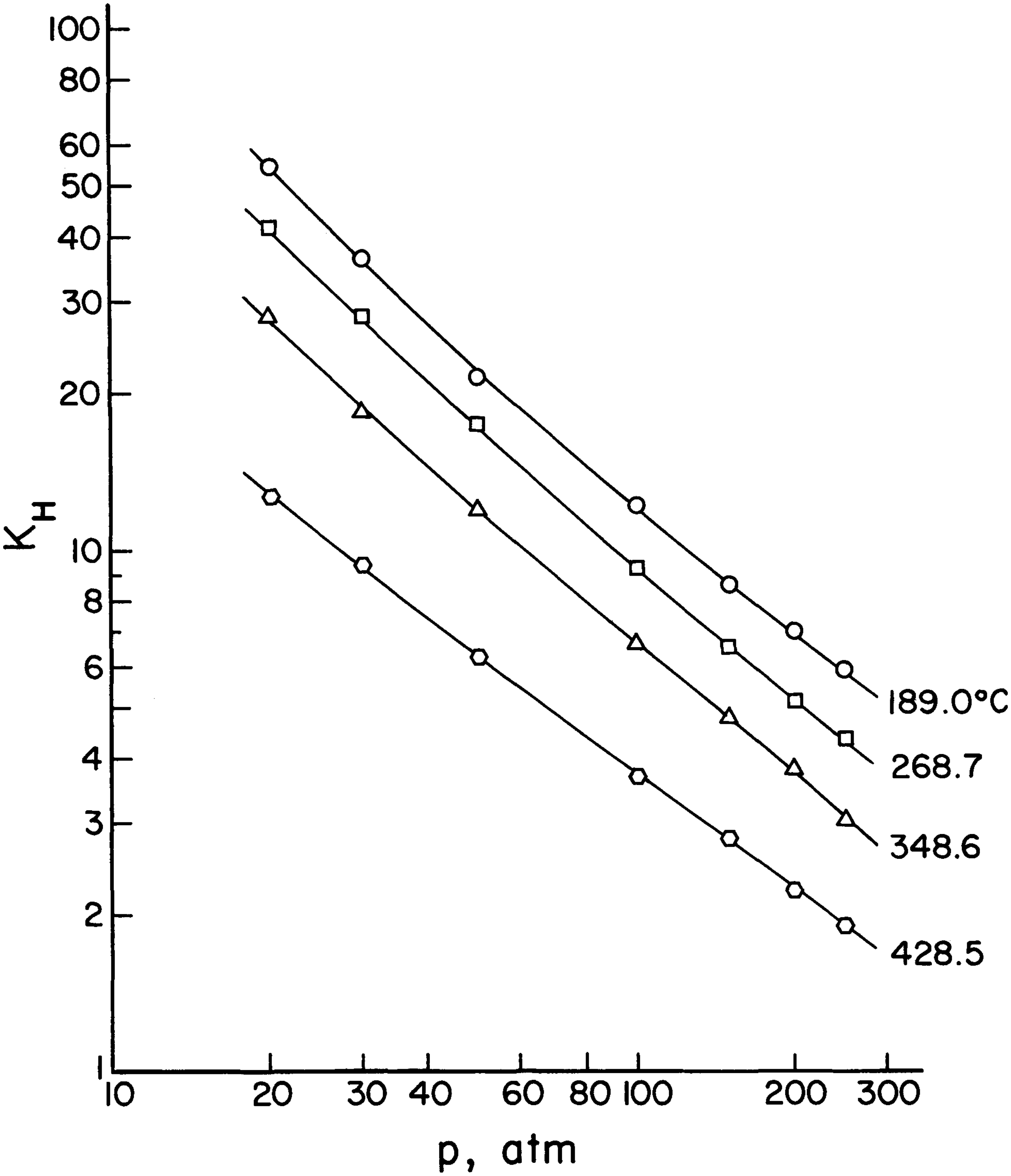


Figure 21. Vaporization Equilibrium Ratio of Hydrogen in H_2/bicyclohexyl.

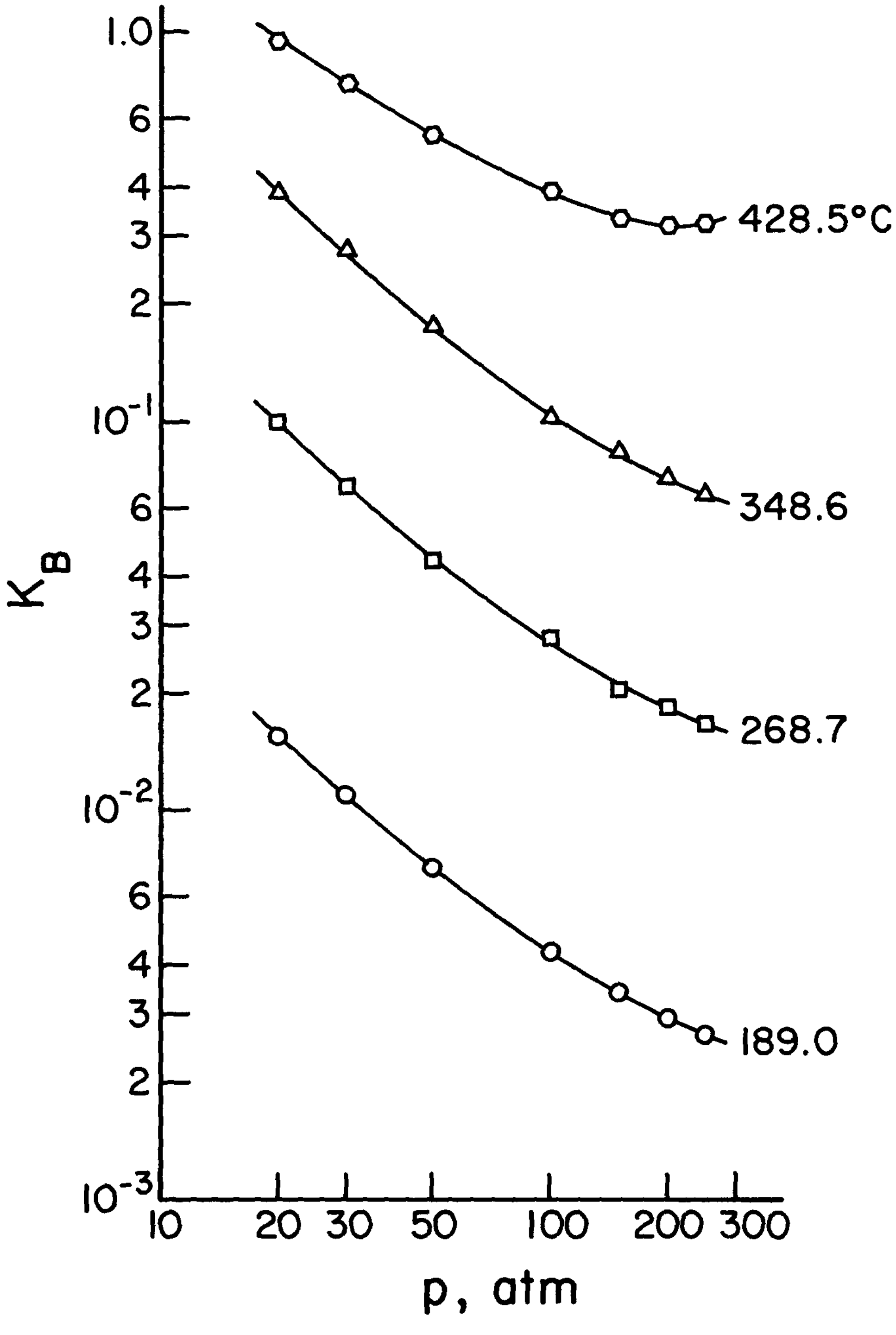


Figure 22. Vaporization Equilibrium Ratio of Bicyclohexyl in H_2/bicyclohexyl.

diphenylmethane up to 760 mm Hg, (Weast, 1969), for 1-methylnaphthalene up to 1500 mm (Wilhoit and Zwolinski, 1971), and for bicyclohexyl up to 736 mm (Eghoff, 1947). Dobry and Keller (1957) measured the vapor pressures for bicyclohexyl, but gave no detailed data. Their result was represented by the Clausius-Clapeyron equation. Interpolation gives the needed vapor pressure values at the lower temperatures of this work.

The quantities $\tilde{V}^E$ and ϕ_i also needed in the calculations are estimated in this work by the method of Prausnitz and Chueh (1968) based on the use of their modified Redlich and Kwong equation of state. The estimation procedures are described in the Appendix.

Since the calculations are relatively complicated and since the quantities $\tilde{V}^E$ and ϕ_i have to be estimated, a test is made of the total procedure by applying it to a set of high pressure gas/liquid data in the literature. Connolly's data on H_2/benzene is chosen for the reason that the system is closest in nature to those studied in this work. The calculated y agrees with the reported experimental values to within the accuracy of the data.

Table 6 shows the comparison of the calculated y_H with the experimental values of this work for H_2/tetralin. The comparison is limited by the available vapor pressure data to the lower temperatures of this work. Agreement between the two sets of y_H values is within 1%. We conclude from these comparisons that the experimental conditions of this work are at equilibrium and the data are thermodynamically consistent to within the uncertainty of the data.

Henry constants H of hydrogen in the solvents studied are generated by the orthogonal collocation calculations, and the results are reported in Table 7. Henry constant is the constant of proportionality in Henry's law which expresses that the fugacity f of the dissolved gas in a liquid is proportional to the mole fraction of the dissolved gas x,

$$f = \lim_{x \to o} Hx \tag{3-1}$$

The reported Henry constants are useful for making estimates of solubility of hydrogen at low pressures. The fugacity is simply equal to the partial pressure in the equilibrium gas mixture at low pressures. The solubilities of hydrogen

Table 6

COMPARISON OF EXPERIMENTAL WITH CALCULATED y_H

x_H	p atm	y_H expt	 calc	Δy_H % dev.
		H_2/tetralin at 189.6°C		
0	0.669	0	0	
.0118	20	.9652	.9619	-0.34
.0176	30	.9748	.9737	-0.11
.0297	50	.9828	.9847	0.19
.0571	100	.9897	.9918	0.21
.0823	150	.9927	.9940	0.13
.1051	200	.9940	.9951	0.11
.1289	250	.9948	.9958	0.10
		H_2/diphenylmethane at 189.6°C		
0	0.151	0	0	
.0123	20	.9903	.9918	0.11
.0183	30	.9935	.9944	0.09
.0300	50	.9963	.9966	0.03
.0591	100	.9980	.9982	0.02
.0830	150	.9985	.9987	0.02
.1055	200	.9988	.9900	0.02
.1240	250	.9989	.9991	0.02
		H_2/diphenylmethane at 268.7°C		
0	1.13	0	0	
.0159	20	.9390	.9343	-0.50
.0244	30	.9580	.9564	-0.17
.0408	50	.9741	.9750	0.09
.0785	100	.9861	.9876	0.15
.1105	150	.9895	.9911	0.16
.1416	200	.9912	.9932	0.20
.1724	250	.9921	.9944	0.23
		H_2/1-methylnaphthalene at 189.0°C		
0	0.257	0	0	
.0103	20	.9863	.9862	-0.01
.0153	30	.9906	.9906	0.00
.0250	50	.9939	.9943	0.04
.0479	100	.9965	.9969	0.04
.0692	150	.9974	.9978	0.04
.0887	200	.9978	.9982	0.04
.1060	250	.9980	.9985	0.05

Table 6 (continued)

x_H	p atm	y_H expt	 calc	Δy_H % dev.
		H_2/1-methylnaphthalene at 268.7°C		
0	1.70	0	0	
.0127	20	.9007	.9021	0.16
.0202	30	.9360	.9355	-0.05
.0342	50	.9625	.9625	0.30
.0641	100	.9801	.9801	0.24
.0931	150	.9860	.9860	0.22
.1191	200	.9890	.9890	0.23
.1452	250	.9908	.9908	0.25
		H_2/bicyclohexyl at 189.0°C		
0	0.300	0	0	
.0181	20	.9842	.9828	-0.14
.0262	30	.9889	.9883	-0.06
.0443	50	.9929	.9933	0.04
.0810	100	.9958	.9964	0.06
.1158	150	.9969	.9974	0.05
.1418	200	.9974	.9979	0.05
.1718	250	.9977	.9982	0.05

Table 7

HENRY'S CONSTANTS OF HYDROGEN

t°C	H atm
in Tetralin	
189.6	1528
in Diphenylmethane	
189.6	1630
268.7	1150
in 1-Methylnaphthalene	
189.0	1890
268.7	1370
in Bicyclohexyl	
189.0	1060

calculated from Henry's law using the reported value of Henry constant are shown in Figure 23 for hydrogen/tetralin at 189.6°C for comparison with experimentally observed values. Increasing pressure produces two effects that cause the system to depart more and more from Henry's law: the effect of pressure on the fugacity of the dissolved gas, and the effect of self-interaction of the dissolved gas molecules. One approach to the development of a general correlation of high pressure gas solubility is to account for these factors. This approach will be discussed in § 4.3.

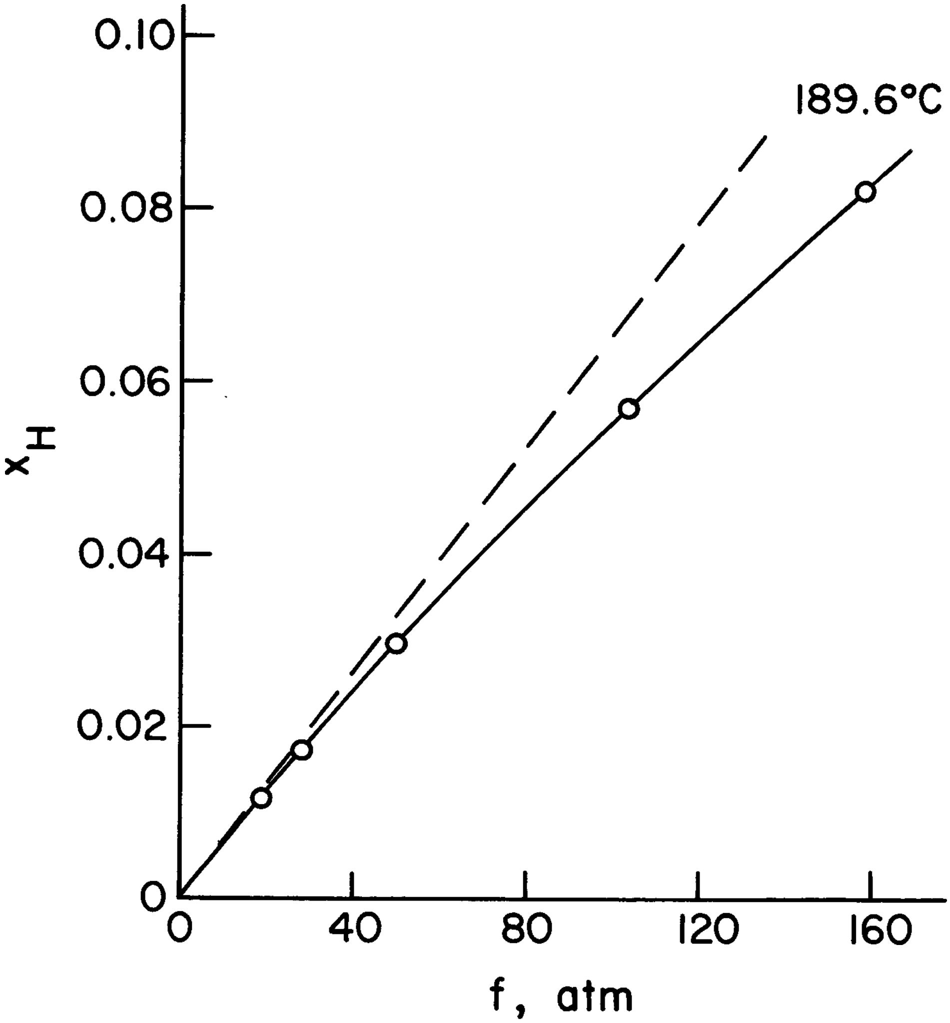


Figure 23. Comparison of Henry's Law and Experimental Solubility Data of Hydrogen in Tetralin at 189.6°C.

Section 4.0

CORRELATION OF VAPOR-LIQUID EQUILIBRIUM

4.1 INTRODUCTION

Vapor-liquid equilibrium data are made useful for engineering work when suitably correlated in the form of K-values or equivalent quantities. The correlations are needed to describe the equilibrium in real systems of interest which may contain a large number of components of various natures in wide ranges of compositions. In addition, the temperature and pressure can vary over wide ranges. The possible combinations of variables of interest is so large that it is impractical to attempt direct experimental observation on all of them and the limited quantity of experimental data must be generalized through the development of correlations. Thus the ultimate usefulness of the data reported here will depend on their bearing with correlations. In the following sections we discuss this bearing in two ways: the test of existing correlations and the development of new correlations with the data. The accuracy of existing correlations can be determined when tested with experimental data. The results will indicate to the engineer the need to use correction factors if and when systematic deviations are uncovered. Any need for the development of new correlations will also become obvious.

4.2 TEST OF THE CHAO-SEADER AND GRAYSON-STREED CORRELATIONS

The Chao-Seader correlation (1961) for vapor-liquid equilibrium in hydrocarbon systems has been in wide use. The correlation is in the form of a set of equations for the K-value,

$$K_i = \nu_i \gamma_i / \phi_i \tag{4-1}$$

where $\nu_i = f^\circ_{iL}/p$ = fugacity coefficient of pure liquid component

$\gamma_i = f_i/(f^\circ_{iL} x_i)$ = activity coefficient of component in liquid mixture

$\phi_i = f_i/(p y_i)$ = fugacity coefficient of component in vapor mixture

f°_{iL} = fugacity of pure liquid component at system temperature and pressure

The pure liquid fugacity coefficient ν_i is a function of T and p only for each component, and is expressed with one generalized equation for all the usual hydrocarbons in reduced temperature $T_r \equiv T/T_c$ and reduced pressure $p_r \equiv p/p_c$. However, a special equation is given for hydrogen because of the very large values of T_r at the conditions of interest.

The pure liquid fugacity coefficient corresponds to the "ideal" K-values. It would indeed be the actual K-value if the liquid solution were ideal and if the vapor were an ideal gas. Deviations from these ideal conditions are respectively accounted for by γ_i and ϕ_i.

The activity coefficient in a liquid mixture γ_i is given by the Hildebrand-Scatchard regular solution equation. It performs the function of an "aromaticity correction factor" for the solubility of gases in hydrocarbon liquids.

The fugacity coefficient in the vapor mixture ϕ_i is calculated with the Redlich and Kwong equation of state. For hydrogen at the temperatures and pressures of this work, it is usually close to 1, showing that the gas mixture is close to being an ideal gas and the fugacity coefficient of hydrogen is not of much interest at these conditions.

The Chao-Seader correlation has been found to agree with data on K-values of hydrogen in hydrocarbon solvents at pressures up to about 550 atm. with an average deviation of about 10%. But the applicable temperature is limited to a maximum of 240°C due to a lack of a data base at higher temperatures. In spite of this stated limitation, use of the correlation at the higher temperatures persisted. It is therefore of interest to test the correlation with the present data to obtain indications as to the direction and magnitude of the 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 H_2/heavy oil systems. The liquid solution activity coefficient and vapor mixture fugacity coefficient calculations remain unchanged. No comparison of the Grayson-Streed correlation has ever been made with data other than their own at the higher temperatures of this work. It is therefore also of interest to test the correlation with the present data.

Comparison of the correlations with the experimental K-values in the H_2/tetralin system are shown in Figures 24 and 25 for hydrogen and tetralin respectively.

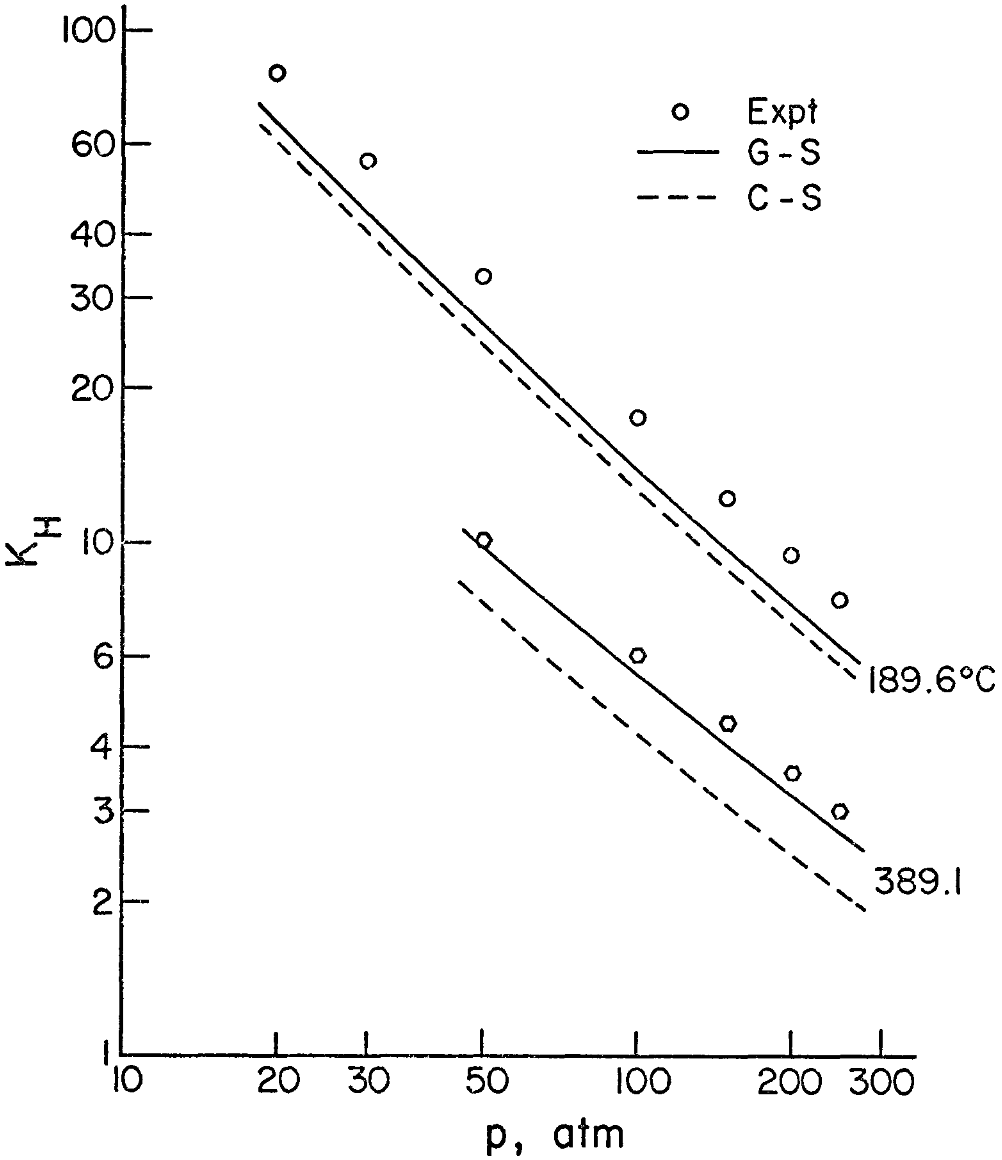


Figure 24. Comparison of K_H Data in H_2/tetralin with Correlations.

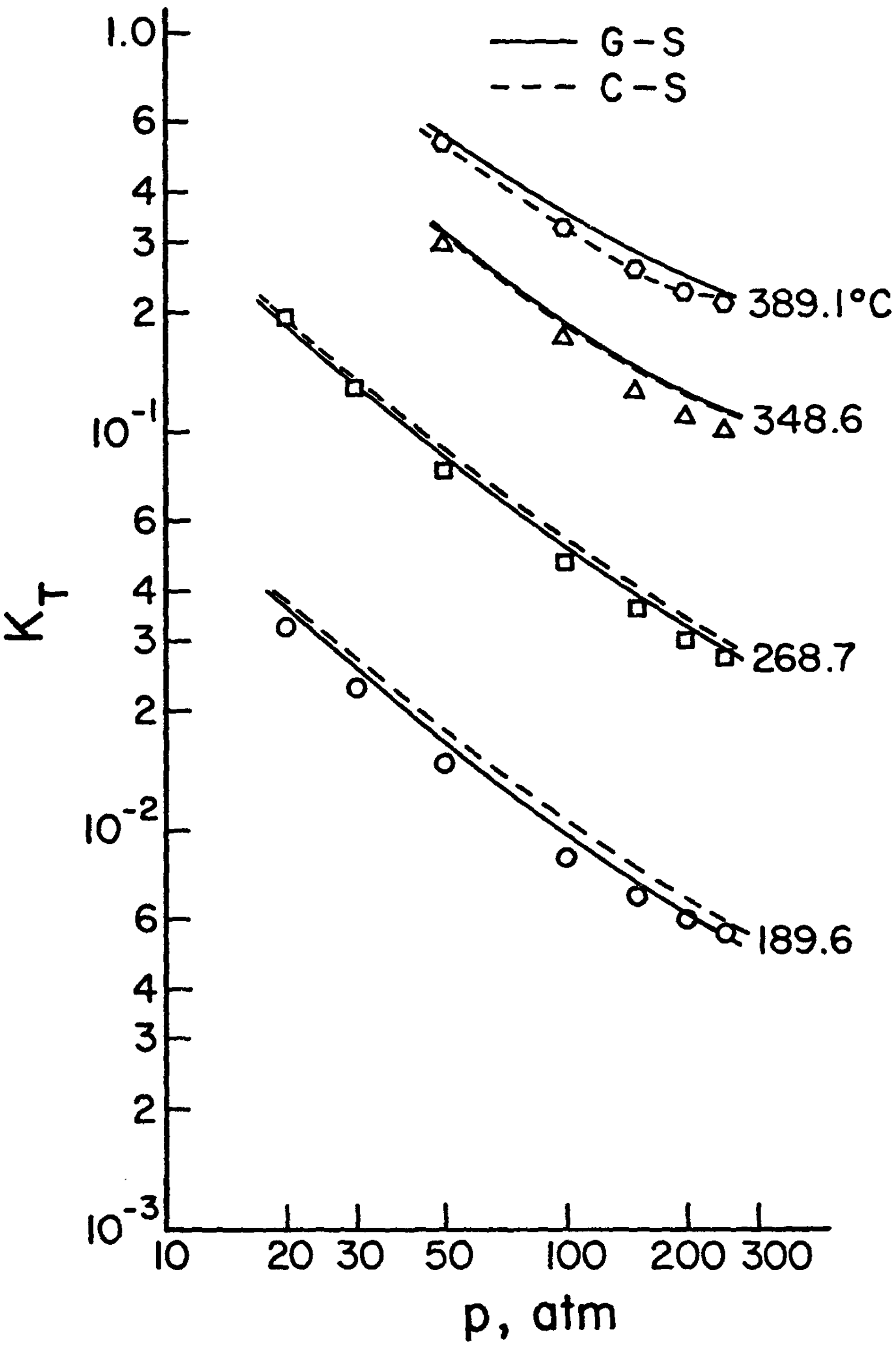


Figure 25. Comparison of K_T Data in H_2/tetralin with Correlations.

Only the lowest and the highest isotherms are shown in Figure 24 since the intermediate isotherms are quite similar. K-values of hydrogen from the Chao-Seader correlation appear consistently low by up to about 37%. The Grayson-Streed correlation also seems to be low by up to about 25%. The K-values of tetralin appear to be well represented by both correlations up to the highest pressure studied.

Similar comparisons of the experimental K-values with the correlations are shown in Figures 26 and 27 for the systems H_2/diphenylmethane, in Figures 28 and 29 for H_2/1-methylnaphthalene, and in Figures 30 and 31 for H_2/bicyclohexyl.

Substantial deviations of the data from the correlations are indicated by the comparisons, up to 37% from the Chao-Seader and up to 30% from the Grayson-Streed.

K-values of hydrogen predicted by the correlations that are used in the comparisons are sensitively dependent on the value of solubility parameter of the solvent that is used in the calculation. Similarly the predicted K-values of the solvents sensitively depend on the critical properties and acentric factors used in the calculations. Unfortunately most of these quantities required in the calculations are estimated since direct experimental data are not available. The estimated values are presented in Table 8. The procedure of estimation is briefly described below.

Values of the critical properties are estimated by Lydersen's method (Reid and Sherwood, 1966), which employs structural contributions to estimate T_c, p_c, and V_c. Structural parameters were originally developed by Riedel, but Lydersen extended the method to treat more types of molecules. The results agree well with those by the method of Forman and Thodos (Reid and Sherwood, 1966) and are comparable with the values reported in the literature (Gould, 1955; Riddick and Bunger, 1970; Reid and Sherwood, 1966). However, Reid, Prausnitz and Sherwood (1977) recommended the values of P_c = 34.7, 29.4, and 35.2 (in atm) for tetralin, diphenylmethane, and 1-methylnaphthalene, respectively, which are significantly higher than the values reported in Table 8, but good agreement in the values of T_c.

The acentric factor, ω, is defined by the vapor-pressure curve at $T_r = 0.7$. Vapor pressure data of tetralin and diphenylmethane are available only up to the normal boiling points, corresponding to $T_r = 0.67$ and 0.698, respectively.

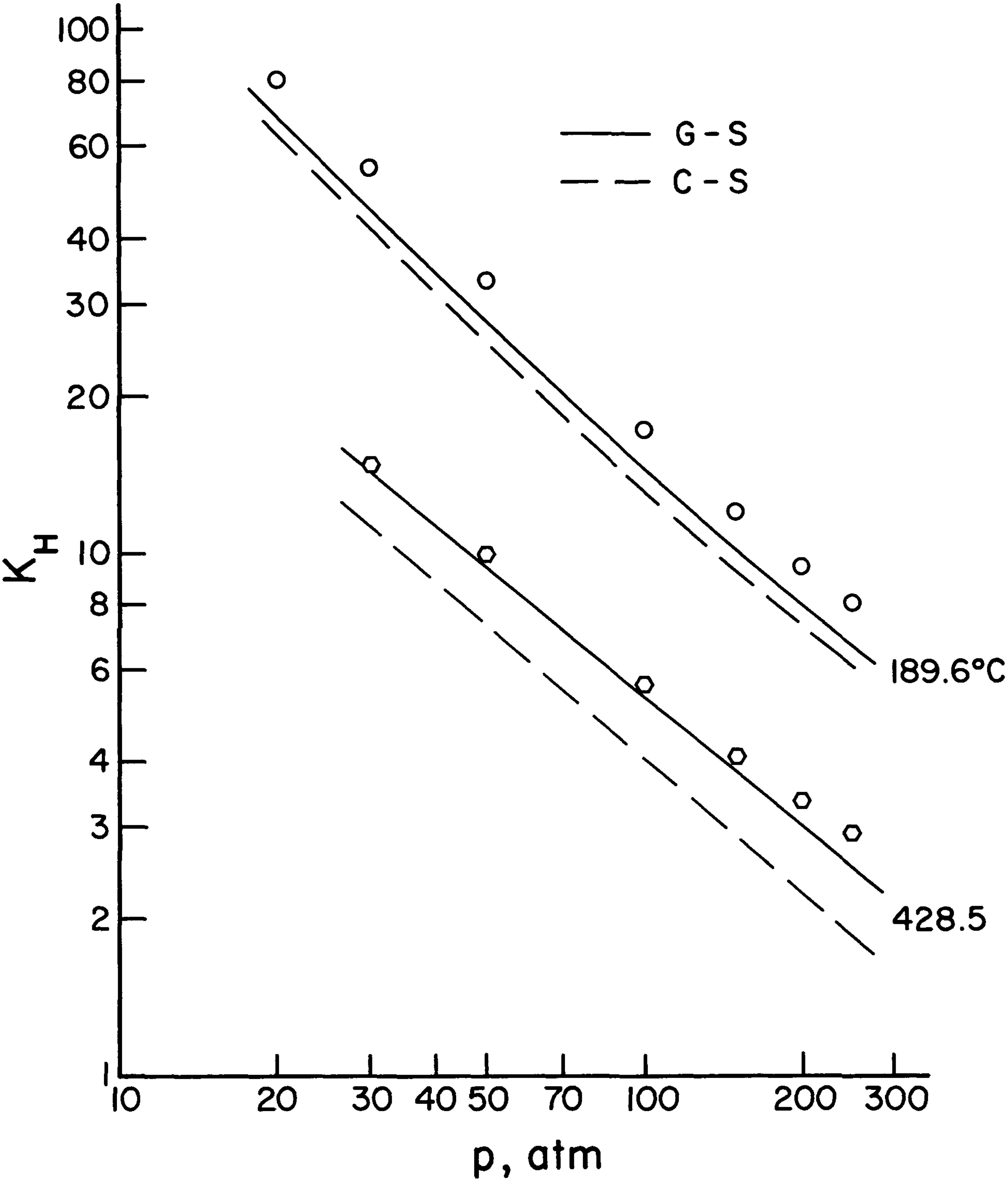


Figure 26. Comparison of K_H Data in H_2/diphenylmethane with Correlations.

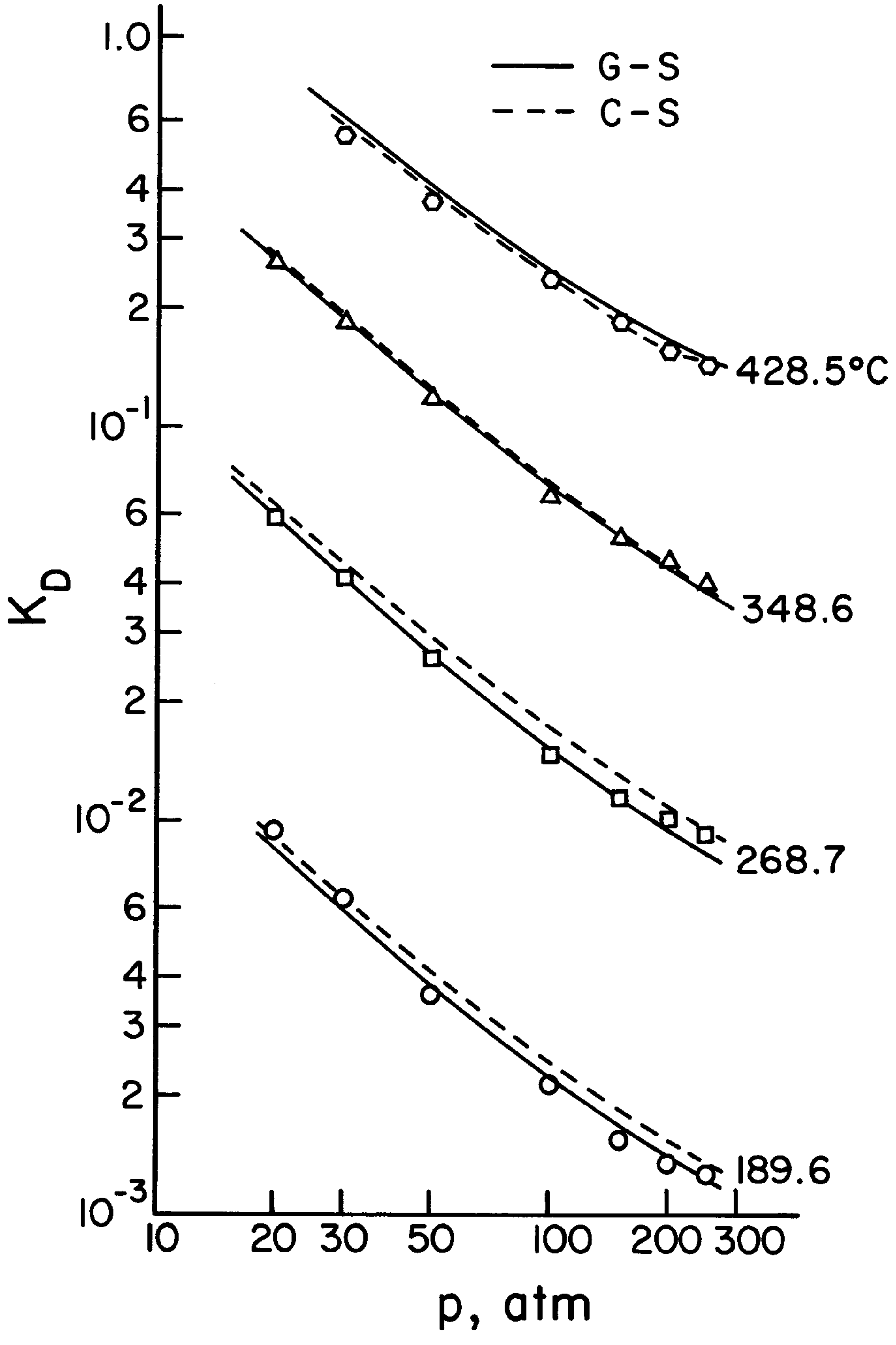


Figure 27. Comparison of K_D Data in H_2/diphenylmethane with Correlations.

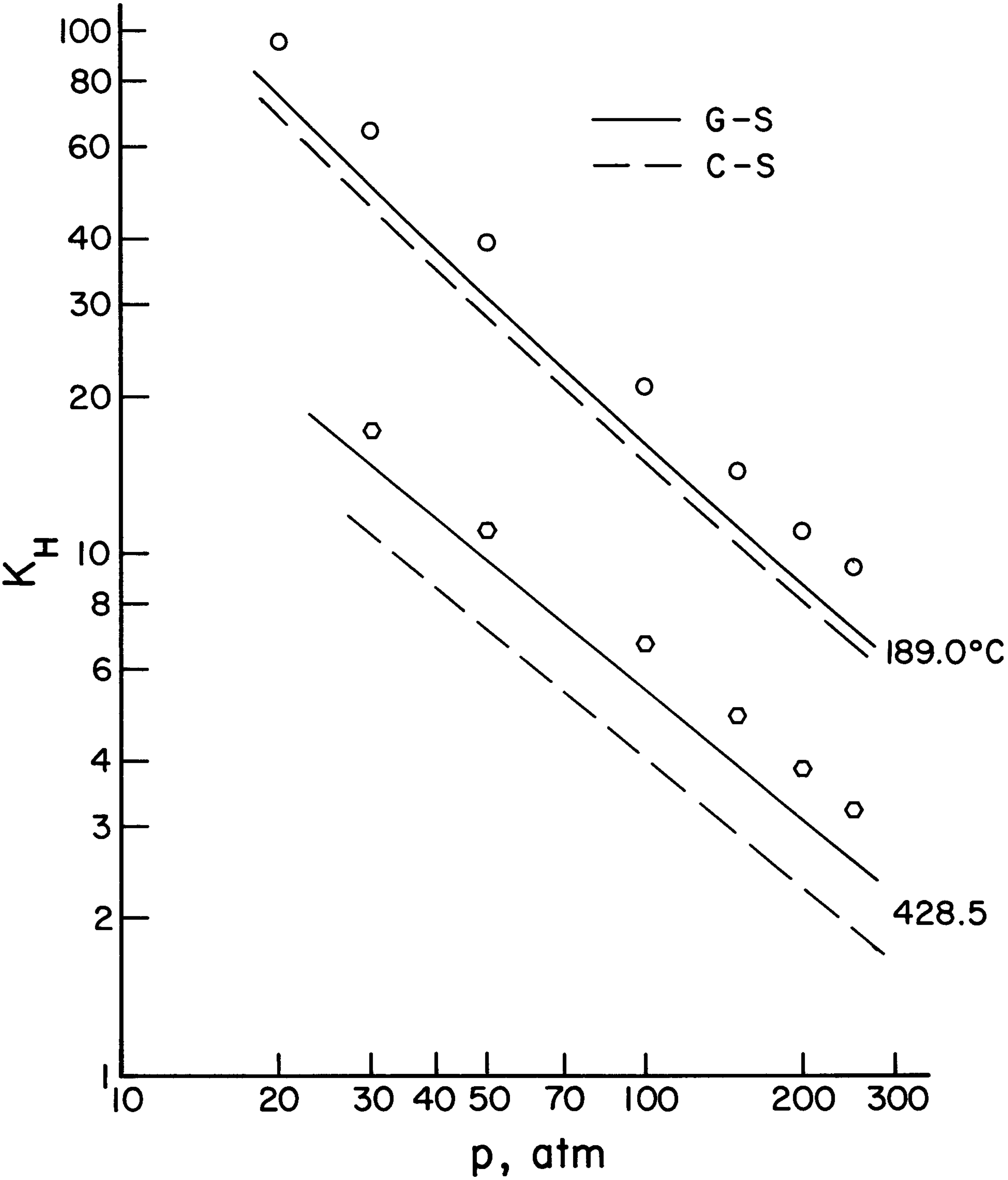


Figure 28. Comparison of K_H Data in H_2/1-methylnaphthalene with Correlations.

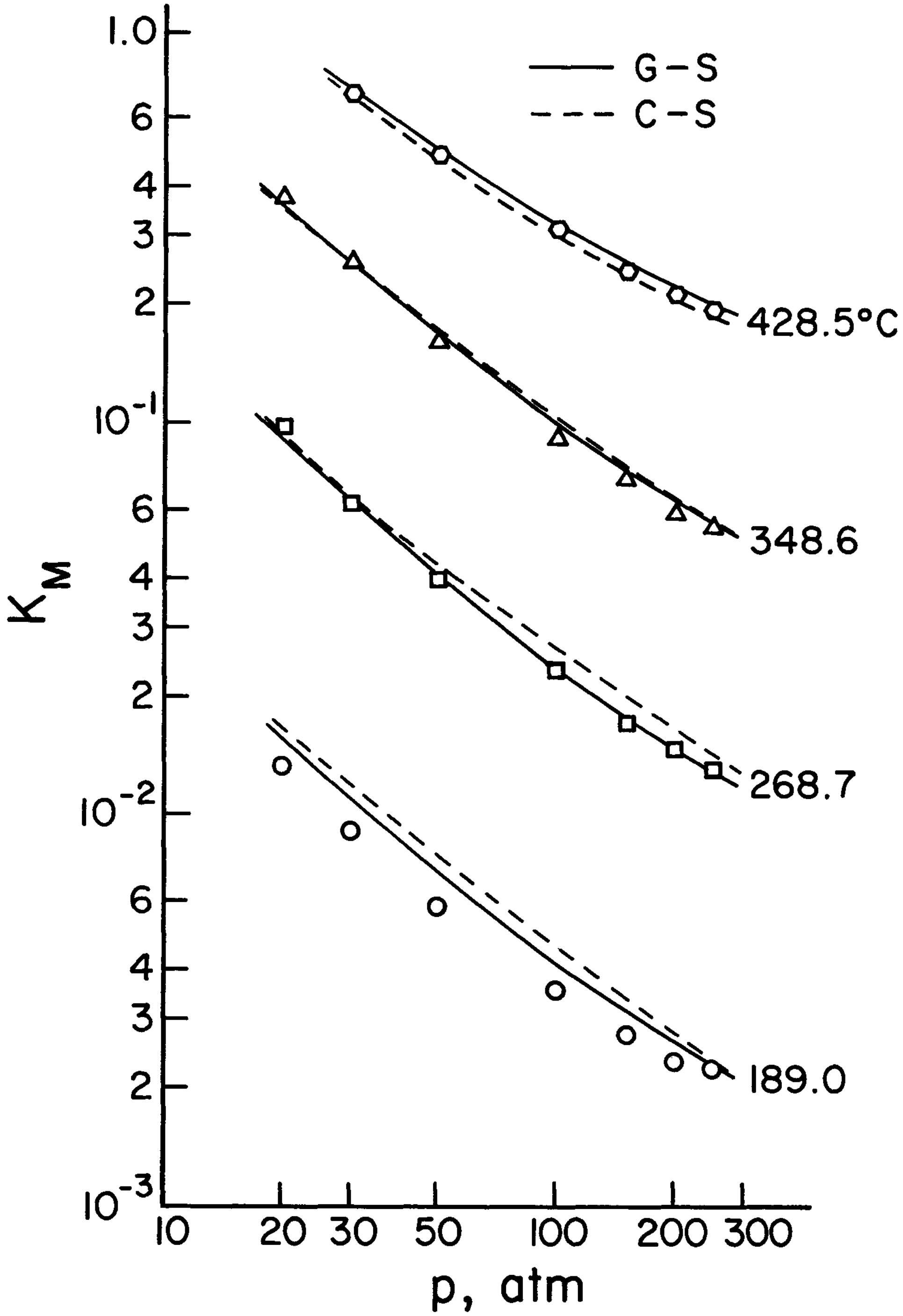


Figure 29. Comparison of K_M Data in H_2/1-methylnaphthalene with Correlations.

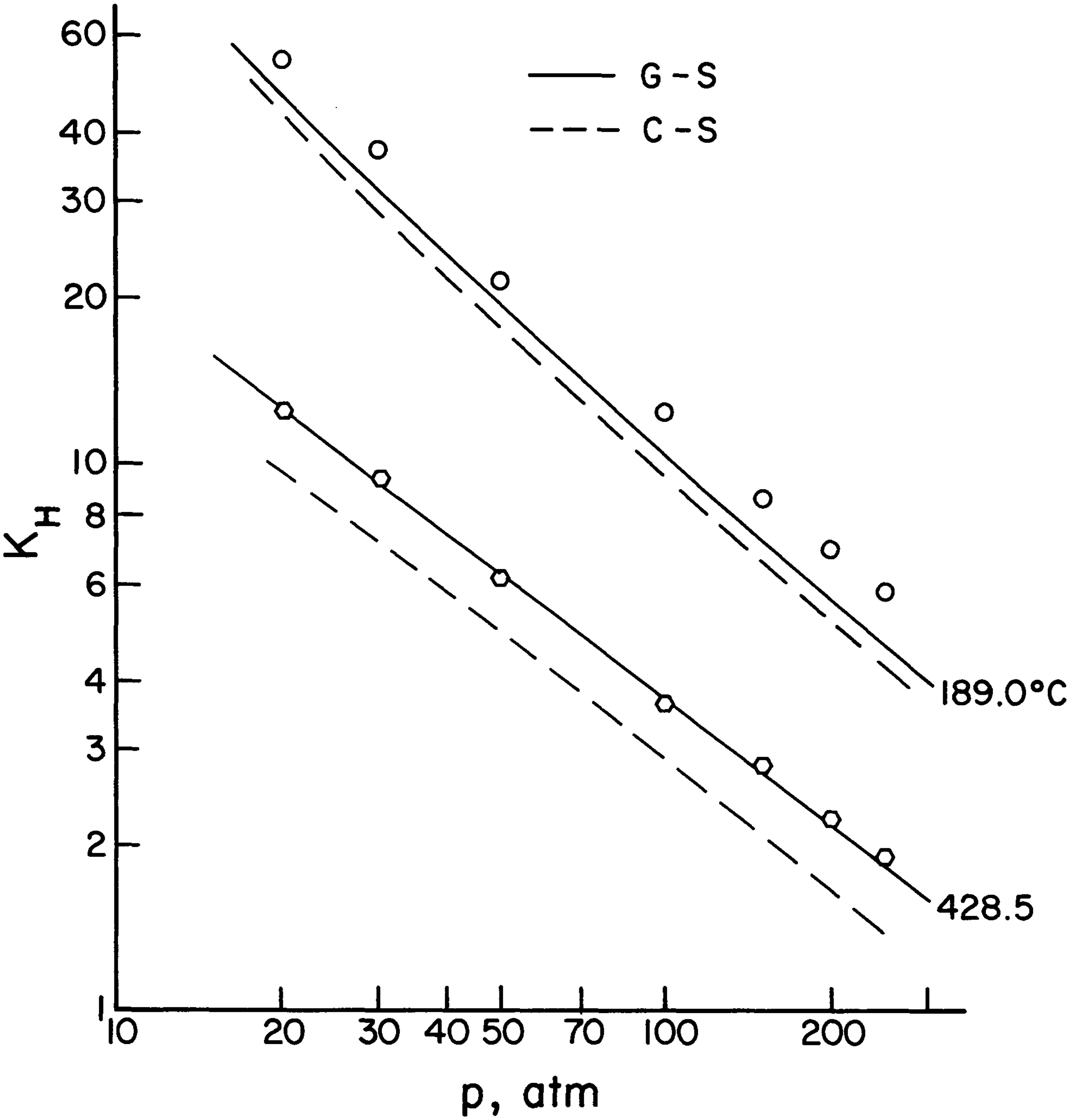


Figure 30. Comparison of K_H Data in H_2/bicyclohexyl with Correlations.

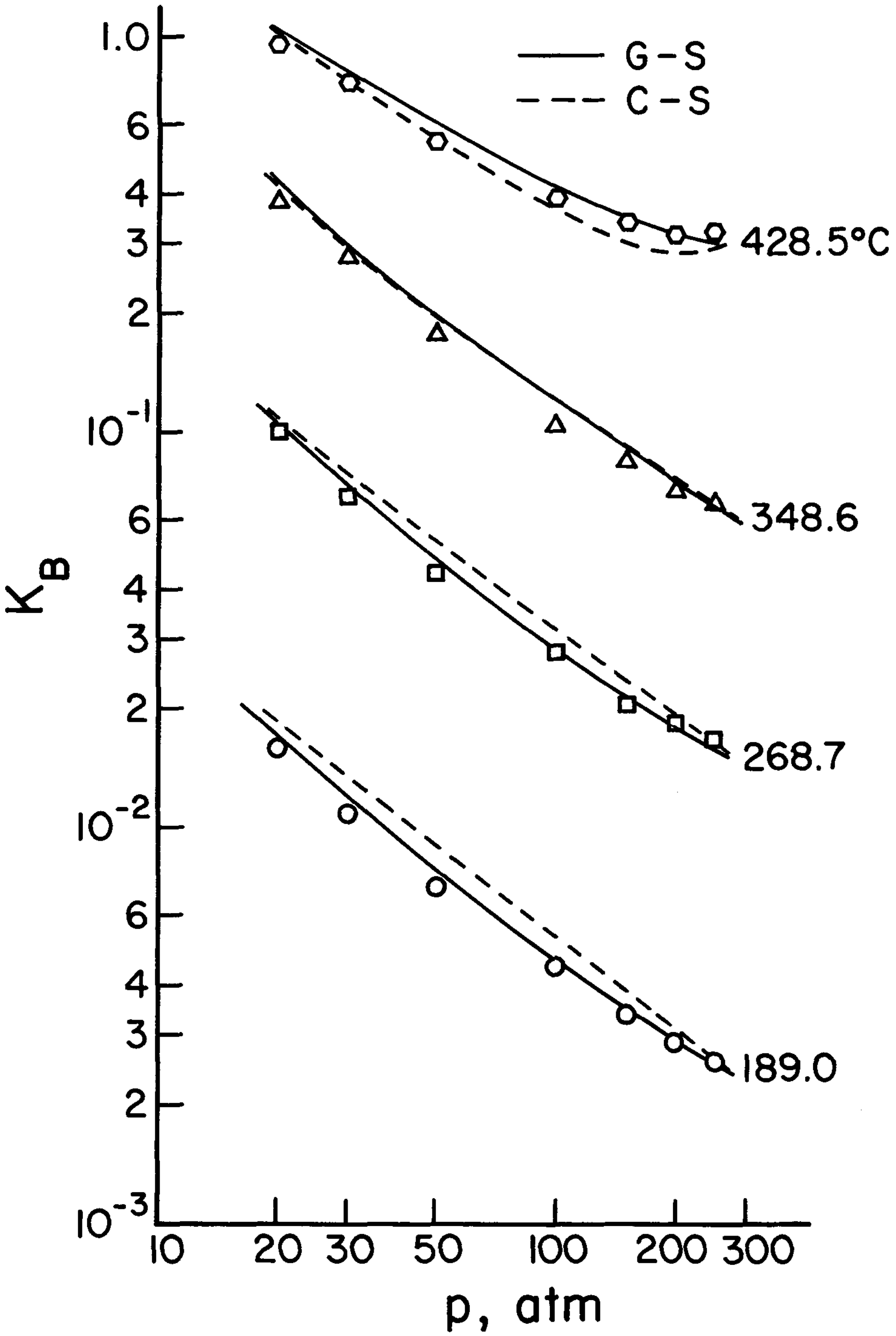


Figure 31. Comparison of K_B Data in H_2/bicyclohexyl with Correlations.

Table 8

SOME PROPERTIES OF SOLVENTS

	Tetralin	Diphenylmethane	1-Methylnaphthalene	Bicyclohexyl
Tc, °K	716.5	770.2	772.2	731.4
Pc, at m	33.05	28.2	32.1	25.3
Vc, cc/g-mole	438.0	527.0	462.0	577.0
ω	0.316	0.434	0.302	0.388
δ, $(cal/cc)^{1/2}$	9.5	9.6	9.8	8.7
$\tilde{V}$,(liq. at 25°C) cc/mole	137.1	167.2	139.9	187.7

Antoine equations fitted to the subatmospheric data are applied to extrapolate the vapor pressures to $T_r = 0.7$, which are then used to find the values of ω. For 1-methylnaphthalene, the vapor pressure data given by Wilhoit and Zwolinski (1971) are used to calculate ω. Reliable experimental data of vapor pressure are not available for bicyclohexyl. The Edmister method (Reid and Sherwood, 1966) is employed to estimate ω for this solvent. This method is essentially an application of the Reduced Kirchoff vapor-pressure equation at T_b and at $T_r = 0.7$ and is described by

$$\omega + 1 = 3/7[\theta/(1-\theta)]\log p_c \qquad (4\text{-}2)$$

where $\theta = T_b/T_c$. Note that Dobry and Keller (1957) applied the Clausius-Clapeyron equation of $\log P = -A/T + B$ with $A = -2715$ and $B = 8.21$ to represent the vapor pressure of bicyclohexyl. This equation leads to a value of $\omega = 0.377$. Reid, Prausnitz and Sherwood (1977) recommended the value of $\omega = 0.303$ for tetralin and revised their earlier values of 0.438 for diphenylmethane and 0.279 for 1-methylnaphthalene (Reid and Sherwood, 1965) to 0.471 and 0.334, respectively. The solubility parameter, δ, is in general calculated from the heat of vaporization, ΔH_v. Several techniques for estimating heats of vaporization of pure liquids have been critically reviewed by Reid and Sherwood (1965) (see also Reid, Prausnitz and Sherwood, 1977). Those methods require the knowledge of at least one of the following physical properties: vapor pressure, normal boiling point, and T_c, p_c, etc.. The selection of methods for calculation of ΔH_v in this work depends on what kind of physical properties are experimentally available or can be estimated with confidence. Generally speaking, the values of the normal boiling points for the liquids of interest are well defined. Such methods as "Hildebrand rules" (Hildebrand and Scott, 1964) and the Kistiakowsky equation (Reid, Prausnitz, and Sherwood, 1977), which require the knowledge of only the normal boiling point, are particularly useful. The "Hildebrand rules" are simply an empirical formula for ΔH_v at 25°C.

$$\Delta H_v(\text{cal/mole}) = -2950 + 23.7\ T_b + 0.020\ T_b^2 \qquad (4\text{-}3)$$

and a similar relation for ΔH_v at the normal boiling point:

$$H_v(\text{b.p.}) = 17.0\ T_b + 0.009\ T_b^2 \qquad (4\text{-}4)$$

Hildebrand's equation is applied to calculate ΔH_v for diphenylmethane, which agrees with the values from the modified Pitzer acentric-factor correlation (Reid and Sherwood, 1966) and from the literature (Gould, 1955). The heat of vaporization reported by Gould (1955) is used to calculate the solubility parameter for tetralin, the result is in agreement with the estimated values from Hildebrand's equation and Pitzer's correlation and also with the value recommended by Riddick and Bunger (1970). API-44-TRC publication (Wilhoit and Zwolinski, 1971) reported the value of ΔH_v at the boiling point for 1-methylnaphthalene, which is in good agreement with the values obtained by the Giacalone equation (Reid and Sherwood, 1966) and the Hildebrand equation. The Fishtine method (Reid and Sherwood, p. 148, 1966) is applied to find the value of ΔH_v, and thus δ, at 25°C from the value at the boiling point. For bicyclohexyl, the heat of vaporization estimated from the Hildebrand equation is used to calculate the solubility parameter. The result agrees with the value obtained from Giacalone's equation. However, Dobry and Keller (1957) suggested the value of $\Delta H_v = 12.4$ Kcal/mole at the boiling point from their vapor pressure equation, which corresponds to $\delta = 9.18$ at 25°C. The values of the solubility parameter reported in Table 8 are comparable with those from most of the estimation methods recommended by Reid and Sherwood (1965), but are higher than those given by Cukor and Prausnitz (1972) for diphenylmethane (9.09) and bicyclohexyl (8.16).

4.3 GENERAL VAPOR-LIQUID EQUILIBRIUM CORRELATION FOR COAL LIQUIDS

Comparison of the new experimental data with the Chao-Seader correlation and the Grayson-Streed correlation indicate large deviations. Either the correlations should be modified to yield acceptable accuracy of about 10% or new correlations should be developed. The data obtained in this work are being used for both purposes in an effort to obtain the best correlation.

Grayson-Streed differs from Chao-Seader only in the expression for fugacity coefficient of pure liquids, while the expressions for activity coefficients in in liquid solutions and fugacity coefficients in vapor mixtures 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 correlation.

A fair indication of the likely success in pursuing the Chao-Seader scheme of correlation is obtained in the regular orderly behavior of the hydrogen K-values with respect to the solubility parameter of the solvent. This is shown in Figures 32 (a) through (d). Increasing solubility parameter of the solvent steadily increases the hydrogen K-value at the same temperature and pressure. Also remarkable is the similarity with which the K-values of hydrogen in different solvents respond to changing pressure at the same temperature. These features

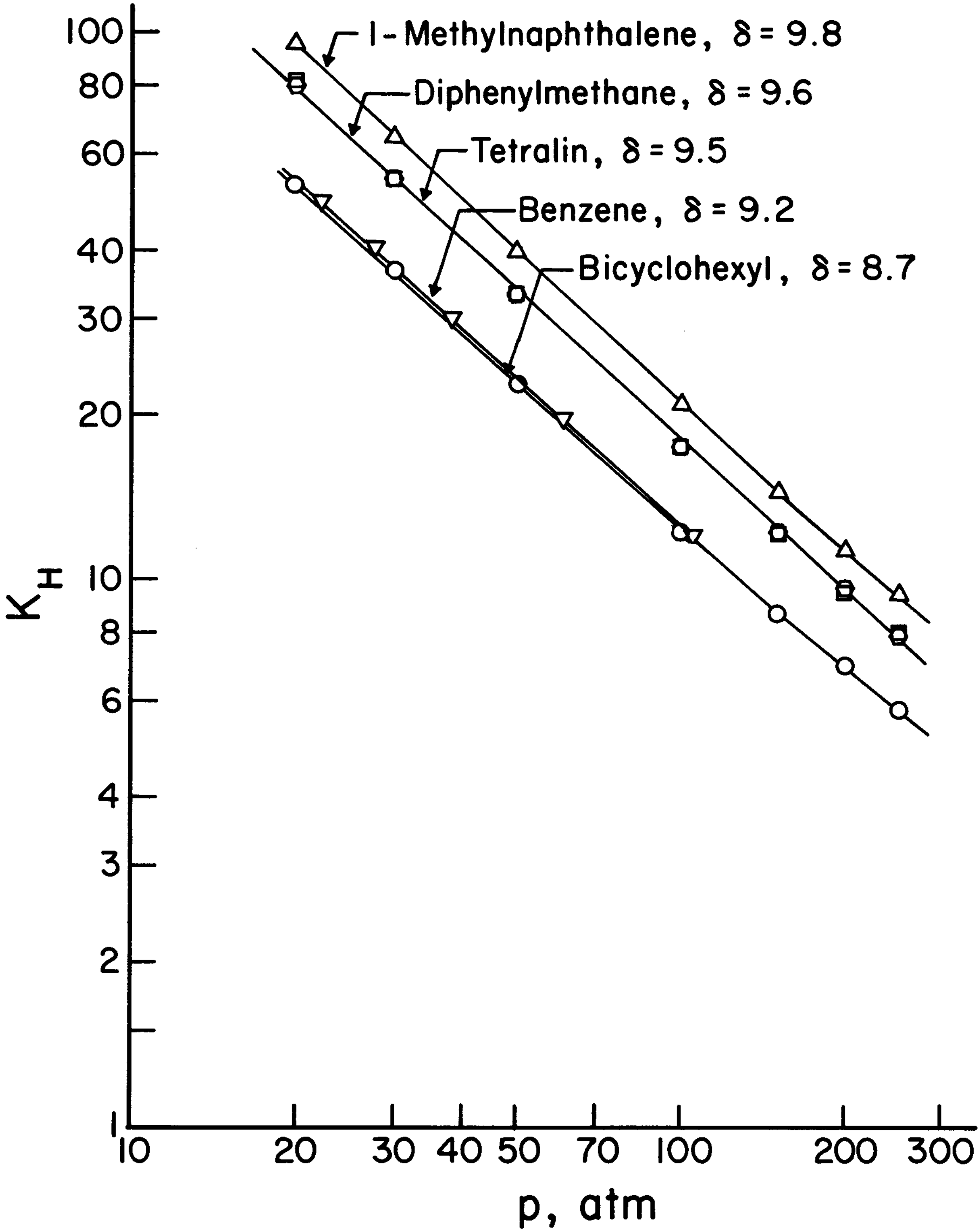


Figure 32 (a). K_H in Various Solvents Showing Dependence on Solubility Parameter of Solvent at 189°C.

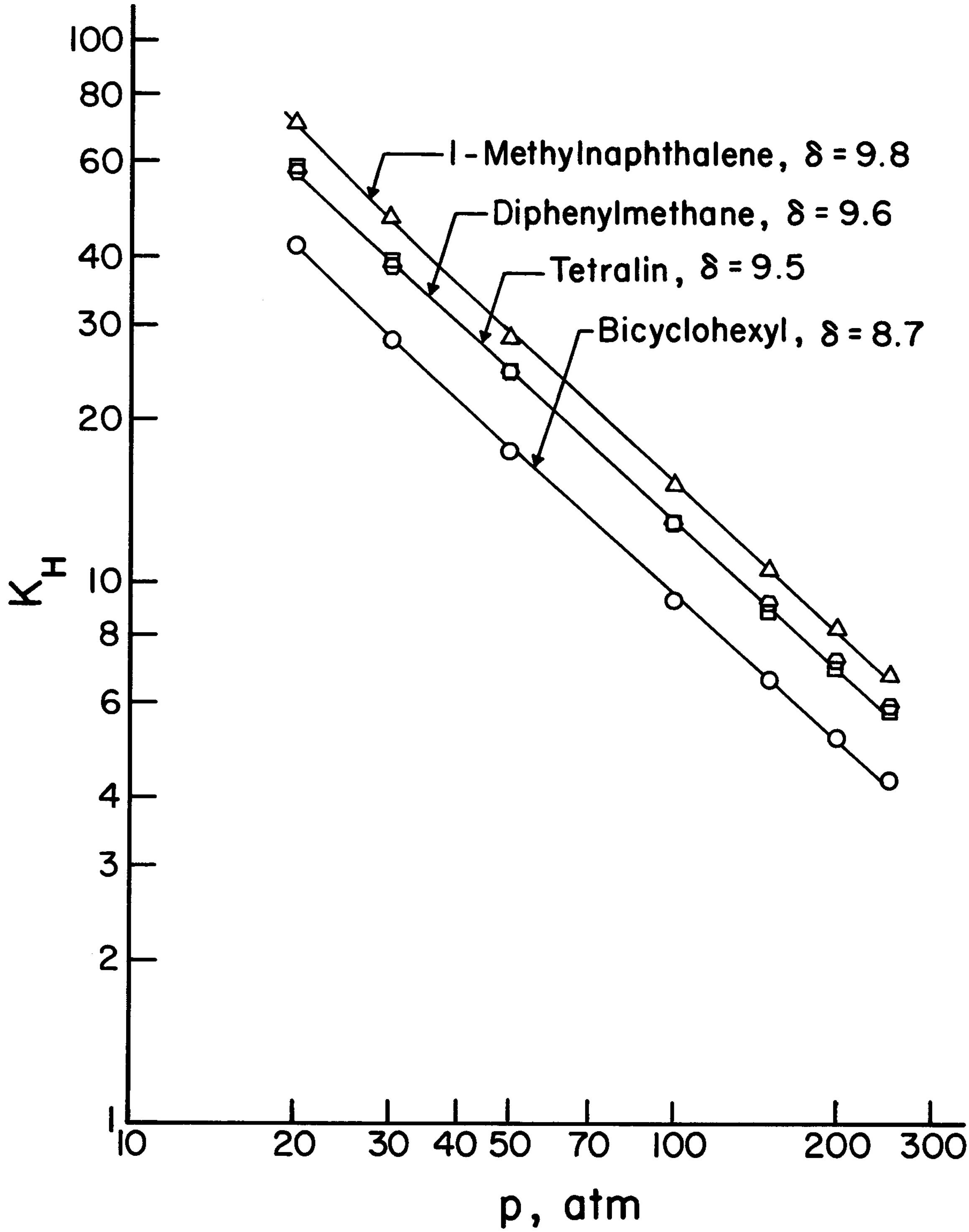


Figure 32 (b). K_H in Various Solvents Showing Dependence on Solubility Parameter of Solvent at 269°C.

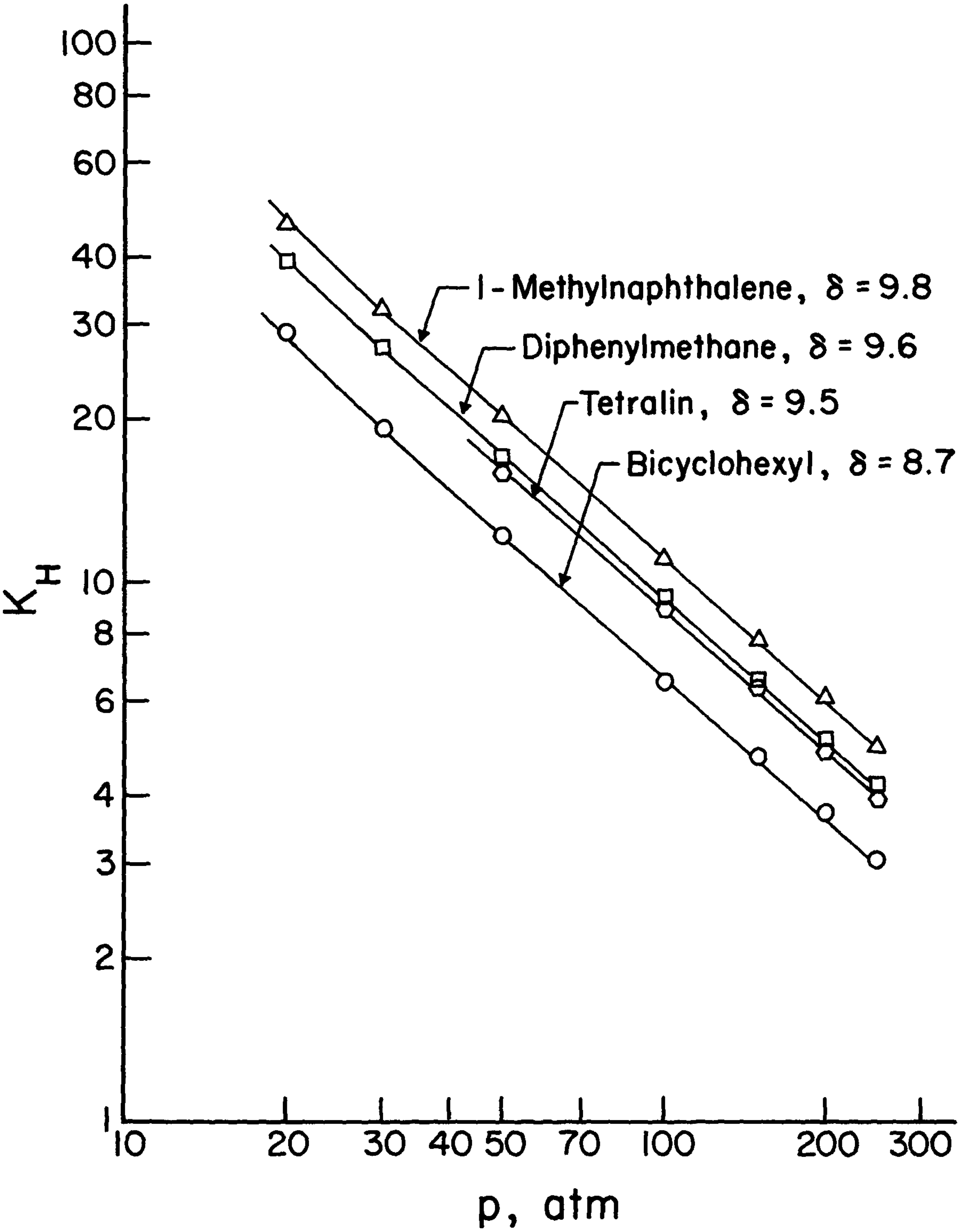


Figure 32 (c). K_H in Various Solvents Showing Dependence on Solubility Parameter of Solvent at 349°C.

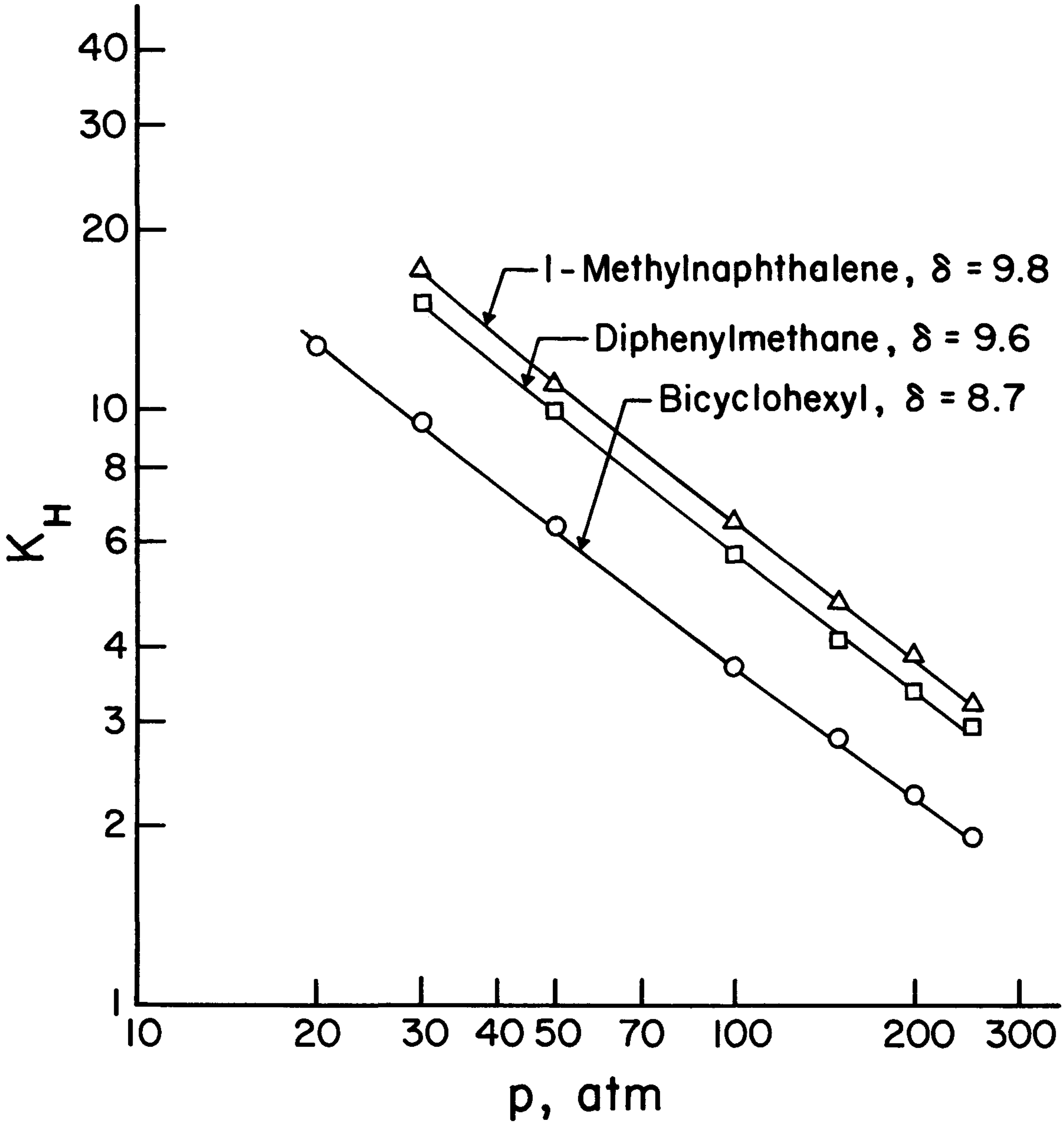


Figure 32 (d). K_H in Various Solvents Showing Dependence on Solubility Parameter of Solvent at 429°C.

are in agreement with the premises on which the Chao-Seader correlation is developed. It appears that the correlation can be modified to reflect the observed behavior.

The use of Henry's law as the basis for the representation for high pressure gas solubility has received considerable attention in recent years. The approach differs from the Chao-Seader scheme in that the pure liquid fugacity is not used for the dissolved gas. Instead a combination of Henry constant and a Poynting correction factor takes its place.

$$H \exp \int_{p_s}^{p} \frac{\overline{V}}{RT}\, dp \Rightarrow \nu$$

The partial molal volume of the dissolved gas $\overline{V}$ is required to be known from the saturation pressure of the solvent p_s to the system pressure p at the compositions of interest. The activity coefficient in the unsymmetric convention γ^* is then applied to correct for non-ideal solution behavior, and a combination of factors replaces the product $\gamma\nu$ in the Chao-Seader scheme as follows:

$$H\gamma^* \exp \int_{p_s}^{p} \frac{\overline{V}}{RT}\, dp \Rightarrow \gamma\nu$$

The treatment of the gas phase fugacities remains unchanged and is to be calculated by means of an equation of state.

The Henry's law approach is described in the monograph by Prausnitz and Chueh, "Computer Calculations for High Pressure Vapor-Liquid Equilibria" (1968) and in various articles by these authors. In order to obtain a generalized correlation by this approach the following tasks must be accomplished:

(1) Henry's constant H of hydrogen is to be described as a function of temperature and solvent. It is likely that the nature of the solvent can be expressed by the solubility parameter δ. If so, the function to be developed will be $H(T,\delta)$.

(2) The activity coefficient γ^* in the unsymmetric convention needs to be formulated and generalized. Brelvi and O'Connell (1972, 1975) developed a corresponding states method for the parameter in the one-term Margules relation for activity coefficients of H_2 in solvents. Test of their method with the recently-published experimental data by Klink et al. (1975) on H_2/butane system shows that the agreement is excellent between the predicted and experimental results. However, extension of their method to high concentration of dissolved hydrogen is necessary to include the conditions of practical interest.

(3) The partial volume $\bar{V}$ of hydrogen must be known. There is no experimental data on this quantity at the high temperatures of interest. The data at low temperatures have been correlated by Brelvi and O'Connell (1972, 1975) who presented a general equation at infinite dilution of hydrogen. The correlation needs to be extended to finite concentration of hydrogen and to higher pressures.

The first part of the needed work to develop a correlation for Henry's constant of hydrogen appears to closest to reality. The other two parts are closely related. If $\bar{V}$ is known, γ^* can be determined from experimental data such as ours and hopefully generalized. Without reliable values of $\bar{V}$, no reliable values of γ^* can be obtained. It would appear that $\bar{V}$ is the key to new developments by the Henry's law approach.

Section 5.0

SUMMARY AND CONCLUSIONS

A vapor-liquid equilibrium apparatus of the flow type has been built and checked out to give reliable equilibrium data. The apparatus is good for temperatures up to 430°C and pressures up to 300 atm. Slightly higher temperatures and pressures may be possible. Equilibrium data have been obtained with this apparatus for four hydrogen-containing binary mixture systems: H_2/tetralin, H_2/diphenylmethane, H_2/1-methylnaphthalene, and H_2/bicyclohexyl.

The experimental data have been used to test the Chao-Seader and the Grayson-Streed correlations. Both are found to give large systematic deviations at the conditions of temperature and pressures of interest. The nature of the deviations suggests that the basic scheme of the Chao-Seader correlation can be used to correlate the new data for substantially improved accuracy.

The Henry's law approach to the correlation of the data has been examined. The partial volume of hydrogen holds the key to this approach. If this quantity can be reliably estimated, a new correlation of hydrogen solubility can probably be developed on the basis of the Henry's law approach.

Appendix

INTEGRATION OF GIBBS-DUHEM EQUATION BY ORTHOGONAL COLLOCATION

For a binary mixture system in vapor-liquid equilibrium at constant temperature, the Gibbs-Duhem equation is expressed by

$$\ell n\ \gamma_1 = g + x_2\left(\frac{dg}{dx_1}\right)_s - \frac{x_2}{RT}\tilde{V}^E\left(\frac{dp}{dx_1}\right)_s \tag{1}$$

$$\ell n\ \gamma_2 = g - x_1\left(\frac{dg}{dx_1}\right)_s + \frac{x_1}{RT}\tilde{V}^E\left(\frac{dp}{dx_1}\right)_s \tag{2}$$

where

γ = activity coefficient

$g = \tilde{G}^E/RT$

$\tilde{G}^E$ = excess Gibbs energy per mole

R = universal gas constant per mole

T = absolute temperature

$\tilde{V}^E$ = excess volume per mole

$= \tilde{V} - x_1\bar{V}_1^{\infty} - x_2\tilde{V}_2$

Subscript 1 denotes the light solute; 2 the heavy solvent; and s saturation conditions. Superscript ∞ represents infinite dilution.

The mole fractions in the vapor phase add up to 1

$$\frac{x_1\gamma_1 f_1{}^{\circ}}{\phi_1} + \frac{x_2\gamma_2 f_2{}^{\circ}}{\phi_2} = p \tag{3}$$

where ϕ stands for the fugacity coefficient in the vapor mixture, and f° the standard state fugacities given by

$$f_1{}^{\circ} = H_1 \exp \int_{p_{2s}}^{p} \frac{\bar{V}_1^{\infty}}{RT}\, dp \tag{4}$$

$$f_2{}^\circ = P_{2s}\phi_{2s} \exp \int_{P_{2s}}^{P} \frac{\tilde{V}_2}{RT}\, dp \tag{5}$$

where

H_1 = Henry constant of the light solute

$= \lim_{x_1 \to 0} (f_1/x_1)$

P_{2s} = vapor pressure of the heavy solvent

In the orthogonal collocation method the derivative $(dg/dx_1)_s$ in Equations (1) and (2) is expressed as a linear combination of point values of g at orthogonal collocation points.

$$\left.\left(\frac{dg}{dx_1}\right)_s\right|_{x_k} = \sum_{j=0}^{N+1} A_{kj}\, g(x_j) \tag{6}$$

where A_{kj} are elements of the discretization matrix determined from Legendre polynomials and N is the number of internal collocation points. Since the two end points are also used in the calculations (N+2) points are actually used.

The collocation abscissas x are in reduced form (liquid mole fraction divided by the maximum liquid mole fraction). The roots of the Legendre polynomial and the two end points, 0 and 1 (corresponding to the maximum liquid mole fraction) are used in the calculations. The Legendre polynomials are given by

$$P_n(u) = \frac{1}{2^n n!} \frac{d^n}{du^n} (u^2 - 1)^n \tag{7}$$

and the recursion formula

$$P_{n+1}(u) = \frac{2n+1}{n+1}\, u\, P_n(u) - \frac{n}{n+1} P_{n-1}(u) \tag{8}$$

In this work we use

$$P_{1+\frac{n}{2}}(x) = P_n(u^2) \qquad n = 0,2,4,.... \tag{9}$$

in order to insure all the roots of nth order Legendre polynomial be in range of 0 and 1.

The first three Legendre polynomials are:

$$P_1 = 1 \tag{10}$$

$$P_2 = 1.5x - 0.5 \tag{11}$$

$$P_3 = 4.375x^2 - 3.75x + 0.375 \tag{12}$$

All the Legendre polynomials up to the eleventh are in our computer program.

The elements of discretization matrix $A_{k\ell}$ can be determined from the Legendre polynomial by the method of Michelsen and Villadsen (1972) as follows:

From Lagrange's form of interpolation polynomial,

$$G(x) = \sum_{\ell=0}^{N+1} L_\ell(x) G(x_\ell) \tag{13}$$

where

$$L_\ell(x) = \prod_{\substack{k=0 \\ k\neq\ell}}^{N+1} \frac{(x-x_k)}{(x_\ell-x_k)} \tag{14}$$

$$\frac{dG(x)}{dx} = \sum_{\ell=0}^{N+1} G(x_\ell) \frac{dL_\ell(x)}{dx} \tag{15}$$

$$\left.\frac{dG}{dx}\right|_{x_k} = \sum_{\ell=0}^{N+1} G(x_\ell) \left.\frac{dL_\ell(x)}{dx}\right|_{x_k} \tag{16}$$

$$\text{discretization matrix } A_{k\ell} = \left.\frac{dL_\ell(x)}{dx}\right|_{x_k} \tag{17}$$

can thus be calculated.

$\frac{dG}{dx}$ values can be expressed as a linear combination of G at selected points by introducing $A_{k\ell}$. The points selected should be the zeros of a Jacobi polynomial in order to make the approximating error minimum. Here we choose the zeros of Legendre polynomial and two end points as our orthogonal collocation points.

Combine Equations (1), (2), (3) and (6) and express the result for a collocation point $x_{1,k}$.

$$\frac{x_{1,k} f^{\circ}_{1,k}}{\phi_{1,k}} \exp \left\{ g(x_{1,k}) + x_{2,k} \left[\sum_{\ell=0}^{N+1} A_{k\ell}\, g(x_{1,\ell}) \right] - \frac{x_{2,k}}{RT} V_k^E \left[\frac{dp}{dx_1}(x_{1,k}) \right]_s \right\}$$

$$+ \frac{x_{2,k} f^{\circ}_{2,k}}{\phi_{2,k}} \exp \left\{ g(x_{1,k}) - x_{1,k} \left[\sum_{\ell=0}^{N+1} A_{k\ell}\, g(x_{1,\ell}) \right] + \frac{x_{1,k}}{RT} V_k^E \left[\frac{dp}{dx_1} (x_{1,k}) \right]_s \right\} = P(x_{1,k}) \tag{18}$$

We smooth our isothermal pressure and mole fraction data by using spline fitting technique

$$p = \left[1 - \left(\frac{x_1}{x_{max}} \right) \right]_{2s} + \sum_{i=1}^{N} C_i P_i \left(\frac{x_1}{x_{max}} \right) \tag{19}$$

where

P_i is Legendre polynomial

$N \leq 4$ depending on data

$\frac{dp}{dx_1}$ can thus be calculated from smoothed data.

Equation (18) is a nonlinear equation of N+2 unknowns, $g(x_{1k})$, k=0, N+1. For N+2 collocation points, we have N+2 equations. The system of differential equations is thus reduced to a set of N+2 nonlinear simultaneous equations. These equations are now solved for g at each collocation point using the Newton-Raphson iteration procedure with the initial estimates of g given by

$$g(x_{1,k}) = 0 \text{ for all } k \tag{20}$$

Steps in the solution procedure are as follows:

1. T, p, and x_i are known as experimental data and V^E, f_i°, ϕ_i, and P_{2s} are estimated by calculation. Also $\frac{dp}{dx}$ is found from smoothed data.
2. ϕ_i depends on the vapor phase composition, since ϕ_i enters into Equation (18). They must be estimated initially by choosing ϕ_i=1, i=1,2, for every collocation point.

3. Solve the nonlinear simultaneous equations made up of Equation (18) and get g values at every collocation point.
4. Substitute back to Equations (1), and (2), and (6) to obtain activity coefficients γ_{1k} and γ_{2k} (k=0,...N+1).
5. Calculate y_i for each chosen value of x_{ik} as follows:

$$y_i = \frac{\gamma_i x_i f_i^\circ}{\phi_i p} \tag{21}$$

6. Calculate new values of ϕ_i using y_i from step 5 and repeat steps (3) to (5) until successive values of y_i agree to within 10^{-4}.
7. Calculate y_i of each data point by interpolation among y_i of the orthogonal collocation points from step 6.

The program flowchart is shown in Figure 33. The major subroutines used in the program are described in Table 9.

The procedures for the estimation of the required thermodynamic quantities are described in the following:

1. Calculation of V^E — the liquid phase molar volumes and mixture volumes are calculated following the methods presented by Prausnitz and Chueh (1968). The partial molar volumes at infinite dilution are determined by using the correlation of Brelvi and O'Connell (1972, 1975). The critical properties and acentric factor ω, required for the estimation are shown in Table 8.
2. Calculation of ϕ_i — Fugacity coefficients can be calculated by using equation of state. The modified Redlich-Kwong equation of state of Prausnitz and Chueh proved to be reasonably accurate by comparison with:

   (1) P-V-T data of pure hydrogen gas: From Hydrogen Technological Survey (McCarty, 1975), P-V-T data of hydrogen gas over a wide range of temperature and pressure are available. Comparison shows that the average percentage difference is about 1% and the maximum is less than 2.7%. Since the P-V-T data are read from a log-scale plot, these percentage differences are insignificant.

   (2) Fugacity coefficient of H_2 in H_2/butane system: Klink, Cheh and Amick (1975) studied the hydrogen/butane system and determined the fugacity of hydrogen in the vapor phase. By definition of fugacity coefficient, $\phi_H = f_H/py_H$, these ϕ_H values are accordingly obtained from

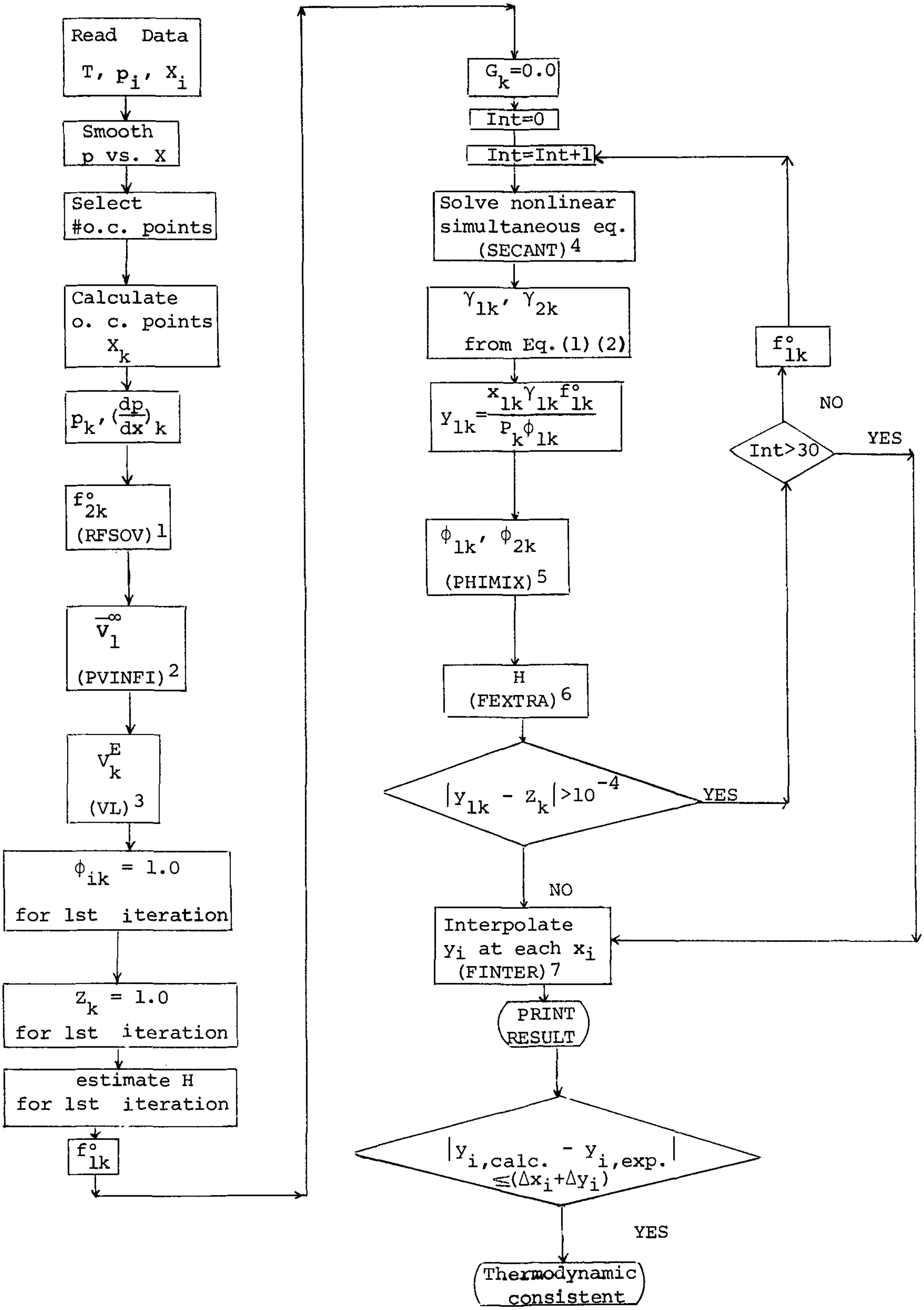


Figure 33. Computer Program Flowchart for Thermodynamic Consistency Test.

Table 9

MAJOR SUBROUTINES FOR ORTHOGONAL COLLOCATION CALCULATIONS

1.	RFSOV	Subroutine for calculating reference fugacity of solvent (component 2) at each orthogonal collocation point.
2.	PVINFI	Calculate partial molar volume of solute (component 1) at infinite dilution.
3.	VL	Calculate molar volume of pure component and mixture.
4.	SECANT	Solve n unknowns from n nonlinear simultaneous equations.
5.	PHIMIX	Calculate fugacity coefficient by using modified Redlich-Kwong equation.
6.	FEXTRA	Extrapolate $\frac{f}{x}$ to zero to get Henry's Constant.
7.	FINTER	Calculate y_i at each data point by using Lagrangian interpolation.

their experimental data and compared with that from the modified R-K equation. Agreement appears to be generally within 1%, and with maximum difference of about 4.2%.

In the modified R-K equation two constants Ω_a and Ω_b need to be known first and their values for some hydrocarbons are listed by Prausnitz and Chueh, but no value can be found for the systems of interest here. Fortunately, these constants can be correlated with acentric factor ω and both increase with increasing ω. The correlations of Ω_a and Ω_b obtained from regression of available values are as follows:

$$\Omega_a = 0.42649+0.084153\omega-0.32663\omega^2+2.2515\omega^3-2.95488\omega^4 \quad (22)$$

$$\Omega_b = 0.086495+0.013397\omega-0.0038014\omega^2+0.23116\omega^3-0.35853\omega^4 \quad (23)$$

Interpolations are made according to these equations to obtain the required constants.

Mikolaj and Dev (1971) had made these correlations early in 1971, but only graph form can be found and that is not convenient for use in computer calculation. Their results are almost the same as this work.

The binary constant k_{ij} representing deviation of T_{cij} from the geometric mean of T_{ci} and T_{cj} is also needed. Data of H_2/hydrocarbon systems are available (Prausnitz and Chueh, 1968) only from methane to hexane, and a correlation has to be developed and extended to the heavier hydrocarbon. For hydrogen containing binary mixtures we find k_{ij} to increase with increasing critical temperature of the heavy component according to

$$k_{ij} = -5.54802\text{x}10^{-3}+1.66279\text{x}10^{-4}T_c+8.22538\text{x}10^{-8}T_c^{\ 2} \quad (24)$$

3. Calculation of f_i° Henry's law is followed by all gases in sufficiently dilute solutions,

$$\lim_{X_H\to 0} f_H = X_H H \quad (25)$$

The Henry's constant H is accordingly given by

$$H = \lim_{X_H\to 0} \phi_H k_H P \quad (26)$$

Thus, the Henry's constant can be found by extrapolating the product $\phi_H k_H P$ to zero mole fraction of dissolved hydrogen from available experimental data.

NOTATION

f	fugacity
H	Henry constant
K	vaporization equilibrium ratio = $\frac{y}{x}$
p	pressure
T	absolute temperature
V	volume
x	mole fraction, liquid phase
y	mole fraction, vapor phase

Greek letters

γ	activity coefficient in liquid mixture
δ	solubility parameter
ν	fugacity coefficient of pure liquid component
ϕ	fugacity coefficient in vapor mixture
ω	acentric factor

Subscripts

B	bicyclohexyl
b	boiling point
c	critical constant
D	diphenylmethane
H	hydrogen
i	component i
M	1-methylnaphthalene
r	reference state
T	tetralin

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