Vapor-Liquid Equilibria in Hydrogen-Benzene and Hydrogen-Cyclohexane Mixtures

RICHARD E. THOMPSON and WAYNE C. EDMISTER

Oklahoma State University, Stillwater, Oklahoma

A new vapor-liquid equilibrium experimental facility has been built for and operated on light gas-hydrocarbon systems. The range of operating conditions are 3 to 1,000 atm. and 25° to 400°C. A dynamic flow type of equilibrium cell is used. This and most of the other apparatus are from designs by Michels. Solubilities of hydrogen in benzene and in cyclohexane were obtained at 150° and 250°F. and at pressures up to 10,000 lb./sq.in.abs.

Compositions of the equilibrium vapor phases were determined so the vapor-liquid *K* ratios could be derived. Thermodynamic consistency tests were applied to the data with the conclusion that the new data are consistent with volumetric properties, predicted by other methods.

The phase behavior of hydrogen-heavy hydrocarbon mixtures is of both theoretical and practical interest, theoretical because of the need for better thermodynamic relationships for coexisting gas-liquid phases and practical because of the need for vapor-liquid equilibrium phase distribution ratios for use in design calculations.

Hydrogen-benzene and hydrogen-cyclohexane systems were selected for this investigation along with a dynamic flow experimental method. In this method the hydrogen is bubbled slowly through the hydrocarbon until the liquid phase is saturated with hydrogen and the gas phase is saturated with the hydrocarbon. Effluent gas and liquid samples are analyzed.

Several variations of this experimental method have been described (*17, 19, 20, 21, 23*). The apparatus and operating procedure used in this work are essentially the same as those of Michels et al. (*19, 20, 21*), except for the sampling and analytical techniques. This and other experimental techniques are described in the technical literature (*2, 12, 26, 30*).

The sources and ranges of available literature data for the binary mixtures hydrogen-benzene and hydrogen-cyclohexane are given in Table 1. Not included in this list are the low-pressure data of Seidell and Linke (*18*) for hydrogen solubility in these solvents. Except for Silver's (*29*) work, the references in Table 1 are for binary systems. Silver (*29*) obtained experimental data for ternary and quaternary mixtures of hydrogen with *n*-hexane, cyclohexane, and benzene at 100° and 200°F. and at 1,000 and 2,000 lb./sq. in. abs. The range of the available data and the limitations of the experimental apparatus were considered in selecting the temperatures used in the present work.

TABLE 1. SOURCES AND RANGES OF VAPOR-LIQUID EQUILIBRIUM DATA FOR HYDROGEN-CYCLOHEXANE AND HYDROGEN-BENZENE

Hydrocarbon	Pressure range, lb./sq. in. abs.	Temperatures, °F.	Type of data	Reference
Cyclohexane	670 to 4,500	77, 302, 464	*P-T-x*	*13*
	1,000 to 2,500	77	*P-T-x*	*8*
	15 to 2,000	95.4	*P-T-x*	*28*
	750 to 10,000	68, 104, 140	*P-V-T-x-y**	*17*
Benzene	380 to 4,600	77, 104, 212	*P-T-x*	*15*
	750 to 4,500	77, 212, 302, 392, 464	*P-T-x*	*13*
	15 to 2,200	95.4, 162.7	*P-T-x*	*28*
	3,500 to 42,000	77, 122, 158, 212, 302	*P-T-x-y*	*14*
	725 to 7,150	77	*P-V-T-x**	*16*
	280 to 2,500	320 to 500 (18-deg. intervals)	*P-V-Y-x-y*†	*6*

* Liquid densities measured.
† Liquid and vapor densities measured.

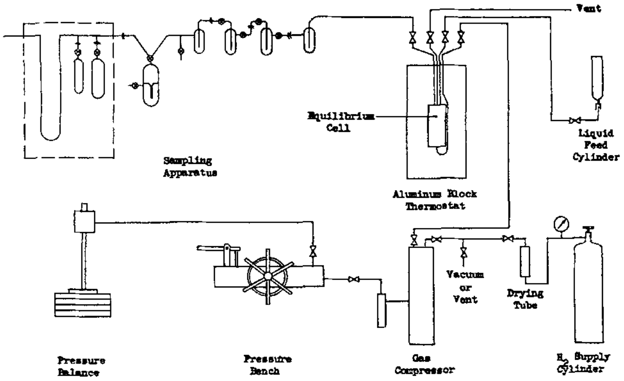

Fig. 1. Schematic flow diagram of apparatus for the isothermal pressure effect on enthalpy.

EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus is shown in Figure 1. The equilibrium cell and constant-temperature bath are shown in Figure 2.

Gas is fed via valve *A* into the bottom of the cell and passes through small grooves in a cone, breaking up into small streams. Further contact of gas and liquid is provided by a section packed with Fiberglas cloth. Liquid feed enters through valve *B*. Vapor and liquid samples are removed through valves *C* and *D*, respectively. All capillary lines are 0.6-mm. I.D.

The cell capacity is about 150 cc. The maximum allowable operating pressure is 1,000 atm. The steel used in the cell and its components is mostly of the composition 16.0% chromium, 0.35% carbon, and 1.0% molybdenum.

The constant-temperature bath is a cylindrical aluminum block, heated by nichrome heating wires in grooves around the outside of the block. Two ½-in. diameter wells are provided for temperature measurement and control sensing elements.

Temperature was measured by use of a chromel-constantan thermocouple. The thermocouple was calibrated in place by comparison with a platinum resistance thermometer. Temperature control was effected by means of an electronic controller. The controller sensing element was a resistance thermometer.

Pressure regulation and measurement were accomplished by use of a Michels pressure balance (*4*) in conjunction with a

---

Richard E. Thompson is at the University of Tulsa, Tulsa, Oklahoma.

gas compressor. A pressure bench was used to obtain and maintain pressure in the system, by addition or removal of hydraulic oil or by adjusting the system volume. The balance is claimed to be accurate to approximately 1 part in 10,000 and to have a precision of 1 part in 100,000.

The gas compressor is a two-compartment vessel with an interconnecting tube. Oil from the pressure bench flows into the lower compartment on top of mercury. The mercury, in turn, flows through the interconnecting tube to the upper compartment, where the gas is confined. The level of the mercury in the upper compartment is measured by a bridge-circuit indicator.

The balance, bench, compressor, equilibrium cell, and aluminum block thermostat are described by Thompson (*30*).

Hydrogen was fed from a supply cylinder, through a drying tube, to the gas compressor. The drying tube was packed with silica gel. Hydrocarbons were fed from a liquid cylinder, through a capillary tube, to the equilibrium cell.

The method of analysis of equilibrium phases consisted of passing the samples through cold traps, freezing out the hydrocarbon, and then measuring the volume and pressure of the hydrogen at a known temperature. Residual hydrogen in the traps was transferred to the volumetric part of the sampling apparatus by means of a Toepler pump. The sample traps were then closed, removed, and weighed to determine the amount of hydrocarbon present.

The sampling apparatus was glass, except for a short, steel capillary tube, which was used to connect the apparatus to the appropriate sampling valve. The volumetric portion was housed in an air bath in order to maintain constant temperature. Volumetric bulbs of 25 cc. to 4 liter capacity were attached to side arms. The sizes of the bulbs used depended on the phase being sampled and the cell temperature and pressure. Pressure was determined by measuring the heights of mercury in a U-tube manometer with a cathetometer. A vacuum was maintained on the leg of the U-tube manometer opposite the sample.

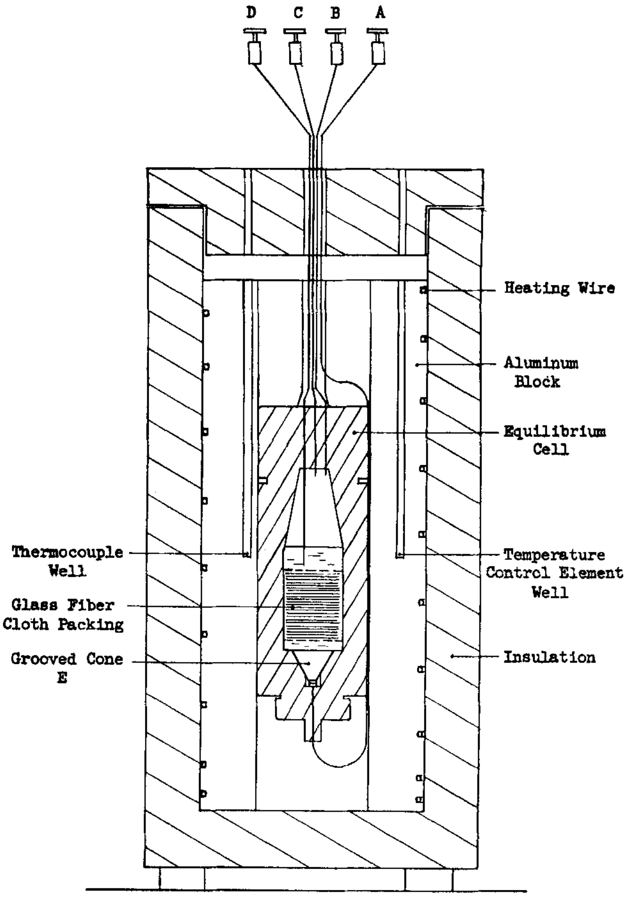

Fig. 2. Calorimeter for isothermal pressure effect on enthalpy.

MATERIALS

The hydrocarbons used in this study were benzene, 99.93 mole % minimum and cyclohexane, 99.94. The purity of these materials was checked by gas chromatography, which showed no significant impurities. The hydrocarbons were dried over calcium chloride before introducing them to the cell.

The hydrogen used was electrolytic grade for the first runs and extra-dry grade for the remainder of the runs. The stated purity of the hydrogen was 99.8 mole %. Mass spectrographic analysis of the electrolytic grade indicated 99.74 mole % hydrogen.

EXPERIMENTAL PROCEDURE

The first step in a series of runs was the evacuation of the gas compressor. Hydrogen was added to flush the system, and the evacuation was repeated. Hydrogen was then introduced to the compressor to a pressure of about 100 lb./sq.in.

The equilibrium cell was evacuated next. A few cubic centimeters of the hydrocarbon to be used were added to flush the cell, and the evacuation was repeated. Following this, approximately 90 cc. of hydrocarbon were added to the cell. The hydrocarbon in the cell was degassed by further evacuation, a few cubic centimeters of hydrocarbon being distilled off. Hydrogen was then bled into the cell.

For a run, the cell was heated to operating temperature, and hydrogen was introduced to obtain the desired pressure. At low operating pressures (up to 3,000 lb./sq.in.abs.) hydrogen was bled into the cell slowly, oil being added to maintain pressure. After 2 to 10 min. the addition of hydrogen was virtually complete. Equilibration was obtained by keeping the cell at pressure for a few hours.

At high operating pressures it became necessary to use more than one filling of the gas compressor to obtain operating pressure in the cell. This was because of the comparatively low pressure (1,500 to 1,700 lb./sq.in. gauge) of the hydrogen in the supply cylinder. Equilibration was obtained, again, by maintaining the cell at pressure for several hours. Minute leaks prevented isolation of the cell during the equilibration period at high operating pressures (above 3,000 lb./sq.in.abs.).

Preparations for sampling were made during the equilibration period. Tare weights were determined for the sample traps. Appropriate volumetric bulbs were attached to the sampling apparatus. The sample line was purged, and the sampling apparatus was evacuated and tested for leaks. Dry ice-acetone baths were applied to the sample traps.

Liquid samples were collected by opening the sampling valve for a very short time. Gas samples were collected by opening the sample valve slightly and allowing the gas mixture to pass through the sample traps. Sampling time varied from 15 min. to 3 hr., depending on the cell pressure and allowable sampling rate.

During gas sample withdrawal the pressure tended to fall continuously. Pressure was maintained by pumping oil into the system at the pressure bench. At the same time, small weights were added to the pressure balance to compensate for the increasing mercury head in the gas compressor.

EXPERIMENTAL RESULTS

Data were taken at eight pressures from 100 to 10,000 lb./sq.in.abs. at temperatures of 150° and 250°F. for the two binary mixtures. A few preliminary runs were made at 280° and 320°F. These were made to perfect the sampling method, check the effect of sampling rate on gas composition, and to compare directly with available data for benzene hydrogen. The x-y data and calculated K values are listed in Tables 2 and 3.

The precision, or variability, of the composition data was studied by the method of propagation of errors and by comparing a few repetitions in measurements. These considerations led to the conclusion that the composition data were repeatable to within about ± 3% of the average value. Measurement and control of temperature and pressure should have introduced negligible error compared with that in the composition data.

Sources of error which might have affected the accuracy of the data were discovered in the course of the work. Heating of the sampling capillary for gas samples was found to be very important, particularly at 150°F. Insufficient heating in some of the early runs forced discarding of several vapor-composition data points.

Runs made at different equilibration times indicated that equilibration time may have been insufficient in the benzene runs. This possible source of error would affect mainly the benzene liquid-phase compositions at 150°F. Equilibration times of 1½ to 5 hr. were used for the benzene data and at least 8 hr. for the cyclohexane data.

The use of stopcock grease in the connections for the sample traps may have introduced error due to absorption of hydrocarbon vapor from the sample. This was more important for vapor samples because of the smaller amount of hydrocarbon collected. Separate tests indicated that error due to this cause might have been as high as 5% in extreme cases, although it was probably smaller.

Sampling rates of up to 150 cc./hr. (at 1 atm.) did not affect vapor compositions appreciably. The lower practical sampling rate was always used and did not exceed 100 cc./hr. at 1 atm. in any case.

In an effort to judge the accuracy of the data, thermodynamic consistency tests were performed and data comparisons were made. The results are discussed below.

CONSISTENCY TESTS

Thermodynamic vapor-liquid equilibria consistency tests, correctly applied, are comparisons of two types of experimental data. In the constant temperature case, volumetric data are compared with equilibrium composition data. In most cases complete volumetric data of the type needed are not determined. It becomes important, then, to study what comparisons can be made in the absence of complete data.

Consistency tests in the form proposed by Adler et al. (*1*) appeared to offer the best possibility for checking because they used experimental quantities and not derived quantities. The use of approximations is, therefore, introduced at a level where the effect of the approximation can best be recognized. Furthermore, the tests can be applied where one component is above its critical temperature.

The equations of Adler et al. (*1*) for the constant temperature case involve the assumption of the Lewis and Randall rule. A rigorous derivation can be made to obtain an expression similar to theirs, which is as follows:

$$\int x_1 (1 + y_1\xi_1)\, d \ln K_1 + \int x_2 (1 + y_1\xi_1)\, d \ln K_2 = \int \left[z^L + y_1 \bar{z}_1^v \left(\frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{z^v}{K_2} \right] d \ln P \qquad (1)$$

where

$$\xi_1 = \frac{1}{RT} \int_0^P \left(\frac{\partial \bar{V}_1^v}{\partial y_1^1} \right)_{P,T} dP$$

$$\bar{z}_1^v = \frac{P\bar{V}_1^v}{RT}$$

Equation (1) is for a binary mixture at constant temperature.

The right-hand side of Equation (1) can be split into two terms, one for the liquid and one for the vapor. The latter, plus further rearrangement, gives the following form:

$$\int x_1 (1 + y_1\xi_1)\, d \ln K_1 + \int x_2 (1 + y_1\xi_1)\, d \ln K_2 = \int (z^L - 1)\, d \ln P + \int z'\, d \ln P \qquad (2)$$

where

$$z' = 1 + \frac{1}{K_2} (\bar{z}_1^v - z^v) - \bar{z}_1^v$$

Table 2. Equilibrium Data for Hydrogen-Benzene System

Temp., °F.	Pressure, lb./sq. in. abs.	Mole fraction hydrogen in liquid	Mole fraction benzene in vapor	$K = y/x$ ratios Benzene	Hydrogen
150	76.2	0.00166	0.125	0.126	529
	194.3	—	0.0500	0.0502	214
	503.1	0.0117	0.0203	0.0205	83.4
	503.0	—	0.0198	0.0200	83.6
	1,026	0.0238	0.0111	0.0114	41.6
	1,026	—	0.0113	0.0116	41.5
	1,707	0.0389	0.00850	0.00884	25.5
	1,707	—	0.00843	0.00877	25.5
	2,508	0.0536	0.00679	0.00718	18.6
	4,000	0.0812	0.00575	0.00626	12.2
	6,998	0.131	0.00497	0.00573	7.57
	9,997	0.176	0.00506	0.00614	5.64
	9,997	0.180	0.00443	0.00540	5.54
250	97.1	0.00186	0.486	0.487	275
	201.0	0.00536	0.247	0.249	140
	499.4	0.0153	0.104	0.106	58.4
	1,003	0.0321	0.0557	0.059	29.4
	1,003	—	0.0571	0.0576	29.4
	1,702	0.0541	0.0379	0.0401	17.8
	1,702	—	0.0383	0.0405	17.8
	2,999	0.0937	0.0268	0.0295	10.4
	2,999	—	0.0264	0.0292	10.4
	5,995	0.167	0.0208	0.0250	5.86
	9,983	0.243	0.0180	0.0238	4.04
320	427.1	0.0144	0.292	0.296	492
	601.8	0.0214	0.206	0.298	371
	778.0	0.0291	0.167	0.172	286
	1,309	0.0506	0.110	0.116	176

Table 3. Equilibrium Data for Hydrogen-Cyclohexane System

Temp., °F.	Pressure, lb./sq. in. abs.	Mole fraction hydrogen in liquid	Mole fraction cyclohexane in vapor	$K = y/x$ ratios Cyclohexane	Hydrogen
150	99.8	0.00362	0.0973	0.0977	249
	199.9	0.00710	0.0477	0.0480	134
	501.9	0.0182	0.0227	0.0231	53.8
	501.6	—	0.0207	0.0211	53.9
	995.9	0.0345	0.0120	0.0124	28.6
	1,694	0.0563	0.00868	0.00920	17.6
	3,002	0.102	0.00680	0.00753	10.2
	5,996	0.178	0.00610	0.00742	5.59
	10,013	0.262	0.00642	0.00869	3.80
	10,013	—	0.00685	0.00928	3.80
250	101.3	0.00317	0.451	0.452	173
	199.9	0.00802	0.237	0.239	95.2
	500.0	0.0225	0.101	0.104	40.0
	999.9	0.0456	0.0565	0.0592	20.7
	1,700	0.0774	0.0377	0.0409	12.4
	3,000	0.131	0.0269	0.0310	7.41
	5,996	0.236	0.0213	0.0279	4.15
	9,999	0.350	0.0188	0.0289	2.80

Table 4. Evaluation of Terms in Equation (2)

		Left side			Right side		
Solvent	°F.	Term 1	Term 2	Total	Term 1	Term 2	Total
Benzene	150	−0.04	−4.60	−4.64	−4.93	+0.27	−4.66
	250	−0.05	−2.86	−2.91	−3.39	+0.47	−2.92
Cyclohexane	150	−0.05	−4.49	−4.55	−4.85	+0.27	−4.58
	250	−0.07	−2.79	−2.86	−3.36	+0.47	−2.89

If the vapor phase is ideal, z' reduces to zero, as does the ξ_1 term. If the Lewis and Randall rule holds for the vapor phase, ξ_1 is zero, and Equation (2) reduces to the form derived by Adler et al.

Each term in Equation (2) was evaluated for the mixtures studied here. The limits of integration used were the vapor pressure of the pure solvent (component 2) and 2,000 lb./sq. in. abs., that is from $x_1 = 0$ to $x_1 = (x_1)_{P=2,000}$. The results are shown in Table 4.

Values of the mole fractions, pressure, and K values for use in Equation (2) came from the experimental data, of course. Volumetric data were needed, then, to complete the calculations.

Evaluation of the liquid compressibility term was based on interpolation or extrapolation of existing volumetric data for the mixtures studied here (*5, 16, 17*). To check the importance of the accuracy of this computation, the liquid volume term for benzene-hydrogen was evaluated with the pure component molar volume of benzene at its vapor pressure over the entire pressure range. The value of the liquid volume integral thus obtained was 4.92, as compared with 4.93 obtained with mixture volumes. A reasonably good estimate of liquid mixture volumes seems to be sufficient.

The Berlin form of the virial equation of state, truncated after the second virial coefficient, was used to evaluate the ξ_1 term. The Leyden form of the virial equation was used to evaluate z^v and $\bar{z}_1^v$. The virial coefficients used are discussed in a later section. The applicability of the virial equation to mixtures like those considered here is discussed elsewhere (*24*).

Several comments may be made concerning the above consistency test. In the first place, the term involving x_1 and K_1 is small and relatively unimportant. The value of K_2 depends mainly on y_2, since x_2 is close to 1.0 and insensitive to error in x_1. Thus, rather large errors in the liquid concentration of hydrogen will not affect the results of the test appreciably.

The terms of y_2 and K_2 are more important. To test the effect of error in y_2, the consistency test was repeated for benzene-hydrogen at 250°F., with values of y_2 that were 10% less than the experimental values. The left side of Equation (2) totalled −3.03 and the right side −2.96. The agreement is not as good as in Table 4, but the effect of error in y_2 is not marked. Equation (2) does not seem to be very sensitive to errors in the x-y data. Furthermore, the equation of state used in evaluating the vapor compressibilities is likely to have appreciable effect on the results of the test.

Prausnitz and Keeler (*24*) suggested a consistency test in which the interaction second virial coefficient (B_{12}) is evaluated for a series of isothermal P-x-y points. Relative constancy of the values of B_{12} calculated indicates self-consistency of the data, since B_{12} is a function of temperature only. The methods consists specifically in the simultaneous solution of the following equations for B_{12}:

$$\bar{f}_2^{\,v} = \gamma_2^L x_2 f_2^{\,v} \exp\left[\frac{1}{RT} \int_{p_2}^{P} V_2^L \, dP \right] \tag{3}$$

$$\ln \bar{f}_2^{\,v} = \ln\left(\frac{y_2 RT}{\underline{V}}\right) + \frac{2}{\underline{V}}\left(y_1 B_{12} + y_2 B_{22}\right) + \frac{3}{2\underline{V}^2}\left(y_1^2 C_{112} + 2 y_1 y_2 C_{122} + y_2^2 C_{222}\right) \tag{4}$$

$$\underline{V} = \frac{RT}{P}\left(1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2}\right) \tag{5}$$

$$B = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \tag{6}$$

$$C = y_1^3 C_{111} + 3 y_1^2 y_2 C_{112} + 3 y_1 y_2^2 + y_2^3 C_{222} \tag{7}$$

TABLE 5. SECOND VIRIAL INTERACTION COEFFICIENTS CALCULATED FROM HYDROGEN SOLUBILITY DATA

Solvent	Temperature, °F.	B_{12}, cc./g. mole
Benzene	150	9 ± 12
Benzene	250	12 ± 2
Cyclohexane	150	−1 ± 8
Cyclohexane	250	17 ± 2

Pure component second virial coefficients for the hydrocarbons were taken from David et al. (*7*) and second and third virial coefficients for hydrogen from Bird et al. (*3*). Third virial coefficients were estimated from the generalized correlation of Prausnitz (*22*) and the following empirical combination rule (*6*):

$$C_{ijk} = \left(C_{iii} C_{jjj} C_{kkk}\right)^{1/3} \tag{8}$$

The effect of including third virial coefficient terms is small. Vapor pressures were taken from API 44 (*27*) and liquid molar volumes from Glanville and Sage (*10*) and Reamer and Sage (*25*). Equation (4) was used in pure component form to evaluate $f_2^{\,v}$ at p_2. Liquid activity coefficients were calculated by the Scatchard-Hildebrand equation (*11*) but could have been taken as 1.0 with very little error.

Values of B_{12} calculated from the present data in the range 500 to 3,000 lb./sq. in. abs. are given in Table 5. Reasonable constancy of B_{12} is seen, particularly at 250°F. Variation in the B_{12} values at 150°F. seems rather large, but it should be stressed that rather small errors in y_2 produce large variations in B_{12}, particularly at low pressures.

Notice that this consistency test does not really test the liquid-phase concentration data. In fact, reasonable estimates of x_2 are all that is required (*23*). Presumably, good values of the pure component second virial coefficient are needed (and are not always available). The effect of varying the pure second virial coefficients was not studied.

Gautreaux and Coates (*9*) have proposed an infinite dilution consistency test that can be applied to gas-liquid data. Their test differs from the above tests in that it does test the liquid-phase solubility data. The equation used is

$$(K_1)_{x_1=0} = 1 - \left(\frac{\partial P}{\partial x_1}\right)_T \left(\frac{V_2^{\,v} - V_2^L}{RT}\right) \tag{9}$$

The vapor and liquid volume terms are for the pure solvent at its vapor pressure. The slope term is evaluated from the isothermal $P - x_1$ data. Isothermal $P - K_1$ data are extrapolated to the vapor pressure of the solvent and compared with the values calculated by Equation (9). Table 6 shows the comparison for the present data. The

TABLE 6. INFINITE DILUTION CONSISTENCY TEST OF HYDROGEN K DATA

		Hydrogen K ratios at infinite dilution		
Solvent	Temp., °F.	Extrapolating y/x	Equation (9)	% diff.*
Benzene	150	4,200	4,430	−5.2
	250	500	607	−1.2
Cyclohexane	150	2,400	2,870	−16.4
	250	395	423	−6.6

* Based on calculated K_1 from Equation (9).

TABLE 7. COMPARISON OF HYDROGEN-BENZENE DATA AT 320°F.

	Hydrogen $K = y/x$ values			Benzene $K = y/x$ values		
Pressure, lb./sq. in. abs.	This work	Connolly (6)	% difference from Connolly	This work	Connolly (6)	% difference from Connolly
427.1	49.3	50.3	−2.0	0.296	0.288	+2.8
601.8	37.1	36.4	+1.9	0.210	0.213	−1.4
778.0	28.6	28.4	+0.7	0.172	0.172	0
1,309.0	17.6	17.3	+1.7	0.116	0.116	0

agreement in the extrapolated and calculated K values is not bad, when one considers the arbitrariness of the extrapolation procedure. The infinite dilution test uses only pure component volumetric data, which may be known fairly accurately. On the other hand, the comparison depends on an extrapolation and presumably tests only in range of low pressures (near infinite dilution).

The results of the consistency tests indicate that the experimental data are fairly consistent. The second test, in which interaction virial coefficients are calculated, would appear to be more informative.

DATA COMPARISONS

Initial hydrogen-benzene data taken at 320°F. were compared with the work of Connolly (*6*). Connolly's data were interpolated on large plots at the pressures used for the initial data. The comparison is shown in Table 7. The results appear to agree within the precision of the present data. Connolly's data were obtained by the bubble and dew point method.

Indirect comparisons were made by cross plotting equilibrium data against temperature at constant pressure. As might be expected, there was some scatter exhibited between the various data from the sources listed in Table 1 and the present data. Detailed comparisons are given by Thompson (*30*). Only general remarks concerning these comparisons are made here. For hydrogen-benzene the agreement is generally good except for the vapor-phase concentrations at 5,000 to 10,000 lb./sq. in. abs., where the Ipatiev et al. data (*14*) are somewhat higher. The same is true for hydrogen-cyclohexane, with generally good agreement, except at 5,000 to 10,000 lb./sq. in. abs. with the vapor-phase data of Krichevskii and Sorina (*17*).

ACKNOWLEDGMENT

Financial assistance of Esso Research and Engineering Company and the Standard Oil Foundation, Incorporated, helped make this research possible. Phillips Petroleum Company donated the hydrocarbons used in the experimental work. The high pressure apparatus was purchased with institutional funds from Oklahoma State University.

NOTATION

B, C = second and third virial coefficients
f = fugacity
K = vapor-liquid equilibrium ratio, y/x
P = pressure
p = vapor pressure
R = gas law constant
T = absolute temperature
V = molar volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction
z = compressibility factor, PV/RT
z' = quantity defined under Equation (2)
γ = activity coefficient, $\bar{f}/f^{o}x$
ξ = defined under Equation (1)

Superscripts

L = quantity associated with liquid phase
V = quantity associated with vapor phase
— = property of component of a mixture
o = property of pure component

Subscripts

1 = quantity associated with component 1 (lighter component)
2 = quantity associated with component 2 (heavier component)

LITERATURE CITED

1. Adler, S. B., L. Friend, R. L. Pigford, and G. M. Rossellini, *A.I.Ch.E. Journal*, **6**, 104 (1960).
2. Barr-David, F. H., Ph.D. thesis, Yale University, New Haven, Connecticut (1956).
3. Bird, R. B., E. L. Spotz, and J. O. Hirschfelder, *J. Chem. Phys.*, **18**, 1395 (1950).
4. Comings, E. W., "High Pressure Technology," McGraw-Hill, New York (1958).
5. Connolly, J. F., "Notes for Applied Thermodynamics Conference," Oklahoma State University, Stillwater, Oklahoma (1961).
6. ———, *J. Chem. Phys.*, **36**, 2897 (1962).
7. David, H. G., S. D. Hamann, and R. B. Thomas, *Australian J. Chem.*, **12**, 309 (1959).
8. Frolich, P. K., E. J. Tauch, J. J. Hogan, and A. A. Peer, *Ind. Eng. Chem.*, **23**, 548 (1931).
9. Gautreaux, M. F., and J. Coates, *A.I.Ch.E. Journal*, **1**, 496 (1955).
10. Glanville, J. W., and B. H. Sage, *Ind. Eng. Chem.*, **41**, 1272 (1949).
11. Hildebrand, J. H., and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).
12. Hipkin, H., "Notes for Conference on Vapor-Liquid Phase Equilibria," Oklahoma State University, Stillwater, Oklahoma (1959).
13. Ipatiev, V. V., and M. I. Levina, *Zhur. Fiz. Khim.*, **6**, 632 (1935).
14. ———, V. P. Teodorovitch, A. P. Brestkin, and V. S. Artemovich, *Chem. Abstr.*, **42**, 8619 (1948).
15. ————————, and I. M. Levine, *Oil Gas. J.*, **32**, No. 20, p. 14 (1933).
16. Krichevskii, I. R., and G. D. Efremov, *Zhur. Fiz. Khim.*, **22**, 1116 (1948).
17. ———, and G. A. Sorina, *ibid.*, **32**, 2080 (1958).
18. Linke, W. F., "Solubilities of Inorganic and Metal Organic Compounds," 4 ed., Vol. 1, Van Nostrand, New York (1958).
19. Michels, A., G. F. Skelton, and E. Dumoulin, *Physica*, **16**, 831 (1950).
20. ———, E. Dumoulin, and J. J. Th Van Dijk, *ibid.*, **25**, 840 (1959).
21. *Ibid.*, **27**, 886-892 (1963).
22. Prausnitz, J. M., *A.I.Ch.E. Journal*, **5**, 3 (1959).
23. ———, and P. R. Benson, *ibid.*, 301.
24. ———, and R. N. Keeler, *ibid.*, **7**, 399 (1961).
25. Reamer, H. H., and B. H. Sage, *J. Chem. Eng. Data*, **2**, 9 (1958).
26. Robinson, C. S., and E. R. Gilliland, "Elements of Fractional Distillation," 4 ed., McGraw-Hill, New York (1950).
27. Rossini, F. D., et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Institute of Technology, Pittsburgh, Pennsylvania (1953).
28. Sattler, H., *Chem. Abstr.*, **36**, 18 (1942).
29. Silver, H. F., Ph.D. thesis, University of Michigan, Ann Arbor, Michigan (1961).
30. Thompson, R. E., Ph.D. thesis, Oklahoma State Univ., Stillwater, Oklahoma (1963).

Manuscript received January 20, 1964; revision received September 22, 1964; paper accepted September 23, 1964. Presented at A.I.Ch.E. Houston meeting.