Solubility of Liquids in Compressed Hydrogen, Nitrogen, and Carbon Dioxide

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The vapor-phase solubilities of carbon tetrachloride, *iso*-octane, toluene, and *n*-decane were measured in compressed hydrogen, nitrogen, and carbon dioxide at 50° and 75°C. and at various pressures between 20 and 90 atm. The virial equation of state was used to describe the volumetric properties of the vapor mixtures, and the second virial cross coefficients were evaluated from the solubility data. The results indicate that the vapor phase departs from ideality very quickly for these systems as the pressure increases, particularly at pressures greater than 10 atm.

The solubility of a liquid in a gas at low pressure is given by the vapor pressure of the liquid. The mole fraction of the heavier component in the gaseous phase is computed by Raoult's Law:

$$y_1 = \frac{(1 - x_2)P_1^0}{P} \qquad (1)$$

At low pressures x_2 is negligible compared with unity, and the solubility is then just the ratio of the vapor pressure to the total pressure. As the total pressure rises, Equation (1) fails, not because of nonidealities in the liquid but because of nonideal mixing in the gaseous phase, which causes the fugacity of the heavier component to be significantly different from its partial pressure. At very high pressures, approaching the critical pressure of the gas-liquid mixture, the nonideality of the liquid phase also becomes important in determining the vapor-phase solubility of the heavier component. In the intermediate pressure range, however, it is the vapor-phase nonideality which determines that solubility. This work reports new data on the solubility of liquids in compressed gases and uses them to compute virial coefficients for the vapor-phase mixtures.

THERMODYNAMIC RELATIONSHIPS

A binary system at temperature T and total pressure P consisting of a heavy (liquid) component 1 and a light (gaseous) component 2 will be considered. At equilibrium the distribution of the heavier component between the two phases L and G is governed by the Gibbs relation

$$\bar{f}_1^L = \bar{f}_1^G \qquad (2)$$

where the bar indicates that component 1 is in solution. The fugacities are related to the mole fractions by

$$\bar{f}_1^L = \gamma_1^L(1 - x_2)P_1^0\phi_1^0 \cdot \exp\left[\frac{v_1^{0L}(P - P_1^0)}{RT}\right] \qquad (3)$$

$$\bar{f}_1^G = \phi_1 y_1 P \qquad (4)$$

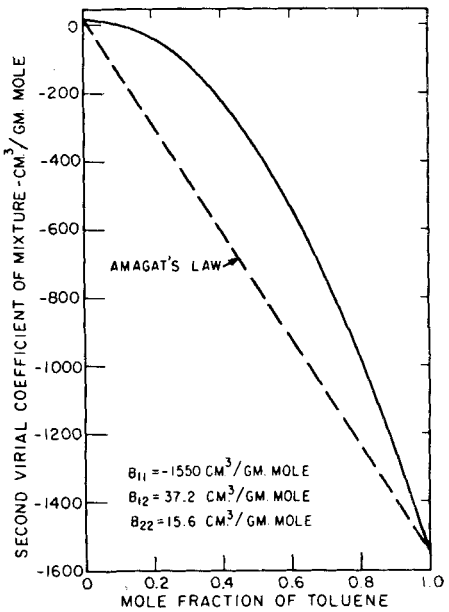

Fig. 1. Second virial coefficient of hydrogen-toluene mixtures at 75°C.

When Equations (3) and (4) are substituted into Equation (2), the vapor-phase solubility is

$$y_1 = \frac{\gamma^{L_1}(1 - x_2)P_1^0\phi_1^0}{\phi_1 P} \cdot \exp\left[\frac{v_1^{0L}(P - P_1^0)}{RT}\right] \qquad (5)$$

Solubilities of gases in nonpolar liquids have been correlated by Jolley and Hildebrand (*5*), and with the help of Henry's Law (and by use of fugacities rather than partial pressures) it is possible to make good estimates of x_2 provided that the total pressure is not extremely large. At such pressures x_2 will be small compared with unity, and thus y_1 is not sensitive to x_2. Also, when x_2 is small, the liquid phase is ideal with respect to the solvent, and $\gamma_1^L = 1$.* The problem of computing the vapor-phase solubility therefore reduces to the calculation of the fugacity coefficient, which can be computed from an equation of state for the gaseous mixture. A particularly convenient equation of state for this purpose is the virial equation; details of this computation are presented elsewhere (*8*). If the virial equation is terminated after the second virial coefficient, the fugacity coefficient in a binary mixture is given by

$$\ln \phi_1 = \frac{2}{v}[y_1B_{11} + y_2B_{12}] - \ln z \qquad (6)$$

Numerical values for B_{11} can be obtained with high accuracy from the recent work of Pitzer and Curl (*7*), and values of B_{12} can be estimated for a variety of systems by methods described previously (*8, 9*). If Amagat's Law is assumed, B_{12} is the arithmetic average of B_{11} and B_{22}, and the fugacity coefficient can be evaluated by the Lewis fugacity rule. This assumption however is a good approximation only at very low pressures (*9, 10, 11*). If components 1 and 2 are both small molecules of low molecular weight, a simple extension of the two-parameter theory of corresponding states may be used to evaluate B_{12} (*3*). Generally however the three-parameter law of corresponding states (*6*) must be used with suitable semiempirical corrections (*9*). To illustrate how remote the value of B_{12} can be from the arithmetic average of B_{11} and B_{22}, one should consider mixtures of toluene and hydrogen. The second virial coefficient of the mixture is given by

$$B_m = y_1^2B_{11} + 2y_1y_2B_{12} + y_2^2B_2 \qquad (7)$$

Figure 1 shows a plot of B_m vs. composition for this system at 75°C.; the second virial coefficients are based on experimental results reported in this work. In this case B_{12} does not even fall between the values of B_{11} and B_{22} but is larger than either one of them. Hence any type of averaging law seeking to compute B_{12} from B_{11} and B_{22} cannot be successful for this system.

At moderate pressures and temperatures $y_1 \ll y_2$. Equation (6) therefore indicates that the fugacity coefficient ϕ_1 is very sensitive to the virial coefficient B_{12}. Measurements of the solubility of liquids in compressed gases, therefore, are particularly useful for obtaining information on the interaction between dissimilar molecules (*2, 10*). This work presents data for the solubilities of carbon tetrachloride, *iso*-octane (2, 2, 4 trimethyl pentane) toluene, and decane in com-

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*If x_2 exceeds about 0.20, a small correction for liquid-phase nonideality may be required. This can be estimated by Hildebrand's equation after an appropriate (empirically determined) solubility parameter for the gaseous component (*4*) has been assigned.

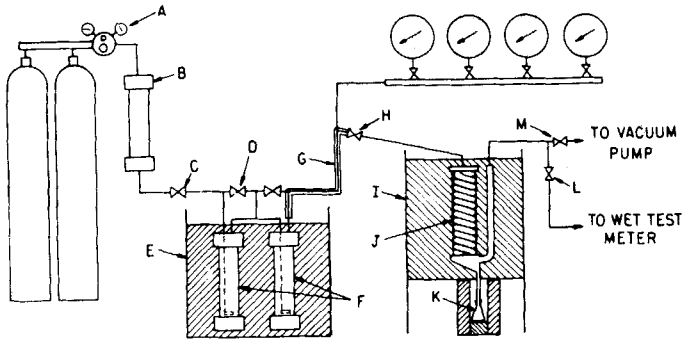

Fig. 2. Schematic diagram of equipment.

pressed nitrogen, hydrogen, and carbon dioxide at 50° and 75°C.

EXPERIMENTAL

The solubility of liquids in a compressed gas was measured in a flow system shown schematically in Figure 2.

The gas was fed from two cylinders into a manifold constructed from copper pipe (11/16-in. O.D., 7/16-in. I.D.). The cylinders of gas were used to maintain a steady supply of high-pressure gas.

From the manifold the gas passed through a Victor GD-62B pressure regulator (A), designed for controlled pressures between 0 and 3,600 lb./sq. in. gauge. Before entering the equilibrium cells (F) the gas was dried with silica gel in the drying tube (B), which was constructed from a 9-in. length of 2½-in. double, extra-strong steel pipe, capped at each end, and sealed with O rings.

Two equilibrium cells connected in series were used to assure saturation of the gas, even though experimental evidence indicated that one cell was sufficient. The cells were made with 2½-in. double, extra-strong stainless-steel pipe, type 347, capped and sealed in the same manner as the drying tube with O rings. A detail drawing of an equilibrium cell is given in Figure 3. The liquid was contained within the cells in Pyrex liners, and the gas was very finely dispersed from a fritted-glass sparger (pore size 14μ) at the bottom of the cells. To prevent entrainment of liquid from the equilibrium cells two layers of 6-mm. glass beads were placed on a Teflon support at the top of the liquid in each cell. The beads caused the finely dispersed gas to form into large bubbles before they broke the surface of the liquid. Any spray from the large bubbles which might have escaped from the cell was trapped by glass-wool plugs at the exits of the cells. The equilibrium cells were immersed in a constant-temperature bath (E), which was controlled to within ±0.05°C.

After leaving the second cell the vapor mixture was led to a Hoke stainless-steel-needle expansion valve (H). This section of tubing and the tubing between the cells was heated with a spiral winding of Nichrome wire and insulated to prevent any condensation of the liquid.

Pressure within the second equilibrium cell was determined from one of the Bourdon tube pressure gauges, connected to a manifold which was constructed from the same pipe as the gas-cylinder manifold. Full-scale pressures of the four gauges were respectively 160, 600, 1,500, and 2,000 lb./sq. in. gauge. The gauge employed at a given pressure was the one which indicated the pressure between one-third and two-thirds full-scale reading. All gauges were calibrated with an Ashcroft dead-weight gauge tester; pressure measurement accuracy was within ±0.6%.

After expansion the vapor mixture entered the condenser (J) in the refrigerated ethylene glycol–water bath (I), operated at −25° ± 0.1°C. for all liquids except carbon tetrachloride, where −22°C. was used to prevent freezing. In the condenser, the vapor was distributed to six spirals of ¼-in. copper tubing, each approximately 3 ft. long. Condensate from the tubes dripped onto the sloping bottom of the condenser and ran into a ⅜-in. copper tube at the lowest point; this tube was joined to a piece of glass tubing which terminated in a standard taper ground-glass joint. A well-insulated 25-ml. flask was connected to this joint to collect the condensate. The gas leaving the condenser passed through a plug of glass wool at the entrance of a vertical section of 1-in. copper tubing. It was assumed that the vapor leaving the condenser was in equilibrium with the condensate. This assumption was checked several times by the adsorption of the remaining trace of condensable vapor from the condenser on activated carbon and the determination of weight increase. The correction calculated in this manner was always the same as the one calculated from the liquid-vapor pressure at the temperature of the condenser, thereby verifying the equilibrium assumption.

From the condenser the flow of gas was measured with a wet-test meter and then vented to the atmosphere. A vacuum pump was connected through a valve at the outlet

Table 1. Equilibria in Binary Systems Containing Hydrogen

Component 1	Temperature, °C.	Total pressure, atm.	y_1
CCl_4	75	39.9	0.0268
	75	54.2	0.0203
	75	69.7	0.0165
i-C_8H_{18}	50	32.9	0.00677
	50	45.2	0.00506
	50	62.0	0.00401
	75	35.3	0.0155
	75	51.6	0.0108
	75	65.8	0.00869
$C_6H_5CH_3$	50	40.4	0.00343
	50	55.5	0.00262
	50	62.9	0.00240
	75	42.8	0.00814
	75	52.8	0.00696
	75	55.4	0.00665
	75	69.2	0.00544
n-$C_{10}H_{22}$	50	30.4	0.000297
	50	41.8	0.000217
	50	50.2	0.000186
	75	32.7	0.000987
	75	45.2	0.000730
	75	55.6	0.000599

Table 2. Equilibria in Binary Systems Containing Nitrogen

Component 1	Temperature, °C.	Total pressure, atm.	y_1
CCl_4	50	28.4	0.0189
	50	42.8	0.0139
	50	63.9	0.0111
	75	30.6	0.0410
	75	53.9	0.0276
	75	71.7	0.0231
i-C_8H_{18}	50	23.5	0.0109
	50	26.4	0.0101
	50	50.7	0.00686
	50	74.3	0.00608
	50	83.4	0.00611
	75	28.5	0.0230
	75	41.2	0.0178
	75	55.2	0.0150
$C_6H_5CH_3$	50	22.9	0.00692
	50	34.8	0.00524
	50	47.3	0.00442
	50	60.2	0.00403
	75	21.2	0.0194
	75	37.1	0.0130
	75	51.9	0.0106
n-$C_{10}H_{22}$	50	28.4	0.000495
	50	53.9	0.000410
	50	71.9	0.000409
	50	87.7	0.000419
	75	27.1	0.00172
	75	34.4	0.00145
	75	41.7	0.00139

Table 3. Equilibria in Systems Containing Carbon dioxide

Component 1	Temperature, °C.	Total pressure, atm.	y_1
CCl_4	50	20.2	0.0238
	50	24.8	0.0200
	50	27.2	0.0187
	75	20.2	0.0540
	75	23.6	0.0476
	75	27.2	0.0415
i-C_8H_{18}	50	20.5	0.0130
	50	23.6	0.0119
	50	27.2	0.0109
	75	20.2	0.0311
	75	23.7	0.0272
	75	27.5	0.0245
$C_6H_5CH_3$	50	20.5	0.00822
	50	23.9	0.00760
	50	27.0	0.00705
	75	20.7	0.0209
	75	24.3	0.0186
	75	27.3	0.0170
n-$C_{10}H_{22}$	50	20.2	0.000761
	50	24.1	0.000714
	50	29.2	0.000703
	75	21.6	0.00225
	75	24.1	0.00216
	75	27.3	0.00204

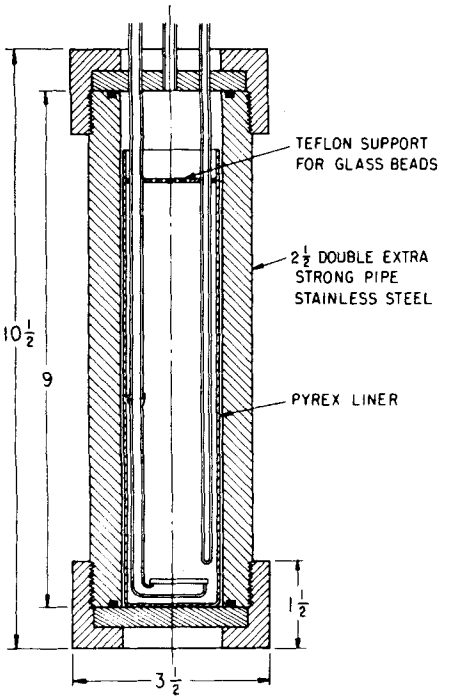

Fig. 3. Equilibrium cell.

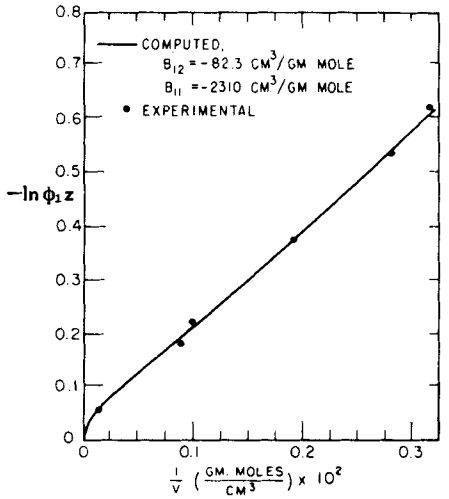

Fig. 4. Phase equilibria for nitrogen–*iso*-octane at 50°C.

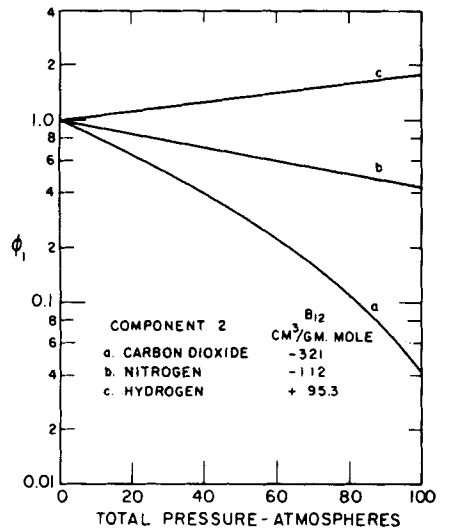

Fig. 5. Fugacity coefficient of decane in hydrogen, nitrogen, and carbon dioxide at 75°C.

of the condenser to permit evacuation of the complete system before all runs.

TEMPERATURE CONTROL AND MEASUREMENT

The constant-temperature bath for the equilibrium cells was controlled to ±0.05°C. The condenser temperature was maintained constant to within ±0.1°C. by the control of the refrigeration evaporator pressure and by an auxiliary 150-w. heater. Temperatures in the second equilibrium cell and in the condenser were measured with copper-constantan thermocouples which were checked against a National Bureau of Standards calibrated thermometer. Temperature measurement was ±0.05°C.

MATERIALS

The purities of the liquids were: carbon tetrachloride, reagent grade; toluene, reagent grade; iso-octane (2, 2, 4 trimethylpentane); and *n*-decane, practical grade.

Each of the liquids was distilled in an eleven-tray glass column at a reflux ratio of approximately 5 to 1. The column was surrounded by a heated jacket, and a dry nitrogen atmosphere was maintained over the system. The nitrogen was dried by bubbling it through concentrated sulfuric acid and then passing it through a long tube of potassium hydroxide flakes. Drierite was placed in the reboiler to remove any traces of water and to act as boiling chips. The first and last 10% of the liquid charged to the still was discarded, and only the 80% heart cut was used for the experimental determinations.

The gases were passed through a bed of activated charcoal to remove any traces of hydrocarbons and then passed through a bed of silica gel to remove any moisture. The activated charcoal and silica gel were renewed each time the equilibrium cells were opened to change liquids.

EXPERIMENTAL PROCEDURE

Details of the experimental procedure are given elsewhere (*1*). Special care was taken to assure attainment of steady state conditions (3 to 12 hr. depending on the percentage condensible in the gas phase) Initially the gas flow rate was varied to determine the rate at which complete saturation of the gas was assured; final data were taken with gas flow rates in the range 0.005 to 0.020 cu. ft./min. as measured by the wet-test meter. During a run the flow rate was held constant to within 1% or better.

To assure that equilibrium between gas and liquid had been attained, several precautions were taken. First, it was ascertained that changes in the gas flow rate did not affect the results; second, it was shown that the results were independent of the liquid height in the equilibrium cells. Finally runs were made at very low pressure, where the observed results were in excellent agreement with those calculated from ideal-gas behavior.

TREATMENT OF DATA

Solubilities of gases in liquids were taken from the literature whenever possible and otherwise estimated from correlations (*5*). In some cases the data and the estimates were not of very high accuracy, although probably within 5%. However since calculation of the liquid fugacity is insensitive to the gas solubility [Equation (3)], these inaccuracies did not seriously impair computation of ϕ_1. In no case did x_2 exceed 0.30; hence even an error of as much as 10% in x_2 would at most produce a 3% error in f_1^L. Where necessary the Hildebrand equation was used to compute γ_1^L, but in no case did γ_1^L differ from unity by more than ½%.

The composition of the vapor phase was calculated from the measured volume of gas and the measured weight of condensate collected, with the necessary correction made for liquid not condensed. Experimental values of the vapor-phase solubility were reproducible to within 1%. For a given gas-liquid pair, vapor-phase compositions were determined for each temperature at a series of pressures, and values of $\ln \phi_1 z$ were plotted as a function of $1/v$ to check the consistency of the data. A typical plot is shown in Figure 4. From Equation (6)

$$\ln \phi_1 z = \ln \frac{\gamma_1 x_1 f_1^L}{y_1 P} + \ln z = \frac{2}{v}(y_1 B_{11} + y_2 B_{12}) \quad (8)$$

The compressibility factor and the molar volume of the gaseous mixture were computed by the virial equation with a preliminary estimate for B_{12}. A value of B_{12} was then computed from Equation (8). This new value of B_{12} was then used to reevaluate z and v, and still another value of B_{12} was calculated. In this way it was possible to converge rapidly upon

Table 4. Second Virial Cross Coefficients for Twelve Binary Systems

Components	Temperature, °C.	B_{12}, (cc./g.-mole)
H_2, CCl_4	75	34.9 ± 5.5
H_2, i-C_8H_{18}	50	37.6 ± 5.9
	75	55.7 ± 6.0
H_2, $C_6H_5CH_3$	50	19.0 ± 5.9
	75	37.2 ± 6.0
H_2, n-$C_{10}H_{22}$	50	81.2 ± 6.9
	75	95.3 ± 7.0
N_2, CCl_4	50	−58.5 ± 5.9
	75	−49.6 ± 5.5
N_2, i-C_8H_{18}	50	−82.3 ± 5.7
	75	−60.3 ± 6.5
N_2, $C_6H_5CH_3$	50	−98.1 ± 6.2
	75	−88.1 ± 7.5
N_2, n-$C_{10}H_{22}$	50	−141 ± 5
	75	−112 ± 7
CO_2, CCl_4	50	−205 ± 8
	75	−163 ± 9
CO_2, i-C_8H_{18}	50	−303 ± 8
	75	−252 ± 9
CO_2, $C_6H_5CH_3$	50	−254 ± 8
	75	−215 ± 9
CO_2, n-$C_{10}H_{22}$	50	−417 ± 7
	75	−321 ± 8

a true value for B_{12}; usually two or three trials were sufficient.

For each temperature and for each system the coefficient B_{12} was calculated at several pressures ranging from 20 to 90 atm. At a constant temperature for a given system the values were almost always reproducible to within 5 cc./g.-mole, and the maximum range was 10 cc./g.-mole.

RESULTS

The solubilities of carbon tetrachloride, *iso*-octane, toluene, and *n*-decane in compressed hydrogen are given in Table 1; the solubilities in compressed nitrogen in Table 2, and those in compressed carbon dioxide in Table 3. Table 4 gives the second virial cross coefficients for the various binary gas-liquid pairs.

The data show that the vapor phase departs from ideality very quickly for these systems as the pressure increases, particularly at pressures greater than 10 atm. Even at 1 atm. pressure the departure from ideality is a few per cent in some cases. For example, for the system nitrogen and iso-octane the vapor-phase fugacity coefficient of the iso-octane at 1 atm. total pressure and 50°C. is 0.967.

For a given liquid the vapor-phase fugacity coefficient (and hence its vapor-phase solubility) is strongly dependent on the nature of the gaseous component. To illustrate, Figure 5 shows the effect of pressure on the vapor-phase fugacity coefficient of *n*-decane in hydrogen, nitrogen, and carbon dioxide at 75°C.

A comparison between the various methods of calculation of vapor-phase compositions is shown in Figure 6, which shows the vapor-phase concentration of *n*-decane in nitrogen at 50°C. as a function of pressure, calculated from the ideal-gas law, the Lewis fugacity rule, and the virial equation of state, with the second virial cross-coefficient as calculated from vapor-phase solubility data. In this particular case the Lewis fugacity rule introduces as much as a sixfold error over a wide pressure range, and the ideal-gas law introduces a two- to fourfold error in the same pressure range. It appears therefore that as a result of compensating errors the Lewis fugacity rule is actually worse in some cases than the ideal-gas law.

A comparison (Figure 7) was also made between equilibrium ratios K, as computed from the virial equation of state and as predicted from standard K-charts for the system nitrogen and *iso*-octane at 50°C. The error introduced by the use of the standard K-charts is small at low pressures but rapidly increases as the pressure exceeds 10 atm.

While vapor-phase fugacity coefficients for liquids in nitrogen and carbon dioxide were always less than unity for the systems studied, the fugacity coefficients were greater than unity for the same

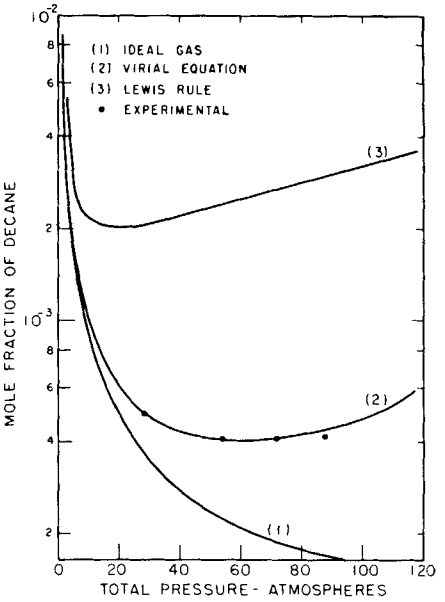

Fig. 6. Vapor-phase solubility of decane in nitrogen at 50°C.

liquids in hydrogen, or at the same temperature and total pressure a liquid is more soluble in nitrogen than in hydrogen and more soluble in carbon dioxide than in nitrogen. This result is not surprising if one remembers that like dissolves like. The difference in physical properties between hydrogen (T_c = 33°K.) and a typical liquid ($T_c \sim$ 500°K.) is certainly larger than that between the physical properties of nitrogen (T_c = 126°K.) or carbon dioxide (T_c = 304°K.) and a typical liquid. In the solubility of liquids in gases one therefore finds a qualitative order quite similar to that found in the solubility of gases in liquids. This selectivity is especially pronounced if the gaseous solvent is slightly above its critical temperature. Thus for example the solubility of naphthalene in ethylene (T_c = 9.2°C.) at 35°C. and 100 atm. is about one thousand times as large as that computed from the ideal-gas-law relation [(Equation (1)], and the solubility in nitrogen at the same temperature and pressure is about two orders of magnitude smaller than that in ethylene (*8*).

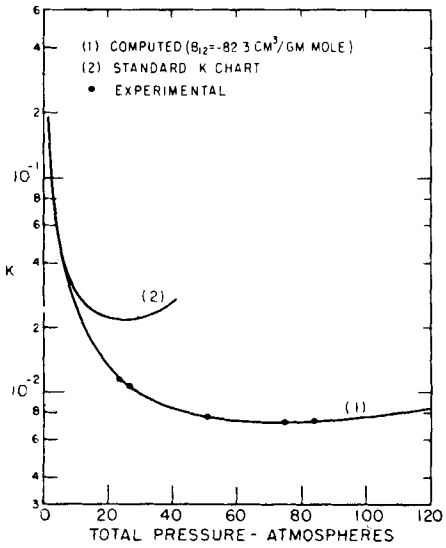

Fig. 7. Equilibrium ratios for *iso*-octane in nitrogen at 50°C.

A method of correlating these as well as previously published gas-liquid equilibrium data will be presented in a separate publication.

ACKNOWLEDGMENT

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NOTATION

B = second virial coefficient
f = fugacity
P = pressure
R = gas constant
T = absolute temperature
v = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
z = compressibility factor

Greek Letters

γ^L = activity coefficient in liquid phase
ϕ = fugacity coefficient in vapor phase

Subscripts

1, 2 = components
m = mixture

Superscripts

L = liquid phase
G = gas phase
o = pure component

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