knowledge of partial molar volumes as a function of concentration. These were calculated from density data (*7*). Density measurements were made for all systems at temperatures ranging from 25° to 60°C and covering the whole concentration range (*13*).

Results and Discussion

Tables I–VII show the experimental differential diffusion coefficients and densities for the systems benzene–chloroform (at 25°, 40°, and 55°C); cyclohexane–carbon tetrachloride (at 25°, 40°, and 55°C); benzene-*n*-heptane (at 25°, 40°, and 55°C); benzene-cyclohexane (at 25°, 40°, and 60°C); benzene-toluene (at 25° and 40°C); and diethyl ether-chloroform (at 25°C). These results are shown graphically in Figures 3–9 as differential diffusivities vs. mole fraction.

The accuracy of the experimental results obtained with the modified diaphragm cell is of the order of 1 to 2% and depends largely on the error involved in reproducing the calibration curves for the capacitance or conductivity measuring cell. The diffusion coefficients for cyclohexane–carbon tetrachloride, benzene–cyclohexane, and diethyl ether–chloroform at 25°C agree with those of other workers (*4, 6, 11*). The agreement is well within the experimental accuracy of 1 to 2%.

Nomenclature

ΔC_o, ΔC_f = initial and final concentration differences between the two compartments of the diffusion cell, g/cc
C_f', C_f'' = final concentrations in the top and lower compartments of the cell
C_o', C_o'' = initial concentrations in the top and lower compartments of the cell
Di = integral diffusion coefficient, cm^2/sec
a = effective area of the diffusion path
l = length of the diffusion path
t = total diffusion time, sec
V', V'' = volumes of the top and lower compartments of the cell, cm^3

Greek Letter

β = diaphragm cell constant, cm^2

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Vapor-Liquid Equilibria of Binary Systems Containing Selected Hydrocarbons with Perfluorobenzene

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Isobaric vapor-liquid equilibria were determined for the binary systems benzene–perfluorobenzene, perfluorobenzene–toluene, perfluorobenzene–methylcyclohexane, and *n*-hexane–perfluorobenzene. All measurements were made in a modified Hipkin-Meyers apparatus at 760 mm Hg pressure. Two azeotropes were observed in the benzene–perfluorobenzene system. These occurred at temperatures of 79.3° and 80.3°C and concentrations of 20.8 and 81.3 mol % perfluorobenzene. The system perfluorobenzene–toluene followed Raoult's Law, although the system exhibits a significant heat of mixing. A minimum boiling azeotrope was observed in the perfluorobenzene–methylcyclohexane system at a temperature of 79.9°C and concentration of 94.9 mol % perfluorobenzene. A minimum boiling azeotrope was observed in the *n*-hexane–perfluorobenzene system at a temperature of 67.9°C and composition of 75.6 mol % *n*-hexane.

The physical and thermodynamic properties of perfluorobenzene were reported by Patrick and Prosser (*12*)and Counsell et al. (3). Duncan and Swinton (*6*) reported solid-liquid phase diagrams for perfluorobenzene with benzene, toluene, and several other hydrocarbons. The excess volumes of mixing for perfluorobenzene with benzene, toluene, and several other hydrocarbons were reported by Duncan et al. (*5*). They also reported the dipole moments of perfluorobenzene in benzene and other hydrocarbons. The enthalpies of perfluorobenzene with hydrocarbons were reported by several investigators (*2, 7, 8*). Gaw and Swinton (*9*) reported vapor-liquid equilibrium data for the system benzene–perfluorobenzene at 70°C and also at 500 mm Hg total pressure.

Apparatus

The equilibrium still was based upon the design of Hipkin and Myers (*11*) as modified by Yen and Reed (*14*). The sampling valves were replaced by septums, and samples were withdrawn with a syringe and injected directly into the chromatograph or refractometer. This eliminated errors owing to liquid holdup in the sampling lines and valves. A schematic is shown in Figure 1.

The temperature was measured with copper–constantan thermocouples and potentiometer. The thermocouples were calibrated at the ice point, steam point, and boiling point of *n*-hexane. The calibration results were fit to a second-order polynominal for interpolation. The temperature was obtained with an accuracy of ±0.1°C. The pressure was maintained constant at 760.0 ± 0.1 mm Hg by a Cartesian manostat with compressed dry nitrogen

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gas. The pressure was read from a large diameter mercury manometer to an accuracy of ±0.01 mm with a cathetometer.

Materials

The benzene was Fisher spectro grade. It was better than 99.99 mol % pure and used without further purification. The toluene was Baker Chemical reagent grade. It was better than 99.9 mol % pure and used without further purification. The *n*-hexane was obtained from Matheson Coleman & Bell. It was subjected to numerous fractionations to obtain a product with a purity greater than 99.5 mol %. The methylcyclohexane was Baker analyzed reagent and had a purity of greater than 99.5 mol %.

The perfluorobenzene was obtained from two sources, Imperial Smelting Co. and Whittaker Corp. The perfluorobenzene obtained from Whittaker Corp. was better than 99.7 mol % pure and used without further purification. The perfluorobenzene obtained from Imperial Smelting Co. was only 95 mol % pure. It was subjected to numerous distillations in a 40-plate packed laboratory column until a product of better than 99.7 mol % purity was obtained. This material was used only in the system benzene–perfluorobenzene.

The purity of all reagents was determined by gas chromatography with a Beckman GC-2A with a thermal conductivity detector and a 6-ft Silicon 550 column. The refractive index, density, and normal boiling points of the pure components were measured and are given with the literature values in Table I.

Analysis

Refractive index composition curves were constructed for the analysis of liquid and vapor samples. These curves were constructed by determining the refractive index of known mixtures. The refractometer prisms were maintained at 30° ± 1.0°C for the benzene–perfluorobenzene system. All other refractive indices were measured at 20° ± 0.1°C. The results have been deposited with the ACS Microfilm Depository Service. The composition could be determined to an accuracy of ±0.1 mol % from these curves for all systems except the *n*-hexane–perfluorobenzene. For this system a minimum in the refractive index composition curve necessitated other analysis in the range of 35–65 mol %. A number of known mixtures were chromatographed to obtain a peak area composition curve which was used for the analysis of the system.

Results

Benzene–perfluorobenzene. The experimental vapor-liquid equilibrium data at 760 mm Hg pressure are given in Table II and Figures 2 and 3.

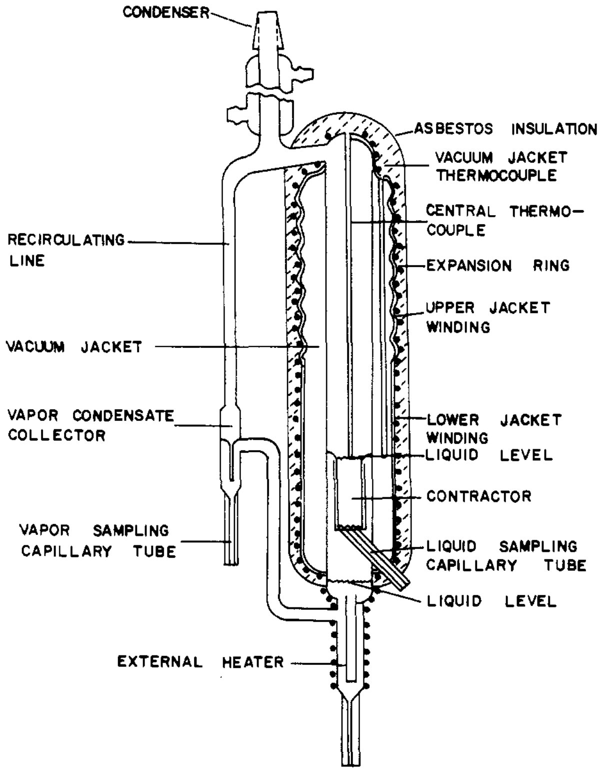

Figure 1. Equilibrium still

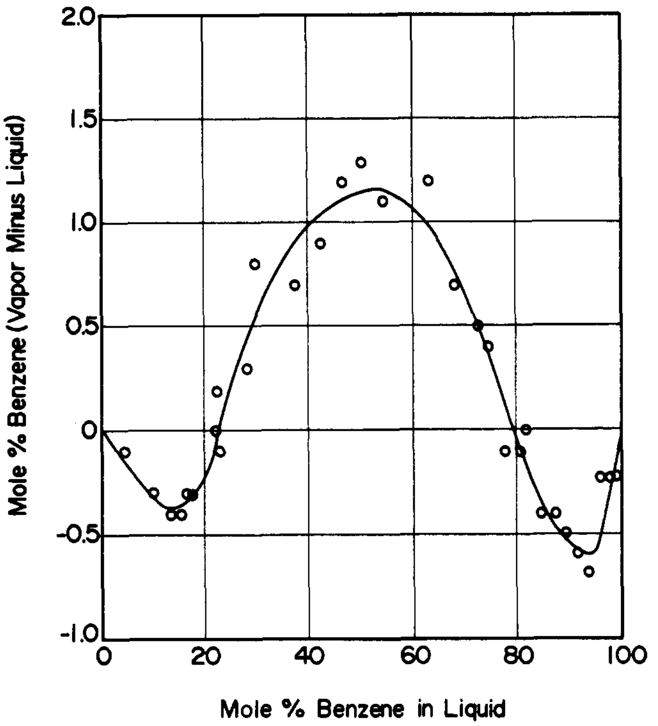

Figure 2. Experimental vapor-liquid composition for system benzene–perfluorobenzene at 760 mm Hg pressure

Table I. Physical Properties

Compound	Refractive index, 20°C		Bp, °C, 760 mm Hg press		Density, g/l., 20°C	
	Measured	Lit.	Measured	Lit.	Measured	Lit.
Benzene	1.49479	1.49468 (*4*)	80.15	80.10 (*4*)	0.8784	0.8791 (*4*)
Perfluorobenzene	1.37783	1.37810 (*13*)	80.27	80.26 (*3*)	1.6155	1.6182 (*3*)
Toluene	1.49664	1.49693 (*4*)	110.78	110.63 (*4*)	0.8669	0.8669 (*4*)
n-Hexane	1.37501	1.37486 (*1*)	68.74	68.74 (*1*)	0.65877	0.65937 (*1*)
Methylcyclohexane	1.42288	1.42312 (*1*)	100.93	100.93 (*1*)	0.76871	0.76939 (*1*)

Table II. Equilibrium Data at 760 mm Hg

Benzene–perfluorobenzene			Perfluorobenzene–toluene		
C_6H_6			C_6F_6		
Liquid, mol %	Vapor, mol %	Temp, °C	Liquid, mol %	Vapor, mol %	Temp, °C
0.0	0.0	80.26	0.0	0.0	110.78
4.2	4.1	80.31	2.3	5.6	108.51
9.7	9.4	80.23	4.8	10.8	107.50
13.0	12.6	80.23	6.2	13.4	106.54
14.9	14.5	80.31	9.1	19.2	105.21
16.1	15.8	80.25	10.4	21.5	104.71
17.1	16.8	80.27	15.0	28.3	103.21
21.9	22.0	80.31	18.0	32.8	102.23
22.5	22.4	80.20	21.9	38.8	100.51
27.9	28.2	80.18	24.6	41.4	99.98
29.3	30.1	80.30	29.6	48.6	98.25
37.5	38.2	80.18	30.8	50.8	97.74
42.3	43.2	80.03	36.6	56.3	96.30
46.1	47.3	80.03	38.0	58.2	95.66
50.3	51.6	79.87	39.8	60.5	95.17
54.2	55.3	79.74	44.8	65.2	93.27
62.8	64.0	79.65	50.2	70.2	92.48
67.8	68.2	79.47	57.6	76.2	90.67
71.7	72.2	79.45	64.6	81.3	88.81
74.2	74.6	79.36	73.2	86.8	86.49
76.6	76.5	79.34	80.7	91.2	84.49
80.6	80.5	79.32	88.0	94.8	82.69
83.7	83.3	79.34	93.0	97.0	81.46
87.0	86.6	79.35	96.8	98.5	80.58
88.5	88.0	79.35	98.5	99.1	80.31
90.6	90.0	79.39	99.0	99.2	80.58
92.5	91.8	79.39	100.0	100.0	80.26
95.6	95.4	79.54			
98.4	98.2	79.65			
98.7	98.5	79.85			
100.0	100.0	80.15			

Perfluorobenzene–methylcyclohexane			*n*-Hexane–perfluorobenzene		
C_6F_6			n-C_6H_{14}		
0.00	0.00	100.00	0.00	0.00	80.25
1.93	7.70	98.77	4.12	10.53	78.04
2.96	10.97	97.80	5.08	13.35	77.42
4.11	13.57	97.10	8.19	20.94	75.83
6.13	19.99	95.30	11.28	26.20	74.95
7.55	22.70	94.24	13.26	28.25	74.15
9.76	28.42	92.50	15.53	34.82	72.26
10.47	29.03	92.37	19.38	40.16	71.91
12.10	33.17	91.06	21.70	42.50	71.24
15.58	38.32	89.66	24.87	43.50	70.50
18.39	42.17	88.63	27.73	47.23	69.95
24.24	48.02	86.70	30.25	48.07	69.75
27.77	52.04	85.49	34.80	49.50	69.36
32.56	54.80	84.62	37.93	51.02	69.27
37.20	58.32	83.70	43.02	54.55	69.06
41.62	61.24	82.92	48.51	57.36	68.60
47.82	64.61	82.21	53.73	61.89	68.27
55.43	68.19	81.68	57.43	63.39	68.21
57.97	70.67	81.22	62.90	64.85	68.16
62.34	73.25	80.87	67.25	69.70	68.09
68.05	76.18	80.61	69.28	71.43	67.99
74.30	79.68	80.32	70.40	71.55	67.92
79.28	82.20	80.06	73.38	74.80	67.93
81.77	82.97	79.87	75.55	75.55	67.94
83.14	86.56	79.95	76.86	75.98	67.94
88.96	89.35	79.81	78.13	77.28	67.96
91.87	92.29	80.01	80.85	79.72	67.80
94.71	94.83	79.85	88.25	85.05	68.02
94.94	94.94	79.87	91.72	89.27	68.12
97.06	96.93	79.97	94.32	92.50	68.36
100.00	100.00	80.25	100.00	100.00	68.74

There are two azeotropes in the benzene–perfluorobenzene system. The azeotropes are formed at temperatures of 79.3° and 80.3°C and at a mol % of perfluorobenzene of 20.8 and 81.3, respectively. The azeotropes were confirmed by subjecting several mixtures of a composition close to two azeotropic compositions to fractionation. The results of Gaw and Swinton (*9*) at 500 mm Hg pressure show two azeotropes at temperatures of 68.7° and 69.2°C and at mol % of perfluorobenzene of 18.0 and 79.5. They also noted this behavior at all temperatures from 30° to 70°C, and the extrapolation of the results in this temperature range indicated azeotropes up to 120°C. This unusual phenomena of double azeotropes is probably due to the close vapor pressures of both pure compounds and an electrostatic interaction of the two components (*2*, *8*). Some investigators proposed a charge transfer interaction leading to the formation of a molecular complex (*6*).

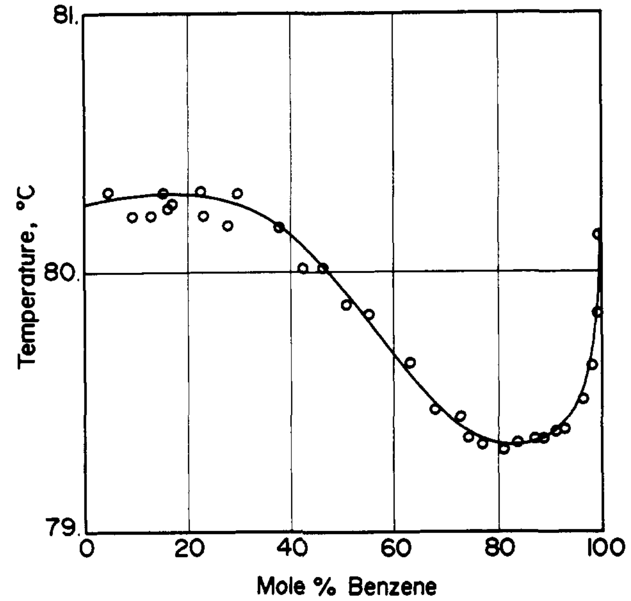

Figure 3. Experimental temperature composition for system benzene–perfluorobenzene at 760 mm Hg pressure

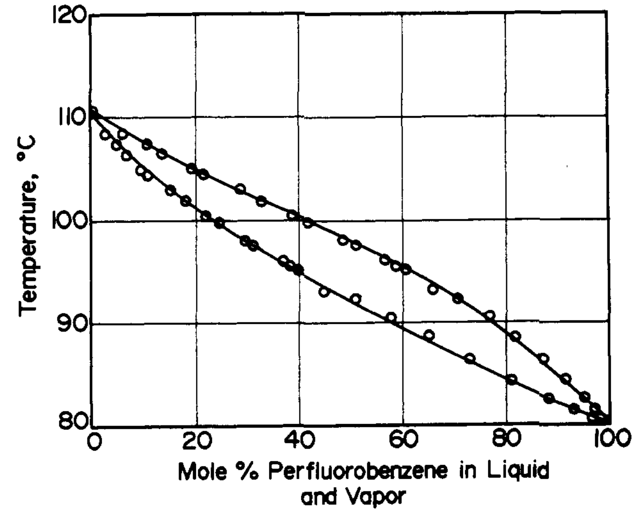

Figure 4. Temperature composition for system perfluorobenzene–toluene at 760 mm Hg pressure

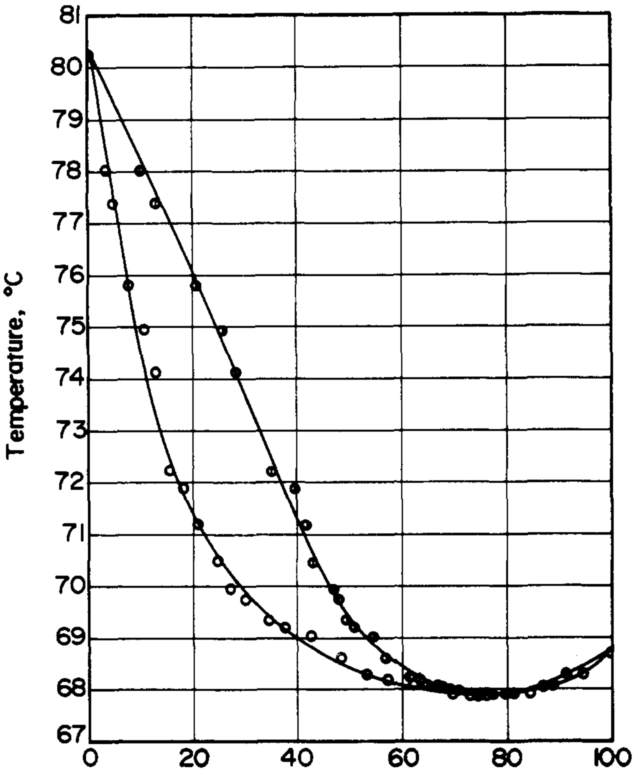

Figure 5. Temperature composition for system *n*-hexane-perfluorobenzene at 760 mm Hg pressure

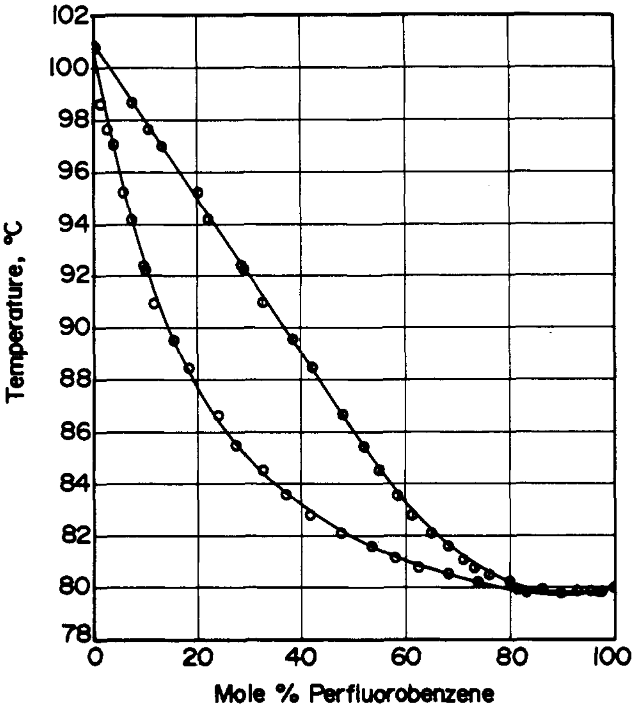

Figure 6. Temperature composition for system perfluorobenzene-methylcyclohexane at 760 mm Hg pressure

Perfluorobenzene-toluene. The experimental vapor-liquid equilibrium data at 760 mm Hg pressure are given in Table II and Figure 4. Although this data indicated approximately ideal behavior similar to the benzene-toluene system, the perfluorobenzene-toluene system exhibits a heat of mixing and is not ideal (*2, 10*).

Perfluorobenzene-hexane. The experimental vapor-liquid equilibrium data at 760 mm Hg pressure are shown in Table II and Figure 5. This system showed a large positive deviation from ideal behavior, having a minimum boiling azeotrope at 75.55% normal hexane. The refractive index composition curve of this system exhibited a minimum at 58 mol % *n*-hexane.

The azeotrope was confirmed by introducing a sample into the packed column described earlier for the benzene-perfluorobenzene system. The results for samples on either side of the azeotrope were identical.

Perfluorobenzene-methylcyclohexane system. The experimental vapor-liquid equilibrium data at 760 mm Hg pressure are shown in Table II and Figure 6. This system showed a large positive deviation from ideality with a minimum boiling azeotrope at 94.94 mol % perfluorobenzene.

The azeotrope was determined in the packed fractionating column described previously. The results were identical confirming an azeotrope at 94.94 mol % perfluorobenzene.

Liquid-phase activity coefficients were calculated and correlated for these systems. The results have been deposited with the ACS Microfilm Depository Service.

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Received for review March 23, 1973. Accepted April 6, 1973. **Supplementary Material Available.** An Appendix, including four tables and three figures, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JCED-73-322.