Two basic differences in experimental method between the previous and present studies are noted. First, an Othmer-type still was used in the present work compared to equilibrium cells in the other investigations. Both techniques have inherent shortcomings, and it is difficult to establish which is more accurate. The other difference is in analytical methods. The present work used mass spectrometric techniques whereas previous investigators used chemical methods. Reamer and Sage measured propylene content by volumetric determination of hydrogen consumption upon catalytic hydrogeneation. Hanson, *et al.*, determined the reduction in gas volume upon absorption of the propylene in sulfuric acid. It would seem that the more recently developed mass spectrometric technique is basically superior to the chemical methods, although evaluation of the quantitative effect on relative volatility would require additional study.

The good agreement between the present and published data tends to confirm the validity of the method used for correlating the isothermal data and provides confidence in the extrapolation of the previous relative volatility data above the 90% propylene level. These results thus increase the reliability of fractionator calculations in the region of high-purity propylene, where the requirements are most severe.

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Vapor-Liquid Equilibria at Atmospheric Pressure

II. 1-Butanol-Benzene System

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Vapor-liquid equilibrium values have been determined at atmospheric pressure for 1-butanol-benzene system, using a modified Gillespie still. Experimental data meet the thermodynamic requirements of Gibbs-Duhem equation. The constants *A* and *B* for van Laar equation have been determined.

LIQUID VAPOR equilibria for the system 1-butanol-benzene have been determined at 20° C. by Tryhorn and Wyatt (*8*), at 25° C. by Allen Lingo and Felsing (*1*) and at 45° C. by Brown and Smith (*3*). No published vapor-liquid equilibrium data at 760 mm. of Hg pressure is available, except that of Bonauguri, Bicelli and Spiller (*2*), who made the measurements at 743 to 758 mm. of Hg pressure. However, no information is given about the temperatures at which x-y data were taken, and whether any corrections were made for pressure deviations. In view of this, present measurements were made to determine the vapor-liquid equilibrium compositions at 760 mm. for 1-butanol-benzene system. The experimental results are given in Table I, and the temperature-composition, and x-y curves are shown in Figure 1 and 2, respectively. The activity coefficients were calculated from the equation

Table I. Experimental Data for 1-Butanol-Benzene at 760 mm. of Hg

Temp., ° C.	x_1	y_1	$y_{1\,\text{calcd.}}$	γ_1	γ_2
80.09	1.000	1.000	1.000	1.0000	. . .
80.16	0.954	0.966	0.961	1.0104	3.4293
80.21	0.948	0.963	0.957	1.0122	3.2943
80.28	0.942	0.960	0.954	1.0132	3.1813
80.39	0.928	0.952	0.947	1.0165	3.0597
80.67	0.897	0.947	0.934	1.0371	2.7719
80.87	0.848	0.920	0.910	1.0591	2.3641
81.36	0.790	0.904	0.892	1.1005	2.0065
81.98	0.714	0.885	0.870	1.1698	1.7159
83.19	0.631	0.867	0.855	1.2501	1.4567
84.54	0.560	0.847	0.844	1.3215	1.3213
86.39	0.475	0.819	0.822	1.4259	1.2074
88.28	0.397	0.787	0.785	1.5509	1.1370
89.69	0.369	0.779	0.782	1.5820	1.0596
92.25	0.308	0.724	0.735	1.6560	1.0575
95.60	0.234	0.660	0.672	1.7905	1.0443
98.70	0.180	0.590	0.595	1.9103	1.0345
100.22	0.161	0.560	0.565	1.9450	1.0201
102.22	0.134	0.510	0.510	2.0091	1.0193
107.10	0.085	0.380	0.386	2.0830	1.0026
112.00	0.040	0.217	0.215	2.2304	1.0005
116.90	0.004	0.025	0.024	2.2754	1.0005
117.70	0	0	0	. . .	1.0000

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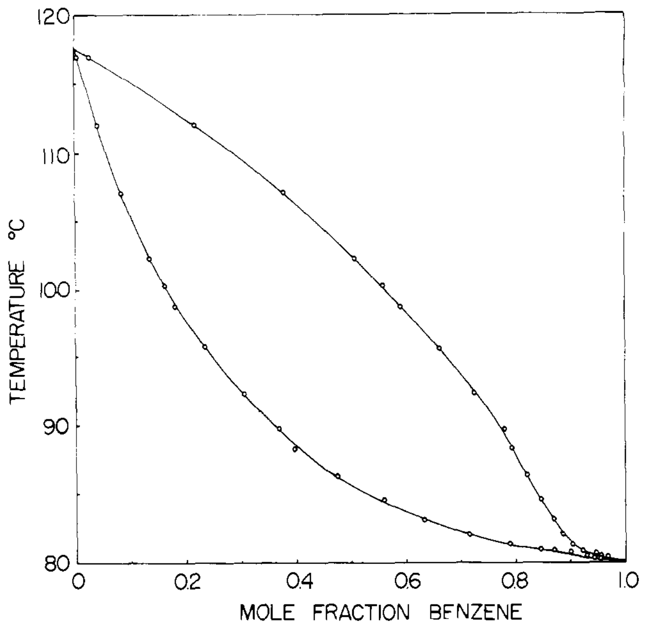

Figure 1. Temperature-composition curve for 1-butanol-benzene system

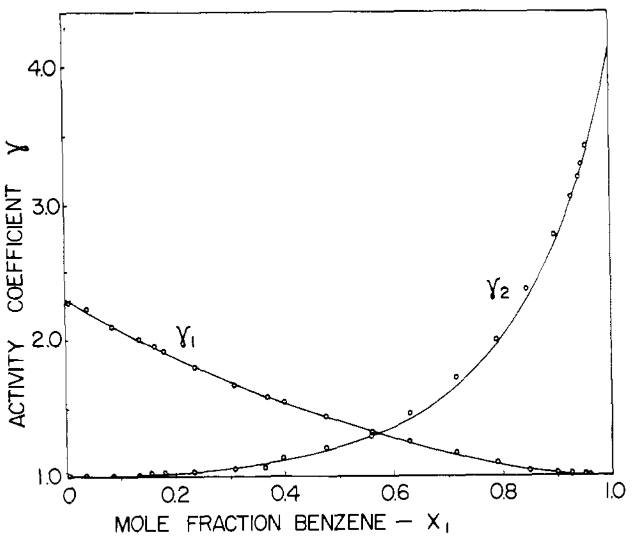

Figure 3. Activity coefficient-composition curve for 1-butanol-benzene system

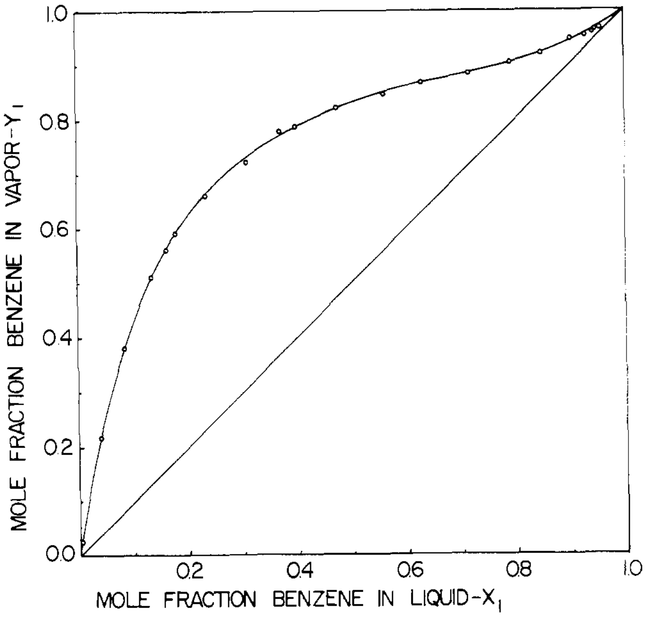

Figure 2. Vapor-liquid equilibrium curve for 1-butanol-benzene system

$\gamma = (y\pi/xP^{\circ})$. P° was calculated for various temperatures from the equations:

$$\text{Benzene: } \log_{10} P^{\circ}(\text{mm.}) = 6.91210 - \frac{1214.645}{221.205 + t}$$

$$\text{1-Butanol: } \log P^{\circ}(\text{mm.}) = 8.19659 - \frac{1781.719}{217.675 + t}$$

Though azeotropes are found in 1-butanol-toluene and propanol-benzene systems, no azeotrope was obtained in 1-butanol-benzene system.

EXPERIMENTAL

The C.P. grade chemicals used were redistilled over CaO, Mg turnings, and activated alumina in turn, and middle cuts used. The distillates used in equilibrium still had boiling ranges of not more than 0.03° C. The physical constants of the materials used are given in Table III.

Binary compositions were determined from refractive indices at 25° C., using a Zeiss Abbe refractometer, and a modified Gillespie still as described in an earlier paper of Mann and Shemilt (5).

Thermodynamic Consistency. The experimentally determined values of γ_1 and γ_2 are in general agreement with the thermodynamically correct values as shown by van Laar equation (9) curve in Figure 3 within the limits of accuracy

Table II. Properties of Pure Compounds

Compound	n_D^{25} Exptl.	n_D^{25} Lit. (7)	B.P. at 760 mm. of Hg, ° C. Exptl.	B.P. at 760 mm. of Hg, ° C. Lit. (7)	D, Gms./ml. at 25° C. Exptl.	D, Gms./ml. at 25° C. Lit. (7)
Benzene	1.4979	1.49807	80.09	80.103	0.87368	0.87368
1-Butanol	1.3974	1.3970	117.7	117.726	0.80560	0.80567

of the analytical procedure. The values of A and B for van Laar equation curves were obtained as 0.38969 and 0.55954 by determining A and B as terminal values of $\log \gamma_1$ at $x_1 = 0$, and $\log \gamma_2$ at $x_2 = 0$, using the Carlson, Colburn (*4*) relationship:

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \cdot \frac{x_1}{x_2}\right)^2}$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A} \cdot \frac{x_2}{x_1}\right)^2}$$

Values of y_1 were calculated based on these values of A and B, and are given as $y_{\text{calcd.}}$ in Table I. The maximum percentage deviation between $y_{\text{exptl.}}$ and $y_{\text{calcd.}} = (100\ \Delta y/y_1)$, is less than 2%. Plots of $\log (\gamma_1/\gamma_2)$ *vs.* x_1 in accordance with Redlich and Kister equation (*6*) showed variation in net area under the curve of less than 2%, which is quite reasonable considering the difference of over 37° C. in the boiling points of benzene and 1-butanol.

NOMENCLATURE

A and B = constants in van Laar equation
P° = vapor pressure, mm.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = activity coefficient
π = total pressure
t = temperature, ° C.
Δy = $y_{\text{exptl.}} - y_{\text{calcd.}}$

Subscripts

1 = benzene
2 = 1-butanol

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Relative Volatility Data for Isopentane: *n*-Pentane Mixtures

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This paper discusses the experimental measurement and the thermodynamic prediction of the relative volatilities of isopentane: *n*-pentane at pressures of 25 to 150 p.s.i.a. A six-stage equilibrium unit was used because of the low relative volatility. The equilibrium samples were analyzed by gas chromatography. Literature values of physical property data were used in the thermodynamic calculations. The agreement of the predicted values with the experimentally measured values given in this paper illustrates that accurate relative volatilities can be predicted for close boiling mixtures, provided adequate physical property data are available.

THE PRESENT INVESTIGATION to determine the relative volatility data for the isopentane: *n*-pentane system is a part of a continuing program to supply the needs of industry with fundamental design data for separational processes.

Accurate experimental vapor-liquid equilibrium data for many close boiling systems such as isopentane (2-methylbutane):*n*-pentane have not been previously determined, mainly because of the difficulties in analyzing accurately the small changes in concentration obtained in the conventional one-stage equilibrium devices.

The present data were determined in a six-stage equilibrium unit covering a pressure range of 34 to 114 p.s.i.a. and the full concentration range of this binary system. Gas chromatography was used to determine accurately the composition of the equilibrium samples.

Because of a lack of experimental data on vapor-liquid equilibrium relationships, many theoretical prediction methods have been proposed to calculate the relative volatility (alpha) of close boiling mixtures. The only experimental vapor-liquid data available in the literature for isopentane:*n*-pentane mixtures are those of Redlich and Kister (*9*) who have predicted that the ratios of the activity coefficients for this system are essentially unity. The method used by these authors is based on total pressure measurements for binary mixtures at constant temperature. The present experimental data, consisting of measured compositions of vapor and liquid phases at equilibrium, serve to check the results of Redlich and Kister as well as the theoretical prediction methods.

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