Vapor-liquid Equilibria of Benzene–n-hexane and Benzene-cyclohexane Systems

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Vapor-liquid equilibria of two binary systems, benzene–n-hexane and benzene-cyclohexane, were measured at pressures from 4 to 18 atm. The three-constant Redlich-Kister equation was found satisfactory for correlation.

With the benzene–n-hexane system no azeotrope occurred; with the benzene-cyclohexane system an azeotrope appeared, and the mole fraction of cyclohexane in it diminished with increase in pressure. Lack of correction for fugacity in the vapor phase introduced a maximum error of 4% in activity coefficients at highest pressure.

Previously published data on these two systems have been restricted to measurements at atmospheric pressure and have conflicted as to the occurrence or absence of an azeotrope in the benzene–n-hexane system. Tonoberg and Johnston (11) reported vapor-liquid-equilibria data on the benzene–n-hexane system at atmospheric pressure and found no azeotrope; Other investigators (13, 5, 7, 6) reported the formation of an azeotrope. Griswold and Ludwig (2), in commenting on the data of Tonoberg and Johnston, stated that the azeotrope perhaps escaped detection because of the small temperature difference, 0.1°C., between the normal boiling points of the azeotrope and n-hexane.

Vapor-liquid equilibria and thermodynamic properties of the benzene-cyclohexane system have been established by Scatchard, Wood, and Mochel (10) and by Wood and Austin (12), who attribute the highly irregular behavior of this system to the large entropy of mixing. Richards and Hargreaves (9) established similar data on this system at atmospheric pressure and found the azeotrope composition to be 50.2 mole % benzene at a normal boiling point of 77.4°C. As the boiling points of the pure components are close together, a slight deviation from ideality readily produces a minimum boiling azeotrope (3).

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used for measuring vapor-liquid equilibria was a continuous liquid-recirculating still similar to that used by Griswold et al. (1), as shown in Figure 1. It consisted of a still, condenser C, reboiler leg B, condensate reservoir CR, and calibrated spring-loaded nonreturn valve N (Figure 2).

Temperature measurements were made with an iron-constantan thermocouple with its cold junction at the melting point of ice.

Temperatures recorded by the thermocouples, being slightly lower than the true values owing to heat losses along the thermocouple wires, were made by use of the following equation for the size of wire used:

$$t_0 = 0.000\ 15686\ t^2 + 0.9996\ t + 0.856 \qquad (1)$$

where t_0 = true temperature and t = observed temperature. Pressures were measured by a Bourdon gauge having a scale range of 0 to 600 lb./sq. in. and a dial 8 in. in diameter with divisions marked at 2 lb./sq. in. intervals. This gauge was calibrated periodically against a dead-weight gauge. A Doran potentiometer in conjunction with a multiflux-spot galvanometer was used to record potentials (Figure 3). Vapor-pressure-temperature relationships were measured for three pure compounds, benzene (b.p. 80.1°C.), cyclohexane (b.p. 80.7°C.), and methanol (b.p. 64.7°C.)

The three reagents, benzene, n-hexane, and cyclohexane, were obtained from the British Drug Houses.

Benzene

> Analytical quality
> Boiling point   80.1°C.
> Density at 30°C., 0.8059 g./ml.
> Density at 28°C., 0.8077 g./ml.

N-*Hexane*

The n-hexane of laboratory quality was dried with anhydrous calcium chloride and refractionated in a glass column. The fraction collected between 67° and 69°C. was refractionated, and the final cut selected had a normal boiling point of 68.6°C. and density of 0.6228 g./ml. at 30°C.
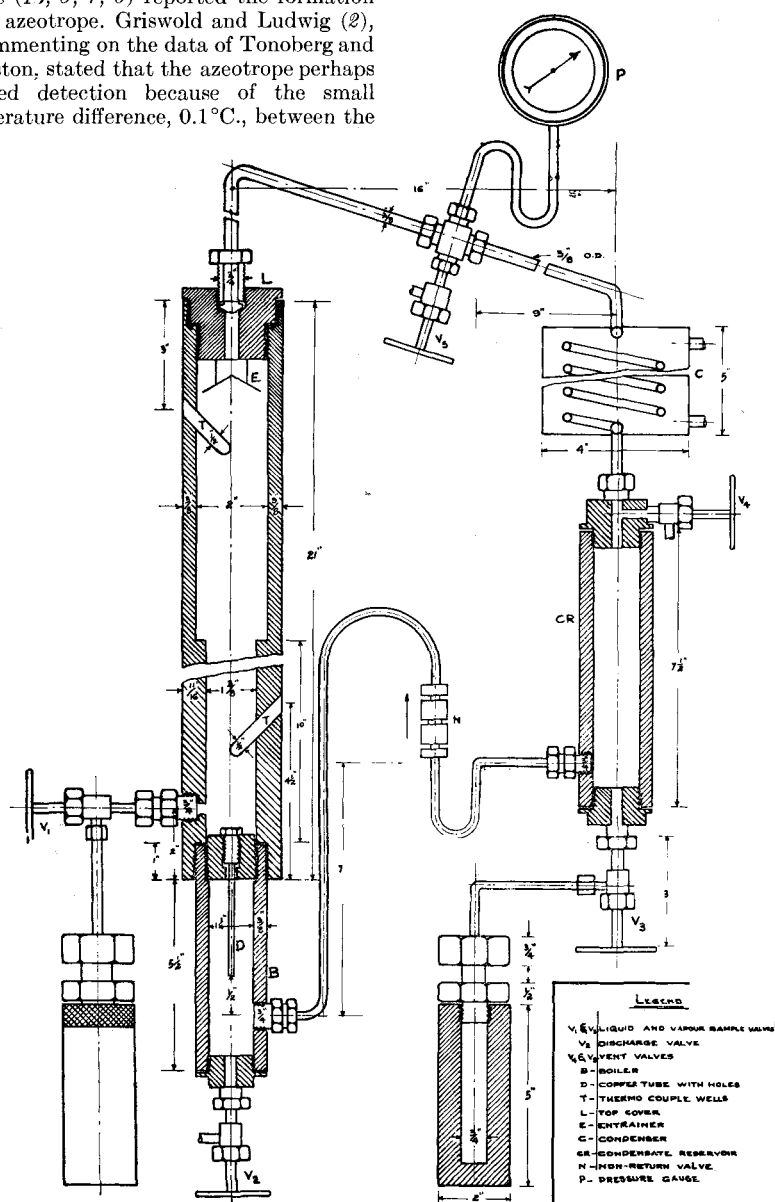

Fig. 1. Continuous liquid-recirculating still.

Cyclohexane

Laboratory reagent quality
Normal boiling point, 80.7°C.
Density at 28°C., 0.7181 g./ml.

The vapor pressures of the three pure components were measured and plotted on large-scale graphs (18 by 28 in.) to facilitate accurate interpolation. Owing to the large differences in the densities of these components the compositions of each binary system could be established with accuracy from density measurements.

CORRELATION OF EXPERIMENTAL DATA

Benzene–*n*-Hexane System

To establish with certainty the presence or absence of an azeotrope in the benzene–n-hexane system experiments were made at high pressures, where a possible azeotrope in the system would be more readily observed. Since the heat of vaporization of n-hexane is less than that of benzene, the n-hexane content of a possible azeotrope in this system would diminish with increased pressure; accordingly studies were made at pressures up to 10 atm.

TABLE 8. BENZENE–n-HEXANE SYSTEM; REDLICH-KISTER CORRELATIONS

x_1	58.8 lb./sq. in. abs. log γ_1/γ_2		88.6 lb./sq. in. abs. log γ_1/γ_2		117.6 lb./sq. in. abs. log γ_1/γ_2		147 lb./sq. in. abs. log γ_1/γ_2	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.0	0.141	0.132	0.111	0.125	0.101	0.119	0.079	0.107
0.1	0.104	0.100	0.083	0.090	0.076	0.085	0.059	0.074
0.2	0.071	0.070	0.055	0.058	0.052	0.054	0.041	0.046
0.3	0.041	0.040	0.031	0.031	0.036	0.028	0.022	0.022
0.4	0.014	0.013	0.007	0.007	0.006	0.005	0.003	0.002
0.5	−0.012	−0.012	−0.014	−0.014	−0.014	−0.014	−0.014	−0.014
0.6	−0.033	−0.034	−0.032	−0.031	−0.031	−0.030	−0.028	−0.027
0.7	−0.048	−0.043	−0.045	−0.045	−0.043	−0.043	−0.037	−0.037
0.8	−0.062	−0.068	−0.056	−0.057	−0.053	−0.052	−0.044	−0.044
0.9	−0.074	−0.078	−0.065	−0.064	−0.060	−0.059	−0.049	−0.048
1.0	−0.085	−0.084	−0.074	−0.071	−0.063	−0.063	−0.052	−0.051

TABLE 9. BENZENE–n-HEXANE SYSTEM, CORRELATION OF REDLICH-KISTER CONSTANTS WITH PRESSURE

π, lb./sq. in. abs.	B Exp.	B Calc.	C Exp.	C Calc.	D Exp.	D Calc.
58.8	0.1131	0.1131	−0.024	−0.024	−0.0049	−0.0049
88.6	0.0958	0.0958	−0.027	−0.026	0.0021	−0.0023
117.6	0.0891	0.0815	−0.028	−0.028	0.0014	0.0014
147.0	0.0757	0.0692	−0.028	−0.030	0.0033	0.0070

TABLE 17. BENZENE-CYCLOHEXANE SYSTEM, REDLICH-KISTER CORRELATIONS

x_1	66.7 lb./sq. in. abs. log (γ_1/γ_2)		116.5 lb./sq. in. abs. log (γ_1/γ_2)		165.9 lb./sq. in. abs. log (γ_1/γ_2)		217 lb./sq. in. abs. log (γ_1/γ_2)		268.7 lb./sq. in. abs. log (γ_1/γ_2)	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.0	0.0780	0.0785	0.0560	0.0529	0.0400	0.0382	0.0360	0.0345	0.0337	0.0309
0.1	0.0720	0.0720	0.0517	0.0508	0.0365	0.0359	0.0326	0.0372	0.0314	0.0312
0.2	0.0650	0.0651	0.0450	0.0456	0.0314	0.0312	0.0282	0.0342	0.0273	0.0277
0.3	0.0560	0.0561	0.0362	0.0374	0.0240	0.0243	0.0225	0.0267	0.0210	0.0212
0.4	0.0430	0.0438	0.0255	0.0262	0.0160	0.0156	0.0140	0.0157	0.0126	0.0124
0.5	0.0265	0.0265	0.0120	0.0120	0.0052	0.0052	0.0030	0.0030	0.0024	0.0024
0.6	0.0027	0.0030	−0.0043	−0.0051	−0.0080	−0.0064	−0.0104	−0.0105	−0.0103	−0.0082
0.7	−0.0297	−0.0285	−0.0218	−0.0249	−0.0213	−0.0209	−0.0240	−0.0235	−0.0234	−0.0188
0.8	−0.0662	−0.0693	−0.0434	−0.0476	−0.0378	−0.0320	−0.0355	−0.0346	−0.0331	−0.0281
0.9	−0.1034	−0.1208	−0.0685	−0.0732	−0.0545	−0.0455	−0.0435	−0.0432	−0.0400	−0.0356
1.0	−0.1390	−0.1845	−0.0955	−0.1009	−0.0730	−0.0590	−0.0480	−0.0465	−0.0443	−0.0405

Activity coefficients in the liquid phase were calculated from the ratio $\gamma_1 = y_1\pi/x_1P_1$. No corrections were made for lack of ideality in the vapor phase. Vapor pressures of pure n-hexane and benzene are tabulated in Tables 1* and 2* and density-composition relations for the binary solutions in Table 3*. In Tables 4 through 7* experimental values of activity coefficients for the benzene–n-hexane system are tabulated. With the benzene–n-hexane system no azeotrope was found.

The experimental values of t, x, y and log γ are shown graphically in Figure 4 for a pressure of 58.8 lb./sq. in. abs. and the experimental y-x data at all pressures are shown in Figure 5.

The experimental data on activity coefficients were correlated with the Van Laar equation and on activity-coefficient ratios by the Redlich-Kister (8) equation. The latter equation gave

TABLE 18. BENZENE-CYCLOHEXANE SYSTEM, CORRELATION OF REDLICH-KISTER CONSTANTS WITH PRESSURE

π, lb./sq. in. abs.	B Exp.	B Calc.	C Exp.	C Calc.	D Exp.	D Calc.
66.7	0.1162	0.0934	0.0530	0.0493	0.0153	0.0143
116.5	0.0775	0.0778	0.0240	0.0240	−0.0006	0.0055
165.9	0.0518	0.0648	0.0104	0.0117	−0.0032	−0.0025
217.0	0.0537	0.0537	0.0060	0.0056	−0.0132	−0.0100
268.7	0.0441	0.0444	0.0048	0.0026	−0.0084	−0.0174

TABLE 19. BENZENE-CYCLOHEXANE SYSTEM x-y CORRELATIONS

x_1	x_1/x_2	66.7 lb./sq. in. abs. y_1	y_1/y_2	116.5 lb./sq. in. abs. y_1	y_1/y_2	165.9 lb./sq. in. abs. y_1	y_1/y_2	217 lb./sq. in. abs. y_1	y_1/y_2	268.7 lb./sq. in. abs. y_1	y_1/y_2
0.1	0.111	0.116	0.131	0.111	0.125	0.112	0.126	0.106	0.119	0.105	0.117
0.2	0.250	0.227	0.294	0.220	0.282	0.217	0.277	0.212	0.269	0.208	0.263
0.3	0.429	0.335	0.504	0.322	0.475	0.320	0.471	0.317	0.464	0.318	0.466
0.4	0.667	0.433	0.764	0.420	0.724	0.420	0.724	0.418	0.718	0.419	0.721
0.5	1.000	0.519	1.079	0.513	1.053	0.513	1.053	0.512	1.049	0.511	1.045
0.6	1.500	0.602	1.519	0.605	1.532	0.608	1.561	0.607	1.545	0.606	1.538
0.7	2.333	0.689	2.215	0.696	2.289	0.700	1.333	0.701	2.344	0.703	2.367
0.8	4.000	0.770	3.348	0.790	3.762	0.790	3.762	0.797	3.926	0.798	3.950
0.9	9.000	0.885	7.696	0.890	8.091	0.890	8.091	0.894	8.434	0.897	8.709

the better results. The three-constant Redlich-Kister equation (8) was found to be satisfactory, namely,

$$\log \frac{\gamma_1}{\gamma_2} = B(1 - 2x_1)$$

$$+ C[6x_1(1 - x_1) - 1]$$

$$+ D(1 - 2x_1)[1 - 8x_1(1 - x_1)] \quad (2)$$

The constants B, C, and D were obtained from data taken at constant pressures with temperatures fixed by pressure and composition. Values of individual coefficients thus calculated at a given pressure differ slightly from those based upon constant temperature and pressure. These constants were evaluated at each pressure and correlated in terms of pressure by the following relations:

$$\log B = -0.00242\pi - 0.8043 \quad (3)$$

$$\log (-C) = 0.00114\pi - 1.6868 \quad (4)$$

$$\log (D + 0.01)$$
$$= 0.00594\pi - 2.6416 \quad (5)$$

where π = total pressure, lb./sq. in. abs.

A comparison of experimental values of γ_1/γ_2 with calculated values is given in Table 8 and Figure 6 for a pressure of 58.8 lb./sq. in. abs.

The experimental values of B, C, and D are plotted in Figure 7 and a comparison of calculated with experimental values is tabulated in Table 9. At high concentrations of n-hexane the y-x vapor-liquid lines nearly coincide with the y-x line but this is not proof of azeotrope formation. The two lines must cross to establish such proof.

Benzene-cyclohexane System

The vapor pressures of pure cyclohexane are tabulated in Table 10* and density-composition relationships for the benzene-cyclohexane system in Table 11*.

Since the y-x differences for this system are small, interpolations of the density-composition data were made by the following equation rather than from graphs.

$$x = 4.004 \, d^3 - 101.08 \, d^2 + 17.096 \, d \quad (6)$$
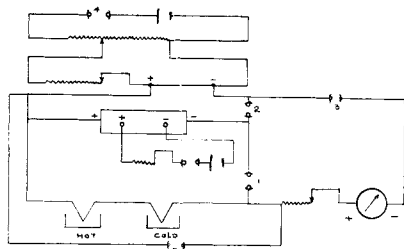
*See footnote on page 192.

Fig. 3. Multiflux circuit.

where

x = mole fraction of benzene
$d = d_m - d_c$

d_m = density of mixture
d_c = density of cyclohexane

Equilibrium data and activity coeffi-

TABLE 21. BENZENE-CYCLOHEXANE SYSTEM, CORRELATION AND PREDICTION OF AZEOTROPIC DATA

| π, lb./ sq. in. abs.	m Exp.	m Calc.	c Exp.	c Calc.	$x_{1_{az}}$ Exp.	$x_{1_{az}}$ Calc.	t_{az}, °C. Exp.	t_{az}, °C. Calc.	% Deviation in $x_{1_{az}}$	% Deviation in t_{az}
14.7	—	—	—	—	0.505	0.522	77.3	74.8	3.4	3.2
66.7	0.8373	0.8496	0.0331	0.0248	0.615	0.594	137.1	140.6	3.0	2.6
116.5	0.9214	0.9122	0.0234	0.0234	0.665	0.649	165.7	168.0	2.4	1.4
165.9	0.9364	0.9372	0.0224	0.0220	0.700	0.691	185.5	186.2	1.3	0.4
217.0	0.9521	0.9511	0.0207	0.0206	0.730	0.725	201.7	200.5	0.7	0.6
268.7	0.9609	0.9597	0.0191	0.0191	0.755	0.763	215.7	212.3	1.0	1.1
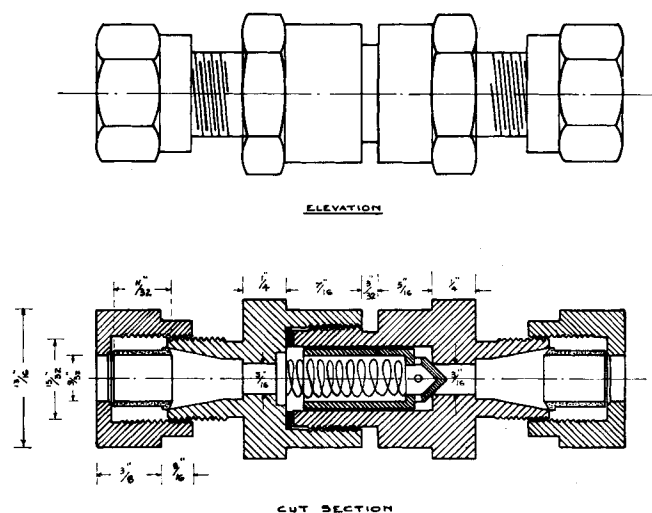
Fig. 2. Spring-loaded nonreturn valve N.
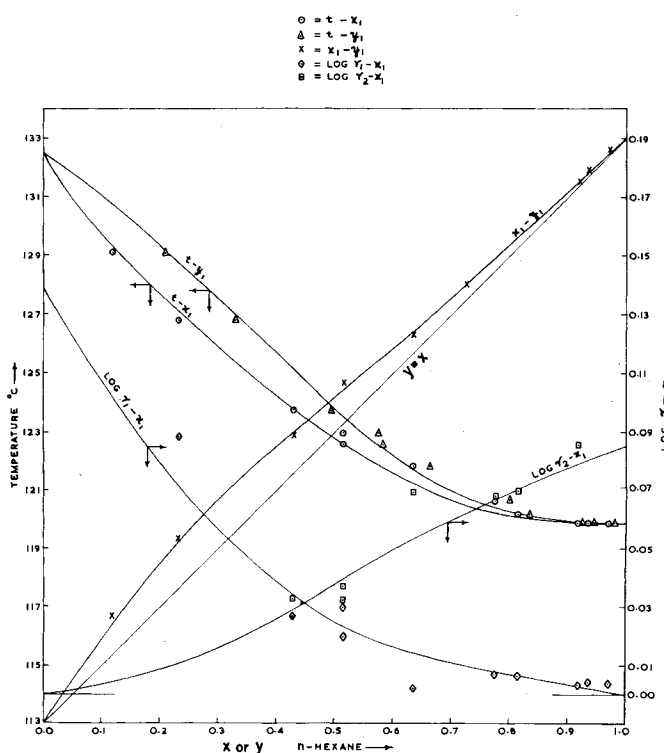
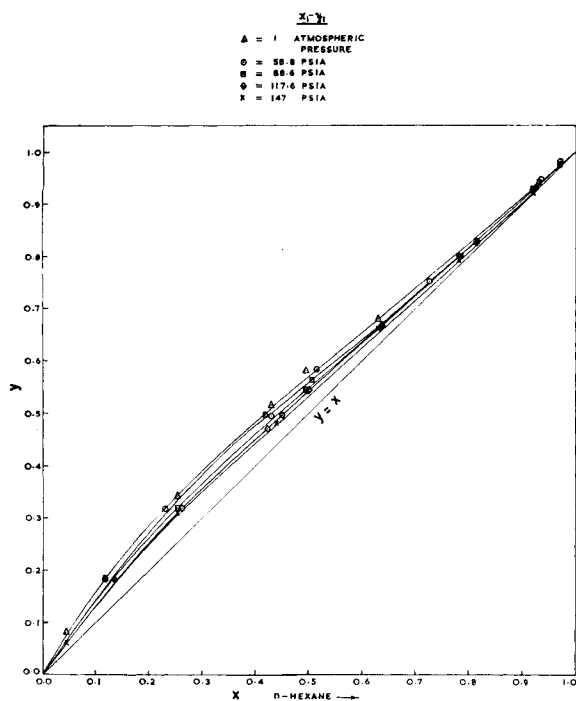Fig. 4. γ, t, x, y diagram at 58.8 lb./sq. in. abs., benzene-n-hexane system.

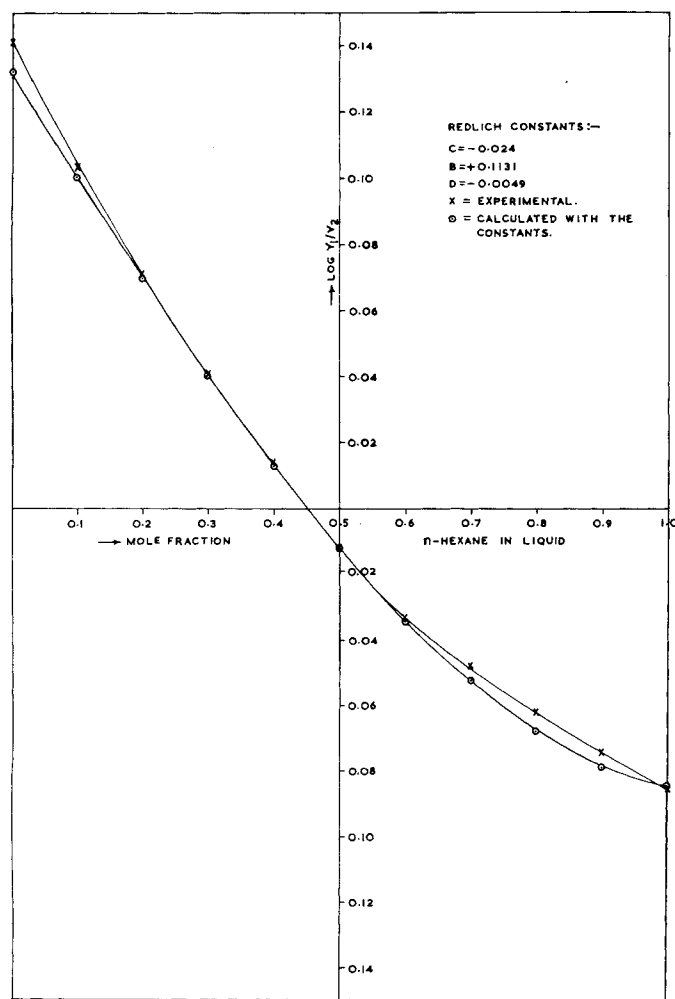Fig. 5. Benzene–n-hexane system y-x diagram at four pressures.

cients are tabulated in Tables 12* to 16* for pressures of 66.7, 116.5, 165.9, 217, and 268.7 lb./sq. in. abs., respectively. Experimental data of t, x, y, and log γ are shown in Figure 8 for a pressure of 66.7 lb./sq. in. abs. and the y-x data at all pressures are shown in Figure 9. The shift of the azeotrope composition with temperature is shown as the dotted straight line in Figure 10.

The activity coefficients of this system were correlated with the three-constant

*See footnote on page 192.

Fig. 7. Benzene–n-hexane Redlich-Kister constants vs. pressure.

Fig. 6. Benzene–n-hexane system log γ_1/γ_2 vs. x at 58.8 lb./sq. in. abs.

Fig. 8. Benzene-cyclohexane γ, t, x, y at 66.7 lb./sq. in. abs.

Redlich-Kister equation, the values of the constants as a function of pressure being related as follows:

$$\log B = -0.0016\pi - 0.9228 \qquad (7)$$

$$\log C = -0.0063\pi - 0.8866 \qquad (8)$$

$$\log (D + 0.1)$$
$$= -0.0007\pi - 0.8948 \qquad (9)$$

Experimental and calculated values of $\log \gamma_1/\gamma_2$ are tabulated in Table 17 and shown graphically in Figure 11 for a pressure of 66.7 lb./sq. in. abs. A comparison of calculated values of constants B, C, and D with experimental values is tabulated in Table 18.

The composition of the azeotrope in the benzene-cyclohexane system shifted with temperature according to the equation

$$t_{az} = 581.1 x_{az} - 220.7 \qquad (10)$$

where

x_{az} = mole fraction of benzene in the azeotrope
t_{az} = temperature of the azeotrope, °C.

Simplified Presentation of y-x data

For simplicity in use the y-x data for these two binary systems were presented in modified form by plotting y_1/y_2 vs. x_1/x_2 on log-log scales as suggested by Hirata (4). The values for benzene-cyclohexane are tabulated in Table 19. A straight line was obtained for each pressure as shown in Figure 13 for benzene-cyclohexane at a pressure of 66.7 lb./sq. in. abs.; thus

$$\log \frac{y_1}{y_2} = m \log \frac{x_1}{x_2} + c \qquad (11)$$

On uniform log scales each line intersects a 45-deg. line at a point corresponding to the azeotropic composition at the given pressure. At this point of intersection

$$\log \frac{x_{1az}}{x_{2az}} = \frac{c}{1 - m} \qquad (12)$$

Comparison of experimental azeotropic compositions with those obtained by Equation (12) are tabulated in Table 20. The constants m and c were correlated with pressure as shown in Figure 14 to give the following:

TABLE 20.
AZEOTROPE COMPOSITIONS FOR THE BENZENE-CYCLOHEXANE SYSTEM

π lb./sq. in. abs.	x_{1az} Exp.	x_{1az} Calc.
66.7	0.615	0.615
116.5	0.665	0.665
165.9	0.700	0.692
217.0	0.730	0.726
268.7	0.755	0.755

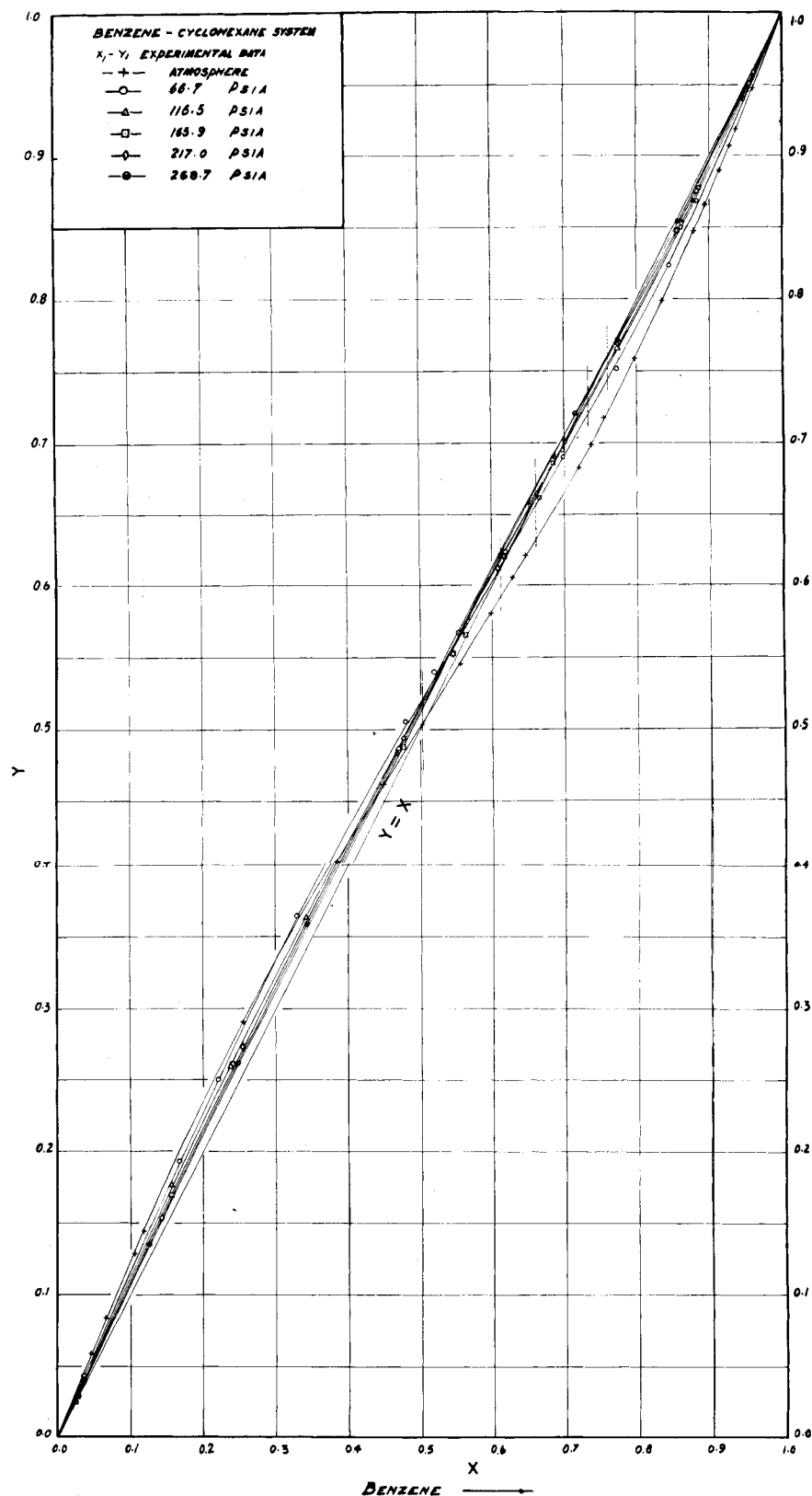
Fig. 9. Benzene-cyclohexane y-x diagram for five pressures.

$$m = \frac{9.7727}{\pi} + 0.9961 \qquad (13)$$

$$c = -2.825(10^{-5})\pi + 0.0267 \qquad (14)$$

Correlation of Azeotrope Data

The relation between the temperature and pressure of the azeotrope in the benzene-cyclohexane system is shown in Figure 15 and expressed by the equation

$$\log T = 2.4074 + 0.1147 \log \pi \qquad (15)$$

where

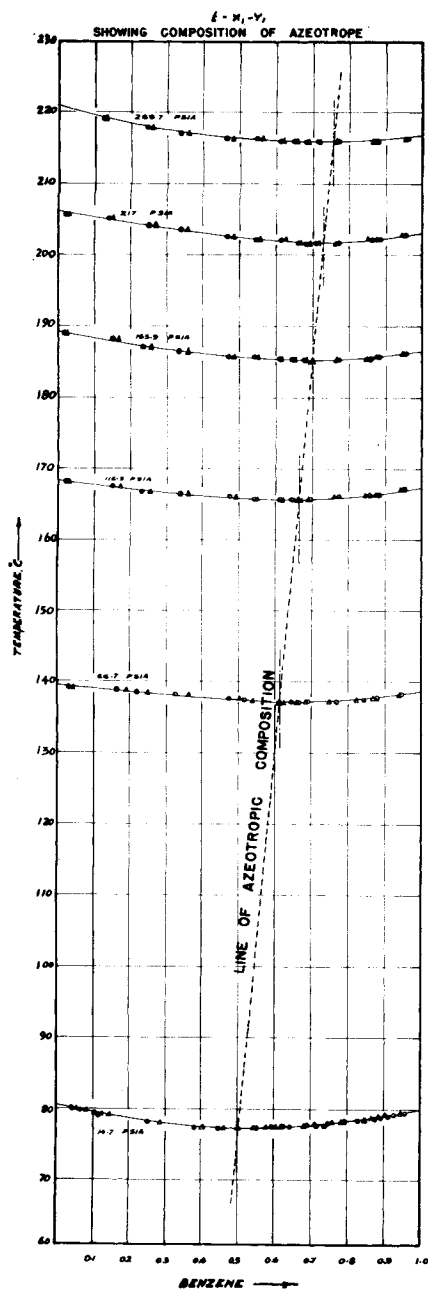T = boiling point of azeotrope in °K.
π = pressure, lb./sq. in. abs.

Fig. 10. Benzene-cyclohexane t, x, p for azeotrope.

At any pressure π the composition of the azeotrope may be derived from Equations (12), (13), and (14) to give

$$x_{1_{az}} = \frac{1}{1 + 10^k} \qquad (16)$$

where

$$k = 0.00724\pi\left[\frac{\pi - 945.1}{\pi + 2505.8}\right] \qquad (17)$$

The azeotropic temperature at the same pressure may also be calculated from Equation (15). A comparison of experimental with calculated values of $x_{1_{az}}$ and t_{az} are tabulated in Table 21.

SUMMARY AND CONCLUSIONS

Vapor-liquid equilibria data are reported on the two binary systems
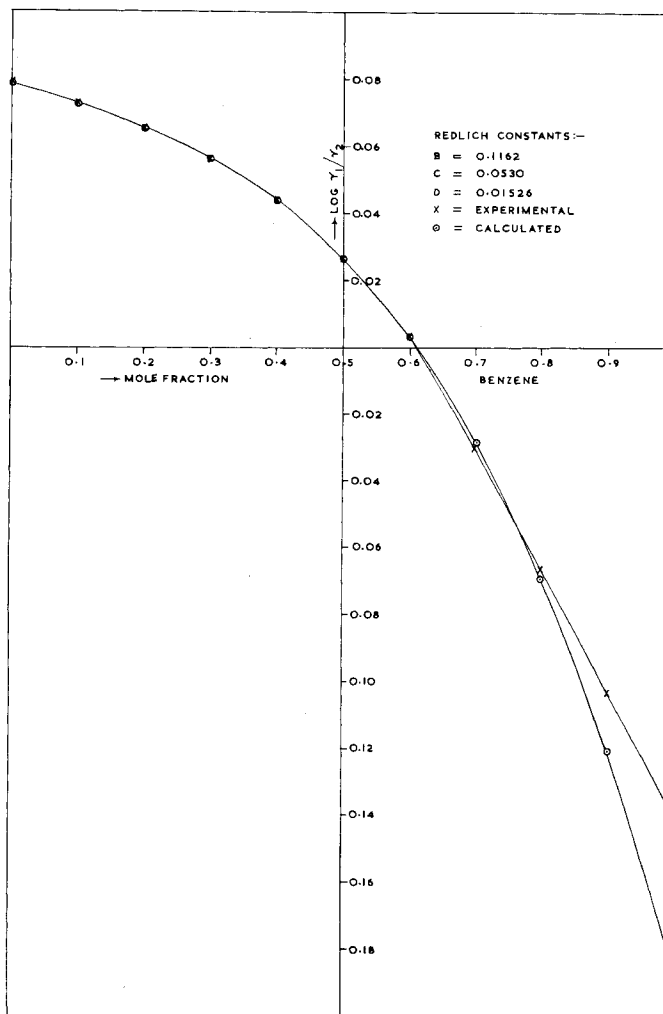
Fig. 11. Benzene-cyclohexane log γ_1/γ_2 vs. x at 66.7 lb./sq. in. abs.
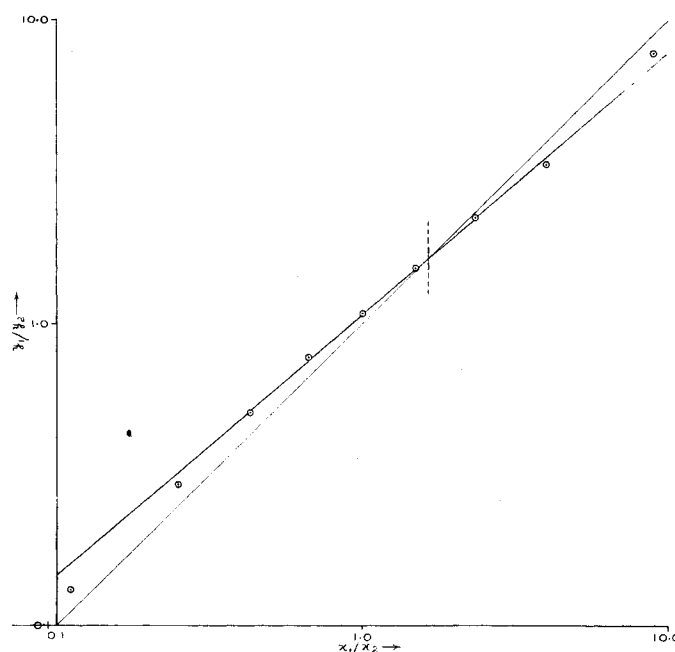

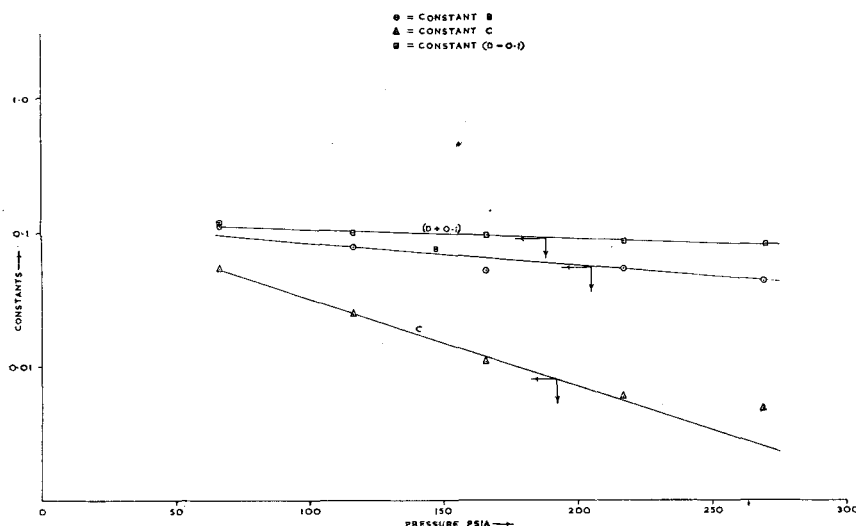Fig. 12. Benzene-cyclohexane Redlich-Kister constants vs. pressure.

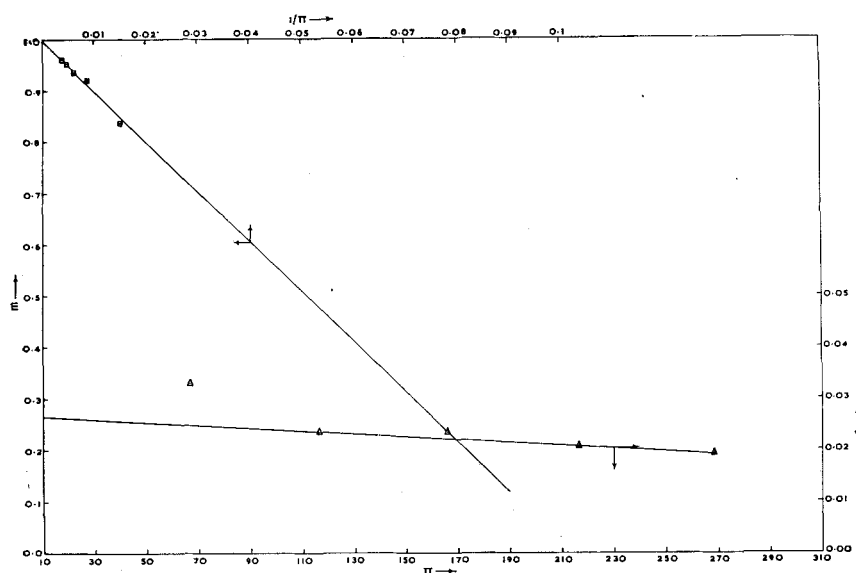Fig. 13. Benzene-cyclohexane log y_1/y_2 vs. log x_1/x_2 at 66.7 lb./sq. in abs.

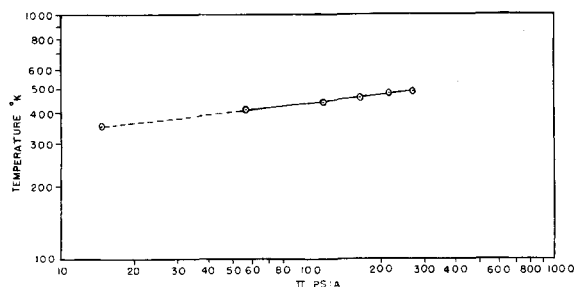Fig. 14 Benzene-cyclohexane m and c vs. pressure.

Fig. 15. Effect of pressure upon temperature of azeotrope of benzene-cyclohexane.

For benzene-n-hexane

$\log B = -0.00242\pi - 0.8043$
$\log (-C) = 0.00114\pi - 1.6868$
$\log (D + 0.01) = 0.00594\pi - 2.6416$

For benzene-cyclohexane

$\log B = -0.0016\pi - 0.9228$
$\log C = -0.0063\pi - 0.8866$
$\log (D + 0.01) = -0.0007\pi - 0.8948$

For the benzene-cyclohexane system empirical correlations are given for the change of the azeotrope composition with temperature and pressure.

A simple modified method is given for representing the y-x data of these two binary systems.

NOTATION

B, C, D = constants of the Redlich-Kister equation
c = empirical constant
m = empirical constant
P_1, P_2 = vapor pressures of the pure components 1 and 2, lb./sq. in. abs.
t_0 = true temperature, °C.
t = temperature recorded by the thermocouple, °C.
x_1, x_2 = mole fraction of components 1 and 2 in the liquid phase
y_1, y_2 = mole fractions of components 1 and 2 in the vapor phase
γ = activity coefficient
π = total pressure, lb./sq. in. abs.

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benzene-n-hexane and benzene-cyclohexane for the pressure range from 4 to 18 atm. Lack of correction for the fugacities in the vapor phase introduces a maximum error of 4% in activity coefficients. The three-constant Redlich-Kister equation satisfactorily represents the ratio of activity coefficients of both binary systems:

$\log \dfrac{\gamma_1}{\gamma_2} = B(1 - x_1)$
$\qquad + C[6x_1(1 - x_1) - 1]$
$\qquad + D(1 - 2x_1)[1 - 8x_1(1 - x_1)]$

With the benzene-n-hexane system no azeotrope was found. The values of B, C, and D are reported as functions of pressure by the following: