Subscripts

1	refers to unburned gas
2	refers to incident detonation wave
3	refers to reflected detonation wave
4	refers to final explosion condition
a	refers to H_2O
b	refers to H_2
c	refers to O_2
d	refers to OH
e	refers to H
f	refers to O
j	refers to *j*th component
k	refers to knallgas
r	refers to reflected wave

ACKNOWLEDGMENT

The authors express their grateful acknowledgment to Oak Ridge National Laboratory and the Union Carbide Nuclear Co., under whose auspices this work was performed.

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RECEIVED for review March 17, 1958. Accepted October 1, 1958.

Vapor-Liquid Equilibria at Atmospheric and Subatmospheric Pressures for System *n*-Hexane–Methylcyclopentane

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Vapor-liquid equilibrium data at pressures of 760, 600, 400, and 200 mm. of mercury were determined for the system *n*-hexane and methylcyclopentane. This particular binary system was investigated because of the different types of hydrocarbon compounds involved, *n*-hexane being a straight-chain saturated paraffin and methylcyclopentane being a saturated cycloparaffin, and the narrow range of boiling temperatures.

The experimental results show that this binary system behaves ideally in the liquid. The experimental results obtained at a pressure of 760 mm. of mercury are compared with the data obtained by Myers (*4*). The agreement between the two sets of experimental data is reasonably good.

Expressions were developed which would be useful to those who wish to use this binary system to calibrate distillation columns.

PURITY OF COMPOUNDS

The methylcyclopentane and *n*-hexane used in the experimental work were pure grade materials obtained from the Phillips Petroleum Co. and had a minimum purity of 99 mole %. These materials were used without further purification. Table I reports the physical constants for these chemicals and for comparison, similar data on the pure compounds.

EXPERIMENTAL METHOD

The vapor-liquid equilibrium data were determined in a Braun still designed by Hipkin and Myers (*3*). The operating procedure used was essentially the same as used by these authors and has been described by Wagner and Weber (*6*) and Nielsen and Weber (*5*).

The composition of the various mixtures was determined by measuring their refractive indices at 25° C. An Abbé refractometer was used, and the possible error in the readings was ±0.0001. For the system *n*-hexane (η = 1.3723) and methyl-

Table I. Properties of Pure Compounds

	Experimental	Literature
Methylcyclopentane		
Density, 25° C., grams/ml.	0.7443	0.74394 (*1*)
Refractive index, 25° C.	1.4070	1.40700 (*1*)
Vapor pressure, mm. Hg.		
760	71.72° C	71.81° C (*1*)
600	64.32	64.33 (*1*)
400	52.29	52.32 (*1*)
200	39.92	33.96 (*1*)
n-Hexane		
Density, 25° C., grams/ml.	0.6542	0.65481 (*1*)
Refractive index, 25° C.	1.3723	1.37226 (*1*)
Vapor pressure, mm. Hg.		
760	68.77° C	68.74° C (*1*)
600	61.40	61.40 (*1*)
400	49.67	49.63 (*1*)
200	31.68	31.61 (*1*)

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cyclohexane (η = 1.4070) a change in value of the refractive index of this magnitude represents a change in the composition of approximately 0.3%.

VAPOR-LIQUID EQUILIBRIUM DATA

From the experimental data, liquid phase activity coefficients of each component were calculated from the expression

$$\gamma = yP/xP_v \qquad (1)$$

Equation 1 is valid only for conditions under which the ratio of f^0_1/f^0_v is equal to the ratio of Pv/P. The majority of the calculated liquid phase activity coefficient values were equal to 1.00 ± 0.02. A difference of 2% in the activity coefficient could, in most cases, be attributed to the fact that the possible error in the compositions was 0.3%. There was no consistent trend observed in the values of activity coefficients—i.e., the number of values slightly greater than unity was approximately equal to the number of values slightly less than unity.

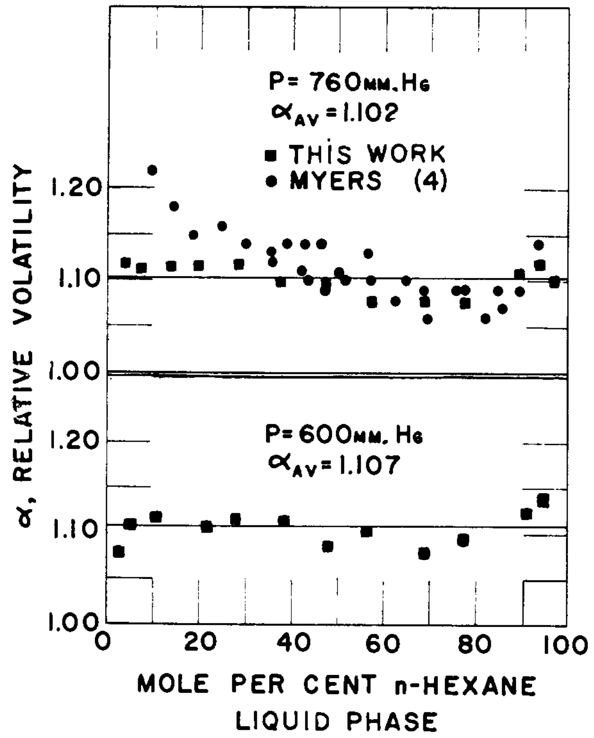

Figure 1. Relative volatility of *n*-hexane in the *n*-hexane–methylcyclopentane system

At pressures of 760 and 600 mm. of mercury

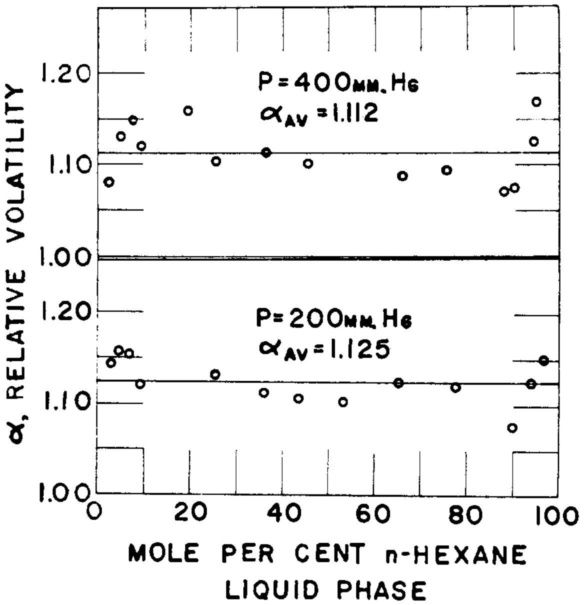

Figure 2. Relative volatility of *n*-hexane in the *n*-hexane–methylcyclopentane system

At pressures of 400 and 200 mm. of mercury

Table II. Vapor-Liquid Equilibrium

(Smoothed data for methylcyclopentane–*n*-hexane system)

Mixture Composition, Mole Fraction *n*-Hexane	Bubble Point, °C.	Dew Point, °C.
P = 760 mm. Hg.	α = 1.102	
0.000	71.72	71.72
0.050	71.48	71.54
0.100	71.23	71.31
0.200	70.82	70.94
0.300	70.46	70.58
0.400	70.13	70.26
0.500	69.82	69.94
0.600	69.55	69.66
0.700	69.30	69.43
0.800	69.07	69.20
0.900	68.90	68.96
0.950	68.82	68.88
1.000	68.77	68.77
P = 600 mm. Hg.	α = 1.107	
0.000	64.32	64.32
0.050	64.17	64.25
0.100	64.00	64.12
0.200	63.70	63.83
0.300	63.43	63.52
0.400	63.14	63.22
0.500	62.81	62.93
0.600	62.52	62.64
0.700	62.23	62.35
0.800	61.94	62.03
0.900	61.67	61.75
0.950	61.53	61.60
1.000	61.40	61.40
P = 400 mm. Hg.	α = 1.112	
0.000	52.29	52.29
0.050	52.08	52.20
0.100	51.87	52.00
0.200	51.48	51.63
0.300	51.11	51.26
0.400	50.75	50.92
0.500	50.40	50.56
0.600	50.11	50.27
0.700	50.00	50.13
0.800	49.89	49.98
0.900	49.78	49.82
0.950	49.70	49.75
1.000	49.67	49.67
P = 200 mm. Hg.	α = 1.125	
0.000	33.92	33.92
0.050	33.75	33.82
0.100	33.61	33.73
0.200	33.35	33.52
0.300	33.13	33.34
0.400	32.93	33.13
0.500	32.71	32.91
0.600	32.50	32.68
0.700	32.26	32.46
0.800	32.02	32.22
0.900	31.82	31.97
0.950	31.75	31.83
1.000	31.68	31.68

In view of this fact, the data were smoothed by using relative volatilities which were determined from the experimental data. Calculated average values of the relative volatilities varied from 1.102 to 1.125 while relative volatilities determined from vapor pressure data ranged from 1.091 to 1.122. The experimental data and the smoothed relative volatility curves for the four pressures are shown in graphical form in Figures 1 and 2. The smoothed vapor-liquid equilibrium data and the bubble point and dew point temperatures are reported in Table II.

Because of the low relative volatilities and narrow range of temperatures involved, the determination of vapor-liquid relationship for this system was a rather severe test of the experimental equipment.

The *n*-hexane–methylcyclopentane has advantages which would recommend its use for the calibration of distillation columns: its ideal behavior, the degree of difficulty encountered in the separation of these compounds, its narrow temperature range, and the general similarity of physical properties.

If this system were used to calibrate a distillation column, an analytical solution for the number of plates would be preferable to a graphical one. For this reason a relationship was developed between composition and refractive index. This relationship can be presented as:

$$\log \eta = 0.14829 - 0.0128x_1 + 0.002x^2_1 \qquad (2)$$

or, solving for x_1,

$$x_1 = \frac{1.28 \times 10^{2} \sqrt{1.6384 \times 10^{-4} - 8 \times 10^{-3} \log \frac{1.4070}{\eta}}}{4 \times 10^{-3}} \qquad (2a)$$

Equation 2 predicts the refractive index at a given composition to ±0.0001 and Equation 2a predicts the composition to 0.001 mole %. The value of the refractive index at 25° C. should be used in these expressions and the following equations.

If Equation 2a is substituted into the Fenske equation (*2*), which relates the number of plates to the distillate and bottom composition and an average relative volatility at total reflux, the result is:

$$N = \frac{\log\left[\left(\frac{3.200 - Z}{Z - 2.200}\right)_d \left(\frac{Z - 2.200}{3.200 - Z}\right)_w\right]}{0.0453} \qquad (3)$$

where

$$Z = \left(10.240 - 500 \log \frac{1.4070}{\eta}\right)^{1/2} \qquad (3a)$$

An average relative volatility of 1.11 was assumed in the development of Equation 3. In the calibration of distillation columns, the refractive indices of the distillate and bottoms need only be measured and their respective values substituted in Equations 3 and 3a for the determination of the number of theoretical stages.

In a more rapid, but perhaps less accurate, graphical solution (Figure 3) the refractive index and number of plates are plotted *vs.* mole per cent of *n*-hexane. To construct Figure 3 a bottoms composition must be assumed. In this instance, a bottoms which contained 5 mole % of *n*-hexane was used. Figure 3 can be used for cases in which the bottoms composition is not 5 mole % of *n*-hexane. The difference can be taken in account by the use of Figure 3 if the bottoms contains more than 5 mole % of *n*-hexane; otherwise, Equations 3 and 3a must be used in conjunction with Figure 3.

The following examples illustrate the use of Figure 3,

Example 1. Given:

η (distillate) = 1.3729
η (bottoms) = 1.4049

Determine: Number of theoretical plates required at total reflux.

From the η *vs.* composition relationship obviously the bottoms contains 5 mole % of *n*-hexane; therefore, the graph can be used directly. The composition of the distillate determined from the graph is 98.3% of *n*-hexane. From the point which represents composition of the distillate, a vertical line can be drawn to the curve which represents the relationship between number of theoretical plates required and composition. At the intersection of the vertical line and this curve, a horizontal line is drawn to the right-hand ordinate, and the number of plates required for the separation is read. In this example:

$$N = 65.3$$

Example 2. Given:

η (distillate) = 1.3729 (same as Example 1)
η (bottoms) = 1.4000

Determine: Number of theoretical plates required at total reflux.

The bottoms contains more than 5 mole % of *n*-hexane, specifically 17.3%. Hence, the number of plates required to produce a 17.3 mole % of *n*-hexane distillate and a 5 mole % of bottoms must be determined. The procedure would be funda-

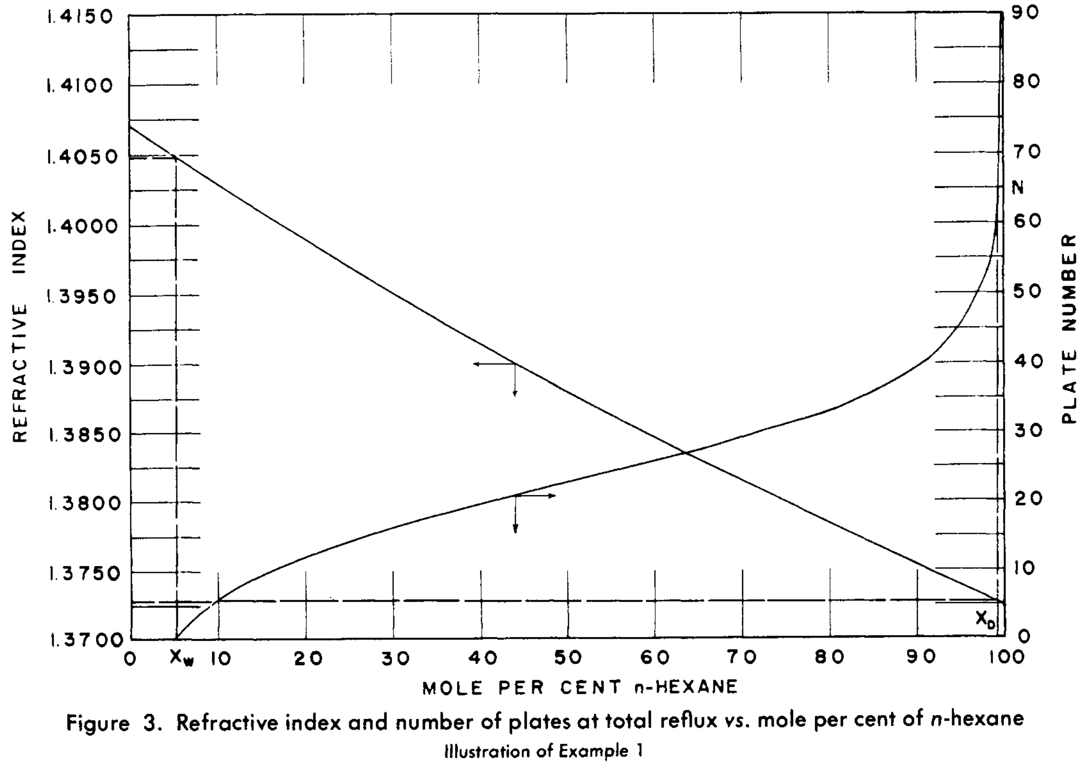

Figure 3. Refractive index and number of plates at total reflux vs. mole per cent of *n*-hexane

Illustration of Example 1

mentally the same as that used in Example 1. The number of theoretical plates required for this separation, obtained from Figure 3, is 13.1. Therefore, to achieve the separation desired, the required number of plates is the difference between the result obtained in Example 1, $\mathcal{N}$ = 65.3, and 13.1, or 52.2 theoretical plates.

NOMENCLATURE

$\mathcal{N}$ = number of plates in distillation column
P = total pressure, mm. of mercury
P_v = vapor pressure, mm. of mercury
f^0 = fugacity of pure component in standard state at temperature and pressure of system
x = mole fraction in liquid phase
y = mole fraction in vapor phase
α = relative volatility
γ = liquid phase activity coefficient
η = refractive index

Subscripts

av refers to average value of property
d refers to distillate
l refers to liquid
v refers to vapor
w refers to bottoms

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RECEIVED for review July 14, 1958. Accepted October 13, 1958.

Vapor-Liquid Equilibria at Subatmospheric Pressures

Binary and Ternary Systems Containing Ethyl Alcohol, Benzene, and *n*-Heptane

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Vapor-liquid equilibrium data were determined for the ethyl alcohol-benzene and benzene-*n*-heptane binary systems at pressures of 400 and 180 mm. of mercury. Similar data at a pressure of 760 mm. of mercury had previously been determined for the ethyl alcohol-benzene system by Barbaudy (*1*) and for the benzene-*n*-heptane system by Myers (*10*) and Sieg (*12*). These binary systems have now been investigated at three pressures. As in the case at atmospheric pressure, the ethyl alcohol-benzene system deviated greatly from ideal liquid phase behavior and showed a minimum boiling azeotrope at each reduced pressure. On the other hand, the benzene-*n*-heptane system departed from ideal liquid phase behavior to a lesser extent.

Vapor-liquid equilibrium data for the ethyl alcohol-benzene-*n*-heptane system at a pressure of 400 mm. of mercury supplement the data on this ternary system, determined at atmospheric pressure by Wagner and Weber (*13*). The information reported in this article and by Katz and Newman (*5*) include ternary vapor-liquid equilibrium data and similar data for the three possible binary systems at a pressure of 400 mm. of mercury for the system ethyl alcohol-benzene-*n*-heptane.

The ternary system showed large deviations from ideal liquid phase behavior, but no ternary azeotrope was found.

PURITY OF COMPOUNDS

The benzene and *n*-heptane used in this study were pure grade materials of 99 mole % minimum purity obtained from the Phillips Petroleum Co. The ethyl alcohol was manufactured by the United States Industrial Chemical Co. These chemicals were used without further purification. Physical constants for the materials appear in Table I.

Binary Systems Ethyl Alcohol-Benzene and Benzene-*n*-Heptane

EXPERIMENTAL METHOD

Vapor-liquid equilibrium data were obtained using a Braun still as described by Hipkin and Myers (*4*), and the experimental technique outlined by these authors was followed. Constant subatmospheric pressures were obtained using a manostat and vacuum pump. Jacket and still pressures were measured using absolute manometers. Samples were drawn by reducing the pressure in the sample receivers to 2 or 3 mm. of mercury below the still pressure, the pressure difference being measured with a differential manometer. The pressures could be read to 0.1 mm. of mercury, and the still pressure was kept within 0.5 mm. of mercury of the desired pressure.

Temperatures in the vapor spaces of the still and jacket were obtained by the use of a Leeds & Northrup Type K potentiometer in conjunction with copper-constantan thermocouples. The thermocouples were placed in thermowells provided in the apparatus. This arrangement allowed temperatures to be read to ±0.1° C. The jacket temperature was matched to within 0.05° C. of the still temperature, the jacket temperature being controlled by adjusting the jacket pressure. Pure benzene was used as the jacket fluid.

Table I. Properties of Pure Compounds

	Ethyl alcohol		Benzene		*n*-Heptane	
	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)
Density, 25°C., g/ml.	0.7843	0.78404	0.8732	0.87368	0.6786	0.67947
Refractive index, 25° C.	1.3591	1.35914	1.4976	1.49790	1.3851	1.38517
Boiling point, °C. at 760 mm. Hg	78.3	78.33	80.0	80.103	98.4	98.428
Boiling point, °C. at 400 mm. Hg	62.6	62.91	60.3	60.60	77.9	77.89
Boiling point, °C. at 180 mm. Hg	45.7	45.81	39.5	39.62	56.1	55.98

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