VAPOR-LIQUID EQUILIBRIA AMONG THE C_6 HYDROCARBONS

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INTRODUCTION

Fractional distillation is defined as a process of separating a mixture of two or more volatile substances into its individual components. Separation is achieved by successive vaporization and condensation into fractions of successively varying composition until the desired degree of separation is reached (9).

A separation of a mixture of volatile liquids by fractional distillation is possible when the composition of the vapor coming from the liquid mixture is different from that of the liquid. The greater the difference between the vapor and liquid compositions, the easier the separation. In order to design fractional distillation equipment it is necessary to know the relation between vapor and liquid compositions. Usually this is obtained from measurements of the vapor and liquid compositions in equilibrium with one another.

When one liquid is dissolved in another the partial pressure of each is decreased (10). When the two liquids are composed of molecules of the same size and structure and mix without such complicating effects as molecular association or chemical combination, the reduction in partial pressure of each is in proportion to its concentration. Such a mixture is termed ideal. In this ideal mixture the partial pressure of each component will be equal to the product of the vapor pressure of the pure component and its mol fraction in the mixture. This generalization is known as Raoult's Law. It is expressed by the relationship,

$$p_a = P_a x_a$$

where: p_a is the partial pressure of component A in the solution

x_a is the mol fraction of A in the solution

P_a is the vapor pressure of pure A at the temperature of the solution.

Because of the nature of the assumptions made in deriving Raoult's law there are relatively few systems to which it applies rigorously. Deviations from Raoult's law range from moderate - for such systems as paraffin and aromatic hydrocarbons - to large for a system such as hydrogen chloride-water.

In non-ideal systems it is necessary to use basic thermodynamic relations to derive expressions for the equilibria involved. These basic thermodynamic expressions may be applied readily to the vapor phase to calculate deviations from ideal behavior but there are no convenient conditions for calculating liquid phase deviations due to association or chemical reaction. For this reason it is customary to use as a basis the pure liquids before they are mixed and then calculate the deviations resulting from mixing. These deviations are then lumped together in what is termed an activity coefficient which is inserted on the right hand side of the equation to make it exact:

$$p_a = \gamma_a P_a x_a$$

At low pressures - two atmospheres or less - deviations from ideal behavior in the vapor phase are small and it is general practice to ignore them. Under these conditions the pressure of any component is equivalent to the product of the system pressure and the mol fraction of that component in the vapor phase. The vapor-liquid equilibrium expression then becomes:

$$\pi y_a = \gamma_a P_a x_a$$

in which π is the system pressure.

A number of attempts have been made to calculate the value of γ from the physical properties of the substances in the mixture and the thermodynamic changes occurring on mixing. Van Laar attempted to calculate the internal energy of mixing by the use of the van der Waals equation of state. It was necessary for him to make certain simplifying assumptions which were (11):

1. The excess partial molal entropy of mixing is zero.
2. There is no volume change on mixing.
3. Van der Waals equation applies to each component and to the mixture, for both liquid and vapor phases.
4. The van der Waals constants of the mixture can be calculated from the constants of the pure constituents.

On the basis of these assumptions Van Laar derived the following equations for expressing the activity coefficients as functions of the van der Waals constants for the mixture:

$$\ln \gamma_1 = \frac{B}{T(1 + A\frac{x_1}{x_2})^2} \quad ; \quad \ln \gamma_2 = \frac{AB}{T(A + \frac{x_2}{x_1})^2}$$

where $A = b_1/b_2$

$B = (b_1/R)\ (\sqrt{a_1}/b_1 - \sqrt{a_2}/b_2)^2$

a and b are the constants in the van der Waals equation of state, $P = RT/(V-b) - a/V^2$

R = Universal gas constant - liter-atmospheres/mol - °Kelvin

Similar expressions were derived by Scatchard and Hildebrand and by Cooper (12) using different assumptions and different expressions for evaluating the internal energy change in mixing per mol of mixture.

On the basis of the derivations, the two constants of the Van Laar equations, or the modifications of them, are related to the physical properties of the two components. However because of the assumptions made in the derivations it is seldom that an actual mixture fits the equations. In general practice the equations are used empirically and the constants chosen to fit the observed data.

Two constants are used in the equations. Since in a binary mixture one vapor-liquid equilibrium point gives the activity coefficients of both components only one measurement is required. Such a procedure has seldom been found satisfactory since any errors involved in the single point measurement will be reflected in the values of the constants. In practice a number of equilibrium points are measured covering the entire concentration range. In this case the Van Laar equations are rearranged to the following:

$$\frac{1}{\sqrt{T \ln \gamma_1}} = \frac{1}{\sqrt{B}} + \frac{A}{\sqrt{B}}\left(\frac{x_1}{x_2}\right) \quad ; \quad \frac{1}{\sqrt{T \ln \gamma_2}} = \frac{A}{\sqrt{AB}} + \frac{1}{\sqrt{AB}}\left(\frac{x_2}{x_1}\right)$$

These are the equations of two straight lines of different but related slopes and intercepts. The constants A and B are readily calculated from the values of the individual slopes and intercepts. Ideally the values of A and B derived from each curve should be equal. Actually because of experimental errors the constants will be different from each plot. The magnitude of the difference is a measure of the accuracy of the data.

Somewhat better data correlation is obtained by eliminating x_1 and x_2 from the Van Laar equations. The resulting equation is:

$$\sqrt{T \ln \gamma_1} = \sqrt{B} - \sqrt{A} \cdot \sqrt{T \ln \gamma_2}$$

This is also the equation of a straight line with slope of $-\sqrt{A}$ and intercept equal to $\sqrt{B}$.

Although x_1 and x_2 do not appear directly they are included indirectly in the $\ln \gamma$ terms. Errors in the values of x are of a smaller magnitude then the corresponding values of $x/(1 - x)$. As a result the data plotted in this manner show less scattering. Also this type of plot gives more weight to points obtained in the middle composition ranges where the effects of analytical errors are minimized whereas the other forms of the Van Laar equations tend to emphasize points obtained in the terminal concentration regions where analytical errors are intensified.

Consequently this form of the Van Laar equations was used to correlate data from the naphthene-naphthene and paraffin-paraffin binary systems which are essentially ideal.

In the design of fractionating columns the concept of relative volatility is often used. This is defined as the volatility of one component with respect to a second. Volatility is defined as the partial pressure of a component in the vapor in equilibrium with a liquid phase divided by the mol fraction in the liquid or:

$$\text{volatility} = \pi y/x$$

$$\text{relative volatility} = \alpha = (\pi y_a/x_a)/(\pi y_b/x_b) = y_a x_b / x_a y_b.$$

In an ideal system the partial pressure in the vapor is equal to the vapor pressure of the pure component times its mol fraction in the liquid. Relative volatility in an ideal system reduces to the ratio of the vapor pressures of the pure components:

$$\alpha = P_a/P_b$$

In systems which are non-ideal the partial pressure of a component in the vapor is the product of its vapor pressure times its mol fraction in the liquid times its activity coefficient. Relative volatility for non-ideal systems then becomes:

$$\alpha = \gamma_a P_a / \gamma_b P_b$$

The utility of the concept of relative volatility is that it shows at a glance the ease or difficulty of making a given separation by distillation. The greater the value of α the more easily may the separation be made. As α approaches unity the separation becomes more difficult. When $\alpha = 1$ separation by distillation is impossible.

In ideal systems relative volatility, or the ratio of the vapor pressures of the pure components, changes only slightly with temperature although the individual volatilities or vapor pressures change greatly. In non-ideal systems the relatively constant vapor pressure ratio is modified by the activity coefficient ratio which may vary greatly with changes in liquid composition. In systems which form constant boiling mixtures, or azeotropes, the relative volatility will range from below unity to above unity over the entire composition range. At the azeotrope composition α is unity and no separation is possible.

In Figures 3, 4, 5, and 6 relative volatilities of the C_6 paraffins, naphthenes and benzene with respect to hexane, methylcyclopentane, cyclohexane, and benzene are plotted as functions of the composition of the liquid phase. For the non-ideal systems the activity coefficients were calculated using the average values of the Van Laar equation coefficients reported in Tables I-XXI. For the paraffin systems which are considered to be ideal the relative volatility is calculated as the vapor pressure ratio.

Although vapor-liquid equilibrium data have been published for a great many systems only a relatively few systems composed of C_6 hydrocarbons have been studied. Of the eight hydrocarbons only 4, hexane, methylcyclopentane, cyclohexane, and benzene have been investigated. This study was made to complete the data involving these compounds.

EXPERIMENTAL MATERIALS AND EQUIPMENT

1. Hydrocarbons. Pure grade hydrocarbons were used in all experiments. In most cases the original stock which had a minimum purity of 99.0 mol per cent was distilled in a 36" x 25mm Podbielniak Heli-grid packed Hyper-Cal Fractionating column. A center-cut from this distillation was used after discarding the initial and final ten per cent distilled. The hydrocarbons are tabulated below along with their refractive indices.

Compound	n_D^{20}	B.P.-°C (760mm Hg)
2,2-dimethylbutane	1.3688	49.74
2,3-dimethylbutane	1.3749	57.82
2-methylpentane	1.3715	60.24
3-methylpentane	1.3765	63.28
n-Hexane	1.3749	68.74
Methylcyclopentane	1.4099	71.80
Cyclohexane	1.4260	80.78
Benzene	1.5011	80.10

Analyses of these materials by gas-liquid chromatography are tabulated in the appendix.

2. An American Optical Company Spencer refractometer was used to measure the refractive index of the paraffin-naphthene, paraffin-aromatic, and naphthene-aromatic mixtures. It has a precision of ±0.0001 refractive index units.

3. An American Instrument Company constant temperature bath was used to circulate water through the prisms of the refractometer. It maintained a temperature of 20±0.05 degrees Centigrade.

4. Vapor-Liquid Equilibrium Stills. A great number of vapor-liquid equilibrium stills have been designed. Barr-David (1) has made a survey of the types of stills most commonly used along with the advantages and disadvantages of each. Ideally the still should require a minimum of attention while operating and should come to equilibrium in a short time.

Two types of stills were used in this work. One was a vapor recirculating still and the other a Cottrell pump with means for separating and collecting the vapor and liquid phases. A number of systems were run in each still. Good agreement was obtained indicating that either still was acceptable.

a. Modified Hipkin and Myers Still, Figure 1. This still was adapted from a design by Hipkin and Myers (4). In their design, heat transfer from or to the still was reduced to a minimum by boiling and condensing a liquid of similar boiling point in the jacket space around the still. Pressure on the jacket was varied so that the boiling point of the jacket liquid would be the same as the mixture under consideration in the still.

Although this system reduces heat transfer to a minimum it requires two heaters and two pressure control systems as well as two sets of thermocouples to record still and jacket temperatures.

In order to simplify operation the separate jacket heating system was omitted. Vapors from the reboiler flowed through the annular space around the still proper to a condenser where they were condensed and returned to the reboiler. As air collected in this condenser it was bled off to the atmosphere to maintain a ring of reflux in the condenser

Other vapors from the reboiler bubbled through the liquid and then passed to a condenser where they were condensed and returned to the reboiler. This second condenser was connected to the pressure control system.

When this still was used it was observed that the liquid level in the liquid sample cup varied with time. This was believed due to a slight flow of heat to or from this portion of the still which would cause refluxing to take place in the vapor space above this point or would boil off some of the liquid phase sample. For this reason a new still of simpler design was constructed from a design by Gillespie (3).

b. Modified Gillespie Still, Figure 2. This still was constructed from the design originated by Gillespie (3). The position of the vapor condenser was altered to provide a more compact unit. Vapor and liquid sample points were changed from the original design and were altered to allow samples to be drawn off by hypodermic syringe.

This still makes use of a Cottrell pump to carry an intimate mixture of liquid and vapor to the disengaging zone in which the two phases are separated. The liquid phase returns directly to the reboiler. The vapor phase is totally condensed in the external condenser. Condensed vapor phase is mixed with the returning liquid phase ahead of the reboiler. Thus the liquid mixture returned to the reboiler is the same composition as the liquid in the reboiler.

5. Temperatures were read from an A.S.T.M. 14C, paraffin melting point thermometer, 79mm immersion, graduated 38-82 °C in 0.1 °C divisions. Temperature readings were precise to ±0.02 °C.

The thermometer was immersed directly in the fluid being measured. An "O" ring sealed the thermometer to the male portion of a standard taper joint which fitted the female joint sealed to the still.

6. Still pressure was held at 760mm mercury pressure by means of an Emil Greiner Cartesion Manostat #6.

7. All stopcocks and ground glass joints were lubricated with Non-Aq stopcock lubricant which is hydrocarbon insoluble.

8. Reboiler heat was supplied by a suitable Glas-Col heating mantle controlled by a Variac.

EXPERIMENTAL PROCEDURES

When the modified Hipkin and Myers still was used it was charged with 200 cc of a pure component. Heat was applied to the reboiler. When reflux was established in the vapor condenser the sample stopcock was turned to shut off flow of condensate to the reboiler. This caused reflux to overflow from the condenser into the liquid sample pot. When sufficient liquid had accumulated the vapor sample stopcock was turned to allow condensate to flow from the condenser back to the reboiler.

Heat input to the reboiler was then adjusted to give the desired amount of reflux in the two condensers. At this point a measured volume of the second component was introduced into the vapor condensate stream. The still was then allowed to operate for 30-35 minutes to come to equilibrium. Equilibration time of the still was determined and found to be less than 30 minutes. Such data are shown in the Appendix. During this interval the jacket condenser was bled off as necessary to prevent the top of the jacket from "gassing-off" with air and the pressure control manostat was adjusted to give the desired pressure in the still.

At the end of the equilibration period the still pressure and temperature were noted and samples taken of the vapor and liquid phases. Vapor phase samples were taken by evacuating the sample system, shutting off the vacuum, and turning the sample stopcock so that condensed vapor flowed into the sample receiver. When a sufficient volume had collected the sample stopcock was returned to its original position.

Liquid samples were taken by first draining off 4-5 cc to flush out the sample line. The sample receiver was then installed and evacuated and the sample collected as for the vapor sample.

After collecting the samples a measured volume of the second component was introduced to the system and the process repeated. This procedure was repeated until approximately equimolar concentrations of the two components were reached. The still was then shut down, drained, and evacuated.

The still was then charged with 200 cc of the second component and the procedure repeated.

The refractive indices of the vapor and liquid phase samples were measured using the Spencer refractometer. Compositions of the two phases were then determined from a calibration curve relating the refractive index of the mixture to its composition. Such calibration curves were made up for each of the paraffin-naphthene, paraffin-aromatic, naphthene-aromatic, and naphthene-naphthene systems studied. These data are tabulated in the appendix.

When the modified Gillespie still was used it was charged with 110-115 cc of one component. Heat was applied to the reboiler and adjusted to give the desired reflux in the vapor condenser. The pressure control manostat was adjusted to give the desired pressure. When the system was operating as desired a measured volume of the second component was added to the reboiler. The still was allowed to operate for a minimum of 30 minutes to allow it to reach equilibrium. Actually a steady state was reached in 10-15 minutes. Equilibration time data for this still are in the appendix.

At the end of the equilibration period samples of the vapor and liquid phases were drawn off with hypodermic syringes and run on the refractometer. In the case of paraffin-paraffin systems the samples were transferred from the syringes to small glass ampoules sealed with rubber serum caps. Samples of the material in the ampoules were then analyzed by gas-liquid partition chromatography.

After sampling, a measured volume of the still contents was withdrawn and replaced with a similar volume of the second component. The still was allowed to reach equilibrium and samples again taken. This procedure was repeated until the mixture was approximately equimolar. At this point the still was shut down, drained and evacuated. It was then charged with the second pure component and the procedure repeated.

METHODS OF CALCULATIONS

Compositions of the vapor and liquid phases were determined either from refractive index measurements or by gas-liquid chromatography.

Vapor pressure - temperature curves for each of the eight hydrocarbons were constructed using the Antoine equation

$$\log P = A - B/(C+t)$$

where P is the vapor pressure in mm Hg

t is the temperature in °C

A, B, C are empirical constants, different for each compound.

Values of A, B, and C for each of the eight hydrocarbons were obtained from the data published by A.P.I. Project 44 (14). The curves so constructed are believed to be accurate to ±0.5 mm Hg. A sample curve is shown in Figure 7.

From the vapor and liquid phase compositions and the vapor pressures of the individual pure components at the observed temperature the activity coefficient was calculated for each component from the following equations

$$\gamma_1 = \pi y_1 / P_1 x_1$$

$$\gamma_2 = \pi y_2 / P_2 x_2$$

where γ_1, γ_2 are the activity coefficients of components 1 and 2 respectively.

y_1, y_2 are the mol fractions of components 1 and 2 in the vapor phase. In a binary system $y_1 + y_2 = 1$.

P_1, P_2 are the vapor pressures of components 1 and 2 respectively at the observed temperature.

x_1, x_2 are the mol fractions of components 1 and 2 in the liquid phase. In a binary system $x_1 + x_2 = 1$.

π is the total pressure on the system, 760 mm Hg in this study.

After calculating γ the value of $1/\sqrt{T \ln \gamma}$ was calculated where T is the absolute temperature and $\ln \gamma$ is the natural logarithm of γ. The values of $1/\sqrt{T \ln \gamma}$ were then plotted on rectangular coordinate paper as a function of the corresponding values of x_1/x_2. Ideally these points should fall on a straight line. By visual inspection of the plots certain points were rejected because of abnormal deviation. In this manner two sets of points were obtained approximating two different straight lines for each system studied. A typical plot of these points is shown in Figure 9.

A straight line was then fitted to each set of points using the method of least squares. This computation was carried out on an I.B.M. C.P.C. computer which derived the equations of the straight lines and determined the probable error of the measurements.

From the slope and intercept values of the two lines the Van Laar coefficients A and B were determined. These values are given in Tables I-XXI along with the observed x-y data on each binary system.

This method of correlation was not suitable for the systems which were only slightly non-ideal. In such systems the observed values of γ are very nearly unity and may be slightly less than unity because of experimental errors. Also a small experimental error in a number close to one becomes an appreciable error in the logarithm of that number. This causes the data to scatter considerably.

In these systems the data were correlated by eliminating x_1 and x_2 from the Van Laar equations. The resulting equation is:

$$\sqrt{T \ln \gamma_1} = \sqrt{B} - \sqrt{A} \cdot \sqrt{T \ln \gamma_2}$$

which is the equation of a straight line. This equation has the advantage of emphasizing points obtained in the middle range of compositions where analytical errors are minimized.

DISCUSSION OF RESULTS

Vapor-liquid equilibrium data for the systems studied are listed in Tables I-XXI and shown in Figures 3- 6. The greatest deviations from ideality are shown for the paraffin-aromatic and naphthene aromatic systems listed in Tables I-VII.
This is to be expected because of the fundamental differences in the nature of the molecules. The observed deviations however are not large compared to systems of chemically dissimilar compounds such as chloroform and acetone or to systems in which molecular association plays an important role such as hydrogen chloride and water.

Maximum deviation from ideality, as measured by the value of B in the Van Laar equations, was observed in the system benzene-neohexane. In this system the value of B was 170. Values of γ for benzene and neohexane, each at zero concentration, are 1.69 and 1.83 respectively. Despite this relatively large deviation the system did not form an azeotrope.

Minimum deviation from ideality, for binaries containing benzene, was observed in the system benzene-cyclohexane. In this system B had a value of 118.5. At zero concentrations of each component values of γ for benzene and cyclohexane respectively were 1.40 and 1.46. This deviation was sufficient for these close-boiling components to result in the formation of an azeotrope.

Azeotrope formation in this system has been reported in the literature. Composition and boiling point data are listed for comparison:

Azeotrope: System Benzene-Cyclohexane

B.P.-°C (760 mm Hg)	Mol Per Cent Benzene	Reference
77.65	54.2	This work
77.5	56.9	Perry (8)
77.7	53.6	Horsley (5)

An azeotrope was also observed in the system benzene-methylcyclopentane. Other investigators have also reported azeotropes. These data are summarized:

Azeotrope: System Benzene-Methylcyclopentane

B.P.-°C (760 mm Hg)	Mol Per Cent Benzene	Reference
71.5	10.0	Horsley (5)
71.68	14.0	This work
71.65	12.8	Myers (7)

A number of investigators have published data on the system benzene-normal hexane. Some report evidence of azeotrope formation, others do not. Inspection of the x-y data reported in Table V do not show evidence of an azeotrope. The values of the Van Laar coefficients however show that an azeotrope does form containing 1.57 mol per cent benzene. It is evident that the volatility of benzene in this mixture, in the region of the azeotrope, is so close to unity that the analytical method was not sensitive enough to show differences in the vapor and liquid compositions. Data reported on this system are shown below:

Azeotrope: System Benzene-Normal Hexane

B.P.-°C (760 mm Hg)	Mol Per Cent Benzene	Reference
68.72	1.57	This work
68.5	5.2	Horsley (5)
None	-	Horsley (5)

The systems benzene-neohexane, benzene-diisopropyl, benzene-2-methylpentane, and benzene-3-methylpentane did not form azeotropes. The relative volatility of benzene at zero concentration, in these mixtures increased with the increasing boiling point of the other component but the maximum was 0.893. For an azeotrope to exist the relative volatility would have to be greater than one.

The paraffin-naphthene systems listed in Tables VIII-XVIII and Figures 3-6 showed slight deviations from ideal solution laws. For systems in which cyclohexane was one of the components the Van Laar constant B varied between 29 and 57. Activity coefficients of the individual components at zero concentration were in the range 1.10-1.20. This indicates a maximum deviation from ideality of 10-20 per cent.

Data from these systems correlated quite well with the Van Laar equations except for the system cyclohexane-3-methylpentane. In this case values of both A and B obtained from the two straight line plots do not agree. The actual deviations are great but it is probable that the average values are reasonably accurate.

Systems in which methylcyclopentane was one of the components showed slightly smaller deviations from the ideal. Values of the Van Laar constant B varied between 10 and 26. Values of the activity coefficient for each component at infinite dilution ranged from 1.03 to 1.17.

A minimum boiling azeotrope of methylcyclopentane and hexane has been reported (2), (5). However, the data obtained in this work do not show an azeotrope. This result agrees with other published data on this system (6). None of the other paraffin-naphthene systems showed any tendency to form azeotropes.

The system cyclohexane-methylcyclopentane appears to be ideal within the limits of experimental error.

Refractive index was used to determine compositons. The total difference in refractive index for the pure components is 0.0265 units. An error of 0.0001 units in the refractive index is equivalent to an error of 0.4 mol per cent. In the concentration ranges in which either component is present at low concentration an error of this magnitude creates a considerable error in the x_1/x_2 ratio.

Data from the three paraffin-paraffin systems studied are presented in Tables XIX-XXI. Within the limits of experimental error these systems may be considered ideal. Analyses for these systems were made by gas-liquid partition chromatography. Composition errors for any component are probably of the order of 0.5 mol per cent. An error of this magnitude can easily lead to deviations of the activity coefficients from unity of several per cent. It is therefore concluded that these systems are ideal.

The three systems studied represent the extremes in boiling point and molecular structure differences. Since they are ideal it was concluded that the other paraffin-paraffin systems are also ideal. It was not considered necessary to study these systems.

SUMMARY AND CONCLUSIONS

Vapor-liquid equilibria have been determined for twenty-one of the twenty-eight binary systems involving paraffin, naphthene and aromatic hydrocarbons containing six carbon atoms. Included in these twenty-one systems are five paraffin-aromatic systems, two naphthene-aromatic, one naphthene-naphthene, ten naphthene-paraffin and three paraffin-paraffin systems.

The data were correlated according to the Van Laar equations and the Van Laar coefficients A and B determined.

As expected, maximum deviations from ideal solution laws were observed for the systems in which benzene was a component. These deviations were moderate when compared to such systems as chloroform-acetone or hydrogen chloride-water. Activity co-efficients for a component at infinite dilution varied from 1.40 to 1.69 for benzene in cyclohexane and neohexane respectively and 1.46 to 1.83 for cyclohexane and neohexane.

The paraffin-naphthene systems showed only slight deviations from ideality. Systems containing cyclohexene deviated 10-20 per cent and those in which methylcyclopentene was a component deviated 3-17 per cent.

The naphthene-naphthene and paraffin-paraffin systems behaved ideally within the limits of experimental error. The methods of analysis employed in these systems are inherently less accurate than those employed in the other systems. Consequently these data are of a somewhat lower order of accuracy.

Three azeotropes were observed: benzene with cyclohexane, benzene with methylcyclopentane, and benzene with hexane. None of the other systems formed azeotropes.

The systems studied in this work cover the paraffin, naphthene, and aromatic hydrocarbons containing six carbon atoms. These compounds are present in natural and straight run gasolines. Several of the compounds are becoming important as chemical raw materials or as blending ingredients in high octane number motor or aviation fuels. The data reported here should find application in the design of fractionating columns to separate the various components from the raw feed stocks.

A much larger field of study, as a natural extension of this work, would be the determination of vapor-liquid equilibria among the C_6 olefins and combinations of them with the paraffins, naphthenes, and aromatics studied here.

TABLE I

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZENE AND NEOHEXANE

Temperature	Mol Fraction Benzene[a]		Temperature	Mol Fraction Benzene[b]	
°C	x	y	°C	x	y
49.60	0.000	0.000	49.84	0.000	0.000
50.04	0.024	0.015	50.12	0.030	0.019
50.08	0.026	0.017	50.78	0.078	0.048
50.40	0.043	0.025	51.62	0.140	0.080
50.84	0.080	0.048	53.14	0.244	0.138
51.60	0.144	0.080	54.60	0.335	0.188
52.44	0.200	0.115	56.02	0.414	0.240
53.90	0.311	0.177	56.38	0.446	0.249
64.00	0.746	0.483	56.48	0.446	0.255
67.64	0.832	0.595	56.52	0.448	0.255
72.88	0.917	0.737	56.56	0.449	0.250
75.42	0.965	0.835	58.10	0.533	0.300
77.42	0.974	0.900	60.34	0.630	0.371
78.58	0.984	0.948	60.56	0.632	0.369
79.82	0.9985	0.998	63.00	0.708	0.432
			65.02	0.762	0.534
			67.42	0.816	0.586
			70.48	0.874	0.657
			74.68	0.934	0.795
			77.18	0.967	0.876
			80.10	1.000	1.000

Van Laar Constants

	A[a]	B[a]	A[b]	B[b]
From Benzene	0.667	171.0	0.780	186.0
From Neohexane	0.789	156.8	0.813	154.0
Average	0.727	163.9	0.796	170.0

Van Laar Equations

Benzene: $T \ln \overset{a}{\gamma}_B = \left(\frac{164}{1 + .727\, x_B/x_N}\right)^2$ $\quad T \ln \overset{b}{\gamma}_B = \left(\frac{170}{1 + .796\, x_B/x_N}\right)^2$

Neohexane: $T \ln \overset{a}{\gamma}_N = \left(\frac{119}{.727 + x_N/x_B}\right)^2$ $\quad T \ln \overset{b}{\gamma}_N = \left(\frac{135}{.796 + x_N/x_B}\right)^2$

a. Modified Hipkin and Myers Still
b. Modified Gillespie Still

TABLE II

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZENE AND DIISOPROPYL

Temperature	Mol Fraction Benzene	
°C	x	y
57.96	0.000	0.000
58.10	0.016	-
58.26	0.033	0.027
58.38	0.051	0.039
58.66	0.089	0.067
59.20	0.149	0.110
60.32	0.258	0.182
61.38	0.360	0.250
63.10	0.478	0.324
63.54	0.499	0.341
65.12	0.590	0.407
65.18	0.599	0.415
67.52	0.708	0.512
71.62	0.845	0.667
75.24	0.922	0.802
77.42	0.962	0.888
78.82	0.982	0.948
79.52	0.990	0.973
80.10	1.000	1.000

Van Laar Constants

	A	B
From Benzene	0.731	164.0
From Diisopropyl	0.806	147.0
Average	0.769	155.5

Van Laar Equations

Benzene: $$T\ln\gamma_B = \frac{155.5}{(1 + .769\ x_B/x_D)^2}$$

Diisopropyl: $$T\ln\gamma_D = \frac{119}{(.769 + x_D/x_B)^2}$$

TABLE III

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZENE AND 2-METHYLPENTANE

Temperature	Mol Fraction Benzene	
°C	x	y
60.30	0.000	0.000
60.46	0.015	0.013
60.56	0.033	0.025
60.76	0.070	0.056
61.24	0.131	0.103
62.42	0.253	0.194
63.36	0.348	0.256
64.98	0.454	0.349
66.42	0.583	0.430
68.96	0.719	0.541
71.16	0.803	0.625
75.04	0.909	0.785
77.40	0.956	0.883
78.82	0.980	0.946
79.46	0.990	0.974
80.10	1.000	1.000

Van Laar Constants

	A	B
From Benzene	0.513	136.1
From 2-Methylpentane	0.680	115.6
Average	0.597	125.8

Van Laar Equations

Benzene: $$T \ln \gamma_B = \frac{126}{(1 + .597\, x_B/x_2)^2}$$

2-Methylpentane: $$T \ln \gamma_2 = \frac{75}{(.597 + x_2/x_B)^2}$$

TABLE IV

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZENE AND 3-METHYLPENTANE

Temperature	Mol Fraction Benzene	
°C	x	y
63.44	0.000	0.000
63.52	0.050	0.049
63.60	0.075	0.060
63.80	0.130	0.111
64.04	0.222	0.193
64.94	0.276	0.229
66.50	0.441	0.340
67.60	0.543	0.413
67.72	0.549	0.418
68.68	0.619	0.472
68.80	0.625	0.479
70.38	0.715	0.560
73.96	0.856	0.718
76.46	0.927	0.833
78.16	0.963	0.911
79.20	0.984	0.958
79.72	0.993	0.980
80.10	1.000	1.000

Van Laar Constants

	A	B
From Benzene	0.736	160.7
From 3-Methylpentane	0.763	128.0
Average	0.750	144.4

Van Laar Equations

Benzene: $$T \ln \gamma_B = \frac{144}{(1 + .750\, x_B/x_3)^2}$$

3-Methylpentane: $$T \ln \gamma_3 = \frac{108}{(.750 + x_3/x_B)^2}$$

TABLE V

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZENE AND N-HEXANE

Temperature	Mol Fraction Benzene[a]		Temperature	Mol Fraction Benzene[b]	
°C	x	y	°C	x	y
68.78	0.000	0.000	68.74	0.000	0.000
68.74	0.017	0.017	68.72	0.015	0.015
68.78	0.034	0.034	68.72	0.027	0.027
68.78	0.050	0.052	68.70	0.043	0.042
68.82	0.083	0.082	68.74	0.065	0.064
68.88	0.118	0.115	68.72	0.065	0.065
68.96	0.149	0.142	68.76	0.075	0.072
69.00	0.211	0.199	68.74	0.081	0.080
69.56	0.337	0.296	68.78	0.123	0.116
69.88	0.430	0.367	68.90	0.193	0.181
70.58	0.507	0.433	69.16	0.272	0.245
70.92	0.549	0.465	69.56	0.358	0.318
71.32	0.592	0.499	70.00	0.441	0.375
71.78	0.631	0.530	70.58	0.513	0.438
73.02	0.720	0.609	71.24	0.581	0.488
74.40	0.805	0.694	71.92	0.646	0.539
76.92	0.912	0.833	72.68	0.699	0.588
78.38	0.958	0.912	73.40	0.746	0.629
79.22	0.982	0.960	74.38	0.799	0.684
79.64	0.990	0.979	74.48	0.807	0.697
80.12	1.000	1.000	75.18	0.839	0.731
			75.60	0.856	0.755
			76.70	0.901	0.814
			77.88	0.931	0.882
			79.08	0.973	0.931
			80.12	1.000	1.000

Van Laar Constants

	A[a]	B[a]	A[b]	B[b]
From Benzene	0.620	131.0	0.706	134.9
From n-Hexane	0.580	126.9	0.682	119.5
Average	0.600	129.0	0.694	127.2

Van Laar Equations

Benzene: $\overset{a}{T\ln\gamma_B} = \frac{129}{(1 + .600\, x_B/x_H)^2}$ $\overset{b}{T\ln\gamma_B} = \frac{127}{(1 + .694\, x_B/x_H)^2}$

Hexane: $\overset{a}{T\ln\gamma_H} = \frac{77.4}{(.600 + x_H/x_B)^2}$ $\overset{b}{T\ln\gamma_H} = \frac{88.3}{(.694 + x_H/x_B)^2}$

a. Modified Hipkin and Myers Still
b. Modified Gillespie Still

TABLE VI

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZNE AND METHYLCYCLOPENTANE

Temperature	Mol Fraction Benzene		Temperature	Mol Fraction Benzene(7)	
°C	x	y	°C	x	y
71.78	0.001	0.001	71.8	0.000	0.000
71.80	0.016	0.018	71.8	0.036	0.036
71.72	0.030	0.037	71.75	0.079	0.079
71.80	0.030	0.035	71.65	0.125	0.125
71.64	0.047	0.054	71.65	0.155	0.154
71.64	0.069	0.069	71.7	0.192	0.185
71.64	0.088	0.089	71.8	0.251	0.238
71.70	0.088	0.089	72.0	0.323	0.296
71.64	0.105	0.106	72.3	0.399	0.362
71.66	0.120	0.122	72.95	0.511	0.452
71.68	0.136	0.137	73.4	0.570	0.500
71.68	0.152	0.152	74.2	0.659	0.575
71.72	0.169	0.168	75.1	0.728	0.642
71.72	0.189	0.185	76.1	0.805	0.722
71.74	0.190	0.185	77.15	0.865	0.794
71.78	0.232	0.221	77.8	0.904	0.845
71.88	0.271	0.255	78.35	0.9305	0.887
72.04	0.380	0.315	79.45	0.975	0.955
72.74	0.476	0.426	80.15	1.000	1.000
72.84	0.606	0.446			
73.30	0.560	0.496			
74.08	0.713	0.574			
74.36	0.672	0.594			
75.14	0.740	0.656			
75.44	0.761	0.685			
76.50	0.896	0.760			
78.14	0.925	0.876			
79.20	0.961	0.937			
79.64	0.984	0.968			
79.98	0.992	0.985			
80.14	1.000	1.000			

Van Laar Constants

	A	B	A(7)	B(7)
From Benzene	0.694	114.9	0.897	123.5
From Methylcyclopentane	0.666	113.0	0.897	108.5
Average	0.680	113.9	0.897	116.0

Van Laar Equations

Benzene $$T \ln \gamma_B = \frac{114}{(1 + .680\ x_B/x_M)^2}$$

Methylcyclopentane: $$T \ln . \gamma_M = \frac{77.4}{(.680 + x_M/x_B)^2}$$

TABLE VII

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: BENZENE AND CYCLOHEXANE

Temperature	Mol Fraction Benzene	
°C	x	y
80.74	0.000	0.000
80.38	0.038	0.046
79.80	0.087	0.115
78.92	0.189	0.226
78.28	0.276	0.307
77.92	0.343	0.379
77.70	0.404	0.435
77.72	0.432	0.449
77.56	0.499	0.504
77.58	0.536	0.519
77.58	0.551	0.550
77.68	0.614	0.601
77.96	0.731	0.703
78.18	0.794	0.761
78.62	0.862	0.833
79.28	0.934	0.913
79.70	0.971	0.960
80.10	1.000	1.000

Van Laar Constants

	A	B
From Benzene	0.933	119.0
From Cyclohexane	0.848	118.0
Average	0.890	118.5

Van Laar Equations

Benzene: $$T \ln \gamma_B = \left(\frac{118}{1 + .890\, x_B/x_C}\right)^2$$

Cyclohexane: $$T \ln \gamma_C = \left(\frac{105}{.890 + x_C/x_B}\right)^2$$

TABLE VIII

VAPOR-LIQUID EQUILIBRIUM AT 760MM HG: CYCLOHEXANE AND NEOHEXANE

Temperature	Mol Fraction Cyclohexane	
°C	x	y
49.74	0.000	0.000
50.84	0.057	0.021
52.20	0.118	0.051
53.78	0.195	0.088
54.78	0.244	0.114
55.42	0.270	0.128
57.20	0.347	0.173
58.84	0.415	0.212
59.08	0.425	0.223
60.48	0.475	0.259
61.18	0.506	0.282
62.20	0.537	0.306
64.16	0.604	0.361
66.32	0.667	0.429
68.70	0.735	0.515
71.00	0.792	0.592
73.60	0.855	0.688
76.16	0.912	0.791
79.10	0.969	0.919
80.78	1.000	1.000

Van Laar Constants

	A	B
From Cyclohexane	0.736	44.4
From Neohexane	0.790	26.8
Average	0.763	35.6

Van Laar Equations

Cyclohexane: $$T \ln \gamma_C = \frac{36}{(1 + .763\ x_C/x_N)^2}$$

Neohexane $$T \ln \gamma_N = \frac{27}{(.763 + x_N/x_C)^2}$$

TABLE IX

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: CYCLOHEXANE AND DIISOPROPYL

Temperature	Mol Fraction Cyclohexane	
°C	x	y
57.90	0.000	0.000
58.02	0.012	0.008
58.08	0.015	0.006
58.50	0.042	0.019
59.54	0.106	0.061
61.20	0.165	0.079
63.00	0.318	0.195
65.76	0.454	0.292
67.60	0.540	0.372
69.72	0.635	0.459
73.18	0.768	0.616
75.70	0.853	0.730
78.10	0.929	0.856
79.44	0.969	0.931
80.22	0.992	0.985
80.78	1.000	1.000

Van Laar Constants

	A	B
From Cyclohexane	0.863	49.5
From Diisopropyl	0.760	33.4
Average	0.812	41.5

Van Laar Equations

Cyclohexane: $$T \ln \gamma_C = \frac{42}{(1 + .812\, x_C/x_D)^2}$$

Diisopropyl: $$T \ln \gamma_D = \frac{34}{(.812 + x_D/x_C)^2}$$

TABLE X

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: CYCLOHEXANE AND 2-METHYLPENTANE

Temperature	Mol Fraction Cyclohexane	
°C	x	y
60.38	0.000	0.000
60.60	0.017	0.010
61.06	0.055	0.032
61.82	0.107	0.068
61.86	0.107	0.066
63.56	0.213	0.136
65.14	0.314	0.205
66.44	0.392	0.269
67.58	0.462	0.324
69.48	0.569	0.410
69.50	0.563	0.410
71.42	0.658	0.499
74.20	0.777	0.640
76.32	0.857	0.749
78.44	0.930	0.819
79.00	0.970	0.938
80.38	0.994	0.981
80.56	1.000	1.000

Van Laar Constants

	A	B
From Cyclohexane	1.535	76.0
From 2-Methylpentane	1.337	38.7
Average	1.436	57.3

Van Laar Equations

Cyclohexane:

$$T \ln \gamma_C = \frac{57}{(1 + 1.436\ x_C/x_2)^2}$$

2-Methylpentane:

$$T \ln \gamma_2 = \frac{82}{(1.436 + x_2/x_C)^2}$$

TABLE XI

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: CYCLOHEXANE AND 3-METHYLPENTANE

Temperature	Mol Fraction Cyclohexane	
°C	x	y
63.28	0.000	0.000
63.80	0.039	0.027
65.36	0.165	0.116
66.54	0.257	0.182
67.72	0.339	0.241
68.94	0.419	0.316
70.08	0.492	0.379
70.44	0.519	0.398
71.36	0.571	0.444
71.80	0.600	0.467
72.38	0.629	0.496
73.24	0.674	0.555
74.62	0.747	0.639
76.08	0.815	0.709
77.48	0.873	0.787
78.68	0.925	0.868
79.70	0.968	0.944
80.74	1.000	1.000

Van Laar Constants

	A	B
From Cyclohexane	1.182	77.4
From 3-Methylpentane	0.259	13.7
Average	0.770	45.6

Van Laar Equations

Cyclohexane: $$T \ln \gamma_C = \frac{46}{(1 + .770\ x_C/x_3)^2}$$

3-Methylpentane: $$T \ln \gamma_3 = \frac{35}{(.770 + x_3/x_C)^2}$$

TABLE XII

VAPOR-LIQUID EQUILIBRIUM DATA AT 760 MM HG: CYCLOHEXANE AND NORMAL HEXANE

Temperature	Mol Fraction Cyclohexane	
°C	x	y
68.74	0.000	0.000
69.12	0.052	0.035
69.64	0.105	0.078
70.26	0.176	0.131
70.26	0.178	0.138
70.94	0.245	0.192
71.72	0.323	0.259
72.56	0.398	0.321
73.42	0.478	0.391
73.70	0.502	0.412
74.30	0.555	0.466
74.52	0.571	0.476
75.14	0.628	0.533
75.30	0.633	0.546
75.06	0.663	0.592
76.08	0.696	0.609
76.90	0.757	0.677
77.76	0.816	0.751
78.56	0.872	0.818
79.30	0.920	0.879
80.06	0.965	0.942
80.76	1.000	1.000

Van Laar Constants

	A	B
From Cyclohexano	1.020	30.3
From Normal Hexane	0.176	27.6
Average	0.598	29.0

Van Laar Equations

Cyclohexane: $$T \ln \gamma_C = \frac{29}{(1 + .598\, x_C/x_H)^2}$$

Hexane: $$T \ln \gamma_H = \frac{17}{(.598 + x_H/x_C)^2}$$

TABLE XIII

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: CYCLOHEXANE AND METHYLCYCLOPENTANE

Temperature	Mol Fraction Cyclohexane	
°C	x	y
71.69	0.000	0.000
72.30	0.060	0.033
72.86	0.130	0.102
73.62	0.220	0.185
74.38	0.318	0.268
75.00	0.391	0.336
75.70	0.469	0.398
76.24	0.531	0.465
76.38	0.531	0.470
77.12	0.624	0.562
77.18	0.630	0.562
77.80	0.703	0.649
78.52	0.777	0.732
79.34	0.843	0.815
80.24	0.940	0.927
80.78	1.000	1.000

Van Laar Constants[a]

A	0.848
B	0.06

[a] Derived from Plot cf $\sqrt{T \ln \gamma_{MCP}} = \sqrt{\frac{B}{A}} - \sqrt{\frac{1}{A}}\sqrt{T \ln \gamma_{CH}}$

Van Laar Equations

Cyclohexane: $T \ln \gamma_C = \frac{0.06}{(1 + .848\, x_C/x_M)^2}$

Methylcyclopentane: $T \ln \gamma_M = \frac{0.05}{(.848 + x_M/x_C)^2}$

TABLE XIV

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: METHYLCYCLOPENTANE AND NEOHEXANE

Temperature	Mol Fraction Methylcyclopentane	
°C	x	y
49.74	0.000	0.000
50.56	0.052	0.029
51.50	0.113	0.058
52.80	0.190	0.108
54.22	0.270	0.161
55.70	0.351	0.218
57.18	0.429	0.280
57.42	0.439	0.290
58.86	0.507	0.345
59.00	0.517	0.356
60.30	0.580	0.410
60.52	0.585	0.415
61.92	0.650	0.480
63.70	0.717	0.561
65.80	0.794	0.657
67.52	0.864	0.750
69.18	0.919	0.843
70.68	0.965	0.935
71.80	1.000	1.000

Van Laar Constants

	A	B
From Methylcyclopentane	0.380	24.4
From Neohexane	0.397	12.6
Average	0.388	18.5

Van Laar Equations

Methylcyclopentane: $$T \ln \gamma_M = \frac{18}{(1 + .388\, x_M/x_N)^2}$$

Neohexane: $$T \ln \gamma_N = \frac{7}{(.388 + x_N/x_M)^2}$$

TABLE XV

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: METHYLCYCLOPENTANE AND DIISOPROPYL

Temperature	Mol Fraction Methylcyclopentane	
°C	x	y
58.00	0.000	0.000
58.60	0.062	0.036
59.30	0.117	0.078
60.22	0.199	0.145
61.14	0.273	0.204
62.08	0.353	0.264
63.34	0.428	0.336
63.82	0.484	0.380
64.22	0.514	0.410
64.86	0.566	0.454
65.16	0.584	0.475
65.88	0.632	0.531
66.82	0.700	0.601
67.78	0.760	0.678
68.80	0.832	0.753
69.78	0.884	0.833
70.80	0.941	0.915
71.80	1.000	1.000

Van Laar Constants

	A	B
From Methylcyclopentane	0.396	14.3
From Diisopropyl	0.487	13.0
Average	0.442	13.6

Van Laar Equations

Methylcyclopentane: $$T \ln \gamma_M = \frac{14}{(1 + .442\, x_M/x_D)^2}$$

Diisopropyl: $$T \ln \gamma_D = \frac{6}{(.442 + x_D/x_M)^2}$$

TABLE XVI

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: METHYLCYCLOPENTANE AND 2-METHYLPENTANE

Temperature	Mol Fraction Methylcyclopentane	
°C	x	y
60.24	0.000	0.000
60.74	0.053	0.044
61.38	0.125	0.092
62.06	0.194	0.154
62.82	0.267	0.210
63.50	0.333	0.267
64.30	0.411	0.330
64.80	0.458	0.376
65.12	0.485	0.403
65.55	0.516	0.434
66.04	0.564	0.476
66.30	0.593	0.500
67.16	0.665	0.579
67.96	0.725	0.650
68.70	0.787	0.724
69.52	0.844	0.795
70.44	0.911	0.872
71.28	0.964	0.952
71.82	1.000	1.000

Van Laar Constants

	A	B
From Methylcyclopentane	0.215	11.8
From 2-Methylpentane	0.392	16.3
Average	0.303	14.0

Van Laar Equations

Methylcyclopentane: $$T \ln \gamma_M = \frac{14}{(1 + .303\, x_M/x_2)^2}$$

2-Methylpentane: $$T \ln \gamma_2 = \frac{4}{(.303 + x_2/x_M)^2}$$

TABLE XVII

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: METHYLCYCLOPENTANE AND 3-METHYLPENTANE

Temperature	Mol Fraction Methylcyclopentane	
°C	x	y
63.28	0.000	0.000
63.64	0.047	0.040
64.12	0.120	0.099
64.68	0.196	0.162
65.34	0.274	0.232
65.96	0.356	0.301
66.58	0.430	0.371
67.00	0.487	0.424
67.18	0.512	0.448
67.56	0.551	0.490
67.80	0.585	0.518
68.16	0.625	0.564
68.32	0.647	0.585
68.74	0.700	0.638
69.32	0.758	0.706
69.98	0.818	0.783
70.66	0.891	0.865
71.20	0.942	0.924
71.80	1.000	1.000

Van Laar Constants

	A	B
From Methylcyclopentame	0.849	14.8
From 3-Methylpentane	0.684	6.9
Average	0.766	10.4

Van Laar Equations

Methylcyclopentane: $$T \ln \gamma_M = \frac{10}{(1 + .766\, x_M/x_3)^2}$$

3-Methylpentane: $$T \ln \gamma_3 = \frac{8}{(.766 + x_3/x_M)^2}$$

TABLE XVIII

VAPOR-LIQUID EQUILIBRIUM AT 760 MM HG: METHYLCYCLOPENTANE AND NORMAL HEXANE

Temperature	Mol Fraction Methylcyclopentane	
°C	x	y
68.74	0.000	0.000
68.84	0.064	0.058
69.00	0.127	0.117
69.14	0.200	0.184
69.34	0.271	0.259
69.54	0.356	0.351
69.70	0.418	0.393
69.72	0.418	0.397
69.88	0.486	0.468
70.08	0.544	0.530
70.10	0.560	0.535
70.28	0.605	0.585
70.36	0.627	0.611
70.60	0.708	0.685
70.58	0.703	0.679
70.84	0.775	0.755
71.04	0.836	0.819
71.38	0.906	0.896
71.64	0.957	0.954
71.80	1.000	1.000

Van Laar Constants

	A	B
From Methylcyclopentane	0.902	21.1
From Normal Hexane	0.400	31.1
Average	0.651	26.1

Van Laar Equations

Methylcyclopentane: $$T \ln \gamma_M = \frac{26}{(1 + .651\, x_M/x_H)^2}$$

Hexane $$T \ln \gamma_H = \frac{17}{(.651 + x_H/x_M)^2}$$

TABLE XIX

VAPOR-LIQUID EQUILIBRIUM: NORMAL HEXANE AND NEOHEXANE

Temperature	Mol Fraction Normal Hexane	
°C	x	y
49.74	0.000	0.000
51.34	0.101	0.058
53.00	0.205	0.124
54.60	0.298	0.170
56.10	0.384	0.250
57.60	0.465	0.302
59.06	0.547	0.392
60.50	0.633	0.482
61.80	0.704	0.549
64.04	0.797	0.694
66.44	0.905	0.842
68.74	1.000	1.000

Van Laar Constants[a]

$A = 7.6$

$B = 2.1$

Van Laar Equations

Hexane: $$T \ln \gamma_H = \frac{2}{(1 + 7.6\, x_H/x_N)^2}$$

Neohexane: $$T \ln \gamma_N = \frac{16}{(7.6 + x_N/x_H)^2}$$

a. Derived from Plot of $\sqrt{T \ln \gamma_{neo}}$ vs $\sqrt{T \ln \gamma_N}$

TABLE XX

VAPOR-LIQUID EQUILIBRIUM: 3-METHYLPENTANE AND NEOHEXANE

Temperature	Mol Fraction 3-Methylpentane	
°C	x	y
49.74	0.000	0.000
50.80	0.100	0.066
51.88	0.190	0.130
53.18	0.299	0.224
54.44	0.424	0.314
55.78	0.482	0.408
55.84	0.509	0.408
57.14	0.605	0.501
60.12	0.806	0.738
60.62	0.803	0.732
61.88	0.910	0.882
63.28	1.000	1.000

Van Laar Constants[a]

$A = 2.8$
$B = 0.5$

Van Laar Equations

3-Methylpentane: $T \ln \gamma_3 = \frac{0.5}{(1 + 2.8\, x_3/x_N)^2}$

Neohexane: $T \ln \gamma_N = \frac{1.4}{(2.8 + x_N/x_3)^2}$

[a] Derived from Plot of $\sqrt{T \ln \gamma_{neo}}$ vs $\sqrt{T \ln \gamma_{3MP}}$

TABLE XXI

VAPOR-LIQUID EQUILIBRIUM: DIISOPROPYL AND NEOHEXANE

Temperature	Mol Fraction Diisopropyl	
°C	x	y
49.74	0.000	0.000
50.76	0.143	0.115
51.64	0.264	0.211
52.68	0.382	0.342
53.54	0.489	0.439
54.42	0.589	0.544
54.74	0.642	0.579
55.80	0.759	0.719
56.76	0.877	0.840
57.82	1.000	1.000

Van Laar Constants[a]

A = 1.1
B = 0.03

Van Laar Equations

Diisopropyl: $$T \ln \gamma_D = \frac{.03}{(1 + 1.1\, x_D/x_N)^2}$$

Neohexane: $$T \ln \gamma_N = \frac{.03}{(1.1 + x_N/x_D)^2}$$

a. Derived from Plot of $\sqrt{T \ln \gamma_{neo}}$ vs $\sqrt{T \ln \gamma_{DIP}}$

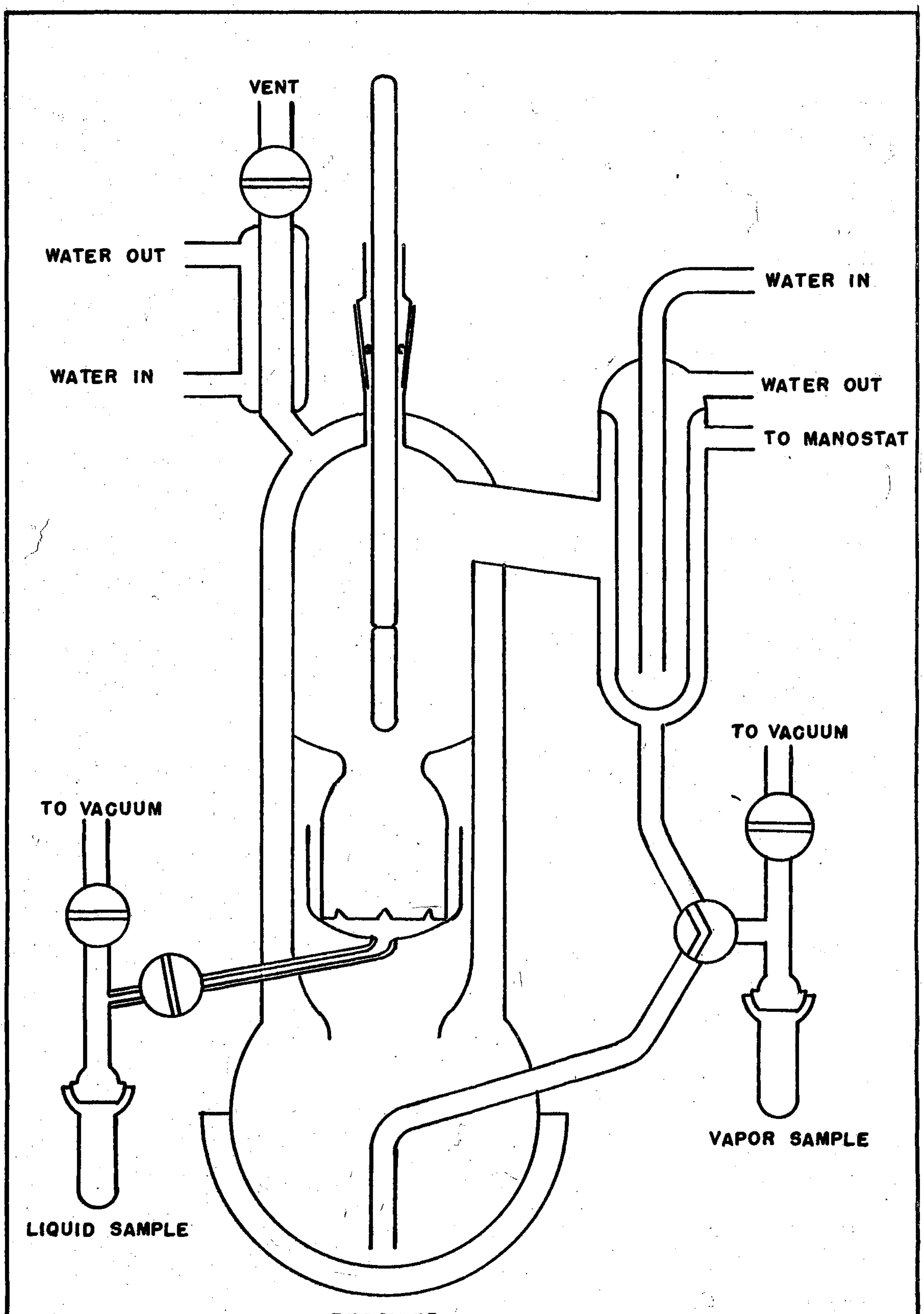


FIG. I MODIFIED HIPKIN AND MYERS VAPOR-LIQUID EQUILIBRIUM STILL

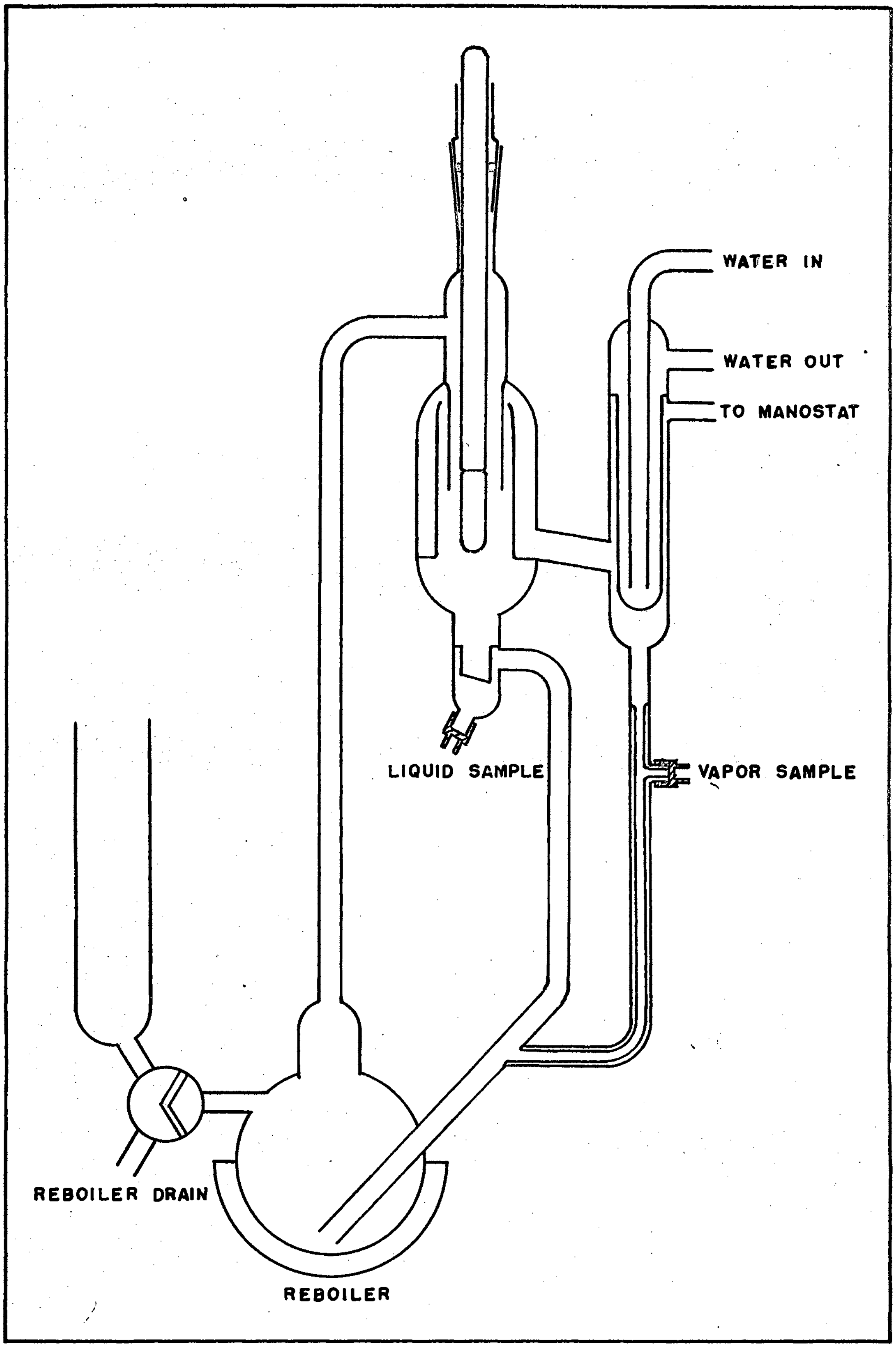


FIG. 2 MODIFIED GILLESPIE VAPOR-LIQUID EQUILIBRIUM STILL

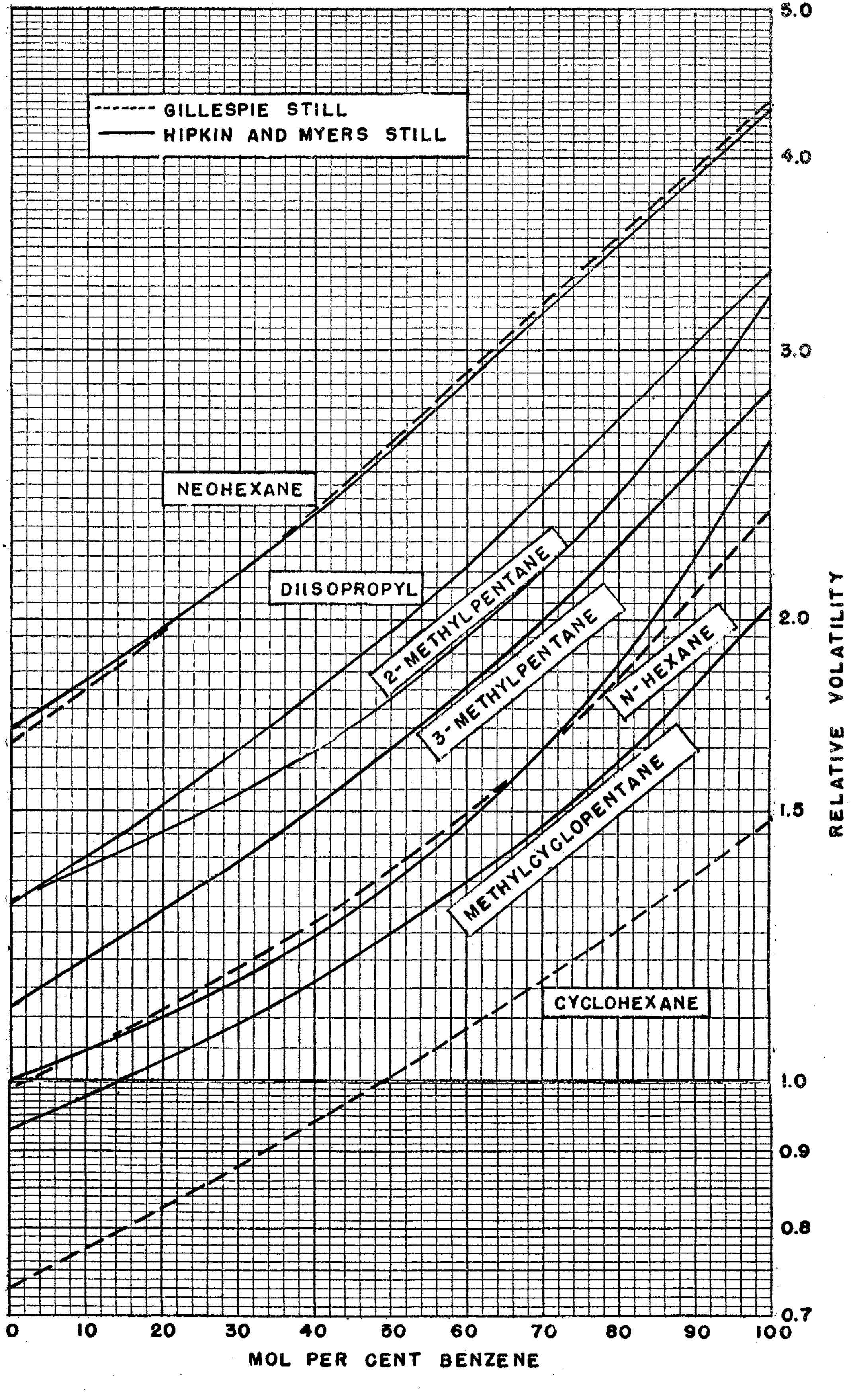


FIG. 3 RELATIVE VOLATILITIES OF C_6 PARAFFINS AND NAPHTHENES WITH RESPECT TO BENZENE

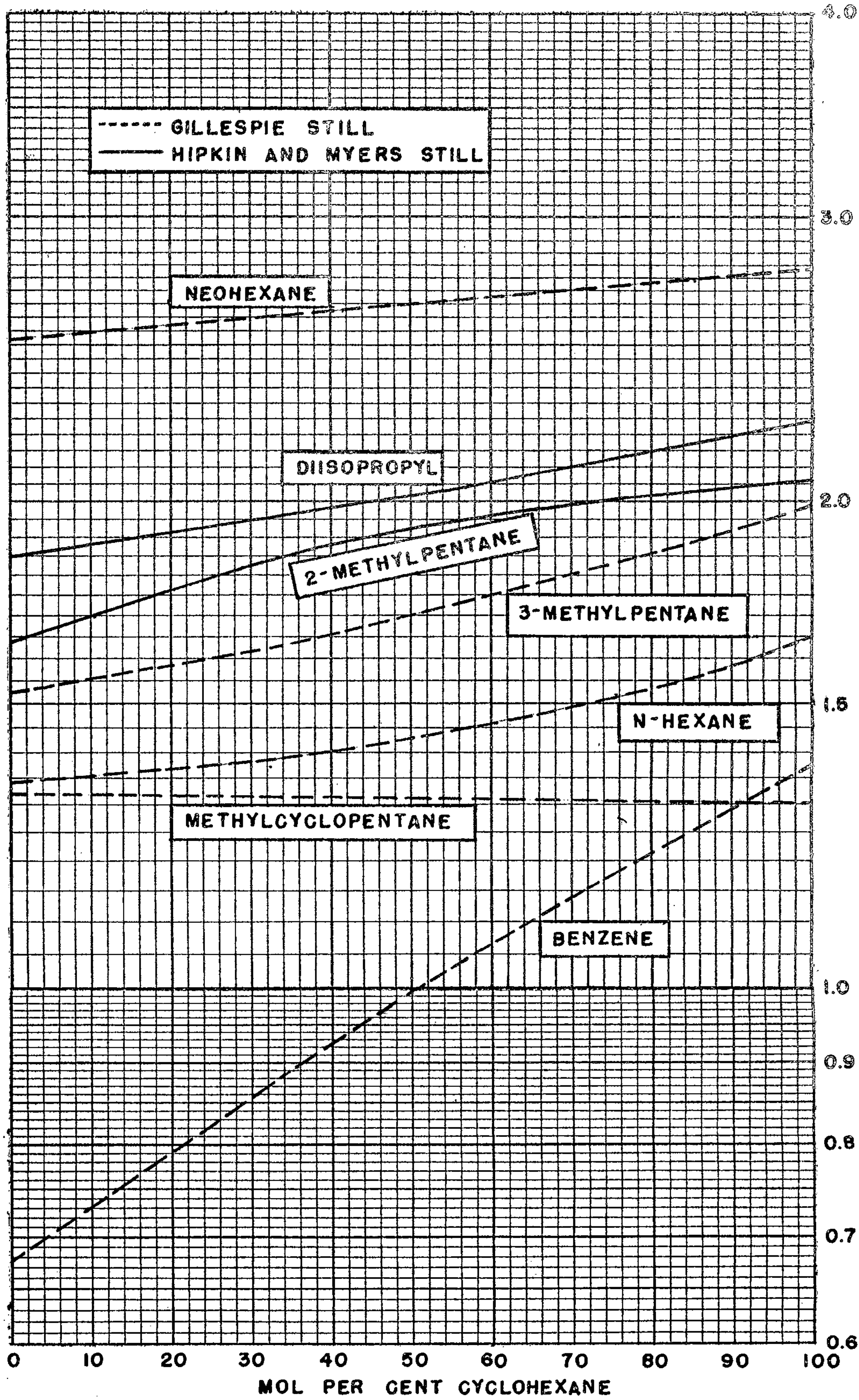


FIG. 4 RELATIVE VOLATILITIES OF C_6 PARAFFINS, NAPHTHENES, AND BENZENE WITH RESPECT TO CYCLOHEXANE

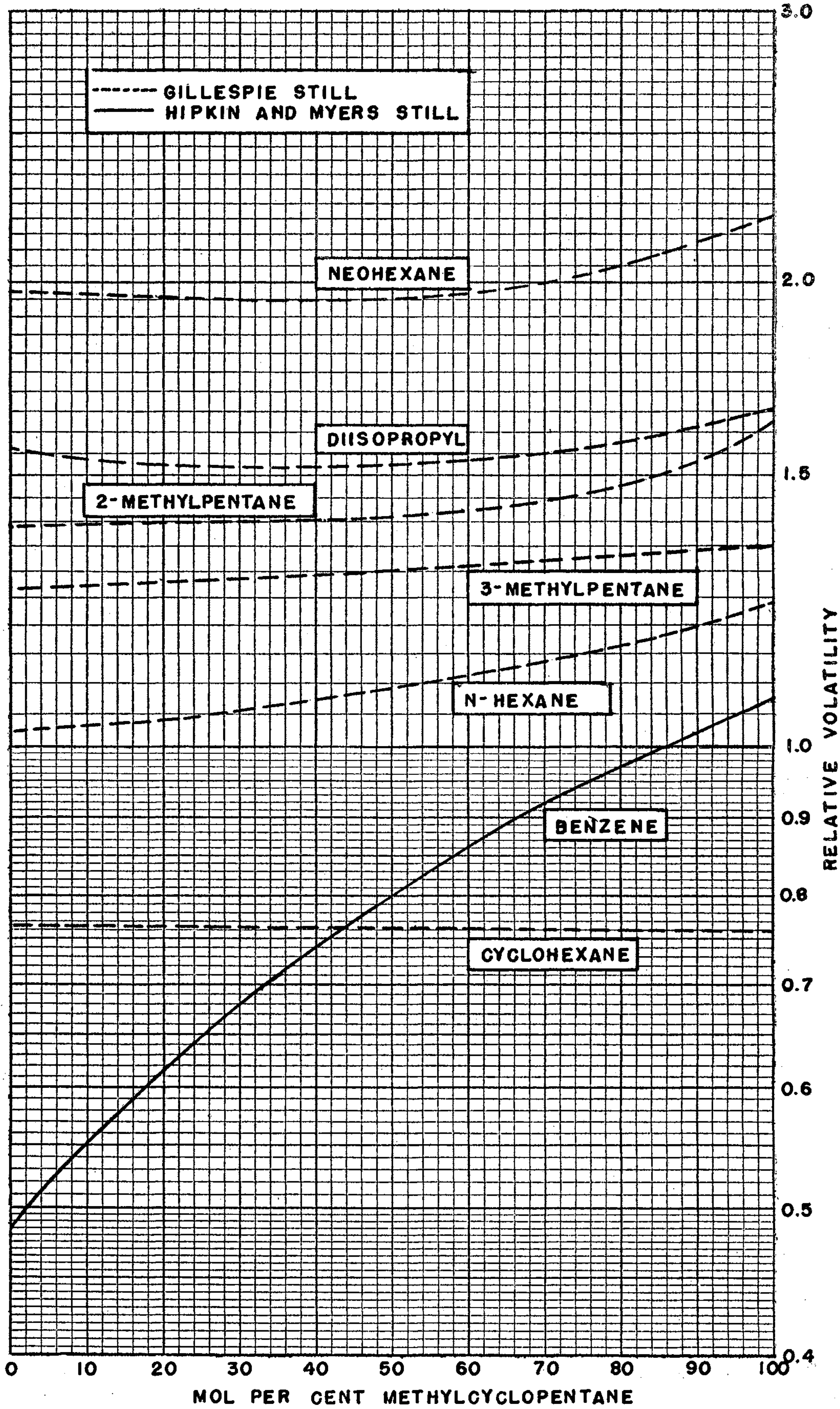


FIG. 5 RELATIVE VOLATILITIES OF C_6 PARAFFINS, NAPHTHENES, AND BENZENE WITH RESPECT TO METHYLCYCLOPENTANE

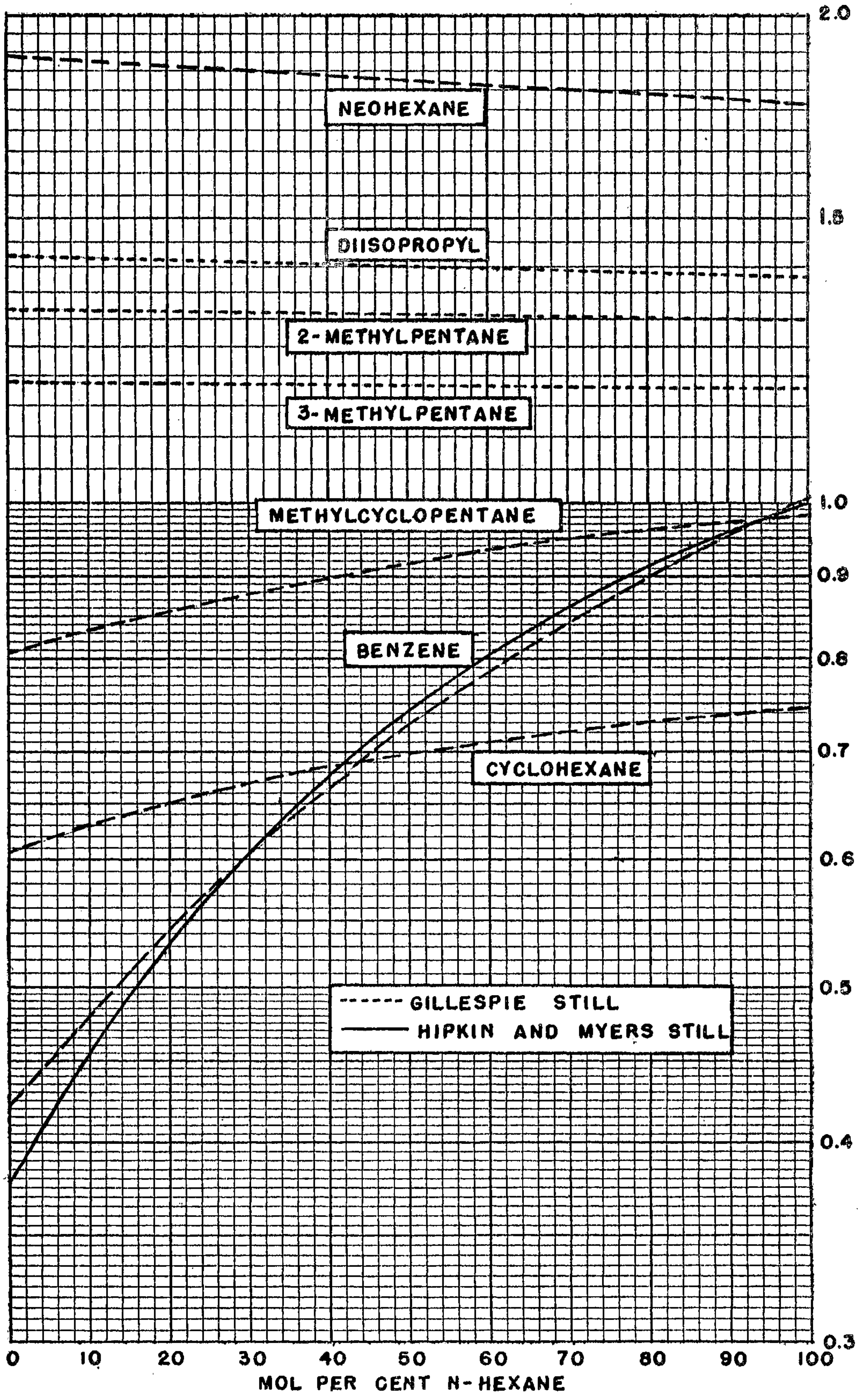


FIG. 6 RELATIVE VOLATILITIES OF C_6 PARAFFINS, NAPHTHENES, AND BENZENE WITH RESPECT TO N-HEXANE

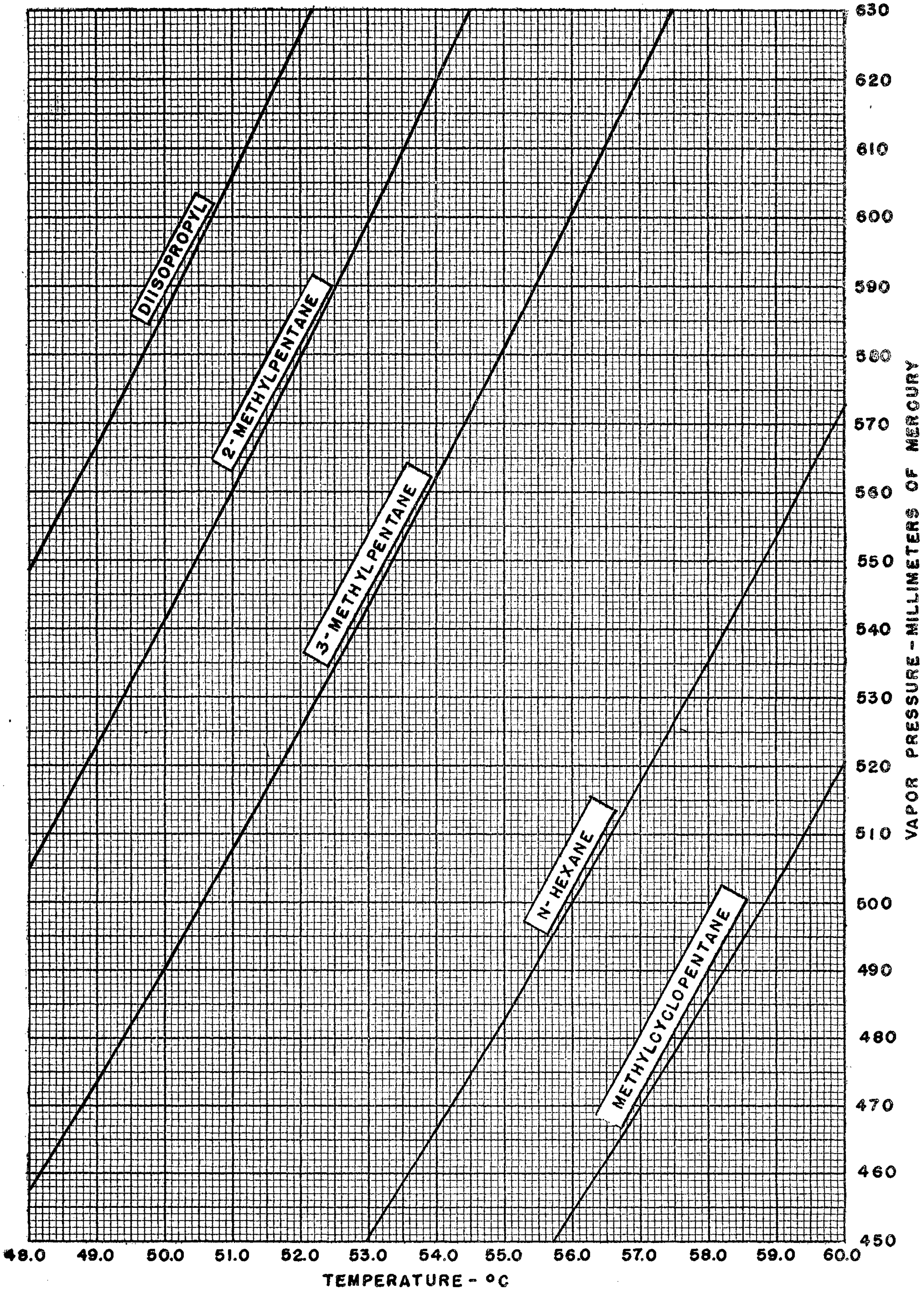


FIG. 7 TYPICAL CURVES FOR DETERMINING VAPOR PRESSURES OF C_6 PARAFFINS, NAPHTHENES, AND BENZENE

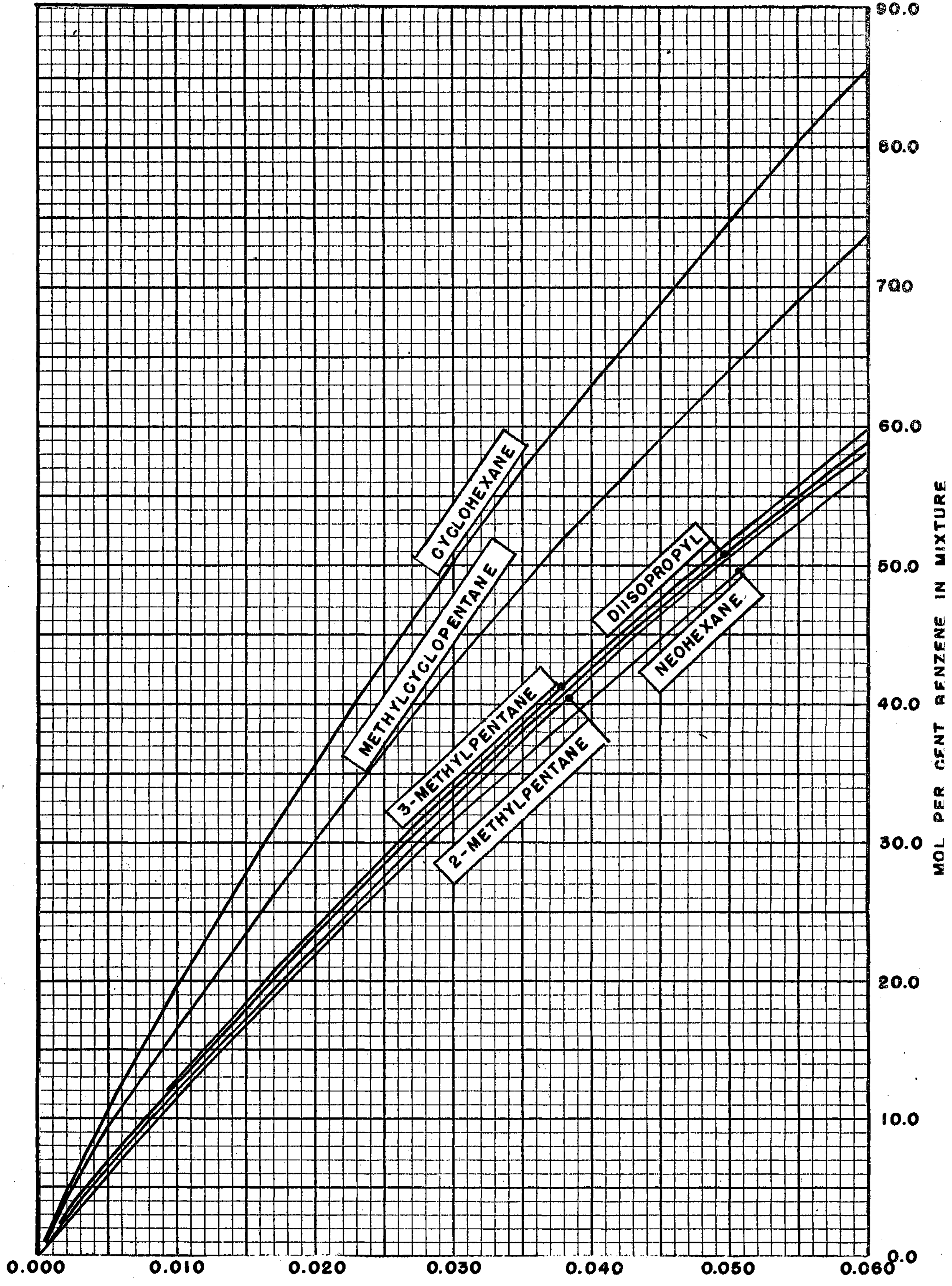
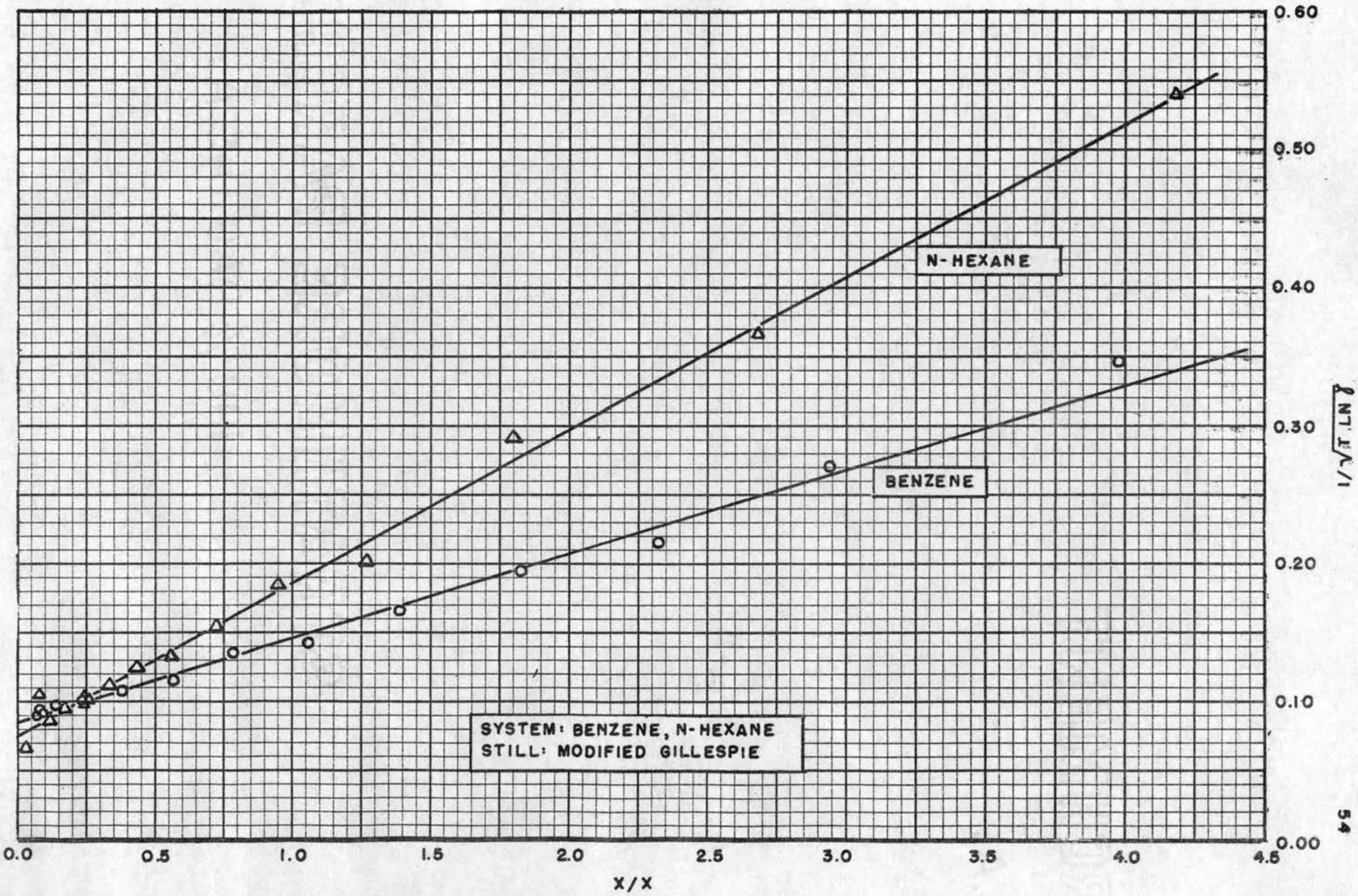


FIG. 8 REFRACTIVE INDEX-COMPOSITION CURVES FOR MIXTURES OF BENZENE WITH C_6 PARAFFINS AND NAPHTHENES


N-HEXANE
BENZENE
SYSTEM: BENZENE, N-HEXANE
STILL: MODIFIED GILLESPIE
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
X/X
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1/√T.NT ℓ

ABSTRACT

Vapor-liquid equilibria have been measured in binary systems comprised of paraffin, naphthene, and aromatic hydrocarbons containing six carbon atoms. These hydrocarbons are: 2,2-dimethylbutane (neohexane), 2,3-dimethylbutane (diisopropyl), 2-methylhexane, 3-methylhexane, n-hexane, methylcyclopentane, cyclohexane, and benzene.

These eight hydrocarbons make a total of twenty-eight binary systems. Of this total twenty-one systems were studied, all possible paraffin-aromatic, naphthene-aromatic, paraffin-naphthene systems and three paraffin-paraffin systems.

Vapor-liquid equilibria for these systems were measured at one atmosphere pressure (760 mm mercury). Data were correlated using the Van Laar equations.

Only three systems formed azeotropes. They were benzene-cyclohexane, benzene-methylcyclopentane, and benzene-normal hexane.

Systems in which benzene was one of the components showed moderate deviations from ideal solution behavior. The naphthene-paraffin systems showed only slight deviations. The naphthene-naphthene and paraffin-paraffin systems behaved ideally.

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(10) Ibid, Chapter 3.

(11) Ibid, p. 57.

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(13) Ibid, p. 60

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APPENDIX A

Table 1

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND NEOHEXANE

Mol Fraction Benzene	n_D^{20}
0.000	1.3688
0.130	1.3802
0.234	1.3903
0.380	1.4062
0.500	1.4199
0.596	1.4323
0.679	1.4451
0.784	1.4618
0.881	1.4783
0.939	1.4899
1.000	1.5011

Table 2

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND DIISOPROPYL

Mol Fraction Benzene	n_D^{20}
0.000	1.3750
0.157	1.3881
0.261	1.3979
0.391	1.4113
0.484	1.4220
0.603	1.4370
0.698	1.4501
0.768	1.4605
0.822	1.4691
0.908	1.4838
1.000	1.5011

Table 3

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND 2-METHYLPENTANE

Mol Fraction Benzene	n_D^{20}
0.000	1.3714
0.129	1.3821
0.229	1.3916
0.308	1.3996
0.425	1.4120
0.598	1.4338
0.749	1.4558
0.832	1.4605
0.882	1.4782
0.937	1.4885
1.000	1.5011

Table 4

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND 3-METHYLPENTANE

Mol Fraction Benzene	n_D^{20}
0.000	1.3765
0.145	1.3880
0.247	1.3975
0.379	1.4109
0.487	1.4231
0.592	1.4359
0.694	1.4499
0.772	1.4617
0.849	1.4738
0.913	1.4848
1.000	1.5011

Table 5

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND HEXANE

Mol Fraction Benzene	n_D^{20}
0.000	1.3749
0.104	1.3831
0.241	1.3956
0.333	1.4048
0.476	1.4201
0.508	1.4243
0.622	1.4388
0.754	1.4578
0.799	1.4648
0.908	1.4833
1.000	1.5010

Table 6

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND METHYLCYCLOPENTANE

Mol Fraction Benzene	n_D^{20}
0.002	1.4099
0.076	1.4144
0.114	1.4170
0.210	1.4237
0.339	1.4333
0.474	1.4446
0.560	1.4522
0.646	1.4607
0.761	1.4726
0.809	1.4780
0.864	1.4842
0.927	1.4918
0.954	1.4952
1.000	1.5011

Table 7

REFRACTIVE INDEX-COMPOSITION DATA: BENZENE AND CYCLOHEXANE

Mol Fraction Benzene	n_D^{20}
0.000	1.4260
0.139	1.4330
0.233	1.4384
0.318	1.4437
0.431	1.4511
0.520	1.4576
0.626	1.4659
0.731	1.4747
0.793	1.4800
0.874	1.4879
1.000	1.5011

Table 8

REFRACTIVE INDEX-COMPOSITION DATA: CYCLOHEXANE AND NEOHEXANE

Mol Fraction Benzene	n_D^{20}
0.000	1.3688
0.150	1.3763
0.249	1.3816
0.333	1.3862
0.445	1.3924
0.544	1.3980
0.666	1.4052
0.755	1.4106
0.831	1.4153
0.901	1.4199
1.000	1.4260

Table 9

REFRACTIVE INDEX-COMPOSITION DATA: CYCLOHEXANE AND DIISOPROPYL

Mol Fraction Cyclohexane	n_D^{20}
0.000	1.3750
0.144	1.3813
0.238	1.3858
0.307	1.3889
0.417	1.3942
0.537	1.4004
0.637	1.4057
0.746	1.4117
0.819	1.4156
0.892	1.4198
1.000	1.4260

Table 10

REFRACTIVE INDEX-COMPOSITION DATA: CYCLOHEXANE AND 2-METHYLPENTANE

Mol Fraction Cyclohexane	n_D^{20}
0.000	1.3715
0.177	1.3796
0.292	1.3851
0.360	1.3886
0.466	1.3940
0.566	1.3994
0.661	1.4047
0.794	1.4128
0.859	1.4168
1.000	1.4259

Table 11

REFRACTIVE INDEX-COMPOSITION DATA: CYCLOHEXANE AND 3-METHYLPENTANE

Mol Fraction Cyclohexane	n_D^{20}
0.000	1.3767
0.145	1.3824
0.242	1.3866
0.314	1.3898
0.434	1.3955
0.550	1.4011
0.649	1.4062
0.750	1.4115
0.822	1.4156
0.890	1.4193
1.000	1.4260

Table 12

REFRACTION INDEX-COMPOSITION DATA: CYCLOHEXANE AND HEXANE

Mol Fraction Cyclohexane	n_D^{20}
0.000	1.3749
0.105	1.3792
0.221	1.3842
0.310	1.3883
0.426	1.3938
0.524	1.3986
0.612	1.4031
0.708	1.4083
0.808	1.4140
0.884	1.4186
1.000	1.4260

Table 13

REFRACTIVE INDEX-COMPOSITION DATA: CYCLOHEXANE AND METHYLCYCLOPENTANE

Mol Fraction Cyclohexane	n_D^{20}
0.000	1.4097
0.136	1.4116
0.206	1.4127
0.286	1.4139
0.402	1.4158
0.504	1.4174
0.613	1.4191
0.721	1.4210
0.786	1.4221
0.883	1.4239
1.000	1.4260

Table 14

REFRACTIVE INDEX-COMPOSITION DATA: METHYLCYCLOPENTANE AND NEOHEXANE

Mol Fraction Methylcyclopentane	n_D^{20}
0.000	1.3687
0.126	1.3735
0.220	1.3771
0.351	1.3824
0.410	1.3848
0.512	1.3890
0.621	1.3935
0.728	1.3980
0.801	1.4010
0.893	1.4050
1.000	1.4098

Table 15

REFRACTIVE INDEX-COMPOSITION DATA: METHYLCYCLOPENTANE AND DIISOPROPYL

Mol Fraction Methylcyclopentane	n_D^{20}
0.000	1.3749
0.114	1.3787
0.236	1.3827
0.307	1.3850
0.447	1.3899
0.507	1.3919
0.599	1.3950
0.733	1.3999
0.792	1.4020
0.879	1.4051
1.000	1.4099

Table 16

REFRACTIVE INDEX-COMPOSITION DATA: METHYLCYCLOPENTANE AND 2-METHYLPENTANE

Mol Fraction Methylcyclopentane	n_D^{20}
0.000	1.3714
0.107	1.3750
0.201	1.3783
0.300	1.3819
0.421	1.3864
0.522	1.3901
0.614	1.3938
0.735	1.3985
0.809	1.4016
0.911	1.4060
1.000	1.4099

Table 17

REFRACTIVE INDEX-COMPOSITION DATA: METHYLCYCLOPENTANE AND 3-METHYLPENTANE

Mol Fraction Methylcyclopentane	n_D^{20}
0.000	1.3765
0.113	1.3800
0.196	1.3824
0.301	1.3858
0.514	1.3928
0.615	1.3960
0.716	1.3995
0.809	1.4029
0.883	1.4056
1.000	1.4099

Table 18

REFRACTIVE INDEX-COMPOSITION DATA: METHYLCYCLOPENTANE AND HEXANE

Mol Fraction Methylcyclopentane	n_D^{20}
0.000	1.3749
0.169	1.3800
0.277	1.3836
0.407	1.3877
0.519	1.3913
0.593	1.3940
0.679	1.3971
0.774	1.4008
0.861	1.4040
1.000	1.4099

APPENDIX B

VALUES OF ANTOINE EQUATION CONSTANTS USED IN CALCULATING VAPOR PRESSURES OF PURE HYDROCARBONS (14)

$$\log P = A - B/(C + t)$$

P = Vapor pressure - mm Hg
t = Temperature - °C

	A	B	C
Neohexane	6.75483	1081.176	229.343
Diisopropyl	6.80983	1127.187	228.900
2-Methylpentane	6.83910	1135.410	226.572
3-Methylpentane	6.84887	1152.368	227.129
Hexane	6.87776	1171.530	224.336
Methylcyclopentane	6.86283	1186.059	226.042
Cyclohexane	6.84498	1203.526	222.863
Benzene	6.90565	1211.033	220.790

APPENDIX C

COMPOSITIONS OF HYDROCARBONS USED

Hydrocarbon:	Neohexane	Diisopropyl	2-Methylpentane	3-Methylpentane	Hexane	Methylcyclopentane	Cyclohexane	Benzene
Component - Wt %								
Isobutane		0.02						
Butane		0.01						
Isopentane		0.10						
Pentane		0.01						
Neohexane	100.00					0.03		
Diisopropyl		99.68	0.46					
2-Methylpentane		0.18	99.54	0.18		0.02		
3-Methylpentane				99.82	0.10	0.04		
Hexane					99.75	0.04		
Methylcyclopentane					0.15	99.68		0.09
Cyclohexane						0.09	99.78	0.03
Benzene						0.10		99.73
Isoheptanes							0.22	
Toluene								0.15
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

APPENDIX D

EQUILIBRATION TIMES OF MODIFIED HIPKIN AND MYERS STILL

Trial I

Charge - Mixture of Benzene and Neohexane: $n_D^{20} = 1.4430$

Pressure mm Hg	Elapsed Time Minutes	Vapor Temperature °C
760	0	52.0
760	5	59.00
760	10	59.28
760	15	59.38
760	20	59.48
760	25	59.46
760	30	59.52
760	35	59.52
760	40	59.52
760	60	59.50

Trial II

Add 25 cc 2-Methylpentane to Mixture of Benzene and 2-Methylpentane

Pressure mm Hg	Elapsed Time Minutes	Vapor Temperature °C
760	0	71.16
760	22	68.92
760	30	68.92
760	45	68.96

Trial III

Add 50 cc 2-Methylpentane to Benzene, 2-Methylpentane Mixture

Pressure mm Hg	Elapsed Time Minutes	Vapor Temperature °C
760	0	68.96
760	13	67.54
760	20	66.50
760	26	66.42
760	34	66.42
760	45	66.42

Trial IV

Add 25 cc Benzene to Benzene, 3-Methylpentane Mixture

Pressure mm Hg	Elapsed Time Minutes	Vapor Temperature °C
760	0	64.04
760	10	64.66
760	15	64.84
760	23	64.90
760	29	64.94
761	35	64.94
761	40	65.00
760	45	64.94

APPENDIX E

EQUILIBRATION TIME OF MODIFIED GILLESPIE STILL

Trial I

Add 5 cc Cyclohexane to Mixture of 3 Mol Per Cent Cyclohexane in Benzene

Pressure mm Hg	Elapsed Time Minutes	Refractive Index of Vapor Sample n_D^{20}
760.5	0	1.4967
760.5	10	1.4918
760.5	25	1.4918
760.5	30	1.4918

VITA

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