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VAPOR-LIQUID EQUILIBRIA --  
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METHYLCYCLOHEXANE-n-HEPTANE-SOLVENT  
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DISSERTATION

Presented to the Faculty of Approved: the School of

The University of Texas in

of the Regu

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DOCTOR OF P

David Andres, B.S., M.S.

Approved:

Austin, Texas

Dean of the Graduate School, 1942

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VAPOR-LIQUID EQUILIBRIA --  
METHYLCYCLOHEXANE-n-HEPTANE-SOLVENT

DISSERTATION

Presented to the Faculty of the Graduate School of

The University of Texas in Partial Fulfillment

of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

David Andres, B.S., M.S.

Austin, Texas

June, 1942

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Appendix

INTRODUCTION

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scale only by combinations of methods and successive treatments which are not economically suited to commercial practice.

The methods which have been used are: distillation at atmospheric and reduced pressure, chemical treatments (nitration, fuming sulfuric and chlorosulfonic acids), azeotropic distillation, fractional crystallization from solvents and/or equilibrium melting, adsorption on silica gel, and solvent extraction.

Chemical methods are too costly for commercial concentration of a dilute material. Fractional crystallization is virtually excluded because of the cost of large quantities of liquid air required for refrigeration.

From an economic point of view, distillation, azeotropic distillation, and solvent and silica gel extraction are industrial possibilities. However, workers at the Bureau of Standards, in the "Bureau and High-Pressure Research, Bur. Standards, 2, 525 (1932) (p. 534).



I

INTRODUCTION

The work reported in this dissertation covers one part of a general project -- the development of methods for the commercial separation of pure paraffin and naphthene hydrocarbons from petroleum. Pure methane, ethane, propane, butane, isobutane, pentane, and isopentane are now being produced commercially from petroleum. Higher molecular weight paraffins and naphthenes, with the exception of the lower boiling isomeric hexanes, cannot be separated in a pure condition by distillation alone, as is done with the lighter paraffins. Higher hydrocarbons have been isolated on a laboratory scale only by combinations of methods and successive treatments which are not economically suited to commercial practice.

The methods which have been used are: distillation at atmospheric and reduced pressure, chemical treatments (nitration, fuming sulfuric and chlorosulfonic acids), azeotropic distillation, fractional crystallization from solvents and/or equilibrium melting, adsorption on silica gel, and solvent extraction.

Chemical methods are too costly for commercial concentration of a dilute material. Fractional crystallization is virtually excluded because of the cost of large quantities of liquid air required for refrigeration.

From an economic point of view, distillation, azeotropic distillation, and solvent and silica gel extraction are industrial possibilities. However, workers at the Bureau of Standards, in the



course of an investigation of the composition of petroleum<sup>1</sup>, found these methods to be relatively ineffective for separation of paraffins from naphthenes. Very rarely did one or a combination of these methods yield satisfactory results without the additional use of chemical treatment or fractional crystallization. Even in the few cases where these four methods effected complete separation, the necessity for a large number of successive applications precludes commercial applicability. (See the paper of Bruun et al<sup>2</sup> on the separation of hexane isomers from a natural gasoline fraction). Aniline extraction<sup>3</sup> is a possibility for the separation of paraffins from naphthenes, although its use was attempted without great success in at least one case<sup>4</sup>.

An economical means of obtaining pure  $C_6$  to  $C_8$  hydrocarbons from petroleum will be of commercial value. A counter-current distillation-extraction process now being developed shows promise of becoming such a method. The process will consist of a solvent passing down through a fractionating column countercurrent to hydrocarbon vapors passing up through it. The method is therefore actually a combination of distillation and extraction into one unit operation. Solvent extraction separates materials almost solely according to structure; distillation separates primarily according to vapor pressure. A combination of these two into a process such as the one being developed should therefore effect separations which would be difficult or impossible with either of

<sup>1</sup>Rossini, Refiner Natural Gasoline Mfr., 16, 547 (1937).

<sup>2</sup>Bruun, Hicks-Bruun, and Faulconer, J. Am. Chem. Soc., 59, 2355 (1937).

<sup>3</sup>Varteressian and Fenske, Ind. Eng. Chem., 29, 270 (1937).

<sup>4</sup>Bruun and Hicks-Bruun, J. Research Nat. Bur. Standards, 8, 525 (1932) (RP 432).



the two processes alone, and in effect accomplish in one step what otherwise requires a number of successive applications of fractionation and solvent refining.

The distillation-extraction process is at present being developed with the binary paraffin-naphthene mixture n-heptane-methylcyclohexane. This system is of special interest. A ready market exists for pure n-heptane; this demand is at present being supplied with material which has its origin in the Jeffrey pine. Bruun and Hicks-Bruun<sup>5</sup> found n-heptane to comprise over 1% of a typical mid-continent petroleum. The 93-100° C. fraction of this petroleum, after removal of toluene, was split into two fractions by distillation in a 30 plate column. The fraction boiling around 98° C. consisted solely of methylcyclohexane and n-heptane. It will be noted that the separation of this mixture from the original petroleum was relatively simple, involving only the preliminary distillation to obtain the 93-100° C. fraction from the crude petroleum, the removal of toluene (this could be accomplished by azeotropic distillation as discussed later), and the final distillation in a 30 plate column to obtain the binary mixture. The resolution of the binary solution is more difficult. Bruun and Hicks-Bruun separated pure n-heptane from the mixture by subjecting it to two distillations in a 35-foot column packed with jack chain and a final treatment with chlorosulfonic acid. A more economical method for the separation of this mixture would greatly simplify the commercial production of n-heptane from petroleum.

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<sup>5</sup>Ibid.



To determine the relative effectiveness of various solvents for the separation of this mixture by the distillation-extraction process, it is necessary to determine the vapor-liquid equilibria of the systems methylcyclohexane-n-heptane-solvent. It is with these equilibria, at and above atmospheric pressure, that this dissertation is primarily concerned. For the systems methanol-water (Fig. 3, Table IV) and benzene-toluene (Fig. 4, Table V) above atmospheric pressure has been obtained in connection with verification of the reliability of the apparatus. These data have been compared to data from the literature<sup>6,7</sup>.

The effect of the addition of various solvents on the separation of methylcyclohexane from n-heptane has been determined at atmospheric and higher pressures (Figs. 5-12; Tables VIII, IX). The values of  $\alpha$ , the relative volatility between the two hydrocarbons, at atmospheric pressure in solutions containing about 50 mol % solvent are given in Table I. The solvents are listed in order of decreasing effectiveness.

number of plates required for a given separation with various values of  $\alpha$ .

Further information on the pressure of solution was obtained at atmospheric pressure. The separation in the distillation column increased slightly as the pressure increased from 1 atm. to 10 atm. and decreased sharply above that pressure.

<sup>6</sup> Fredig and Bayer, Z. Phys. Chem. **135**, 1 (1927).

<sup>7</sup> von Hahn, Forschung auf dem Gebiete des Ingenieurwesens, **A2**, 129 (1931).

## II

## SUMMARY OF RESULTS AND CONCLUSIONS

## Relative Effectiveness of Solvents at Atmospheric Pressure

A new apparatus for determining vapor-liquid equilibria at high pressures has been developed (Fig. 2). A small amount of data on the vapor-liquid equilibria of the systems methanol-water (Fig. 3, Table IV) and benzene-toluene (Fig. 4, Table V) above atmospheric pressure has been obtained in connection with verification of the reliability of the apparatus. These data have been compared to data from the literature<sup>6,7</sup>.

The effect of the addition of various solvents on the separation of methylcyclohexane from n-heptane has been determined at atmospheric and higher pressures (Figs. 5-12; Tables VIII, IX). The values of  $\alpha$ , the relative volatility between the two hydrocarbons, at atmospheric pressure in solutions containing about 80 mol % solvent are given in Table I. The solvents are listed in order of decreasing effectiveness.

Maximum separation in the presence of solvents was obtained at atmospheric pressure. The separation in the absence of solvents increased slightly up to 240° C. (about 250 p.s.i. abs.) and decreased sharply above that temperature, as shown in Table II.

<sup>6</sup>Bredig and Bayer, Z. Phys. Chem. 130, 1 (1927).

<sup>7</sup>von Huhn, Forschung auf dem Gebiete des Ingenieurwesens, A2, 129 (1931).



Table I

Relative Effectiveness of Solvents at Atmospheric Pressure

Solvent	Mol % Solvent	Relative Volatility $\alpha$
Aniline <sup>8</sup>	80	1.40
Furfural	79	1.35
Phenol	81	1.33
Nitrobenzene	82	1.32
Chlorex	81	1.29
Aminocyclohexane	76	1.16
None <sup>9</sup>	--	1.07

The vapor-liquid equilibria of all except the aniline system and the binary hydrocarbon system are given (Figs. 5-9, Table VIII). Various methods for calculating these equilibria have been attempted, but none has given satisfactory results. An illustrative problem is worked out in the appendix, section G, showing the difference in number of plates required for a given separation with various values of  $\alpha$ .

Maximum separation in the presence of solvents was obtained at atmospheric pressure. The separation in the absence of solvents increased slightly up to 240° C. (about 250 p.s.i. abs.) and decreased sharply above that temperature, as shown in Table II.

<sup>8</sup>Van Berg, M.S. Thesis in Ch.E., U. of Texas, 1940.

<sup>9</sup>Bromiley and Quiggle, Ind. Eng. Chem., 25, 1136 (1933).



Table II

SELECTION OF ANILINE AS THE OPTIMUM SOLVENT  
Binary Equilibria for Methylcyclohexane-n-Heptane

T, °C.	P P.S.I.	A. Azeotrope-Forming Solvents		$\alpha$	Equilibrium constant for MCH $K = y/x$
		Mol fraction n-H in liquid (1 - x)	Mol fraction n-H in vapor (1 - y)		
150	50.3	.456	.477	1.09	.962
190	107	.454	.477	1.10	.958
240	253	.454	.479	1.11	.955
260	325	.456	.471	1.04	.980

The binary system follows Raoult's law closely up to 150° C., but shows increasing deviations above that temperature.

The vapor pressure of methylcyclohexane from 150° C. to 275° C. has been determined (Fig. 15, Table XII). A partial chart of equilibrium constants (K values) for methylcyclohexane has been constructed using the experimental values (Table II, Fig. 16).

The critical solution temperature of the following systems were obtained: nitromethane-n-heptane, nitromethane-methylcyclohexane, and furfural-n-heptane (Table XI).

The boiling points of the binary azeotropes formed by methylcyclohexane and n-heptane with acetone, acetic acid, and pyridine have been determined (Table VII). Azeotropic distillation as a means of separating pure hydrocarbons from petroleum is discussed.

<sup>10</sup> Rossini, *Op. cit.*

<sup>11</sup> Rose and White, J. Research Nat. Bur. Standards, 21, 167 (1938) (RP 1123).

<sup>12</sup> Swietoslawski, *Ebulliometry*, p. 100, New York, Chemical Publishing Co., 1937.



## III

## SELECTION OF ANILINE AS THE OPTIMUM SOLVENT

## A. Azeotrope-Forming Solvents

Some work has been done recently by Rossini and coworkers<sup>10</sup> at the Bureau of Standards on the use of azeotrope-forming solvents for the separation of mixtures of hydrocarbons by distillation. This method was found to be very successful in removing aromatics from close boiling mixtures of aromatics, naphthenes, and paraffins<sup>11</sup>. It is rumored to be in commercial use for the separation of toluene from hydrocarbon mixtures.

According to Swietoslawski,

It has long been known that when a mixture of two azeotropes is distilled, it behaves just as if it were composed of two individual components which obey strictly Raoult's law or give only slight positive or negative deviations from it<sup>12</sup>.

The results of certain experiments indicate that there exists no such general rule. Rose and White were able to obtain nearly quantitative separation of a mixture of azeotropes boiling only 3° C. apart in a column containing approximately 25 theoretical plates. This degree of separation would not be obtained if the mixture obeyed Raoult's law or deviated from it only slightly. These investigators ascribe the high degree of separation to the fact that

<sup>10</sup>Rossini, Op. cit.

<sup>11</sup>Rose and White, J. Research Nat. Bur. Standards, 21, 167 (1938) (RP 1123).

<sup>12</sup>Swietoslawski, Ebulliometry, p. 100, New York, Chemical Publishing Co., 1937.



the relation existing between the concentrations in the liquid and vapor phases is considerably more favorable than usually encountered in simple distillation without an added component.

Insufficient data on mixtures of azeotropes containing paraffins and naphthenes or paraffins and isoparaffins exist to allow any conclusion with regard to their behavior on distillation except that it is more nearly "ideal" than that of mixtures containing aromatics. Commercial practice, and attention was turned to selective solvents.

In view of the above considerations, data on the boiling point spreads between the binary azeotropes formed by methylcyclohexane and by n-heptane with various solvents are of questionable value in predicting the separation of these two hydrocarbons by distillation with azeotrope-forming solvents. However, the existing boiling point data are given in Table VII. Boiling points of azeotropes of these hydrocarbons with acetic acid, acetone, and pyridine were obtained by the author. These were determined as follows: 15 cc. of the hydrocarbon under investigation were heated to boiling in the modified Cottrell apparatus (Fig. 17). The solvent was then added in 0.1 cc. portions through the condenser. The boiling point of the mixture was recorded after each 0.1 cc. addition. The minimum boiling temperature obtained was recorded as the boiling point of the azeotrope. The acetic acid data reported in the literature were found to be in error.

Azeotropic distillation, in combination with other methods, has been used extensively in attempts to separate paraffins from naphthenes and from isoparaffins. In no case, however, has it been possible to obtain pure hydrocarbons using azeotropic distillation alone or in combination with ordinary distillation. It has always

Hair, Glasgow, and Bossini, *ibid.*, 27, 39 (1941) (RP 1402).



been necessary to resort to fractional crystallization or chemical treatment to obtain the pure compounds. Although the data<sup>13,14</sup> indicate that in some cases, at least, better separation is effected by azeotropic distillation than by ordinary distillation, this separation is of limited scope and very incomplete. Consequently, it was considered unlikely that this process would be successful in commercial practice, and attention was turned to selective solvents, brims flash distillation<sup>16</sup>, and the recirculation method (Otmer apparatus, Fig. 1)<sup>17</sup>.

#### B. Selective Solvents

Research in the petroleum industry has shown that, of a large number of these solvents investigated, those most selective for liquid, the separation of paraffins from naphthenes (and from aromatics and asphaltenes) are propane, acetone, acrolein, aniline, chlorex, crotonaldehyde, furfural, phenol, and nitrobenzene. Since it seemed likely that these solvents would be the most selective in distillation processes also, aniline, chlorex, furfural, phenol, and nitrobenzene were chosen for investigation. Aminocyclohexane was investigated to determine whether a substituted anphthene would show marked paraffin-naphthene selectivity. It was much poorer in this respect than the other solvents.

The equilibrium flash method utilizes a packed chamber which provides a large contact surface between liquid and vapor. The chamber is kept at constant temperature. Solution is fed continuously; part of the solution is flashed to vapor, and the vapor

<sup>13</sup>White and Rose, J. Research Nat. Bur. Standards, 17, 943 (1936) (RP 955).  
<sup>14</sup>Good, Ind. Eng. Chem., 12, 453 (1927).  
<sup>16</sup>Mair, Glasgow, and Rossini, *ibid.*, 27, 39 (1941) (RP 1402).



## IV

and liquid are continuously drawn off. This also requires large quantities of liquid.

CHOICE OF METHODS -- THE DEVELOPMENT OF AN APPARATUS FOR DETERMINING VAPOR-LIQUID EQUILIBRIA AT HIGH PRESSURES

In the Othmer apparatus, vapor from the boiling liquid passes through a condenser into a liquid storage chamber, from which it overflows.

A. Atmospheric Pressure Equilibria

The methods used for the determination of ternary equilibria at atmospheric pressure are: differential distillation<sup>15</sup>, equilibrium flash distillation<sup>16</sup>, and the recirculation method (Othmer apparatus, Fig. 1)<sup>17</sup>.

The differential distillation method consists of the distillation of a small vapor sample from a relatively large body of liquid, the vapor sample being so small that its removal causes no appreciable change in the composition of the liquid. Reflux is carefully eliminated; the vapor is therefore in equilibrium with the liquid from which it was formed. Due to the large quantity of liquid required to obtain sufficient vapor sample for analysis, this method is cumbersome for dilute solutions and those in which the solute is much more volatile than the solvent. Since the systems under investigation were of the latter type, this method was rejected.

The equilibrium flash method utilizes a packed chamber which provides a large contact surface between liquid and vapor. The chamber is kept at constant temperature. Solution is fed continuously; part of the solution is flashed to vapor, and the vapor of

<sup>15</sup>Zawidzki, Z. Phys. Chem., 25, 129 (1900).

<sup>16</sup>Leslie and Good, Ind. Eng. Chem., 19, 453 (1927).

<sup>17</sup>Othmer, Ind. Eng. Chem. Anal. Ed., 4, 232 (1934).



and liquid are continuously drawn off. This also requires large quantities of material, and requires a constant temperature bath as well.

In the Othmer apparatus, vapor from the boiling liquid passes through a condenser into a liquid storage chamber, from which it overflows back into the distillation chamber. The circulation is continued until the boiling liquid and the material in the vapor condensate chamber are in equilibrium. This is by far the most convenient of the three methods wherever it can be used, since the apparatus is easy to operate and relatively small quantities of material are required. The Othmer apparatus was used in this work for all equilibria determined at atmospheric pressure.

#### B. High Pressure Equilibria

Of the three types of equipment discussed above, the differential distillation apparatus<sup>18</sup> and one type of recirculation apparatus<sup>19</sup> have been used for determining vapor-liquid equilibria at high pressures. Equilibrium flash distillation is a possible method, but has not been used for this purpose. The method of Kay<sup>20</sup> is applicable only to binary systems. It is based on the fact that, in binary systems, a mixture having a dew point at a particular temperature and pressure is in equilibrium with the mixture which has its bubble point at that same temperature and pressure. Since there are in general, for any three given components, a series of

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<sup>18</sup>Bredig and Bayer, Op. cit.

<sup>19</sup>Scheeline and Gilliland, Ind. Eng. Chem., 31, 1050 (1939).

<sup>20</sup>Kay, Ind. Eng. Chem., 30, 459 (1938).



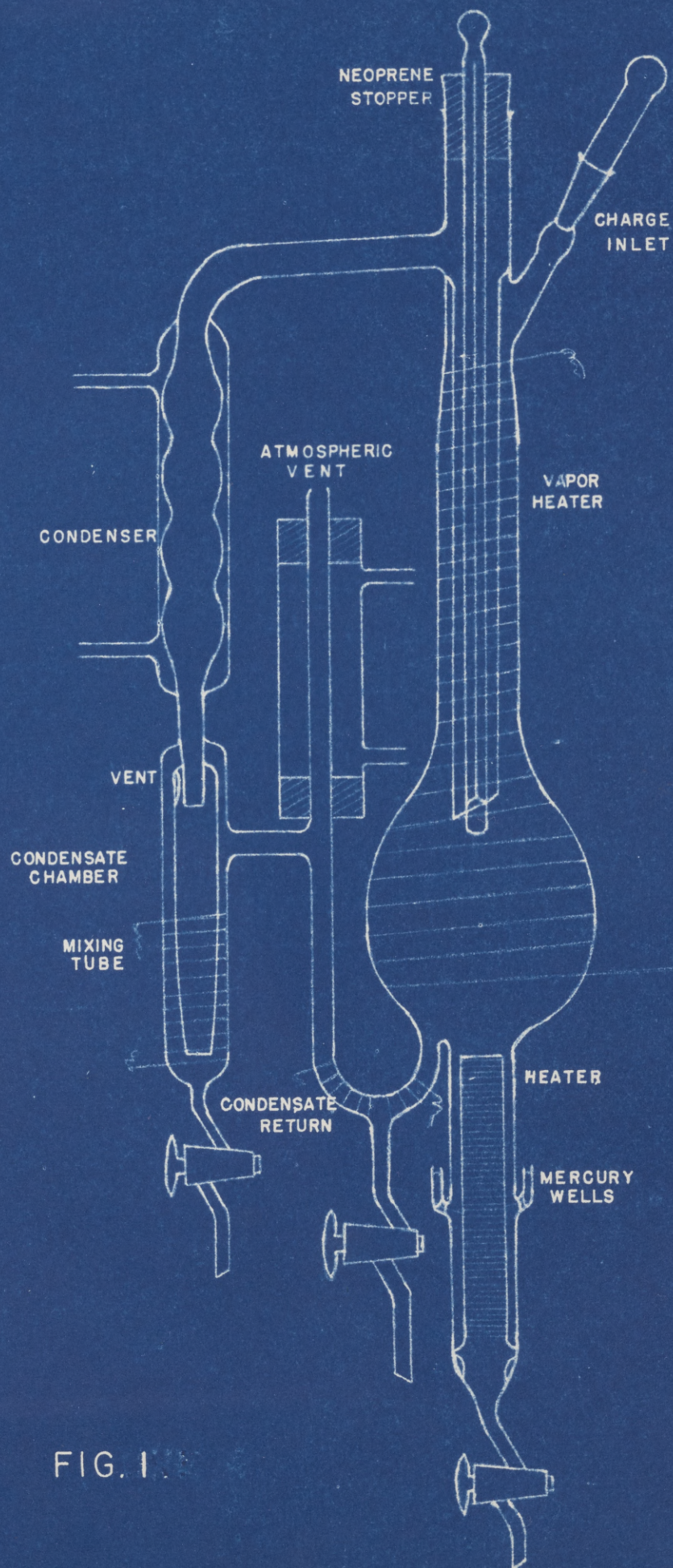


FIG. 1



or by balancing of heat input against heat removed. Since the compositions having equal bubble points and dew points, the method former method is the simpler and less delicate of the two, it was cannot be used for ternary systems.

Differential distillation and the equilibrium flash method were rejected for reasons already given. The recirculation apparatus described in the literature was part glass and part metal, and involved glass-to-metal seals. This construction is not well adapted to high pressures and elevated temperatures.

Since the recirculation apparatus offers many advantages, it was decided to develop one for use at high pressure, to be built entirely of steel. In the first model sufficient head room over the boiling liquid was allowed to give no entrainment according to the Souders and Brown equation<sup>21</sup>. However, it was found that the vapor condensate composition varied with distillation rate. This could be caused by spray or entrainment and also by incomplete mixing, resulting in flashing in the still. The apparatus was then rebuilt to give more head room, and larger cross-sectional area in the disengaging section. A device to insure thorough mixing of the liquid in the still was also included. Provision was made for disassembling the apparatus so that any further internal changes could be made which might prove necessary. A check valve was installed between the vapor condensate chamber and the still to prevent backflow and contamination of the vapor condensate sample with still liquid during sampling or on sudden surges while in operation.

Pressure and temperature could be controlled by the presence of an inert gas at the desired pressure (as in the Othmer apparatus)

<sup>21</sup>Souders and Brown, Ind. Eng. Chem., 26, 98 (1934).

<sup>22</sup>Winkler, Z. Phys. Chem. 501424 (1922).



or by balancing of heat input against heat removed. Since the former method is the simpler and less delicate of the two, it was the first to be tried. It was realized that the inert gas would dissolve to some extent in the vapor condensate, but it was hoped that this solubility could be made negligible by controlling the vapor condensate temperature. It was found that changing the vapor condensate temperature under set conditions of temperature and pressure changed the composition of the vapor in equilibrium with a given liquid. A study of the literature<sup>22</sup> revealed that there is a definite temperature of minimum solubility for any gas-liquid combination, with the solubility increasing at both higher and lower temperatures. The effect of solubility on vapor-liquid equilibria even at this point might not be negligible. Therefore, this method of temperature control had to be abandoned. The second method -- that of balancing heat input against heat removal -- proved satisfactory. Figure 2 shows the apparatus in the form finally used. Several improvements suggested themselves in the course of the experimental work. These are given in the appendix, section E.

The limits of operating conditions are given in Table III.

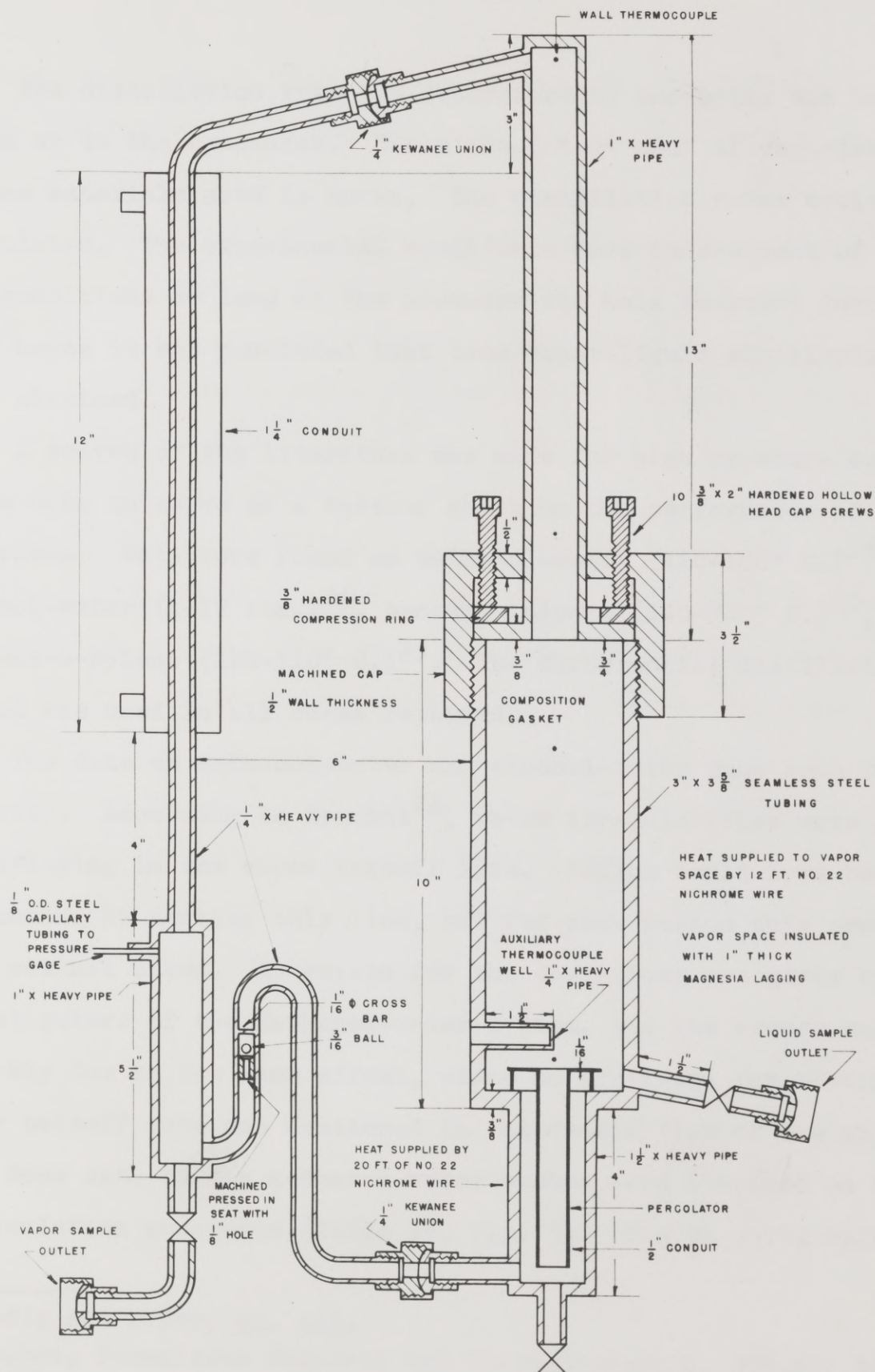
Table III

Range of Operating Conditions

	Maximum	Minimum
Distillation Rate, cc. vapor/min.	6000	500
Total Liquid Charge, cc.	600	350
Time of Operation after Attainment of Steady Conditions, Hrs.	5	1/2

<sup>22</sup>Winkler, Z. Phys. Chem. 9, 171 (1892).





HIGH PRESSURE VAPOR-LIQUID EQUILIBRIUM APPARATUS



The distillation rate was determined by measuring the heat given up to the condenser. Since the latent heat of vaporization of the materials used is known, the distillation rates could be calculated. The experimental equilibria were independent of operating conditions so long as the pressure was held constant during a run; hence it was concluded that true vapor-liquid equilibrium data were obtained.

A search of the literature was made for high pressure equilibrium data to serve as a further check on the performance of the apparatus. Data were found on methanol-water (120-180° C.)<sup>23</sup>, ethanol-water (1-15 atm.)<sup>24</sup>, benzene-toluene (120-300° C.)<sup>25</sup>, and benzene-m-xylene (120-310° C.)<sup>25</sup>. The differential distillation method was used in all cases reported.

The data on methanol-water and ethanol-water show some irregularity. According to Grumbdt<sup>24</sup>, these irregularities were caused by refluxing in the vapor takeoff line. Reflux could have been eliminated by heating this line, but for some reason this precaution was not taken. No reason for the deviations was given by the investigators of the methanol-water system, but the errors were probably due to the same effect, since no provision for heating the vapor takeoff tube was mentioned in the description of the apparatus.

Some data on the methanol-water system were obtained on the recirculation apparatus (Table IV, Fig. 3). Though quite self-con-

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<sup>23</sup>Bredig and Bayer, Op. cit.

<sup>24</sup>Grumbdt, Technische Mechanik und Thermodynamik I, 309-15; 349-57 (1930).

<sup>25</sup>von Huhn, Op. cit.



sistent, they show a slightly lower separation than was found by Bredig and Bayer. This substantiates the belief that the previous data are somewhat high due to refluxing.

Von Huhn's data on benzene-toluene are self-consistent. However, in an attempt to check them, it was discovered that the author's equilibria showed greater separation (see Table V, Fig. 4). The benzene-toluene system is known to obey Raoult's law at atmospheric pressure (80-110° C.)<sup>26</sup>. Von Huhn's data at 120° C. show 30% less separation than is predicted by Raoult's law. The author's data at 120° using the recirculation apparatus follow Raoult's law to within the limit of analytical error. From the description of apparatus and procedure given by von Huhn, it seems probable that not enough head room was allowed in his bomb, that the vapor sample was taken off too rapidly, and that liquid was entrained with the vapor.

The consistency of the data obtained on the recirculation apparatus over the wide range of distillation rates and the foregoing considerations are conclusive evidence of the satisfactory operation of this piece of equipment.

<sup>26</sup>Rosanoff, Bacon, and Schulze, J. Am. Chem. Soc., 36, 1994 (1914).



Vapor - Liquid Equilibrium  
of Methanol - Water at  
180° C. (Table IV)

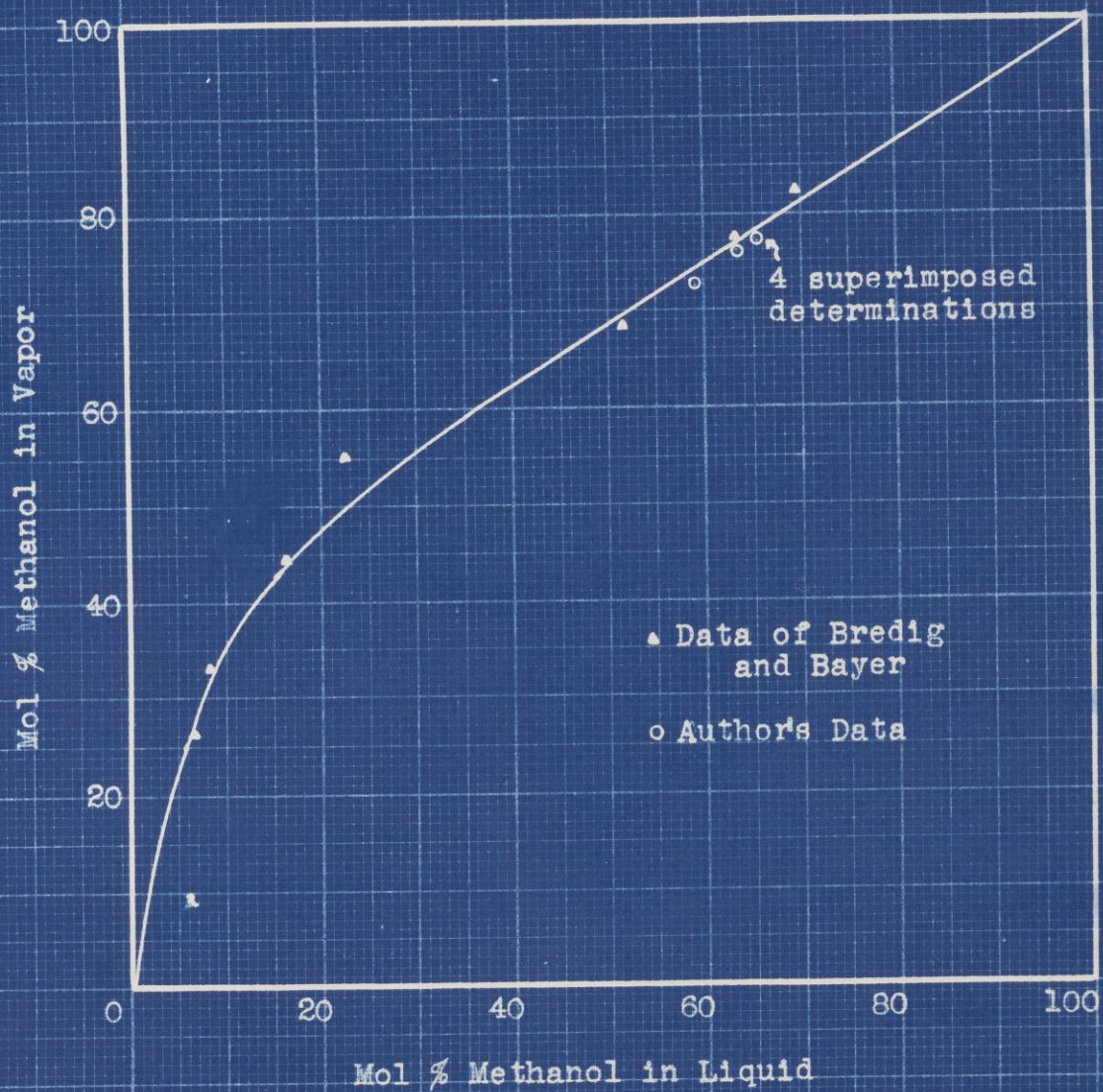


FIG. 3



Vapor - Liquid Equilibrium of  
Benzene - Toluene at  
120° C. (Table V)

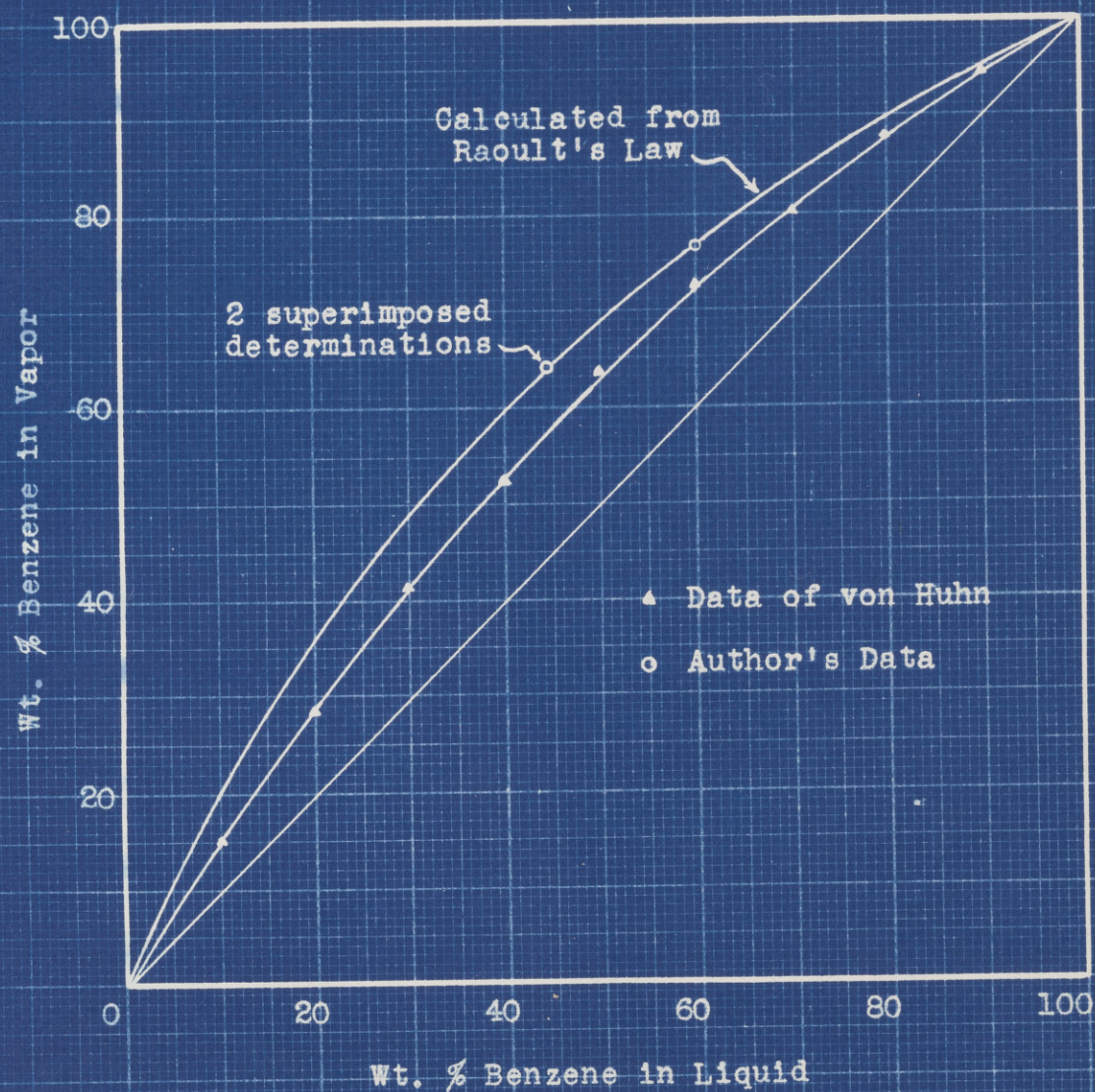


FIG. 4



Table IV

## Data on Methanol-Water (Fig. 3)

Determination No.	Mol % Methanol in Liquid	Mol % Methanol in Vapor	Temp., °C.	Pressure, p.s.i. abs.
1	65.2	77.4	180	328
2	59.0	73.3	180	315
3	63.3	76.6	180	325
4	66.2	77.6	180	330
5	65.3	77.0	180	327
6	65.5	77.5	180	328

Table V

## Data on Benzene-Toluene (Fig. 4)

Determination No.	Mol % Benzene in Liquid	Mol % Benzene in Vapor	Temp., °C.	Pressure, p.s.i. abs.
1	48.4	68.4	120	19
2	48.4	67.8	120	19
3	63.7	79.7	120	21
4	56.0	69.6	180	115
5	49.4	64.1	180	108
6	47.8	55.3	280	465
7	47.8	55.0	280	463



## V

## SUMMARIZED DATA AND RESULTS

The solvents chosen for study were aniline, nitrobenzene, furfural, phenol, chlorex, and aminocyclohexane. Vapor-liquid equilibrium curves were determined at atmospheric pressure on the ternary systems methylcyclohexane-n-heptane-solvent at a constant solvent concentration of approximately 80 mol % in the liquid phase (Figs. 5-9, Table VIII). This concentration was chosen, since it is near the optimum for commercial separation. The relative volatility for methylcyclohexane-n-heptane in this solution was found to be substantially independent of hydrocarbon ratio. Since this is so, only one determination is needed at a given pressure and solvent concentration.

At pressures above one atmosphere, the solvent concentration and temperature were systematically varied. One determination was made at each concentration and at each temperature. Data for aniline were taken at 150° C., 200° C. and 250° C. (Fig. 10, Table IX); for phenol at 200° C. and 250° C. (Fig. 11, Table IX); and for nitrobenzene at 200° C. (Fig. 12, Table IX). The results were plotted as isotherms of relative volatility of the two hydrocarbons vs. mol per cent solvent.

In order to detect any chemical reaction between the solvents and the hydrocarbons, 25 cc. of the hydrocarbons with 25 cc. of each solvent in turn were enclosed in a bomb and heated at 250° C. for four hours. In every case there was no change in quantity or composition of the hydrocarbon mixture. However, nitrobenzene,



furfural, and chlorex were unstable at this temperature, darkening and forming some gas. Since the presence of even moderate quantities of inert gas seriously interfered with the equilibrium determinations, these solvents could not be investigated at 250° C. Nitrobenzene was sufficiently stable to use at 200° C., but chlorex and furfural were not.

The values of  $\alpha$ , the relative volatility between the two hydrocarbons at various temperatures in solutions containing 80 mol % solvent, are listed in Table VI.

Table VI

The Relative Volatility of Methylcyclohexane-n-Heptane  
in Solutions Containing 80 Mol % Solvent  
(Figs. 5-12; Tables VIII, IX)

Solvent	Values of $\alpha$ at Indicated Pressure or Temp.			
	at 1 atm.	at 150°	at 200°	at 250°
Aniline	1.40 <sup>27</sup>	1.34	1.30	1.26
Furfural	1.35	--	--	--
Phenol	1.33	--	1.31	1.26
Nitrobenzene	1.32	--	1.28	--
Chlorex	1.29	--	--	--
Aminocyclohexane	1.16	--	--	--
None	1.07 <sup>28</sup>	1.09	1.10	1.08

In all cases, the solvents were more effective at atmospheric pressure than at higher pressures and temperatures. However, in-

<sup>27</sup>Van Berg, *Op. cit.*

<sup>28</sup>Bromiley and Quiggle, *Op. cit.*



Methylcyclohexane - n-Heptane - Furfural  
Vapor - Liquid Equilibrium at Atmospheric  
Pressure in Solutions Containing 80 Mol  
% Furfural (Solvent-Free Basis)  
(Table VIII)

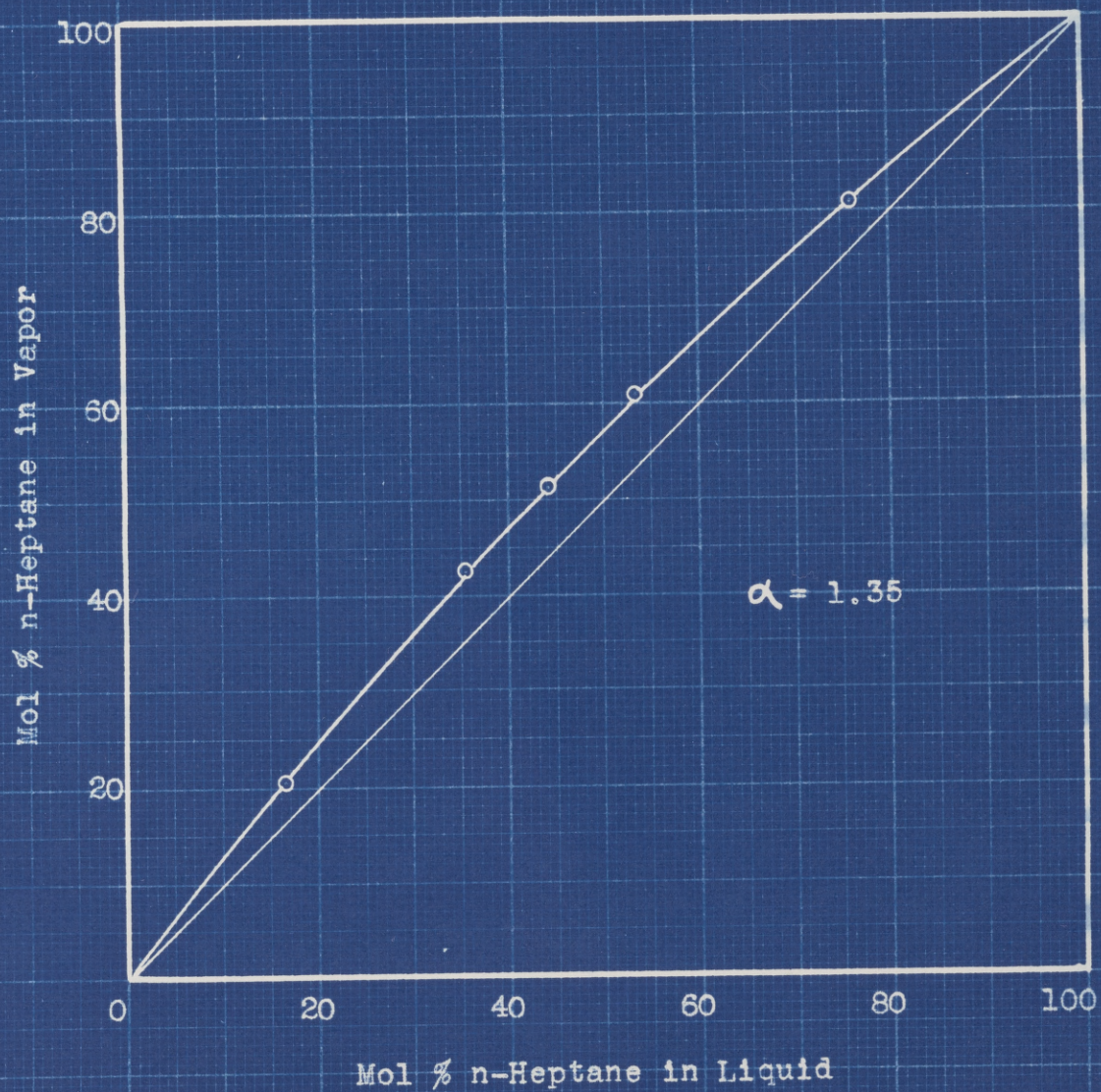


FIG. 5



Methylcyclohexane - n-Heptane - Phenol  
Vapor - Liquid Equilibrium at Atmospheric  
Pressure in Solutions Containing 80 Mol  
% Phenol (Solvent-Free Basis)  
(Table VIII)

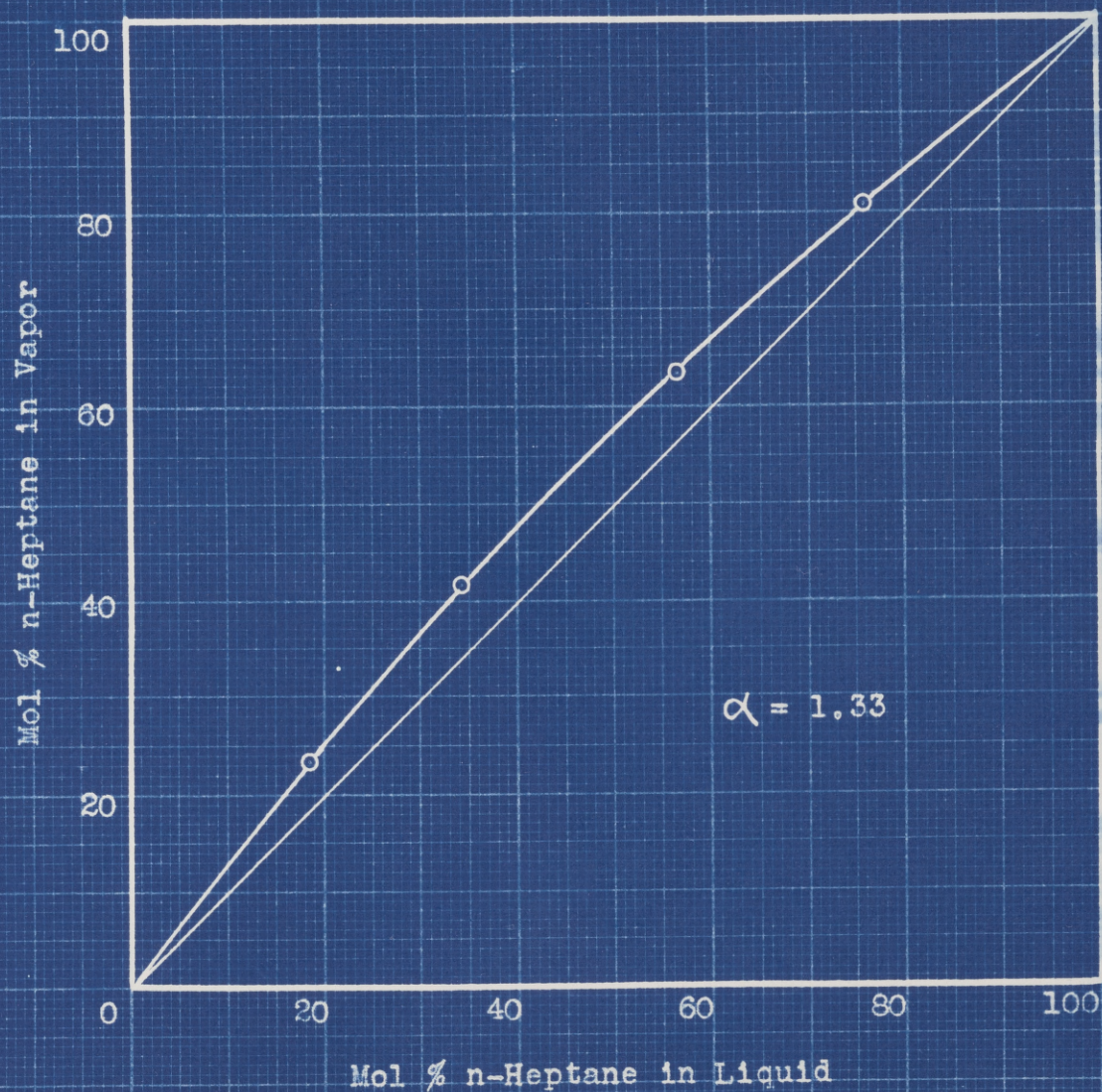


FIG. 6



Methylcyclohexane - n-Heptane - Nitrobenzene  
Vapor - Liquid Equilibrium at Atmospheric  
Pressure in Solutions Containing 80 Mol  
% Nitrobenzene (Solvent-Free Basis)  
(Table VIII)

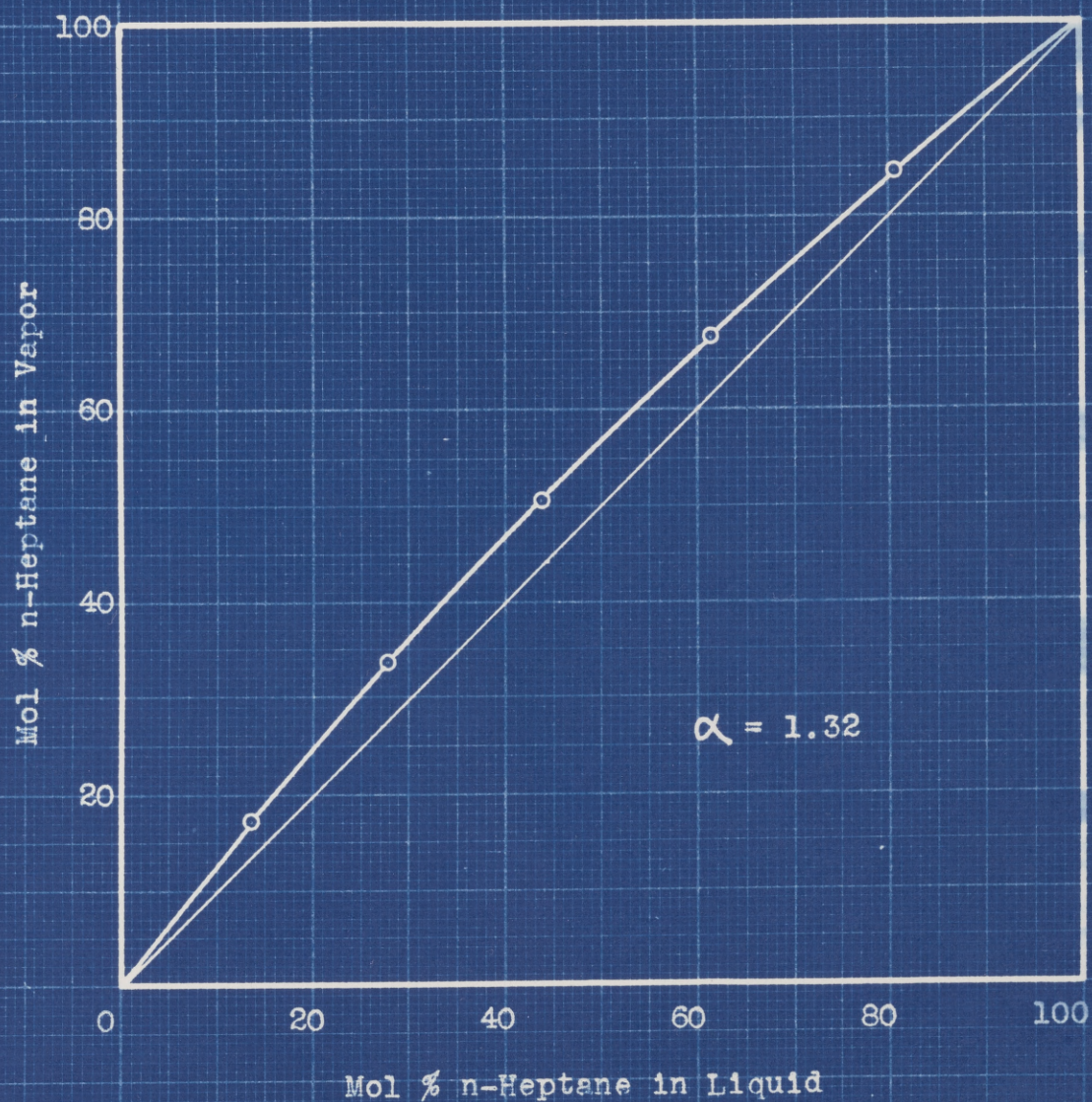


FIG. 7



Methylcyclohexane - n-Heptane-Chlorex  
Vapor - Liquid Equilibrium at Atmospheric  
Pressure in Solutions Containing 80 Mol  
% Chlorex (Solvent-Free Basis)  
(Table VIII)

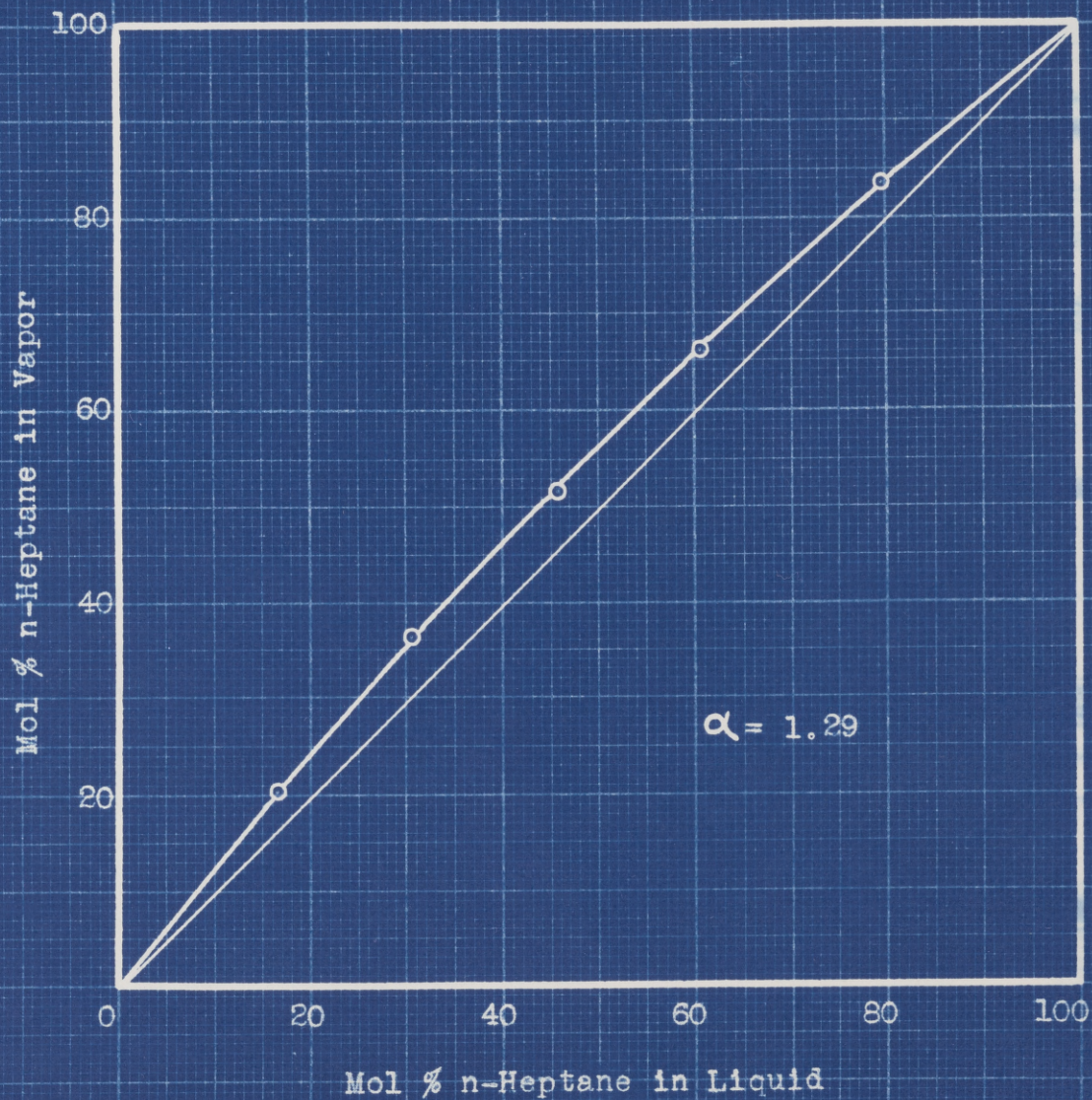


FIG. 8



Methylcyclohexane - n-Heptane - Aminocyclohexane  
Vapor - Liquid Equilibrium at Atmospheric  
Pressure in Solutions Containing 80 Mol  
% Aminocyclohexane (Solvent-Free Basis)  
(Table VIII)

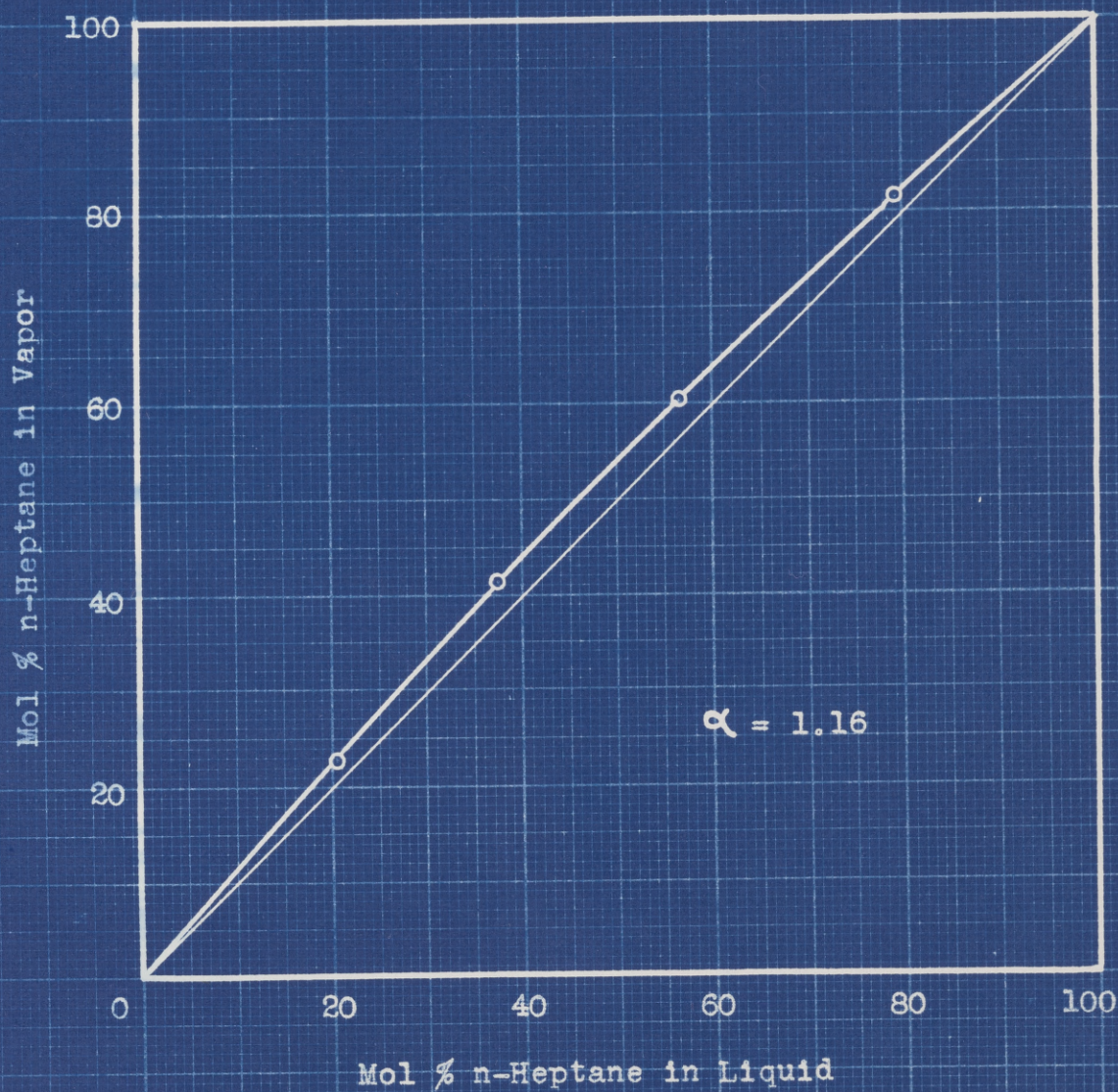


FIG. 9



Relative Volatility of Methylcyclohexane

- n-Heptane in Aniline at

150° C., 200° C., and 250° C.

(Table IX)

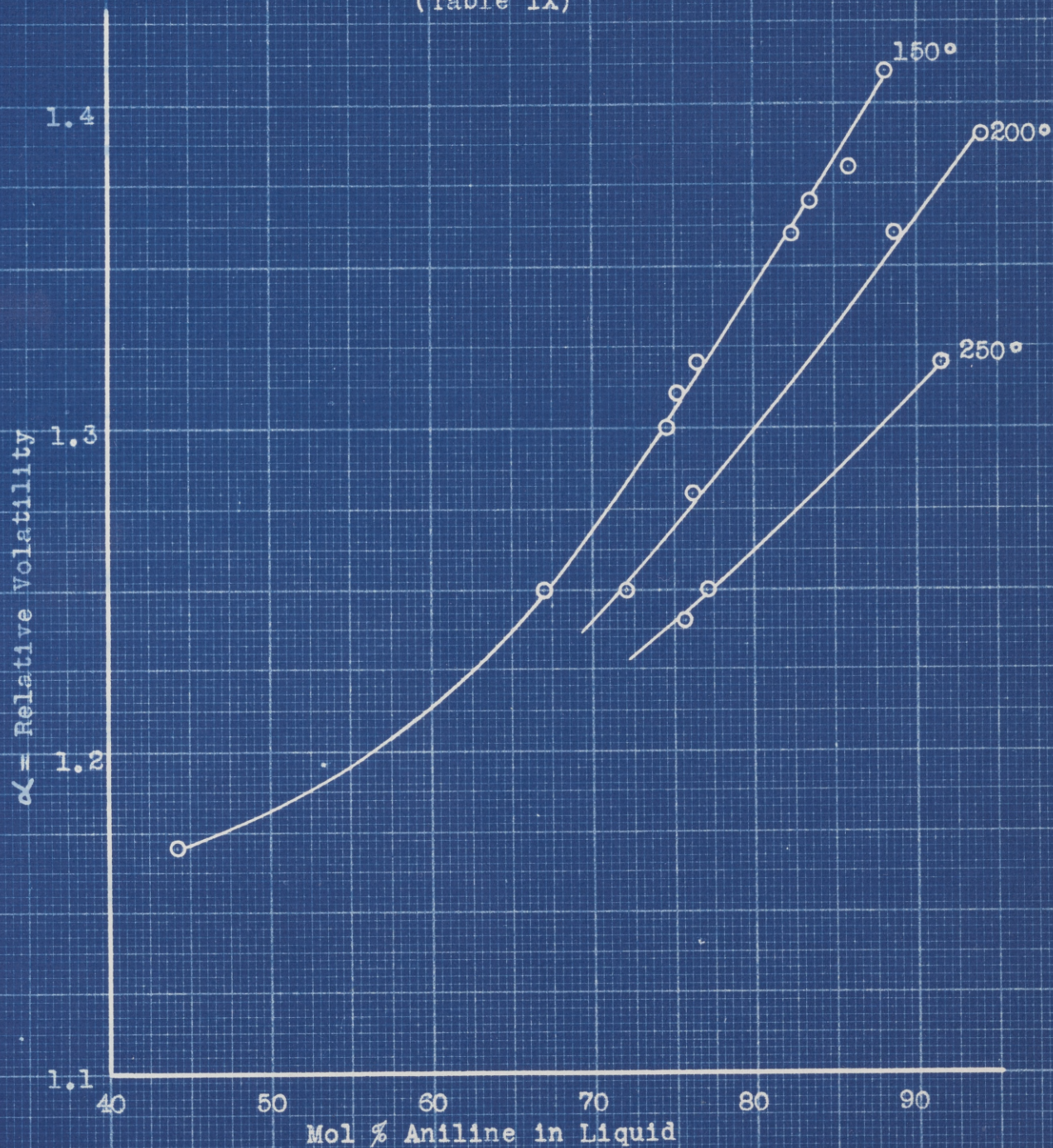


FIG. 10



Relative Volatility of Methylcyclohexane -  
n-Heptane in Phenol at 200° C. and 250°C.

(Table IX)

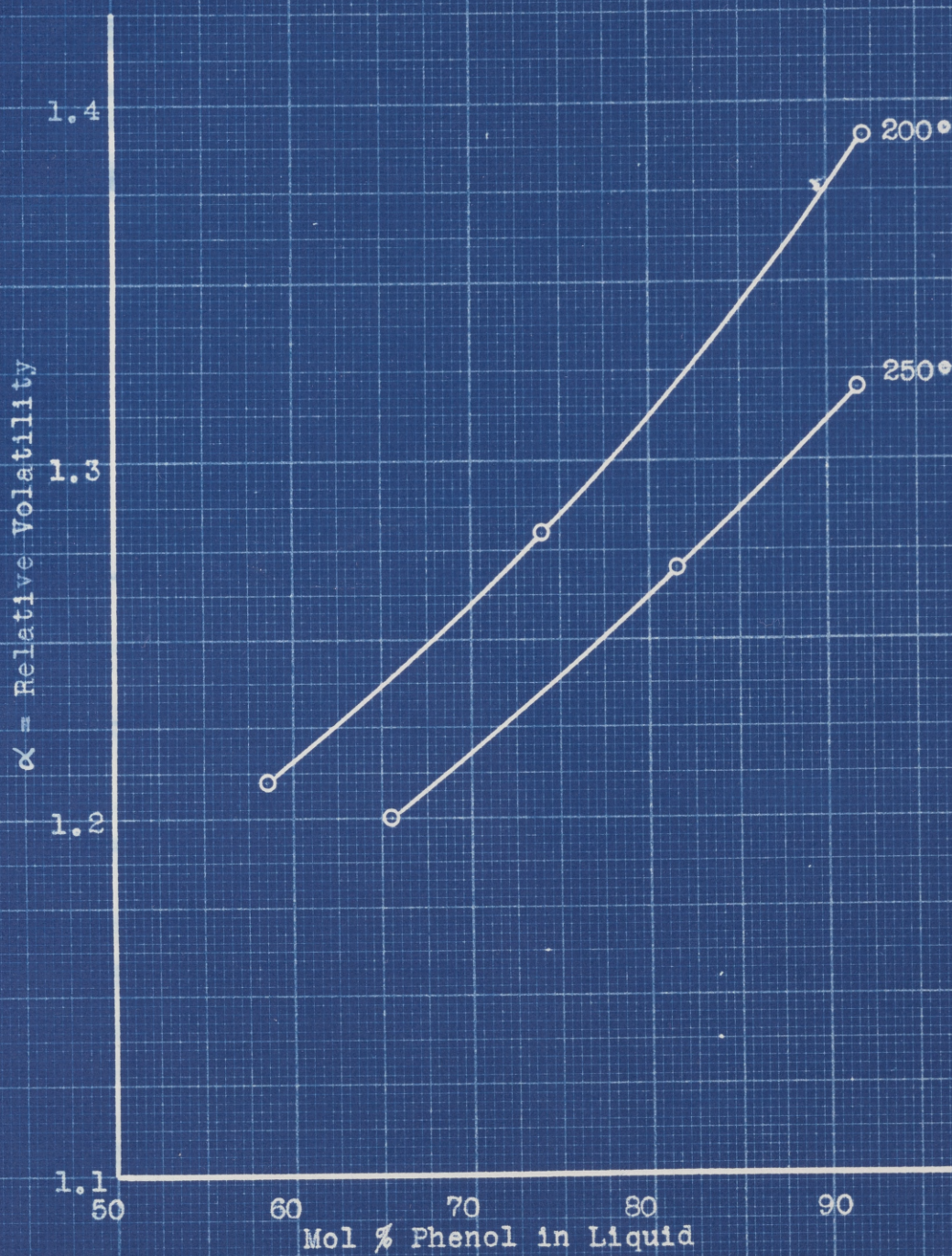


FIG. 11



Relative Volatility of Methylcyclohexane  
- n-Heptane in Nitrobenzene at 200° C.  
(Table IX)

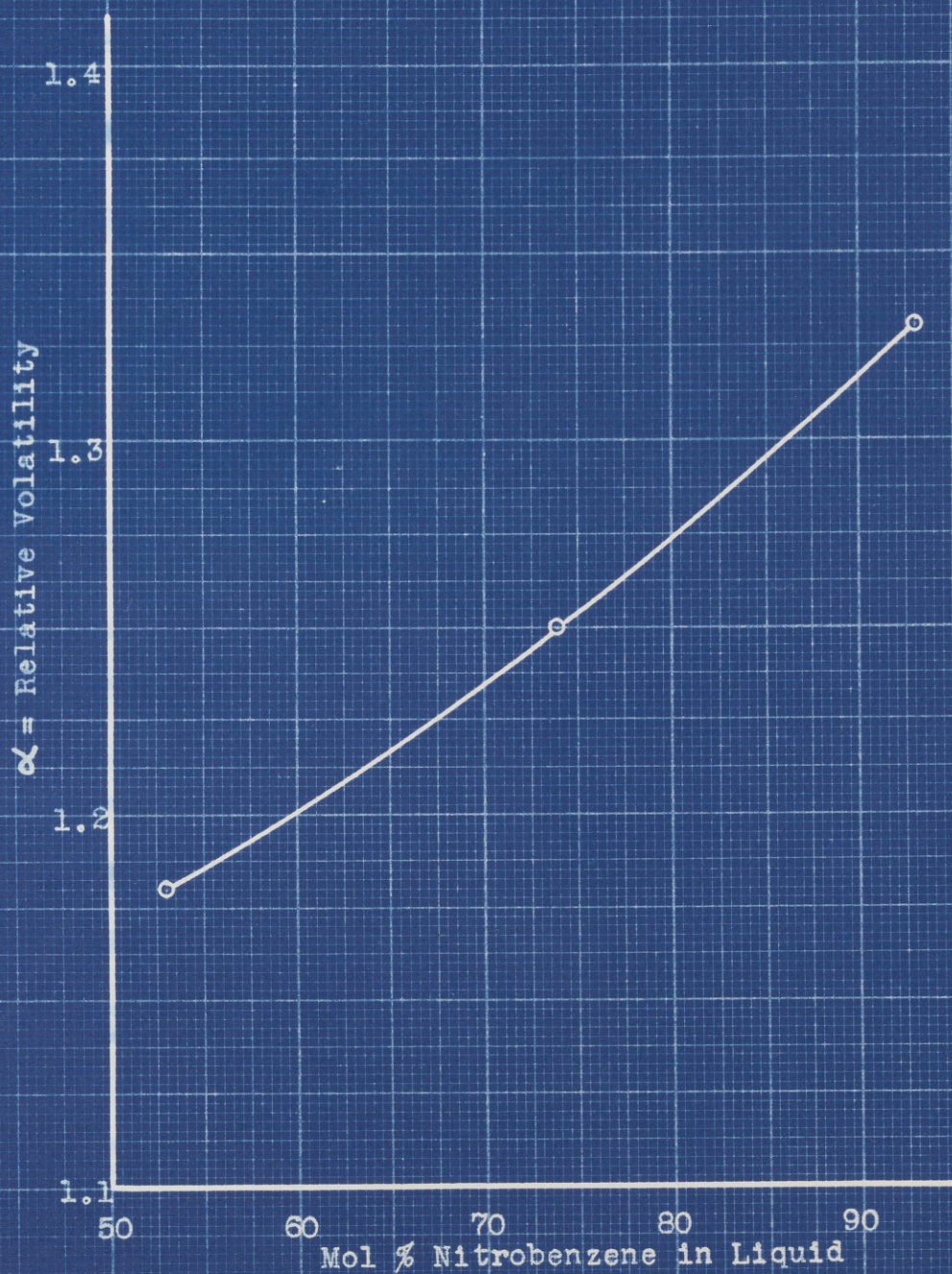


FIG. 12



creased temperature and pressure reduced the effectiveness of some solvents more than others.

The data on the binary system methylcyclohexane-n-heptane have been presented in the summary of results, Table II.

## VI

### ATTEMPTED CORRELATIONS

All attempts to calculate the ternary equilibria from data on the individual components and their binary mixtures failed; Raoult's and Henry's laws could not be applied. Experimental K values for n-heptane in the ternary solutions were approximately twice as large as those read from the M. I. T. K chart for n-heptane in crude oil. Attempts were made to calculate the ternary equilibrium chlorex-methylcyclohexane-n-heptane from the binary equilibria chlorex-methylcyclohexane (Fig. 13, Table X) and chlorex-n-heptane (Fig. 14, Table X). It was first assumed that in the ternary mixtures each hydrocarbon behaved like the other toward the solvent; for instance, in a solution containing 80 mol % chlorex, 10 mol % methylcyclohexane, and 10 mol % n-heptane, the n-heptane and methylcyclohexane were taken to have the same K values as in 80 mol % chlorex-20 mol % hydrocarbon binary systems. Equilibria calculated on this assumption did not agree with the experimental values. It was then assumed that each hydrocarbon behaved as solvent toward the other; by this assumption the hydrocarbons in the above solutions should have the same K values as in binary systems of 90 mol % chlorex-10 mol % hydrocarbon. Equilibria calculated on this basis also showed no agreement with experimental values.



Methylcyclohexane - Chlorex  
Vapor - Liquid Equilibrium  
at Atmospheric Pressure  
(Table X)

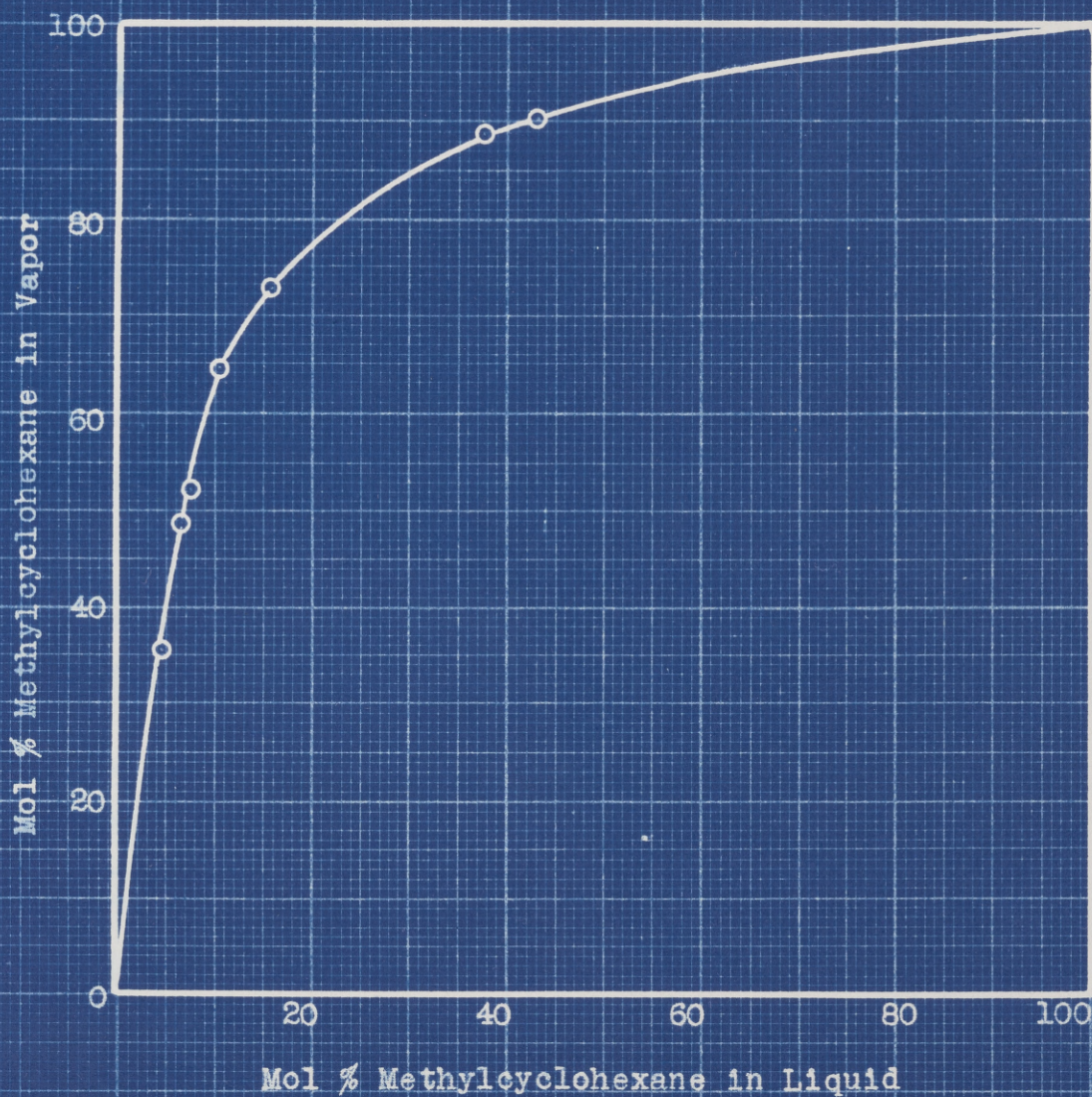


FIG. 13



n-Heptane - Chlorex  
Vapor - Liquid Equilibrium  
at Atmospheric Pressure  
(Table X)

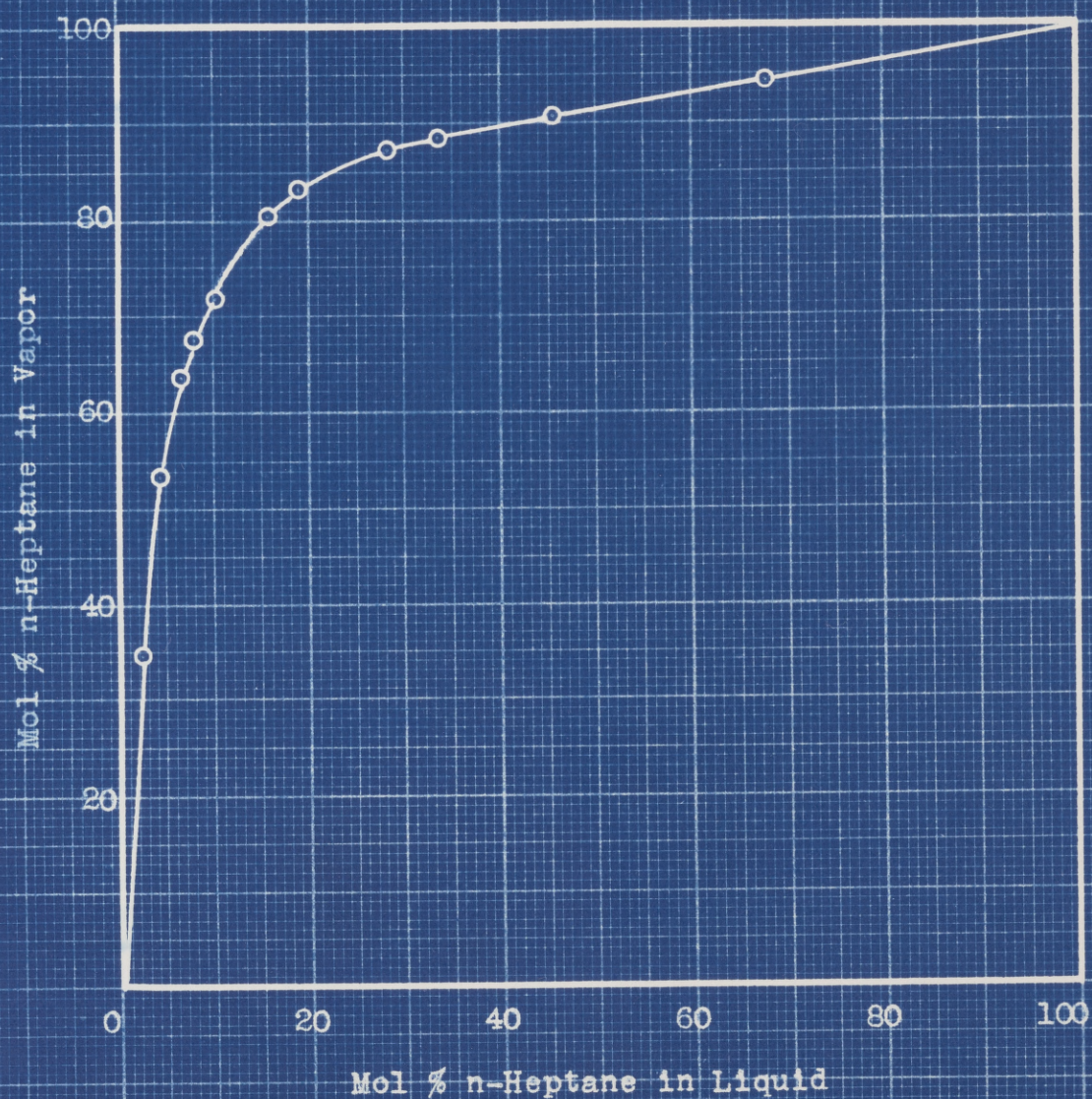


FIG. 14



## VII

## K CHART FOR METHYLCYCLOHEXANE

An attempt was made to calculate equilibrium constants for methylcyclohexane from approximate fugacities obtained by means of the Lewis compressibility chart. The vapor pressure of methylcyclohexane from 150 to 275° C. was determined in connection with this correlation (Fig. 15, Table XII). The calculated values deviated from those experimentally determined. This method of calculation could therefore not be used. The chart given in Fig. 16 was constructed from the experimental values and the Brown and M. I. T. charts for n-heptane. The experimentally determined values for methylcyclohexane were superimposed on the n-heptane charts, and lines were drawn from these values by interpolation between n-heptane lines.





Vapor Pressure of Methylcyclohexane  
Above 1 Atmosphere  
(Table XII)

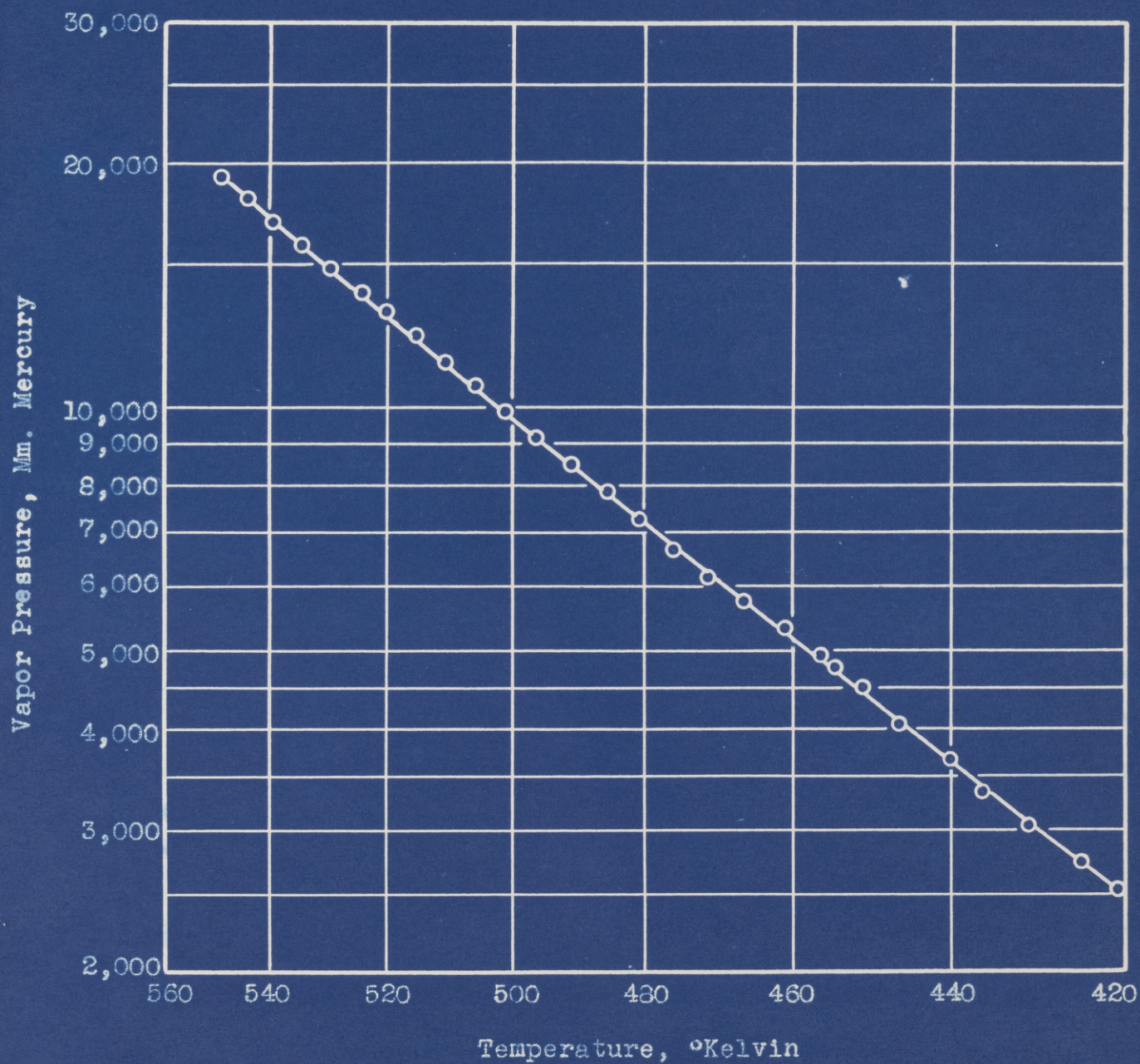
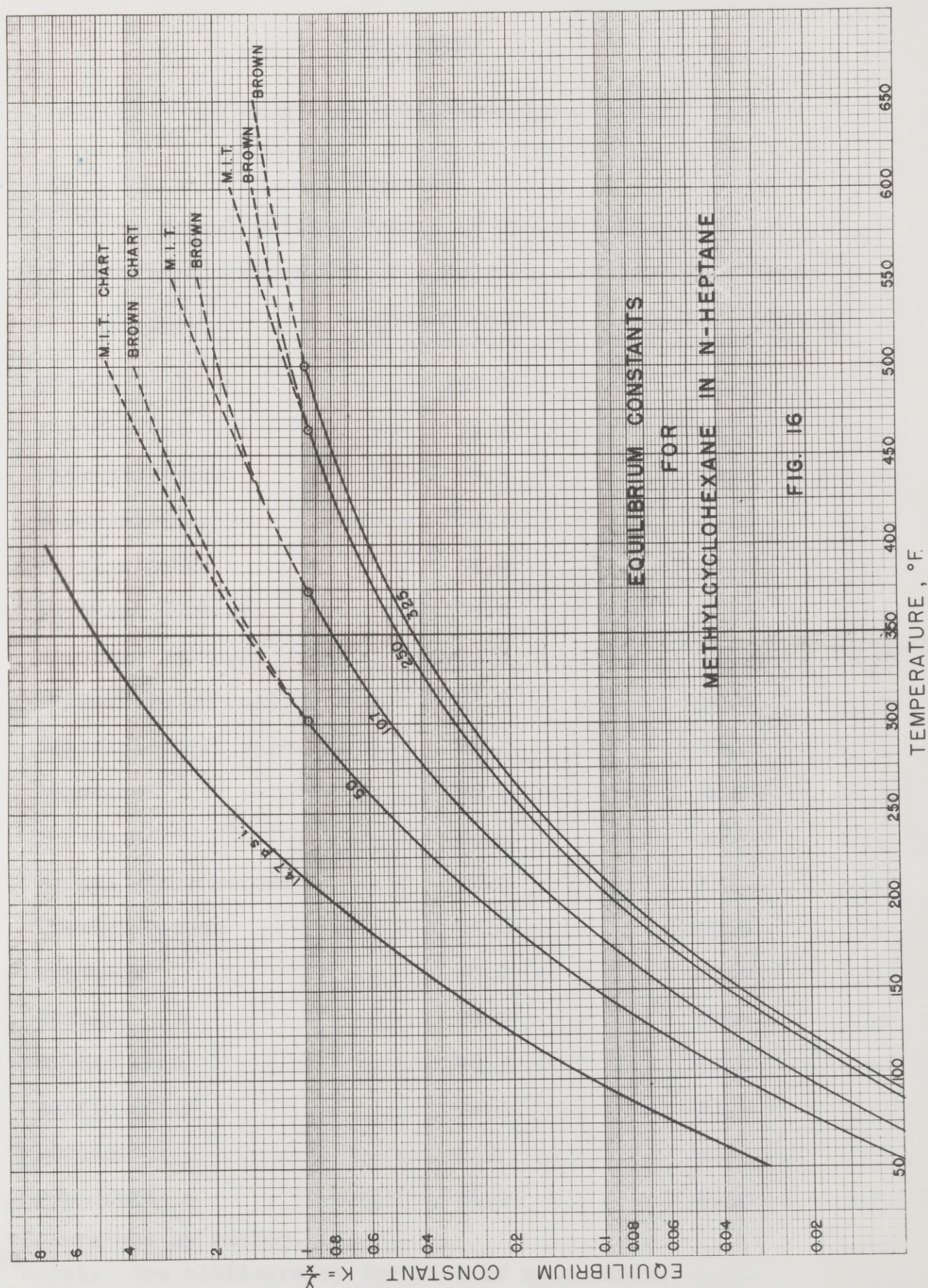


FIG. 15







## APPENDIX

Ternary Equilibria A. Data and Results *n*-Heptane-Solvent  
at Atmospheric Pressure (Figs. 5-9)

Table VII

Normal Boiling Points of Binary Azeotropes  
of Methylcyclohexane and of *n*-Heptane with other Compounds<sup>29</sup>

Solvent	Boiling Point of MCH Azeotrope, °C.	Boiling Point of <i>n</i> -H Azeotrope, °C.
Glycol	100.8	98.3
Isopropanol	77.4	76.4
Isoamyl nitrite	95.5	95.0
Chloropicrin	100.7	98.4
Allyl alcohol	85.0	84.5
Isobutyl carbinol	100.0	97.7
Tertiary butanol	78.2	78.0
Primary isobutanol	93.2	90.8
Dimethyl ethyl carbinol	93.4	91.2
<i>n</i> -Butanol <sup>29</sup>	96.4	94.4
<i>n</i> -Propanol	86.0	84.8
Methyl ethyl ketone	78.0	77.0
Diethyl ketone	95.0	93.5
Methanol	60.0	60.5
Ethanol	73.0	72.0
Acetic acid	96.3	91.9
Acetic acid*	93.0	91.0
Acetone*	55.1	55.0
Pyridine*	96.0	92.0

\*Determined by author.

<sup>29</sup>Lecat. See bibliography for list of references.

\*Values on solvent-free basis.



Table VIII

Ternary Equilibria: Methylcyclohexane-n-Heptane-Solvent  
at Atmospheric Pressure (Figs. 5-9)

Determi- nation No.	Solvent	Mol % Solvent in Liquid	Mol % n-H in Liquid*	Mol % n-H in Vapor*	$\alpha$
1	Furfural	78.4	16.3	20.8	1.35
2	"	78.5	53.4	60.9	1.36
3	"	80.0	76.0	80.9	1.34
4	"	79.5	44.1	51.2	1.33
5	"	79.5	35.4	42.5	1.35
6	Phenol	80.0	18.6	23.3	1.33
7	"	82.4	34.2	41.7	1.37
8	"	81.1	56.6	63.1	1.31
9	"	81.5	76.0	80.8	1.33
10	Nitrobenzene	81.5	13.6	17.1	1.31
11	"	82.0	43.7	50.5	1.31
12	"	82.1	61.2	67.3	1.31
13	"	82.5	80.5	84.6	1.33
14	"	81.5	27.8	33.6	1.32
15	Chlorex	80.5	79.7	83.6	1.30
16	"	80.5	60.6	66.2	1.27
17	"	81.0	45.9	51.8	1.27
18	"	81.0	30.7	36.3	1.29
19	"	81.5	16.5	20.2	1.28
20	Aminocyclo- hexane	75.6	20.4	22.9	1.16
21	"	76.2	37.5	41.2	1.17
22	"	76.6	56.6	60.2	1.16
23	"	77.0	79.1	81.4	1.16

\*Values on solvent-free basis.



Table IX

## High Pressure Ternary Equilibria (Figs. 10-12)

Chlorox-Methylcyclohexane (Fig. 13) and Chlorox-n-Heptane (Fig. 14)

Determin- ation No.	Solvent	Mol % Solvent in Liquid	Temp. °C.	Pressure, p.s.i., abs.	Mol % n-H in Liquid*	Mol % n-H in Vapor*	$\alpha$
1	Aniline	76.5	150	33.5	56.2	62.9	1.32
2	"	75.1	150	31.5	25.1	30.5	1.31
3	"	74.5	150	31.5	25.9	31.2	1.30
4	"	82.5	150	28.5	37.8	45.4	1.37
5	"	82.5	150	29.0	38.1	45.6	1.36
6	"	85.9	150	26.0	37.1	44.9	1.38
7	"	82.2	150	28.0	23.5	29.4	1.36
8	"	88.1	150	27.0	71.0	77.6	1.41
9	"	67.0	150	35.0	42.8	48.3	1.25
10	"	44.2	150	40.0	44.4	48.3	1.17
11	"	94.0	200	43.5	36.3	44.1	1.39
12	"	72.0	200	81.5	40.8	46.2	1.25
13	"	76.2	200	76.5	42.9	49.0	1.28
14	"	88.6	200	56.5	40.6	48.2	1.36
15	"	77.1	250	156	41.0	46.5	1.25
16	"	91.5	250	113	41.6	48.6	1.32
17	"	75.7	250	165	42.7	48.1	1.24
18	"	69.7	280	264	63.9	68.0	1.20
19	Phenol	58.5	200	100.5	43.4	47.9	1.21
20	"	74.0	200	88.0	44.8	50.9	1.28
21	"	92.0	200	54.0	40.3	48.5	1.39
22	"	65.5	250	200	43.8	48.4	1.20
23	Hydrocarbon	81.5	250	165	43.9	49.8	1.27
24	"	91.6	250	125	39.0	45.8	1.32
25	Nitrobenzene	53.0	200	91.0	43.1	47.3	1.18
26	n-Heptane	73.9	200	68.0	42.3	47.8	1.25
27	n-Heptane	93.0	200	31.0	41.7	48.7	1.33

\*Values on solvent-free basis.



Table X

## Binary Equilibria at Atmospheric Pressure

Chlorex-Methylcyclohexane (Fig. 13) and Chlorex-n-Heptane (Fig. 14)

Determi- nation No.	Temp. °C.	Vapor Pressure mm. Hg.	Mol % MCH in Liquid	Mol % MCH in Vapor	Temp. °C.	Vapor Pressure mm. Hg.	Mol % n-H in Liquid	Mol % n-H in Vapor
1	178	4500	7.5	52.2	228	67.6	94.2	
2	173	4030	6.5	48.2	228	8.0	67.6	
3	167	3670	6.8	49.3	233	4.3	53.5	
4	163	3360	4.5	35.5	238	45.5	90.8	
5	158	3050	15.8	72.7	243	33.6	88.7	
6	152	2740	10.3	64.6	248	28.2	87.4	
7	148	2535	43.0	90.1	253	19.0	83.3	
8	193	5740	37.8	88.9	258	15.8	80.7	
9	188	5230			263	10.1	71.8	
10	183	4910			268	6.7	63.6	
11	178	4500			273	2.2	34.8	
	173	4080			278		18070	
	168	3720			267		16900	
	163	3360			257		14900	

Table XI

Critical Solution Temperatures of  
Three Hydrocarbon-Solvent Systems

Hydrocarbon	Solvent	Critical Solution Temp., °C.
Methylcyclohexane	nitromethane	95.1
n-Heptane	nitromethane	109.0
n-Heptane	furfural	95.1



Table XII

Vapor Pressure of Methylcyclohexane (Fig. 15)

Temp. °C.	Vapor Pressure mm. Hg	Temp. °C.	Vapor Pressure mm. Hg.
181	476	218	8490
178	4500	223	9150
173	4030	228	9890
167	3670	233	10600
163	3360	238	11390
158	3050	242	12280
152	2740	247	13130
148	2535	252	13880
193	5740	257	14900
188	5230	262	15890
183	4910	267	16910
178	4500	276	19300
173	4080	272	18070
168	3720	267	16900
163	3360	257	14900
188	5330	247	13120
198	6150	223	9150
203	6620	198	6150
208	7250	188	5330
213	7860		



## B. Original Data

Table XV

Table XIII

Benzene-Toluene Equilibria (See Table V)

Methylcyclohexane-n-Heptane Binary Equilibria (See Table II)

Determin- ation No.	$n_D^{20}$ Liquid Sample	$n_D^{20}$ Vapor Sample	Pressure, p.s.i. abs.	Temp. °C.
1	1.40557	1.40483	50.3	150
2	1.40565	1.40483	107	190
3	1.40565	1.40479	252	240
4	1.40542	1.40506	325	260
5				
6				
7				

Table XIV

Methanol-Water Binary Equilibria (See Table IV)

\*Corrected to 760 mm.

Determin- ation No.	$d_4^{20}$ Liquid Sample gm./cc.	$d_4^{20}$ Vapor Sample gm./cc.	Pressure p.s.i. abs.	Temp. °C.
1	.8548	.8316	328	180
2	.8668	.8395	315	180
3	.8581	.8333	325	180
4	.8528	.8312	330	180
5	.8543	.8321	327	180
6	.8540	.8313	328	180



Table XVI

Table XV

## Vapor-Liquid Equilibria of Ternary

## Benzene-Toluene Equilibria (See Table V)

Determination No.	Determination No.	Liquid Samples		Vapor Samples		Temp. °C.
		B.P. of Liquid Sample*, °C.	Vol. cc.*	B.P. of Vapor Sample*, °C.	Pressure p.s.i. abs.	
1	1	93.7	14.7	87.9	19.5	120
2	2	93.7	15.5	88.1	19.5	120
3	3	89.2	15.1	85.0	21	120
4	4	91.4	15.0	87.6	115	180
5	5	93.4	13.9	89.1	108	180
6	6	93.9	12.5	91.6	465	280
7	7	93.2	13.5	91.0	463	280
8	8	108.2	24.6	108.4	23.5	108.2
9	9	108.2	22.3	108.4	23.5	108.2
10	10	108.2	23.3	108.4	23.5	108.2
11	11	108.2	24.2	108.4	23.6	108.2
12	12	108.2	23.3	108.4	23.6	108.2
13	13	108.2	23.3	108.4	23.6	108.2
14	14	108.2	23.3	108.4	23.6	108.2
15	15	55.1	11.6	55.1	20.2	55.1
16	16	55.1	11.6	55.1	20.2	55.1
17	17	55.1	11.7	55.1	20.7	55.1
18	18	55.1	11.6	55.1	20.6	55.1
19	19	55.0	11.8	55.1	20.4	55.1
20	20	41.4	13.5	41.4	13.2	41.4
21	21	41.3	13.4	41.4	11.1	41.4
22	22	41.4	13.5	41.4	13.3	41.4
23	23	41.4	13.5	41.4	13.5	41.4

\*Corrected for treating loss.



Table XVI

## Vapor-Liquid Equilibria of Ternary

Systems at 1 atm. (See Table VIII)

Deter- mina- tion No.	Solvent	Liquid Samples			Vapor Samples		
		Wt. Sam- ple, gm.	Vol. Hydro- carbons, cc.*	<sup>20</sup> n <sub>D</sub> Hydro- carbons	Wt. Sam- ple, gm.	Vol. Hydro- carbons, cc.*	<sup>20</sup> n <sub>D</sub> Hydro- carbons
1	Furfural	49.2	14.7	1.41731	19.5	21.8	1.41501
2	"	50.5	15.5	1.40327	19.5	22.0	1.40037
3	"	51.3	15.1	1.39545	19.5	22.0	1.39370
4	"	51.0	15.0	1.40659	19.5	22.1	1.40373
5	"	50.9	15.0	1.40982	19.5	22.0	1.40689
6	Phenol	48.8	13.9	1.41636	18.7	23.3	1.41401
7	"	49.3	12.5	1.41027	18.7	23.3	1.40720
8	"	48.9	13.6	1.40214	18.7	23.4	1.39961
9	"	49.0	13.5	1.39545	18.6	23.6	1.39370
10	Nitrobenzene	108.2	24.6	1.41845	18.9	23.5	1.41643
11	"	109.2	22.3	1.40674	18.9	23.5	1.40400
12	"	108.8	23.3	1.40052	18.9	23.5	1.39824
13	"	108.4	24.2	1.39392	18.8	23.6	1.39242
14	"	108.8	23.3	1.41271	18.8	23.6	1.41016
15	Chlorex	55.1	11.6	1.39422	20.2	20.9	1.39276
16	"	55.1	11.6	1.40071	20.2	20.9	1.39857
17	"	55.1	11.7	1.40595	20.2	20.7	1.40356
18	"	55.1	11.6	1.41160	20.2	20.6	1.40914
19	"	55.0	11.8	1.41724	20.4	20.4	1.41522
20	Amino-cyclo- hexane	41.4	13.5	1.41567	19.8	13.2	1.41464
21	"	41.3	13.4	1.40903	17.1	11.1	1.40768
22	"	41.4	13.5	1.40214	19.7	13.3	1.40085
23	"	41.4	13.5	1.39441	19.7	13.5	1.39363

\*Corrected for treating loss.



Table XVII

## Vapor-Liquid Equilibria of Ternary Systems Above one Atmosphere

(See Table IX)

Deter- mina- tion No.	Solvent	Liquid Sample			Vapor Sample			Temp. °C.	Pressure, p.s.i. abs.
		Wt. Sam- ple, gm.	Hydro- carbons, cc.*	n <sub>D</sub> <sup>20</sup>	Wt. Sam- ple, gm.	Hydro- carbons, cc.*	n <sub>D</sub> <sup>20</sup>		
1	Aniline	50.7	17.6	1.40188	23.7	26.7	1.39958	150	33.5
2	"	50.3	17.8	1.41318	23.3	26.0	1.41108	150	31.5
3	"	49.5	18.0	1.41280	24.6	25.9	1.41081	150	31.5
4	"	48.9	11.7	1.40832	24.2	27.9	1.40556	150	28.5
5	"	52.4	13.4	1.40822	23.7	27.1	1.40533	150	29.0
6	"	51.2	10.6	1.40859	24.5	27.3	1.40574	150	26.0
7	"	51.5	13.0	1.41372	24.0	24.5	1.41148	150	28.0
8	"	52.2	9.3	1.39678	23.1	25.9	1.39456	150	27.0
9	"	48.6	23.2	1.40649	23.3	24.2	1.40455	150	35.0
10	"	48.1	36.1	1.40593	23.4	28.7	1.40455	150	40.0
11	"	52.6	4.5	1.40888	25.7	16.7	1.40605	200	43.5
12	"	52.5	21.2	1.40724	24.9	25.2	1.40529	200	81.5
13	"	53.0	18.4	1.40646	24.7	25.4	1.40428	200	76.5
14	"	54.5	8.9	1.40728	25.8	21.6	1.40459	200	56.5
15	"	53.7	17.0	1.40717	25.5	21.4	1.40515	250	156
16	"	55.9	7.0	1.40695	27.2	15.8	1.40443	250	113
17	"	53.2	18.6	1.40653	25.3	22.2	1.40455	250	165
18	"	50.7	22.8	1.39916	25.1	20.5	1.39785	280	264
19	Phenol	51.6	30.5	1.40631	24.0	26.8	1.40466	200	100.5
20	"	55.0	20.5	1.40578	24.1	25.5	1.40360	200	88.0
21	"	59.2	6.8	1.40743	26.3	20.8	1.40447	200	54.0
22	"	52.1	25.6	1.40616	24.5	22.7	1.40451	250	200
23	"	56.0	14.9	1.40612	26.0	20.6	1.40402	250	165
24	"	59.1	7.1	1.40788	28.0	15.8	1.40541	250	125
25	Nitrobenzene	55.0	31.6	1.40638	24.1	28.5	1.40489	200	91.0
26	"	61.6	19.1	1.40668	25.2	26.9	1.40470	200	68.0
27	"	64.6	5.0	1.40691	27.1	21.3	1.40443	200	31.0

\*Corrected for treating loss.



## C. Analytical Methods, Procedures and Curves

Table XVIII

## Binary Equilibria of Methylcyclohexane-Chlorex

and n-Heptane-Chlorex (See Table X)

Determin- ation No.	<sup>25</sup> <sub>4</sub> Liquid Sample	<sup>25</sup> <sub>4</sub> Vapor Sample	<sup>25</sup> <sub>D</sub> Liquid Sample	<sup>25</sup> <sub>D</sub> Vapor Sample	weighing
1	1.1757	.9686	1.4032	1.3880	
2	1.1805	.9864	1.4482	1.4032	
3	1.1790	.9809	1.4514	1.4127	
4	1.1910	1.0438	1.4183	1.3897	
5	1.1354	.8776	1.4271	1.3908	
6	1.1617	.9126	1.4313	1.3915	
7	1.0096	.8042	1.4387	1.3937	
8	1.0332	.8091	1.4414	1.3952	
9			1.4463	1.4005	

Boiling points of the samples were determined by a still type of boiling point apparatus (Fig. 17). The boiling points were read from a boiling point-composition curve plotted from the data of Rosanoff, Bacon, and Schulze<sup>32</sup> as modified by Todd<sup>33</sup> (Fig. 18). The approximate error was  $\pm 0.3$  mol %.

<sup>30</sup> Osborne, Bull. U. S. Bur. Standards, 2, 371 (1913).

<sup>31</sup> Dittmar and Fawsitt, Trans. Roy. Soc. Edinburgh, 33, 509 (1887) via International Critical Table, Vol. III, p. 115, New York, McGraw-Hill, 1928.

<sup>32</sup> Rosanoff, Bacon, and Schulze, Op. cit.

<sup>33</sup> Todd, Ind. Eng. Chem., 32, 287 (1940).



### C. Analytical Methods, Procedures and Curves

#### Methanol-Water

The samples were analyzed by a density determination at 20° C. The densitometer was constructed by supporting an analytical balance over a thermostat. The test tube containing the sample was placed in the thermostat beneath the balance. A cylindrical plumb weighing approximately 5 grams was suspended from one arm of the balance beam by a tungsten wire .002" in diameter. The wire passed through a hole in the floor of the balance, suspending the plumb in the test tube containing the sample<sup>30</sup>. The density was calculated from the weight of the plumb in air, the weight of the plumb in water, and the weight of the plumb in the sample. The mol fraction of methanol was then read directly from a table given in the literature<sup>31</sup>. The approximate error was  $\pm 0.1$  mol %.

#### Benzene-Toluene

Boiling points of the samples were determined by a Cottrell type of boiling point apparatus (Fig. 17). Compositions were read from a boiling point-composition curve plotted from the data of Rosanoff, Bacon, and Schulze<sup>32</sup> as modified by Todd<sup>33</sup> (Fig. 18). The approximate error was  $\pm 0.3$  mol %.

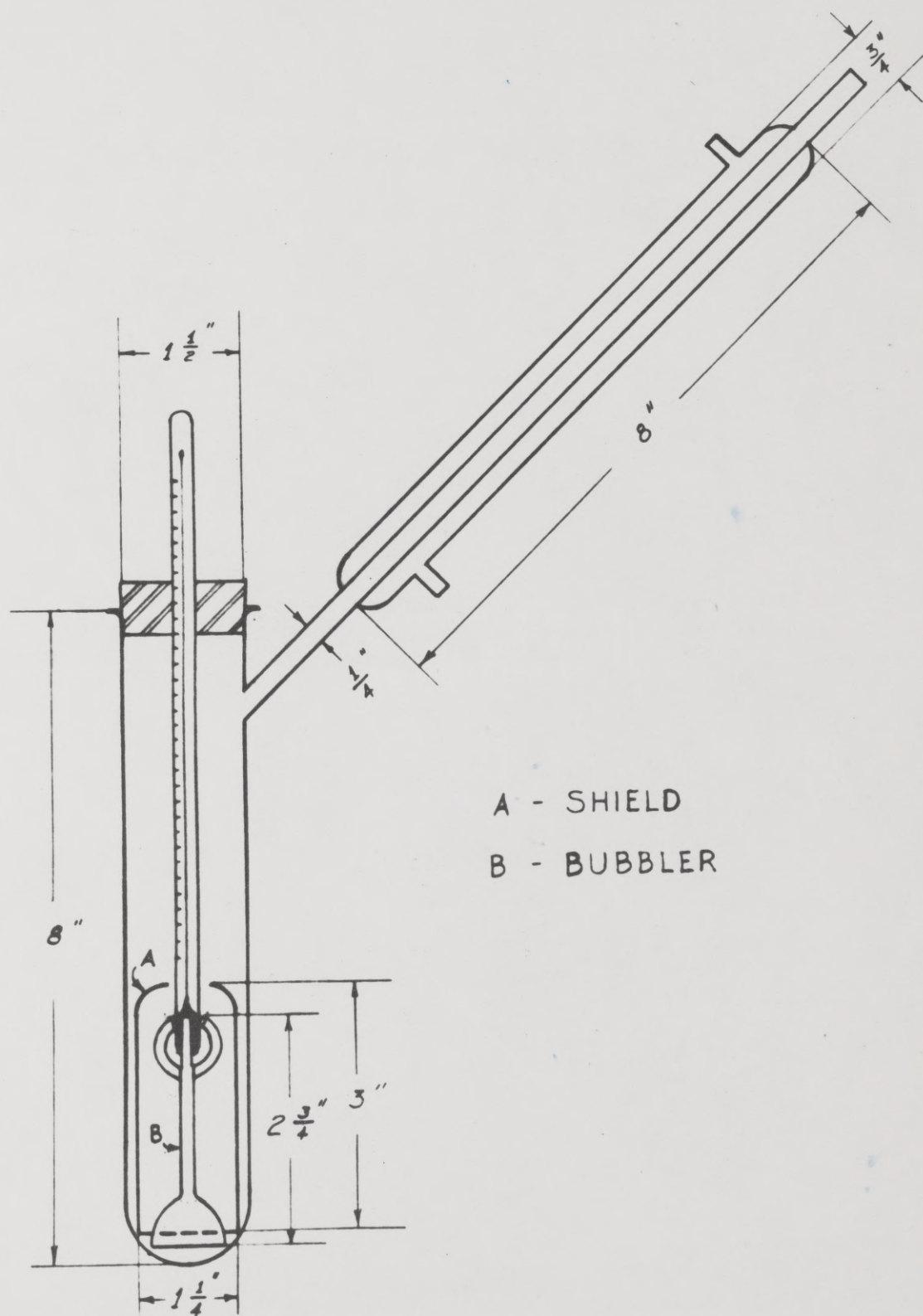
<sup>30</sup>Osborne, Bull. U. S. Bur. Standards, 2, 371 (1913).

<sup>31</sup>Dittmar and Fawsitt, Trans. Roy. Soc. Edinburgh, 33, 509 (1887) via International Critical Table, Vol. III, p. 115, New York, McGraw-Hill, 1928.

<sup>32</sup>Rosanoff, Bacon, and Schulze, Op. cit.

<sup>33</sup>Todd, Ind. Eng. Chem., 32, 287 (1940).





COTTRELL BOILING POINT  
APPARATUS  
FIG. 17



Boiling Point - Composition Curve  
for Benzene - Toluene Mixtures  
at 760 Mm.

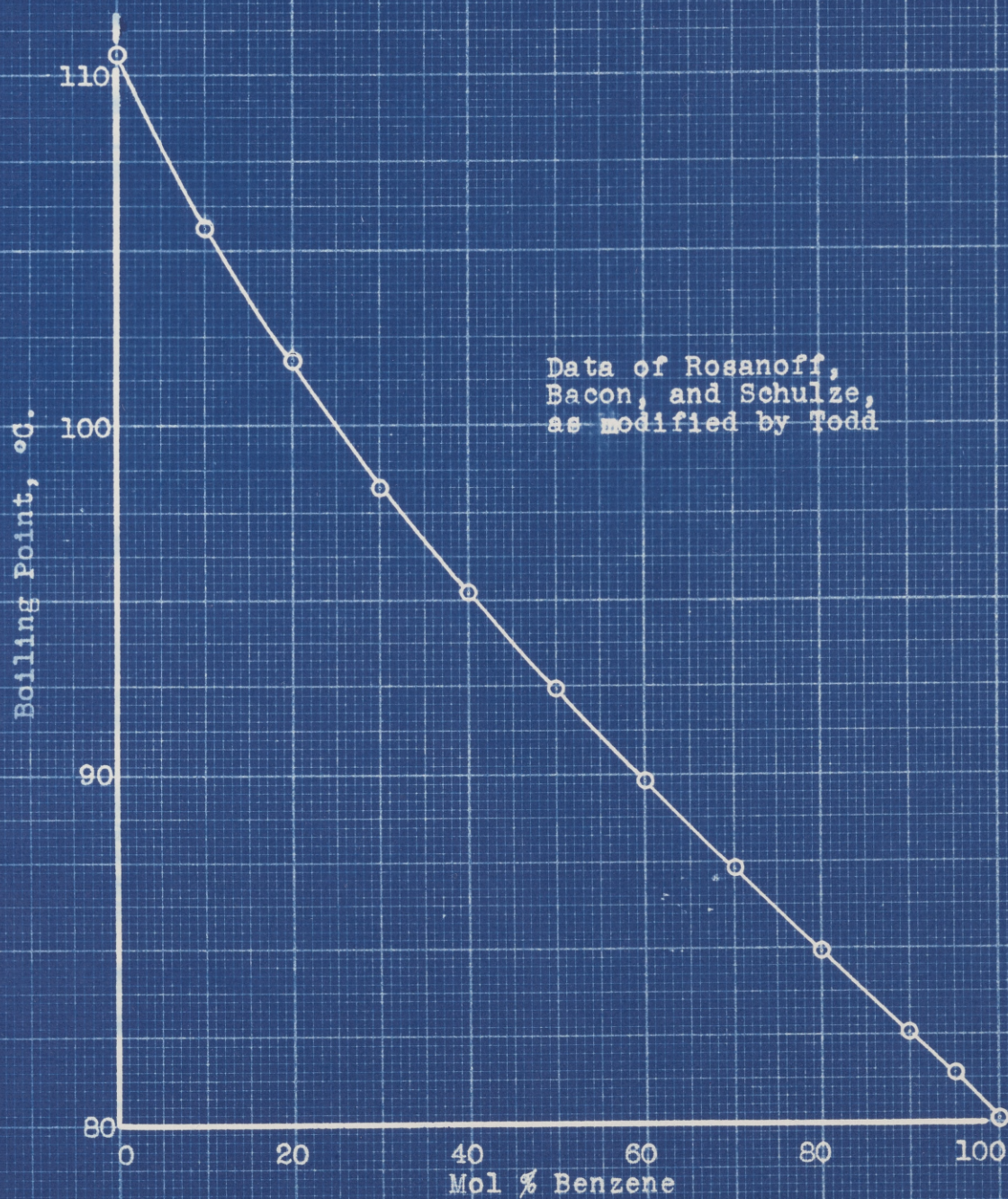


FIG. 18



### Chlorex-Methylcyclohexane

A composition curve was constructed from densities taken on known mixtures at 25° C. (Fig. 19, Table XIX). The densities were determined in a pycnometer of approximately 1 cc. volume. The approximate error in testing samples was  $\pm 0.1$  mol %.

### Chlorex-n-Heptane

A refractive index-composition curve was determined at 25° C. (Fig. 20, Table XX) for the analysis. The refractive indices were determined with an Abbe type refractometer. The approximate error was  $\pm 0.1$  mol %.

### Methylcyclohexane-n-Heptane

A refractive index-composition curve (Fig. 21) was made from the data of Bromily and Quiggle<sup>34</sup>, corrected for the fact that both the methylcyclohexane and n-heptane used had refractive indices .0001 units lower than the materials used by these investigators. Refractive indices of unknown samples were determined with a dipping refractometer and their compositions read from the curve. The approximate error was  $\pm 0.1$  mol %.

### Ternary Mixtures

The general method of analysis for all ternary mixtures was the same. The hydrocarbons in a weighed quantity of solution were separated from most of the solvent by distillation in a Podbielniak

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<sup>34</sup>Bromily and Quiggle, Op. cit.



Density - Composition Curve for  
Methylcyclohexane - Chlorex  
at 25° C.  
(Table XIX)

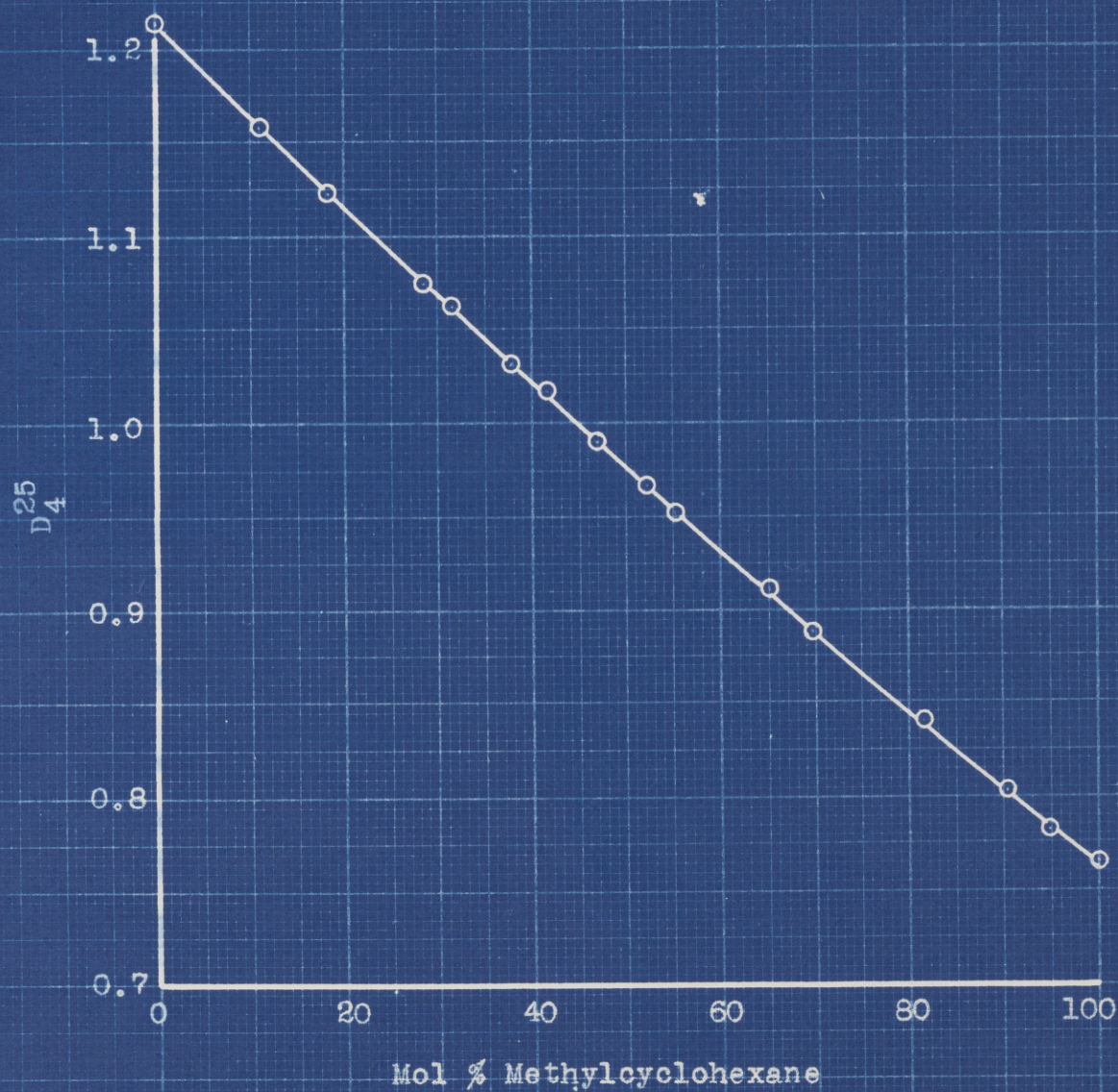


FIG. 19



Refractive Index - Composition Curve for  
n-Heptane - Chlorex at 25° C.

(Table XX)

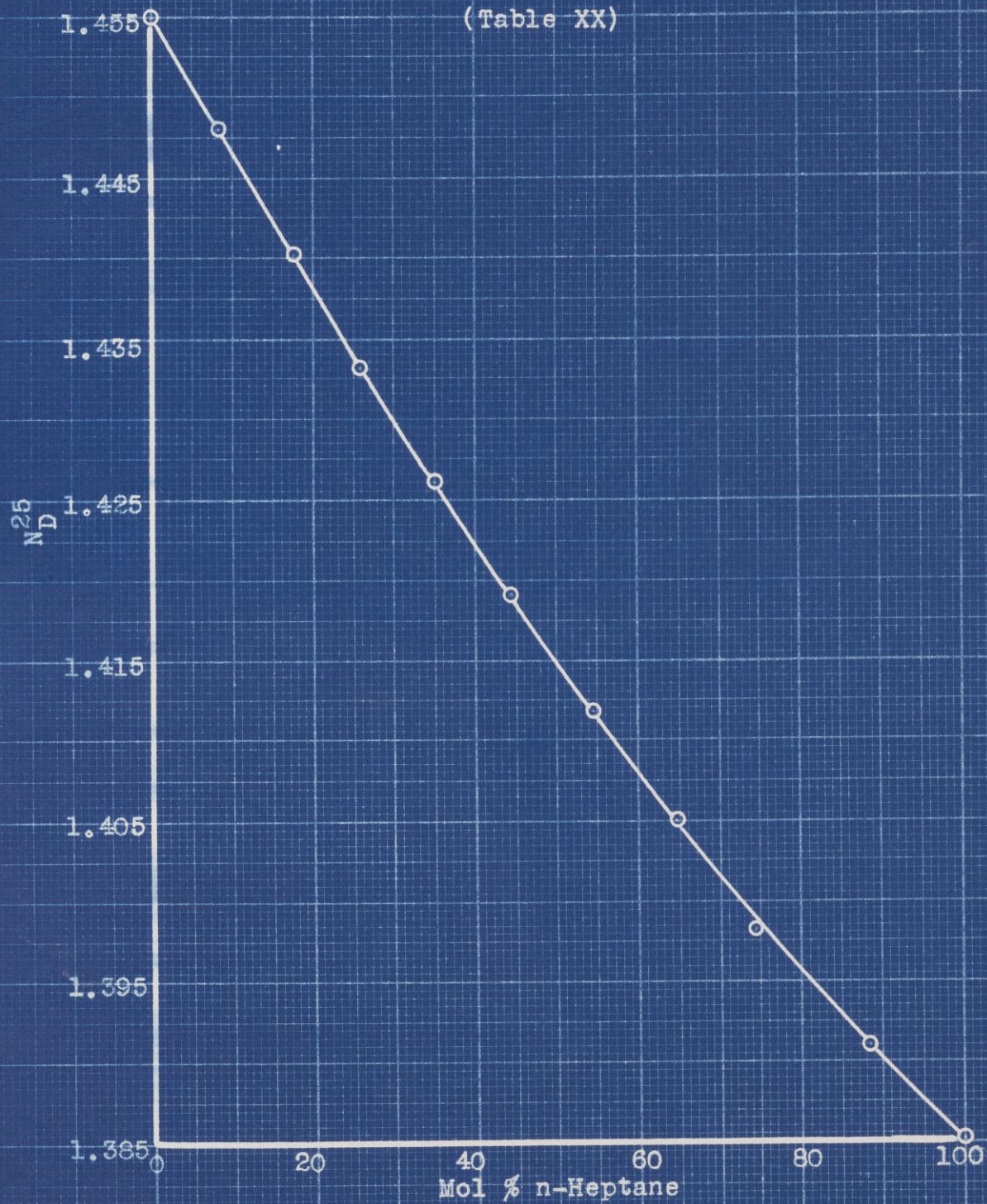


FIG. 20



Refractive Index - Composition  
Curve for Methylcyclohexane -  
n-Heptane Mixtures at 20° C.

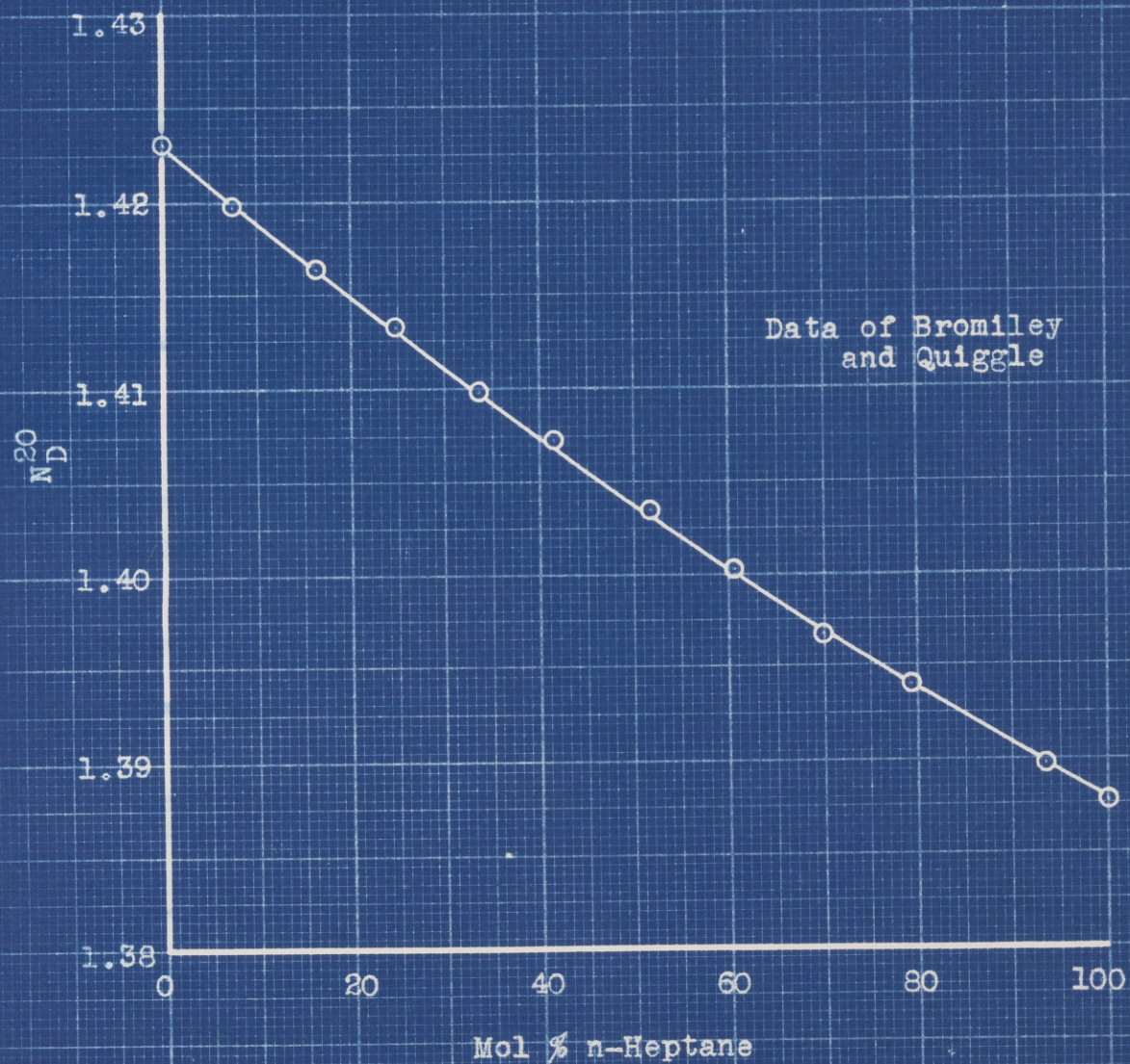


FIG . 21



model apparatus, which has a four foot column packed with a single wire spiral. The hydrocarbons and a small amount of solvent were distilled directly into a separator which consisted of a 50 ml. burette sealed to the mouth of a 125 ml. separatory funnel (Fig. 22). The distillate was treated with the proper material (see following paragraph) to remove the remaining traces of solvent and it was then washed with water. The hydrocarbons were floated into the burette section by introducing water at the top of the separator. Their volume and temperature was recorded. A small sample was pipetted off and its refractive index determined with the dipping refractometer. The weight of the hydrocarbons was determined from the volume and density<sup>35</sup>. This weight was subtracted from the weight of the original solution to give the weight of solvent.

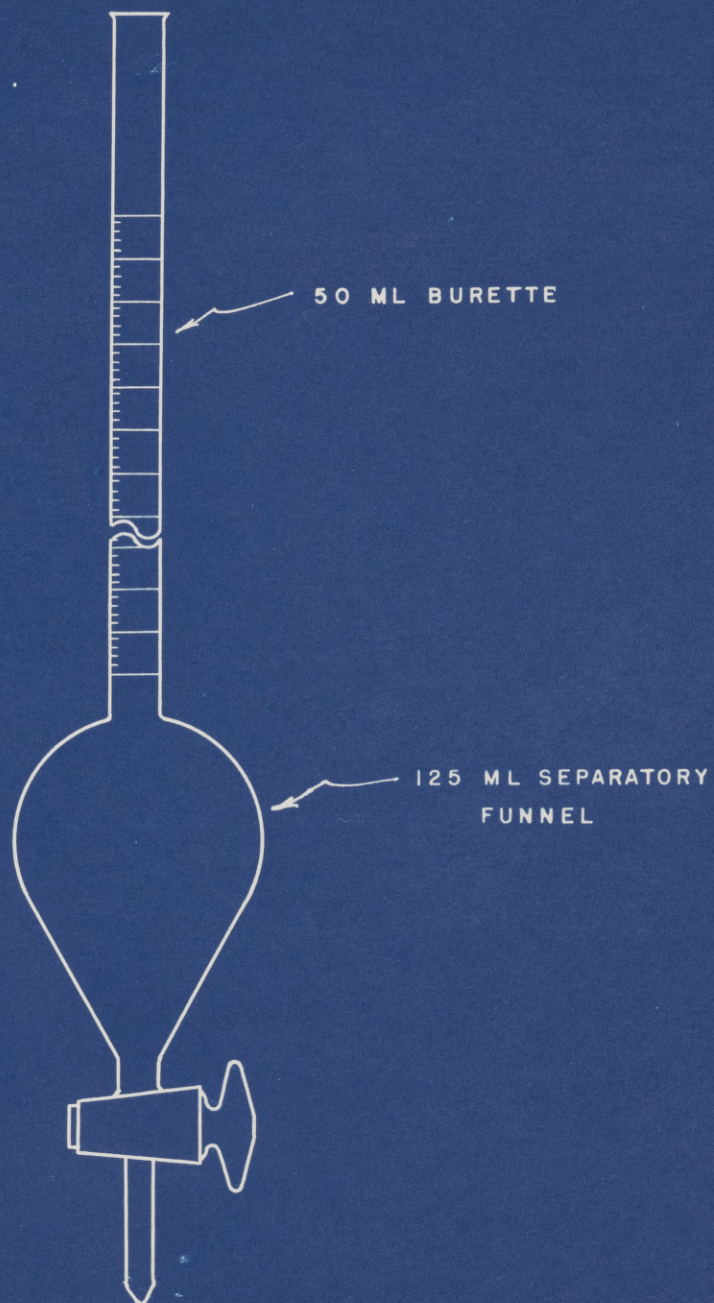
Details of the treatment to remove the last traces of solvent from the hydrocarbons follow. Chlorex and nitrobenzene were removed by washing twice with concentrated sulfuric acid (Sp. gr. 1.84) and twice with water. Aniline and aminocyclohexane were removed by washing once with concentrated hydrochloric acid (Sp. gr. 1.19), once with concentrated sulfuric acid, and twice with water. The phenol mixture was treated once with 20% sodium hydroxide, once with water, once with concentrated sulfuric acid, and twice with water. Hydrocarbons containing furfural were treated once with sulfuric acid (50 wt. %), once with concentrated sulfuric acid, and twice with water.

The loss of hydrocarbons in the analysis was 0.4 cc. in all cases. This quantity was independent of the volume of hydrocarbons

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<sup>35</sup>Egloff, Physical Constants of Pure Hydrocarbons Vol. I, p. 40; Vol. II, p. 81. A.C.S. Monograph No. 78, Reinhold Publishing Co.





HYDROCARBON-SOLVENT SEPARATOR

FIG. 22



treated (from 5 to 50 cc.). In the analysis of unknowns, it was added to the observed volume of the hydrocarbons as an arbitrary correction.

Numerous analyses of known ternary mixtures showed these procedures to give correct results in every case.

Mol % n-H	Density, gm./cc.	Mol % n-H	Density, gm./cc.
25.8	1.0730	55.1	.9535
37.7	1.0320	47.0	.9912
52.0	.9669	41.7	1.0157
56.2	.9468	31.4	1.0613
90.1	.8042	18.3	1.1234
94.9	.7848	10.9	1.1594
69.8	.8896	100	.7652

Table XX

#### Refractive Index of n-Heptane-Chloroform Solutions at 25° C.

Mol % n-H	$n_D^{25}$	Mol % n-H	$n_D^{25}$
25.8	1.4321	55.1	1.3910
35.0	1.4260	100	1.3852
44.3	1.4192	17.3	1.4402
54.9	1.4117	8.1	1.4480
64.8	1.4050	0	1.4550
74.4	1.3983		



Table XIX

Density of Methylcyclohexane-Chlorex Solutions at 25° C.

Mol % MCH	Density, gm./cc.	Mol % MCH	Density, gm./cc.
0	1.2145	64.9	.9168
28.8	1.0730	55.1	.9535
37.7	1.0320	47.0	.9912
52.0	.9669	41.7	1.0157
56.2	.9468	31.4	1.0613
90.1	.8042	18.3	1.1234
94.9	.7848	10.9	1.1594
69.8	.8896	100	.7652

Samples were drawn off while the apparatus was in operation.

They were analyzed as described in the previous section.

Table XX

Refractive Index of n-Heptane-Chlorex Solutions at 25° C.

Mol % n-H	$n_D^{25}$	Mol % n-H	$n_D^{25}$
25.8	1.4321	88.4	1.3910
35.0	1.4260	100	1.3852
44.3	1.4192	17.3	1.4402
54.9	1.4117	8.1	1.4480
64.8	1.4050	0	1.4550
74.4	1.3983		

Distillation was continued for two hours after steady conditions had been attained.



#### D. Operating Technique on the Othmer Apparatus and the High Pressure Apparatus

##### Othmer Apparatus

Heat input to the heaters was regulated by the use of three variable resistances. Equilibrium was insured by boiling the liquid for three hours after steady conditions had been attained, this being the time necessary to distill a volume equal to three times that of the liquid charged (250 cc.).

The heat supplied by the external winding around the wall of the vapor space was regulated so that condensation was just eliminated.

##### Pressure Apparatus

Samples were drawn off while the apparatus was in operation. They were analyzed as described in the previous section.

##### High Pressure Apparatus

Approximately 450 cc. total liquid was charged to the apparatus. The apparatus was evacuated by means of an aspirator. The still and wall heaters were then turned on. When the desired temperature was reached, the variable transformer regulating the heat supply to the still heater and the flow of coolant through the condenser were adjusted so that this temperature was maintained. The variable transformer controlling the heat input to the vapor space heater was adjusted to maintain the wall temperature about 1° C. above that of the still liquid. Distillation was continued for two hours after steady conditions had been attained.



The sampling bombs were made from sections of 1" extra heavy pipe with nipples of 1/4" extra heavy pipe welded into either end. Valves were screwed on to these nipples. The volumes of the vapor and liquid sampling bombs were 30 cc. and 60 cc., respectively.

To take samples, the bombs were attached to the proper outlets of the apparatus by means of unions (see Fig. 2). The bombs were evacuated. The valves on the vapor condensate and liquid outlets were then opened simultaneously. After the bombs were charged, both these valves and the valves on the bombs were closed. The bombs were then disconnected from the apparatus.

#### E. Suggestions for Improvements of High Pressure Apparatus

Several improvements suggested themselves in the course of the experimental work. Although none was of sufficient importance to justify rebuilding the apparatus, they are given here for future use. The condenser should be divided into a 1/2" section, a 1" section, a 3" section, and a 6" section, each having individual cooling fluid connections so that any section can be used alone. The most unsatisfactory feature of the present apparatus is its large condenser surface, which necessitates the use of air as a coolant. With short sections, water could conveniently be used except possibly at very high temperatures. The cap, gasket junction, and section of 1" pipe shown in the drawing should be eliminated, as they are not necessary. A nipple of 1/4" pipe should be welded into the vapor line just above the condenser to facilitate evacuation of the apparatus. The two unions joining the still



side to the condenser and vapor condensate section should be eliminated, leaving nothing but welded joints in the apparatus.

Although the apparatus was designed for use at high pressures, with the above changes it could readily be used at sub-atmospheric pressures also.

#### F. Materials and Instruments Used

The n-heptane was obtained from the California Chemical Company. Its physical constants, as determined by the Bureau of Standards, were b.p. = 98.4° C. at 760 mm.,  $d_4^{20} = .6836$ ,  $n_D^{20} = 1.38769$ . This material was used without further purification.

The methylcyclohexane was obtained from Rohm and Haas Company. It was treated for 36 hours with 100% sulfuric acid. The material was separated from the acid, washed twice with water, and then distilled through a 2 foot laboratory column packed with glass helices. Only the central fraction (about 80% of the total) was retained for use. The constants of the fraction used were: b.p. = 100.6-101.0° C. at 760 mm.,  $d_4^{20} = .7693$ ,  $n_D^{20} = 1.42310$ .

The methanol was obtained from Carbide and Carbon Chemicals Company. Its constants were: b.p. = 64.5° C. at 760 mm.,  $d_4^{20} = .7913$ ,  $n_D^{20} = 1.3287$ . This material was used without further purification.

Each of the materials listed below was distilled through a 2 foot laboratory column before use. Only the central fraction of each was retained. The size of this fraction varied somewhat, depending on the material, but it generally comprised about 80% of the total quantity processed.



The benzene and toluene came from Merck and Company. The constants of the purified benzene were: b.p. = 80.1° C. at 760 mm.,  $d_4^{20} = .8789$ ,  $n_D^{20} = 1.5011$ . The constants of the purified toluene were: b.p. = 110.5 ° C. at 760 mm.,  $d_4^{20} = .8670$ ,  $n_D^{20} = 1.4969$ .

The aniline and nitrobenzene were obtained from the General Chemical Company. The constants of the purified aniline were: b.p. = 183.9° C. at 750 mm.,  $d_4^{20} = 1.0217$ ,  $n_D^{20} = 1.5860$ . The constants of the purified nitrobenzene were: b.p. = 210.3° C. at 750 mm.,  $d_4^{25} = 1.1982$ ,  $n_D^{20} = 1.5524$ .

The aminocyclohexane and phenol were obtained from the Eastman Kodak Company. The constants of the purified aminocyclohexane were: b.p. = 134.5° C. at 760 mm.,  $d_4^{20} = .8670$ ,  $n_D^{20} = 1.4350$ . The constants of the purified phenol were: m.p. = 41° C., b.p. = 182.4° C. at 750 mm.

The furfural was obtained from Schaar and Company. The constants of the purified fraction were: b.p. = 161.0° C. at 745 mm.,  $d_4^{20} = 1.1590$ ,  $n_D^{20} = 1.5255$ .

The chlorex was obtained from Carbide and Carbon Chemicals Company. The constants of the purified fraction were: b.p. = 177.2° C. at 746 mm.,  $d_4^{25} = 1.2145$ ,  $n_D^{25} = 1.4550$ .

Pressure gauges used were calibrated by a dead weight tester at intervals of approximately two months during the course of the experimental work. Their calibrations were found not to vary. The wall and auxiliary thermocouples shown in Fig. 2 were calibrated by boiling water in the apparatus while holding the pressure constant at various levels. The temperatures corresponding to the various steam pressures were read from the steam tables of



Keenan and Keyes. The effect of secondary junctions in the wall couples was found to be negligible, as these couples gave the same calibration as the completely insulated auxiliary couple.

G. Illustrative Problem Showing Difference in Plate Requirements with Various Values of  $\alpha$ , the Relative Volatility

According to Fenske<sup>36</sup>, the number of plates necessary at the total reflux to effect a given separation in a binary mixture is given by the following equation:

$$\frac{y_a}{y_b} = (\alpha_{ab})^n \frac{x_a}{x_b}$$

where  $y_a$  = the concentration of the more volatile component in the distillate,

$y_b$  = the concentration of the less volatile component in the distillate,

$x_a$  = the concentration of the more volatile component in the feed,

$x_b$  = the concentration of the less volatile component in the feed,

$\alpha_{ab}$  = the relative volatility of the lighter to the heavier component,

$n$  = the number of theoretical plates required for this separation.

<sup>36</sup>Fenske, Ind. Eng. Chem., 24, 482 (1932).



The problem may be stated as follows: given five mixtures of relative volatilities  $\alpha_1 = 1.07$ ,  $\alpha_2 = 1.16$ ,  $\alpha_3 = 1.30$ ,  $\alpha_4 = 1.40$ , and  $\alpha_5 = 1.90$ . These mixtures have the same composition with respect to light and heavy components ( $x_{a1} = x_{a2} = x_{a3} = x_{a4} = x_{a5}$ ). It is required to effect the same degree of separation in each of these mixtures ( $y_{a1} = y_{a2} = y_{a3} = y_{a4} = y_{a5}$ ). Assuming that 100 plates are necessary to obtain the desired separation in mixture 1 ( $n_1 = 100$ ), how many plates are required for each of the other mixtures?

Under the given conditions, the ratios  $y_a/y_b$  for all the mixtures are equal, as are the ratios  $x_a/x_b$ . Dividing the Fenske equation for mixture 1 by the Fenske equation for mixture 2, we obtain

$$(\alpha_1)^{n_1} = (\alpha_2)^{n_2}$$

$$\frac{n_1}{n_2} = \frac{\log \alpha_2}{\log \alpha_1}$$

Substituting the values given,

$$\frac{100}{n_2} = \frac{\log (1.16)}{\log (1.07)}$$

$$\text{and } n_2 = 45.6 \text{ plates.}$$

Similarly,  $n_3 = 25.8$  plates,  $n_4 = 20.2$  plates, and  $n_5 = 10.5$  plates.



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