

VAPOR-LIQUID EQUILIBRIUM STUDY
OF
BENZENE-PROPANOL AND BENZENE-PENTANOL

LE 367
1951 A7
H6 V2
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by
GEORGE ROBERT ALEXANDER HOWEY

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE
in the Department
of
Chemistry

We accept this thesis as conforming to the
standard required from candidates for the
degree of MASTER OF APPLIED SCIENCE

Members of the Department of
Chemistry

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1951

ABSTRACT

A study has been made of the vapor-liquid equilibria for the benzene-propanol and benzene-pentanol systems at atmospheric pressure using a Fowler-Gillespie still. Refractive index curves for the complete systems were also obtained at 25°C. Thermodynamic consistency of the results was checked with the Van Laar integration of the Gibbs-Duhem equation. This theoretical correlation of the experimental values showed an average deviation of approximately 10% between the experimental and theoretical values. A vapor-liquid equilibrium plot of the benzene-alcohol series from methanol to pentanol was made and the general shape of the curves was discussed with regard to the disappearance of the azeotrope.

ACKNOWLEDGMENT

The author wishes to express his appreciation of the helpful instruction given by Dr. L.W. Shemilt under whose supervision this research was carried out. He acknowledges too the constructive suggestions of Mr. C. Larkam and the advice of Mr. A. Werner on the purification of the alcohols.

Special thanks are also due to Mr. M. Waldichuk for introducing the author to the theory and techniques involved.

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INTRODUCTION

The separation of a mixture of volatile liquids by means of fractional distillation is possible when the composition of the vapor coming from the liquid mixture is different from that of the liquid. The relation between the vapor and liquid compositions must be known in order to design a fractionating column, or even to determine the number of theoretical plates needed for the given separation of a binary mixture. Since few systems form ideal solutions so that equilibrium data can be calculated from Raoult's Law, it is necessary to have some means of determining data for a binary mixture over the whole range of composition.

The method of obtaining vapor-liquid equilibrium compositions can be considered under two main headings: 1) the experimental determination of equilibrium compositions by the use of a vapor-liquid equilibrium still and 2) the theoretical relationships.

A number of methods have been developed to determine experimentally vapor-liquid equilibrium data. The first of these is the simple distillation of a very small sample of the vapor from a flask containing a large quantity of a liquid. This method can be inaccurate since some reflux almost always takes place, and in addition, a large sample is required. A second method is to pass vapor of constant composition through a liquid until equilibrium is reached. A third method consists of collecting and analyzing several successive fractions from a batch distillation and then extrapolating back to a point where zero distillate would be obtained. A fourth method and by far the

most satisfactory, is that developed by Othmer (1) and consists of vaporizing a liquid, condensing the vapors, and then recirculating the condensate through the cycle until equilibrium is reached. To make such a still operate efficiently without error the liquid must be vaporized and condensed without allowing any reflux between the time of the first vaporization and final condensation. Reflux would tend to give a vapor richer in the more volatile component than is actually the case in true equilibrium. In addition entrainment of liquid in the vapor must be avoided since the carrying over of unvaporized material will give an equilibrium value containing less^{of} the actual amount of lower boiling component in the vapor. Thirdly, no part of the apparatus should be superheated sufficiently to cause total instead of equilibrium vaporization, which would also give a value of vapor composition too low in the more volatile component. Fourthly, the composition of the material in the still should remain constant.

Various investigators have taken care of the above requirements in different ways. One vapor-liquid equilibrium still that meets the requirements was designed by Gillespie (2) and later modified by Fowler (3). This still was used in this research on the benzene-propanol and benzene-pentanol systems and will be described later.

The theoretical methods used to obtain vapor-liquid compositions without recourse to experiment are discussed later.

Of the two binary systems, benzene-propanol and benzene-pentanol, studied in this research only the benzene-propanol system has been examined previously. In 1918 Lecat (4) reported that this system formed an azeotrope at 0.791 mole fraction of benzene with a boiling point of 77.1°C. at 760 mm. of pressure.

Lee (5) in 1931 reported the partial pressure isotherms of the system at 40°C.

Although no practical use could be ascertained for data on either system, a study of these is of interest for consideration of vapor-liquid equilibrium data for the benzene-alcohol systems from C_1 to C_5 . This allows an attempt to be made to explain the disappearance of the azeotrope with the systems benzene-butanol and benzene-pentanol.

The object of this research, therefore, is to obtain the vapor-liquid equilibrium composition curves for the binary mixtures of benzene-propanol and benzene-pentanol at constant pressure, and to check the thermodynamic consistency of the results by an application of at least one of the integrated forms of the Gibbs-Duhem equation. The vapor-liquid equilibrium data for the five benzene-n-alcohol systems methanol to pentanol will be plotted and discussed.

THEORETICAL DISCUSSION

The most convenient and simple relation between liquid and vapor compositions is that expressed by Raoult's Law:

$$p_1 = P^\circ x_1 \quad (1)$$

in which p_1 is the partial pressure of a component in the vapor phase in equilibrium with its solution at a molar concentration x_1 and P° is the vapor pressure of the pure component at the same temperature. A system obeying Raoult's Law is considered ideal, but unfortunately few do. Deviations from ideality may be due either to the liquid phase, the vapor phase or both. These deviations can be both physical and chemical in nature. The most important of these are that the molecules have definite volume, and that they exert attractive or repulsive forces upon each other. Actual chemical effects may also be involved especially when the components are chemical dissimilar, e.g. belonging to different homologous series. It has been shown experimentally that substances having similar chemical structure deviate only slightly from Raoult's Law.

Carlson and Colburn (6) have pointed out that a convenient method of expressing the deviation of a given system from Raoult's Law and also of indicating the thermodynamic consistency of vapor-liquid equilibrium data is to plot the logarithm of the activity coefficients against the liquid compositions. For a given component the activity coefficient is defined by the equation:

$$\gamma_1 = \frac{Py_1}{P_1 x_1} \quad (2)$$

where P is the pressure of the system in millimeters of mercury, P_1 is the pressure of the pure component in millimeters of mercury at the solution temperature, x_1 and y_1 are the mole fractions of component 1 in the liquid and vapor phases, respectively.

A number of attempts have been made to describe the behaviour of systems which deviate from ideality in terms of general equations based on thermodynamic relations and depending upon a general equation of state. According to Clark (7) the following method can be used to give these general equations.

The exact thermodynamic relation describing a phase in equilibrium within itself was expressed by Gibbs:

$$- Sdt + Vdp - \sum_i n_i d\mu_i = 0$$

in which n_i is the number of molecules of the i th component in the phase and μ_i is the chemical potential of that component. For equilibrium between the phases the μ for each component shall be equal at the same temperature and pressure.

For a vapor phase which is a perfect gas at a fixed temperature,

$$d\mu_1 = RT d \ln p_1$$

The equation for 1 mole of a liquid phase of components at constant temperature may be written:

$$V_{\text{liq.}} dP = x_1 d\mu_1 + x_2 d\mu_2$$

If this phase is in equilibrium with a vapor phase, $d\mu_1$ and $d\mu_2$ are the same and by substitution we obtain:

$$V_{\text{liq.}} dP = RT (x_1 d \ln p_1 + x_2 d \ln p_2)$$

For RT we can write $PV_{\text{vap.}}$ in which $V_{\text{vap.}}$ is the molar volume of the vapor phase. By re-arrangement:

$$\frac{V_{\text{liq.}}}{V_{\text{vap.}}} \frac{dP}{P} = x_1 d \ln p_1 + x_2 d \ln p_2$$

At ordinary pressures, $\frac{V_{\text{liq.}}}{V_{\text{vap.}}}$, the ratio of the molar volumes of the two phases is very small and the left-hand side of this equation may be equated to zero without serious error. We then obtain as the condition of equilibrium at constant temperature:

$$x_1 d \ln p_1 + x_2 d \ln p_2 = 0$$

This is a derivative of the Gibbs equation attributed to Duhem and Margules (8). Alternately the relation between liquid and vapor compositions may be expressed in terms of activity coefficients, γ , using the definition

$$p = P \gamma x$$

in which γ appears as the correction factor in the statement of Raoult's Law. By differentiation and substitution for $d \ln p$ the Gibbs-Duhem equation is readily obtained in the form

$$x_1 \left(\frac{d \ln \gamma_1}{d x_1} \right)_{\text{T.P.}} = x_2 \left(\frac{d \ln \gamma_2}{d x_2} \right)_{\text{T.P.}} \quad (3)$$

Equation 3 is of value in studying experimental data on vapor-liquid equilibrium by relating the curves of a plot of the activity coefficient against the liquid compositions of the binary mixture. Inasmuch as the magnitude of the slopes are difficult to determine precisely, however, studies have been made to obtain convenient mathematical solutions of this differential equation.

The most useful of the integrated forms of Equation 3 are the equations of Margules (8) and Van Laar (9).

Margules Equations

Margules integrated the Gibbs-Duhem equation in terms

of a pair of exponential series with unlimited numbers of terms and then derived the constants for one of the equations from those of the other by applying Equation 3. As expressed by Carlson and Colburn (6) the two-term equations of Margules are:

$$\begin{aligned}\log \gamma_1 &= (2B - A) x_2^2 + 2(A - B) x_2^3 \\ \log \gamma_2 &= (2A - B) x_1^2 + 2(B - A) x_1^3\end{aligned}$$

One finds at $x_1 = 0$, $\log \gamma_1 = A$ and $\log \gamma_2 = 0$, at $x_1 = 1$, $\log \gamma_1 = 0$ and $\log \gamma_2 = B$. It is of interest to note that for these equations, at $x_1 = 0.5$, $\log \gamma_1 = \frac{B}{4}$ and $\log \gamma_2 = \frac{A}{4}$ regardless of the values of A and B.

Van Laar Equations

Van Laar derived solutions to Equation 3 from a thermodynamic study and these are given below in the form expressed by Carlson and Colburn

$$\begin{aligned}\log \gamma_1 &= \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \\ \log \gamma_2 &= \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2}\end{aligned}$$

In this form, constants A and B have the property of being equal to the terminal values of the $\log \gamma$ of the plot of Equation 2 for γ_1 and γ_2 . Thus, at $x_1 = 0$, $\log \gamma_1 = A$, and at $x_1 = 1$ when $x_2 = 0$, $\log \gamma_2 = B$. It is of interest, also, to see that at $x_1 = 0$, $\log \gamma_2 = 0$ or $\gamma_2 = 1$, and at $x_1 = 1$, $\log \gamma_1 = 0$ or $\gamma_1 = 1$.

In all attempts to find suitable solutions to the differential form of the Gibbs-Duhem equation the object has been to derive separate equations for the activity coefficients of the two components, which can be used, in conjunction with their vapor pressures, in the pure state, to determine the relations between the two phases. In using these equations at constant pressure, and consequently with varying temperature, it must be assumed that the activity coefficient varies to a negligible extent with temperature over the range extending between the boiling points of the two components. This assumption is increasingly difficult to justify as the boiling points become further and further apart.

APPARATUS

A. The Liquid Recirculation Apparatus

The apparatus used to determine the vapor-liquid equilibrium compositions on the benzene-propanol and benzene-pentanol systems was the same as that used by Waldichuk (10). It was designed to be similar to that proposed by Fowler (3) with the following additional improvements:

(1) A capillary stopcock was introduced into the liquid trap for removal of the liquid sample. This eliminated the larger quantities of liquid which stagnate in an ordinary stopcock.

(2) The drop counter of the Gillespie still (2) was retained in the small bulb above the capillary leading to the boiler. This aids in adjusting for a proper rate of heating to the boiler.

(3) The vapor condensate trap was made smaller in order to achieve equilibrium more quickly.

(4) A type of container where dry ice and acetone mixture can be used for the cooling material was introduced above the vapor condensate trap.

The still as shown in Fig. 1 was made of Pyrex glass. Tungsten leads were sealed into the standard taper stopper of the filling tube for electrical input to the internal heater. This heater consisted of about 10 inches of 28-gauge platinum wire, wound into a small coil at the end and brazed to the tungsten leads with constantin as flux. A current of 5 amp. controlled by a variac was suitable for proper pumping in the Cottrell tube. The boiler, Cottrell tube, disengagement chamber, and thermometer well were insulated with asbestos cord and asbestos cement. The external heater for the boiler was wound on the asbestos lagging

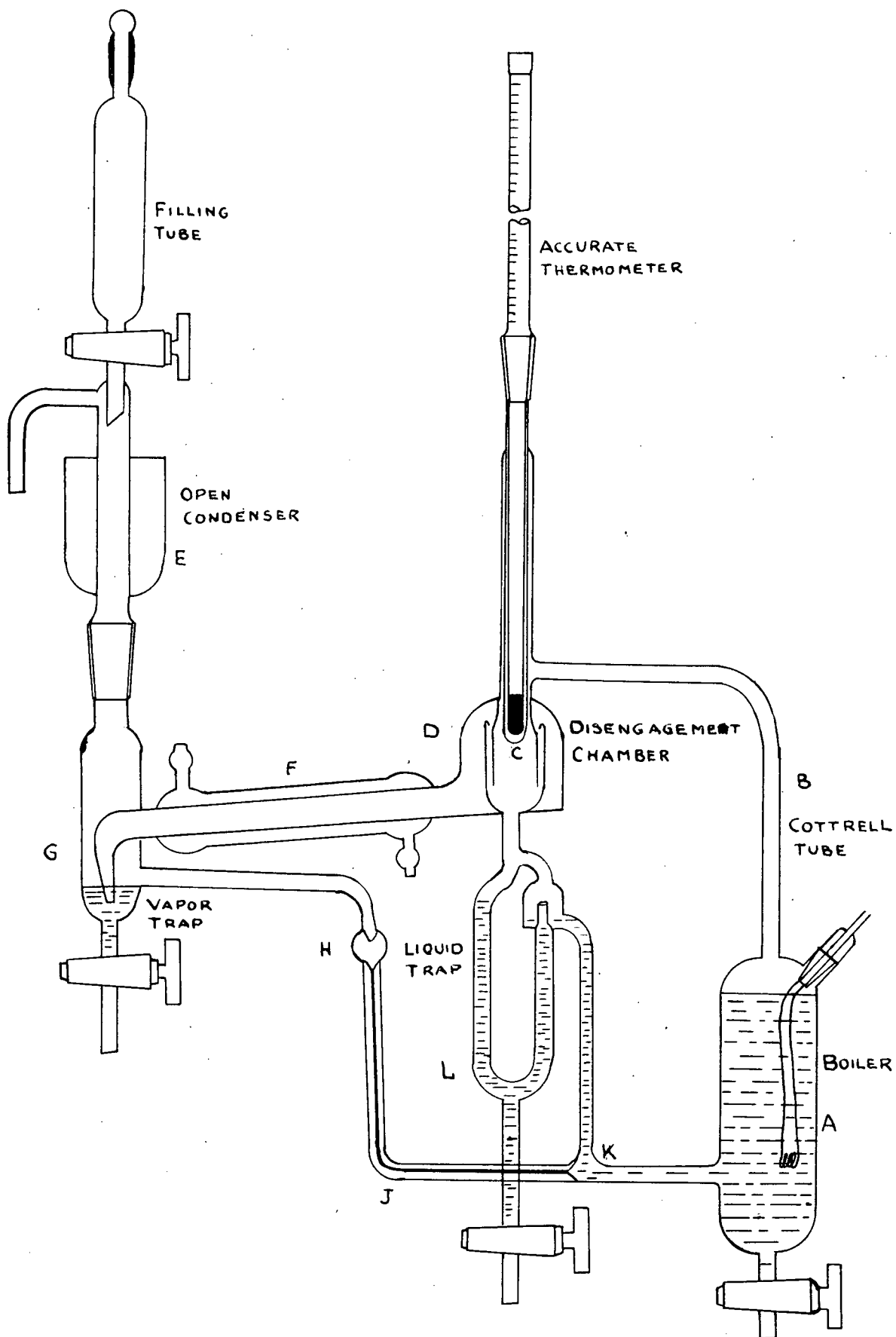


FIG. 1 FOWLER - GILLESPIE STILL

from the stopcock at the bottom of the boiler to the base of the filling tube. It consisted of 28 turns of No. 22 nichrome resistance wire. A potential of 38 to 50 volts was found necessary to give the proper heat for boiling. The external heater was covered with a layer of asbestos cement and paper for electrical insulation. The whole apparatus was mounted on a platform 24" by 16" with upright steel support rods located 14" apart.

The vapor-liquid equilibrium still used does an effective job of preventing condensation of the vapors in the still while at the same time causing circulation of both vapors and liquid, and keeping entrainment at a minimum. Although the apparatus is based on the vapor recirculation principle, it differs essentially from others of this type in that the boiling liquid is also circulated rapidly. The liquid is boiled in the boiler A, but differing from other vapor-liquid equilibrium apparatus, the vapor and liquid are not permitted to separate in this chamber. They are maintained in intimate contact as they pass up the modified Cottrell pump B to the thermometer C, and hence to the disengagement chamber D. In D the liquid continues to circulate down through L, while the vapor passes to the condenser F, and then to the condensate trap G. The overflow from G returns to the boiler through the small drip counter H and capillary J. At K the overflow combines with the liquid flow from L and both return to the boiler. The rate of condensate return should be such that the level of liquid fluctuates gently just above the capillary in the drip counter.

B. Refractometer

The analysis of the vapor and liquid compositions is

carried out with a refractometer of the Spencer-Abbe type. It is equipped with Amici compensating prisms so that a white light source can be used instead of monochromatic light. The scale of the instrument is calibrated directly in refractive index as measured with the D line of the sodium spectrum. Readings may be read directly to the third decimal place and the fourth may be estimated with an accuracy of ± 0.0002 . The temperature of the prisms was kept at $25^{\circ}\text{C.} \pm 0.2$ with a water bath controlled to $25^{\circ}\text{C.} \pm 0.1$. The temperature of the prisms could be read to 1°C. and estimated to $\pm 0.2^{\circ}\text{C.}$ on a thermometer supplied with the instrument. No closer check on the temperature was necessary since a change of 0.2°C. only altered the refractive index of benzene, propanol and pentanol by approximately 0.0001 units.

C. Thermometers

The two thermometers used in this research had ranges from $50^{\circ} - 100^{\circ} \text{C.}$ and from $0^{\circ} - 200^{\circ} \text{C.}$ and were the ordinary mercury-in-glass type. Both were calibrated by Waldichuk (10) against a platinum resistance thermometer No. 169314 with National Bureau of Standards Certificate dated August 17, 1937, for use in his research. The short-range one was calibrated at 5° intervals from $50^{\circ} - 100^{\circ} \text{C.}$ and the long-range one at 10° intervals from $100^{\circ} - 200^{\circ} \text{C.}$ The short-range thermometer could be read accurately to the nearest 0.05°C. The long-range thermometer could be read accurately to the nearest 0.1°C.

MATERIALS

A. Benzene

The benzene used was a commercially pure grade as supplied by Merck and Company, Inc. It conformed to A.C.S. standards and a lot analysis for the benzene's maximum impurities was given as follows:

Non-volatile - - - - -	0.001%
Acid or alkali - - - - -	passes test
Substances darkened by H_2SO_4 - - -	passes test
Sulphur compounds (as S) - - - - -	0.005%
Thiophene - - - - -	0.000%
Water - - - - -	passes test

This benzene was subjected to further purification as follows:

In about 1500-ml. lots the benzene was agitated with C.P. concentrated sulfuric acid in a 2-liter separating funnel. The acid was allowed to settle out, and it was drained off. The benzene was washed twice with 500-ml. portions of distilled water, then with two 500-ml. portions of 1 N sodium hydroxide. The benzene was washed further with distilled water. About 150 ml. of purified mercury was agitated with the benzene. A greyish-black scum was left on the surface of the mercury. The mercury was removed and the benzene was finally washed with several portions of distilled water. The benzene was poured from the separating funnel into a 3-liter container to which was added freshly cut sodium ribbon. The container was stoppered lightly and the benzene was allowed to stand for a week. Any hydrogen formed from the reaction of the sodium with the water would be

evolved during that time.

The still used for the benzene distillation is shown in Fig. 2. The column is a silvered, vacuum-jacketed one, packed with a mixture of glass-beads and helices. It has 14 theoretical plates. It is 122 cm. long and has an internal diameter of 25 cm. A 1-liter flask is used for the boiler and heat is supplied through a Glas-Col heating mantle controlled by a variac. A reflux adjustment could be made in the head of the still to give the reflux ratio desired.

After standing for a week the benzene was refluxed over Na ribbon for ten hours in the benzene still. The reflux ratio was then set for 15:1 and distillation carried out in which the first 150 ml. distilled were discarded. About 650 ml. of benzene were collected in the middle fraction. This benzene distillation was repeated twice and only the middle fractions distilling at constant temperature were collected each time.

The distilled benzene was placed in a 250-ml. erlenmeyer flask, about 150 ml. at a time, and was frozen in a dry ice-acetone mixture. The last few mls. to freeze were discarded and the first 25 ml. to melt were discarded also. The purified benzene was then stored in a ground glass stoppered flask over activated alumina. Over 2 liters of purified benzene were collected.

Three separate checks on the purity of this benzene were made - refractive index, boiling point, and density.

a) Refractive Index

The refractive index of the purified benzene was checked at 20°C. and 25°C. and the values of the refractive index found were 1.5012 and 1.4979, respectively, in good agreement with the reported values listed in Table I.

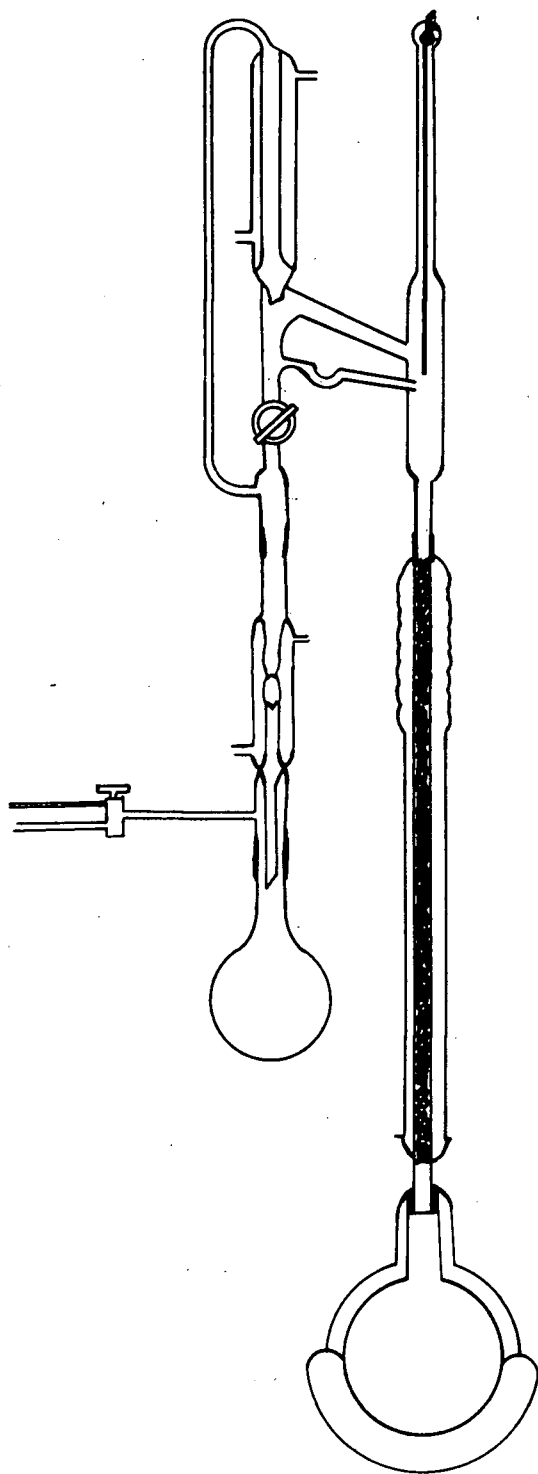


FIG. 2 BENZENE STILL

b) Boiling Point

The determination of the boiling point of benzene was carried out in a Cottrell-Chopin boiling-point determination apparatus shown in Fig. 4. It is a standard form of ebulliometer. The boiling point was found to be 80.1°C . This result checks favourably with the boiling points reported in Table I.

c) Density

Density measurements were carried out in a vacuum-jacketed 25-ml. pycnometer bottle which was calibrated with double distilled water at 25°C . The bottle was carefully weighed and benzene was added. The pycnometer was then placed in a constant temperature bath, the temperature being controlled at 25.00°C . ± 0.02 . After two hours the bottle was removed from the bath, the excess benzene was cleaned off with lens tissue and the bottle and benzene were weighed carefully as before. The density of the benzene at 25°C . was found to be 0.8735. Comparative values are given in Table I.

The balance used for the weighings was a Chainomatic balance with a sensitivity of 3 scale divisions per milligram and the weights used were calibrated by the method of substitution. Correction for air buoyancy was made after each weighing.

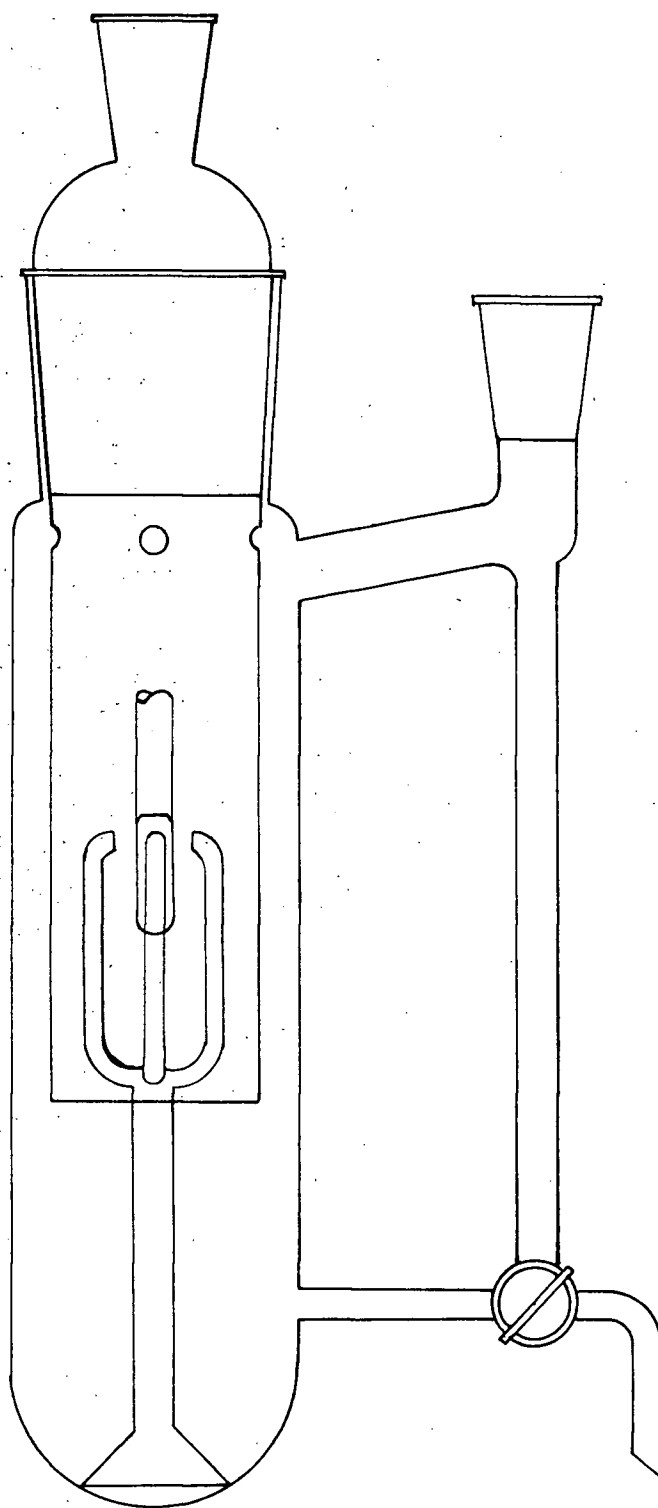


FIG. 4 COTTRELL-CHOPIN BOILING-POINT APPARATUS

TABLE I
PHYSICAL DATA FOR BENZENE FROM THE LITERATURE

Author	R.I.	B.P.	Density
Waldichuk (10)	$n_D^{25} = 1.4979$		$d_4^{25} = 0.87368$
Wojciechowski (11)	$n_D^{25} = 1.4981$	80.1°C.	$d_4^{25} = 0.87366$
I.C.T. (12)	$n_D^{20} = 1.5014$	80.12°C.	$d_4^{20} = 0.8788$
Allen, Lingo and Felsing (13)	$n_D^{20} = 1.4980$		$d_4^{25} = 0.8732$
Glanville and Sage (28)	$n_D^{20} = 1.5014$		
Handbook of Chemistry and Physics (14)	$n_D^{20} = 1.5014$	80.1°C.	$d_4^{20} = 0.8794$
Gibbons et al. (15)	$n_D^{25} = 1.4979$		

B. Propanol

The propanol used was a commercially pure grade as supplied by the Fisher Scientific Company with a lot analysis for maximum impurities as follows:

Acidity (CH_3COOH)	- - - - -	0.002%
Boiling range	- - - - -	96° - 97.5°C.
Non-volatile matter	- - - - -	0.000%
Substs. ppt. by H_2O	- - - - -	None

The propanol was further purified by treating 2 liters of it with about 5 ml. of Br_2 . The bromine was added to remove any allyl alcohol (B.P. 97°C.) which might be present. After standing overnight the alcohol was fractionated in the alcohol distilling column (illustrated in Fig. 3).

This column is similar to the one used for the benzene distillation except that its length is only 100 cm. and its diameter is 3 cm. It is silvered, vacuum jacketed and packed with very small helices giving an estimated 20 theoretical plates. The still pot was a 2-liter flask heated with a Glas-Col mantle, the heat input to it being controlled by a variac. Any desired reflux ratio could be obtained by the adjustment of a stop-cock in the head of the column.

At a reflux ratio of 15:1 the fraction distilling overhead between 96.8° to 97.4°C. was collected. This fraction was dried over Ca for several days, then redistilled. The portion coming over between 97° - 97.3°C. was collected and was finally dried over freshly ignited CaO for a week, then fractionated. The middle cut distilling at 97.2°C. at 760 mm. pressure was collected. The purified propyl alcohol was stored over activated

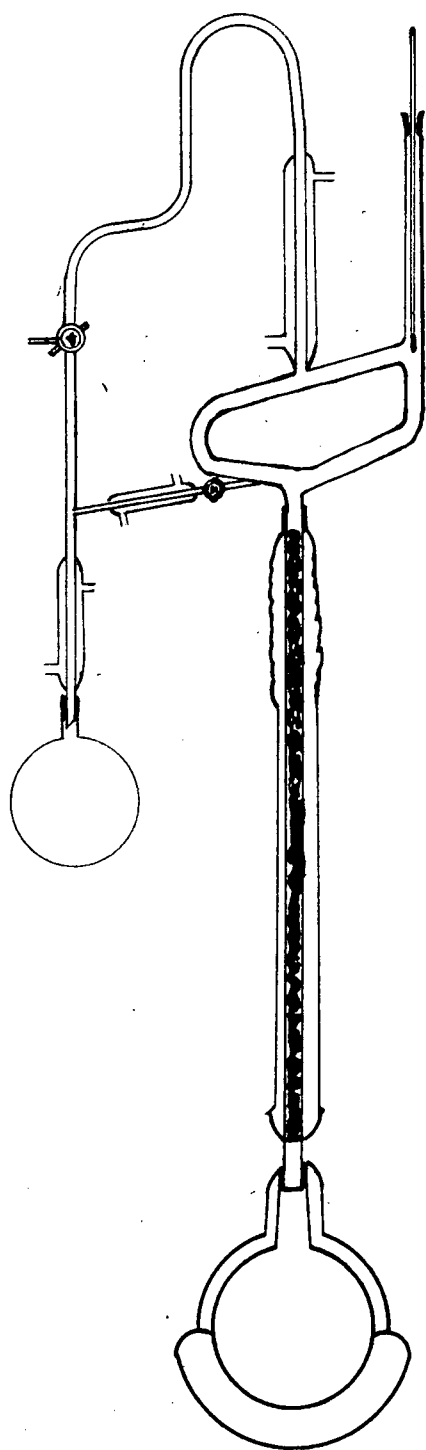


FIG.3 ALCOHOL STILL

alumina in a glass-stoppered flask. About 1000 ml. of alcohol was purified in this fashion.

Three separate checks on the purity of the propanol were made - refractive index, boiling point, and density.

a) Refractive Index

The refractive index of the alcohol was checked at 20°C. and 25°C. and gave values of 1.3838 and 1.3858, respectively. Comparative values are given in Table II.

b) Boiling Point

The boiling point determination was carried out in the apparatus shown in Fig. 4. The value obtained was 97.2°C., agreeing well with the literature values.

c) Density

The density of the propanol was found in the same way as that used for benzene. The value of 0.8023 obtained checks well with the one reported in Table II.

TABLE II
PHYSICAL DATA FOR PROPANOL FROM THE LITERATURE

Author	R.I.	B.P.	Density
Trev and Watkins (16)	$n_D^{25} = 1.3834$	96.96 ₇₅₄ °C.	$d_{25}^{25} = 0.80236$
Wojciechowski (17)		97.21°C.	
Brunel (18)	$n_D^{25} = 1.3835$	97.25°C.	
Denzler (19)	$n_D^{20} = 1.3860$		
Webb and Lindsley (20)	$n_D^{20} = 1.3855$	97.25°C.	

C. Pentanol

The pentanol used was a technical grade of alcohol supplied by the Fisher Scientific Company.

A search of the literature revealed that the isomers of n-pentanol have boiling points that differ from that of the pure pentanol by at least 5°. The closest isomer of n-hexanol that could be found had a b.p. that differed by 2°. It was decided therefore to purify the pentanol by fractionation without any further treatment.

About 3500 ml. of the technical pentanol had been obtained and this was charged to the still pot in two 1750-ml. batches. After two successive fractionations on each batch at a 15:1 reflux ratio about 2000 ml. of pentanol had been collected with a b.p. range of 137.5° to 138°C. This was carefully distilled once more and dried over CaO for a week. Two more fractionations were then carried out at a reflux ratio of 20:1 to remove all traces of impurities. This gave a volume of about 750 ml. of pentanol that came over at 137.9°C.

Only two checks on the purity were carried out - refractive index and boiling point. The values of refractive index, density, and b.p. varied over considerable range as reported in the literature. Of these the boiling point offered the best agreement and this seemed the most reliable check on the purity.

a) Refractive Index

The refractive index was obtained at 20°C. and 25°C. and the values are 1.4113 and 1.4095, respectively. Comparative

values are given in Table III.

b) Boiling Point

The boiling point determination was carried out in the same apparatus used in the determination of b.p. of benzene and propanol. A value of 137.9°C. was obtained. Literature values are reported in Table III.

TABLE III
PHYSICAL DATA FOR PENTANOL FROM THE LITERATURE

Author	R.I.	B.P.
Butler et al. (21)	$n_D^{20} = 1.4111$	137.75°C.
Timmermans (22)	$n_D^{20} = 1.4119$	
Simons (23)		138.00°C.
Wojciechowski (17)		138.2°C.

EXPERIMENTAL PROCEDURES

A. Determination of the Refractive-Index Composition Curve at 25°C.

Benzene-Propanol

In constructing the refractive-index composition curve for benzene-propanol calculated amounts of benzene were pipetted into carefully cleaned and weighed weighing bottles. To each bottle in turn, after the benzene and bottle were weighed, was added definite amounts of propanol so as to make up compositions ranging from approximately 0.1 - 1.0 mole fraction of benzene. The bottle was again weighed and the refractive index was taken of the mixture on the Abbé refractometer with the temperature of the refractometer prisms controlled at $25^{\circ}\text{C.} \pm 0.2$. Readings were taken at 1-minute intervals over a 4-minute period after the mixture on the prisms was allowed to come up to temperature. No change was noticed in the refractive index readings, showing that the liquid between the prisms was not volatilizing. The liquid was placed on the prisms by forcing a few drops of it between the clamped prisms with an eye dropper.

Care was exercised to see that the period of time the weighing bottle was uncovered was kept to a minimum so as to reduce the loss of the volatile components. The transfer of the liquid took approximately 10 secs., and weighings made in order to calculate the loss of benzene during this period showed a small loss of about 0.5 milligrams.

B. Vapor-Liquid Determination on the Fowler-Gillespie Still

Initially the boiler of the still was charged with approximately 180 ml. of pure benzene by way of the internal heater opening. The internal heater was set in place, the leads

attached and A.C. voltage applied to both the external and internal heaters - about 35 and 7 volts, respectively. When pumping in the Cottrel tube had commenced the internal heater was adjusted to give smooth operation. It was difficult to place the correct quantity of liquid in the boiler at the start so adjustments were made after the condensate trap was filled. On boiling the liquid level should gently fluctuate in the small bulb above the capillary tube and in the small bulb at the top of the liquid trap.

After the temperature of boiling of the benzene was recorded, the power to the still was shut off, some benzene was removed from it, and an approximately equal volume of propanol added to it. The power was reapplied.

Attainment of equilibrium usually took about two hours. When the temperature fluctuation was no greater than $\pm 0.05^{\circ}\text{C}$. the boiling temperature was recorded and samples of the liquid and vapor condensate were removed as quickly as possible. Each outlet from the traps was flushed out before the sample was taken. Samples were collected in small glass vials and were tightly corked thereafter with cork stoppers. Refractive index readings were taken soon after in a similar fashion to that used for the refractive index-composition curve. Atmospheric pressure readings were taken at almost the same time as the other readings on a Fortin-type of barometer, located about 15 feet above the level of the vapor-liquid still.

In subsequent runs benzene-rich mixtures were removed from the condensate trap and pure propanol was added to the required height in the boiler to affect changes in composition.

For the determination of the vapor-liquid compositions

of the benzene-pentanol systems the same procedure as above was followed except that more heat was applied through the external heater to boiler to give equilibrium conditions. Instead of carrying out the runs at atmospheric conditions, pressure was applied through a barostat (see Fig. 5) to keep it at 760 ± 2 mm. of pressure.

C. Determination of Refractive Index-Composition Curve at 25°C.

Benzene-Pentanol

This refractive index-composition curve determination was carried out in a similar manner to that used for the benzene-propanol system, the only difference being that the pentanol was added first to the weighing bottle since it was less volatile than the benzene.

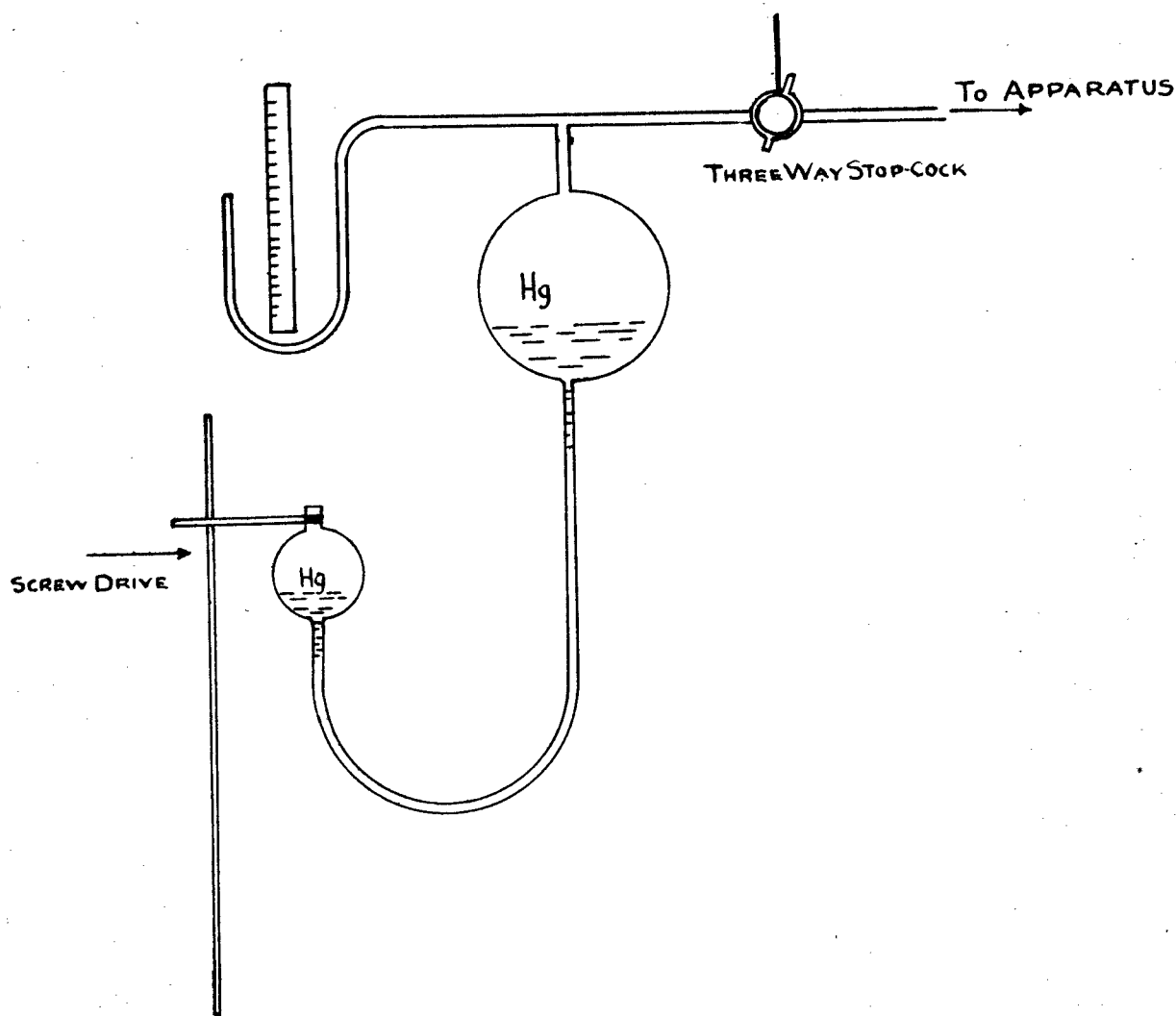


FIG.5 MERCURY BAROSTAT

RESULTS

A. Benzene-Propanol

The refractive index values found using varying mole fractions of the benzene-propanol system are shown in Table IV. An estimation of the error due to volatilization of the volatile components during the weighings showed it to be approximately 0.03%. No significant error was detected during the refractive index determinations. A large plot of the refractive index versus the composition was made and it was used to determine the compositions during the vapor-liquid equilibrium runs. Fig. 6 shows a reduced plot of the large one.

TABLE IV

REFRACTIVE INDEX-COMPOSITION DATA FOR BENZENE-PROPANOL AT 25°C.

<u>MOLE FRACTION OF BENZENE</u>	<u>REFRACTIVE INDEX</u>
0.000	1.3838
0.094	1.3959
0.183	1.4070
0.270	1.4173
0.375	1.4298
0.488	1.4428
0.580	1.4528
0.654	1.4610
0.754	1.4714
0.802	1.4769
0.904	1.4876
1.000	1.4979

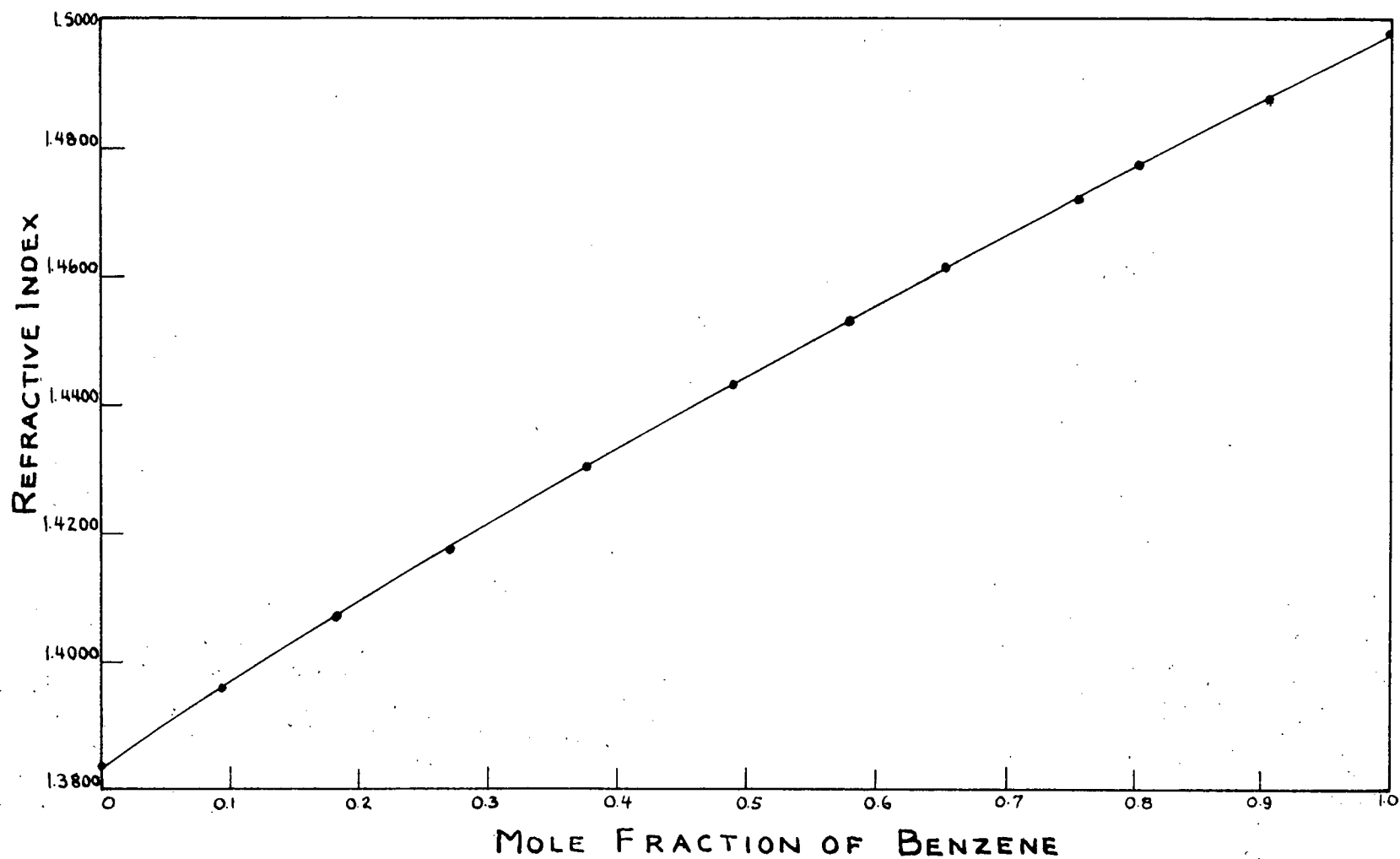


FIG.6 REFRACTIVE INDEX OF BENZENE-PROPANOL MIXTURES AT 25°C

In Table V are tabulated the results of the vapor-liquid equilibrium determinations on the Fowler-Gillespie still. The temperature was read on a 50° - 100°C. thermometer read to the nearest 0.05°C. The pressure was read on a Fortin-type barometer and all runs were made when the atmospheric pressure was constant between 740 - 742 mm. of Hg.

TABLE V

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR BENZENE-PROPANOL
AT ATMOSPHERIC PRESSURE

Run	Duration of Run (Hrs.)	Temp. °C.	Atm. Press. mm. Hg	Liquid Phase		Vapor Phase	
				R.I.at 25°C.	Mol. Fr. C ₆ H ₆	R.I.at 25°C.	Mol. Fr. C ₆ H ₆
1		79.30	741	1.4979	1.000	1.4979	1.000
2	2	77.70	741	1.4937	0.960	1.4888	0.915
3	2	77.0	741	1.4908	0.935	1.4852	0.883
4	2	76.4	742	1.4860	0.888	1.4814	0.847
5	2 1/2	76.3	742	1.4840	0.870	1.4798	0.832
6	2 1/2	76.2	742	1.4795	0.831	1.4775	0.810
7	2 1/2	76.2	740	1.4716	0.755	1.4741	0.777
8	2	76.3	740	1.4646	0.687	1.4714	0.755
9	2 1/2	76.60	741	1.4577	0.623	1.4695	0.735
10	2	76.8	741	1.4543	0.596	1.4686	0.727
11	2	78.40	741	1.4360	0.427	1.4613	0.660
12	2 1/2	79.10	741	1.4307	0.380	1.4595	0.635
13	2 1/2	80.2	740	1.4228	0.316	1.4549	0.600
14	2	83.00	740	1.4114	0.219	1.4460	0.518
15	2	84.90	740	1.4060	0.175	1.4390	0.455
16	2 1/2	90.10	740	1.3940	0.080	1.4179	0.274
17		96.40	740	1.3838	0.	1.3838	0

A large scale plot of the equilibrium values was made, and also a plot of the temperature against the liquid and vapor composition of the more volatile component. The reduced graphs are shown in Fig. 7 and Fig. 8, respectively.

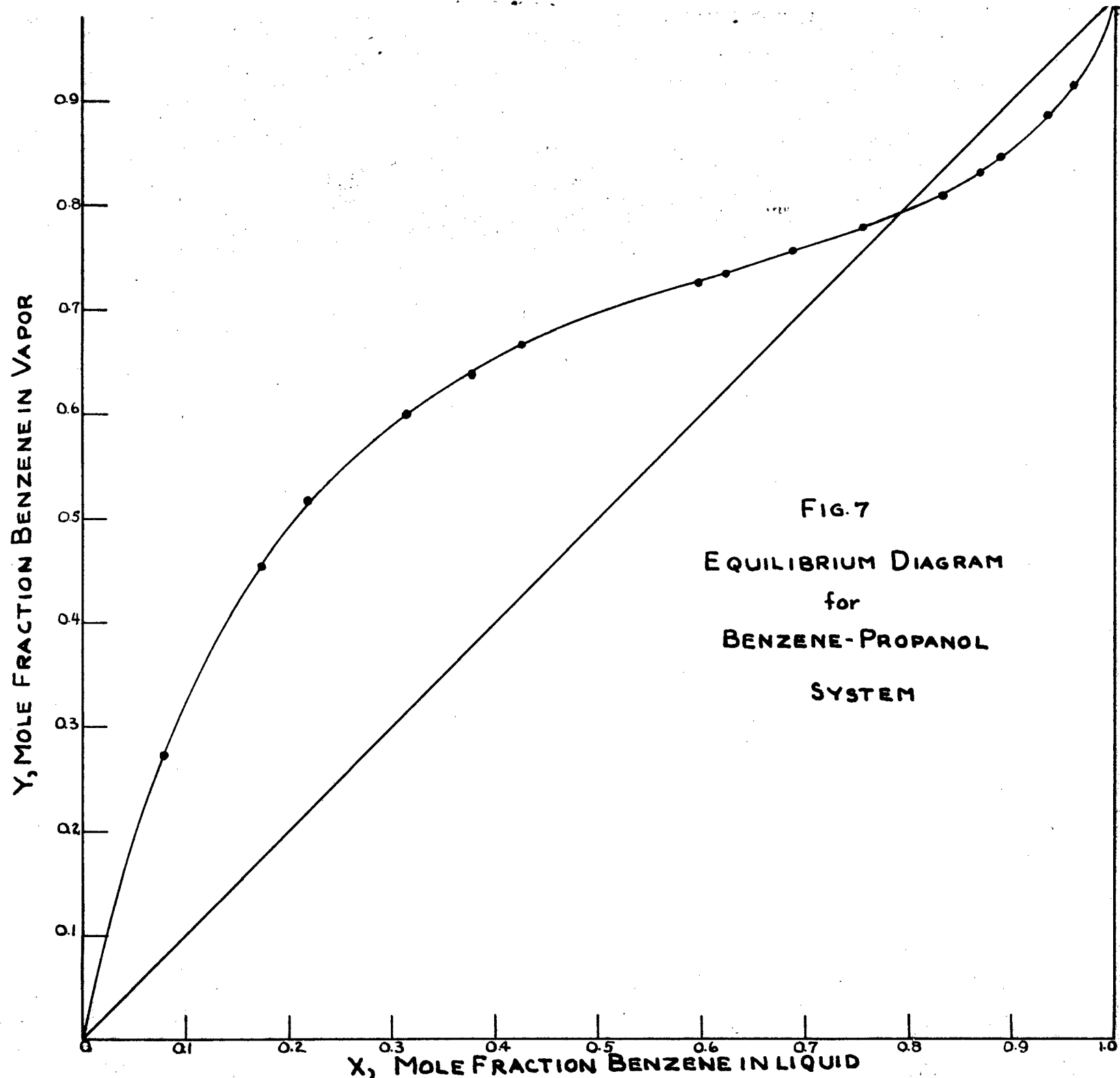
The graphs indicate an azeotrope at $x_1 = 0.795$ with a normal boiling point of 76.2°C . at 740 mm. pressure. Similar values reported by Lecat (4) give the azeotrope at $x = 0.791$ and a b.p. of 77.12°C . at 760 mm. pressure. The boiling-point curve for the liquid is almost horizontal in the vicinity of the minimum, and a change in composition from 68% to 83% benzene is accompanied by a temperature change of only 0.11°C .

To check the thermodynamic consistency of the system the values of the activity coefficients obtained experimentally were compared with those calculated theoretically. The activity coefficients were computed from the equation

$$\gamma = \frac{Py}{P^\circ x} \quad (1)$$

where γ = activity coefficient; P = the total pressure of the system, in this case 740 - 742 mm. of mercury; P° = the vapor pressure of the pure component at the solution temperature in mm. of mercury; and x = mole fraction of the component in the liquid phase. The calculated values are shown in Table VIII.

Pressures of the pure components, benzene and propanol, at the particular boiling temperatures were taken from vapor pressure curves. For benzene, the vapor pressure data for the range of temperature used for both the benzene-propanol and benzene-pentanol systems were obtained from various sources. Over the lower temperature range the vapor pressure values are computed



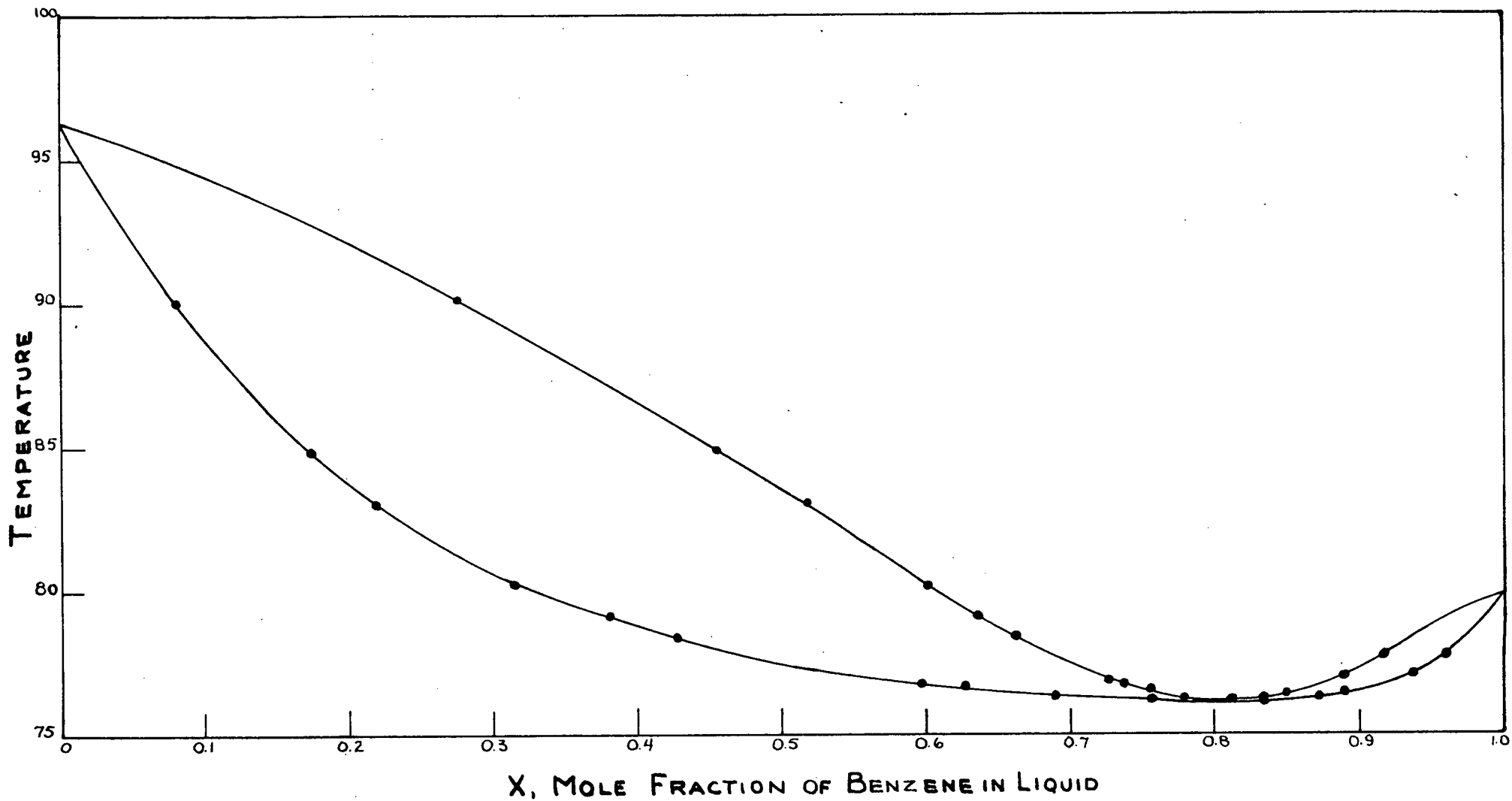


FIG.8 BOILING POINT DIAGRAM OF BENZENE- PROPANOL SYSTEM

by the equation

$$\log P \text{ (mm.)} = - \frac{0.05223 a}{T} + b$$

where T is the absolute temperature, and a and b are constants having the following values:

0° to 42°C.	a = 34,172	42° to 100°C.	a = 32,295
	b = 7.9622		b = 7.6546

For the region of temperature from 100° to 140°C. the experimental values of Smith and Menzies (24) and Gornowski et al. (25) were used. Table VI shows the vapor pressure values over the temperature range concerned and Fig. 9 a plot of these values.

TABLE VI
VAPOR PRESSURE DATA FOR BENZENE

Temp.	Pressure mm. Hg	Source of Data
60	390	Calculated
70	548	"
80	754	"
90	1022	"
100	1360	"
110	1751	Smith and Menzies (24)
120	2240	" " "
130	2825	Gornowski et al. (25)
140	3518	" " "

The vapor pressure data for propanol were taken from Chemical Engineers' Handbook (26) and are shown in Table VII and a plot of it in Fig. 10.

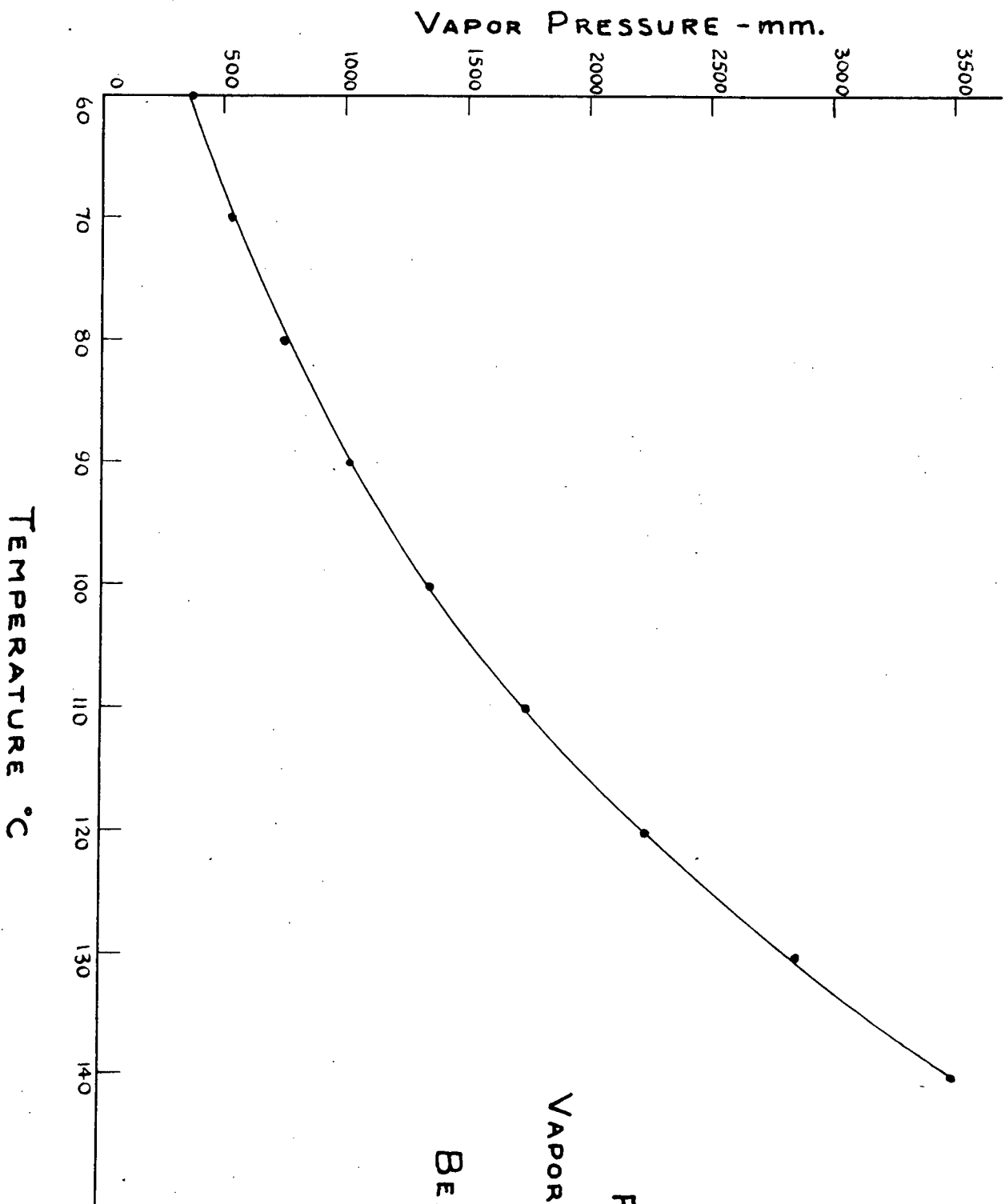


FIG. 9
VAPOR PRESSURE
of
BENZENE

TABLE VII
VAPOR PRESSURE DATA FOR PROPANOL

Temp. °C.	Pressure mm. Hg
66.6	200
75.4	300
82.0	400
87.3	500
91.6	600
95.8	700
97.2	760

VAPOR PRESSURE - mm.

800

700

600

500

400

300

200

65

70

75

80

85

90

95

100

TEMPERATURE - °C

FIG.10

VAPOR PRESSURE
of
PROPANOL

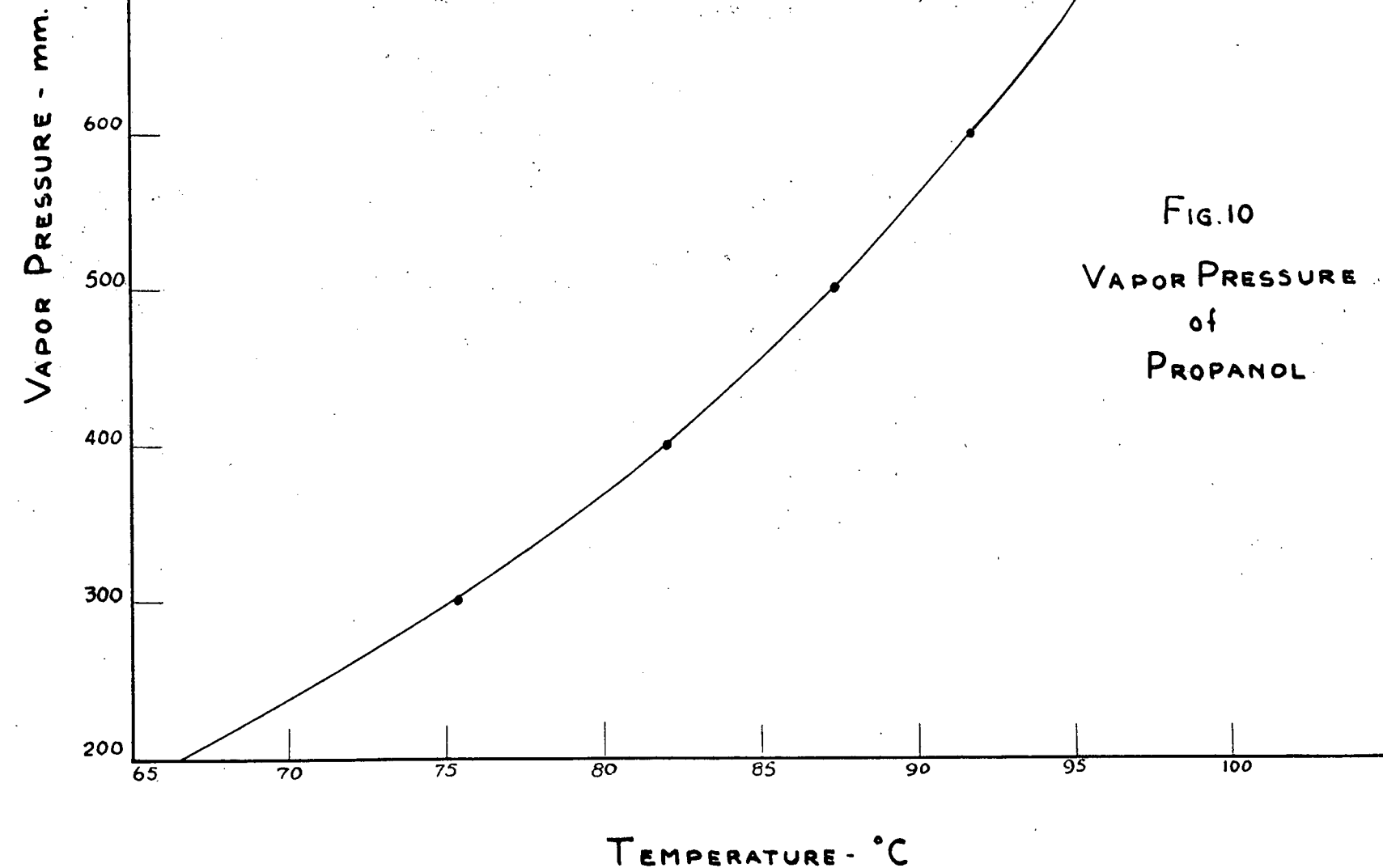


TABLE VIII

ACTIVITY COEFFICIENTS OF BENZENE AND PROPANOL
FROM EXPERIMENTAL DATA

T°C.	P mm. Hg	P ₁ mm. Hg	P ₂ mm. Hg	x ₁	y ₁	Y ₁	Y ₂
79.3	741			1.000	1.000	1.0	
77.7	741	700	337	0.960	0.915	1.010	4.66
76.97	741	685	324	0.935	0.883	1.022	4.10
76.42	741	673	304	0.888	0.847	1.05	3.33
76.31	742	670	300	0.870	0.832	1.056	3.19
76.21	742	668	298	0.831	0.810	1.08	2.80
76.24	741	669	299	0.755	0.777	1.129	2.25
76.31	741	670	300	0.687	0.755	1.216	1.93
76.6	741	675	305	0.623	0.735	1.295	1.705
76.78	741	683	322	0.596	0.727	1.325	1.55
78.4	740	720	347	0.427	0.660	1.585	1.28
79.1	740	731	355	0.380	0.635	1.69	1.228
80.21	740	761	372	0.316	0.600	1.847	1.165
83.0	741	830	418	0.219	0.518	2.11	1.085
84.9	740	882	455	0.175	0.455	2.18	1.078
90.1	740	1025	563	0.08	0.274	2.479	1.055
96.44	741	0	740	0	0	2.768	1.000

The theoretical values of the activity coefficients are calculated from the Van Laar solutions of the Gibbs-Duhem equation which are given below in the form presented by Carlson and Colburn (6):

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2}$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2}$$

where A and B are the values of $\log \gamma_1$ and $\log \gamma_2$ for $x_1 = 0$ and $x_2 = 0$, respectively; the values giving the best fit of the plot of the experimental activity coefficients extrapolated to zero are $A = 0.443$ and $B = 0.752$. Figure 11 shows the agreement between the observed data and the calculated values and in Table IX the experimental and theoretical values are given.

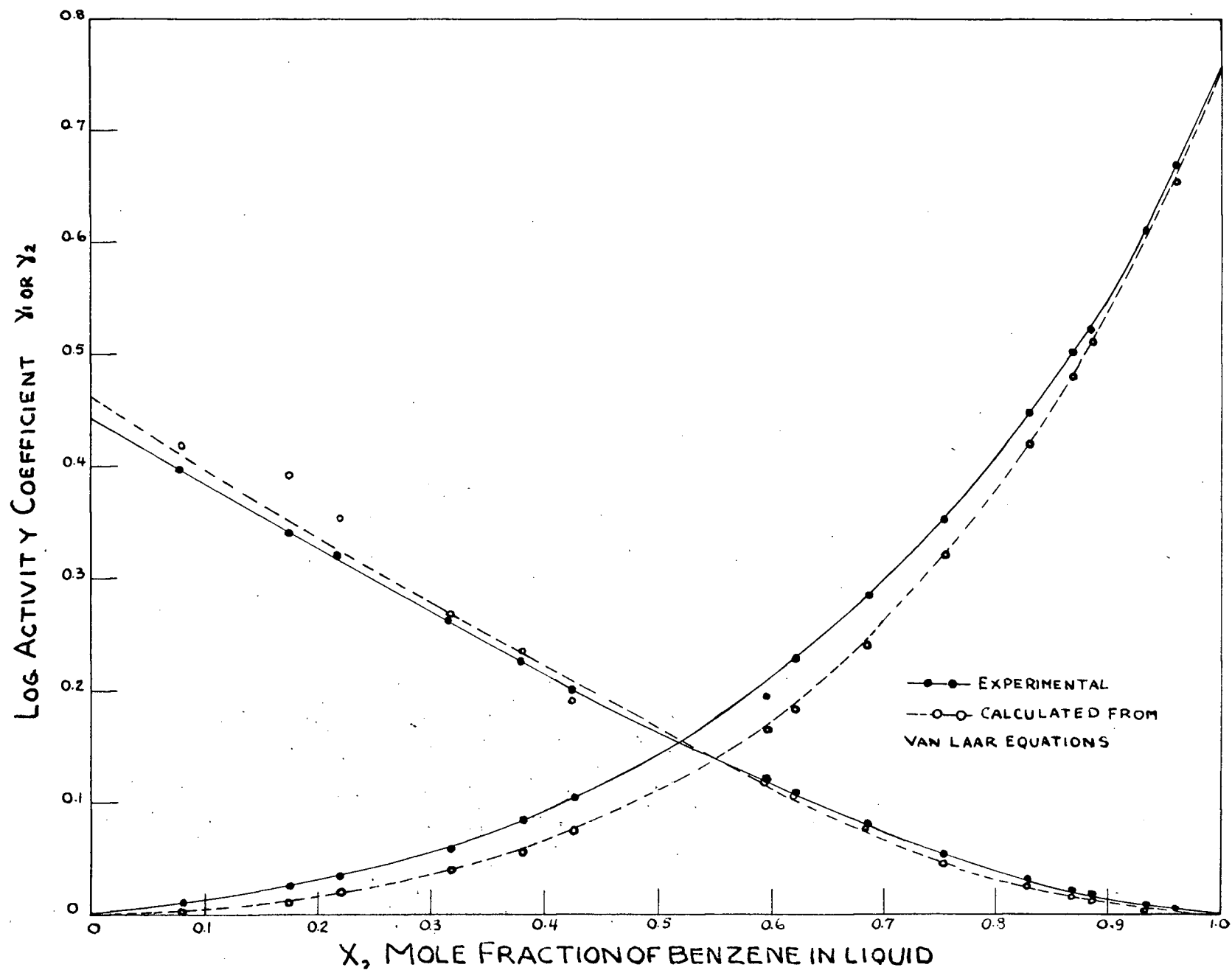


FIG. II ACTIVITY COEFFICIENTS FOR BENZENE-PROPANOL SYSTEM

TABLE IX
EXPERIMENTAL AND THEORETICAL ACTIVITY COEFFICIENTS
OF BENZENE AND PROPANOL

x_1	γ_1 Expt.	γ_1 Calc.	γ_2 Expt.	γ_2 Calc.
0	0	2.768	1.000	1.000
.080	2.479	2.630	1.055	1.005
.175	2.180	2.472	1.078	1.021
.219	2.110	2.394	1.085	1.051
.316	1.847	1.873	1.165	1.074
.380	1.690	1.732	1.128	1.131
.427	1.585	1.551	1.280	1.181
.596	1.325	1.323	1.550	1.454
.623	1.295	1.298	1.705	1.520
.687	1.216	1.212	1.930	1.736
.755	1.129	1.138	2.250	2.110
.831	1.080	1.070	2.800	2.620
.870	1.056	1.042	3.190	3.010
.888	1.050	1.032	3.330	3.230
.935	1.022	1.012	4.100	4.100
.960	1.010	1.005	4.660	4.520
1.000	1.000	1.000		5.640

B. Benzene-Pentanol

The refractive index values found using varying mole fractions of the benzene-pentanol system are shown in Table X and a graphical representation of these in Fig. 12. An estimation of

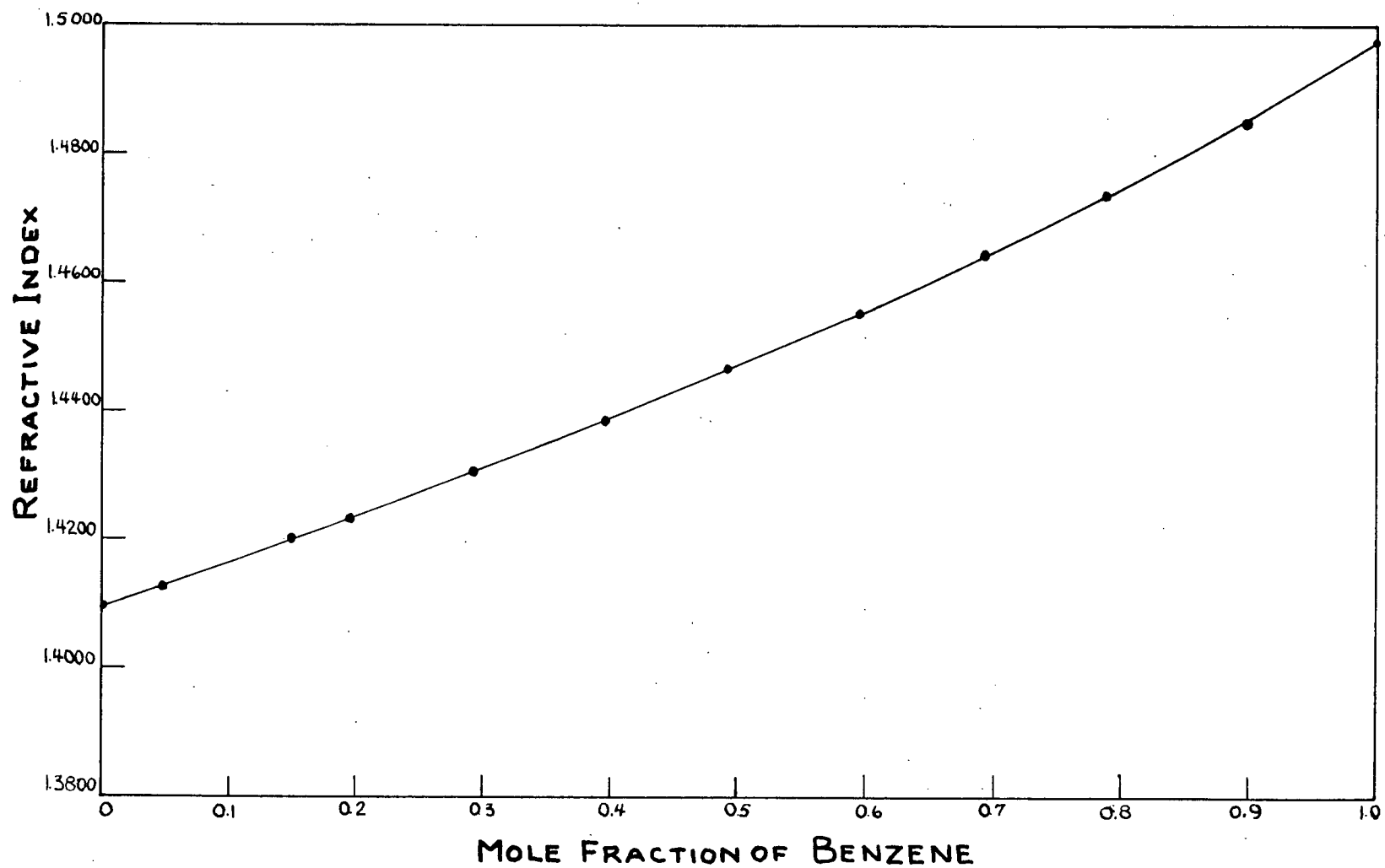


FIG.12 REFRACTIVE-INDEX OF BENZENE-PENTANOL MIXTURES AT 25°C

the error due to volatilization of the volatile components during the weighings showed it to be approximately 0.03%. No significant error was detected during the refractive index determinations. A large plot of the refractive index versus the composition was made and it was used to determine the compositions during the vapor-liquid equilibrium runs.

TABLE X

REFRACTIVE INDEX-COMPOSITION DATA FOR BENZENE-PENTANOL AT 25°C.

Mole Fraction of Benzene	Refractive Index
0.000	1.4095
0.048	1.4128
0.149	1.4200
0.195	1.4232
0.292	1.4304
0.395	1.4383
0.492	1.4465
0.595	1.4550
0.692	1.4642
0.788	1.4739
0.896	1.4848
1.000	1.4979

In Table XI are tabulated the results of the vapor-liquid equilibrium determinations on the Fowler-Gillespie still. The temperatures over the range, 80° - 138°C., were read on two separate thermometers to the nearest 0.1°. The pressure was kept constant at 760 mm. \pm 2 mm. by a mercury barostat.

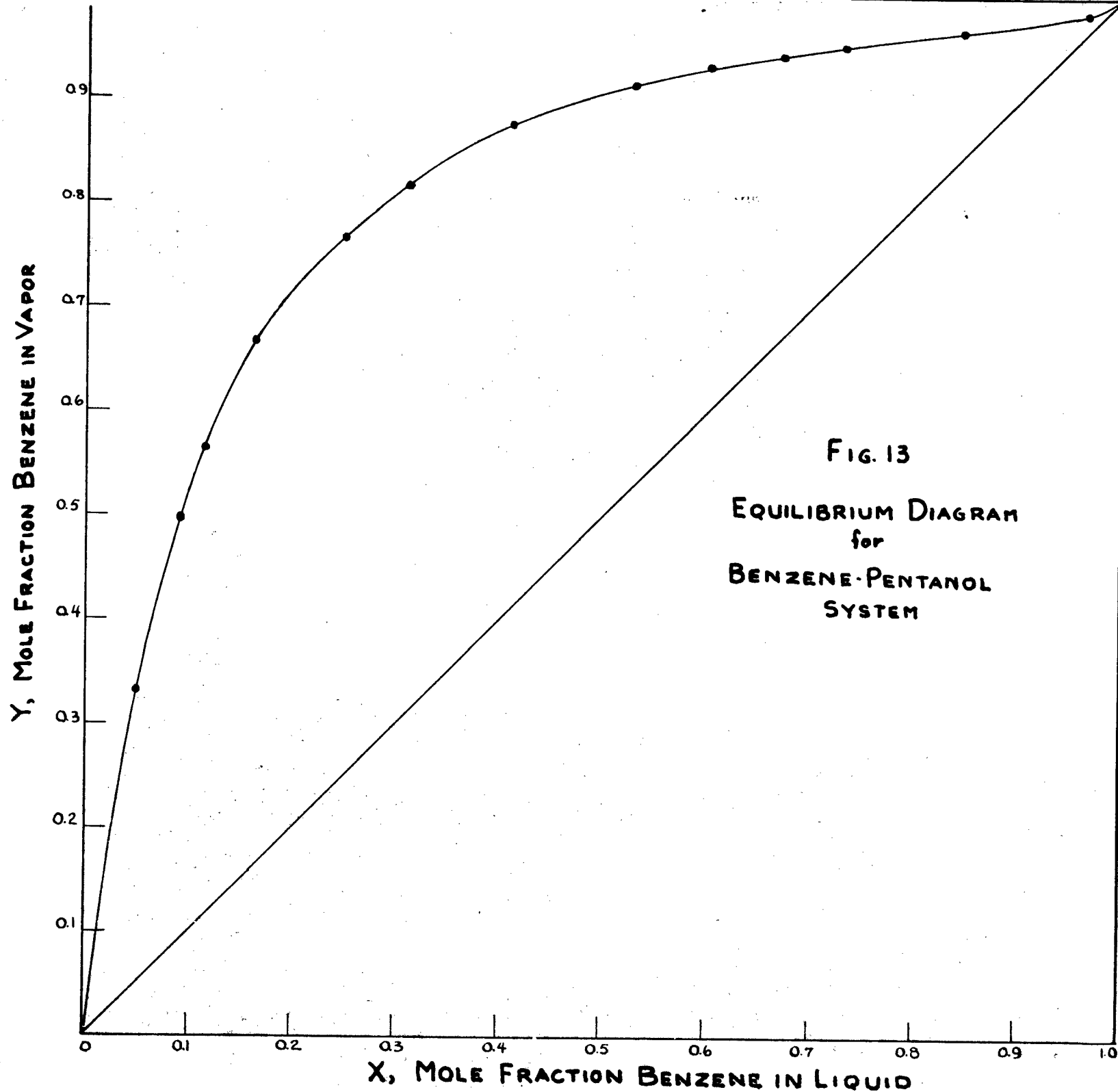


FIG. 13
EQUILIBRIUM DIAGRAM
for
BENZENE-PENTANOL
SYSTEM

TABLE XI

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR BENZENE-PENTANOL
AT ATMOSPHERIC PRESSURE

Run	Duration of Run (Hrs.)	Temp. °C.	Atm.Press. mm. Hg	Liquid Phase		Vapor Phase	
				R.I.at 25°C.	Mol.Fr. C ₆ H ₆	R.I.at 25°C.	Mol.Fr. C ₆ H ₆
1		80.1	760	1.4979	1.0	1.4979	1.0
2	3	80.3	"	1.4930	0.965	1.4960	0.983
3	3	82.0	"	1.4796	0.845	1.4931	0.966
4	3	84.5	"	1.4679	0.729	1.4912	0.951
5	3 1/2	85.7	"	1.4620	0.670	1.4900	0.943
6	3	87.7	"	1.4549	0.600	1.4889	0.934
7	4	90.3	"	1.4471	0.527	1.4866	0.913
8	3	94.3	"	1.4395	0.410	1.4827	0.875
9	3 1/2	100.1	"	1.4319	0.310	1.4768	0.817
10	3 1/2	104.5	"	1.4273	0.250	1.4715	0.765
11	4	111.6	"	1.4210	0.164	1.4612	0.660
12	4 1/2	116.8	"	1.4175	0.115	1.4525	0.565
13	3	120.4	"	1.4157	0.090	1.4467	0.497
14	3	127.1	"	1.4128	0.050	1.4336	0.333
15		137.9	"	1.4095	0	1.4095	0

A large-scale plot of the equilibrium values was made and also a plot of the temperature against the liquid and vapor compositions. Reduced graphs of these are shown in Fig. 13 and Fig. 14, respectively.

The large graphs indicate no possible formation of an azeotrope.

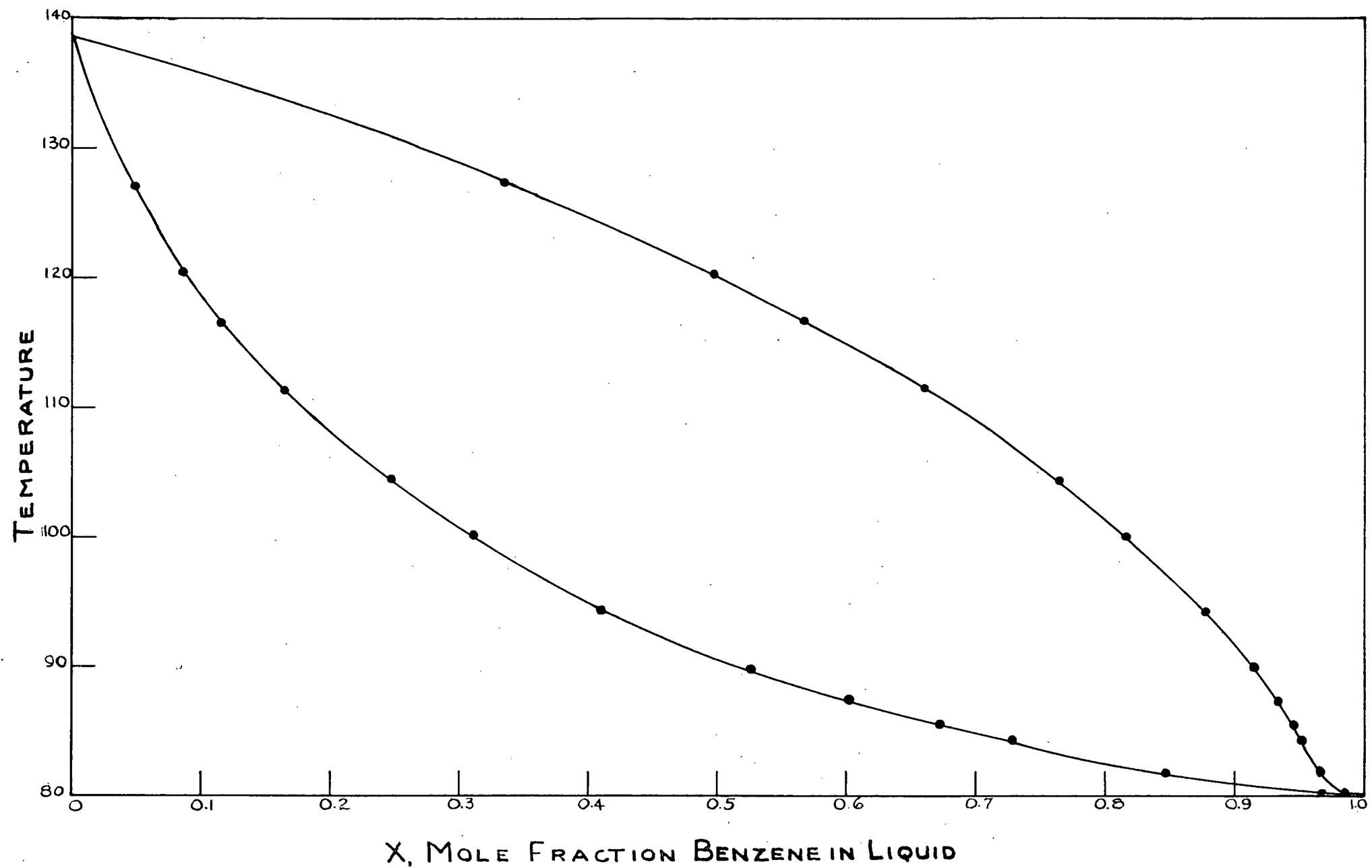


FIG.14 BOILING POINT DIAGRAM OF BENZENE-PENTANOL SYSTEM

The thermodynamic consistency of the system was checked in a similar way to that of benzene-propanol system and the results are shown in Table XIII and Fig. 16.

Values of A and B for $\log \gamma_1$ and $\log \gamma_2$ for $x_1 = 0$ and $x_2 = 0$ were chosen as 0.280 and 0.835, respectively, as the ones giving the best plot of the Van Laar equations.

The vapor pressure of pure pentanol was taken from the work of Butler, Ramchandani, and Thomson (21) and are presented in Table XII and Fig. 15.

TABLE XII
VAPOR PRESSURE DATA FOR PENTANOL

Temp. °A	Pressure mm. Hg
333.27	26.01
343.45	46.15
348.58	
353.74	77.74
363.99	125.8
374.32	198.0
383.35	286.9
393.71	424.1
404.04	611.9
410.91	760.0

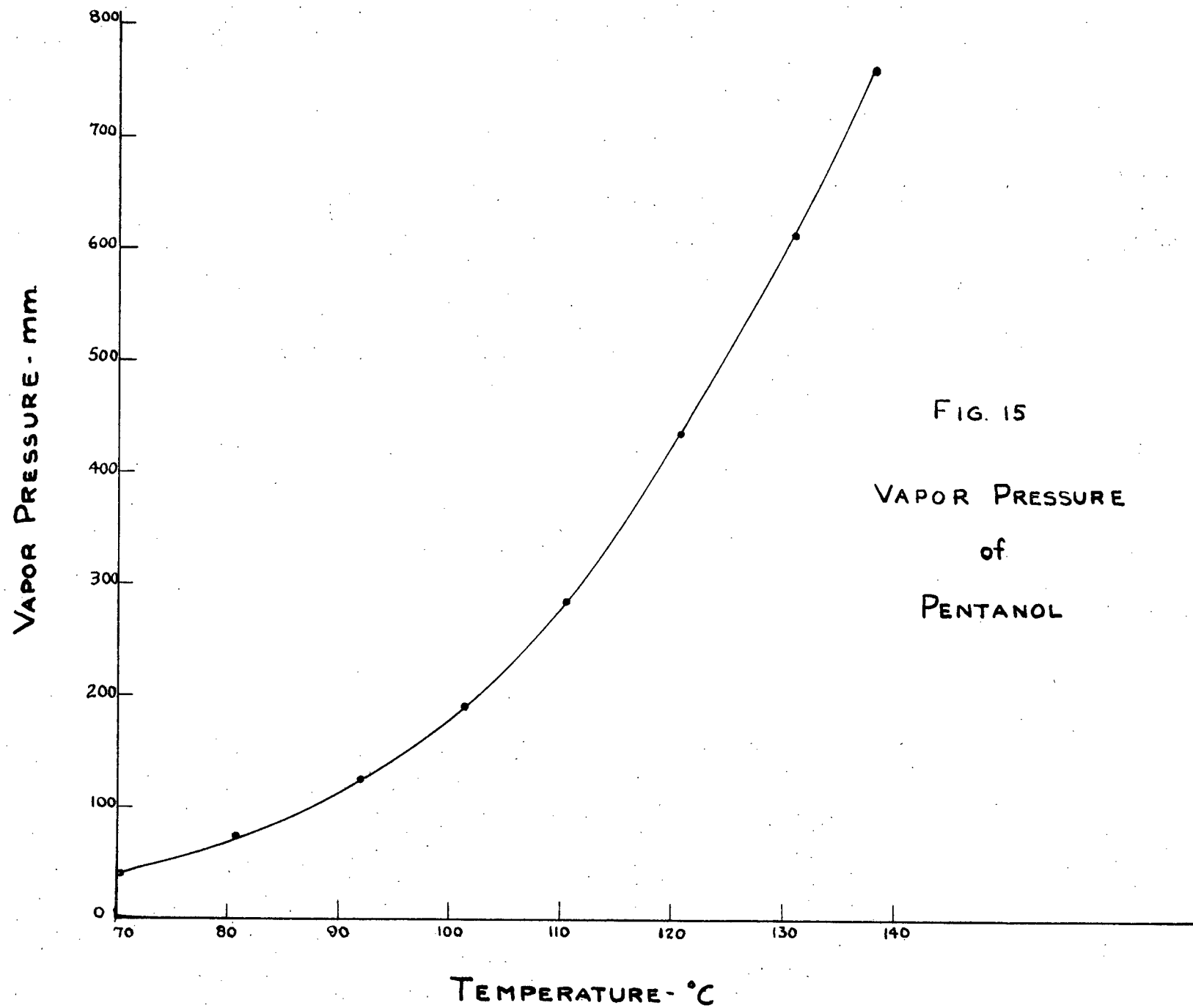


TABLE XIII

ACTIVITY COEFFICIENTS OF BENZENE AND PENTANOL FROM EXPERIMENTAL DATA

T°C.	P mm. Hg	P ₁ mm. Hg	P ₂ mm. Hg	x ₁	y ₁	Y ₁	Y ₂
80.1	760	760	-	1.0	1.0	1.000	
80.28	"	765	72	0.965	0.983	1.011	5.130
82.00	"	810	80	0.845	0.966	1.071	2.060
84.52	"	880	92	0.729	0.951	1.125	1.497
85.69	"	912	98	0.670	0.943	1.175	1.340
87.67	"	960	107	0.600	0.934	1.231	1.245
90.3	"	1030	121	0.527	0.913	1.300	1.158
94.25	"	1170	148	0.410	0.875	1.392	1.088
100.1	"	1360	190	0.310	0.817	1.472	1.060
104.5	"	1525	228	0.250	0.765	1.520	1.042
111.6	"	1820	303	0.164	0.660	1.680	1.021
116.8	"	2070	372	0.115	0.565	1.830	1.010
120.4	"	2270	420	0.090	0.497	1.845	1.002
127.1	"	2650	534	0.050	0.333	1.909	1.000
137.9	"	-	760				1.000

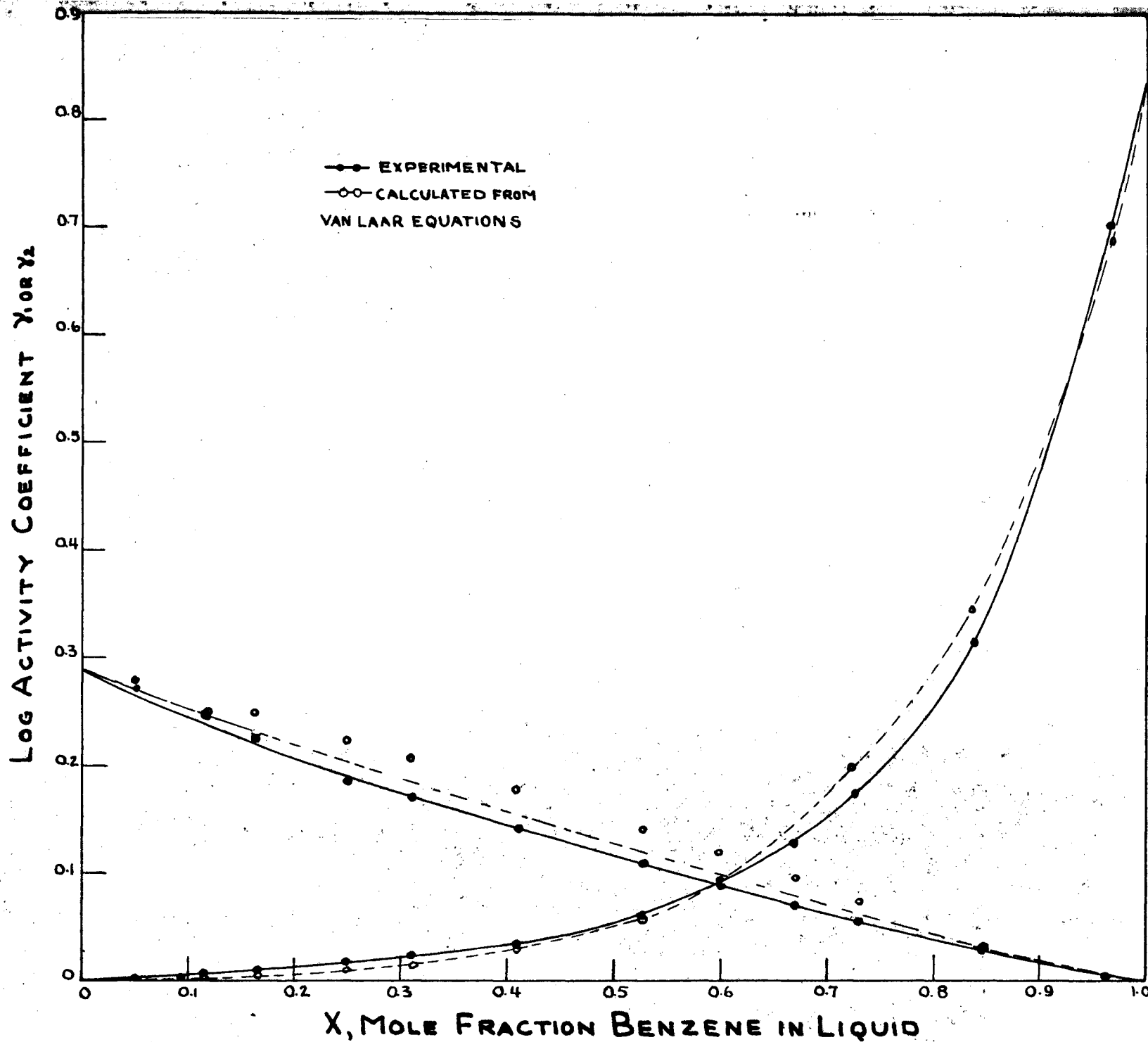


FIG.16 ACTIVITY COEFFICIENTS FOR BENZENE-PENTANOL SYSTEM

TABLE XIV

EXPERIMENTAL AND THEORETICAL ACTIVITY COEFFICIENTS
OF BENZENE AND PENTANOL

Mol. Fr. C_6H_6	γ_1 Expt.	γ_1 Calc.	γ_2 Expt.	γ_2 Calc.
0.000	0	1.90	1.000	1.000
0.050	1.909	1.870	1.000	1.000
0.090	1.845	1.865	1.002	1.002
0.115	1.830	1.835	1.010	1.004
0.164	1.680	1.78	1.021	1.015
0.250	1.520	1.685	1.042	1.025
0.310	1.472	1.630	1.060	1.035
0.410	1.392	1.520	1.088	1.070
0.527	1.30	1.405	1.158	1.147
0.600	1.231	1.332	1.245	1.230
0.670	1.175	1.256	1.340	1.370
0.729	1.125	1.190	1.497	1.605
0.845	1.071	1.082	2.060	2.230
0.965	1.011	1.006	5.130	4.900
1.000	1.000	1.000		6.700

DISCUSSION OF RESULTS

A. Benzene-Propanol

A plot of the log of the activity coefficients of benzene and propanol gives a reasonably good curve. According to Carlson and Colburn (6) when this so, the system shows some thermodynamic consistency. As a further check on consistency, at $x = 0.5$ the log γ_2 curve should fall below the log γ_1 curve since the log γ_2 curve has a higher end value.

A thermodynamic check on the consistency of the experimental values from a theoretical consideration of the Gibbs-Duhem equation showed the theoretical activity coefficients to deviate from the experimental ones. An estimation of the deviation of the values showed an error that ranged from 1% to 17% with the average deviation to be about 10%. Gilliland (27) claims an average error of 10% between the experimental and theoretical values of the activity coefficients is fair correlation. A plot of the Margules integration showed no closer correlation so these values have been omitted.

The value for the azeotrope of 0.795 mole fraction of benzene in the liquid at 76.2°C. and 740 mm. of pressure for the benzene-propanol system is in keeping with the value reported by Lecat (4) of 0.791 at 77.1°C. and 760 mm. of pressure.

A plot of the vapor-liquid equilibrium compositions gave a smooth curve, as well as the plot of the temperature against the compositions.

B. Benzene-Pentanol

The benzene-pentanol system showed no tendency toward an azeotrope. The plot of the vapor-liquid equilibrium values gave a

smooth curve as well as the temperature composition curve.

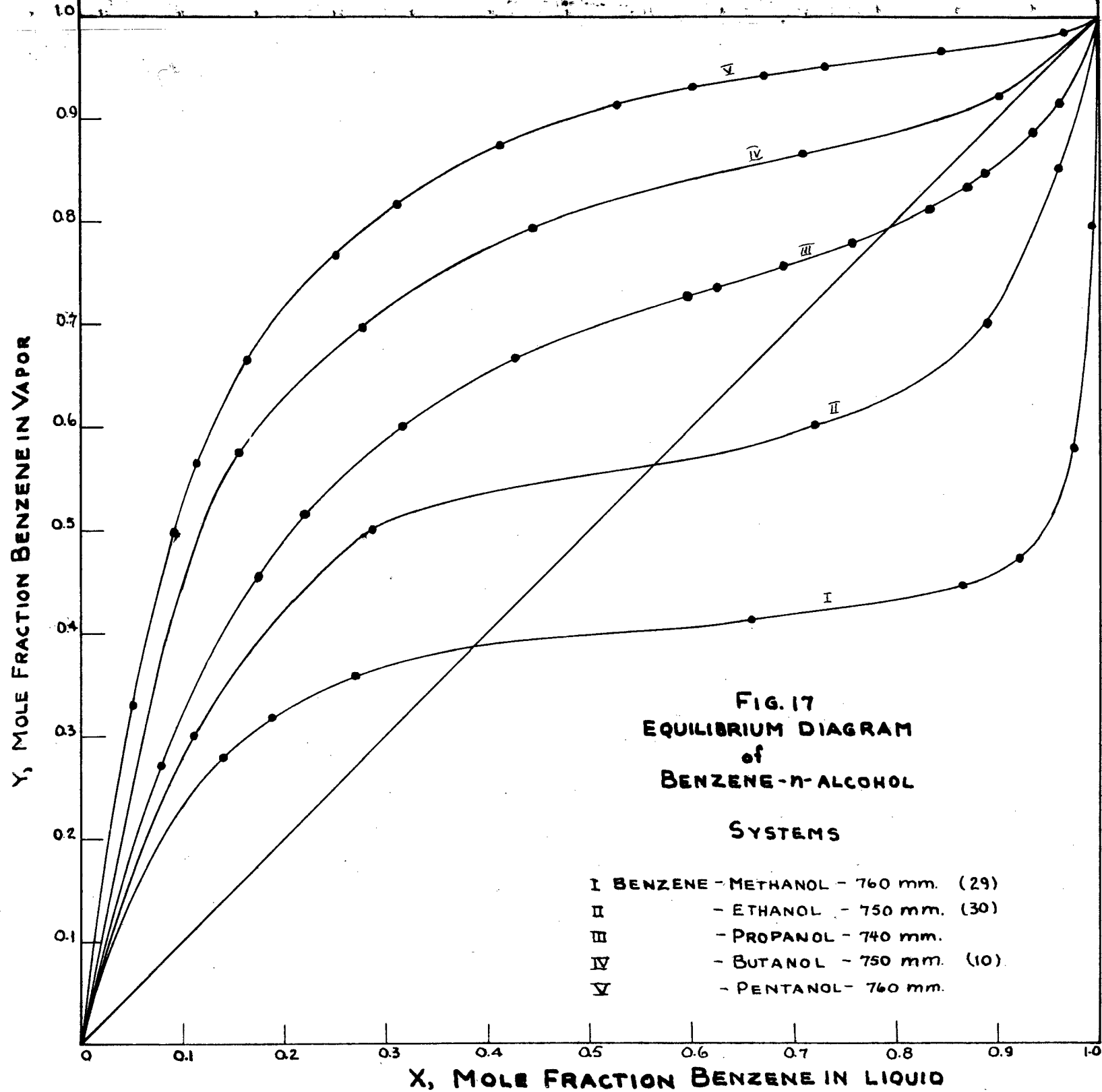
A plot of the log of the activity coefficients for benzene and pentanol gave smooth graphs showing thermodynamic consistency. The $\log \gamma_2$ curve fell below the $\log \gamma_1$ curve at $x = 0.5$ as it should do.

Again, the correlation of the theoretical and experimental values showed an average deviation of 8%, the values ranging from less than 1% to 15%. Margules values showed no closer correlation and were omitted.

Van Laar (9) based his integration of the Gibbs-Duhem equation on the thermodynamic changes occurring on the mixing of liquids. In deriving his equations he made the following assumptions:

1. No change of entropy on mixing.
2. No volume change on mixing.
3. The van der Waals equations apply to each of the components and to the mixture, both as liquids and vapors.
4. The van der Waals constants of the mixture can be calculated from the constants of pure components.

On the basis of his derivations the theoretical validity of the Van Laar equations is questionable and the quantities A and B which were assumed to be constant in these equations will vary somewhat over the temperature range involved. Hence the deviation of the experimental and calculated theoretical coefficient is not too unreasonable.



DISCUSSION ON THE BENZENE-n-ALCOHOL SYSTEMS

On. Fig. 17 are plotted the vapor-liquid equilibrium curves for the benzene-methanol, benzene-ethanol, benzene-propanol, benzene-butanol and benzene-pentanol systems. The data for the benzene-methanol, ethanol, and butanol systems were taken from the literature (29, 30, 10).

An examination of these curves shows that the first three benzene-alcohol systems cut the $y = x$ line and form azeotropes, while the last two systems manifest the same general shape of curve somewhat displaced from each other.

All the systems deviate in a positive manner from Raoult's Law. Skolnik (31) says that four factors contribute to such non-ideality: internal pressure, polarity, length of the analogous groups, and association of a component, while Lee (5) says that heat of solution and the tendency to separate into two layers are contributing factors to non-ideality.

All the five alcohols are miscible with benzene with miscibility increasing as the molecular weight of the alcohol is increased, yet water which resembles methanol in many ways is only slightly miscible with benzene. Methanol may be salted out from benzene with sodium iodide which shows that the degree of miscibility of methanol with benzene verges on that of a partially immiscible system. A plot of the total pressure of the benzene-methanol vapor pressure isotherms shows a total pressure curve that resembles that of a partially immiscible system. It may be concluded, then, that the contributing factor to non-ideality for the benzene-methanol system is the tendency to separate into two layers. This factor is less pronounced as the molecular weight of the alcohol

is increased. Ethanol cannot be salted out from benzene with sodium iodide. Yet the benzene-ethanol system gives an equilibrium curve that could be attributed to a system showing some immiscibility.

Of course the wide deviation from ideality for the lower benzene alcohol systems may be argued from the point of view of the great difference in polarity of the two components. The polar molecules have an abnormally great attraction for each other, producing greater surface tension, cohesion, etc., and tend to squeeze out non-polar molecules from their midst. As a result of the tendency of a liquid of high internal pressure to squeeze out a liquid of low internal pressure, it is expected that the partial pressure would deviate in a positive manner from Raoult's Law. This concept of association does not admit any definite polymers like double molecules. The polar affinities act within the liquid to form groups of molecules which become impregnable to a non-polar molecule-like benzene.

As the length of the carbon chain of the alcohols is increased the polar effect of the OH group is decreased and for systems like benzene-butanol and benzene-pentanol the alcohols would tend to act more like straight chain hydrocarbons which do not form azeotropes with benzene. At a low concentration of alcohol, molecules are sparsely distributed, to such an extent that each is without influence on the other; hence the alcohols with benzene would have no reason to form an azeotrope.

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