VAPOR-LIQUID EQUILIBRIA,
BINARY MIXTURES OF METHYL ALCOHOL, ISOPROPYL ALCOHOL
AND
n-BUTYL ALCOHOL WITH BENZENE.

by

William A. Flynn

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Master of Science
with a major in Chemical Engineering
in the
Graduate Division
at the
Newark College of Engineering

April, 1953

Table of Contents

ACKNOWLEDGEMENT

The author wishes to express his
appreciation to Doctor Carl W. Carlson
for his encouragement and guidance during
the experimental and write-up phases of
this work.

LIST OF ILLUSTRATIONS

INTRODUCTION

The primary objective of the work described in this paper
was to determine vapor-liquid equilibria for three binary systems,
viz., methyl alcohol, isopropyl alcohol and n-butyl alcohol with
benzene. It was also decided to calculate the activity coefficients
in order to indicate the deviations from Raoult's Law. Based on a
literature search, the system benzene-methyl alcohol was found to
have been previously investigated and was therefore used in this
study as a means of developing a technique and to standardize the
apparatus. The only published data found for the system benzene-
isopropyl alcohol was a minimum boiling point (10) and a reference to
the vapor pressure at 25°C (22). There were no references to the
system benzene-n-butyl alcohol except for data on the total and
partial pressures at 25°C (23).

The basic reason for undertaking this study was twofold.
First, in the application of organic pigments, in the protective
coatings and printing ink fields, there are a number of operations
which require the use of suitable solvent combinations for
evaluations, synthesis and other purposes. Among these are the
binary mixts. involving various lower alcohols and hydrocarbons.
From the research and development, as well as the operating points
of view, a complete knowledge of the behavior of these systems is
of great importance. Secondly, these combinations were chosen in
an attempt to provide an empirical basis for a theoretical
discussion of such topics as hydrogen bonding, polarity and
azeotrope formations.

An examination of vapor-liquid equilibria data (1)
reveals that the majority of the binary mixtures do not even
approximate Raoult's Law and therefore the vapor-liquid equilibria
relationships must be determined by experimental means. There
are various methods described in the literature for experimental
determination of these relationships, such as the method of
Carveth (2), Petit (3), Rosanoff, Bacon and White (4), Carey and
Lewis (5), Scatchard (6), Othmer (7) and others (8), (9).

In order to determine vapor-liquid equilibria empirically,
it is necessary to establish and maintain an equilibrium between
the boiling liquid and the refluxing vapor. Various types of
apparatus have been used as equilibrium stills, the operation of
which is based on the reflux equilibrium principle.

SUMMARY OF RESULTS

The vapor-liquid equilibrium curves expressing boiling point as a function of composition, were determined at atmospheric pressure for the three systems. The apparatus and method used were found to yield excellent results, good duplicability and curves in agreement with the literature in the case of the known system, Benzene-Methyl Alcohol.

The still was checked for accuracy and performance by running a system cited in the literature, viz., Benzene-Methyl Alcohol (8). Experimental data are summarized in Tables 1, 2 and 3. Vapor-liquid composition curves were plotted and the following information was obtained:

For the system Benzene-Methyl Alcohol, the reported minimum boiling point of 58.3°C at 64% by weight benzene (8) (10) was verified. The system Benzene-Isopropyl Alcohol was also observed to have a minimum boiling point, occurring at 71.9°C with 66.7% by weight benzene. This is in close agreement with a minimum boiling point reported in the literature (10). Benzene-n-butyl Alcohol yielded a normal smooth curve without maximum or minimum which is characteristic of the ideal mixtures following Raoult's Law over the greater portion of their concentrations.

The equilibrium diagrams or x-y curves were characteristic of their respective type binary mixture. The sigmoid curve, indicative of the minimum boiling-point mixture, was obtained for the systems Benzene-Methyl Alcohol and Benzene-Isopropyl Alcohol.

In both plots for the systems with minimum boiling points, the curves crossed the diagonal with slopes flatter than the slope of the diagonal.

At points of intersection, the composition at minimum boiling point was obtained. The equilibrium diagram for the system Benzene-b-Butyl Alcohol was a gradually rising symmetrical curve with no intersection of the diagonal.

The equilibrium data were used to calculate the activity coefficients which indicated positive deviations from Raoult's Law for the systems Benzene-Methyl Alcohol, Benzene-Isopropyl Alcohol and Benzene-n-Butyl Alcohol.

Deviations from the ideal behavior are discussed and explained under a separate heading, "Theoretical Considerations".

THEORETICAL BACKGROUND

When a binary mixture is formed by dissolving two liquids
in each other, the composition of the vapor differs from that
of the liquid, if the vapor pressures of the two components are
different; each component lowers the vapor pressure of the other.
The extent to which the vapor pressure is lowered for practically
ideal solutions at all concentrations and for many non-ideal
solutions at all concentrations can be determined by reference to
Raoult's Law which states that at a given temperature, the partial p
pressure of any constituent in a mutually soluble liquid mixture
is equal to its vapor pressure multiplied by its mole fraction
in solution. This is stated mathematically by the expression

$$p_A = \frac{N_A}{N_A + N_B} = x_A \, P_A$$

and
$$p_B = \frac{N_B}{N_A + N_B} = (1 - x_A) \, P_B = x_B \, P_B$$

where p_A and p_B = partial vapor pressure of components
A and B, respectively.

P_A and P_B = vapor pressure of components A and B
respectively, in the pure state at the temperature of the liquid.

N_A and N_B = mols of components A and B, respectively

x_A = mol fraction of component A in the liquid. x_B and $(1 - x_A)$
= mol fraction of component B in the liquid.

This expression applies only for binary liquids where
there is no chemical reaction nor molecular association between
constituents. In addition, the molecules of each component
must be approximately the same size. In an ideal solution, eg.,
a mixture of methyl and ethyl alcohols, the molecules of one
component are not changed by the surrounding molecules of the
other component. In general, however, in most solutions one
constituent exerts some type of interaction on the other so that
Raoult's Law does not hold. There may be compound formation
as in the case of chloroform and acetone. Another type involves
the formation of non-volatile ions which results in one component
being less volatile in the presence of the other. A third
phenomenon occurs in solutions where the second liquid breaks
down the larger units of the first liquid and in so doing, renders
the first liquid more volatile.

A low vapor pressure is indicative of a high boiling
temperature and generally the boiling-point composition curves
are directly opposite to the vapor pressure -- composition curves.
Homogeneous binary mixtures fall under three types:

1. Mixtures with vapor pressures intermediate between
those of the pure constituents over the entire range of composition.

2. Mixtures whose vapor pressures over a certain range
of composition are greater than that of either of the pure
components.

3. Mixtures with vapor pressures over a certain range of
composition lower than that of either of the pure components.

In an ideal solution, the vapor and liquid composition curves run smoothly between the two boiling points, but in a non-ideal solution, particularly where the boiling points are quite close, the variation in volatility resulting from the chemical influence of the other component may cause a minimum or maximum in the boiling point curve (corresponding to a maximum or minimum in the vapor pressure curve).

Henry's law states that the partial pressure of the component present in the smallest concentration, the solute, is proportional to its mol fraction in the solution, i.e.,

$$p_A = K x_A$$

where p_A = partial vapor pressure of the solute

x_A = mol fraction of the solute

K = constant which depends on temperature of the solution.

Raoult's and Henry's Laws then, are actually special cases of each other differing only by the proportionality constant which determines the slope of the line. The constant is   in Raoult's Law, whereas it must be experimentally determined in the other. For ideal solutions, the two laws are identical.

As has been stated earlier under Discussion of Results, the relationship between the vapor and liquid curve at equilibrium is derived from the principle which states that the vapor phase is relatively richer in the component which results in a lowering of the boiling point when added to the mixture or alternatively, the liquid phase is richer in the higher boiling point constituent.

This principle is based on Konowaloff's rule (1881) which was arrived at empirically, although anticipated by the theoretical considerations of J.W. Gibbs (1876). After Gibbs, P. Duhem (1886) and M. Margules (1895) both independently of each other and Gibbs, derived what is generally known as the Duhem-Margules equation which can be written in the form

$$\frac{x_A}{p_A} \cdot \frac{dp_A}{dx_A} = \frac{x_B}{p_B} \cdot \frac{dp_B}{dx_B}$$

where x_A and x_B are again the respective mole fractions and p_A and p_B the respective partial pressures. Since $dx_A = -dx_B$, the above expression becomes

$$\frac{x_A}{p_A} \cdot \frac{dp_A}{dx_A} + \frac{x_B}{p_B} \cdot \frac{dp_B}{dx_A} = 0$$

$$\therefore \frac{dP}{dx_A} = \frac{dp_A}{dx_A} + \frac{dp_B}{dx_A} = \frac{dp_B}{dx_A}\left(1 - \frac{x_B \, p_A}{x_A \, p_B}\right)$$

where P is the total vapor pressure. The value of dp_B/dx_A, which is equal to $-dp_B/dx_B$, must be negative; then if dP/dx_A is to be positive

$$x_B \, p_A > x_A \, p_B \quad \text{or} \quad \frac{p_A}{p_B} > \frac{x_A}{x_B}$$

the meaning of which, is that the vapor is richer in A than is the liquid from which it evolves.

In the same manner, if dP/dx_A is negative, i.e., dP/dx_B is positive, the vapor will be relatively richer in B. The vapor, therefore, is relatively richer in the constituent which by its presence in the liquid results in an increase in total vapor pressure. If the vapor pressure curve has a maximum or minimum, dP/dx_A in the above equation, must be zero; therefore, either dp_B/dx_A must be zero, or $x_A p_B = x_B p_A$ i.e., $x_A/x_B = p_A/p_B$. The first condition is not probable, since it would mean that the partial vapor pressure would remain constant regardless of a change in concentration and therefore for a maximum or minimum total vapor pressure, $p_A/p_B = x_A/x_B$

The molecular ratio of the two vapor constituents is given by p_A/p_B , if the gas law is obeyed; and so the conclusion is that when the vapor pressure is a maximum or minimum, the vapor composition is equal to that of the liquid with which it is in equilibrium.

EXPERIMENTAL METHOD AND APPARATUS

Principle

The method employed in obtaining vapor-liquid equilibrium data is similar to that of Othmer (7). Vapors in equilibrium with a boiling liquid mixture are condensed and returned to the boiler. The equilibrium still is operated so that when the composition and quantity of vapor leaving the boiling liquid are identical with the composition and quantity of distillate returning to the boiler, equilibrium is established and the boiling point remains constant at a given pressure. Temperature and pressure can be directly measured and samples of liquid and corresponding vapor are removed and their compositions determined by physical or chemical analysis.

Apparatus

A diagram of the apparatus is shown in Figure 1. It consists of a modified Cottrell boiling point unit and is essentially the same as that used by J.W. Rogers, J.W. Knight and A.R. Choppin (8). The column is fitted with a three-way T-type stopcock, which is used to return the condensate to the boiler or to withdraw liquid or vapor samples. A precision grade thermometer graduated in 0.1 $^{\circ}$ C and calibrated against a Bureau of Standards thermometer was used to determine the boiling points at equilibrium.

To provide in greater measure for good equilibrium between boiling liquid and refluxing vapor, some modification of the apparatus as described in the cited article was employed.

This consisted in the installation of insulating material in the form of a cylindrical wrapping of asbestos tape. Aluminum foil was then placed over the tape and was also used as a thermometer shield to eliminate errors in temperature readings. A nichrome wire heating unit was also added.

Procedure

In operating the still, a charge of 100 cc of binary liquid was introduced into the boiler, with the stopcock in position for distillate return. Samples of binary liquid ranging from 0% to 100% of one component, in 5% increments were used. Heat was then applied via the nichrome wire heating unit. (A microburner, properly shielded was also found to give satisfactory results). The heat was applied at a rate which permitted 1) the Cottrell pumps to eject a rapid flow of boiling liquid over the thermometer bulb and 2) the condensate to return from the condenser at a constant rate. The boiling was continued until the temperature became constant, the pressure being checked and controlled with a manometer and pump. The heating unit was then turned off and samples were withdrawn by moving the three-way stopcock to the proper position. The sampling tube was flushed out each time by a portion of the liquid remaining in the vapor return tube and the small amount of this wash liquid was then quickly drained by touching the tip with a piece of filter paper. The vapor sample was then collected in a small vial which was immediately sealed. A similar procedure was used for liquid sampling.

Analysis

The refractive index of the samples were determined with an Abbe Refractometer and the composition was then obtained by referring to reference curves, Figures 2, 3 and 4 which were previously prepared by measuring the refractive index of liquid samples of various known compositions. Series of mixtures of the binary liquids were made up, individual samples ranging from 5 cc to 95 cc in 5 cc increments. These samples were prepared from reagents maintained at 20°C. From the known densities of the two constituents, the weight per cent of each was calculated from the volume percent. The refractive index of these samples was measured at 20°C, the temperature being controlled to 0.1°C by circulating water from a 20 liter jar equipped with copper coils and a constant input head.

Purity of Material

In order to insure liquid purity, all the solvents used were selected from C.P. stock. The benzene was thiophene free and was redistilled before use, B.P. = 80.1°C, R.I. = 1.5014. Methyl Alcohol was acetone free and was redistilled over lime, B.P. = 64.7°C, R.I. = 1.3312. Isopropyl Alcohol was redistilled over lime, B.P. = 82.3°C, R.I. = 1.3776. n-Butyl Alcohol was redistilled at 117.7°C, R.I. = 1.3993.

PRECISION OF MEASUREMENTS

Precision was evaluated using the observed values for the refractive indices of the pure solvents and the binary liquids. For each sample, four separate refractive indices were taken and the arithmetic mean or average of each was taken as the most probable value of the correct result. The precision of an individual result was measured by its deviation from the average result, and the average precision was measured by the average deviation of the single results from the mean.

The following procedure as recommended by W.C. Pierce and E.L. Haenisch (10) was employed to determine the average deviation of the individual results in the series of refractive index measurements;

1. The arithmetic mean was computed.

2. The numerical deviation of each result from the mean was computed without regar d to algebraic sign.

3. The deviations of the individual results were averaged.

4. Each deviation from the mean was expressed in parts per 1000.

The deviation of a doubtful result was compared with the deviations of other results from the average. If the deviation of a single result was greater than four times the average deviation of the remaining results, the single result was discarded.

A summary of evaluation of precision for observations made on the pure solvents is shown in Table 4.

ACTIVITY COEFFICIENTS

The deviation from ideality is expressed by the activity coefficient γ, which is defined as the activity divided by the mole fraction or

$$\gamma_1 = \frac{a_1}{x_1} \text{ and } \gamma_2 = \frac{a_2}{x_2}$$

where the activity, a is the relative fugacity; or the ratio between the fugacity of a substance in solution and its fugacity in the pure state, the fugacity being an ideal vapor pressure, identical with the partial pressure p, where the conditions are specified by the perfect gas laws. If the components behave according to the perfect gas laws, then the fugacity is equivalent to the partial pressure and the expression for the activity coefficients then becomes

$$\gamma_1 = \frac{p}{P_1 x_1} = \frac{P y_1}{P_1 x_1} \text{ and } \gamma_2 = \frac{P y_2}{P_2 x_2}$$

where P_1 is the vapor pressure of the pure component and P is the total pressure.

In determining correlation with the Van Laar equation, the experimental data on the vapor-liquid equilibria of the systems studied in this paper were calculated in terms of deviation factors from Raoult's Law by substituting in the above equations. Vapor pressures were obtained by referring to curves plotted from data contained in the literature (15), (16), (17), (18), (19).

Figures 17, 18, 19 and 20. The constants A and B were obtained from the plot of $x_1 x_2 / x_1 \log \gamma_1 + x_2 \log \gamma_2$ vs x_1, the $x_1 = 0$ intercept being the constant $1/A$ and the $x_1 = 1.0$ intercept being $1/B$ according to the procedure used by P.H. Miller (23). Using the method described by Carlson and Colburn (12), a new activity coefficient was then calculated by using a slightly rearranged form of the Van Laar equation.

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B}\frac{x_1}{x_2}\right)^2} \quad \text{and} \quad \log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A}\frac{x_2}{x_1}\right)^2}$$

The corresponding new value of was then calculated by substituting in the equation $y = \frac{\gamma_1 x P_1}{P}$ Percent Deviation was calculated according to the formula given by Robinson and Gilliland (13), viz., % Deviation $= \frac{y_{calc} - y}{y - x} \times 100$

As pointed out by Carlson and Colburn (12) the constants A and B as represented in the above symmetrical form of the Van Laar equation have the property of being equal to the terminal values of $\log \gamma$ of the two curves. Therefore at $x_1 = 0$, $\log \gamma_1 = A$, and at $x_1 = 1$ when $x_2 = 0$, $\log \gamma_2 = B$.

It should be emphasized that at $x_1 = 0$, $\log \gamma_2 = 0$ or $\gamma_2 = 1$, and at $x_1 = 1$, $\log \gamma_1 = 0$ or $\gamma_1 = 1$, which satisfies the limiting condition that Raoult's Law holds for a component whose concentration approaches 100 mol %.

Benzene-Ethyl Alcohol

Referring to Figure 14, the intercepts at $x_1 = 0$ and $x_1 = 1$ are both equal to 1.24, the reciprocal being 0.81 and the slope of the line is zero. The semi-log plot, see Figure 11, is typical of a non-ideal system. At $x_1 = 0$, $\log \gamma_1 = A$ or $\log 6.5 = A$, $A = 0.81$. Similarly, at $x_1 = 1$, $\log \gamma_2 = B$ or $\log 6.5 = B$, $B = 0.81$. This is an example of the special case where $A = B$. At $x_1 = 0.5$, the curves represented by the Van Laar equations have an unusual property which is manifest at the midpoints on the curves,

$$\frac{\log \gamma_1}{A} = \frac{\log \gamma_2}{B} = \frac{AB}{(A+B)^2}$$

If $A = B$, the term $AB/(A+B)^2 = 1/4$. As A and B differ, the ratio decreases slightly. According to the preceding "midpoint" equation then, the halfway value on one curve is approximately one fourth the end value on the other curve. Referring to Figure 11 again, it is evident that at $x_1 = 0.5$, $\log \gamma = \frac{A}{4}$, $\gamma = 1.594$.

The deviations from ideality in the liquid state are positive in this system, i.e., the activity coefficients are greater than unity so that the logarithms of the activity coefficients are positive numbers. Referring to Table 6, the maximum % deviation is 20.0 and the average % deviation —6.4 According to the classification of Mason (14) the agreement of the Van Laar equations for a system is poor, if the average deviation is greater than 11%.

Benzene-Isopropyl Alcohol

The plot of $x_1 x_2 / x_1 \log \gamma_1 + x_2 \log \gamma_2$ Figure 15 reveals A and B to be equal to 0.593 and 0.842, respectively. Referring to the semi-log plot Figure 12 at $x_1 = 0$, $\log \gamma_1 = A$ or $\log 3.92 = A$, $A = 0.593$ and at $x_1 = 1$, $x_2 = 0$ and $\log \gamma_2 = B$ or $\log 6.95 = 0.842$, $B = 0.842$. In this case, the values of $\log \gamma_1$ and $\log \gamma_2$ at the midpoint are approximately one quarter of B and A respectively i.e., at $x_1 = 0.5$, $\log \gamma_1 = B/4$ or $\log 1.9 = 0.279$, $B = 1.1$ and at $x_1 = 0.5$, $\log \gamma_2 = A/4$ or $\log 1.35 = 0.130$, $A = 0.52$. The curve for Isopropyl Alcohol which has the higher end value is the lower at $x_1 = 0.5$, which is essentially in agreement with the "midpoint" equation. In this system, the activity coefficients being greater than unity, the deviations from Raoult's Law are also positive. The maximum % deviation is 50 and the average % deviation 25, Table 7. According to Mason (14) then, the agreement of the Van Laar equations for this system is poor.

Benzene-n-Butyl Alcohol

The straight line plot of $\alpha_1 \; x_2/x_1 \; \log \gamma_1 + x_2 \log \gamma_2$ resulted in intercepts, the reciprocals of which were equal to $A = 0.478$ and $B = 0.424$, Figure 16.

A plot of the data on semi-log paper according to the method previously described, yielded activity coefficient curves which intersected at $\alpha_1 = 0.635$ Figure 13. Calculation of the β deviation resulted in a maximum of $- 91.7$ and an average of $- 6.3$. According to Lason (14), this represents good correlation with the Van Laar equation, which is to be expected with a system which has a normal boiling point curve. The curves obtained in Figure 13 are apparently the result of plotting the activity coefficients of a system which although it has a normal boiling point curve, is not completely ideal over the entire concentration range and yields activity coefficient curves indicating positive deviations.

Further discussion of the results appears under the next heading, Theoretical Considerations.

Nomenclature

A and B = arbitrary constants in Van Laar equation and equal
to $\log \gamma_1$ at $x_1 = 0$ and $\log \gamma_2$ at $x_2 = 0$ respectively.

x = mol fraction in liquid

y = mol fraction in vapor

γ = activity coefficient

P = total pressure of system, mm Hg

P_1, P_2 = vapor pressures of pure components, mm Hg.

Subscripts

1 = Component of binary mixture with lower boiling point

2 = Component of binary mixture with higher boiling point

DISCUSSION OF RESULTS

Graphical representation of the equilibrium relationships between the liquid and vapor phases, based on experimental data, can be constructed by various methods, but the most useful of these are the boiling point and the equilibrium diagrams.

1. The first part of this discussion deals with the vapor-liquid curves. The data are plotted in the conventional manner with the compositions as abscissae and the boiling points as ordinates. Of the two resulting curves, one gives the composition of the liquid, the other that of the vapor with which it is in equilibrium at the boiling point. The relation between the two curves depends on a principle which follows from Konovaloff's rule, (previously discussed under Theoretical Background) viz., the vapor phase is relatively richer in the component which lowers the boiling point when added to the mixture; the liquid phase being richer in the component which raises the boiling point.

a) Benzene-Methyl Alcohol System, Figure 5.

These curves are typical of a system having a minimum boiling point. At the intersection of the vapor and liquid curves, the compositions of both phases are identical at 60.4% benzene by weight, with a minimum boiling point of 58.3 ° C.

A liquid of this composition then, will boil at a constant
temperature and distil over without change in composition, this
type liquid being defined as an azeotrope. If a liquid composed
of less than 60.4% benzene were fractionally distilled, the
distillate would eventually equal this azeotropic composition,
while the final residue would approach 100% methyl alcohol.
This, of course, is because the more volatile constituent benzene,
would be distilled off with resultant lowering of the boiling
point. A liquid with composition higher than 60.4% benzene would
yield on fractionation, distillates approaching the azeotropic
composition whereas the liquid residue would tend toward 100%
benzene. The vapor phase at any given boiling point is relatively
richer in the less volatile component, viz., methyl alcohol.
Therefore the liquid residue on fractionation becomes richer in
the more volatile benzene, which results in a progressive rise
in boiling point.

b) Benzene - Isopropyl Alcohol System, Figure 6.
This system also proved to be of the minimum boiling point type, an
azeotropic mixture occurring at 66.7% benzene by weight with a
boiling point of 71.9 ° C. Similar conclusions may be drawn.
Binary mixtures containing less than 66.7% benzene, will eventually
on fractionation, form an azeotrope. The final liquid residue will
approach 100% isopropyl alcohol with a progressive rise in boiling
point.

Fractional distillation of mixtures above 66.7% benzene will yield
distillates which approach the azeotrope in composition, while the
liquid residue will approach 100% benzene with a progressive drop
in boiling point.

The two systems benzene-methyl alcohol and benzene-isopropyl
alcohol, having boiling-point curves with minima belong to the
more common group of which approximately four hundred are listed
in the International Critical Tables. These systems, as is to be
expected, showed definite deviations from the ideal situation as
expressed by Raoult's Law. The vapor pressure curves all have
maxima.

c) Benzene-n-Butyl Alcohol System, Figure 7.
These curves indicate that the system is a member of the group
whose boiling point increases regularly with change of liquid
composition from the more volatile constituent, benzene, to the less
volatile, n-butyl alcohol. The vapor thus always contains more
of the lower boiling point component, benzene. For example, a
liquid composed of 67.5% benzene by weight will boil at 83.0 ° C
and the vapor will be 89% benzene. In a distillation where the
vapor phase is removed, it is evident that since the vapor phase
is richer in the more volatile benzene, the liquid remaining becomes
relatively richer in n-butyl alcohol and the boiling point
gradually rises.

2) Equilibrium or $x-y$ diagrams are a more direct method of representing the equilibrium relationships between liquid liquid and vapor composition. In this type of diagram, the concentration of the more volatile component in the liquid phase is plotted as ordinates against the equilibrium concentration in the vapor phase as abscissae. A 45° reference line is also included; a point on this line representing a state where **vapor** and liquid compositions are identical. Equilibrium diagrams prove particularly useful in solving distillation **problems** at constant pressure, because the vapor-liquid equilibrium relationships are only slightly affected by moderate changes in pressure. In plotting a boiling-point curve however, a slight pressure change results in an appreciable variation in the boiling-point composition relationships.

a) Benzene-Methyl Alcohol System, Figure 8. This equilibrium diagram indicates that when the liquid concentration of benzene is low, i.e., less then 38 mol %, a vapor is evolved which is richer in benzene. At the intersection with the diagonal, the compositions of liquid and vapor phase are identical, viz., 38 mol % benzene, which corresponds to the minimum boiling point of a 60.4% benzene by weight liquid, Fig., 5. Above this concentration of benzene in the liquid, the liquid begins to evolve vapor which is less rich in benzene. The volatility of the components is reversed. It is to be noted that the curve crosses the diagonal with a slope flatter than the slope of the diagonal. This is characteristic of curves which possess minimum boiling points at the intersection.

b) Benzene-Isopropyl Alcohol System, Figure 9.
Examination of the equilibrium diagram for this system reveals
another minimum boiling point type. Here, it is again evident
that when the liquid contains relatively low amounts of benzene,
i.e., less than 53.5 mol %, the vapor is richer in benzene. When
the benzene concentration in the liquid rises to 53.5 mol %,
the composition of the vapor is the same. Above this level a
reversal occurs, the liquid evolving vapor which is less rich in
benzene. The curve crosses the diagonal with a slope flatter
than the slope of the diagonal at 53.5 mol % benzene which
corresponds to the minimum boiling point of a 66.7% benzene by
weight liquid, Fig., 6.

c) Benzene-n-Butyl Alcohol System, Figure 10.
The equilibrium diagram indicates the normal type for binary
mixtures which obey Raoult's Law over the entire range of
composition. The vapor evolved always contains more of the
lower boiling point, more volatile component than the corresponding
liquid. In this type, there cannot be any intersection of the
curve with the diagonal.

THEORETICAL CONSIDERATIONS

The behavior of the three systems studied in this paper, considered from the viewpoint of ideality, may be analyzed in terms of a number of theoretical concepts.

The poor agreement of the systems Benzene-Methyl Alcohol and Benzene-Isopropyl Alcohol with the Van Laar equations is not surprising if explained on the basis of alcohol - benzene miscibility. It is known that in mixtures approaching immiscibility, i.e., those having y, x curves which are nearly horizontal over an appreciable concentration range, poor agreement is the rule rather than the exception. Both Methyl Alcohol and Isopropyl Alcohol with benzene have y, x curves which tend to be nearly horizontal over a relatively wide concentration range, Figures 8 and 9. The entropy of **mixing** is not the same in a partially immiscible solution as it would be in an ideal solution and for complete immiscibility the entropy of mixing would be zero. In the case of Benzene-n-Butyl Alcohol where the y, x curves do not approach the horizontal, Figure 10, the agreement is fair. This is to be expected since the miscibility of alcohols with a non polar solvent such as benzene increases as the alcohol becomes more hydrocarbon in nature.

Methyl Alcohol is only weakly miscible with benzene as may be shown by adding sodium iodide which results in a separation into two layers. Methyl Alcohol, since it is a water-like substance has chemical and physical properties halfway between water and ethyl alcohol. It is more miscible in benzene than in water and as the length of the hydrocarbon chain increases in ascending the series, the alcohols become progressively more soluble in benzene.

The tendency to follow Raoult's Law also increases with the length of the hydrocarbon portion of the molecule. This implies that the degree of association decreases with the higher alcohols. A possible explanation for the decrease in association is that as the length of the hydrocarbon chain in the alcohol increases, the distance between the hydroxyl and methyl groups also increases. The methyl group, which supplies electrons in the sense than an electron drift is set up toward the oxygen, favoring hydrogen bonding, is placed at a greater distance from the hydroxyl. This of course means the likelihood of hydrogen bonding is lessened.

Another theory which helps to explain the phenomenon can be set up on the basis of polarity. In a system which behaves ideally and follows Raoult's Law, molecule A has the same attractive force for molecule B as it does for another molecule of A. However, because of the wide difference in polarity between Methyl Alcohol and Benzene, the polar alcohol groups exert an unusually high attractive force on each other with resultant higher surface tension and cohesion. There is a tendency to displace or force out the non-polar benzene molecules and therefore the system deviates from Raoult's Law because of the unequal forces of attraction. The strong affinity set up between the polar alcohol molecules results in the formation of aggregates (which can be identified with products formed by association in the hydrogen bond theory) acting as barriers to the non-polar benzene molecule.

The analysis can be taken a step further in an attempt to explain the mechanism of hydrogen bonding and azeotrope formation. The term hydrogen bonding may be defined as the tendency of a proton such as hydrogen to act as an acceptor of electrons which may be donated by an oxygen or a nitrogen atom. In this way larger units are bound together. Hildebrand (21) states that hydrogen bond formation offers a satisfactory explanation for the higher solubilities of aniline and phenol in water compared to benzene. He proposes that the oxygen atom of water acts as a donor and the hydrogen atoms of the amino and hydroxyl groups behave as acceptors. Hildebrand presented evidence of hydrogen bonding from solubility relationships, stating that in order for a substance to be soluble there should be strong attractive forces between solute and solvent molecules. The source of such attraction probably arises from either the mutual electrostatic attraction of molecular dipoles or the chemical coordinative forces such as are produced in the formation of hydrogen bonds.

Based on the strength of hydrogen bonds or on the lack of such bonds, organic liquids have been grouped according to five classifications (20). Methyl, Isopropyl and n-Butyl Alcohols belong to class II which includes liquids composed of molecules containing active hydrogen atoms and donor atoms such as oxygen, nitrogen and fluorine. This includes alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with hydrogen atoms, nitriles with hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.

Benzene belongs to class V which consists of liquids having no hydrogen bond forming capabilities. This class includes hydrocarbons in general, carbon disulfide, sulfides, mercaptans, halohydrocarbons without active hydrogens, nonmetallic elements such as iodine, phosphorus, sulfur, etc. Combinations of classes II and V if non-ideal, yield deviations from Raoult's Law which are always positive. Systems which show positive deviations from Raoult's Law and also from azeotropes are always minimum boiling. Further, according to this classification with combination of classes II and V, hydrogen bonds are broken only.

Empirical proof of this may be derived from the systems studied. The combinations of benzene with methyl and isopropyl alcohol form azeotropes because there is a tendency for the RO-H ... O bonds to be broken. In mixtures of benzene and n-butyl alcohol, the higher alcohol is more soluble in benzene and less associated. The attractive forces are equal, the polarity of the two components is closer, so that the trend is toward ideal behavior.

LITERATURE CITED

1. Carey. "Chemical Engineer's Handbook". Perry, Editor. Section 12, Distillation, 1105. McGraw-Hill, 1934.

   Badger and McCabe. "Elements of Chemical Engineering". 2nd edition, 323, McGraw Hill, (1936).

   Walker, Lewis, McAdams and Gilliland. "Principlesof Chemical Engineering". 3rd edition, 514. McGraw-Hill (1937).

   Chemical Engineer's Handbook. Perry, editor. Distillation 561-660. McGraw-Hill (1950).

2. Carveth. "The Composition of Mixed Vapors". J. of Phys. Chem. 3, 193 (1899).

3. Petit, J.H. "Minimum Boiling Point and Vapor Composition". J. of Phys. Chem. 3, 360 (1899).

4. Rosanoff, Bacon and White. "A Rapid Laboratory Method of Measuring the Partial Vapor Pressure of Liquid Mixtures". J. of American Chemical Society, 36, 1803 (1914).

5. Carey and Lewis. "Studies in Distillation". Ind. Eng. Chem. 24, 882 (1935).

6. Scatchard. "Vapor-Liquid Equilibrium, I - Apparatus for the Study of Systems with Volatile Components. II - Chloroform-Ethanol Mixtures". J. of American Chemical Society, 60, 1275-1278 (1938).

7. Othmer, D.F. "Composition of Vapors from Boiling Binary Solutions". Ind. Eng. Chem. 20, 743-746 (1928).

   Othmer, D.F. "Composition of Vaporsfrom Boiling Binary Solutions". Ind. Eng. Chem., Anal. Ed., 4, 232-234 (1932).

   Othmer, D.F. "Composition of Vapors from Boiling Binary Solutions". Anal. Chemistry 20, 763 (1948).

8. Rogers, J.W., Knight, J.W., and Choppin, A.R. "An Improved Apparatus for Determining Vapor-Liquid Equilibrium". J. of Chem. Ed. 24, 491-493 (1947).

9. Langdon, W.M. and Keyes, D.B. "Vapor-Liquid Equilibrium Data on Ethyl Alcohol-Water and on Isopropyl Alcohol Water". Ind. Eng. Chem., 34, 938-42 (1942).

LITERATURE CITED, CONT'D

10. Young, S. "Distillation Principles and Processes" (49) Macmillan, 1922.

11. Pierce, W.C. and Haenisch, E.L. "Quantitative Analysis" 2nd edition, (41), Wiley, 1940.

12. Carlson, H.C. and Colburn, A.P. "Vapor-Liquid Equilibrium of Non-Ideal Solutions". Ind. Eng. Chem., 34, 581-9 (1942).

13. Robinson, C.S. and Gilliland, E.R. "Elements of Fractional Distillation", 4th edition, 61, McGraw Hill, 1950.

14. Mason; M.S. thesis in chemical engineering, M.I.T. 1948.

15. Lange, N.A. Handbook of Chemistry, 4th edition, 124, 1951.

16. Handbook of Chemistry and Physics 30th edition, 1844 Chemical Rubber Publishing Co.

17. Mellan, I. "Industrial Solvents" 224, Reinhold, 1947.

18. Scatchard, et al. J. American Chemical Society 61, 3206-10 1934.

19. J. Physical Chemistry 43, 119-130, 1939.

20. Carney, T.P. "Laboratory Fractional Distillation". Ch. XX Macmillan, 1949.

21. Hildebrand "Science" 83, 21 (1936).

22. Olsen, A.L., Washburn, E.R. "The Vapor Pressure of Binary Solutions of Isopropyl Alcohol and Benzene at 25°C." J. Phys. Chem. 41, 457-62 (1934).

23. Allen, B.B., Lingo, S.P., Felsing, W.A. "Total and Partial Pressures of Binary Solutions of the Butyl Alcohols in Benzene at 25°C." J. Phys. Chem. 43, 425-30, 1939.

24. Miller, P.H. "Study of Vapor Liquid Equilibrium Data Analyzed by Van Laar's and Frahl's Method." M.S. thesis in chemical engineering, Newark College of Engineering, 1952.

LITERATURE SEARCH AND BIBLIOGRAPHY

A literature search was made on the subject of Vapor-Liquid Equilibrium prior to starting experimental work on the specific systems involved. The literature on distillation was examined.

Chemical Abstracts were searched from 1907 - 1953, inc. under the following topics:

Vapor-liquid equilibrium -- Equilibrium, liquid vapor

Equilibrium stills

Distillation

Vapor pressure

Binary liquids -- Mixtures

Benzene

Methyl alcohol

n-Butyl alcohol

Isopropyl alcohol

The following handbooks and reference works proved to be valuable:

1. Daniels, F.; Mathews, J.H.; Williams, J.W. "Experimental Physical Chemistry". McGraw-Hill, New York, 1941.

2. Swietoslawski, W. "Ebulliometric Measurements". Reinhold Publishing Corp., New York, 1945.

3. Weissberger, A. "Technique of Organic Chemistry". Vol. I - Physical Methods, Part 1 - 2nd edition. Interscience Publishers, In., New York, 1949.

4. Durrans, T.H. "Solvents". Van Nostrand Co., New York, 1931.

5. Morton, A.A. "Laboratory Technique in Organic Chemistry". McGraw-Hill, New York, 1938.

6. Glasstone, S. "Textbook of Physical Chemistry". 2nd edition. Van Nostrand Co., New York, 1946.

7. Taylor, H.S. "A Treatise on Physical Chemistry", Vol. I,
    2nd edition. Van Nostrand Co., New York, 1930.

8. Mellon I. "Industrial Solvents". Reinhold Publishing Corp.,
    New York, 1939.

9. McCormack, H. "The Application of Chemical Engineering".
    Van Nostrand Co., New York, 1940.

10. Robison - Gilliland. "The Elements of Fractional Distillation".
    3rd edition. McGraw-Hill, 1939.

11. Young, S. "Distillation Principles and Processes".
    Macmillan and Co., Ltd., London, 1922.

12. Gattermann, L. "Laboratory Methods of Organic Chemistry".
    trans. from the 24th German edition. Macmillan and Co., Ltd.,
    London, 1943.

13. Zimmerman, O.T., and Lavine, I. "Chemical Engineering Labor-
    atory Equipment". Industrial Research Service, Dover, N.H.
    1943.

14. Walker, W.H., Lewis, W.K., McAdams, W.H., Gilliland, E.R.
    "Principles of Chemical Engineering". McGraw-Hill, New York,
    1937.

15. Gregory, T.C. and Turner, F.M. "TheCondensed Chemical
    Dictionary". Reinhold PublishingCorp., New York, 1942.

16. "Handbook of Chemistry and Physics". 34th edition.
    Chemical Rubber Publishing Co., Cleveland, O. 1952-53.

17. Perry. "Handbook of Chemical Engineering".

18. "A Source Book of Technical Literature on Fractional
    Distillation". Gulf Research and Development Co.

19. Hausbrand. "Principles and Practice of Industrial
    Distillation". Wiley, 1928.

The following non-cited literature references were found to be of interest:

Mertes, T.S. and Colburn, A.P. "Binary Mixtures of n-Butane, Isobutane and 1-Butene with Furfural. Vapor-Liquid Equilibria and Thermodynamic Properties". Ind. Eng. Chem., 39, 787 (1947).

Sage, B.H., and Lacey, W.N. "Phase Equilibria in Hydrocarbon Systems". Ind. Eng. Chem., 26, 103-6 (1934).

Beatty, H.A., and Calingaert, G. "Vapor-Liquid Equilibrium of Hydrocarbon Mixtures". Ind. Eng. Chem., 26, 504-8 (1934).

Kay, W.B. "Liquid-Vapor Phase Equilibrium Relations in the Ethane-n-Heptane System". Ind. Eng. Chem. 30, 459-65 (1938).

Carlson, H.C. and Colburn, A.P. "Equilibrium Still for Miscible Liquids. Data on Ethylene Dichlorice - Toluene and Ethanol-Water". Ind. Eng. Chem. 35, 666-72 (1943).

Benedict, M., Solomon, E., and Rubin, L.C. "Liquid-Vapor Equilibrium in Methane - Ethylene - Isobutane System". Ind. Eng. Chem. 37, 55-9 (1945).

THERMOMETER, PRECISION GRADE, 0.1°C. DIVISIONS (卫 BUSHING ADAPTER)

19/38 卫 JOINT

10" WEST CONDENSER

45/50 卫 JOINT

19/38 卫 JOINT

VAPOR OUTLET HOLES

THERMOMETER SHIELD

VAPOR RETURN TUBE

COTTRELL PUMP

3 WAY STOPCOCK

SAMPLING TUBE

FIGURE I. DIAGRAM OF APPARATUS

CALIBRATION CURVE
CORRECTIONS FOR STILL THERMOMETER BASED
ON BUREAU OF STANDARDS THERMOMETER

FIGURE 1a

FIGURE 2

REFERENCE CURVE FOR
BENZENE-ISOPROPYL ALCOHOL

REFRACTIVE INDEX

WEIGHT PER CENT BENZENE

FIGURE 3

REFERENCE CURVE FOR
BENZENE—n BuOH

REFRACTIVE INDEX

WEIGHT PER CENT BENZENE

FIGURE 4

Table 1

Benzene-Methyl Alcohol System

Experimental Data

760 mm pressure

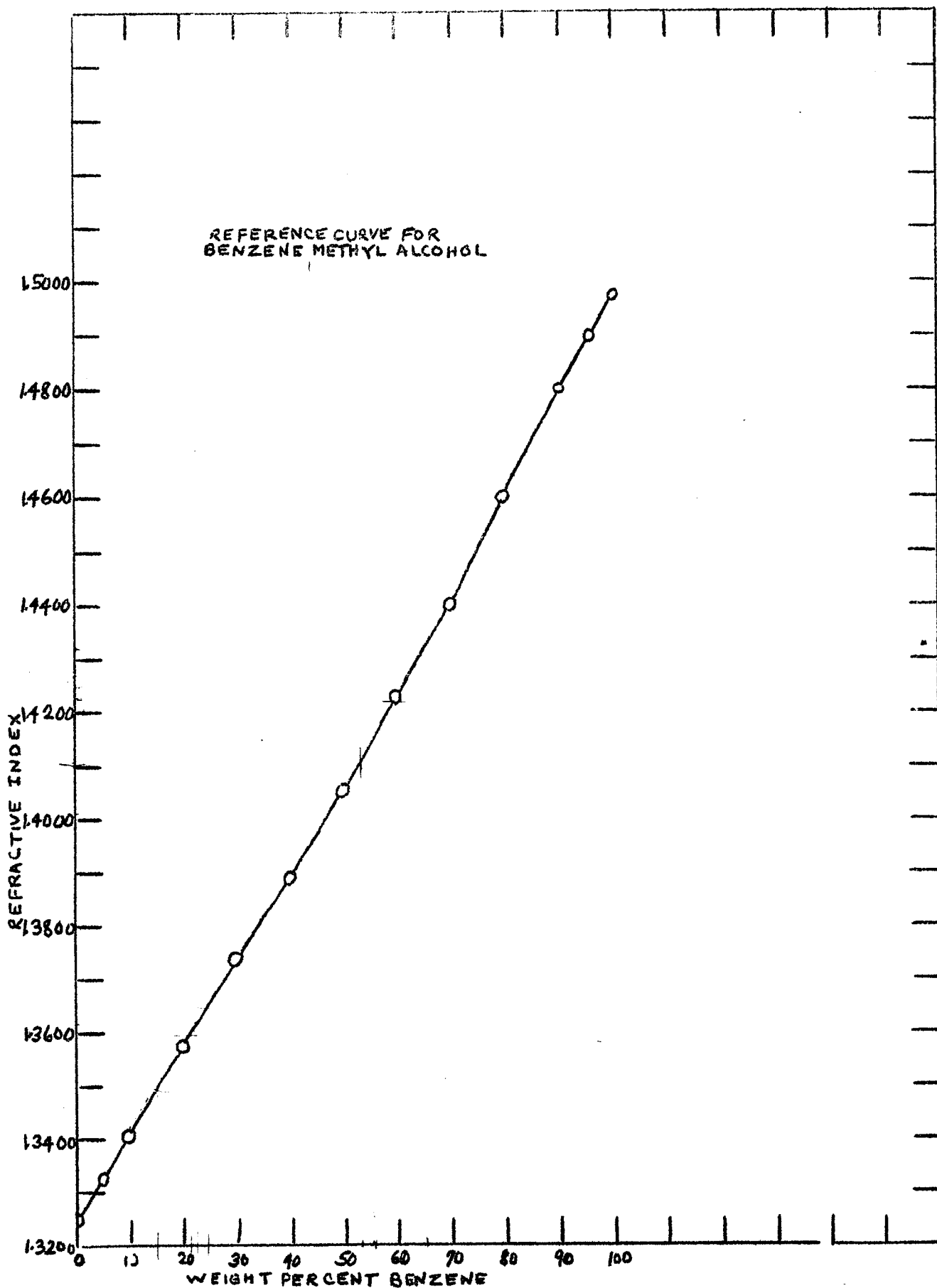| Benzene in Vapor		Benzene in Liquid		Temperature °C
Wt. %	Mol. %	Wt. %	Mol. %	
100.0	100.0	100.0	100.0	80.3
90.0	78.0	98.0	95.3	73.5
78.0	59.3	97.0	93.0	68.0
72.5	52.0	95.5	89.5	64.5
70.0	48.9	95.0	88.5	62.5
66.0	44.4	93.0	84.5	60.4
65.0	43.2	90.0	84.1	59.6
64.0	42.2	87.5	74.0	59.2
63.0	41.1	84.5	69.1	58.9
62.0	40.0	80.0	62.8	58.5
60.4	38.4	60.4	38.4	58.3
58.0	36.2	44.0	24.4	58.4
57.0	35.8	38.0	20.0	58.6
52.0	30.7	31.5	15.9	59.2
48.0	27.5	23.0	10.9	59.8
38.0	20.0	17.0	7.8	60.8
31.5	15.8	11.5	5.0	61.8
21.5	10.1	7.5	3.2	63.0
16.5	7.5	5.0	2.0	63.6
7.5	3.2	2.0	0.8	64.1
0.0	0.0	0.0	0.0	64.7

Table 2

Benzene-Isopropyl Alcohol System

Experimental Data

760 mm Pressure

Benzene in Vapor		Benzene in Liquid		Temperature °C
Wt. %	Mol. %	Wt. %	Mol. %	
100.0	100.0	100.0	100.0	80.0
97.0	96.1	98.5	98.1	78.7
93.5	91.8	96.5	95.5	77.1
90.5	88.0	95.0	93.6	76.0
86.5	83.2	93.0	91.2	74.8
82.0	77.8	91.0	88.6	73.6
77.5	72.6	87.5	84.4	72.7
71.0	65.3	75.0	69.8	72.1
66.7	60.6	66.7	60.6	71.9
60.0	53.6	47.5	41.0	72.1
55.5	48.9	42.5	36.3	72.25
50.0	43.5	32.5	27.2	73.4
44.0	37.7	22.0	17.8	75.3
36.5	30.7	16.0	12.8	76.7
28.0	23.0	10.5	8.3	78.2
22.5	17.9	8.0	6.3	79.2
16.5	13.2	6.0	4.7	80.1
10.0	7.8	2.5	2.0	81.3
0.0	0.0	0.0	0.0	82.3

Table 3

Benzene-n-Butyl Alcohol System

Experimental Data

760 mm Pressure

Benzene in Vapor		Benzene in Liquid		Temperature °C
Wt. %	Mol. %	Wt. %	Mol. %	
100.0	100.0	100.0	100.0	80.0
98.5	98.3	96.0	95.8	80.1
97.5	97.0	95.0	94.6	80.3
92.5	92.1	80.0	79.3	81.5
89.0	88.4	67.5	66.3	83.0
86.0	85.4	55.5	54.2	85.0
84.0	83.3	47.5	46.1	87.0
82.5	81.7	41.5	40.2	88.5
77.5	76.6	33.5	32.3	91.5
71.0	69.9	27.0	26.0	94.2
69.0	67.9	25.5	24.5	95.0
63.5	62.3	21.0	20.2	97.2
57.5	56.2	17.0	16.3	99.4
52.5	51.2	14.5	13.9	101.2
46.5	45.2	11.5	11.0	103.3
41.5	44.8	9.5	9.1	105.1
27.0	26.0	5.0	4.8	109.8
16.5	15.8	2.5	2.4	113.0
7.5	7.2	1.0	0.9	115.5
4.0	3.8	0.5	0.5	116.5
0.0	0.0	0.0	0.0	117.7
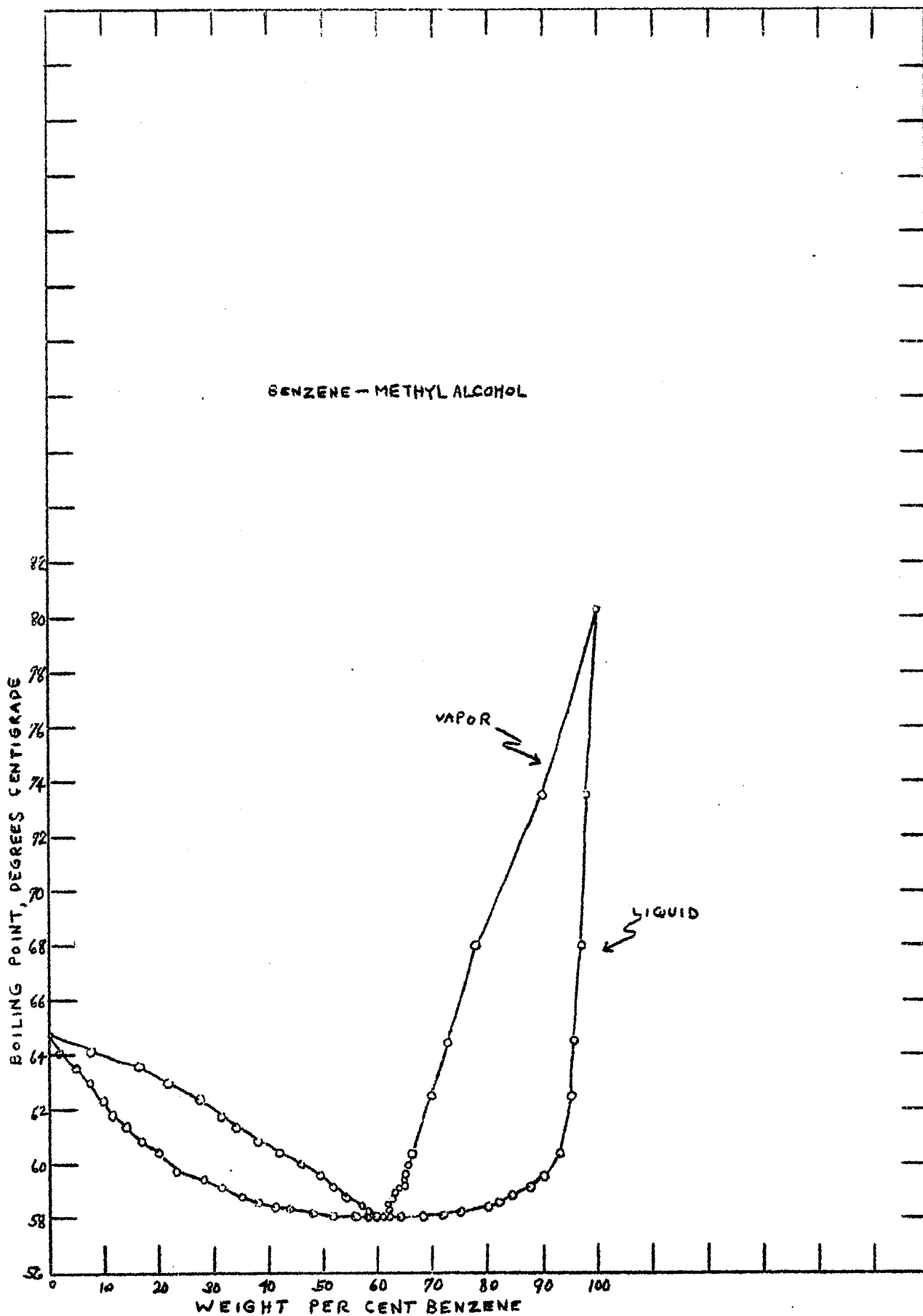
FIGURE 5

BENZENE ISOPROPYL ALCOHOL

VAPOR

LIQUID

WEIGHT PER CENT BENZENE   FIGURE G

BENZENE—n BUTYL ALCOHOL

BOILING POINT DEGREES CENTIGRADE

WEIGHT PER CENT BENZENE
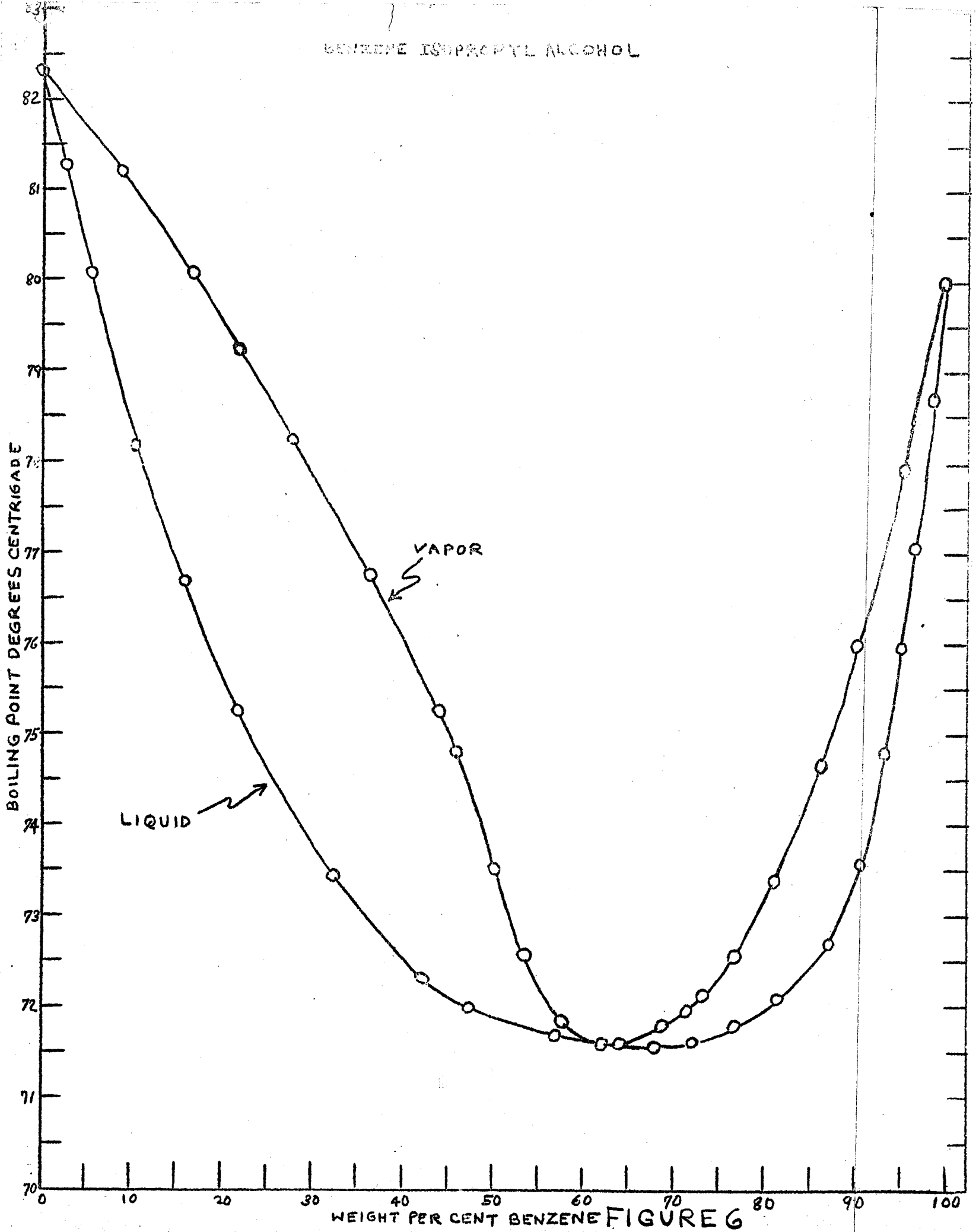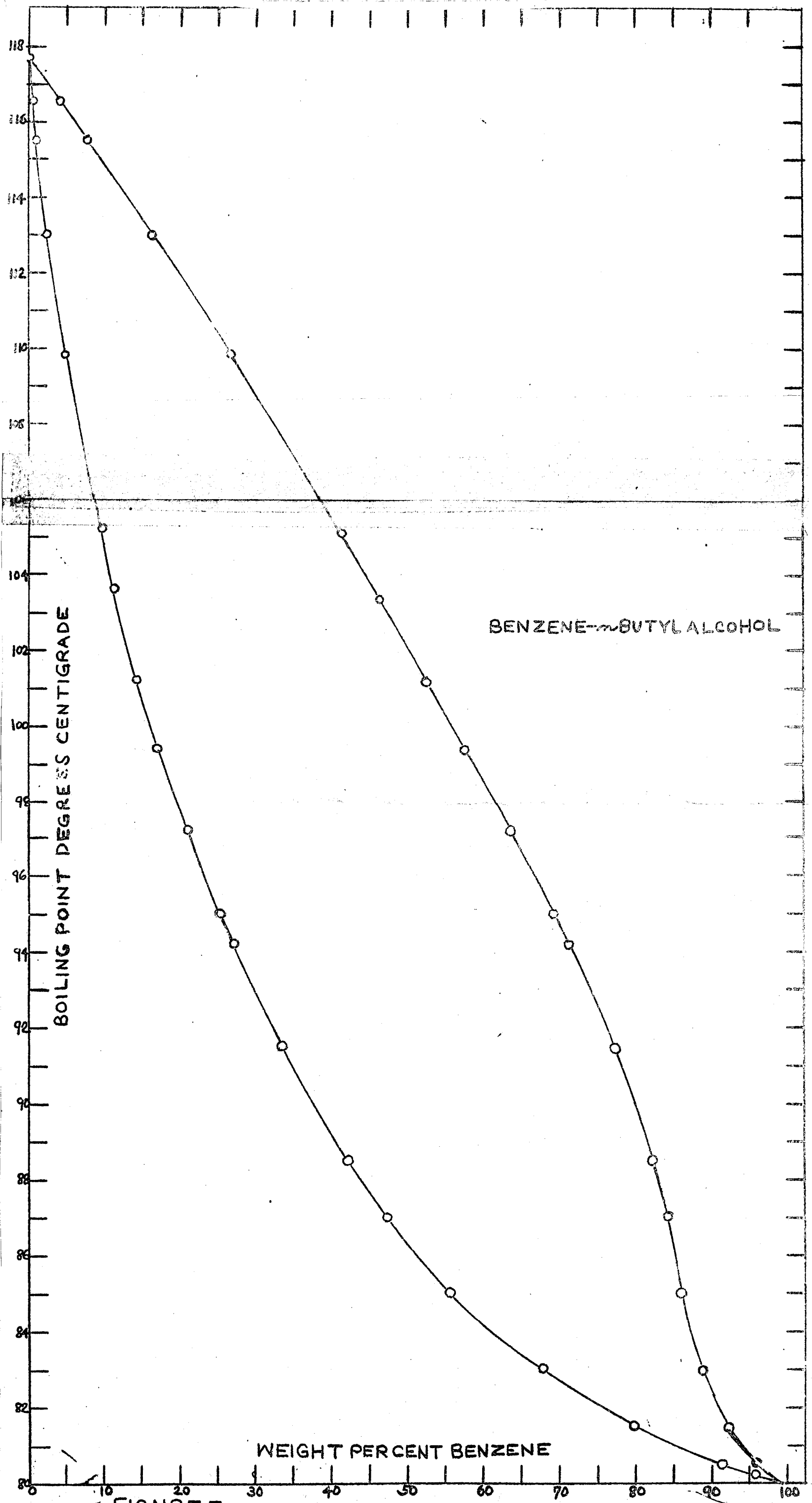
FIGURE 7

BENZENE – METHYL ALCOHOL

BENZENE MOL % IN VAPOR

BENZENE MOL % IN LIQUID

FIGURE 8

BENZENE/ISOPROPYL ALCOHOL

BENZENE MOL % IN VAPOR

BENZENE MOL % IN LIQUID
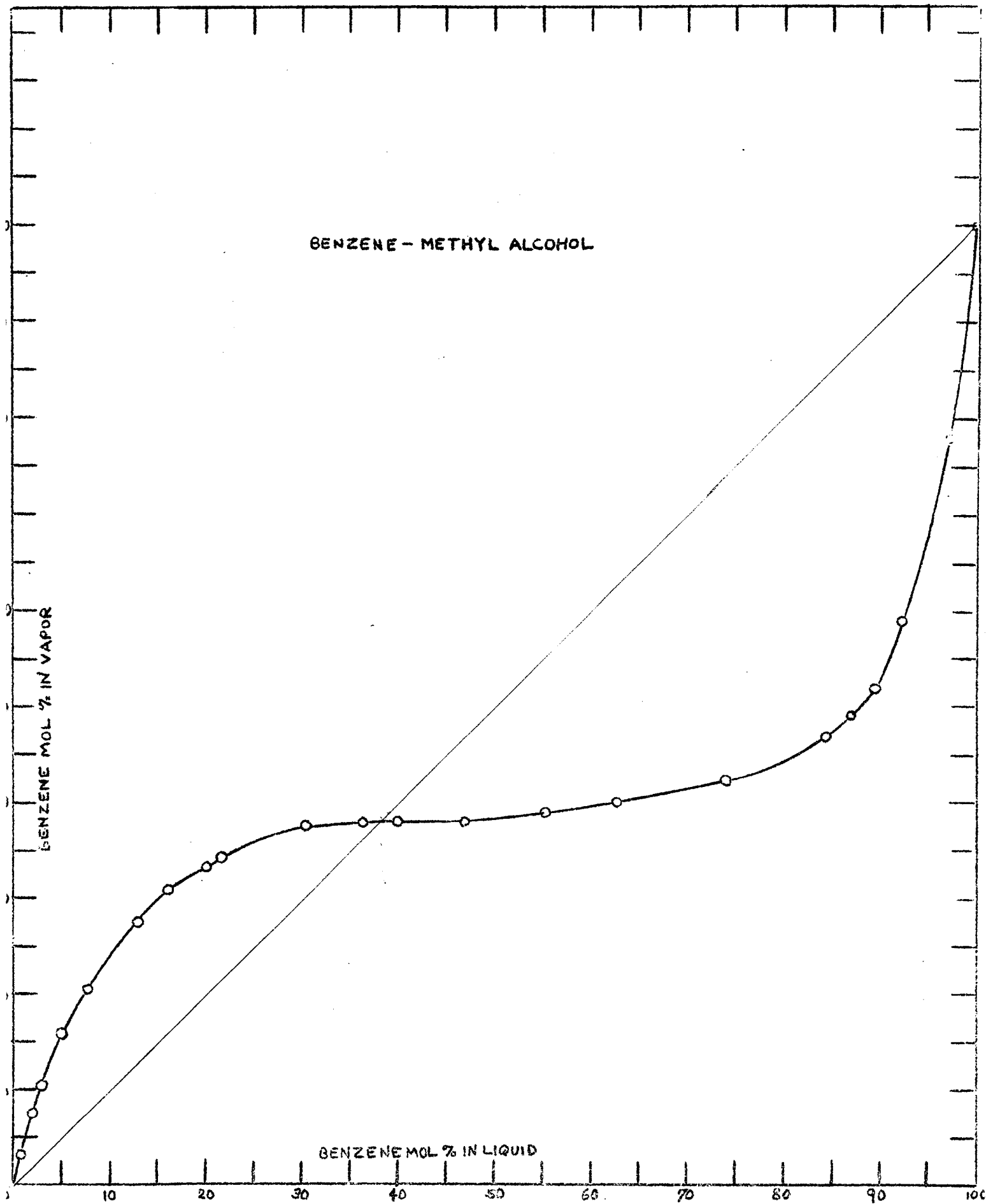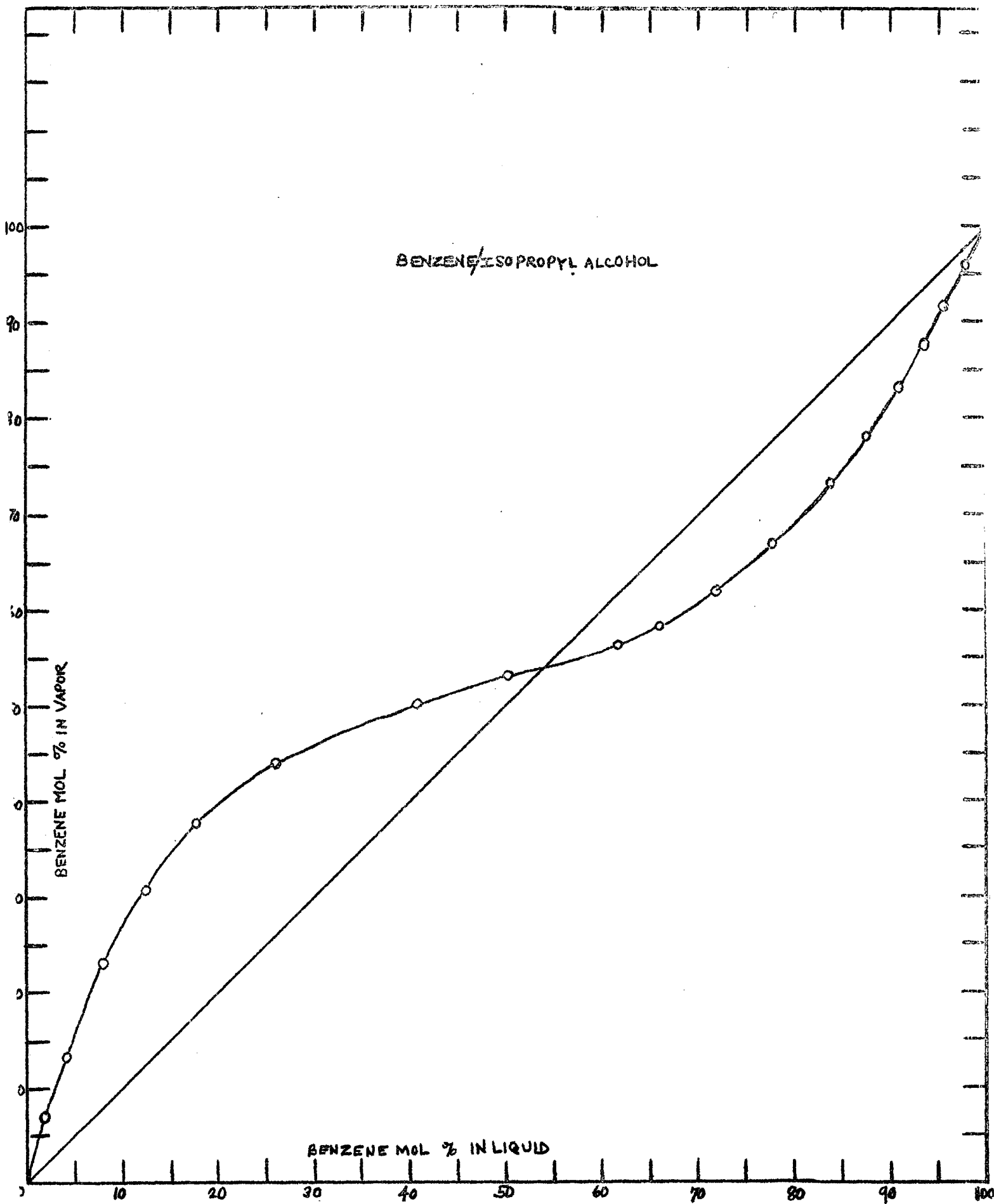
FIGURE 9

FIGURE 10

Table 4

Evaluation of Precision

I Pure Components

a) Benzene Lit. Values: R.I. 1.50142^{20} B.P. $80.1^{o}C$
(Handbook of Chemistry and Physics)

Observed values:

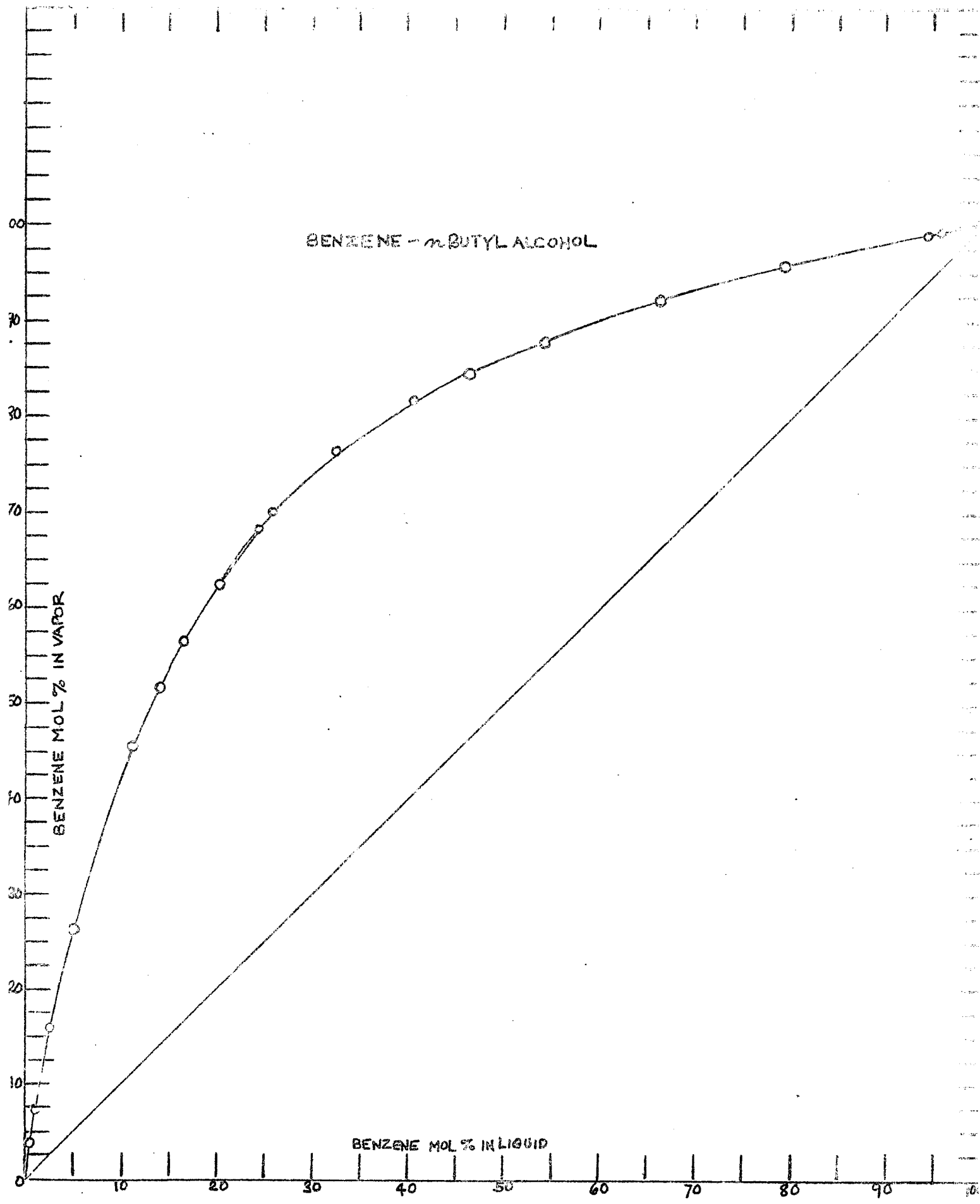| R.I.	Deviations	Deviations in parts per 1000	B.P.^{o}C	Deviations	Deviations in parts per 1000	
1.5015	0.000125	0.083	80.05	0.025	0.30	
1.5013	0.000750	0.488	80.10	0.025	0.30	
1.5013	0.000750	0.488	80.10	0.025	0.30	
1.5014	0.000125	0.083	80.05	0.025	0.30	
1.501375	0.0004375	0.2855	80.075	0.025	0.3	Av.

b) Methyl Alcohol Lit. Values: R.I. 1.3318^{20} B.P. $64.7^{o}C$

Observed values:

R.I.	Deviations	Deviations in parts per 1000	B.P.^{o}C	Deviations	Deviations in parts per 1000	
1.3312	0.0000	0.000	64.65	0.00	0.00	
1.3311	0.0001	0.075	64.60	0.05	0.80	
1.3313	0.0001	0.075	64.65	0.00	0.00	
1.3312	0.0000	0.000	64.70	0.05	0.80	
1.3312	0.00005	0.0375	64.65	0.025	0.40	Av.

c) Isopropyl Alcohol Lit. Values: R.I. 1.37757^{20} B.P. $82.3^{o}C$

Observed values:

R.I.	Deviations	Deviations in parts per 1000	B.P.^{o}C	Deviations	Deviations in parts per 1000	
1.3776	0.0000	0.000	82.30	0.06	0.73	
1.3777	0.0001	0.074	82.15	0.09	1.10	
1.3775	0.0001	0.073	82.25	0.01	0.12	
1.3776	0.0000	0.000	82.25	0.01	0.12	
1.3776	0.00005	0.0365	82.24	0.04	0.51	Av.

d) n-Butyl Alcohol Lit. values: R.I. 1.39931[20] B.P. 117.7°C

Observed values:

R.I.	Deviations	Deviations in parts per 1000	B.P.°C	Deviations	Deviations in parts per 1000
1.3992	0.0001	0.0715	117.60	0.06	0.51
1.3992	0.0001	0.0715	117.70	0.04	0.34
1.3994	0.0001	0.0715	117.65	0.01	0.10
1.3994	0.0001	0.0715	117.70	0.04	0.34
1.3993	0.0001	0.0715	117.66	0.0375	0.032 Av.

Table 5

Activity Coefficients - Benzene-Methyl Alcohol

Temp., °C	y_1	x_1	P_1 mm Hg	P_2 mm Hg	γ_1	γ_2	$x_2/x_1 \log \gamma_1 + x_2 \log \gamma_2$	% Dev. *
73.5	0.220	0.047	1070	600	3.440	1.035	1.13	8.1
68.0	0.407	0.070	864	510	5.130	0.950	0.93	- 2.67
64.5	0.480	0.105	752	468	4.620	0.942	1.01	- 2.02
62.5	0.511	0.115	696	428	4.850	0.980	1.175	-16.75
60.4	0.556	0.155	636	396	4.280	1.005	1.32	-16.50
59.6	0.568	0.159	616	380	4.410	1.030	1.182	-20.00
59.2	0.578	0.260	604	376	2.800	1.155	1.18	- 1.25
58.9	0.589	0.309	600	374	2.410	1.205	1.22	1.79
58.5	0.600	0.372	592	368	2.060	1.315	1.22	2.19
58.3	0.616	0.616	586	366	1.295	2.070	1.24	--
58.4	0.638	0.758	588	367	1.090	3.080	1.255	-16.95
58.6	0.642	0.800	592	369	1.030	3.680	1.29	-17.7
59.2	0.693	0.841	604	376	1.034	3.900	1.25	-10.1
59.8	0.725	0.891	620	388	0.995	4.940	1.255	-11.4
60.8	0.800	0.922	644	400	1.025	4.850	1.125	7.36
61.8	0.842	0.950	674	412	1.000	5.820	1.242	0.9
63.0	0.899	0.968	710	436	0.995	5.500	1.15	-10.15
63.6	0.925	0.980	728	444	1.010	6.400	0.98	- 2.73
64.1	0.968	0.992	742	448	0.998	6.800	1.05	- 8.34

$$* \quad \% \, Dev. = \left[\frac{y_{calc.} - y_{exp.}}{(y-x)_{exp.}} \right] 100$$

Table 6

Activity Coefficients -- Benzene-Isopropyl Alcohol

Temp., °C	y_1	x_1	P_1 mm Hg	P_2 mm Hg	γ_1	γ_2	$\frac{x_1 x_2}{x_1 \log \gamma_1 + x_2 \log \gamma_2}$	% Dev.*
78.7	0.961	0.981	724	666	1.03	2.34	0.94	131
77.1	0.918	0.955	688	620	1.06	2.23	1.088	140
76.0	0.880	0.936	668	592	1.07	2.40	1.165	71.4
74.8	0.832	0.912	648	568	1.07	2.56	1.287	47.5
73.6	0.778	0.886	620	532	1.075	2.78	1.298	29.6
72.7	0.726	0.844	604	512	1.082	2.60	1.410	13.6
72.1	0.653	0.698	588	494	1.212	1.768	1.588	- 8.9
71.9	0.606	0.606	582	490	1.305	1.55	1.705	---
72.1	0.536	0.410	488	494	1.691	1.21	1.705	39.7
72.25	0.489	0.363	596	504	1.715	1.205	1.695	15.0
73.4	0.435	0.272	612	520	1.985	1.13	1.650	48.4
75.3	0.377	0.178	654	576	2.46	1.005	2.050	25.6
76.7	0.307	0.128	680	610	2.68	0.988	1.890	24.6
78.2	0.230	0.083	705	646	2.99	0.988	1.730	-69.4
79.2	0.179	0.063	724	672	2.985	0.99	1.745	21.1
80.1	0.132	0.047	760	700	2.81	0.988	1.745	42.1
81.3	0.073	0.020	772	748	3.83	0.955	1.730	- 2.4

$$* \quad \% \text{ Dev.} = \left[\frac{y_{calc.} - y_{exp.}}{(y-x)_{exp.}} \right] 100$$

Table 7

Activity Coefficients – Benzene-n-Butyl Alcohol

Temp., °C	y_1	x_1	P_1 mm Hg	P_2 mm Hg	γ_1	γ_2	$x_1 x_2 / x_1 \log \gamma_1 + x_2 \log \gamma_2$	% Dev. *
80.1	0.983	0.958	757	172	1.03	2.00	1.893	-60.0
80.3	0.970	0.946	760	174	1.03	2.44	2.192	-91.7
81.5	0.921	0.793	792	180	1.12	1.61	2.041	85.0
83.0	0.884	0.663	828	192	1.22	1.36	2.180	-38.1
85.0	0.854	0.542	879	208	1.36	1.17	2.408	-27.9
87.0	0.833	0.461	932	225	1.47	1.05	2.842	-21.8
88.5	0.817	0.402	972	236	1.59	1.00	2.990	-20.0
91.5	0.766	0.323	1060	266	1.70	1.00	2.941	-13.3
94.2	0.699	0.260	1156	302	1.77	1.02	2.726	- 0.7
95.0	0.679	0.245	1176	310	1.79	1.04	2.452	1.2
97.2	0.623	0.202	1240	332	1.89	1.08	1.954	36.3
99.4	0.562	0.163	1324	372	1.97	1.07	1.893	9.2
101.2	0.512	0.139	1388	400	2.02	1.08	1.680	33.2
103.3	0.452	0.110	1468	440	2.13	1.06	1.639	12.9
105.1	0.448	0.091	1540	472	2.43	1.00	2.357	0.0
109.8	0.260	0.048	1740	563	2.36	1.04	1.371	31.3
113.0	0.158	0.024	1860	652	2.69	1.01	1.612	6.8
115.5	0.072	0.009	2004	712	3.03	1.00	1.872	- 3.2
116.5	0.038	0.005	2052	736	2.82	1.00	2.210	6.1

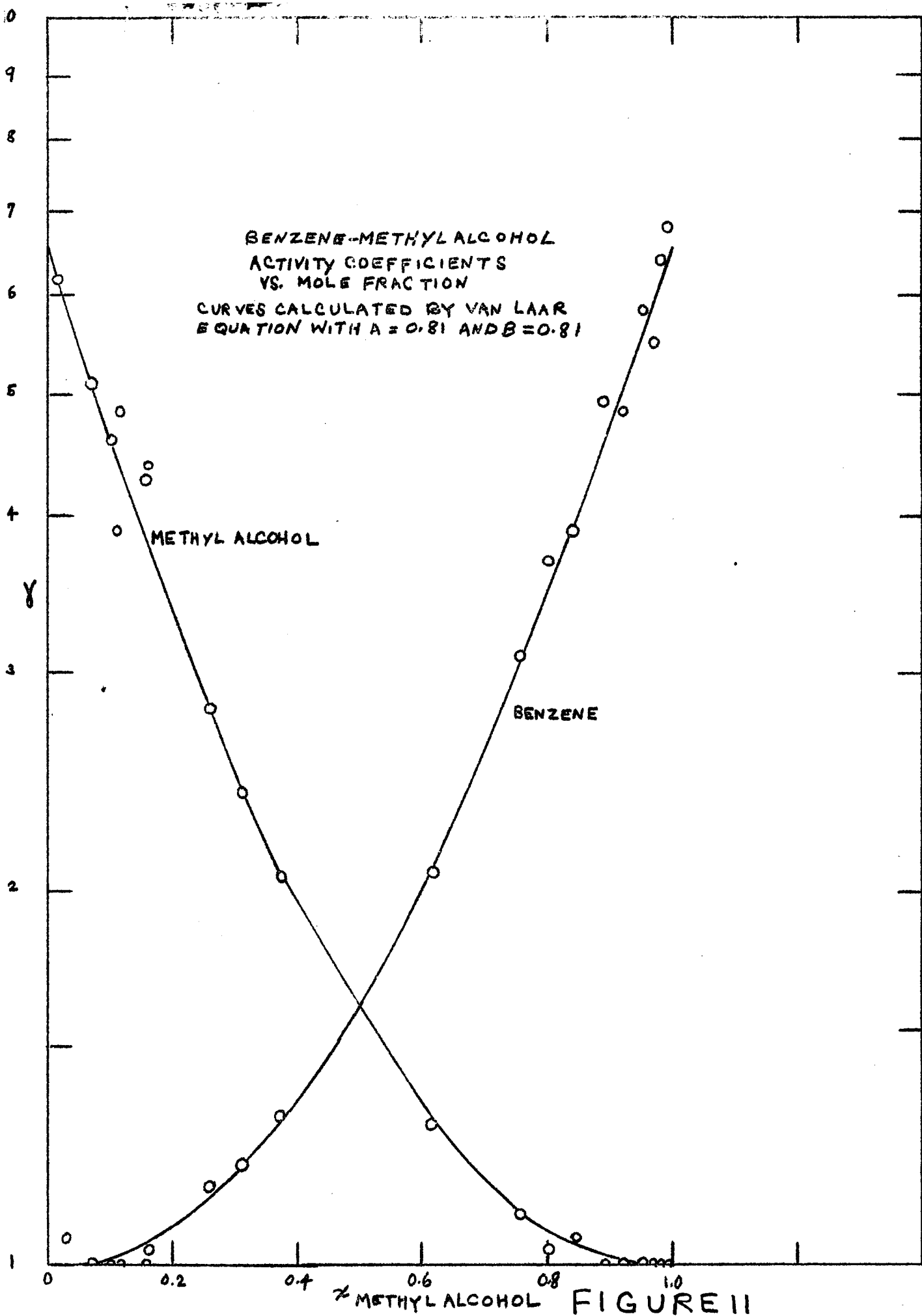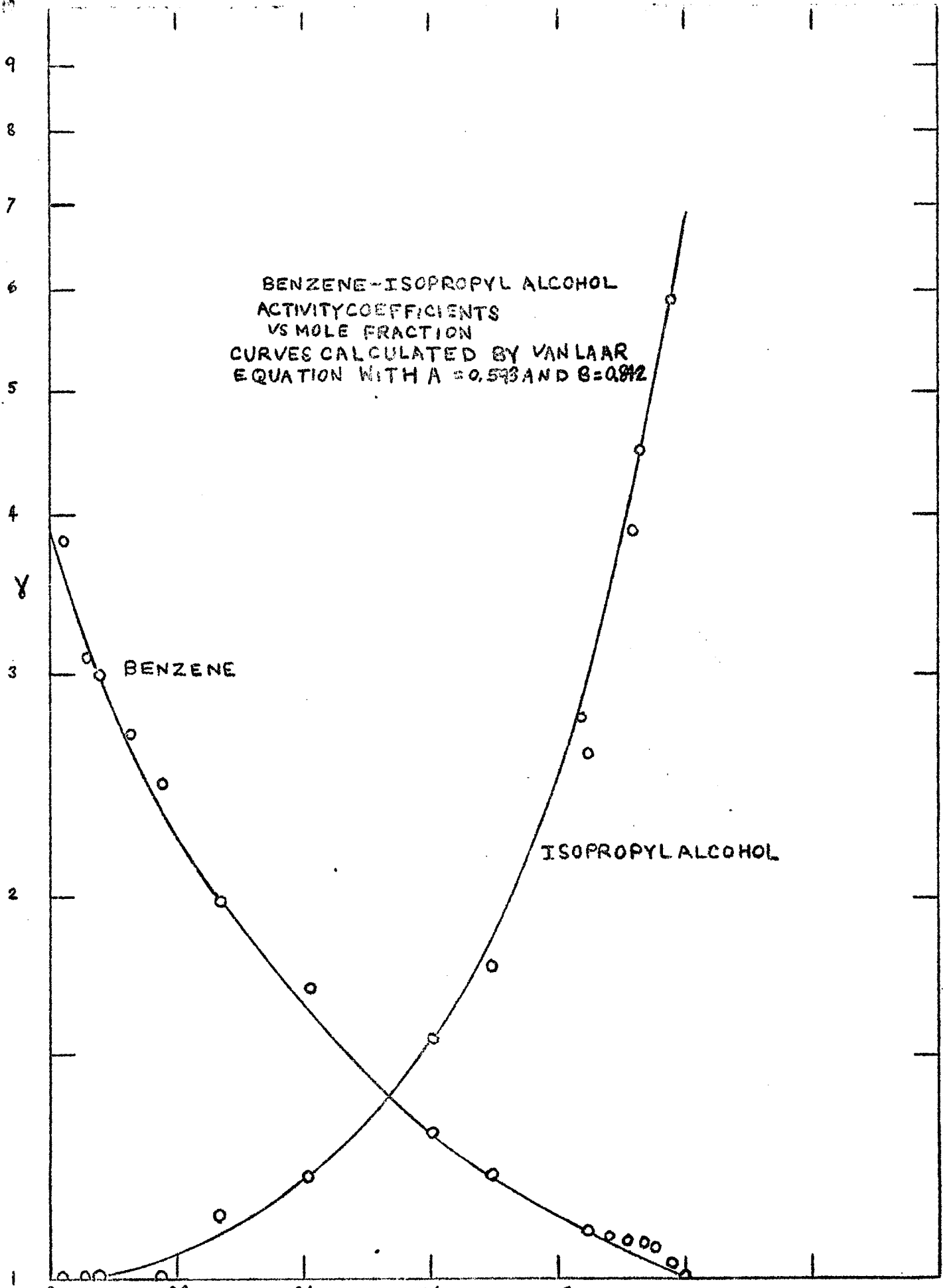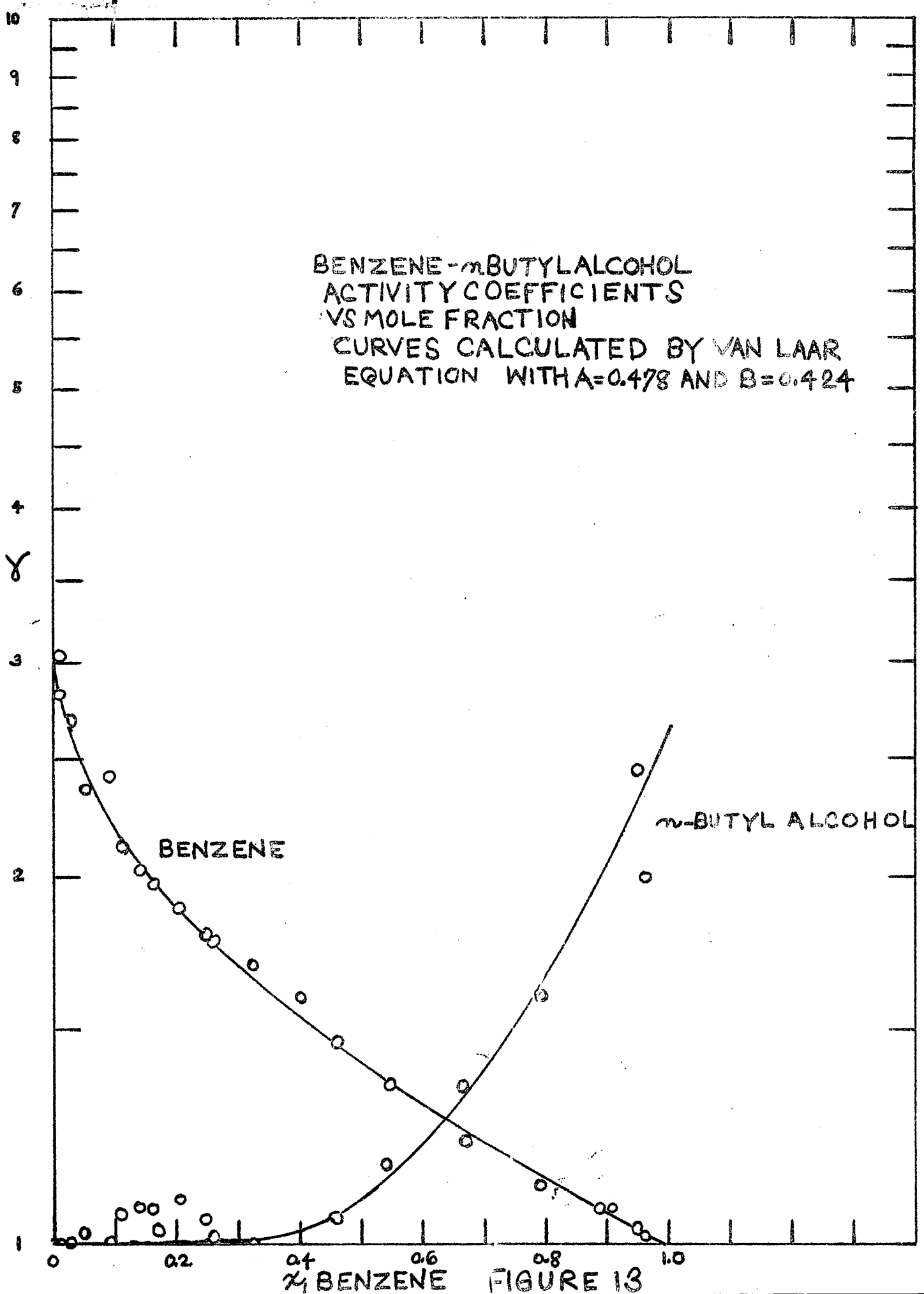$$* \quad \% \text{ Dev.} = \left[\frac{y_{calc.} - y_{exp.}}{(y-x)_{exp.}} \right] 100$$

BENZENE-METHYL ALCOHOL
ACTIVITY COEFFICIENTS
VS. MOLE FRACTION
CURVES CALCULATED BY VAN LAAR
EQUATION WITH A = 0.81 AND B = 0.81

METHYL ALCOHOL

BENZENE

x METHYL ALCOHOL

FIGURE II

BENZENE-ISOPROPYL ALCOHOL
ACTIVITY COEFFICIENTS
VS MOLE FRACTION
CURVES CALCULATED BY VAN LAAR
EQUATION WITH A = 0.593 AND B = 0.842

BENZENE

ISOPROPYL ALCOHOL

γ

x_1 BENZENE

FIGURE 12

BENZENE-nBUTYLALCOHOL
ACTIVITY COEFFICIENTS
VS MOLE FRACTION
CURVES CALCULATED BY VAN LAAR
EQUATION WITH A=0.478 AND B=0.424

BENZENE

n-BUTYL ALCOHOL

x_1 BENZENE   FIGURE 13

BENZENE Vs METHYL ALCOHOL

$x_1 \dfrac{x_2}{?} / x_1 \log \gamma_1 + x_2 \log \gamma_2$
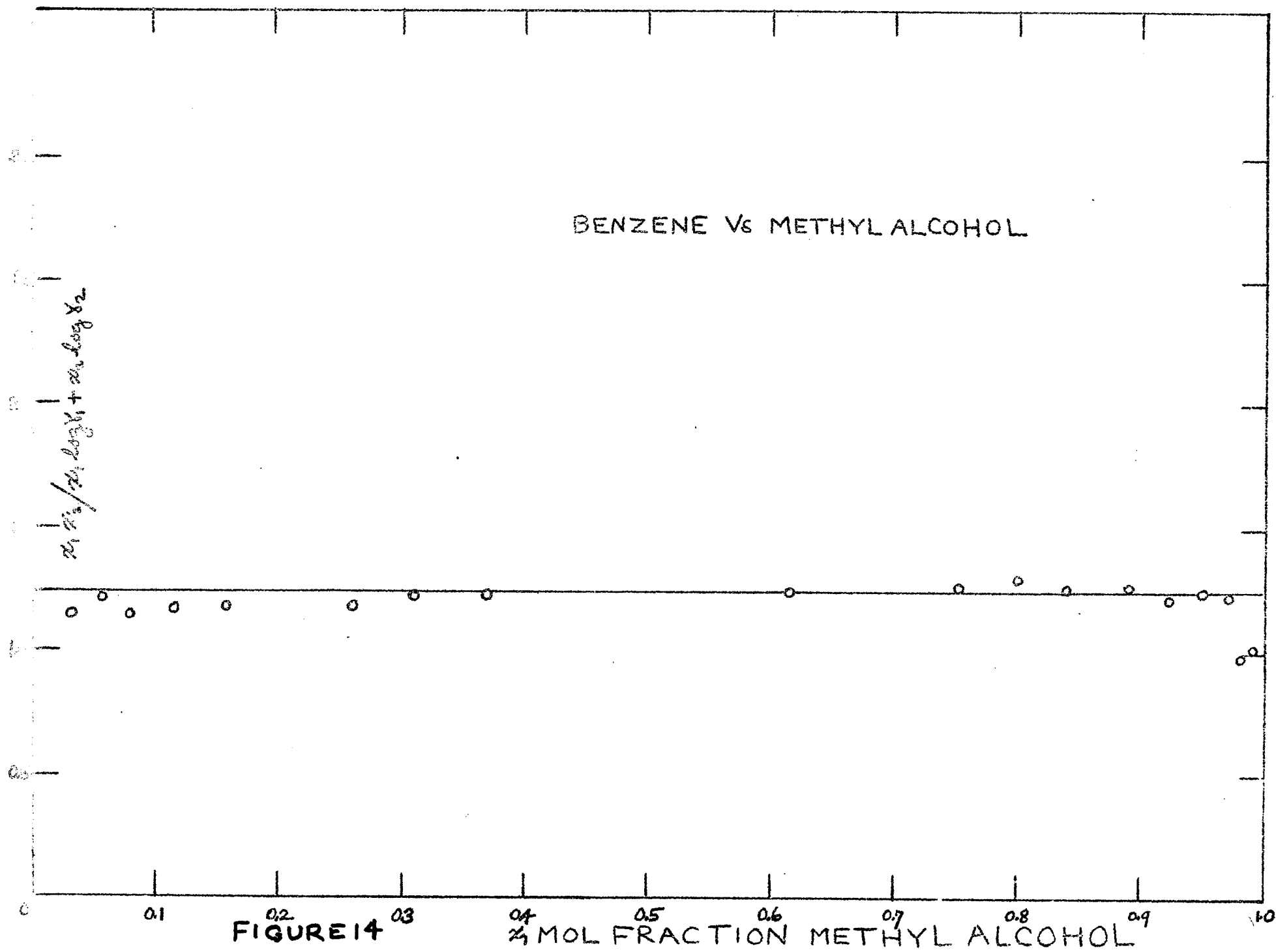
FIGURE 14 x_1 MOL FRACTION METHYL ALCOHOL

ISOPROPYL ALCOHOL Vs BENZENE

FIGURE 15

x_1 MOL FRACTION BENZENE

$\dfrac{\Delta F}{2.3 RT} = x_1 \log \gamma_1 + x_2 \log \gamma_2$

FIGURE 16

n BUTYL ALCOHOL VS BENZENE

% MOL FRACTION BENZENE

VAPOR PRESSURE CURVE
BENZENE 70°-120°C RANGE

FIGURE 17

VAPOR PRESSURE CURVES
BENZENE 30°-90°C RANGE
ISOPROPYL ALCOHOL

FIGURE 18

VAPOR PRESSURE CURVE
METHYL ALCOHOL

PRESSURE MM of Hg

TEMP °C

FIGURE 19

VAPOR PRESSURE CURVE
n - BUTYL ALCOHOL

PRESSURE MM OF Hg

TEMP °C

FIGURE 20