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VAPOR-LIQUID EQUILIBRIA DATA AND DISTILLATION PACKING EVALUATION AT HIGH VACUUM

BY

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ABSTRACT

Vapor pressure data and vapor-liquid equilibria data at 1-30 m.m. pressure are presented for benzyl alcohol and benzyl-n-butyl ether system. Activity coefficients for the system are symetrical, the Margules constants are $A_{1-2} = A_{2-1} = .301$. HETP values observed at a condenser pressure of 1 m.m. for 1/4" and 3/4" Berl saddles, 1" Intalox saddles, Fibre Glass Combination packings # 076 and # 476, and a Knitted Wire Mesh packing are presented as a function of the mass throughput and column pressure drop. At a condenser pressure of 1 m.m. the pressure drop per foot in terms of the mass throughput is observed for each packing. HETP values at high vacuum are greater than those observed in the same equipment at atmospheric pressure.

PURPOSE OF THE WORK

Vacuum fractionation of aromatic chain compounds is a method of purification in the Fine Chemical Industry. It is essential for quality and quantity of product that condenser pressures of from one to four millimeters of mercury be used. Performance characteristics of distillation packings under these conditions are scarce. The thesis presents operating characteristics of various distillation packings at high vacuum, and employs a binary test liquid of aromatic chain compounds. The purpose of this study is;

1. To determine if the vapor-equilibria data of these compounds may be handled by established methods.

2. To observe operating characteristics of various distillation packings under high vacuum conditions and to determine how they compare with available data in the literature.

SCOPE OF THE WORK

The thesis presents the selection and evaluation of a test liquid, and studies the operating characteristics of distillation packings at high vacuum and compares them with data in the literature.

The following topics are discussed in the test liquid study:

1. Selection of the test liquid.
2. Analysis of the test liquid.
3. Purification of the compounds.
4. Vapor pressure data of the pure compounds.
5. Correlation of the vapor pressure data.
6. Vapor-liquid equilibria data.
7. Correlation of the vapor-liquid equilibria data.
8. Calculation of an average vapor-liquid equilibria curve over the range of pressures investigated.
9. Calculation of a direct method of obtaining theorectical plates in a distillation unit operating at total reflux from analysis of the vapor and pot compositions.

Various packing performances at high vacuum are studied in terms of:

1. Calculation of HETP values.
2. Measurement of throughput rates and pressure drop data.
3. Comparison of experimental data on packing performances with data available in the literature.

FUNDAMENTAL THEORY AND PRESENT STATE OF KNOWLEDGE

Vapor pressure data of many compounds are available in the literature. Several methods employed in the correlation and extrapolation of vapor pressure data are; plots of the modified Clausius-Clapeyron equation (4), the Cox chart (5), the Duhring rule (6), and the Othmer plot (14).

The Clausius-Clapeyron equation may be used over small temperature ranges as follows:

$$\frac{d \ln p}{d T} = \frac{L}{RT^2}$$

Assuming that L (molal latent heat of vaporization) is constant over the temperature range to be used, the equation assumes the form,

$$d \ln p = \frac{L}{R} \frac{dT}{T^2}$$

Integrated form,

$$\ln P)_{P_0}^{P_1} = \frac{L}{R} \frac{1}{T})_{T_0}^{T_1}$$

Thus, a plot of ln p vs. 1/T will give a straight line as long as L remains constant.

Cox developed a method for hydrocarbons which gives a straight line relationship. The log of the vapor pressure of a family of hydrocarbons is plotted against an arbritrary temperature scale calibrated to give a straight line for the vapor pressure of water. He observed that curves of the same family of hydrocarbons pass through a common point.

Duhring's rule states that there is a linear relationship between the temperatures of two components exerting identical vapor pressures. This rule will hold for absolute or relative temperature scales. This rule is a variation of the Ramsay and Young relationship.

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + C(T_A' - T_B')$$

T_A', T_B' and T_A, T_B are absolute temperatures at which compounds A and B respectively, have identical vapor pressures. C is a constant which approaches zero as the two components are more closely related. Thus, the Duhring rule may be employed to correlate vapor pressure data using a reference substance. The error or deviation from a straight line will be a function of the relationships between the reference and test compounds.

Othmer's method, the logarithmic plot of the vapor pressure of a liquid against the vapor pressure of a reference liquid at the corresponding temperatures, gives straight lines over a wide range of temperatures. It offers a more accurate and convenient method for correlating vapor pressure data. Best results are obtained when a related reference substance is used. Water, however, is a convenient reference substance and gives a good correlation. The theoretical background for the Othmer method is based on the Clausius-Clapeyron equation and is derived as follows:

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \qquad \frac{d \ln p_R}{dT_R} = \frac{L_R}{RT_R^2} \qquad \text{if } T = T_R$$

$$\frac{R\ d \ln p}{L} = \frac{dT}{T^2} = \frac{dT_R}{T_R^2} = \frac{R\ d \ln p_R}{L_R}$$

$$\frac{d \ln p}{d \ln p_R} = \frac{L}{L_R} \quad \text{integrates to}$$

$$(1) \quad \ln p = \frac{L}{L_R} \ln p_R + C$$

Either form may be used, the latter being the more convenient. The relationship holds because the L/L_R remains constant through a wide range of temperatures. The Othmer plot may be used in the estimation latent heats of vaporization from the slope of the curve. Latent heat of vaporization may be estimated from the other methods also.

Vapor-liquid equilibria data may be predicted from an ideal solution providing the gas laws hold in the vapor phase. Raoult's law states (15) that the partial pressure of any component in the vapor is equal to the product of its mole fraction in the liquid and the vapor pressure of the pure component at the same temperature.

$$p_1 = P_1 x_1 \qquad p_2 = P_2 x_2$$

$$P y_1 = P_1 x_1 \qquad P y_2 = P_2 x_2$$

Thus, in an ideal binary solution, the relationship of the two components in the vapor and liquid is:

$$\frac{y_1}{x_2} = \frac{P_1}{P_2}\frac{x_1}{x_2}$$

The relative volatility, which is a measure of the difficulty of separation of compounds, is defined in the ideal solution as,

$$\alpha = \frac{P_1}{P_2} \qquad \frac{y_1}{y_2} = \alpha \frac{x_1}{x_2}$$

A convenient relationship for presenting y-x data is from the equation

$$\frac{y_1}{y_2} = \alpha \frac{x_1}{x_2} \qquad y_2 = 1 - y_1$$

$$x_2 = 1 - x_1$$

by rearrangement of the terms this form is obtained.

$$(2) \qquad y_1 = \frac{\alpha x_1}{1+(\alpha-1)x_1}$$

Few liquid systems follow Raoult's law. They are limited to:

1. Homologue series and isomers.

2. Certain other mixtures labeled as "quasi-ideal", classified by Ewell, Harrison and Berg (7).

3. For all non-ideal mixtures where any component approaches 100%.

Non-ideal liquid mixtures are approached using Raoult's law. Deviations from ideality are expressed as thermodynamically significant activity coefficients, as defined for ideal gasses,

$$(3) \quad P y_1 = \gamma_1 P_1 x_1 \text{ or } P y_2 = \gamma_2 P_2 x_2$$

$$\frac{y_1}{y_2} = \frac{\gamma_1}{\gamma_2} \frac{P_1}{P_2} \frac{x_1}{x_2}$$

The relative volatility for a non-ideal binary mixture is defined as,

$$(4) \alpha_{1-2} = \frac{\gamma_1}{\gamma_2} \frac{P_1}{P_2}$$

Vapor-liquid relationships are:

$$\frac{y_1}{y_2} = \alpha_{1-2} \frac{x_1}{x_2} \qquad \text{and}$$

$$\text{Eq. } (2) \quad y_1 = \frac{\alpha_{1-2}\, x_1}{1+(\alpha_{1-2}-1)\, x_1}$$

Activity coefficients vary with concentration and temperature. The fundamental thermodynamic equation relating activity coefficients and composition is the Gibbs-Duhem relation (8) at constant temperature and pressure,

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{TP} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{TP} + - - = 0$$

For binary mixtures, ${}_1x_1 = - x_2$ Therefore,

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_T = - x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_T$$

These equations relate the slopes of the activity coefficient curves on a log against composition plot. The equations are cumbersome to handle and integrated forms are available, namely the Margules equation (10) and the Van Laar equation (20).

The Margules equation is given below as a two constant equation. If necessary the number of constants may be increased to accurately correlate data, however, two constants are sufficient for most cases.

$$(5) \quad \log \gamma_1 = x_2^2 \;(A_{1-2} + 2\, x_1 \,(A_{2-1} - A_{1-2}))$$

$$(6) \quad \log \gamma_2 = x_1^2 \;(A_{2-1} + 2\, x_2 \,(A_{1-2} - A_{2-1}))$$

One method of evaluating the two constants Margules equation is, from the following derivation:

$$\log \gamma_1 = x_2^2 \;(A_{1-2} + 2 \,(A_{2-1} - A_{1-2})\, x_1)$$

$$\frac{\log \gamma_1}{x_2^2} = A_{2-1} + 2(A_{2-1} - A_{1-2})\, x_1 \qquad x_i = 1 - x_2$$

$$(7) \quad \frac{\log \gamma_1}{x_2^2} = 2\, A_{2-1} - A_{1-2} - 2(A_{2-1} - A_{1-2})\, x_2$$

$$(8)\quad \frac{\log \gamma_2}{x_1^2} = 2A_{1-2} - A_{2-1} - 2(A_{1-2} - A_{2-1})x_1$$

The values of A_{1-2} and A_{2-1} may be read from plots of $\frac{\log \gamma_1}{x_2^2}$ vs. y_2 plotted from left to right and from a plot of $\frac{\log \gamma_2}{x_1^2}$ vs. x_2 plotted right to left, by alligning $x_1 = 0$ with $x_2 = .5$ and $x_1 = .5$ with $x_2 = 0$, and reading the values at $x_1 = 0$ and $x_1 = .5$ respectively. This may be seen from the original equations that when

$$x_1 = 0 \quad \frac{\log \gamma_1}{x_2^2} = A_{1-2} \qquad x_2^2 = 1 \quad \therefore \log \gamma_1 = A_{1-2}$$

and when

$$x_2 = 0 \quad \log \gamma_2 = A_{2-1} \qquad x_1^2 = 1 \quad \therefore \log \gamma_2 = A_{2-1}$$

This method is illustrated in the Presentation of data.

The Van Laar equations are:

$$(9)\quad \log \gamma_1 = \frac{A_{1-2}}{\left(1 + \frac{A_{1-2}x_1}{A_{2-1}x_2}\right)^2}$$

$$(10)\quad \log \gamma_2 = \frac{A_{2-1}}{\left(1 + \frac{A_{2-1}x_1}{A_{1-2}x_2}\right)^2}$$

A_{1-2} and A_{2-1} are the same as given in the Margules equation. A method for obtaining the Van Laar constants is as follows. The terms of the equations are rearranged to give the following forms.

(11)
$$\frac{1}{\sqrt{\log \gamma_1}} = \frac{\sqrt{A_{1-2}}}{A_{2-1}} \frac{x_1}{x_2} + \frac{1}{\sqrt{A_{1-2}}}$$

(12)
$$\frac{1}{\sqrt{\log \gamma_2}} = \frac{\sqrt{A_{2-1}}}{A_{1-2}} \frac{x_2}{x_1} + \frac{1}{\sqrt{A_{2-1}}}$$

A plot is made of $1/\sqrt{\log \gamma_1}$ vs. x_1/x_2, and $1/\sqrt{\log \gamma_2}$ vs. x_2/x_1. The values of A_{1-2} and A_{2-1} are obtained by adjusting the two curves until the respective values agree.

In the symmetrical case the Margules equation and the Van Laar equation give identical curves of the activity coefficients. Differences in the two equations occur as the ratio of A_{1-2} to A_{2-1} changes from unity.

Fractionation is a distillation in which contact is made between the vapor from the pot and liquid condensed from this vapor. The transfer of material and interchange of heat results in a greater enrichment of the more volatile component than could be secured in a single distillation with the same amount of heat. Returning condensed vapors to the still is called reflux. The reflux ratio is defined as the ratio of the liquid take off to the liquid returned to the column. Total reflux is the return of all of the condensed vapors to the column.

Methods used to effect fractionation in a distillation unit are:

1. Bubble cap plate towers are a series of trays mounted

horizontally in a column. Bubble caps, which allow vapor to pass through a liquid seal and prevent the liquid to flow down through the vapor riser, are spaced in the tray. A height of liquid is maintained on each tray by weirs, sealing the vapor from the tray below. The excess liquid is carried to the tray below by downspouts. The vapor makes contact with the liquid as it rises through the liquid seal of the bubble cap.

2. Sieve tray and perforated plate columns are a series of trays mounted horizontally and spaced at intervals in the column. The liquid and vapor make contact as the vapor rises through the holes in the plates. Weirs and downspots are used to handle the liquid.

3. Packed columns employ a variety of packings designed to effect an efficient transfer of material. In general, the smaller the size packing, the smaller the column height will be required. Those forming continuous films rather than dropwise formation are seen to give better efficiencies. Packed columns have applications in:

   a. Columns under one foot in diameter where high efficiencies are required for low height.
   b. Where low pressure drop is desired as in vacuum distillation.
   c. Where low holdup is required as in batch distillation.

Distillation packings are easily evaluated at total reflux, and the performance data presented in terms of Height of a Transfer Unit or Height Equivalent to a Theoretical Plate.

HTU is the height of packing in a given column necessary to produce one transfer unit. A Transfer Unit is defined from the equation:

$$N_{OG} = \int_{y_2}^{y_1} \frac{dy}{y^{*}-y} \quad \text{Gas Film controlling} \qquad N_{OL} = \int_{x_2}^{x_1} \frac{dx}{x-x^{*}} \quad \text{Liquid Film controlling}$$

In distillation the transfer units are usually calculated based on the gas film controlling. The integration may be handled by several methods suggested in the literature or by graphical methods. HETP is defined as the height of packing in a given column required to produce one theoretical plate. A Theoretical Plate is defined as a condition of equilibrium between a boiling liquid and its vapor. HETP is a more convenient method for evaluating packing performance. The relation of HETP to HTU is given for the following conditions:

1. If the operating line and equilibrium line are parallel, HETP = H_{OG}.

2. If the operating line and equilibrium line are straight but are not parallel,

$$\frac{HETP}{H_{OG}} = \frac{(m\,G_m/L_m) - 1}{\ln\,(m\,G_m/L_m)} \qquad m = \frac{dy^{*}}{dx}$$

The McCabe Thiele method (11) for calculating theoretical plates relates the equilibrium conditions of the solution to the operating conditions in the column, with the following assumptions:

1. Sensible heat changes through the tower are negligible in comparison with the latent heats.

2. The molal latent heats of all of the compounds are equal.

3. The heat of mixing of the components is negligible.
4. Heat losses from the tower are negligible.

A material balance around the top of the column and the n th tray, relates the operating conditions in the column in terms of vapor and liquid concentration of one component. At the top, numbering the trays from the top down,

$$V_{n+1} = L_n + P$$

V_{n+1} = Vapor Rising to the n+1 tray.

L_n = Liquid leaving the n th tray.

P = Product leaving the top.

In terms of one component in a two component system,

$$V_{n+1} y_{n+1} = L_n x_n + P x_p$$

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{P}{V_{n+1}} x_p$$

$$R = \frac{L_n}{P} \qquad L_n = R\,P \qquad V_n = (R+1)\,P$$

$$(13) \quad y_{n+1} = \frac{R}{R+1} x_n + \frac{1}{R+1} x_p$$

A similar derivation may be made from a material balance around the reboiler. The trays are numbered from the bottom up.

$$y_n = \frac{V/B + 1}{V/B} x_{m+1} - \frac{1}{V/B} x_B$$

These equations when plotted on an y-x type curve are called operating lines and represent the operating conditions in the column. When operating a column at total reflux these lines become identical and have a slope of 1.0, passing through the points, y_1 & x_1 = 0, and y_1 & x_1 = 1. If the equilibrium curve for a binary solution is plotted on the same y-x plot, conditions are fulfilled for the theoretical plate, thus, liquid and vapor compositions may be stepped off in horizontal and vertical steps, each complete step representing a theoretical plate.

Thus, at total reflux, if samples are taken of the vapor at the top of the column and liquid in the reboiler, the number of theoretical plates in the still may be calculated. The number of plates in the column is found by subtracting the one plate for the reboiler and the condenser from the total number of plates in the still.

$$(14) \qquad N = N_T - 1$$

The HETP of the packing is obtained by dividing the length of the packing by the number of plates in the column.

$$(15) \qquad HETP = \frac{L}{N}$$

Performance data is available on a variety of packings in the literature. HETP or H_{OG} values are listed for many packings in Perry's Handbook (16). Recently Murch (13) presented a general correlation of HETP values with; throughput, tower diameter, relative volatility, liquid viscosity, liquid density, and three constants predicted from experimental data.

$$HETP = K_1 \; G^{K_2} \; d^{K_3} \; h^{1/3} \; \frac{\alpha \mu}{\rho}$$

HETP = height equivalent to a theoretical plate, inches.

G = mass velocity of the vapor, lb./hr./ft.

d = tower diameter in inches.

α = relative volatility.

μ = liquid viscosity - centipoises.

ρ = liquid density - grams/cc.

Average values from top and bottom.

K_2 = an expoential constant applied to the mass velocity term G. This constant is the numerical slope obtained when G is plotted against HETP on logarithmic coordinates.

K_1 = proportionality constant, obtained directly from experimental data.

K_3 = an exponential constant applied to the tower diameter. This constant is the numerical slope of the line obtained when tower diameter is plotted against HETP on a logarithmic plot. Murch reports an accuracy of ± 10% in calculating the HETP values of the packings investigated. The effect of pressure was not included in the correlation because the data in the literature were scattered and did not give any definite trend.

Pressure drop data and methods of correlation are available in the literature. Flow of a single fluid through a uniform packed bed is correlated by Chilton and Colburn (2) and Brown (1). Pressure drop as a function of the mass rate at different rates are correlated by Forshet (18), Tillson (19), and many others. Loading and flooding velocities have been correlated by Tillson (19) and many others (17). The flooding velocity is defined physically as that point in the operation of a column where the vapor rising up the column holds up the liquid coming down the column. It is recognized by an increase in column holdup and pressure drop. This is seen from a logarithmic plot of the pressure drop against the gas mass velocity. The pressure drop is approximately proportional to the square of the gas velocity (9), as the gas rate is raised the ratio becomes greater than the square, this is defined as loading. Further increase of the gas rate will increase the proportion, this is the flooding point. Loading is physically described as the complete wetting of the packing.

DESCRIPTION OF THE EQUIPMENT

Figure 11 shows a drawing of the distillation unit which was used in purifying the test compounds and running experimental data on the packings. Descriptions of the components of the unit are:

1. Pot - 12 liter glass flask with 1-75/105 ball joint (to column), 1-24/40 tapered joint, a thermometer well, electrically heated insulated jacket controlled by a rheostat.

2. Columns- 2, one six feet by two and seven-eighths inches in diameter, and one four feet in length with the same diameter, all glass.

3. Still head - all glass, with magnetically controlled reflux splitter.

4. Condenser - all glass, mounts on an angle of approximately 30 degrees, coil inside, condensate runs back to the splitter.

5. Receiver - Standard vacuum receiver.

6. Manometers - two, one for vapor pressure and one for pot pressure

7. Sampling device - glass tube to the pot beneath the liquid level, connected to a standard vacuum receiver.

8. Vacuum source - mechanical vacuum pump (Duo-Seal), in series with a air bleed port and a liquid air vapor trap.

Figure 2 shows the Othmer Still (15) with attachments for vacuum operation. The pressure was measured with a McLeod gauge (Stokes). The vacuum source was the same as for the still.

Table 13 lists descriptions of the various packings.

All the refractive index readings were made on a Bausch and Lomb Refractometer, the temperature was kept constant with a constant temperature bath.

OPERATING TECHNIQUES

The benzyl alcohol and benzyl-n-butyl ether were purified in the distillation equipment shown in Figure 11. They were fractionated at a 10/1 reflux ratio through six feet of 1/4" Berl saddles. The column was first brought to flooding conditions and then operated at conditions just below flooding. Ten per cent fractions were taken and bulked according to refractive index. A condenser pressure of one millimeter was used in each distillation. The benzyl alcohol was an N. F. grade before fractionation. The benzyl-n-butyl ether was a plant fractionated grade before fractionation.

Vapor pressure data and the vapor-liquid equilibria data were measured in the Othmer still, Figure 2. The pressures in the Othmer still were measured with the McLeod vacuum gauge, this gauge was overhauled and calibrated by the Stokes Co. before this investigation was begun. The temperatures were measured on a 0-200 degree, in one degree divisions, thermometer. This thermometer was calibrated with a standard .1 degree division thermometer and was found to be correct within the precision with which it could be read.

In collecting the vapor pressure data, a charge of 200 cc. of purified material was used. The pressure was set by regulating the flow of air through two stopcocks at a port between the vacuum pump and the trap. It was found that if the system was tight, excellent control could be maintained using this system. The still was maintained at adiabatic conditions by lagging with cotton cheese cloth and electrical heating tape. The material was heated using a platinum wire coil immersed in the liquid. Equilibrium was assumed when the temperature remained constant for a period of from 15 to 20 minutes at a distillation rate of from one to two seconds per drop of distillate. This temperature and pressure were taken as the vapor pressure data. A constant check was maintained on the pressure throughout each run.

Vapor-liquid equilibria data were run at total pressures of 20 mm and check runs were made at 5 mm. Approximately 200 cc of solution was charged to the Othmer still. The total pressure on the system was maintained as above. An average of 15 minutes was taken to fill the receiver. Equilibrium conditions were attained after one and one-half hours or 6 recycles of the distillate. This was checked by repeat runs of the same composition. The method of sampling was to vent the still to the atmosphere and drain samples of the vapor and pot by gravity. A close check was made when venting the still to see if any mixing of the solutions was caused. This method proved very satisfactory because any loss of either compound due to evaporation was eliminated. The low vapor pressure of these compounds at these temperatures, prevent their vaporization at atmospheric pressure. The samples were analyzed on the Bausch and Lomb Refractometer. The sample size was about 2 cc.

All the runs on packing performance were made at total reflux. Approximately 2 liters of test solution was charged to the pot and the system was evacuated. The column was brought to a visual flooding condition and then the heat was regulated to give the pressure drop desired. Equilibrium was obtained in approximately 3 hours after the pressure drop was set. This was checked by runs for a longer equilibrium time under the same condition.

Samples of the vapor were obtained by directing the flow of the refluxing liquid into a vacuum receiver. The receiver was quickly isolated from the still and vented to atmospheric pressure. Samples of the reboiler solution were obtained by raising the pressure in the still to approximately 50 mms. to allow the liquid to be pushed into an evacuated receiver. This receiver was quickly isolated and vented. The quick venting was necessary to prevent evaporation in the vacuum receiver. Vaporization losses at atmospheric pressure were assumed to be negligible because of the low vapor pressure of the compounds at these temperatures. Samples were analyzed by refractive index in a Bausch and Lomb refractometer at 20°C.

After the material in the pot was sampled, the still was allowed to return to the previous operating condition. The through-put was measured at about 30 minutes after the still returned to the operating condition, by directing the flow of the reflux into a graduated receiver for a measured period of time, usually one minute.

CALCULATION OF THE AVERAGE EQUILIBRIUM CURVE

In the range of pressure that has been investigated, there are two ratios which determine the relative volatility.

1. The relation of the vapor pressures of benzyl alcohol and benzyl-n-butyl ether which varies with temperature.

2. The ratio of the activity coefficients which varies with composition.

Average relative volatilities at various compositions are calculated, and it is shown that the average curve over the range of from 1-30 mm, is accurate for the calculation of a vapor liquid equilibrium diagram to be used in the packing evaluation.

A sample calculation of an equilibrium curve at 20 mm total pressure is as follows. The relative volatility is

$$\text{Eq. (4)} \quad \alpha_{1-2} = \frac{\gamma_1}{\gamma_2} \frac{P_1}{P_2}$$

The relationship of $1/2$ is read directly from figure 8. The change of P_1/P_2 at this pressure is small and an average value is used. The ratio of the vapor pressures at the boiling points of the two compounds $P_1/P_2 = 1.360$ and 1.368; the average is 1.364. The sample calculation at .1 mf benzyl alcohol the relative volatility is $= 1.804 \quad 1.364 = 2.46$. Using the equation $y = \frac{\alpha x}{1 + (\alpha - 1)x}$ a vapor composition of the more volatile component (benzyl alcohol) is calculated. Tables 8, 9, and 10 list the calculations for the x-y curves for total pressures of 20 mm., 10 mm. and 1.35 mm. Figure 9 shows these curves and indicates that little error would be realized with an average value of the relative volatility was used. Table 11 lists the calculations of the arithmetic average relative volatility. This average value is plotted against mole fraction of Benzyl Alcohol, (Figure 10). This curve is used in the calculation of the equilibrium curve used in the packing evaluation.

METHOD OF CALCULATING THE NUMBER OF PLATES IN A STILL

At a constant relative volatility the Fenske equation (16) is used to calculate the number of theoretical plates in a distillation unit operating at total reflux. When the relative volatility changes, a graphical method by stepping off the plates on a y-x curve is used. A more convenient form of this method is to plot the number of theoretical plates against the function used as the analysis. Figure 11 shows the number of plates at total reflux vs. the refractive index of the benzyl alcohol, benzyl-n-butyl ether solution. It relates the distance required per theoretical plate in terms of liquid composition.

The calculations are as follows: A liquid composition is selected which is at the extreme range to be used. The refractive index of this composition is read from figure 2. The vapor in equilibrium with this liquid is calculated from equation

$$\text{Eq. (2)} \quad Y_1 = \frac{\alpha_{1-2}\, x_1}{1 + (\alpha_{1-2} - 1)x_1}$$

The value of α is read from figure 10 which shows the average variation over the pressure range tested of the relative volatility with composition. This vapor composition is also the composition of the liquid on the next plate as the column is operated at total reflux. The refractive index of this composition is read from figure 1. The difference in refractive index represents 1 theoretical plate in the separation. Table 12 lists completed calculations used to construct figure 12.

PRESENTATION AND INTERPRETATION OF DATA

Selection of the test solution of benzyl alcohol and benzyl-n-butyl ether was based on the following:

1. It gave a reasonable number of theoretical plates at a good spread of composition difference.

2. Enabled analysis by refractive index having an average of 5 divisions on the instrument for each mol percent of benzyl alcohol in the test solution.

3. Both compounds are typical of those required in the purpose of the work, namely high boiling aromatic compound prevalent in the Fine Chemicals Industry.

Table I shows the constants of purified benzyl alcohol and benzyl-n-butyl ether. Figure I shows the refractive index at 20°C. of the solution vs mol fraction of benzyl alcohol. Benzyl alcohol was taken as the reference compound because it was the more volatile component in the test solution used in packing evaluation. The vapor pressure data were obtained from the literature and experimentally in an Othmer still. No vapor pressure data was available in the literature on benzyl-n-butyl ether. Table 2 lists experimental data and data obtained from the literature. Figure 3 shows the Othmer Plot of the vapor pressure data of both compounds based on Eq. (1). Water was used as the reference substance. All the data available correlated well on the Othmer plot. Table 3 and Figure 4 show the correlated vapor pressure in mm. of mercury against temperature in degrees centigrade.

Presentati

Table 4 lists vapor-liquid equilibria data taken at 20 mm. total pressure and the check runs at 5 mm. An azeotrope was observed at .70 mol fraction benzyl alcohol.

The data were checked for thermodynamic consistency using Margules equation and also tested with the Van Laar equation. Activity coefficience are calculated,

Eq. (3) $\gamma_1 = \frac{P_1}{P}\frac{y_1}{x_1}$ $\gamma_2 = \frac{P_2}{P}\frac{y_2}{x_2}$

and are listed in table 5. A corrected temperature was used in reading the P_1 and P_2 values off the vapor pressure curve. The temperatures obtained from figure 5 which is a plot of the boiling point of the solution at 20 mm. total pressure vs mol fraction benzyl alcohol. This correction was necessary because a small error in reading the temperature results in a large error in the vapor pressure. This is caused by the steep vapor pressure curves typical of high molecular weight compounds.

Correlation of the data to the 2 constant Margules equation discussed in the theory section was made as follows: Table 6 lists calculations necessary to make the plot shown in figure 6 using Eqs. (7) and (8). The results showed the Margules equation to be symetrical for this system. Thus the constants A_{1-2} and A_{2-1} are equal. The curve drawn was weighted because of the azeotropic points which are more reliable. The constants for the Margules equation for this system are $A_{1-2} = A_{2-1} = .301$. The activity coefficient curve thermodynamically correlated to the Margules equation has the form Eq. (5) $\text{Log}\,\gamma_1 = .301X_2^2$ Eq. (6) $\text{Log}\,\gamma_2 = .301X_1^2$

A check was made on these constants by applying them to the Van Laar equation using the method described in the theory section, Eqs. (11 and 12). Table 7 shows the necessary calculations and figure 7 shows the plot of

$$\frac{1}{\sqrt{\log \gamma_2}} \text{ vs } \frac{x_2}{x_1} \quad \text{and} \quad \frac{1}{\sqrt{\log \gamma_1}} \text{ vs } \frac{x_1}{x_2}$$

This compares favorably with the correlation of the Margules equation. For the symetrical case the Van Laar and Margules equations are identical.

Figure 8 shows the correlated activity coefficient curves with experimental data as points. This curve is assumed to hold in the range of 1 to 30 mm. pressure and 50 to 120°C. on the basis of the check points and the change in temperature from the range at 20 mm. pressure is not excessive. A comparison of activity coefficients for iso propyl ether and iso propyl alcohol (12) in the temperature range of 68 to 82°C. are $A_{1-2} = .42$ and $A_{2-1} = .60$. In general it can be said that the activity coefficients were consistent with these values since the heavier molecular weight compound usually show lower activity coefficients. In a homologus series this relationship is more prevalent.

The McCabe-Thiele method of calculating theoretical plates was assumed to be accurate because four assumptions mentioned in the theory section were adhered to. Molal heats of vaporization are practically equal. This was derived from the Othmer Plot from which a relation that the slope of the vapor pressure curve is the ratio of the latent heat of the compound and the reference compound. Benzyl alcohol and benzyl-n-butyl ether have slopes close to each other, thus practically equal heats of vaporization. Heat losses were minimized by careful lagging of the still. Sensible heat changing and heats of mixing were assumed to be negligible.

Experimental values of total plates, pressure drop, and through put data are presented in table 14. The 1/4" Berl saddles and both Fibre Glass combination packings were operated up to flooding conditions. Overloading the condenser prevented rates up to flooding with the other packing. The shorter column was used in the more efficient packing to stay within the limits of the test solution. Calculated H. E. T. P. and mass velocity values are listed in table 15. Figure 13 shows the variation of H. E. T. P. with the mass velocity and Figure 14 shows H. E. T. P. values vs. pressure drop for 1" intalox and 3/4" Berl saddles. Figures 15 and 16 show the H. E. T. P. with mass velocity and pressure drop respectively for 1/4" Berl saddles and Fibre Glass Combination #076 and #476.

Comparison of the H. E. T. P. values obtained at high vacuum and those from the literature is listed in table 16. Only 1/4" Berl saddles and Fibre Glass Combination packings #076 and #476 data can be assumed to be usable. The 3/4" Berl saddles and 1" Intalox saddles could not be brought to flooding conditions and also should be operated in a larger size column for a fair comparison.

Pressure drop data on the packings are listed in table 17. Figure 17 shows a plot of the pressure drop, in terms of inches of water per foot of packing.vs. the mass rate of flow,

G. The data for #476 Fibre Glass Combination packing showed visual flooding below the #076 packing which is a more dense packing. This was probably caused by a slight difference in vacuum at the condenser. It is logical to assume that #076 would flood before #476 because it has less free volume. The data could not be correlated with any of the methods in the literature. The effect of the gas density and superficial velocity are the factors which caused the deviation.

CONCLUSION

It is concluded that -

1. Vapor pressure and vapor-liquid equilibrium data, at 1 to 30 m.m. pressure of aromatic chain compounds similar to those evaluated may be successfully correlated by methods available in the literature. Results obtained in this paper validate this assumption. Experimental precision must be exercised to obtain good data. This is caused by the rapid change of vapor pressure with temperature, a characteristic of high molecular weight compounds.

2. HETP data are higher than those reported by the same packing operated at atmospheric pressure. In comparing the 1/4" Berl saddles and the two Fiber Glass Combination packings, increases of from 20 to 100% in HETP values are observed in operation at vacuum as compared with atmospheric pressure. Both series of runs were made in the same equipment, the differences being the test liquid or the relative volatility of the systems and the operating pressures. The Fiber Glass Combination packings operated at high efficiency over a wider range of gas mass velocity than the 1/4" Berl saddles.

3. Pressure drop appears to be an exponential function, which varies with types of packing, of the mass rate G. This data could not be correlated with methods in the literature to give reasonable results. The reason for this may be in the effect of the gas density or high superficial velocity on these correlations.

SUMMARY - SUGGESTION FOR FUTURE WORK

The benzyl alcohol - benzyl-n-butyl ether Test was evaluated in an Othmer still at high vacuum. Various relationships are presented.

1. Analysis - A spread 1.5400 - 1.4867 of refractive index at 20° gave 1 mole % per .0005 divisions.
2. Vapor pressure data - are presented from 1 to 760 m.m.
3. Activity coefficients are correlated at 20 m.m. pressure and are symmetrical, having a Margules and a Van Laar constant of A = .301.
4. Vapor-liquid equilibrium data at 1.35, 10 and 20 m.m. are calculated from vapor pressure and activity coefficient relationships.

Distillation packings, 3/4" and 1/4" Berl saddles, Fibre Glass Combination (York # 076, # 476), Knitted wire mesh and 1" Intalox saddles, are evaluated as follows:

1. HETP values are related to G, the mass throughput.
2. HETP values are related to P, pressure drop.
3. Pressure drop data is presented.
4. HETP values are compared with values at atmospheric pressure.

Suggestions for future work on distillation packing performance at the high vacuum range of 1 - 100 m.m. in terms of HETP and throughput data are discussed.

1. The effect of pressure on HETP has not been definitely established in the literature. An expanded study varying types of packings, diameter of column, and

heights of column in the pressure range of 1 - 100 mm. appears necessary to make a correlation. This correlation might be included in an equation as offered by Murch (12) to enable extrapolation of packing performance at atmospheric pressure.

2. Throughput performance data in the high vacuum range are scarce. A study varying liquid and gas rates at pressures in the high vacuum range to determine normal, loading and flooding conditions would be of considerable importance.

NOMENCLATURE

A = Constant in Margules and Van Laar equations.

B = Bottoms product.

G = Mass gas rate/area of column.

HETP = Height equivalent to one theorectical plate.

H_{OG} = Height of a transfer unit based on the overall gas film.

L = Mass liquid rate/area of column.

L = Length of the column.

L = Molal latent heat of vaporization.

L = Liquid down the column.

m = Slope of the equilibrium curve.

N = Plates in the column.

N_T = Total plates in the still.

N_{OG} = Number of transfer units based on the overall gas film.

N_{OL} = Number of transfer units based on the overall liquid film.

P = Overhead product.

P = Pressure.

p = Partial pressure.

R = Gas constant.

R = Reflux ratio - vapor returned to the column/product withdrawn.

T = Absolute temperature.

V = Vapor rate up the column.

y = Vapor composition - mol fraction.

y^* = Vapor equilibrium concentration.

x = Liquid composition - mol fraction.

x = Liquid equilibrium concentration.

α = Relative volatility.

γ = Activity coefficient.

ρ = Density.

SUBSCRIPTS:

A = Different compounds.

B = Different compounds.

1 = Different components.

2 = Different components.

R = Reference compounds.

BIBLIOGRAPHY

1. Brown, "Unit Operations", Wiley and Sons, (1950).
2. Chilton and Colburn, Trans. Amer. Ins. Chem. Eng.,26,178,(1931).
3. Chilton and Colburn, Ind. & Eng. Chem., 27, 255, (1935).
4. Clausius - Claperyron Equation, Perry, "Chemical Engineers Handbook", McGraw Hill, (1950).
5. Cox, Ind. & Eng. Chem., 15, 592, (1923).
6. Duhring's Equation, Perry, "Chemical Engineers Handbook", Third Edition, McGraw Hill, (1950).
7. Ewell, Harrison and Berg, Ind. & Eng. Chem., 36, 871, (1944).
8. Gibbs-Duhem, Lemis and Randall " Thermodynamics and the Free Energy of Chemical Substances. "- McGraw-Hill, New York, (1923).
9. Leva, "Tower Packing and Packed Tower Design" U.S. Stoneware (1951).
10. Margules Equation, Carlson and Colburn Ind. & Eng. Chem. 34, 581, (1942).
11. McCabe and Theile, Ind. & Eng. Chem., 17, 605, (1925).
12. Miller and Bliss, Ind. & Eng. Chem,, 32, 123, (1940).
13. Mursh, Ind. & Eng. Chem. 45, 2616, (1953).
14. Othmer, Ind. & Eng. Chem., 32, 841, (1940).
15. Othmer, Ind. & Eng. Chem.,
16. Perry, "Chemical Engineers Handbook," Third Edition, McGraw-Hill, (1950).
17. Raoults Law, Perry's Handbook.
18. Sarchet, Trans. Amer. Inst. Chem. Eng. 38, 283, (1942).
19. Tillson, "Thesis" Massachusetts Institute of Technology, (1939).
20. Van Laar Equation, Carlson and Colburn Ind. & Eng. Chem. 34, 581, (1942).

APPENDIX

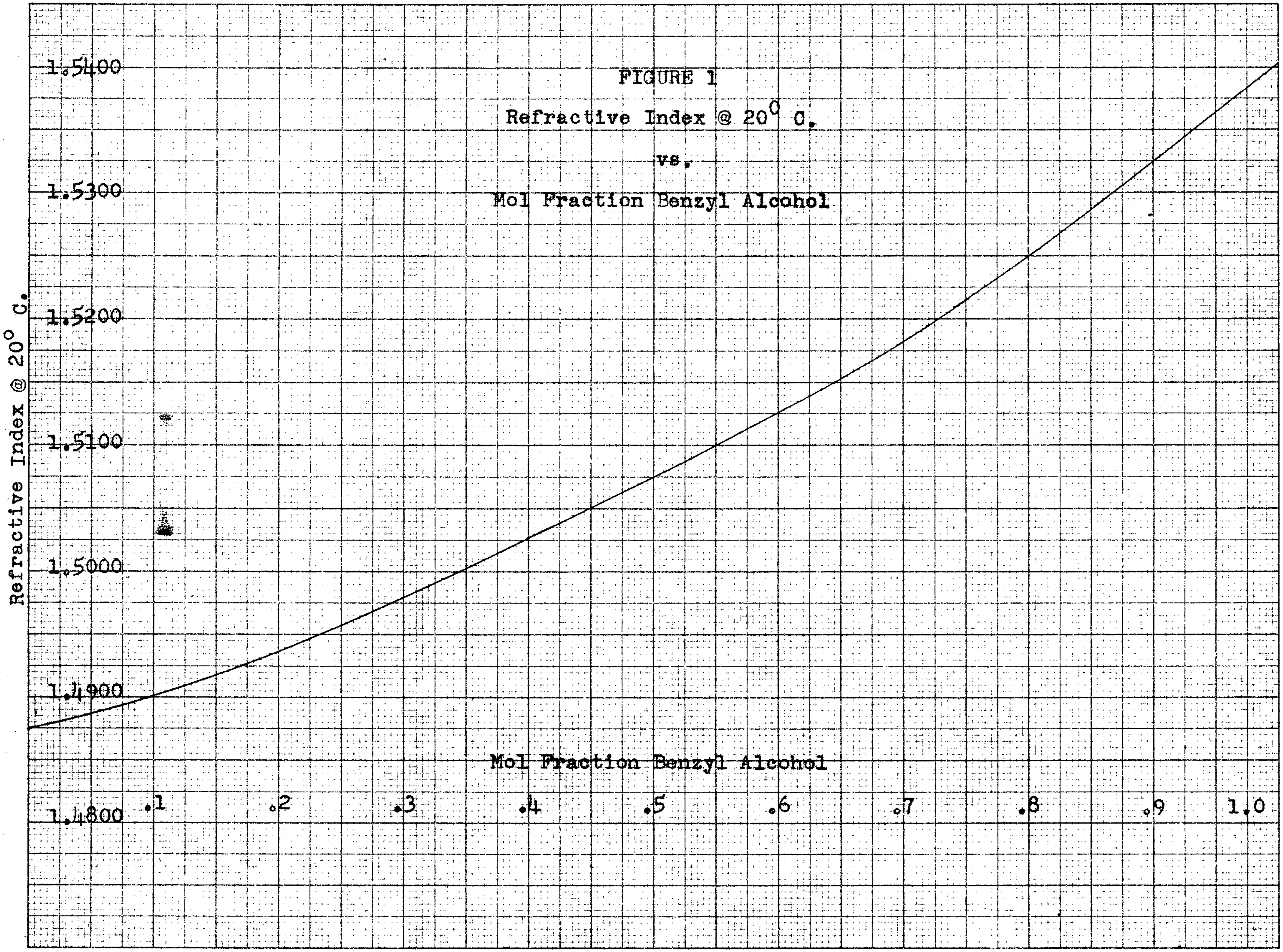


FIGURE 1

Refractive Index @ 20° C.

vs.

Mol Fraction Benzyl Alcohol

FIGURE 2.

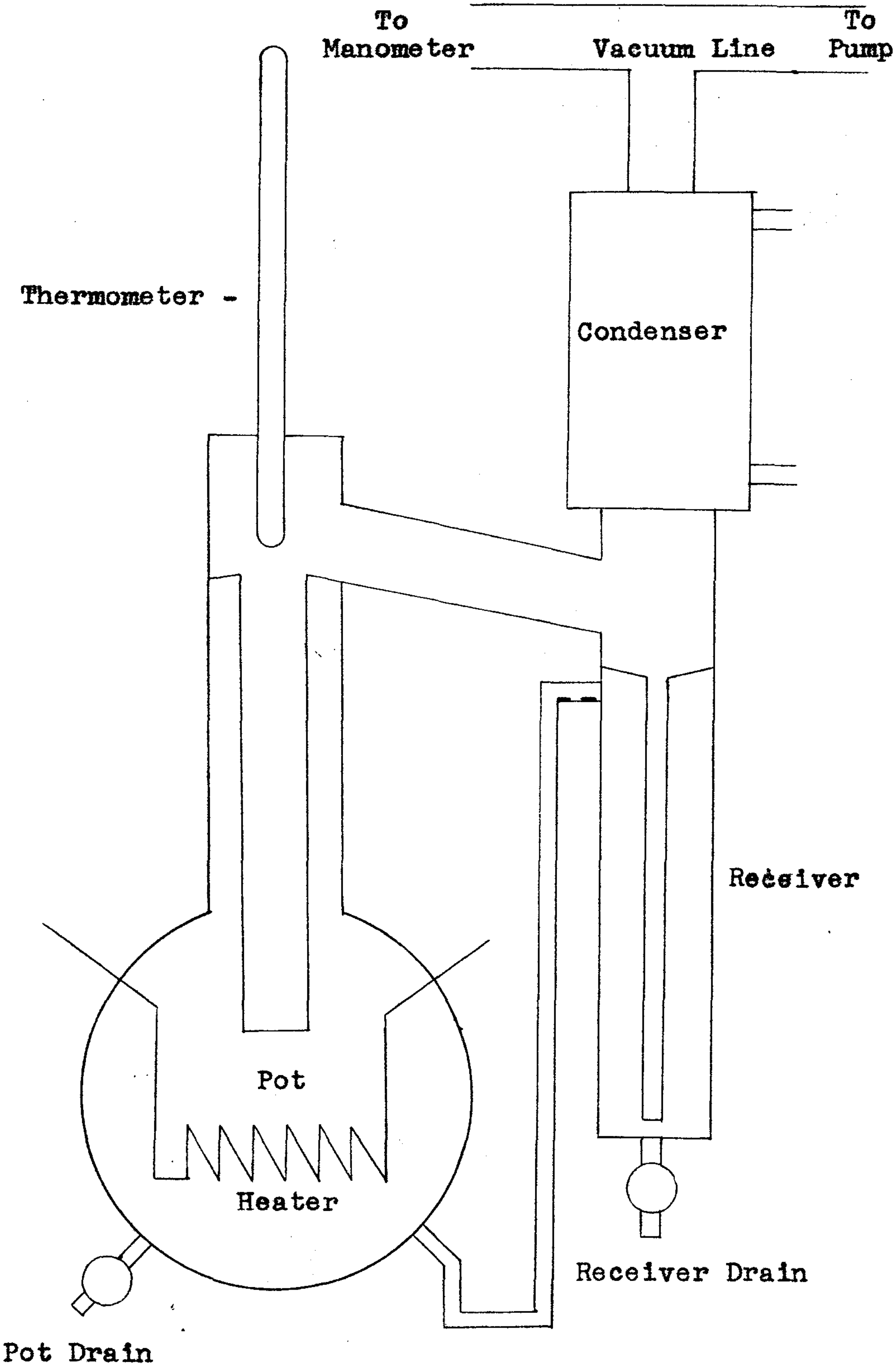


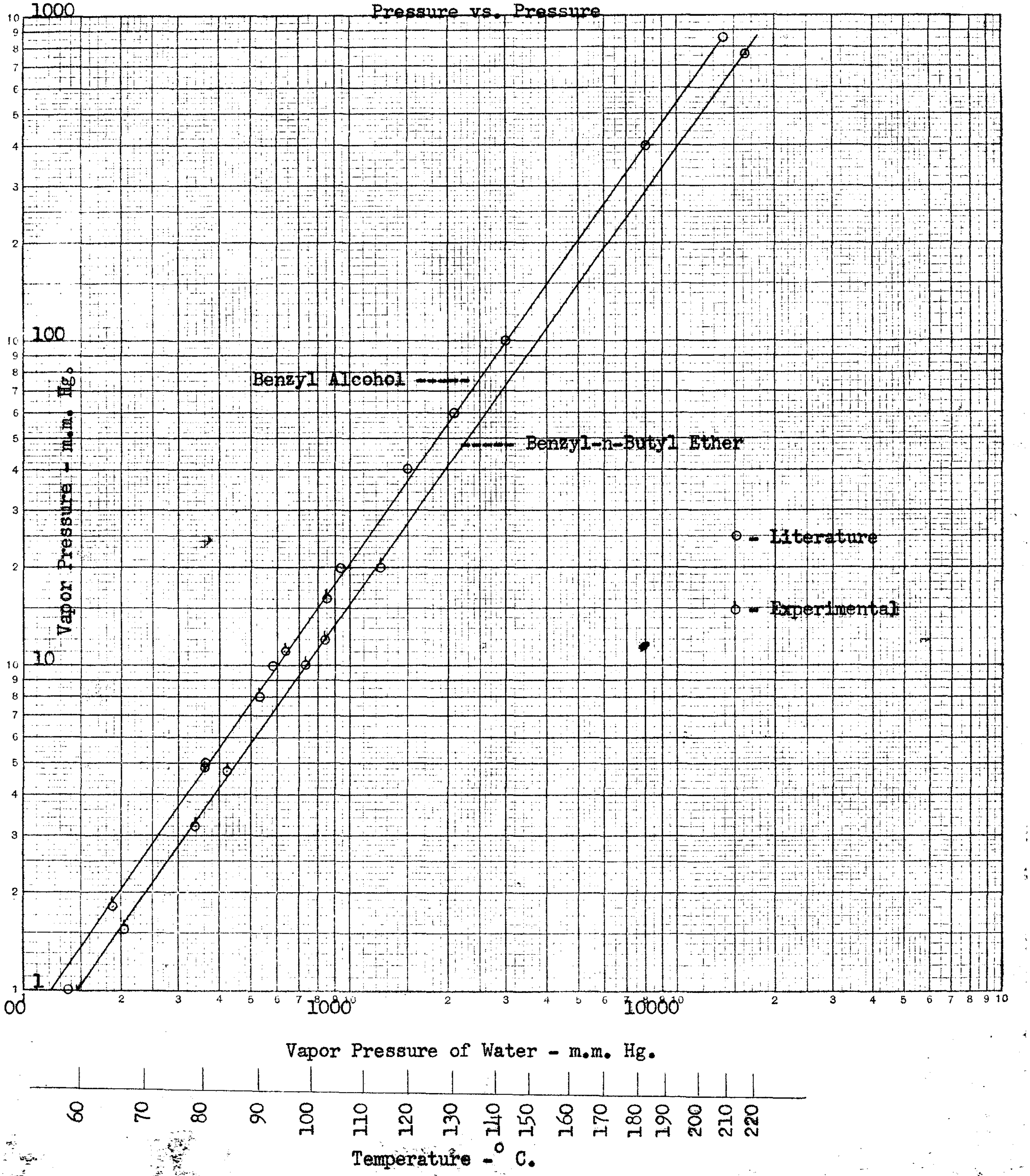
Diagram of the Othmer Still with Modifications to Vacuum

FIGURE 3

Othmer Plot of the Vapor Pressure Data

of Benzyl Alcohol and Benzyl-n-Butyl Ether

Pressure vs. Pressure



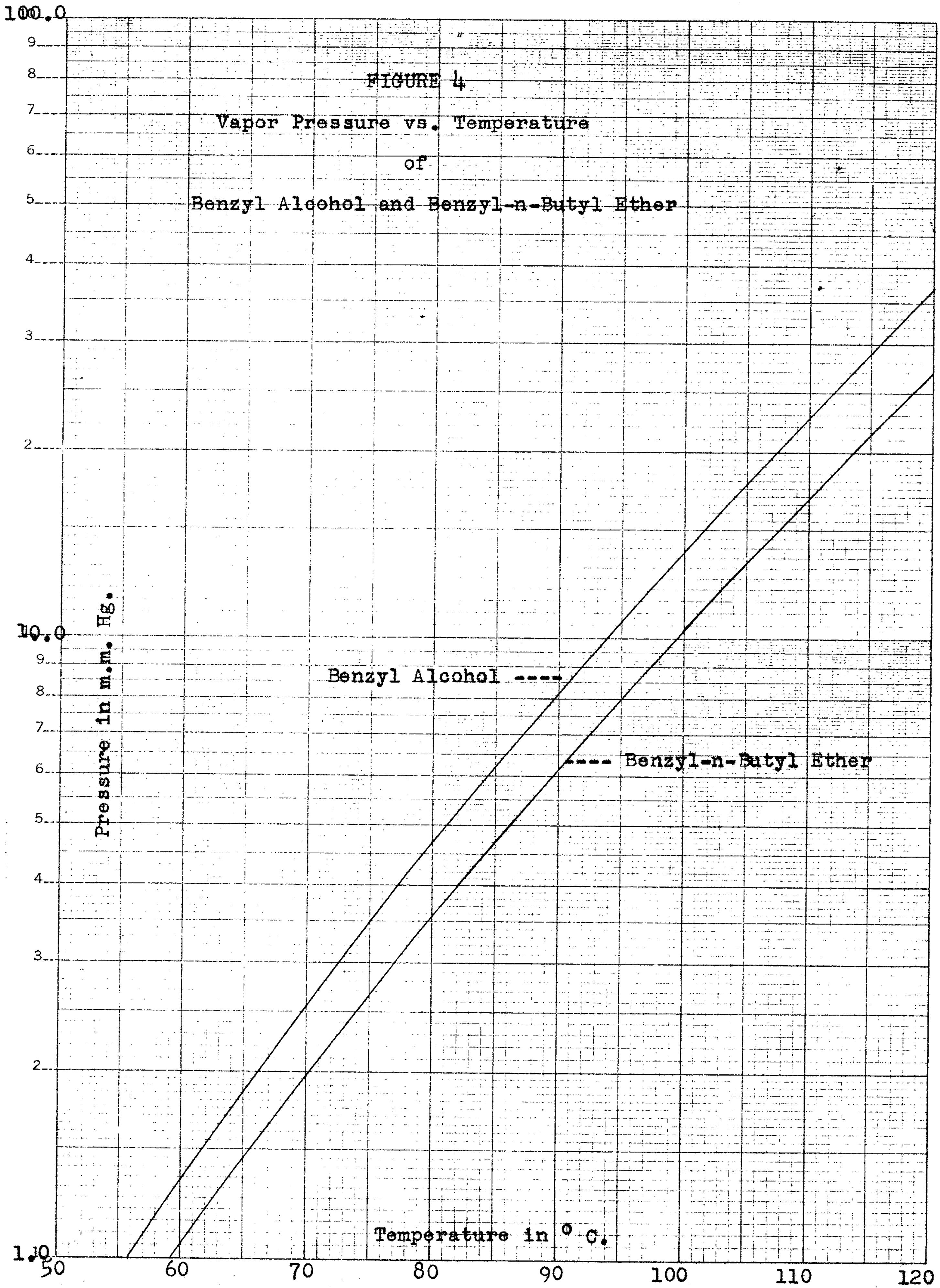


FIGURE 4

Vapor Pressure vs. Temperature

of

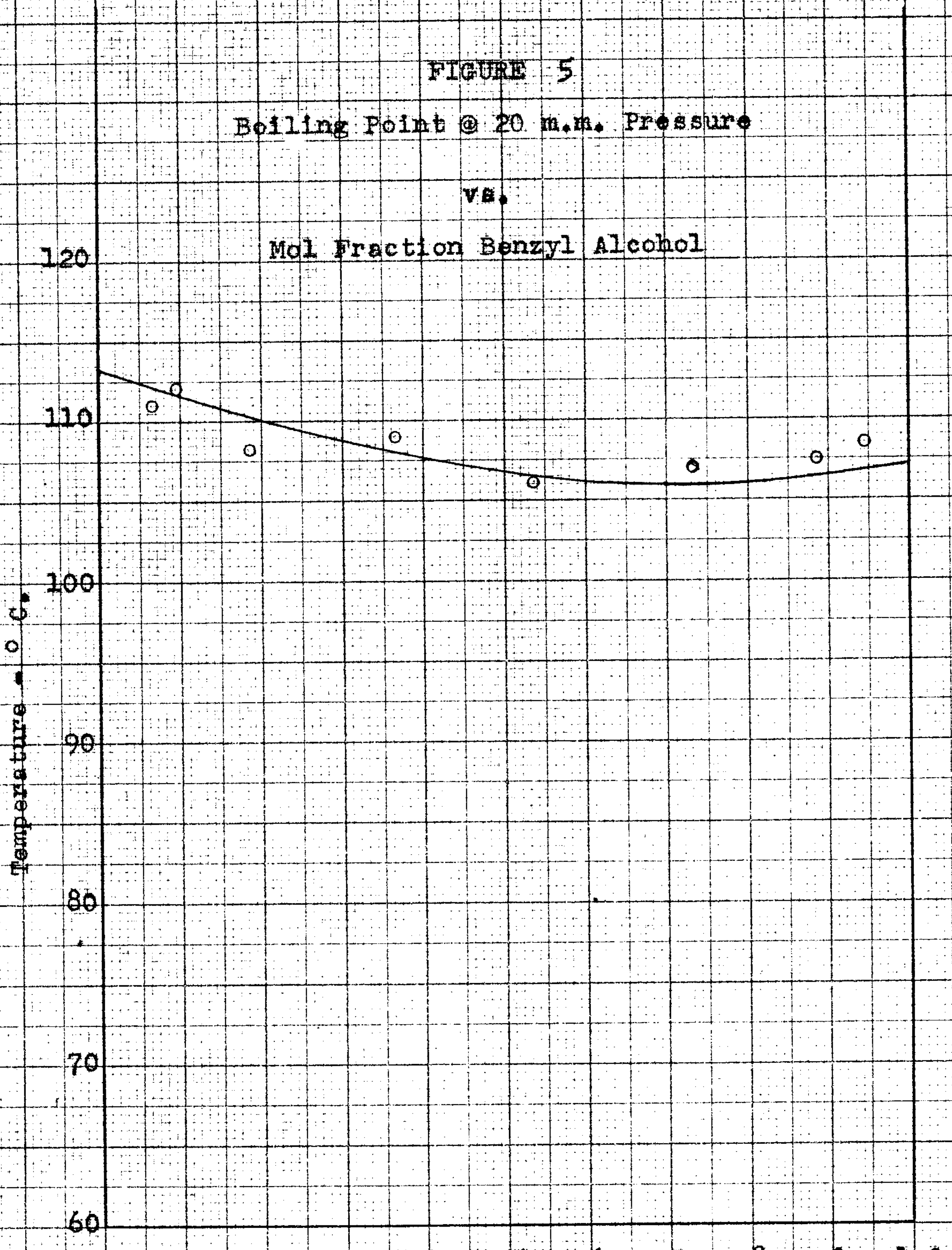
Benzyl Alcohol and Benzyl-n-Butyl Ether

FIGURE 5

Boiling Point @ 20 m.m. Pressure

vs.

Mol Fraction Benzyl Alcohol



Mol Fraction Benzyl Alcohol

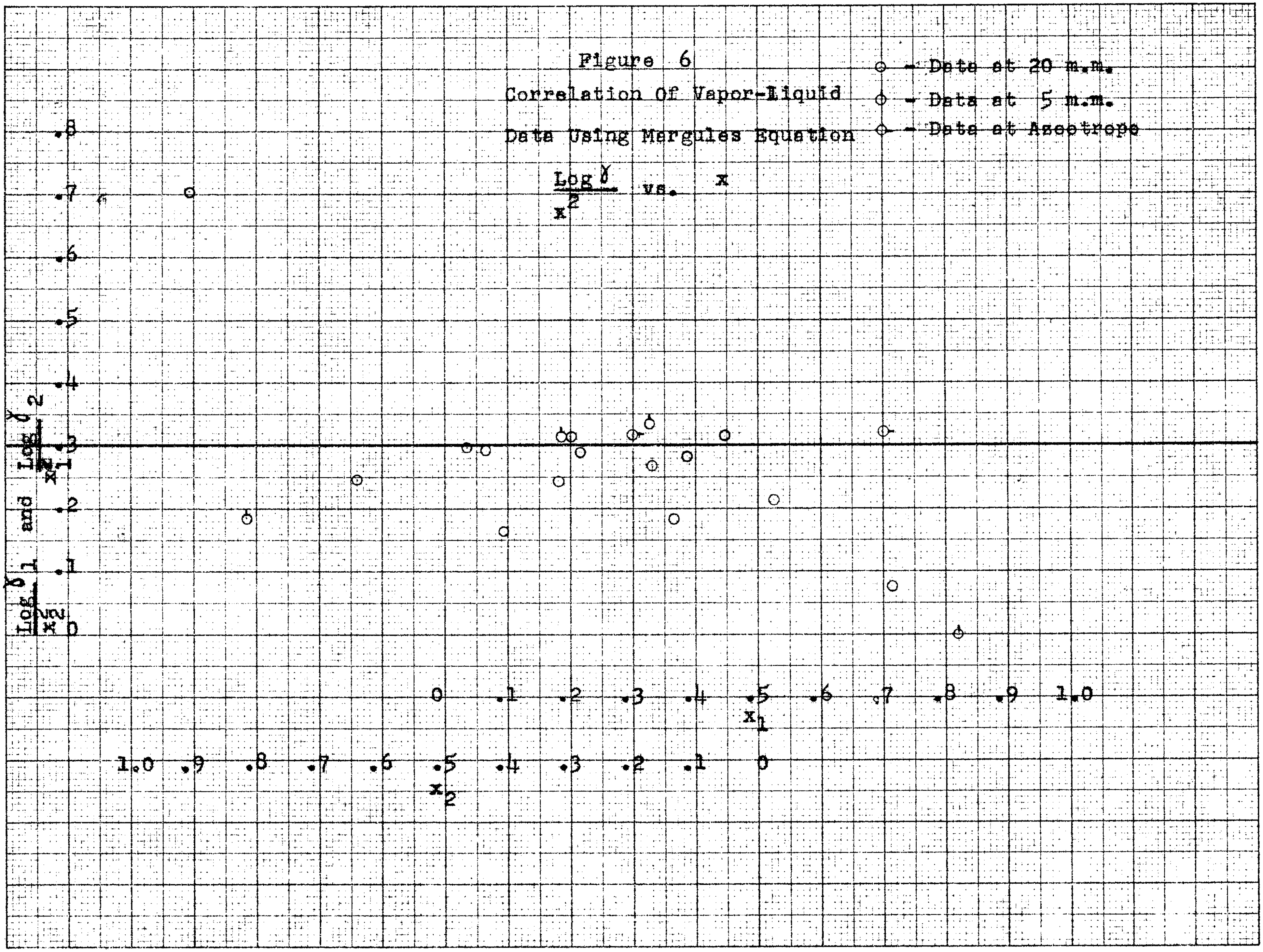
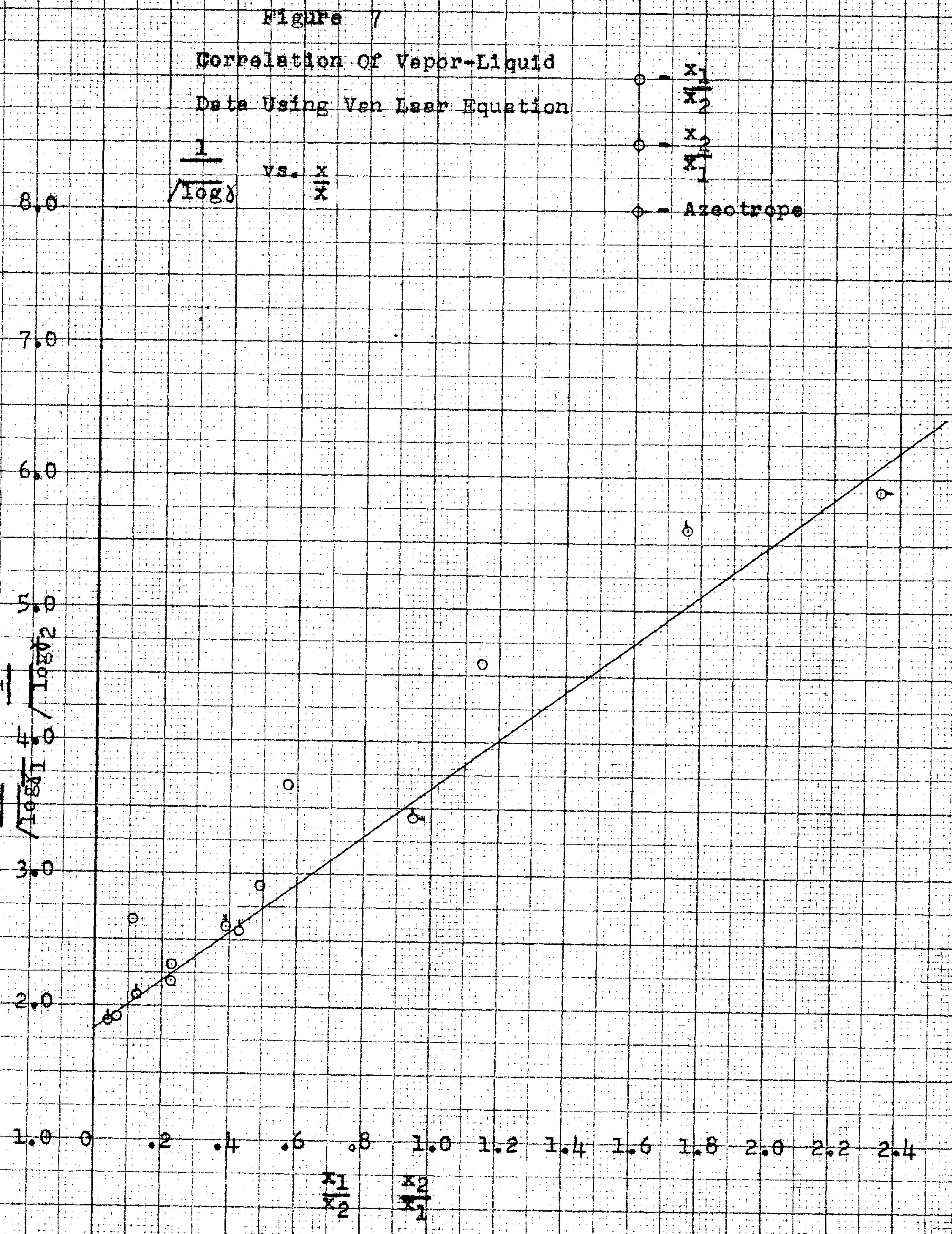


Figure 6

Correlation Of Vapor-Liquid Data Using Margules Equation

$\frac{\text{Log } \gamma}{x^2}$ vs. x

Figure 7
Correlation Of Vapor-Liquid
Data Using Van Laar Equation
$\frac{1}{\sqrt{\log\gamma}}$ vs. $\frac{x}{x}$
○ - $\frac{x_1}{x_2}$
○ - $\frac{x_2}{x_1}$
○ - Azeotrope
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
$\frac{1}{\sqrt{\log\gamma_1}}$ $\frac{1}{\sqrt{\log\gamma_2}}$
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
$\frac{x_1}{x_2}$ $\frac{x_2}{x_1}$

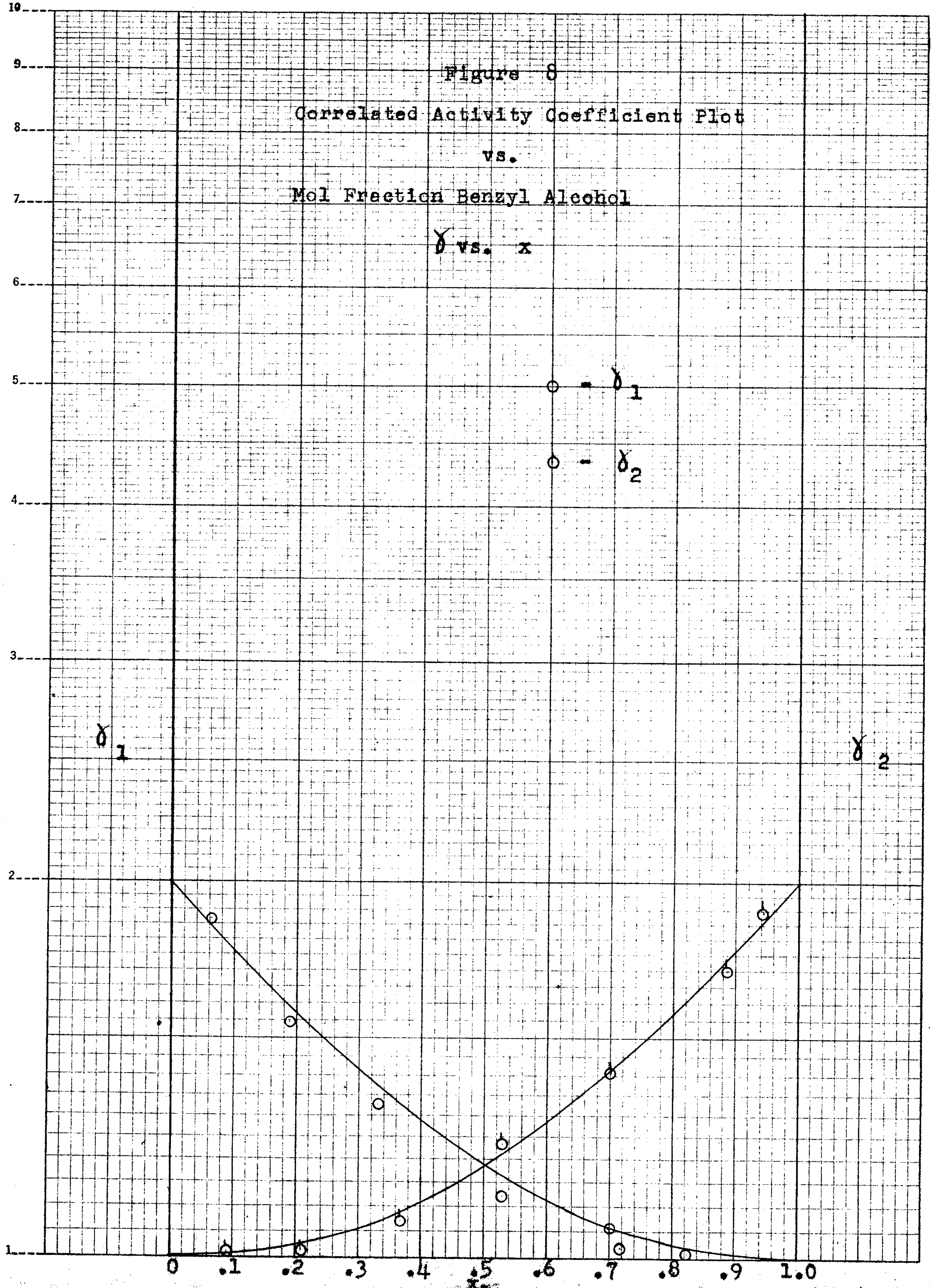


Figure 8

Correlated Activity Coefficient Plot

vs.

Mol Fraction Benzyl Alcohol

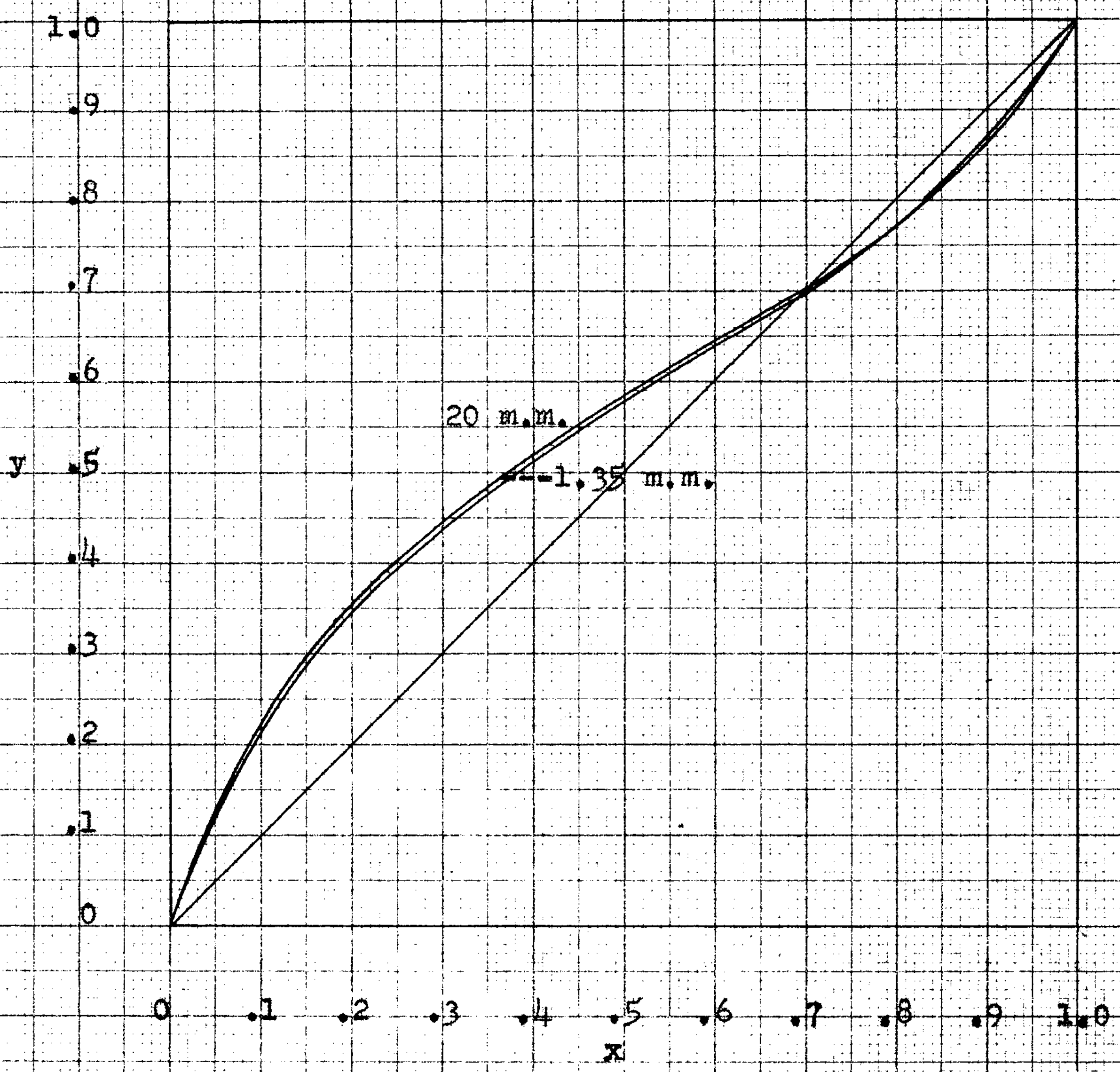
γ vs. x

Figure 9

Vapor-Liquid Data at

1.35, 10 and 20 m.m.

y vs. x



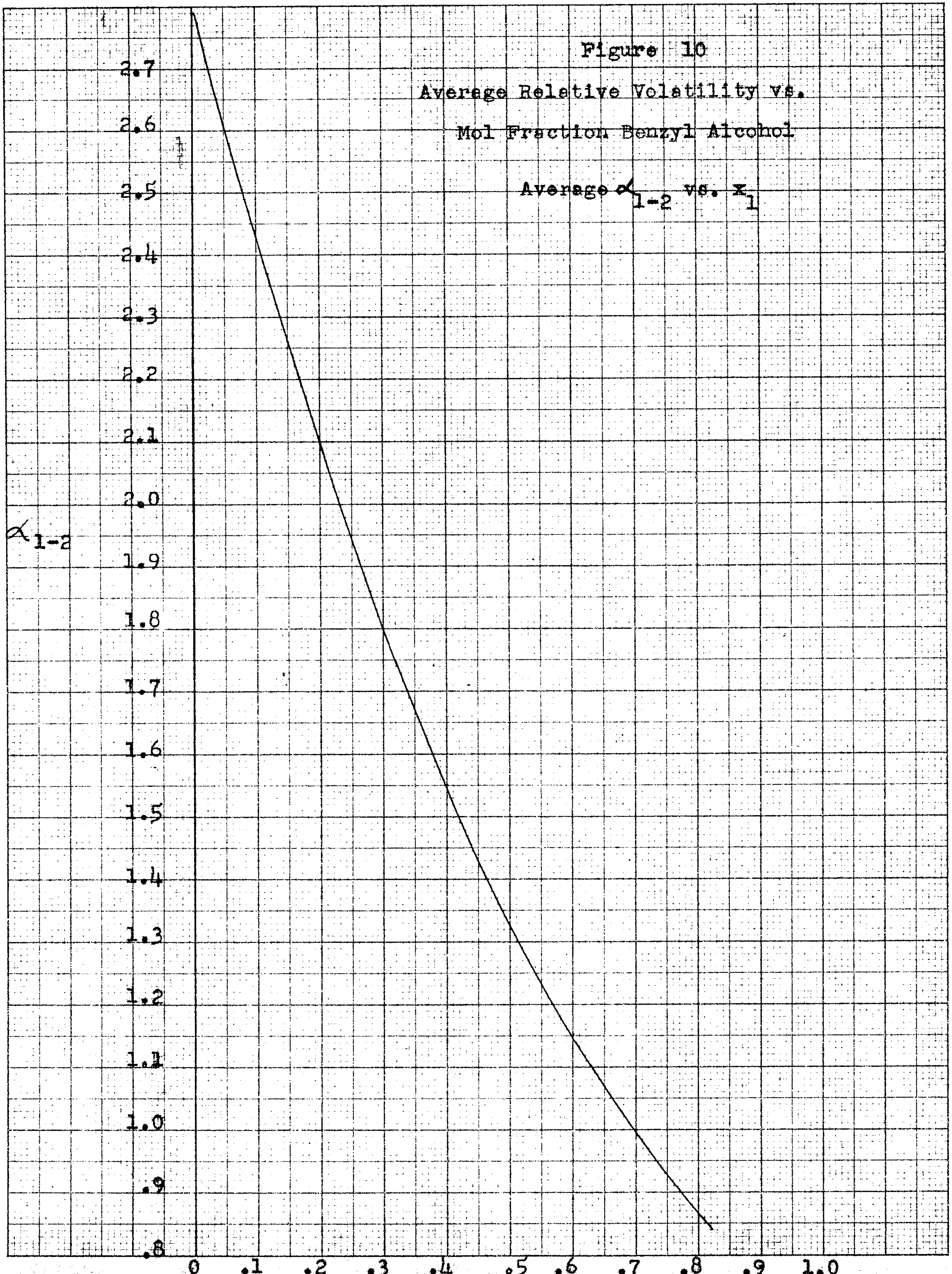
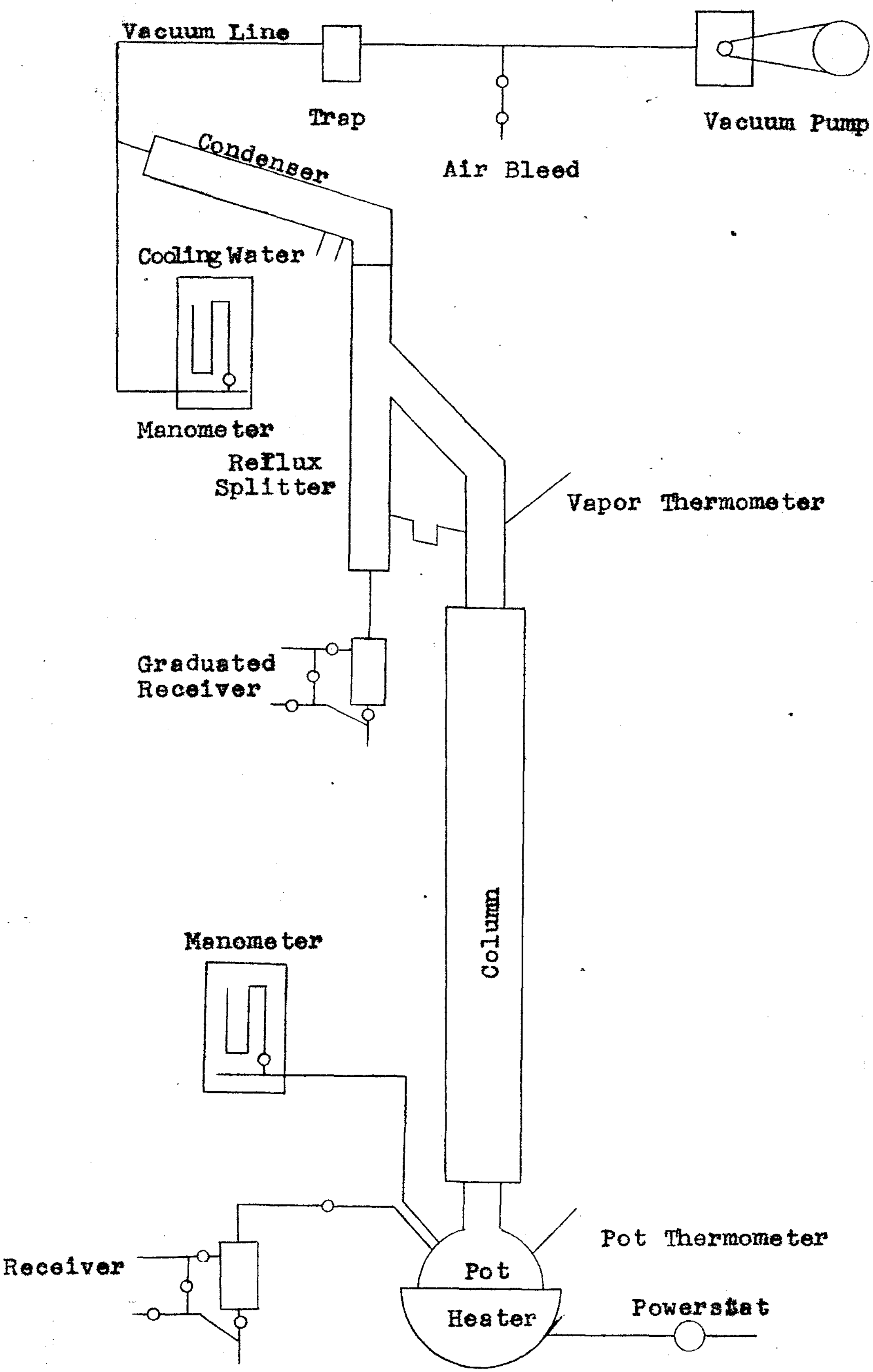


Figure 10
Average Relative Volatility vs.
Mol Fraction Benzyl Alcohol
Average α_{1-2} vs. x_1
α_{1-2}
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

Figure 11

Still Used In Packing Efficiencies



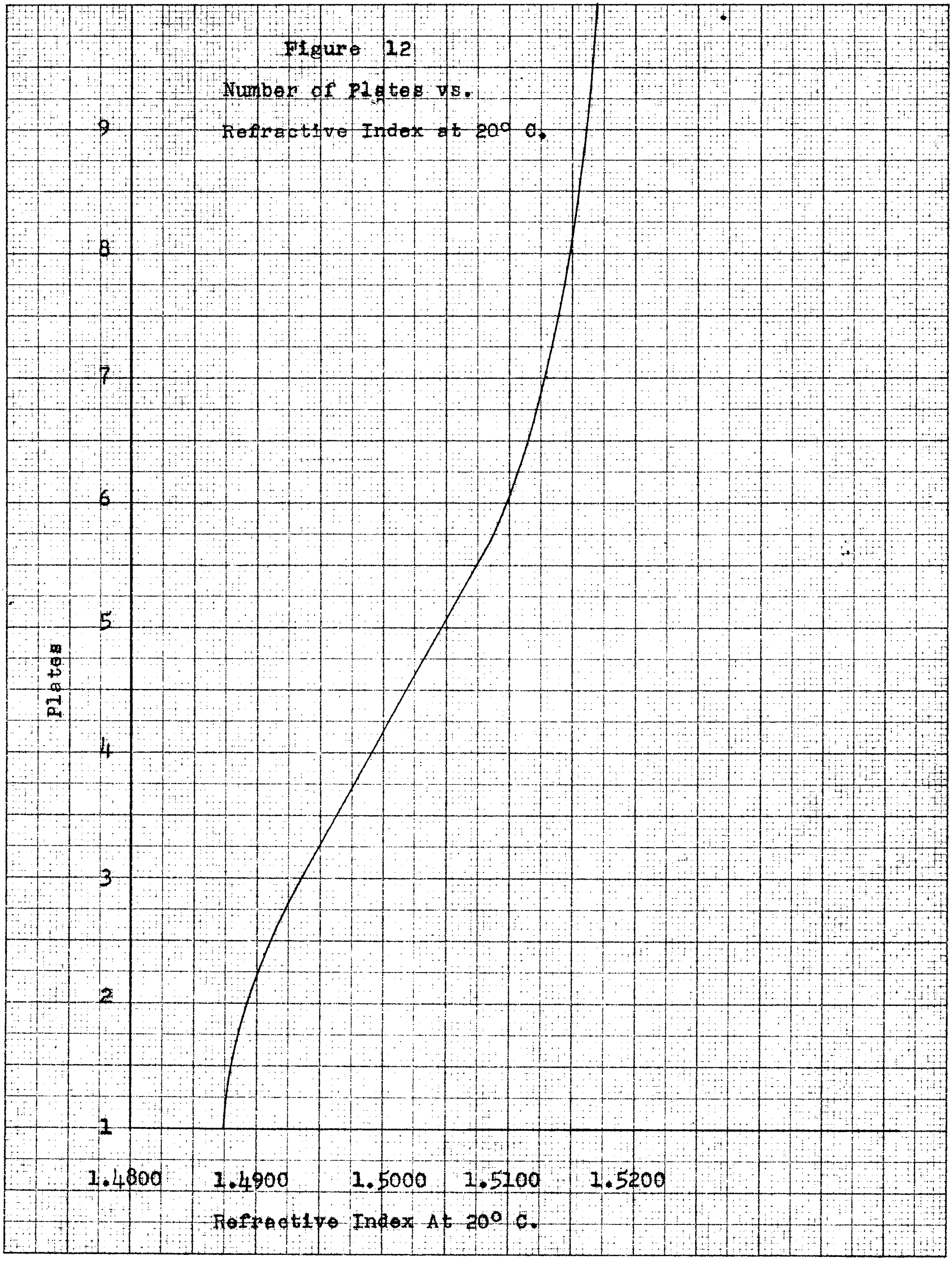


Figure 12

Number of Plates vs.

Refractive Index at 20° C.

Figure 13

HETP vs. G for 1" Intalox and 3/4" Berl Saddles

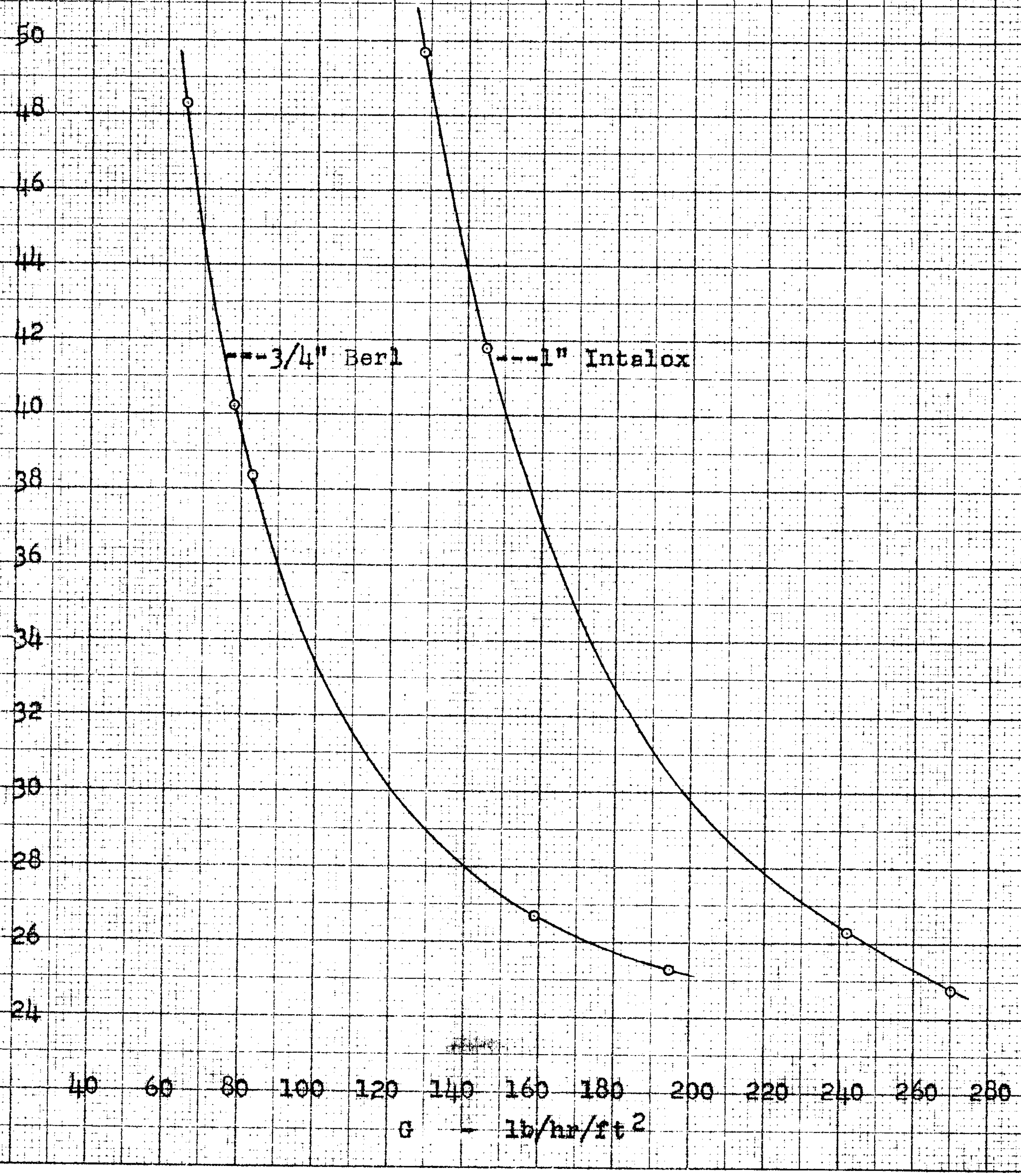


Figure 14
HETP vs. Pressure Drop for 1"
Intalox and 3/4" Berl Saddles.

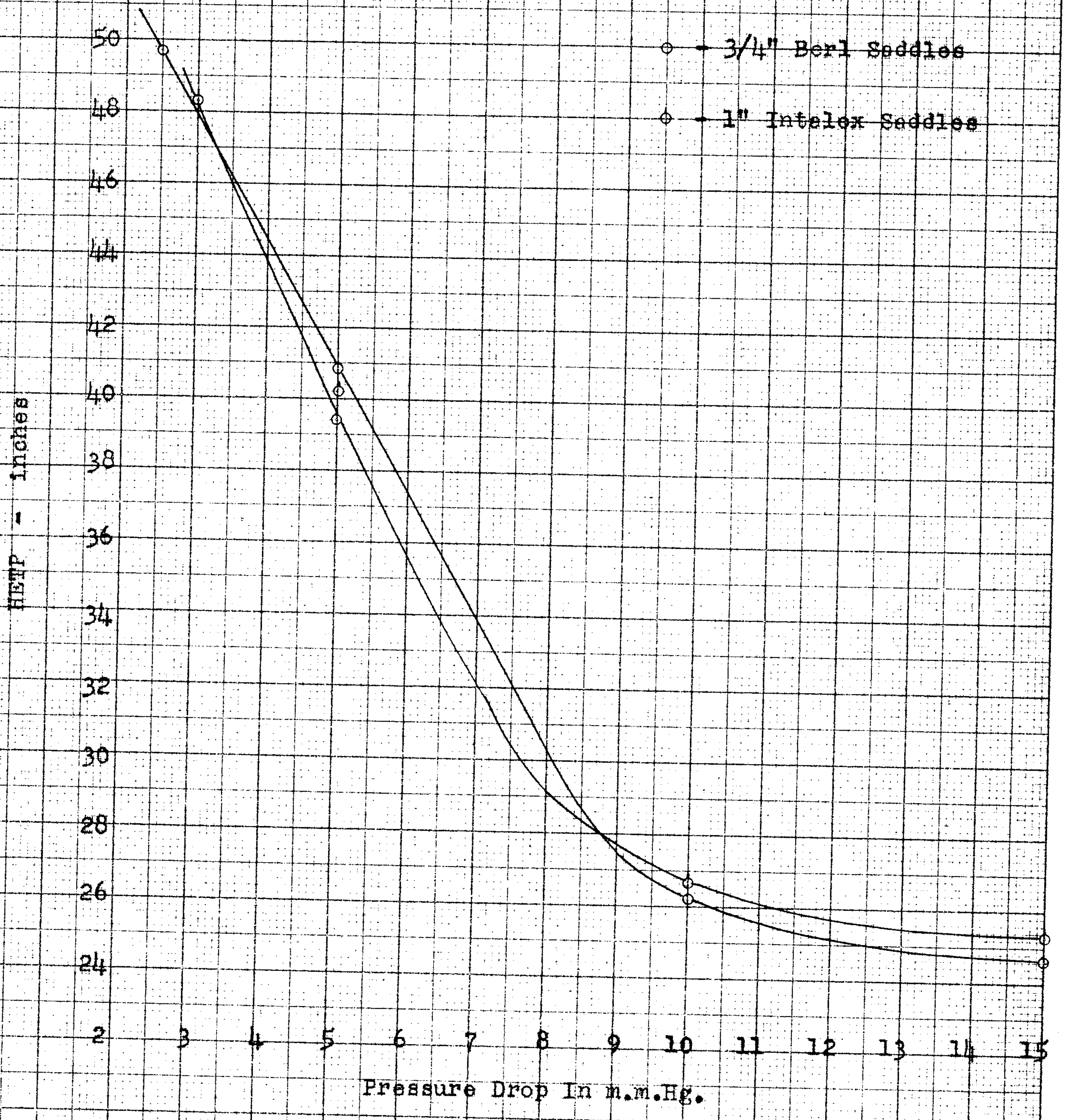


Figure 15

HETP Values vs. G for 1/4" Berl Saddles, Fibre Glass Combination # 076 and # 476.

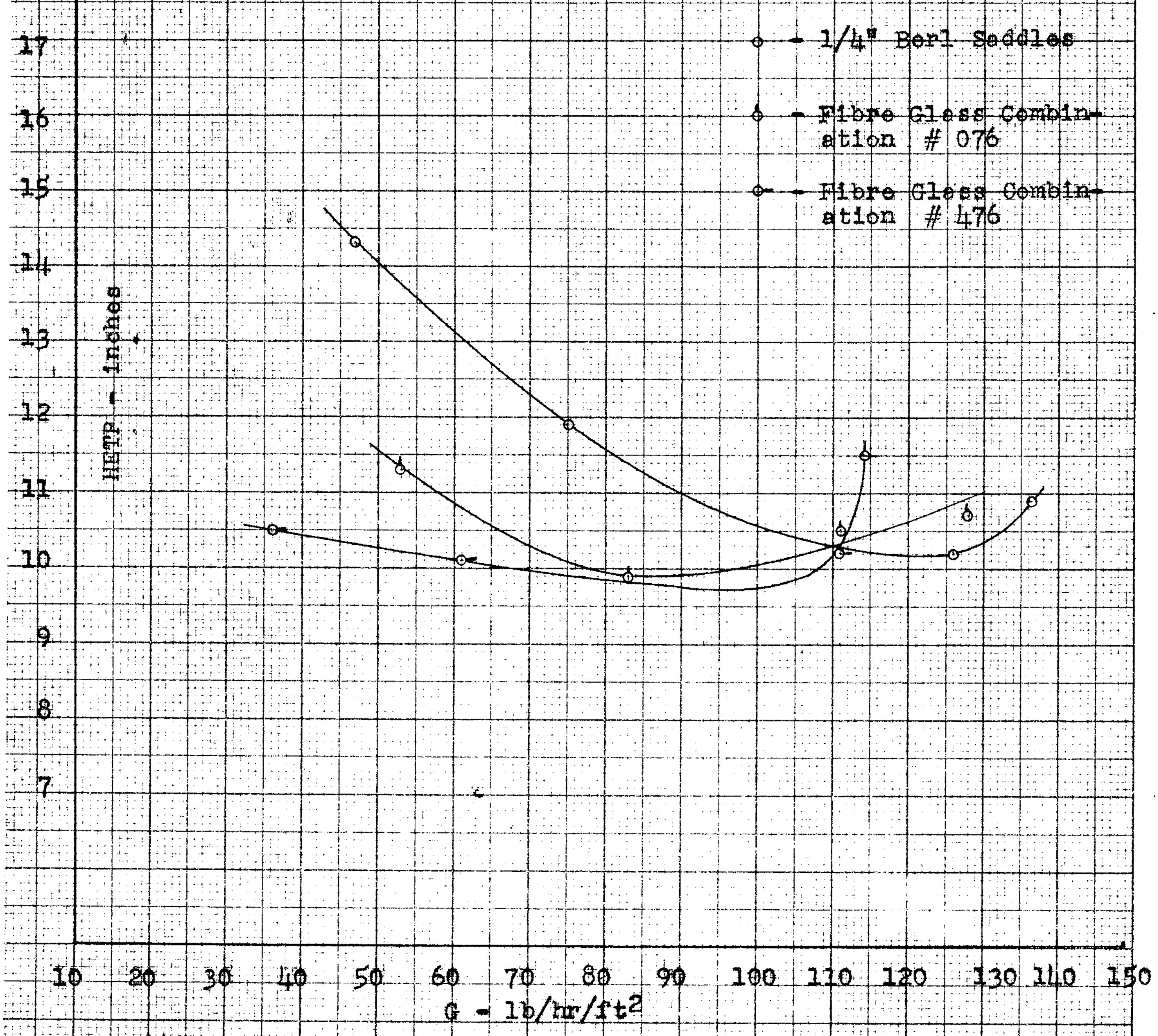


Figure 16

HETP Values vs. P for 1/4" Berl Saddles,

Fibre Glass Combination # 076 and # 476.

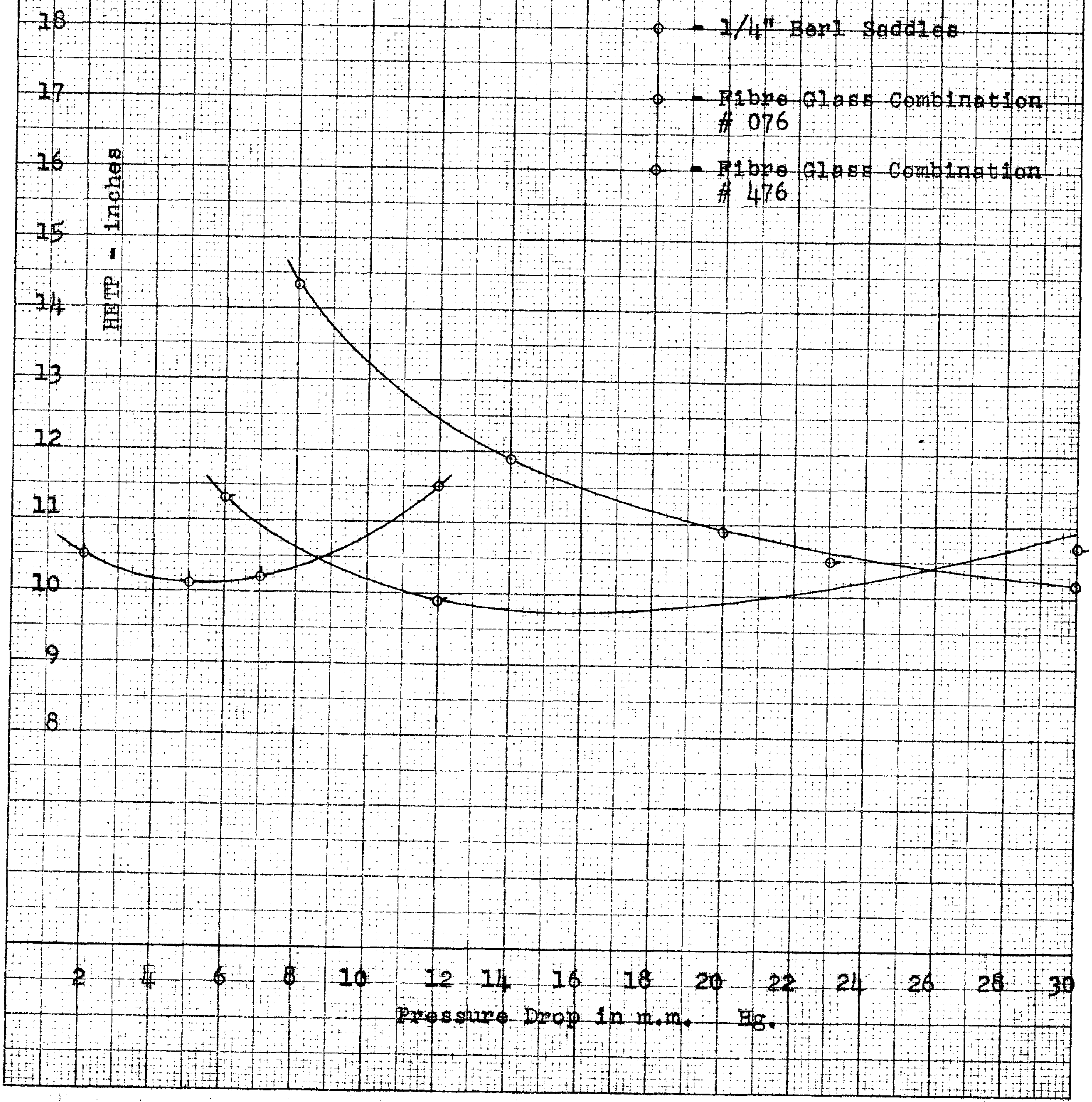


Figure 17

Pressure Drop in Inches of Water per Foot

vs.

G for All Packings

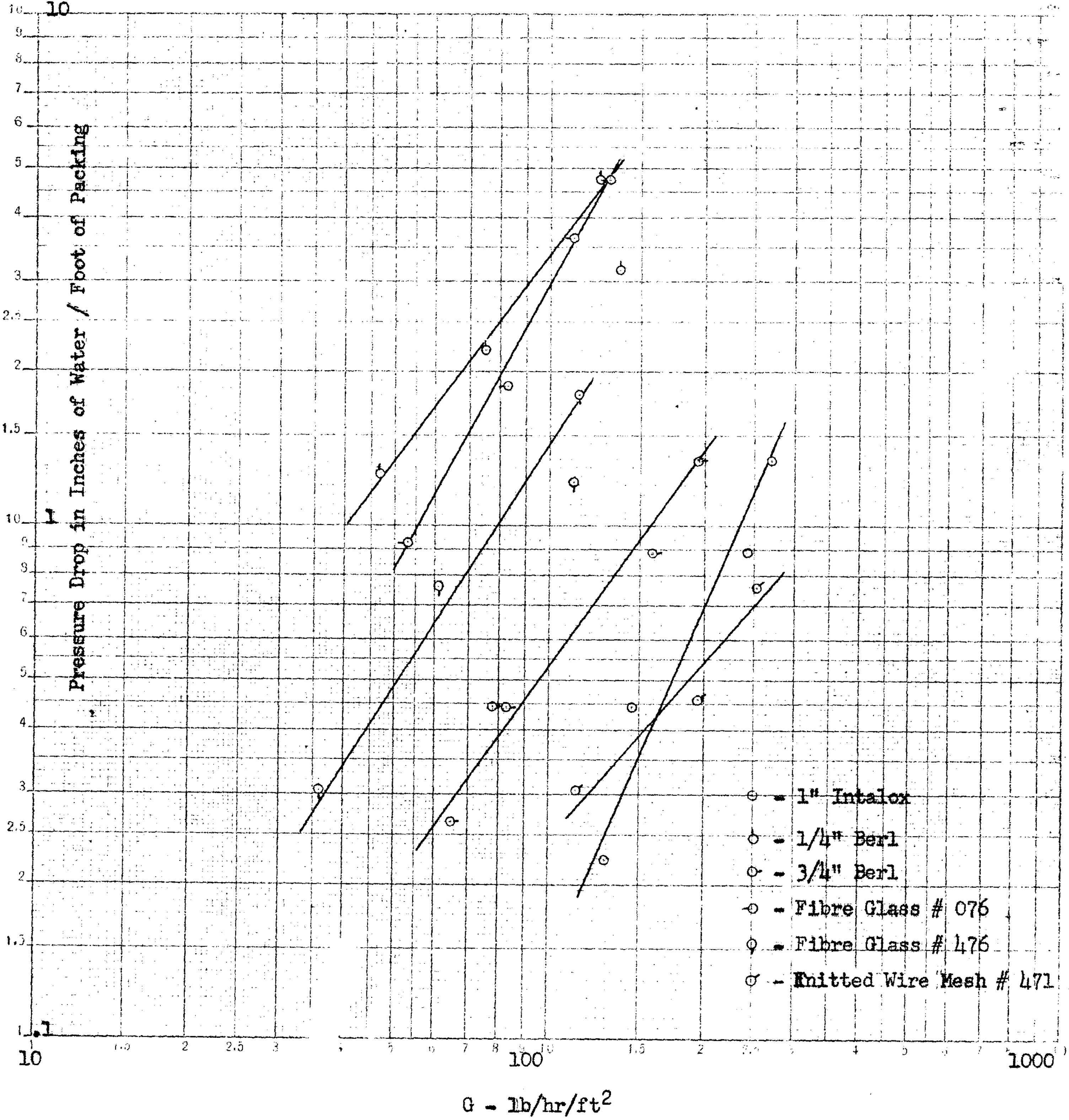
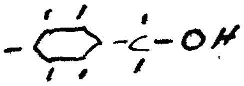


TABLE 1

Physical Properties of Purified Test Compounds

Benzyl Alcohol

Structure - $C_7 H_{10} O$



Molecular Weight - 108.13

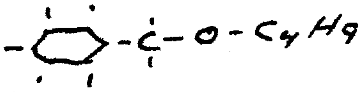
Density @ 20°C 1.043 grams/c. c.

Refractive Index @ 20°C - 1.5405

Viscosity @ 27°C - 5 c. p.

Benzyl n-Butyl Ether

Structure - $C_{11} H_{16} O$



Molecular Weight - 164.24

Density @ 20°C .909 grams/c. c.

Refractive Index @ 20°C 1.4867

Viscosity @ 27°C - 2.5 c. p.

TABLE 2

Vapor Pressure Data

Benzyl Alcohol

Literature (16)		Experimental	
Temp °C	Press mm Hg	Temp °C	Press mm Hg
58	1.0	65.2	1.8
80.8	5.0	79.5	4.8
92.6	10.0	90.0	8.0
105.8	20.0	94.4	10.9
119.8	40.0	103.2	16.4
129.3	60.0	103.0	16.4
141.7	100.0		
160.0	200.0		
183.0	400.0		
204.7	760.0		

Benzyl-n-Butyl Ether

Literature (16)		Experimental	
Temp °C	Press mm Hg	Temp °C	Press mm Hg
216	760	67	1.55
		79	3.2
		84	4.7
		98	10.0
		103	12.0
		115	20.0

TABLE 3

Correlated Vapor Pressure Data

Benzyl Alcohol		Benzyl n-Butyl Ether	
Temp°C	**Press mm Hg**	**Temp°C**	**Press mm Hg**
55.8	1.0	59	1.0
60	1.35		
65	1.89	65	1.42
70	2.60	70	1.94
75	3.50	75	2.6
80	4.7	80	3.45
85	6.3	85	4.55
90	8.2	90	5.9
95	11.0	95	7.75
100	14.0	100	9.8
105	18.0	105	12.5
110	23.3	110	16.0
115	29.5	115	20.0
120	36.5	120	25.0

TABLE 4

Experimental Vapor - Liquid Data

Run No	Vapor Temp °C	Total Pressure m. m.	Vapor Comp M. F. BzOH	Liquid Comp M. F. BzOH
1	108.5	19.5	.919	.943
2	107.5	19.55	.857	.885
3	107.0	19.4	.711	.716
4	106.1	19.65	.587	.534
5	109.0	19.6	.460	.362
6	112	19.9	.162	.092
7	111	19.5	.154	.063
8	106.2	19.6	.476	.331
9	108.2	19.6	.340	.182
10	80.0	4.6	.313	.186
11	84.0	4.7	.744	.823

TABLE 5

Activity Coefficient Calculations

Run No.	x_1	y_1	P_1mm	$P_T$mm	γ_1	x_2	y_2	P_2mm	γ_2	corrected T° C.
1	.943	.919	19.7	19.5	.965	.057	.081	14.6	1.898	106.8
2	.885	.857	19.3	19.6	.982	.115	.143	14.3	1.697	106.5
3	.716	.711	19.0	19.4	1.014	.284	.289	14.0	1.407	106.0
4	.534	.587	19.3	19.7	1.117	.466	.413	14.3	1.216	106.5
5	.362	.460	21.0	19.6	1.186	.638	.540	15.4	1.075	108.1
6	.092	.162	25.2	19.9	1.390	.908	.838	18.1	1.014	111.8
7	.063	.154	25.7	19.5	1.856	.937	.846	18.9	.932	112.3
8	.331	.476	21.4	19.6	1.317	.669	.524	15.7	.978	108.4
9	.182	.340	23.4	19.6	1.544	.818	.660	17.4	.913	110.3
10	.186	.313	4.8	4.6	1.61	.814	.687	3.53	1.10	80
11	.822	.714	5.2	4.7	1.00	.178	.256	4.0	1.69	82

TABLE 6

Margules Plot Calculations

Run No.	X_1	X_2	X_1^2	X_2^2	Log γ_1	Log γ_2	$\frac{\text{Log}\ \gamma_1}{X_2^2}$	$\frac{\text{Log}\ \gamma_2}{X_1^2}$
1	.943	.057	.890	.00325	-.065	.278	-[illegible]5	.312
2	.885	.115	.797	.0132	-.008	.228	- .607	.285
3	.716	.284	.512	.0808	.006	.148	.0743	.290
4	.534	.466	.286	.217	.048	.085	.222	.298
5	.362	.638	.131	.408	.074	.032	.1815	.245
6	.092	.908	.0085	.836	.143	.006	.171	.705
7	.063	.937	.00397	.910	.268	-.031	.295	-
8	.331	.669	.110	.448	.119	-.010	.266	-
9	.182	.881	.0332	.778	.189	-.040	.244	-
10	.186	.814	.0346	.662	.207	.041	.313	1.85
11	.822	.178	.677	.0318	0	.226	0	.333
(12)*	.700	.300	.49	.09	.028	.153	.322	.313

*Azeo. est.

TABLE 7

Van Laar Calculations

Run No	X_1	X_2	$\frac{X_2}{X_1}$	γ_1	Log γ_1	$1/\text{Log}\,\gamma_1$	$\frac{X_1}{X_2}$	γ_2	Log γ_2	$1/\text{Log}\,\gamma_2$
1	.943	.057	.0603	.965	-.015	-	16.5	1.898	.278	1.90
2	.885	.115	.130	.982	-.008	-	7.69	1.697	.228	2.09
3	.716	.284	.397	1.014	.006	12.75	2.53	1.407	.148	2.61
4	.534	.466	.873	1.117	.048	4.58	1.146	1.216	.085	3.44
5	.362	.638	1.766	1.186	.074	3.69	.568	1.075	.032	5.60
6	.092	.908	9.87	1.390	.143	2.65	.1014	1.014	.006	12.75
7	.063	.937	14.87	1.856	.268	1.93	.0673	.932	-.031	-
8	.331	.669	2.03	1.317	.119	2.91	.495	.978	-.01	-
9	.182	.818	4.51	1.544	.189	2.31	.223	.913	-.04	-
10	.186	.814	4.38	1.61	.207	2.20	.229	1.10	.041	4.95
11	.822	.178	.217	1.02	0	-	4.63	1.69	.226	2.21
(12)	.70	.300	.428	1.07	.029	5.88	2.34	1.42	.152	2.57

TABLE 8

Calculation of Vapor-Liquid Equilibria Data at 20 mm Pressure

P_1/P_2 (Avg.) = 1.354

X_1	γ_1/γ_2	α_{1-2}	αX_1	$1 + (\alpha-1)X_1$	Y_1
0	2.08	2.835	-	-	0
.1	1.804	2.460	.246	1.146	.215
.2	1.570	2.145	.428	1.229	.349
.3	1.343	1.834	.549	1.250	.440
.4	1.160	1.584	.632	1.234	.512
.5	1.00	1.354	.682	1.182	.578
.6	.862	1.174	.705	1.103	.638
.7	.743	1.01	.707	1.008	.700
.8	.642	.876	.701	.911	.770
.9	.558	.762	.685	.794	.863
1.0	.482	.658	-	-	1.000

TABLE 9

Calculation of Vapor-Liquid Equilibria Data

at 10 mm Pressure

P_1/P_2 (avg.) = 1.346

X_1	γ_1/γ_2	α_{1-2}	αX_1	$1 \neq (\alpha-1)X_1$	Y_1
0	2.080	2.80	-	-	0
.1	1.804	2.43	.243	1.143	.2125
.2	1.570	2.11	.421	1.222	.344
.3	1.343	1.81	.542	1.243	.436
.4	1.160	1.56	.623	1.224	.509
.5	1.00	1.346	.673	1.173	.574
.6	.862	1.160	.697	1.096	.637
.7	..743	.999	.699	1.00	.699
.8	.642	.863	.689	.891	.773
.9	.558	.752	.677	.777	.872
1.0	.482	.650	-	-	1.000

TABLE 10

Calculation of Vapor-Liquid Equilibria Data

at 1.35 mm

P_1P_2 1.302

X_1	γ_1/γ_2	α_{1-2}	αX_1	$1 \neq (\alpha-1)X_1$	Y_1
0	2.080	2.71	-	-	0
.1	1.804	2.35	.235	1.135	.2125
.2	1.570	2.05	.408	1.210	.344
.3	1.340	1.75	.525	1.243	.436
.4	1.160	1.512	.603	1.224	.509
.5	1.00	1.302	.652	1.173	.574
.6	.862	1.122	.673	1.096	.637
.7	.743	.955	.668	1.00	.699
.8	.642	.837	.669	.891	.773
.9	.558	.728	.655	.777	.872
1.0	.482	.628	-	-	1.0

TABLE 11

Calculation of Average Relative Volatilities

X_1	Relative Volatility			Average Relative Volatility
	20 mm	10mm	1.35 mm	
0	2.835	2.80	2.71	3.79
.1	2.46	2.43	2.35	2.42
.2	2.145	2.11	2.05	2.105
.3	1.834	1.81	1.750	1.800
.4	1.584	1.56	1.512	1.55
.5	1.364	1.346	1.302	1.337
.6	1.174	1.160	1.122	1.153
.7	1.010	0.999	.955	.988
.8	,876	.863	.837	.858
.9	.762	.752	.728	.748
1.0	.658	.650	.628	.650

TABLE 12

Calculations for Number of Plates vs. Refractive Index Plot

X_1	α (avg)	αX_1	$1 + (\alpha - 1)X_1$	Y_1	n_D @20°C
.030	2.67	.081	1.037	.071	1.4892
.078	2.50	.195	1.117	.1745	1.4917
.1745	2.18	.380	1.206	.315	1.4989
.315	1.78	.560	1.246	.448	1.5050
.448	1.45	.651	1.202	.542	1.5098
.542	1.26	.683	1.141	.598	1.5129
.598	1.15	.688	1.090	.633	1.5148
.633	1.09	.694	1.060	.655	1.5160
.655	1.06	.694	1.038	.668	1.5169

TABLE 13

Packing Description

Run		
1-4	1" Intodox Saddles (Ceramic)	Free Space 74% Area 78 ft^2/ft^3
5-8	1/4" Berl Saddles (Ceramic)	Free Space - 60% Area 274 ft^2/ft^3
9-12	3/4" Berl Saddles (Ceramic)	Free Space - 66% Area 82 ft^2/ft^3
13-16	Fibre Glass Combination (York & Co.) #076	Free Volume 92%
17-20	Fibre Glass Combination (York & Co.) #476	Free Volume 96.5%
21-23	Knitted Wire Mesh (York & Co.) #471	Free Volume 97.7%

TABLE 14

Performance Data

Run No	Length of Packing	Type of Packing	Time at Equilibrium hrs.	n_D @20°C	Pot Comp Plates	n_D @20°C	Vapor Comp Plates	Plates in Still	Boilup Rate ml/min.	Condenser Pressure mm	Pot Pressure mm	ΔP mm
1	72"	1" Intalox	3 1/2	1.4882	1.6	1.5067	5.35	3.75	87	1.0	11	10
2	72"	"	"	1.4910	2.46	1.5112	6.39	3.93	108	1.0	16	15
3	72"	"	"	1.4942	3.10	1.5090	5.82	2.72	52	1.0	6	5
4	72"	"	"	1.4947	3.18	1.5082	5.63	2.45	46	1.0	3.5	2.5
5	40.5"	1/4" Berl	5	1.4918	2.63	1.5137	7.35	4.72	49	1.0	21	20
6	40.5"	"	3 1/2	1.4895	2.07	1.5131	7.05	4.98	45*	1.0	31	30
7	40.5"	"	"	1.4918	2.63	1.5130	7.02	4.39	27	1.0	15	14
8	40.5"	"	3	1.4923	2.73	1.5118	6.57	3.84	17	1.0	9	8
9	72"	3/4" Berl	3 1/2	1.4917	2.62	1.5091	5.85	3.23	57	1.0	11.0	10
10	72"	"	"	1.4906	2.37	1.5106	6.22	3.85	70	1.0	16	15
11	72"	"	"	1.4933	2.93	1.5085	5.73	2.80	28	1.0	6	5

TABLE 14

(continued)

Run No	Length of Packing	Type of Packing	Time at Equili-brium hrs.	n_D@20°C	Pot Comp Plates	n_D@20°C	Vapor Comp Plates	Plates in Still	Boilup Rate ml/min.	Condenser Pressure mm	Pot Pres-sure mm	ΔP mm
12	72"	3/4" Berl	3	1.4930	2.87	1.5066	5.36	2.49	23.5	1.0	4	3
12a	72"	"	"	1.4927	2.82	1.5084	5.70	2.88	30	1.0	6	5
13	41" Fibre Glass	#076	"	1.4877	1.4	1.5106	6.23	4.83	46*	1.0	31	30
14	41"	#076	"	1.4877	1.4	1.5108	6.28	4.88	40	1.0	24	23
15	41"	#076	3 1/2	1.4875	1.25	1.5113	6.42	5.17	30	1.0	13	12
16	41"	#076	3	1.4882	1.62	1.5106	6.23	4.61	19	1.0	7	6
17	42"	Fibre Glass #476	"	1.4874	1.15	1.5086	5.7	4.63	41*	1.0	13	12
18	42"	"	"	1.4876	1.32	1.5113	6.42	5.10	40	1.0	8	7
19	42"	"	"	1.4876	1.10	1.5106	6.23	5.13	22	1	6	5
20	42"	"	"	1.4877	1.25	1.5106	6.23	4.98	13	1	3	2
21	42"	Knitted Mesh #471	"	1.4902	2.35	1.4958	3.03	.78	40	1	3	2
22	42"	"	"	1.4896	2.10	1.4930	2.87	.77	90	1	4	3
23	42"	"	"	1.4906	2.35	1.4942	3.10	.75	90	1	6	5

*flooding at top

TABLE 15

HETP Values

un No	Packing Material	Total Plates	Length of Packing	Plates in Column	HETP in	Boilup Rates		Δp m.m.
						ml/min	lb/hr/ft^2	
1	1" Intalox	3.75	72 in.	2.75	26.3	87	242	10
2	" "	3.93	" "	2.93	24.6	108	270	15
3	" "	2.72	" "	1.72	41.8	52	145	5
4	" "	2.45	" "	1.45	49.7	46	128	2.5
5	¼" Berl	4.72	40.5 in.	3.72	10.9	49	136	20
6	" "	4.98	" "	3.98	10.2	45	126	30 *
7	" "	4.39	" "	3.39	11.9	27	75	14
8	" "	3.84	" "	2.84	14.3	17	47	8
9	3/4" "	3.70	72 "	2.70	26.7	57	159	10
10	" "	3.85	" "	2.85	25.3	70	195	15
11	" "	2.80	" "	1.80	40.2	28	78	5
12/12a	" "	2.49/2.88	" "	1.49/1.88	48.3/38.4	235/30	65/83	3/5
13	Fibreglass #076	4.83	41 in.	3.83	10.7	46	128	30 *
14	"	4.88	" "	3.88	10.5	40	111	23
15	"	5.17	" "	4.17	9.9	30	83	12
16	"	4.61	" "	3.61	11.3	19	53	6
17	Fibreglass #476	4.63	42 in.	3.63	11.5	41	114	12*

TABLE 15 (Cont.)

Run No	Packing Material	Total Plates	Length of Packing	Plates in Column	H E T P in	ml/min	Boilup Rates lb/hr/ft^2	Δ p m.m.
18	Fibreglass #476	5.10	42 in.	4.10	10.2	40	111	7
19	"	5.13	" "	4.13	10.1	22	61	5
20	"	4.98*	" "	3.98	10.5	13	36	2
21	Knitted Wire Mesh #471	1.0+	" "	----	----	40	112	2
22	"	" "	" "	----	----	70	196	3
23	"	" "	" "	----	----	90	252	5

* Flooding at top column.

TABLE 16

Comparision of HETP Data

Packing	Packing Depth ft	Column Diameter	Mixture	G lb/hr/ft^2	HETP inches	Pressure	Source
¼" Berl Saddles	8.5	2 in.	n-Heptane Methylcyclo-hexane	200	7.0	1.0 atm.	(16)
" " "	"	"		700	6.7	" "	"
" " "	"	"	"	1000	6.25	" "	"
" " "	3.38	2 7/8 in.	"	748	8.4	" "	Data at Shulton
" " "	"	"	"	587	8.1	" "	" " "
" " "	"	"	"	428	9.2	" "	" " "
" " "	"	"	"	469	8.4	" "	" " "
" " "	"	"	"	374	9.2	" "	" " "
" " "	"	"	Benzyl Alcohol Benzyl-n-Butyl Ether	136	10.9	1 m.m. Condenser Pressure	Thesis Data
" " "	"	"		126	10.2		" "
" " "	"	"	"	75	11.9	"	" "
" " "	"	"	"	47	14.3	"	" "
Fibre Glass Combination #076	3.89	"	n-Heptane Methylcyclo-hexane	662	4.7	1.0 atm	Data at Shulton
	"	"		448	4.8	"	" " "
"	"	"	"	214	4.8	"	" " "
"	"	"	"	75	4.8	"	" " "

TABLE 16 (Cont.)

Packing	Packing Depth ft	Column Diameter	Mixture	G lb/hr/ft^2	H E T P inches	Pressure	Source
Fibre Glass Combination #076	3.38	2 7/8 in.	Benzyl Alcohol Benzyl-n-Butyl Ether	128	10.7	1.0 atm.	Data at Shulton
	"	"		111	10.5	"	" " "
"	"	"	"	83	9.9	"	" " "
"	"	"	"	53	11.3	"	" " "
Fibre Glass Combination #476	4.00	"	n-Heptane Methylcyclo-hexane	623	6.8	"	" " "
	"	"		481	6.4	"	" " "
"	"	"	"	428	6.8	"	" " "
"	"	"	"	406	6.8	"	" " "
"	"	"	"	235	7.0	"	" " "
"	3.5	"	Benzyl Alcohol Benzyl-n-Butyl Ether	114	11.5	1 m.m. Condenser Pressure	Thesis Data
"	"	"		111	10.2		" "
"	"	"	"	61	10.1	"	" "
"	"	"	"	36	10.5	"	" "
1" Intalox	6.0	"	"	270	24.6	"	" "
"	"	"	"	242	26.3	"	" "
"	"	"	"	145	41.8	"	" "
"	"	"	"	128	49.7	"	" "

TABLE 16 (Cont.)

Packing	Packing Depth ft	Column Diameter	Mixture	G lb/hr/ft^2	H E T P inches	Pressure	Source
1" Ceramic	9.0	12 in.	Ethanol-Water	960	13.2	1 m.m.	Thesis Data
"	"	" "	" "	150	16.8	Condenser Pressure	" "

TABLE 17

Pressure Drop and G. Data

Run No	Packing	Length Ft	ΔP mm Hg	ΔP in H_2O	ΔPm H_2O per ft	G. lb/hr/ft^2
1	1" Intalox	6'	10	5.35	.892	242
2	"	6'	15	8.03	1.34	270
3	"	6'	5	2.68	..447	145
4	"	6'	2.5	1.34	.224	128
5	1/4" Berl	3.38	20	10.7	3.19	136
6	"	3.38	30	16.05	4.77	126
7	"	3.38	14	7.48	2.22	75
8	"	3.38	8	4.27	1.265	47
9	3/4" Berl	6'	10	5.35	.892	159
10	"	6'	15	8.03	1.34	195
11	"	6'	5	2.68	.447	78
12	"	6'	3	1.611	.268	65

TABLE 17

(continued)

Run No	Packing	Length	ΔP mm Hg	ΔP in H_2O	ΔPm H_2O per ft	G lb/hr/ft^2
12A	3/4" Berl	6'	5	2.68	.447	83
13	Fibre Glass .076	3.42	30	16.05	4.70	128
14	"	"	23	12.3	3.61	111
15	"	"	12	6.42	1.88	83
16	"	"	6	3.21	.938	53
17	Fibre Glass 476	3.53	12	6.43	1.81	114
18	"	"	8	4.28	1.22	111
19	"	"	5	2.68	.76	61
20	"	"	2	1.07	.307	36
21	Knitted Wire Mesh	3.5	2	1.07	.307	112
22	"	"	3	1.61	.46	196
23	"	"	5	2.68	.76	252

SAMPLE CALCULATIONS

1. Activity coefficients (Table 4) Run 1.

$$\gamma_1 = \frac{P_T \; y_1}{P_1 \; x_1} = \frac{(19.5)(.919)}{(19.7)(.943)} = .965$$

$$\gamma_2 = \frac{P_T \; y_2}{P_2 \; x_2} = \frac{(19.7)(.081)}{(14.6)(.057)} = 1.898$$

P_1 and P_2 are read from Figure 5.

2. Margules plot (Table 6) Run 4.

$$\frac{\log \gamma_1}{x_2^2} = \frac{\log 1.117}{(.446)^2} = .222$$

$$\frac{\log \gamma_2}{x^2} = \frac{\log 1.216}{(.534)^2} = .298$$

3. Van Laar plot (Table 7) Run 4.

$$\frac{1}{\sqrt{\log \gamma_1}} = \frac{1}{\sqrt{\log 1.117}} = 4.58$$

$$\frac{x_1}{x_2} = \frac{.534}{.466} = 1.146$$

$$\frac{1}{\sqrt{\log \gamma_2}} = \frac{1}{\sqrt{\log 1.216}} = 3.44$$

$$\frac{x_2}{x_1} = \frac{.466}{.534} = .873$$

4. Vapor-liquid data (Tables 8, 9, 10, &11) for $x_1 = .1$ at 20 m.m. total pressure.

$$\alpha\ 1\text{-}2 = \frac{\gamma_1}{\gamma_2} \; \frac{P_1}{P_2} = (1.804)(1.364) = 2.460$$

$$\frac{\gamma_1}{\gamma_2} \quad \text{from Figure 8} = 1.804$$

$$\frac{P_1}{P_2} = 1.364$$

$$y_1 = \frac{\alpha_{1-2} \; x_1}{1+(\alpha_{1-2} - 1)\; x_1} = \frac{(2.460)(.1)}{1+(2.460-1)(.1)} = .215$$

5. Number of plates vs. refractive index (Table 12)

a. Assume value of liquid composition $x_1 = .030$

b. Read refractive index at composition

$$x_1 - n_D \text{ @ } 20^{\circ}\text{C} = 1.4892$$

c. Eq. (2) $y_1 = \dfrac{\alpha_{1-2}\; x_1}{1+(\alpha_{1-2}-1)\; x_1} = \dfrac{(2.67)(.030}{1+(2.67-1)(.1)} = .078$

x_{1-2} is read from Figure 10 = 2.67

d. Read refractive of $y_1 = .078$ is 1.4917 .

e. This .078 is used to repeat step (C).

f. $x_1 = .030$ to $x_1 = .078$ is one plate.

g. Repeat calculations until a sufficient number of plates are obtained.

6. Mass rate (Table 15) Run 1.

$G = \text{lb/hr/ft}^2$ density = .95 (average)

$$G = \frac{(87 \text{ ml/min})\ (.95 \text{ grs/ml})\ (60 \text{ min/hr})}{454 \text{ grs/lb})\quad (\ \frac{\pi}{4}\ (\frac{2.875}{12})^2} = 242\text{lb/hr/ft}^2$$

7. HETP (Table 15) Run 1.

$N = N_T - 1$ HETP $= \frac{N}{L}$

$N_T = 3.75$

$N = 2.75$

$L = 72$ inches

HETP $= \frac{72}{2.75} = 26.3$ inches.