

SEPARATION OF BENZENE AND TOLUENE
IN A PACKED COLUMN

125

A THESIS

Presented to
the Faculty of the Graduate Division

by

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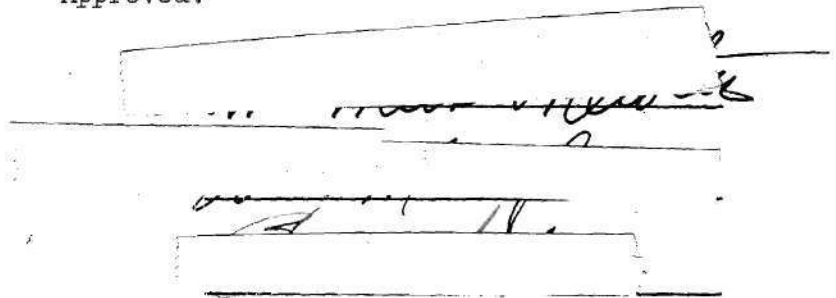
In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemical Engineering

Georgia Institute of Technology

November 1952

SEPARATION OF BENZENE AND TOLUENE
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Approved:

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Date Approved by Chairman: Dec. 19, 1952

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. William Meese Newton for his advice and suggestions in directing the progress of this investigation.

Thanks are also extended to the author's wife, Ruth Thompson Hutton, for her assistance in tabulation and other problems concerned in the investigation, to T. A. Wastler, Harry Chung, V. D. Holt, and E. F. Ward for their aid in the experimental and literature work, and to Mrs. T. A. Wastler for the editing and typing of this report.

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SUMMARY

The purpose of the investigation was to determine the effect of operating variables such as reflux ratio and superficial vapor velocity on the separation of benzene and toluene in a column packed with 1/4-inch Raschig rings.

Glass construction was used throughout. The packed section was of 2.0 inches inside diameter, packed to a height of 5.0 feet.

The column was operated at superficial vapor velocity ranges of 0.18-0.24, 0.45-0.53, and 0.83-0.96 feet per second. In each of these velocity ranges, the value of L/V was varied from 0.4 to 1.0, and corresponding values of $(HTU)_{OV}$, the over-all height of a transfer unit based on the change in vapor composition, were determined.

In all three velocity ranges, it was found that the value of $(HTU)_{OV}$ changed relatively slowly as L/V was decreased from 1.0 to 0.8; at values of L/V below 0.8, $(HTU)_{OV}$ rose rapidly and appeared to become asymptotic to the line $L/V = 0$.

At a given value of L/V , $(HTU)_{OV}$ for the highest vapor velocity was found to be lower than that for the lowest velocity. At the intermediate vapor velocity, the curve of $(HTU)_{OV}$ appeared to be slightly lower than, but essentially the same as, that for the highest velocity.

From theoretical considerations, Colburn (1) has derived the equation

$$(HTU)_{OV} = (HTU)_V + (HTU)_L \frac{mV}{L},$$

relating $(HTU)_{OV}$ to the height of the vapor and liquid film transfer units $(HTU)_V$ and $(HTU)_L$, the slope of the equilibrium curve m , and the reciprocal of the operating line slope, V/L . If the behavior of the system investigated can be represented by this equation, and if $(HTU)_V$ and $(HTU)_L$ are independent of velocity, a plot of $(HTU)_{OV}$ vs. $m_a V/L$ should yield a straight line with the intercept $(HTU)_V$ and the slope $(HTU)_L$, permitting the calculation of these values from a study of the curve.

The data obtained as described above were plotted in this form; considerable curvature was noted, indicating that the value of $(HTU)_L$ may also be a function of the operating variables. Because of this curvature, determination of $(HTU)_V$ by extrapolation to $m_a V/L = 0$ was not feasible.

Values of $(HTU)_{OV}$ varied from 0.64 to 11.5 feet over the L/V range investigated. These values compare favorably with those reported in the literature for this system.

CHAPTER I

INTRODUCTION

Packed columns have been used in distillation since the latter part of the nineteenth century. For many years after their introduction, no attempt was made to learn the fundamental relationships governing the behavior of packed columns, and all design work was merely the result of experience.

Not until comparatively recent years, in fact, have methods evolved for the calculation of the height of column necessary to effect a given separation. One of the first of these methods to be generally accepted involved the concept of HETP (height equivalent to a theoretical plate), as proposed by Peters. (2) This method is an adaptation of the methods used in plate column calculations; the composition of the vapor and liquid entering and leaving the column is determined, and the number of theoretical plates required for this separation is stepped off on a McCabe-Thiele diagram. When the value thus obtained is divided into the column height, the result is the HETP for that column under the conditions of the experiment.

The values obtained by this method can be used with satisfactory results to calculate the height of column necessary to perform any given separation under conditions similar to those under which the HETP was determined. The method cannot, however, be satisfactorily extended to cover new situations or different systems without extensive investigations to determine the HETP under the desired conditions.

A large amount of work has been done to determine the effect of column variables and operating variables on the HETP; many inconsistent and even conflicting results have been obtained. A few generalizations may be made, however, which illustrate the effects of some of these variables. Carney (3) reports the following:

- (1) HETP generally increases as column diameter increases, although the magnitude of this effect varies with different types of packings. This increase may be due to "channeling" of the liquid reflux, so that all of the body of the liquid does not make contact with the rising vapor.
- (2) HETP increases as throughput increases in a given column, again because of inefficient contact between liquid and vapor. This poor contact may be due either to channeling or to poor heat exchange at the higher vapor velocities.
- (3) Increased reflux ratio (ratio of overhead condensate returned as reflux to overhead condensate withdrawn as product) decreases the HETP, other variables remaining constant, and this effect is proportionally greater at low values of reflux ratio than at high ones.

Although the above statements are true as generalizations, data have been taken with certain systems and types of columns that are not consistent with them. In some cases, the inconsistency is due to interrelationships between variables, i.e., with certain types of packing, a decrease in reflux ratio can decrease the effective column diameter, affecting vapor velocity accordingly. The combined effect of all these changes on the HETP may be exactly opposite to the one expected. In many other cases, however,

inconsistency in results may be due to the fundamental inaccuracy of the HETP concept.

In a packed column, changes in composition of vapor and liquid occur continuously rather than in finite steps, as in a plate column. Since the HETP concept is based on finite changes in concentration, it is accurate only when the number of theoretical plates involved is quite large, so that the stepwise relationships in HETP determination approach the differential nature of the changes occurring in packed columns. Some design method based on a rigorous mathematical treatment of the nature of packed column distillation is therefore desirable.

Chilton and Colburn (4), considering the differential nature of packed column distillation and absorption, proposed the concept of the "transfer unit." The over-all number of transfer units necessary to perform a given separation, expressed in terms of changes in vapor composition, is defined as

$$(NTU)_{OV} = \int_{y_1}^{y_2} \frac{dy}{y^* - y}, \quad (1)$$

where y_1 = mole fraction of lower-boiling component in entering vapor,

y_2 = mole fraction of lower-boiling component in leaving vapor,

y = mole fraction of lower-boiling component in vapor at any part of column,

y^* = equilibrium mole fraction of lower-boiling component corresponding to y .

From this relation, the over-all "height of a transfer unit," $(HTU)_{OV}$, is found by dividing the column height H by $(NTU)_{OV}$, and a differential

equation relating H , $(HTU)_{OV}$, and the compositions may be derived:

$$\frac{dH}{(HTU)_{OV}} = \frac{dy}{y^* - y}. \quad (2)$$

The treatment leading to equation 1 leads also to the definition of the over-all height of a transfer unit based on changes in liquid concentration, $(HTU)_{OL}$, and to the heights of the liquid- and gas-film transfer units, $(HTU)_L$ and $(HTU)_V$. Differential equations similar to equation 2 show the relation of column height to composition and to these HTU values (1):

$$\frac{dH}{(HTU)_{OL}} = \frac{dx}{x - x^*}, \quad (3)$$

$$\frac{dH}{(HTU)_V} = \frac{dy}{y_1 - y}, \quad (4)$$

$$\frac{dH}{(HTU)_L} = \frac{dx}{x - x_1}, \quad (5)$$

where $(HTU)_{OL}$ = over-all height of a transfer unit, based on changes in liquid concentration,

$(HTU)_V$ = height of gas-film transfer unit,

$(HTU)_L$ = height of liquid-film transfer unit,

H = column height,

x = mole fraction of lower-boiling component in liquid at any point,

y = mole fraction of lower-boiling component in vapor at any point,

and where * refers to equilibrium concentrations,

sub i refers to interfacial concentrations.

Since interfacial concentrations are usually not known, calculation of $(HTU)_V$ or $(HTU)_L$ is possible only when one film offers the controlling resistance to mass transfer or when the interfacial concentrations are known. In the case of the gas film's controlling, $(HTU)_V$ is equal to $(HTU)_{OV}$. In many distillation and absorption problems, however, the resistance of both films must be considered. For evaluation of $(HTU)_V$ and $(HTU)_L$ in these cases, some relation between these quantities and the overall value of HTU must be derived.

Colburn (1) obtained such a relation from theoretical considerations, which may be expressed by the equation

$$(HTU)_{OV} = (HTU)_V + (HTU)_L \frac{mV}{L},$$

where m = slope of the equilibrium curve,

V/L = reciprocal of the slope of the operating line.

If this equation is obeyed, and if $(HTU)_V$ and $(HTU)_L$ are independent of velocity, a plot of $(HTU)_{OV}$ as a function of mV/L will appear as a straight line with slope $(HTU)_L$ and intercept $(HTU)_V$ at $mV/L = 0$.

Colburn plotted the absorption data of Adams (5) and the data of Kowalke, Hougen, and Watson (6) on the absorption of ammonia by water from an air mixture in this fashion and obtained straight lines. Other investigators, however, are in disagreement concerning the validity of this equation.

Duncan, Koffolt, and Withrow (7) investigated the systems methanol-water, ethanol-water, carbon tetrachloride-benzene, acetone-water, and

trichloroethylene-toluene and plotted values of $(HTU)_{OV}$ against m_a , the average slope of the equilibrium curve, with L/V as a parameter. The resulting plot appeared as a series of straight lines which intersected at a common point.

Deed, Schutz, and Drew (9) plotted data for the packed-column rectification of isopropyl alcohol in the form $(HTU)_{OV}$ vs. $m_a V/L$ and found that the plots showed considerable curvature.

Carter (10) prepared plots for carbon tetrachloride-toluene in the manner suggested by the Colburn equation and found that the plot of $(HTU)_{OV}$ vs. $m_a V/L$ showed definite curvature and that it exhibited a minimum value of $(HTU)_{OV}$ in the range of $m_a V/L$ from 0.7 to 1.0.

Very few data of this nature for the system benzene-toluene have been gathered; those which have been obtained scatter badly when plotted in accordance with the Colburn equation.

The purpose of this investigation was to obtain further data on the separation of benzene and toluene in a column packed with 1/4-inch Raschig rings and to determine the effect of operating variables on $(HTU)_{OV}$.

CHAPTER II

THEORY OF HTU

In a bubble-cap distillation column, transfer of material from one phase to the other is conducted in a series of finite steps--plates. On each tray, the ascending vapor and descending liquid are mixed, and exchange of material takes place; the concentration of a given component in either phase then remains constant until the next tray is reached. In a packed column, however, continuous exchange occurs, and the calculation of the tower height necessary to effect a given separation should therefore be approached on the basis of a differential, rather than on a stepwise process such as the McCabe-Thiele method. In view of this fact, Chilton and Colburn (4) advanced the concept of the transfer unit. The development of this concept and its application to distillation problems, as explained by Chilton and Colburn, are discussed below:

In a packed column used for distillation, an ascending stream of vapor passes countercurrent to the liquid reflux. At all points in a column operating properly, the concentration of the lower-boiling component in the vapor at the vapor-liquid interface is greater than that in the vapor stream. As a result, there is a diffusion of the lower-boiling component away from the liquid surface and of the higher-boiling component to it. It is assumed that the continual evaporation of liquid and condensation of vapor at the interface proceed at a rate so great that the surface layer of vapor is always in equilibrium with the liquid, and the only resistance to the exchange of material is that of diffusion in the

vapor phase. The concentration of the lower-boiling component in the vapor increases continuously as the vapor passes upward, rather than in steps as in a plate column. A treatment of the transfer of material in a packed column must be based, therefore, on a consideration of the differential nature of the changes.

In order to obtain a functional relationship between the variables involved, Chilton and Colburn (4) considered that over a differential element of height, dH , the partial pressure of the lower-boiling component in the vapor is increased by the differential amount dp , and since in distillation the total moles of vapor passing successive points remains essentially constant, the differential rate of increase of moles of lower-boiling component in the vapor is given by the equation

$$dw = \frac{dp}{\pi} \frac{G}{M_m} S, \quad (1)$$

where w = rate of transfer of diffusing component, lb. moles/hr.,

p = partial pressure of diffusing component, atm.,

G = mass velocity of vapor, lb./hr.-ft.²,

S = cross-sectional area (over which G is measured), ft.²,

π = total pressure, atm.,

M_m = average molecular weight of vapor stream.

This rate must be equal to the rate of transfer by diffusion, which may be expressed as

$$dw = K \Delta p \, dA = K a \Delta p \, S \, dH, \quad (2)$$

where K = absorption coefficient (gas film), lb. moles/hr.-ft.²-atm.,

$$\Delta p = p^* - p,$$

p^* = equilibrium partial pressure of diffusing component out of liquid, atm.,

A = interface area, ft.²,

a = surface area of packing per unit of packed volume, ft.²/ft.³,

H = height of packed section, ft.

For this case, where diffusion occurs equally in both directions, the mass transfer coefficient K is theoretically independent of the partial pressure of the component considered (11).

Equations 1 and 2 can be combined and rearranged to give the relation

$$\frac{dp}{\Delta p} = \frac{K a \pi M_m}{G} dH, \quad (3)$$

which becomes on integration

$$\int_{p_1}^{p_2} \frac{dp}{p} = \frac{K a \pi M_m H}{G}. \quad (4)$$

Thus the required height of column for any separation can be determined by a solution of equation 4 for H , provided that the value of K is known or can be predicted.

There is another way of looking at the problem, however, which has proved to be more convenient. The quantity $\int_{p_1}^{p_2} \frac{dp}{p}$ can be considered a measure of the difficulty of a desired separation, just as the required number of theoretical plates is a measure of the difficulty of a separation to be carried out in a plate column. Because of the similarity of the two concepts, the authors have called the solution of the integration above the "number of transfer units." Thus the number of transfer units, NTU, is

$$NTU = \int_{p_1}^{p_2} \frac{dp}{\Delta p}. \quad (5)$$

This equation can be expressed in terms of the mole fraction in the vapor, y , as well as partial pressures, i.e.,

$$NTU = \int_{y_1}^{y_2} \frac{dy}{\Delta y} = \int_{y_1}^{y_2} \frac{dy}{y^* - y}, \quad (6)$$

where y = mole fraction of diffusing component in gas = p/π ,

y^* = equilibrium mole fraction of diffusing component out of

liquid = p^*/π .

By this means, without any consideration being given to the calculation of the total number of moles being transferred, any problem can be directly expressed as a required number of transfer units. Then if experimental data are available as values of height per transfer unit, (HTU), the determination of column height involves merely the multiplication of NTU by HTU.

Comparison of HTU and HETP.---It has been suggested by Peters (12) that a given separation be treated as though it were carried out in a plate column and be expressed as a required number of theoretical plates. The height of the packed column is then divided by this number to give the height equivalent to a theoretical plate, (HETP). The theoretical plate concept implies that the change in composition of the vapor passing through the plate is equal to the difference between the composition of the entering vapor and the corresponding equilibrium vapor, or $y_p - y_a = y_a^* - y_a$ (see Fig. 1). On the other hand, a transfer unit is so defined that $y_b' - y_a = (y^* - y)_m$ = average of $y_b^* - y_b$ and $y_a^* - y_a$. If the mean value, $(y^* - y)_m$, is equal to $y_a^* - y_a$, the two concepts are identical. This

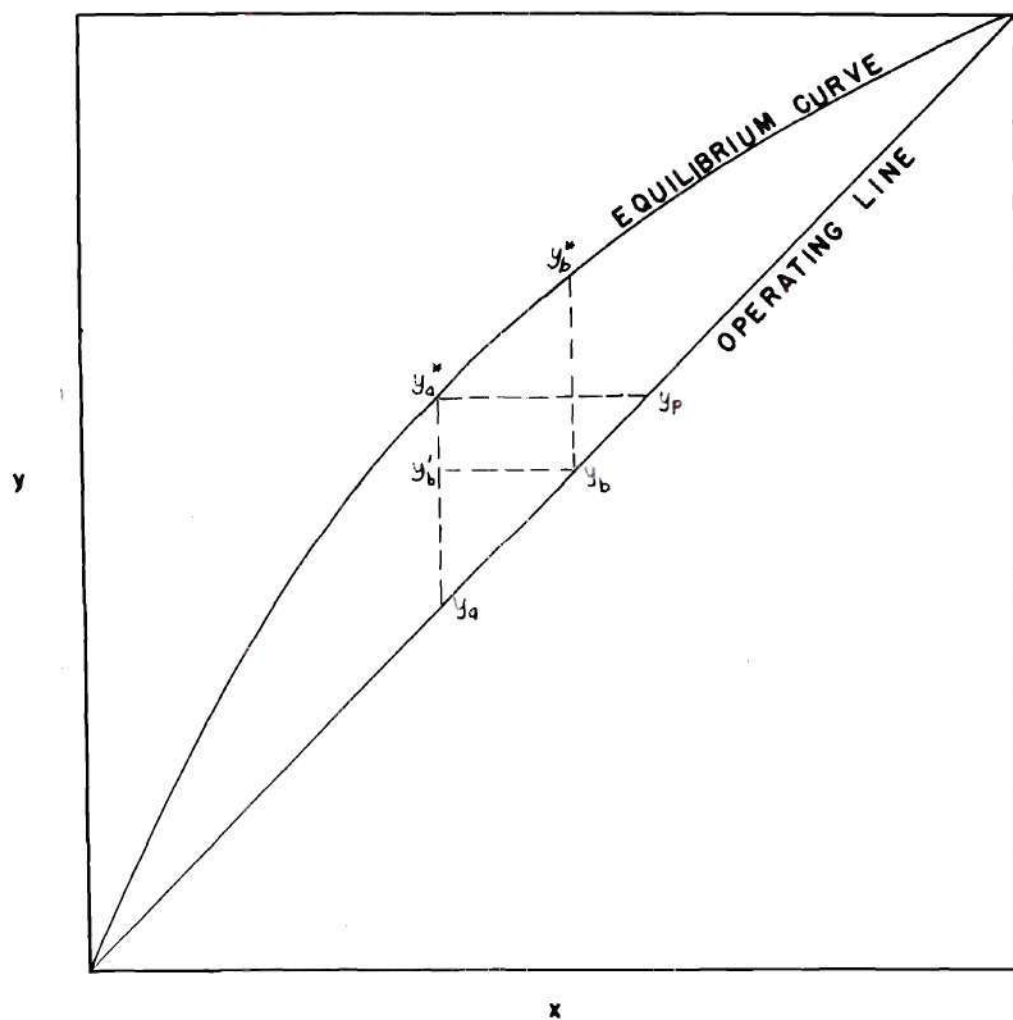


FIGURE I
RELATIONSHIP BETWEEN
H.T.U. AND H.E.T.P.

occurs when the equilibrium curve is parallel to the y vs. x or operating line, a condition rarely occurring for appreciable ranges of y .

One of the chief difficulties encountered in the calculations of vapor-liquid diffusion processes is the presence of considerable resistance to transfer in each of the fluids, which necessitates the use of two diffusion coefficients. These coefficients usually must be estimated or determined from the scarce available data. When one film or the other is controlling, calculations can be greatly simplified by basing equations on the controlling film only, since the other is then of negligible resistance. In the case of distillation and absorption processes, where both films usually must be considered, it is desirable to have a relation between over-all resistance to transfer and individual film resistances. Colburn (1) derived such a relation between the over-all height of a transfer unit, $(HTU)_{OV}$, and the liquid and gas film transfer units, $(HTU)_L$ and $(HTU)_V$, in which the following nomenclature applies:

- y = mole fraction of diffusing component in gas at any point,
- y^* = equilibrium mole fraction of diffusing component in gas,
- y_i = mole fraction of diffusing component in gas at vapor-liquid interface,
- x = mole fraction of diffusing component in liquid at any point,
- x^* = equilibrium mole fraction of diffusing component in liquid,
- x_i = mole fraction of diffusing component in liquid at vapor-liquid interface,
- H = height of packed section,
- V = molal flow rate of vapor,
- L = molal flow rate of liquid,

m = slope of equilibrium curve,

$(HTU)_{OV}$ = over-all height of a transfer unit, based on the change in vapor composition,

$(HTU)_{OL}$ = over-all height of a transfer unit, based on the change in liquid composition,

$(HTU)_V$ = height of gas-film transfer unit,

$(HTU)_L$ = height of liquid-film transfer unit.

For equimolar counter diffusion at any given point in an absorption column, over-all and film values of HTU are defined by the differential equations

$$\frac{dH}{(HTU)_{OV}} = \frac{dy}{y^* - y}, \quad (1)$$

$$\frac{dH}{(HTU)_{OL}} = \frac{dx}{x - x^*}, \quad (2)$$

$$\frac{dH}{(HTU)_V} = \frac{dy}{y_i - y}, \quad (3)$$

$$\frac{dH}{(HTU)_L} = \frac{dx}{x - x_i}, \quad (4)$$

Eliminating the derivative dH/dy from equations 1 and 3,

$$\frac{dH}{dy} = \frac{(HTU)_{OV}}{y^* - y} = \frac{(HTU)_V}{y_i - y},$$

$$\text{or} \quad (HTU)_{OV} = (HTU)_V \frac{(y^* - y)}{(y_i - y)}. \quad (5)$$

$$\text{However,} \quad \frac{y^* - y}{y_i - y} = \frac{y^* - y_i + y_i - y}{y_i - y} = \frac{1 + y^* - y_i}{y_i - y}. \quad (6)$$

Substituting equation 6 into equation 5,

$$(\text{HTU})_{\text{OV}} = (\text{HTU})_{\text{V}} + (\text{HTU})_{\text{V}} \frac{(y^* - y_1)}{(y_1 - y)}. \quad (7)$$

Considering the equilibrium curve to be a straight line over the small range $y^* - y_1$, the following equality holds:

$$y^* - y_1 = m (x - x_1). \quad (8)$$

Substituting equation 8 into equation 7,

$$(\text{HTU})_{\text{OV}} = (\text{HTU})_{\text{V}} + (\text{HTU})_{\text{V}} (m) \frac{(x - x_1)}{(y_1 - y)}. \quad (9)$$

However, by dividing equation 3 by equation 4, it may be seen that

$$\frac{x - x_1}{y_1 - y} = \frac{(\text{HTU})_{\text{L}}}{(\text{HTU})_{\text{V}}} \frac{dx}{dy}. \quad (10)$$

Substituting equation 10 into equation 9, there results

$$(\text{HTU})_{\text{OV}} = (\text{HTU})_{\text{V}} + (\text{HTU})_{\text{L}} (m) \frac{dx}{dy}. \quad (11)$$

However, dx/dy is simply the reciprocal of the slope of the operating line or V/L . Making this substitution, equation 11 becomes

$$(\text{HTU})_{\text{OV}} = (\text{HTU})_{\text{V}} + (\text{HTU})_{\text{L}} \frac{mV}{L}. \quad (12)$$

It will be noted that equation 12 can be used in the form above only when the equilibrium curve is a straight line over the range involved in the calculations. The equation can be applied when the equilibrium curve is not straight, however, by employing the average slope of the

equilibrium curve, m_a , between the limits of integration used in determining $(HTU)_{OV}$. This average slope, expressed in terms of y^* , is defined as

$$m_a = \frac{\int_{y^*_1}^{y^*_2} m \, dy^*}{y^*_2 - y^*_1}.$$

CHAPTER III

MATERIALS

The benzene and toluene used in the investigation were Merck C. P. materials; the boiling ranges were specified as 0.5° C for benzene and 1.0° C for toluene. Upon ASTM distillation in the laboratory, however, the boiling ranges for benzene and toluene were found to be 0.8° and 1.3° C, respectively.

The liquids were therefore further purified by distillation. The distillation was conducted in the column used in the investigation at a reflux ratio of about three to one; the first and last 20 per cents of each product were discarded. After this further purification the benzene and toluene boiling ranges were found to be 0.3° and 0.6° C, respectively, by ASTM distillation.

CHAPTER IV

EQUIPMENT

All parts of the equipment which were in contact with the distillation mixture were made of Pyrex glass. A diagram of the main assembly is shown in Fig. 9.¹

Still and heater.--The still consisted of a standard 12-liter, three-neck distillation flask, with an additional length of 7-mm. glass tubing sealed into the top of the flask and extending almost to the bottom. The still was joined to the other portions of the equipment by standard ball-and-socket ground-glass joints and was seated in a Glas-col heating mantle equipped with two 450-watt heating elements. The heat supply to the still was regulated by means of a variable autotransformer in series with each heating element.

Column.--The center neck of the still was attached to a glass column, 2.00 inches inside diameter, which was packed with 1/4-inch Raschig rings to a height of five feet. At intervals of one foot along the length of the packed section, short pieces of 7-mm. tubing were sealed into the column to permit placing thermocouples inside the packed section. The entire column was insulated with asbestos and magnesia. For the purpose of supplying any heat lost through the length of the column, the bottom, middle, and top portions were wound with nichrome wire buried in the insulation. Thermocouples were also buried in the insulation halfway between the column

¹Figures 9 through 21 may be found in the Appendix.

wall and the heating coils at points corresponding to the positions of the thermocouples inside the packed section. The thermocouple placement is shown in Fig. 10.

Substantially adiabatic operation of the column was assured by adjustment of the current input to the three separately controlled heater coils in such a way that the inside column temperature was equal to the temperature just outside the wall. In this manner, no temperature differential through the wall was permitted, so that no heat could pass in or out of the packed section.

Superheater.--Immediately above the column proper was located a section of 35-mm. glass tubing approximately two feet long, equipped with a stopcock, insulated in the same manner as the column, and wound with a nichrome heating element in the insulation. The purpose of this was simply to convey the vapor leaving the top of the column to the overhead condenser without permitting further condensation of the product. A thermocouple was located inside the superheater, and heat input to the heater coil was so adjusted that the temperature of the vapor passing through the superheater was considerably higher than that of the vapor passing through the topmost thermocouple in the column. The purpose of the stopcock was to reduce the flow of vapor through the column during the runs in which a portion of the still vapor was passed through the vapor line, as will be explained later.

Vapor line.--To one neck of the still was attached a section of 35-mm. glass tubing approximately eight feet long which was wound with nichrome heater coils and insulated. At the top of the vapor line was located a standard 20-inch Pyrex condenser, so that a portion of the still vapor could be passed through the vapor line, condensed, and returned to the

column as reflux, thus permitting operation at ratios of L/V greater than unity. The heat input to the vapor line was controlled by a variable autotransformer in series with each of the two heater windings and simply adjusted so that none of the vapor was allowed to condense on the walls of the vapor line. When the vapor line was not in operation, flow from the still was blocked by a stopcock in the line.

Flowmeters.--At the downstream end of the main condenser at the top of the column was located a Y-tube, equipped with a stopcock on each fork, in which the condensate stream was divided into two portions, one passing through a flowmeter into the top of the column as reflux, the other passing through a flowmeter and returning to the still through the sealed-in tubing mentioned previously. The condensate leaving the vapor-line condenser also was passed through a flowmeter before entering the top of the column as reflux. These meters were of the orifice discharge type as shown in Fig. 11 and were so constructed that any meter could be replaced by another meter containing a different-sized orifice. By means of these flowmeters, any liquid flow rate from 10 to 130 cc./min. could be ascertained quite accurately.

Reflux heater and distributor.--The condensate returned to the column as reflux passed through the reflux heater, which consisted of a section of 19-mm. tubing approximately one foot in length, wound with nichrome wire, and insulated. The heat input to the reflux heater was controlled by a variable autotransformer and was so adjusted that the liquid was heated almost to the boiling point. A reflux distributor made in the shape of a funnel and covered with a perforated glass plate was located in the lower portion of the superheater just above the column packing.

Sample collectors.--To the third neck of the still flask was attached a small condenser, the downstream end of which was sealed to the top of one leg of a U-tube bent from 11-mm. glass tubing. This tube had a capacity of about 50 cc. and was equipped with a tap at the bottom of the U. The second leg of the collector was attached to a length of tubing which was sealed into the still return line. This assembly continuously condensed a portion of the vapor rising from the still, passed it through the collector, and returned it to the still.

Collectors of the type described, but without the condenser, were also placed below the vapor-line condenser, in the overhead condensate line, and in the reflux return line. The purpose of these collectors was to permit the accumulation of a sample of about 50 cc. for analysis by boiling point determination. Upon analysis of the samples obtained from the appropriate collectors, the composition of the still vapor (y_1), the overhead condensate (y_2), and the reflux (x_2) could be determined, and by measurement of the liquid flow rates the L/V ratio could be calculated, fixing the operating line for a given run.

Packing.--The packing used consisted of 1/4-inch stoneware Raschig rings. The following physical properties are given for this material (13):

O.D. and length:	1/4 inch
Wall thickness:	1/32 inch
Density:	46 lb./ft. ³
Surface area:	240 ft. ² /ft. ³
Voids:	73 per cent

The rings were packed in such a manner as to allow random arrangement. This was accomplished by filling the column with toluene and dropping the

rings singly into the top of the column, thus allowing each ring to settle independently.

The following measurements apply to the packed section employed in this investigation:

Diameter: 2.0 in.
 Height: 5.0 ft.
 Volume: 0.109 ft.³

Heating equipment.--As mentioned previously, heat was supplied to the various parts of the equipment by heater circuits wound of nichrome wire controlled by variable autotransformers. Nine of these transformers were employed: one for each of the two elements in the still heating mantle, one for each of the three heater coils supplying heat to the column walls, one for each of the two coils heating the vapor line, one for the superheater, and one for the reflux heater. These transformers were so arranged that the voltage and current supplied by each could be measured at any time, as shown by Fig. 12.

Thermocouples.--Fourteen copper-constantan thermocouples were employed in the system, distributed as follows:

<u>T.C. No.</u>	<u>Location</u>
1,3,5,7,9	Placed at 1-ft. intervals outside column wall (see Fig. 10),
2,4,6,8,10	Placed at 1-ft. intervals inside column wall (see Fig. 10),
11	Inside reflux flowmeter,
12	Inside vapor-line condenser, just above top of vapor line,

<u>T.C. No.</u>	<u>Location</u>
.13	Inside superheater,
14	Inside reflux heater.

These thermocouples were so arranged that, through a switching system, each could be paired with a common cold junction which was maintained at 0° C by an ice-water bath. The thermocouple wiring diagram is shown in Fig. 13. In addition, the wiring leading to couples Nos. 1 through 10 was so arranged that the cold junction could be bypassed and No. 1 paired with No. 2, No. 3 with No. 4, etc., to form a difference thermocouple. Since these pairs were so placed in the column that one was inside the column and the other just outside the column walls, it was only necessary to adjust the current to the heater coils so that the emf between a given pair was essentially zero, indicating that the two couples were at the same temperature and, therefore, that the column was operating adiabatically at that point.

A General Electric self-balancing potentiometer (Autopot), whose output current was measured by a milliammeter, was used to measure the emf developed by the thermocouples.

Boiling point determination apparatus.--Samples drawn from the column were analyzed by boiling point determination, using the modified Cottrell apparatus described by Griswold, Andres, and Klein (14). Corrections for barometric pressure and exposed thermometer stem were applied as described in Chapter V.

CHAPTER V

CALIBRATION OF INSTRUMENTS

Flowmeters.--The flow meters were calibrated by passing benzene from a large reservoir through a valve into the meter. The time required for a given volume of benzene to pass through the meter at a given meter reading was determined, and a plot of flow rate as a function of meter reading was prepared, as shown in Fig. 14. It will be noted that these curves appear as straight lines on log-log grid, indicating that the meter orifices behaved substantially as sharp-edged orifices.

Thermocouples.--The thermocouples were calibrated against a sensitive mercury thermometer in a heated glycerin bath. Thermometer and couples were immersed in the agitated bath in close proximity, and heat was supplied to the bath through a heating mantle controlled by a variable autotransformer. Readings of the thermometer and output current from the potentiometer were then recorded. The calibration curve for the thermocouples is shown in Fig. 15.

Boiling point determination apparatus.--The mercury thermometer employed in the modified Cottrell apparatus was calibrated for total immersion and graduated from 70° to 150° C in divisions of 0.2° C. Corrections for exposed stem were applied according to ASTM designation D850-50, which specifies corrections calculated from the equation

$$C_1 = KN(T - t),$$

where C_1 = correction, °C, for emergent stem,

$$K = 0.000154,$$

N = number of degree graduations exposed,

t = emergent stem temperature, °C,

T = observed reading, °C.

The thermometer was so placed that the top of the cork was at the 76° graduation; the value of N , therefore, was $t - 76$. The equation could thus be written

$$C_1 = (0.000154)(t - 76)(T - t),$$

and C_1 was plotted as a function of T with t as the second variable, producing a family of curves.

The observed temperature reading was corrected for changes in barometric pressure; this correction was also made in accordance with the ASTM method designated above, in which the correction is calculated from the equation

$$C_2 = k(760 - p),$$

where C_2 = correction, °C, to boiling point at 760 mm.,

p = barometric pressure, mm. Hg at 0° C,

k for benzene = $0.0427 + 0.000025 (760 - p)$,

k for toluene = $0.0463 + 0.000027 (760 - p)$.

A plot of C_2 as a function of p and mole fraction benzene was prepared by assuming that the factors determining k are additive in terms of mole fraction benzene, x , so that the equation could be put into the form

$$C_2 = (760 - p) \left\{ 0.0427 x + 0.0463 (1 - x) + [0.000025 x + 0.000027 (1 - x)] (760 - p) \right\}.$$

The plots described above were used to determine boiling point corrections for analyses of all runs. The boiling point apparatus was initially calibrated using weighed samples of known composition; the observed boiling point for each sample was determined, the proper corrections added, and a curve of corrected boiling point as a function of real mole fraction benzene was prepared. From this curve, a plot of corrected boiling point as a function of "fictitious" (see Chapter VI) mole fraction benzene was drawn, as shown in Fig. 16.

CHAPTER VI

PROCEDURE

In the graphical determination of $(NTU)_{OV}$, the compositions of gas and liquid at any point in the column are determined from the operating line, which is a representation of these values drawn on the x-y diagram (see Sample Calculations in the Appendix). If it may be assumed that the operating line is straight, the line can be determined by a knowledge of the compositions of the inlet and outlet gas and liquid; they fix two points on the x-y diagram and, hence, the entire operating line. Assumption of a straight operating line may be made, provided the following conditions are fulfilled:

1. Sensible heat in liquid and gas is negligible in comparison with heat of vaporization.
2. Heat of mixing of the components is negligible.
3. The column operates substantially adiabatically.
4. The condensation of one mole of vapor furnishes sufficient heat to vaporize one mole of liquid, regardless of composition.

In this investigation, condition 1 above could be assumed because of the relatively small temperature difference between the bottom and top of the column. Condition 2 was fulfilled by the nature of benzene-toluene mixtures. As has been mentioned previously, the column wall was heated in such a manner that essentially adiabatic operation could be assumed, fulfilling condition 3.

Condition 4 holds only if the molar heats of vaporization of the two components of the system are substantially equal. While the molar heats of vaporization of benzene and toluene are quite close to each other, they are not the same; hence, it was necessary to calculate a "fictitious molecular weight" for one of the components and to base all calculations on this value.

At approximately the boiling point of toluene, the latent heats of vaporization of benzene and toluene are as follows:

$$\text{Benzene: } \Delta H_v = 12,430 \text{ Btu/lb.-mole,}$$

$$\text{Toluene: } \Delta H_v = 14,300 \text{ Btu/lb.-mole.}$$

Thus, the fictitious molecular weight of benzene = $\frac{(78.11)(14,300)}{(12,430)} = 89.8$.

The vapor-liquid equilibrium relations for the benzene-toluene system were then recalculated on the basis of the fictitious molecular weight of benzene, and all results throughout the remainder of the investigation are reported in terms of fictitious mole fraction benzene.

The "fictitious" vapor-liquid equilibrium relations were calculated from the real vapor-liquid equilibrium relations in the following manner:

x = real mole fraction benzene,

x' = fictitious mole fraction benzene,

X = real moles benzene/mole toluene,

X_p = pounds benzene/pound toluene,

X' = fictitious moles benzene/mole toluene.

$$X = \frac{x}{1 - x},$$

$$X_p = \frac{x}{(1 - x)} \frac{(78.1)}{(92)},$$

$$X' = X_p \frac{(92)}{(89.8)} = \frac{x}{(1-x)} \frac{(78.1)}{(92)} \frac{(92)}{(89.8)} = \frac{x}{(1-x)} \frac{(78.1)}{(89.8)}$$

$$= \frac{0.87 x}{1-x},$$

$$x' = \frac{X'}{1+X'} = \frac{0.87 x}{1-0.13 x}.$$

The relation between the real and fictitious vapor-liquid equilibrium data may be seen in Table 1 in the Appendix; the real and fictitious vapor-liquid equilibrium curves are shown in Figs. 17, 18, and 19.

At the start of a day's operations, the column was first operated at a relatively high throughput and total reflux for one to two hours, assuring the thorough wetting of the packing before a run was begun. The heat input to the still, column, and reflux heater was then adjusted roughly to the required conditions, and the desired reflux ratio was approximated by adjustment of the stopcocks below the main condenser. Finer adjustments of heat input and flow rates were made as the column operation approached the desired conditions. Readings were made of the temperatures inside and outside the column and of the superheated vapor, overhead condensate, and reflux temperatures, as well as of the product and reflux flow rates. Complete sets of readings were taken at approximately 15-minute intervals, and any required adjustments were made as the column approached thermal and dynamic equilibrium. The attainment of equilibrium required about one hour from the time the final adjustments were made and was shown by the fact that all temperatures and flow rates remained constant. After the column had operated under steady-state conditions for at least 20 minutes, samples of the overhead condensate, reflux, and still

vapor were drawn for analysis.

After determination of the overhead and reflux compositions by boiling points, the point x_2, y_2 was located on the fictitious vapor-liquid equilibrium curve. (See Fig. 19; large-scale plots of this curve were employed in the actual runs.) Before the L/V ratio could be calculated, it was necessary to determine the molal flow rates of the overhead and reflux streams. For this purpose, a plot of liquid density as a function of temperature and fictitious mole fraction benzene was prepared. The values for this plot were based on the density-temperature relations for benzene and toluene as given in the International Critical Tables (15), and the density of a mixture of benzene and toluene was calculated assuming ideal solution. This plot may be seen in Fig. 20. Also, the average molecular weight of the mixture in each case was calculated from the relation

$$M_{\text{avg}} = x M_b + (1 - x) M_t,$$

where x and M_b refer to the fictitious mole fraction of benzene and the fictitious molecular weight of benzene, respectively.

Thus, when composition and temperature of the overhead and reflux streams were known, the density and molecular weight of each stream could be calculated; these quantities, with the liquid flow rate for each stream, permitted the calculation of the molal flow rates of each stream. At this point in each run, the superficial vapor velocity for the run was calculated from the molal vapor rate and the column cross-section, on the assumption that the vapor mixture behaved as an ideal gas.

From the molal flow rates of the overhead and reflux streams, the L/V ratio (the slope of the operating line) was calculated. After the

composition of the still vapor has been determined, this value and the operating line slope permit the calculation of the x_1 value according to the equation

$$x_1 = x_2 - \frac{V}{L} (y_2 - y_1).$$

The entire operating line may now be drawn on the fictitious vapor-liquid equilibrium curve, and the value of NTU may be calculated by

$$(NTU)_{OV} = \int_{y_1}^{y_2} \frac{dy}{y^* - y}.$$

The integration was performed by the numerical method of Gauss (16). In sample trials, it was found that a four-point Gauss integration duplicated the results of graphical integration with an error of less than 0.5 per cent for runs in which the minimum value of $y^* - y$ was greater than 0.05; when this minimum value was less than 0.05, a six-point Gauss integration was employed.

After the calculation of $(NTU)_{OV}$, the value of $(HTU)_{OV}$ was determined simply by dividing the height of the packed section, 5.0 feet, by $(NTU)_{OV}$.

The value of m_a , average slope of the operating line, was calculated from the equation

$$m_a = (1.82) \frac{[(1 - 0.565 y^*_1)^3 - (1 - 0.565 y^*_2)^3]}{y^*_2 - y^*_1}.$$

The derivation of this equation may be seen in the section Sample Calculations of the Appendix.

The procedure described above is that used for runs in which the

column was operated as a stripping column; in this case, the reflux composition was different from the composition of the overhead condensate. In the majority of the runs made, however, the column was operated as a rectifying column. The procedure in this case is essentially the same as that shown above but somewhat simplified in that the composition of the reflux was the same as the overhead composition.

A complete run, showing all calculations, is shown in the section Sample Calculations of the Appendix.

CHAPTER VII

DISCUSSION OF RESULTS

Runs were made at three different ranges of superficial vapor velocity; in each range an attempt was made to vary the L/V ratio over the range 0.4-1.0. The vapor velocity ranges chosen were 0.18-0.24, 0.45-0.53, and 0.83-0.96 feet per second. Although it was not possible to control the vapor velocity exactly for a given run, control within the ranges shown could be easily maintained.

The range 0.18-0.24 feet per second vapor velocity was found, by preliminary experiments, to be the lowest at which the column could be operated under steady conditions. Because of the very low product and reflux flow rates at this velocity, accurate determination of flow rates at an L/V less than about 0.55 and between 0.8 and 1.0 could not be made; this was due to the fact that liquid flow rates of less than 10 cc./min. could not be accurately measured with the flowmeters employed. Runs were made in this velocity range, however, at total reflux and at an L/V range of about 0.55-0.8. The value of $(HTU)_{OV}$ was determined for each of these runs and the results are plotted in Fig. 2. It may be seen from this figure that the value of $(HTU)_{OV}$ appears lowest at total reflux ($L/V = 1.0$), rises gradually to an L/V value of about 0.7, and continues to rise more sharply as L/V is further decreased.

It was desired that the highest velocity range chosen be somewhere near the flood point for the packing used. Calculation from summarized

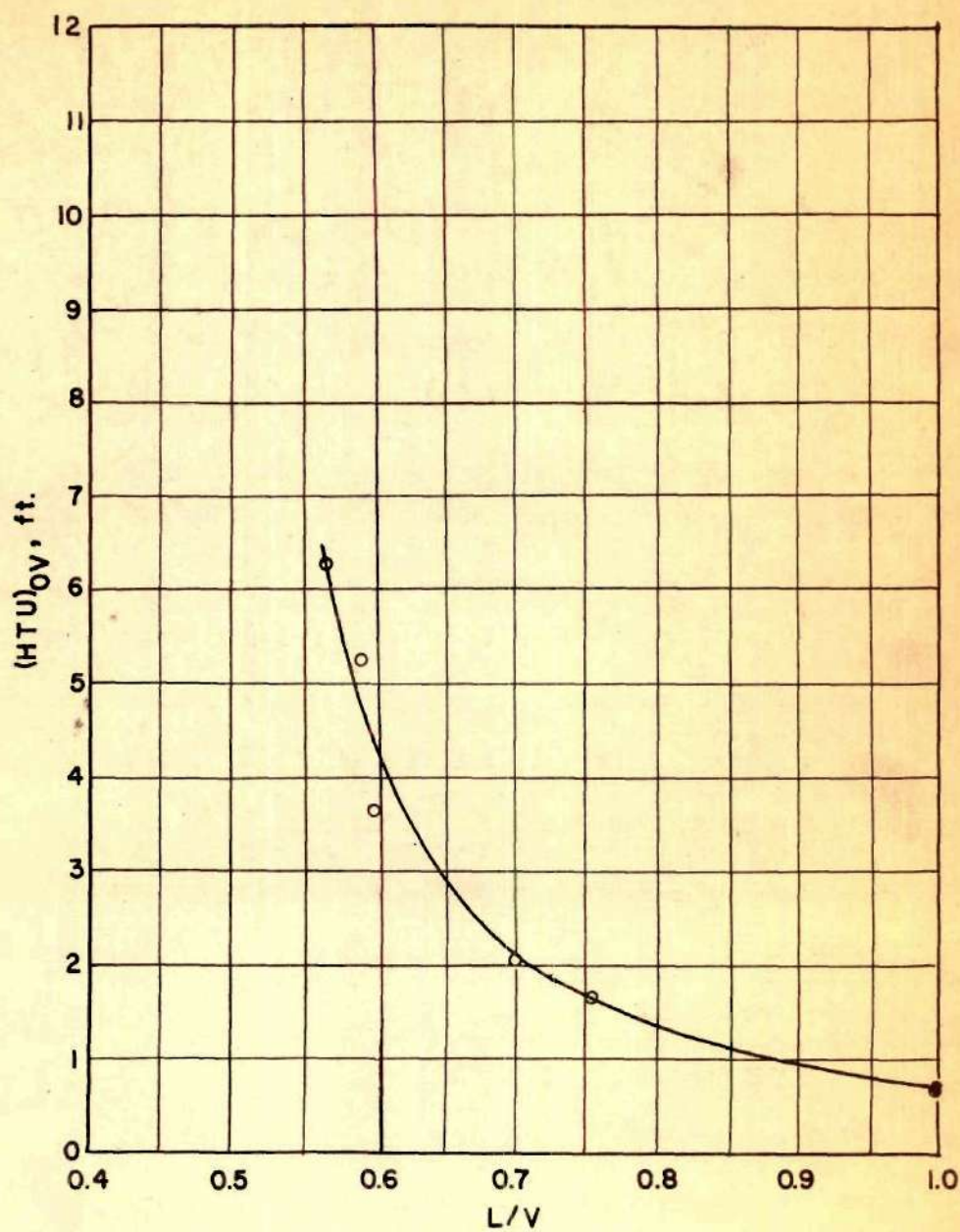


FIGURE 2
 $(HTU)_{OV}$ vs. L/V
Sup. Vap. Vel. = 0.18-0.24 ft./sec.

data for ring packings (17) yielded a value of approximately 1.5 feet per second as the flooding velocity for this packing (based on the empty column); an actual test showed that flooding began at about 1.3 feet per second.

The second series of runs was therefore made at a superficial vapor velocity of 0.83 to 0.96 feet per second. L/V was varied from 0.4 to 1.0, and the values of $(HTU)_{OV}$ were calculated. The results are shown in Fig. 3. It will be noted that the curve of Fig. 3 follows approximately the same trend as that of Fig. 1, although the value of $(HTU)_{OV}$ is lower for the high range of vapor velocity than for the low range at a given value of L/V , the difference becoming greater as L/V decreases. At total reflux, $(HTU)_{OV}$ is essentially the same for both velocity ranges (0.70 feet at the low range and 0.64 feet at the high range).

The third series of runs was made at a velocity range intermediate between the two extremes discussed above. The results of this series are plotted in Fig. 4. Again the value of $(HTU)_{OV}$ is essentially the same at total reflux as the values obtained from the first two series; the curve again falls below that of the first series and appears also to fall slightly below that obtained from the second series, although this difference is not believed great enough to be significant.

Correlation with $m_a V/L$.--Attempts at correlation of $(HTU)_{OV}$ with $m_a V/L$ were not so successful as the correlation with L/V . Considerable scattering of experimental points may be noted from an examination of Figs. 5, 6, and 7, which are plots of $(HTU)_{OV}$ vs. $m_a V/L$ for the same three velocity ranges. These plots were made in an attempt to determine the values of $(HTU)_V$ and $(HTU)_L$ for this system in accordance with Colburn's equation,

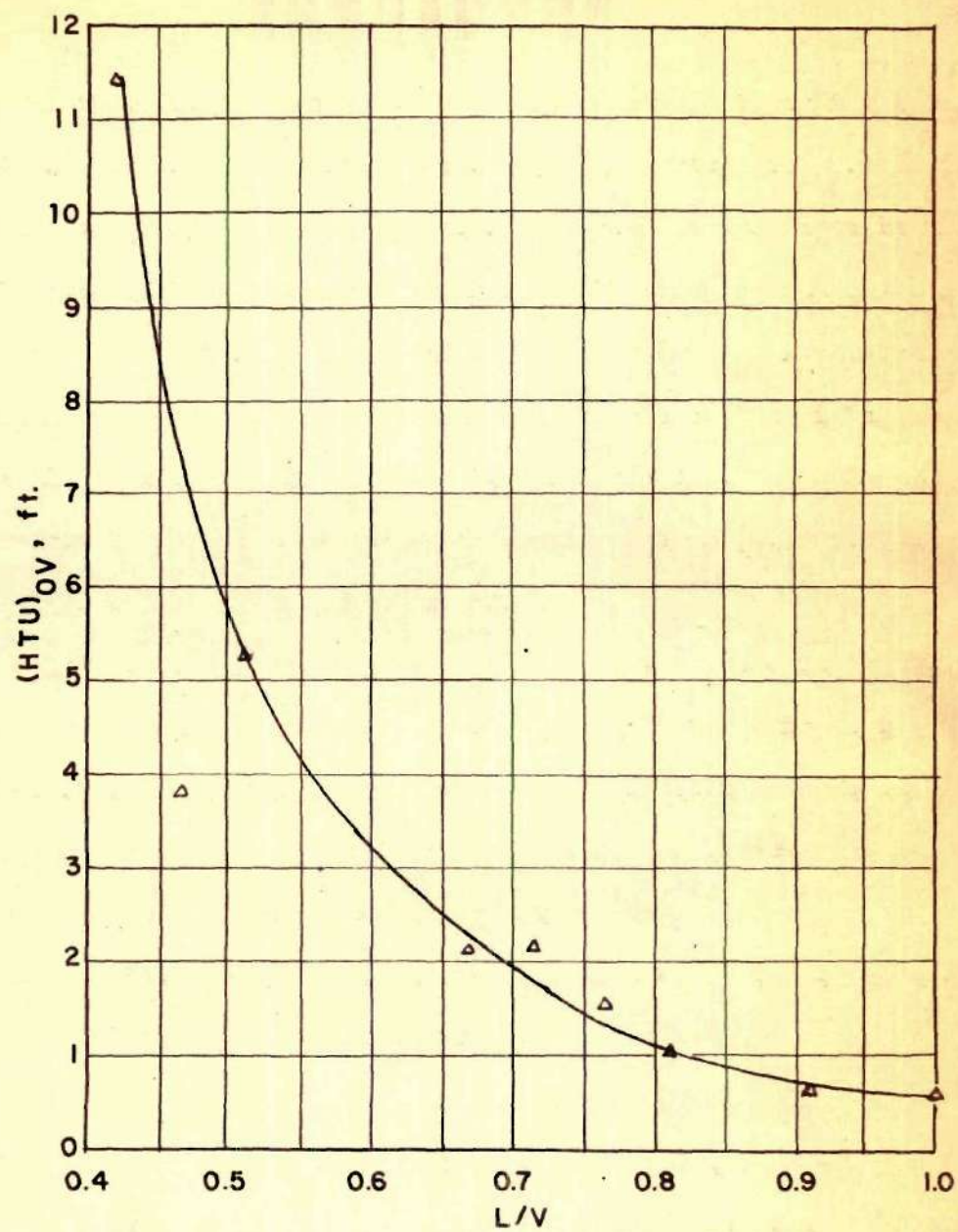


FIGURE 3

 $(HTU)_{OV}$ vs. L/V

Sup. Vap. Vel. = 0.83 - 0.96 ft./sec.

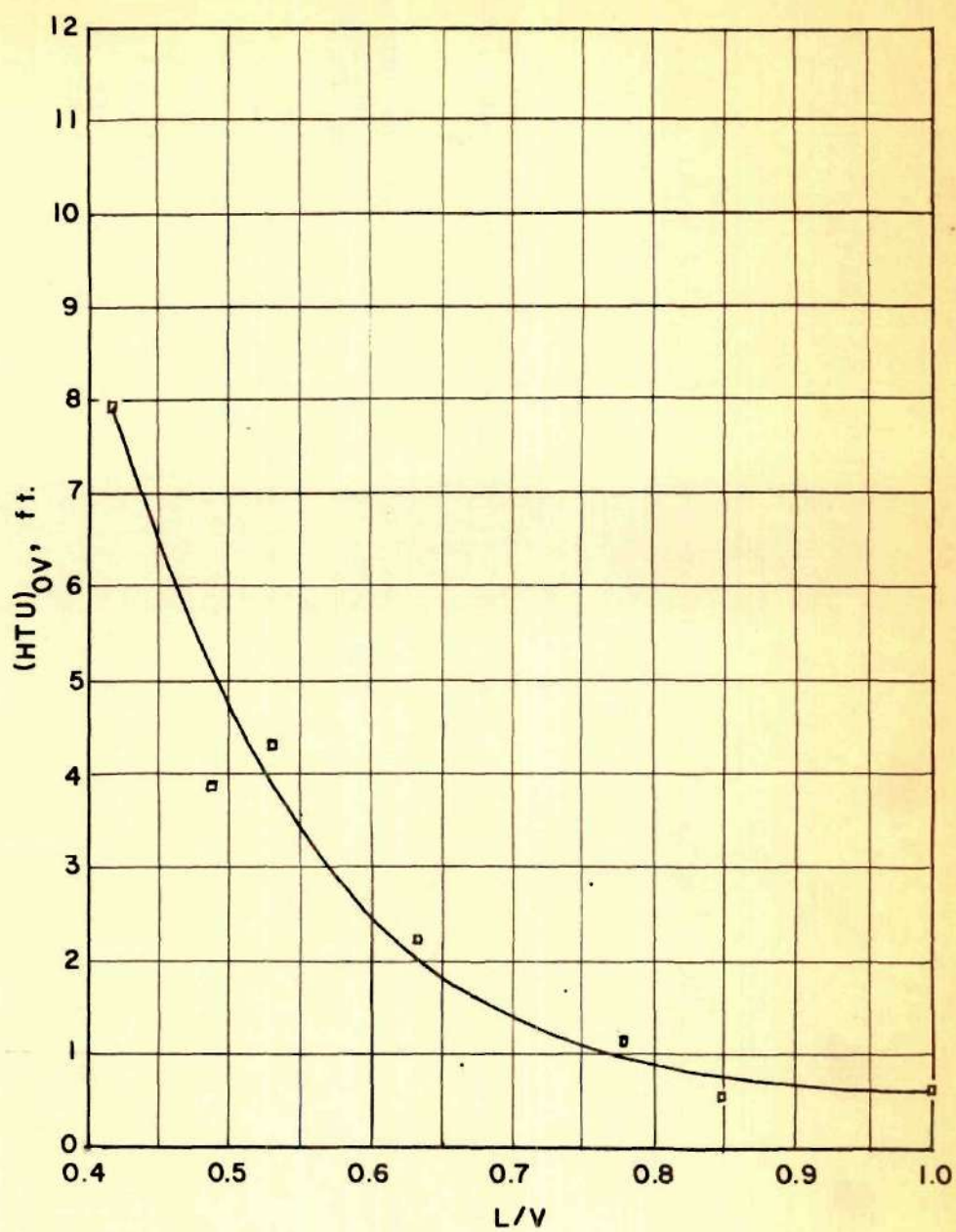


FIGURE 4

 $(HTU)_{OV}$ vs. L/V

Sup. Vap. Vel. = 0.45–0.53 ft./sec.

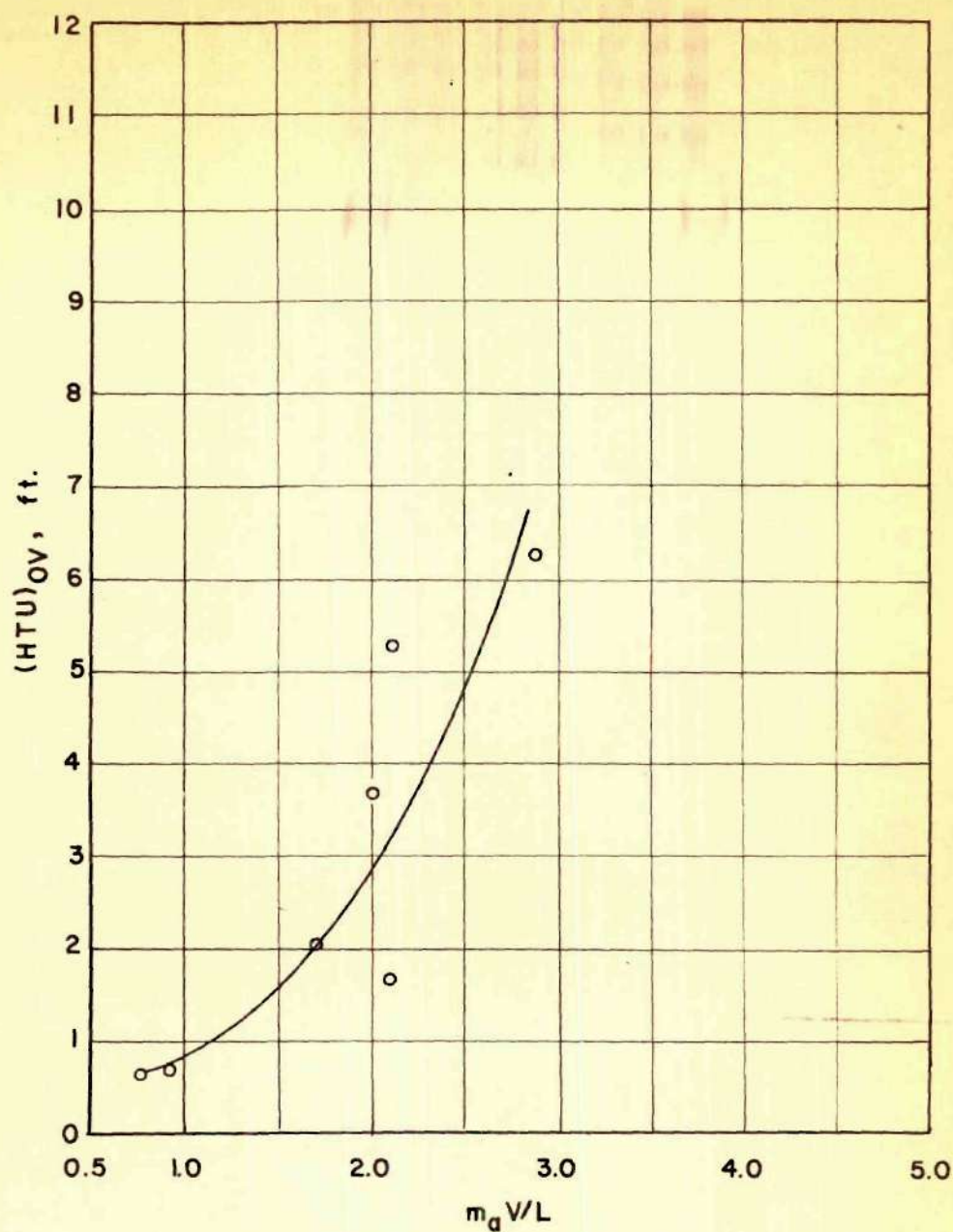


FIGURE 5
 $(HTU)_{OV}$ vs. $m_a V/L$
Sup. Vap. Vel. = 0.18–0.24 ft./sec.

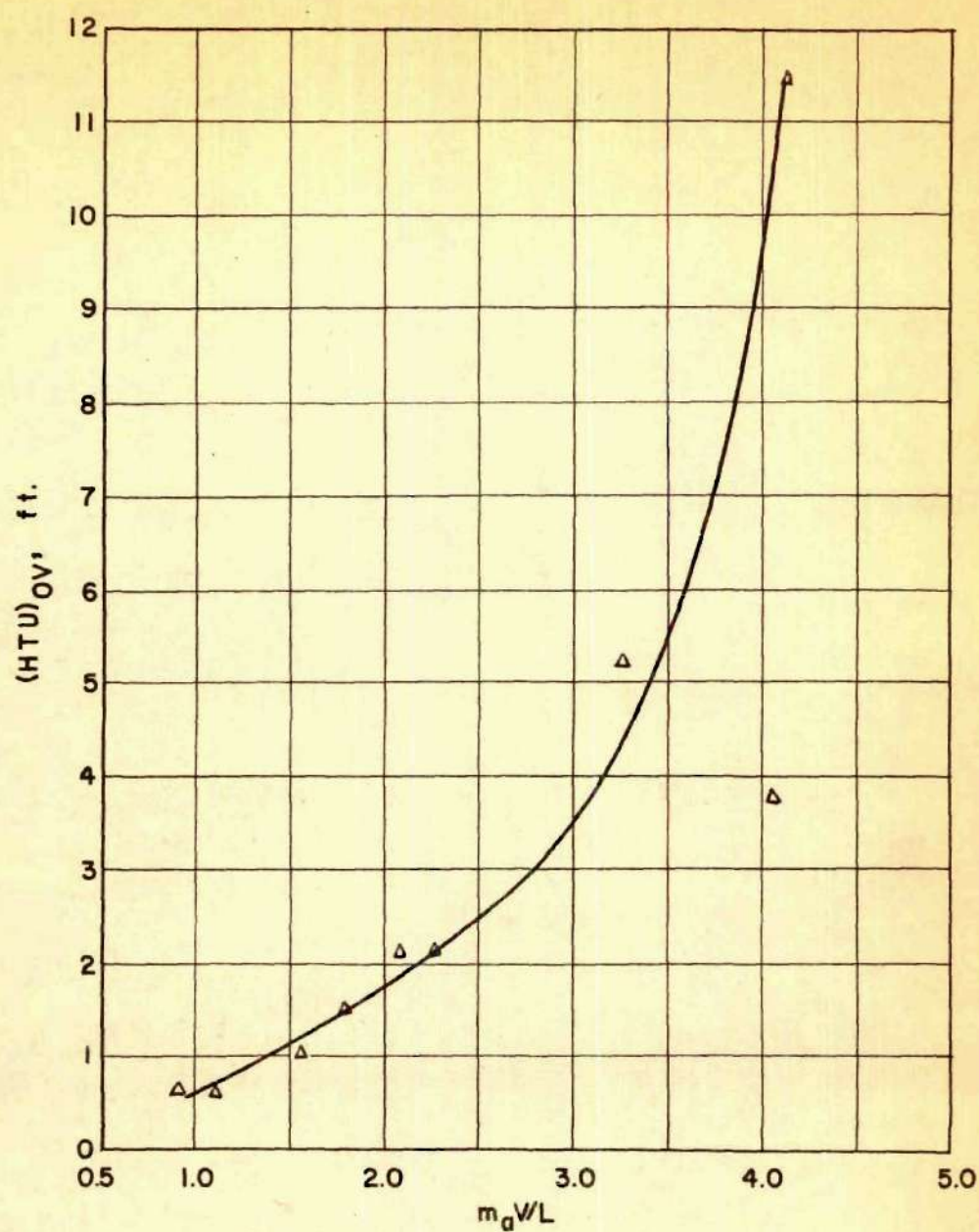


FIGURE 6

 $(HTU)_{OV}$ vs. $m_a V/L$

Sup. Vap. Vel. = 0.83–0.96 ft./sec.

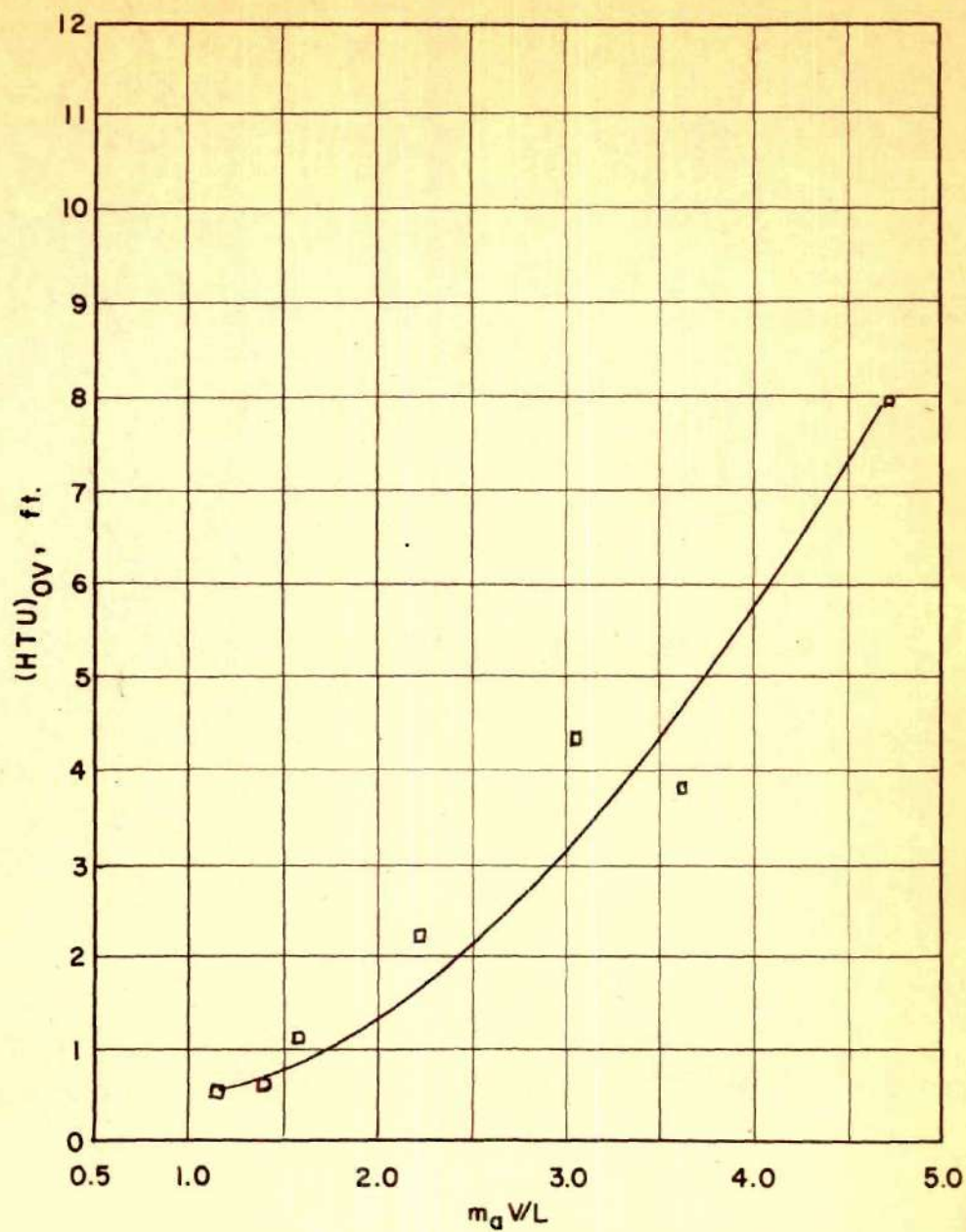


FIGURE 7

 $(HTU)_{OV}$ vs. $m_a V/L$

Sup. Vap. Vel. = 0.45–0.53 ft./sec.

$$(\text{HTU})_{\text{OV}} = (\text{HTU})_{\text{V}} + (\text{HTU})_{\text{L}} \frac{mV}{L}.$$

If this equation were obeyed, a plot of $(\text{HTU})_{\text{OV}}$ vs. $m_a V/L$ would appear as a straight line with the intercept $(\text{HTU})_{\text{V}}$ and the slope $(\text{HTU})_{\text{L}}$. Although considerable scattering of points may be seen, it is obvious that the best line which can be drawn through these points shows a significant curvature. This may indicate that the value of the liquid-film HTU, $(\text{HTU})_{\text{L}}$, is also a function of operating variables, since different values of the slope of the curve may be determined at different values of L/V and of vapor velocity. Because of the considerable curvature of these plots, extrapolation to a value of zero for $m_a V/L$ is not feasible, so that a measure of $(\text{HTU})_{\text{V}}$ could not be obtained.

It will be further noted that these three curves follow essentially the same pattern as that observed in the curves of $(\text{HTU})_{\text{OV}}$ vs. V/L , i.e., the curve for the low-velocity runs is considerably above the other two, and the intermediate-velocity curve falls slightly below that for the highest velocity.

No attempt was made to observe any effect of over-all composition on $(\text{HTU})_{\text{OV}}$ except that, in the first series of runs, over-all compositions of approximately 0.15, 0.20, and 0.31 fictitious mole fraction benzene were studied. No significant effect of over-all composition was noted, either in correlation of $(\text{HTU})_{\text{OV}}$ with V/L or of $(\text{HTU})_{\text{OV}}$ with $m_a V/L$. Fluctuations in over-all composition could be responsible for the scattering of points in the plot of $(\text{HTU})_{\text{OV}}$ vs. $m_a V/L$, although no relation was observed which indicated a definite composition effect.

Comparison with literature data.--Comparison of the data obtained in this work with those of other investigators shows that values of $(\text{HTU})_{\text{OV}}$ for

1/4-inch Raschig rings are similar to those exhibited by other packings. $(HTU)_{OV}$ in this investigation varied from 11.5 to 0.64 feet over the range of L/V from 0.4 to 1.00; the values of $(HTU)_{OV}$ obtained by Carter (18) for benzene-toluene separation in a Fiberglas-packed column varied from 8.97 to 0.27 feet over the L/V range 0.49-1.00. Reported values of $(HTU)_{OV}$ for the benzene-toluene system at total reflux in a column packed with 0.275-inch glass rings are 0.75 and 0.45 feet (19). Values of $(HTU)_{OV}$ reported in the literature (18) for a number of systems and types of packing vary from 0.04 to 2.8 feet at total reflux.

Operation of the column as a stripping section.--Several attempts were made to determine values of $(HTU)_{OV}$ for L/V values greater than unity--the condition which exists in a stripping column. In practically all of these runs, a condition of extreme "pinch" between the operating line and the equilibrium curve was noted at the upper end of the operating line, i.e., the operating line approached the equilibrium curve so closely that reliable values of HTU could not be obtained. Since the function to be integrated in this determination is the reciprocal of the vertical difference between the equilibrium curve and the operating line, a very small error in analysis of the overhead condensate may cause a very large error in the value of $(HTU)_{OV}$. In all but two of the runs made at L/V values greater than one, this "pinched" condition was obtained; the difference between the operating line and the equilibrium curve was less than the experimental error in the boiling point curve used for analysis of the product samples. It was therefore necessary to abandon stripping-region studies of this system.

The exceptions to the analysis above were Runs 10 and 11, which were

made at an L/V of 1.50 (thereby falling within the stripping region) and superficial vapor velocities of 0.296 and 0.292 feet per second, respectively. The results from these runs are quite close; the $(HTU)_{OV}$ values obtained were 1.14 and 1.15 feet, respectively. Although no reliable conclusions may be drawn from these two points, they may indicate the presence of a minimum value in the curve of $(HTU)_{OV}$ vs. V/L , as found by Carter (10).

It is believed that the reason for the results described above may be found in the design of the equipment used in the investigation. As may be seen from the description in Chapter IV and from Fig. 9, the still flask employed was of 12-liter capacity, equipped with a standard heating mantle. This necessitates that approximately five to six liters of mixture be charged to the still so as to prevent superheating of the vapor entering the column. The holdup in the upper section of the column is therefore negligible in comparison to the liquid in the still, so that the composition of the still liquid cannot change as operating conditions change. Furthermore, since the area of the boiling liquid surface in the still is quite large compared to the area of the column from which reflux is descending, the composition of the still vapor is essentially constant at a given over-all composition. This condition does not permit the column to adjust itself freely as operating conditions are changed, leading to the "pinched" condition described above.

The same type of result was occasionally noted at the lower end of the operating line at the lower values of L/V . It was observed that, as L/V was decreased, the composition of the still vapor remained essentially constant at a given over-all composition, causing the operating line to move closer to the equilibrium curve. If this condition had remained,

runs at L/V values below about 0.55 would not have been possible. Further runs were made using the procedure described below.

Before the operating line had approached the equilibrium curve too closely for accurate determination of $(HTU)_{OV}$, about one liter of the benzene-toluene mixture was withdrawn from the still and replaced with an equal amount of pure toluene. The composition of the still liquid, and hence of the still vapor, was thus decreased by about 0.04 (fictitious mole fraction benzene). A run was then made at the new composition, and although the value of $(HTU)_{OV}$ continued the previous trend, the lower end of the operating line was found to be farther from the equilibrium curve than in the previous run. The series was then continued at progressively lower values of L/V .

A proposal for the solution of the problem described above is outlined in Chapter IX of this work.

CHAPTER VIII

CONCLUSIONS

The conclusions obtained from the investigation are as follows:

1. The value of $(HTU)_{OV}$ changes relatively slowly as L/V is decreased from 1.0 to about 0.8. At values of L/V below this point, $(HTU)_{OV}$ rises rapidly and appears to become asymptotic to the line $L/V = 0$.

2. At a given value of L/V , $(HTU)_{OV}$ at the superficial vapor velocity 0.83-0.96 feet per second is somewhat lower than $(HTU)_{OV}$ in the velocity range 0.18-0.24 feet per second. For the velocity range 0.45-0.53 feet per second, the curve of $(HTU)_{OV}$ appears slightly lower than for the 0.83-0.96 range although this difference is not believed to be significant.

3. Correlation of $(HTU)_{OV}$ with $m_a V/L$ yields curves which follow the general pattern of the curves of $(HTU)_{OV}$ vs. L/V although a relatively large degree of scatter, as compared with the L/V plots, may be seen.

4. The plots of $(HTU)_{OV}$ vs. $m_a V/L$ exhibit definite curvature, indicating either that the equation

$$(HTU)_{OV} = (HTU)_V + (HTU)_L \frac{mV}{L}$$

does not apply to this system or that $(HTU)_L$ and $(HTU)_V$ are functions of operating variables.

5. The values of $(HTU)_{OV}$ obtained in this work are similar to those found by other investigators, both with benzene-toluene and with other systems.

6. The equipment employed in this study is not entirely satisfactory for an investigation of this nature.

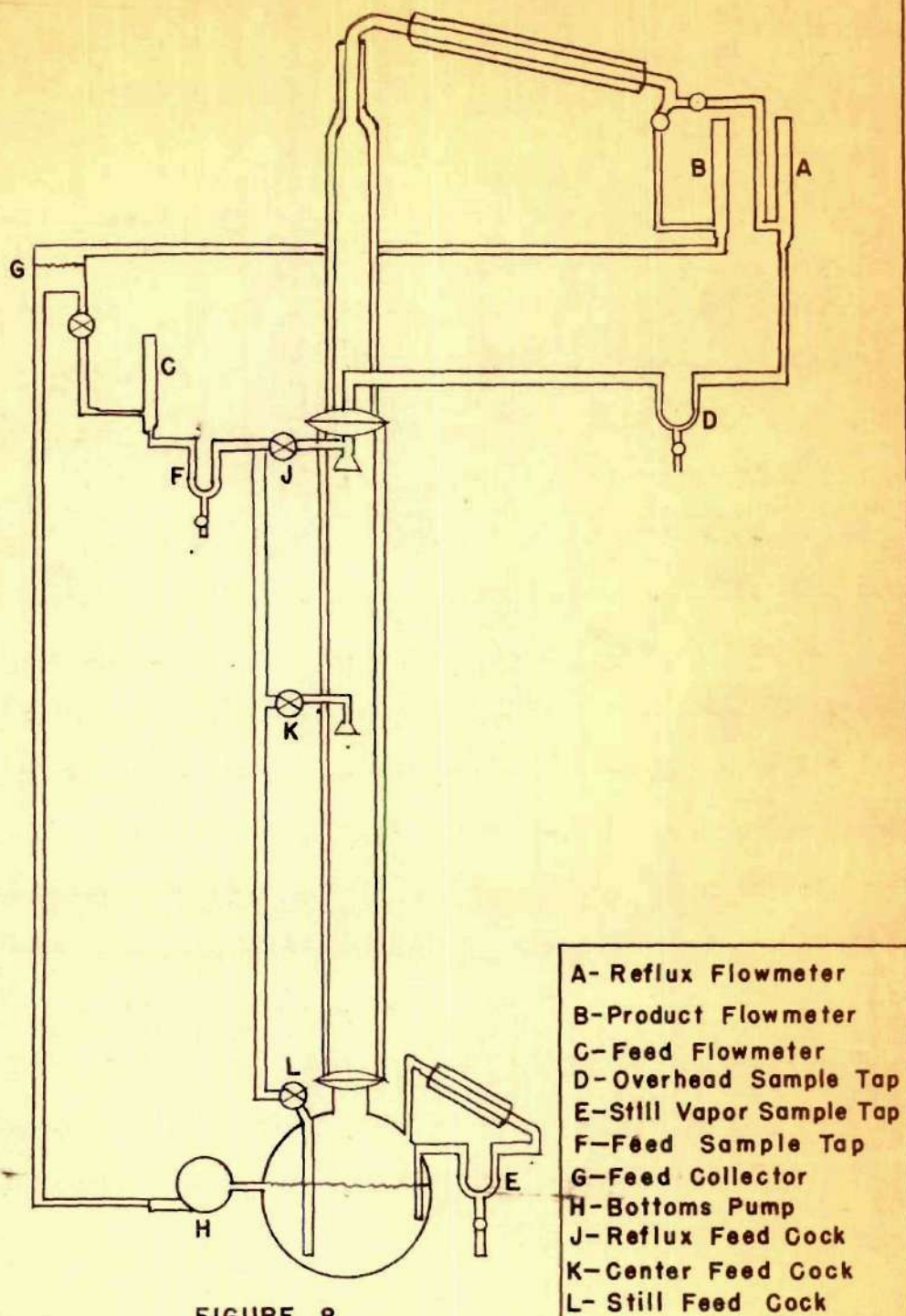
CHAPTER IX

RECOMMENDATIONS

The difficulties encountered in the study are thought to be due to the fact that the composition of the still vapor was not allowed to change freely as operating variables were changed. The proposed equipment shown in Fig. 8 is designed to circumvent this difficulty. Many of the features of the proposed equipment are essentially the same as those of the equipment employed, a schematic diagram of which is shown in Fig. 9.

One of the essential changes in the proposed equipment is the size of the still flask. It is recommended that the capacity of this flask be not more than two liters so that the total volume of the still liquid is not more than one liter. Another important feature is the provision made for continuously withdrawing a portion of the still liquid through a simple overflow arrangement and pumping this liquid back to the feed collector G, where the still liquid is mixed with the overhead product not returned as reflux. In this manner, overhead and bottoms products are continuously withdrawn from the column, mixed, and returned to the column as feed. It is believed that this arrangement will permit the composition of the still vapor to vary more freely as the operating variables are adjusted.

The flow rate of the liquid feed is adjusted by the valve just below the feed collector (see Fig. 8), metered at the flowmeter C, and sampled at the sample collector F. The feed may be admitted to the column



through cock J and the reflux distributor, through cock K to the center of the column, or through cock L to the still, permitting the operation of the column as a stripping, stripping-rectifying, or rectifying column as desired.

The heating windings along the column, the still heaters, superheaters, and reflux heaters remain essentially the same as in the column used. The vapor line and vapor-line heaters are, of course, discarded, and a heater is supplied for the feed line so that feed may enter the column as a saturated liquid.

Recommendations for further minor changes in the equipment are as follows:

Thermocouples Nos. 2, 4, 6, 8, and 10 should be sealed into the column wall rather than enter through a ball-and-socket joint so as to eliminate unnecessary joints which may develop leaks during column operation. In this connection, the entire assembly should be constructed with as few joints as possible, particularly if used with the benzene-toluene system. No method of sealing joints against these liquids and their vapors has been found completely satisfactory.

It is suggested that another thermocouple be placed directly at the column outlet, about eight inches above the present location of couple No. 10, so that the temperature of the vapor leaving the column may be more accurately determined.

Proper venting of the system to the atmosphere is essential if the column is operated at atmospheric pressure; at points where the liquid temperature is close to the boiling point, these vents should, of course, be effected through reflux condensers.

APPENDIX

SAMPLE CALCULATIONS

The data of Run 33, made on October 23, 1952, were selected for the sample calculations. All computations involved in this run are shown below.

The following temperatures were recorded after the column reached equilibrium; determined from Fig. 15:

Thermo- couple No.	Location	Potentiometer Output Current, ma.	Temp., °C
1	Inside Insulation	4.20	105.8
3	Inside Insulation	3.74	99.2
5	Inside Insulation	3.34	85.5
7	Inside Insulation	3.56	90.9
9	Inside Insulation	3.01	77.0
2	Inside Column	4.02	101.6
4	Inside Column	3.96	100.2
6	Inside Column	3.89	98.6
8	Inside Column	3.69	94.0
10	Inside Column	3.47	88.7
11	In Reflux Flowmeter	1.68	42.9
12	In Vapor-Line Condenser	--	--
13	Superheater	3.85	97.7
14	Reflux Heater	2.99	76.6

The other measurements which were recorded are given here, along with the values used in correcting the boiling point analyses.

Power Input to Heaters

<u>Location</u>	<u>Volts</u>	<u>Amps</u>
Column--bottom	61	1.9
Column--middle	53	2.4
Column--top	--	---
Vapor Line--bottom	--	---
Vapor Line--top	--	---
Superheater	68	3.1
Reflux Heater	41	1.8
Still Heater--top	83	3.7
Still Heater--bottom	85	3.7

Flow Rates (see Fig. 14)

<u>Meter</u>	<u>Reading</u>	<u>Flow, cc./min.</u>
Product (A)	4.0	12.9
Reflux (D)	12.3	45.3

Boiling Point Analyses

<u>Sample</u>	<u>Observed Boiling Point, °C</u>	<u>Barometric Pressure, mm. Hg</u>	<u>Exposed Stem Temp., °C</u>	<u>Corrected B.P., °C</u>
Overhead	82.35	742.5	31	83.10
Still Vapor	95.75	742.5	34	96.74

The corrected boiling points indicate (see Fig. 16) fictitious mole fractions of benzene of 0.843 and 0.341 for the overhead condensate and

for the still vapor condensate, respectively. Since the composition of the reflux is the same as the product composition, the point $x_2 = y_2 = 0.843$ is fixed on the x-y diagram. From the product and reflux flow rates, the slope of the operating line, L/V , is calculated as

$$\frac{45.3}{45.3 + 12.9} = 0.780.$$

If the values of x_2 , y_2 , y_1 , and the operating line slope are known, the value of x_1 may be calculated by a material balance, according to the relation

$$L (x_2 - x_1) = V (y_2 - y_1),$$

whence

$$x_1 = x_2 - \frac{V}{L} (y_2 - y_1),$$

where x_1 = mole fraction benzene in liquid leaving column,

x_2 = mole fraction benzene in liquid entering column (reflux),

y_1 = mole fraction benzene in vapor entering column (still vapor),

y_2 = mole fraction benzene in vapor leaving column (overhead),

L = liquid flow rate, moles/hr.,

V = vapor flow rate, moles/hr.

Therefore,
$$x_1 = 0.843 - \frac{(0.843 - 0.341)}{0.780} = 0.209.$$

The entire operating line may now be drawn in on the x-y diagram. The number of transfer units based on the gas film, $(NTU)_{OV}$, is now calculated according to the equation

$$(NTU)_{OV} = \int_{y_1}^{y_2} \frac{dy}{y^* - y}.$$

This value could be calculated by graphical integration by preparing a curve of $\frac{1}{y^* - y}$ vs. y and determining the area under the curve. The same purpose may be achieved, however, by the use of Gauss numerical integration (16) as follows:

$$\text{Let } a = \text{lower integration limit} = y_1 = 0.341,$$

$$b = \text{upper integration limit} = y_2 = 0.843,$$

$$b - a = 0.843 - 0.341 = 0.502.$$

Then, for integration purposes,

$$y_1 = (0.502)(0.0694) + 0.341 = 0.376,$$

$$y_2 = (0.502)(0.33) + 0.341 = 0.507,$$

$$y_3 = (0.502)(0.67) + 0.341 = 0.677,$$

$$y_4 = (0.502)(0.9306) + 0.341 = 0.808.$$

The values of y_i^* corresponding to y_i above are then taken from the x - y diagram, and the function $f(y_i) = \frac{1}{y_i^* - y_i}$ is calculated for each value as follows:

$$f(y_1) = \frac{1}{0.450 - 0.376} = 13.51,$$

$$f(y_2) = \frac{1}{0.639 - 0.507} = 7.57,$$

$$f(y_3) = \frac{1}{0.815 - 0.677} = 7.19,$$

$$f(y_4) = \frac{1}{0.910 - 0.808} = 9.80.$$

Therefore, $(NTU)_{OV}$

$$= (0.502) \left[(0.1739)(13.51 + 9.80) + (0.3261)(7.57 + 7.19) \right]$$

$$= 4.45.$$

Then
$$(\text{HTU})_{\text{OV}} = \frac{5.0}{4.45} = 1.12 \text{ ft.}$$

To calculate the value of m_a , some expression of the equilibrium line slope as a function of y^* is necessary, since by definition

$$m_a = \frac{\int_{y_1^*}^{y_2^*} m \, dy^*}{y_2^* - y_1^*} \quad (1)$$

The value of m for any value of y^* may be immediately determined, provided the equation of the equilibrium curve is known; it is therefore necessary to determine the equation of the fictitious curve of y^* vs. x . If the fictitious vapor-liquid equilibrium relations obey Raoult's Law, the equation of the curve will have the form

$$y^* = \frac{x}{a + bx} \quad (2)$$

This equation may be rearranged to the form

$$\frac{y^*}{x} = \frac{1}{a} - \frac{(b)}{(a)} y^*, \quad (3)$$

so that a plot of y^*/x vs. y^* will yield a straight line of slope $-b/a$ and intercept $1/a$.

Fig. 21 shows a plot of the data of Table 1, plotted in the form above. A straight line may be drawn through these points with a maximum error of somewhat under 6 per cent, corresponding to a y^* value of 1.00. The average error of this line is less than 2 per cent.

From the slope and intercept of this line, the values of a and b may be calculated, yielding the equation

$$y^* = \frac{x}{0.421 + 0.565 x} \quad (4)$$

for the equilibrium curve. Differentiating equation 4,

$$\frac{dy^*}{dx} = \frac{(1 - 0.565 y^*)^2}{0.42} \quad (5)$$

Substituting dy^*/dx from equation 5 into equation 1,

$$m_a = \frac{\int_{y^*_1}^{y^*_2} \frac{(1 - 0.565 y^*)^2}{0.421} dy}{y^*_2 - y^*_1}$$

$$= \frac{(1.82) [(1 - 0.565 y^*_1)^3 - (1 - 0.565 y^*_2)^3]}{y^*_2 - y^*_1}$$

In Run 33, the values of y^*_1 and y^*_2 were 0.388 and 0.933, respectively. Therefore,

$$m_a = \frac{(1.82) \{ [1 - (0.565)(0.388)^3] - [1 - (0.565)(0.933)^3] \}}{0.933 - 0.388}$$

$$= 1.24.$$

The value of $m_a V/L$ is then $\frac{1.24}{0.780} = 1.59$.

The superficial vapor velocity for this run may be calculated from the following data:

Total overhead flow rate: 58.2 cc./min.,

Barometric pressure: 742.5 mm. Hg,

Overhead condensate temperature: 42.9° C,

Overhead condensate composition: 0.843 (fictitious mole

fraction benzene),

Column cross-sectional area: 0.0218 ft.^2 ,

Average vapor temperature: $95.1^\circ \text{ C} = 368.1^\circ \text{ K}$.

Consultation of Fig. 21 shows a density of 0.852 for a mixture of liquid benzene and toluene of the composition above at 42.9° C . The average molecular weight of the mixture is calculated as 90.2. From the data above,

$$V = \frac{58.2 \text{ cc.}}{\text{min.}} \times \frac{0.852 \text{ g.}}{\text{cc.}} \times \frac{1 \text{ lb.}}{454 \text{ g.}} \times \frac{60 \text{ min.}}{\text{hr.}} \times \frac{1 \text{ lb.-mole}}{90.2 \text{ lb.}}$$

$$= 0.0727 \frac{\text{lb.-mole}}{\text{hr.}}$$

The superficial vapor velocity

$$= \frac{0.0727 \frac{\text{lb.-mole}}{\text{hr.}}}{0.0218 \text{ ft.}^2} \times \frac{359 \text{ ft.}^3}{\text{lb.-mole}} \times \frac{(368)}{(273)} \times \frac{(760)}{(743)} \times \frac{\text{hr.}}{3600 \text{ sec.}}$$

$$= 0.457 \frac{\text{ft.}}{\text{sec.}}$$

Table 1. Relation Between Real and Fictitious
Vapor-Liquid Equilibrium Data
for the Benzene-Toluene System at 760 mm. Pressure.

Real Mole Fraction Benzene (20)		Fictitious Mole Fraction Benzene ¹	
Liquid	Vapor	Liquid	Vapor
0	0	0	0
0.10	0.208	0.088	0.186
0.20	0.372	0.179	0.340
0.30	0.507	0.272	0.473
0.40	0.619	0.367	0.585
0.50	0.713	0.465	0.684
0.60	0.791	0.566	0.768
0.70	0.859	0.670	0.840
0.80	0.912	0.775	0.900
0.90	0.959	0.887	0.951
0.95	0.980	0.943	0.977
1.00	1.000	1.000	1.000

¹Calculated by the author on the basis of a fictitious molecular weight of 89.8 for benzene.

Table 2. Boiling Points of
Benzene-Toluene Mixtures at 760 mm. Pressure.

Real Mole Fraction Benzene	Boiling Point, °C		Fictitious Mole Fraction Benzene
	Literature (21)	Experimental ¹	
0	110.56	110.4	0
0.10	105.71	106.3	0.088
0.20	101.78	102.6	0.179
0.30	98.25	99.1	0.272
0.40	95.24	95.8	0.367
0.50	92.43	92.7	0.465
0.60	89.82	89.8	0.566
0.70	87.32	87.3	0.670
0.80	84.97	84.6	0.775
0.90	82.61	82.2	0.887
0.95	81.34	81.1	0.943
1.00	80.01	80.0	1.000

¹Corrected boiling point obtained in modified Cottrell apparatus.

Table 3. Experimental Data:
Vapor Velocity, L/V , $m_a V/L$, and $(HTU)_{OV}$.

Run No.	Superficial Vapor Velocity, feet/sec.	L/V	$m_a V/L$	$(HTU)_{OV}$, feet
1	0.156	1.000	---	1.215 ¹
2	0.195	1.000	---	0.695 ¹
3	0.209	1.000	0.942	0.700
4	0.200	0.701	1.689	2.07
5	0.223	0.600	1.999	3.64
6	0.216	0.591	2.12	5.28
7	0.182	0.568	2.86	6.27
8	--- ²	---	---	---
9	--- ²	---	---	---
10	0.296	1.500	0.923	1.138
11	0.292	1.500	0.907	1.155
12	--- ¹	---	---	---
13	--- ²	---	---	---
14	---	---	---	---
15	0.237	1.000	0.761	0.690
16	0.217	0.754	2.11	1.68
17	0.959	1.000	0.913	0.642
18	0.936	0.910	1.11	0.642
19	0.882	0.810	1.57	1.044
20	0.890	0.764	1.80	1.54
21	0.857	0.715	2.07	2.16
22	0.864	0.670	2.26	1.51
23	--- ²	---	---	---
24	---	---	---	---
25	0.854	0.421	4.13	11.47
26	0.844	0.467	4.05	3.81
27	--- ²	---	---	---
28	---	---	---	---
29	0.489	1.000	1.42	0.711
30	0.532	0.847	1.15	0.549
31	--- ²	---	---	---
32	---	---	---	---
33	0.457	0.780	1.59	1.12
34	0.454	0.634	2.22	2.20
35	0.505	0.533	3.04	4.31
36	0.478	0.418	4.72	7.96
37	0.481	0.481	3.62	3.83
38	0.930	0.516	3.27	5.29

¹Rejected because of error in sampling.

²Rejected because of extreme "pinch" between operating line and equilibrium curve.

Table 4. Experimental Data:
Still Vapor, Overhead, and Equilibrium Compositions,
and Average Slope of Equilibrium Curve.

Run No.	y_1	y_2	y^*_1	y^*_2	m_a
1	0.268	0.905	0.472	0.960	--- ¹
2	0.450	0.990	0.671	0.995	--- ¹
3	0.372	0.995	0.595	0.997	0.942
4	0.415	0.733	0.487	0.879	1.184
5	0.433	0.631	0.516	0.817	1.198
6	0.417	0.571	0.529	0.773	1.251
7	0.432	0.570	0.548	0.771	1.623 ²
8	0.308	0.807	0.522	0.819	--- ²
9	0.250	0.711	0.447	0.681	--- ²
10	0.218	0.757	0.400	0.777	1.385
11	0.240	0.731	0.433	0.769	1.360 ²
12	0.225 ¹	0.660	0.412	0.660	--- ²
13	---	---	---	---	---
14	0.193	0.836	0.285	0.815	--- ²
15	0.170	0.989	0.332	0.995	0.761
16	0.230	0.570	0.250	0.771	1.59
17	0.408	0.996	0.632	0.997	0.913
18	0.378	0.989	0.535	0.995	1.013
19	0.312	0.859	0.355	0.940	1.27
20	0.297	0.703	0.332	0.862	1.37
21	0.288	0.588	0.328	0.785	1.48
22	0.288	0.551	0.315	0.757	1.51 ²
23	0.201	0.925	0.320	0.919	--- ²
24	0.162	0.890	0.281	0.885	--- ²
25	0.265	0.328	0.347	0.548	1.74
26	0.227	0.329	0.233	0.549	1.89 ²
27	0.214	0.333	0.223	0.552	--- ²
28	0.196	0.362	0.209	0.586	--- ²
29	0.075	0.974	0.164	0.989	1.42
30	0.448	0.996	0.572	0.998	0.974 ²
31	0.394	0.967	0.385	0.986	--- ²
32	0.430	0.881	0.415	0.950	---
33	0.341	0.843	0.388	0.933	1.24
34	0.340	0.589	0.370	0.785	1.41
35	0.284	0.424	0.320	0.658	1.62
36	0.275	0.358	0.318	0.583	1.97
37	0.261	0.377	0.290	0.602	1.74
38	0.265	0.382	0.313	0.607	1.69

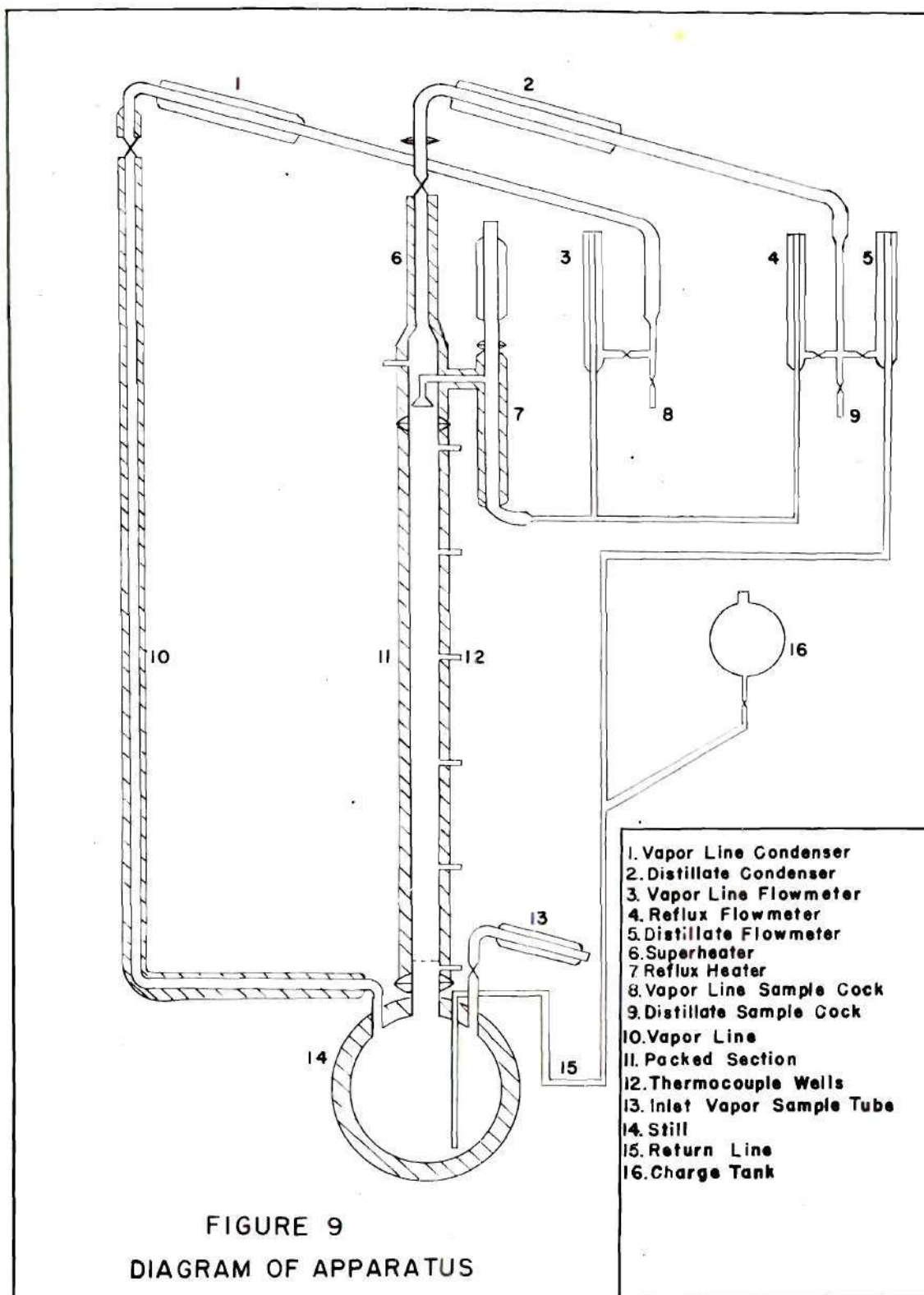
¹ Rejected because of sampling error.

² Rejected because of extreme "pinch" between operating line and equilibrium curve.

Table 5. Operating Conditions:

Column Inlet, Column Outlet, and Condensate Temperatures.

Run No.	Temperature, °C		Overhead Condensate
	Column Inlet	Column Outlet	
1	106.4	93.3	27.0
2	97.7	79.6	30.5
3	101.4	79.9	30.5
4	99.3	95.6	32.0
5	98.9	97.3	32.7
6	98.9	97.5	31.8
7	98.0	96.8	29.3
8	99.6	83.8	31.6
9	103.0	90.0	32.0
10	104.0	86.6	37.2
11	103.5	85.6	35.7
12	105.1	89.5	29.5
13	104.0	90.9	35.9
14	109.2	87.3	25.7
15	108.5	81.1	25.6
16	108.5	101.6	28.0
17	98.9	78.3	67.4
18	98.4	77.7	65.0
19	99.4	85.8	63.7
20	100.2	93.3	60.0
21	100.7	96.6	58.7
22	104.3	100.5	60.8
23	105.9	82.3	67.4
24	107.7	83.6	67.5
25	104.5	102.3	50.7
26	102.5	100.0	58.6
27	102.5	100.0	57.3
28	102.9	100.5	63.6
29	103.1	81.5	45.6
30	99.3	79.7	45.9
31	99.6	81.4	44.5
32	99.8	87.1	44.0
33	101.6	88.7	42.9
34	101.2	97.1	39.9
35	102.3	100.5	42.4
36	103.5	99.6	41.7
37	---	---	43.3
38	---	---	46.0



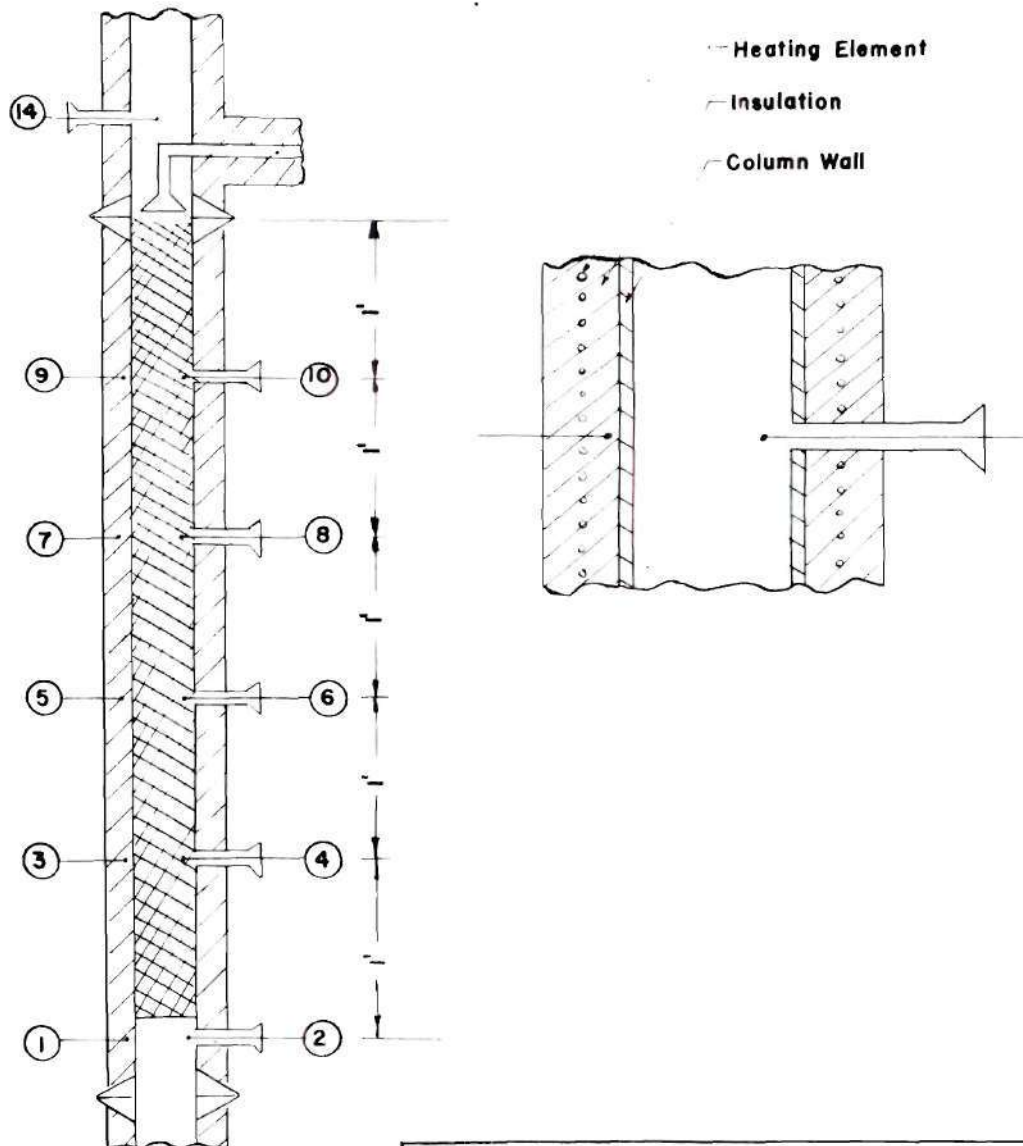


FIGURE 10
THERMOCOUPLE LOCATION

FIGURE 12
WIRING DIAGRAM
HEATER CIRCUIT

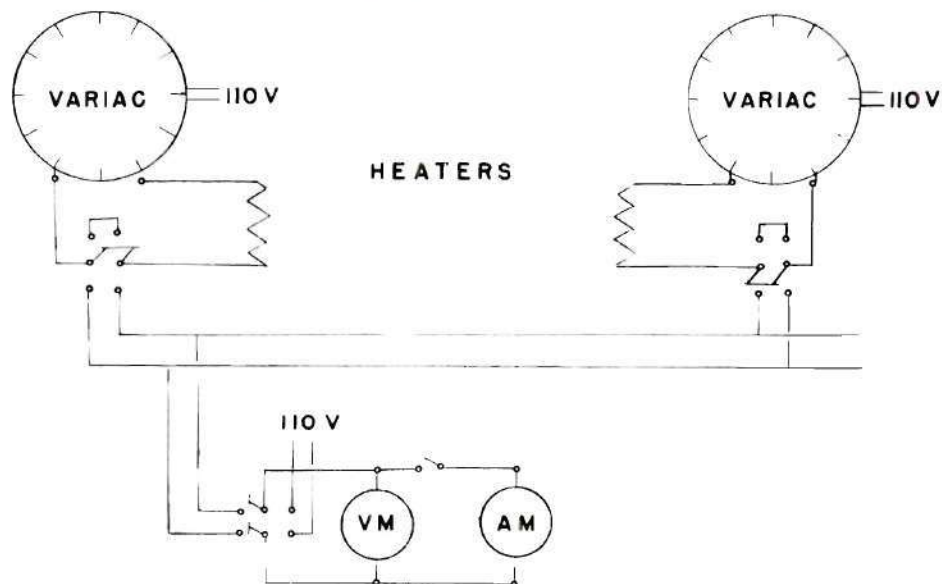


FIGURE 11
DETAIL OF
FLOWMETER

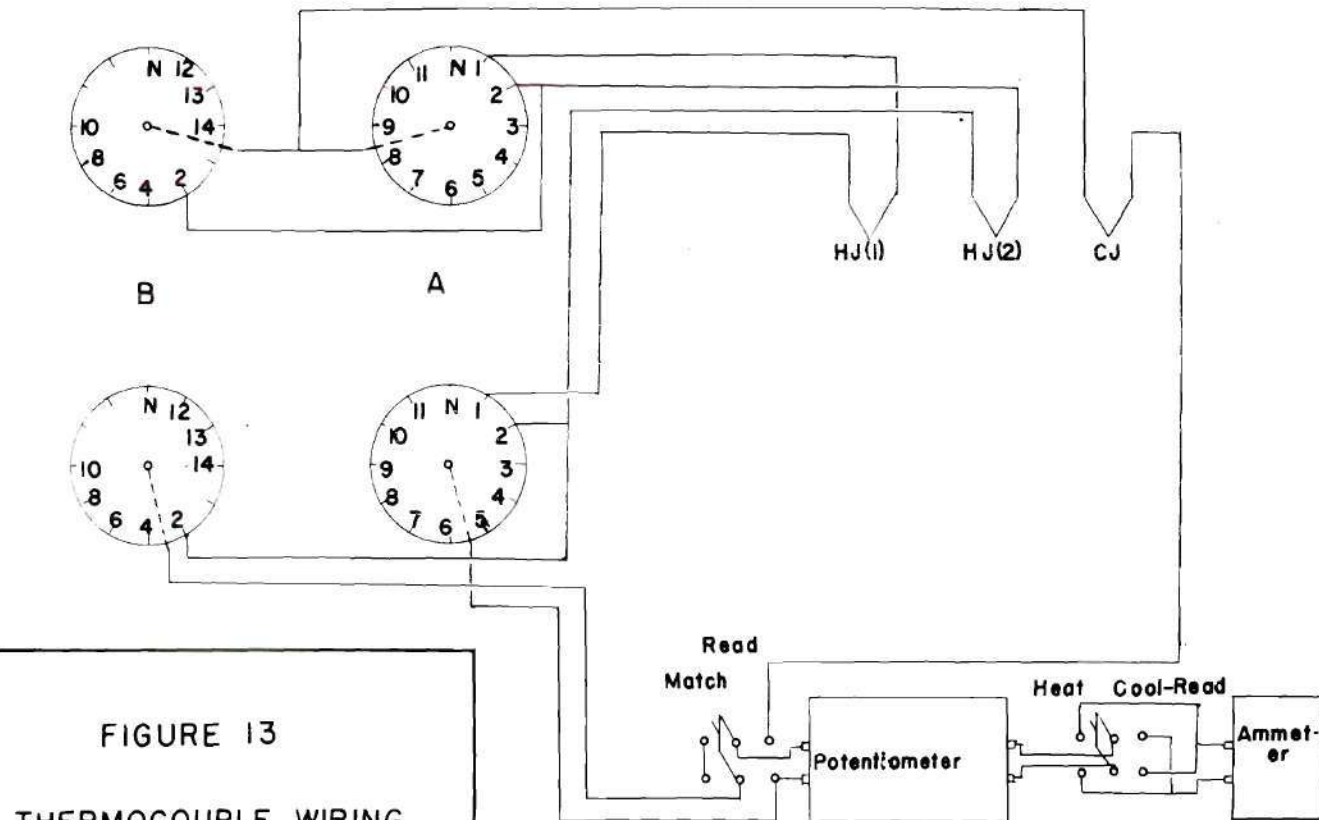
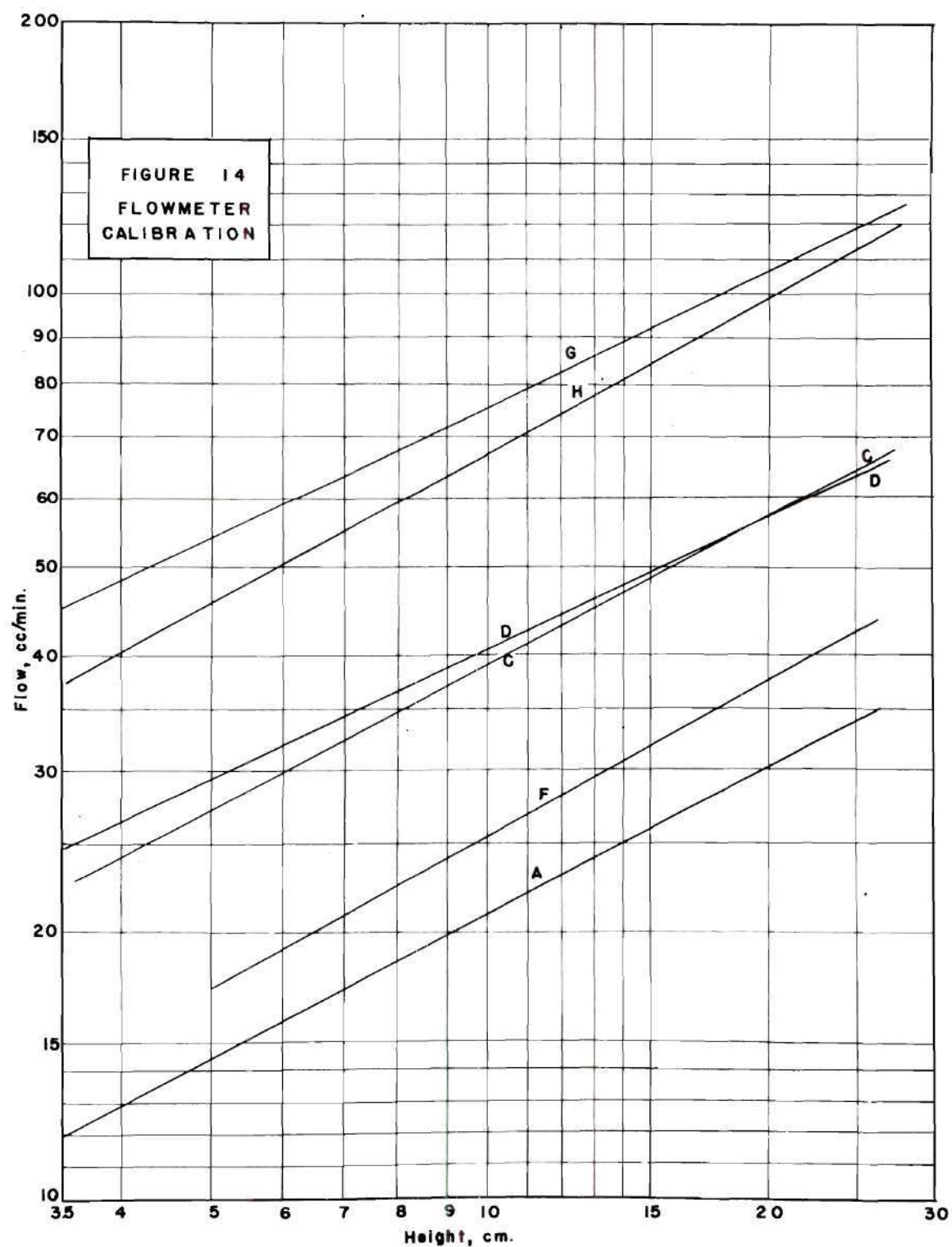


FIGURE 13
THERMOCOUPLE WIRING



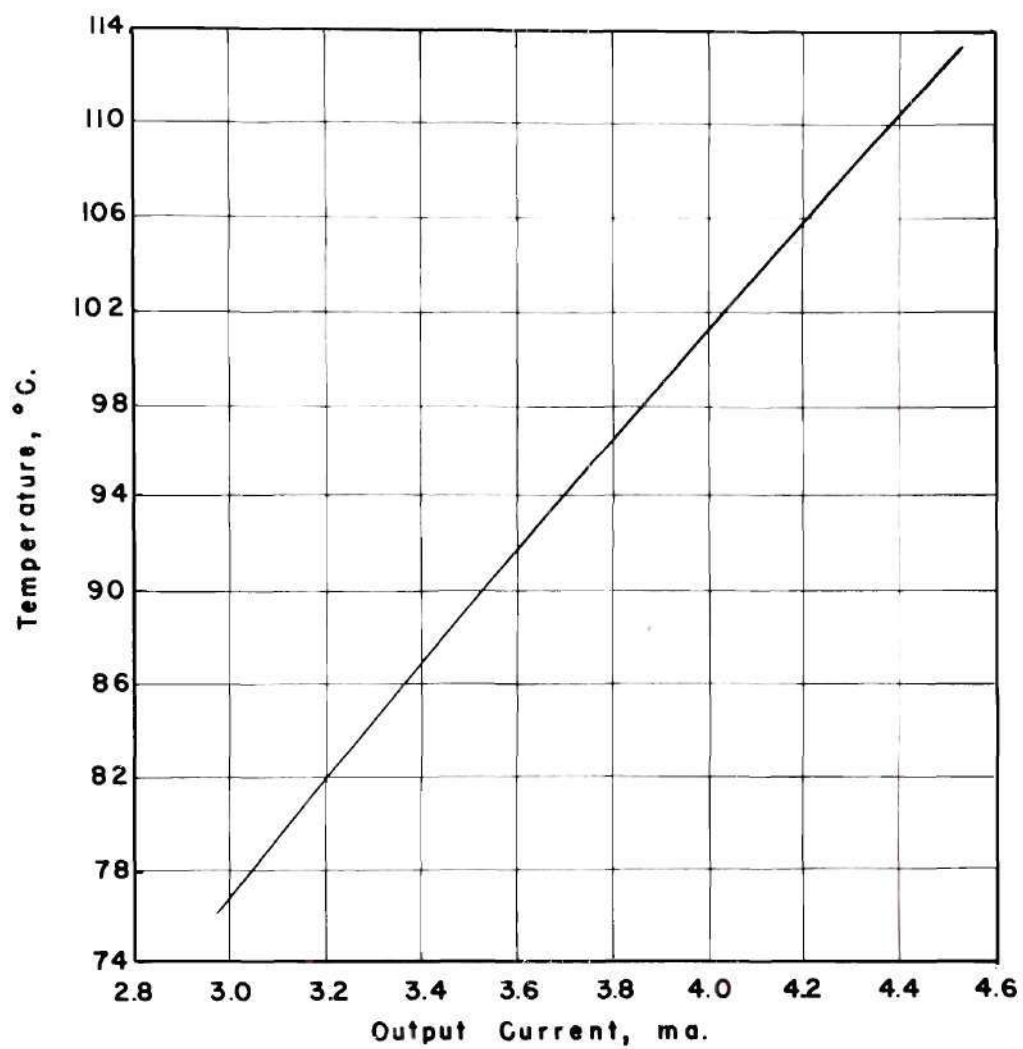
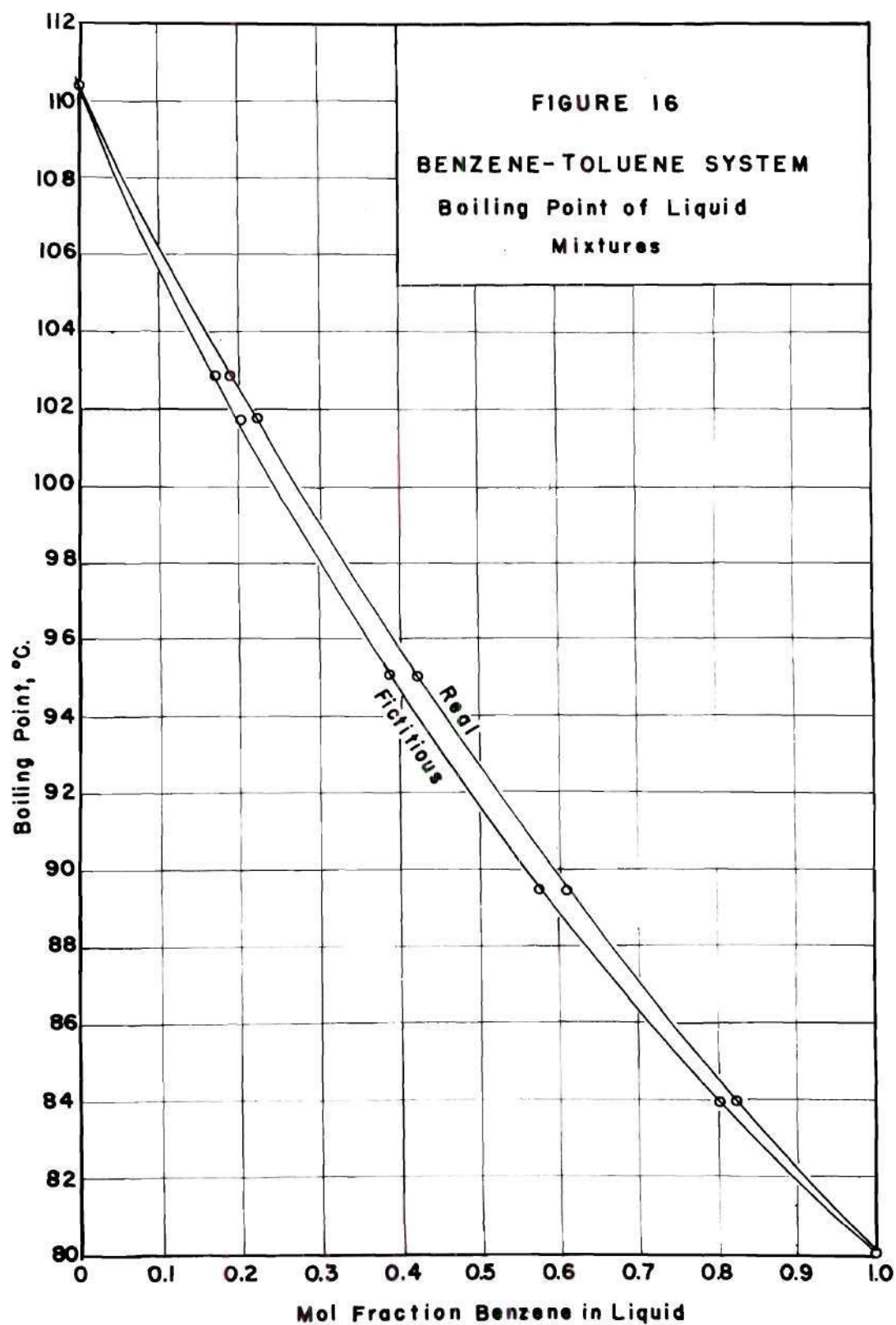


FIGURE 15
THERMOCOUPLE CALIBRATION



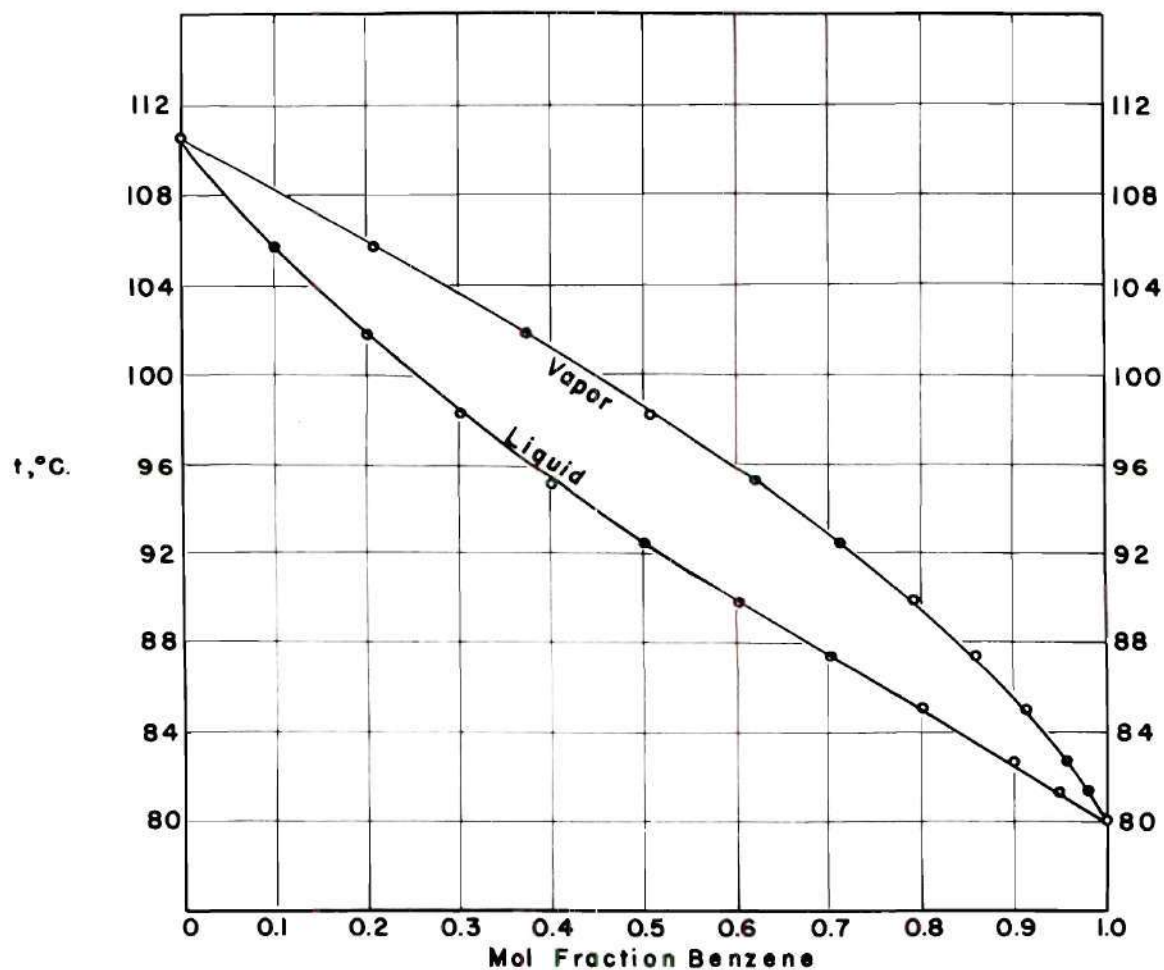


FIGURE 17
BENZENE-TOLUENE SYSTEM:
Real Vapor-Liquid Equilibrium
Relations at 760 mm.

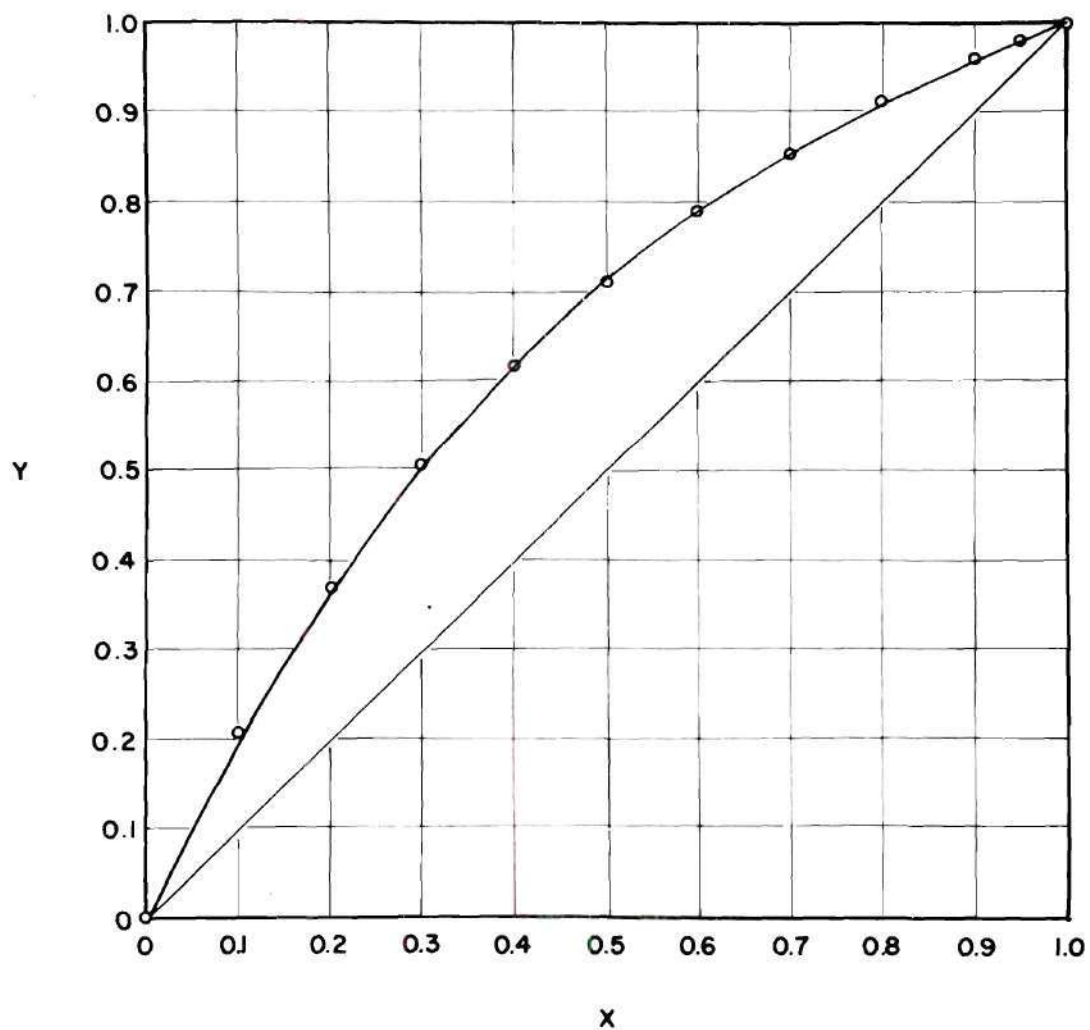


FIGURE 18
BENZENE-TOLUENE SYSTEM:
Real Vapor-Liquid Equilibrium
Relations at 760 mm.

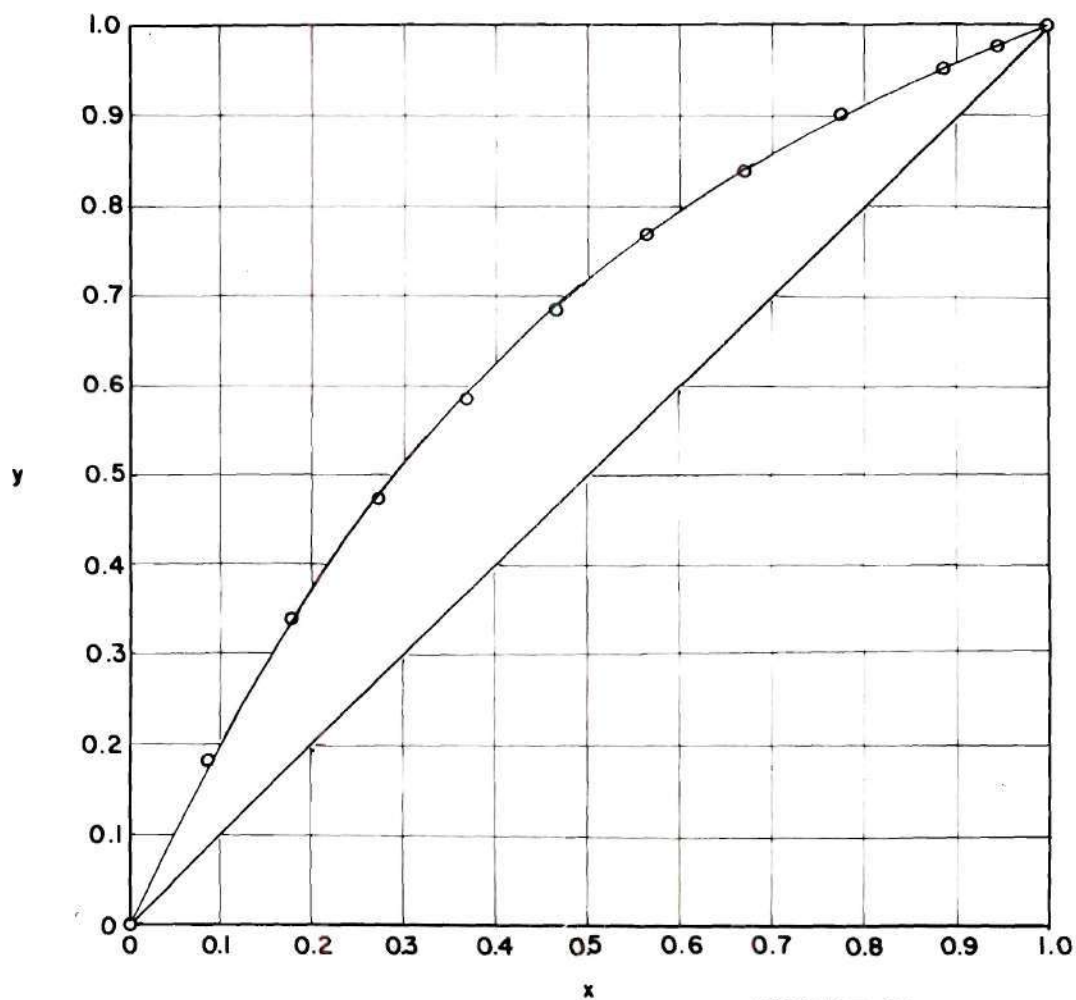


FIGURE 19
BENZENE-TOLUENE SYSTEM
Fictitious Vapor-Liquid Equilibrium
Relations at 760 mm.

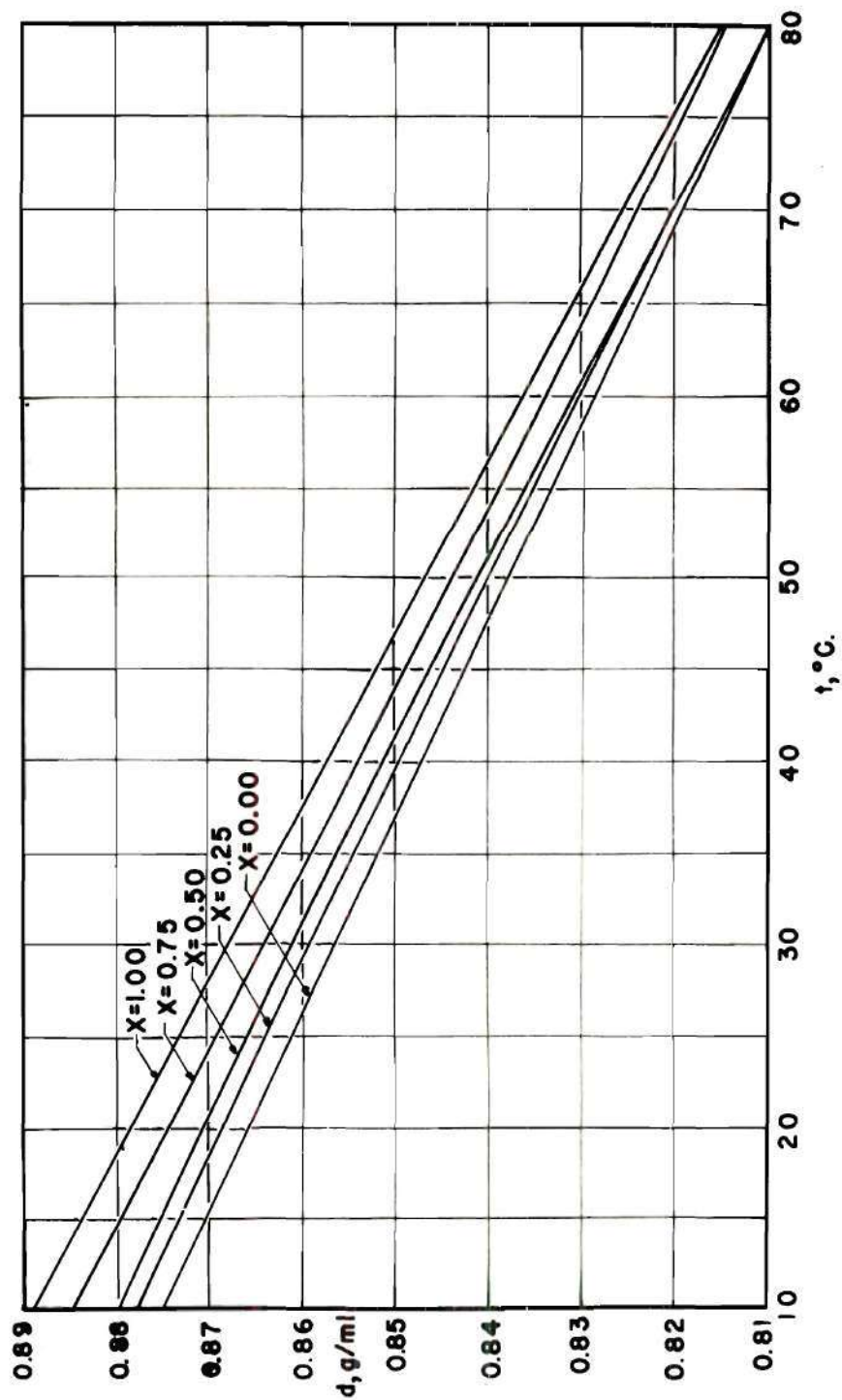


FIGURE 20
BENZENE-TOLUENE SYSTEM
Density of
Liquid Mixtures

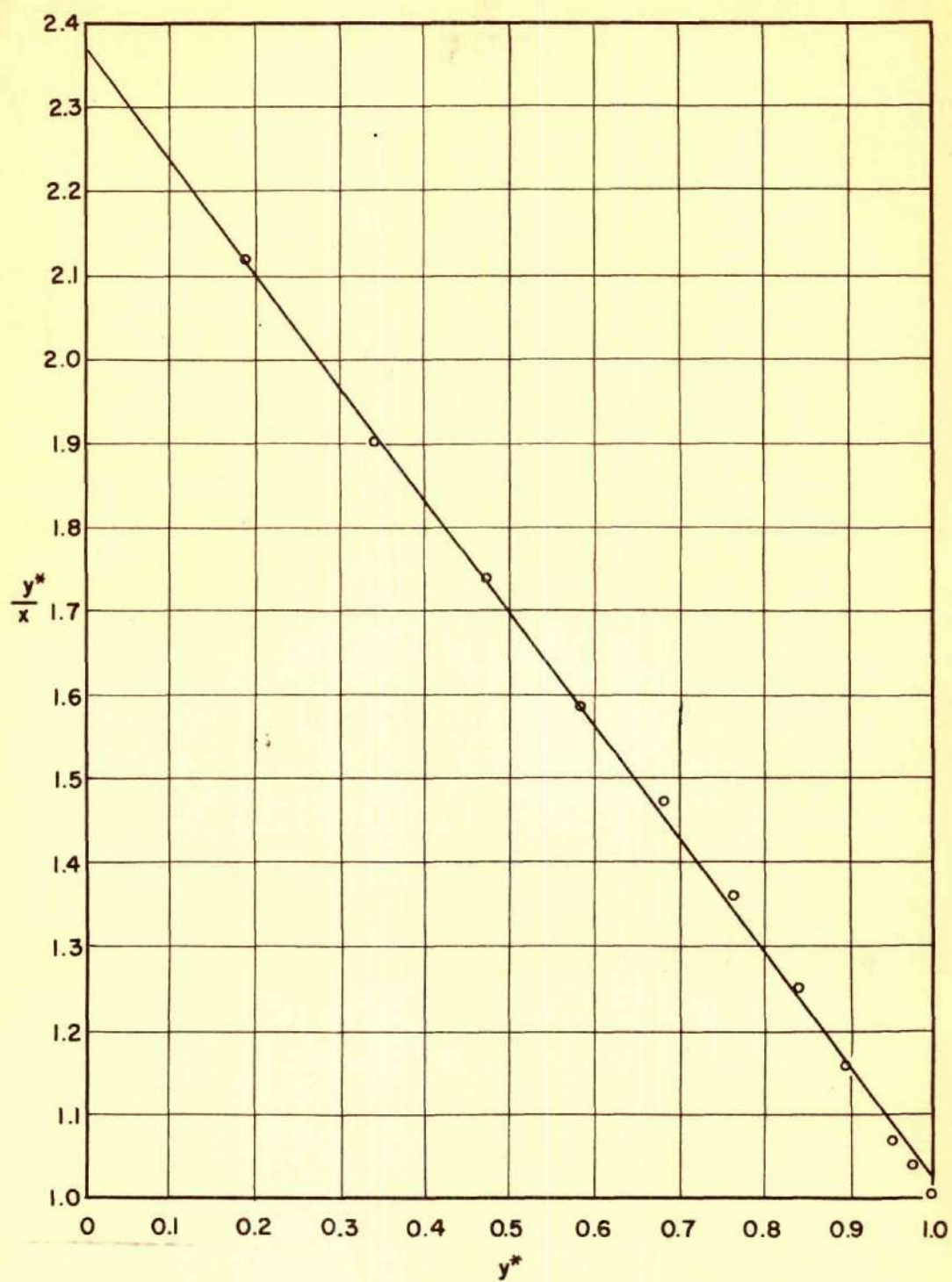


FIGURE 21
BENZENE-TOLUENE SYSTEM
Fictitious y^*/x vs. y^*

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