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A STUDY OF LOW PRESSURE DISTILLATION
IN A PACKED COLUMN

A THESIS

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Master of Science in Chemical Engineering

By
John Loflin Ergle
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A STUDY OF LOW PRESSURE DISTILLATION
IN A PACKED COLUMN

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I wish to express my appreciation to Dr. W. M. Newton who proposed this problem, gave his advice and assistance in carrying it out, and whose many and varied interests are an inspiration to his students.

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Table 1. SYMBOLS

Symbol	Meaning	Units
a	Relative volatility	-
C	Compressibility	-
F	Correlation Factor	-
HETP	Height equivalent to a theoretical plate	ft
HTU	Height of a transfer unit	ft
L	Reflux rate based on the cross section of the empty column	lbs/min-ft^2
M	Molecular weight	-
N	Boil-up rate	Moles/min
n_D	Refractive index	-
P	Pressure at the top of the main condenser	mm Hg
ΔP	Pressure drop across the column	mm dibutylphthalate
R	Gas law constant	mm Hg-ft^3/lb mole-°K
r	Reflux ratio	-
T	Temperature	°K or °C
U	Vapor velocity based on the cross section of the empty column	ft/sec
V	Boil-up rate	ft^3/min
X	Mole fraction	-

Symbol	Subscripts
A	Average
CB	Chlorobenzene

Table 1 (Continued)

Symbol	Subscripts
D	Distillate
EB	Ethylbenzene
S	Still pot vapor
T	Total
W	With X, weight fraction

CHAPTER I

INTRODUCTION

Packed distilling columns.--Interest in the subject of packed columns exists for a number of important reasons. Of these, inexpensive construction and the ability to separate mixtures efficiently are noteworthy considerations. There are disadvantages, and in large diameter columns foremost of these is usually poor reflux distribution known as channeling.

The efficiency of a packed column is based on the height of packed section necessary to produce a certain separation. The measure of column efficiency is the number of theoretical plates or transfer units that a certain column represents. Data are, however, usually presented in a more convenient form. The HTU, height of a transfer unit, and HETP, height equivalent to a theoretical plate, are inversely proportional to efficiency.

Packed columns have advantages in the following types of applications: where materials corrosive to metals must be separated; where low pressure prop is desired, as in vacuum distillation; where low hold-up is desired, as in batch distillation; for semi-commercial operation where the column diameter is small; and where a very large number of plates must be realized in a relatively low height, as in analytical laboratory distillations.

There is a large variety of types and sizes of packings, and as might be expected, the same type packing is quite often used for both absorption and distillation. Generally the most efficient packings are those that cause the reflux to present large liquid surface areas to the vapor and also limit liquid stagnation. The size of packing is important in that the separating efficiencies of smaller sizes of the same type are usually better. This advantage is limited by larger pressure drops and channeling in the smaller sizes.

Low or subatmospheric operating pressures are normally used when lower temperatures are needed to avoid decomposition or polymerization of the products, or where improved equilibrium relations result.

Theoretical considerations.--For operations of interest to both research and production phases of industry, there is the desire to predict distilling column capabilities for design or improved operation purposes. The necessity of determining what are the operating variables and their effects becomes immediately evident, and a number of distillation studies have been made throughout the world.

Murch (1) has suggested that the variables to be considered are liquid and vapor rates; shape, size, and material of packing; degree of wetting; tower diameter; packed height; ratio of tower diameter to packing size; liquid distribution; operating pressure; and the physical properties of the liquid system.

When the operating pressure of a column is reduced, the vapor velocity will increase if the boil up rate is held constant. This reduces the gas film resistance which tends to improve diffusion across the vapor-liquid interface, allows a closer approach to equilibrium, and an improved separation. On the other hand, the increased vapor rate results in a reduced time of contact for the vapor, an increase in the mixing of the vapor in the direction of the column axis, and an increase in entrainment, all of which tend to make the separation poorer. The lower temperatures resulting from lower operating pressures will decrease the vapor viscosity, improving diffusion, and as a rule increase the liquid viscosity, making diffusion poorer. Lower pressures can either improve, make poorer, or leave unchanged the equilibrium relations.

Daniel's experimental work.--Reports in the literature demonstrated to Daniel (2) the importance of the liquid reflux velocity and the vapor velocity. This led him to suggest that the most important variables in packed columns might be the time of contact for both reflux and vapor. This statement is made with the provision that column height and diameter, packing, composition of the mixture, and reflux ratio remain fixed. The time of contact considerations indicated a probability approach, and Daniel put forth the idea that column efficiency could best be correlated at total reflux by the product of the two variables, vapor velocity and liquid velocity, regardless of the pressure. Of course, the actual vapor velocity and liquid reflux velocity through the packing are usually unknown, and while they can be estimated, a somewhat different approach was made by Daniel. Daniel suggested that the actual vapor velocity was very nearly proportional to a superficial vapor velocity calculated on the basis of an average column pressure and the cross sectional area of the empty column. This proportionality also assumes no changes in wetting of the packing or hold-up. Daniel also suggested that by neglecting changes in wetting and changes in liquid density in the packed section, the actual liquid velocity would be directly proportional to a superficial velocity based on the cross section of the empty column. The above lead to the conclusion that efficiency at total reflux could be correlated by the product of the superficial vapor and liquid velocities.

For Daniel's data this was indeed true, and a logarithmic plot of HTU versus L times U resulted in a single straight line with a positive slope. This plot is presented as Figure 1. on the next page. In addition, Daniel was able to correlate his results at all reflux ratios by using the above product multiplied by an empiracal factor, F, involving reflux ratio and operating pressure.

$$F = \left[\frac{r + 1}{r}\right]^{1 + P^{-0.35}}$$

For this equation, P is in atmospheres.

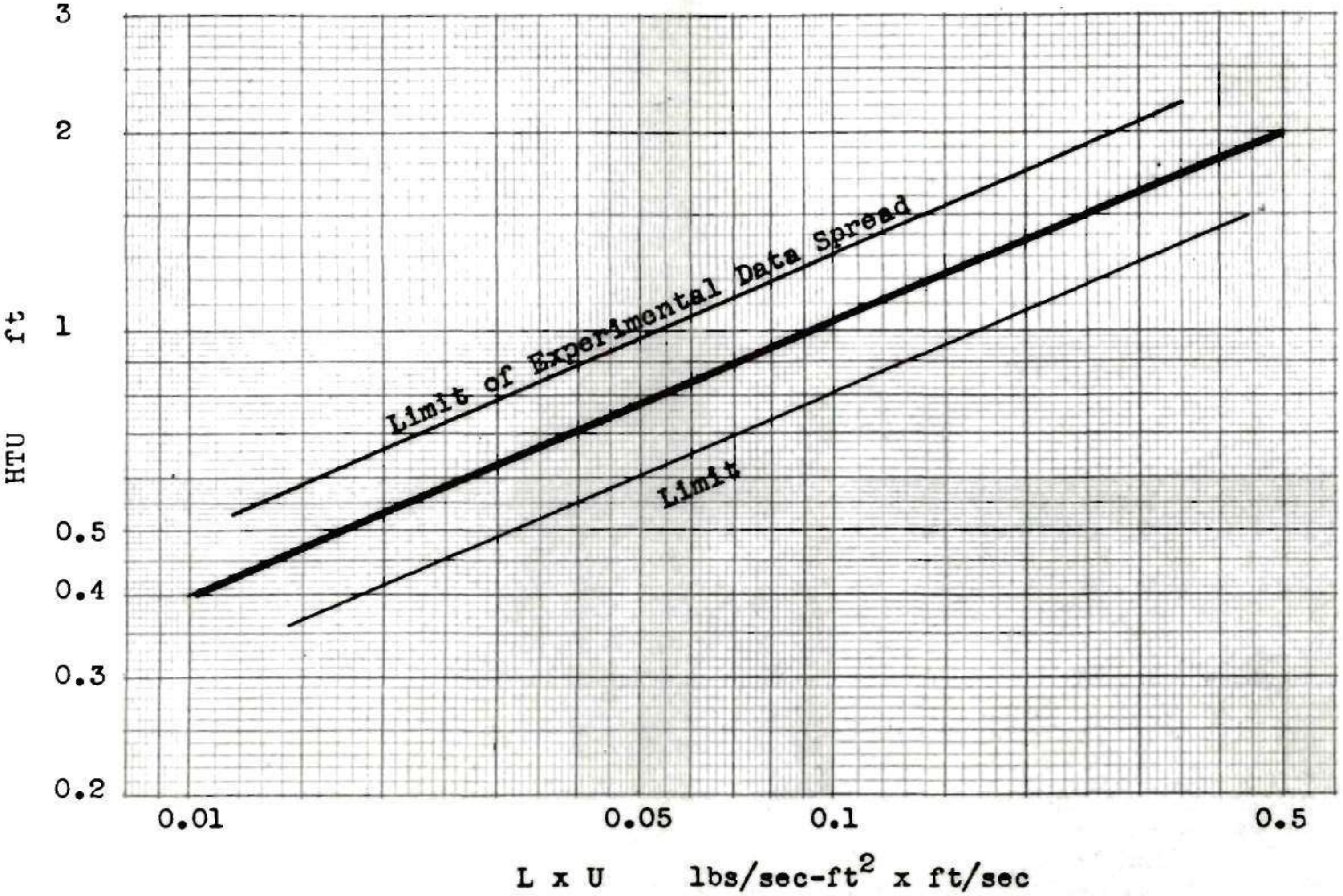

Figure 1. HTU Versus Reflux Rate Times Vapor Velocity

This plot is presented as Figure 2.

In view of the fact that Daniel made his study using only the system methyl and isopropylbenzoate and that other work in the literature does not strongly support his theories, it was decided to extend the work. This was to be done by making a study with chlorobenzene and ethylbenzene mixtures with a rebuilt apparatus using the same packing and general set-up as before.

Literature reports.--A literature survey yielded some 17 papers of direct interest. Of the group reviewed by Daniel (2): Nandi and Jalota (3), Smoker (4), and Schofield (5) report slightly lower efficiencies at subatmospheric pressures. Feldman, Myles, Wender, and Orchin (6) and Berg and Popovac (7) obtained results indicating essentially no change in efficiency with pressure change. Skoble and Driatskaya (8), Struck and Kinney (9), and Myles, Feldman, Wender, and Orchin (10) all have done work indicating improved efficiencies at subatmospheric pressures.

It must be kept in mind that even though efficiencies at lower pressures may compare favorably with those at atmospheric pressure, the boil-up rates may or may not be the same for the point of comparison. Experimental data are quite often presented as a plot of HTU or HETP versus boil-up rate for the case of total reflux, the plot having different curves for each operating pressure.

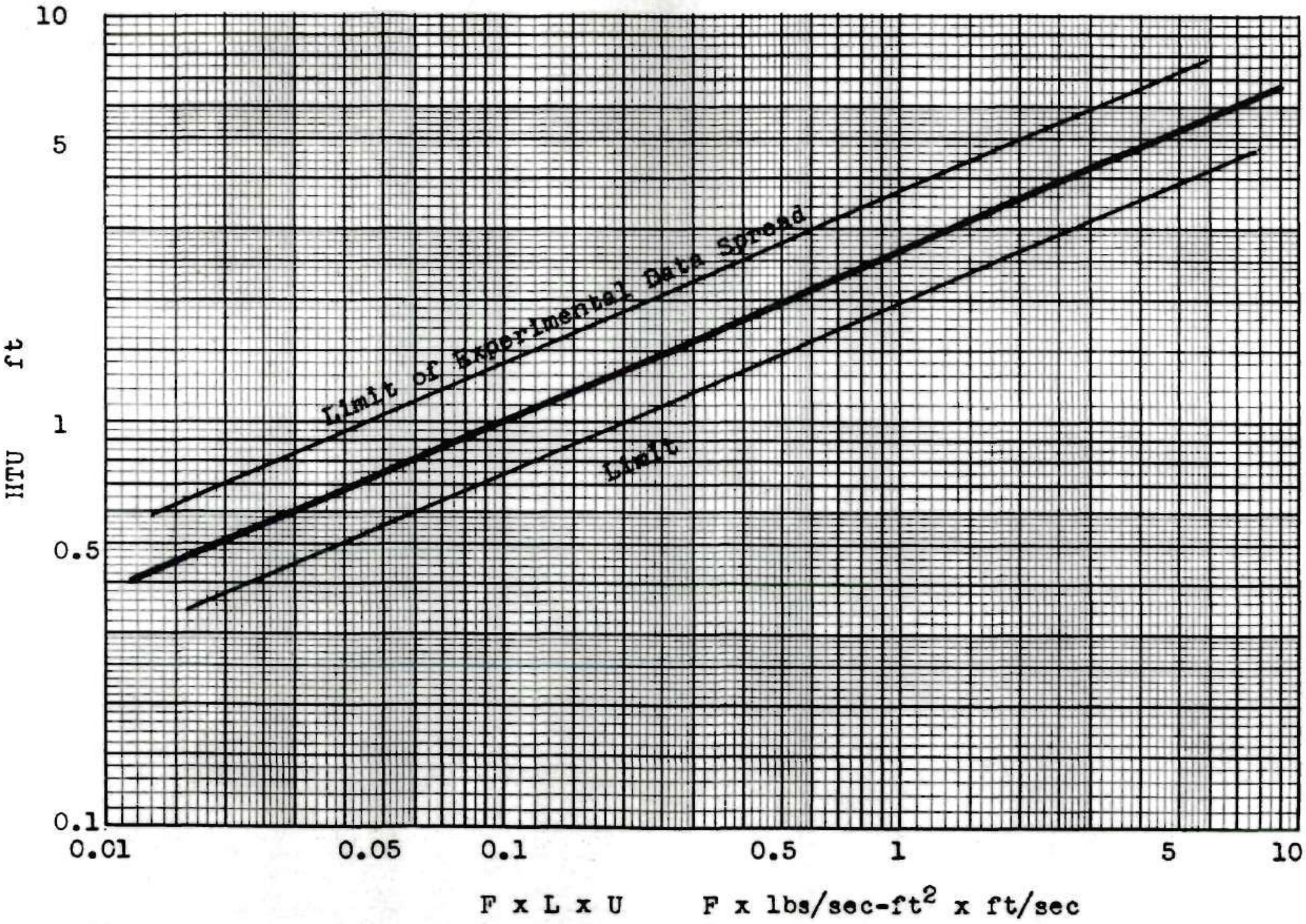

Figure 2. HTU Versus Correlating Factor Times Reflux Rate Times Vapor Velocity

More recently additional work has been reported. Morton (11) has studied the operation of commercial and semi-commercial columns with Steadman packing which were used for separating petroleum fractions. He found the most efficient operating pressure depended on the boil-up rate and that efficiencies decreased rapidly as the boil-up rate increased.

Hawkins (12) ran tests using two small columns and two binary systems in each. The first column contained a spiral screen packing in an annular cross section and the other glass Raschig rings in a conventional column. One binary was a mixture of ethylbenzene and chlorobenzene and the other a mixture of normal heptane and methyl cyclohexane. Runs using the benzenes in the first column indicated slightly higher efficiencies at 20 millimeters of mercury than at 760. In the second column with the same binary, results were just reversed. A study at 760 and 300 millimeters with the first column and the heptane mixture indicated the more efficient operating pressure depended on boil-up rate. In the second column this mixture was separated to a slightly greater degree at 760 millimeters for all boil-up rates. In all four cases efficiency decreased with increased boil-up rate.

Bliss, Eshaya, and Frish (13) have conducted experiments using a mixture of orthodichlorobenzene and orthodiethylbenzene. They carried out their experiments in two different columns. One of these was about three inches in diameter and packed to a height of five feet with one-half inch carbon Rashig rings. The other was also about three inches in diameter and packed with bell-shaped pieces of brass strung on several wires running the length of the column. The height of this packed section was about three feet. The experimental pressure range was ten to one hundred millimeters of mercury, and there was a marked decrease in efficiency as the pressure was lowered. At all pressures the efficiency was independent of boil-up rate.

Peters and Cannon (14) report studies on a number of packings using both chlorobenzene-ethylbenzene and normal decane-trans-decalin test mixtures. The packings were 0.16 and 0.24 inch square stainless steel protruded pieces, 0.25 inch McMahon, and 0.25 inch Berl saddles. The column was two inches in diameter and packed to a height of two feet. The pressure range extended from 10 to 735 millimeters of mercury.

The decane mixture when used with the 0.16 inch protruded packing gave results showing the most efficient operating pressure depended on the boil-up rate selected. Efficiencies decreased as the boil-up rate increased at all pressures.

Using the chlorobenzene mixture in this set up indicated improved efficiencies at lower pressures and efficiencies essentially independent of boil-up rate.

Results with the decane mixture and Berl saddles indicated somewhat improved efficiencies at lower pressures and gave efficiency versus boil-up rate curves having minimums for each pressure.

An interesting plot of HETP versus pressure at a constant boil-up rate was used to compare the two protruded and the McMahon packings. The most efficient was the 0.16 inch protruded packing with the McMahon next. The three packings gave essentially straight and parallel lines, with HETP decreasing as the pressure decreased, except that the smaller protruded and the McMahon packings gave minimums near the low pressure ends of the curves.

Kirschbaum and David (15) have conducted experiments in a one hundred millimeter diameter column packed to a height of one meter with eight millimeter porcelain Raschig rings. The systems studied were ethyl alcohol-water, hexane-dichloroethane, and acetic acid-water. Separation was more efficient at the higher pressures, the range of study being 50 to 760 millimeters of mercury. A plot of number of plates versus vapor velocity gave a saddle shaped curve with two maximums, a dip between these, and a rapid drop off at each extreme.

Walsh, Sugimura, and Reynolds (16) have made studies using several columns and a test mixture of dodecane and cyclohexylcyclopentane. The columns ranged in size from 19 to 29 millimeters in diameter and were packed to heights of six to seven feet. Runs with a number of packings, including three-sixteenths inch glass helices, gave results such that the spread of the data was greater than any pressure effect. The range of study was 200 to 760 millimeters of mercury.

Another packing, Podbielniak Heligrid, showed higher efficiencies at lower pressures, the range investigated being 20 to 760 millimeters of mercury. Efficiencies were essentially unaffected by vapor velocity at the lower pressures but decreased with velocity increase at 760 millimeters.

Lloyd (17) and Bowman, Byron, and Coull (18) have presented theoretical arguments pertaining to the effect of reduced pressures. The latter predicted a maximum in the efficiency-pressure plot, while Lloyd predicted a decrease in efficiency with pressure lowering.

Murch (1) has presented a summary of the effects of variables based on a collection of experimental work but declines to comment on effect of operating pressure due to conflicting experimental reports.

In summary, it can be seen that the variety of experimental results indicates the complexity of the relationship between operating pressure and efficiency, and it is not too surprising that the knowledge and ability to predict column performance for design purposes is, indeed, in an incomplete state of development.

CHAPTER II

APPARATUS AND MATERIALS

Introduction.--The experimental apparatus was composed of the liquid-vapor handling system; the heating, condensing, and temperature measuring systems, the pressure control and pressure measuring systems, and the sampling system. These systems and their components were connected by means of "Pyrex" and rubber tubing.

The liquid-vapor handling system.--The test mixture was boiled in a five-liter "Pyrex" flask having three necks with ground glass taper joints. Glass cappillary tubes, some standing on end on the bottom of the flask, were used to reduce bumping. The vapor passed up through the center neck, through an enlarging adapter, and into the column. The column was constructed from a "Pyrex" tube, was about 46 inches long and 1.77 inches inside diameter, and had ground taper joints at each end. The lower packing support was made of a perforated glass cone, opening upward, and was fixed to the wall of the column six inches from the bottom of the column.

The packing consisted of eight-turn glass helices, each piece being one-eighth inch in diameter and three-eighths inch long. For this packing Daniel (2) reported an 83 per cent free volume and a static hold-up of 26 milliliters per

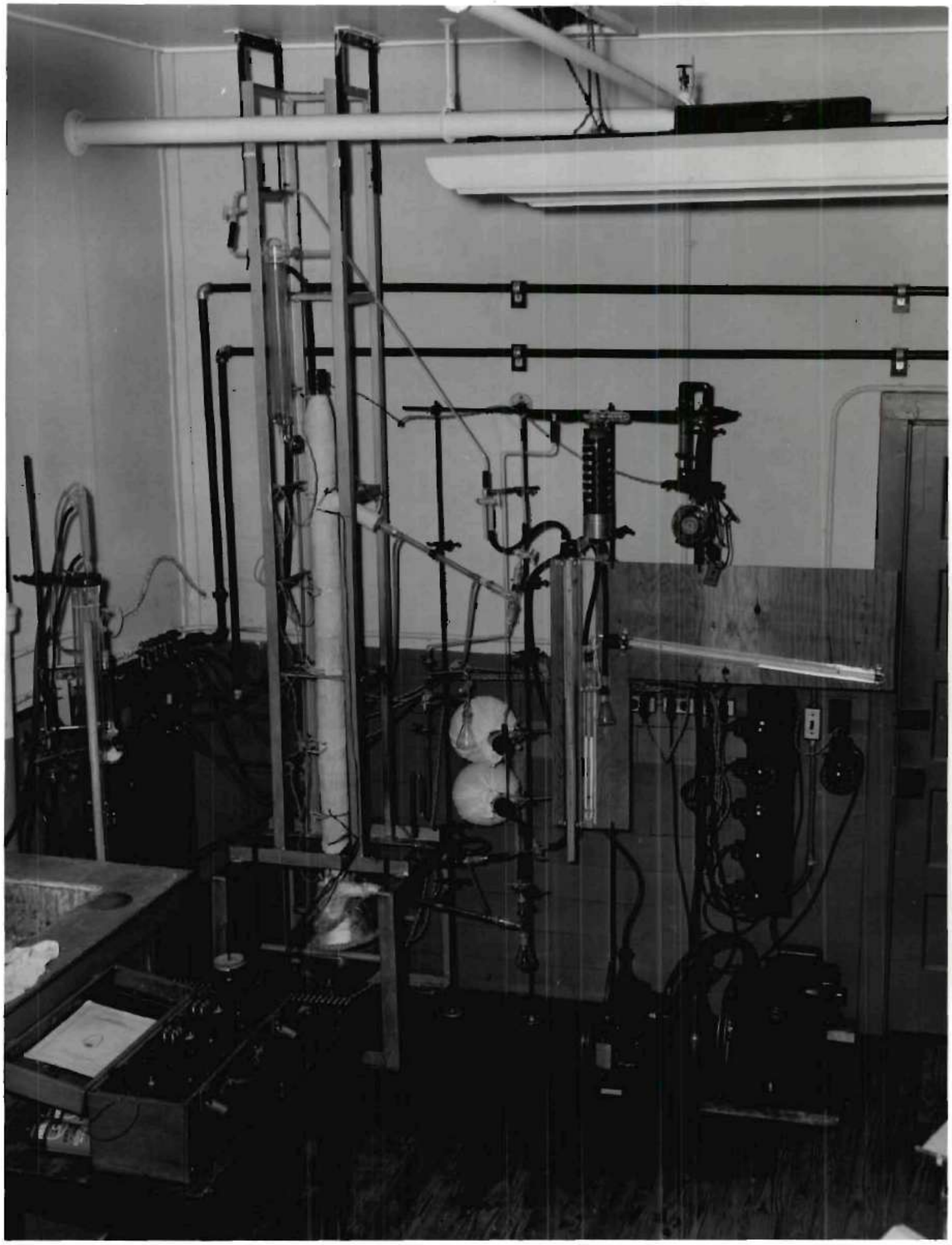

Figure 3. Picture of Experimental Apparatus

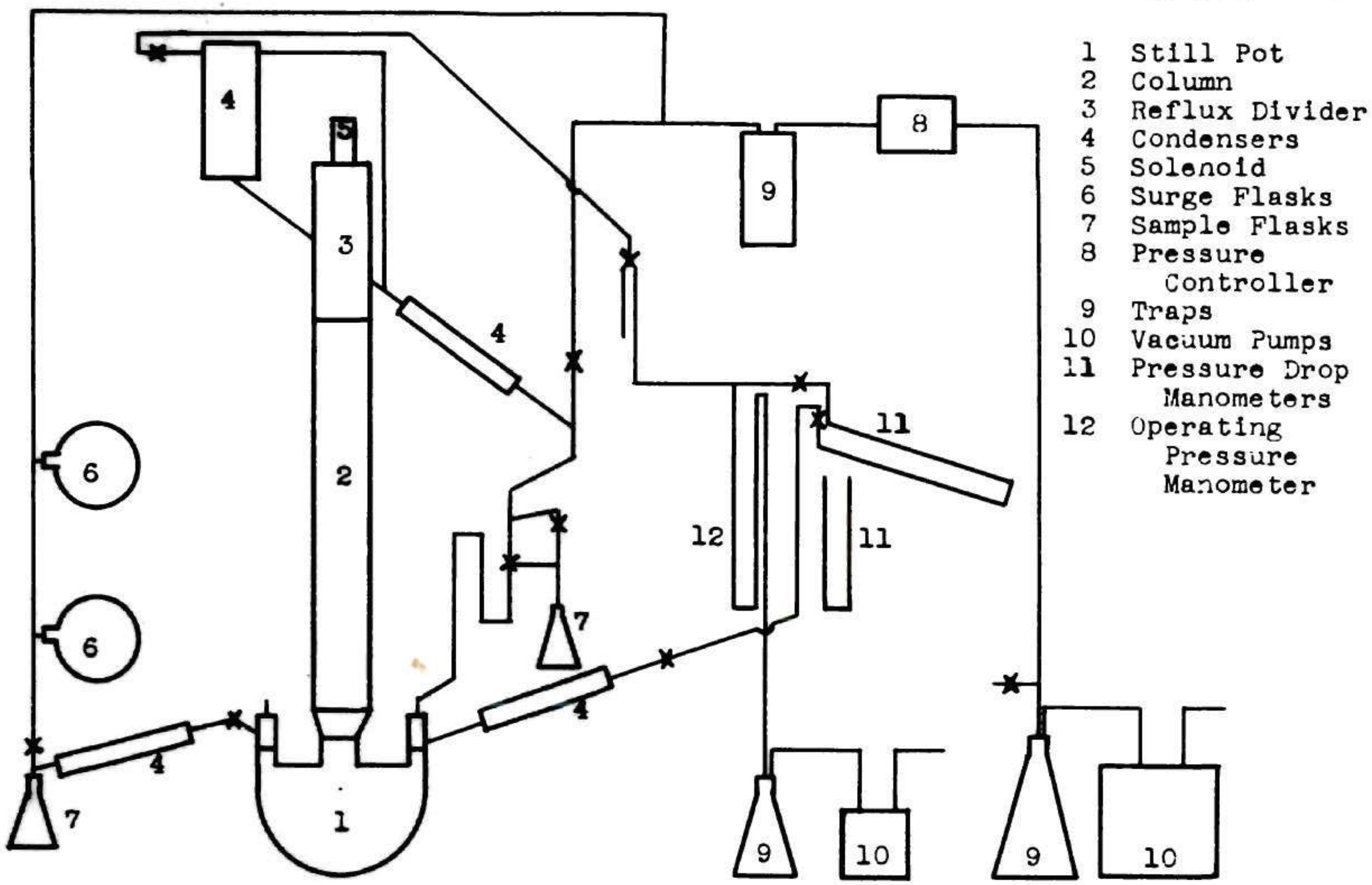

Figure 4. Schematic Diagram of Experimental Apparatus

foot of column for his benzoate test mixture. The column was packed by dropping the pieces into the column one at a time while bouncing the column on a rubber stopper. Occasionally during the filling the column was pounded gently with a piece of rubber tubing. The column was packed to a height of 29 3/4 inches between supports. During his experiments, Daniel noticed that this packing was quite often disturbed when the column was flooded. In order to prevent this during the present experiments, the top of the packing was secured by a parabolic-shaped wire screen made of stainless steel. The parabolic screen opened downward and was held to the bottom support by a wire running through the packing. Early experiments with this arrangement using air and water indicated flooding originated at the bottom support.

After passing through the packing and upper column, the vapor passed up through a reflux divider and into a total condenser. The condenser was joined to the side of the reflux divider by a large ball and socket joint. The liquid condensate followed a path counter-current to the vapor and ran back into the reflux divider.

At this point the position of a solenoid-operated ball and socket valve determined whether the condensate would be returned to the column as reflux or removed as product. When open, the valve allowed the removal of all condensate as product and when closed all as reflux. The solenoid was operated by a General Electric timer with a ten second cycle time and a zero to 100 per cent of cycle time closed circuit setting. With this any desired reflux ratio could be set.

Condensate removed as product passed through a cooler, an adapter connected to the pressure control system, and into the return line to the still. In the return line a product sampling device was inserted. The return line carried the product into the still pot by means of an adapter in the rear small neck. The product was released in the boiling liquid about one inch above the bottom of the flask. This arrangement, of course, allowed operation at steady state and finite reflux ratio without an external feed. The return line was bent to trap enough liquid to provide a seal between the still pot and the top of the column. Since all runs for this study were made at total reflux, this section of the apparatus found use only during sampling operations.

The liquid-vapor handling system was constructed of glass throughout; use of standard adapters, condensers, stopcocks, etc. being made where practical. The ground glass joints of these parts were first sealed using a high vacuum silicone grease distributed by the Dow Corning Corporation. The test mixture readily removed this grease causing contamination of samples and foaming in the still. It was found that for joints coming in contact with the hot liquid, satisfactory operation could be obtained by putting the joints together dry and sealing the lip with a rubbery potting compound. This compound was 1120 PC Potting Compound distributed by the

Minnesota Mining and Manufacturing Company of Detroit. Stopcocks in contact with the liquid were operated without lubrication. When subjected to heat and the liquid mixture for some time, this sealing substance became somewhat porous but was easily resealed with a little lacquer. Some ease in dismantling and cleaning or repairing was lost, but the rubbery material could be removed by scraping and peeling without too much difficulty.

The column, packing, and divider used in this apparatus were constructed by the Ace Glass Company of Vineland, New Jersey.

Heating, condensing, and temperature measurement.--The still pot was seated in a "Glas-col" heating mantle and the upper part of the flask covered by still another heating mantle, each controlled by a variable transformer.

Adiabatic conditions were maintained in the column and reflux divider. These were insulated to a thickness of one-half inch by wrapping with strips of sheet asbestos. A paste of asbestos was used over irregular sections. This insulation was then wrapped with turns of twenty gauge "Nichrome V" resistance wire spaced one-fourth inch apart. This winding was divided into four sections which included the lower column and first ten inches of the packed section, the middle ten inches of packed section, the upper ten inches of packed section, and the upper column and reflux divider. Each of these four sections of winding was connected to a zero to 135 volt variable transformer. Another one-fourth inch of insulation was placed on top of the windings. When adiabatic conditions were desired, enough current was admitted to windings such that the temperature at the winding was equal to the temperature at the column wall. Small unheated and exposed portions of the top of the still pot and lower column were insulated with "Pyrex" glass wool.

Temperature measurement was made using a number of copper-constantan thermocouples. The couples were made from Leeds and Northrup, 24 gauge duplex wire with a silicone resin impregnated double glass wrap. The ends of the wire were twisted and a short length fused in a welding flame. The thermocouples were calibrated in a constant temperature bath before they were installed. The difference in output between any two couples at the same temperature was less than 0.02 millivolts. The calibration of thermocouples agreed with Leeds and Northrup standard conversion tables to less than one degree centigrade. The voltage of the couples was measured with a double range precision potentiometer indicator manufactured by Leeds and Northrup. The couples were connected to the potentiometer through a Leeds and Northrup twelve point rotary selector switch, which made only one ice bath junction necessary and eliminated the necessity of changing leads.

Twelve thermocouples were located as follows: one at the wall and one at the coil of the reflux divider, one in a well in the divider, one at the wall of the upper column, one at the wall and one at the coil of the upper packed section, one at the wall and one at the coil of the middle packed section, one at the wall and one at the coil of the lower packed section, one between the upper still pot heater and the pot, and one in a well in the still pot.

The condensing and cooling system, consisting of the main condenser, the product cooler, the condenser used when removing a vapor sample from the still, and the condenser on the pressure measuring connection to the still, could all be cooled by either tap water or ice water. The ice water system consisted of a 55 gallon barrel, a pump, and necessary connections.

An air conditioning unit and thermostat eliminated abrupt changes in room temperature.

Pressure control and measurements.--As previously mentioned, the pressure control system was connected to the product cooler by means of a "T" adapter at one end of the product cooler. Gases being removed from the system passed first through a connection to the surge system, an ice trap, a pressure control device, a bleeder valve, a surge flask and trap, and finally through a Cenco-Megavac Vacuum Pump made by the Central Scientific Company.

The pressure control device was a cartesian diver type of manostat manufactured by the Emil Greiner Company of New York. The column and equipment could be pumped down to the desired pressure, and then by manipulating a stopcock, this control pressure was trapped beneath a hollow glass float resting in mercury. When the column pressure began to rise, the float would sink, opening a valve to the pump. The pump ran continuously. As the pressure in the column dropped, the float would rise and again close the valve when the column pressure dropped to the control pressure. This device operated unsatisfactorily at 760 millimeters pressure, possibly due to the large pressure drop across it. Some experience was necessary to effectively adjust this device for satisfactory control at lower pressures, and even then the column pressure would sometimes slowly drift. The device controlled the pressure during a run to within 2 per cent. The fact that the pressure control system was connected to one end of the product cooler did not cause pressure control to be impaired when product was being removed. The cooler never ran full of liquid. Also, the connection between the reflux divider and product cooler included a line running to the top of the main column condenser, making the operation of the reflux divider valve unimportant to pressure control.

A surge system to smooth pressure fluctuations was attached by means of a "T" in the line connecting the product cooler to the ice trap. This system consisted of two, five-liter flasks and connecting tubing. This system could be connected to the still pot through a vapor-sampling device to be described later.

Pressure measurements were made using three manometers. One leg of a "U" tube mercury manometer for determining operating pressure was connected to the top of the main condenser and the other leg of this tube connected to a trap and small vacuum pump. This pump was designed to produce pressures as low as 0.0001 millimeters of mercury, and its use allowed the absolute pressure of the column to be read without reference to a barometer. The other manometers were "U" tube manometers filled with dibutyl phthalate and used to measure pressure drop across the column. One of these manometers was inclined to increase its sensitivity ten-fold. Only one of these manometers at a time was used, depending on the magnitude of the pressure drop. The top connection for these manometers was the same as for the operating pressure manometer. The still connection for the pressure drop manometers was made through a condenser and the adapter in the rear small neck of the still pot.

<ins>Sampling and analysis.</ins>--As previously mentioned, the product sampler was attached to the product return line. It was constructed from a ground glass tapered joint over which a sample flask could be fitted. This joint was connected at one side

to the product return line by means of a "T" stopcock in the line. The top of the joint was also connected through a plug-bored, three-way stopcock to the return line. Adjustment of this stopcock allowed either of the two lines that it normally connected to be vented to the atmosphere. Without disturbing column operation, manipulation of these stopcocks allowed the evacuation of the sample bottle, the filling of the bottle, and the venting of the bottle to the atmosphere.

A still pot vapor sample could be removed via an adapter in the front small neck of the flask, a stopcock, a condenser, a "T" adapter, and a sample bottle. The other connection of this last adapter passed up through a plug-bored stopcock to the surge flasks. Opening the latter to the surge system evacuated the condenser and sample bottle to a pressure lower than the still pot pressure by an amount equal to the pressure drop across the column. Upon opening the stopcock to the still pot, a vapor sample flowed into the condenser and the condensate into the sample bottle. Upon closing this stopcock, the sampling set up could be vented to the atmosphere by means of the plug-bored stopcock. This set-up operated quite efficiently and seemed to disturb the column operation very little.

Analysis of samples was made by refractive index using a Bausch and Lomb modified Abbe type precision refractometer. The results of the calibration runs are presented in Figure 6.

Analysis was made at thirty degrees centigrade, the temperature of the samples in the refractometer being controlled by a constant temperature bath manufactured by the Precision Scientific Company, Chicago. Temperature control was to plus or minus 0.04 degrees centigrade or better. This deviation produced negligible errors in the compositions determined. The refractometer had divisions and vernier for one part in 7,200 and could be estimated to one part in 14,400. A change of one part in 14,400 entailed a refractive index change of 0.00003 and a mole fraction change of about 0.001. The refractometer was frequently checked and recalibrated.

Test mixture.--The binary mixture used in the apparatus was composed of chlorobenzene and ethylbenzene obtained from the Matheson Company. The materials were further purified in this laboratory by distilling in a Precise Fractionation Assembly manufactured by Todd Scientific Company at reflux ratios greater than ten to one. The resulting properties of the middle cut are given and compared below:

	Chlorobenzene	Ethylbenzene
Boiling Point (760 mm)		
This work	131.7±0.2 C	136.2±0.2 C
Dreisbach (19)	131.70	136.186
Refractive Index (30°C)		
This work	1.51880	1.49029
Dreisbach (19)	1.51837	1.4904

This binary system was suggested by Walsh, Sugimura, and Reynolds (16), and they presented the equilibrium data used in this study. The components have the normally desired properties of availability in nearly pure form, reasonable cost, stability, and non-corrosiveness. Disadvantages include the toxic effects of chlorobenzene and the low boiling points at reduced pressures, which made some refrigeration necessary in condenser systems. The mixtures have nearly ideal equilibrium relations, a relative volatility essentially unaffected by composition and only slightly affected by pressure.

The equilibrium data presented by Walsh, Sugimura, and Reynolds included a large number of runs at 760 millimeters and at 20 millimeters of mercury pressure. Because only three runs were made at 300 millimeters, a good average value of relative volatility could not be determined, and linear interpolation between the 20 and 760 values was used instead. Relative volatility at 760 millimeters pressure was 1.10 and at 20 millimeters was 1.12. The relative volatilities calculated for Raoult's Law, making use of Antoine equations were 1.13 and 1.20 respectively.

Physical properties other than boiling points, refractive index, and equilibrium data were taken from <u>Physical Properties of Chemical Compounds</u> by Dreisbach. (18)

CHAPTER III

PROCEDURE

Preliminaries.--The normal procedure for beginning a run was to fill the still pot about half full with twenty-five hundred milliliters of a mixture having a composition of 0.4 to 0.5 mole fraction chlorobenzene. For studies at fifty millimeters pressure the charge was reduced to about one thousand milliliters, for this practice was found to appreciably reduce bumping tendencies. Experimental checks made indicated that neither varying the composition of the charge or the amount of charge had any noticeable effect on the results.

Cooling water was then admitted to all the condensers and the lower still pot heater turned up to maximum capacity. When the vapors began to reach the main condenser, the vacuum pump was started and the apparatus was evacuated. Since the heater capacity and packing was such that the column would not flood continuously except when the pressure was reduced to about 50 millimeters of mercury and in order to insure initial flooding of the packing, this evacuating was done even if the runs were to be made at atmospheric pressure. However, it was not necessary to drop the operating pressure to fifty millimeters to produce momentary flooding sufficient to wet the packing. The pressure could be reduced rapidly enough to cause the boiling mixture to flash and the column to flood. The flooding action was observed through a view port in the insulation at the top of the packing. Flooding was performed with column heaters off in order to provide for maximum condensation and wetting.

If the run was to be made at four hundred millimeters or atmospheric pressure, the operating pressure was then allowed to rise slowly to the desired level. Boiling was not necessarily maintained during this pressure rise. If the operating pressure was to be four hundred millimeters, this pressure was set with the regulator; but if atmospheric, the system was left open to the atmosphere through the bleeder valve. The column was then allowed to operate for a few moments at the maximum boil up rate.

The desired rate was then set by the bottom still heater control, and the top still and column heaters brought slowly up to operating temperatures. This tedious operation required from one to two hours. The column heaters were set so that about one degree centigrade drop across the one-half inch insulation existed. Temperature measurements and small adjustments, when needed, were made about every one-half hour.

The run.--As soon as temperature equilibrium was reached, the first product sample was taken and other initial readings such as pressure drop, pressure, and room temperature also recorded.

All runs in this study were made at total reflux. Product samples were about five to ten milliliters in size and were taken and analyzed about every one-half hour to one hour. These were removed by operating the column at a reflux ratio of about fifty to one, and it was not expected that this would upset column operation appreciably. The frequency of sampling depended on the boil-up rate and how rapidly it was estimated that equilibrium was being approached. Careful rinsing of the refractometer and pipette used to introduce samples into the refractometer practically insured agreement to less than 0.001 difference in mole fractions for two duplicate analyses of one sample. The test mixture was such an excellent solvent that no other rinsing substance was needed for the analytical equipment.

When the composition of the overhead product held constant for two or more samples or oscillated slightly probably indicating small oscillations in the operating conditions, the first sample was removed from the still. Samples were taken continually until agreement was reached, these samples being about the same size and subjected to the same analytical procedure as the product. The second and third samples from the still practically always had the same compositions. The first sample usually had a slightly different composition, probably due to the fact that it rinsed out a small amount of residual material left from the previous run.

Next, boil-up rates were determined by removing all the condensate as product for a measured time interval, catching it in the product sampler, and weighing it. Fifteen or thirty second samples were taken. The pressure drop manometer was watched closely during this determination and as a rule no effects were noted. Three timed samples were usually taken for each run and differences as much as 10 to 20 per cent in sample weight noted. This was due, in part at least, to the fact that short times were employed in sampling, and oscillations in the boil-up rate had periods of the same order of magnitude. Hence the three determinations were made in order that an average value might be used. The taking of samples for such a short period of time was of course necessary to eliminate any effect that returning no reflux to the column might have.

It was felt that taking all the overhead samples first, the bottom samples next, and then determining boil-up rate, in that order, provided a technique such that the sampling itself would not cause changes in column operation which would affect the subsequent samples.

At the end of the run another series of readings was recorded.

Quite often another run was begun at this point simply by modifying the boil-up rate and resetting the column heater controls. This was always done from a higher to a lower boil-up rate, for some difficulty in reproducing results was otherwise encountered. Results from runs begun from a cold start or following another higher boil-up run were, as a rule, in good agreement.

CHAPTER IV

DISCUSSION OF RESULTS

Range of study.--In this investigation measurements were made at three operating pressures, 740, 400, and 50 millimeters of mercury. The boil-up or reflux rate ranged from about 2 to 13 pounds per minute per square foot for all operating pressures. The lower of these two rates represents the lowest practical rate, and the higher of the two corresponds to the maximum capacity of the still heater except at an operating pressure of fifty millimeters. At this pressure the column flooded near the maximum heater capacity. On a weight basis this range was considerably greater than and included the range studied by Daniel (2) except at atmospheric pressure. Here Daniel's upper limit was greater by two pounds per minute per square foot. The above conditions resulted in superficial vapor velocities of about 0.13 to 1.2 feet per second at 740 millimeters, 0.13 to 2.3 at 400, and 1.3 to 12 at 50.

Figure 5 on the following page presents the best picture of the results obtained in this investigation. While it is obvious that there is considerable spread of the data, it is felt that the trends indicated are well established. A large number of runs were made. The earlier runs were devoted to gaining experience in technique and improving the equipment.

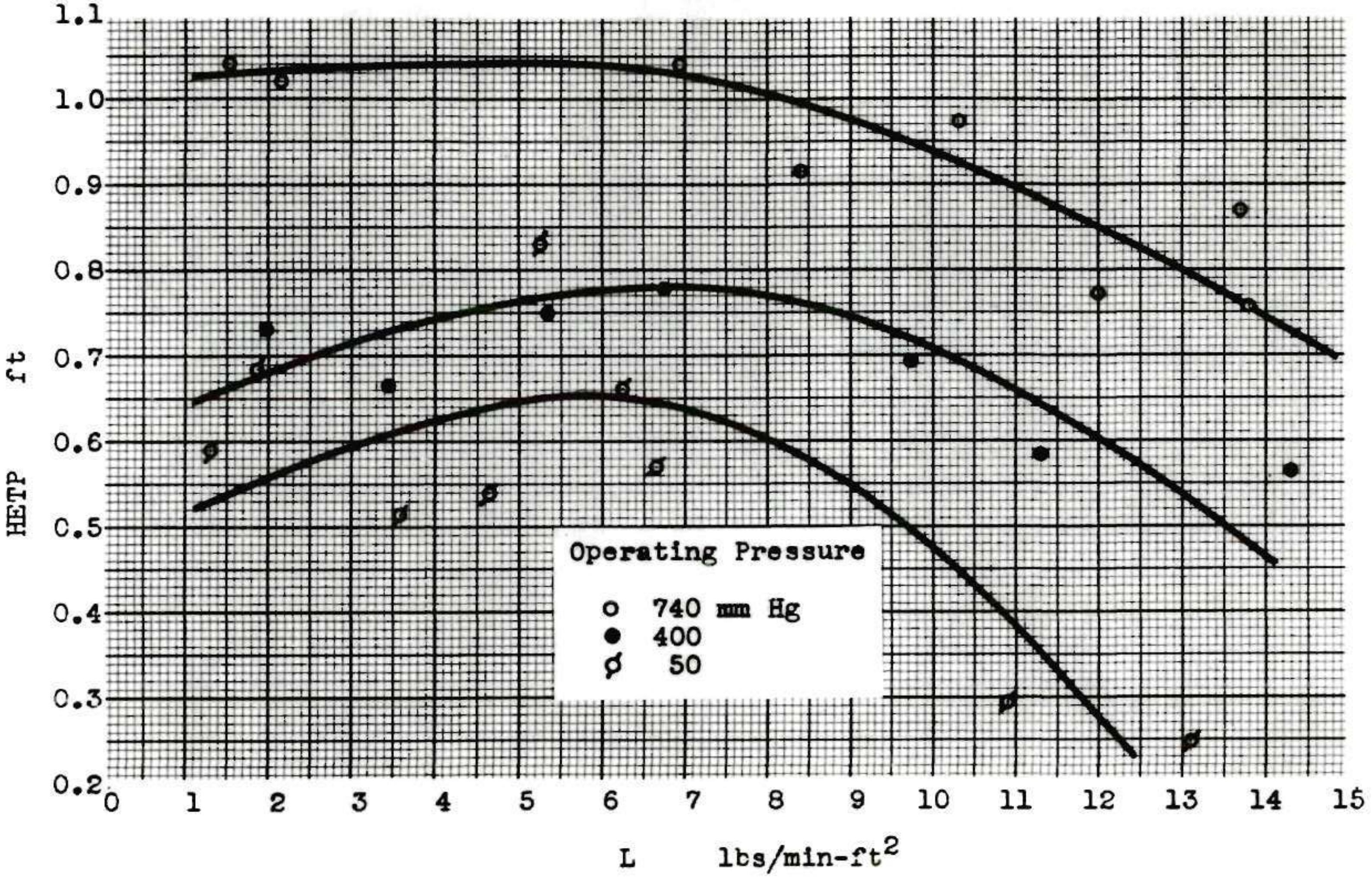

Figure 5. HETP Versus Reflux Rate

Only the data for the final runs when column operation was satisfactory are presented.

The range of HETP values for this work, 0.25 to 1.05 feet, compare with Daniel's HTU values of 0.4 to 2 feet. Dodge (20) states that for close-boiling ideal liquid systems HTU and HETP results will be in good agreement. A check was made at six points and agreement to within about 2 per cent obtained.

Figure 5 indicates that for this work there is a definite improvement of efficiency at lower pressures. It also presents efficiency curves that tend to have a minimum at the two lower operating pressures considered. A number of experimenters report improved efficiencies at lower pressures. As previously mentioned, Kirschbaum and David (15), while reporting improved efficiencies at higher pressures, have presented data that show minimums also. Peters and Cannon's work (14) with Berl saddles indicated slightly improved efficiencies at lower pressures and curves having minimums.

Daniel's correlation.--As previously mentioned, Daniel's correlation, which consisted in plotting HTU versus L times U for operation of total reflux, was based on the hypothesis that the most important variables were the time of contact for the liquid and vapor. Daniel's hypothesis predicts that an increase in L at constant operating pressure would cause the efficiency to fall, for the time of contact for both the reflux and vapor would decrease. The results of this investigation presented in Figure 5 are not in agreement with Daniel's prediction, for efficiency increased as L increased for a portion of the boil-up range studied.

In addition, Daniel's hypothesis predicts that a decrease in pressure at constant L should result in a decrease in efficiency because the vapor velocity would increase and the time of contact decrease. Figure 5 presents results of this investigation which are not in agreement with the above statement, for efficiency increased as operating pressure decreased for all cases studied in this work.

The data of the present study are plotted in Figure 6 using Daniel's method and it can be seen that this method does not correlate the data.

Comparison of systems.--A comparison of the binary mixture used in this study with that of Daniel's revealed some differences. Not much data was available for isopropyl benzoate, but using the data for methyl benzoate as a basis for comparison, the heats of vaporization of the two mixtures are about the same on a weight basis, the viscosity of the benzoate system about twice that of the benzenes, the surface tension some 10 to 20 per cent greater than the benzenes, and the specific gravity of all components about one at room temperature except for ethylbenzene. Ethylbenzene has a specific gravity of about

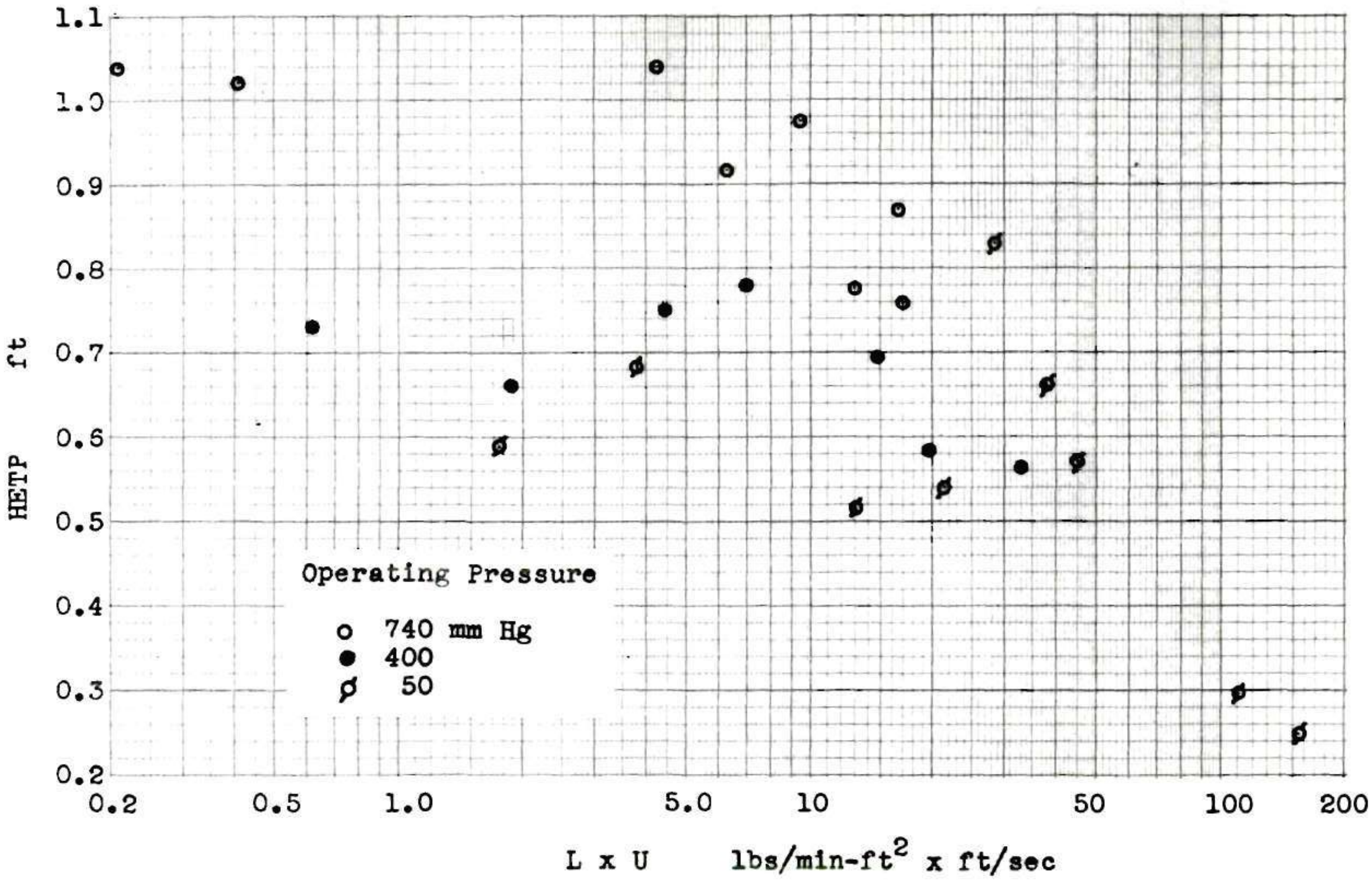

Figure 6. HETP Versus Reflux Rate Times Vapor Velocity

0.85. The difference in boiling points of the benzoates was about 19 degrees centigrade at 760 millimeters mercury pressure and only about 4.5 degrees centigrade for the benzenes. The relative volatility of the benzoates varied from about 1.4 to 1.6 over the range covered in this study. It may be recalled the range for the benzenes was 1.10 to 1.12. The benzoate mixture obeyed Raoult's law very closely.

The increased surface tension and viscosity of the benzoates may account for the greater ease with which Daniel could flood the column.

Pressure drop.--Figure 7 shows a plot of pressure drop versus reflux or boil-up rate. Several extra runs were made at atmospheric pressure, under adiabatic conditions but without waiting for steady state vapor-liquid mass transfer, to verify the strange unexplained behavior evidenced by the shape of the curves. Insufficient data are presented at pressures of four hundred and fifty millimeters to determine the shape at low rates, but the possibility of similar behavior is not excluded. The smooth curves above the dips plot as straight lines on log-log graphs as suggested by Daniel and others.

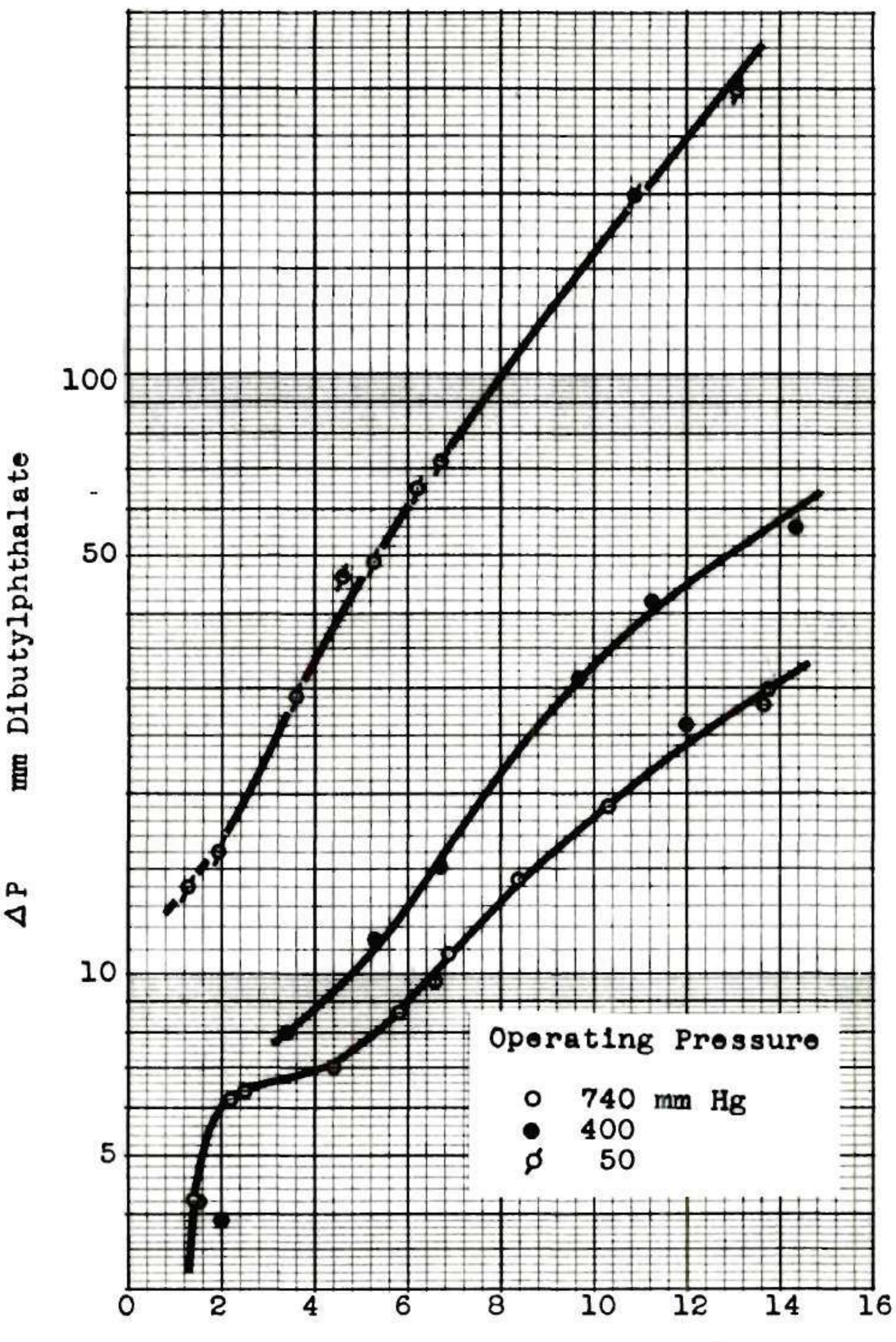

Figure 7. Column Pressure Drop Versus Reflux Rate

CHAPTER V

CONCLUSIONS

For the results obtained in this investigation it may be concluded that:

1. For this experimental apparatus and binary system operating at total reflux and constant boil-up rate, the efficiency of the packing increased as the operating pressure decreased from 740 to 50 millimeters of mercury. At a given operating pressure the efficiency of the packing may increase, decrease, or remain unchanged as the boil-up rate is increased, depending on the operating pressure and the range over which the boil-up rate is varied.
2. Daniel's correlation (2) and the hypotheses upon which it is based are not confirmed by the results of this investigation.

APPENDIX

SAMPLE CALCULATIONS

Calculations were made on the basis that the experimental data were correct to three significant figures and the calculated results reported to this same significance. This accuracy easily exceeds that which is indicated by the experimental spread of the data.

The data from run 9 were used in the sample calculations and a data sheet appears on the following page.

Sample Calculations (Continued)

Data sheet for run 9

Date: June 23

Room Temperature: 28.5°C at start, 28.5°C at end

Reflux: Total

Pressure: 398 mm Hg at start, 398 mm Hg at end

Charge: Continued from run 35 (about 2000 ml)

Bottom still heater setting: 135 volts

Time:		
	Start run	8:00 A.M.
	Temperature equilibrium	10:45 A.M.
	End run	2:20 P.M.

Thermocouple readings 10:45 A.M.:

Location	Wall		Heater Winding	
	TC no.	Reading	TC no.	Reading
Divider and upper column	0	4.85 mv	1	4.79 mv
	2	4.81		
	3	4.81		
Upper packed	4	4.84	5	4.76
Middle packed	6	4.87	7	4.80
Lower packed	8	4.90	9	4.86
Still	11	5.04	10	4.98

Compositions:

Time	Sample	Analysis	Refractometer reading
11:00	X_D 1	1	18.000
		2	18.000
11:30	X_D 2	1	18.010
		2	18.015
1:30	X_D 3	1	18.015
		2	18.015
	X_S 1	1	17.450
		2	17.450
	X_S 2	1	17.430
		2	17.425
	X_S 3	1	17.425

Sample Calculations (Continued)

Column pressure drop:	Condenser leg	Still leg
	310 to 210	490 to 590

mm dibutylphthalate

(Range shows size of oscillations)

Boil-up:	% of time open	Sample time	Sample weight plus flask	Flask no.
	100	15 sec	107.2 g	1
	100	15	108.9	1
	100	15	106.8	1

Remarks: Cold start. Flooded. Moisture negligible.

1. The determination of compositions. X_D and X_S were determined directly from Figure 8, the plot of refractometer scale reading versus composition. Data for this figure are recorded in Table 4. When there was some oscillation in X_D, the last value was selected rather than an average, for it was decided this would probably best represent column operating conditions recorded at that time.

	Refractometer reading	X
Distillate	18.015	0.562
Still vapor	17.425	0.448

2. Condenser pressure, P. Condenser pressure, read on the absolute reading manometer in millimeters of mercury, was not corrected other than for the density of mercury at an average

Sample Calculations (Continued)

room temperature.

$$P = 398 \text{ mm Hg}$$

Density for all runs = 13.5 g/ml

<u>3. Pressure drop over column, ΔP.</u> For the inclined manometer,

$$P = \frac{(B - T) + (T_Z - B_Z)}{10},$$

where B = still pot leg reading

T = condenser leg reading

$T_Z - B_Z$ = difference in readings for ΔP of zero

= 277

Taking an average difference,

$$P = \frac{(540 - 260) + 277}{10}$$

$$= 55.7 \text{ mm dibutylphthalate}$$

<u>4. Average column pressure, P_A.</u>

$$P_A = 398 \text{ mm Hg} + \frac{(55.7)\left(\frac{1.04}{13.5}\right)}{2}$$

$$= 400 \text{ mm Hg}$$

Sample Calculations (Continued)

5. Average column temperature, T_A.

Thermocouple EMF top packed section	4.84 mv
Bottom section	4.90
Average	4.87

$T_A = 113^\circ C$

6. Superficial reflux or boil-up rate, L.

Weight of sample 1 and flask 1	107.2 g
2	108.9
3	106.8
Average	107.6
Weight flask 1	79.8
Average sample weight	27.8

Cross sectional area of column $= 0.0171\ \text{ft}^2$

$$L = \left(\frac{27.8\ \text{g}}{15\ \text{sec}}\right)\left(\frac{60\ \text{sec}}{\text{min}}\right)\left(\frac{1\ \text{lb}}{453.6\ \text{g}}\right)\left(\frac{1}{0.0171\ \text{ft}^2}\right)$$

$$= 14.3\ \text{lbs/min-ft}^2$$

7. Height of a theoretical plate, HETP. Using the Fenske equation,

Sample Calculations (Continued)

$$\text{No. of plates} = \frac{\log\left[\left(\frac{X_D}{1 - X_D}\right)\left(\frac{1 - X_S}{X_S}\right)\right]}{\log a}$$

$$X_D = 0.562$$

$$X_S = 0.448$$

$$a = 1.110$$

$$\text{No. of plates} = 4.39$$

$$\text{HETP} = \frac{29.75 \text{ in}}{(12)(4.39)}$$

$$= 0.566 \text{ ft}$$

8. Superficial vapor velocity, U. Deriving an expression for U,

$$\frac{(X)(M_{CB})}{(X)(M_{CB}) + (1-X)(M_{EB})} = X_W, \text{ weight fraction}$$

chlorobenzene.

$$\frac{N_T}{A} = \frac{(L)(X_W)}{M_{CB}} + \frac{(L)(1-X_W)}{M_{EB}}, \text{ boil-up rate in moles}$$

based on column cross sectional area.

Applying the gas law,

$$\frac{V}{A} = U = \frac{(C)(N_T)(R)(T)}{(P)(A)}$$

Since C was 0.96 to 1.00 for the experimental range and both components, it was taken to be 1.00 throughout the calculations. Substituting into the above and simplifying,

Sample Calculations (Continued)

$$U = \frac{(R)(T_A)(L)}{P_A} \left[\left(\frac{X_A}{(X_A)(M_{CB} - M_{EB}) + M_{EB}} \right) \left(1 - \frac{M_{CB}}{M_{EB}} \right) + \frac{1}{M_{EB}} \right]$$

where $T_A = 386°K$

$P_A = 400$ mm Hg

$L = 14.3/60$ lbs/sec-ft^2

$X_A = 0.505$

$M_{CB} = 112.557$

$M_{EB} = 106.160$

$R = 1005$ mm Hg-ft^3/lb mole-°K

$U = 2.28$ ft/sec

Table 2. EXPERIMENTAL DATA

Run No.	Approximate operating pressure	Refractometer reading		Condenser pressure
		Distillate	Still vapor	
-	mm Hg	-	-	mm Hg
1	740	18.105	17.705	738-737
2	"	18.000	17.690	737-736
3	"	17.960	17.670	736-736
4	"	17.950	17.655	745-744
5	"	17.925	17.635	742-740
6	"	17.875	17.480	738-736
7	"	17.790	17.460	736-736
8	"	17.695	17.345	742-742
9	400	18.015	17.425	398-398
10	"	17.870	17.390	399-399
11	"	17.805	17.380	399-402
12	"	17.955	17.460	399-397
13	"	17.825	17.370	398-399
14	"	17.910	17.470	401-403
15	"	17.990	17.430	402-402
16	50	18.320	17.705	50-50
17	"	18.205	17.520	51-52
18	"	18.125	17.605	49-50
19	"	17.935	17.505	50-51
20	"	17.980	17.450	51-52
21	"	18.300	17.650	51-52
22	"	18.150	17.550	50-51
23	"	18.770	17.400	48-49
24	"	18.435	17.250	49-50

Table 2. Experimental Data (Continued)

Run No.	Pressure drop			Thermocouple EMF	
	Condenser leg *	Still leg	Type Manometer	Top Packed Section	Bottom Packed Section
-	mm dibutylphthalate		-	mv	mv
1	396	380-420	Inclined	5.87	5.91
2	439	337-353	"	5.87	5.91
3	476	297-307	"	5.92	5.95
4	496	279-281	"	5.90	5.94
5	504	269-269	"	5.94	5.93
6	416	360-400	"	5.88	5.91
7	463	312-330	"	5.88	5.91
8	326	292-298	Vertical	5.90	5.94
9	310	490-590	Inclined	4.84	4.90
10	411	386-456	"	4.86	4.91
11	471	326-346	"	4.87	4.90
12	500	397-303	"	4.86	4.89
13	518	278-280	"	4.86	4.89
14	484	312-322	"	4.86	4.89
15	368	430-510	"	4.85	4.89
16	413	335-341	Vertical	2.29	2.40
17	286	251-257	"	2.30	2.36
18	188	164-172	"	2.26	2.29
19	205	146-156	"	2.30	2.38
20	211	130-146	"	2.31	2.40
21	197	143-151	"	2.30	2.38
22	179	159-165	"	2.26	2.30
23	477	140-180	"	2.27	2.62
24	417	200-220	"	2.27	2.57

* Corresponds to smaller reading of range given under still pot leg.

Table 2. Experimental Data (Continued)

Run no.	Boil-up rate				
	Sample Time	Sample Weight			
		1	2	3	4
-	sec	g	g	g	g
1	15	27.5	25.4	27.3	-
2	15	20.3	19.8	-	-
3	15	12.7	13.9	13.5	13.7
4	15	3.9	4.3	4.3	-
5	30	6.4	6.0	5.4	-
6	15	22.7	24.0	23.6	-
7	15	16.4	16.1	16.8	-
8	15	26.2	27.4	26.6	-
9	15	27.4	29.1	27.0	-
10	15	17.0	20.2	19.4	-
11	15	12.9	14.4	13.2	-
12	15	6.9	6.2	4.9	7.0
13	30	7.3	7.8	8.0	-
14	15	10.2	10.1	10.8	-
15	15	20.6	22.0	23.4	21.7
16	15	12.7	13.3	12.8	-
17	15	6.9	7.3	6.7	-
18	30	7.7	7.7	6.6	-
19	15	9.3	10.9	10.5	-
20	15	11.9	12.6	11.7	-
21	15	8.7	9.0	9.2	-
22	45	7.3	8.7	6.7	-
23	15	24.7	24.4	27.0	-
24	15	21.5	20.8	21.2	-

Table 2. Experimental Data (Continued)

Special additional runs at 740 mm Hg operating pressure for pressure drop data.

Pressure drop			Boil-up rate			
Condenser leg*	Still leg	Type Manometer	Sample Time	Sample Weight		
				1	2	3
mm dibutylphthalate		-	sec	g	g	g
518	281-283	Inclined	30	5.1	5.7	-
500	298-320	"	15	12.3	13.3	-
501	296-310	"	15	10.5	11.8	11.2
509	288-296	"	15	5.0	4.8	-
507	290-300	"	15	9.2	7.8	-

*Corresponds to smaller reading of range given under still pot leg.

Table 3. CALCULATED RESULTS

Run no.	X_D	X_S	ΔP	P_A	T_A
-	-	-	mm dibutyl-phthalate	mm Hg	°C
1	0.580	0.502	30.1	738	134
2	0.560	0.499	19.1	737	134
3	0.522	0.495	10.8	744	135
4	0.550	0.492	6.2	742	134
5	0.545	0.488	4.2	740	135
6	0.535	0.458	26.1	737	134
7	0.519	0.454	14.4	737	134
8	0.500	0.432	28	743	134
9	0.562	0.448	55.7	400	113
10	0.534	0.441	32.2	400	113
11	0.522	0.439	15.2	403	113
12	0.551	0.454	8.0	397	113
13	0.525	0.437	3.9	399	113
14	0.542	0.456	11.5	403	113
15	0.558	0.448	41.9	404	113
16	0.622	0.502	72	53	57
17	0.600	0.466	29	53	57
18	0.584	0.483	16	50	56
19	0.547	0.463	49	52	57
20	0.556	0.451	65	55	57
21	0.618	0.491	46	54	57
22	0.589	0.472	14	52	56
23	0.710	0.443	297	60	60
24	0.644	0.413	197	58	59

Table 3. Calculated Results (Continued)

Run No.	L	HETP	U
-	lbs/min-ft^2	ft	ft/sec
1	1.38	0.758	1.24
2	1.03	0.973	0.927
3	0.693	1.04	0.615
4	0.215	1.02	0.192
5	0.153	1.04	0.137
6	1.20	0.773	1.08
7	0.842	0.916	0.753
8	1.37	0.871	1.22
9	1.43	0.566	2.28
10	0.973	0.693	1.52
11	0.674	0.778	1.04
12	0.345	0.665	0.549
13	0.198	0.732	0.312
14	0.534	0.749	0.830
15	1.13	0.585	1.75
16	0.666	0.569	6.76
17	0.359	0.514	3.63
18	0.188	0.686	2.02
19	0.527	0.829	5.43
20	0.623	0.662	6.08
21	0.463	0.539	4.61
22	0.131	0.591	1.35
23	1.31	0.248	11.8
24	1.09	0.295	10.1

Table 3. Calculated Results (Continued)

Special pressure drop runs at 740 mm Hg operating pressure.

ΔP mm dibutyl-phthalate	L lbs/min-ft^2
4.2	0.139
9.7	0.659
8.6	0.582
6.4	0.253
7.0	0.438

Table 4. REFRACTOMETER CALIBRATION DATA

X_{CB}	Refractometer reading	n_D
-	-	-
0.3767	17.070	1.50069
0.4337	17.355	
0.5465	17.925	
0.6258	18.340	
0.6525	18.480	
0.7069	18.770	1.51014

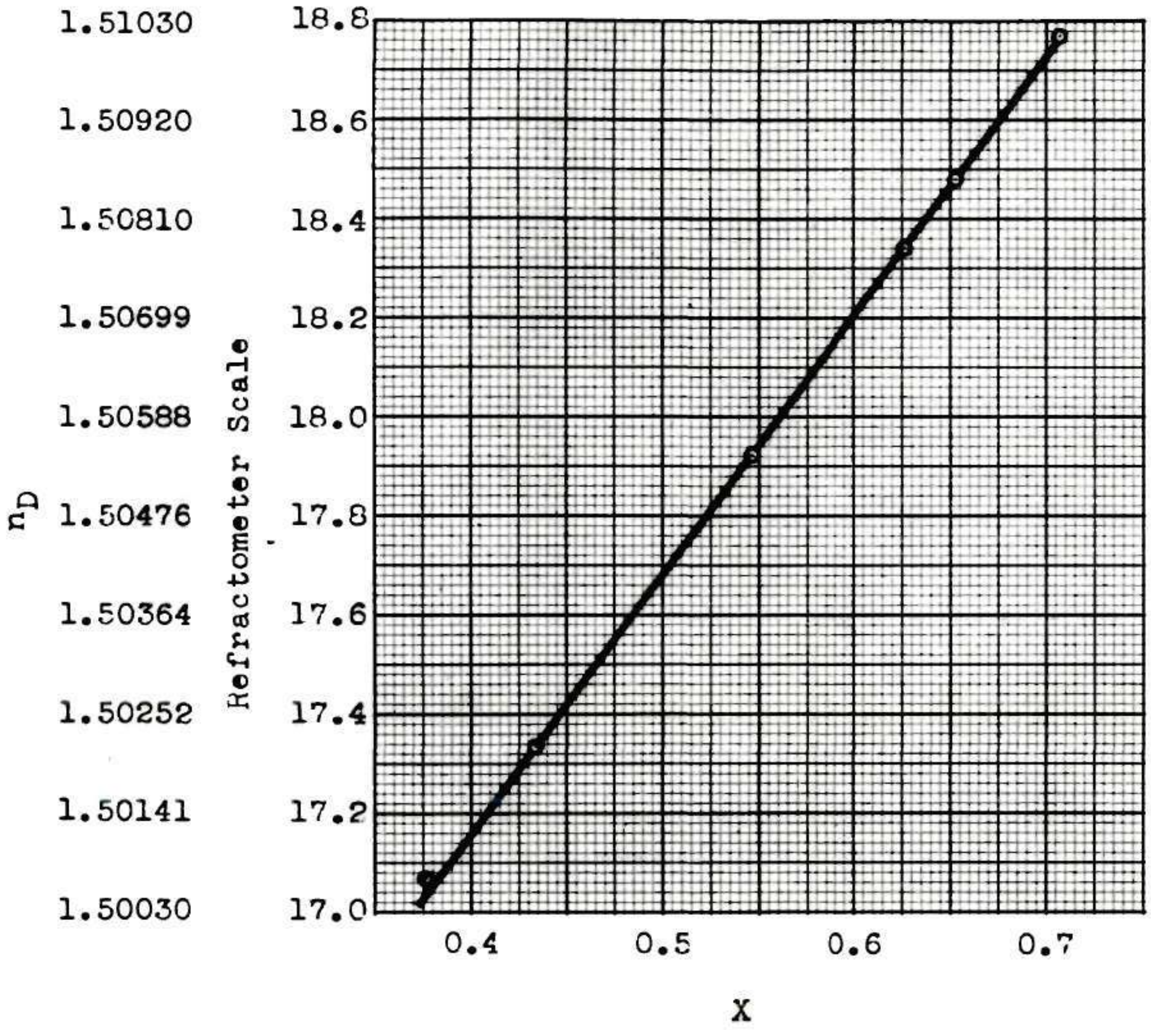

Figure 8. Refractive Index and Refractometer Scale Versus Mole Fraction Chlorobenzene in Binary Mixture

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