TEST OF WIRE-GAUZE PACKED FRACTIONATING COLUMN

By

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(1939)

Signature of the author:_____

Department of CHEMICAL ENGINEERING, May 18, 1939

Signature of Professor
in charge of research:_____

Jamaica Plain,
Massachusetts.
May 18, 1939.

Professor George W. Swett,
Secretary of the Faculty,
Massachusetts Institute of Technology,
Cambridge, Massachusetts.

Dear Sir:

I respectfully submit this thesis, entitled,
"Test of Wire-Gauze Packed Fractionating Column," as
a partial fulfillment of the requirements for the
degree of Bachelor of Science in the Department of
Chemical Engineering.

Sincerely yours,

ACKNOWLEDGMENT

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PURPOSE

The purpose of this thesis was to continue and amplify the work of Dowding and Kangas in investigating the efficiency of a new type of wire-gauze packed fractionating column, borrowed from the Foster Wheeler Corporation and designed by D. F. Stedman (U. S. Patent 2,047,444 of July 14, 1936).

Whereas Dowding and Kangas, in their thesis of last year entitled, "Test of Wire-Gauze Packed Distilling Column," investigated the efficiency of the column in separating a mixture of benzene and ethylene dichloride at total reflux, the purpose of this thesis was to investigate the efficiency of the packing at reflux ratios greater and less than unity, and in this way to see if varying the reflux ratio had any effect upon the efficiency of separation. The effect of varying the vapor velocity was studied also.

The same binary was used in this thesis, since the extremely close boiling points of the two components makes this mixture a very difficult one to separate and consequently a good one for testing the efficiency of the packing. The efficiency under the varying conditions of operation will be expressed as the number of transfer units between the limits of the separation.

ABSTRACT

As originally proposed, this thesis was to study
the effect on the fractionating efficiency of varying
the reflux ratio over ranges greater than as well as
less than unity. Actually, however, a thorough study
over the range greater than unity only was accomplished.

The set-up of the apparatus was such as to per-
mit operating with a reflux ratio greater than unity,
and reach a continuous state of equilibrium, without
having to supply feed or withdraw bottoms or distillate
continuously. Heat was supplied continuously to the
still through an electric heater, and part of the vapor
generated in the still was by-passed around the frac-
tionating column, condensed, and returned to the top of
the column as liquid condensate, where it joined the
reflux from the vapor which went up through the column,
and thus the net result was a ratio of reflux to vapor
greater than unity. The operation was continuous, none
of the original charge ever leaving the system.
Equilibrium was reached in about four or five hours,
as was indicated by a check analysis of samples from
the top and bottom of the column. The analyses were made
easily and quickly by refractive index, data on refractive
index vs. composition being found available for the binary
benzene-ethylene dichloride.

A constant level gauge, for which a calibration
plot was constructed previous to the efficiency runs,

measured the rate of flow of the condensed by-pass vapor, the flow of which could be controlled by a valve in the vapor line between the still and the condenser. A blue-print is shown on page 2^{f}. The quantity of vapor generated in the still was determined from a knowledge of the heat input to the still and the latent heat of vaporization of the binary. The quantity of vapor passing up through the column was taken as the difference between the total vaporization and what was by-passed, as indicated by the constant level meter. Thus the reflux ratio, or ratio of reflux to vapor in the column, could be calculated, and, also, the velocity of the vapor in feet/second could be calculated from the gas laws. The efficiency of separation as shown by the difference in the benzene content of the top and bottom samples was calculated for each run in terms of the number of transfer units (See Method of Calculation, page 3^{6}).

Twelve runs were made, three at a reflux ratio of unity (vapor by-pass valve closed, gauge level zero), and three at each of three other reflux ratios greater than one. The reason for making three runs at each reflux ratio was to investigate the effect of varying the vapor velocity. Low, medium, and high vapor velocities were used. An upper limit on the reflux ratio of about 1.3 was necessitated by the flat nature of the equilibrium curve for the binary used.* Reflux

(*) (See Calculations, page 3^{6}). If the operating line, whose slope is the reflux ratio, is so steep as to cut the equilib-rium curve, it is impossible to get an accurate value of the number of transfer units.

ratios of approximately 1.1 and 1.2 were also used, and the vapor velocities were in the neighborhood of 0.34, 0.67, and 0.85 feet/second.

Tables and graphs of the results are given from page 11 through page 14. It is apparent that the effect of varying the reflux ratio is very marked, and at the higher reflux ratios an increase in vapor velocity cuts down the efficiency of fractionation considerably, this effect not being so great at total reflux. At low reflux ratios the number of transfer units is greater than at higher ratios, and at total reflux the optimum separation is obtained.

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INTRODUCTION

Since the purpose of this thesis is to determine the effect on the separating efficiency of the fractionating column of two variable factors of operation, namely, reflux ratio and vapor velocity, it would be appropriate at this point to state the definitions of these terms as they are employed in this thesis.

Definitions.   The fractionating efficiency of the wire-gauze packing under the various conditions of operation will expressed as the "number of transfer units" corresponding to the separation effected. This is the accepted method of reporting packing efficiencies, an alternative method being the theoretical plate equivalent, which, however, does not take into account the differential nature of the rectification process in a packed column as contrasted with a plate tower. The definition of the number of transfer units corresponding to a given separation is the integral, between the lower and upper limits of separation, of the change in concentration of the rising vapor, divided by the instantaneous driving force expressed as the difference between the actual vapor composition at a given point in the column and the vapor composition which is in equilibrium with the liquid reflux at that same point in the column. That is, vapor phase resistance is assumed, the driving force being the difference in

concentration of the main body of the vapor and the equilibrium composition of the vapor at the vapor-liquid interface.

Therefore,
$$N.T.U. = \int_{y_1}^{y_2} \frac{dy}{y^*-y}$$

where y is the actual vapor concentration, expressed as mols benzene per mol of vapor, and y^* is the equilibrium concentration corresponding to the liquid composition at that point in the packing.

The so-called McCabe-Thiele diagram presents graphically the conditions of vapor and liquid reflux compositions at all points in the packing from the bottom to the top. It consists essentially of an equilibrium or y vs. x diagram, which gives the equilibrium vapor composition for a given liquid, together with an "operating line," which gives the relationship existing between the actual vapor composition and that of the liquid at any point in the packing. By drawing up a total material balance between any point in the column and either end it becomes apparent that the "operating line" will be a straight line, between the upper and lower compositions, with a slope equal to the ratio of the mols of reflux divided by the mols of rising vapor, which ratio is the same throughout the column.

In a stripping column, where the ratio of reflux to vapor is greater than unity, the equilibrium curve will be above the operating line on a McCabe-Thiele

diagram, since the interfacial or equilibrium vapor con-
centration is greater than the main body concentration
thus resulting in diffusion from liquid to vapor, as con-
trasted with an absorption column, where the operating line
lies above the equilibrium curve since the driving force
is from gas to liquid, the gas concentration being greater
than the equilibrium interfacial concentration.

In cases where the equilibrium curve is essentially
a straight line over the region of fractionation, a
logarithmic mean of the concentration differences at the
two ends of the column may be used in place of integrating,
and the number of transfer units then becomes equal to the
ratio of the separation effected divided by this mean driv-
ing force. By reference to the equilibrium chart for the
system benzene-ethylene dichloride, it is apparent that for
the separation obtained by this small column the logarithmic
mean may be used.

That is,
$$N.T.U. = \frac{y_2 - y_1}{\Delta y_{l.m.}}$$

In cases where the equilibrium curve and the operating line
are essentially parallel in the region of operation, the
N.T.U. becomes equal to the number of theoretical plates
required for the separation.

Since for a given column the number of transfer units
does not vary over a very great range, it is apparent from
the above equation that certain generalisation can be made as
to the best method of operating a stripping column. Since a

high reflux ratio (reflux divided by vapor) tends to raise the operating line nearer the equilibrium curve, Δy log mean becomes smaller, and hence $y_2 - y_1$, or the separation, becomes less. The term reflux ratio as applied to a stripping column, as opposed to the above definition, usually means the ratio of reflux to the vapor drawn off as product, most of the vapor rising in the column being condensed in a partial condenser at the top. A little consideration will show that as the ratio of reflux to product is increased the ratio of reflux to rising vapor in the column becomes less, approaching unity. Thus the results of R. F. Mackie, S.B. M.I.T. (1924)* presented on the accompanying graph, should not be construed as disproving the above deductions regarding the McCabe-Thiele diagram. That is, his results, continuously feeding a mixture of benzene and toluene into the top of a column and regulating the amount of product by varying the temperature of the oil in the jacket of his partial condenser, indicate that with a reflux ratio of 5:1 he obtains much sharper separation than by using a reflux ratio of 1:1. His curves indicate the boiling point of the distillate plotted against the volume of the distillate, and it is apparent that for the high reflux ratio a much better separation is obtained between the benzene (b. p. 80.1) and the toluene (b. p. 110.8).

Data such as this support the general conclusion to be drawn from the McCabe-Thiele diagram that better separation is effected in a stripper by using a ratio of reflux to rising vapor near unity, but afford no indication of how the packing

* (9)

Benzene-Toluene
Stripping Column.
(Mackie).

Reflux ratio
= 5:1

Reflux ratio
= 1:1

Boiling Point °C.

Volume of Distillate (c.c.)

FORM 1 T
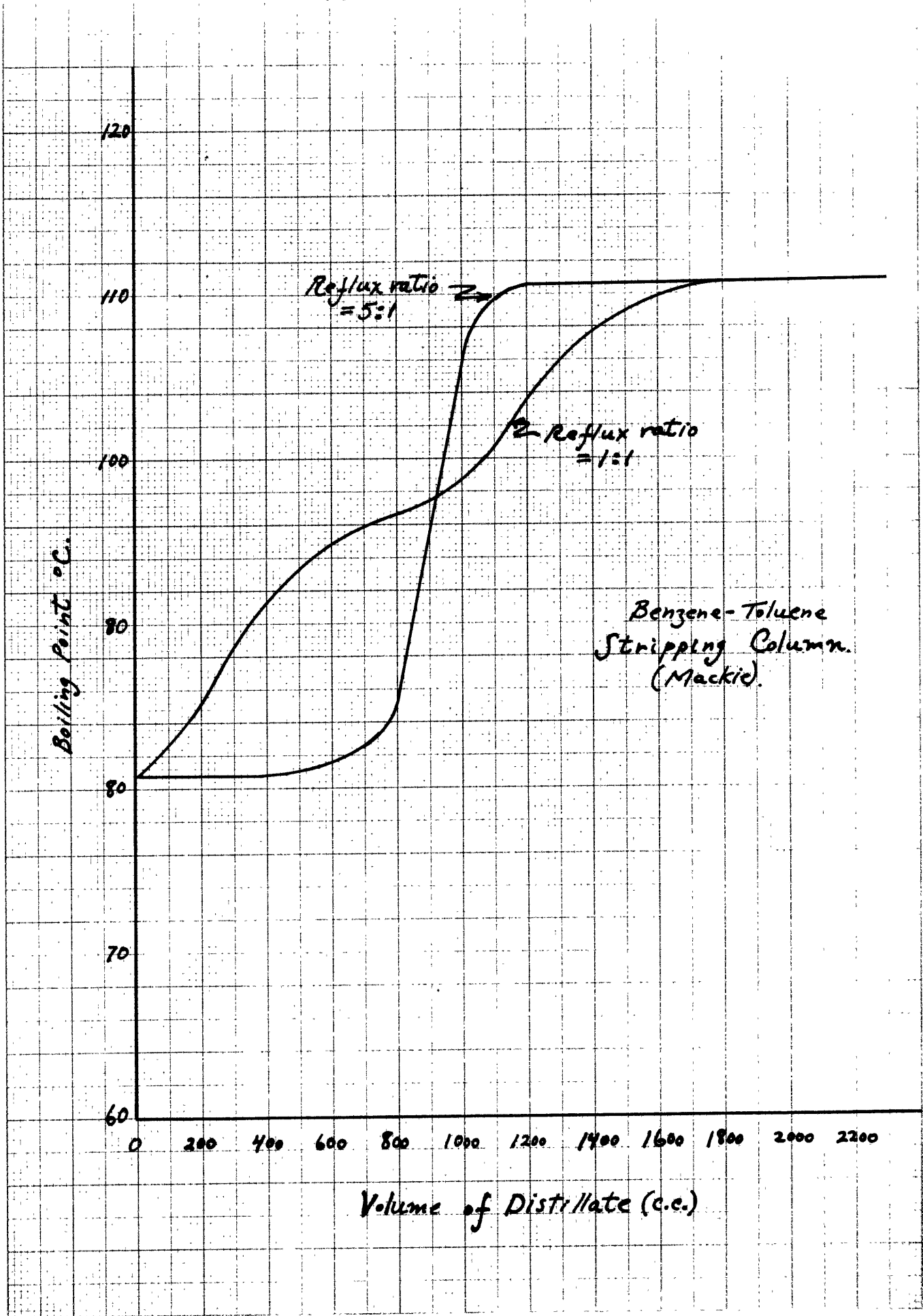
efficiency, expressed as transfer units, changes with changing refulx ratio.

To determine this is the purpose of this thesis, using the Stedman wire-gauze packed column and the binary benzene-ethylene dichloride. The effect of varying the vapor velocity is also studied.

Procedure. As outlined in the abstract, the procedure will be to by-pass part of the vapor generated in the still, measuring this condensed by-pass by means of a constant level gauge, and determine the vapor rising in the column as the difference between the total vapor generated, as calculated from a knowledge of the latent heat of the binary and the heat input to the still, and the by-passed vapor. The reflux is equal of course to the total vapor generated, since no vapor leaves the system. The reflux ratio can then be calculated for each run, and can be varied by opening or closing the valve on the by-pass line. The degree of fractionation obtained is found from the analysis of samples taken from the still and from a sample trap just below the condenser at the top of the column. The velocity of the vapor in inches or feet per second can be calculated from the vapor rate as mols per unit time. For further details see Description of Apparatus, Operating Technique, and Method of Calculation.

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RESULTS

Run No.	Heat Input	Vapor Velocity	Reflux Ratio	N. T. U.
1	135	0.67	1.0	10.3
2	75	0.32	1.0	11.9
3	150	0.65	1.19	5.15
4	140	0.65	1.08	5.31
5	160	0.64	1.31	2.82
6	175	0.90	1.0	10.1
7	180	0.83	1.08	4.75
8	190	0.81	1.15	5.01
9	205	0.83	1.25	3.52
10	105	0.33	1.41	4.51
11	95	0.32	1.22	8.90
12	85	0.33	1.15	8.92

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RESULTS (cont'd)

The data on the previous page can be put into categories as indicated below.

The figures in parentheses refer to the run numbers as given above.

The data in the form given below were used for drawing up the accompanying graphs. The figures are the N. T. U.

Vapor Velocity	Reflux Ratio			Total
	High	Medium	Low	Reflux
High	3.52 (9)	5.01 (8)	4.75 (7)	10.0 (6)
Medium	2.82 (5)	5.15 (3)	5.31 (4)	10.3 (1)
Low	4.51 (10)	8.90 (11)	8.92 (12)	11.9 (2)

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Benzene-Ethylene Dichloride Transfer Units vs. Vapor Velocity at Different Reflux Ratios.

KEY: △ – R.R. approx. 1.0
     * – R.R. " 1.1
     ▢ – R.R. " 1.2
     + – R.R. " 1.3

(Run nos. in Roman numerals)

Number of Transfer Units (N.T.U.)
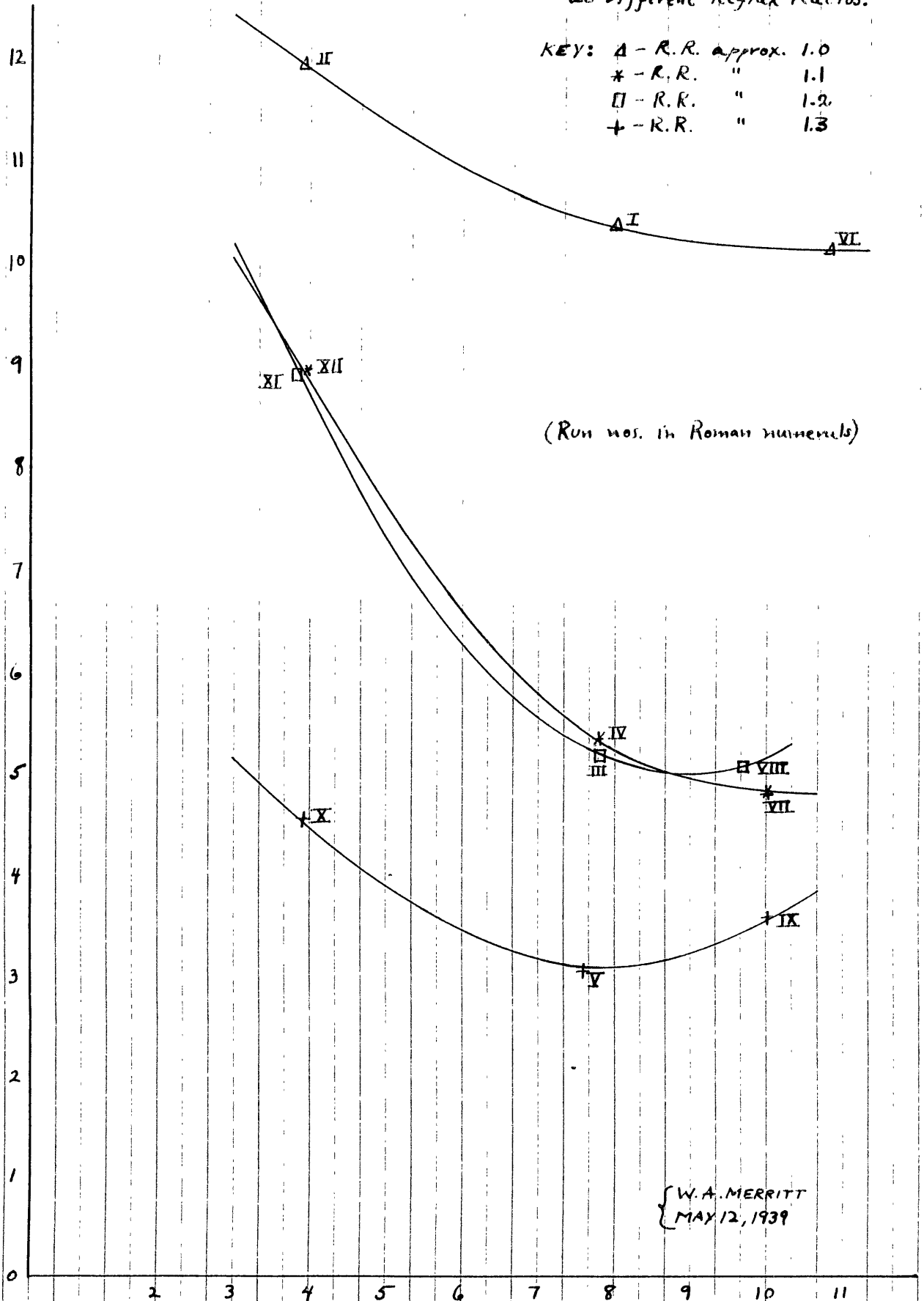
Vapor Velocity (inches per second)

W. A. MERRITT
MAY 12, 1939

Benzene - Ethylene Dichloride
Transfer Units vs. Reflux Ratio
at Different Vapor Velocities.

KEY: △ - V.V. appry 0.32 ft/sec.
✳ - V.V. " 0.65 "
☐ - V.V. " 0.84 " .

Curves A, B, C respectively.

(Run nos. in Roman numerals)

Number of Transfer Units (N.T.U.)

Reflux Ratio (°/v)

DISCUSSION OF RESULTS

It is apparent from the results obtained in the twelve runs that for a given vapor velocity the number of transfer units is greater for the lower reflux ratio, being a maximum at total reflux, or a ratio of unity. And at a given reflux ratio the number of transfer units is greater the lower the vapor velocity. Of course the curves are of necessity averaged, since it was experimentally impossible to adjust the reflux ratio and vapor velocity to any desired value.
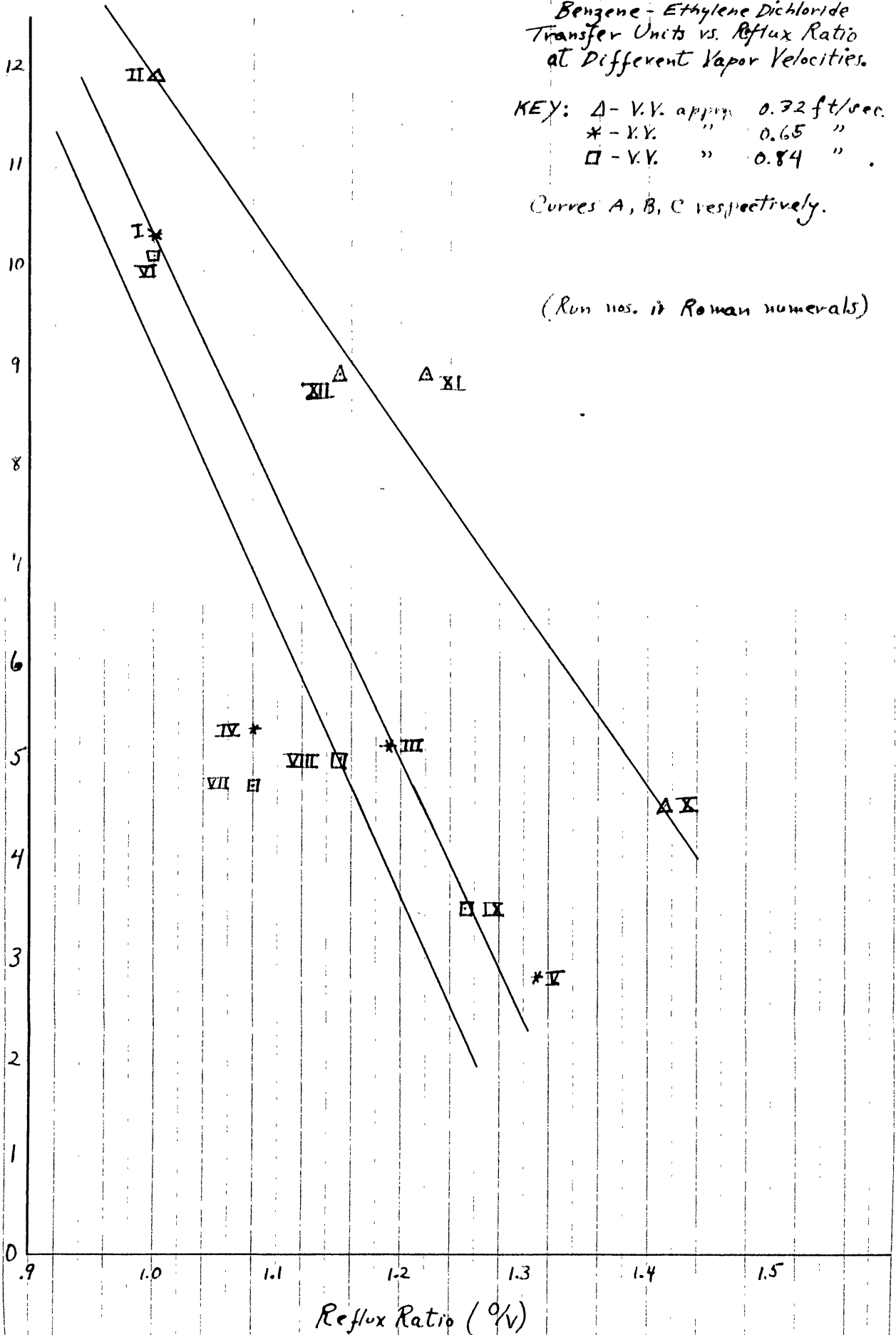
The variation in N.T.U. at total reflux is much less, proportionately, than at higher reflux ratios, with varying vapor velocity, but in all cases the N.T.U. decreases with increasing vapor velocity. This is apparently quite a common phenomenon, the explanation being that due to the increased rate of flow the vapor has less time of contact with the liquid reflux. H. C. Carlson, in his M.S. thesis of 1934,[*] studied the rectification of benzene-toluene mixtures in a column packed to a depth of eighteen inches with 7 mm. rings, and found that the N.T.U. decreased "slightly" with increasing vapor velocity, but began to increase up near the flooding point. T.J.Coleman,[†] however, using benzene-ethylene dichloride in a two-inch column packed 9.5 feet with 7 mm. Peter's rings, reports that the number of transfer units were substantially independent of vapor velocity, being greatly affected, on the other hand, by the concentration of the still mixture employed.
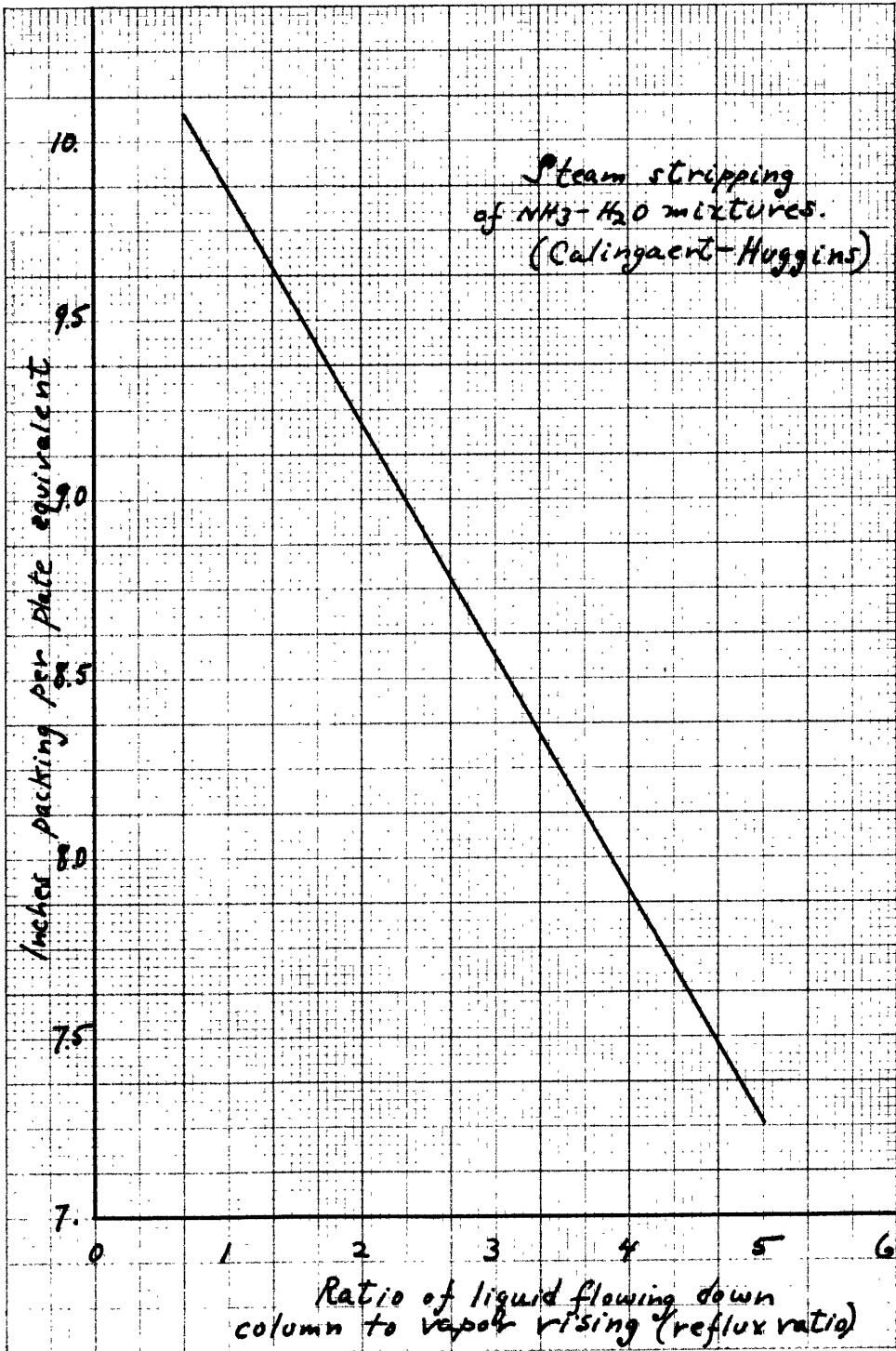
In the matter of the effect of vapor velocity and reflux ratio on the packing efficiency, Calingaert and Huggins,[‡]

[*] (4)   [†] (5)   [‡] (2)

investigating the performance of a coke-packed rectifying column in the continuous steam stripping of an ammonia-water mixture, report results that are just the opposite of the trends found in this thesis, with variable reflux ratio. The wide divergence of results prevailing in the various experimental theses on this subject is in my opinion an indication of the extreme complexity of the problem. There are undoubtedly many different influencing factors involved in the variation of packing efficiency with varying reflux ratios.

By way of example the results of Calingaert and Huggins are presented here in graphical form. According to their data the inches per plate equivalent fall from ten to seven, roughly, as the ratio of liquid flowing down the column to the amount of vapor rising rises from one to about five. That is, the plate efficiency rises with increasing reflux ratio. This is also apparent from their plot of inches of packing per plate equivalent vs. superficial vapor velocity, where, although for a given reflux ratio the packing efficiency decreases with increasing vapor velocity, as was found to be the case in this thesis and in most of the other theses referred to, for a given vapor velocity the efficiency is greater for greater feed rates, which amounts to greater reflux ratios since the feed comes in at the top. The column they used was packed to a depth of five feet with 3/8 - 5/8 inch coke.

A. J. Ullman,* studying the effect of vapor velocity using benzene and carbon tetrachloride in a four plate column,

(*)-17

Steam stripping
of $NH_3 - H_2O$ mixtures.
(Calingaert-Huggins)

Inches packing per plate equivalent

Ratio of liquid flowing down
column to vapor rising (reflux ratio)

Inches packing per plate equivalent.

Superficial vapor velocity (ft. per. sec.).

7.

8.

9.

10.

11.

12.

0   .5   1.0   1.5   2.0   2.5   3.0

← 20 liters/hr.

16 ℓ/hr.

12 ℓ/hr.

8 ℓ/hr.

Steam stripping
of $NH_3 - H_2O$ mixtures.
(Calingaert - Huggins).

23.
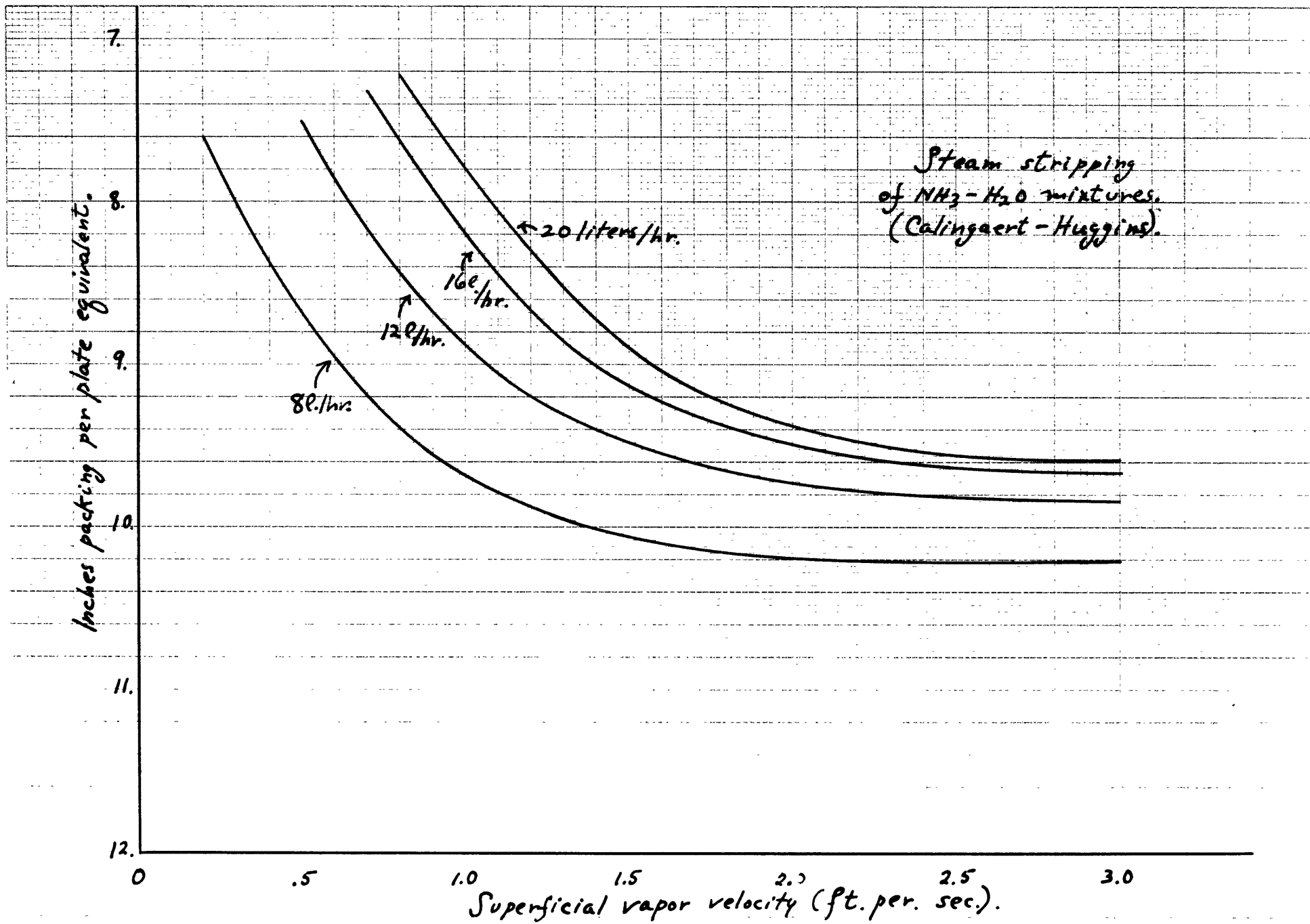
obtained results in accordance with this thesis and the
majority of other observers. His results were a sub-
stantiation of J. S. Carey's* observations that the plate
efficiency (Murphree) is independent of vapor velocity in
the low range up to one foot per second, where the vapor
is just bubbling up through the liquid on the plates, but
as the vapor velocity increases, the effect of spray is to
increase the contact between vapor and liquid between plates,
thus raising the efficiency due to increased vapor-liquid
contact. Above a certain critical velocity the efficiency
is cut down due to entrainment to the plate above. Thus
these observations substantiate the conclusion that with
low vapor velocites in a packed column better fractionation
is obtained due to more thorough vapor-liquid contact.

Although the data on the effect of vapor velocity
seem entirely in accordance, such is not the case in the
matter of the effect of reflux ratio. Apparently few data
are reported in this connection, and most of the obser-
vations I was able to find were rather general. For example,
Wheeler and Woodruff! in studying the rectification of an
acetone-water mixture, brought out the desirability of having
the column lagged with a partial condenser on top rather
than to have it unlagged, since then the overflow would not
flow down over so much of the packing and there would not
be so much chance for enrichment. But they give no data
on the actual N.T.U. obtained at various reflux ratios.

(*)-3

(ƒ)-19

At this point it would be appropriate to mention
the possible sources of error in my determination of the
number of transfer units. From the tabulated results it
is apparent that the N.T.U. undergoes a great change.
It seems improbable that the change should be quite as
great as that indicated, and probably the greatest source
of error is the measurement of the by-passed vapors. A
small error in this would affect the slope of the operating
line somewhat, and this might conceivably raise or lower
the mean concentration difference to a fairly great extent,
since the equilibrium curve for benzene and ethylene di-
chloride lies so close to the diagonal.

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CONCLUSIONS

Over a range of vapor velocities from roughly one-third to one foot/second and of reflux ratios from unity to 1.3, the data indicate that optimum separation is attained at total reflux, and at the lower vapor velocities.

Increasing the vapor velocity and maintaining the reflux ratio constant decreases the efficiency of fractionation, and raising the reflux ratio at a constant vapor velocity decreases the efficiency, also, although this last effect is not so marked as the first, except for the transition from a reflux ratio of unity to one greater than unity.

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RECOMMENDATIONS

As mentioned before, it was originally intended in this thesis to obtain data at reflux ratios less than unity, but this was not accomplished.

It would be interesting to see how this data would compare with that which I obtained at reflux ratios greater than one. The apparatus could be set up so that the distillation would be continuous, without continually feeding and drawing off product, by arranging to send all the vapor generated in the still up the column, pass it through a total condenser, and split the condensate, sending part back to the top of the column as reflux and part directly back to the still. This would of course yield a reflux ratio less than unity.

In connection with the method of heat supply to the still, before using the electric stove as an external source of heat I tried using a heating coil of Chromel resistance wire placed directly inside the still, the purpose being to cut down heat loss. At high heat inputs the ethylene dichloride tended to decompose, giving among other things, hydrogen chloride and carbon, so this method of heating had to be abandoned. My recommendation is the use of an external stove, heavily lagged, or probably an internal heating wire could be used if carefully sealed within a piece of pyrex glass tubing. In this case heat loss from the ends would have to be avoided.

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APPENDIX

DESCRIPTION OF APPARATUS

General.   As a whole, the apparatus consisted of the
wire-gauze fractionating column connected at the
bottom to a flask, which served as the still, and at
the top to an atmospheric condenser; a variable reflux
ratio was accomplished by by-passing part of the vapor
generated in the still up to the top of the column by
way of an external vapor line equipped with a regulating
valve, the vapor being condensed and the condensate
metered before being passed back into the top. Hence,
for every ten mols vaporized in the still, if 1 mol
was by-passed, then the reflux ratio O/V would be

$$\frac{10}{10-1} = 1.11.$$

This set-up thus affords a means of obtaining
a reflux ratio greater than unity. It was originally
proposed also to make some runs using a reflux ratio
less than unity by arranging to pass all the vapor up
through the column, but split the condensate, allowing
only part to come back down as reflux, the rest being
returned directly to the still. Both set-ups have the
advantage of continuous operation without having to
feed the still continuously or draw off bottoms and
distillate continuously.

Packed Column.   The column used was a Foster Wheeler
    Corporation laboratory distilling column containing
    a comparatively new packing designed by D. F. Stedman
    (U. S. Patent 2,047,444, July 14, 1936). As men-
    tioned above this was the same column that was used
    by L. F. Dowding and O. J. Kangas in their thesis of
    May 1938, for making tests at total reflux. The
    packing consisted of 3/8 inch triangular pyramids
    made of stainless steel wire screen 0.009 inches in
    diameter and 40x60 mesh. 18 inches of this packing
    was enclosed in a flanged, stainless steel column
    with a 1 1/8 inch hexagonal cross section. Following
    is part of a description of the packing given in the
    U. S. Patent Office Gazette:

    "Packing for fractionating columns and the
    like comprising a column of capillary material,
    the capillary openings of which seal with liquid
    under treatment, arranged to provide a multip-
    licity of cells uniformly distributed through-
    out the column, vapour passages through said
    capillary material larger than said capillary
    openings whereby each cell receives vapour from
    at least two other cells and uniformly disposed
    contact surfaces throughout the column to provide
    for repeated subdivision and recombination or
    liquid passing through the column."

Still.   The still consisted of a two-liter, three-
    necked, round bottom pyrex glass distilling flask,
    which was flanged, and could thus be attached to the
    bottom of the flanged column by means of a thin, hard
    rubber gasket. This means of attachment was found to
    be much less troublesome and damaging to the column

← PREHEATER FOR AIR FROM LAB. LINE

← CONSTANT LEVEL GAUGE

← VAPOR BYPASS LINE (HOT AIR JACKETED)
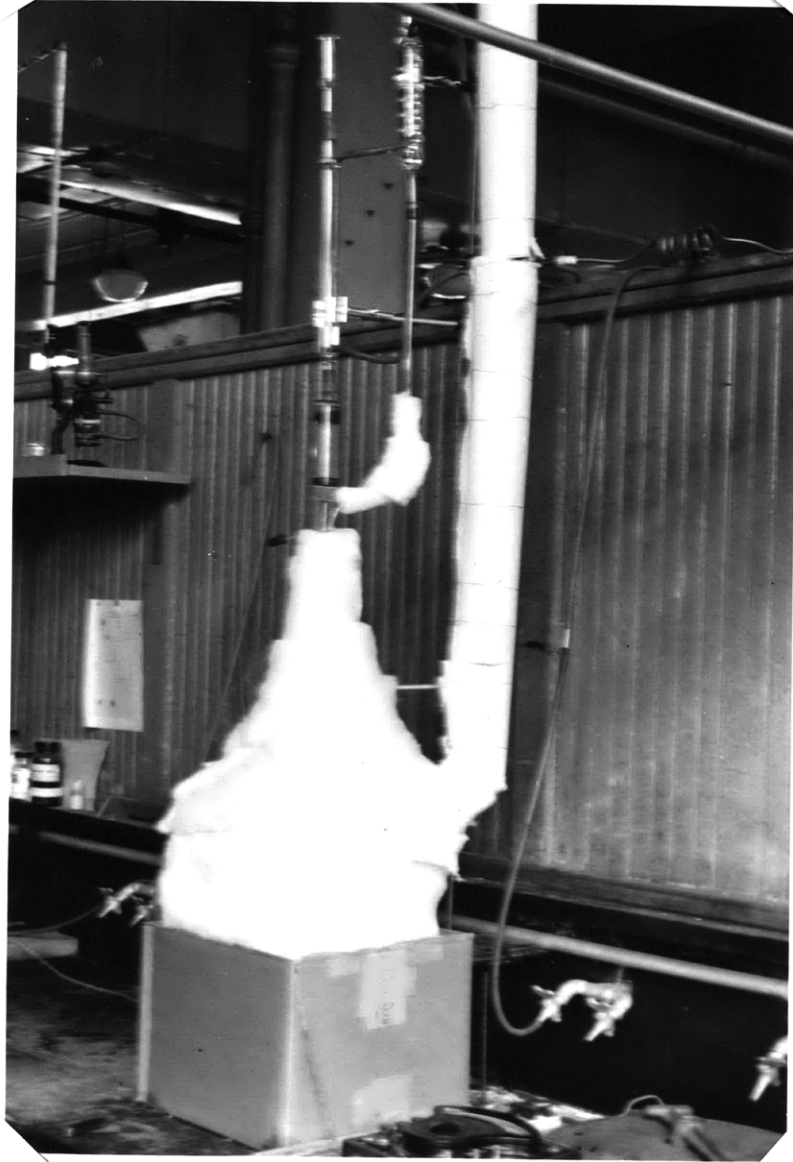
← RHEOSTAT

TOP SAMPLING TUBE →

COLUMN AND STILL → (LAGGED)

STILL SAMPLING TUBE → (OBSCURED)

↑ WATTMETER

SET-UP OF APPARATUS.

[%V > 1.0]

than using porcelain cement, and the gasket was not
attacked by the vapors. Through one of the two side-
necks a sampling tube was extended to the bottom of
the flask, extending on the outside to a point below
the liquid level in the still, so that samples for
analysis could be siphoned off. The external vapor
line extended from the other side-neck.

Heat was supplied to the still by means of an
electric stove heater, the current through which could
be regulated by means of a rheostat. The power input
to the still was measured by a wattmeter. The stove
and still were lagged with asbestos and cotton (outside),
with a thick layer of wood shavings surrounding the
stove, in a large box; a piece of asbestos pasteboard
separating the shavings from the heating wires. This
means of insulation proved quite effective.

By-pass Line and Meter, Lagging. A picture of the ap-
paratus is shown, with a diagrammatic blueprint of the
arrangement. The by-pass line was equipped with a
valve to vary the flow of vapor. The vapor by-passed
was condensed and the condensate metered through a
constant level gauge which had been previously
calibrated in terms of cc./sec. flow at various levels
for mixtures of various compositions. This metered
condensate was then sent to the top of the column.
Particular care had to be taken to prevent condensation
in the by-pass line, and so besides being heavily

SET-UP OF APPARATUS
FOR REFLUX RATIO GREATER THAN 1.0

OPEN TO ATMOSPHERE

←WATER

←WATER

CONDENSERS

TOP SAMPLE

LINE LAGGED
AND HOT-AIR
JACKETED

CONSTANT-LEVEL
GAUGE FOR METER-
ING BYPASS

←VALVE

WIRE-GAUZE PACKED
FRACTIONATING COLUMN

LAGGED→

LINE FOR
BYPASSED VAPOR

BOTTOMS
SAMPLING TUBE

STILL

ELECTRIC STOVE
CONNECTED TO RHEOSTAT

W.A.M.
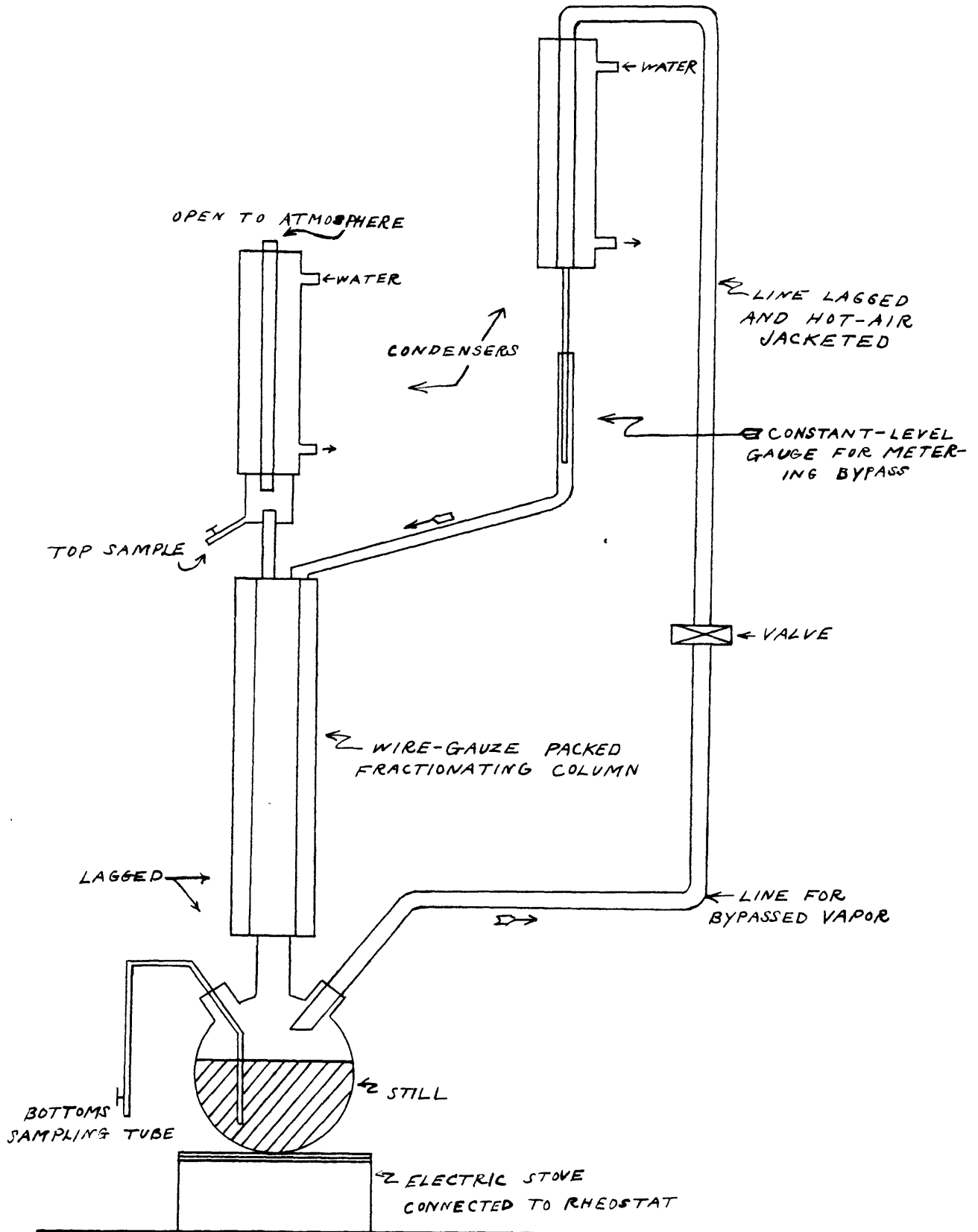
lagged with cotton it was externally heated by means of a hot air stream maintained at slightly above 80 C. at its coolest point, so that no condensation could take place. The hot air was obtained by heating air from a compressed air tap as it passed through a coil of copper tubing. A Bunsen flame was used to heat the coil.

That portion of the vapor which was generated in the still and passed up through the column was condensed at atmospheric pressure and refluxed. Samples of this reflux were taken from a sampling tube extending from a trap just beneath the condenser and above the top of the column. Both condensers were of the spiral type, tap water being the cooling medium.

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OPERATING TECHNIQUE

Introduction.   The efficiency runs usually took from
five to eight hours to reach equilibrium, and fur-
thermore, at low heat inputs, sometimes as much as
a half hour was consumed in bringing the still and
its contents up to the boiling point. So it was
very seldom that two runs could be made in a single
day. Equilibrium was assumed to have been reached
when the analyses of the top and bottom samples
checked those previously taken an hour before.

The still usually contained about one liter
of the binary, whose composition was about 40 mol %
benzene. After equilibrium had been established the
fraction of the original solution which was distributed
throughout the system was so small that the quantity
and composition of the still liquid was altered very
little from the initial conditions.

Procedure.   The procedure used was to start the daily
run at 9:00 A.M., and take samples for analysis ap-
proximately every hour until equilibrium was reached
late in the afternoon. As a general rule it was found
that equilibrium was reached in a shorter time for the
runs at the higher vapor velocities. Note was also
made, when the samples were taken, of the level in
the constant level gauge for the by-passed vapor, and

if it was not assuming the desired level adjustments could be made with the valve on the vappr by-pass line. The heat input to the column was checked by the wattmeter, also, and if this was not constant, due to motors or other electrical apparatus around the Institute being cut in or out, the rheostat could be adjusted.

A check was also made periodically on the temperatures at each end of the hot-air jacket, to make sure no condensation was taking place in the vapor line.

Before the run was made a rough estimate of the desired heat input and gauge level was made, so that the vapor velocity at equilibrium and the reflux ratio would be such as to fit fairly well into the table of the twelve desirable sets of conditions presented on page *12*. In other words, if the run the day before had been for a medium vapor velocity and medium reflux ratio, and the run proposed for the day at hand was to be for medium vapor velocity and high reflux ratio, then a slightly greater heat input to the still would be required in order to vaporize the extra vapor for by-passing. Similarly, if the reflux ratio was to stay the same, but the vapor velocity increased, additional heat would be required. As it finally turned out the data divided fairly well into the twelve parts of the table. It was necessarily a matter of trial and error.

Heat Loss. Heat loss from the column and still was determined in the same way as that used by Dowding and Kangas, i. e., it was assumed equal to the heat input required to just carry the vapors up to the condensers. This was found to be very small, about twenty watts for low heat input. Since the temperature within the still would not change with varying heat inputs, the heat loss, most of which is due to conduction, would not, theoretically, change with increasing heat inputs. However, a small allowance was made at the higher heat inputs.

Meter Calibration. The constant level gauge was calibrated by noting for different levels the volume in cc. of a liquid mixture of given composition which passed through within a given time interval, four minutes. The data are given on page *55*, and the calibration chart, for use in calculating the reflux ratio, on page *57*. As indicated from the data, the effect of varying the liquid composition on the flow rate was very slight, and so a single calibration curve was plotted for 50 mol % benzene.

- - - - -

METHOD OF ANALYSIS

The method of analyzing the samples from the top of the column and the still was measuring the refractive index of the sample, by means of an Abbé refractometer, and referring to the refractive index-composition curve, which is given on the photostat, page 37. Taking a reading from the refractometer required only a few seconds, and also had the advantage that only a few drops of the sample were required. The readings are good to four decimal places. Density measurements might have been made, but this method of analysis would have been slower and less simple, with no better accuracy.

The Abbé refractometer was calibrated with the monobronaphthalene standard, the index of which at 25°C. is 1.638.

The pure benzene and ethylene dichloride used have the following indices and boiling points.

	Refractive Index (25.2°C.)	Boiling point °C.
Benzene - -	1.4962	80.25
Ethylene dichloride - -	1.4418	83.70

- - - - - -

SOURCE OF EQUILIBRIUM DATA

The same equilibrium data were used in this thesis as were used by Dowding and Kangas, i. e., the data calculated from Raoult's law employing a relative volatility of 1.111. These were the equilibrium data presented by T. J. Coleman, S. M. Thesis, M. I. T., 1934, page 110.

These data are reproduced in Table $\mathbb{II}$, page 35 and were used in constructing the y-x curve given on the photostat, page 37.

The analytical data, refractive index vs. composition, are from Zawadzki, Z. Physik Chem., 35, 145 (1900). They are presented in Table $\mathbb{III}$, on the previous page 36.

- - - - - -

TABLE

EQUILIBRIUM DATA*

(vapor-liquid compositions)

Based on Raoult's law, using a relative volatility α of 1.111.

$$\frac{y^*}{1 - y^*} = \alpha \; \frac{x}{1 - x}$$

α equals the ratio of the equilibrium vapor composition to the liquid composition (mol fraction B) *as molal ratio*.

x_B	y_B^*
0.00	0.00
.05	.05524
.10	.10988
.20	.21735
.30	.32255
.40	.4255
.50	.5263
.60	.6250
.70	.7216
.80	.8162
.85	.8630
.90	.9090
.95	.9548
.9625	.9661
.975	.9775
1.000	1.000

(*) Coleman, T. J., S.M. Thesis, M.I.T., 1934, p.110

TABLE

ANALYTICAL DATA*

Mol % benzene	Refractive Index (25.2°C.)
100.00	1.49779
91.81	1.49294
80.71	1.48641
74.46	1.48273
64.26	1.47696
51.48	1.47270
45.73	1.46687
45.35	1.46643
34.06	1.46041
25.42	1.45572
11.37	1.44842
0.00	1.44225

(*) Zawadzki, Z. Physik Chem., 35, 145 (1900)

FIGURE 3
EQUILIBRIUM CURVE
SYSTEM BENZENE-ETHYLENE CHLORIDE
AS CALCULATED FROM RAOULT'S LAW
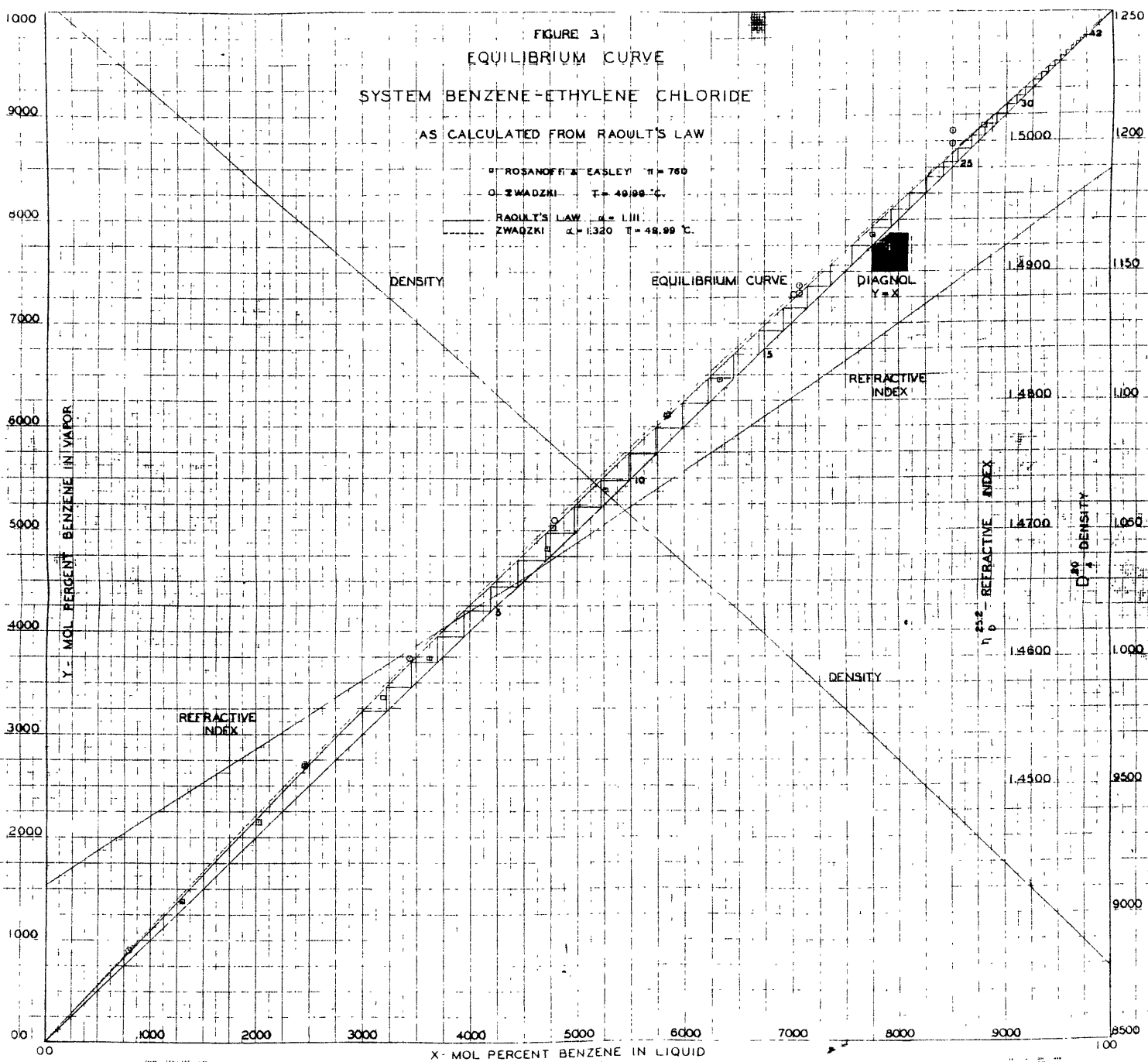
METHOD OF CALCULATION

<u>Example</u> <u>Run</u> <u>No. 3</u> (see Data) :-

Temperature and pressure changes through the column were considered negligible.

The latent heat of a 50 mol per cent benzene mixture was calculated from Trouton's Law as follows:

$$\frac{L_V}{T_s} = 8.75 + 4.571 \ln T_s$$ (see Table of Nomenclature, page 60)

Benzene: $L_V = 357 \ (8.75 + 11.68) = 7300$

Ethylene Dichloride: $L_V = 353.3 \ (8.75 + 11.67) = 7260$

approximately for the binary, $L_V = 7280$ cal./gm. mol

$$= 13100 \ B.T.U./lb. \ mol$$

This value for the latent heat was used for all the still mixtures since the slight variations from 50 mol per cent benzene would not appreciably affect the 13,100.

1 K.W.H. = 3412 B.T.U.

net heat input = 150 - 20 = 130 watts

Total mols/hr. vaporized from still:

$$\frac{.130 \times 3412}{13100} = 0.0339$$

For convenience in calculations the linear plot on page 58 was constructed for finding the mols/hr. vaporized from the net heat input.

Mols/hr. by-passed (through gauge):

Rate of flow through gauge = 0.056 cc./sec. from the calibration plot, page 57.

CALCULATIONS (cont'd)

Besides giving a plot of equilibrium vapor-liquid compositions, the photostat also includes a plot of refractive index and density versus liquid composition. The density of the mixture by-passed is found from the photostat as being that of a liquid having the composition of the vapor leaving the still, i. e., in equilibrium with the still liquid, whose index is 1.4700. This density is found to be 1.058.

$$\text{lbs./hr. by-passed} = \frac{.056 \times 1.058 \times 3600}{454} = 0.470$$

From the photostat it is seen that the composition of the mixture by-passed is 54.4 mol per cent benzene.

$$\text{mols/hr. by-passed} = \frac{470}{(.544 \times 78) \quad (.456 \times 99)} = .00535$$

Mols/hr. through column as vapor:

$$0.03390 - .00535 = 0.02855$$

Reflux ratio: $\quad \dfrac{O}{V} = \dfrac{.03390}{.02855} = 1.19$

Vapor velocity through column:

cross sectional area of column = .00571 sq.ft.

$$\frac{.02855 \times 359 \times 353}{.00571 \times 3600 \times 273} = 0.65 \text{ ft./sec.}$$

as can be verified from the plot on page 59.

CALCULATIONS (cont'd)

Number of Transfer Units (N. T. U.) -

By definition, the number of transfer units in a given separation is given by

$$N.T.U. = \int_{Y_1}^{Y_2} \frac{dy}{y^*-y}$$, where y^* and y represent

the equilibrium and actual gas concentrations respectively at any point in the column where the reflux composition is X. Y_2 and Y_1 refer to the top and bottom of the column respectively.

On the diagram given on the following page the top line represents the equilibrium curve (exaggerated), and the straight line above the diagonal is the "operating line," which gives the value of Y for any value of X. Its slope is the reflux ratio O/V or 1.19 in this case. The dotted arrows show the two ends of the separation.

The vapor rising from the top has the same composition as the top sample of condensate, hence Y_2 is 0.644. X_s is 0.518.

In the region between the dotted lines a graphical integration for the N.T.U. may be replaced by using a logarithmic mean value for Y^*-Y, since the equilibrium curve is so nearly straight over this short distance.

$$N.T.U. = \frac{Y_2-Y_1}{\frac{(Y^*-Y)_1 - (Y^*-Y)_2}{\ln\frac{(Y^*-Y)_1}{(Y^*-Y)_2}}} =$$

$$\frac{.644 - .546}{\frac{(.572-.546)-(.657-.644)}{\ln\frac{.026}{.013}}} = 5.15$$

- - - - - -

$Y_2^* \\ (.657)$

$Y_2 \\ (.644)$

$slope \\ =1.19$

$Y_1^* \\ (.572)$

Y

$Y_s^* \\ (.546)$

$X_s \\ (.518)$

X_1

X_2

$X \rightarrow$
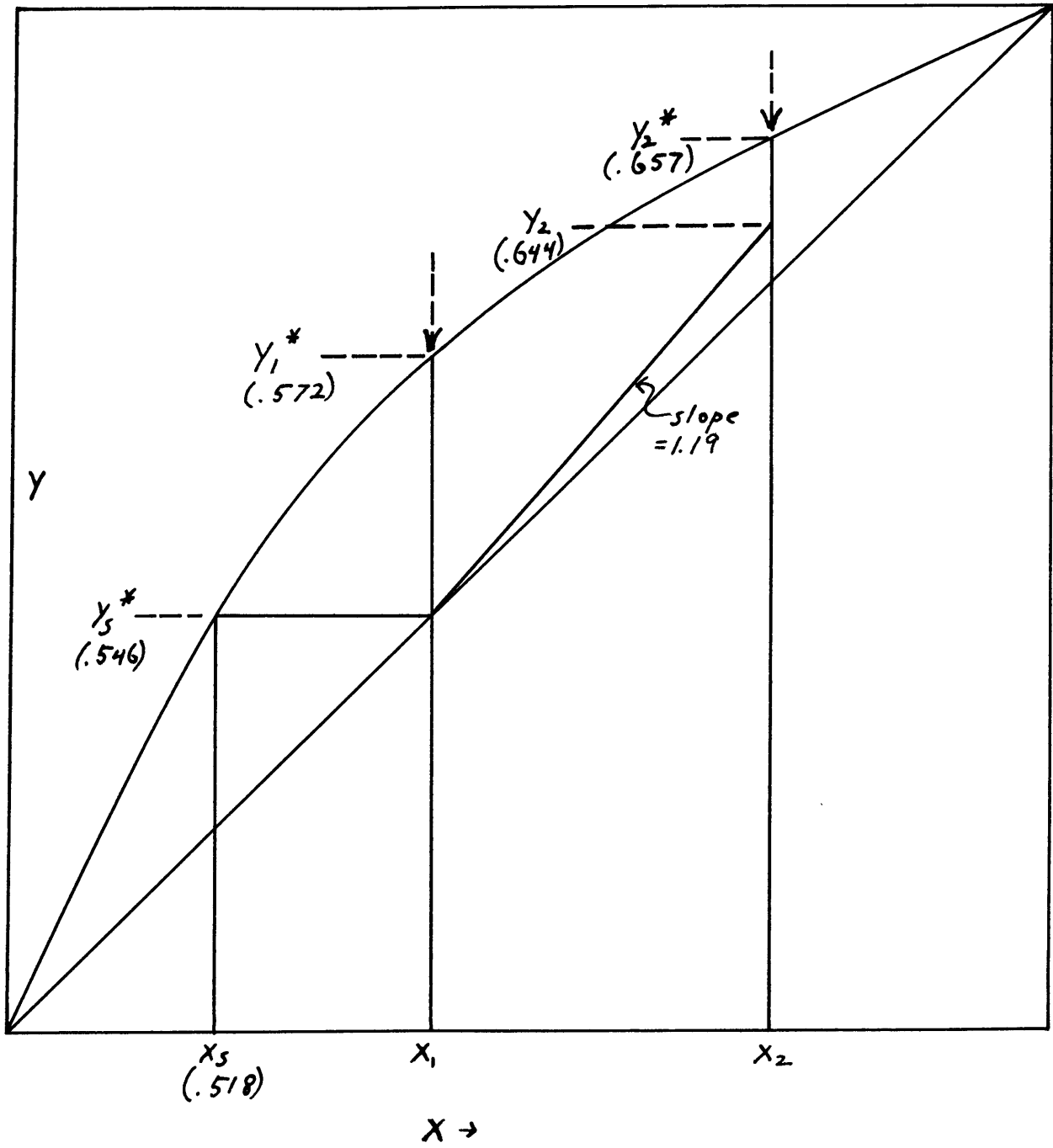
$(X_s \text{ and } Y_s^* \text{ refer to the still})$

O B S E R V E D   D A T A

F O R   E F F I C I E N C Y   R U N S

at varying reflux ratios

and vapor velocities.

EFFICIENCY DATA

RUN I

April 2.

Conditions: Medium vapor velocity

Reflux ratio unity (total reflux)

Data: Started at 9:45 A.M.

Time	Index (top)	Index (still)	Gross heat
11:45 A.M.	1.4704	1.4579	135 watts
12:45 P.M.	1.4718	1.4574	135
1:45	1.4733	1.4565	135
2:45	1.4733	1.4564	135
3:45	1.4733*	1.4564*	135
equilibrium compositions†	0.575	0.330	

heat loss 20 w.

* denotes equilibrium value of index.

† as mol fraction benzene.

- - - - - -

EFFICIENCY DATA

RUN II

April 3.

Conditions: Low vapor velocity

Reflux ratio unity

Data: Started at 9:00 A.M.

Time	Index (top)	Index (still)	Gross heat
1:30 P.M.	1.4699	1.4560	75 watts
2:30	1.4708	1.4553	75
3:30	1.4717	1.4548	75
4:30	1.4721	1.4544	75
5:30	1.4735	1.4554	75
6:30	1.4735*	1.4554*	75
equilibrium compositions	0.580	0.3175	

heat loss 20 w.

- - - - - -

EFFICIENCY DATA

RUN III

April 4.

Conditions: Medium vapor velocity

                Medium reflux ratio

Data: Started at 9:00 A.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
10:15 A.M.	33 (32nds)	1.4765	1.4700	150 watts
11:15	40	1.4770	1.4700	150
12:15 P.M.	40	1.4770	1.4700	150
1:15	40	1.4770*	1.4700*	150
	equilibrium compositions	0.644	0.518	

heat loss 20 w.

- - - - - -

EFFICIENCY DATA

RUN IV

April 6.

Conditions: Medium vapor velocity

Low reflux ratio

Data: Started at 9:00 A.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
10:30 A.M.	16 (32nds)	1.4755	1.4690	140 watts
11:30	16	1.4760	1.4690	140
12:30 P.M.	16	1.4766	1.4689	140
1:30	16	1.4766*	1.4689*	140
	equilibrium compositions	0.638	0.498	

heat loss 20 w.

- - - - - -

EFFIC IENCY DATA

RUN V

April 7.

Conditions: Medium v apor velocity

High reflux ratio

Data: Started at 9:00 A.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
10:30 A.M.	48 (32nds)	1.4709	1.4685	160 watts
11:30	56	1.4718	1.4683	160
12:30 P.M.	56	1.4721	1.4683	160
1:30	56	1.4728	1.4682	160
2:30	56	1.4728*	1.4682*	160
	equilibrium compositions	0.568	0.485	

heat loss 20 w.

- - - - - -

EFFICIENCY DATA

RUN VI

April 8.

Conditions: High vapor velocity

Reflux ratio unity

Data: Started at 9:00 A.M.

Time	Index (top)	Index (still)	Gross heat
11:00 A.M.	1.4769	1.4660	175 watts
12:00	1.4790	1.4658	175
1:00 P.M.	1.4798	1.4658	175
2:00	1.4806	1.4658	175
2:45	1.4806*	1.4658*	175
equilibrium compositions	0.708	0.440	

heat loss 20 w.

- - - - - -

EFFICIENCY DATA

RUN VII

April 8.

Conditions: High vapor velocity

Low reflux ratio

Data: Started at 2:45 P.M. (still already up to heat)

Time	Gauge level	Index (top)	Index (still)	Gross heat
3:45 P.M.	16 (32nds)	1.4710	1.4656	180 watts
4:50	16	1.4717	1.4656	180
5:45	16	1.4722	1.4654	180
6:30	16	1.4722*	1.4654*	180
	equilibrium compositions	0.558	0.432	

heat loss 25 w.

- - - - - -

EFFICIENCY DATA

RUN VIII

April 9.

Conditions: High vapor velocity

Medium reflux ratio

Data: Started at 2:00 P.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
4:00 P.M.	40 (32nds)	1.4712	1.4665	190 watts
5:00	40	1.4718	1.4663	190
5:45	40	1.4723	1.4663	190
6:30	40	1.4723*	1.4663*	190
	equilibrium compositions	0.558	0.450	

heat loss 30 w.

- - - - -

EFFICIENCY DATA

RUN IX

April 10.

Conditions: High vapor velocity

High reflux ratio

Data: Started at 9:00 A.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
10:30 A.M.	56 (32nds)	1.4686	1.4660	205 watts
11:30	56	1.4691	1.4658	205
12:30 P.M.	56	1.4699	1.4658	205
1:30	56	1.4699*	1.4658*	205
	equilibrium compositions	0.519	0.437	

heat loss 35 w.

- - - - - -

EFFICIENCY DATA

RUN X

April 10.

Conditions: Low vapor velocity

High reflux ratio

Data: Started at 1:30 P.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
2:30 P.M.	60 (32nds)	1.4698	1.4658	105 watts
3:30	60	1.4705	1.4655	105
4:30	60	1.4712	1.4655	105
5:45	60	1.4712*	1.4655*	105
	equilibrium compositions	0.538	0.437	

heat loss 20 w.

- - - - - -

EFFICIENCY DATA

RUN XI

April 11.

Conditions: Low vapor velocity

Medium reflux ratio

Data: Started at 9:00 A.M.

Time	Gauge level	Index (top)	Index (still)	Gross heat
10:30 A.M.	44 (32nds)	1.4745	1.4680	95 watts
11:35	40	1.4753	1.4677	95
12:30 P.M.	40	1.4758	1.4677	95
1:30	40	1.4758*	1.4677*	95
	equilibrium compositions	0.623	0.472	

heat loss 20 w.

- - - - - -

DATA FOR FLOWMETER CALIBRATION

(See calibration plot page 57)

I.   30 mol per cent benzene solution.

Gauge level (32nds)	Volume (cc.)	Time (sec.)	Rate of flow (cc. per sec.)
16	5.76	240	0.024
20	6.72	240	0.028
30	9.60	240	0.040
40	13.13	240	0.0545
50	13.15	180	0.073
65	18.70	180	0.104
75	23.20	180	0.129

II. 50 mol per cent benzene solution.*

Gauge level (32nds)	Volume (cc.)	Time (sec.)	Rate of flow (cc. per sec.)
16	6.00	240	0.025
20	6.96	240	0.029
30	9.84	240	0.041
40	13.42	240	0.056
50	13.30	180	0.074
65	19.10	180	0.106
75	23.65	180	0.131

* (these data used for the mean calibration plot)

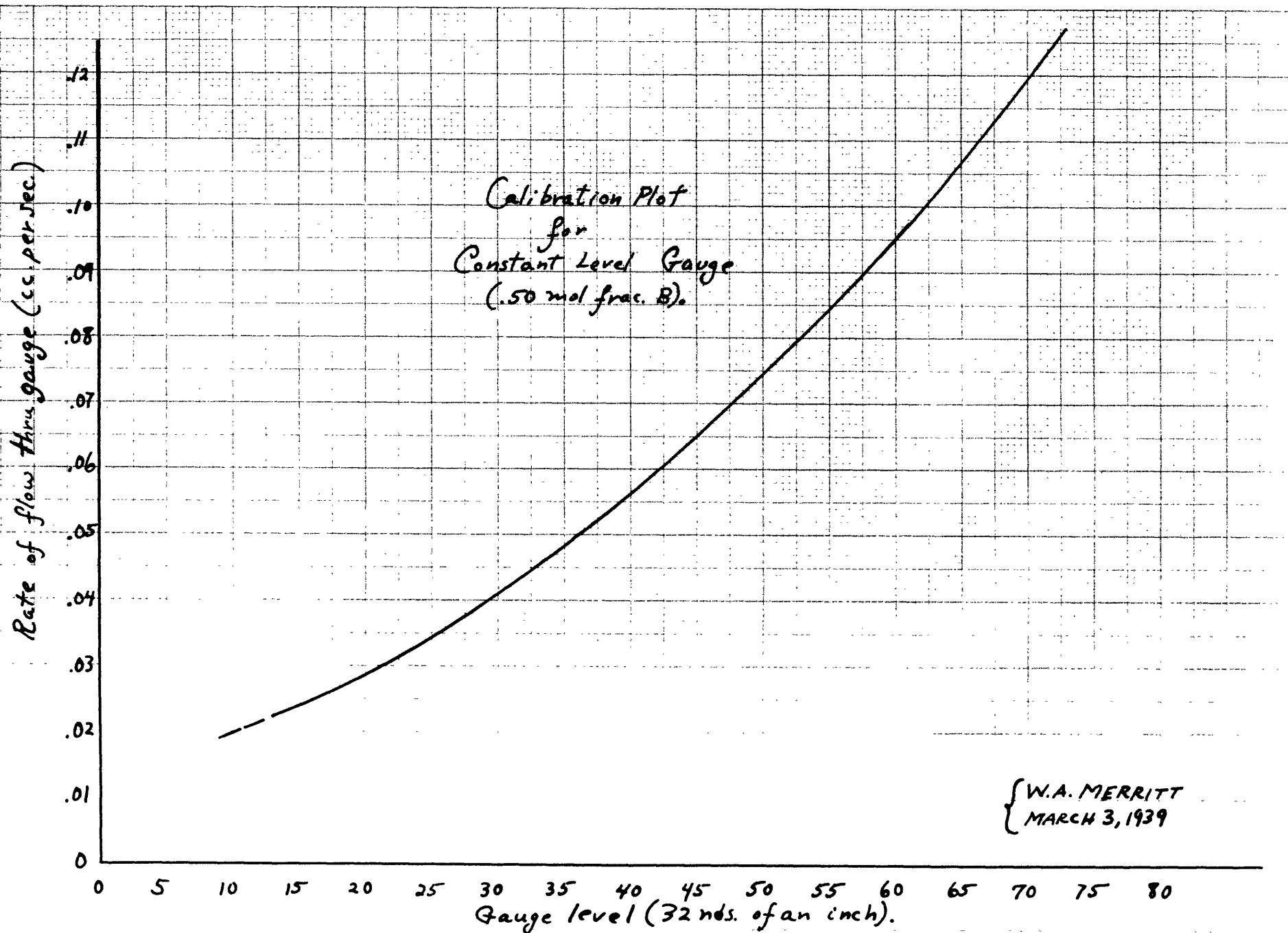# DATA FOR FLOWMETER CALIBRATION

(continued)

III.   70 mol per cent benzene solution.

Gauge level (32nds)	Volume (cc.)	Time (sec.)	Rate of flow (cc. per sec.)
16	6.25	240	0.026
20	7.20	240	0.030
30	10.12	240	0.042
40	13.80	240	0.0575
50	13.60	180	0.0752
65	19.25	180	0.107
75	23.90	180	0.133

- - - - - -

Calibration Plot
for
Constant Level Gauge
(.50 mol frac. B).

{ W.A. MERRITT
MARCH 3, 1939

Rate of flow thru gauge (c.c. per sec.)

Gauge level (32 nds. of an inch).

Mols Vaporized
per Hour
vs.
Heat Input (net)
(for convenience in calcs.)

{ W.A. MERRITT
MAY 8, 1939

Mols vaporized per hour

Heat Input in Watts (net)

Vapor Velocity
vs.
Mols per Hour
thru Column
(for convenience in calcs.)

Vapor Velocity (ft. per second).

1.2
1.1
1.0
.90
.80
.70
.60
.50
.40
.30
.20
.10
0

0   .01   .02   .03   .04   .05

Mols per hour thru column as vapor.

{ W.A. MERRITT
{ MAY 9, 1939

FORM 1 T

TABLE OF NOMENCLATURE

B   - Benzene

ED   - Ethylene dichloride

H.E.T.P.   - Height of the equivalent theoretical plate

H.T.U.   - Height of a transfer unit

L_v - Molal latent heat in Trouton's Law

N,n   - Refractive index

N.T.U.   - Number of transfer uj

O   - Overflow or reflux rate

P   - Vapor pressure

T_s - Temperature, absolute, in Trouton's Law

V   - Vapor rate

X   - Mol fraction benzene in the liquid

X_1, X_2, X_s - Mol fraction benzene in liquid at bottom, top, still.

Y, Y^* - Vapor composition at any point, equilibrium vapor composition

Y_1, Y_2, Y_s^* - Vapor composition at bottom, top, leaving still

α - Relative volatility

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