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Construction and Testing of Equipment to be used in Extractive Distillation Experiments

By

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CONSTRUCTION AND TESTING OF EQUIPMENT TO BE USED IN

EXTRACTIVE DISTILLATION EXPERIMENTS

by

Orrin C. Holbrook

A THESIS

Presented to the Graduate Faculty of Lehigh University

in partial fulfillment of the requirements

for the degree of

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fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering.

Date: _D. E. Mach_
                          Professor in Charge

Date: _____
                          Head of Department

Acknowledgment

This work was undertaken under the supervision
and guidance of Dr. D. Mack. The author wishes to
express his gratitude to Dr. Mack for the valuable
assistance rendered through his continuous suggestions
and constructive criticisms.

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Introduction

Many binary liquid mixtures, either because of their narrow boiling range or due to the presence of azeotropes, cannot be separated by conventional fractionation. If the two components are of different chemical structure, however, the addition of a third component or solvent to the mixture can greatly increase the relative volatility of the original two components. The process of fractionation in the presence of a foreign substance added to improve the relative volatility is called extractive distillation and is used at present on a commercial scale for the separarion of many liquid mixtures.

The object of the work on which this report is based wa; the construction and testing of laboratory equipment to be used in extractive distillation experiments. One of the items constructed was an Othmer still (7) with which the vapor-liquid equilibrium relationships of liquid mixtures can be determined. A thorough knowledge of these relationships is necessary for the evaluation and design of any extractive distillation system. The other piece of equipment built was a continuous extractive distillation column of the Dicks and Carlson (2) type. Use of this column gives a comparison of the separation obtained with conventional distillation and with extractive distillation. A description of both units is given as well as the operating procedures used on each. Their use is illustrated by a study of the system water-acetic acid-glycol diacetate.

Summary of Acetic Acid Dehydration

The possibility of separating water and acetic acid mixtures on a commercial scale by extractive distillation with glycol diacetate as solvent cannot be fully evaluated with the data obtained at present. However, some very important generalizations can be made. The presence of solvent does produce a considerable increase in the relative volatility of the water. Roughly stepping off the number of plates required for the separation of such a mixture into products of 99 percent purity at total reflux shows that twenty plates are needed when no solvent is used while only five plates are required when 80 percent solvent is present in the still. Fractionation in the presence of solvent, however, causes hydrolysis when separating a charge containing less than 65 percent acid and esterification with a charge containing more than this amount of acid. The monoacetate produced in hydrolysis, though harmful to the separation, does not become sufficiently concentrated to materially affect it until more than thirty minutes of refluxing.

In a commercial unit, the solvent, assumed to be pure glycol diacetate, would enter at the top of the column and descend through a region of very low acetic acid concentration. Hydrolysis would take place rapidly, but, providing the residence time of the solvent in this region

was not more than ten or fifteen minutes, the effectiveness
of the solvent in aiding the separation would not be
seriously impared. From here, the solvent would pass
into a region of moderate acid concentration where
hydrolysis would take place slowly. Next, the solvent
would pass into a region of high acid concentration
where esterification would take place. There are two
important consequences of this esterification reaction
in the lower part of the column. First, it regenerates
the diacetate and, providing the reaction were allowed to
go to completion, would permit the return of pure
diacetate to the top of the column. Second, it produces
water in the lower part of the column. This is undesirable
and constitutes a serious threat to the process which
will require further investigation. However, the
principle advantage of extractive over azeotropic
distillation for this mixture lies in the lower heat
requirements of extractive distillation of dilute acid
mixtures. If a case were found in which it were desired
to concentrate a dilute acid solution to one of 80 or 90
percent acid, this method might prove more economical then
azeotropic distillation.

Equilibrium Still

The vapor-liquid still is of the Othmer Type (7) and has the following principle parts (fig. 1):

    A-still body (50 cc distillation flask)

    B-vapor tube

    C-condenser

    D-condensate trap (capacity approx 1.7 cc)

    E-heater, 28 cm of No. 26 nichrome wire

    F-vent

    G-thermometer, 30 to 300 F

In operation, approximately 25 cc of liquid is charged to the still through the opening at the top of the flask and the opening closed with a cork stopper containing the thermometer and heater lead wires. The current is turned on and adjusted so that the liquid in the flask boils vigorously. The vapors pass up through the vapor tube and into the condenser. After condensation, the liquid passes through the condensate trap and back into the flask. Because of the change in composition of the liquid in the flask, it is necessary to continue distillation until equilibrium has been reached. Tests on the mixture benzene-methanol indicated that approximately twenty minutes of boiling after the sample trap has filled is necessary for equilibrium to be attained. After reaching equilibrium, the current is turned off, the condensate sample removed from stopcock D (Fig. 1), and a
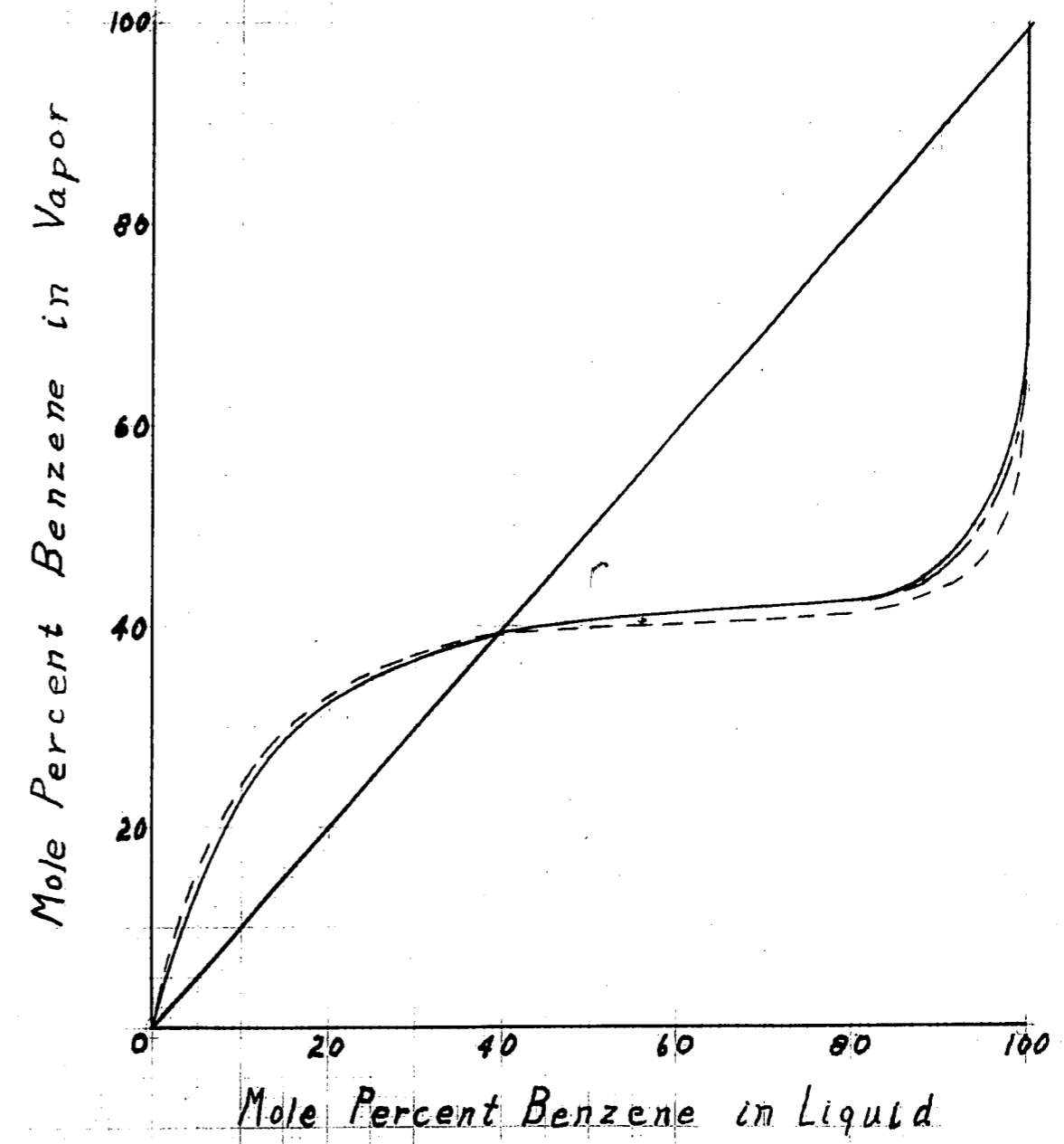
Fig. 1

Equilibrium Still
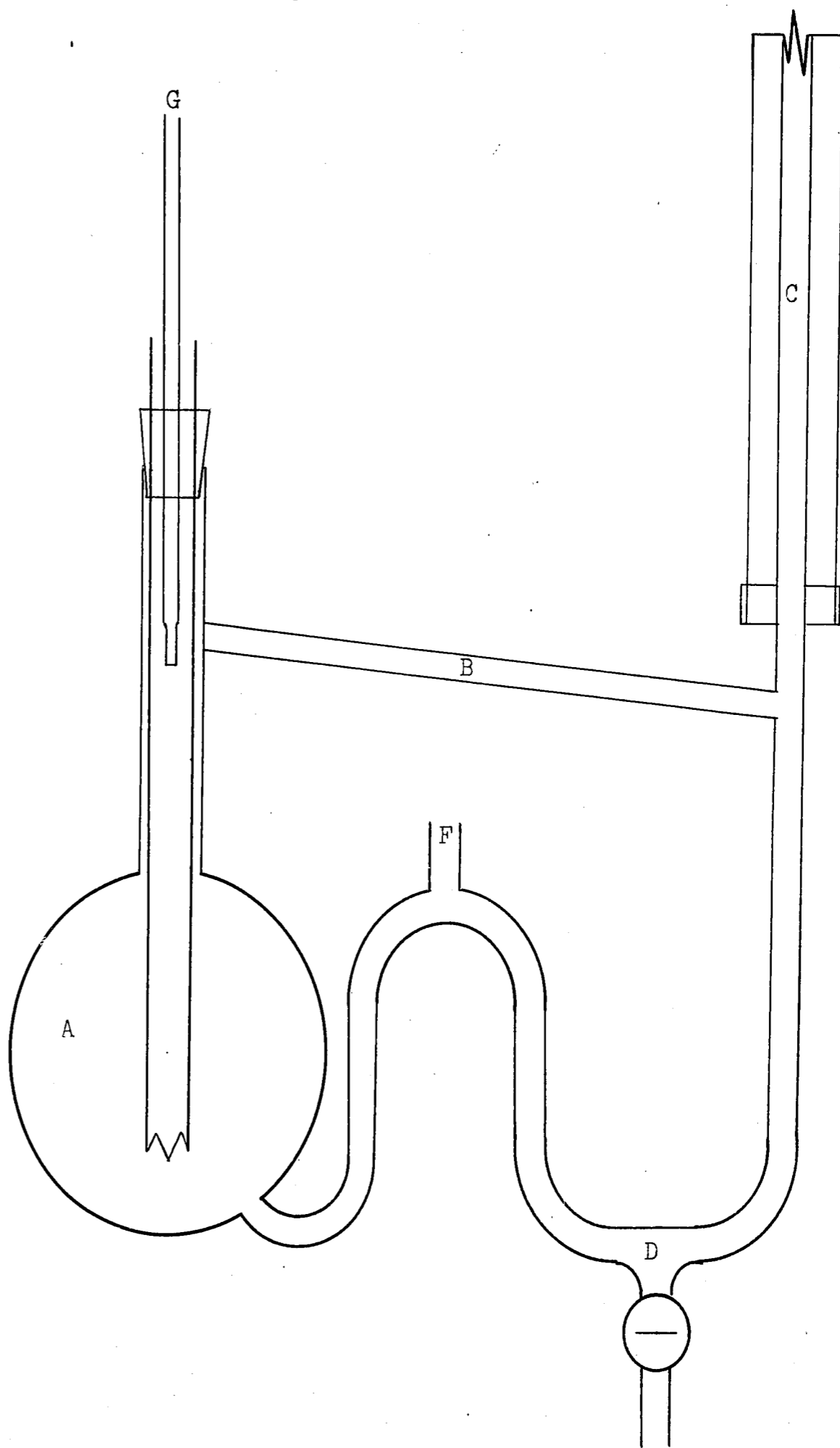
sample of residue removed from the flask with a pipette. The process is repeated after the addition of the desired amount of one of the components.

To check the performance of the still, the vapor-liquid equilibrium of the system benzene-methanol was determined in the still at one atmosphere pressure and compared with that found in the literature. The data is given in Table I and a graph of the equilibrium curves obtained both from the still and from the literature (10) is shown in Figure 2. Analysis of the mixture was by refractive index at 20 ±.5 C (automatic temperature control equipment was not available).

It is seen in Figure 2 that the curve obtained with this still lies slightly outside of the curve found in the literature. This was thought to be due to a small amount of refluxing taking place between the rising vapors and the liquid condensing on the walls of the still. To decrease the amount of this reflux, approximately one half inch of asbestos insulation was placed around the neck and bulb of the flask and the experiment repeated. The results obtained under these conditions (Fig. 2 and Table II) followed the literature values much more closely than before. The benzene and methanol used in the experiments on the insulated flask were of a higher grade than before, necessitating slightly different refractive index standards (Fig. 3).

Figure 2

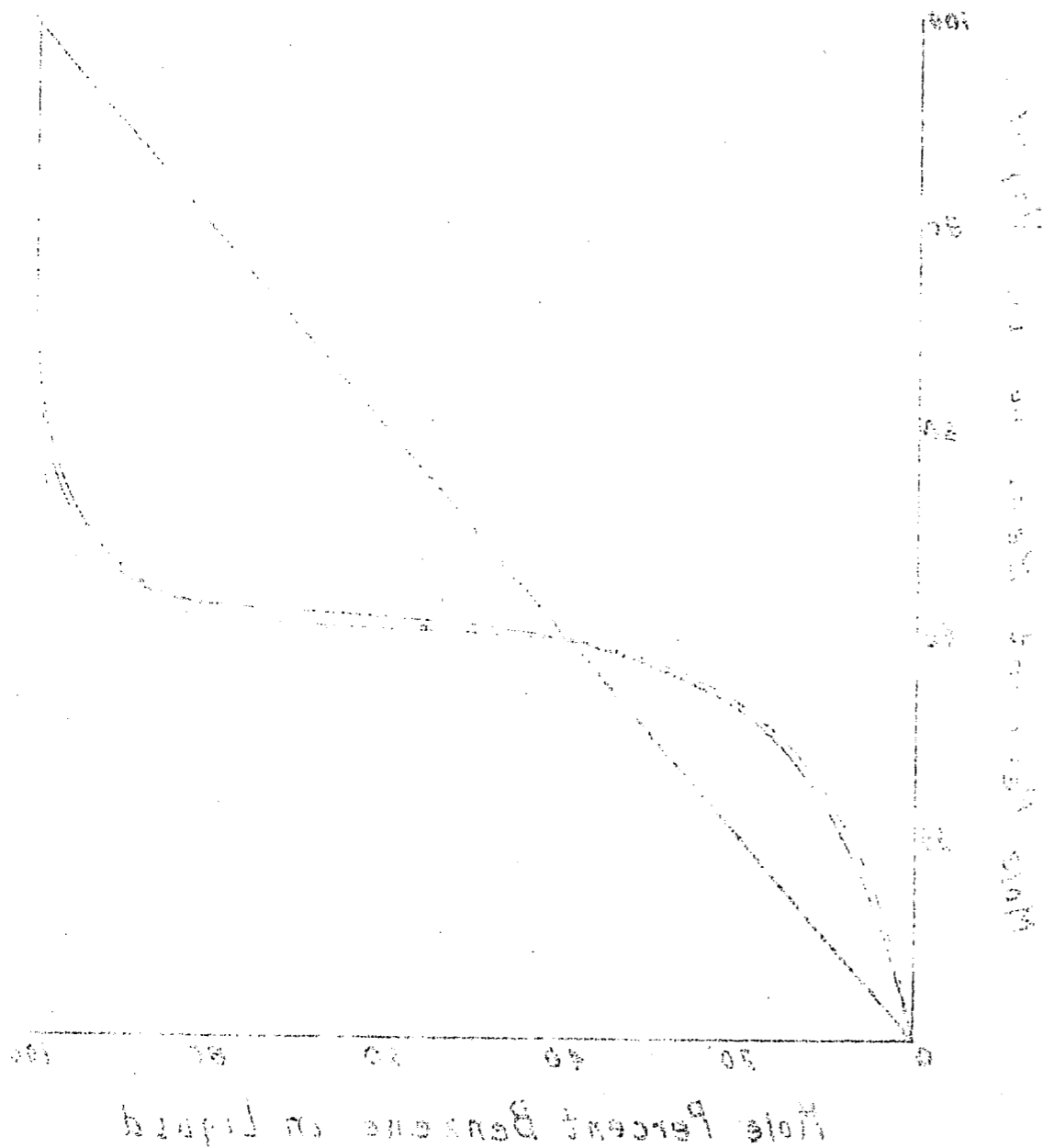Equilibrium Diagram of Benzene-Methanol

Mole Percent Benzene in Liquid

Mole Percent Benzene in Vapor

Literature
Runs 1-18
Runs 19-24

Figure 2

Equilibrium Diagram of Benzene-Methanol

Mole Percent Benzene in Liquid

Literature ——
Runs 1-18 -----
Runs 19-24 ········

Table I

Vapor-Liquid Equilibrium of Benzene-Methanol

Run no.	Time min.	Temp. F.	R. I. Condensate	R. I. Residue	Mole Fr. Benzene Condensate	Mole Fr. Benzene Residue
1	20	148	1.3379	1.3322	2.5	1
2	20		1.3468	1.3331		1
3	20	146	1.3588	1.3340	8	2
4	20	143	1.3793	1.3455	15	5
5	20	139	1.4069	1.3672	25	12
6	20	138	1.4163	1.3842	30	18
7	20	137	1.4262	1.4124	36	29
8	20	137	1.4269	1.4288	36	38
9	20	137	1,4308	1.4440	39	48
10	20	137	1.4325	1.4560	40	56
11	20	137	1.4313	1.4649	40	63
12	20	137	1.4344	1.4800	42	76
13	20	138	1.4343	1.4863	42	84
14	20	174	1.4974	1.4993	97	100
15	20	172	1.4937	1.4996	98	99.9
16	20	164	1.4829	1.4991	73	9..9
17	20	162	1.4572	1.4998	56	99.9
18	45	137	1.4308	1.4716	39	68

Table II

Vapor -Liquid Equilibrium of Benzene-Methanol

Run	Time	Temp	R. I.		Mole Fr. Benzene	
No.	min.	F	Condensate	Residue	Condensate	Residue
19	20	137	1.4330	1.4885	43	85.5
20	20	137	1.4304	1.4690	41.5	65.5
21	20	136	1.4295	1.4485	41	51.5
22	20	137	1.4203	1.4206	36.3	36.5
23	20	137	1.4211	1.4000	37	26.3
24	20	137	1.4125	1.3732	34	21

Figure 3
Refractive Index of Benzene-Methanol

Mixture used in runs 1-19

Mixture used in runs 19-24

Refractive Index

Mole Fraction Benzene

Figure 3

Refractive Index of Benzene-Methanol

Mole Fraction Benzene

100 80 60 40 20 0
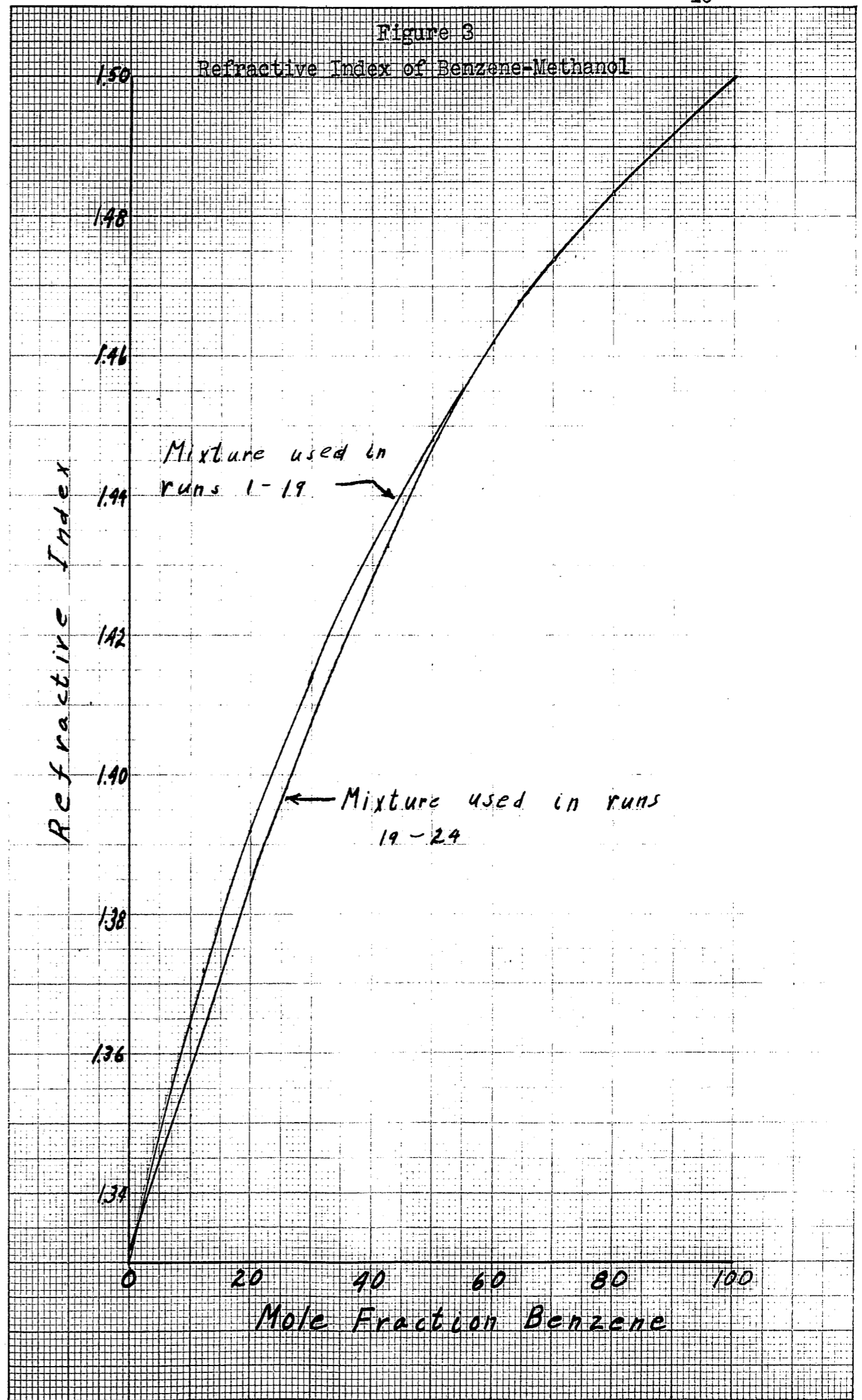
Continuous Extractive Distillation Column

The continuous still is a modification of the type
described by Dicks and Carlson (2). The principle parts
are (see Fig. 4):

    A-condenser and sample cup

    B-solvent circulation system

    C-contacting section, 24 in. long, 5/8 in. diam.,

        packed to a height of 20 in. with pieces of 5 mm

        glass tubing approx. 5/16 in. long

    D-residue trap and withdrawal tube

    E-reservoir, capacity 159 cc

    F-tube between contacting section and reservoir

    G-stripping section, 17 in. long, 5/8 in. diam.,

        packed to a height of 14 in. with pieces of 5mm

        glass tubing approx. 5/16 in. long

    H-tube between reservoir and stripping section

    I-solvent siphon

    J-still and heater

The principle sections of the apparatus are insulated
with approximately one inch of crumpled aluminum foil.
The stripping and contacting sections and the reservoir
are all made of condenser jackets. Use is made of the
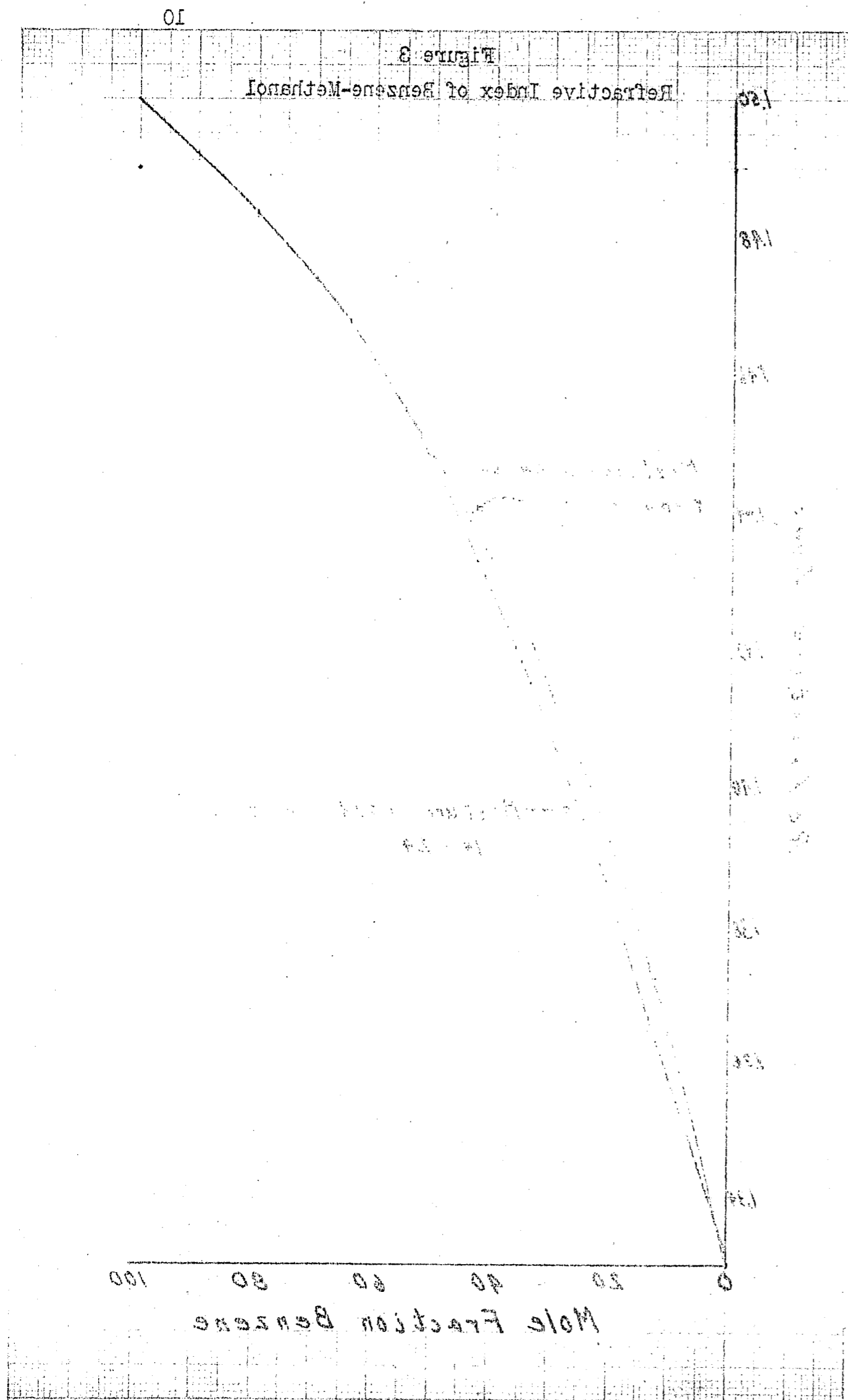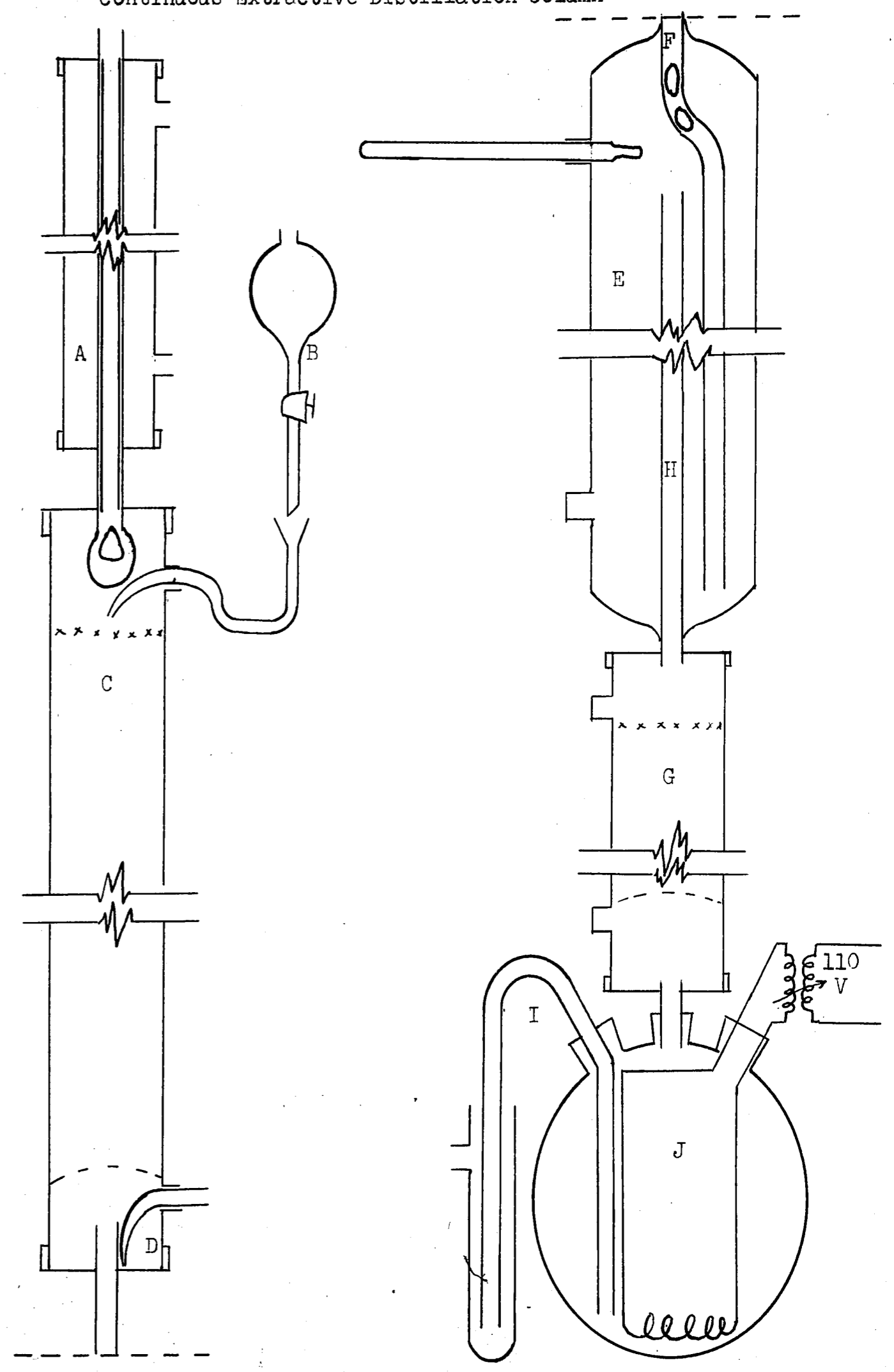water connections on the jackets as shown in Figure 4.

Figure 4

Continuous Extractive Distillation Column

The still is first operated as a conventional distillation column by determining the separation accomplished in the contacting section with no solvent present. The number of plates under these conditions is calculated from the equilibrium diagram of the system and the condensate and residue sample analyses. The still is then operated as an extractive distillation column by circulating solvent down through the contacting section. The number of plates under these conditions is calculated from the equilibrium diagram and the sample analyses on a solvent free basis. A comparison of the number of plates under the two conditions reveals the improvement in separation due to the presence of the solvent.

In operating as a conventional distillation column, the contacting section is connected directly to the still. The mixture is distilled until constant values of the sample analyses indicate that equilibrium has been reached. Since total reflux is used, the number of plates can be calculated from the Fenske equation (5)

$$n = \frac{\log\left(\frac{X'}{X''}\right)_D \left(\frac{X''}{X'}\right)_W}{\log a_{avg.}}$$

where

  $n =$ number of theoretical plates

  $X' =$ concentration of more volatile component in
     liquid

  $X'' =$ concentration of less volatile component in
     liquid

a = relative volatility

subscripts;

    D = distillate

    W = residue

When operating as an extractive distillation column, approximately 300 cc of solvent is placed in the reboiler and heated to boiling. When the solvent vapors reach the top of the stripping section, the reservoir is filled with the desired mixture of solvent and charge which has been heated to just below the boiling point. Circulation of the solvent through the contacting section is then started by opening the stopcock in the solvent storage line and, when liquid starts to overflow from the reservoir into the stripping section, the siphon from the still is filled. Entry of the solvent from the contacting section into the reservoir causes the mixture in the reservoir to overflow into the stripping section. As this mixture descends into the stripping section against the ascending solvent vapors, the charge is stripped from the solvent and passes up through tubes F and K (Fig. 4) into the contacting section. Here the charge is fractionated in the presence of the solvent, all of the vapors passing overhead being condensed and returned as reflux.

This column differs from the one of Dicks and Carlson in that tube F extends all the way to the bottom of the reservoir and has holes near the top to permit the passage of vapors from the stripping section up into the contacting section. In this way, the level of liquid in the reservoir is held constant at the level of the overflow tube and mixing of the contents of the reservoir is provided for by introducing liquid at the bottom and withdrawing it at the top. In the Dicks and Carlson still, the tube connecting the contacting section and the reservoir ended immediately after entering the reservoir. The liquid level in the reservoir was then controlled by a stopcock between the bottom of the reservoir and the top of the stripping section. This method was tried on the present equipment, but it was found that almost perpetual adjustment of the stopcock was required to maintain a constant liquid level. Introduction of this new feature greatly simplified the operation of the still.

Dehydration of Acetic Acid

The equilibrium curve for the system water-acetic acid is decidedly pinched in the region of high water concentration (Fig. 5), making separation into pure components by conventional fractionation impossible on a commercial scale. Most acetic acid manufactured today is separated from water by azeotropic distillation using benzene as the entrainer (6). Since extractive distillation should also facilitate the separation of such a mixture, it was decided to investigate the possibility of separating water from acetic acid by extractive distillation using the equipment described.

Considerable difficulty was encountered in the selection of a solvent, since most organic compounds of sufficiently high boiling point are insoluble in water and many of those that are soluble react with acetic acid. In view of the sucessful use of acetate esters in the azeotropic distillation of acetic acid, it was decided to attempt the use of an ester for this purpose. Glycol diacetate was decided upon since its boiling point (190 C) is sufficiently high to permit separation from acetic acid, and its solubility in water (16.1 g per 100 cc water at 22 C) was thought to be high enough to avoid the complication of a two phase mixture in the column.

Figure 5

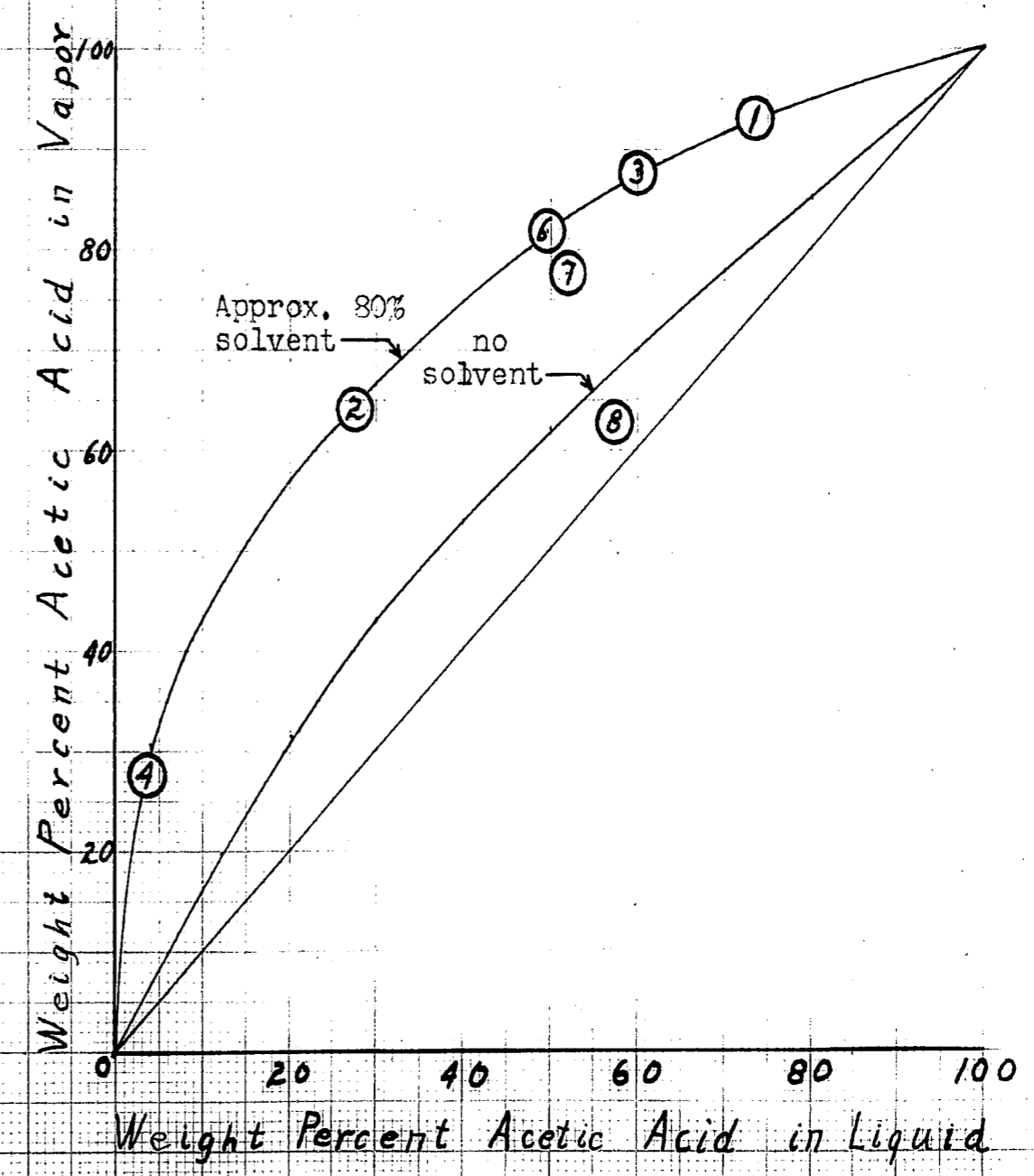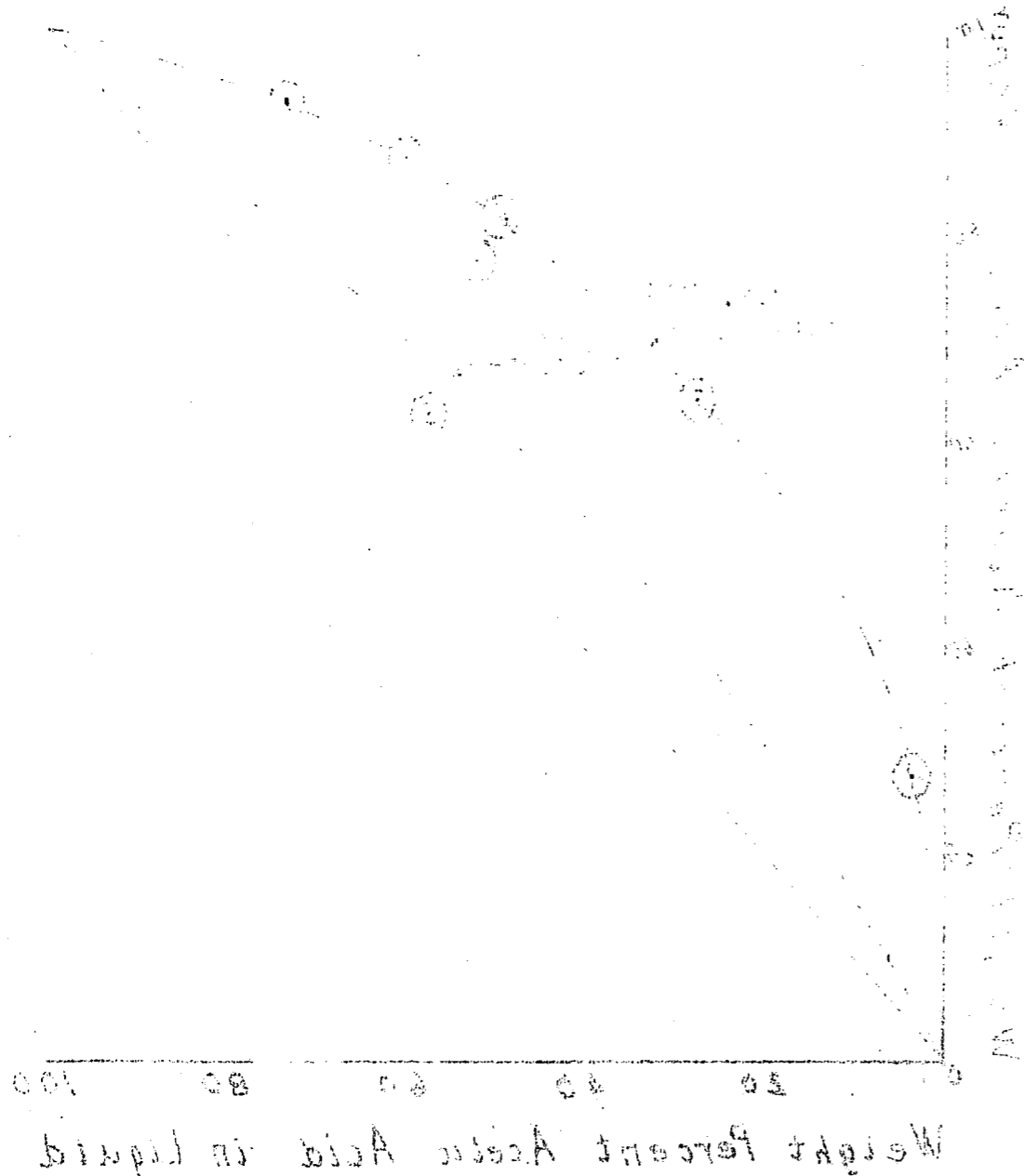Equilibrium Curve for Water-Acetic Acid

Figure 5

Equilibrium Curve for Water-Acetic Acid

Weight Percent Acetic Acid in Liquid

The glycol diacetate used in these experiments was obtained from Carbide and Carbon Company and was found by titration to have negligible residual acidity. Analysis of the ternary mixture water-acetic acid-glycol diacetate was by a combination of titration and refractive index. The refractive indices of mixtures having a constant ratio of water to glycol diacetate were observed after the addition of varying amounts of acetic acid (Table III). The volume percent acetic acid was then plotted against the refractive index with the volume ratio of water to glycol diacetate as parameter, and a similar graph on a weight basis prepared (Fig.6). In operation, the refractive index of the sample is determined and the remaining sample weighed. The sample is then titrated with sodium hydroxide using phenolphthalein as the indicator. The weight percent acetic acid is calculated from the titration and the weight of the sample and the ratio of water to acetate is then found by interpolation on Figure 6. Because of the convergence of the ratio lines at concentrations of acetic acid over 50 percent, analyses in this region would be hazardous. Consequently, when it is suspected that a sample will contain over 50 percent acid, a known quantity of water is added before the refractive index is taken. The true content of the sample can then be found by subtracting the weight of water added from the weight of water found .

Figure 6
Refractive Index of Water-Acetic Acid-
Glycol Diacetate
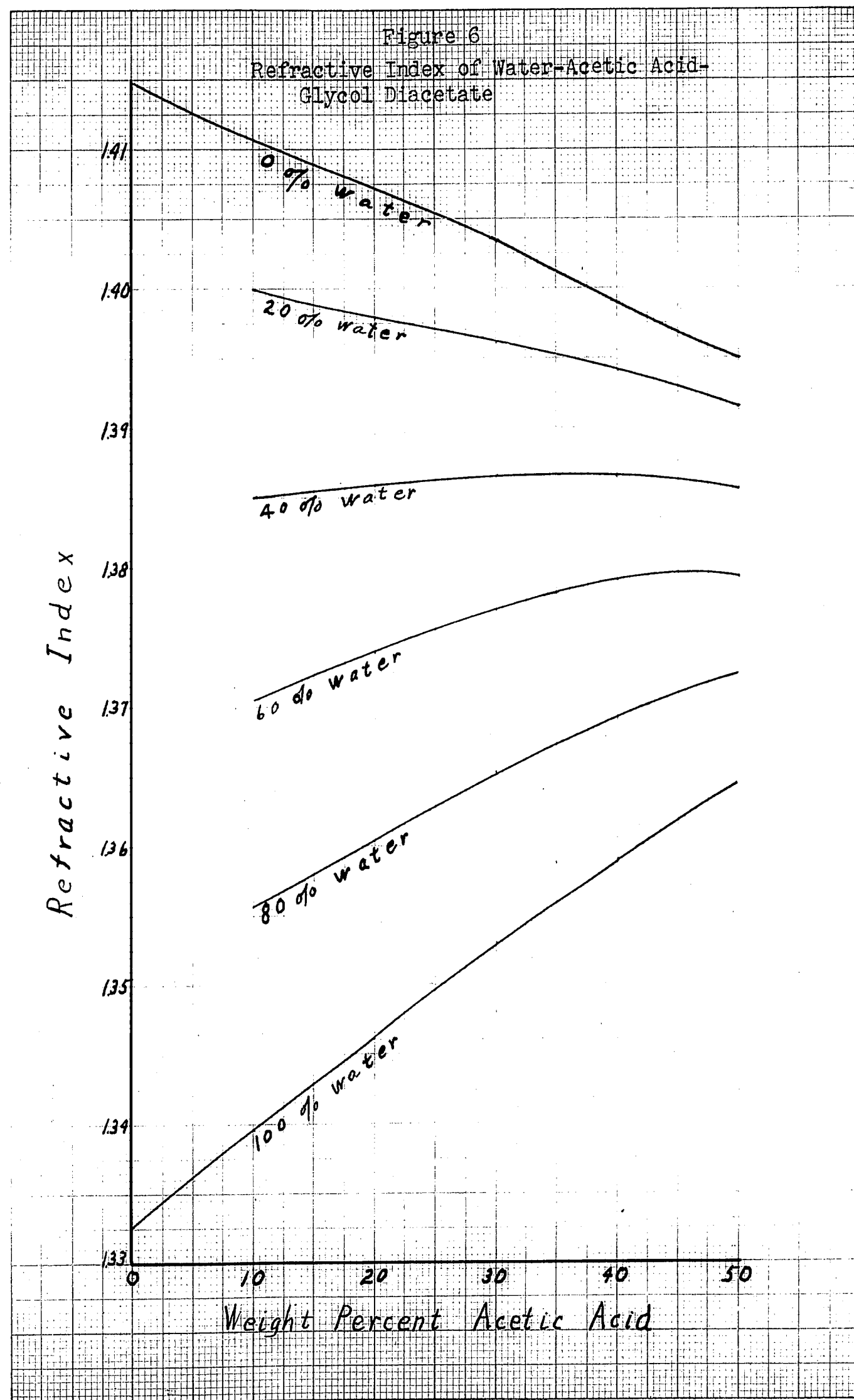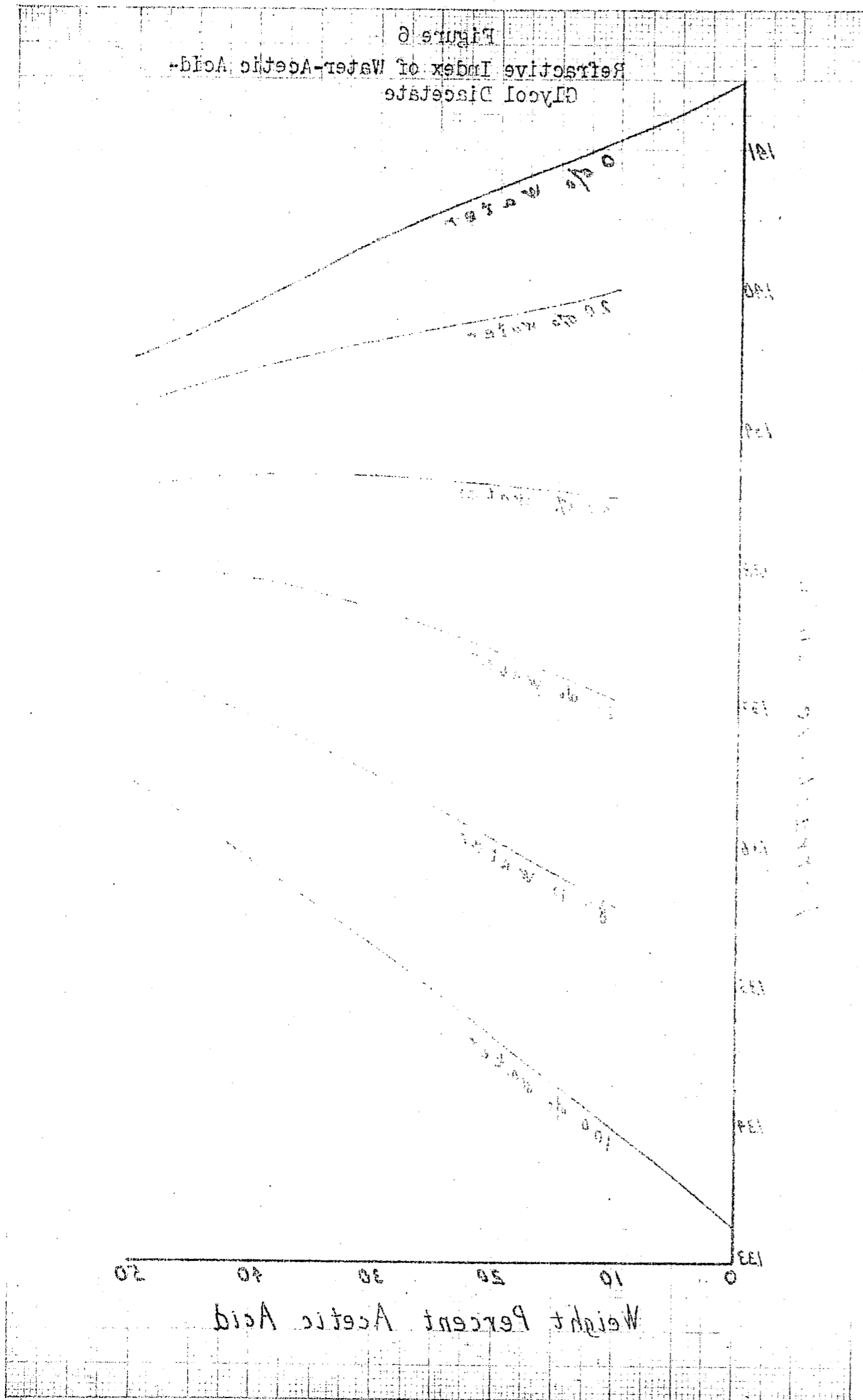
Table III

Refractive Indices of Water-Acetic Acid-Glycol Diacetate

Mixtures

Glycol cc	Water cc	Acetic Acid, cc					
		0	1.1	2.5	4.3	6.7	10.0
0	10	1.3329	1.3400	1.3468	1.3536	1.3595	1.3649
2	8		1.3567	1.3610	1.3652	1.3692	1.3728
4	6		1.3720	1.3746	1.3763	1.3785	1.3796
6	4		1.3861	1.3872	1.3872	1.3870	1.3864
8	2		1.006	1.3988	1.3967	1.3943	1.3919
10	0	1.4149	1.4112	1.4072	1.4030		1.3950

Figure 6

Refractive Index of Water-Acetic Acid-Glycol Diacetate

Weight Percent Acetic Acid

The equilibrium curve of water and acetic acid in the presence of the solvent was determined in the Othmer still. The standard operating procedure for the still was used except that the residue was removed after each run and a fresh charge added. The data obtained is shown in Table IV. The compositions of the condensate and residue samples were determined from this data, but material balances for each component based on these compositions showed considerable errors. The most logical explanation of these errors was that the following reaction took place during the distillation:

$$(CH_3CO_2CH_2)_2 + HOH \rightleftharpoons CH_3COOH + CH_3CO_2CH_2CH_2OH$$
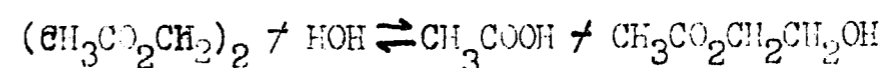
If this were the case, analyses of acetic acid could be made in the usual manner but the accuracy of the analyses of water and solvent would be endangered by the presence of a new component. Both the mono and diacetates are relatively non-volatile in comparison with acetic acid and water, however, so very little of either are contained in the condensate. Therefor, the analysis of the condensate was assumed to be correct and the composition of the residue was calculated by a material balance. Thus, the amount of each component in the residue was assumed to be equal to the difference between the amount charged and the amount withdrawn in the condensate. The compositions arrived at in this manner are shown in Table V. The water-acetic acid equilibrium concentrations were then plotted in Figure 5 on a solvent free basis.

Table IV

Equilibrium Still

System Water-Acetic Acid-Glycol Diacetate

Run no.	1	2	3	4	5	6	7	8
Charge, cc								
acetate	15	15	15	15	15	15	15	15
water	4	2	3.5	.5	.25	3	3	3
acid	1	3	1.5	4.5	4.75	2	2	2
Time, min.	30	40	50	15	15	10	40	180
Temp., F	215	223	220	243	250	217	213	227
Condensate								
R. I.	1.3510	1.3652	1.3523	1.3820	1.3810	1.3598	1.3625	1.3753
weight	1.631	1.855	1.793	1.773	1.832	1.880	1.836	2.069
titration*	13.2	96.3	31.5	172.4	203.6	45.8	54.0	93.7
Residue								
R. I.	1.4070	1.4090	1.4020	1.4083	1.4070	1.4089	1.4089	1.4106
weight	1.825	1.966	2.237	2.259	1.073	1.820	1.800	1.655
titration*	17.6	45.6	33.2	67.0	32.8	29.1	29.0	24.3

*titration, cc of 0.0984 N NaOH

Table V

### Compositions of Equilibrium Mixtures of Water-Acetic Acid-Glycol Diacetate (Weight Percent)

Run no.	1	2	3	4	5	6	7	8
Charge								
% acetate	75	75	75	75	75	75	75	75
% water	20	10	17.5	2.5	1.25	15	15	15
% acid	5	15	7.5	22.5	23.3	10	10	10
Residue								
% acetate	81.2	81.6	81.8	80.4		81.4	81.2	80.9
% water	13.8	5	11	.62		9.1	7.7	10.9
% acid	5	13.3	7.2	19		9.5	9.2	8.1
Condensate								
% acetate	16.2	13.9	12.6	21.3	15.2	19.7	20.6	23.6
% water	79.2	55.5	77	21.2	13.6	65.9	62	44.6
% acid	4.6	30.6	10.4	57.5	66.2	14.4	17.4	26.8

A study of Figure 5 shows that the presence of
glycol diacetate greatly facilitates the separation of
acetic acid-water mixtures. The hydrolysis reaction,
however, introduces an element of uncertainty into the
picture which requires a study of the influence of the
r action on the separation. The position of equilibrium
in the hydrolysis reaction was determined from an acetic
acid balance by plotting the percent acetic acid in the
charge (on a solvent free basis) against the ratio of the
acetic acid present after distillation to the weight of
acetic acid in the charge(Table VI and Fig. 7). It is
seen in Fig. 7 that, with a charge containing less than
65 percent acetic acid, more acid is present after
distillation than before, indicating that, since the acid
is one of the products of hydrolysis, hydrolysis has
taken place. When the charge contains more than 65 percent
acetic acid, less acid is present after distillation,
indicating that esterification has occured. This also
indicates that some glycol monoacetate was present in the
solvent.

The influence of the time of distillation on
the reaction was determined in runs 6, 7, and 8. In these
runs, all using the same charge, distillation was continued
for 10, 40, and 180 minutes respectively. It is seen in
Figure 7 that this results in a steady increase in the
amount of acetic acid present in the system. The influence
of the distillation time on the equilibrium curve is seen
in Figure 5, where the points approach the 45 degree line

Figure 7

Change in Acetic Acid Content of Mixture
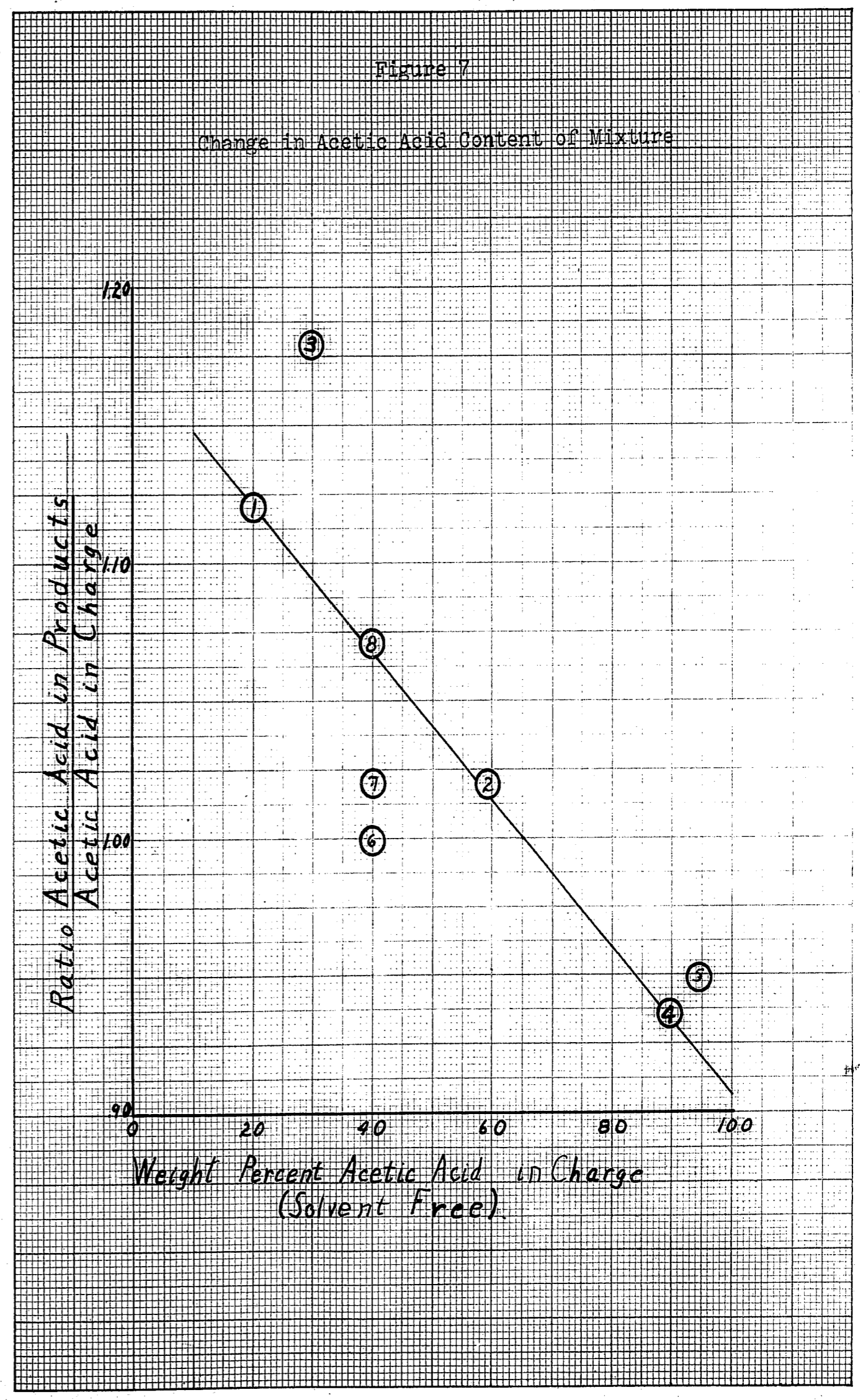
Figure 7.

Change in Acetic Acid Content of Mixture
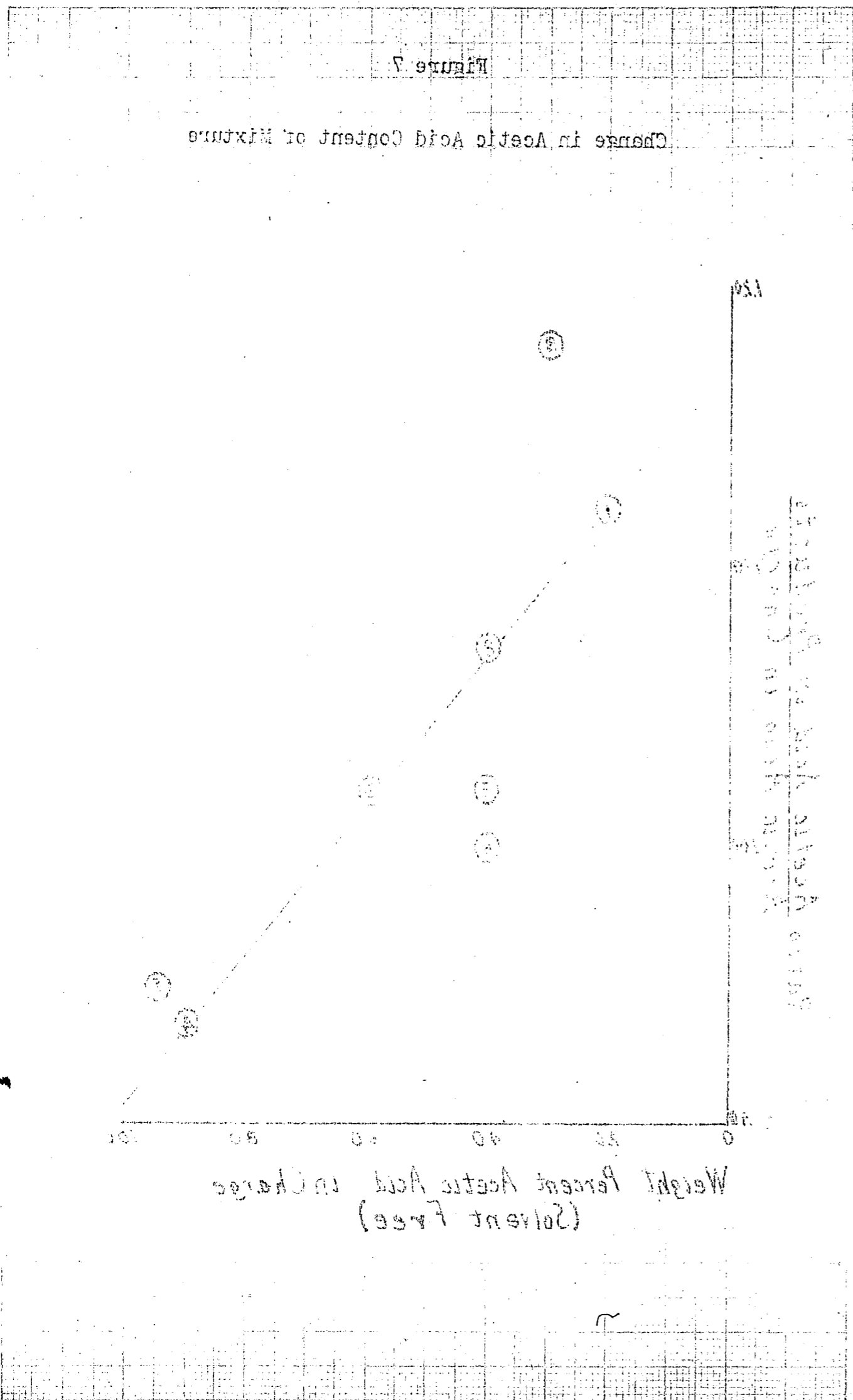
Table VI

Acetic Acid Balance

Run no.	1	2	3	4	5	6	7	8
Grams of acetic acid in;								
charge	1.05	3.14	1.57	4.72	4.99	2.10	2.10	2.10
residue	1.10	2.64	1.66	3.40	3.52	1.33	1.83	1.69
condensate	.08	.57	.19	1.02	1.21	.27	.32	.56
residue plus condensate	1.18	3.21	1.85	4.42	4.73	2.10	2.15	2.25
$\dfrac{\text{Residue condensate}}{\text{Charge}}$	1.12	1.02	1.18	.94	.95	1.0	1.02	1.07

with increasing time. In fact, the equilibrium point for
run 8 lies below the equilibrium curve for the system
with no solvent present. This is easily understood,
since the diacetate originally present is chemically
similar to the acid and therefore increases the volatility
of the water. The monoacetate, howev.r, has a strong
affinity for water because of its one hydroxy group and
consequently decreases the volatility of the water.
As the concentration of the monoacetate increases, the
effectiveness of the solvent in enhancing the separation
decreases to a point where it actually retards the
separ tion.

Two separate attempts were made to run the system
water-acetic acid-glycol diacetate in the continuous
extractive distillation column. The charge to the
reservoir in both cases consisted of 60 percent solvent,
24 percent water, and 16 percent acid. In the first
attempt, the solvent was introduced at room temperature
at the top of the contacting section. Solvent circulation
and vigorous boiling were continued for five hours, but
at the end of that time the vapors had ascended only one
quarter of the way up the contacting section. In the
second attempt, the solvent was introduced at
approximately 100 C and boiling continued for six hours.
The solvent rate was increased almost to the point of

flooding the stripping section. Nevertheless, the vapors
rose only half way up the contacting section. This
clearly illustrates the need for reducing the heat
losses from the column, prefferably by electric heating
coils or vapor jackets.

Theory of Extractive Distillation

The purpose of extractive distillation is to
make possible the separation of mixtures having nearly
equal relative volatilities or, in the extreme, mixtures
which form azeotropes. Before proceeding to the theory
involved, it would be advisable to investigate the factors
which cause mixtures of this kind. Two equations directly
involved are:

$$a_{12} = \frac{y_1 x_2}{y_2 x_1} \tag{2}$$

and

$$a_{12} = \frac{\gamma_1 P_1}{\gamma_2 P_2}$$

where

a_{12} = relative volatility

y = composition of the vapor

x = composition of the liquid

P = partial pressure

γ = activity coefficient

subscripts refer to components.

It is seen from equation 3 that a low value of the
relative volatility will result from nearly equal values
of the activity coefficients and partial pressures for
both components, or from the ratio of the activity
coefficients being nearly equal to the inverse of the ratio
of the partial pressures. The first case is

exemplified by ideal solutions (activity coefficients
near one for both components at all concentrations) both
components of which have nearly equal vapor pressures.
Examples of the second case are nonideal solutions in
which the ratios of the activity coefficients varies
considerably while the ratio of the partial pressures
remains nearly constant. An azeotrope is the extreme
example of this case, the ratio of the activity
coefficients being equal to the inverse of the ratio of
the partial pressures at one composition.

In mixtures of the second type, it has been found
that the addition of appreciable amounts of a dissimilar
material causes a marked alteration in the activity
coefficients of the original components. If the added
component, 3, is more similar to component 2 than to 1,
the ratio γ_1/γ_2 will increase. Considering component 1
to be the more volatile of the original two, it is seen
from equation 3 that the highest relative volatility will
result from the activity coefficient of 1 being increased
and that of 2 decreased. Consequently, it is advantageous
to select a third component which is more similar
chemically to the least volatile component of the mixture
being separated. Inasmuch as the solvent must be present
as a liquid during fractionation but must be easily
separated afterwards, it should boil considerably higher
than either component of the original mixture and should
form no azeotrope.

Since extractive distillation always involves at least
three components and analyses of such mixtures is difficult,
considerable attention has been paid to methods of
predicting the equilibrium relationships of three component
mixtures from those of the three two component mixtures
involved. In the procedures developed by Van Laar (2),
Margules (11), and White (9), the activity coefficient of
one component of a binary mixture is related to the
composition of the mixture by equations involving constants
which can be determined experimentally. Reddich and
Kister (9) have developed an equation for the ratio of the
activity coefficients of the two components which is very
convenient since multipication of this ratio by the ratio
of the partial pressures gives the relative volatility
directly. All of these equations can be expanded to
include ternary mixtures, though in some cases (8,1)
additional constants must be determined from the three
component mixture. The equations of Reddich and Kister
and of White, however, require no additional constants
and are much more convenient to use. It is also possible
to determine the activity coefficients in a ternary mixture
by a special method of plotting the activity coefficients
of the binary mixtures (3). This reference also describes
a very convenient method of estimating the Van Laar
constants from data on mutual solubilities. Such a
procedure is useful when considering a large number of
solvents for a given separation.

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