1936

Vapor-liquid equilibrium data and other physical properties of the ternary system ethanol, glycerine, and water

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Recommended Citation

UNIVERSITY OF LOUISVILLE

VAPOR-LIQUID EQUILIBRIUM DATA AND
OTHER PHYSICAL PROPERTIES OF THE TERNARY SYSTEM
ETHANOL, GLYCERINE, AND WATER

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

In Chemical Engineering

Department of Chemical Engineering

By

CHARLES H. WATKINS

1936

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ACKNOWLEDGEMENT

The author wishes to express his ap-
preciation for the helpful suggestions
rendered by Dr. Robert C. Ernst, who
directed this research.

CHAPTER I

INTRODUCTION

INTRODUCTION

The purpose of this investigation is to obtain vapor-liquid equlibrium data and to determine specific heats, boiling points, latent heats, and vapor pressures for the ternary system-ethanol, glycerine, and water. In a previous investigation (1) densities, viscosities, surface tensions, and refractive indicies were reported. The Data of these two investigations are to be used in the study of distillation of this ternary mixture in a semi-commercial eight plate fractionating column.

Neiman (2) investigated the system, butanol, acetone, and water for vapor-liquid equilibrium data and concluded that these pure materials can be separated by: 1. distilling in a fracti ning column giving almost pure acetone, 2. separating the butanol from the water because of their immiscibility and, 3. purification of the materials by further fractionation. It is hoped that some similar correlation can be made for the system--ethanol, glycerine and water.

Brunjes and Furnas (8) prepared vapor-liquid equilibrium diagrams of two binary mixtures of commercially important organic solvents: n-butanol-n-butyl acetate and n-butanol-acetone. The Othmer apparatus was used in obtaining the data, and it was found that n-butanol-n-butyl

acetate formed an azeotropic mixture at 72.9 mole %
alcohol, boiling at 116.5°C, at 760 mm. Mercury: however,
the system n-butanol-acetone formed no azeotropic mixture.

Ernst, Litkenhous, and Spanyer determined the boil-
ing points, and other physical properties, of the system-
n-butanol, acetone and water using a modification of the
Cottrel Apparatus (10). All boiling points were found to
be intermediate between those of the pure substances.

The determination of vapor-liquid equilibrium data,
specific heats, latent heats, boiling points, and vapor
pressures was undertaken in this investigation and these
properties are reported herein, both graphically and in
table form.

CHAPTER II

THEORETICAL

THEORETICAL

The determination of the physical properties undertaken in this investigation include those necessary and directly used in the study of distillation on a commercial scale. These properties are all heat functions. In commercial distillation, the liquid feed to be distilled is usually in storage at room temperature. On leaving storage the feed is passed through preheaters where its temperature is raised to the boiling point. Immediately after entering the still at its boiling point, the feed is vaporized and the vapors are continuously condensed and vaporized on each plate in the column. The vapors from the top plate are condensed and caught in the receiver.

When the feed is passed through the preheater, heat is added to it, which raises the temperature and increases the vapor pressure. When the Vapor pressure is raised to the pressure of the surroundings, the boiling point of the liquid is reached. At this temperature latent heat must be added to vaporize the liquid. When the liquid is vaporized, its composition can be obtained from vapor-liquid composition data. In this way, the properties determined are applied to the study of distillation. For instance, latent heats and specific heats are used in calculating the steam consumption. Boiling points indicate the steam temperature

and pressure to be used. From the vapor-liquid equilibrium data, can be calculated the result at any stage of distillation.

According to the kinetic theory there is a continuous flight of particles of vapor from the surface of a liquid into the free space above it. Simultaneous to this emmission of vapor particles, there is a reverse process of condensation at the surface of the liquid. If this system of vapor and liquid is in a closed vessel, there will exist a definite equilibrium between the liquid and its vapor when the rate of emmission is exactly equal to the rate of condensation. The pressure exerted by the vapor in equilibrium with the liquid phase at a certain temperature is the vapor pressure of the liquid at that temperature. This equilibrium is dependent upon the temperature. For every temperature, then, there is a definite equilibrium pressure, and conversely, for every pressure there exists a definite temperature at which vapor and liquid are in equilibrium with each other. The temperature corresponding to the equilibrium pressure of 760 mm. of mercury is the boiling point of the liquid. The vapor pressure of a liquid is a constant at a definite temperature, and is entirely independent of the amounts of liquid and vapor present: however, it increases as the temperature is increased. Fig. I shows the vapor

pressure of ethanol, glycerine, and water at various temperatures.

To increase the temperature of a liquid, energy is supplied in the form of heat and is called specific heat. Specific heat may be defined as the amount of heat necessary to raise a unit quantity of substance a unit change in temperature, or to be specific, it may be defined as the number of calories necessary to raise one gram of the liquid one degree centigrade.

In order to transform a liquid into a vapor, energy is required to overcome intermolecular attraction of the molecules and also to increase the volume of the fluid against atmospheric pressure. This energy is supplied in the form of heat and is called latent heat of vaporization and may be defined as the number of calories of heat necessary to convert one gram of a liquid at its boiling point into vapor at the same temperature. The liquid referred to in this discussion may be a single substance or a mixture of two, three, or four liquids.

A useful relation between vapor pressure, temperature, and heat of vaporization was developed by Clapeyron (7). It may be developed in an approximate manner with the help of a single thermodynamical cycle similar to Carnot's.

FIG. 1
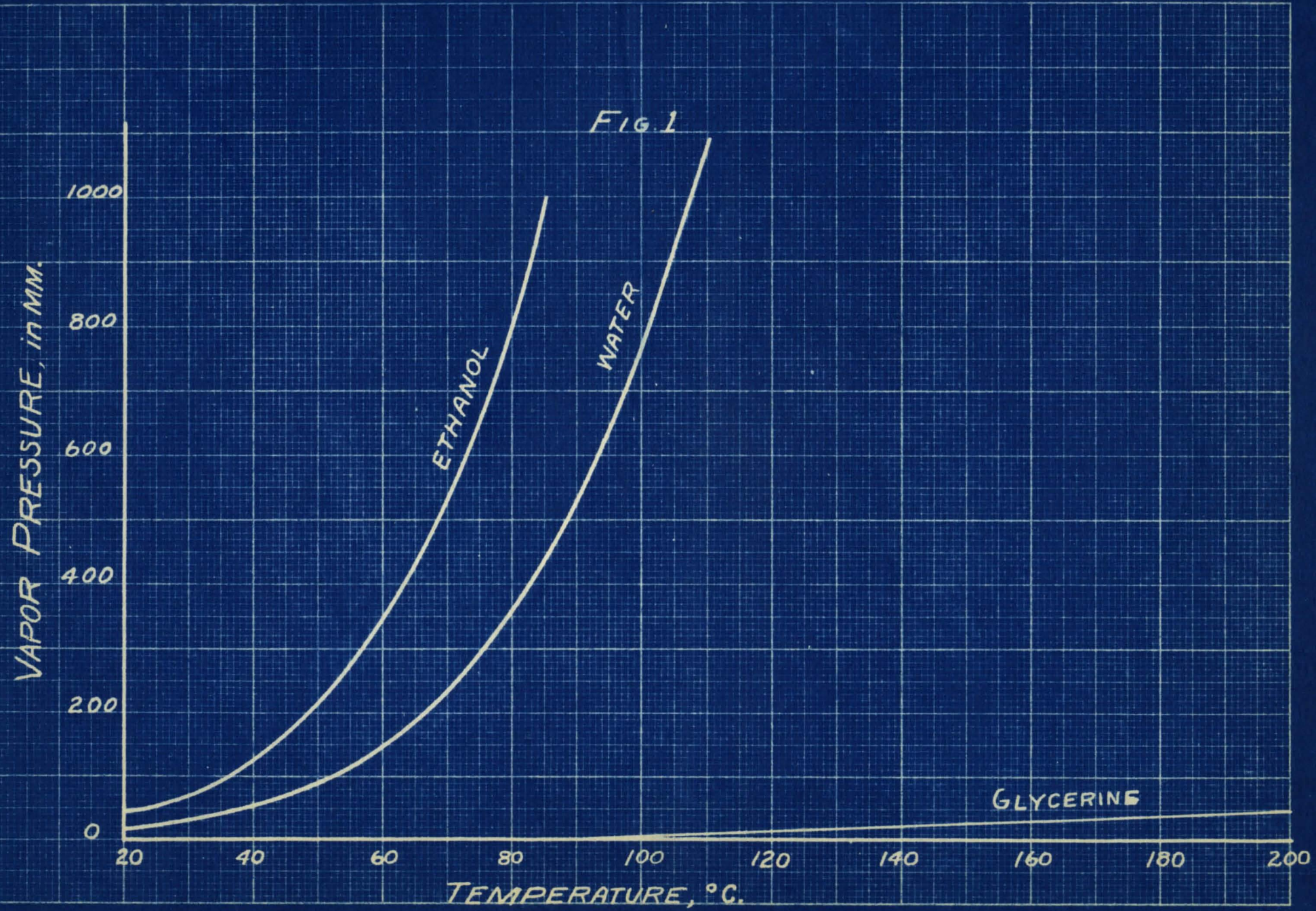
Applying Carnot's cycle and the second law of thermodynamics, the differential form of the equation may be written:

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \cdot \qquad (1)$$

which is known as the Clapeyron equation.

Where L = latent heat of vaporization.

        T = absolute temperature.

        V_2 = volume fluid in gaseous state.

        V_1 = volume of liquid

        $\frac{dp}{dT}$ = derivative of the pressure with respect to the temperature.

Clausius showed how the Clapeyron equation may be simplified by assuming that the vapor obeys the ideal gas law. Clausius changed from the basis of one gram to the basis of one mole. Neglecting V_1 which is small compared to V_2 and substituting RT/p for V_2 (according to the ideal gas law). He obtained:

$$\frac{dp}{dT} = \frac{Lp}{RT^2} \qquad (2)$$

On separating the variables and integrating on the basis L and R are constants.

$$\log_e p = \frac{-L}{RT} + C \qquad (3)$$

where C is the constant of integration. This equation is linear in $\log_e P$ and $1/T$, and when these quantities are plotted a straight line results, the slope of which is $-L/R$. Using this fact the vapor pressures determined in this investigation are shown graphically in Figures 10, 11, and 12 with log p plotted against $1/T$.

If equation (2) is integrated between the limits of P_2, P_1 and T_2, T_1, the following equation results:

$$\log_e \frac{P2}{P1} = \frac{-L}{R} \div \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{4}$$

Where P_2 is the vapor pressure at T_2 and P_1 is the vapor pressure at T_1. Solving equation (4) for L,

$$L = 2.303R \log_{10} \frac{P_2}{P_1} \div \left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{5}$$

Where L is the latent heat in calories per mole. Equation (5) is used in this investigation for calculating latent heats as described in Chapter IV.

CHAPTER III

APPARATUS and PROCEDURE

APPARATUS AND PROCEDURE

Specific heats (6) were determined by intro-
ducing a measured quantity of electricity into the
sample and recording the temperature rise. A portable
watt second meter and a thermometer with one-tenth de-
gree graduations were used to determine these values.
A carbon resistor was used as a heating element. This
apparatus was inclosed in a silver plated glass tube
surrounded by an evacuated jacket, a sketch of which is
shown in Fig. 2.

VAPOR LIQUID EQUILIBRIUM. A modification of the
Othmer Apparatus (7) was used to obtain the vapor-
liquid equilibrium data. The apparatus (Fig. 3) con-
sists of a still, a condenser, a receiver, and an over-
flow or r flux connection. The sample is placed in the
still body from which it is vaporized. The condensed
vapors fall from the condenser into the receiver. When
the latter is filled, the liquid is refluxed to the
still body and the cycle is repeated. As the liquid
falls from the condenser, it is fed to the bottom of the
receiver: this operation insures thorough mixing and
equilibrium conditions. The temperature rises at the
beginning of the run until the receiver is filled.
After refluxing begins, little change in temperature

14

TO MOTOR

TO WATT SEC. METER

A   B   C
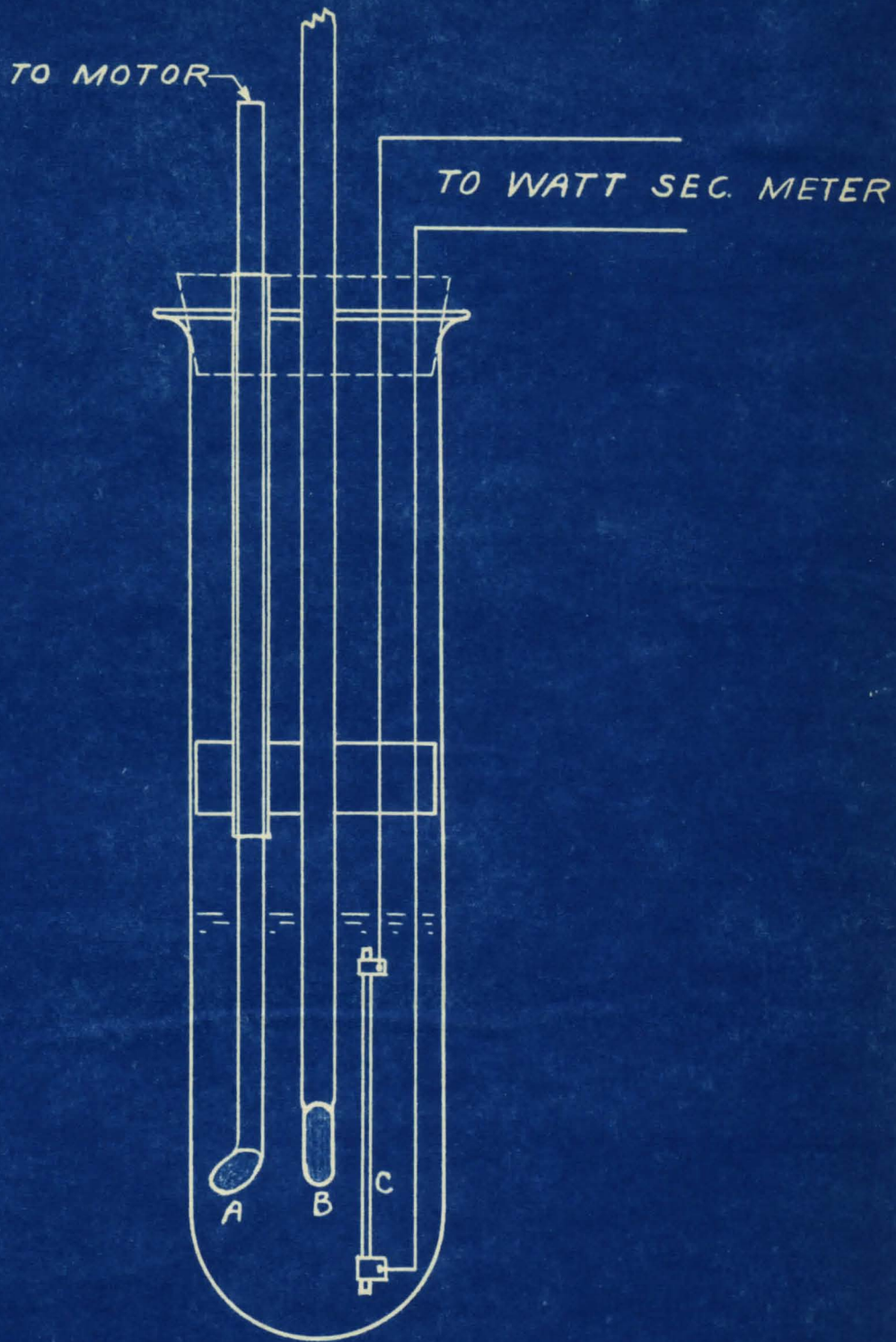
FIG. 2

SPECIFIC HEAT APPARATUS
A. STIRING ROD, B. THERMOMETER,
C. CARBON HEATING ELEMENT.

C.H.W.
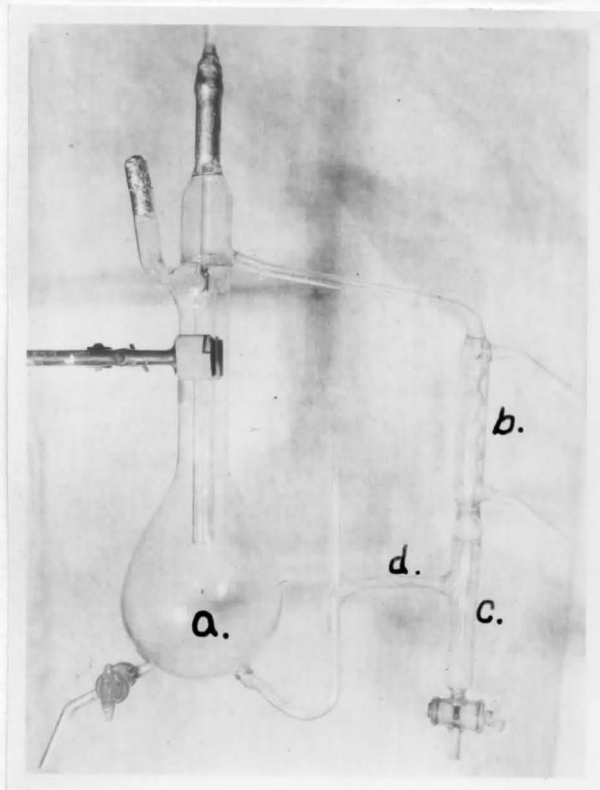
Fig. 3

OTHMER APPARATUS

a. Still body, b. Condenser,

c. Receiver, and d. Reflux

overflow.

is noted. After two hours of constant temperature
operation, in which time the liquid in the receiver
is changed eight to ten times, the liquid and vapor
samples are taken. The pressure was maintained at
760 mm. mercury throughout the run. The composition
of the samples was found by determining the refractive
index and density. The data from a previous in-
vestigation (1) were used in preparing Fig. 4. The inter-
section of the constant density line and constant refrac-
tive index line locates a point on the triangular diagram
which represents the composition of the sample. Thus
point A represents a sample having a refractive index of
1.3900 and a density of 1.0200. Its composition is 40.0%
water, 33.5% glycerol, and 26.5% ethanol.

The thermometer used was a 0-200°C. thermometer,
calibrated by the Bureau of Standards (No. 58330).
The densities of the vapor and liquid samples were
determined using a Westphal balance. An Abbe refract-
ometer (5) was used to obtain the refractive index.
These properties were run at 25°C. using a constant tem-
perature bath as described in a previous dissertation(1).
VAPOR PRESSURE AND BOILING POINT. Fig. 5 is a diagram
of a modification of the Cottrell apparatus (10). Boil-
ing points and vapor pressures were determined in this
apparatus. The sample is admitted into the tube at A

FIG. 4

GLYCERINE

WATER

ETHANOL

TO CONDENSER, B

TO PUMP

S

M

R
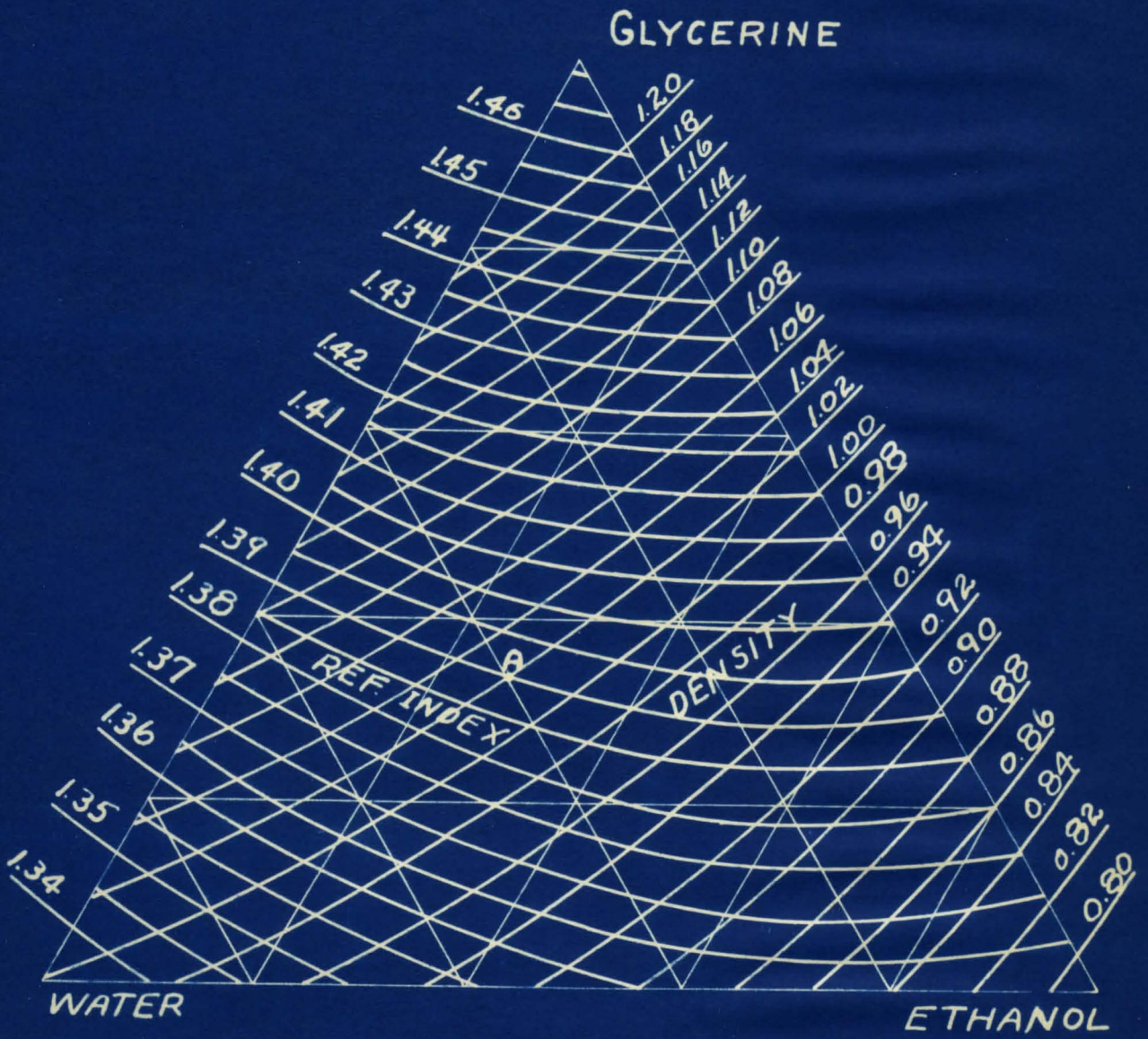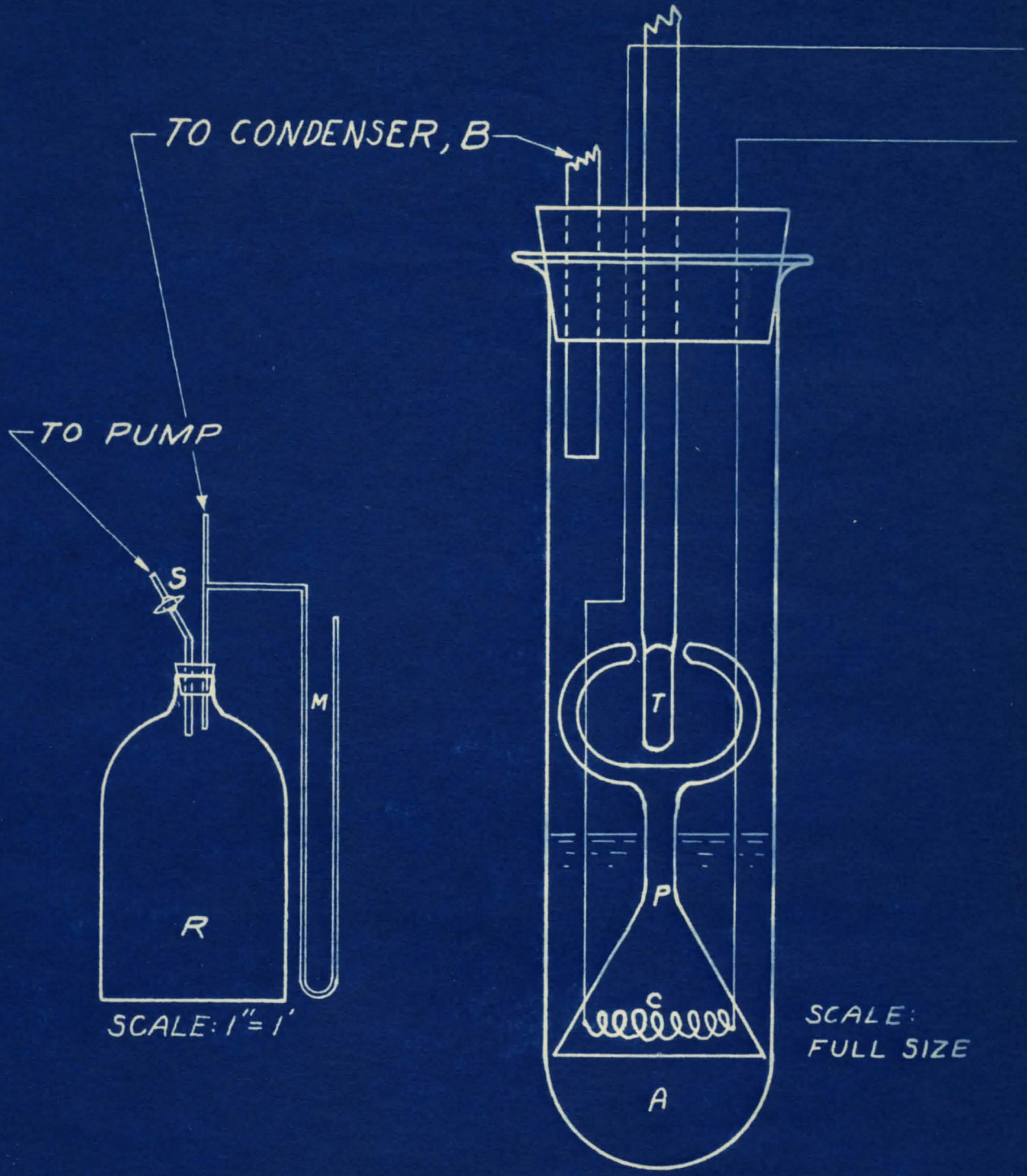
SCALE: 1"= 1'

SCALE:
FULL SIZE

T

P

C

A

FIG. 5

BOILING POINT APPARATUS
T, THERMOMETER BULB, P, PER-
COLATOR, C, HEATING COIL, A,
LIQUID SPACE, M, MANOMETER,
R, PRESSURE REGULATOR

and the heating element. c, heats the liquid to boiling.
As the liquid boils it rises through the percolator, p,
and is forced continuously upon the thermometer bulb, t.
Any vapors that escape are condensed at B and returned
to the system A, and the cycle is repeated. The pres-
sure on the system was kept constant with the use of the
receiver and manometer, shown in diagram.

To determine vapor pressure the stopcock, a,
was opened to the suction, and the pressure on the sys-
tem was reduced to 150 mm. mercury absolute. The heat-
ing coil was turned on; and after continuous percolation
and constant temperature and pressure were maintained,
readings were taken. The pressure, calculated by sub-
tracting the difference in levels of the mercury
in the manometer columns from the barometer reading,
and the temperature, recorded by the thermometer, re-
present a point on a vapor pressure curve. The pres-
sure is now changed by opening stopcock s and another
such reading is taken. When the pressure is 760 mm.
mercury, the temperature recorded is the boiling point.
Thus, with this apparatus, both boiling points and vapor
pressures were determined. The thermometer used was
calibrated by comparison with a Bureau of Stand-
ards' thermometer. A mercury barometer was used. Latent

heats were calculated from the vapor pressure data
using the Clausius-Clapeyron equation as discussed
in Chapter II.

CHAPTER IV.

EXPERIMENTAL

EXPERIMENTAL

MATERIALS: Ethyl alcohol of the C. P. grade was treat-
ed with metallic calcium and metallic sodium, then dis-
tilled repeatedly.

Chemically pure glycerine was distilled repeatedly
under reduced pressure until a density determination using
a calibrated pycnometer showed the absence of water.

Distilled water was treated with potassium perman-
ganate to remove any oxidants and then distilled. Treat-
ment with barium hydroxide and successive distillations
followed. The physical properties of the resulting mater-
ials and values given by other experimenters are shown in
Table I.

PREPARATION OF SAMPLES. The Samples were prepared on a
weight percent basis in increments of ten per cent. The
correct amount of glycerine was added to a ground glass
stoppered flask and the correct weight of ethanol and
water added by means of burettes (number of C.C. were cal-
culated from density determination). The compositions of
the resulting sixty-six Samples are shown in Table II.

Specific heats, boiling points, latent heats and va-
por pressures were determined for the sixty-six Samples.
Both binoidal and triangular diagrams have been prepared
for the first two mentioned properties. Specific Heats,
boiling points, and latent heats for the system are given
in Table III.

TABLE I

PHYSICAL CONSTANTS OF PURIFIED MATERIALS

	Density	Viscosity	Surface Tension	Refractive Index	Specific Heat	Boiling Point
Ethanol	0.7851 * 0.78506(22) 0.78510(23)	1.10 * 1.101(19)	22.0 * 22.03(13)	1.3596 * 1.35941(15)	0.536 * 0.54 (16)	78.3 * 78.4(27) 78.3(29)
Glycerine	1.2580 * 1.2580(26) 1.25802(11)	934 * 945(24)	62.5 * 63.0(14)	1.4729 * 1.4730(4)	0.555 * 0.541(25) 0.589(25)	289 *— 290*(28)
Water	0.99707' 0.99707(18) 0.99707(12)	0.893' 0.894(17) 0.893(20)	72.0' 72.0(16) 71.86(30)	1.3332 * 1.3325(21) 1.3333(9)	1.00'	1.00'

* Author's experimental values.
' Values accepted for calibration of instruments.
— Glycerine decomposes slowly at 200°C. and above.

TABLE II

COMPOSITION OF SAMPLES

Sample No.	Wt. Pct. Glycerol	Wt. Pct. Ethanol	Wt. Pct. Water
1		100	
2	100		
3			100
4		10	90
5		20	80
6		30	70
7		40	60
8		50	50
9		60	40
10		70	30
11		80	20
12		90	10
13	90		10
14	80		20
15	70		30
16	60		40
17	50		50
18	40		60
19	30		70
20	20		80
21	10		90
22	10	90	

TABLE II Cont'd.

COMPOSITION OF SAMPLES

Sample No.	Wt. Pct. Glycerol	Wt. Pct. Ethanol	Wt. Pct. Water
23	20	80	
24	30	70	
25	40	60	
26	50	50	
27	60	40	
28	70	30	
29	80	20	
30	90	10	
31	80	10	10
32	70	10	20
33	60	10	30
34	50	10	40
35	40	10	50
36	30	10	60
37	20	10	70
38	10	10	80
39	70	20	10
40	60	20	20
41	50	20	30
42	40	20	40
43	30	20	50
44	20	20	60

TABLE II Cont'd.

COMPOSITION OF SAMPLES

Sample No.	Wt. Pct. Glycerol	Wt. Pct. Ethanol	Wt. Pct. Water
45	10	20	70
46	60	30	10
47	50	30	20
48	40	30	30
49	30	30	40
50	20	30	50
51	10	30	60
52	50	40	10
53	40	40	20
54	30	40	30
55	20	40	40
56	10	40	50
57	40	50	10
58	30	50	20
59	20	50	30
60	10	50	40
61	30	60	10
62	20	60	20
63	10	60	30
64	20	70	10
65	10	70	20
66	10	80	10

Table III

Physical Properties

Sample No.	Specific Heat	Boiling Point °C.	Latent Heat Cal./Mol
1.	0.537	78.3	9,736
2.	0.555	239.0	17,740
3.	1.00	100.0	9,074
4.	1.036	91.7	9,920
5.	1.040	87.3	10,150
6.	0.995	84.7	10,150
7.	0.964	83.2	9,830
8.	0.915	81.8	9,830
9.	0.859	80.3	9,920
10.	0.784	80.1	9,742
11.	0.700	79.2	9,736
12.	0.618	78.4	10,392
13.	0.579	142.0	10,057
14.	0.610	121.1	10,011
15.	0.665	113.5	9,965
16.	0.715	109.9	9,920
17.	0.770	106.1	9,920
18.	0.810	104.0	9,220
19.	0.870	103.0	9,920
20.	0.930	101.3	9,920
21.	0.967	101.0	9,830
22.	0.550	79.3	9,742

Table III (Continued)

Sample No.	Specific Heat	Boiling Point °C.	Latent Heat Cal./Mol
23.	0.550	80.5	9,656
24.	0.549	81.7	9,656
25.	0.548	82.9	9,656
26.	0.550	84.6	9,4??
27.	0.549	86.2	9,366
28.	0.549	89.3	9,247
29.	0.551	97.0	9,169
30.	0.552	113.4	9,093
31.	0.5?1	103.4	9,656
32.	0.622	97.3	9,614
33.	0.675	94.7	9,530
34.	0.741	93.4	9,?30
35.	0.790	92.5	9,742
36.	0.856	92.1	9,?75
37.	0.921	91.3	9,875
38.	0.966	91.6	9,488
39.	0.538	90.6	9,530
40.	0.635	83.6	9,920
41.	0.631	87.5	9,?30
42.	0.735	87.1	9,656
43.	0.810	87.0	9,656
44.	0.835	87.0	9,920

Table III (Continued)

Sample No.	Specific Heat	Boiling Point °C.	Latent Heat Cal./Mol
45.	0.953	87.1	9,742
46.	0.591	86.3	9,706
47.	0.644	85.1	9,786
48.	0.690	84.5	9,330
49.	0.754	84.3	9,614
50.	0.831	84.3	9,614
51.	0.910	84.5	9,614
52.	0.592	84.1	9,614
53.	0.642	83.4	9,656
54.	0.702	83.0	9,330
55.	0.775	82.8	9,614
56.	0.860	82.8	9,330
57.	0.591	82.6	9,699
58.	0.648	82.0	9,330
59.	0.720	81.8	9,330
60.	0.809	81.7	9,330
61.	0.592	81.5	9,920
62.	0.660	80.8	9,920
63.	0.741	80.8	9,920
64.	0.610	80.4	9,920
65.	0.677	80.2	9,920
66.	0.616	79.4	9,920

SPECIFIC HEATS

The apparatus used in determining specific heats is shown in Fig. 2. Experimentally, the values of Δt, w, and g are obtained, where

Δt = temperature rise of sample, $^{\circ}$C.

w = watt second = $1/4.186$ gram calories and

g = grams of sample used.

Specific Heats are calculated from the experimental data by means of the equation:

$$\frac{\frac{w}{4.186} - K\Delta t}{g\Delta t} = \text{sp. ht. in Cal. per gram per } ^{\circ}\text{C.}$$

Where K is the calorimeter constant (7.42) and 4.186 electrical equivalent of heat. $\Delta t \cdot K$ represents amount of heat lost to apparatus.

SAMPLE CALCULATION: Values given are those obtained for Sample No. 47:

Δt = 6.00 $^{\circ}$C

$w/4.186$ = 143.0 gram calories

$K\Delta t$ = 44.50 calories

g = 25.42 Grams

Substituting in formula one obtains:

$$\frac{143.0 - 44.5}{25.42 \times 6.00} = \frac{98.5}{152.52} = .644$$

This is a sample of the calculations used for determining the specific heats of the sixty-six samples, the results of which are shown in Table III.

Fig. 6 is a binoidal graph which shows the specific heat of the system plotted against composition. The specific heats of the water-ethanol binary system reach a maximum at eighty percent water; then the values drop on a smooth curve to that of pure ethanol. The values of the binary system glycerine-ethanol lie on a smooth curve which is almost a straight line. The constant percent glycerine lines show a curvature similar to that of the ethanol-water curve: however the sixty percent and higher glycerine curves approach a straight line.

The triangular diagram of Fig. 7 is another graph of the properties. Each line on this graph joins points which represent compositions having the same specific heat. This diagram is prepared from Fig. 6.

The curvature of the lines in Fig. 7 can be explained by the fact that the constant percent glycerine lines and the ethanol-water lines reach maximums.

FIG. 6
SPECIFIC HEAT
(cal /gm /°c)
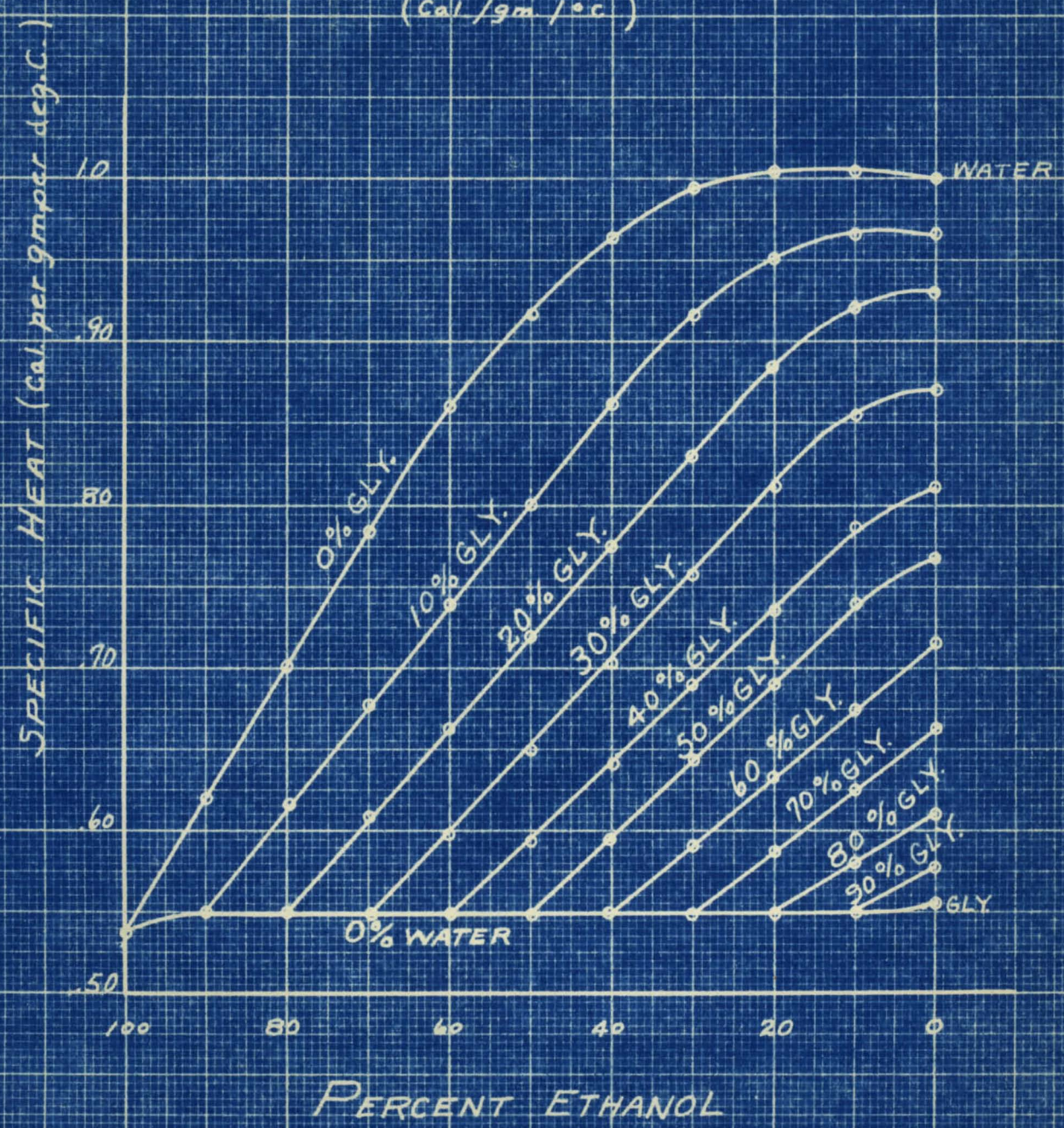
FIG. 7
SPECIFIC HEAT

GLYCEROL

WATER

ETHANOL

33

C.H.W.
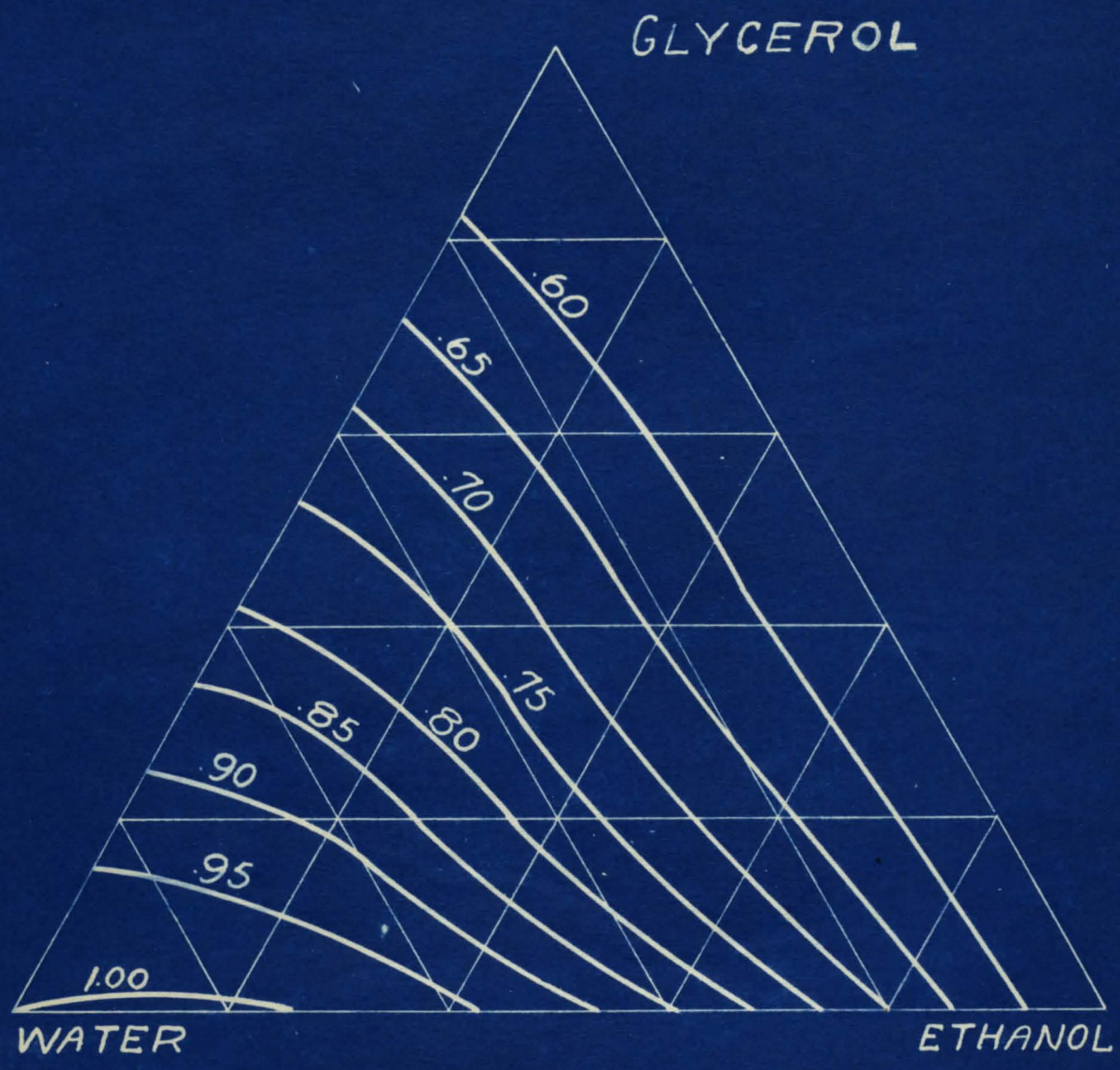
BOILING POINTS

The boiling points of pure ethanol, water and glycerine are 7 .3, 100.0, and 290° C respectively. The vapor pressure of glycerine (see Fig.1) is less than five mm. mercury at 100°C. and is only 45 mm. mercury at 200°C. From these two facts it can be seen that the glycerine, in small percentages, will not have a very great effect on the boiling point of the ternary system. The graph of the boiling points (Fig.) shows this to be true for samples whose glycerine percentage is fifty percent and less. Especially true is this statement when the sample contains ten percent or more of ethanol. The boiling points for the binary system, ethanol-water lie on a smooth curve between the values for the pure components. The constant percent glycerine lines have a curvature similar to that of the latter, but are displaced to the right as the glycerine percentage is increased.

The triangular diagram (Fig.9), containing the constant boiling point lines shows the latter to be almost parallel to the constant percent ethanol lines. This shows that the ethanol content governs the boiling point.

FIG. 8
BOILING POINT DIAGRAM
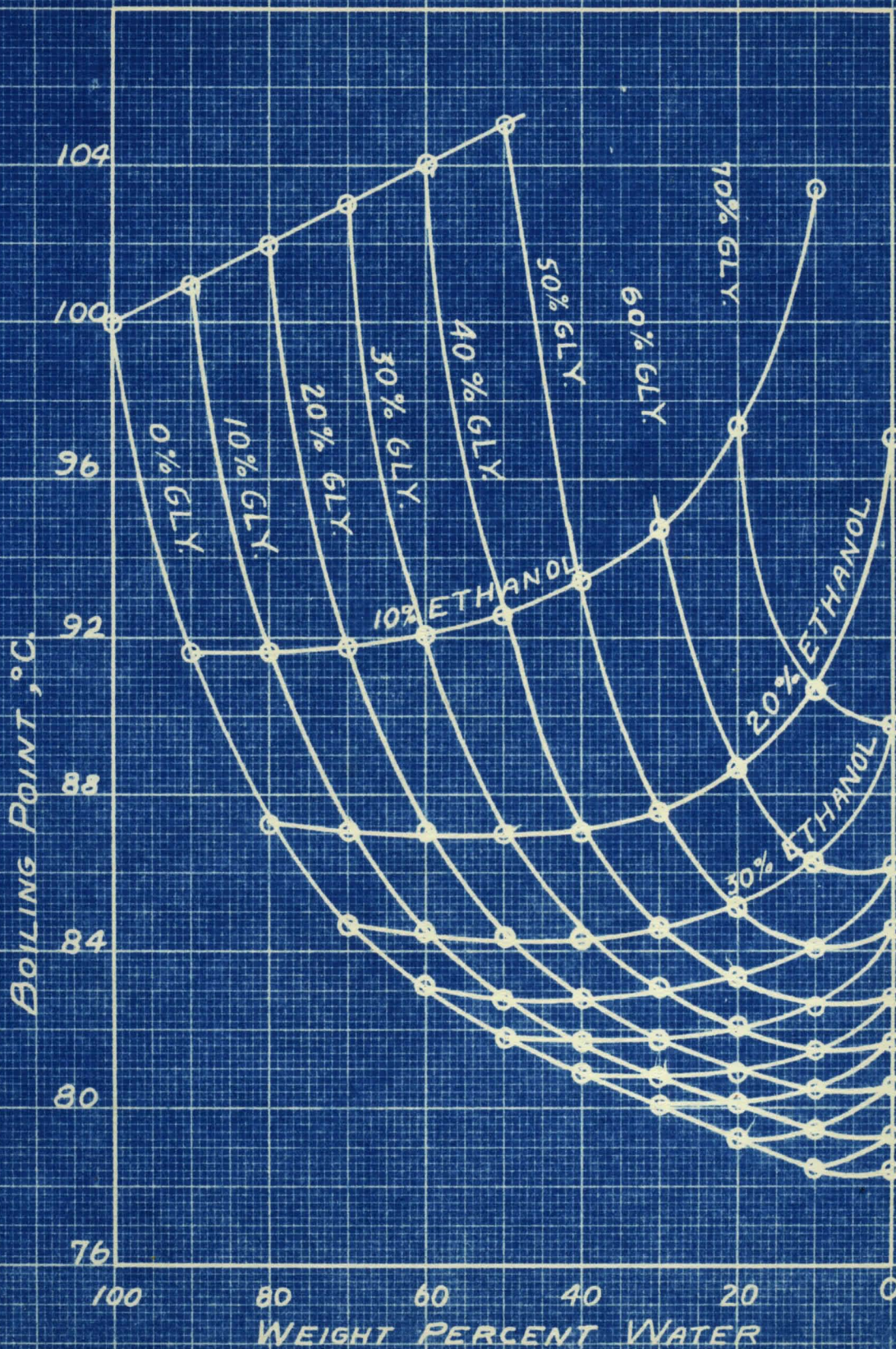
FIG. 9
BOILING POINT DIAGRAM

GLYCERIN

100.0

90.0

86.0

84.0

83.0

82.0

81.0

80.0

79.0
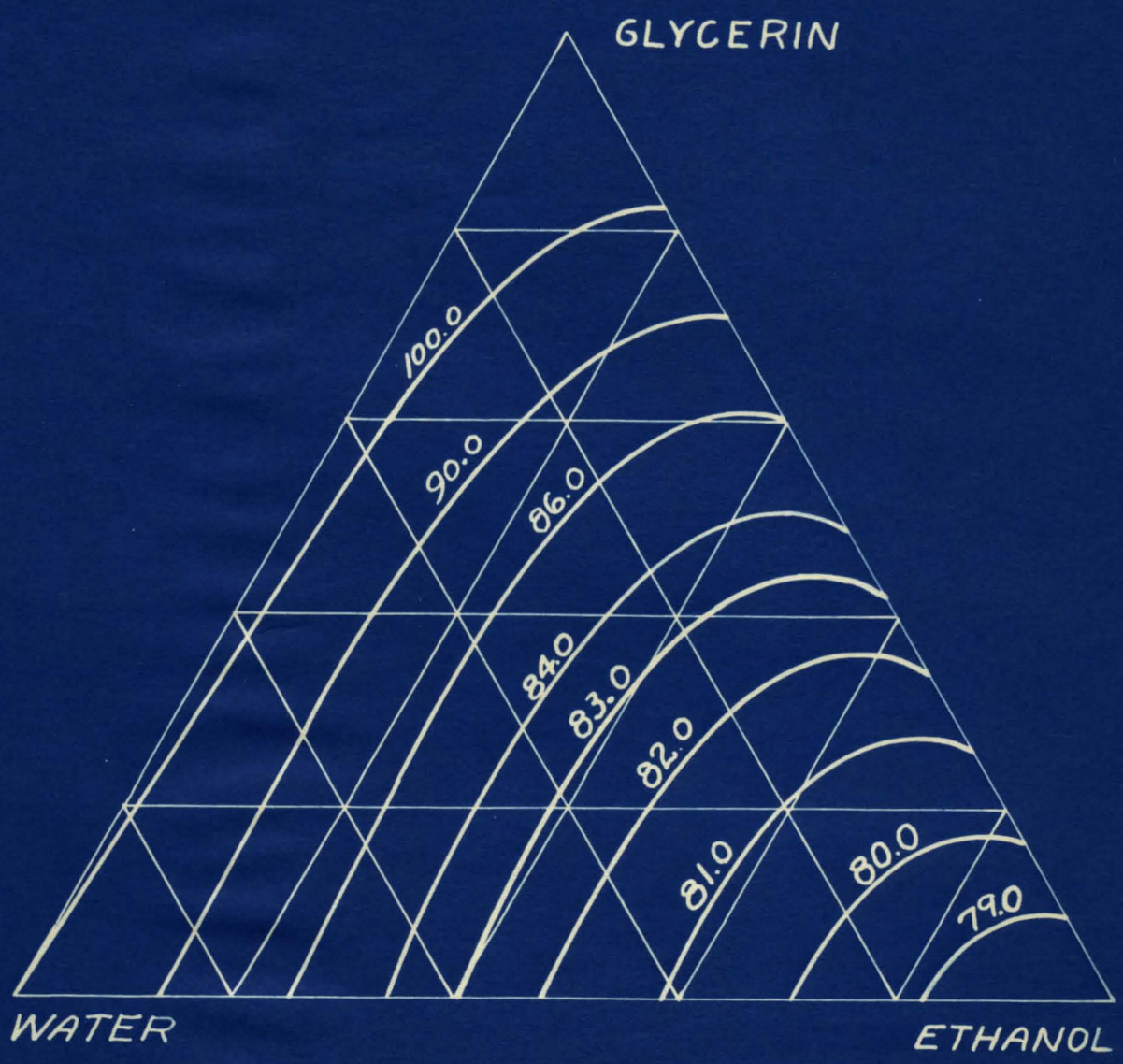
WATER

ETHANOL

VAPOR PRESSURES

Vapor pressure data for the sixty-six Samples are shown in Table IV. These data for the binary systems ethanol-water and water-glycerin are shown graphically in Fig. 10. This graph shows the effect that ethanol and glycerin exert upon the vapor pressure of the systems. As the percent ethanol is increased, the vapor pressure lines are successively displaced to the right of the vapor pressure line for water. This means that, at a given temperature, the vapor pressure of the ethanol-water series is respectively increased with increase in ethanol content. The vapor pressure lines to the left of that for water are those for the glycerin-water system. The glycerin percentage increases as the distance of the vapor pressure lines from that of water is increased. Thus, it shows that any increase in glycerin percentage decreases the vapor pressure of the system.

Figures 11 and 12 show vapor pressure lines for some of the samples of the ternary system. Others have been omitted because they coincide with those shown in the figures: but in all cases the rise of the vapor pressure due to the glycerin is apparent.

Table IV

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature degrees Cent.	Reciprocal of Abs. Temp. x 1000
1.	115.0	54.73	3.052
	303.1	76.1	2.865
	454.0	86.1	2.765
	607.3	93.9	2.726
	760.0	100.0	2.681
	905.5	105.0	2.746
2.	281.0	55.1	3.043
	550.0	70.4	2.912
	760.0	78.3	2.847
	916.0	83.1	2.809
3.	23.0	170.0	2.257
	100.0	227.0	2.000
	200.0	246.0	1.927
	395.0	268.0	1.848
	605.0	282.0	1.802
	760.0	289.0	1.779
4.	120.0	49.0	3.106
	432.0	77.3	2.855
	572.0	84.3	2.799
	760.0	91.7	2.742
5.	110.0	44.2	3.153
	451.0	74.2	2.880
	600.0	81.3	2.822
	760.0	87.3	2.776
6.	290.6	60.2	2.995
	474.1	72.9	2.891
	626.6	79.7	2.835
	760.0	84.7	2.796
7.	276.6	59.2	3.010
	467.7	71.2	2.907
	640.7	79.9	2.842
	760.0	83.2	2.808
	902.7	87.8	2.772

Table IV (continued).

Vapor Pressure Data.

Sample No.	Vapor Pressure mm. mercury	Temperature degrees Cent.	Reciprocal of Abs. Temp. x 1000
8.	140.0	44.1	3.154
	306.7	60.3	3 .000
	560.2	74.4	2. 79
	760.0	82.1	2. 16
	902.2	86.4	2.785
9.	154.7	44.8	3.147
	29 .	58.9	3.013
	563.3	73.6	2.882
	760.0	80.8	2. 24
	905.3	85.7	2.789
10.	170.5	46.9	3.126
	297.0	5 .0	3.116
	555.5	72.3	2. 96
	760.0	0.1	2.832
	917.5	85.0	2.793
11.	71.0	30.1	3.299
	2 0.5	56.0	3.040
	552.0	71.3	2.905
	760.0	79.2	2. 39
	907.5	83.7	2. 04
12.	77.0	30.	3.300
	2 7.0	55.7	3.043
	562.0	70.1	2.90
	760.0	7 .4	2. 45
	913.0	82.2	2. 15
13.	145.0	90.0	2.757
	294.0	110.0	2.611
	476.0	12 .1	2.493
	760.0	141.	2.411
	910.0	14 .6	2.372
14.	145.2	75.9	2. 66
	2 9.2	93.0	2.732
	472.2	106.	2.633
	760.0	120.1	2.53
	89 .7	125.5	2.509

Table IV (continued)

Vapor Pressure Data.

Sample No.	Vapor Pressure mm. mercury	Temperature degrees Cent.	Reciprocal of Abs. Temp. x 1000
15.	141.7	6 .9	2.925
	290.7	6.1	2.7 5
	4 2.2	100.1	2.6 0
	760.0	113.3	2.5 9
	91.7	117.4	2.562
16.	140.0	65.	2.957
	300.1	3.6	2. 04
	430.0	96.9	2.704
	760.0	109. 7	2.613
	93.0	114.	2.579
17.	140.2	63.9	2.968
	2 0.7	79.7	2.835
	479.7	92.9	2.733
	760.0	106.1	2.734
	99.7	111.0	2.604
13.	146.2	62.1	2.9 1
	290.2	77.	2. 51
	479.7	90.1	2.74
	760.0	103.9	2.653
	90.7	10 .6	2.621
19.	142.5	60.1	2.995
	291.5	77.2	2. 56
	430.5	90.2	2.753
	7 0.0	102.9	2.661
	97.0	107.6	2.62
20.	14 .0	60.0	3.001
	293.0	7 .4	2. 63
	433.0	90.0	2.762
	760.0	101.	2.66
	97.0	106.2	2.637
21.	147.0	59.9	3.001
	292.0	75.5	2. 69
	4 3.0	.4	2.767
	760.0	100.9	2.674
	91 .5	105.9	2.639

Table IV (continued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature degrees Cent.	Reciprocal of Abs. Temp. x 1000
22.	86.0	33.0	3.263
	2 9.0	56.6	3.034
	55 .0	71.6	2.902
	760.0	79.3	2.83
	899.0	83.7	2.804
23.	140.0	42.5	3.175
	296.0	53.1	3.021
	555.1	72.3	2. 90
	760.0	80.5	2.827
	893.5	85.0	2.793
24.	4.0	34.0	3.257
	297.0	59.1	3.011
	569.5	74.4	2.87
	760.0	81.7	2. 19
	900.0	6.4	2.703
25.	0.0	34.0	3.257
	310.0	61.1	2.993
	577.5	75.	2. 67
	760.0	2.9	2. 10
	94.5	7.2	2.776
26.	255.5	57.8	3.023
	430.0	69.9	2.916
	5 7.5	77.8	2. 51
	760.0	84.6	2.796
	904.0	89.5	2.753
27.	2 1.6	60.9	2.995
	461.6	72.5	2. 95
	5 5.6	79.2	2.839
	760.0	86.1	2.784
28.	2 2.0	63.3	2.973
	44 .0	74.9	2. 74
	5 0.0	2.1	2. 16
	760.0	9.8	2.757
	92.0	94.2	2.724

Table No.IV (continued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature degrees Cent.	Reciprocal of Abs. Temp x 1000
29.	157.5	61.4	2.990
	357.0	76.6	2.861
	557.5	90.4	2.752
	760.0	97.0	2.702
	900.0	106.3	2.637
30.	142.5	70.4	2.912
	209.5	90.5	2.751
	430.5	103.4	2.657
	760.0	110.5	2.555
	909.5	127.7	2.495
31.	139.5	61.0	2.994
	295.0	76.7	2.860
	420.5	88.5	2.766
	760.0	103.2	2.658
	906.0	107.8	2.626
32.	142.1	54.	3.051
	296.5	70.	2.909
	473.5	84.2	2.800
	760.0	97.3	2.701
	900.0	102.2	2.665
33.	144.5	54.2	3.057
	291.0	70.6	2.911
	470.0	82.	2.827
	760.0	94.7	2.725
	904.0	100.8	2.675
34.	143.1	53.6	3.062
	289.1	69.0	2.924
	477.6	81.0	2.824
	760.0	93.4	2.750
	904.6	98.6	2.691
35.	145.2	52.2	3.076
	295.2	66.4	2.930
	473.7	79.7	2.835
	760.0	92.5	2.736
	904.7	97.4	2.700

Table IV (continued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature deg. cent.	Reciprocal of Abs. Temp. x 1000
36.	152.7	53.9	3.060
	290.7	67.8	2.934
	473.7	79.5	2.837
	760.0	92.0	2.739
	913.2	97.2	2.702
37.	143.7	52.7	3.070
	293.7	63.0	2.932
	483.2	79.9	2.834
	760.0	91.8	2.742
	903.2	96.8	2.704
38.	149.0	53.2	3.066
	292.0	66.7	2.944
	488.5	79.8	2.834
	760.0	91.6	2.740
	906.0	96.2	2.709
39.	143.0	49.8	3.098
	293.0	65.6	2.953
	485.0	78.1	2.848
	760.0	90.6	2.752
	900.0	95.1	2.717
40.	145.5	49.5	3.101
	298.0	65.1	2.953
	485.0	76.7	2.860
	760.0	88.6	2.765
	907.0	92.4	2.737
41.	146.5	48.7	3.108
	284.0	63.2	2.935
	433.0	75.0	2.873
	760.0	87.5	2.747
	906.0	92.4	2.737
42.	158.5	50.0	3.096
	293.5	63.3	2.974
	480.5	74.8	2.875
	760.0	87.1	2.777
	895.5	91.6	2.743

Table IV (continued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature deg. cent.	Reciprocal of Abs. Temp. x 1000
43.	153.0	49.7	3.099
	294.5	63.7	2.970
	436.5	75.7	2.863
	760.0	87.0	2.730
	906.5	92.2	2.738
44.	152.5	50.3	3.093
	297.5	64.3	2.965
	437.5	75.9	2.867
	760.0	87.0	2.730
	896.0	91.6	2.753
45.	146.5	49.5	3.101
	293.5	64.2	2.966
	437.5	75.8	2.867
	760.0	87.1	2.777
	902.5	91.8	2.741
46.	146.5	46.5	3.130
	293.5	62.2	2.983
	467.5	74.3	2.879
	760.0	86.3	2.734
	909.0	91.6	2.743
47.	140.5	46.3	3.132
	283.0	60.7	2.997
	471.0	72.9	2.891
	760.0	85.1	2.793
	902.5	89.5	2.759
48.	143.5	46.3	3.132
	289.0	61.1	2.994
	471.0	72.4	2.895
	760.0	84.5	2.797
	893.0	89.1	2.762
49.	139.5	45.7	3.131
	284.0	60.5	2.999
	467.5	72.0	2.893
	760.0	84.5	2.797
	907.5	89.2	2.761

Table IV (continued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature deg. cent.	Reciprocal of Abs. Temp x 1000
50.	136.4	45.3	3.142
	201.4	60.3	3.000
	472.4	72.2	2.897
	760.0	84.3	2.799
	910.4	89.1	2.762
51.	135.0	45.0	3.145
	290.5	61.0	2.994
	476.5	72.5	2.895
	760.0	84.5	2.797
	923.5	89.8	2.756
52.	146.0	46.4	3.131
	303.0	61.6	2.989
	483.0	72.6	2.894
	760.0	84.1	2.801
53.	157.7	47.1	3.124
	303.7	60.8	2.996
	483.7	72.2	2.897
	760.0	83.4	2.806
	997.7	90.8	2.749
54.	140.0	45.5	3.139
	305.6	60.8	2.996
	490.0	72.0	2.899
	760.0	83.4	2.809
	927.5	88.4	2.767
55.	277.0	59.4	3.002
	403.0	68.5	2.928
	577.3	76.5	2.861
	760.0	83.3	2.803
	901.8	88.7	2.765
56.	170.3	49.6	3.100
	385.3	66.1	2.949
	555.8	75.0	2.874
	760.0	82.3	2.811
	894.3	87.0	2.777

Table IV (continued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature deg. cent.	Reciprocal of Abs. Temp x 1000
57.	202.5	51.6	3.011
	379.0	65.3	2.957
	533.0	75.6	2.863
	760.0	82.6	2.812
	903.5	87.7	2.777
58.	219.3	52.9	3.068
	370.3	65.0	2.959
	561.3	74.2	2.880
	760.0	82.0	2.810
	900.3	86.4	2.783
59.	201.9	51.2	3.035
	372.9	64.6	2.962
	532.4	75.3	2.871
	760.0	81.8	2.810
	910.4	86.9	2.779
60.	242.5	54.9	3.049
	412.5	66.7	2.944
	567.0	74.3	2.879
	760.0	81.7	2.320
	795.0	86.0	2.796
61.	276.5	56.4	3.036
	404.5	65.5	2.954
	591.5	74.6	2.877
	760.0	80.9	2.825
	900.5	85.3	2.791
62.	223.0	53.9	3.068
	393.0	65.1	2.958
	570.5	73.2	2.888
	760.0	80.8	2.826
63.	177.0	47.5	3.120
	370.0	63.4	2.972
	561.5	73.2	2.889
	760.0	80.3	2.826
	903.5	84.3	2.794

Table IV (conctinued)

Vapor Pressure Data

Sample No.	Vapor Pressure mm. mercury	Temperature deg. cent.	Reciprocal of Abs. Temp x 1000
64.	249.5	54.7	3.052
	394.0	64.6	2.962
	565.0	73.1	2.?90
	760.0	?0.4	2.?29
	?96.5	?4.9	2.794
65.	153.0	44.5	3.150
	349.1	61.5	2.990
	549.6	72.6	2.?94
	760.0	?0.2	2.?32
	902.1	?4.7	2.796
66.	151.0	43.6	3.15?
	354.5	61.1	2.993
	566.5	72.2	2.?97
	760.0	79.4	2.?37
	905.5	?3.9	2.?02
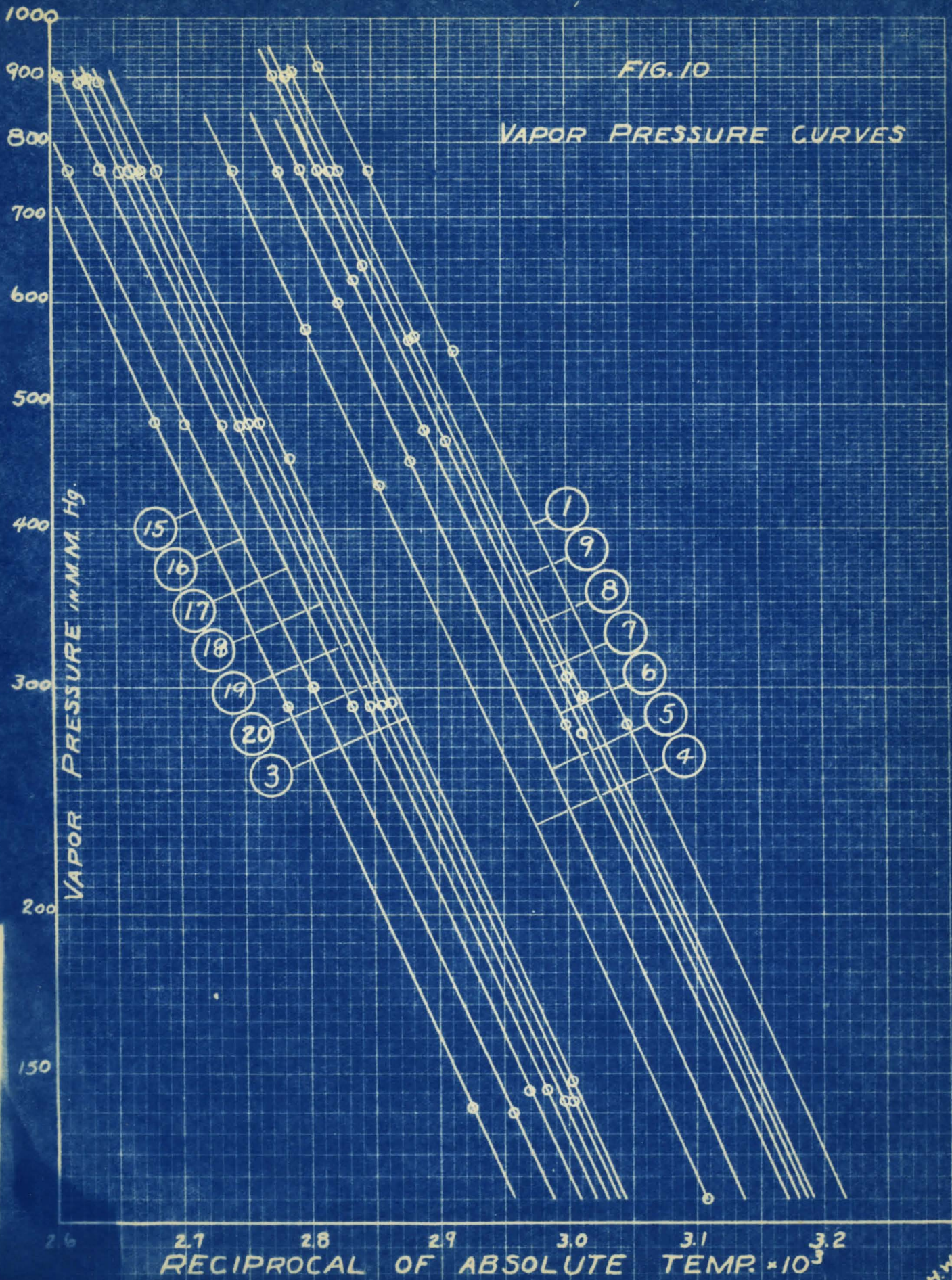
FIG. 10

VAPOR PRESSURE CURVES

FIG. II

VAPOR PRESSURE CURVES

FIG. 12
VAPOR PRESSURE
CURVES

VAPOR PRESSURE IN M.M. Hg.

RECIPROCAL OF ABSOLUTE TEMP. × 10³
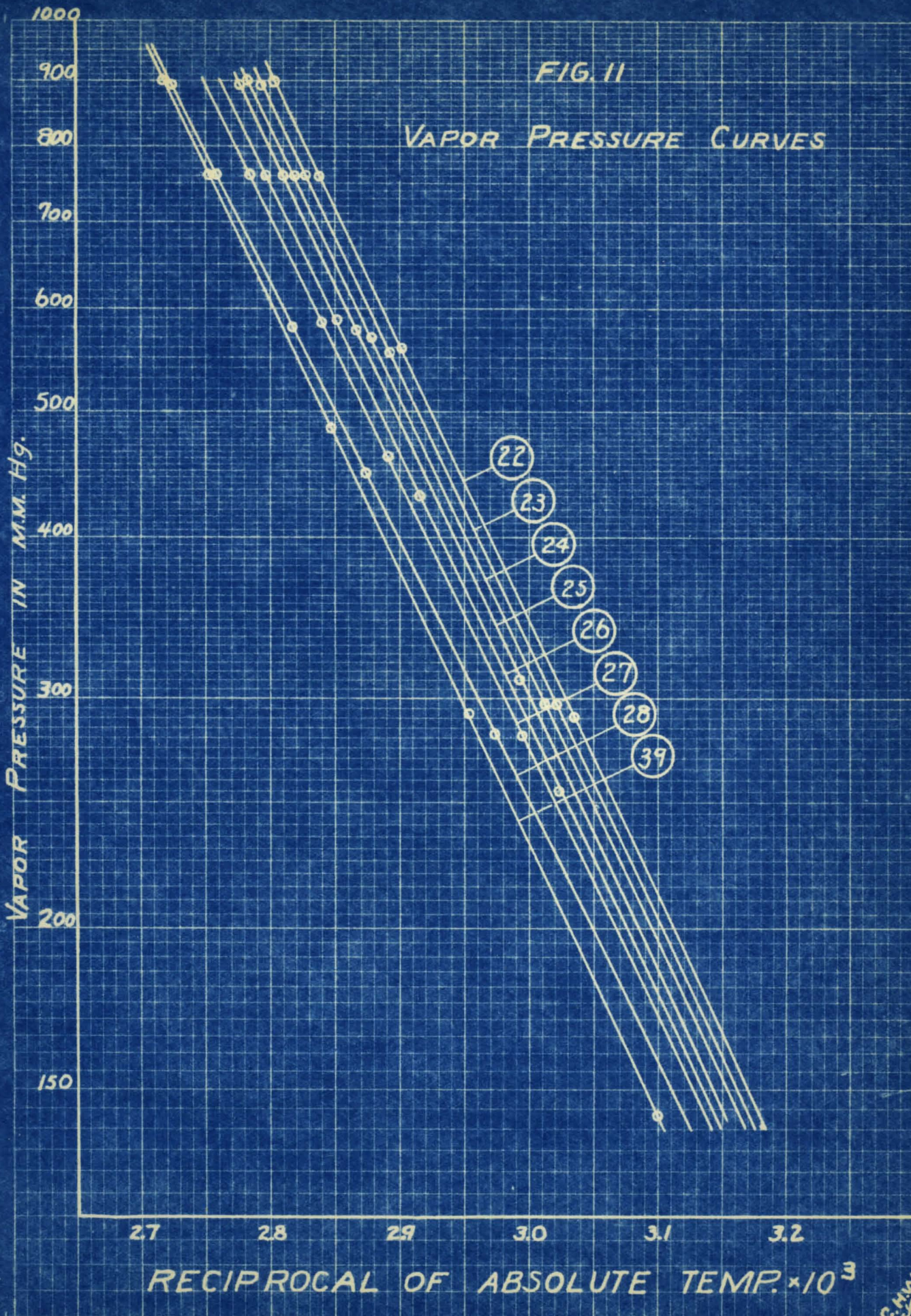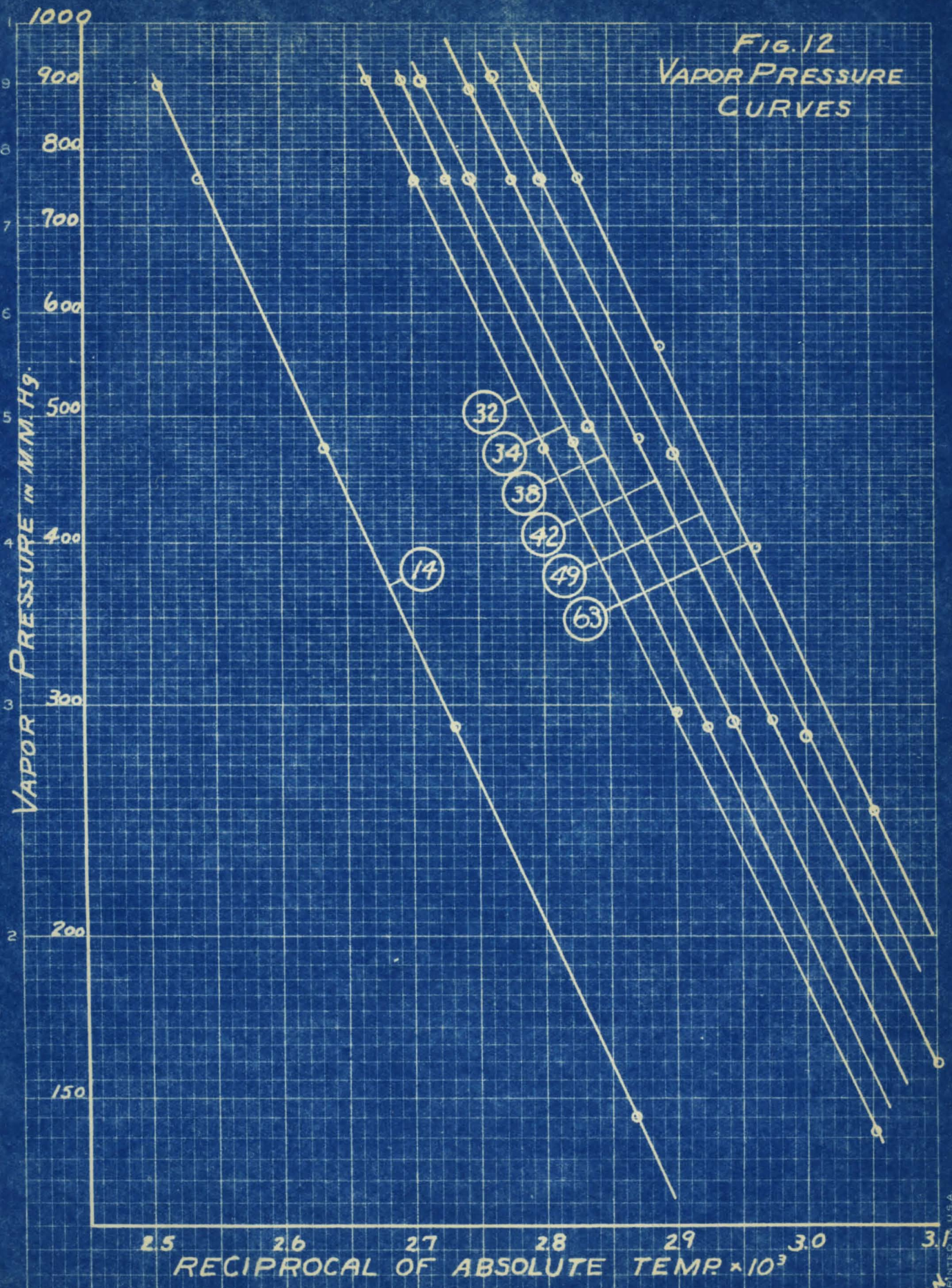
LATENT HEATS

The latent heats have been calculated for the entire system using the Clausius-Clapeyron equation as discussed in Chapter II. These values are tabulated in Table III in gram calories per mole.

Sample Calculations:

Equation used, $L = R \log \frac{p_2}{p_1} \div \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

Values obtained from vapor pressure curve of sample number 42 are as follows-

$1/T_1 = .002968$

$1/T_2 = .002742$

$p_1 = 300$ mm. Hg.

$p_2 = 900$ mm. Hg.

$1/T_1 - 1/T_2 = .000226$

$\log_e P_2/P_1 = 2.303 \log_{10} 3.000 = 2.303 \times 0.47712$

Substituting in equation (5),

$L = \dfrac{2.30 \times 0.47712 \times 1.986}{.000226} = 9,650$ calories per mole

It is noted that in arriving at equation (5) it was assumed that L was a constant, and this is not true. We know that the latent heat of liquids varies with the pressure at which vaporization takes place. This variation in latent heat is proportional to the change in slope of the vapor pressure lines (log p vs. 1/T). Since the vapor pressure data are used in this investigation to calculate the latent heats, some error is encountered; however it is small.

It is understood that the latent heats calculated here
do not represent the value at a definite temperature and
pressure but over a definite range. This is the range
of temperature and pressure selected to substitute in equa-
tion (5), which in this investigation was between 300 and
900 mm. mercury absolute.

These data are useful in the study of heat exchange
in distillation, that is, in calculating steam consump-
tion, quantity of condenser water, etc.

VAPOR-LIQUID EQUILIBRIUM DATA

Vapor-liquid equilibrium data for the ternary system are shown graphically in Fig. 13. The composition of the liquid phase is represented by the position of the small circle. That is, the percent of water that any sample contains is proportional to the distance of the point representing that sample from the side of the triangle opposite the vertex labled water. Then to find the composition of any sample proceed as follows: From the point representing the composition of the sample, draw perpendiculars to each of the three sides of the triangle. The percent by weight of any component is equal to the ratio of the corresponding perpendicular to the altitude of the triangle. Thus, sample No. 6 contains approximately 39% glycerine, 21% ethanol, and 40% water.

The vapor phase is represented by a small dot. Each small circle has a corresponding dot bearing the same numbers. Thus, a small circle and a dot with the same number represent equilibrium compositions of the liquid and vapor phases respectively.

From Fig. 13 it can be seen that the liquid compositions vary over a wide range, while the vapor phase in equilibrium with the liquid contains no glycerine.

The absence of glycerine in the vapor phase is to be expected, because of the low vapor pressure of glycerine below 100 deg. cent. as shown in Fig. 1. It was found in this investigation that regardless of the composition of the liquid, the vapor phase contained no glycerine except where the liquid sample contained above 60 per cent glycerine, and then only a trace was in the vapor.

Table V shows the refractive index and density of the vapor and liquid samples, from which Fig. 13 was prepared with the aid of Fig. 4.

Curve 2 in Fig. 14 shows equilibrium compositions of the binary system ethanol-water from the data of Carey and Lewis (31). The graph is plotted weight percent ethanol in liquid phase versus weight percent ethanol in the vapor phase.

Curve 1 in Fig. 14 is plotted using the same coordinates, but the data were taken from a ternary system instead of a binary system as in the case of curve 2. It can be seen that curve 1 lies above curve 2 throughout. Now consider two mixtures, No. 1 and No. 2, both containing 30% ethanol, but No. 1 is a ternary system containing ethanol, glycerine, and water while No. 2 is a binary system of ethanol and water. From Fig. 14 it can be seen that sample No. 1 will contain more ethanol in vapor phase than No. 2. No. 1 has 35% ethanol in

vapor phase and No. 2 has only 70% ethanol in vapor.

It must be borne in mind that curve 1 does not represent all possible conditions, but is an average of the data contained. As the glycerine composition of the ternary system decreases, curve 1 approaches curve 2. This is to be expected, since, when the glycerine percertage is zero, the system will be a binary system (curve 2). Table VI, containing the data for curve 1 Fig. 14, was obtained from Fig. 13.

It has been concluded that the three components, ethanol, glycerine, and water in a mixture can be separated as follows:

1. By Fractionation, obtaining almost pure ethanol, and

2. By distilling the residue from 1 in a vacuum. The latter will remove all the water before the glycerine distills.

TABLE V

Properties of Vapor and Liquid Phases

Sample No.	Liquid Refractive index	Density	Boiling point degrees Cent.	Vapor Refractive index	Density
1.	1.3904	0.9990	80.0	1.362	0.8270
2.	1.3549	1.0187	91.1	1.3614	0.8993
3.	1.3730	1.0450	87.2	1.3620	0. 663
4.	1.3366	1.0042	99.5	1.3560	0.9 70
5.	1.369	1.0707	100.0	1.3335	0.9990
6.	1.3949	1.0490	78.8	1.3621	0. 141
7.	1.4103	1.0079	79.0	1.3618	0.8053
8.	1.4300	1.0380	78.2	1.3616	0.8032
9.	1.3995	1.1005	87.4	1.3622	0. 753
10.	1.3912	1.1116	98.4	1.3420	0.9750
11.	1.3591	1.0500	99.6	1.3350	0.9922
12.	1.34 2	1.02 0	99.9	1.3340	0.9957
13.	1.369	0.9975	82.9	1.3630	0. 530

TABLE V (cont.)

Properties of Vapor and Liquid Phase

Sample No.	Liquid Refractive index	Density	Boiling point deg. Cent.	Vapor Refractive index	Density
14.	1.3722	0.9495	81.0	1.3630	0.8445
15.	1.3700	0.8890	79.6	1.3623	0.8235
16.	1.3877	0.9520	79.3	1.3632	0.8290
17.	1.3750	0.8640	70.3	1.3630	0.8233
18.	1.4240	1.1500	87.3	1.3630	0.8770
19.	1.4171	1.0860	79.5	1.3640	0.8303
20.	1.3622	0.9736	83.3	1.3637	0.8565
21.	1.3427	0.9910	91.4	1.3610	0.9060
22.	1.3740	1.0230	84.7	1.3636	0.8593
23.	1.4410	1.1790	82.7	1.3640	0.8500
24.	1.3602	0.8324	70.3	1.3629	0.8096
25.	1.3342	0.9183	70.6	1.3632	0.8134

FIG. 13

VAPOR LIQUID EQUILIBRIUM

COMPOSITION DATA
○ LIQUID PHASE
• VAPOR PHASE

GLYCERINE

○23

○18   ○8

○19

○7

○9
○10   ○6

○5
○3   ○22   ○1
○11   ○16   ○25

○2   ○13   ○17
○12   ○14   ○24
○20   ○15

○4   ○21

WATER   ETHANOL

⑤ ⑫ ⑪ ④ ⑩   ㉑ ② ⑱ ⑨ ③ ㉒ ⑳ ⑬ ㉓ ⑭ ⑲ ⑯ ⑮ ① ⑥

㉕ ⑰ ㉔ ⑦ ⑧

C.H.W.
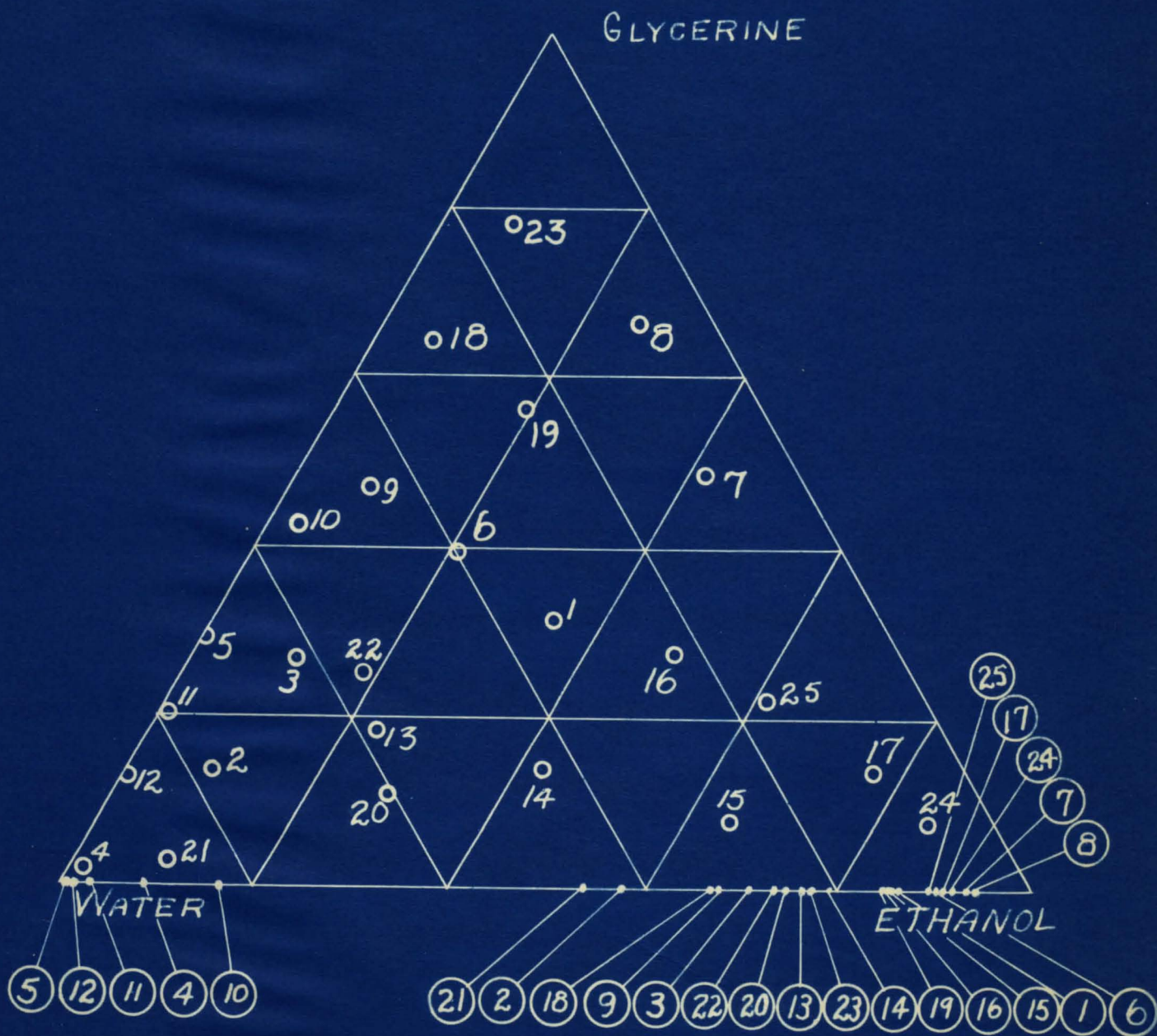
TABLE VI

Vapor-Liquid Composition

Sample No	ETHANOL CONTENT Wt. Pct.	
	LIQUID	VAPOR
1	35.1	36.0
2	8.8	58.0
3	11.0	70.3
4	1.5	9.0
5.	0.5	0.8
6	21.0	90.0
7	42.0	93.0
8	25.5	94.0
9	3.1	63.0
10	7.5	16.8
11	1.0	3.4
12	0.6	1.6
13	23.3	76.5

TABLE IV (Cont'd)

VAPOR-LIQUID COMPOSITION

Sample	ETHANOL CONTENT Wt. Pct.	
	LIQUID	VAPOR
14.	42.5	79.0
15.	64.7	85.5
16.	49.0	85.0
17.	76.2	90.5
18.	6.0	86.8
19.	19.0	84.5
20.	23.0	74.5
21.	9.8	84.0
22.	13.0	73.5
23.	7.2	77.5
24.	84.9	91.5
25.	61.4	89.0

FIG. 14

VAPOR-LIQUID EQUILIBRIUM CURVES FOR ETHANOL

① TERNARY SYSTEM

② BINARY SYSTEM

WT. PCT. ETHANOL IN VAPOR PHASE

WT. PCT. ETHANOL IN LIQUID PHASE
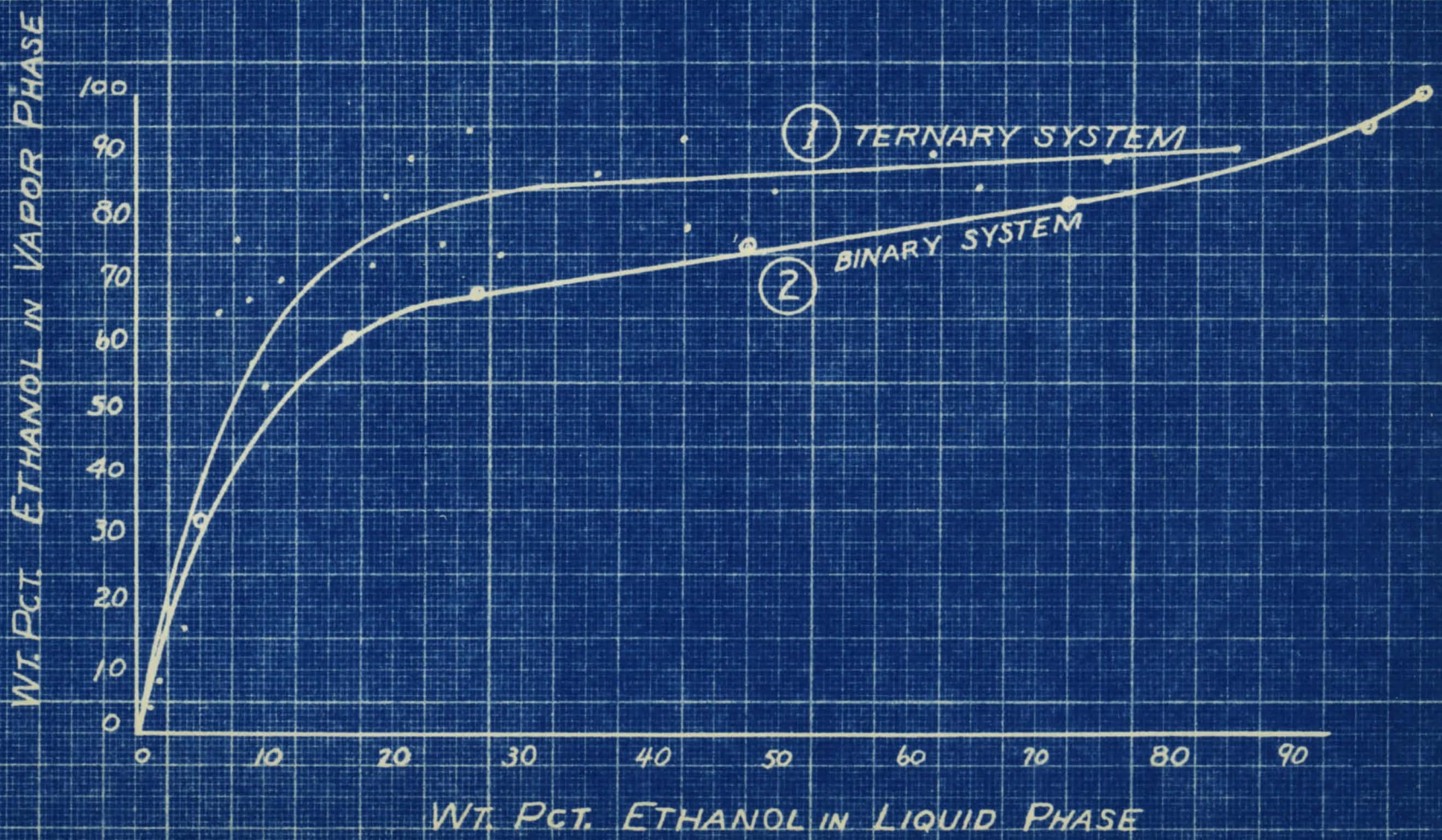
FREEZING POINTS

The primary object of this investigation was to determine those properties that are directly related to distillation-namely, specific heats, boiling points, vapor pressures, latent heats, and vapor-liquid equilibrium data: but, since the three materials are important in binary mixtures as commercial antifreeze solutions, freezing points were determined.

Acetone, cooled with solid carbon dioxide, was used as the freezing mixture. A toluene thermometer, graduated in one degree subdivisions, was used to determine the temperatures. Samples containing less than fifty per cent water did not give definite freezing points. These samples usually resulted in the formation of gelatinous masses, and gave no definite freezing point. Table VII contains the freezing points that were obtained. Fig. 15 is a plot of these values. The values for the binary system Glycerine-water agree with those of Lane (32).

The constant per cent water lines reach a minimum
when ethanol and glycerine contents are equal. This
means that for an antifreeze with a certain freezing
point, a greater water content may be used if the
resulting per cent is made up of equal parts of
ethanol and glycerine instead of being made up of
either one separately.

The triangular diagram (Fig. 16) shows all the
possible compositions having the same freezing point.
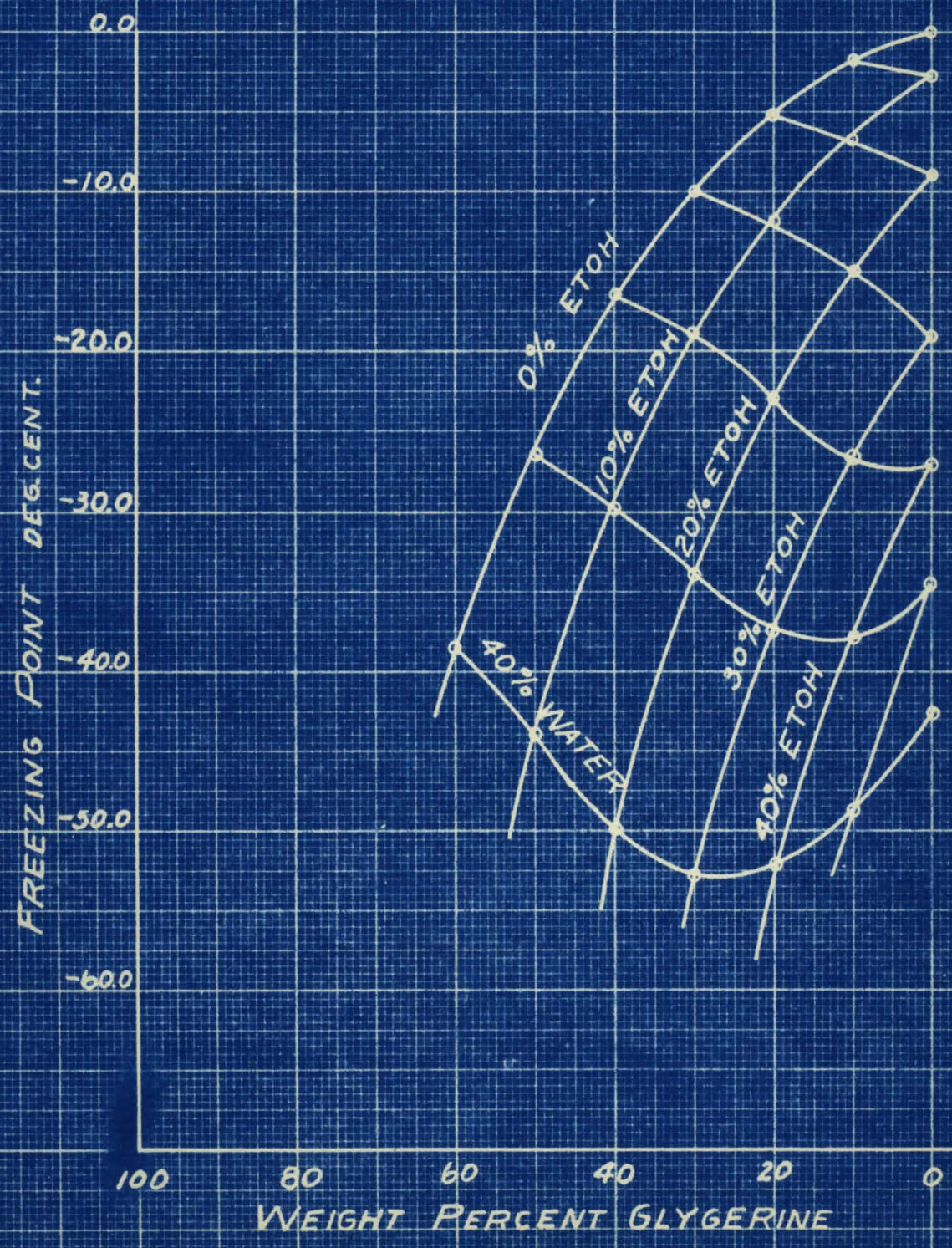
TABLE VII

Freezing Points

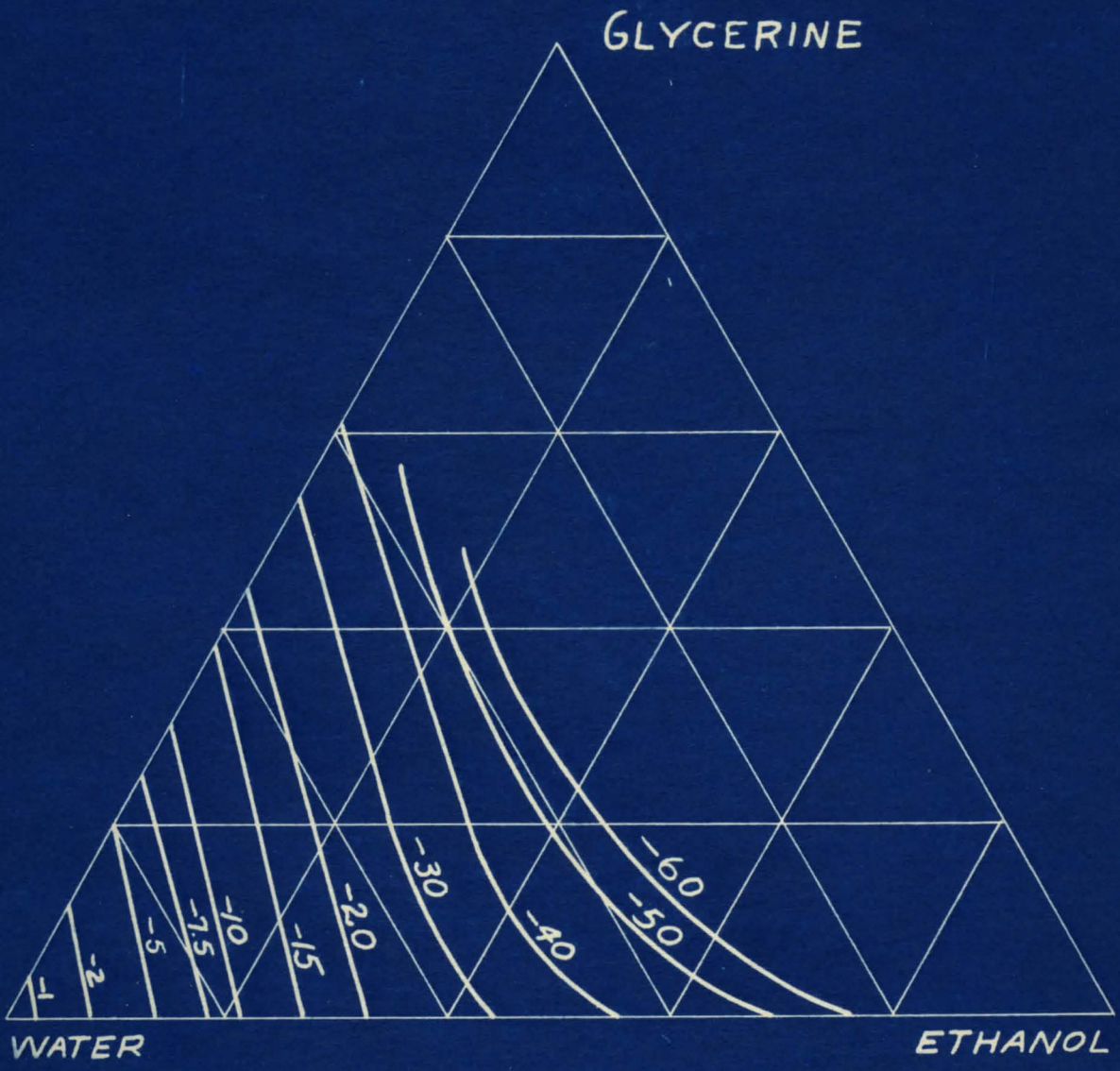| Sample No.	Freezing Points degrees Cent.	Sample No.	Freezing Point degrees Cent.
1.	-115.0	34.	-44.0
3.	-0.0	35.	-30.0
4.	-2.0	36.	-19.0
5.	-9.0	37.	-12.0
6.	-19.0	38.	-7.0
7.	-27.0	42.	-50.0
8.	-34.6	43.	-34.0
9.	-42.5	44.	-23.0
10.	-53.0	45.	-15.0
16.	-38.5	49.	-53.0
17.	-26.5	50.	-37.5
13.	-16.5	51.	-27.0
19.	-9.6	55.	-52.0
20.	-5.7	56.	-33.0
21.	-2.5	60.	-50.0

FIG. 15

FREEZING POINT DIAGRAM

FIG.16
FREEZING POINT DIAGRAM

CHAPTER V

CONCLUSIONS

CONCLUSIONS

Specifies heats, boiling points, vapor pressures, latent heats, and vapor-liquid equilibrium data have been reported in this dissertation. These properties and the properties reported in a previous investigation (1) complete the preliminary work on this system in the study of distillation of ternary mixtures. Freezing points have been added because ethanol and glycerine in aqueous solutions are of interest as commercial anti-freeze mixtures.

The properties reported in the previous investigation (1) were presented before the Mid-west regional meeting of the American Chemical Society, November 1, 1935 in Louisville, Kentucky, and were accepted by the Journal of Physical Chemistry for publication and will appear in May, 1936 Edition.

CHAPTER VI

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