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Physical Properties of The Ternary System: Ethylene Glycol - Disthylene Glycol - Water

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PHYSICAL PROPERTIES OF THE TERNARY SYSTEM: ETHYLENE GLYCOL--DIETHYLENE GLYCOL--WATER

being

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by

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Date Jan 12, 1950 Approved Harold S. Choguill
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INTRODUCTION

Since approximately two-thirds (12) of the energy from the fuel in automobile engines is converted to unusuable heat, it is necessary that a method of cooling the engines be provided. In most present-day engines of this type, an indirect method is utilized, namely, the transfer of heat to a liquid and thence from the liquid to the surrounding air by means of radiators. Water is universally used for the coolant liquid because of its availability and high heat transfer properties. However, water has its limitations.

A significant limitation of water as a coolant is its corrosive action causing rust clogging and metal perforation. Water is a very stable compound, but it attacks certain cooling system metals vigorously under the influence of heat and aeration. Even more significant than these is its high freezing point.

Ever since the automobile reached the point of perfection that made it usable in the colder seasons of the year, men have been searching for coolants with freezing points lower than that of water and possessing the desirable coolant characteristics of water. In addition to an adequately lower freezing point, it is a necessary requirement that an antifreeze does not impart undesirable properties that would interfere with cooling engines efficiently. It is also highly desirable that the substance reduce the corrosive tendency.

Many substances have been tested that could be used in below-freezing temperatures. Some of these are oils, sugars, inorganic and organic salts, various alcohols, glycerol, and several glycols. The oils, sugars, and salts have proven highly unsatisfactory (12). Of the usable materials so far tested, the glycols have generally proved to be the most satisfactory.

Ethylene glycol (sometimes called "glycol" or "ethandiol-1,2") has been in use the longest of any of the glycol compounds. It probably first appeared on the market under the trade name of "Eveready Prestone", manufactured by the National Carbon Company. More recently diethylene glycol (β,β'-dihydroxyethyl ether or glycol ether) and propylene glycol (propandiol-1,2) have become commercially available.

In 1941, approximately one-third of the automobiles in use in the United States used antifreezes having an ethylene glycol base (12). The reasons for the present wide use of these glycols for antifreezes are many. First of all, they have freezing points lower than that of water and when mixed with water (they are soluble in water in all proportions due to their polar nature) in varying proportions, exhibit freezing points of the pure glycols are as follows: ethylene glycol -13.5°C. (2), diethylene glycol -10.45°C. (14). These glycols also show boiling points higher than that of water. The literature lists these temperatures as follows: ethylene glycol 197.40°C. (11), diethylene glycol 244.33°C. (11), and propylene glycol 189°C. (14). They are also generally less corrosive on metals. Tabulated below (12) are the weight losses in mg./12 sq. in./200 hrs. at 170°F. of various metals found in engine cooling systems for ethylene glycol and distilled water.

	Iron	Aluminum	Copper	Brass	Solder
Ethylene Glycol Solution*	793	45	101	101	267
Distilled Water	1524	5	93	93	234

In their study of the thermal conductivities of ethylene glycol-water solutions, Bates and Hazzard (1) found the following values at 80°C.:

Ethylene Glycol (% by weight)	K_t
100	0.000580
50	0.001000
0	0.001630

K_t is in g.-cal.,sec.$^{-1}$,cm.$^{-2}$,$^{\circ}$C.$^{-1}$,cm.

However, Green, Lamprey, and Sommer (12) found no measurable difference in the heat transfer properties of water and ethylene glycol. The two prominent undesirable properties of the glycols as antifreezes, namely, foaming and creepage, can be effectively reduced by adding the proper antifoaming and anticreep agents (12). Likewise corrosion may be reduced by the proper inhibitors (cf. 17, 21).

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*Solution of ethylene glycol and water having a freezing point of 0°F.

General Properties of Solutions

Some of the aspects of the theory of liquids and solutions must now be considered. A liquid may be regarded as a condensed gas or as a melted solid (6). In this work it is more advantageous to consider a liquid as a melted solid.

At any instant liquids do possess something analogous to a definite arrangement between neighboring molecules, as shown by the patterns they exhibit when X-rays are passed through them (6). Moreover, they require the expenditure of energy when one layer of liquid is forced past another. These facts seem to be explained best on the hypothesis that the molecules are squeezed together by their own forces of mutual attraction but that each molecule has a free volume surrounding it, in which it behaves effectively as an ideal gas. In a solid the molecules cannot move from one place to another, but in a liquid they can, provided that a small amount of energy is supplied. The differences in the properties of viscosity and heat transfer between different liquids depends, at least partially, upon the differences of their mutual attraction forces.

A solution may be defined as a homogeneous system composed of two or more different chemical substances. Such a homogeneous system exhibits the same chemical composition and physical properties in every part. Since a solution is formed by an interdispersion of single molecules rather than groups of molecules, it is reasonable to expect that they should exhibit to a modified degree some new properties in much the same manner that elements do when combined to form a chemical compound. This reasoning is exemplified by the freezing points of certain binary solutions.

An ideal solution (6) is one in which no special force of attraction exists between the components of the solution, and no change in internal energy is produced on mixing. Under these conditions no change in the character of liquids is produced by mixing, merely a dilution of one liquid by the other. When two liquids are mixed to give an ideal solution, there is no heat effect, and the properties are strictly additive. While the freezing points of some binary solutions may theoretically be linear functions of the compositions, most of them exhibit maxima or minima. This means that, in the case of a minimum, a solution would have a freezing point lower than that of either of its pure components. The same type of phenomena is found in boiling points of solutions.

Several different types of composition--freezing point curves (22, 8) are exhibited by binary solutions. The following figures represent some of the simpler freezing point curves found in binary solutions. Figures 1 and 2 show freezing point depressions with two types of single minima, while Figure 3 is an example of compound formation with a congruent melting point. Figure 4 exhibits a maximum in a freezing point elevation.

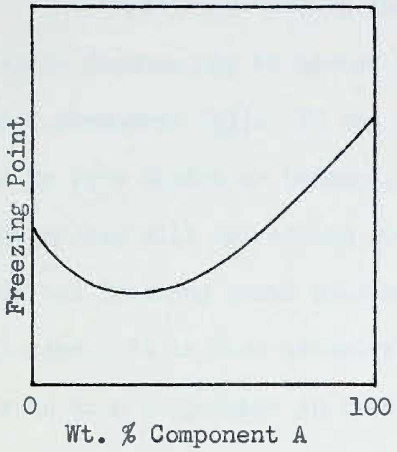

Fig. 1 Simple Freezing Point Depression

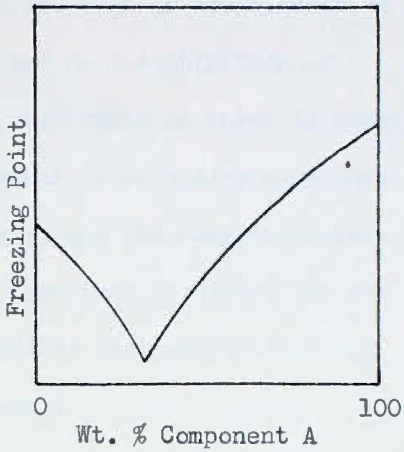

Fig. 2 Eutectic Freezing Point Depression

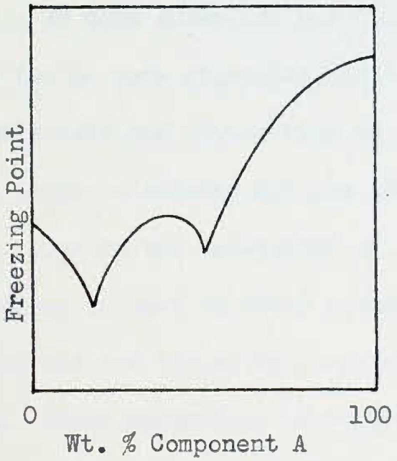

Fig. 3 Compound Freezing Point Depression

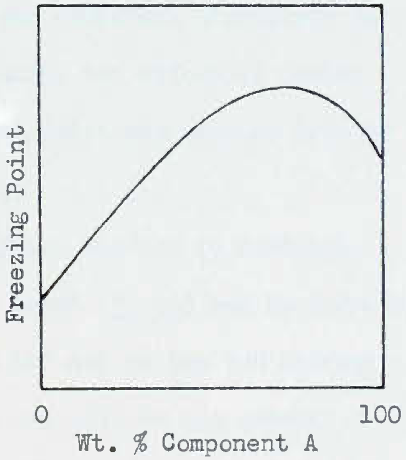

Fig. 4 Simple Freezing Point Elevation

The deviations causing abnormalities such as those shown in the above figures may be caused by any one or a combination of several phenomena (23). If one of the components is known to associate to form dimers or trimers, the number of effective molecules in the system will be reduced accordingly, and the observed lowering of the freezing point will be less than that predicted for the ideal case. It is also conceivably possible that association may occur in both components in some instances.

Another very common form of deviation occurs when components A and B partially combine in the liquid phase to form a third substance AB. In such cases, the deviation from ideality is often said to be due to solvation, or molecular compound formation.

In some cases the molecules of one component dissociate to form two or more molecules, thus increasing the effective number of molecules and giving rise to freezing point depressions greater than those calculated for the ideal case.

One of the mechanisms of interaction leading to nonideal solutions is that in which a "hydrogen bond" (9, 26) can be formed, making the A-B attraction greater than the A-A or the B-B attraction. Other mechanisms of association may well be the common dipolar (27) and induced dipolar (10) effects.

It is known that the freezing point of a binary system such as ethylene glycol-water is not a linear function of the composition (5). Rather, each component present tends to lower the freezing point of the other and the minimum freezing point of the system will be exhibited by compositions intermediate between the two pure substances. In this type of binary system the minimum freezing point is lower than that of either of the pure components. According to Romstatt (18) the eutectic point of the composition-freezing point curve of ethylene glycol-water occurs at 35 per cent water and -67°C.

It follows theoretically that in a ternary system each of the three components would tend to lower the freezing point of the other two and thereby the system as a whole would exhibit a greater freezing point depression than that found in the binary system designated above. It also follows that, given a minimum freezing point of a two-component system, such as ethylene glycol-water, the same freezing point depression would be accomplished in a three-component system, such as ethylene glycol--diethylene glycol--water, by the use of a smaller percentage of combined glycols.

No method has as yet been reported for calculating mathematically the freezing point lowering in a ternary system of volatile components. It is, therefore, the purpose of this investigation to determine experimentally whether there is a greater freezing point depression in the ternary system ethylene glycol--diethylene glycol--water than in either of the binary systems ethylene glycol--water or diethylene glycol--water and to determine quantitatively the differences in the freezing point depressions of these systems. It is the further purpose to determine other suitable physical constants for the identification of compositions and to gain additional information concerning the comparative desirabilities of these solutions as antifreezes.

METHOD OF INVESTIGATION

Since the freezing point of a solution is a function of its composition, it is necessary that an ample number of solutions of varying composition be studied in order to determine the type of freezing point curve and to locate the eutectic point, if one be present. The freezing point of any composition may be obtained from a smooth curve plotted from the experimental data. It is possible then from these curves to compare the differences in the freezing point depressions of the systems ethylene glycol--diethylene glycol--water, ethylene glycol--water, and diethlene glycol--water.

Theoretically freezing points and melting points are the same. However, in actual practice a small difference is found between the two values. Spangler and Davies (20) found in their work that the two values differed by 0.02° to 0.05°C. The difference may be greater, depending upon the method and apparatus used. Freezing points rather than melting points were chosen for this investigation because the value of an antifreeze substance is based upon the temperature at which it freezes or solidifies. As a matter of fact, the minimum safe temperature is actually below the freezing point. For an ethylene glycol--water solution that freezes at 0°F., Green, Lamprey, and Sommer (12) report that the minimum safe temperature is from -8.0° to -11.5°F. They further state that since this "safe" temperature varies with the composition, the only practical basis for determining antifreeze protection is the use of actual freezing points.

The value of an antifreeze substance also depends upon its boiling point. It is highly desirable that an antifreeze have a boiling point higher than that of water to prevent it from boiling off during use. Since it is not possible to calculate mathematically the boiling points of ternary solutions, the determination of these constants were included in the present study. Boiling points are also useful to a limited extent for identification of compositions.

Since the boiling point varies with atmospheric pressure, it becomes necessary to determine these constants for all solutions at the same pressure or to use a means for correcting to the same pressure the values read at various pressures of the atmosphere. One method of correcting boiling point temperatures at various barometric pressures to normal pressure involves the use of the Sydney Young equation (15).

$$C_c = 0.00012(760-P)(273+t_c) \qquad (1)$$

C_c is the correction to be made on the observed temperatures t_c on the Centigrade scale and P is the actual barometric pressure in millimeters of mercury. However, as pointed out by Hoyt (15), the Sydney Young equation is applicable only to non-polar substances with low lielectric constants. Ethylene glycol ($HOCH_2 \cdot CH_2OH$), diethylene glycol ($HO \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$), and water are all polar compounds; hence, this formula is not valid for the present work.

Equation (1) may be made applicable to other types of compounds by the substitution of K for the constant 0.00012, where K

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is given a specific value for each type of compound. The invalidity of this modification arises in the present work from the fact that no constant has been determined for the glycols. The matter is further complicated by the fact that the present investigation deals with solutions instead of pure liquids.

Other correction methods are given in the literature (24), but all involve a previous determination of constant values for each liquid or solution studied. Due to the foregoing difficulties encountered in corrections of boiling points from atmospheric to standard pressure, the method of determining boiling points at standard pressure was utilized in the present investigation.

A necessary criterion of a study of numerous solutions such as encountered in the present ternary system involves the use of some physical constants for identification purposes. It is highly desirable that these constants can be quickly and accurately determined. To conform with these specifications, the index of refraction (Abbé) and the relative density were chosen for the problem at hand (2, 13).

The interpretation of the accumulated data necessitates the plotting of a sufficient number of curves showing the relationship between physical constants and compositions.

EXPERIMENTAL

Materials Used

The ethylene glycol and the diethylene glycol were the purest grades commercially available from Paragon Laboratories Inc. They were not further pruified because of the impracticability of further purification for antifreeze use on a commercial scale. Distilled water was obtained from the laboratory supply and was not redistilled. The constants of the materials are shown in Table I.

TABLE I. PHYSICAL CONSTANTS OF MATERIALS USED

Ethylene Glycol

Constant	Literature	Experimental
n_D^{25}	1.4300 (20)	1.4321
D_4^{25}	$1.1101^{\#}$ (20)	1.1147
BP^{76}(°C)	197.2 (14)	195.4
FP(°C)	-13.2 (11)	-13.1

. . . .

\# absolute density
n_D^{25} indicates refractive index for the D line of sodium at 25°C.
d_4^{25} indicates density at 25°C. assuming the density of water as 1 at 4°C.
BP^{76} indicates boiling point determined at a pressure of 76 cm.
FP is freezing point

TABLE I. PHYSICAL CONSTANTS OF MATERIALS USED (Continued)

Diethylene Glycol

Constant	Literature	Experimental
n_D^{25}	1.4475* (20)	1.4467
d_4^{25}	1.1177* (14)	1.1169
BP^{76}(°C)	244.3 (11)	239.2
FP(°C)	-6.5 (14) -10.45 (14)	- - -

. . . .

Water

Constant	Literature	Experimental
n_D^{25}	1.3330* (15)	1.3345
d_4^{25}	0.99707 (15)	1.0010
BP^{76}(°C)	100.0	100.5
FP(°C)	0.0	-0.4

* determination made at 20°C.

Preparation of Samples

To be able to plot valid smooth curves and detect eutectic points, it was deemed necessary to make up solutions varying in composition by 10 per cent by weight. Master solutions of ethylene glycol and diethylene glycol were first made up varying by 10 per cent by weight from 100 per cent glycol to 100 per cent diethylene glycol. Six hundred grams of each composition was prepared.

TABLE II. COMPOSITION OF MASTER SOLUTIONS

	Composition (% by weight)	
Series Number	Ethylene Glycol	Diethylene Glycol
I	0	100
II	10	90
III	20	80
IV	30	70
V	40	60
VI	50	50
VII	60	40
VIII	70	30
IX	80	20
X	90	10
XI	100	0

From each of these series, solutions were made with water by varying the composition by 10 per cent steps, as shown in the example below.

TABLE III. EXAMPLE OF THE COMPOSITION OF TERNARY SOLUTIONS

Solution Number	Composition (% by weight) Series I	Water
1	100	0
2	90	10
3	80	20
4	70	30
5	60	40
6	50	50
7	40	60
8	30	70
9	20	80
10	10	90

One hundred gram samples of each of these final solutions were prepared. Thus a total of 110 solutions were prepared (including the two pure glycols). All solutions were weighed into Erlenmeyer flasks of appropriate size on an Ohaus trip balance. In the manner used, this balance had a sensitivity of 0.05 gram.

Freezing Points

A Beckmann molecular weight freezing point apparatus was used for all determinations. In place of a Beckmann differential thermometer, a low temperature, toluene-filled thermometer was employed.

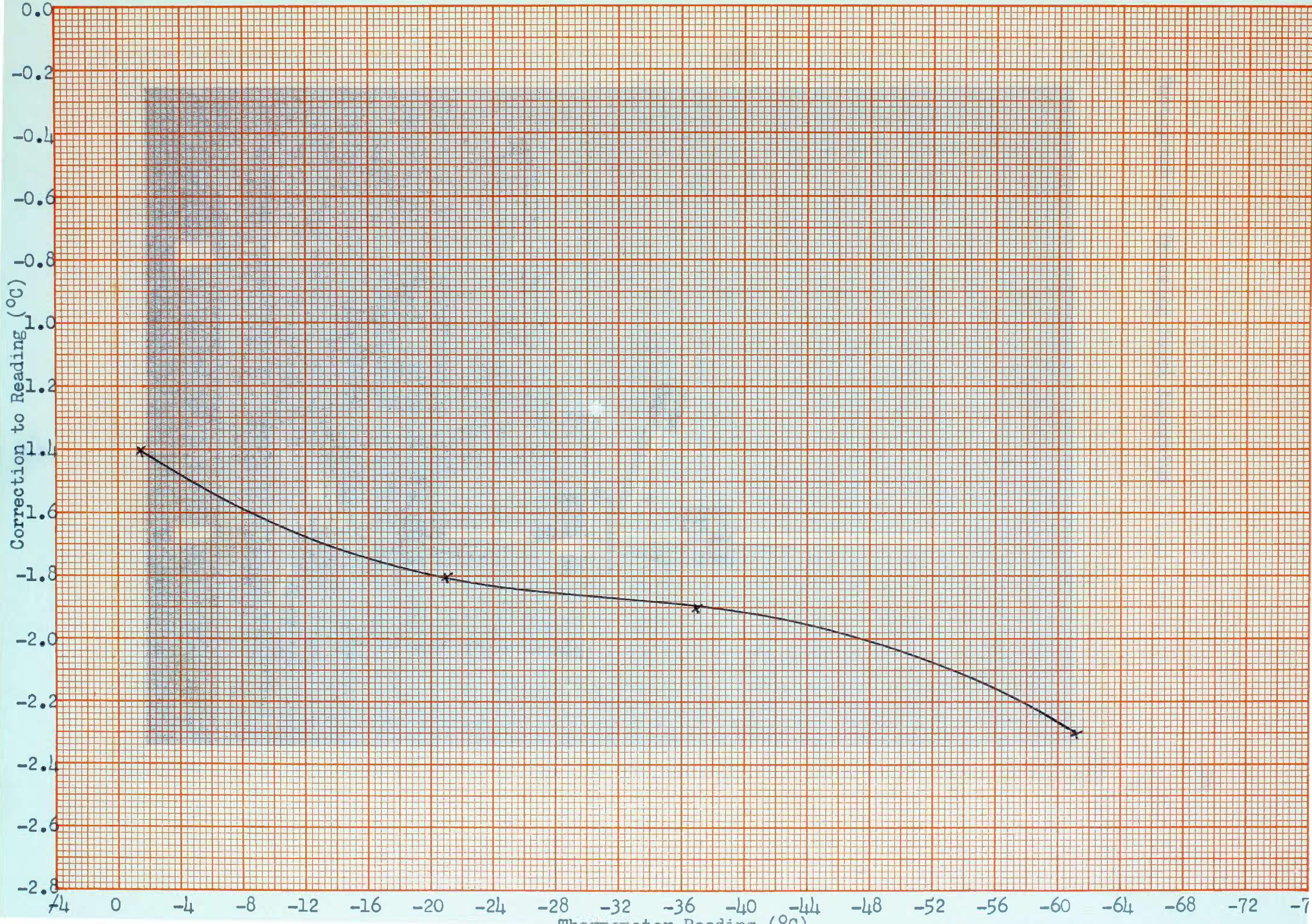
The thermometer was calibrated by determining the apparent freezing points of pure substances. No stem correction was necessary as the thermometer was used in the same position at all times in both calibration and determinations.

The chloroform and carbon tetrachloride samples used were redistilled from chemically pure laboratory stock. Only the middle third fraction was used. The water was redistilled from laboratory supply distilled water. It was collected through a block tin condenser and only the middle third fraction was used. The mercury was from redistilled laboratory stock.

TABLE IV. CALIBRATION OF FREEZING POINT THERMOMETER

Substance	Thermometer Reading	Freezing Point I.C.T. (16)	Correction
Water	+ 1.4°C	0.0°C	-1.4°C
CCl_4	-21.1	-22.9	-1.8
Mercury	-37.0	-38.87	-1.9
$CHCl_3$	-61.2	-63.5	-2.3

Figure 5. Freezing Point Thermometer Calibration



Photograph 1. Freezing Point Apparatus

Supercooling is usually present in any freezing point determination. To overcome this, the solution being frozen was stirred almost continually and somewhat vigorously near the freezing point. As soon as a few crystals appeared, the solution was removed from the freezing bath and stirred slowly until the temperature rose to a value that was constant for several seconds (19). It was found to be a matter of only a few seconds until the temperature lowering due to supercooling disappeared. Due to this technique, little error was introduced by the supercooling effect.

With a few exceptions none of the solutions containing less than 40 per cent water exhibited freezing points. Instead, these solutions simply became very viscous at low temperatures--with no crystallization even when cooled to 40 or 50 degrees below the extrapolated freezing points.

A mixture of approximately equal parts of methanol and crushed solid carbon dioxide served as the freezing mixture in all cases. The average temperature attained was -78°C.

Due to water vapor in the air, frost appeared on the walls of the air chamber. Since this condition reduced the visibility, it had to be completely eliminated. At times it was found difficult even under the most favorable visibility conditions to detect crystal formation. A small amount of dehydrated calcium chloride in the bottom of the air chamber reduced frost formation only slightly. Blowing dry air into the chamber before assembly was likewise ineffective. It was found that a few milliliters of methanol in the bottom of the air chamber was entirely satisfactory.

For those solutions freezing below -45°C., it was necessary to fill the air chamber with methanol because air was not a good enough conductor to bring the temperature of the sample to within 30 degrees of that of the freezing mixture.

A minimum of three readings were taken on each solution. In most cases at least four were recorded. The values shown in the following tables are the arithmetic means of the determinations. The average deviations (3) of the readings farthest from the means ranged from 0.15° near -2°C. to 0.47° near -46°C. A few erratic readings were completely discarded (4).

TABLE V. BINARY FREEZING POINTS: ETHYLENE GLYCOL--WATER

Composition	Freezing Point (°C)		
Ethylene Glycol (Weight %)	Present Work	Conrad, Hill, and Ballman (2)	Bureau of Standards (20)
0	-0.4	- - -	0.0
10	-3.6	-3.6	-2.9
20	-8.8	-8.3	-9.7
30	-16.0	-14.4	-17.6
40	-25.2	-22.6	-26.0
50	-38.6	-34.6	-37.0
60	-53.8	-49.3	- - -
90	-31.8	- - -	- - -
100	-13.1	-13.5	- - -

TABLE VI. BINARY FREEZING POINTS: DIETHYLENE GLYCOL--WATER

Composition	Freezing Point (°C)	
Diethylene Glycol (Weight %)	Present Work	Literature (14)
0	-0.4	0.0
10	-2.0	- - -
20	-5.1	- - -
30	-10.0	- - -
40	-17.3	- - -
50	-27.8	- - -
60	-42.7	- - -
100	- - -	-10.45

TABLE VII. BINARY FREEZING POINTS: ETHYLENE GLYCOL--DIETHYLENE GLYCOL

Composition	Freezing Point (°C)	
Ethylene Glycol (Weight %)	Present Work	Literature (14)
0	- - -	-10.45
10	- - -	- - -
20	-24.7	- - -
30	- - -	- - -
40	- - -	- - -
50	- - -	- - -
60	- - -	- - -
70	-29.0	- - -
80	-21.8	- - -
90	-18.8	- - -
100	-13.1	-13.5*

* Reference (2).

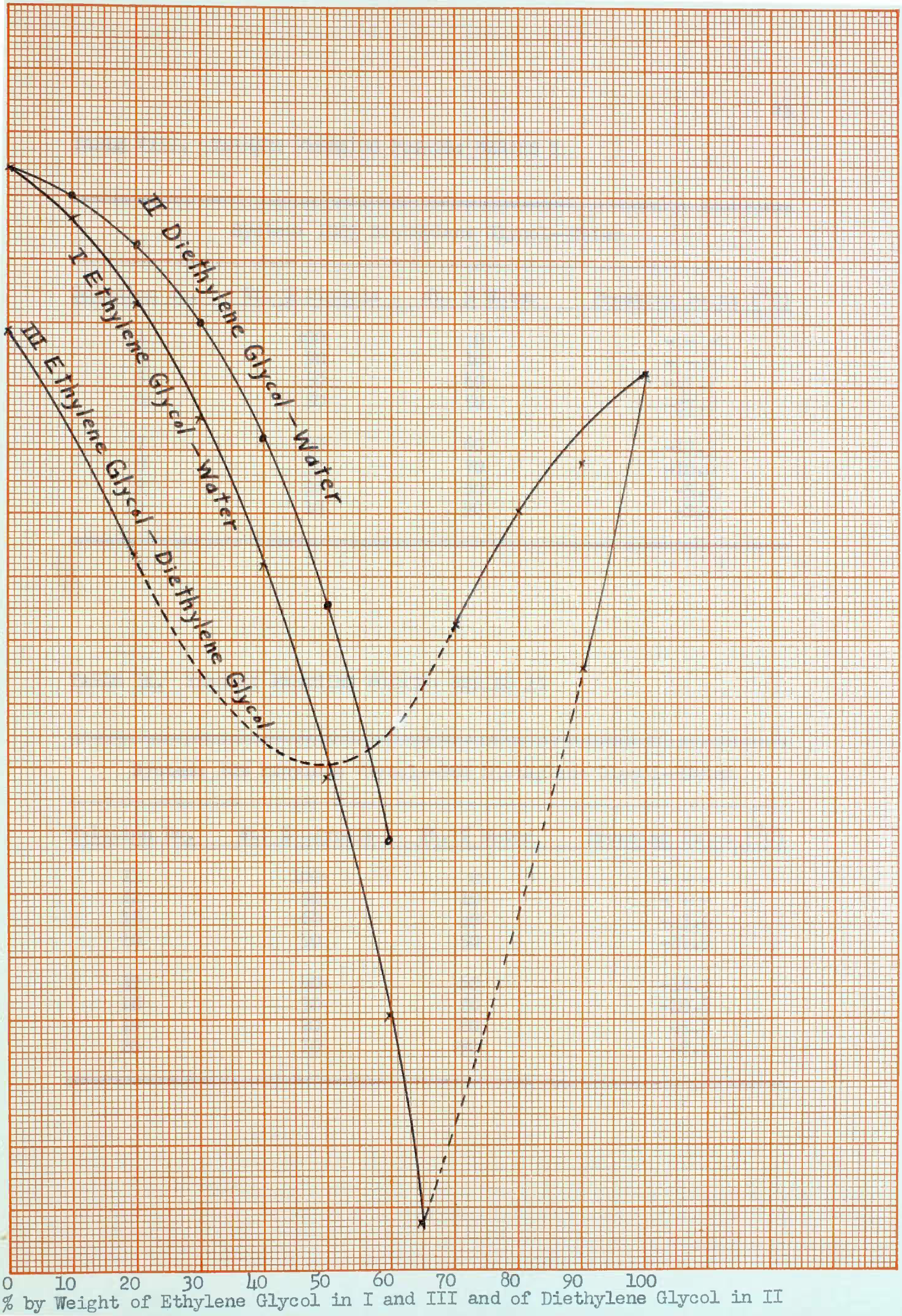

II Diethylene Glycol - Water
I Ethylene Glycol - Water
III Ethylene Glycol - Diethylene Glycol
0
10
20
30
40
50
60
70
80
90
100
% by Weight of Ethylene Glycol in I and III and of Diethylene Glycol in II

TABLE VIII. TERNARY FREEZING POINTS: SERIES I

System: 100% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
1	100	0	- - -
2	90	10	- - -
5	50	40	-42.7
6	50	50	-27.8
7	40	60	-17.3
8	30	70	-10.0
9	20	80	-5.1
10	10	90	-2.0

TABLE IX. TERNARY FREEZING POINTS: SERIES II

System: 10% Ethylene Glycol--90% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
11	100	0	- - -
12	90	10	- - -
15	60	40	-43.6
16	50	50	-28.9
17	40	60	-18.3
18	30	70	-10.8
19	20	80	-5.8
20	10	90	-2.4

TABLE X. TERNARY FREEZING POINTS: SERIES III

System: 20% Ethylene Glycol—80% Diethylene Glycol—Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
21	100	0	-24.7
22	90	10	- - -
25	60	40	-44.4
26	50	50	-30.1
27	40	60	-19.1
28	30	70	-11.6
29	20	80	-6.3
30	10	90	-2.8

TABLE XI. TERNARY FREEZING POINTS: SERIES IV

System: 30% Ethylene Glycol—70% Diethylene Glycol—Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
31	100	0	- - -
32	90	10	- - -
35	60	40	-45.1
36	50	50	-30.8
37	40	60	-20.2
38	30	70	-12.2
39	20	80	-6.5
40	10	90	-2.6

TABLE XII. TERNARY FREEZING POINTS: SERIES V

System: 40% Ethylene Glycol--60% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
41	100	0	- - -
42	90	10	- - -
45	60	40	-45.7
46	50	50	-31.6
47	40	60	-21.1
48	30	70	-12.5
49	20	80	-6.8
50	10	90	-2.9

TABLE XIII. TERNARY FREEZING POINTS: SERIES VI

System: 50% Ethylene Glycol--50% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
51	100	0	- - -
52	90	10	- - -
55	60	40	-46.0
56	50	50	-32.9
57	40	60	-21.9
58	30	70	-13.4
59	20	80	-7.0
60	10	90	-3.1

TABLE XIV. TERNARY FREEZING POINTS: SERIES VII

System: 60% Ethylene Glycol--40% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
61	100	0	- - -
62	90	10	- - -
65	60	40	-46.2
66	50	50	-33.4
67	40	60	-22.6
68	30	70	-13.9
69	20	80	-7.3
70	10	90	-3.0

TABLE XV. TERNARY FREEZING POINTS: SERIES VIII

System: 70% Ethylene Glycol--30% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
71	100	0	-29
72	90	10	- - -
75	60	40	-49.2
76	50	50	-34.4
77	40	60	-23.8
78	30	70	-14.5
79	20	80	-7.7
80	10	90	-3.4

TABLE XVI. TERNARY FREEZING POINTS: SERIES IX

System: 80% Ethylene Glycol--20% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
81	100	0	-21.8
82	90	10	- - -
85	60	40	-49.9
86	50	50	-35.4
87	40	60	-24.5
88	30	70	-15.0
89	20	80	-8.3
90	10	90	-3.3

TABLE XVII. TERNARY FREEZING POINTS: SERIES X

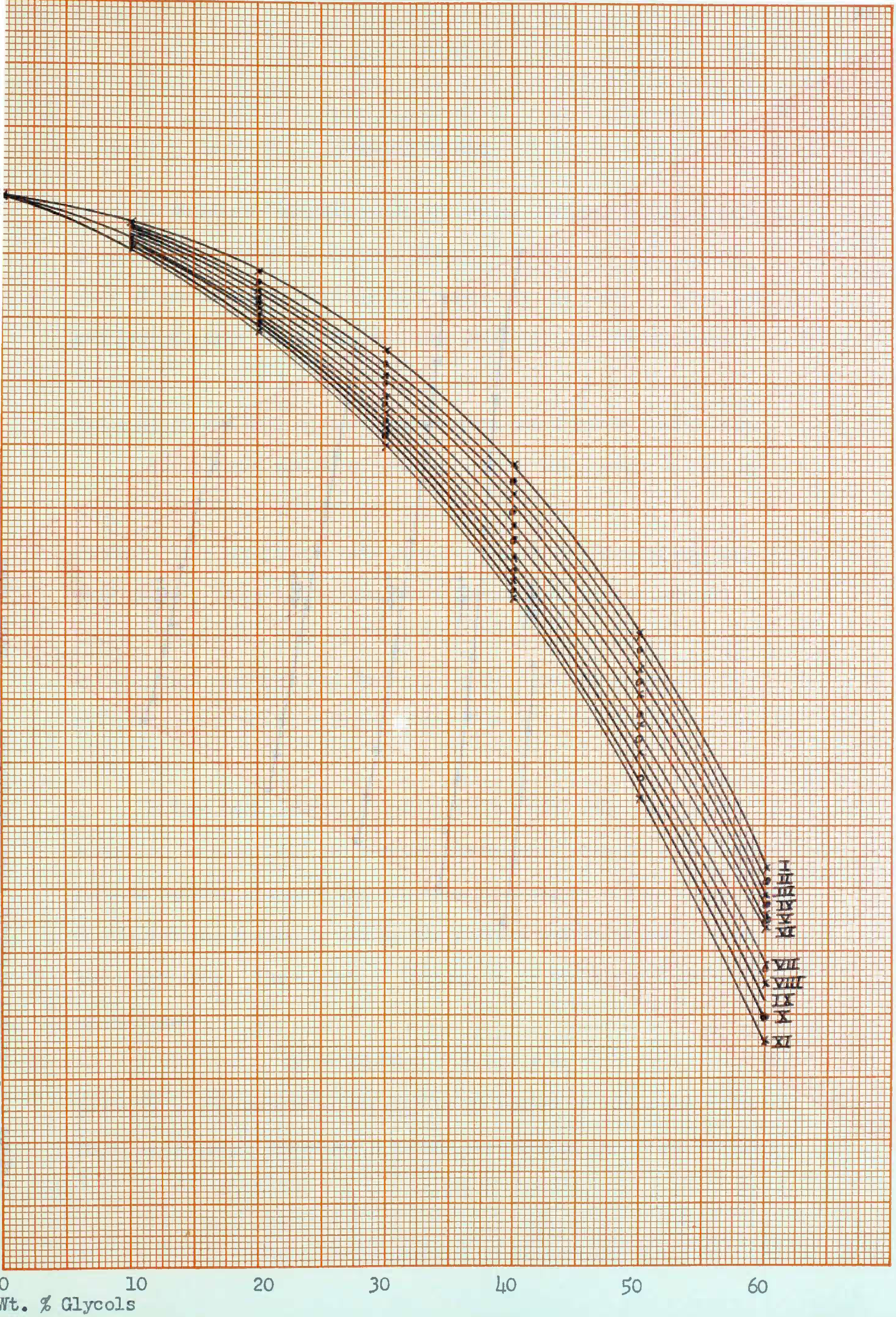
System: 90% Ethylene Glycol--10% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
91	100	0	-18.8
92	90	10	- - -
95	60	40	-52.2
96	50	50	-37.0
97	40	60	-25.6
98	30	70	-15.2
99	20	80	-8.3
100	10	90	-3.4

TABLE XVIII. TERNARY FREEZING POINTS: SERIES XI

System: 100% Ethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Freezing Point (°C)
101	100	0	-13.1
102	90	10	-31.8
105	60	40	-53.5
106	50	50	-38.3
107	40	60	-25.2
108	30	70	-16.0
109	20	80	-8.8
110	10	90	-3.6
111	0	100	-0.3


I
II
III
IV
V
VI
VII
VIII
IX
X
XI
0
10
20
30
40
50
60
Wt. % Glycols

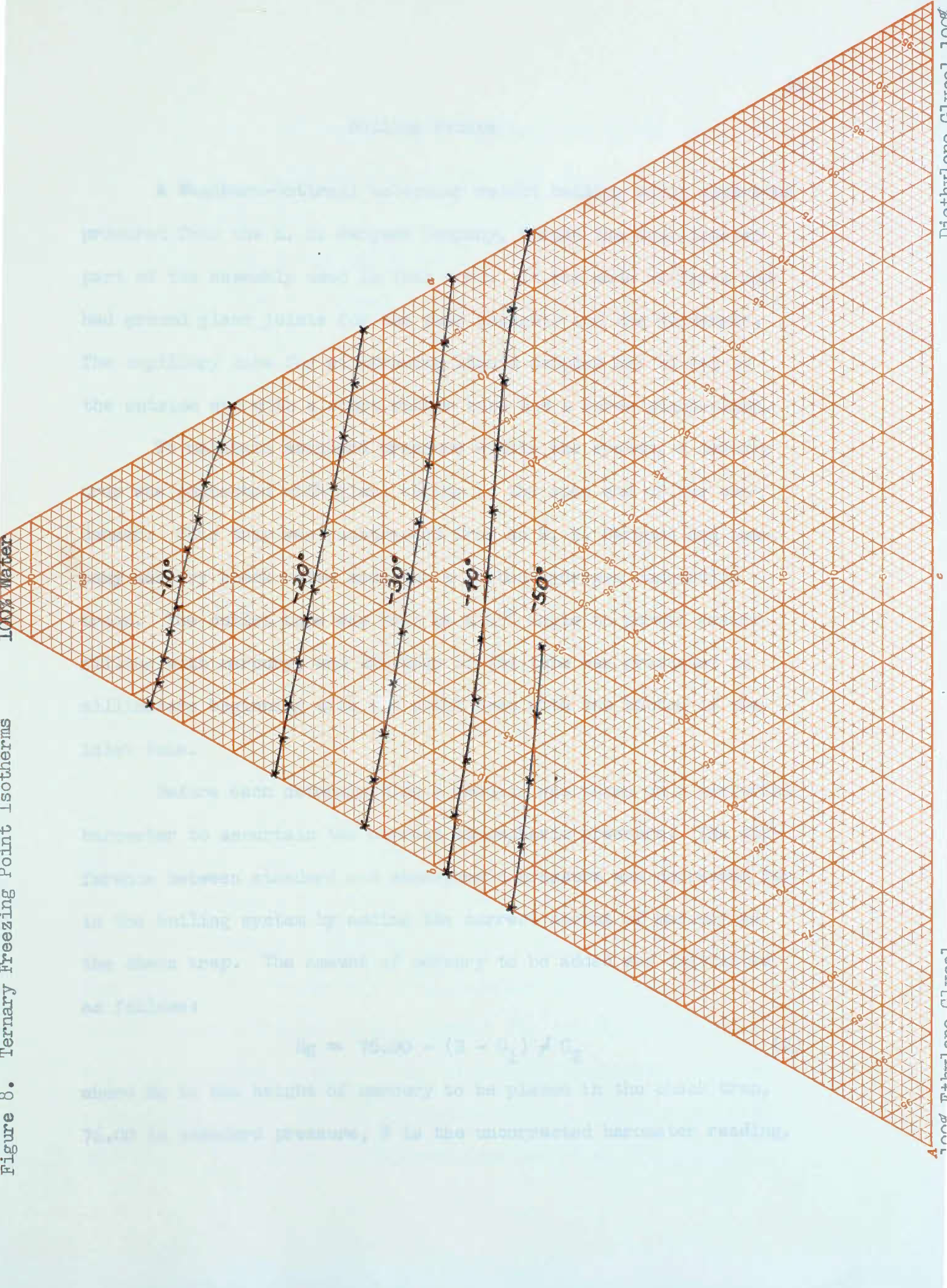


Figure 8. Ternary Freezing Point Isotherms

Boiling Points

A Washburn-Cottrell molecular weight boiling point apparatus procured from the E. H. Sargent Company, formed the ebulliometer part of the assembly used in this work. It was made of Pyrex and had ground glass joints for the pump assembly and the condenser. The capillary tube for withdrawing liquid samples was closed at the outside end with a short rubber tube and a screw pinch-clamp.

To maintain standard pressure within the system, a mercury trap was connected with glass tubing to the open end of the condenser. This trap was constructed from an E. H. Sargent and Company mercury check valve made for a carbon-hydrogen combustion train. The outlet tube was bent to a 45° angle to permit easier filling with mercury, and the body of the tube was graduated in millimeters beginning with the point even with the bottom of the inlet tube.

Before each determination a reading was taken on a mercurial barometer to ascertain the correct atmospheric pressure. The difference between standard and atmospheric pressure was corrected for in the boiling system by adding the correct amount of mercury to the check trap. The amount of mercury to be added was calculated as follows:

$$Hg = 76.00 - (B - C_1) + C_2 \qquad (2)$$

where Hg is the height of mercury to be placed in the check trap, 76.00 is standard pressure, B is the uncorrected barometer reading,

C_1 the correction for the barometer reading, and C_2 the temperature correction for the mercury in the trap. All values are heights of mercury in centimeters.

Before the burner under the boiler was lighted, the system was entirely closed. Heating caused expansion of the entrapped air, which increased the pressure of the system. When the pressure exceeded seventy-six centimeters, the excess bubbled out through the mercury in the trap.

The boiling point was detected by the constant temperature registered on the thermometer. A small temperature fluctuation was observed at the boiling point. This ranged from about 0.4 degree near the boiling point of water to approximately 2 degrees at the boiling points of those solutions containing 10 per cent water. The mean of this fluctuation was taken as the boiling point. Only one determination of each solution was deemed necessary.

The thermometer was a mercury filled, yellow back, partial immersion type with a range of -10° to $\neq 250^\circ C$. It was calibrated against an Eimer and Amend EA39 mercury filled, standard thermometer. The standard thermometer was calibrated by the National Bureau of Standards on December 22, 1948, and carried the number NBS93594. Both thermometers were graduated only in degrees. Readings were estimated to 0.1 degree. The calibration of the experimental thermometer was carried out in the complete Cottrell ebulliometer with a bath of diethylene glycol. The experimental thermometer was placed in the exact position it was to occupy during the boiling point determinations, and the standard thermometer was placed so that the bulbs of the two were together. Since the standard was of the total immersion type, a third thermometer was attached to the standard by means of rubber bands for the purpose of calculating stem correction. The bulb of the stem-correction thermometer was shifted with changing temperatures to keep it in the middle of the emergent stem of the standard thermometer (25).

The stem correction was calculated for the standard thermometer by the equation (28):

$$S.C. = Kn(T^{\circ} - t^{\circ}), \tag{3}$$

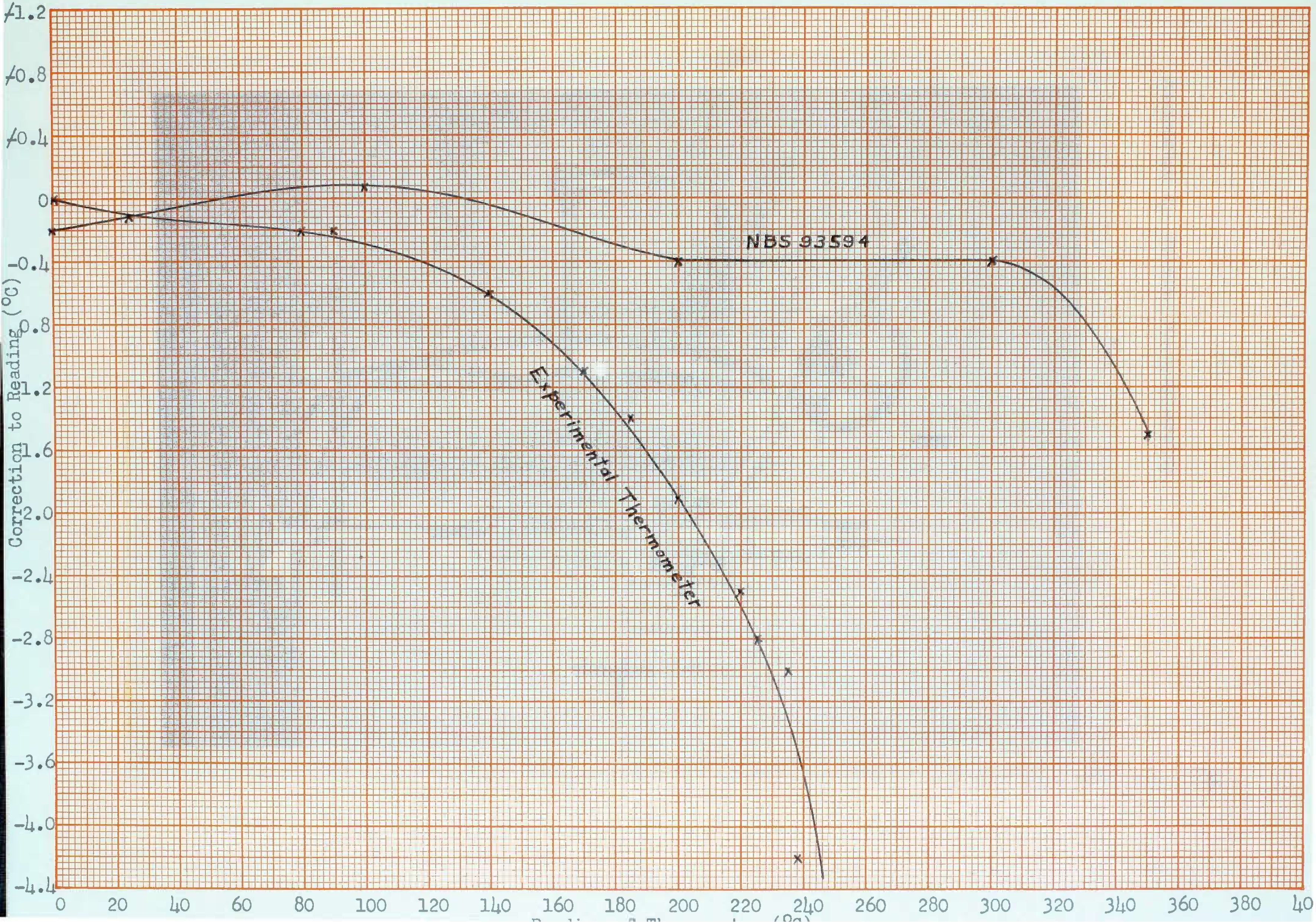
where K is the differential expansion coefficient of mercury in glass ($K = 0.00016$), n is the number of degrees emergent from the bath, T° the temperature of the bath, and t° the mean temperature of the emergent stem.

TABLE XIX. CALIBRATION OF BOILING POINT THERMOMETER

Temperatures (°C)

Reading of Standard Thermo., T°	Emergent Stem Temp., t°	Stem Corr.	NBS Corr.	True Temp.	Reading of Exp. Thermo.	Correction to Exp. Thermo.
0.0	----	----	-0.2	-0.2	-0.2	0.0
25.0	----	----	-0.1	+24.9	+ 25.0	-0.1
79.7	----	----	+0.1	79.8	80.0	-0.2
89.7	----	----	+0.08	89.8	90.0	-0.2
139.4	45.0	0.04	-0.05	139.4	140.0	-0.6
168.5	51.2	0.59	-.24	168.9	170.0	-1.1
183.0	54.5	0.95	-0.34	183.6	185.0	-1.4
197.0	57.8	1.34	-0.39	198.0	200.0	-2.0
216.0	63.0	1.93	-0.40	217.5	220.0	-2.5
220.5	63.0	2.10	-0.40	222.2	225.0	-2.8
230.0	67.7	2.42	-0.40	232.0	235.0	-3.0
231.8	71.0	2.44	-0.40	233.8	238.0	-4.2

Figure 9. Boiling Point Thermometer Calibration



Photograph 2. Boiling Point Apparatus

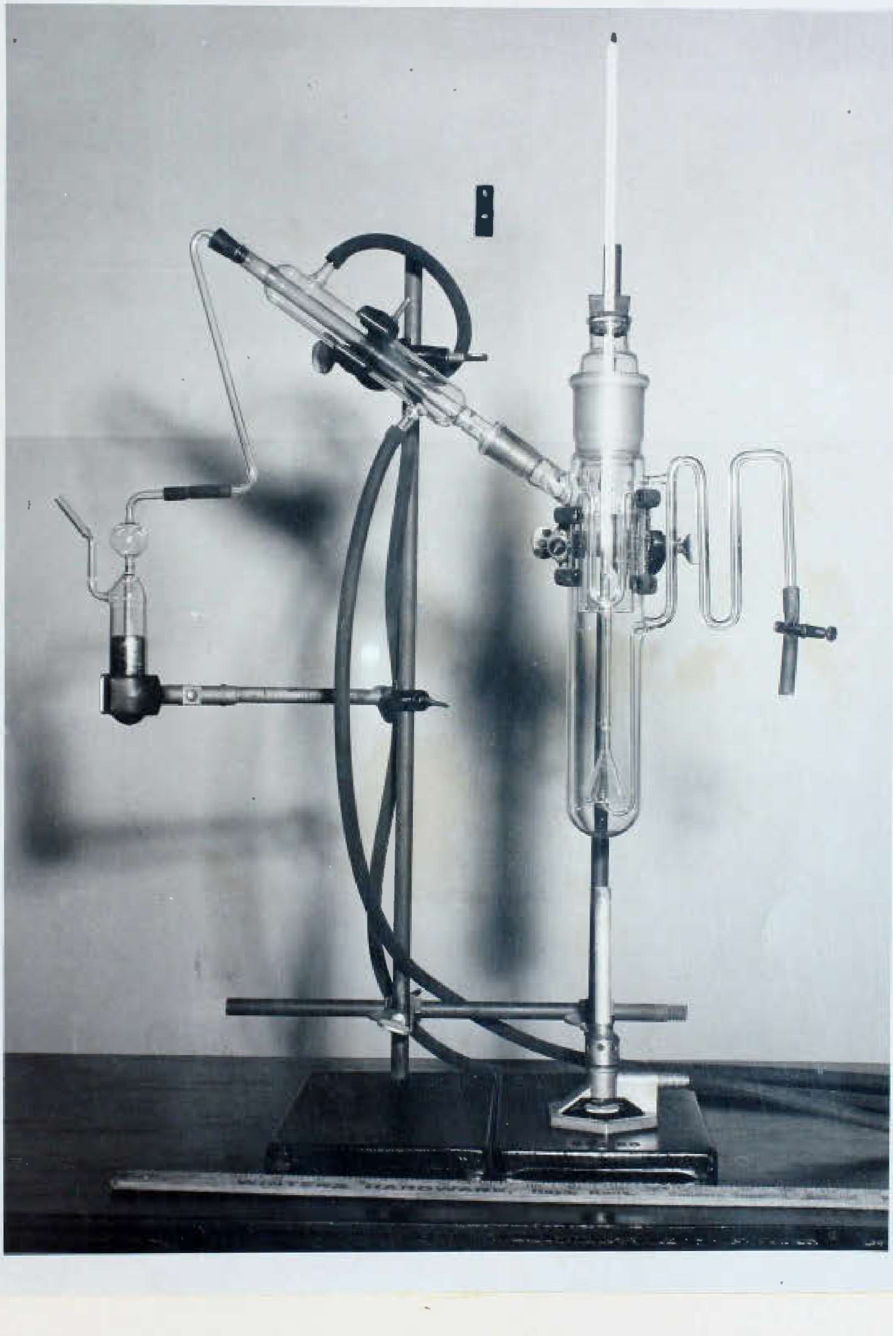


TABLE XX. BINARY BOILING POINTS: ETHYLENE GLYCOL--WATER

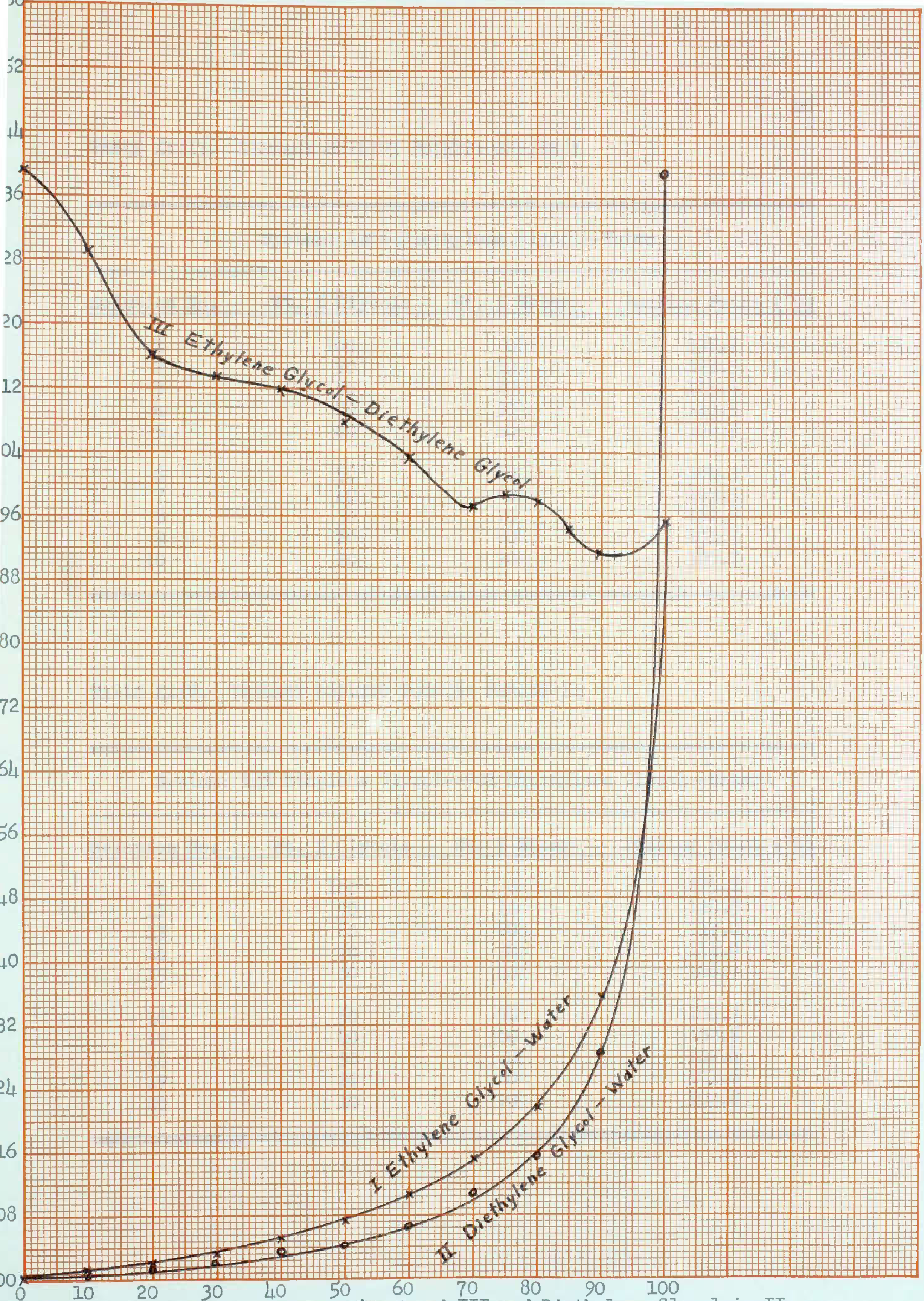
Composition	Boiling Point (°C)	
Ethylene Glycol (Weight %)	Present Work	Literature (11)
0	100.5	100.0
10	101.4	- - -
20	102.0	- - -
30	103.4	- - -
40	105.0	- - -
50	107.6	- - -
60	110.5	- - -
70	115.3	- - -
80	121.7	- - -
90	135.7	- - -
100	195.4	197.4

TABLE XXI. BINARY BOILING POINTS: DIETHYLENE GLYCOL--WATER

Composition	Boiling Point (°C)	
Diethylene Glycol (Weight %)	Present Work	Literature (11)
0	100.5	100.0
10	100.7	- - -
20	101.7	- - -
30	102.5	- - -
40	103.5	- - -
50	104.3	- - -
60	106.7	- - -
70	110.5	- - -
80	115.6	- - -
90	128.5	- - -
100	239.2	244.3

TABLE XXII. BINARY BOILING POINTS: ETHYLENE GLYCOL--DIETHYLENE GLYCOL

Composition	Boiling Point (°C)	
Ethylene Glycol (Weight %)	Present Work	Literature (11)
0	239.2	244.3
10	229.2	- - -
20	216.5	- - -
30	213.8	- - -
40	211.9	- - -
50	207.8	- - -
60	203.4	- - -
70	197.4	- - -
75	198.8	- - -
80	198.1	- - -
85	194.6	- - -
90	191.6	- - -
100	195.4	197.4



% by Weight of Ethylene Glycol in I and III and Diethylene Glycol in II

TABLE XXIII. TERNARY BOILING POINTS: SERIES I

System: 100% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
1	100	0	239.2
2	90	10	128.5
3	80	20	115.6
4	70	30	110.5
5	60	40	106.7
6	50	50	104.3
7	40	60	103.5
8	30	70	102.5
9	20	80	101.7
10	10	90	100.7

TABLE XXIV. TERNARY BOILING POINTS: SERIES II

System: 10% Ethylene Glycol--90% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
11	100	0	229.2
12	90	10	128.5
13	80	20	117.0
14	70	30	111.0
15	60	40	106.7
16	50	50	104.7
17	40	60	103.5
18	30	70	102.4
19	20	80	101.6
20	10	90	100.8

TABLE XXV. TERNARY BOILING POINTS: SERIES III

System: 20% Ethylene Glycol--80% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
21	100	0	216.5
22	90	10	128.5
23	80	20	116.6
24	70	30	111.8
25	60	40	107.9
26	50	50	104.7
27	40	60	103.5
28	30	70	102.6
29	20	80	101.7
30	10	90	100.0

TABLE XXVI. TERNARY BOILING POINTS: SERIES IV

System: 30% Ethylene Glycol--70% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
31	100	0	213.8
32	90	10	131.4
33	80	20	118.8
34	70	30	111.7
35	60	40	108.1
36	50	50	105.7
37	40	60	103.9
38	30	70	102.7
39	20	80	101.9
40	10	90	100.7

TABLE XXVII. TERNARY BOILING POINTS: SERIES V

System: 40% Ethylene Glycol--60% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
41	100	0	211.9
42	90	10	131.0
43	80	20	118.2
44	70	30	112.6
45	60	40	108.7
46	50	50	104.7
47	40	60	103.9
48	30	70	102.9
49	20	80	102.0
50	10	90	101.2

TABLE XXVIII. TERNARY BOILING POINTS: SERIES VI

System: 50% Ethylene Glycol--50% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
51	100	0	207.8
52	90	10	133.0
53	80	20	119.6
54	70	30	113.0
55	60	40	108.7
56	50	50	105.8
57	40	60	104.4
58	30	70	103.0
59	20	80	102.1
60	10	90	101.0

TABLE XXIX. TERNARY BOILING POINTS: SERIES VII

System: 60% Ethylene Glycol--40% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
61	100	0	203.4
62	90	10	132.7
63	80	20	119.6
64	70	30	113.6
65	60	40	108.7
66	50	50	106.6
67	40	60	104.1
68	30	70	103.0
69	20	80	102.2
70	10	90	101.1

TABLE XXX. TERNARY BOILING POINTS: SERIES VIII

System: 70% Ethylene Glycol--30% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
71	100	0	198.3
72	90	10	132.8
73	80	20	119.7
74	70	30	114.0
75	60	40	109.1
76	50	50	106.8
77	40	60	104.7
78	30	70	103.2
79	20	80	102.2
80	10	90	101.2

TABLE XXXI. TERNARY BOILING POINTS: SERIES IX

System: 80% Ethylene Glycol--20% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
81	100	0	198.1
82	90	10	136.4
83	80	20	121.6
84	70	30	114.6
85	60	40	109.7
86	50	50	106.9
87	40	60	104.9
88	30	70	103.3
89	20	80	102.1
90	10	90	101.0

TABLE XXXII. TERNARY BOILING POINTS: SERIES X

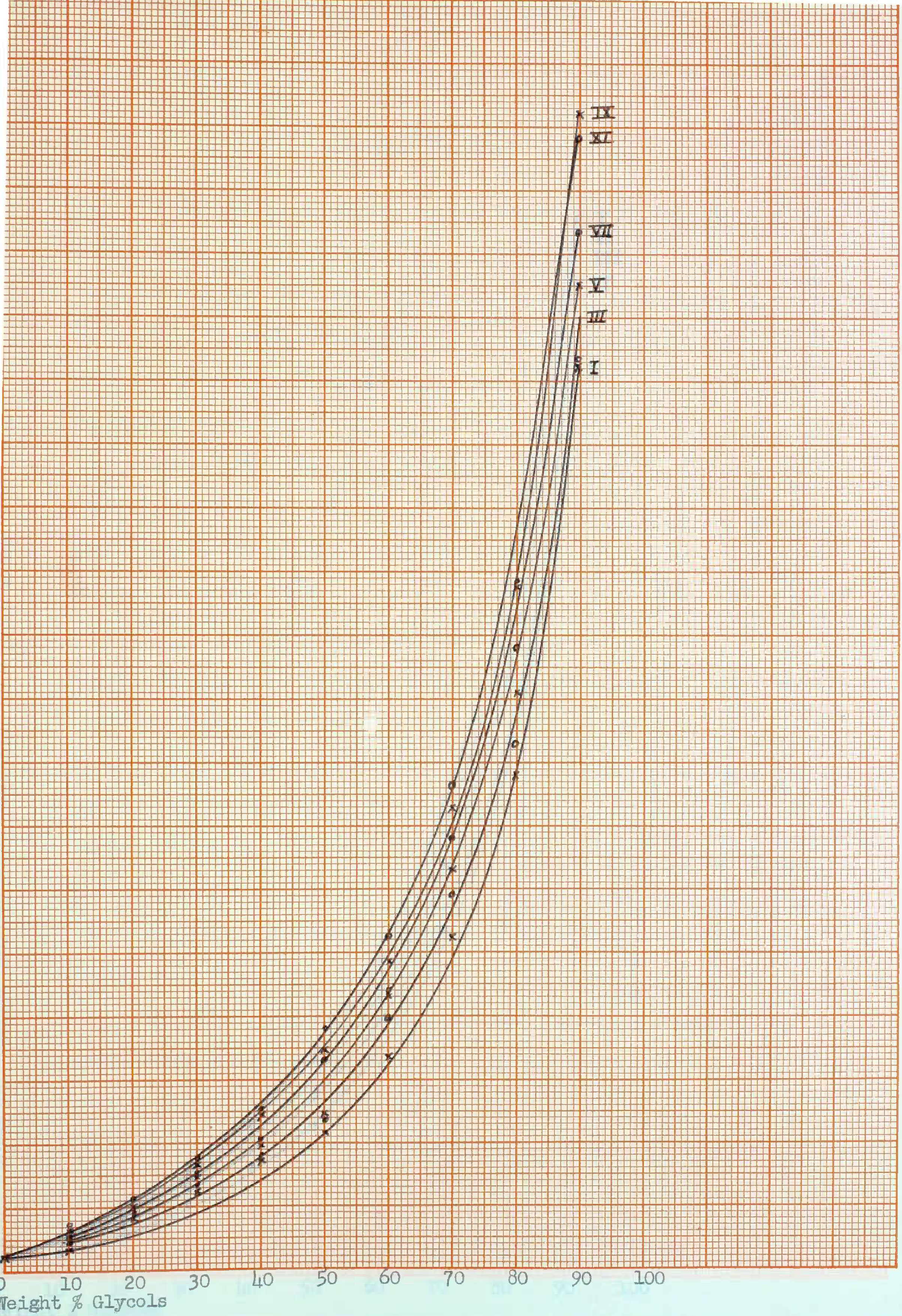
System: 90% Ethylene Glycol--10% Diethylene Glycol--Water

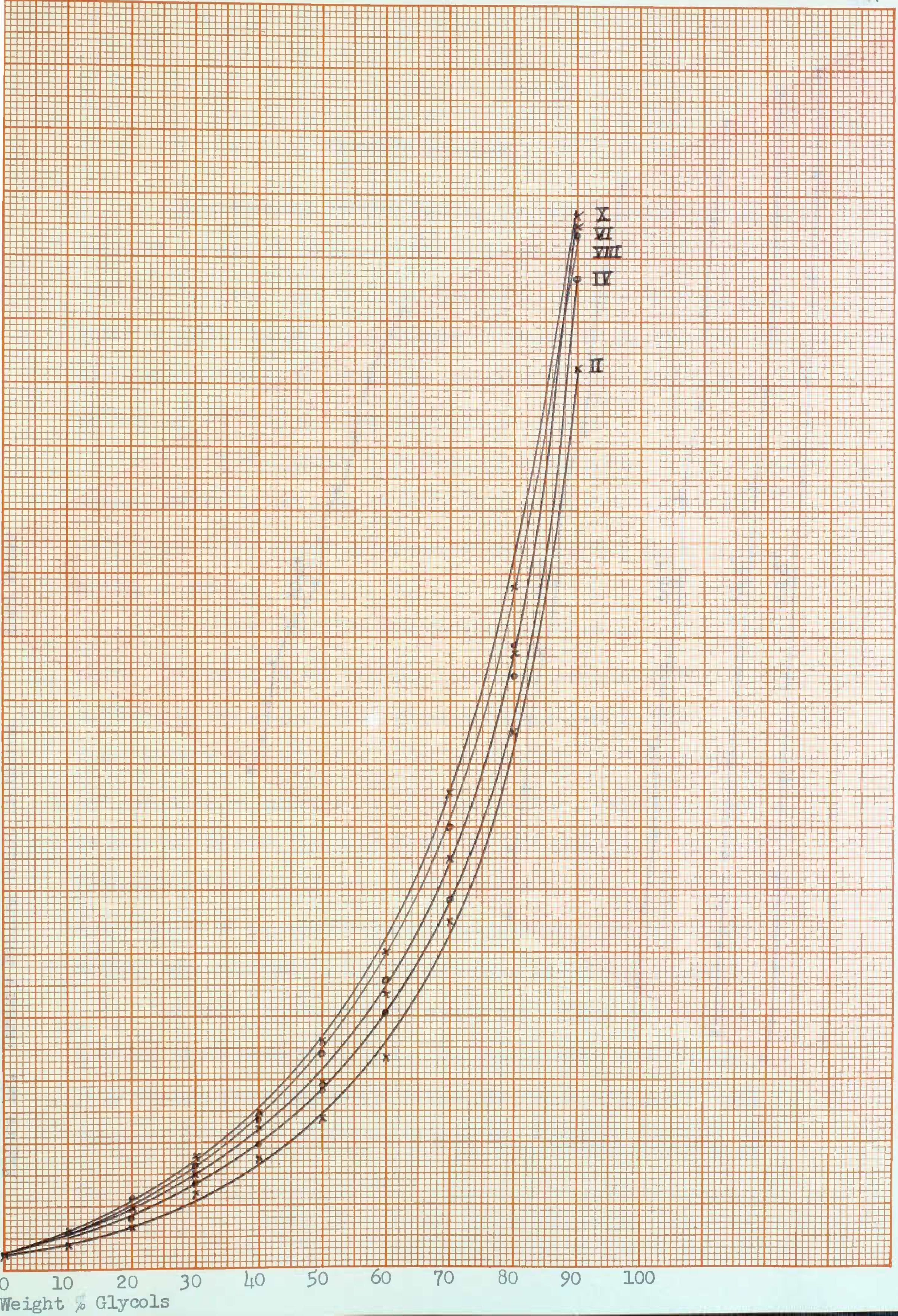
Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
91	100	0	191.6
92	90	10	133.3
93	80	20	121.6
94	70	30	115.1
95	60	40	110.0
96	50	50	107.2
97	40	60	104.7
98	30	70	103.5
99	20	80	102.1
100	10	90	101.2

TABLE XXXVIII. TERNARY BOILING POINTS: SERIES XI

System: 100% Ethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Boiling Point (°C)
101	100	0	195.4
102	90	10	135.7
103	80	20	121.7
104	70	30	115.3
105	60	40	110.5
106	50	50	107.6
107	40	60	105.0
108	30	70	103.4
109	20	80	102.0
110	10	90	[illegible].4
111	0	100	100.5


IX
XI
VII
V
III
I
0
10
20
30
40
50
60
70
80
90
100
Weight % Glycols


X
VI
VIII
IV
II
0
10
20
30
40
50
60
70
80
90
100
Weight % Glycols

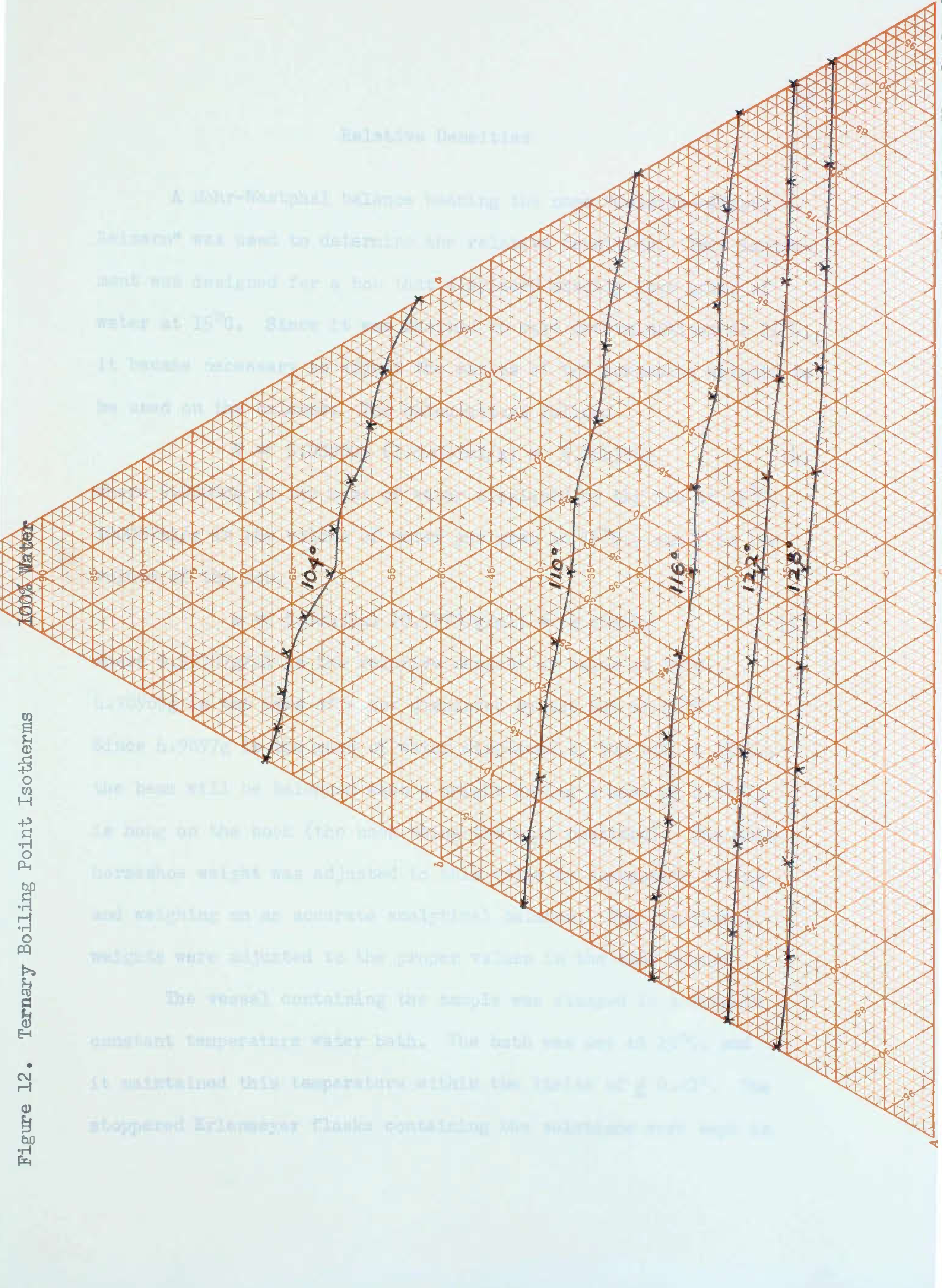


Figure 12. Ternary Boiling Point Isotherms

Relative Densities

A Mohr-Westphal balance bearing the name "Celsius--Körper n. Reimann" was used to determine the relative densities. This instrument was designed for a bob that displaced exactly five grams of water at 15°C. Since it was desired to make determinations at 25°C., it became necessary to adjust the masses of the horseshoe weights to be used on the balance. The calculations follow:

$$V = 5.00000g\ (1.00087ml/g) = 5.00435ml \qquad (4)$$

where 5.00000g is the mass of water displaced by the bob at 15°C., 1.00087ml/g is the volume of water per gram at 15°C., and V is the volume of the bob.

$$m = 5.00435ml\ (0.99707g/ml) = 4.98969g \qquad (5)$$

where 0.99707g/ml is the relative density of water at 25°C., 4.98969g is the mass of water displaced by the bob at 25°C. Since 4.9897g is the mass of water displaced by the bob at 25°C., the beam will be balanced when a weight having a mass of 4.9897g is hung on the hook (the hook being the unit position). The unit horseshoe weight was adjusted to this value by successive filing and weighing on an accurate analytical balance. The fractional weights were adjusted to the proper values in the same manner.

The vessel containing the sample was clamped in a Sargent constant temperature water bath. The bath was set at 25°C. and it maintained this temperature within the limits of ± 0.01°. The stoppered Erlenmeyer flasks containing the solutions were kept in the bath for at least one hour before they were poured into the weighing vessel.

A minimum of three readings was taken on each solution. The mean was used as the correct value. On the average the readings farthest from the mean deviated from the mean by about two points in the fourth decimal place.

TABLE XXXIV. BINARY DENSITIES: ETHYLENE GLYCOL--WATER

Composition	Relative Densities (d_4^{25})	
Ethylene Glycol (Weight %)	Present Work	Spangler & Davies (20)
0	1.0001	0.9970
10	0.0138	0.0097
20	1.0267	1.0231
30	1.0407	1.0367
40	1.0543	1.0495
50	1.0661	1.0619
60	1.0778	1.0733
70	1.0889	1.0848
80	1.0989	1.0946
90	1.1067	1.1032
100	1.1137	1.1101

TABLE XXXV. BINARY DENSITIES: DIETHYLENE GLYCOL--WATER

Composition	Relative Densities (d_4^{25})	
Diethylene Glycol (Weight %)	Present Work	Literature*
0	1.0001	
10	1.0141	
20	1.0291	
30	1.0437	
40	1.0592	
50	1.0729	
60	1.0859	
70	1.0970	
80	1.1056	
90	1.1128	
100	1.1159	

*No values given in the literature.

TABLE XXXVI. BINARY DENSITIES: ETHYLENE GLYCOL--DIETHYLENE GLYCOL

Composition	Relative Densities (d_4^{25})	
Ethylene Glycol (Weight %)	Present Work	Literature*
0	1.1159	
10	1.1159	
20	1.1158	
30	1.1156	
40	1.1157	
50	1.1150	
60	1.1155	
70	1.1143	
80	1.1142	
90	1.1138	
100	1.1137	

*No values given in the literature.

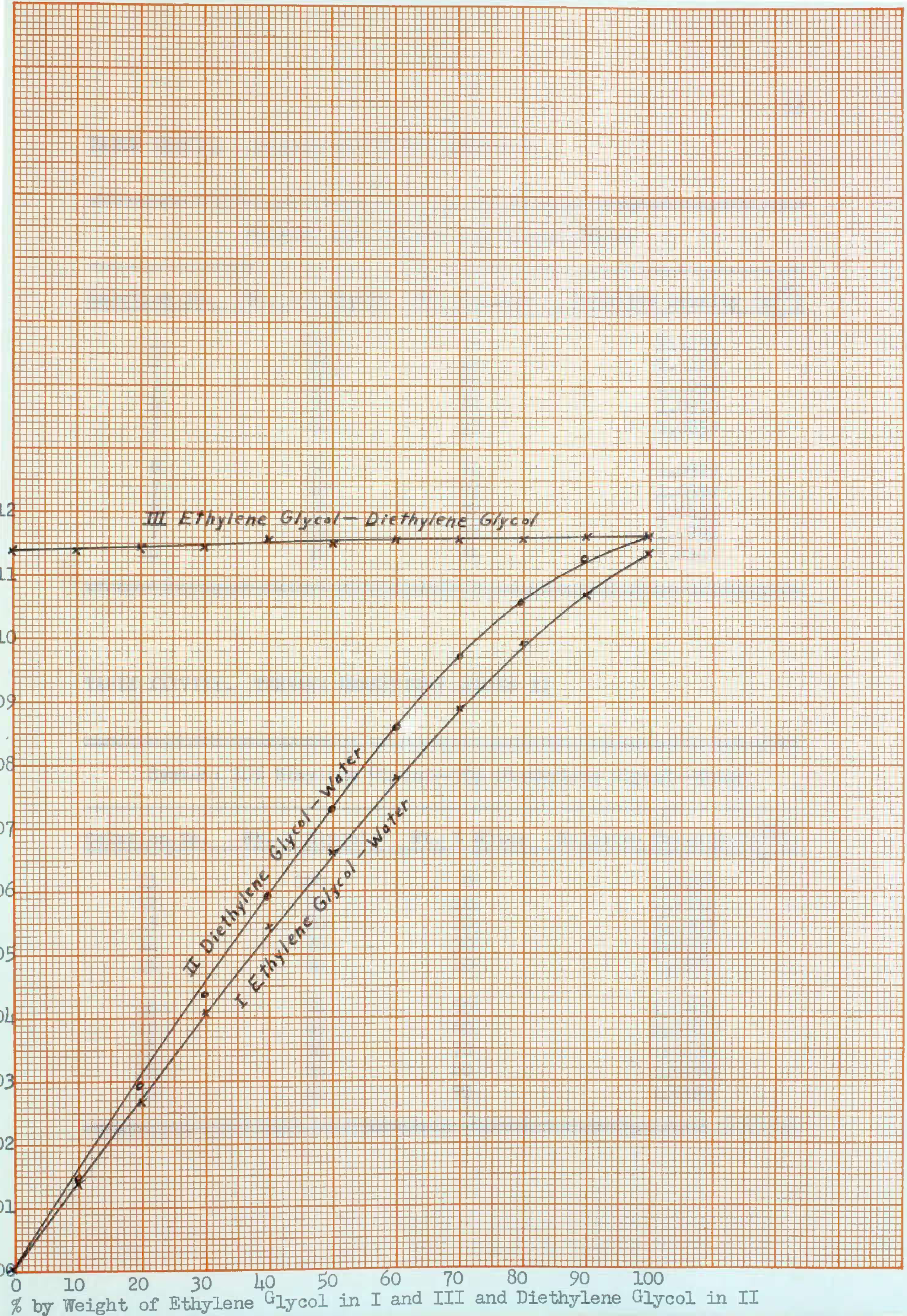

III Ethylene Glycol – Diethylene Glycol
II Diethylene Glycol – Water
I Ethylene Glycol – Water
12
11
10
09
08
07
06
05
04
03
02
01
00
0
10
20
30
40
50
60
70
80
90
100
% by Weight of Ethylene Glycol in I and III and Diethylene Glycol in II

TABLE XXXVII. TERNARY DENSITIES: SERIES I

System: 100% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
1	100	0	1.1159
2	90	10	1.1128
3	80	20	1.1056
4	70	30	1.0970
5	60	40	1.0859
6	50	50	1.0729
7	40	60	1.0592
8	30	70	1.0437
9	20	80	1.0291
10	10	90	1.0141

TABLE XXXVIII. TERNARY DENSITIES: SERIES II

System: 10% Ethylene Glycol--90% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
11	100	0	1.1159
12	90	10	1.1115
13	80	20	1.1052
14	70	30	1.0965
15	60	40	1.0854
16	50	50	1.0720
17	40	60	1.0583
18	30	70	1.0436
19	20	80	1.0286
20	10	90	1.0149

TABLE XXXIX. TERNARY DENSITIES: SERIES III

System: 20% Ethylene Glycol--80% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
21	100	0	1.1158
22	90	10	1.1113
23	80	20	1.1046
24	70	30	1.0960
25	60	40	1.0843
26	50	50	1.0714
27	40	60	1.0590
28	30	70	1.0434
29	20	80	1.0291
30	10	90	1.0141

TABLE XL. TERNARY DENSITIES: SERIES IV

System: 30% Ethylene Glycol--70% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
31	100	0	1.1156
32	90	10	1.1112
33	80	20	1.1033
34	70	30	1.0947
35	60	40	1.0832
36	50	50	1.0703
37	40	60	1.0581
38	30	70	1.0428
39	20	80	1.0284
40	10	90	1.0141

TABLE XLI. TERNARY DENSITIES: SERIES V

System: 40% Ethylene Glycol--60% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
41	100	0	1.1157
42	90	10	1.1098
43	80	20	1.1023
44	70	30	1.0932
45	60	40	1.0823
46	50	50	1.0699
47	40	60	1.0571
48	30	70	1.0431
49	20	80	1.0287
50	10	90	1.0157

TABLE XLII. TERNARY DENSITIES: SERIES VI

System: 50% Ethylene Glycol--50% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
51	100	0	1.1150
52	90	10	1.1094
53	80	20	1.1020
54	70	30	1.0922
55	60	40	1.0815
56	50	50	1.0694
57	40	60	1.0566
58	30	70	1.0428
59	20	80	1.0281
60	10	90	1.0143

TABLE XLIII. TERNARY DENSITIES: SERIES VII

System: 60% Ethylene Glycol--40% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
61	100	0	1.1155
62	90	10	1.1089
63	80	20	1.1013
64	70	30	1.0919
65	60	40	1.0814
66	50	50	1.0686
67	40	60	1.0572
68	30	70	1.0422
69	20	80	1.0281
70	10	90	1.0150

TABLE XLIV. TERNARY DENSITIES: SERIES VIII

System: 70% Ethylene Glycol--30% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
71	100	0	1.1143
72	90	10	1.1082
73	80	20	1.1009
74	70	30	1.0913
75	60	40	1.0799
76	50	50	1.0680
77	40	60	1.0552
78	30	70	1.0422
79	20	80	1.0276
80	10	90	1.0142

TABLE XLV. TERNARY DENSITIES: SERIES IX

System: 80% Ethylene Glycol--20% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
81	100	0	1.1142
82	90	10	1.1072
83	80	20	1.0995
84	70	30	1.0909
85	60	40	1.0799
86	50	50	1.0677
87	40	60	1.0560
88	30	70	1.0422
89	20	80	1.0286
90	10	90	1.0139

TABLE XLVI. TERNARY DENSITIES: SERIES X

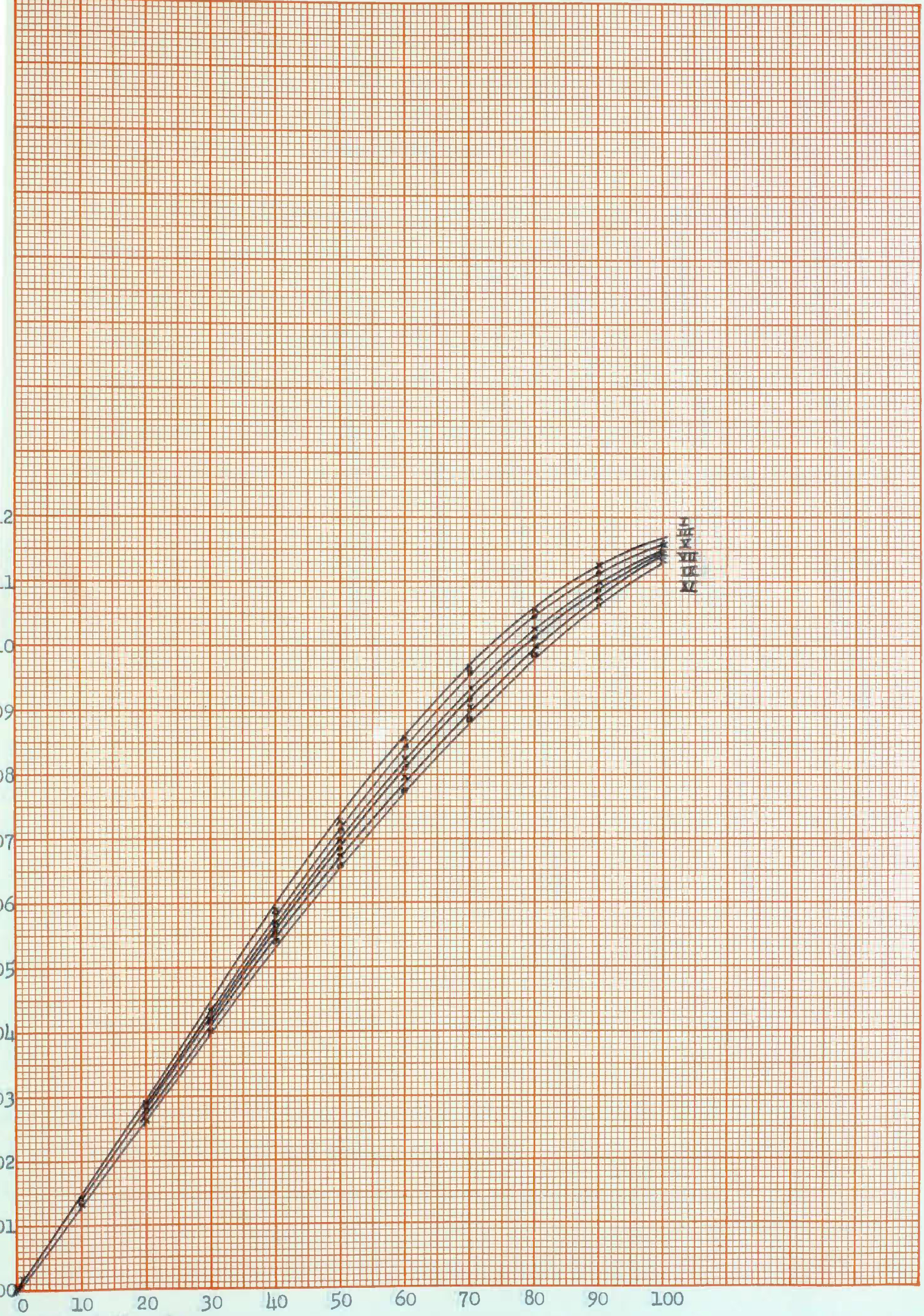
System: 90% Ethylene Glycol--10% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
91	100	0	1.1138
92	90	10	1.1065
93	80	20	1.0990
94	70	30	1.0897
95	60	40	1.0789
96	50	50	1.0663
97	40	60	1.0550
98	30	70	1.0411
99	20	80	1.0275
100	10	90	1.0137

TABLE XLVII. TERNARY DENSITIES: SERIES XI

System: 100% Ethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Relative Density (d_4^{25})
101	100	0	1.1137
102	90	10	1.1067
103	80	20	1.0989
104	70	30	1.0889
105	60	40	1.0778
106	50	50	1.0661
107	40	60	1.0543
108	30	70	1.0407
109	20	80	1.0267
110	10	90	1.0138
111	0	100	1.0001


12
11
10
09
08
07
06
05
04
03
02
01
00
0
10
20
30
40
50
60
70
80
90
100
Weight % Glycols
I
III
V
VII
IX
XI

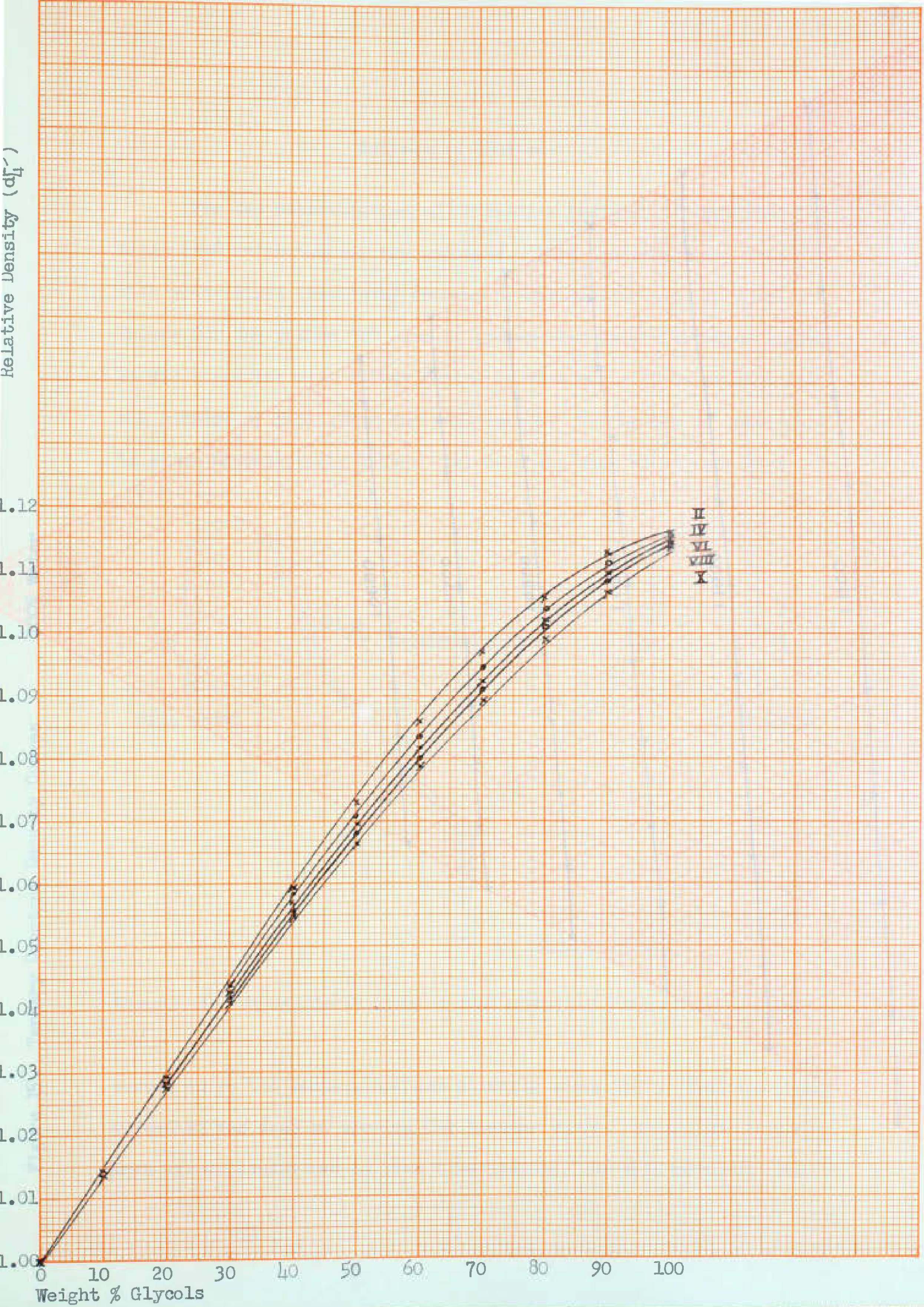
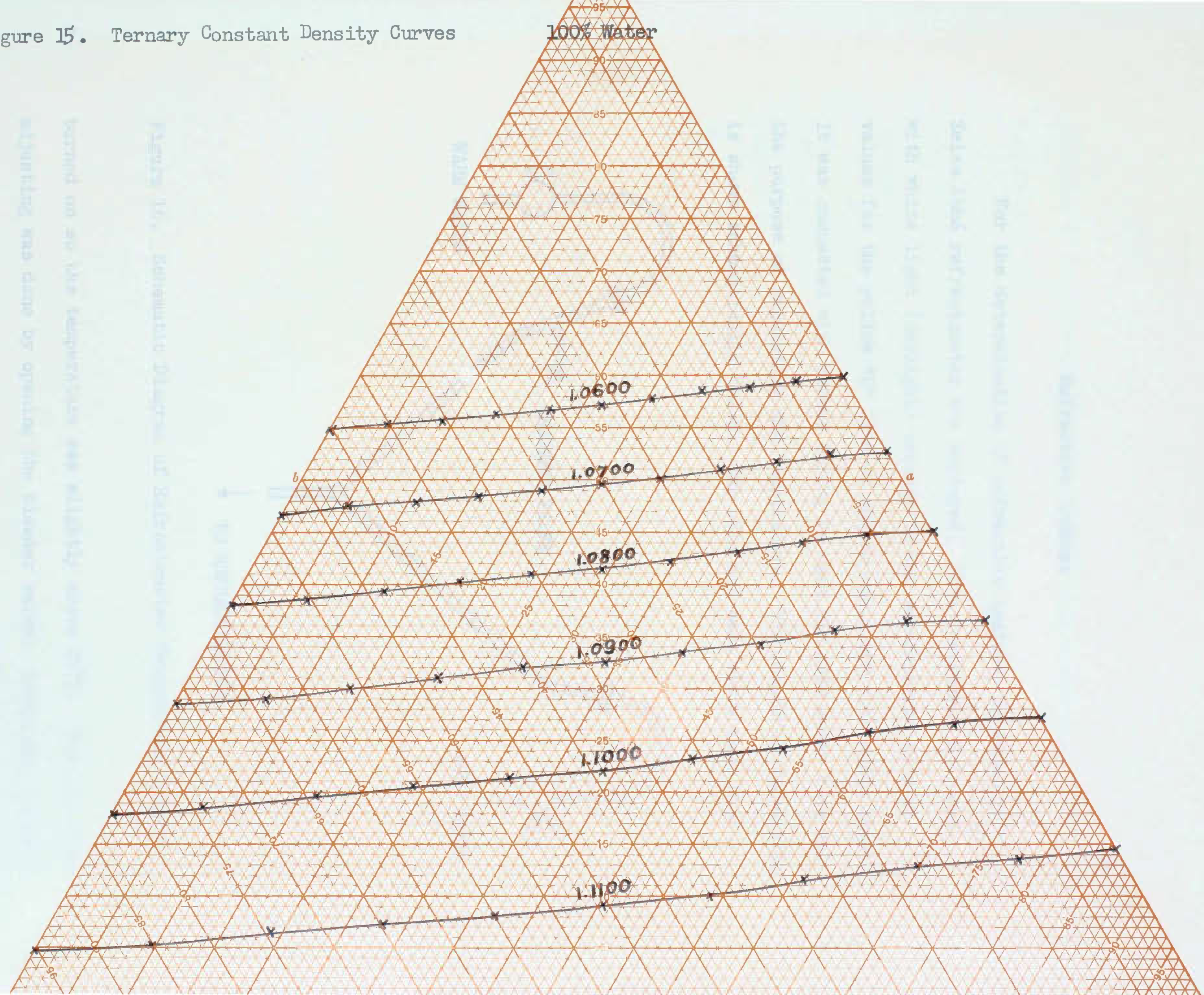

Relative Density ($d_4^{\prime}$)
1.12
1.11
1.10
1.09
1.08
1.07
1.06
1.05
1.04
1.03
1.02
1.01
1.00
0
10
20
30
40
50
60
70
80
90
100
Weight % Glycols
II
IV
VI
VIII
X

Figure 15. Ternary Constant Density Curves



Refractive Indices

For the determination of refractive indices, an excellent Zeiss Abbé refractometer was employed. This instrument was used with white light (daylight) because it was manufactured to give values for the yellow "D" line of sodium when used with white light. It was connected with rubber tubing to warm and cold water taps for the purpose of regulating the temperature. The method of connection is shown schematically below. The cold and warm water taps were turned on so the temperature was slightly above 25°C. Then the fine adjusting was done by opening the bleeder valve. Occasional adjustment was necessary due to line fluctuations. By this method it was

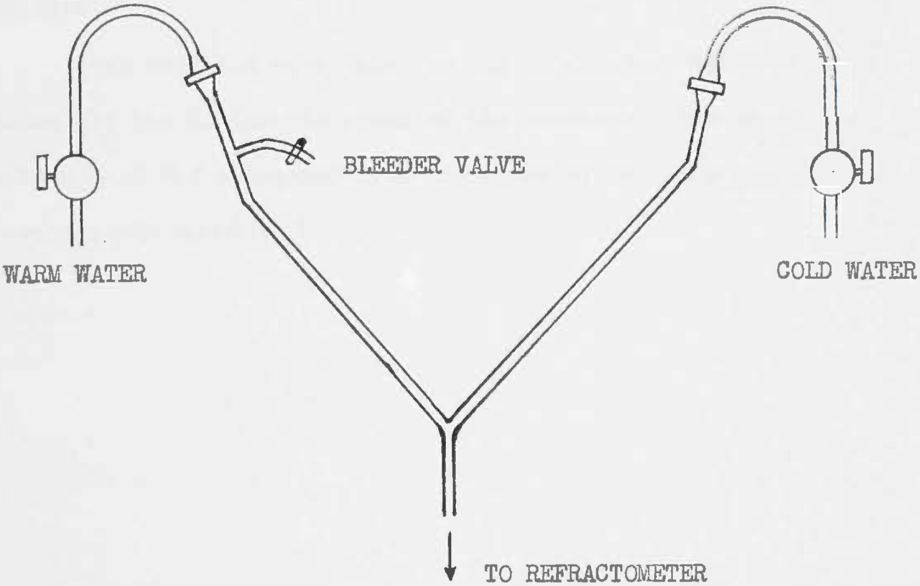


Figure 16. Schematic Diagram of Refractometer Temperature Control

possible to keep the temperature at 25°C. with a variation not exceeding ± 0.2°.

The refractometer was adjusted by means of the crystalline test piece and α-bromonaphthalene provided with the instrument. Ten readings were taken with the test piece to insure good adjustment.

Clean, dry capillary tubes were used to place two drops of solution on the prisms. To remove the solution, the prisms were swabbed thoroughly several times with ethanol on absorbent cotton. The prisms were allowed to dry before the addition of the next solution.

Four readings were taken on all solutions. The tabulated values are the arithmetic means of the readings. The average deviation of the extreemes from the means of the readings was approximately 0.00012.

TABLE XLVIII. BINARY REFRACTIVE INDICES: ETHYLENE GLYCOL--WATER

Composition	Refractive Indices (n_D^{25})	
Ethylene Glycol (Weight %)	Present Work	Davies (20)*
0	1.3345	- - -
10	1.3440	1.3416
20	1.3539	1.3517
30	1.3639	1.3621
40	1.3741	1.3723
50	1.3844	1.3828
60	1.3943	1.3927
70	1.4042	1.4025
80	1.4140	1.4118
90	1.4230	1.4210
100	1.4321	1.4300

*Determined at 20°C.

TABLE XLIX. BINARY REFRACTIVE INDICES: DIETHYLENE GLYCOL--WATER

Composition	Refractive Indices (n_D^{25})	
Diethylene Glycol (Weight %)	Present Work	Literature#
0	1.3345	
10	1.3458	
20	1.3576	
30	1.3693	
40	1.3812	
50	1.3937	
60	1.4054	
70	1.4169	
80	1.4275	
90	1.4385	
100	1.4467	

#No values given in the literature.

TABLE L. BINARY REFRACTIVE INDICES: ETHYLENE GLYCOL--DIETHYLENE GLYCOL

Composition	Refractive Indices (n_D^{25})	
Ethylene Glycol (Weight %)	Present Work	Literature*
0	1.4467	
10	1.4433	
20	1.4435	
30	1.4426	
40	1.4410	
50	1.4396	
60	1.4382	
70	1.4363	
80	1.4352	
90	1.4333	
100	1.4300	

*No values given in the literature.

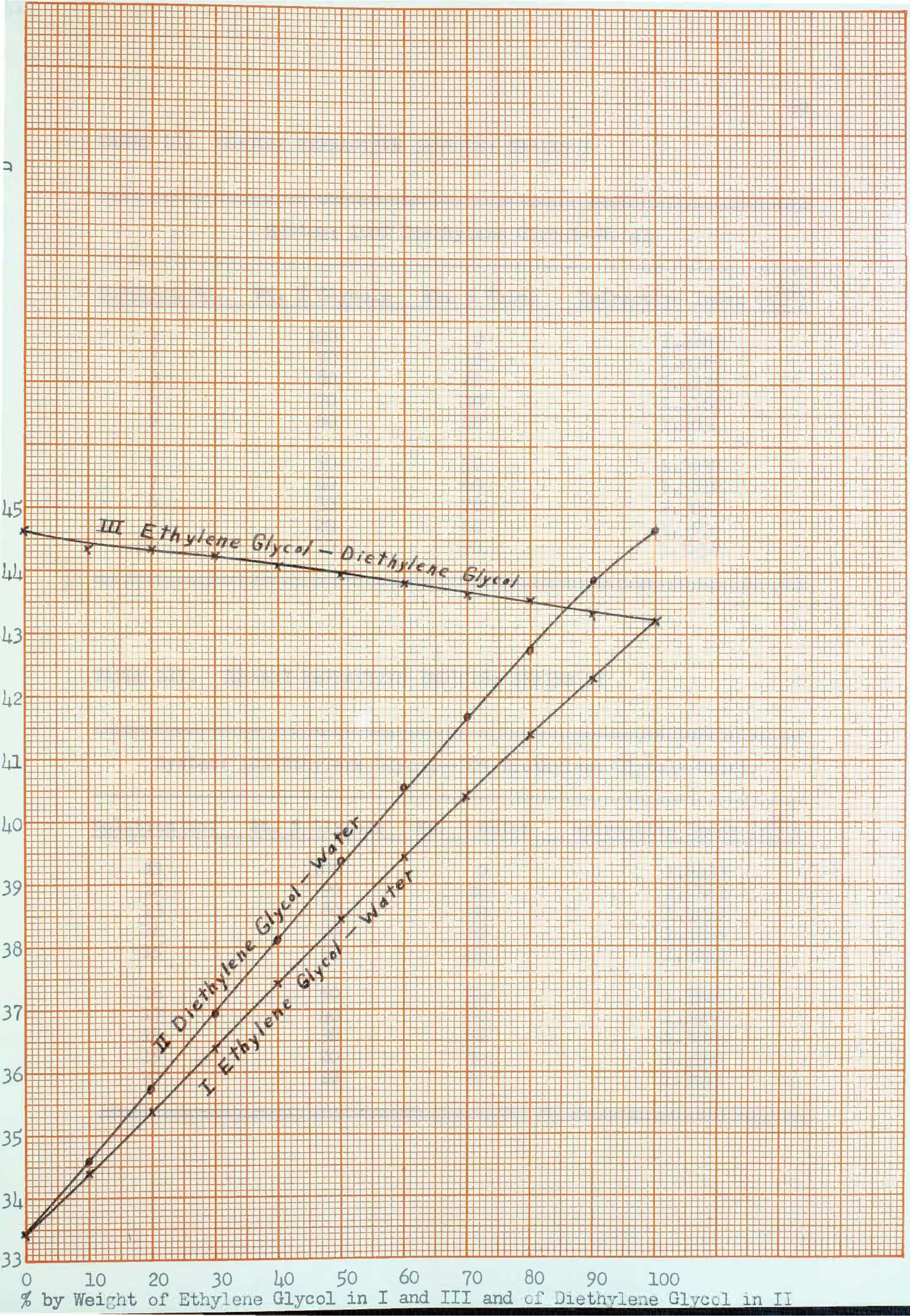

III Ethylene Glycol – Diethylene Glycol
II Diethylene Glycol – Water
I Ethylene Glycol – Water
45
44
43
42
41
40
39
38
37
36
35
34
33
0
10
20
30
40
50
60
70
80
90
100
% by Weight of Ethylene Glycol in I and III and of Diethylene Glycol in II

TABLE LI. TERNARY REFRACTIVE INDICES: SERIES I

System: 100% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
1	100	0	1.4467
2	90	10	1.4385
3	80	20	1.4275
4	70	30	1.4169
5	60	40	1.4054
6	50	50	1.3937
7	40	60	1.3812
8	30	70	1.3693
9	20	80	1.3576
10	10	90	1.3458

TABLE LII. TERNARY REFRACTIVE INDICES: SERIES II

System: 10% Ethylene Glycol--90% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
11	100	0	1.4433
12	90	10	1.4363
13	80	20	1.4259
14	70	30	1.4156
15	60	40	1.4041
16	50	50	1.3926
17	40	60	1.3806
18	30	70	1.3684
19	20	80	1.3569
20	10	90	1.3455

TABLE LIII. TERNARY REFRACTIVE INDICES: SERIES III

System: 20% Ethylene Glycol--80% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
21	100	0	1.4435
22	90	10	1.4345
23	80	20	1.4249
24	70	30	1.4144
25	60	40	1.4031
26	50	50	1.3913
27	40	60	1.3796
28	30	70	1.3679
29	20	80	1.3562
30	10	90	1.3452

TABLE LIV. TERNARY REFRACTIVE INDICES: SERIES IV

System: 30% Ethylene Glycol--70% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
31	100	0	1.4426
32	90	10	1.4335
33	80	20	1.4236
34	70	30	1.4180
35	60	40	1.4018
36	50	50	1.3905
37	40	60	1.3789
38	30	70	1.3675
39	20	80	1.3560
40	10	90	1.3450

TABLE LV. TERNARY REFRACTIVE INDICES: SERIES V

System: 40% Ethylene Glycol--60% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
41	100	0	1.4410
42	90	10	1.4313
43	80	20	1.4217
44	70	30	1.4117
45	60	40	1.4010
46	50	50	1.3892
47	40	60	1.3785
48	30	70	1.3669
49	20	80	1.3559
50	10	90	1.3450

TABLE LVI. TERNARY REFRACTIVE INDICES: SERIES VI

System: 50% Ethylene Glycol--50% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
51	100	0	1.4396
52	90	10	1.4304
53	80	20	1.4209
54	70	30	1.4101
55	60	40	1.3999
56	50	50	1.3888
57	40	60	1.3774
58	30	70	1.3666
59	20	80	1.3553
60	10	90	1.3449

TABLE LVII. TERNARY REFRACTIVE INDICES: SERIES VII

System: 60% Ethylene Glycol--40% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
61	100	0	1.4382
62	90	10	1.4292
63	80	20	1.4196
64	70	30	1.4094
65	60	40	1.3989
66	50	50	1.3879
67	40	60	1.3778
68	30	70	1.3668
69	20	80	1.3556
70	10	90	1.3451

TABLE LVIII. TERNARY REFRACTIVE INDICES: SERIES VIII

System: 70% Ethylene Glycol--30% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
71	100	0	1.4363
72	90	10	1.4274
73	80	20	1.4181
74	70	30	1.4080
75	60	40	1.3972
76	50	50	1.3874
77	40	60	1.3769
78	30	70	1.3660
79	20	80	1.3550
80	10	90	1.3445

TABLE LIX. TERNARY REFRACTIVE INDICES: SERIES IX

System: 80% Ethylene Glycol--20% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
81	100	0	1.4352
82	90	10	1.4259
83	80	20	1.4163
84	70	30	1.4070
85	60	40	1.3967
86	50	50	1.3860
87	40	60	1.3760
88	30	70	1.3660
89	20	80	1.3547
90	10	90	1.3446

TABLE LX. TERNARY REFRACTIVE INDICES: SERIES X

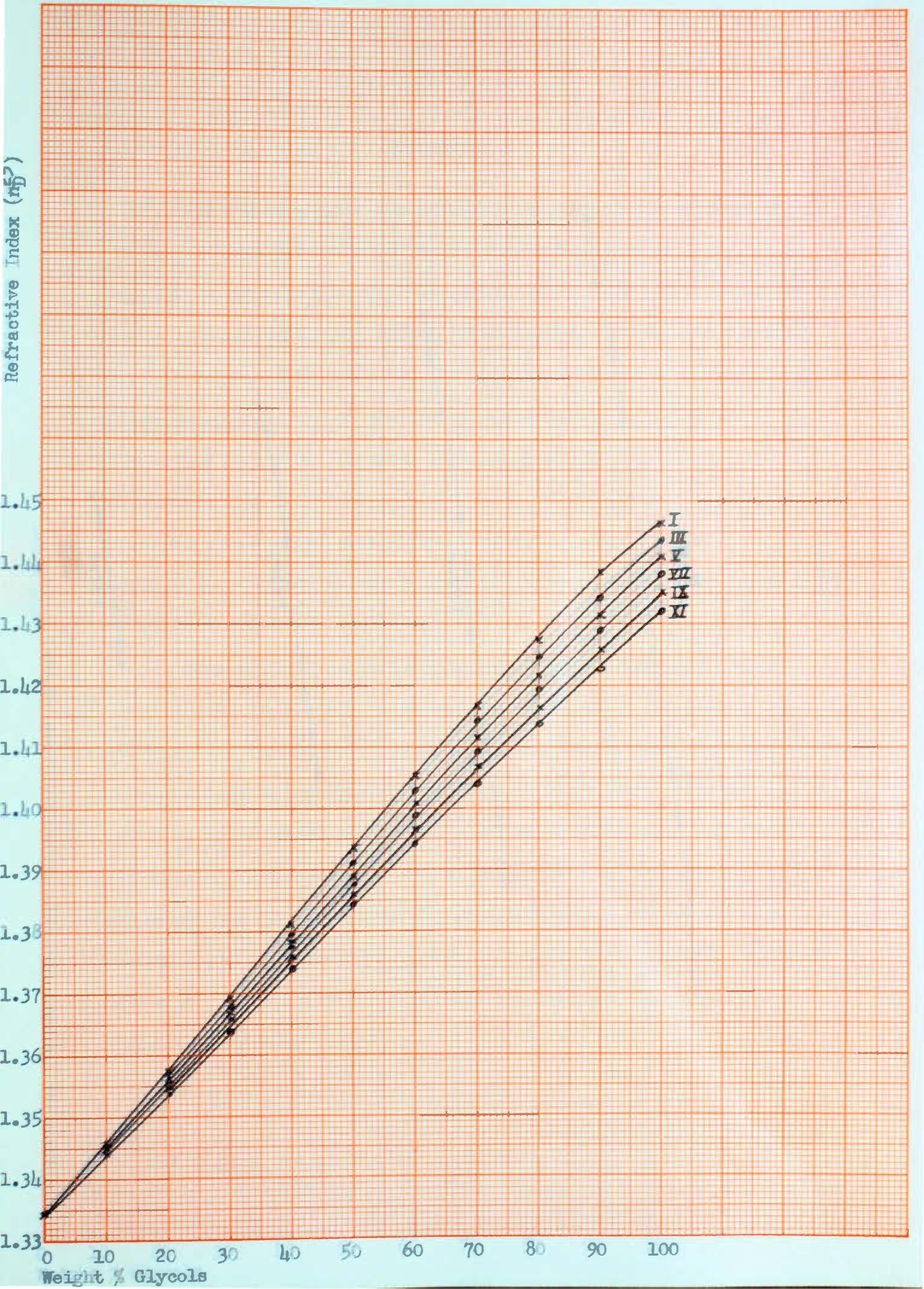
System: 90% Ethylene Glycol--10% Diethylene Glycol--Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
91	100	0	1.4333
92	90	10	1.4248
93	80	20	1.4153
94	70	30	1.4057
95	60	40	1.3953
96	50	50	1.3850
97	40	60	1.3750
98	30	70	1.3646
99	20	80	1.3542
100	10	90	1.3443

TABLE LXI. TERNARY REFRACTIVE INDICES: SERIES XI

System: 100% Ethylene Glycol—Water

Solution No.	Wt. % Glycols	Wt. % Water	Refractive Index (n_D^{25})
101	100	0	1.4321
102	90	10	1.4230
103	80	20	1.4140
104	70	30	1.4042
105	60	40	1.3943
106	50	50	1.3844
107	40	60	1.3741
108	30	70	1.3639
109	20	80	1.3539
110	10	90	1.3440
111	0	100	1.3345


Refractive Index (n_D^{25})
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.35
1.34
1.33
0
10
20
30
40
50
60
70
80
90
100
Weight % Glycols
I
III
V
VII
IX
XI

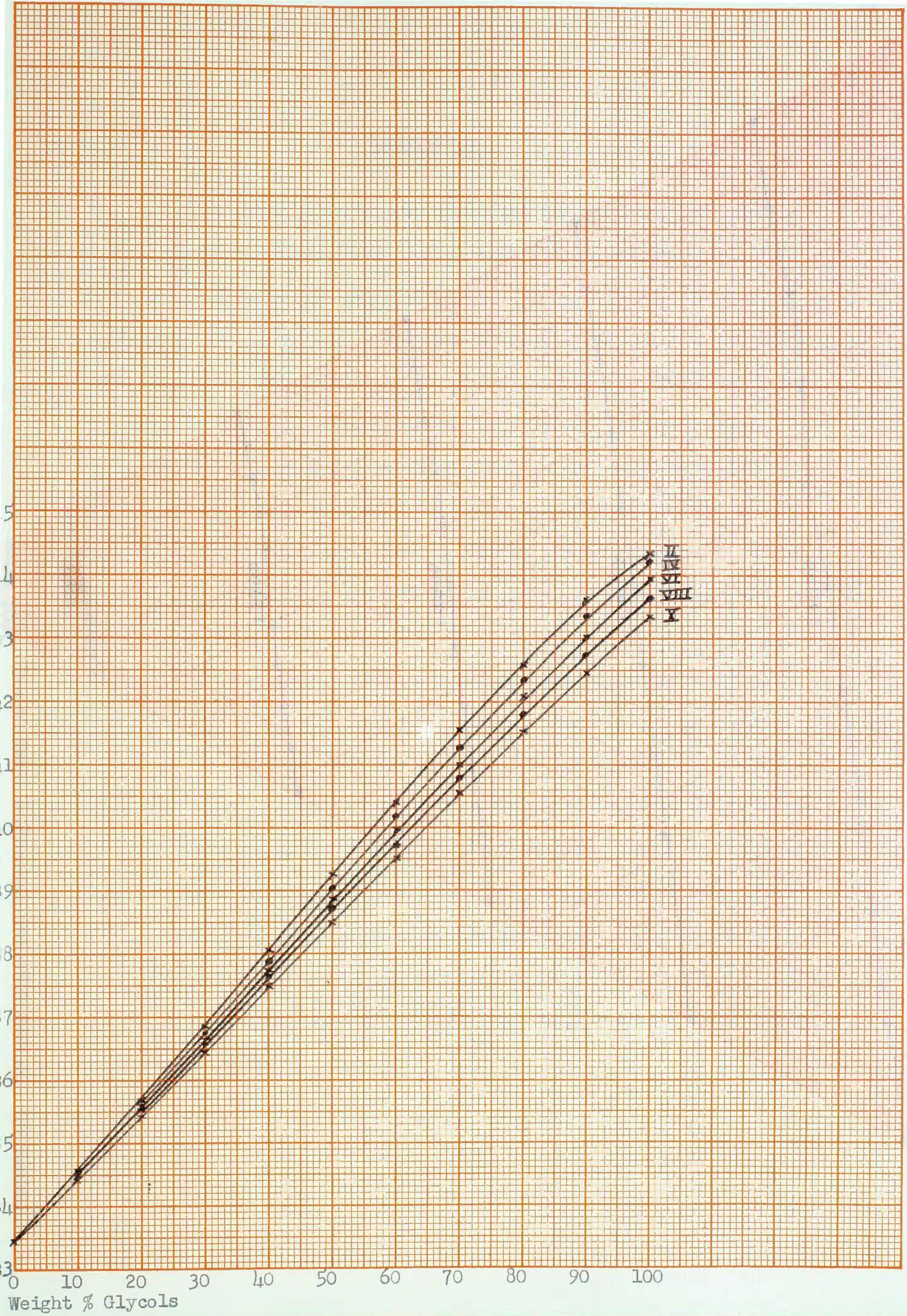
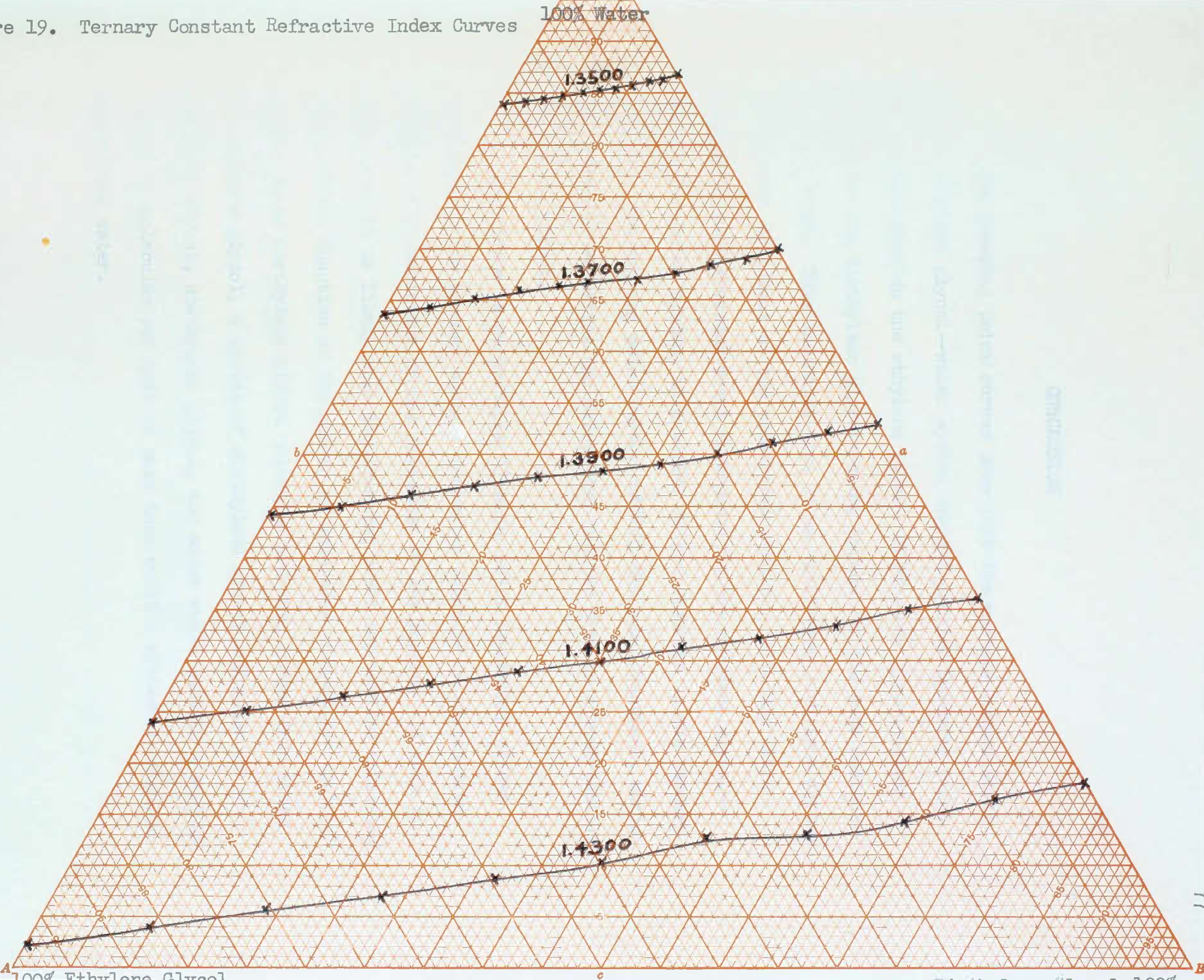

5
4
3
22
11
0
9
8
7
36
5
4
33
0
10
20
30
40
50
60
70
80
90
100
Weight % Glycols
II
IV
VI
VIII
X

Figure 19. Ternary Constant Refractive Index Curves



CONCLUSION

The freezing point curves show that the various compositions of the ethylene glycol--water system exhibit greater freezing point depressions than do the ethylene glycol--diethylene glycol--water systems or the diethylene glycol--water system for the same percentages of water. This indicates that as an antifreeze, ethylene glycol is the most efficient of the substances studied. Although there appears to be a freezing point depression in the ethylene glycol--diethylene glycol system, this effect is not observed in the ternary systems. The boiling point curves exhibit the same phenomena, while the curves of densities and refractive indices show an almost additive-properties effect.

That there is no multiple freezing point depression effect exhibited in the ternary systems indicates there is no association between or dissociation of the molecules of the system. If this is true, then it is likely that the freezing point depressions exhibited are a direct function of the number of molecules present per unit of mass. Since diethylene glycol molecules are much larger than those of ethylene glycol, a system of diethylene glycol and water or of ethylene glycol, diethylene glycol, and water would contain a smaller number of molecules per unit of mass than would a system of ethylene glycol and water.

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