

---

Masters Theses

Student Theses and Dissertations

---

1955

## Further studies of vapor-liquid equilibria of methanol-ethylene glycol-water

Herbert Benjamin Sachs

Follow this and additional works at: [https://scholarsmine.mst.edu/masters\\_theses](https://scholarsmine.mst.edu/masters_theses)



Part of the [Chemical Engineering Commons](#)

Department:

---

### Recommended Citation

Sachs, Herbert Benjamin, "Further studies of vapor-liquid equilibria of methanol-ethylene glycol-water" (1955). *Masters Theses*. 2201.

[https://scholarsmine.mst.edu/masters\\_theses/2201](https://scholarsmine.mst.edu/masters_theses/2201)

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).

FURTHER STUDIES OF VAPOR-LIQUID EQUILIBRIA  
OF METHANOL-ETHYLENE GLYCOL-WATER

BY

HERBERT BENJAMIN SACHS

A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI  
in partial fulfillment of the work required for the  
Degree of  
MASTER OF SCIENCE IN CHEMICAL ENGINEERING  
Rolla, Missouri  
1955

86234

Approved by

Frank H. Conrad  
Professor of Chemical Engineering

### ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to Dr. Frank H. Conrad for his timely suggestions, guidance and general aid throughout this entire investigation.

## TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENT .....	11
LIST OF FIGURES.....	1v
LIST OF TABLES .....	v
INTRODUCTION .....	1
REVIEW OF THE LITERATURE .....	2
MATERIALS .....	7
ANALYTICAL METHOD .....	9
APPARATUS .....	12
PROCEDURE .....	16
RESULTS AND DISCUSSION .....	20
SUGGESTIONS FOR OTHER EQUILIBRIUM STUDIES .....	27
SUMMARY .....	29
APPENDIX A - FIGURES .....	30
APPENDIX B - TABLES .....	38
LITERATURE CITED .....	45
VITA .....	49

## APPENDIX A

LIST OF FIGURES

FIGURE		PAGE
1	Diagram of Improved Othmer Equilibrium Still.....	30
2	Diagram of Constant Pressure Apparatus..	31
3	Photograph of Experimental Apparatus....	32
4	Equilibrium Diagram of Methanol-Water System.....	33
5	Equilibrium Diagram of Glycol-Water System.....	34
6	Equilibrium Diagram of Methanol-Glycol System.....	35
7	Determination of Water in the Equilibrium Vapor of Methanol-Glycol-Water System...	36
8	Determination of Methanol in the Equilibrium Vapor of Methanol-Glycol-Water System.....	37

## APPENDIX B

LIST OF TABLES

TABLE		PAGE
I	Vapor-Liquid Equilibria Compositions of the System, Methanol-Water.....	38
II	Vapor-Liquid Equilibria Compositions of the System, Methanol-Glycol.....	39
III	Vapor-Liquid Equilibria Compositions of the System, Glycol-Water.....	40
IV	Densities, Refractive Indexes and Boiling Points of Mixtures of Methanol-Glycol-Water.....	41
V	Equilibrium Compositions of Methanol- Glycol-Water Mixtures.....	43

## INTRODUCTION

The freezing points of the ternary system methanol-glycol-water have been investigated by Conrad, Hill and Ballman (5). The vapor-liquid equilibria of the same system was studied by Sjoberg (25). These investigations were carried out to determine the properties of the system relative to its possible use as an anti-freeze mixture.

Since Sjoberg's work in 1948, the improved Othmer equilibrium still (20) has been introduced for vapor-liquid experimental determinations. It is therefore the purpose of the present investigation to evaluate the use of this still, compare results with those obtained by Sjoberg, and analyze ternary mixtures for the entire range of glycol concentrations.

The system has been completely covered in the present work, and is presented graphically. The figures and tables are in Appendix A and Appendix B respectively.

## REVIEW OF THE LITERATURE

An intensive review of the literature was made for investigations of ternary systems, and pertinent binary ones. Binary systems of interest in this present investigation are those of methanol-water, glycol-water, and glycol-methanol.

Previous work done on the vapor-liquid equilibria of the methanol-glycol-water system is that of Sjoberg (25). There have been other ternary system investigations which were useful in the present work because of the methods of analysis and presentation of data.

The system, methanol-ethanol-water was investigated by Dinwiddie and Griswold (12). These authors used a scheme of analysis in which the boiling points and densities of various mixtures were correlated. Their vapor-liquid diagrams were rectangular coordinate plots and not the usual triangular plot.

Othmer, Chudgar and Levy (21) present an excellent work on the analysis and correlation of vapor-liquid equilibria of acetone-methyl ethyl ketone-water system. This investigation may be followed as an excellent method for correlating vapor-liquid data of a ternary system.

There is an abundance of data on the vapor-liquid equilibria of binary systems. Only those of interest to this investigation were studied in the literature.



The binary system of methanol-water has been investigated very thoroughly. Data by H. Bergstrom are presented by Hausbrand (13). Data for this system were presented by Blocher and Trschetziak (13). These data have been checked very closely by Cornell and Montonna (6) using a method developed by Rosanoff, Bacon, and White (24).

There have been few investigations of the glycol-water system. Trimble and Potts (27) presented data at several pressures ranging from 220 mm. of mercury to 747 mm. of mercury. Another study of this binary system is one by Taylor and Rinkenbach (26) which is apparently even more acceptable than the work of Trimble and Potts.

Sjoberg (25) presented data on the glycol water system at 760 mm. of mercury. These data are in very close agreement with the data of Taylor and Rinkenbach (26), and that of the present investigation.

The only data on the system methanol-glycol are those of Sjoberg (25) at 760 mm. of mercury. The present investigation also presents data for this system at the same pressure.

The only discussion of the methods used for experimental determinations of vapor-liquid equilibria relations up to 1922, is that of Young (30). After that time no organized discussion of the subject is presented as thoroughly as Young's. Investigators using very similar methods to those discussed by Young

have accounted for recent vapor-liquid equilibria determination methods. Othmer (20) gives an excellent method for binary systems which has widespread use.

The most widely accepted method discussed in the literature concerning the analysis of a ternary system is that used by Baker (2) et al. This method is further discussed by Othmer, Chudgar and Levy (21). The latter also provides a good method of presentation of data as does Dinwiddie and Griswold (12).

There has been a great variety of literature on stills to be used for experimental determination of vapor-liquid equilibria. Robinson and Gilliland (23) describe the general types of apparatus used. Carney (3) summarizes the methods used for vapor liquid equilibria and gives an excellent description of apparatus used for each method. He further states very thoroughly the requirements of a still in order to operate efficiently and without appreciable error. These are:

1. The liquid must be vaporized and condensed without allowing any reflux between the time of the first vaporization and final condensation. Reflux would yield a vapor richer in the more volatile component than is actually the case in a true equilibrium.
2. Entrainment of liquid in the vapor must be avoided. Carrying over of unvaporized

material will give a condensate containing less than the equilibrium amount of lower boiling component in the vapor.

3. The composition of the material in the still should remain constant.
4. No part of the apparatus should be superheated sufficiently to cause total instead of equilibrium vaporization, which would also give a value of vapor composition too low in the more volatile component.
5. The boiling should be completely homogeneous.

Various investigators have taken care of the above requirements in different ways. Wiley and Harder (29) used a three-necked flask as a vapor-equilibrium still. Although simple in construction and operation, manipulation of the auxiliaries of the still to maintain equilibrium conditions is difficult.

Another somewhat useful still for vapor-liquid equilibrium is an apparatus for determining equilibrium by passing vapor through a liquid of constant composition. The designers, Jones, Schoenborn and Colburn (16) claim the use of the apparatus is best carried on by very experienced investigators.

Gillespie (10) designed a recirculation type of still where both liquid and vapor are circulated. It is difficult to maintain a steady boiling rate in this type of still.

The most widely accepted and used vapor-equilibrium still is that developed by Othmer (20). This apparatus is known as the Othmer improved equilibrium still, and was used in the present investigation. See Figure 1.

There is a great deal of information available in the literature on the three compounds used in this study. It is worthy to mention the references used. An excellent method for the purification of methanol is given by Vogel (28). The American Chemical Society Monograph, Number 44 (18) discusses ethylene glycol and describes an excellent method for its purification.

Other investigations of the methanol-glycol-water system are those of Meyer (19) and Flint (9). Meyer determined the densities and refractive indexes of various mixtures of methanol-glycol-water up to a glycol concentration of twenty mole per cent. He also presented a design for an equilibrium still and made some preliminary distillations.

Flint developed a qualitative chemical test for glycol in the presence of methanol and water. The test can detect glycol when present in quantities as small as 0.01 per cent. This test was used in the present investigation for detection of glycol in the vapor at small mole per cents of glycol in the liquid.

## MATERIALS

The materials used in this investigation were methyl alcohol, ethylene glycol, and distilled water. They were purified until their purity checked very closely with known physical properties of refractive index and boiling point.

The methyl alcohol used was obtained from Commercial Solvents Corporation. This was synthetically produced methanol which, according to its density, 0.8119 (17) at 25°C, proved to be 99.4 per cent methanol.

A very excellent method of purification (28) of the methanol was use of a rod and cone type fractionating column. Magnesium metal was used in the distilling flask with the raw methanol to remove the last traces of water. The pure distillate was collected in a side-necked flask with a calcium chloride tube attached to the side neck to prevent contamination of the distillate by moisture from the air.

The methanol was checked at short intervals for refractive index and density. Only the middle third which distilled at a temperature of 64.5°C was retained for use. This methanol had a refractive index of 1.3290 at 20°C, and a density of 0.7867 at 25°C. Accepted values are 1.3288 for the refractive index, and 0.7869 for the density (15).

The ethylene glycol used was obtained from the Carbide and Chemicals Corporation. The glycol was purified by distillation with a rod and cone type fraction-

ating column at a pressure of 50 mm. of mercury. The distilling flask, a 2 liter round bottom type, was heated in an oil bath. Bumping had to be prevented by passage of air dried with calcium chloride into the flask.

The middle third of the glycol distillate was retained for use. Its boiling point was 122°C at a pressure of 50 mm. of mercury. The refractive index of the purified glycol was found to be  $1.4317 n_D^{20^\circ}$ , and it had a density of 1.1109 at 25°C. Acceptable values for the refractive index and density are given as  $1.4318 n_D^{20^\circ}$ , and  $1.1104 d_{40}^{25^\circ}$  (17) respectively. Other values found for the refractive index were  $1.43176 n_D^{20^\circ}$  (14), and  $1.4316 n_D^{20^\circ}$  (8). Other values found for density at 25°C were 1.1106 (22), and 1.1105 (8).

The water used in this investigation was ordinary laboratory distilled water which was further purified by distillation. A small amount of sulphuric acid and potassium permanganate was added to the distilling flask, and distillation was carried out using a rod and cone type of fractionation column. The water thus obtained had a refractive index of  $1.3333 n_D^{20^\circ}$ . This was checked against the value given in Lange's Handbook as  $1.3333 n_D^{20^\circ}$  (17).

The purified water was stored in aged Pyrex glass bottles to prevent a change in the refractive index.

## ANALYTICAL METHOD

A binary system may be easily analyzed for vapor-liquid equilibria by first correlating one of the three physical properties against standards of the most volatile substance of the system. The investigator may use the boiling point, density or refractive index. Since the refractive index is the most rapid, it usually gains preference.

Before undertaking the analysis of the methanol-glycol-water system, three binary systems were run. These were analyzed using the refractive indexes as a standard.

The refractive index was measured with a Spencer refractometer number 1182, manufactured by the American Optical Company. The instrument was calibrated using a standard crystal of  $1.5167 n_D^{20}$  furnished with the instrument. The cementing agent used with the crystal was alpha-bromonaphthalene liquid.

All readings were taken at  $20^\circ\text{C}$  using the Sodium D-line. Water of constant temperature was circulated through the prism jackets of the refractometer. The water temperature was controlled at  $20^\circ\text{C} \pm 0.1^\circ\text{C}$ .

The instrument's thermometer was very carefully calibrated against the freezing point of water and a Bureau of Standards thermometer. The correction factor was found to be  $+0.02^\circ\text{C}$  at  $20^\circ\text{C}$ . The water bath thermo-

meter was calibrated by these methods also, and was found to have a correction of  $\pm 0.03^{\circ}\text{C}$  at  $25^{\circ}\text{C}$ .

A ternary system must be analyzed by measuring two physical properties of the mixture. This work used refractive index and density which appear as the most widely used and the most rapid.

The refractive indexes were measured as previously discussed. The density measurements were performed using a Weld type density bottle. All density measurements were made at  $25^{\circ}\text{C}$  after samples had been immersed in a water bath controlled to  $25^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$ . The water bath thermometer was calibrated as previously mentioned.

In order to correlate the two physical properties required for finding the equilibrium vapor and liquid values of the system of methanol-glycol-water, Sjoberg measured the densities and refractive indexes of several known mixtures of this system. A triangular diagram was constructed presenting these values as lines of constant densities and refractive indexes. These lines were then constructed at regular intervals by interpolation. The reliability of this diagram was checked and found to be very accurate by Conrad, Sjoberg et al (4).

Thus the values for the equilibrium vapor and liquid of a mixture of methanol-glycol-water may be found by measuring the refractive indexes and densities of the equilibrium vapor condensate, and equilibrium liquid yielded by distilling a mixture of methanol-glycol-water until



equilibrium conditions have been reached. These density and refractive index values may then be found on Sjoberg's triangular diagram, and the corresponding values of the equilibrium vapor read from the axes.

## APPARATUS

In the investigation performed by Sjoberg, an equilibrium still was constructed very similar to that used by Jones, Schoenborn and Colburn (16). This still was successful, but it had several disadvantages. The main one was the many necessary joints which allowed leakages and deviation from constant pressure.

Following the suggestion of Sjoberg, this investigator used the improved Othmer equilibrium still. This type of still was designed by Othmer (20) specifically for equilibrium data. The equilibrium still used was obtained from Emil Greiner and Company, New York.

Figure 1 shows the improved Othmer still as used in the present work. All available attachments were obtained with the apparatus.

The boiling flask, A, is an 800 ml. Kjeldahl type with a diameter of 4.5 inches. The sample to be tested is introduced into the flask through the ground glass joint, O.

The short neck of the flask is necessary to minimize radiation losses and reflux of the vapor. The sample is heated by an internal heater consisting of a coiled 250 watt, 110 volt nichrome wire. The internal heater was supported by the two ground glass spherical joints, D. These joints had binding posts as shown at E, to which the wire connections were made.

An external heater also consisting of 250 watt nichrome wire, is wrapped around the circulation leg G of the flask A. The leg G is very successful in promoting good convection type circulation of the sample. The tubes B are the central and outlet tubes.

The vapor from the sample in the flask rises through the central tube, and then through the outlet tube. The vapor rises through the condenser, H, which is approximately 8 x 1.25 inches with 1 inch diameter balls, constrictions varying from a maximum opening at the bottom to about 0.25 inches at the top. The outlet, I, is a connection to either vacuum or pressure.

The vapor after going to the condenser becomes condensate and falls through a drop counter, J, which has a 3/16 inch outlet. The condensate collects in the sample receiver, L, which is about 4 inches in length and has a volume of approximately 30 ml.

The condensate after filling L overflows through the condensate cooler, M, and circulates through the tube, N, back to the bottom of flask A.

After equilibrium has been reached, a sample of the liquid to be analyzed may be removed from the liquid sample cock, F, and a vapor sample may be removed from the condensate sample cock, K.

In order to record temperatures of the equilibrium systems, a thermometer was placed in the opening above

the central vapor tube, B, by means of a rubber stopper.

Since any system being studied for vapor-liquid equilibria data must be distilled under constant pressure conditions, apparatus to maintain these conditions must be used. The apparatus used for this purpose during this study is shown in Figure 2.

As shown, there are four lines used from an air reservoir, P. This reservoir may be a steel tank or a five gallon glass jar as used in this case. The reservoir helps dampen air line fluctuations.

The line, Q, is from an air supply. Line R is attached to the connection, I, on the equilibrium still. A calcium chloride drying tube is used to keep the air dry when entering the apparatus. The line, S, connects to a standard Meriam type manometer, T. The manometer has a scale calibrated so that when filled with water at 25°C it will record millimeters of mercury.

The line, U, has a small hook shape on the end, and is immersed in water in the glass jar, V.

The apparatus is operated by simply allowing air from the line Q to enter the reservoir. This air bubbles through the water in V. The manometer is zeroed at room pressure. Adjustment of the water column, V, will increase pressure by raising the column until the desired setting is attained. This apparatus is used only to obtain pressures above that of the room.

Figure 3 is a photograph of the equilibrium still and pressure control apparatus as assembled and used in this investigation.

## PROCEDURE

Ternary mixtures to be distilled were prepared by measuring the individual components from 250 ml. dispensing burettes. These burettes were protected from the air by means of calcium chloride drying tubes inserted in stoppers and placed in the tops of the burettes. A separate burette was used for each of the liquids, methanol, glycol and water. In this manner contamination was avoided.

The range of concentrations of the samples was from one mole per cent glycol to ninety-six mole per cent glycol. The samples were 400 milliliters in volume. This was determined as the best volume sample from trial distillation runs.

Before distilling a sample, the apparatus was thoroughly cleaned, dried and checked for correct operation. All stop cocks and stoppers were treated with silicone type grease.

After the apparatus was made ready, the sample was introduced through a glass-stopper in the boiling flask. The stopper, however, was not placed into position until a few minutes after the still was operating. This was necessary in order to rid the apparatus of any trapped air.

The internal and external flask heaters were adjusted by means of variac controls for supply of heat

to the still. The constant pressure apparatus was adjusted to record pressure on the manometer of 760 mm. mercury minus the daily barometric pressure corrected to 0°C.

After boiling began, the distillation rate was adjusted at about four to six ml. per minute. The Othmer apparatus generally requires about three minutes for the vapor distillate trap to fill up. Then recirculation of the condensed vapor into the boiling flask liquid starts.

This recirculation continues until equilibrium is established. Equilibrium is indicated by a constant temperature reading on the thermometer in top of the boiling flask. The average time required for a ternary sample was about twelve minutes. However, twenty to thirty minutes were allowed to insure good equilibrium conditions. With samples containing a large concentration of glycol, sometimes 50 to 60 minutes were allowed. This was necessary because of the high boiling point of ethylene glycol at 760 mm. of mercury.

After equilibrium conditions were reached, samples of the liquid and of the vapor (distillate) were taken in small stoppered 30 ml. bottles. The first ten milliliters of the liquid sample and the vapor distillate were rejected. This reduced possible contamination by accumulation of previous samples in the stopcocks.

The samples of liquid and vapor distillate were taken as nearly simultaneously as possible, and before any appreciable change due to the removal of some of the

more volatile components from the system could occur. After the sample bottles were filled, they were immersed in cold water to prevent serious losses due to evaporation. This operation also served a dual purpose of cooling the sample to a temperature below  $25^{\circ}\text{C}$  before placing it in the specific gravity bottles. Normally room temperature was above  $25^{\circ}\text{C}$ .

The results were recorded by sample number. For each sample there were two labelled bottles. One bottle was for the liquid sample, and the other was for the vapor distillate sample. They were labelled "x" and "y" respectively.

All the samples were analyzed by the immediate determination of their refractive indexes and densities. The analytical plot constructed by Sjoberg (25) was used for the final analysis.

In order to study operations of the Othmer equilibrium still, and to gain experience, three binary systems were distilled. The systems were methanol-water, methanol-glycol, and glycol-water.

These binary systems were analyzed by means of the relationship between the concentration of the more volatile component, and the refractive index. The diagrams for the analysis of these systems were constructed by Sjoberg (25). The refractive index was measured on several known mixtures of the particular binary system. The mole fraction of the more volatile component in the system is



plotted as the independent variable and the refractive index as the dependent variable. A smooth curve is constructed through several points.

After distilling the binary system until equilibrium conditions are reached, the refractive indexes of the equilibrium vapor condensate and liquid are measured. These refractive indexes are then used on the plot to determine the equilibrium value of the more volatile component in the liquid and in the vapor.

## RESULTS AND DISCUSSION

A binary mixture may be analyzed by measuring only one physical property. The investigator has a choice of the boiling point, density or refractive index. The refractive index is the simplest and quickest, and is, therefore preferred.

In this work the refractive index was used, and the analysis of a binary mixture was obtained as shown in Table 1. This system was that of methanol and water.

The system was represented graphically by the usual "y" - "x" plot as shown in Figure 4. In this diagram "y", the ordinate, represents the more volatile component in the vapor, and "x", the abscissa, represents the more volatile component in the liquid.

The data for this mixture as determined by Cornell and Montonna (6) and Sjoberg (25) are also plotted in Figure 4. The present work agrees more closely with that of Cornell and Montonna, but there was also fairly good agreement with Sjoberg's work.

The deviation of results from those of Sjoberg may be partially due to his difficulty in holding constant pressure with the apparatus used. However, the deviations are not excessive.

The vapor-liquid equilibria data of the binary mixture of glycol and water was experimentally determined as discussed above. Table 2 shows the analysis

of this system.

The usual "y" - "x" diagram is shown by figure 5, and the data of Sjoberg (25) and Trimble and Potts (27) are shown also. Although Trimble and Potts analyzed the system at 747 mm. of mercury, their data agree well with that of Sjoberg and the present investigation analyzed at 760 mm. of mercury. This is probably due to the fact that the small pressure difference would be balanced out in the overall equilibrium curve.

Table 3 shows the analysis of the third binary mixture in this work. The system was that of methanol and glycol. Figure 6 is the "y" - "x" diagram. The data of Sjoberg (25) are plotted also for comparison. The agreement is fairly good; however, the curve has a tendency to have more spread from the ordinate at lower concentrations in this investigation than in Sjoberg's. The only explanation is that there were possible pressure variations during the runs made by Sjoberg.

The analysis of these systems was made to gain experience with the Othmer still, and check results from it with other results of investigators using a different type of still. Robinson and Gilliland (23) clearly state that most investigations vary from 10 to 15 per cent on the results of a given binary system.

It is a very difficult task to estimate the percentage error between the experimental investigations of one system. A more accurate check is perhaps obtained

by plotting data of the various investigators, and noting the overall trend of the data. Of course the most accurate check would be investigations of the vapor pressure and consequent mathematical analysis of one system. In this case perhaps an average percentage error could be calculated.

The binary mixtures experimentally determined in this investigation might be more amply analyzed by the aid of vapor pressure data on each. With these data, the law of Raoult and Dalton could be assumed to hold true and "x" and "y" values could be calculated.

Once the vapor pressure of the system is determined at different temperatures, the expressions (1)

$$x_a = \frac{P - P_b}{P_a - P_b} \quad \text{where } x_a = \text{mole fraction of component a in liquid}$$

$$y_a = \frac{P_a x_a}{P} \quad \text{and } y_a = \text{mole fraction of component a in vapor}$$

$$P_a = \text{vapor pressure of pure component a}$$

$$P_b = \text{vapor pressure of pure component b}$$

$$P = \text{total pressure}$$

could be utilized to calculate the "y" and "x" values for an equilibrium diagram.

These values could be further verified by use of the Van Laar equations which may be expressed as follows (7):

$$A = \log \gamma_A \left[ 1 + \frac{(1-x) \log \gamma_B}{x \log \gamma_A} \right]^2 \quad \text{and}$$

$$B = \log \gamma_B \left[ 1 + \frac{x \log \gamma_A}{(1-x) \log \gamma_B} \right]^2$$

in which A and B are constants and  $\gamma$  is the activity coefficient. Consequently one may calculate the Van Laar constants A and B, and hence obtain the y, x equilibrium curve without the necessity of any other composition data.

Table 4 lists the densities, refractive indexes and observed boiling points for the distillation of the ternary mixture of methanol-glycol-water. The analysis for these samples is shown in Table 5. The plot used for an analysis was that constructed by Sjoberg (25). The accuracy of this plot is clearly indicated by the work of Conrad et al. (4).

As indicated by Sjoberg, it would have been desirable to carry out the distillations of the ternary mixtures with one of the components kept at some constant value for the duration of the run. However, this is not practical since the analysis of the samples could not be done quickly enough to enable adjustments of the concentrations between samples.

The equilibrium still was charged with a liquid of a composition in the desired range and the distillation was carried out without addition of anything to the liquid between samples.

Withdrawals could be made until the liquid volume in the still reached a value of about 100 ml. A series of samples could be thus arranged covering the entire glycol concentration range.

The data obtained in this manner could be adjusted as is done by Baker (2). Samples with nearly the same glycol concentration in the liquid, and liquid and vapor compositions, could be adjusted to the same glycol concentration in the liquid by assuming that the relative volatilities of the three components were constant over the small concentration range involved.

In this system, however, the relative volatility values of the three components are very far apart. An accurate adjustment could be made only in a system composed of nearly equal relative volatile components.

Sjoberg (25) used the assumption discussed, and adjusted compositions by means of relative volatility. However, the small adjustment would not alter the data to any extent, nor change the correlations when plotted.

Figure 7 consists of the binary systems, glycol-water and methanol-water. Each is plotted using the mole per cent water present in the liquid and vapor.

The results of the analysis of the ternary mixtures were plotted first using the axis values of Figure 7. The value of the glycol concentration corresponding to the particular sample being plotted was placed at the point of intersection of the axes values. Lines were then drawn through each glycol concentration. These lines met at the origin, and intersected the glycol-water binary system curve. By interpolation these lines

were spaced at intervals of ten mole per cent corresponding to the procedure used by Griswold and Dinwiddie(12).

Figure 7 presents a method of finding the mole per cent of water in the equilibrium vapor of the ternary system.

Figure 8 is constructed in a similar manner with the use of the binary mixtures, methanol-glycol and methanol-water. However, the mole per cent methanol in the liquid and vapor is plotted in this case. Again lines of constant glycol composition were constructed from experimental data.

This figure then enables one to establish the mole per cent of methanol in the equilibrium vapor. The mole per cent glycol in the vapor is then found by difference.

The results of the present work on the system, methanol-glycol-water, are shown in Figures 7 and 8. These diagrams show the relationship between all three components in the mixture, and they present a method of obtaining equilibrium vapor compositions of known liquid mixtures.

Thus by use of figures 7 and 8, one may find the equilibrium vapor compositions of a known mixture of methanol-glycol-water. A specific example will serve to demonstrate the use of these diagrams. It is supposed that a known mixture of this system contains 40 mole per cent methanol, 40 mole per cent glycol, and 20 mole per cent water. The 40 mole per cent glycol line

of Figure 7 is followed to the intersection of the abscissa value of 20 mole per cent water. The ordinate value read from this intersection is 13 mole per cent, and this is the concentration of the water in the equilibrium vapor. By following the 40 mole per cent glycol line in Figure 8 to the intersection of the abscissa value of 40 mole per cent methanol in the liquid, the value of 86 mole per cent methanol in the equilibrium vapor is found on the ordinate. The mole per cent glycol in the equilibrium vapor is found by difference, and this is 1 mole per cent.

From the data of Table 5, it may be seen that a considerable concentration of glycol must be in the liquid before appearing in the vapor. The method of Flint (9), which consists of oxidizing the glycol to oxalic acid by nitric acid and precipitating it as barium oxalate from samples containing glycol concentrations, was used to test the vapor condensate from mixtures containing from one mole per cent glycol to twenty mole per cent glycol. The method gave positive results in each case.

This would lead to the probable conclusion that the method used in this investigation was not sensitive enough for lower and middle glycol concentrations. However, since there is no known method for greater sensitivity, for all practical purposes, the analysis as determined would be satisfactory.



## SUGGESTIONS FOR OTHER EQUILIBRIUM STUDIES

The improved Othmer still is an excellent piece of experimental apparatus for liquid vapor equilibrium studies. This apparatus, however, is not sufficient to investigate a system thoroughly.

Along with the Othmer still, there should be a vapor pressure determination apparatus. Also advisable would be an improvement of the constant pressure apparatus. An excellent type apparatus for this purpose would be a Cartesian manostat type as described by Gilmont (11).

It would enable an investigator to study a system thoroughly to have a vapor pressure apparatus and an Othmer equilibrium still. Many systems could be obtained for study from the petrochemical field which has a growing demand for vapor-liquid equilibrium data.

The investigator could utilize the vapor pressure apparatus to study a binary system and obtain necessary data to utilize a combination of Raoult's and Dalton's Law to calculate the usual "y" - "x" plot. These data could be checked by the use of the Van Laar equations, and a third check in the system could be made by experimental results from the improved Othmer still.

Thus the properties of a binary system would be determined from every important aspect known to the field. A ternary system could be treated similarly, but the

mathematical analysis would be very sketchy since these analyses have not been fully developed at this time for a ternary system.

Eventually this work could be organized to include many systems and provide an excellent source for useful industrial and academic information. At the present writing there are many systems to be investigated, but very few investigators.

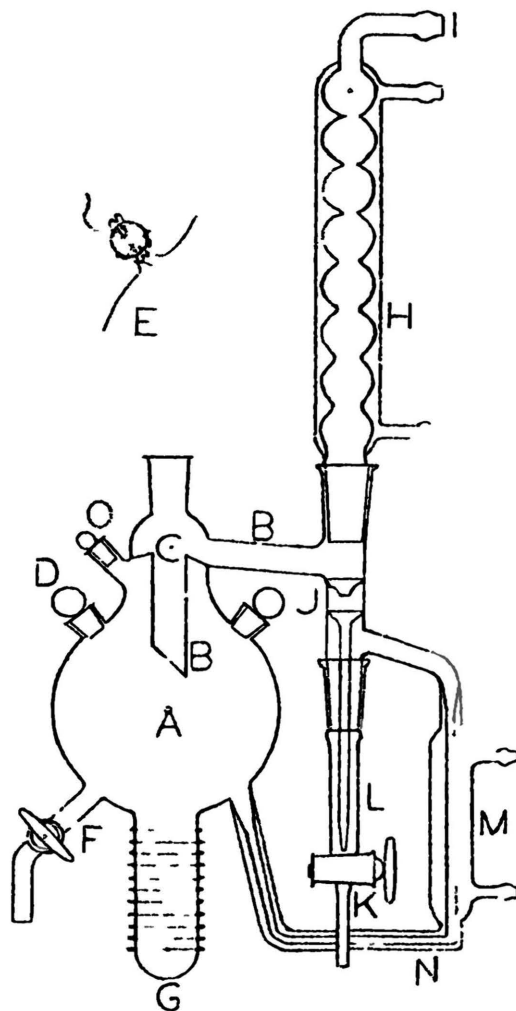
## SUMMARY

1. Experimental vapor-liquid equilibrium data were determined for the binary systems methanol-water, glycol-water and methanol-water. The usual "y" - "x" plot was made for each, and compared with data of other investigators.
2. The improved Othmer equilibrium still was evaluated and used for this investigation. Two samples from each binary system were duplicated, and four samples from the ternary system were redistilled to ascertain duplicating results from the still. In each case there was very good agreement. The improved Othmer equilibrium still is therefore considered as an excellent apparatus for experimental vapor-liquid equilibrium studies. Its ease of operation, compactness, and consistency in experimental values are noteworthy.
3. The equilibrium vapor-liquid compositions of mixtures of methanol-glycol-water for glycol concentrations from one mole per cent to ninety-six mole per cent were determined experimentally.
4. Equilibrium diagrams were constructed for the ternary system. The data and plots were compared with those of Sjoberg, and were in good agreement over the concentration duplicated.

APPENDIX A

FIG. 1

- | LEGEND                           |                            |
|----------------------------------|----------------------------|
| A - Boiling Flask                | I - Pressure Connection    |
| B - Vapor Outlet Tubes           | J - Drop Counter           |
| C - Flask Vapor Outlet           | K - Condensate Sample Cock |
| D - Ground Glass Spherical Joint | L - Condensate Receiver    |
| E - Binding Post                 | M - Condensate Cooler      |
| F - Liquid Sample Cock           | N - Circulation Tube       |
| G - Wire Wrapped Circulation Leg | O - Ground Glass Joint     |
| H - Condenser                    |                            |



IMPROVED OTHMER  
EQUILIBRIUM STILL

FIG. 2

## LEGEND

- P - Five Gallon Glass Jar, Air Reservoir
- Q - Air Supply
- R - Connection to Apparatus, Line I
- S - Manometer Connection
- T - Manometer
- U - Tube for Pressure Control
- V - Water Column

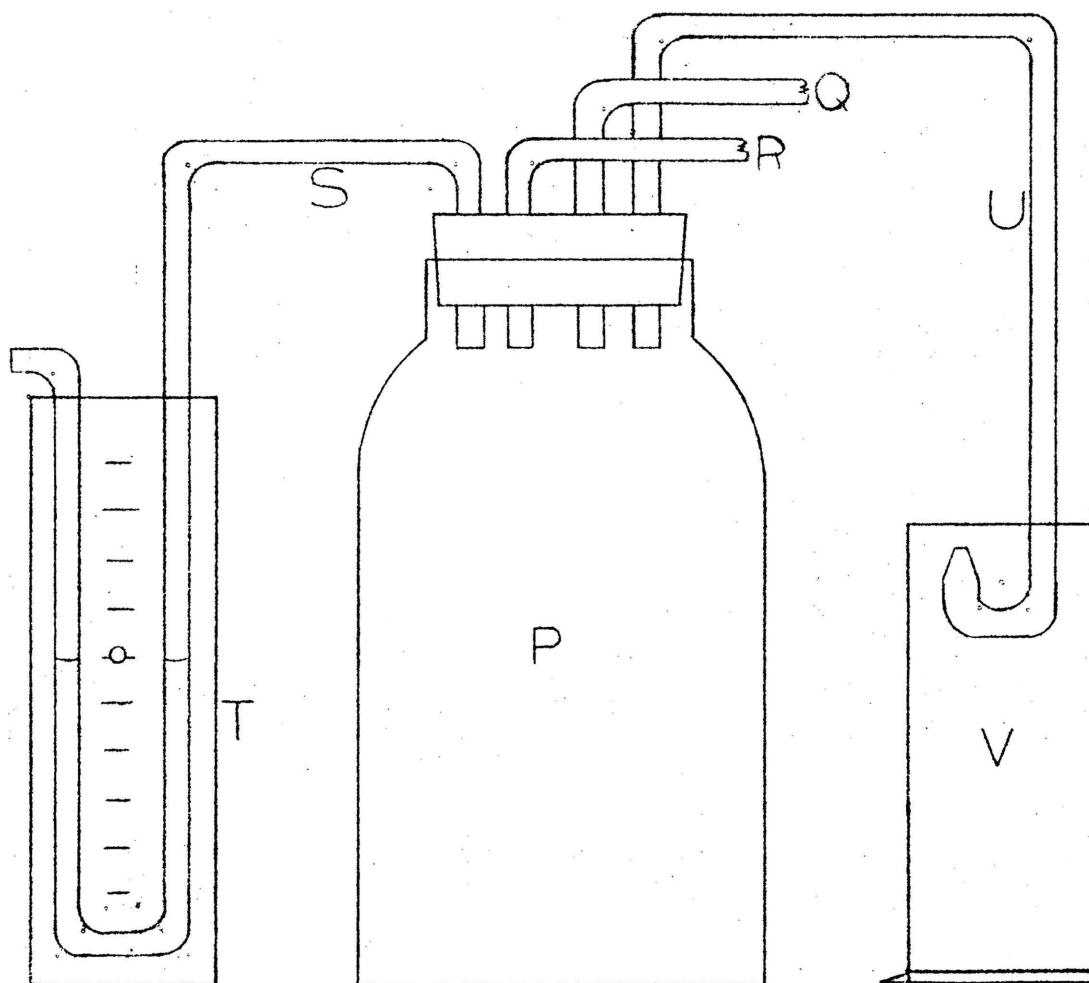
CONSTANT PRESSURE  
DEVICE

FIGURE 3

PHOTOGRAPH OF EXPERIMENTAL APPARATUS

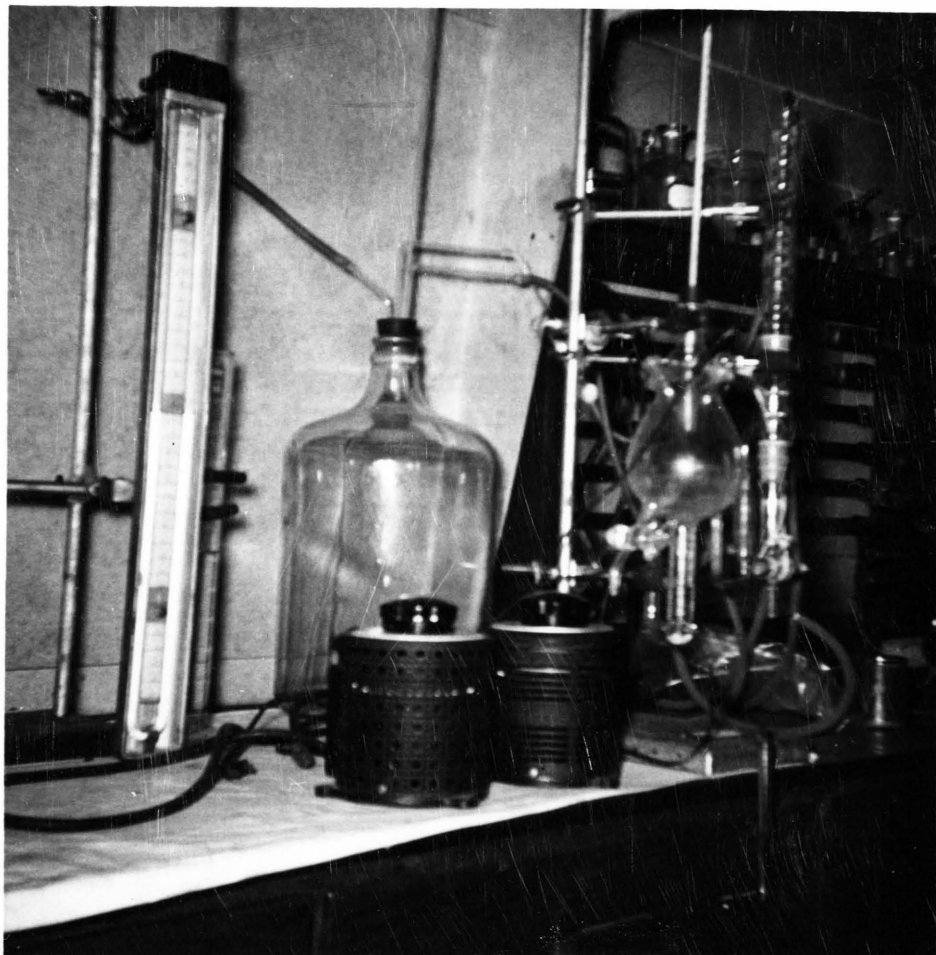


FIG 4

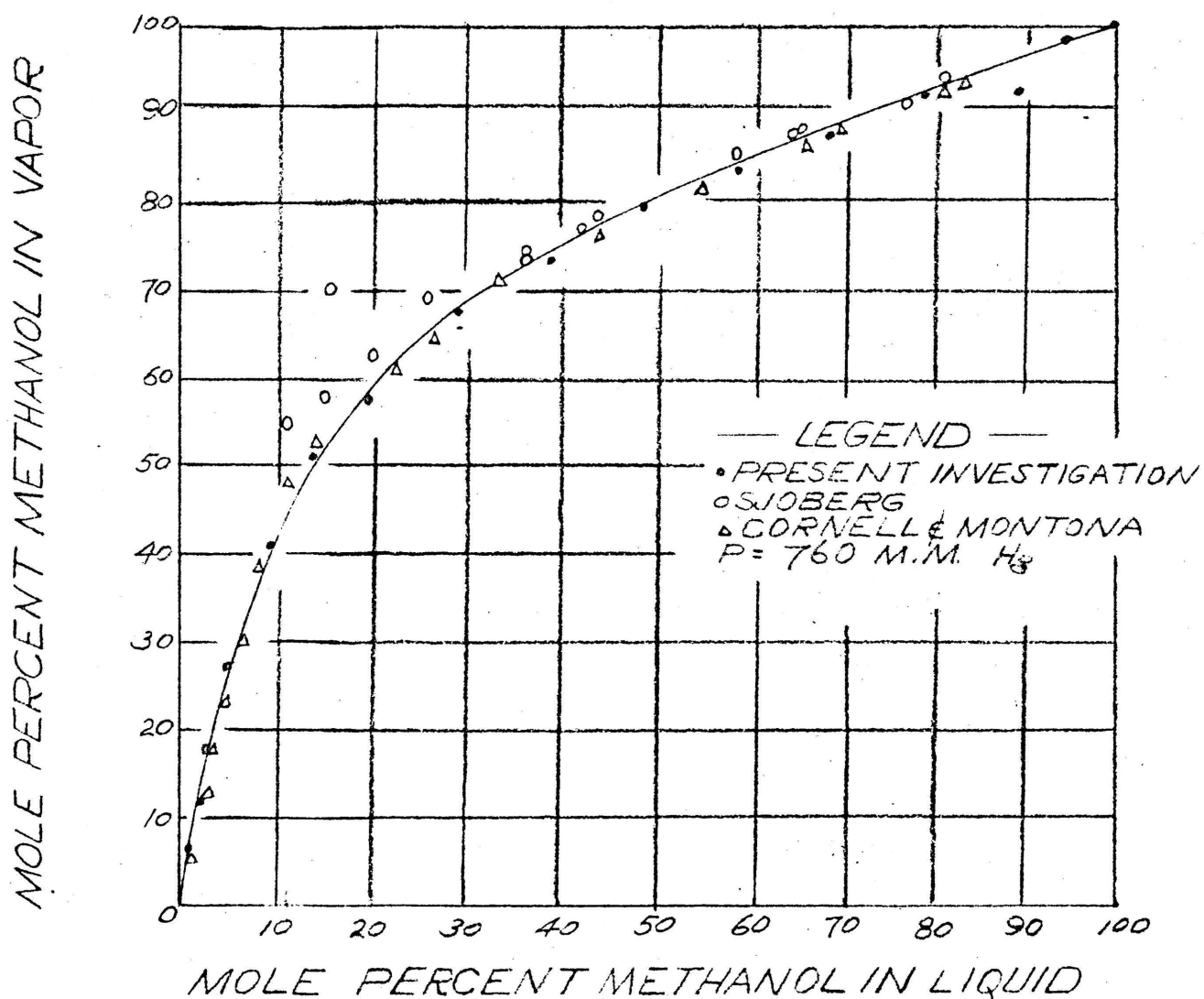
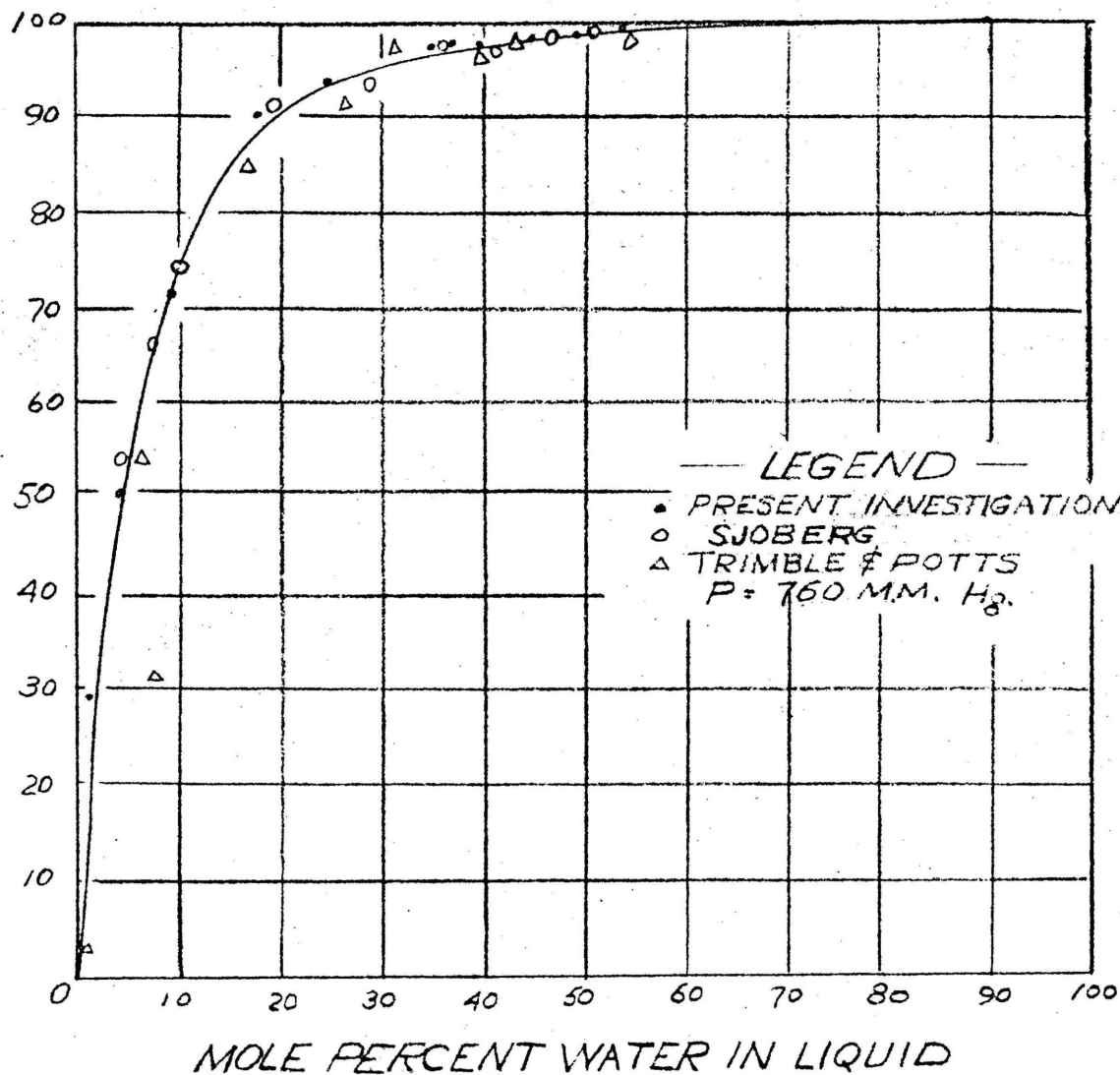
VAPOR-LIQUID EQUILIBRIUM OF  
METHANOL-WATER



FIG. 5

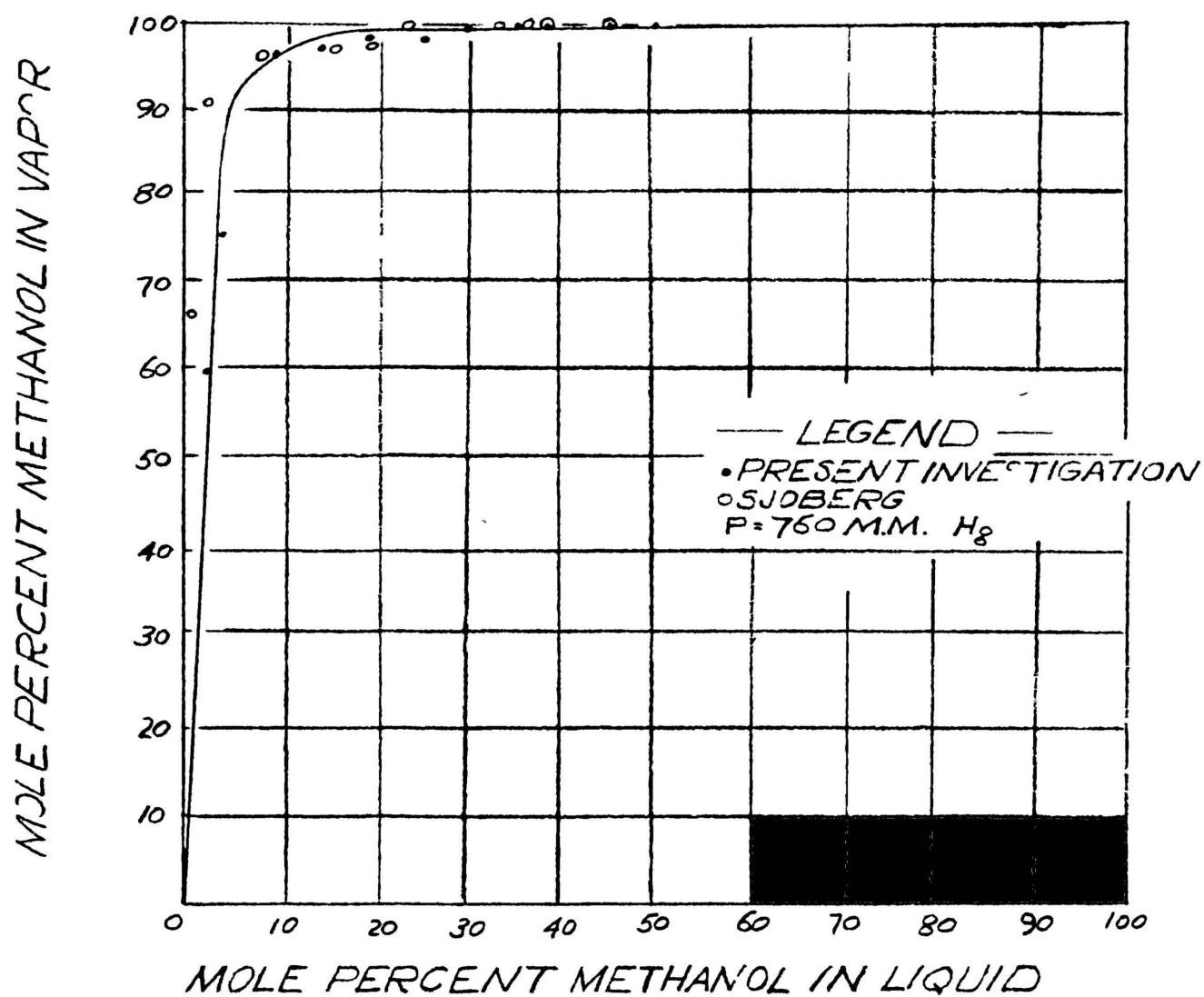
VAPOR-LIQUID EQUILIBRIUM OF  
GLYCOL-WATER

MOLE PERCENT WATER IN VAPOR



MOLE PERCENT WATER IN LIQUID

FIG. 6

VAPOR-LIQUID EQUILIBRIUM OF  
METHANOL-GLYCOL

DETERMINATION OF MOLE PERCENT OF WATER IN EQUILIBRIUM VAPOR AT CONSTANT GLYCOL CONCENTRATIONS

FIG 7

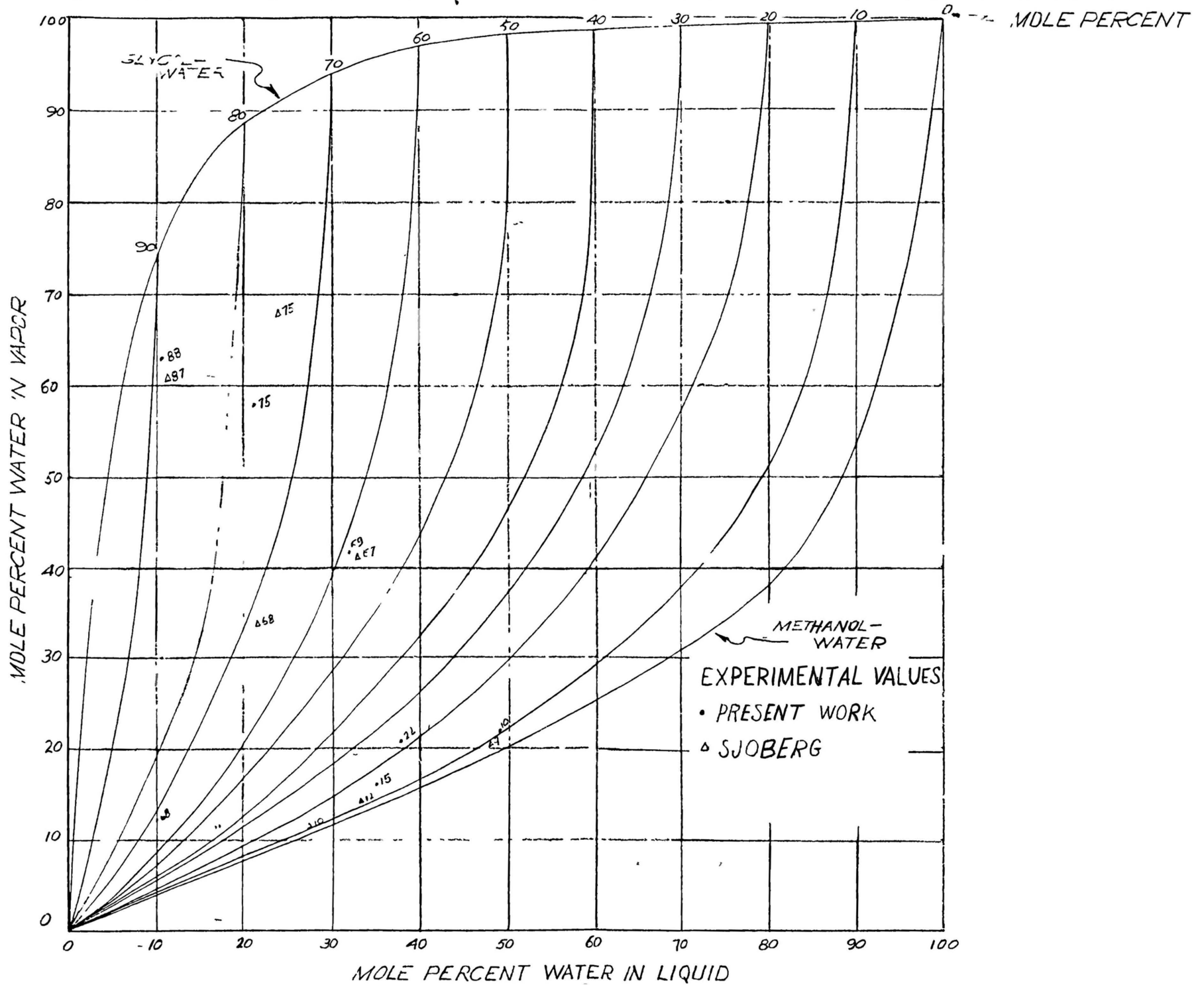
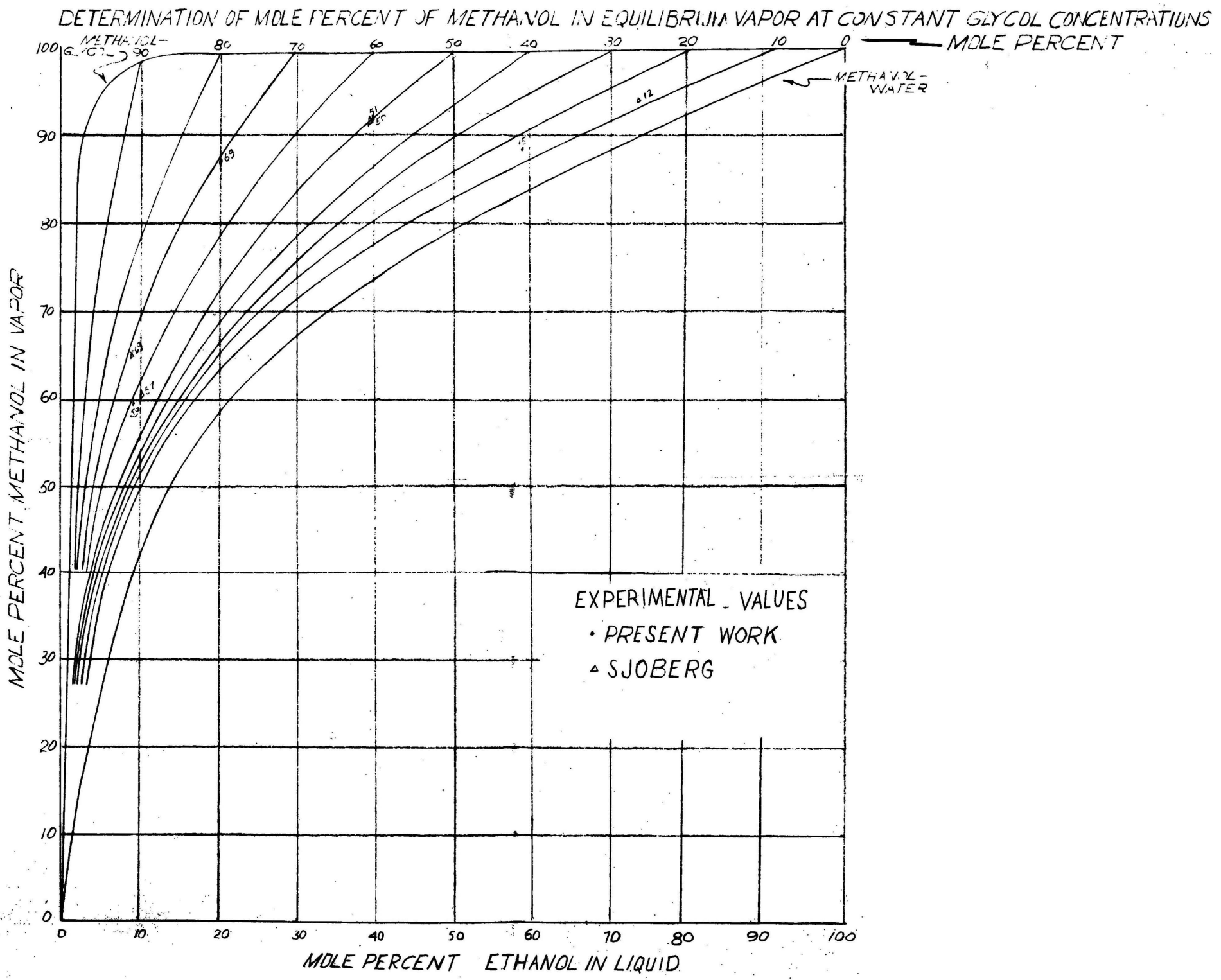


FIG. 8



**APPENDIX B**

TABLE I  
 VAPOR-LIQUID EQUILIBRIA COMPOSITIONS OF THE SYSTEM,  
 METHANOL-WATER; P = 760 mm. Hg.

SAMPLE NUMBER	OBSERVED BOILING POINT °C	MOLE PER CENT METHANOL IN LIQUID	MOLE PER CENT METHANOL IN VAPOR
1	99.2	1	6.2
2	97.0	3	18.1
3	95.8	5	27.3
4	88.0	10	41.5
5	85.1	15	51.6
6	81.5	20	58.1
7	78.0	30	67.2
8	75.2	40	73.1
9	73.0	50	79.0
10	71.1	60	83.0
11	69.2	70	86.8
12	67.5	80	91.7
13	65.9	90	92.1
14	65.1	95	98.1
15	64.5	100	100.0

TABLE II  
VAPOR-LIQUID EQUILIBRIA COMPOSITIONS OF THE SYSTEM,  
METHANOL-GLYCOL; P = 760 mm. Hg.

SAMPLE NUMBER	OBSERVED BOILING POINT °C	MOLE PER CENT METHANOL IN LIQUID	MOLE PER CENT METHANOL IN VAPOR
1	145.6	2	60.3
2	140.7	10	98.1
3	120.0	15	98.6
4	109.1	20	99.0
5	105.2	25	99.2
6	95.0	30	99.5
7	91.2	37.5	99.7
8	87.9	40	99.8
9	85.2	45	99.8
10	83.1	50	99.9

TABLE III  
VAPOR-LIQUID EQUILIBRIA COMPOSITIONS OF THE SYSTEM,  
GLYCOL-WATER; P = 760 mm. Hg.

SAMPLE NUMBER	OBSERVED BOILING POINT °C	MOLE PER CENT WATER IN LIQUID	MOLE PER CENT WATER IN VAPOR
1	186.1	1.2	29.5
2	181.1	5.0	50.1
3	174.0	10.0	71.2
4	160.1	18.1	90.0
5	142.5	25.0	93.6
6	134.0	35.0	97.0
7	131.1	37.0	97.2
8	127.5	40.0	97.5
9	124.0	45.0	98.0
10	121.2	50.0	98.2
11	119.5	54.2	99.1



TABLE IV  
 DENSITIES, REFRACTIVE INDEXES AND BOILING POINTS OF  
 MIXTURES OF METHANOL-GLYCOL-WATER

SAMPLE NUMBER	LIQUID		VAPOR		B.P. °C
	$d_{25}^{\circ}$	$n_D^{20}$	$d_{25}^{\circ}$	$n_D^{20}$	
1	0.9963	1.3397	0.9421	1.3401	98.8
2	0.9801	1.3512	0.8720	1.3412	94.2
3	0.8605	1.3492	0.7937	1.3297	73.5
4	0.9320	1.3601	0.8301	1.3371	78.2
5	0.8508	1.3492	0.7935	1.3305	74.6
6	0.9205	1.3601	0.8205	1.3341	82.6
7	0.9605	1.3685	0.8341	1.3370	86.4
8	0.9104	1.3602	0.8200	1.3356	84.6
9	0.9120	1.3647	0.8010	1.3314	87.3
10	0.9324	1.3674	0.8105	1.3325	89.9
11	0.9651	1.3752	0.8261	1.3360	91.7
12	0.9159	1.3670	0.7941	1.3310	87.4
13	0.9479	1.3770	0.8111	1.3334	93.5
14	0.9389	1.3748	0.8017	1.3309	95.7
15	0.9620	1.3821	0.8117	1.3335	97.9
16	1.0256	1.3911	0.8289	1.3380	102.0
17	0.9956	1.3891	0.8290	1.3355	105.1
18	1.0481	1.3979	0.8302	1.3395	109.8
19	0.9775	1.3910	0.8311	1.3390	106.1
20	0.9800	1.3902	0.8341	1.3345	103.2
21	1.0651	1.4052	0.9050	1.3462	105.0

TABLE IV (Continued)

SAMPLE NUMBER	LIQUID		VAPOR		B.P. °C
	$d_{25}^{\circ}$	$n_D^{20}$	$d_{25}^{\circ}$	$n_D^{20}$	
22	1.0532	1.4040	0.8519	1.3425	109.0
23	1.0111	1.3980	0.8330	1.3341	108.2
24	1.0321	1.4021	0.8381	1.3372	111.2
25	1.0688	1.4107	0.8890	1.3425	115.5
26	1.0756	1.4119	0.8651	1.3455	119.1
27	1.0689	1.4081	0.8309	1.3356	121.2
28	1.0792	1.4130	0.8507	1.3409	124.5
29	1.0881	1.4165	0.8709	1.3420	129.2
30	1.0492	1.4125	0.8157	1.3389	127.5
31	1.0650	1.4137	0.8341	1.3390	129.9
32	1.0690	1.4155	0.8350	1.3392	131.1
33	1.0722	1.4162	0.8129	1.3361	133.5
34	1.0852	1.4185	0.8621	1.3421	137.8
35	1.0610	1.4183	0.8361	1.3385	137.0
36	1.0901	1.4321	0.9009	1.3505	142.7
37	1.0857	1.4215	0.8480	1.3410	145.0
38	1.0875	1.4239	0.8780	1.3490	147.6
39	1.0815	1.4225	0.8392	1.3400	148.2
40	1.1105	1.4269	0.8852	1.3456	149.1
41	1.1118	1.4279	0.9091	1.3511	151.0
42	1.0800	1.4265	0.8320	1.3419	152.6
43	1.0908	1.4288	0.8709	1.3501	153.7
44	1.1103	1.4295	0.8952	1.3589	154.6
45	1.1104	1.4315	0.9610	1.3812	156.2
46	1.1201	1.4398	0.9817	1.3946	163.1

TABLE V  
EQUILIBRIUM COMPOSITIONS OF METHANOL-GLYCOL-WATER MIXTURES\*

SAMPLE NUMBER	LIQUID, MOLE PER CENT			VAPOR, MOLE PER CENT		
	G	M	W	G	M	W
1	1.5	4.0	94.5	0	25.0	75.0
2	5.5	14.5	80.0	0	55.0	45.0
3	9.4	80.0	10.6	0	95.0	5.0
4	10.2	40.8	49.0	0	78.0	22.0
5	11.0	83.4	5.6	0	97.0	3.0
6	12.1	47.4	40.5	0	82.4	17.6
7	15.0	35.0	50.0	0	75.0	25.0
8	15.0	59.1	25.9	0	88.0	12.0
9	18.5	65.0	16.5	0	92.2	7.8
10	21.2	58.8	20.0	0	90.0	10.0
11	22.0	40.2	37.8	0	80.0	20.0
12	25.0	70.0	5.0	0	97.0	3.0
13	27.2	52.8	20.0	0	89.0	11.0
14	30.1	60.9	9.0	0	95.2	4.8
15	31.4	47.3	21.3	0	87.8	12.2
16	33.3	20.7	46.0	0.3	65.7	34.0
17	35.6	30.5	33.9	0	75.9	24.1
18	38.1	15.6	46.3	0.6	60.3	39.1
19	40.4	40.2	19.4	1.1	86.2	12.7
20	43.7	50.2	6.1	1.6	93.6	4.8
21	44.9	5.1	50.0	2.1	43.8	55.1

\* The ternary analysis diagram of Sjoberg (25) was used.

TABLE V (Continued)

SAMPLE NUMBER	LIQUID, MOLE PER CENT			VAPOR, MOLE PER CENT		
	G	M	W	G	M	W
22	48.3	16.4	35.3	1.9	64.4	33.7
23	50.0	40.1	9.9	1.6	92.2	6.2
24	51.5	28.4	20.1	0.5	81.8	17.7
25	52.8	7.7	40.1	0.8	49.0	50.2
26	58.5	9.2	32.3	1.8	57.1	42.1
27	60.1	25.0	14.9	1.6	84.6	13.8
28	61.9	12.0	26.1	0.7	65.3	34.0
29	63.5	6.5	30.0	1.9	54.2	43.9
30	66.8	26.7	6.5	2.1	91.5	6.4
31	67.9	21.8	10.3	2.2	84.9	12.9
32	69.8	20.0	10.2	2.6	84.7	12.7
33	70.2	24.2	5.6	1.2	91.8	7.0
34	71.5	8.2	20.3	2.0	63.1	34.9
35	73.7	21.0	5.3	1.9	89.1	9.1
36	75.0	3.9	21.1	5.5	49.0	45.5
37	77.2	11.0	11.8	2.0	74.0	24.0
38	79.6	6.8	13.6	6.0	65.0	29.0
39	81.7	10.0	8.3	2.3	77.4	20.3
40	83.4	2.8	13.8	2.1	49.8	48.1
41	87.9	2.4	9.7	5.8	49.5	44.7
42	89.5	8.4	2.1	6.1	87.4	6.5
43	90.8	5.7	3.5	10.2	75.8	14.0
44	92.0	4.0	4.0	17.9	62.2	19.9
45	94.5	4.1	1.4	35.0	56.2	8.8
46	96.8	2.0	1.2	43.6	46.4	10.0

## LITERATURE CITED

- (1) Badger, W.L. and W.L. McCabe. Elements of Chemical Engineering. New York, McGraw Hill, Second Edition, (1936).
- (2) Baker, E.M., J.H. Hubbard, J.H. Huget and S.S. Michalowski. Equilibria in the Systems Ethanol-Water, Ethanol-Cellosolve and Cellosolve-Water. Ind. Eng. Chem. 31, 1261-3, (1939).
- (3) Carney, T.P. Laboratory Fractional Distillation. New York, Macmillan, (1939).
- (4) Conrad, F.H., M.C. Flint, R.H. Meyer, and J. W. Sjoberg. Ind. Eng. Chem. Anal. Ed., 24 837, (1952).
- (5) Conrad, F.H., E.F. Hill and E.A. Ballman. Freezing Points of the System Ethylene Glycol-Methanol-Water. Ind. Eng. Chem., 32, 542 (1940).
- (6) Cornell, L.W. and R.E. Montonna. Studies in Distillation II, Liquid-Vapor Equilibria in the Systems Ethanol-Water, Methanol-Water and Acetic Acid-Water. Ind. Eng. Chem., 25, 1331-35, (1933).
- (7) Dodge, B.F. Chemical Engineering Thermodynamics. New York, McGraw-Hill, (1944).
- (8) Encyclopedia of Chemical Technology. New York, Interscience Publishing Co., 2, (1951).
- (9) Flint, M.C. Equilibria between Liquid and Vapor in the System Methanol-Glycol-Water. Unpublished B.S. Thesis. Missouri School of Mines and Metallurgy, Rolla, Mo., (1942).

- (10) Gillespie, D.T.C. Boiling Composition of Binary Systems. Ind. Eng. Chem. Anal. Ed., 18, 575, (1946).
- (11) Gilmont, R., Design and Operational Characteristics of Cartesian Manostats. Ind. Eng. Chem. Anal. Ed., 23, 157, (1951).
- (12) Griswold, J. and J. Dinwiddie. Analysis of the Ternary System Ethanol-Methanol-Water. Ind. Eng. Chem., 34, 1188-91, (1942).
- (13) Hausbrand, E. Principles and Practices of Industrial Distillations by Tripp, E.H. New York, John Wiley and Sons, Fourth Edition, (1926).
- (14) Huborn, I.M. Dictionary of Organic Compounds, New York, Oxford University Press, 2, (1936).
- (15) International Critical Tables. New York, McGraw Hill, 3.
- (16) Jones, C.A., E.M. Schoenborn, and A.P. Colburn. A New Vapor-Liquid Equilibrium Still. Ind. Eng. Chem., 35, 666, (1943).
- (17) Lange, N.A. Handbook of Chemistry. Sandusky, Ohio, Handbook Publishers, Inc., Eighth Edition, (1952).
- (18) Lawrie, J.W. Glycerol and the Glycols. American Chemical Society Monograph Number 44. New York, The Chemical Catalog Co., (1928).
- (19) Meyer, R. Equilibria between Liquid and Vapor in the System Methanol-Glycol-Water. Unpublished B.S. Thesis, Missouri School of Mines and

Metallurgy, Rolla, Mo. (1941)

- (20) Othmer, D.F. Composition of Vapor from Boiling Solutions, Improved Equilibrium Still. Ind. Chem. Anal. Ed., 20, 763, (1948).
- (21) Othmer, D.F., M.M. Chudgon, and S.L. Levy. The Ternary System Acetone-Methyl Ethyl Ketone-Water. Ind. Eng. Chem., 44, 1872-81 (1952).
- (22) Physico-Chemical Constants of Pure Organic Compounds, New York, Elsevier Publishing Co., (1950).
- (23) Robinson, C.S. and E.R. Gilliland. Elements of Fractional Distillation. New York, McGraw-Hill, Fourth Edition, (1954).
- (24) Rosanoff, M.A., C.A. Bacon, and R.H. White. A Rapid Method of Measuring the Partial Vapor Pressures of Liquid Mixtures. J. Am. Chem. Soc., 36, 1803-25, (1914).
- (25) Sjoberg, J.W. Liquid-Vapor Equilibria in the System Methanol-Ethylene Glycol-Water. Published M.S. Thesis, Missouri School of Mines and Metallurgy, Rolla, Missouri, (1948).
- (26) Taylor, C. and W. Rinkenbach. Ethylene Glycol. Ind. Eng. Chem., 18, 676, (1926).
- (27) Trimble, H. and W. Potts. Glycol-Water Mixtures. Ind. Eng. Chem., 27, 66-68, (1935).
- (28) Vogel, A.I. Textbook of Practical Organic Chemistry. New York, Longmans Green, (1951).

- (29) Wiley, R.M. and E.H. Harder. Vapor-Liquid Equilibrium Apparatus Studies. Ind. Eng. Chem. Anal. Ed., **7**, 349, (1935).
- (30) Young, S. Distillation Principles and Processes. London, Macmillan, (1922).



## VITA

Herbert Benjamin Sachs was born in Bonne Terre, Missouri on February 21, 1922. He attended Harris Junior College from September 1940 to June 1942. After serving three and one-half years in the United States Navy during World War II as a Naval Aviator, he entered the Missouri School of Mines and Metallurgy in January 1946. He was graduated with a B.S. in Chemical Engineering in January 1948.

He then was employed as a Chemical Engineer by the United States Bureau of Mines for two and one-half years, and for the Cities Service Oil Company for one year. He was recalled in October 1951 into the United States Navy during the Korean Emergency. After serving two years, he was released from active duty in December 1953.

Mr. Sachs married the former Mary McAuliffe in December of 1953. In February 1954 he entered the Missouri School of Mines to engage in studies for his M.S. degree in Chemical Engineering, which he received in May 1955. Mr. and Mrs. Sachs have one daughter named Betsy.