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**A Report on the Preliminary Work on the  
Experimental Simultaneous Determination  
of Vapor-Liquid Equilibrium, and Enthalpy  
Concentration Data, and A Proposed  
Design of an Improved Apparatus**

By

SIMON MENCHER

A REPORT ON THE PRELIMINARY WORK ON THE EXPERIMENTAL  
SIMULTANEOUS DETERMINATION OF VAPOR-LIQUID  
EQUILIBRIUM, AND ENTHALPY CONCENTRATION  
DATA, AND A PROPOSED DESIGN OF AN  
IMPROVED APPARATUS

by  
Simon Mencher

A REPORT OF RESEARCH  
presented to the Graduate Faculty  
of Lehigh University in candidacy  
for the degree of Master  
of Science

Lehigh University  
Bethlehem, Pennsylvania  
1957

CERTIFICATE OF APPROVAL

This report of research is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

May 31, 1957  
Date

Curtis W. Clump  
Louis Maurer  
Professors in Charge

\_\_\_\_\_  
Head of the Department

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The assistance which has been received from the Staff of the Chemical Engineering Department is gratefully acknowledged.

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## ABSTRACT

An apparatus to determine simultaneously, vapor-liquid equilibrium and enthalpy concentration data, was designed, constructed, and tested with an ethanol-water mixture. The design is one which attempts to remove the sources of error which are present in the usual type of equilibrium still.

The operation of the apparatus is quite flexible. Data may be obtained relatively quickly for various types of binary and ternary systems at desired pressures.

Difficulties were encountered in the determination of data because of the reaction of the ethanol-water mixture on the rubber that was present in the system. An apparatus which is made entirely of glass was therefore designed.

## INTRODUCTION AND LITERATURE REVIEW

Many types of apparatus have been built for the determination of vapor-liquid equilibrium and enthalpy concentration data. Latent heats have been determined by calorimetric measurements with good accuracy but a satisfactory investigation of the accuracy of the various experimental methods of determining equilibrium data has not been made. There is quite a discrepancy when data for the same systems are compared, even when comparing investigations employing essentially the same technique.

Common methods that have been used for obtaining equilibrium data are:

- 1) Circulation method. (1,2,3)
- 2) Bomb method. (4,5)
- 3) Dynamic flow method. (6,7)
- 4) Dew and boiling point method. (8,9,10)
- 5) Dynamic distillation method. (11,12,13)
- 6) Continuous distillation method. (14,15,16,17,18)

The most common sources of error in the above methods are:

- 1) Not having true equilibrium between vapor and liquid.
- 2) Difficulty in withdrawing samples without disturbing equilibrium conditions.
- 3) Difficulties in analysis.



The apparatus discussed in this report was designed to attempt to eliminate the above errors involved in the determination of equilibrium data, and to obtain this data simultaneously with latent heats of condensation.

The problem of obtaining true equilibrium in the system was approached by using an indirect procedure to obtain the usual x, y data. The system does not have to come to equilibrium but only to a steady state condition where all temperatures, pressures, and compositions, are constant with time at any portion of the system. Steady state for a run may be obtained in from 1/2 to 1 hour.

The problem of the disturbance of steady state due to the withdrawal of a sample for analysis has been eliminated. Only a sample of the condensate is needed for analysis and this may be obtained after all other necessary data has been taken at steady state conditions.

The system ethanol-water was used for preliminary work. Data for this system was obtained but did not agree with the values in the literature. It was found that the neoprene used in the construction of the apparatus was dissolving in the alcohol and because of this a design of an all glass-apparatus is included in this report.

## THEORY OF OPERATION

The apparatus is shown in Figure I. A critical point in the operation of the apparatus is to free it from noncondensable gases, as will be explained later. Assume that the system is free from noncondensibles, and consider the liquid in the flask (1). The liquid is boiling and the vapors rise through the heated tube (5). These vapors become superheated and travel from the flask to the adaptor (6). A portion of the adaptor serves as a heat leak and some of the vapors will condense and run back down the sides of the superheater. Here they are revaporized and sent back to the heat leak. This process is continually repeated. It should be noted that there is no liquid returning to the flask, since fractionation can not be tolerated.

Since the vapor is condensing in the adaptor it should be a saturated vapor and its temperature at 760 mm pressure is the dew point of the vapor. A check for possible superheat is made by observing the droplet of liquid in (6). If the droplet does not disappear as the vapor passes over it the vapor is saturated. By controlling the heat addition in the superheater, saturated vapor may be obtained.

The vapor enters the condenser (7) at its dew point and leaves as saturated liquid at its bubble point.

No subcooling occurs in the condenser because the pressure is maintained at 760 mm and there are no noncondensibles present in the system. The pressure is maintained constant by the pressure regulator (16).

Low water rates are used in the condenser. At low rates the difference in temperature between the cooling water and the fluid in the condenser is small, and any tendency for pressure reduction and subcooling due to a temperature driving force is negligible. The water enters the condenser at room temperature and leaves at essentially the dew point of the vapor. This large temperature change reduces the error in calculating the heat of condensation.

The liquid leaving the condenser passes through a flow meter (11), where its rate is measured. The liquid is then recycled to the boiler.

The system is operated continuously in the above manner until steady state conditions are reached.

The condensate has a composition equal to the vapor entering the condenser. A sample of the condensate is obtained at (10) and analyzed. Since the bubble and dew points at this composition are known, two points on a temperature-composition diagram may be plotted. From data at various compositions an entire temperature-composition curve may be plotted.

An energy balance is made around the condenser and the heat of condensation of the alcohol-water mixture is determined at this composition.

## OPERATING PROCEDURE

1. The system is evacuated as completely as possible with a vacuum pump. The system is then heated to approximately 70°C under vacuum to eliminate adsorbed vapors in the flask and superheater.
2. The cooling water rate is set at approximately 2 cc per minute and the system is cut off from the vacuum pump.
3. 1 pint of absolute alcohol is fed into the boiler. The internal heating circuit is turned on and the pressure is allowed to build up to 760 mm.
4. At this time a check on the bubble and dew point of the absolute alcohol usually shows the bubble point to be lower than the dew point. This is due to the presence of noncondensibles. Purging therefore is necessary. The system is purged with an aspirator until the bubble and dew points are equal.
5. The voltage applied to the internal heater is regulated for the most rapid time cycle of the relay.
6. By controlling the heat input of the superheater and internal heating coil steady state conditions may be obtained within 30-60 minutes.
7. At steady state, flow rates and temperatures are recorded and a sample of condensate is withdrawn. The sample must be analyzed immediately to avoid any

loss of volatile material. Collecting the sample in a previously cooled container reduces the tendency for some of the volatile constituent to vaporize from the container during withdrawal.

8. 200 ml of distilled water are added to the system to change the composition in the boiler. The water should be boiled prior to introduction to eliminate any dissolved air.
9. Additional data may now be obtained by repeating Steps 5-9.

## DESCRIPTION OF PROPOSED APPARATUS

The following description of the proposed apparatus differs from that originally used only in the substitution of ground glass joints where rubber was previously used.

All lengths of the glass parts that make up the apparatus are nominally sized because of the difficulty in making glass apparatus to exact specification. The system should be made and put together one section at a time to insure an air-tight system.

The ground glass joints which are specified also specify the size of tubing to be used. All glass is Pyrex.

- (1) One 5 liter 3 neck flask, with  $\text{N} 24/40$  ground glass joints. Glass hooks should be added to the flask.
- (2) Two adaptors. The main joint of each being a male  $\text{N} 24/40$  joint which fits into the external arms of the five liter flask. The top joint is a  $\text{N} 10/30$  female. The side arms are different on each adaptor. One is a  $\text{N} 10/30$  female, and the other a  $12/5$  socket joint. Glass hooks are placed as shown on the diagram.
- (3) Two glass tubes with  $\text{N} 10/30$  male joints. A wire lead is sealed in the tube as shown on the

diagram. This lead is used for the internal heater.

- (4) One 200 ml dropping funnel with a  $\text{N} 10/30$  male joint. The funnel must be less than 4 inches in diameter.
- (5) One 24 inch condenser wired with nicrome wire. Sauerisen adhesive cement is used to hold the wire in place. Male and female  $\text{N} 24/40$  joints are on either end as are the glass hooks shown in the diagram.
- (6) (a) One straight tube with  $\text{N} 24/40$  joints and glass hooks.
- (6) (b) One adaptor. This may be made from the usual type  $\text{N} 24/40$  adaptor since the required angle is ready made. Additions are glass hooks and an indentation which is blown to serve as a liquid trap. A thermometer well  $3/8$  inch in diameter is inserted that the bottom of the well should be approximately  $3/4$  of the way into the main tube. Care must be taken when inserting the well, that no reduction in diameter occurs. This can therefore be used as either a thermometer or a thermocouple well. When in use mercury is used to fill a small portion of the well as explained on page 11.
- (7) One 24 inch condenser with  $\text{N} 24/40$  joints. No additions except glass hooks are necessary.

- (8) One adaptor, consisting of a straight tube with a  $\text{F}$  24/40 female joint, 3 side arms and a thermometer well. The upper arm has a 12/5 socket joint and the bottom arm has a 12/5 ball joint. The other arm is 7 mm tubing fitted with a stopcock. The thermometer well is 3/8 inch diameter tubing that extends into the indentation blown into the main tube. This well is also filled approximately with 1/4 inch of mercury when in operation.
- (9) One straight tube with one 12/5 ball and one 12/5 socket joint.
- (10) This piece may be made entirely from a 3 way stopcock. Additions are a 12/5 socket and a  $\text{F}$  male joint. A 3/8" thermometer well is inserted in the blown indentation.
- (11) One Fischer and Porter O2F 1/8-12-5 flow meter with a  $\text{F}$  ground glass joints.
- (12) One 90 degree bend with a 12/5 ball joint and a  $\text{F}$  male joint.
- (13) One straight tube with two 12/5 ball joints.  
See (13)\*.
- (13)\* A Teflon tube approximately 1-1/2 inches long is inserted in (13). This enables adjustments to be made in fitting the apparatus together.
- (14-16)- The pressure regulator was made of two 3 inch glass funnels which were attached by a wooden clamp.



Between the funnels was a neoprene diaphragm on one side of which was a layer of 1 inch of mercury. The rise and fall of the mercury as the pressure on the diaphragm changed, opened and closed an electric circuit through a small relay. This relay in turn, controlled the flow of current through the internal heating coil.

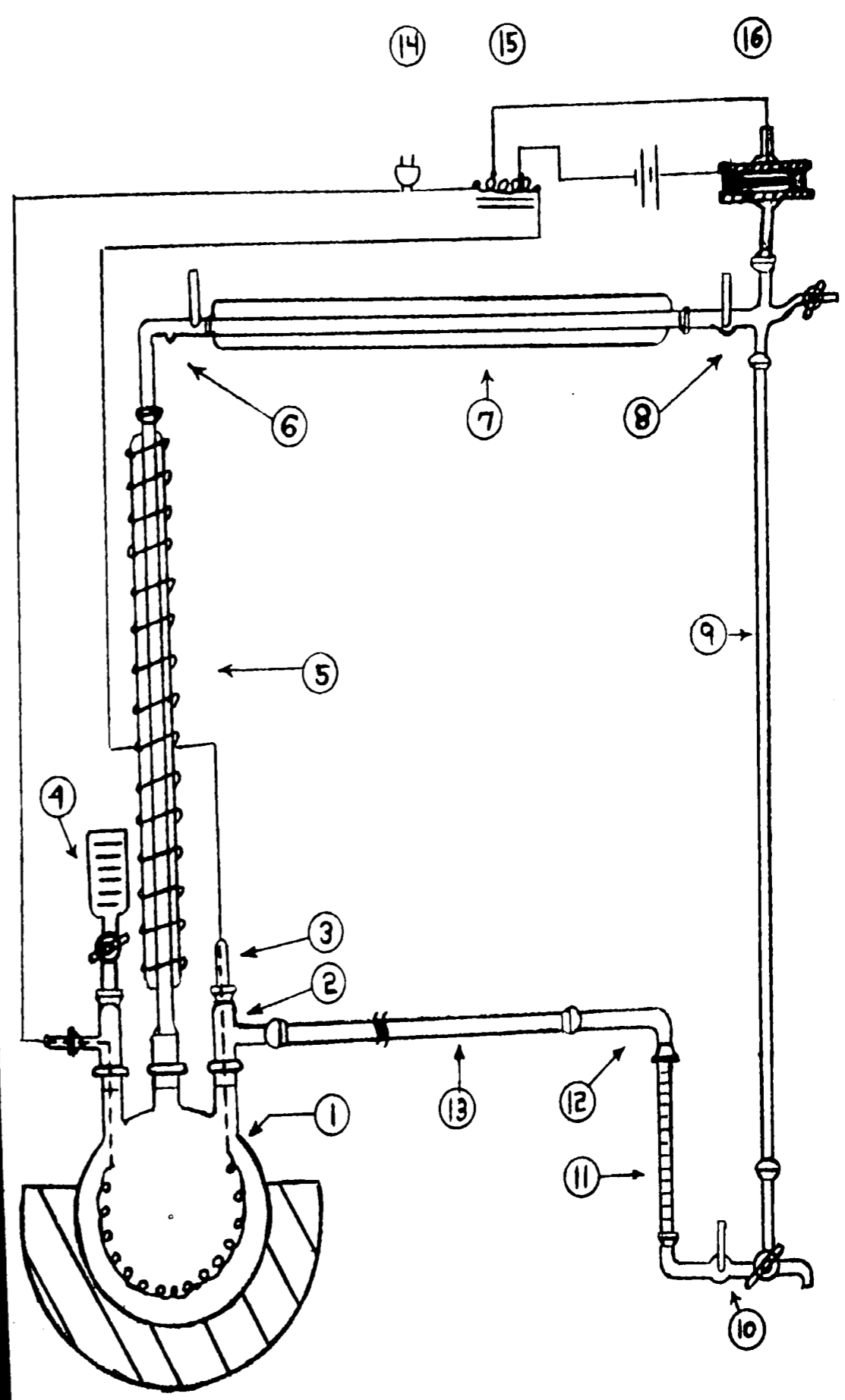
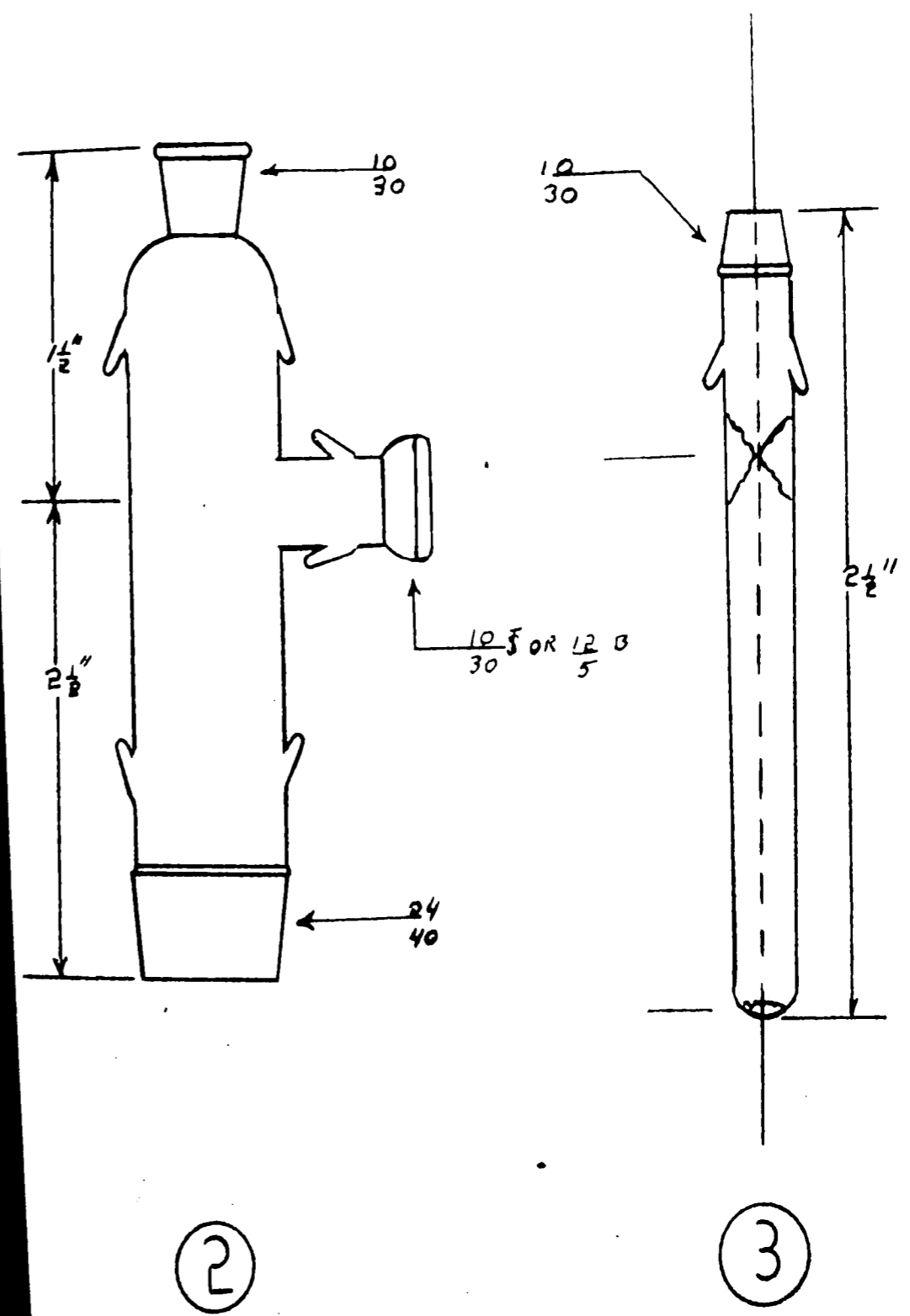
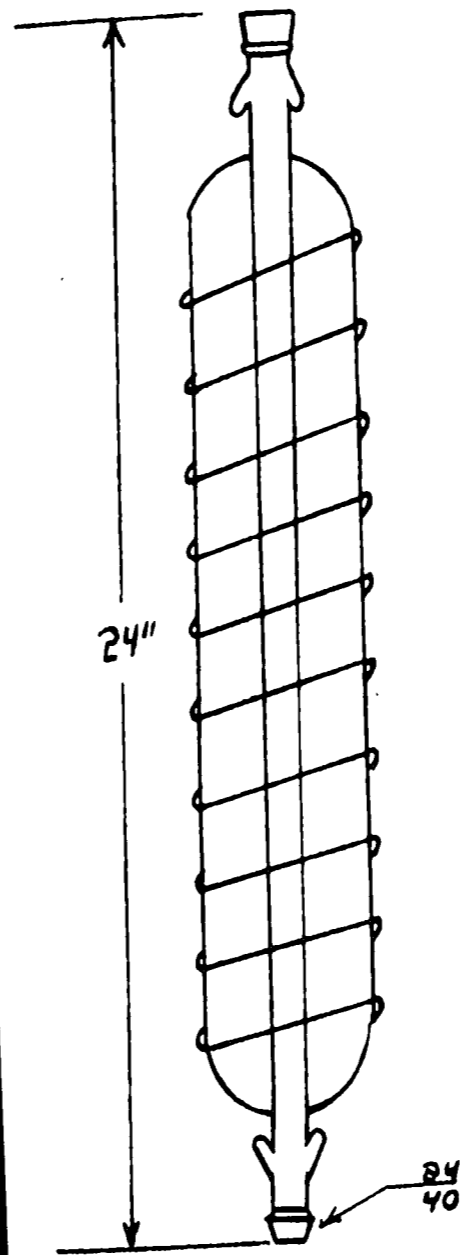
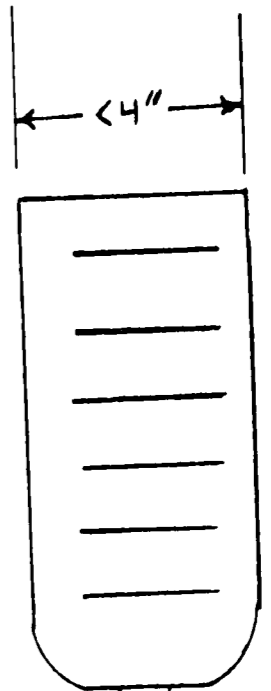


FIG. I

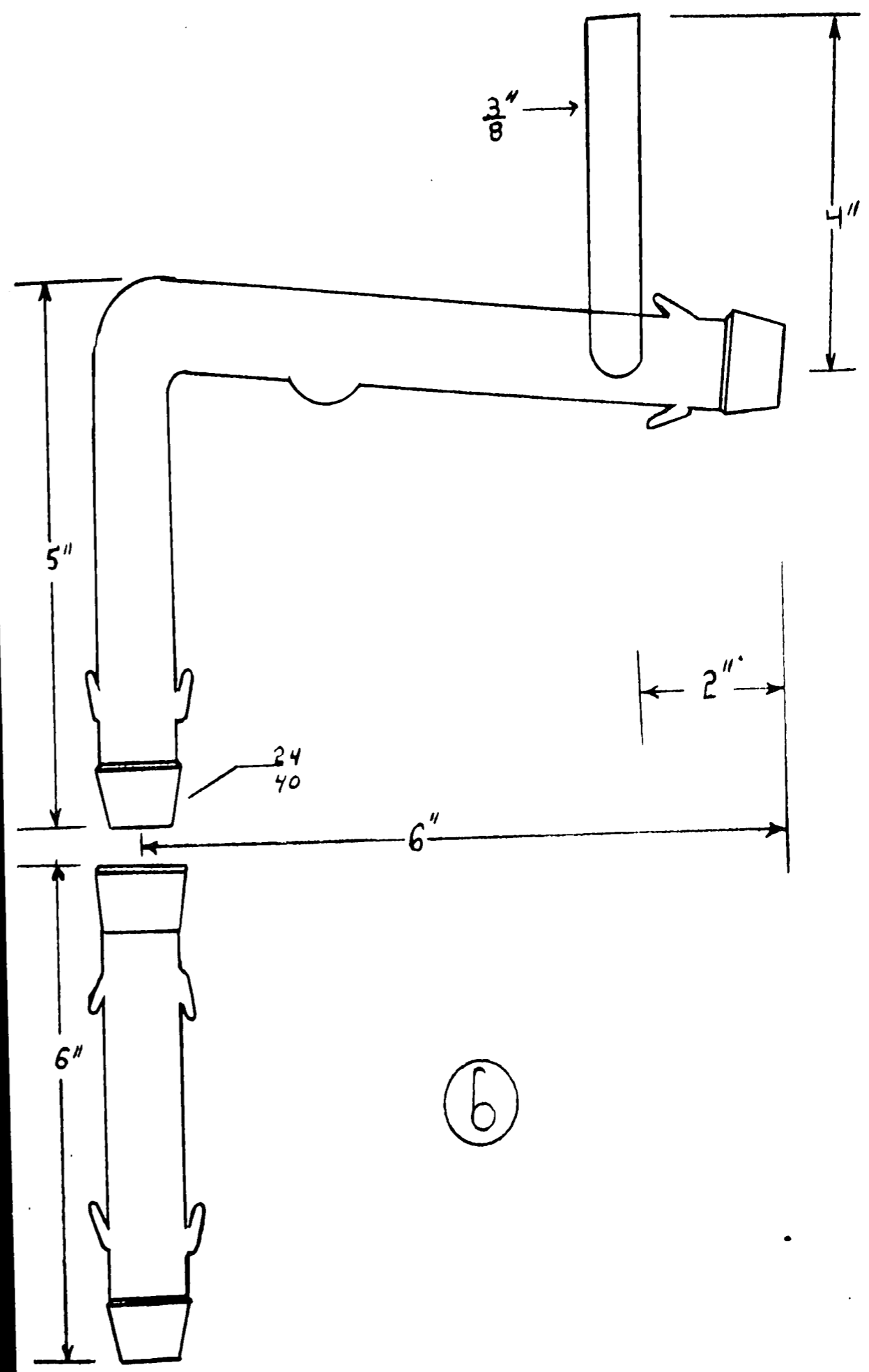


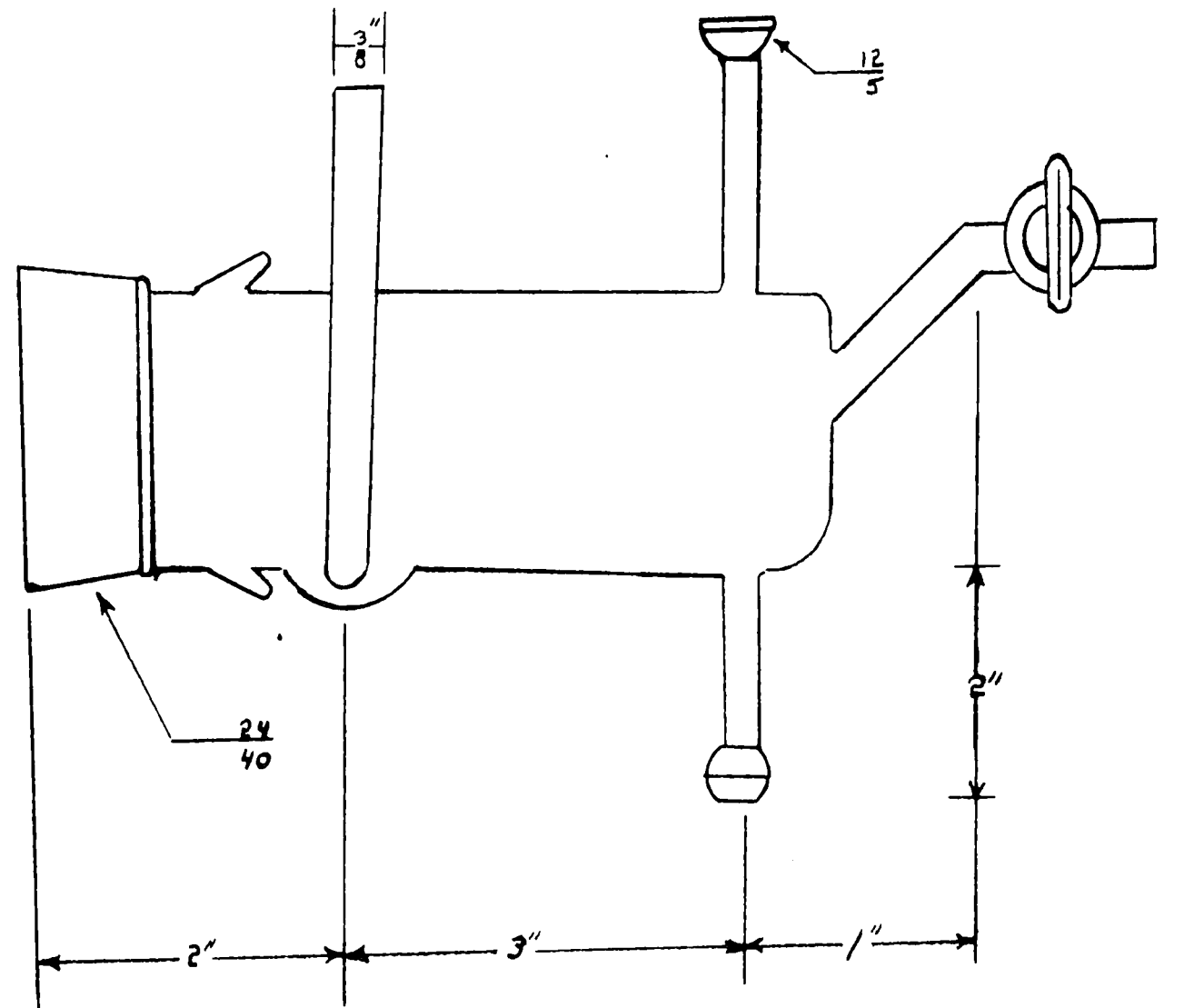


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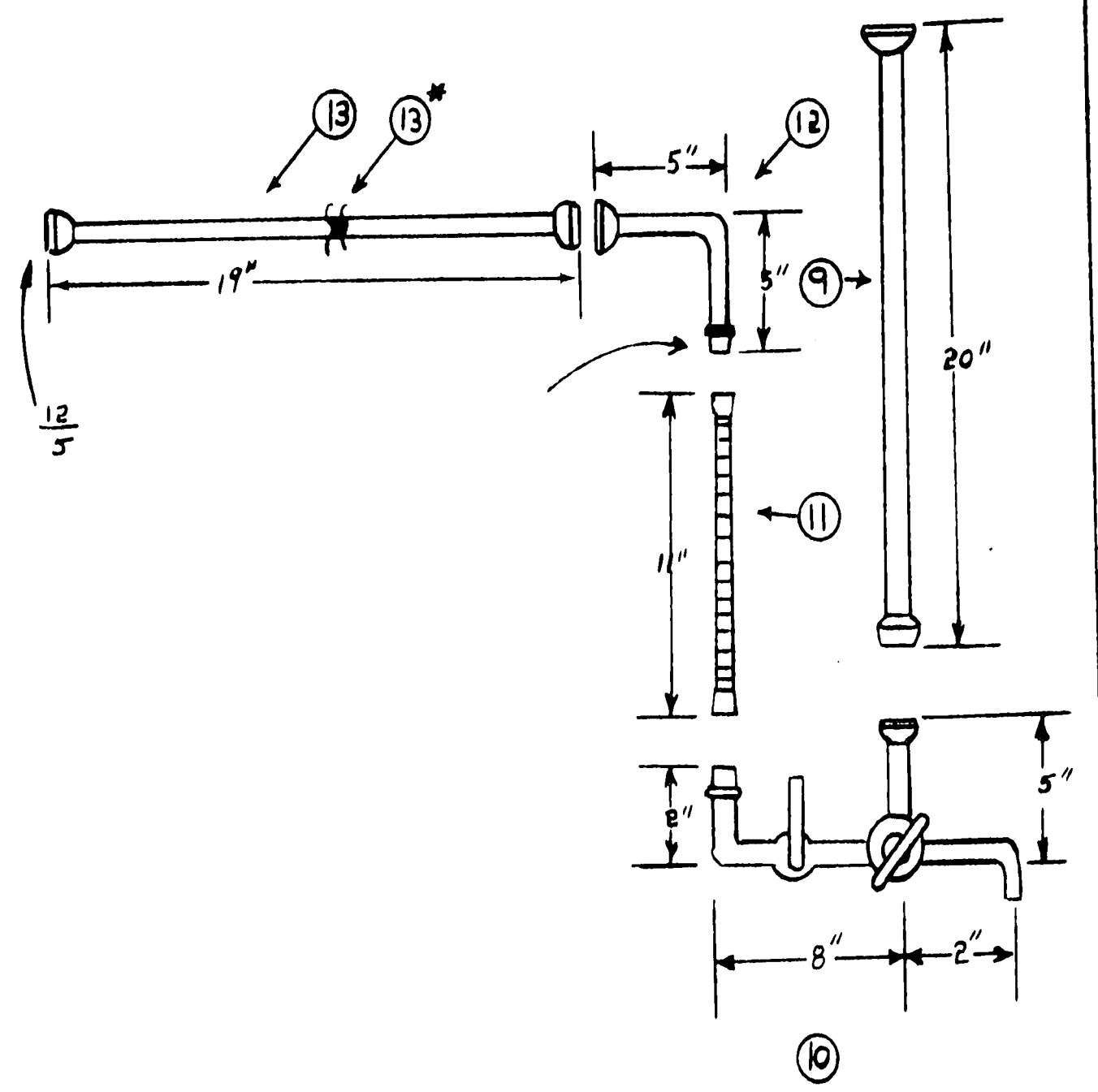


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## CONTROLS AND ACCESSORIES

A 55 gallon constant temperature tank and a 5 gallon constant head tank were used to provide cooling water for the condenser. A 1/50 H.P. centrifugal pump, pumped the water from the storage tank to the constant head tank. From there the water was gravity fed at a controlled rate through the condenser.

The intermittent internal heater was made of coiled nicrome wire. The potential across the wire was set to obtain the most sensitive pressure balance. The heater was controlled by the pressure sensing element.

The external heater was a 600 watt Clas Co. heating mantle.

Temperature measurements were made with 1/1000 inch diameter copper constantan thermocouples. The small diameter was used to prevent heat leaks: by conduction through the lead to the surroundings. The addition of a small amount of mercury in the well increased the sensitivity of the temperature measurements greatly. The thermocouples were protected from the mercury with a coating of Glyptal resin.

A Leeds and Northrup 8662 potentiometer was used for the thermocouple measurements. These measurements were precise to  $0.1^{\circ}\text{C}$ .



A Beckman thermometer was used at the inlet to the water side of the condenser. This provided a check on the effect of variations in room temperature on the inlet temperature of the cooling water.

Analyses of compositions were made with a Bausch and Lomb 33-45-56 and T-46648 refractometers. The latter analysis was precise to  $\pm 0.5$  percent concentration ethanol.

The insulation on the apparatus consisted of magnesia, asbestos rope, and glass wool. Glass wool was used for the portions of the apparatus requiring periodic inspection.

## DIFFICULTIES ENCOUNTERED IN PRELIMINARY OPERATION

Extreme care must be taken to avoid the presence of noncondensibles in the system or erratic data will result. They may be detected by the large amount of sub-cooling of the condensate. This will occur if even a small amount of noncondensibles are present. Any liquid added to the system must be boiled to free it from dissolved air.

The system should be made entirely of glass except for the Teflon joint (13\*). The original apparatus had a number of neoprene joints. It was found that the neoprene was dissolving into the alcohol.

The pressure regulator previously described was not sufficiently sensitive to pressure changes. Additional work on this part of the apparatus should be carried out.

Compositions were determined by refractive index. This method was used because of the ease and rapidity of analysis. If more accurate work is desired another method should be employed.

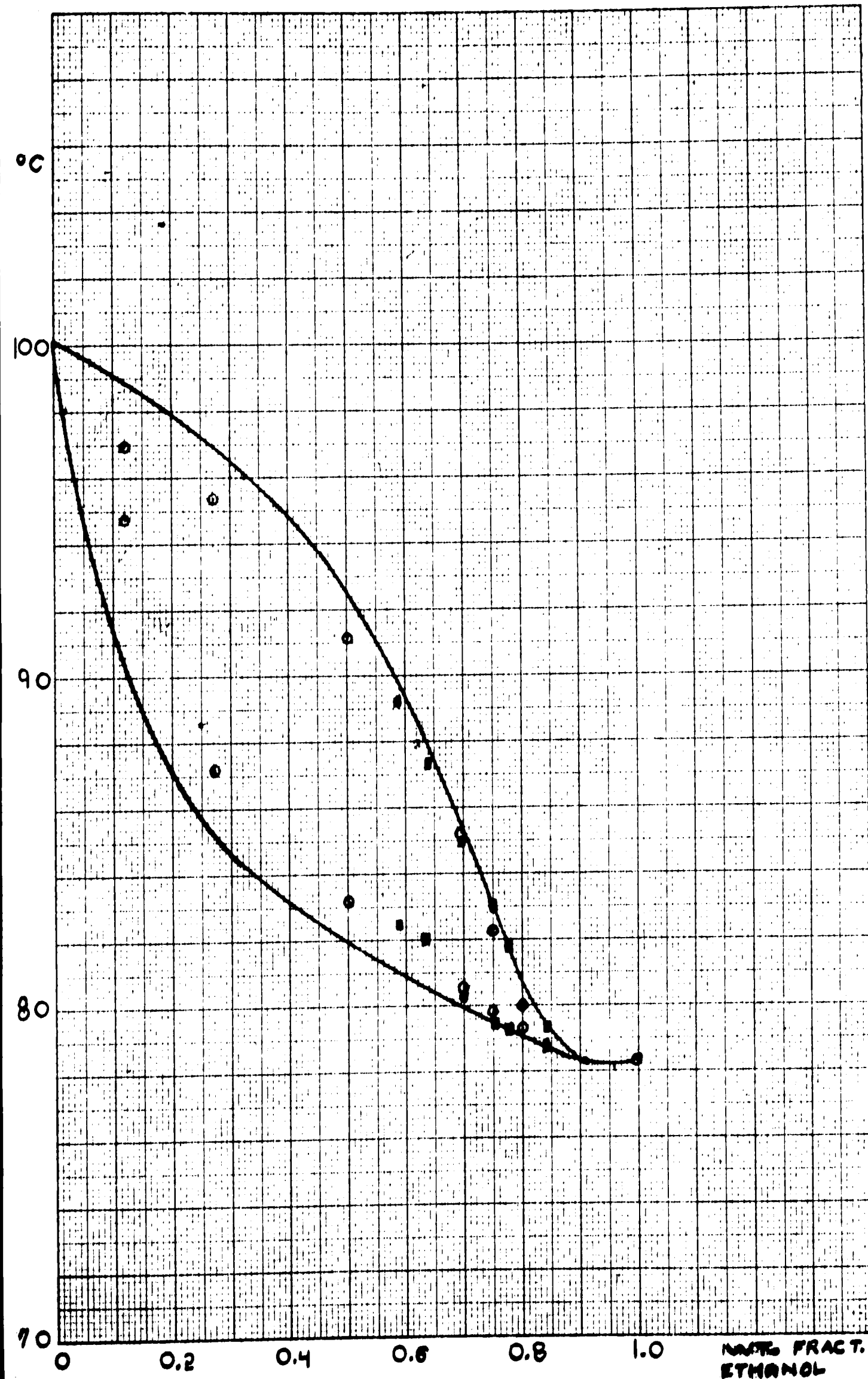
## EXPERIMENTAL DATA

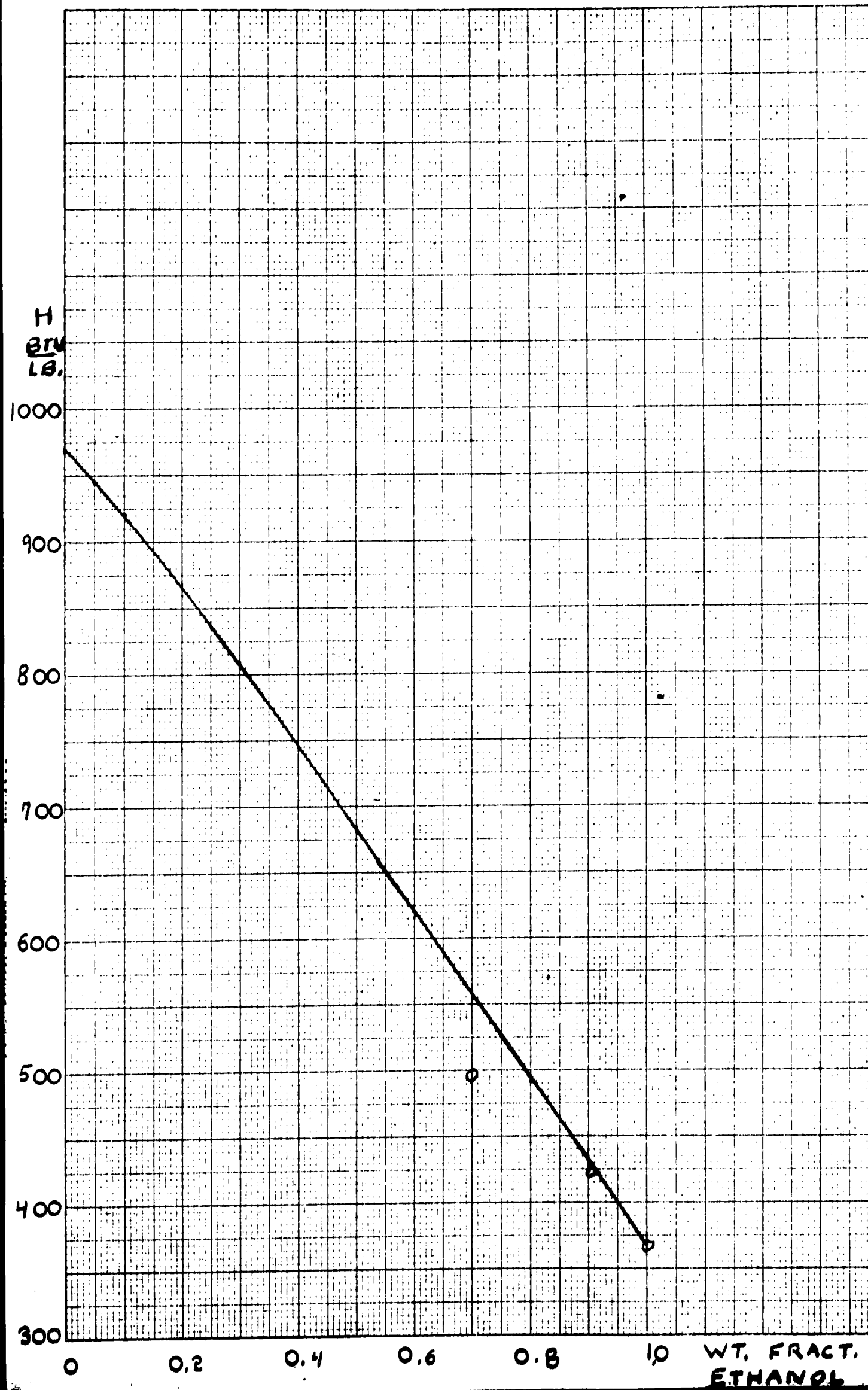
Curves of temperature and heats of condensation versus composition were plotted from the data given in Refs. (20,21,22).

As was explained previously the rubber used in the apparatus had an appreciable solubility in the ethanol-water system. Poor agreement resulted when these data were compared to the literature.

Two methods for obtaining data were used. The first was to determine the entire curve continuously in a single day. This method allowed impurities to build up in the system and the data showed a marked deviation with time.

The other method used was to accumulate data at one concentration, then discontinue operation for cleaning. This method gave better results for the first few points, but as the water concentration was increased the temperature in the system became high enough to cause appreciable solubility of the impurities in a relatively short time. The results for high water to alcohol ratios were therefore poor also.





**ADDITIONAL SUGGESTIONS**

The problem of obtaining a suitable pressure sensing instrument has not been solved. Suggested improvements on the method described in this report are:

- (1) The acquisition of a sensitive and reproducible diaphragm, that could replace neoprene.
- (2) A mercury manometer type of device described on page 12 of reference 20.
- (3) A magnanum wire strain gage instrument described in reference 23.

A method of obtaining self regulation of pressure may be possible by making some changes in the apparatus presently used. A small boiler with an internal heater that protrudes above the surface of the liquid could be used to replace the one in the proposed design. If a large hold up of condensate were incorporated in the apparatus between the condenser and flow meter a steadier recycle rate into the boiler could be obtained although the boil up rate in the system varied. If variations in boil up rate in the system occurred, the level of the liquid in the boiler and consequently the amount of liquid being evaporated would change in directions that would tend to return to the original operating conditions.

## LITERATURE CITED

1. Dodge and Dunbar, J. Am. Chem. Soc. 49, 591 (1927).
2. Ferguson and Funnell, J. Phys. Chem. 33, 1 (1929).
3. Rosanoff, Lamb, and Breithut, J. Am. Chem. Soc. 48, 2055 (1909).
4. Freeth and Verschoyle, Proc. Royal Soc. (London) A 130, 453 (1931).
5. Verschoyle, Trans. Roy. Soc. (London), A 230, 189 (1931).
6. Dobson, J. Chem. Soc., 127, 2866 (1925).
7. Ordorff and Carrell, J. Phys. Chem., 1, 753 (1897).
8. Calingaert and Hitchcock, J. Am. Chem. Soc., 49, 750 (1927).
9. Cummings, Ind. Eng. Chem., 23, 900 (1931).
10. Kay, Ind. Eng., Chem., 30, 459 (1938).
11. Brown, Trans. Chem. Soc. 35, 547 (1879).
12. Rosanoff, Bacon, and White, J. Am. Chem. Soc., 36, 1993 (1914).
13. Taylor, J. Phys. Chem., 4, 290 (1900).
14. Colburn, Jones, and Schoenborn, Ind. Eng. Chem., 35, 666 (1943).
15. Othmer, Ind. Eng. Chem., 20, 743 (1928).
16. Scatchard, Raymond, and Gilmann, J. Am. Chem. Soc., 60, 1275 (1938).
17. Scheeline and Gilliland, Ind. Eng. Chem., 31, 1050 (1939).
18. Smyth and Engel, J. Am. Chem. Soc., 51, 2646 (1929).
19. Carey, Sc. D. Thesis in Chemical Engineering, M.I.T., 1929.

20. Robinson and Gilliland, Elements of Fractional Distillation, Fourth Edition, McGraw-Hill.
21. A Source Book of Technical Literature on Fractional Distillation, Gulf R. and O. Co.
22. Carey and Lewis, Ind. and Eng. Chem. 24, 882 (1932).
23. Cornell and Montanna, Ind. and Eng. Chem. 25, 1331 (1933).
24. Noyes and Warfel, J. Am. Chem. Soc., 23, 463 (1901).