1959

An apparatus for the determination of vapor-liquid enthalpy and phase equilibrium data

Arthur Henry Koeckert
Lehigh University

AN APPARATUS FOR THE DETERMINATION OF VAPOR-LIQUID ENTHALPY AND PHASE EQUILIBRIUM DATA

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A Dissertation

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

Lehigh University

1959

This dissertation is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

(Date) — Professor in Charge

Head of the Department

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ABSTRACT

An equilibrium still has been designed, built, and tested which may be used to determine liquid-vapor equilibrium compositions, the equilibrium pressure and temperature, and the isobaric heat of vaporization at the vapor composition. Investigations are limited by the apparatus to pressures near atmospheric and to miscible systems not highly volatile at room temperatures. The pressure may be held at one atmosphere within 0.7 mm Hg. Equilibrium temperatures may be measured to within 0.1 degree (C). From the 480 ml of liquid required for operation, about 80 ml forms the vapor phase. The vapor is condensed in a reflux condenser where the latent heat is determined from the rise in temperature of the cooling water. A countercurrent contacting section below the condenser insures that only the latent heat is measured. The condensed vapor circulates by gravity through a rotameter at from 2 to 5 gm per minute and is revaporized in a tubular boiler. A bubble cap is used to contact the vapor with the equilibrium liquid held in a flask. Adiabatic walls of heated aluminum pipe reduce the heat transfer between the system and the surroundings. The apparatus was tested with the ethanol-water system for which enthalpy-composition charts are available. The experimental latent heats fall within 5% of the literature values. The liquid line on a temperature-composition diagram agrees well with the literature, but the vapor line shows enrichment due to internal reflux. Design changes are proposed which will eliminate the reflux, improve the accuracy of the device and reduce the operating time.

INTRODUCTION

A knowledge of enthalpy values for vapor-liquid systems is necessary for the accurate determination of stage requirements in distillation column design. With phase equilibrium data the enthalpy values may be used to construct the entire enthalpy-composition diagram for graphical solutions or may be used in tabular form for analytic solution. In addition, the latent heat values make possible the application of rigorous thermodynamic theory to the testing of the consistency of the equilibrium data as shown by Dodge (1). The necessary data for the construction of the thermodynamic network even for binary systems is scattered throughout the literature and is frequently of doubtful accuracy, and for most systems is simply non-existent. Therefore, diagrams for only a few binary systems have been constructed. Graphical treatment and computer methods for multicomponent systems using enthalpy-composition data are currently undergoing study. To make such methods useful, enough data to permit the accurate construction of the network must be made available.

Four kinds of data are required to construct the thermodynamic network from experimental measurements. These are phase compositions and corresponding temperatures and pressures at equilibrium, heat of mixing, specific heat, and heat of vaporization. All must be determined over the full range of compositions. The relationships among them may be visualized by considering the construction of an enthalpy-composition diagram. Heat of mixing data determined along an isotherm provide a base line above which specific heats, bubble points and heats of vaporization are used to construct the saturated liquid and vapor enthalpy lines. The phase equilibrium data provide the tie lines which complete the diagram. The thermodynamic network so constructed is as accurate as the data. The only assumption is that the data points be close enough to permit interpolation between related points at adjacent compositions.

The apparatus described in this report is the result of a complete revision of equipment which was constructed and operated to test the basic features of the design. The present form was designed with more consideration for insulation, is more compact, and incorporates changes found necessary from operation of the original apparatus.

Provision for the measurement of the specific heat was omitted because no unique features would have been employed. Attention was directed to the more challenging problem of latent heat measurement. The heat of mixing was left unexplored simply to limit the scope of the investigation.

I want to thank the Texas Company for providing the fellowship which made this work possible, and the

faculty and staff of Lehigh University for their many helpful suggestions.

DEVELOPMENT OF THE DESIGN

The General Design

Three of the four kinds of data needed to determine the enthalpy-composition network are so closely associated that when the conditions required to measure one are met, the other two may also be measured. These are the phase equilibrium compositions, the heat of vaporization of the saturated vapor, and its mean specific heat in the condensed state. Construction and operation of a single apparatus to determine all three, if not too complex, saves the time spent constructing and operating three pieces of equipment. In principle, a liquid mixture of the components at the composition to be tested is brought to its bubble point, then is vaporized and brought into contact with a liquid mixture of equilibrium composition at the same temperature. To obtain the necessary data an apparatus must be constructed in which the first mixture follows the precise thermodynamic path described above at constant composition. Appropriate measurements of changes in the surroundings permit the determination of the enthalpy values. It is evident that a bomb calorimeter or equilibrium cell is inadequate because the fluids must pass from point to point through the apparatus.

A flow calorimeter may be chosen which provides either a single pass or a recirculating path for the phase at the vapor composition. Both designs offer important advantages. In the single pass design, the moving phase flows from a holding tank into the enthalpy measuring and phase equilibrium regions; it then flows into a receiving tank. Since the mass flow rate may be accurately measured by weighing the receiver, the design has been the principle method used for enthalpy measurements. The design by Dana (2) and modified by Tallmadge, Schroeder, Edmister, and Canjar (3) is of this type, and both are examples of accurate heat measurement by electrical means. Both apparatus contained a stationary liquid phase through which the moving phase was passed, and the latter reference combined equilibrium measurements with the enthalpy values. But it was felt that the liquid did not represent the composition in equilibrium with the moving phase, that it was difficult to keep the volume of liquid constant, and that uncertainties, mentioned by Weissberger (4), in corrections for heat leaks prevented confidence in the enthalpy measurements. The advantage in flow rate measurement was exploited by McCracken and Smith (5) through the use of automatic valves in the product lines, and in highly accurate measurements by Callendar and Barnes (6), but neither design is applicable to equilibrium measurements. A variation of the once-through design by Rosanoff, Bacon, and White (7) and used by Cornell and Montonna (8) operated as a differential distillation, and since no steady state can ever be reached with that form of apparatus, the design was dropped from consideration. The long operating time that most authors find necessary before phase equilibrium is considered established would seem to preclude the use of a once-through design because of the large quantities of liquid components which would be required to supply the moving phase for periods longer than a half hour.

The other alternative design, in which the moving phase is recirculated through the apparatus for as long a time as is necessary, has become widely accepted for making equilibrium measurements. This design, in which the recirculating phase continually repeats the exact thermodynamic path required for the desired enthalpy measurements, is the form used in the present study. The chief disadvantage appears in the attempt to make accurate flow rate measurement. Direct mass flow rate determination is not easily accomplished, since the flow of fluid must be diverted into a weighing tank for a period of time, before and after which a weighing must be made. The resulting depletion in some other section of the apparatus and the cessation of flow into parts downstream of the weighing point cause the steady state operation to be disrupted. Usually the recirculation is caused by a natural convection process and is maintained at a constant rate with constant liquid levels. If weighings were to be made, a pump would be required to maintain

the constant rate necessary for accurate enthalpy values. The direct mass method for flow rate would unnecessarily complicate the equipment. Rate measuring devices which may be inserted into a fluid stream and which operate without disturbing a steady state flow were investigated. Of these, the ball type rotameter was chosen as the most accurate of the direct reading devices for the low flow rate expected.

Equilibrium

The development of the design features of contemporary equilibrium stills is outlined in two excellent reviews by Fowler (9) and Ridgway (10). In the design most favored today, vapor generated externally or in the equilibrium chamber is condensed into a vapor trap. The condensate recirculates either into a vaporizer attached to the equilibrium chamber or flows directly into the equilibrium flask to be revaporized.

Recent designs by Jones, Schoenborn, and Colburn (11) and by Murti (12, 13) suggest that the recirculating phase be vaporized before contacting the equilibrium liquid. With this provision the liquid in the equilibrium flask more nearly represents the true equilibrium liquid. The Othmer design (14, 15, 16) which employs the direct return of recirculating liquid to the boiling flask seems to prevent the establishment of the equilibrium liquid composition. The recirculating phase may be thought of as residing as liquid in the flask for some period of time before revaporizing. Depending upon the amount of flask liquid, the recirculating rate, and this indeterminate residence time, the flask liquid is more or less too highly concentrated in the volatile components to have the true equilibrium composition.

The comments of Swientoslawski (17) seem to indicate that the vapor formed by boiling a flask of liquid is superheated. He noted that his apparatus, using a Cottrell vapor lift to direct a vapor and liquid mixture onto an accurate thermometer, indicated a higher temperature when the boil-up rate was increased, even when the design provided a long contact time between vapor and liquid. Vapor leaving the liquid surface within a heated flask would be in contact with the liquid for a far shorter time and would probably be much more highly superheated. For these two reasons, a separate vaporizing chamber was incorporated into the design.

It is sufficient in a study of binary systems to monitor the approach to equilibrium by noting the temperature of the equilibrium liquid and waiting for that temperature to become constant. But it may be possible for multicomponent systems to have a series of equilibrium points at the same temperature for a given total composition. By equilibrium points is meant the mass distribution between the phases, and the compositions. A still could operate at a constant temperature while the mass distribution or the composition of one of the phases as well as the temperature.

A convenient method of watching the mass distribution is to restrict the system to two liquid phases by design, then monitor one of the liquid levels.

A check of the composition would require either periodic sampling with the chance of upsetting the operation or an in-line composition analyzer. Since it would be difficult to make sample analyses during a run and since no continuous analyzer was available, the method of liquid levels was chosen.

With these considerations in mind, a tubular boiler was chosen with inlet at a slightly higher level than the exit, as used by Jones, Schoenborn, and Colburn, and by Murti. The liquid level was fixed at the inlet of the downward sloping boiler, and the amount of liquid in the recirculating loop was fixed by the liquid level at the point where the condensate collected from the condenser. As explained in the "Description of Apparatus," the latter level was brought outside the insulation so that the level could be observed. The single other liquid level was at the equilibrium flask. There were, therefore, only two liquid containers, and only two liquid levels capable of change. One level could be watched accurately, changes noted, and control action taken. The distribution of mass between the two phases was measured by the visible level, and a constant level would be indicative of a steady state operation.

The validity of this analysis depends upon preventing the formation of any other liquid hold-up which cannot be measured and controlled in volume, such as an accumulation of liquid at the low end of the boiling tube.

It was thought that an external boiler could be operated in such a manner that superheating of the vapor could be prevented. Control of the heat input to the vaporizer would control the vapor temperature at its outlet. This temperature would then be matched with the temperature of the flask liquid and that of the vapor leaving the equilibrium flask. The equilibrium vapor would then be at its saturation point throughout its contact with the equilibrium liquid. The analysis of the control of the boiler proved to be incorrect, as is shown later.

The only alternate boiler design consists of using an auxiliary boiling flask in which the vapor is generated prior to contact with the equilibrium liquid. Such a system was described by Chilton (18) and used by Scatchard, Raymond, and Gilmann (19). The system suffers from having three containers of liquid among which the contents of the still are distributed. In two of the containers, the boiling flask and the equilibrium flask, the liquid levels are turbulent and cannot be determined or controlled. Thus the distribution of liquid among the containers cannot be readily determined. Additional arguments against this design are presented by Othmer (16).

The design chosen for the equilibrium flask was a simple bubble cap. It was felt that this design would provide effective vapor-liquid contact, reducing the recirculation time required to achieve equilibrium. The vapor was forced to bubble through a two inch liquid head as it contacted the liquid, causing a pressure drop of about 3 mm Hg. For operation at 1 atmosphere this represented 0.3% change in pressure and had but a small effect upon the equilibrium. Noyes and Warfel (20) report for the ethanol-water system a change of 0.03 degree (C) in boiling point per mm change in pressure. Thus the change of 3 mm Hg in the equilibrium flask could be expected to produce a 0.1 degree (C) uncertainty in the reported equilibrium temperature.

<u>Enthalpy Measurement</u>

The recirculating still causes a stream at the saturated vapor composition to follow a thermodynamic path ideally suited for the enthalphy measurements needed in the construction of enthalpy-composition diagrams. The two heat effects which can be measured are the isobaric latent heat of vaporization or condensation and the heat capacity of the liquid, all at the vapor composition. To understand the advantages of the various design alternatives, it is of help to consider the circulating fluid as a thermodynamic system operating in a cycle between two temperature levels as shown in Fig. 1. The system serves only to transfer heat between the hot and cold reservoirs. This it does by

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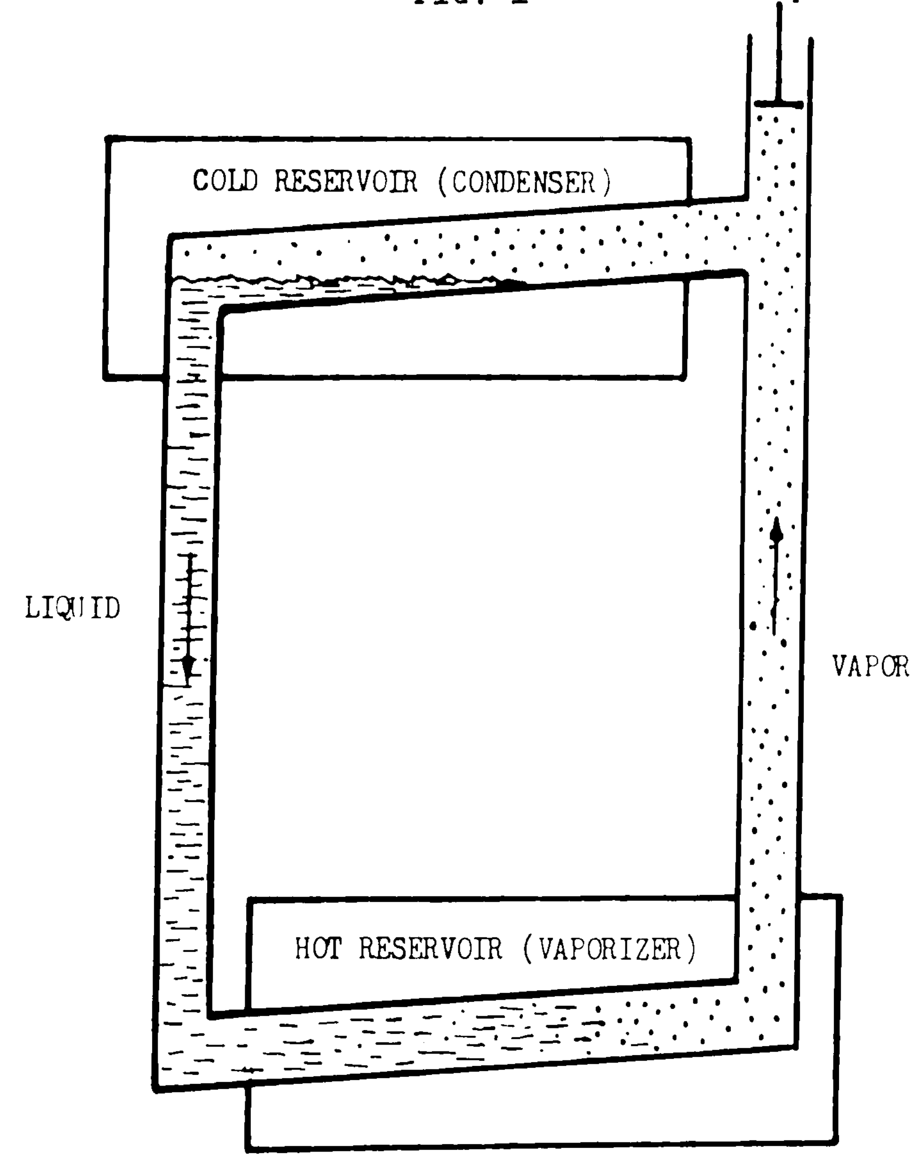
THE EQUILIBRIUM STILL

A THERMODYNAMIC CYCLE

FIG. 1



being heated to the bubble point, vaporized and superheated at the hot reservoir, and condensed and subcooled at the cold reservoir. The enthalpy change between vapor and liquid may then be measured by some known change in the surroundings at either reservoir. The problem is to separate the latent and sensible heat effects so that both may be measured independently.

At the hot reservoir, a subcooled liquid would have to be brought to its bubble point without producing vapor, using a measured heat input to determine the specific heat. This would prepare a saturated liquid for additional heating to determine the heat of vaporization. The temperature of a mixture undergoes a more or less regular rise from the subcooled liquid state to the completely vaporized state without the occurrence of a discontinuity in temperature or region of constant temperature. Supposedly the bubble point temperature is unknown, the purpose of the experiment being to determine it. The stream may not be viewed to notice bubble formation because of the necessity of insulating the measuring region. It would seem that no convenient characteristic of the stream could be used to establish the point where vaporization begins, and thus the latent and sensible effects could not be isolated at the hot reservoir.

A simple design has been devised to isolate the latent and sensible heat effects at the cold reservoir. The equilibrium determination associated with the apparatus provides a supply of saturated vapor which may be fed to a condenser. The problem is to insure that a saturated liquid leaves the condenser, thereby removing no more heat than the integral isobaric heat of condensation. Vapor condensing on a condenser tube wall is subcooled as the liquid film builds in thickness. If the incoming vapor contacts the subcooled liquid leaving the condenser, some of the vapor will condense into the liquid and heat the condensate towards its bubble point.

A reflux condenser provides a means of contacting the vapor and condensate. The vapor condenses in the condenser, yielding its latent heat and some sensible heat to the water used for the enthalpy measurement. The condensate flows down the wall of the condenser countercurrent to the rising vapor. If an insulated section of tubing is provided below the condenser, then the downflowing subcooled liquid is exposed to the rising vapor and partially condenses until the liquid reaches its saturation point. Since a saturated vapor and liquid at the same composition are at different temperatures, the driving force to heat the liquid is substantial. If a trap is provided at the bottom of the contacting section, the liquid is prevented from returning to the equilibrium flask, and may be discharged to the recirculating system. Since a saturated vapor flows into the condenser and a saturated liquid of the same composition leaves the region, only the latent heat is removed by the condenser. The ability of this condenser arrangement to degas the departing saturated liquid was noted in a recent article by Othmer (16), and the design forms the basis for a patent for gas-free distilled water (21).

The various designs of recirculating stills which use a sealed system and regulate the pressure by the adjustment of heating and cooling offer no advantages over the designs which use a direct control of a confining pressure, with the possible exception of operation at high pressures where the confining gas might have appreciable solubility in the condensed vapor at the bubble point. Indeed, these designs offer distinct disadvantages for enthalpy measurement at the condenser. During adjustment of the cooling rate, conditions unfavorable to accurate enthalpy measurements may be set up. Maintainance of the coolant ΔT within the desired measuring range may be impossible, with the resultant inaccuracy in measurement of ΔT and the opportunity for excessive heat leaks from the coolant to its surroundings. The problem is basically the fact that with a purged sealed system, the total inside condenser area must be used to condense vapor. The condenser may be operating in such a manner as to attempt to remove too much heat from the system, thereby tending to reduce the pressure. Various experimenters have attempted to correct for this by using only small portions of the outside area of the condenser (22) or by changing the coolant from water to air (22, 23) in order to reduce the ability of the coolant to remove heat from the system. One other possibility, which has not been tried, would be to adjust the recirculation rate to match the condensing capacity of the coolant. But such a method would prevent a much desired flexibility in operation.

The use of a reflux condenser connected at the top to a reservoir of confining gas automatically compensates for the changing demands of the system for cooling and permits simple measurement and control of the system pressure. The average coolant temperature and rate may be adjusted arbitrarily as long as vapor is confined to the condenser. At whatever conditions of recirculation rate or coolant rate are chosen, the vapor inside the condenser rises to just the height necessary for it to be condensed. In so doing it draws in or pushes out the confining gas in the reservoir. This phenomenon undoubtedly took place in the recent elevated pressure apparatus by Othmer, et. al, (23) although to a small degree. The reflux design with communication to a gas reservoir permits the use of a coolant whose specific heat is accurately known, namely water. Keeping the ΔT at a low value and the average temperature at room temperature reduces the heat leak without elaborate insulation. The use of cool water means that the upper section of the condenser may be kept at a low temperature to reduce the amount of vapor diffusion into the gas reservoir. A supply of room temperature water is easy to maintain at constant temperature and to supply for use in the enthalpy measurement.

One disadvantage involves the condensation temperature at the condenser. The condensation temperature depends upon the system under study and upon the confining pressure. For the ordinary solvent systems likely to be studied with this apparatus at one atmosphere pressure, the boiling points are substantially above room temperature and a water condenser operating near room temperature will condense the vapor. However, an example of a specific system system which presents problems is ethylene oxide which boils at 10 C and cannot be condensed using room temperature water. One other shortcoming, the opportunity for the diffusion of volatile components into the gas reservoir, must be mentioned.

Adiabatic Operation

Heat lost from the equilibrium flask would cause partial condensation of vapor. Such refluxing would destroy the equilibrium and deplete the amount of the recirculating phase. Heat lost from the contacting section would produce error in the enthalpy measurement. Such losses had to be brought below the allowable limits of error. The highest recirculation rate which would not produce excessive splashing from high vapor rate in the equilibrium flask was found by calculation (Appendix, pg. 97) to provide a heat flux of about 2000 cal per min and to represent a liquid flow of from 5 to 35 gm per min, depending upon the compounds chosen. Because of expected uncertainty approaching one percent in the measurements for enthalpy, it was proposed that heat losses not be reduced below one percent, or 20 cal per min. Both the equilibrium flask and contactor operate at up to 100 C, and a simple insulating material would produce too great a heat loss. The use of a silvered vacuum jacket would practically eliminate heat losses, but it was felt that an untried design which might require extensive revision should not be constructed in complex glassware. The construction and operation of an adiabatic wall seemed a simple expedient. In principle, an enclosure about the apparatus is brought to the same temperature as the apparatus. Since the region between apparatus and enclosure is then isothermal, no heat is transferred through the region, and the apparatus operates adiabatically. The use of good insulation between the apparatus and enclosure reduces the heat loss in case the two temperatures do not match. This method is used in an equilibrium still by Chao and Hougen (24). The principle was used for the precise determinations made by Callendar and Barnes and is applied to modern adiabatic calorimeters in which the adiabatic walls automatically follow the temperature of the calorimeter.

At the reflux condenser, since the cool water jacket lay between the hot vapor and the cool surroundings, little insulation and no adiabatic wall were necessary. Assuming a 5 degree (C) difference between the water jacket and surroundings, and the use of three inch thick efficient insulation, a heat loss of about 3 cal per min was estimated (Appendix, p. 99). This was less than 0.2% of the expected heat flux. The actual heat transfer probably amounted to only a small fraction of this value.

The condenser was stacked above the equilibrium flask as close to it as possible to make the path for the vapor as short as possible. Thus the opportunity for heat transfer with the surroundings near the region between the points of equilibrium and enthalpy measurement was reduced as much as possible while still leaving enough area for heat transfer.

DESCRIPTION OF APPARATUS

Recirculating System Components

In order to eliminate contamination problems, pyrex glass and Teflon were used to fabricate all equipment which might come in contact with the system under study. Since modification and flexibility were expected to be necessary, joints were used to attach the parts together. The use of Teflon tubing and ground glass ball joints and taper joints permitted ease in glassblowing, and flexibility in design and construction. However, once a successful design has been tested, it should be constructed without glass joints, thus eliminating the possibility of leaks. It was found necessary to use silicone grease to eliminate leakage in the ball joints at the rotameter and to make the large taper joints vapor-tight. The use of silicone grease is to be discouraged in apparatus for serious phase studies. Traces of the high molecular weight silicones have a pronounced effect on the equilibrium. Short sections of 0.25 inch ID Teflon tubing provided excellent flexible, leak-proof sleeves with which to attach fire-polished 7 mm (0.27 in.) OD glass tubing.

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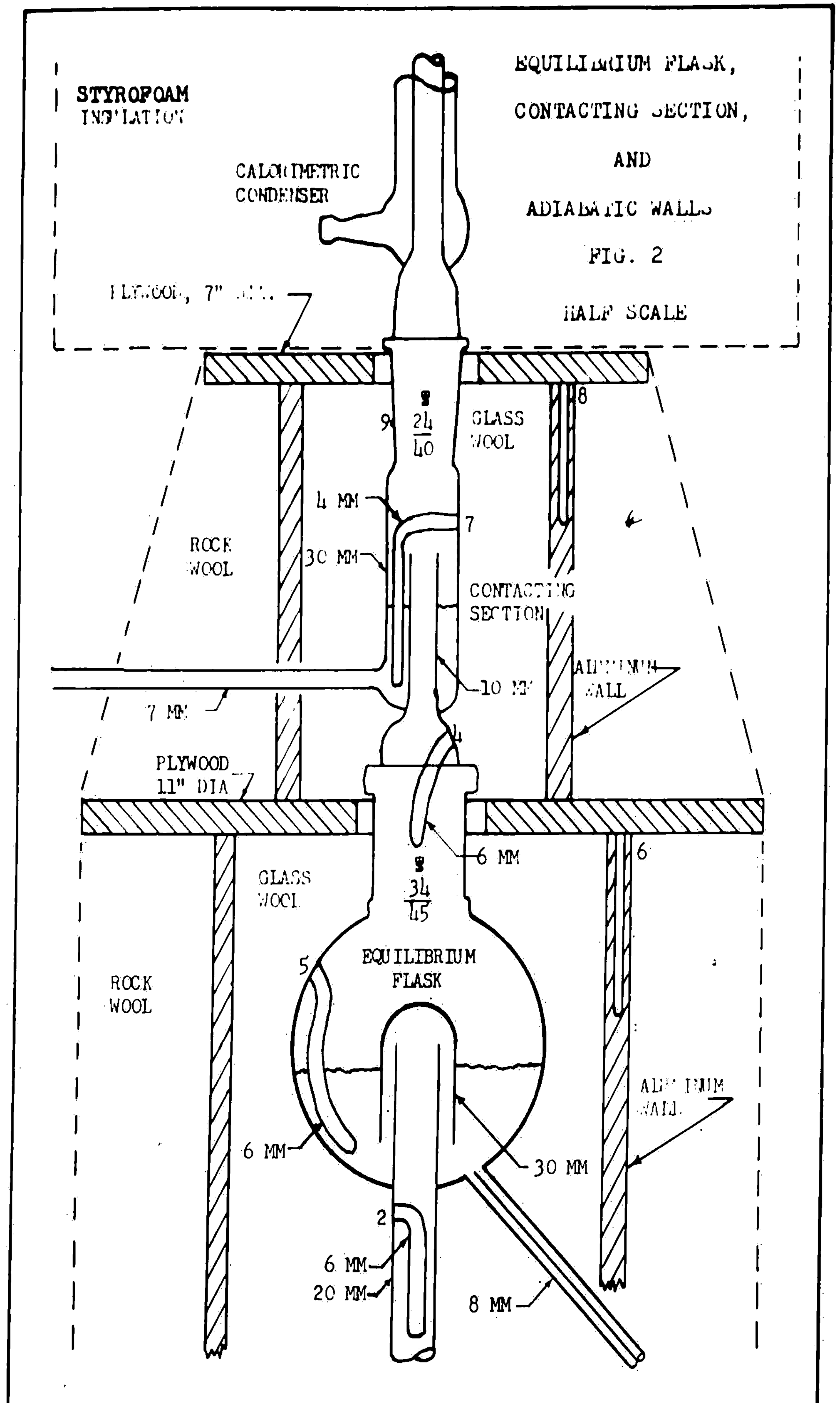

EQUILIBRIUM FLASK, CONTACTING SECTION, AND ADIABATIC WALLS

FIG. 2

HALF SCALE

A small bore sample tube from the bottom of the flask permitted the removal of the equilibrium liquid for analysis. The long tube length was necessary because of the thick adiabatic wall in that section. Slots were cut into the bubble cap in an attempt to break up the bubbles and cause better contact with the liquid. The flask held 530 ml before liquid overflowed into the inlet tube, and 400 ml was considered an adequate charge. The large open volume above the liquid level permitted the vapor to disengage from the liquid.

The condensate contactor fitted into the flask outlet where the vapor outlet thermocouple, T4, was located. Vapor passed through the inner tube and contacted the condensate which trickled down the side of the contactor. The adiabatic section reached to the lowest point of the condenser jacket, a point about one inch above the top of the contactor. A small thermocouple well, T7, dipped into the pool of condensate near the outlet of the collector. Five to ten small chips of broken ceramic measuring about 0.3 cm in the largest dimension were placed in the bottom of the contactor to eliminate the possibility of the condensate being superheated. A side arm led the condensate through the adiabatic insulation. A thermocouple, T9, was taped against the outside of the contactor to give, along with T7, the average contactor temperature and to tell if the contactor was excessively long.

Heat was removed and enthalpy was measured with a standard 300 mm long West type condenser inserted into the contactor. Condensation took place inside a half inch diameter tube around which water flowed in a one inch diameter jacket.

Two clamps for large ball joints were filed oversize and used to clamp the tapered joints between the equilibrium flask and contactor, and between the contactor and condenser.

The condensate passed through a Teflon sleeve joint and into a small Liebig type water cooler (Fig. 3) which reduces the temperature to about 25 C by the use of cooling water from the constant temperature bath. It is at this cooler that the sensible heat effect may be measured. Cooling at this point prevented a loss of volatile components out of the vent of the next element, the leveler (Fig. 3). The leveler permitted the liquid level in the condensate contactor to be measured, and controlled above a minimum. Teflon sleeves on the inlet and outlet provided flexibility for raising and lowering the position of the leveler. Thus the thermocouple well T7 was kept immersed in a pool of condensate and unexposed to warm vapor. Also vapor was prevented from entering the side arm where condensation would constitute a heat loss. By bringing the liquid level outside of the enshrouded condensate contactor, a sensitive measure of the operation of the still was brought to view. A rise or fall in this level meant that the mass of the

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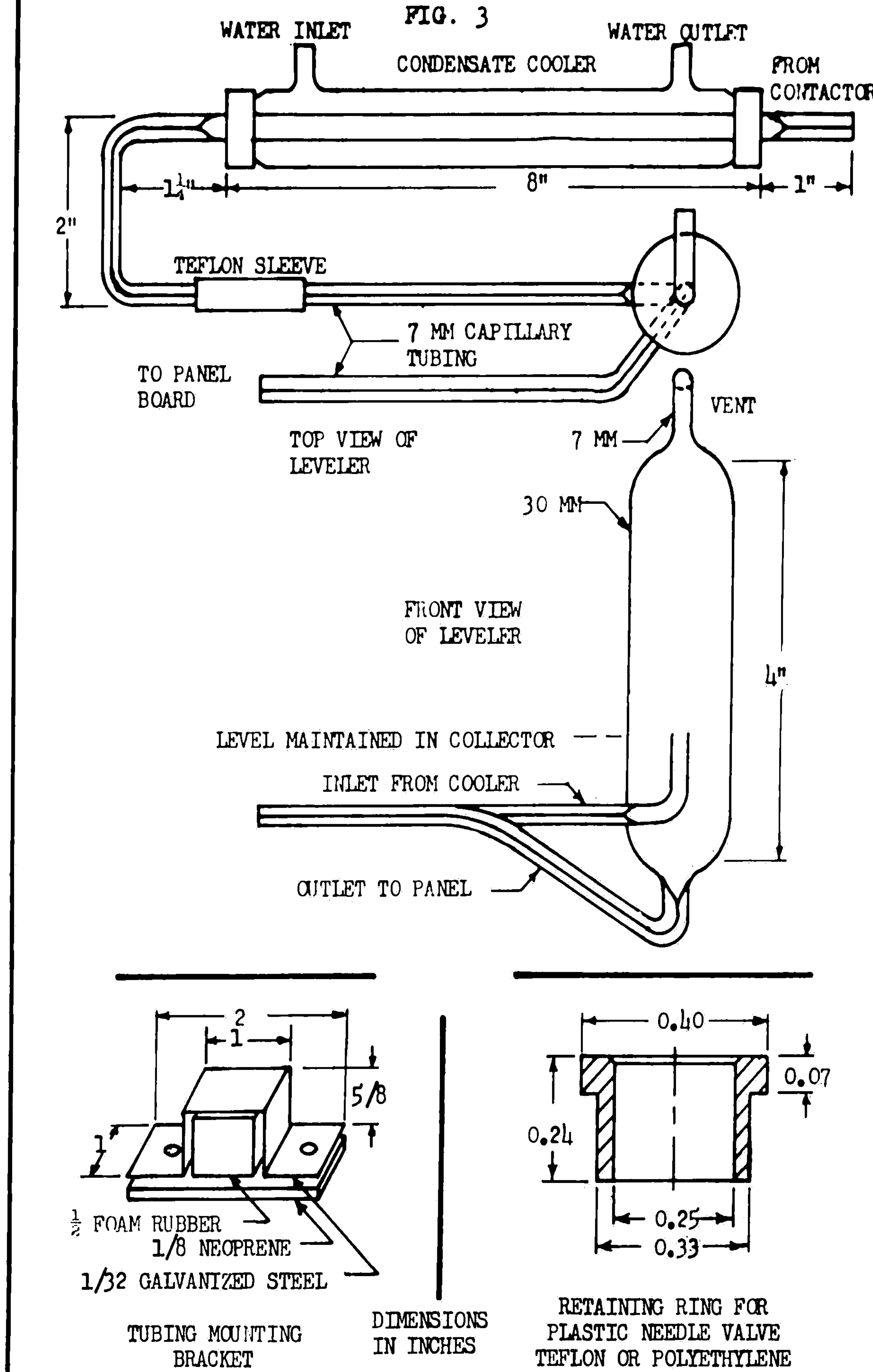
RECIRCULATING SYSTEM COMPONENTS

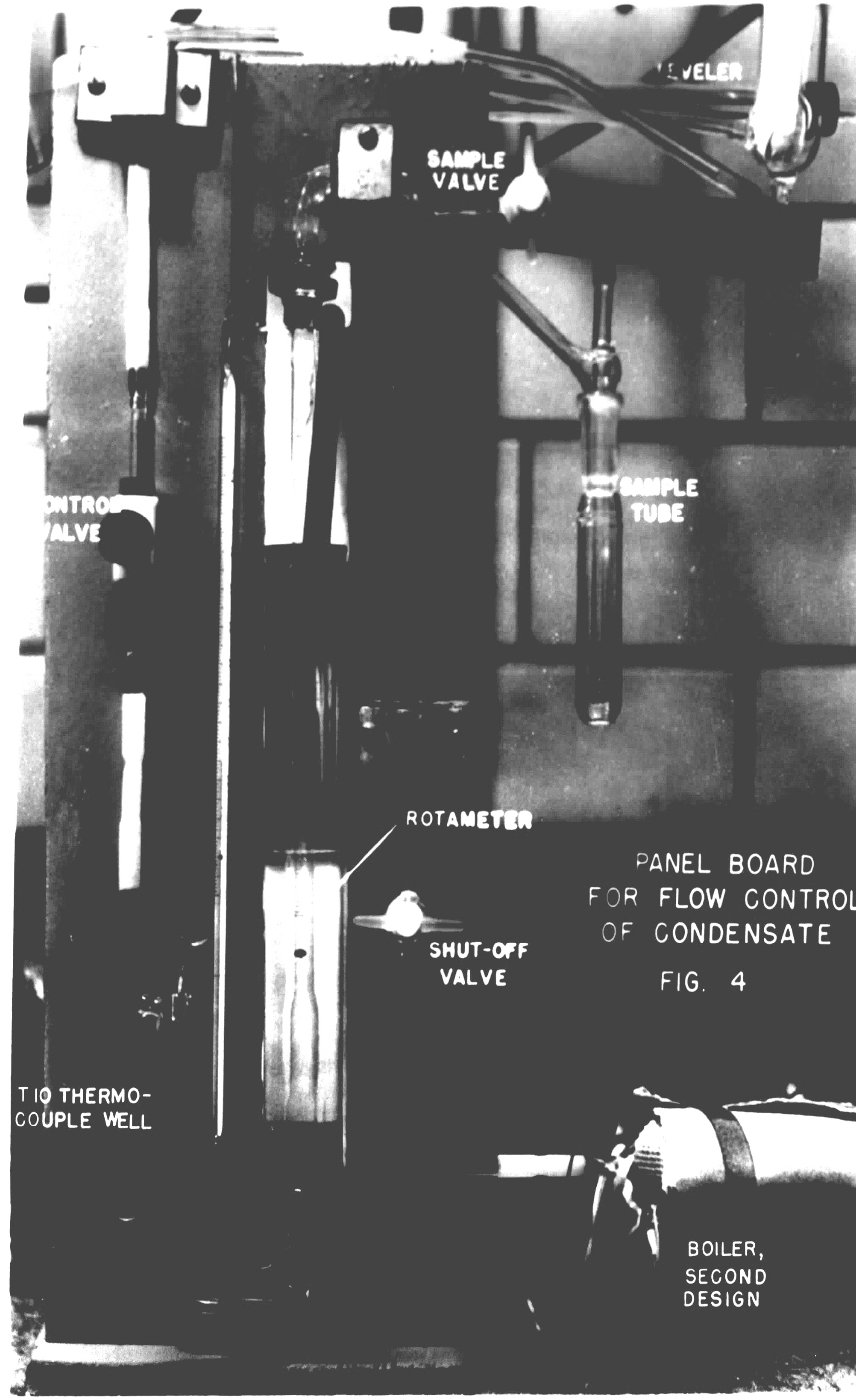
FIG. 3



recirculating phase was changing, and that equilibrium was not established. A piece of tape on the leveler was marked in half centimeters so that levels could be recorded.

The outlet from the leveler lead to tubing mounted on a plywood panel board, Fig. 4, where the flow control valve, thermocouple well, rotameter, sample valve and shut-off valve were mounted. The rotameter produced a piping problem in that it had to be mounted vertically. To make the flow system compact, the fluid had to traverse an S-shape, passing down from the leveler, up through the rotameter, and finally down to the boiler inlet. Since the flow of the system depended upon the small hydraulic leg between the leveler and boiler, air bubbles which would stop the flow had to be eliminated at the start and prevented during a run. The use of capillary tubing, of proper placement of shutoff, sample, and control valves, and of certain operating procedures (see p. 50) eliminated air bubbles. The use of capillary tubing reduced the volume of the recirculating phase, thereby causing a greater turn-over at a given flow rate and hastening the approach toward equilibrium. The components in the circulating system were designed in such a manner that the flow of condensate swept out all regions where liquid might lie. In this way, stagnant regions were prevented.

The Teflon and glass needed valve was manufactured by the Manostat Corp. The valve had a 1 mm bore and provided much closer control than could have been obtained



PANEL BOARD FOR FLOW CONTROL OF CONDENSATE

FIG. 4

from a stopcock, but had a tendency to leak at the inlet and outlet. The slip rings originally sent were considered unsatisfactory and new ones shown in Fig. 3 were designed and constructed. Liquid still leaked past the new slip rings even after the plastic nuts were tightly screwed into the valve body. This is believed to be the result of bending forces on the inlet and outlet tubes. The use of Teflon sleeves on both sides of the valve and the elimination of rigid mounting for the valve eliminated leakage. It is to be noted that the new slip rings do not fit a manufacturer's design change in inlet and outlet glass tubes and that a return to the original slip rings will be necessary if the glass fittings are changed.

The thermocouple well, T10, Fig. 4, was to have measured the temperature at the rotameter so that the efficiency of the cooler could be checked and so that temperature could be duplicated during calibration of the flowmeter. When the effect of temperature upon the indication of the flowmeter was discovered during calibrations, provision was made to jacket the flowmeter with water from the constant temperature bath. Thus the fluid inside the rotameter was brought to 25 C during operation and calibration of the flowmeter. The flowmeter was a Fisher and Porter Tri-Flat Rotameter with specifications 02F-1/8-12-5/36, pyrex tube and sapphire float. Practical range was 0.4 to 23 gm water per minute on a scale of 1 to 12. Ball joints were glassblown onto the rotameter ends to provide flexibility in the mounting and to permit removal of the rotameter for cleaning. A mirror was cemented on the panel immediately behind the rotameter so that errors of parallax in reading the rotameter would be eliminated.

The condensate sample valve was connected to the point where the fluid turned downward toward the boiler. Bubbles collecting at this high point could be vented through the sample line to prevent the stoppage of circulation which would occur if bubbles became trapped in the lines through which flow was downward. The position provided clearance for sample tubes above the boiler. Placement of the sample line between the control valve and the boiler permitted the sample line to be used as an air intake at the time of shut-down. Without this vent, liquid from the equilibrium flask would be drawn into the boiler as vapor condensed in the boiler. This precaution was taken by Jones, Schoenborn, and Colburn, and by Kurti. A stopcock between the sample line and the boiler was used to shut off the path to the boiler when a sample of the recirculating phase was being taken. Both sample valves and the shut-off valve were Fisher and Porter Lab-Crest stopcocks, the manufacturer's name for special stopcocks using Teflon plugs. They needed no lubrication, did not stick or leak, and were excellent for this application.

Condensed vapor samples of 10 cc were drawn by gravity or vacuum through the capillary tubing, Teflon stopcock and ground fitting into short tubes provided with ground joints, shown in Fig. 4 and 5. The sample was introduced through the long capillary below the liquid level in the sample tube. Ice in a beaker placed around the sample tube readily cooled the sample because of the small diameter of the sample tube. Both precautions were taken to reduce volatilization losses. A similar sampling system of capillary tubing, stopcock and ground joint was attached with a section of Teflon tubing to the capillary tube of the equilibrium flask so that a sample of the equilibrium liquid could be taken.

The recirculating system held 30 ml in the region between condensate collector and boiler inlet. The liquid head which provided recirculation was about 17 inches high.

Two boiler designs shown in Fig. 5 have been tested. Liquid passing through a Teflon sleeve and a short 7 mm capillary tube entered the 14 mm tubing of the boiler where the condensate was vaporized as it trickled down the tube in a thin stream. An elbow at the end directed the vapor into the equilibrium flask. Heat was supplied by two four foot long heating tapes wound one on top of the other on the glass tube of the boiler. A 30 mm tube used for the second design was flattened along its length on the bottom side in an attempt to distribute the boiling liquid over a large area. The top half cylinder was insulated with asbestos, and an eight foot heating tape was laid longitudinally against the flat bottom so as to supply most of the heat to the bottom of the boiler in an attempt to eliminate

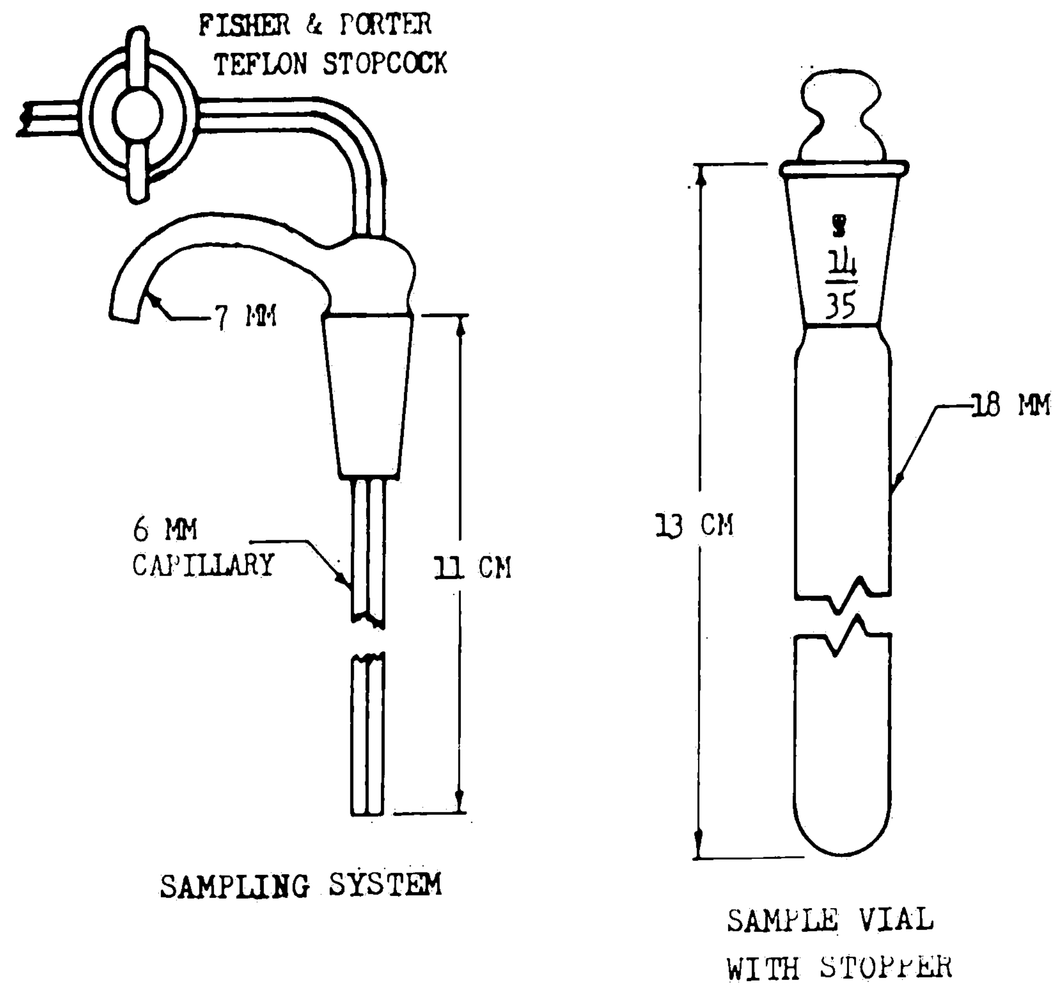
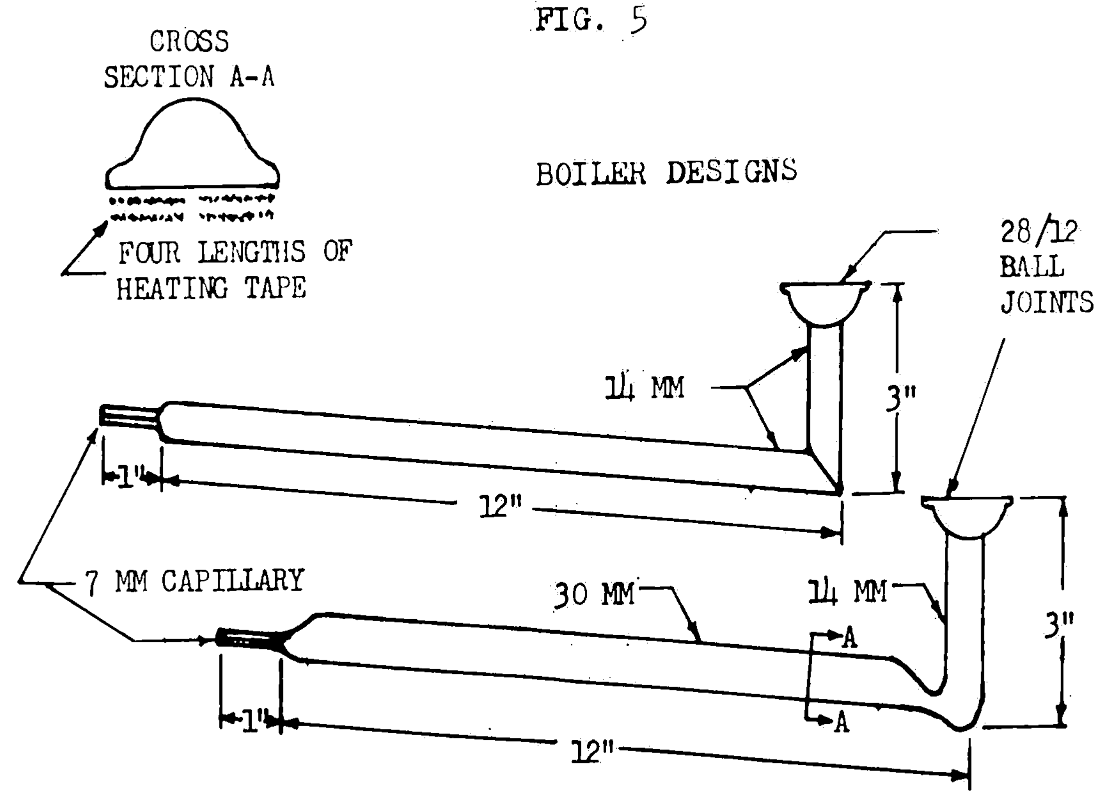

FISHER & PORTER
TEFLON STOPCOCK
7 MM
6 MM
CAPILLARY
11 CM
SAMPLING SYSTEM
14
35
13 CM
18 MM
SAMPLE VIAL
WITH STOPPER

FIG. 5


CROSS
SECTION A-A
FOUR LENGTHS OF
HEATING TAPE
BOILER DESIGNS
28/12
BALL
JOINTS
14 MM
3"
1"
12"
7 MM CAPILLARY
30 MM
14 MM
A
A
3"
1"
12"

superheating of the vapor. The boilers were wrapped with asbestos and mounted in position to slope one inch in twelve.

An addition tube with side arm was inserted in the top of the condenser. The side arm provided an outlet for pressure measurement, and the addition tube and funnel and the Teflon and glass needle valve provided the means to introduce liquids for study.

Adiabatic Walls

Two lengths of schedule forty aluminum pipe were used for the enclosures shown in Fig. 2: a six inch diameter section around the equilibrium flask, and a four inch diameter section around the contractor. These were separated and supported by plywood circles and three wooden legs. Deep thermocouple wells were drilled into the tube walls. Glass wool was packed between the glassware and the pipes. Two heating tapes, 6 ft and 4 ft long, were wound on the six and four inch pipes respectively. Heavy blotting paper was used to hold rock wool insulation against the outside of the aluminum pipes. This outside insulation was used to eliminate the effect of changes in ambient conditions. After an early run of the apparatus, rock wool was packed between the table and lower plywood circle, the region around the elbow at the end of the boiler. It was thought that accumulation of liquid at the end of the boiler was due to condensation in the tube running to the equilibrium

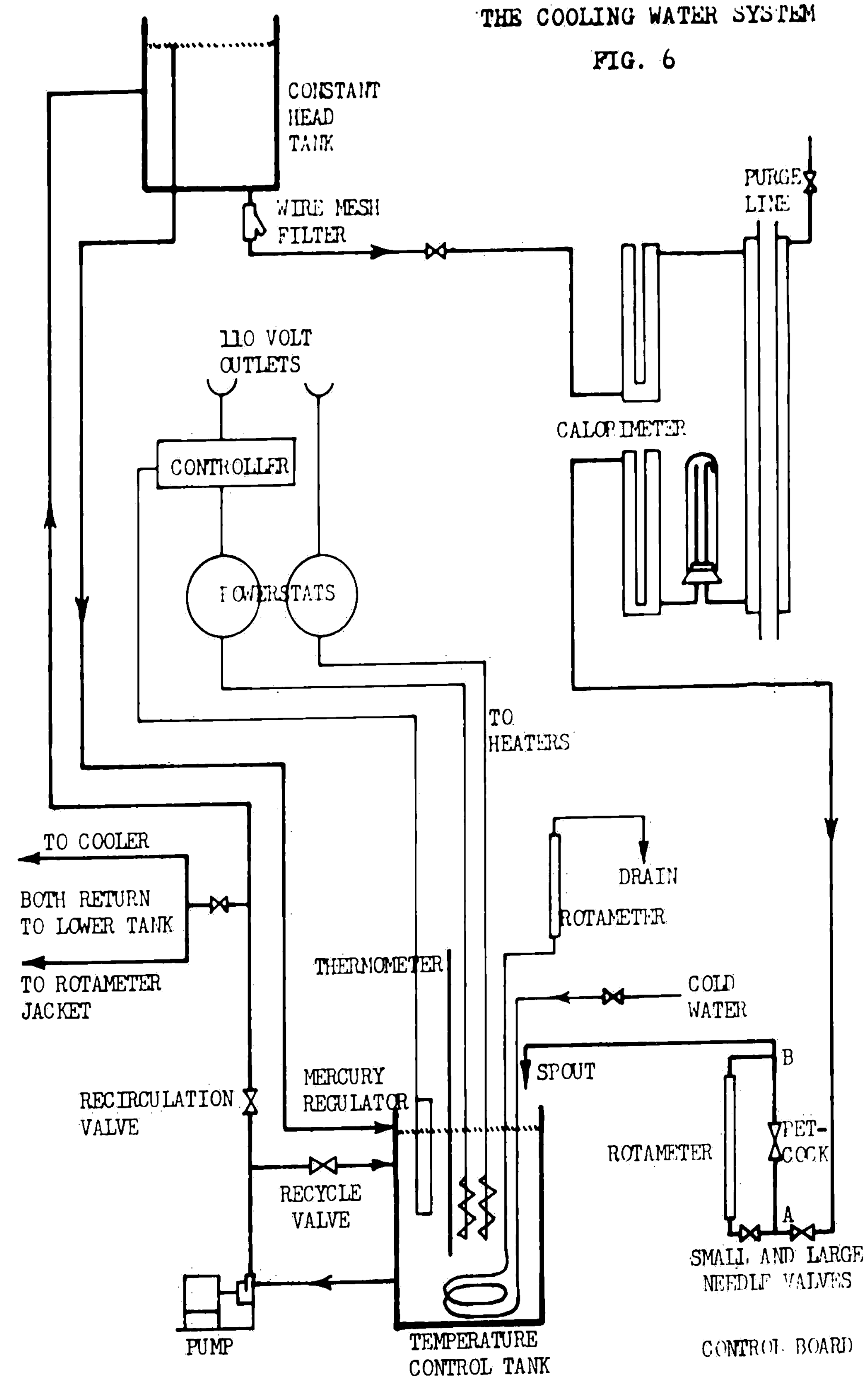
flask and that insulation would prevent this. A test tube for a view port and a flashlight bulb were inserted into the insulation in order to observe the amount of liquid at the elbow.

Power Supply

Since power requirements were below 1000 watts, the 110 volt laboratory outlet was considered a satisfactory source. Voltage regulation became necessary when it was discovered that the line voltage fluctuated, producing erratic operation of the equipment. A simple expedient requiring occasional operator attention was adopted. A single 110 volt powerstat transformer was plugged into the lab outlet, and its output voltage monitored with a vacuum-tube voltmeter. The output power was fed to three control powerstats. The voltage to the three control powerstats could then be adjusted to maintain a constant voltmeter reading. One control powerstat supplied power to two heating tapes in parallel for the boiler, and the other two supplied power to the two adiabatic walls.

The Cooling Water System

The purpose of the cooling water system was to provide water at 25 C and at a constant controlled rate to the calorimeter condenser. The system consisted of a temperature control tank with heaters and a cooling coil, a pump, valves, an auxilliary water supply, a constant head tank, the calorimeter and a control board shown in Fig. 6.



THE COOLING WATER SYSTEM

FIG. 6

For the two tanks, five gallon cans were modified with appropriate pipe fittings and coated with "Tygon" paint in an attempt to prevent rusting. The temperature control tank was set at table height and contained two heaters, a cooling coil, and a mercury regulator. The regulator and a controller were used during operation to supply power through a powerstat to a 50 watt immersion heater. A 750 watt immersion heater, controlled with a powerstat, was used to bring the water system up to 25 C at the start of a run. Cold tap water was circulated through a cooling coil of 8 ft of 1/4 in. copper tubing. The rate of tap water was controlled by a 1/8 in. bore needle valve at the tap, and was observed on a rotameter of 200 gm per min capacity.

A small centrifugal pump with a 1/50 horsepower motor was connected to the piping system with short hose connections to reduce vibration. From the bottom of the temperature control tank, water could be pumped either in recycle to the top of the tank or to the constant head tank. The latter was supported on an angle iron frame at a height of five feet off the table. A half inch copper tube running through the bottom of the upper tank and into the lower tank served as a constant head device. Depending upon the setting of the two valves, the water could be recycled to the lower tank when a constant temperature bath was needed, or circulated through both tanks when a constant head, constant temperature water source was needed.

When it was discovered that a water jacket was necessary for the system rotameter, a stream was taken from a point above the recirculating valve for circulation through the jacket. This auxilliary water supply was also used for the jacket of the condensate cooler at the exit of the condensate collector. Water from the jacket and cooler was returned to the lower tank.

Water for enthalpy measurement was taken from the upper tank through a fine mesh filter. The water flowed through a section of neoprene tubing into the condenser calorimeter. The calorimeter consisted of two thermocouple wells, a mixing tube, and the West type reflux condenser described previously. Both wells were formed entirely from glass tubing. Each was formed of an 11 cm long 6 mm glass tube sealed at one end and jacketed with a 12 cm long 9 mm glass tube, both tubes having standard wall thickness. Inlet and outlet tubes were of 7 mm glass tubing. The mixing tube was used to reduce fluctuations in the temperature at the condenser outlet. It was constructed from a three inch long section of 30 mm glass tubing, sealed off at one end and plugged with a No. 6 two hole rubber stopper at the other end. Inlet and outlet tubes of 7 mm glass tubing, inserted through the stopper, reached to the top of the tube. The top of the inlet tube was bent over so that the incoming water could be directed downward into the tube for mixing.

An extra side arm with hose and pinch clamp was installed at the top of the condenser jacket to remove entrapped air. Air collected there because of the decision to introduce water at the top of the condenser and to remove it at the bottom. Air bubbles would have reduced the available heat transfer area of the condenser.

Two blocks of Styrofoam were used as insulation around the calorimeter. These 4 x 12 x 13.5 inch blocks were hollowed out to accept the condenser, thermocouple wells, mixing tu , and air purge line and to fit around the clamp holding the condenser and contactor together. These components, attached with short sections of neoprene tubing, were sandwiched between the two blocks of Styrofoam. The blocks were bound and glued together. A 3/8 inch thick annulus between condenser and Styrofoam was packed with glass wool. When in place, the Styrofoam insulated the region extending from the top plywood circle to the pressure connection of the addition tube above the condenser.

The cooling water from the calorimeter flowed to a panel board where the rate was observed and controlled. A 1/4 inch bore needle valve was used to control the rate. The flow was divided and a side stream passed through a rotameter and small control valve to give a measure of the flow rate. Adjustment of the small control valve kept the rotameter float on scale for a wide range of flow rates through the calorimeter. A petcock on the main line provided a small pressure drop between points A and B of Fig. 6. The flow through the rotameter was a measure of the pressure drop from A to B. Since the orifice equation shows that pressure drop is proportional to the square of the flow rate, the rotameter gave a sensitive indication of the constancy of the flow rate through the calorimeter. The rate could be controlled between 300 and 1000 gm per min.

From the top of the control board, a long spout returned the water to the lower tank. A compression fitting at the control board served as a swivel joint so that the spout could be swung horizontally over a 500 ml beaker for flow rate determination. Flow measurements taken in this manner prevented any upset in the flow through the calorimeter since no valves or liquid levels were disturbed. Direct mass flow determination eliminated any problems of calibration and accuracy which would be involved in the use of a rotameter.

Thermoregulator and Controller

A regulator and controller for the water system were constructed with a sensitivity of 0.01 degree (C) for use during calibration to check the potential vs. ΔT relation for the calorimeter thermocouples. The control was also used during runs of the apparatus in order to keep an isothermal bath in the jacket of the system rotameter.

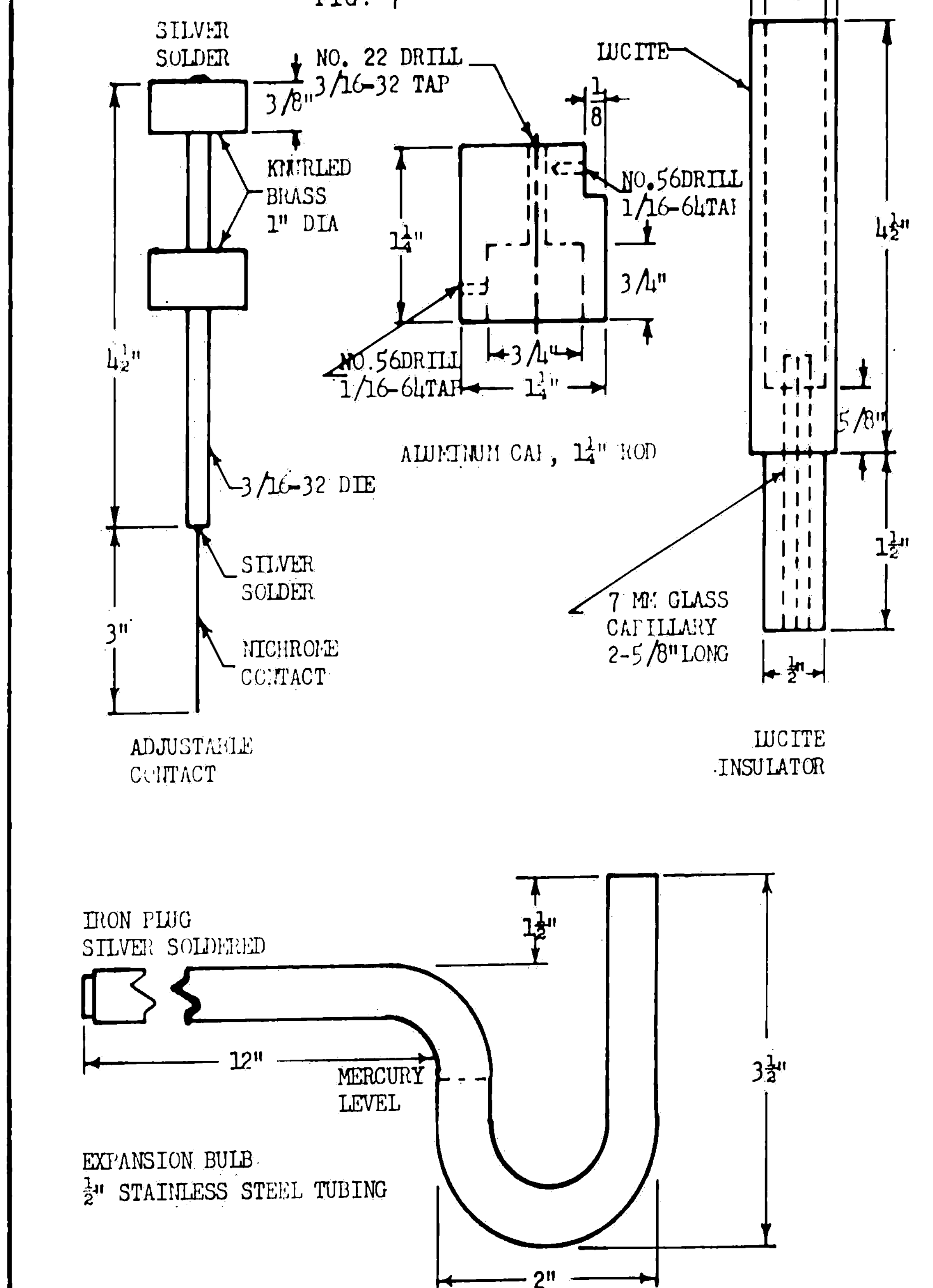
Thermoregulator designs are available in profusion (6, 25, 26). Most rely upon the thermal expansion of a fluid in a bulb to force a capillary column of mercury into making or breaking contact with a fine wire inserted in the capillary tube. This switching action provides the signal to a controller, and the level of the fine wire determines the temperature level. The expansion coefficient of the fluid and the volume of the bulb in comparison to the capillary diameter determine the sensitivity.

The expansion fluid chosen was carbon tetrachloride instead of the usual choice of toluene because of the greater expansion coefficient of carbon tetrachloride. The greater volatility of carbon tetrachloride was not considered a hindrance for room temperature operation. The bulb shown in Fig. 7 was fabricated from 1/2 inch stainless steel tubing instead of glass to avoid accidental breakage and distribution of mercury over the copper parts of the water system. A half inch stainless steel compression union was used to attach the bulb to a section of 7 mm glass capillary fit snugly into a lucite sleeve. To seat the lucite in the union, a short section of rubber tubing was used instead of the stainless steel compression sleeve.

The adjustable contact was nichrome wire silver soldered into a length of threaded brass rod. One section of one inch diameter knurled brass rod served as a turning knob, another section as a set screw. The contact screwed into an aluminum cap mounted on the lucite which also served as an insulator. The capillary tube extended above the bottom of the large hole in the lucite to form a well for excess mercury. One binding post was screwed into the aluminum cap and the other was silver soldered onto the stainless steel union. The procedure for assembling and

THERMOREGULATOR COMPONENTS

FIG. 7



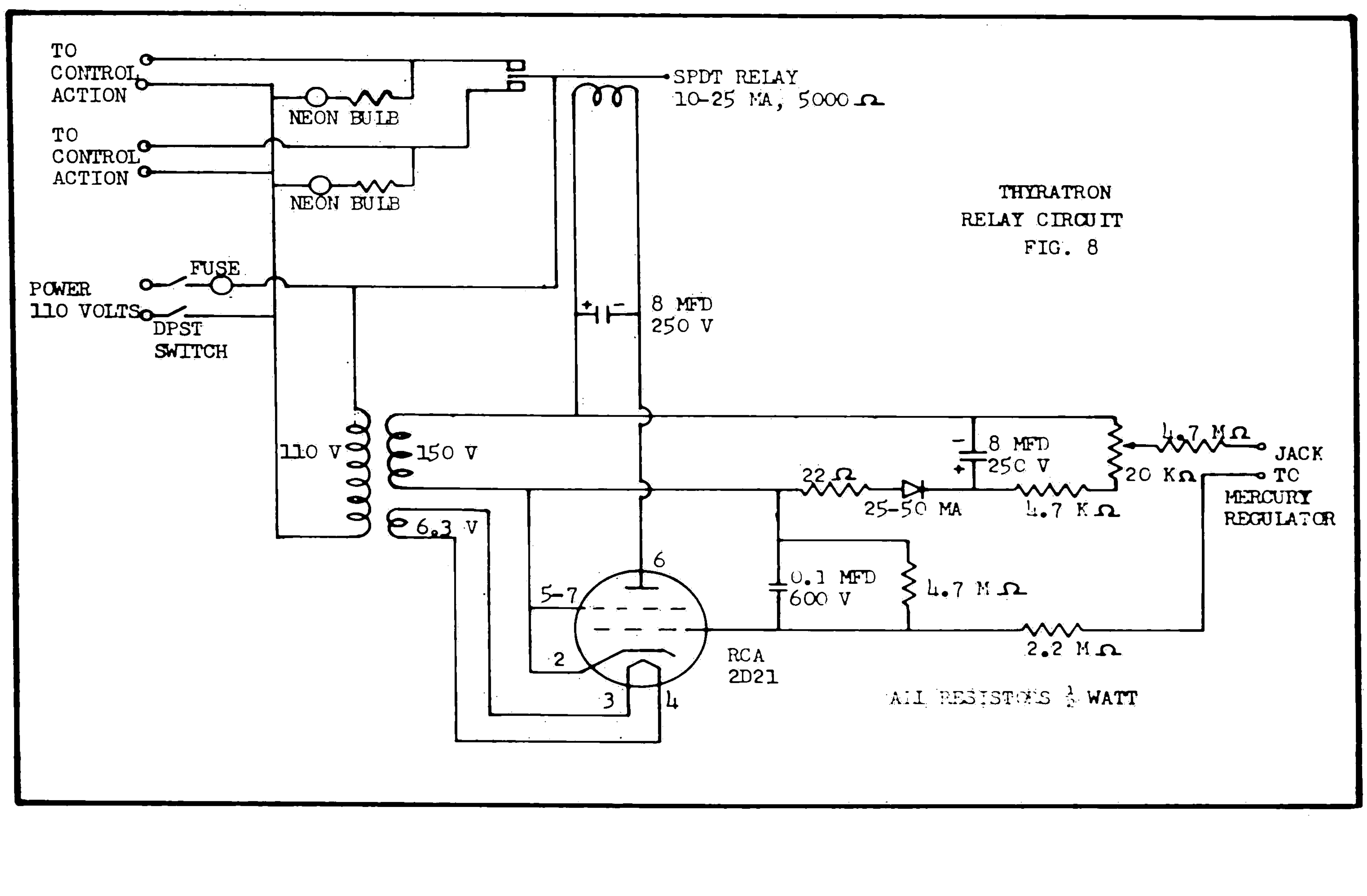
adjusting the regulator may be found in the appendix, p. 115

A variety of control circuits are available (27, 28, 29), and the design of control for constant temperature baths is analyzed qualitatively (6, 30) as well as analytically (28, 31). On-off control was deemed satisfactory. A standard Thyratron relay circuit, Fig. 8, was chosen because of the low power carrying capacity of the regulator. Mercury regulators which directly switch the power to heaters are subject to erratic operation from arcing and mercury oxide formation at the contact. The relay could control 1000 watts at each control outlet, switching from one to the other as the control point was passed. A heater and cooler could both be operated. Capacitance in the circuit introduced a short time lag to reduce unnecessary switching as the control point was passed.

Temperature Measurement

A Leeds and Northrup Type K-3 potentiometer and galvanometer were used with copper-constantan thermocouples for all temperature measurements. The instrument, used with guarded lead and standard cells and with the elimination of stray potentials in the thermocouple circuit, was accurate to ± 0.5 microvolt or 0.02 degree (C) for the enthalpy measurement, and to ± 1.1 microvolt or 0.05 degree (C) for the equilibrium temperatures. The temperature tolerances are computed for a single junction.

Early difficulties over the stability of the

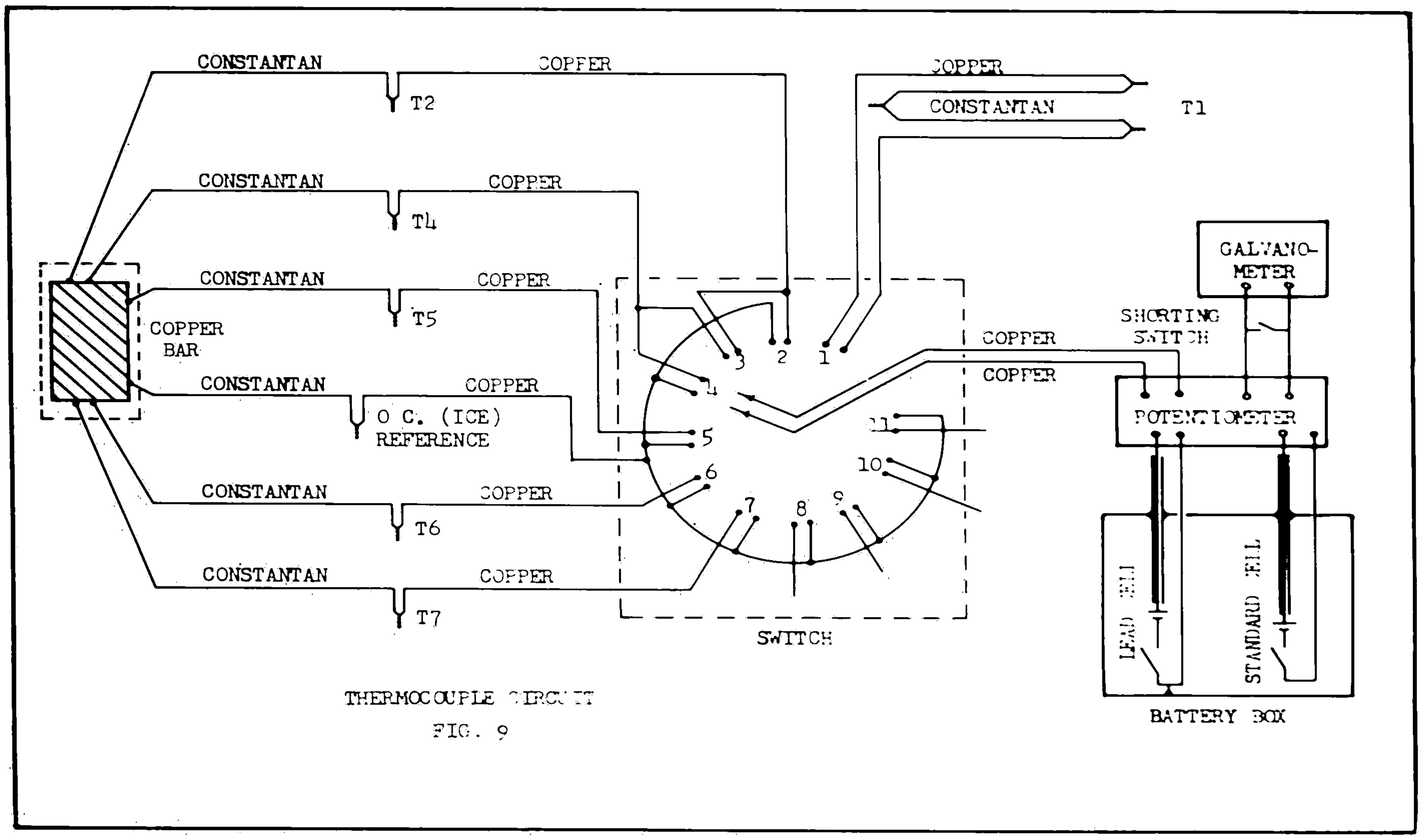


THYRATRON RELAY CIRCUIT
FIG. 8

potential measurements were eliminated when a special switching circuit was built as shown in Fig. 9. The copper bar and the switch, regions assumed to be isothermal, are shown surrounded by a dotted line. The junctions created inside an isothermal region yield no net potential as long as the same conducting material enters and leaves the region. Only constantan wires were connected to the copper bar, and only copper wires were attached to the switch. As long as the two regions were isothermal, no stray junction potentials could be generated in the thermocouple circuit. The compact mass of those two components and their enclosure in a small box made the fulfilment of the isothermal condition more likely. It should be pointed out that the two regions did not need to be at the same temperature, or at a constant temperature from day to day.

A battery box with guarded leads was constructed according to the design suggested in the operating manual for the potentiometer. The lead and the standard cells were placed in a plywood box which was lined with sheet aluminum. The negative terminal of the lead cell was attached to the aluminum and to shielding around the positive leads from both cells. A switch wired into the circuit of each cell prevented the potentials from being used except when needed. A shorting switch on the galvanometer protected the instrument against chance mechanical shock when not in use.

The potential at switch position 1 was a direct



THERMOCOUPLE CIRCUIT
FIG. 9

measure of the potential difference between the thermocouples at condenser inlet and outlet, independent of the reference junction potential. Likewise, position 3 presented the potential difference between T2 and T4. Positions 2 and 4 through 11 used the reference junction. The circuits for thermocouples T8 through T11 have been omitted from the drawing.

Thermocouple junctions were formed by twisting the wire ends and soldering them together. About 0.5 cc of mercury was placed in each of the glass thermocouple wells to improve heat transfer in the vicinity of the junction. Glass backed adhesive tape was used over the thermowells to prevent spillage of mercury and to keep thermocouples in place during assembly of the glassware. Thermocouples T1, 2, 4, 5, and 7 were 24 B & S gage wire which barely fit into 4 mm glass tubing. Thermocouples T6, 8, 9, and 10 were 20 B & S gage.

For the reference junction, a bare thermocouple with soldered junction was immersed in a dewar flask along with ice from an ice machine.

<u>Pressure Measurement and Control</u>

The pressure was controlled by a volume of air connecting the top of the condenser to a water manometer. A connection was also made to the top of the leveler. The trapped air exerted its pressure on the vapor in the condenser, the liquid in the leveler, and on the water in the manometer. Water was chosen for the manometer fluid instead of mercury because of the greater change in height with pressure. The pressure was controlled by introducing or removing air through a blow tube provided with a pinch clamp. The system pressure was kept at 760 mm Hg using a barometric reading to determine the height of water required to increase or decrease the pressure of the atmosphere.

To prevent a substantial change in pressure when the vapor level in the condenser changed, a reservoir of air was provided by a one gallon bottle. A change in vapor level over the length of the condenser changed the air volume about 0.1% and changed the pressure by the same amount. Therefore a change in the vapor level of the condenser, occuring as a changing demand by the system for heat exchange area, would effect neither the water level in the manometer nor the pressure on the system. During early runs, rapid pressure fluctuations were observed at the water manometer. To suppress these, a four inch section of drawn 6 mm capillary tubing was inserted in the neoprene hose. Communication between the condenser and leveler was not impeded by the restriction.

Composition Analysis

Chemical methods of analysis for ethanol-water mixtures are tedious and are accurate only at low alcohol concentrations (32). Refractive index undergoes a maximum at about 0.8 mass fraction while no maxima or minima are observed in the density. No Westphal balance sensitive to 0.1% in composition was available, and the pycnometer method was considered both too time consuming and likely to err from volatilization losses. Since an interferometer, which accurately and rapidly measures differences in refractive index, was available in the chemistry department, refractive index was chosen as the analytical method.

The Carl Zeiss Jena Interferometer consists of optical elements and a water bath contained in an insulated cylinder set horizontally in an air bath controlled to within 0.05 degree (C). Measuring cells, mounted in pairs in cell holders, are equipped with cover glasses to reduce evaporation losses. Each cell has two windows which permit light from the instrument to pass through the cell to the optical section. When the holder is mounted in the water bath of the instrument, a light beam which passes through each cell and a second beam which passes through the water bath produce two interference patterns which are observed in an eyepiece. The positions of the patterns are brought into match by turning a thumbscrew linked to a mirror in the instrument. The thumbscrew is marked to give readings which are linear in the difference in refractive index between the liquids in the two cells. Sensitivity and range are directly and inversely proportional to the path length of light through each cell. A set of cell holders with cells of path lengths 0.5, 1.0, 2.0, and 4.0 cm are available. Because of the large change in refractive index with composition of ehanol-water mixtures at compositions away from the maximum, the 0.5 cm cell which has the greatest range and least sensitivity was used. The effect of temperature upon the analysis is largely reduced because both unknown and known have about the same temperature coefficient.

OPERATING PROCEDURES

Program of Test Runs

The use of ethanol-water as a test system and of refractive index for analysis restricted the operation of the still to regions away from the refractive index maximum where compositions could not be accurately determined. It was felt desirable to operate in the region where there would be the greatest temperature difference between saturated vapor and liquid in the condensate collector, since runs with the pure components would check operation in which vapor and liquid in the contactor were at the same temperature. These considerations limited operation to the range between 0 and 0.6 mass fraction ethanol, away from the azeotrope and refractive index maximum. Since the ethanol-water system was being used simply to test the operation and accuracy of the equipment, the entire composition range did not need to be covered.

Runs were first made with water to discover shortcomings requiring changes in the apparatus. After a successful run with water, the equipment was dried and then charged and run with ethanol. Runs on mixtures were begun by charging a single mixture to the entire still. Calculations showed that an initial charge of 480 ml at about 0.18 mass fraction would produce a vapor phase of about 0.6, the upper limit in mass fraction for accurate analysis. Water added after each run to make up for sampling losses was used to change the point of equilibrium of the next run. The distilled water tap in the laboratory was used as the source of water. Absolute ethanol of U. S. P. grade supplied by United States Industries was used without further purification.

Start-Up

The addition funnel was filled with the mixture to be tested, and the addition valve was opened to allow a trickle of liquid to flow into the condensate collector. The U-bend between the cooler and leveler was temporarily elevated about one inch to prevent bubble accumulation in the cooler as liquid flowed from the collector to leveler. The control valve was used to keep the liquid level in the leveler above the outlet to prevent bubbles from entering the lines to the panel board. The shutoff valve was closed as liquid began to enter the boiler. A sample tube was used to collect a sample from the sample line, and lung pressure was used to reverse the flow, forcing the sample back into the lines. Bubbles which had formed at the Teflon sleeves and in the thermocouple well could thus be forced back into the leveler to be eliminated. With all but the smallest bubbles eliminated, the control valve and sample valve were shut. The remaining 400 ml of the charge were rapidly added and quickly filled the condensate

collector, then ran down the vapor tube into the equilibrium flask. The stopcock in the equilibrium liquid sample line was kept shut. The addition valve was shut after the charge was completely added.

To warm up the equipment the powerstats were turned on to heat the two adiabatic walls and insulation. The voltage to the two heaters was kept below forty volts to prevent overheating.

It was necessary to have the switch to the lead cell turned on for about half an hour before the potentiometer standardization became stable. The lead cell required that time to reach a nearly constant potential. At no time was the switch to the standard cell left turned on for a time longer than that required to make a standardization.

The cooling water system was also brought into operation at this time. The cooling water system was filled with distilled water to eliminate any uncertainty as to the exact specific heat, and to avoid any tendency to foul the water system lines. The pump was started, and the valves set to recirculate water between the two tanks and through the calorimeter, cooler, and rotameter jacket. Either the auxiliary heater or the cooling coil was used to bring the water temperature to within a few tenths of a degree of 25 C. The controller was turned on and the heating circuit set to deliver full power to the 50 watt heater during the heating part of the control cycle. The adjustment screw on the regulator was raised or lowered to bring about control at 25.00 C. The loose nut on the adjustment screw was used as a locknut against the aluminum cap to hold the screw in place at the set point. The auxiliary heater was used at about five volts to supply heat under conditions of low ambient temperatures.

The boiler heater was to be turned on and recirculation started when the flask liquid became heated to its boiling point. But the liquid in the equilibrium flask became heated only by overheating the lower aluminum tube for a few hours. To reduce the warm-up time, recirculation was begun before the flask liquid was completely heated.

The powerstat serving the heaters on the boiler was set at 40 volts for a few minutes to bring the boiler up to temperature. During the start of an early run, 120 volts were applied with the result that the heater became red hot and the glass insulation became baked and embrittled. Recirculation was started by opening the shut-off valve to the boiler and regulating the flow rate with the needle valve. The recirculating phase vaporized in the boiler and condensed in the flask, thereby heating the liquid. The depletion of the recirculating phase was made up by drawing a full sample of the flask liquid and introducing it into the recirculating phase at the other sampling point. This was repeated a sufficient number of times to heat the flask liquid to its bubble point. At this point the vapor stopped condensing and began to travel the route through the calorimeter and leveler. Thus self-sustained recirculation was brought about quickly despite the lack of direct heating at the flask.

Steady State Operation

Many pairs of recirculation rates and heating rates at the boiler would yield steady state conditions. The choice to fix one rate and adjust the other to it had to be made. Operation at a fixed flow rate was chosen because the rotameter could not be read accurately at points between the etch marks on the rotameter tube. The rate was maintained by adjustment of the Teflon and glass needle valve.

The liquid height in the leveler was not deliberately held constant, and was used to gage the approach to steady operation. A change in the level would indicate an exchange of mass between the two phases and would also mean that the flow rate through the condenser was not the same as that through the rotameter. Thus neither equilibrium nor enthalpy measurements would be valid during such time.

A drop in level in the leveler would be due to condensation within the equilibrium flask and/or accumulation of liquid at the end of the boiler. The two possibilities could be distinguished by looking at the elbow of the boiler. Accumulation then could be corrected by temporarily increasing the power to the boiler. If there were no accumulation at the boiler, condensation at the equilibrium flask could be the only alternative. It was thought that such condensation could only be caused by heat transfer to the surroundings and could be eliminated by the proper adjustment of the adiabatic wall temperature.

A rise in level at the leveler would be due to evaporation of the flask liquid by either a superheated vapor leaving the boiler or improper adjustment of the adiabatic wall temperature. The cause could be determined by a comparison of the temperatures at the flask inlet, flask liquid and lower adiabatic wall. Adjustment of the heat to the boiler or adiabatic wall was to have corrected the problem.

It may be seen that indications of improper operation were available and that proper remedial action could be taken to correct any anticipated improper operation.

As the previously mentioned variables moved towards steady values, attention was turned toward the operation of the calorimeter and cooling system. It became necessary to turn off the auxiliary heater in the lower water tank and use the cooling coils to remove the heat picked up by the water in the calorimeter and cooler. The cooling water flow rate was decreased from its maximum until the potential difference T1 rose to a value within the calibrated range. The valve in the branch line to the rotameter on the panel board was adjusted to give a mid-range rotameter reading. The remainder of the operation consisted of adjusting the water temperature regulator, the system flow rate valve, the powerstat settings, the supply voltage and the pressure; and of occasional checks of the barometric reading.

<u>Data Collection</u>

Data from Runs 8 and 9 are shown in Table II and Table III, Appendix, p. 82 and 83. The time was recorded at the beginning and end of each set of data, after which new powerstat values were set and recorded. Changes in the two rotameter values, water temperature, and pressure were made as each value was read, and the new value was recorded. Standardization of the potentiometer was carried out before each set of potentials were read. The thermocouple potentials were read to the nearest 0.01 millivolt to save time at the beginning of a run, and all thermocouples were read to the nearest microvolt or 0.1 microvolt as a steady state was approached and the final readings were being made. About six minutes were required to make a standardization and to read the ten potentials to 0.1 microvolt. The thermocouple readings were converted from potentials to temperatures. A section to the right of each table briefly indicates the observations made about operating conditions each time data were recorded.

When it was determined that a steady state had been reached, a complete set of data was taken without making changes of any variable. The calorimeter water rate was then determined by swivelling the spout from its place over the lower tank to a point over a 500 ml beaker for from half to one minute as measured by a stopwatch. The rotameter on the condenser water panel board, and the potential T1 were watched to certify their invariance throughout the determination. At the end of the time period, the spout was swivelled back over the lower tank, and the water was weighed. The measurement was repeated immediately.

Shutdown

The stopcock before the boiler and the three powerstats were shut off, and the system was opened to the atmosphere at the blow tube in the pressure system. Clean, dry, labeled sample tubes set in an ice bath were used to take samples of condensate and equilibrium liquid. The sample tubes were closed with ground stoppers and set aside in the ice bath for a few minutes before analyses were made. The Teflon needle valve was shut to prevent recirculation, and the condensate and shutoff stopcocks were opened to allow air into the boiler. This procedure was followed to prevent liquid from being drawn into the boiler from the flask. A half hour after the end of the run, the water circulating system was shut down. Flow through the calorimeter, condensate cooler, and rotameter jacket was shut off; the two valves at the pump outlet were reset to recycle the water to the lower tank, and the pump was shut off to end the run.

RESULTS

Measurements

The experimental latent heat values given in Table I, Fig. 10, fall within 5% of the reference values and show no systematic error. This large error may be explained by the failure of the apparatus to reach a steady state in the liquid level of the leveler and as a result of a surging condition in the condenser. Both conditions are discussed more fully under "CONCLUSIONS AND RECOMMENDATIONS."

The reference enthalpy data for the pure component Runs 5, 6, and 7 was taken from Perry (33). The reference enthalpy data for mixtures was found in graphical form and in only two references, Bosnjakovic (34), and Smith, Tuong, Brown, and White (35). The latter chart was used in the textbook by Brown, et. al. The method of calculation used by Bosnjakovic is not known, but Smith, et. al., used a variety of references on heats of mixing, ΔH_v of the pure components, boiling curves, equilibria, and C_p values. The two sources are compared numerically in Table I, the values having been interpolated from the graphs with the aid of a vernier caliper. The literature values are those given at the vapor composition determined in the present work. It is of interest to note a disagree-

TABLE I

LATENT HEAT MEASUREMENTS

THE ETHANOL - WATER SYSTEM

AT 1 ATM.

FIG. 10

REFERENCE	BOSN-JAKOVIC	BROWN	THIS WORK	BOSN-JAKOVIC	BROWN	THIS WORK
VAPOR PHASE COMPOSITION, MASS FRACTION	0.597	0.597	0.597	0.572	0.572	0.572
SATURATED VAPOR TEMPERATURE, C	89.4	89.4	90.4	90.7	90.2	91.1
SATURATED LIQUID TEMPERATURE, C	79.9	81.0	83.4	80.2	81.3	81.9
SATURATED VAPOR ENTHALPY, CAL PER GM	408.8	410.8	--	418.7	419.1	--
SATURATED LIQUID ENTHALPY, CAL PER GM	64.8	64.8	--	65.8	65.8	--
LATENT HEAT, H_v, CAL PER GM	344.0	346.0	330	352.9	353.3	360

	THIS WORK	REFERENCE (33)
LATENT HEAT, CAL PER GM, WATER, RUN 5	525	540
LATENT HEAT, CAL PER GM, ETHANOL, RUN 6	204	204
LATENT HEAT, CAL PER GM, ETHANOL, RUN 7	213	204

ment of 0.5% in the enthalpy values of the two references, appearing in the value of enthalpy of the saturated vapor. No enthalpy measurements were made in Run 10. The method of calculation used in the present report is given in the Appendix, p. 100.

Fig. 11 shows the fairly large disagreement among the literature sources concerning the temperature-composition diagram. There are a large number of sources which list phase equilibrium concentrations, but only a few include the equilibrium temperatures. The few additional points from other sources not included here fall within the same gunshot patterns. The boiling point data of Noyes and Warfel (20), the oldest reference, and the equilibria of Otsuki and Williams (36), the most recent data, are the most complete and consistent sets in the desired range. The two form liquid lines which fall within 0.005 mole fraction of one another. Values for Run 8 and Run 9 fall within this narrow band, while the liquid composition for Run 10 falls somewhat lower. The vapor curve is much less well defined. The data of Otsuki and Williams form a set which falls from 0.02 to 0.04 mole fraction below the data of Carey and Lewis (37) and that of Jones, Schoenborn, and Colburn. The vapor compositions of the present study show considerable enrichment over those of any study except that of Evans (38). Other experimenters conclude that considerable reflux within Evans' apparatus caused the high values. It was concluded that internal reflux was the cause of the

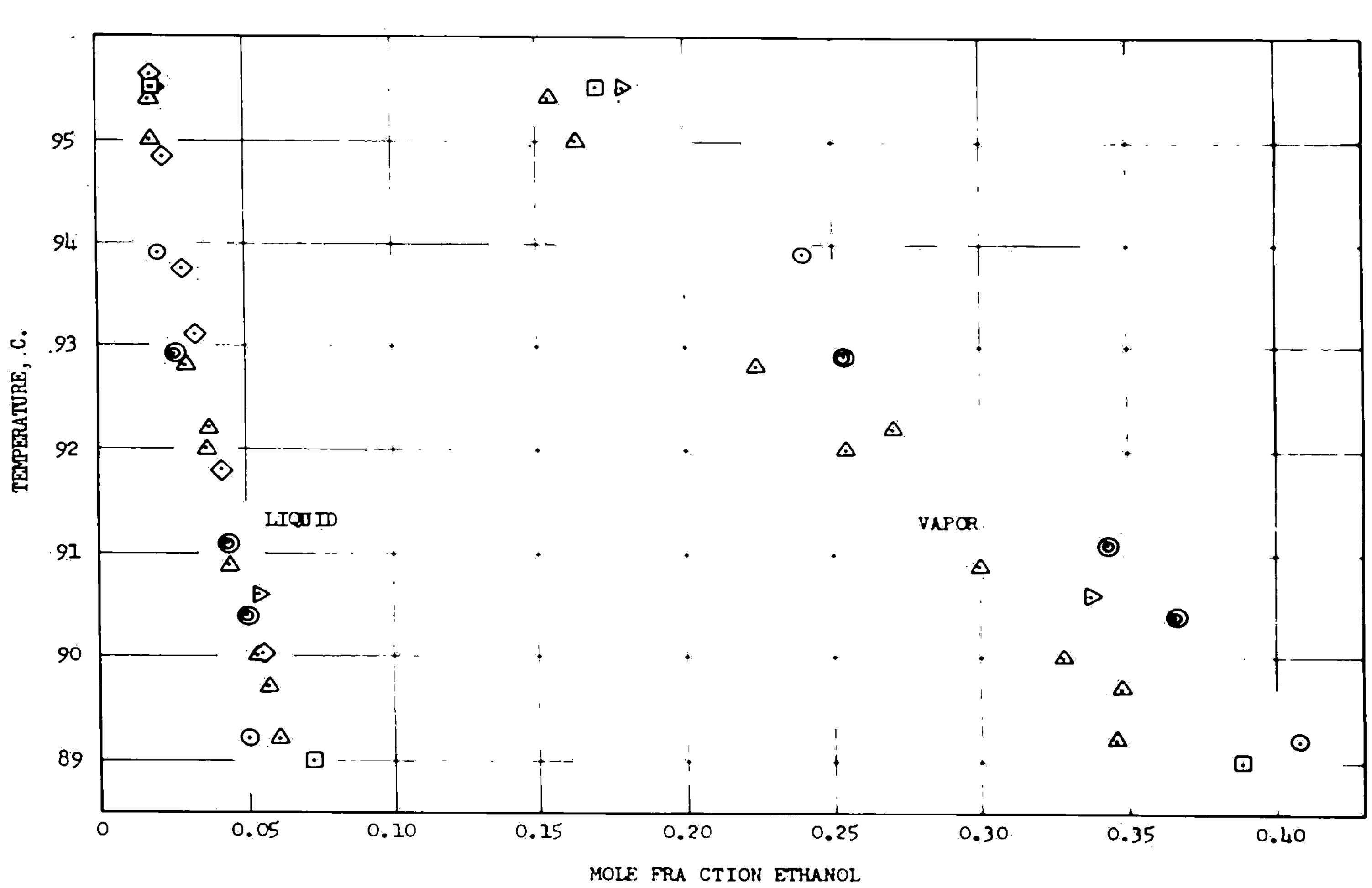
TEMPERATURE - COMPOSITION DIAGRAM

FOR THE ETHANOL - WATER SYSTEM

AT ONE ATMOSPHERE

FIG. 11

SOURCES OF DATA
- ◎ THIS WORK
- △ OTSUKI AND WILLIAMS (36)
- ⊡ CAREY AND LEWIS (37)
- ▷ JONES, SCHOENBORN, AND COLBURN (11)
- ⊙ EVANS (37)
- ◇ NOYES AND WARFEL (20)



high vapor compositions found in the present study. Such reflux, causing the return of condensed vapor to the equilibrium flask would not have much effect on the liquid composition because of the large amount of liquid present. The source of reflux is considered in the next section.

The saturated liquid line in the composition range of the recirculating phase has been plotted in Fig. 12. The reference data form a curve definite to 0.01 mole fraction or 0.1 degree (C). The temperature T7 at the outlet of the condensate collector is the temperature plotted for the points of the present study. The temperatures appear to be too high by about 2.2 degrees (C) and 0.5 degree (C) for Run 8 and Run 9 respectively. It appears that the liquid was superheated as it left the contactor, but that the amount of superheat was substantially decreased in Run 9. The reasons are treated in the section on mechanical performance.

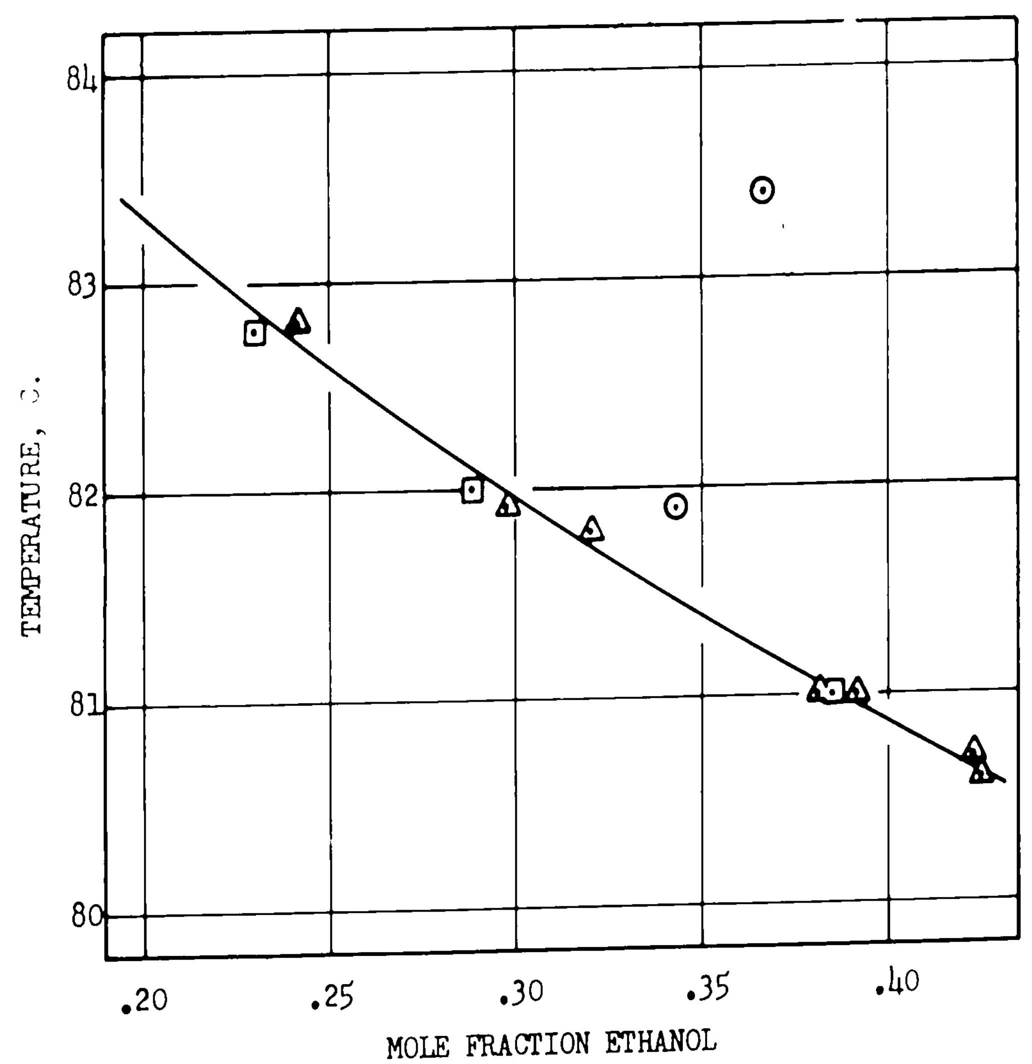
Difficulties of Operation

The operating variables in Run 8 differed significantly in two ways from the conditions set out as necessary for steady operation. They were the amount of superheat permitted in the vapor leaving the boiler and the temperature difference across the lower adiabatic wall. These have the effect of tending to increase the mass of the recirculating phase. The steady operation at the end of Run 8 indicates that these conditions were necessary to offset

TEMPERATURE - LIQUID COMPOSITION DIAGRAM

FOR THE ETHANOL - WATER SYSTEM AT 1 ATM.

FIG. 12



DATA SOURCES

⊙ THIS WORK

⊡ JONES, SCHOENBORN, AND COLBURN (11)

△ OTSUKI AND WILLIAMS (36)

some condition which tended to reduce the mass of the recirculating phase. Operation during Run 9 with low superheat resulted in a steady depletion of the recirculating phase as shown by the dropping level in the leveler. The material could only have condensed inside the equilibrium flask or escaped from the apparatus. The latter seems unlikely. Calculations (Appendix, p. 101) show that the observed depletion was due to heat transfer at the vapor riser of the condensate collector. The lower temperature of the condensed binary vapor caused condensation of the vapor entering the contactor, and the condensate flowed back into the flask. Additional computations (Appendix, p. 107) on the steady operation of Run 8 show that the superheat of the incoming vapor and the heat supplied by the hot lower wall equate roughly with the internal condensation losses calculated for Run 9. The mechanism of depletion by condensation and return to the flask liquid is further confirmed by the high vapor compositions shown in Fig. 11.

Perhaps the most disturbing feature of the operation was a cyclic fluctuation in the vapor flow rate through the equilibrium flask and calorimeter. During Run 8, an uneven bubbling rate was heard coming from within the equilibrium flask. A surge of bubbles, lasting for about one second, could be heard at about 16 sec intervals. The surge of vapor condensing in the calorimeter undoubtedly accounted for the large cyclic fluctuations in the temperature difference across the calorimeter and in the pressure at the water manometer. There was no apparent fluctuation in the flow rate at the system rotameter or at the water rotameter. The restriction in the tube connecting the condenser with the pressure system reduced the fluctuations at the manometer. The mixing tank at the water outlet of the condenser substantially reduced the temperature fluctuation. In Run 6 the temperature varied between 3.6 and 5.4 degrees (C), but in Run 7 after the mixing tank had been inserted, the fluctuation was reduced and a reading of 5.90 ± 0.05 degrees (C) was obtained. The surging was more noticeable during the two component runs and during the early parts of all runs. At the end of Run 8, the temperature was 6.0 ± 0.3 degrees (C), while the final value for Run 9 was 6.55 ± 0.07 degrees (C). The most plausible explanation for the surging is that vapor built up pressure in the boiler to overcome the liquid head in the equilibrium flask. Once the liquid head was overcome, vapor continued to bubble through the flask until the pressure in the boiler returned to some low value at which time bubbling practically stopped. The surging seemed to decrease as operation progressed toward a steady state. A comparison of the fluctuations in the value of ΔT in Runs 8 and 9 indicates that the amount of surging decreased when less superheating was present.

<u>Performance of Equipment</u>

The temperature measured at the liquid outlet of the condensate collector was identical with the temperature in the equilibrium flask during runs on the pure components. It may be concluded that sufficient contacting area was provided over which the reflux from the condenser could be heated by the vapor. The superheating of the condensed liquid indicated in Fig. 12 for the binary runs may have been caused by the heat transfer through the vapor riser which caused refluxing. Ceramic chips introduced into the condensate contactor between Runs 8 and 9 may have depressed the tendency toward the superheating by providing sources for nucleation, thereby causing the closer agreement between the temperature in Run 9 and the reference values. The apparent superheating may be partly due to the position of the thermowell T7. The well extended through the path of the hot vapor entering from the equilibrium flask and may have been heated sufficiently to give an erroneous temperature reading.

The temperature near the top of the contactor, T9, showed that the temperature of the contactor wall and probably that of the liquid inside were below the saturation values. Thus the distance from the condenser and T9, about two inches, did not supply sufficient contacting area between liquid and vapor, and the rest of the contacting area was needed to insure the elimination of subcooling from the condensate. The difference between the two temperatures T7 and T9 (Appendix, Tables II and III) indicates the impossibility of maintaining truly adiabatic conditions in the contacting section with the use of the present adiabatic wall.

Considerable difficulty accompanied efforts to match the temperature of the lower adiabatic wall with that of the equilibrium flask. The principle problem was the sensitivity of the aluminum wall temperature to small changes in the settings of the controlling powerstats. It became necessary to estimate and make one-tenth of a volt changes in the powerstat settings to reverse drifts of 0.1 degree per 10 min. The large number of other chores requiring the operator's attention, the time lag in heating and cooling the adiabatic walls, and the fact that no steady state was truly reached, caused the temperatures of the lower wall to differ from the flask temperature by a degree most of the time.

Movement of the position of the system rotameter float was due only to changes in liquid level in the leveler and to composition changes, although fluctuation was noted whenever there was enough liquid at the end of the boiler to cause bubbling. The change during the time interval between successive recordings of data rarely exceeded a few tenths of a millimeter. The Teflon needle valve proved to be a little coarse for the desired degree of control required. A stick-slip phenomenon at the valve stem caused small jumps in the rotameter reading, first to one side then to the other of the desired set point, as adjustment was attempted. Because of this, it was difficult to keep the float at the desired position.

Difficulty was encountered in the attempt to vaporize totally the recirculating phase without superheating the vapor and without accumulating much liquid at the elbow. The temperature at the entrance to the equilibrium flask was found to fluctuate over a few tenths of a degree within a minute and to vary widely over a half hour period depending upon the amount of liquid at the end of the boiler, and the amount of heat supplied. The presence of liquid at the elbow cannot be considered proof that the vapor entering the equilibrium flask is at saturation. For example, at the 10:52 data entry during Run 8 (Appendix, Table II), superheating of 28 degrees (C) was noted at a time when the amount of liquid at the elbow was increasing. Run 9 was a deliberate attempt to reduce the amount of superheat despite the effect of such operation upon the attainment of a steady operation. Superheat was kept below 5 degrees (C), and uncontrollable increases of liquid at the elbow were not observed. This shows that the revised boiler design with wide area for boiling the liquid and with little or no contact between vapor and heated walls appears to have permitted a reduction in the amount of superheat not possible with the helically heated tubular boiler. But it should be mentioned that the flow rate could not be substantially increased without a return of the difficulties of superheating and incomplete vaporization. Difficulty was encountered with the lack of sensitivity of the powerstat used to supply power to the heater around the boiler.

Bubbles which were trapped in the recirculating lines at the start of a run disappeared after about an hour of operation by disolving in the recirculating fluid. This demonstrates the performance of the reflux design of the condenser in eliminating disolved gases from the recirculating phase. The subcooler operated effectively in reducing the temperature of the recirculating phase to room temperature and reduced the likelyhood of evaporation from the liquid level in the leveler.

About a half hour after the end of a run, liquid from the equilibrium flask filled the boiler despite the precautions taken to open the boiler to the atmosphere. Since this did not effect the sampling or start-up, the situation was ignored.

The impossibility of draining the boiler was first noticed when the still was drained of water so that pure ethanol could be tested. The still was finally dried by attaching a vacuum pump with a trap to the top of the leveler. Both sampling valves and the top of the condenser were opened to the air and heat was supplied to the boiler. About half an hour was required for drying.

Ethanol vapor could be smelled at the blow tube of the pressure system when pressure changes were being made, indicating that ethanol was escaping from the condenser.

Presumably, the air in the condenser became saturated with ethanol and water, and, because of the surging which carried air out of and into the condenser, mixed with the rest of the air of the pressure system.

Leakage from various connections in the system was noticed at three sources. Some leakage was occasionally noticed around the tubing nuts of the Teflon needle valve, despite the precautions taken to eliminate bending thrusts on the tubing system at that point. Additional tightening of the nuts with pliers was found effective in eliminating the leaks. The ball joints at the system rotameter were the second source on leaks. Ethanol vapor could be detected in the region but liquid was rarely noticed. The third source may be inferred from the results of a pressure test made with the recirculating lines filled with water. The pressure was raised in the pressure system until the water leg registered full scale. The entire system was shut off from the atmosphere and the drop in pressure with time was noted. The pressure dropped from 30 to 20 cm water in about 10 sec. The source was not in the pressure system, for during a test with the pressure system sealed off from the glassware, the drop in pressure was negligible. The source was the tapered joints on the custom glassware. No leakage was noticed at the joints held with the Teflon tubing.

The needle value which controlled the flow rate of water through the calorimeter did not seem to provide sufficiently stable control. The mercury regulator was found to change its set point from day to day as a result of evaporation of the carbon tetrachloride. No change was noticed during individual runs and the set point was restored when necessary by the addition of mercury. It was necessary to turn off the valve in the line leading from the pump to the constant head tank at the time the pump was shut off. This step prevented water from flowing back into the lower tank and there causing an overflow. During warm weather, the cooling coils were found to be barely adequate for removing the heat picked up from the condenser and from the warm room.

CONCLUSIONS AND RECOMMENDATIONS

System Design

It should be evident from the long run times required to operate the present apparatus and from the constant error due to heat loss which is characteristic of this type of equipment that as high a flow rate as possible should be used. The importance of the use of equipment as small as possible which has been designed for as high a flow rate as possible cannot be overstated. Potential errors stemming from uncertainties in the heat losses which cannot be calibrated must be eliminated at the design stage. Weissberger (4) should be consulted for the common errors in heat loss calibrations. The water flow rate determination and the calorimetric calculation may be better made when there is a higher recirculation rate, and the length of a run may be sharply decreased. The author suggests that a design be attempted which recirculates at about 20 gm per min and has about 50 gm in the recirculating phase so that an entire recirculation cycle is completed in less than 5 min. Some of the design features of Altscheller might be incorporated, especially the features which separate the phases after contact.

Since the limiting accuracy in the enthalpy measurement appears in the system flow rate, perhaps the once-through design should be reviewed with the thought of using a smaller quantity of equilibrium liquid and a highly effiaient device for contacting the vapor and liquid. Accurate direct mass flow measurement could then be utilised for the system flow rate as well as for the water rate.

The problem of surging has not been adequately explored in this investigation. Surging has been reported in the literature by Brown (39). But it appeared to occur only in apparatus which incorporated the direct return of condensate to a flask boiler, and the possibility of its occurence in the present design was not anticipated. It can merely be noted that surging appeared to lessen as the operation more nearly produced equilibrium conditions, that is, proper compositions and lack of superheating.

Instrumentation

Although the error analysis for the flow rate determination (Appendix, p. 110) points to errors of about 0.1% obtainable at higher flow rates when the float is maintained to within a tenth of a millimeter of the set point, the difficulty of keeping close tolerances in float position during runs of the whole apparatus must be considered. Calibrations at low rates were made to within 0.1%, suggesting even greater accuracies during calibrations at higher rates, but such flow control requires constant concentration to avoid steady drifts in the float position. Such preoccupation with flow control was not possible during operation because of the other factors requiring attention. Perhaps an alternative in-line flow meter such as the thermistor, magnetic, acoustic, or pottermeter type could be used and the flow rate recorded and later integrated over the run time. One of these might prove to be inherently more accurate than the rotameter. If the jacketed rotameter is still to be used, the jacketing should extend over a greater length of tubing below the rotameter to insure that the recirculating liquid is at the desired temperature when it passes the float.

The K-3 potentiometer is capable of high accuracy but was used with very low potentials from the thermocouples. The use of the thermopile arrangement given by Weissberger would add significant figures for both the enthalpy and the equilibrium determinations. The thermocouple wire should be a smaller size to reduce heat leaks out the end of the wire and to make the wires more flexible. If an automatic multipoint recorder were used to monitor the approach to equilibrium, the operator would be freed from time consuming data gathering and a better record of the operation would be produced. The K-3 potentiometer could then be used to make the final determinations. The material such as ice used for the bath at the reference junction must be pure so that the temperature may be accurately known.

Devices which automatically control the pressure in an equilibrium still are widely used. A suitable design should be picked from the literature and constructed, or purchased.

A question arose concerning the difference in pressure between the top of the condenser where the pressure was measured and the liquid level where the measurement was to apply. Calculations (Appendix, p. 113) show that the head of vapor and the drag of viscous flow produced no appreciable pressure gradient.

Equipment

The reflux design, apparently an innovation in latent heat measurements, has proved to be a promising device, isolating the latent effect with but two drawbacks. These are the problem of producing adiabatic conditions and the possibility of diffusion losses. Suggested improvements are the use of a double walled tube for the vapor inlet to the condensate chamber, the placement of the thermocouple well T7 out of the vapor region, and the use of a silvered vacuum jacket around the contacting and condensing section to form an adiabatic wall. A good example of vacuum jacket design is found in Altsheler (32). Without the first change it is impossible to operate the apparatus in such a manner that it will both supply the proper conditions for enthalpy and equilibrium measurements and also reach a steady state operation.

The method used to establish equilibrium leaves much to be desired. The inherent uncertainties resulting from the liquid head in the flask are too great for determinations of the highest accuracy. Probably some design in which the equilibrium liquid is also circulated should be adopted. Designs of this type usually employ the vapor lift principle. The apparatus of Altsheler is a good example, while more conventional Swientoslawski designs by Brown (39, 40) might be considered. In any event the amount of the liquid phase should be greatly reduced to about 100 ml. Some provision should be included to directly heat the equilibrium liquid. The liquid may then be quickly heated at the start of a run and during a run the distribution of mass between the phases may be adjusted.

The decision made at the outset, to monitor the phase distribution by observing liquid levels, is not an entirely satisfactory method. A far more sensitive monitor would be a composition analyzer mounted in the recirculating system line. Such a device would have the sdvantage that it would make part of the composition analysis which is required anyway. For instance, the fluid leaving the rotameter could be passed through a refractometer cell before entering the boiler. A record of the refractive index would show what changes in composition were taking place as the still was being guided to steady operation. The problems of acquiring, modifying, and installing a refractometer would have to be surmounted. Perhaps conductivity or some other property could be continuously measured instead.

The problem of superheat and residual liquid at the boiler might be solved by providing holding time for the superheated vapor leaving the boiler. A length of tubing from elbow to entrance of the equilibrium flask could be used as a controlled heat leak to remove the superheat. A small heater at the low point of the apparatus, the elbow, is recommended for controlling the build-up of liquid at this point. Although the main boiler could be run at high superheat to prevent liquid buildup at the elbow, the extra heater is recommended so that the superheat may be eliminated at the boiler, leaving only slight superheat, say 1 to 5 degrees (C), to be removed by the proposed heat leak. Liquid which is not vaporized in the boiler or which trickles back from the heat leak will be vaporized by the small heater. In connection with this, it is recommended that a stopcock be placed at the lowest point in the equipment so that the entire still may be readily drained.

Three factors limit the usefulness of the heated adiabatic walls used in this apparatus. They are the impossibility of using the heated adiabatic wall to match the temperature gradients along the condensate collector, the heat leak from heated wall into the calorimeter, and the difficulty of manipulating the temperature of the wall to the desired point. The silvered vacuum jacket mentioned above might be heated and insulated much like the adiabatic walls in the present arrangement. The vacuum jacketed region should surround the equilibrium liquid.

Short sections of capillary tubing were glass blown onto all standard tubing at places where Teflon sleeves were used. It was felt that forces produced while attaching the sleeves might result in breakage of ordinary tubing. Use of the sleeves has shown that attachment is readily made and that the precaution was unnecessary. Restriction of the line between the contactor and leveler by capillary tubing is undesirable since the same level is to be maintained in both.

The Teflon and glass needle valve should be eliminated. Other designs are available (41), and a more rugged and accurate type should be designed and constructed.

The use of a constant voltage power supply would further reduce the difficulty of operation and assure a more reliable supply. The powerstats controlling the boiler and adiabatic walls failed to give close enough control of power, and should be replaced by more sensitive controls, perhaps in the form of slidewire resistance.

The water system operated with but little difficulty. Tygon paint used to coat the two tanks was not successful in preventing corrosion. A permanent system should be constructed from copper. It may become necessary to insulate the tanks and lines to prevent heating during warm weather which would overload the cooling coil or cause the delivery of water at the wrong temperature to the rotameter jacket or calorimeter. The mercury thermo-regulator had a large time lag which was probably due to the use of stainless steel for the bulb. Flattened aluminum tubing would provide a much faster response.

Scope of Investigation

Tests of the reliability of a combined apparatus should place the most stringent conditions on both the equilibria and enthalpy measurement. Equilibrium determinations should be made on a system of high relative volatility and compared with other literature references, a method advocated by Brown (39). The operation of the still should be smooth during such operation. Reliability tests of the enthalpy determination are difficult to set up. Runs on pure components provide comparisons with accurate literature values, but the operation of the contacting section during multicomponent runs is difficult to check since highly accurate values, experimental or calculated, are not available.

No consideration has been given towards apparatus for immiscible systems. Fowler reports a variety of designs, and any which supply a sufficiently great recirculation rate could conceivably be modified with the addition of a calorimetric condenser. Flow metering of the vapor phase constitutes a problem because the condensate would split into two phases.

Construction of the enthalpy-composition diagram is usually made with data taken or computed at 1 atmosphere pressure. For plant design calculations where the pressure may be different from one atmosphere, the effect upon the enthalpy-composition chart should be determined. Liquid heats of mixing and specific heats are not affected, but equilibria and the heat of vaporization show considerable pressure dependance (42). Thus design data must often be determined at the pressures to be encountered under process conditions.

Throughout the experimental part of this study, the assistance provided by thermodynamic methods in the construction of the enthalpy-composition chart has been overlooked. It is not always necessary to have all four kinds of data available over the composition range. In particular, if the heats of vaporization of mixtures are unavailable, the dew point curve may still be constructed by the method outlined by Dodge (43). The heat of vaporization of the pure components, the specific heats of the pure component vapors and the dew point temperature of mixtures form the basis of computation, with the assumption that the heat of mixing of the vapor mixtures is negligible. Other assumptions are usually incorporated into the values of the latent heats of the pure components when computed from vapor pressure data. These assumptions become the subjects for investigation by researchers with such apparatus as that of the present study. An experimental and thermodynamic analysis of the terms comprising the latent heat of any two-component mixture was made by Dana. His work on the oxygen-nitrogen system led to the conclusion that latent heats at intermediate compositions could be determined to within 0.1% of the experimental values, using the experimental values of the pure component latent heats and the assumption of negligible heat of mixing to get the calculated values. But the validity of the assumption with other systems appears to be unchecked by anyone else.

Perhaps the most crucial question to be answered in regard to continuing experimental measurement of enthalpy involves knowing what accuracy of the enthalpy values is necessary for the use to which they are to be put. If the purpose be a thermodynamic investigation of the ideality assumptions, then the experimental investigations should be continued, remembering that the latent heat may have to be determined to within 0.1% before non-idealities are detected. If the purpose is the accumulation of enough information to construct enthalpy-composition diagrams with accuracy sufficient for column design applications, then the calculation method, combined with equilibrium determinations, may give satisfactory results.

If the decision is made to continue at the level of thermodynamic investigation, the more recent literature should be consulted for methods of calculating the heat of mixing and the other excess thermodynamic properties from equilibrium measurements. Work has been done in this field by Murti, and by Scatchard and co-workers (44). This work should be investigated anyway to see if experimental determination of the heat of mixing of the liquid may be made unnecessary.

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APPENDIX

FIG. 13
TABLE II. DATA OF RUN 8

TIME PM	SYSTEM ROTAMETER	LEVELER NUMBER IN CM	WATER ROTAMETER	WATER TEMPERATURE IN LOWER TANK	PRESSURE WATER LEG CM OF WATER	POWERSTAT SETTINGS VOLTS I	II	III	THERMOCOUPLE READINGS CENTIGRADE ΔT 1	2	4	5	6	7	8	9	10	TIME PM	NEW POWERSTAT SETTINGS VOLTS I	II	III	COMMENT ON CONDITIONS OF OPERATION
2:38	0	13	---	24.6	0	0	30	25	---	---	63.8	---	101	56.4	81.4	---	---	2:41	0	40	25	
2:52	0	13.1	---	24.8	0	50	40	25	---	---	64.7	48.5	104	60.4	83.1	---	---	2:54	50	30	25	
2:58	2.6	9.8	---	---	0	70	30	25	---	77	66.6	55.2	103	62.9	85.0	59.[illegible]	24	3:07	70	15	25	FOUR FULL LIQUID SAMPLES TRANSFERRED FROM FLASK TO RECIRCULATING LINE
3:18	4	8.1	---	---	0	70	15	25	---	95.4	87.6	87.8	96.8	82.3	87.2	78.9	---	3:25	70	25	25	
3:32	5	10.9	8	24.95	10	65	25	25	4	98.0	88	89.9	95.8	81.3	89.5	79.3	24.5	3:41	65	25	15	
4:20	5.00	11.7	7.3	24.90	11.2	65	25	15	5.6-6.3	111.6	91.4	92.1	94.2	84	82.1	79.8	24.1	4:31	60	15	20	
4:40	5.00	11.5	7.3	25.00	11.3	52	15	20	4.5-5.4	170	91.6	91.7	89.9	84.8	83.5	79.9	---	[illegible]	[illegible]	[illegible]	[illegible]	LIQUID BELOW BUBBLING LEVEL IN ELBOW OF BOILER
7:02	4.98	10.2	6.7	24.97	8.1	50	22	18	4.4-4.5	156	90.9	91.0	86.5	84.1	81.3	79.[illegible]	24.2	7:13	47	25	19	ELBOW EMPTY, FEW DROPS AT 7:31, ABOUT 1.5 ML AT 7:33.
7:33	5.00	9.9	6.6	25.00	11.0	47	25	19	4.3	135.1	90.8	90.9	87.7	84.1	81.8	79.7	24.3	7:41	48.5	25.5	18.5	
7:47	5.00	9.6	6.6	25.02	11.7	48.5	30	18.5	---	131	90.8	90.8	88.6	84.0	81.8	79.7	24.2	7:55	48.5	30	18.5	ABOUT 1 ML.
8:21	5.00	9.2	6.5	25.02	11.1	48.5	30	18.5	---	132.2	90.7	90.7	93.2	83.8	81.7	79.7	24.4	8:30	48.0	25	18.5	ELBOW EMPTY OF LIQUID
8:43	5.00	9.0	5	25.00	10.8	48	25	18.6	4.6-5.4	131	90.7	90.7	92.7	83.8	82.0	79.7	24.3	8:52	48.0	20	18.[illegible]	FEW DROPS [illegible] AT 9:02
9:04	5.00	8.9	4.8	25.01	11.7	47.7	20	18.6	---	127.7	90.6	90.6	91.0	83.7	81.9	79.8	24.3	9:13	47.8	24.5	18.[illegible]	A FEW DROPS AT 9:14
9:29	5.00	8.6	4	25.02	11.6	47.8	24.5	18.4	---	124.0	90.5	90.5	91.0	83.6	81.9	79.7	24.5	9:38	47.8	24.5	18.3	ELBOW EMPTY
9:47	5.01	8.4	3.2	25.00	11.1	47.7	24.5	18.2	---	125	90.5	90.5	90.9	83.5	81.9	79.7	24.4	9:54	47.4	24.5	17.9	
10:19	5.00	8.1	3.1	25.01	11.9	47.5	40	17.8	5.3-6.1	122	90.5	90.5	101	83.5	81.4	79.7	24.3	10:29	47.0	40	17.8	FEW DROPS
10:52	5.00	8.0	3.2	25.00	11.6	47.1	40	17.8	5.6-6.2	119	90.5	90.4	111	83.4	81.9	79.8	24.6	11:0[illegible]	47.1	4[illegible]	17.8	LIQUID IS INCREASING
11:16	5.00	8.2	3.4	25.00	11.2	47.2	40	17.8	5.96	118	90.6	90.5	114	83.6	82.5	79.9	24.2	11:25	47.2	0	17.0	LEVEL IS ABOUT ¼" BELOW BUBBLING AND INCREASING.
11:40	4.98	8.2	3.7	25.02	5	47.2	0	17.0	---	116	90.4	90.4	102	83.4	82.5	79.7	24.1	11:49	OFF	OFF	OFF	HEATING LOWER FLASK TO PUT MORE MAT'L INTO RECIRCULATING PHASE

FIG. 11.
TABLE III. DATA OF RUN 9.

TIME PM	SYSTEM ROTAMETER	LEVELER NUMBER IN CM	WATER ROTAMETER	WATER TEMPERATURE IN LOWER TANK	PRESSURE WATER LEG CM OF WATER	POWERSTAT SETTINGS VOLTS I	II	III	THERMOCOUPLE READINGS CENTIGRADE ΔT 1	2	4	5	6	7	8	9	10	TIME PM	NEW POWERSTAT SETTINGS VOLTS I	II	III	COMMENT ON CONDITIONS OF OPERATION
1:45	5.0	8	-	25	0	60	25	20	---	97.8	91.4	91.5	85.4	83.3	80.3	79.8	24.8	2:02	60	26	19	ELBOW FULL OF LIQUID
2:32	5.00	10.2	-	25.6	0	60	26	19	---	94	93.1	93.2	87.3	82.7	81.0	80.0	24.3	2:39	50	30	17	BARELY BUBBLING
2:56	5.00	10.2	-	25.05	-6.5	50	30	17	---	105	92.8	92.9	88.0	82.4	80.0	79.6	24.6	3:06	50	30	17	JUST BELOW LEVEL OF BUBBLING
4:42	5.00	5	-	23.6	-8.5	50	30	17	---	99.5	91.4	91.5	97.7	81.9	79.1	79.5	--	4:47	50	25	18	SAMPLE LINE BROKEN, REPAIRED. RUN WAS NOT STOPPED.
6:46	4.8	1.8	-	24.4	-9	50	25	18	---	144	90.9	90.9	93.7	81.7	81.5	79.5	25.0	6:51	46	20	17	LEVEL ALMOST OUT OF LEVELER. RUN STOPPED, SAMPLE LINE ATTACHED, SAMPLES FED INTO RECIRC. LINE TO RAISE LEVEL. RUN RESUMED.
7:52	5.0	9.5	-	25.15	0	71	20	17	---	93.1	92.6	92.7	87.5	82.4	79.3	79.9	25.7	8:01	50	25	20	
8:21	5.00	9.9	-	24.95	4	50	24	20	---	95.5	92.5	92.6	88.3	82.3	81.3	79.7	25.6	8:29	48	28	18	BARELY BUBBLING-STOPPED-BEGAN AGAIN
8:35	5.00	9.5	-	24.97	4	46.8	28	18	---	99.1	92.3	92.4	89.5	82.2	81.3	79.7	25.3	8:42	47	28	17.5	
8:45	5.00	9.0	7	24.97	4.5	47	28	17.5	4.25	94.7	92.0	92.2	90.7	82.1	81.2	79.6	25.0	8:52	47	25	17.5	BARELY BUBBLING
9:39	6.00	6.8	6.6	25.00	5	54	25	17.5	6.2-6.6	91.2	91.5	91.5	91.0	82.0	80.6	79.6	24.9	9:43	54	25	17.5	RAISED RECIRC. RATE TO INCREASE T1.
10:01	5.8	4.4	6.5	24.98	4	60	25	17.5	6.68	91.1	91.1	91.2	91.0	81.9	80.5	79.7	25.1	10:08	55	24.8	17.5	BARELY BUBBLING FROM 8:00 TO 10:48 FOUR SAMPLES FED INTO RECIRCULATING LINE
10:29	5.8	5	6.4	25.00	1.5	70	24.8	17.7	---	93.6	91.5	91.6	90.8	82.2	80.4	79.9	25.2	10:35	70	25.1	18.1	SURGING
10:39	6.01	8.9	-	25.00	2	60	30	18	---	93.9	92.3	92.4	92.0	82.5	80.7	80.1	25.1	10:53	60	29	18.5	BARELY BUBBLING
10:56	6.00	8.9	7	25.01	2	60	29	18.4	7.4-8.0	94	92.3	92.3	92.9	82.5	80.8	[illegible]	25.0	11:02	60	25	18.4	BARELY BUBBLING
11:04	6.00	8.8	7	24.95	2	60	25	18.4	---	95.3	92.1	92.2	92.8	82.4	81.0	80.0	25.0	11:09	58	25	18.4	BARELY BUBBLING
11:23	6.00	8.4	7	24.95	-2.6	57	25	18.4	---	98.6	91.8	91.9	92.6	82.3	81.2	79.8	24.7	11:27	57.5	26	18.3	NO BUBBLING
11:40	6.00	7.6	7.1	25.02	-2.6	57.4	25.1	18.2	---	94.8	91.6	91.6	92.5	82.1	81.3	79.8	[illegible]	---	57.4	25.1	17.5	
12:10	5.79	4.9	7.1	25.00	-5.5	57.4	25.1	17.5	---	92.5	91.1	91.2	92.1	81.9	80.9	79.7	24.3	12:17	OFF	OFF	OFF	T1 STEADY

CALIBRATIONS

Calorimeter Thermocouples

The pair of thermocouples used for the enthalpy determination was calibrated for a 5 to 10 degree (C) difference with the lower temperature at 25 C. Therefore two controllable constant temperature baths were required. The thermocouple to be used at the calorimeter inlet was inserted with a drop of mercury into a sealed six mm. glass tube and immersed six inches into the lower tank of the cooling water system. The pump was used to recycle the water directly back to the tank to provide agitation, and the tank was controlled at 25 C. The other thermocouple was similarly immersed in a four gallon constant temperature oil bath. A motor driven agitator and a 500 watt immersion heater, the latter operated through a manually controlled powerstat, were used to maintain the bath at levels between 30 and 35 C.

Two Brooklyn Thermometer Co. mercury in glass thermometers, range 19 to 35 C, interval to 0.01, with auxiliary 0 C scale, and supplied with factory certification, were used to determine the two temperatures. Corrections reported in the certificates were applied, and were no greater than 0.01 degree. Emergent stem corrections were found to be of significance in only one case, for which a correction of 0.01 degree was applied. It is estimated that the temperature difference between the two baths could be determined to 0.01 degree, an error no greater than 0.2% for the 5 to 10 degree range of temperature difference.

The water tank could be maintained to within 0.01 degree indefinitely, and the oil bath could be maintained to within 0.1 degree indefinitely and to 0.005 degree for a half minute. The change in temperature difference between the two baths was on the order of 0.005 degree during the time required to read both thermometers, standardize the potentiometer, make the potential determination twice, and record the data.

To check the reproducibility of the potential measurements, a series of thirteen determinations was made over a seven hour period with the baths at 25 and 35 C. The actual temperature difference was not more than 0.05 degree different from 10 degrees, and each potential was corrected by 0.4 μv for each 0.01 degree between the actual temperature difference and 10 degrees. The corrected values of potential showed a spread of 1.1 μv or 0.3% from the average potential value of 412.1 μv. An additional check on stability of the circuit was made two days later, and three determinations averaged 412.2 μv with a spread of 0.6 μv. It was felt that confidence in the stability and reproducibility of the thermocouple and potentiometer circuits had been established.

It was not known at first whether the thermocouple potential corresponding to the condenser water ΔT would be, for a given ΔT, independent of the temperature at the inlet of the condenser. Another set of calibrations was made to determine the effect of a change in the temperature levels in the two baths at a constant temperature difference. The potential was determined for a five degree difference at temperature pairs of 24.50 C and 29.50 C, of 24.90 C and 29.90 C, and of 25.00 C and 30.00 C. The potentials at all three 5 degree intervals were identical, showing that determination of the inlet temperature and corrections for its variations would be unnecessary.

Calibration of the thermocouples at intermediate temperature differences in the range between 5 and 10 degrees established the relation between potential and temperature difference. The factor k in the relation $\Delta T = k\mathcal{E}$ has been plotted as a function of $\mathcal{E}$, the potential, in Fig. 15. The relation may be seen to be not quite linear.

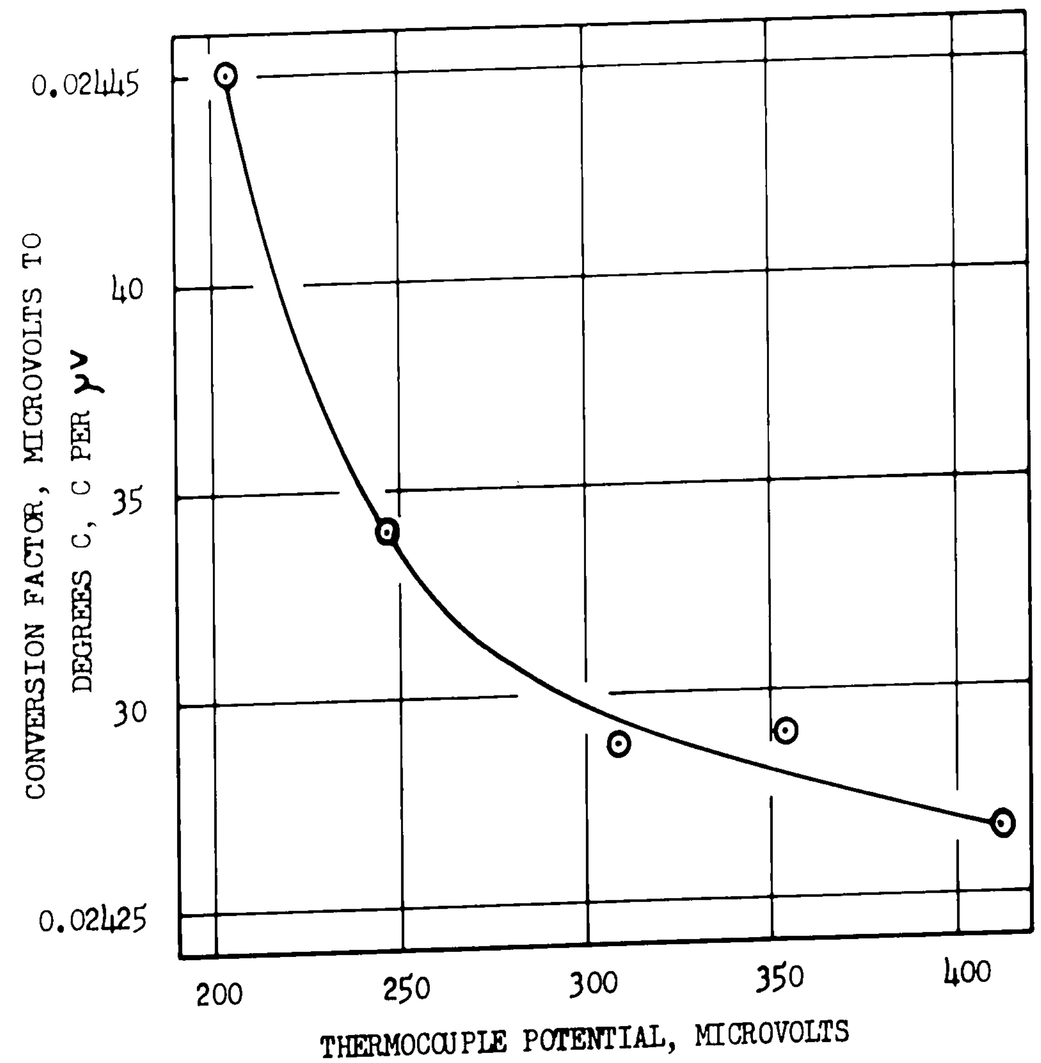
The calibration showed that the potential at T1 could be relied upon as an accurate measure of the temperature difference across the calorimeter, and would be independent of small changes in the temperature of the cooling water system.

<u>Equilibrium Temperature Thermocouples</u>

The oil bath was used to calibrate the potentials

THERMOCOUPLE CALIBRATION
FOR ENTHALPY MEASUREMENT
FIG. 15

COPPER-CONSTANTAN JUNCTIONS (T1
COOLER JUNCTION AT 25 ± 0.5 C.



potentiometer circuits had been established.

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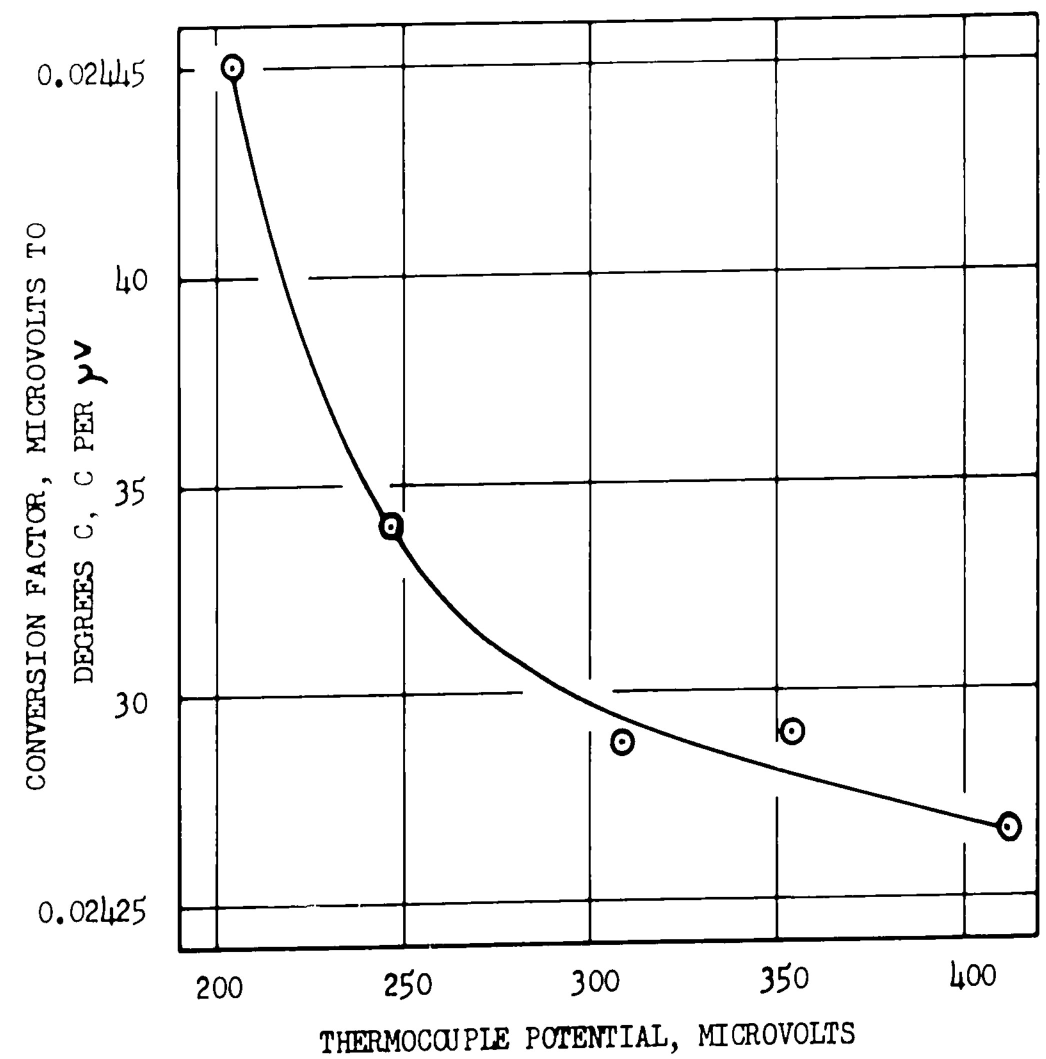


of the seven thermocouples used at the equilibrium flask, contacting section and adiabatic walls. The thermocouples were inserted with a drop of mercury in individual six inch long glass tubes and immersed in the bath with the agitator, 750 watt heater, and two unstandardized ASTM mercury in glass thermometers with 50 C to 100 C ranges in one tenth graduations. The thermometers agreed to within 0.05 degree or closer over their ranges. They were read with magnifiers to 0.01 degree and stem corrections of as much as 0.3 degree were applied. The seven potentials were recorded to the nearest microvolt at calibration points of 70, 80, 90, and 100 C. The potentials agreed to within 3 μ v at each temperature, which indicated uniformity of composition in the thermocouple wire. The calibration followed practically a straight line displaced from the calibration values found in handbook tables (45) by 20 microvolts, equivalent to 0.4 degree. The probable cause is a difference in the composition of the thermocouple wires from those used in the handbook determinations. It seems unlikely that impurities in the ice at the reference junction could cause a 0.4 degree difference from 0 C, that the thermometers used in the calibration could be that inaccurate, or that the potentiometer would be in error by that much. The displacement demonstrates the necessity for calibrating thermocouples for accurate work.

Pressure

To determine the height of the water leg required to bring the pressure in the system to 760 mm Hg, a barometer and two correction and conversion charts were used. The reading of a mercury in glass barometer was corrected for temperature effects, and the difference between the barometric reading and 760 mm Hg was converted to the equivalent water leg height. The water leg was adjusted using the blow tube in the pressure system. The pressure could be maintained to within 1 cm water or 0.7 mm Hg of one atmosphere as a conservative estimate. This variation would cause a change of no greater than 0.05 degree in the boiling point, so that operation at 760 mm Hg could be assured to within the expected accuracy of the temperature measurement of 0.1 degree.

Heat Leak

Because of the arrangement of equipment, there was opportunity for heat transfer between the upper aluminum cylinder and the water in the condenser jacket through the plywood and Styrofoam. The heat transfer was independent of the vapor flow rate into the condenser. Heating rates of the condenser water were determined with the aluminum walls at 80, 90, and 100 C and with no fluid recirculating in the system. The heating amounted to 13, 18, and 23 cal per min at the three temperatures, or a correction of about 1% to be applied to the expected latent heat flux of 2000 cal per min. Since the correction was accurately known and was taken into account during enthalpy calculations, it could not be a cause of inaccuracy or uncertainty.

<u>System Flow Rate</u>

Calibration of the rotameter was made after the run of the apparatus so that the same composition could be used in the calibration. After analysis of the vapor sample, about 500 cc of an ethanol-water solution were prepared to within 0.1% of the vapor concentration for use in the calibration. The recirculating line was dismantled above the Teflon needle valve. The solution was charged to a flask provided with a two hole stopper. An inverted U-tube of capillary tubing, in sections joined by Teflon sleeves for flexibility, ran from the bottom of the flask, out of the flask, and down to the inlet of the needle valve. A bit of glass wool in a short Teflon sleeve, which was slipped over the capillary tubing at the bottom of the flask, served as a filter to prevent solid material from interfering with the operation of the needle valve or rotameter. The flask was mounted above the panel board so that about a two foot liquid head was established between liquid level in the flask and the outlet from the vapor sample line. Liquid flowed from the flask through the filter, U-tube, Teflon needle valve, thermocouple well, rotameter, Teflon sample valve, and into a 100 ml Erlenmeyer flask set on a laboratory pan balance. The Teflon valve in the line to the boiler was kept shut. An Ohaus 311 gm capacity balance reading to 0.01 gm was used. Water was circulated in the rotameter jacket at 25.00 C.

Bubbles were removed with difficulty by replacing the Erlenmeyer flask with a sample tube, draining a full sample, then using lung pressure to force liquid from the sample tube back into the system. Eventually the bubbles were forced up the U-tube and into the flask where they escaped from the system.

Calibrations were made by adjusting the flow rate with the needle valve to the same rotameter reading as observed during operation. Liquid flowing from the sample outlet was caught in the Erlenmeyer flask on the balance. As the balance arm passed the rest point, a stopwatch was started. The balance counterweight was increased by 30 gm, and the stopwatch was stopped as the balance arm passed the rest point. The sample valve was then shut off until the next determination. The time required for each calibration ranged from eight to twenty minutes. Throughout each calibration, the needle valve was adjusted to maintain the proper rotameter reading.

Early difficulty in obtaining reproducible calibrations led to jacketing the rotameter to make the temperature of the fluid constant. Calibrations differed by 2% when water was tested at 25.00 and 26.00 C at a rotameter reading of five. The viscosity of water changes 2% per degree at room temperature, while the density changes 0.03%. After the effect of temperature was eliminated, a series of four successive calibrations with water agreed within 0.14% of one another. Calibrations with ethanol agreed to within 0.5%. Calibrations at intermediate compositions agreed to within 0.3%.

An approximate determination of evaporative losses was made for the calibrations with ethanol and with mixtures. Ethanol was left standing in the Erlenmeyer flask on the balance for a period of time until a change in weight could be noted. Based on this evaporation rate, a loss was calculated for the length of time of each calibration. The loss was added to the value of mass collected and the sum divided by the time of the calibration to determine a corrected rate. Corrections amounted to about 0.3%. The determination of the correction represented only an approximation of the error and was probably low because the mass transfer from a droplet falling into the Erlenmeyer flask would be greater than the transfer from a stagnant liquid surface.

The position of the float in the rotameter was maintained to within a few tenths of a millimeter during runs and calibrations. The calibration chart from the manufacturer has been used with the dimensions of the rotameter scale to estimate the rate of change of flow rate with float position at various float positions (Appendix,

p. 110). The following table shows the error in flow rate corresponding to an error of 1 mm in the position of the rotameter float from the desired reading.

TABLE IV. EFFECT UPON FLOW RATE OF ERROR

IN POSITION OF ROTAMETER FLOAT

FIG. 16

Scale Reading	Nominal Flow Rate, cu cm per min (water)	Error in Flow Rate, cu cm per mm change in float position	Error, Percent of Flow Rate
3	1.0	0.093	9.3
5	3.7	0.17	4.6
8	10.6	0.21	2.0
10	16.4	0.20	1.2

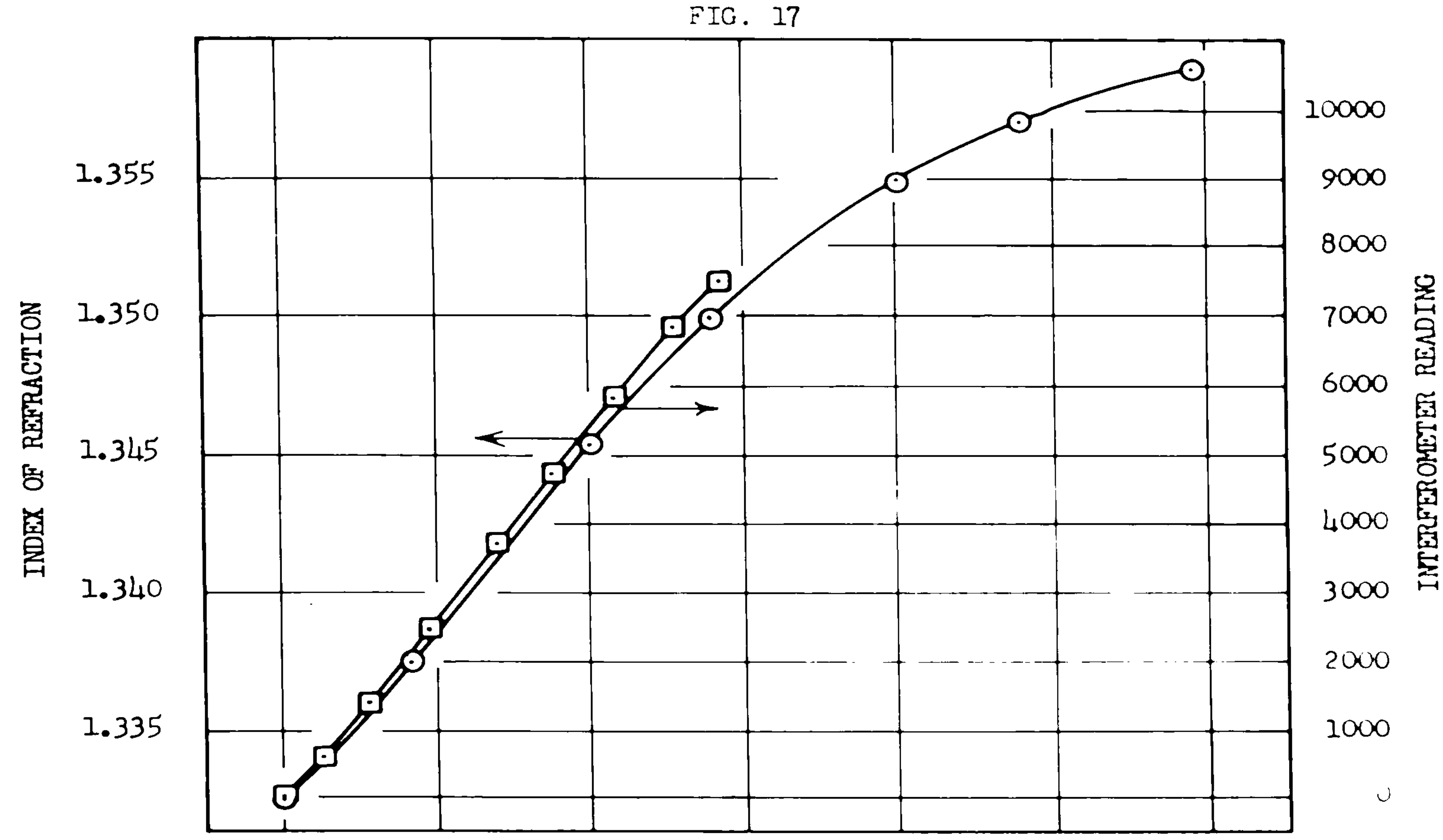
The third and fourth columns show that although the rotameter is more sensitive at low flow rates, the accuracy of the device for flow measurement is greater at the higher flow rates.

To keep the float position as constant as possible during a run and to achieve reproducibility of float position between runs and calibrations a somewhat unusual spacial relation between float and rotameter markings was chosen as a convention for making readings. The top of the ball float was chosen to represent the float position, and the top of each etch mark on the rotameter glass was chosen as the level represented by that etch mark. With the aid of the needle valve the top of the ball was brought tangent to the top of the etch mark, and the flow rate was considered to be set at the value corresponding to the etch mark. Since the etch marks were about 0.2 mm wide, the choice among levels represented by the etch mark was important.

Composition Analysis

The interval in refractive index between mixtures and either of the two pure components extended past the largest interval covered with the smallest interferometer cell. Therefore mixtures of known concentrations were required as standards for the determinations of samples having refractive indexes outside the range covered by the pure components. Although the relation between the refractometer reading and refractive index is linear, the relation between refractive index and composition is not, and unknown compositions could not be determined by simple interpolation of the interferometer reading. To determine the direct relation between interferometer reading and composition, a series of six known concentrations was prepared in the range 0.1 to 0.6, in 0.1 increments of mass fraction. Interferometer readings were determined for successive pairs beginning with distilled water vs. 0.1 ethanol, then 0.1 ethanol vs. 0.2 ethanol, and so on. A reading for distilled water vs. distilled water was used as a zero correction. Cumulative values of readings were plotted on a large graph against composition, a small reproduction of which appears in Fig. 17. To more accurately determine the shape of the curve between

CALIBRATION OF REFRACTOMETER
FOR COMPOSITION ANALYSES
FIG. 17



experimental points, refractive index data (46) for the system were plotted on the same graph. The shape of the reference curve was followed by eye as the calibration points were connected. Components were taken from the same sources used for operation of the still. The known solutions were prepared on the Ohaus balance to 0.1% in composition. The samples, of 50 gm each, were weighed into four ounce bottles having screw caps with polyethylene seals to reduce composition changes through evaporation. It is believed that the composition of samples taken from runs of the apparatus could be determined to the nearest 0.001 mass fraction.

HEAT AND FLOW RATE DETERMINATION

A test run with air blowing through a tube inverted in a beaker of water showed that a rate of about 9000 cc per min was the greatest rate above which excessive splashing occurred. Since the geometry of the equilibrium flask was similar and splashing of liquid up into the condensate contactor was considered undesirable, this figure was taken as the maximum for design purposes. From that number and physical data of some common solvents, the following table has been prepared:

TABLE V. DESIGN DATA

FIG. 18

Compound	CC Vapor Per CC Liquid	ΔH_v Cal/Gm	Heat Flux Cal/Min at 9000 CC Vapor Per Min	Liquid Flow Rate CC/Min
Ethanol	521	204.3	2780	17.3
Water	1700	540	2850	5.3
Methanol	723	262.8	2590	12.4
Benzene	344	94.1	2160	26.2
Acetic Acid	590	96.7	1550	14.7
Ethyl Ether	256	83.8	2110	35.1

From this calculation it was concluded that the recirculating liquid could be expected to transfer at least 2000 cal per min to the condenser. Heat exchange between the surroundings and the recirculating saturated vapor would produce an error in the 2000 cal per min rate, so that figure was used as a basis for percentage calculations.

INSULATION OF THE CALORIMETER

Heat could only be transferred from the water jacket to the surroundings. Assume that the cooling water is at 30 C, that the ambient temperature is 25 C. The inside diameter of the insulation, the outside diameter of the condenser jacket, is 0.75 inches = 0.0625 ft. The length of the insulation is 17.5 inches = 1.46 ft, and the thickness is 3 inches. Assume that the insulation has $k = 0.02$ Btu/hr-ft-F. For heat transfer through a cylinder,

$$q = \frac{2\pi l k \, \Delta T}{\ln (r_2/r_1)}$$

$\Delta T = 5$ degrees (C) = 9 (F).

$$\ln r_2/r_1 = \ln \frac{3.375}{0.375} = \ln 9 = 2.20$$

$$q = \frac{0.02 \text{ Btu}}{\text{hr-ft-F}} \Big| \; 9 \text{ F} \; \Big| \; 2\pi \; \Big| \; 1.46 \text{ ft} \; \Big| \frac{\text{hr}}{60 \text{ min}} \Big| \frac{252 \text{ cal}}{\text{Btu}} \Big| \frac{}{2.20}$$

$q = 3.2$ cal per min.

Since the expected heat flux through the condenser was about 2000 cal per min, this represents an uncertainty, in the form of a possible error of about $\frac{3.2}{2000} \times 100 = 0.16\%$.

LATENT HEAT CALCULATION

FROM EXPERIMENTAL DATA

The latent heats were determined by a heat balance around the calorimeter, made as follows:

$$m_w \; C_p \; \Delta T = \Delta H_v m_s + Q$$

where $m_{w,s}$ = the mass of water and system flowing through the calorimeter in a given time interval,

C_p = specific heat of water,

ΔT = the difference in inlet and outlet water temperatures,

ΔH = the latent heat,

Q = the heat leak as described on pg. 89.

The equation may be arranged as follows for the purpose of calculation:

$$\Delta H_v = \frac{m_w}{m_s} \; C_p \; \Delta T - \frac{Q}{m_s}$$

SOURCES OF LOSSES IN THE RECIRCULATING PHASE, RUN 9

Amount of Loss

The level in the leveler was recorded with time as part of the data of all runs. Since the dimensions of the leveler and contactor are known, the change in level may be converted to a change in mass of recirculating phase. When the level in the leveler was above the 7.5 cm mark, the level could change in both the leveler and the contactor (Fig. 2 and 3). Below that level, only the leveler could drain. The cross-sectional area of liquid above that level was $A_1 = \pi(r_1^2 + r_2^2 - r_3^2 - r_4^2)$, where r_1 and r_2 are the inside diameters of the leveler and contactor respectively, and r_3 and r_4 are the outside diameters of the tube in the leveler and the vapor riser in the contactor respectively.

$r_1 = r_2 = 1.4$ cm, $r_3 = 0.35$ cm, $r_4 = 0.5$ cm, $A_1 = 11.1$ cm^2.

The cross sectional area of liquid below that level was

$A_2 = \pi(r_1^2 - r_3^2) = 5.78$ cm^2.

From the data of Run 9, the liquid level dropped faster after the value of 7.6 cm at 11:40 PM so a different height change corresponded to each area.

Drop in height at level over 7.5 is $\frac{8.9 - 7.6 \text{ cm}}{45 \text{ min}} = 0.029$ cm/min.

Drop in height at level under 7.5 is $\frac{7.6 - 4.9 \text{ cm}}{30 \text{ min}} = 0.09$ cm/min.

Rate of loss of mass $= \pi r^2 h \rho$

$= (11.1 \text{ cm}^2)\ (0.029 \text{ cm/min})\ (0.887 \text{ gm/cm}^3) = 0.286 \text{ gm/min}$

for a level over 7.5 cm.

$= (5.78 \text{ cm}^2)\ (0.09 \text{ cm/min})\ (0.887 \text{ gm/cm}^3) = 0.461 \text{ gm/min}$

for a level below 7.5 cm.

The values do not agree because of the inaccuracy of the measurements and the changes in operating variables which took place during the run. This computation gives an average loss of 0.37 gm per min during Run 9.

The condensate formed from heat losses would be at about the composition of the saturated liquid. The saturated liquid in Run 9 was at 0.043 mole fraction ethanol, with a latent heat of 480 cal per gm as determined from the two references (34, 35). The heat transferred to produce this mass loss was (480 cal/gm) (0.37 gm/min) = 178 cal/min = 42 Btu/hr.

<u>Source of Heat Leak, Run 9</u>

The depletion was not a result of overflow from the condensate contactor into the flask since the liquid level in the leveler never became high enough to cause overflowing. There are three regions where the loss could have taken place.

<u>Source 1. Expansion of Vapor While Bubbling Through the Liquid Phase.</u> The drop in pressure through 2 in. of liquid is about 0.069 psi. The Molier chart for water shows that an idiabatic expansion of saturated steam produces a superheated vapor, and would result in a tem-

perature drop of 0.5 degree (C) under the present situation. Although the material undergoing the expansion was only 0.4 mass fraction water, the behavior would be similar and the expansion would cause no condensation.

<u>Source 2. Condensation on the Wall of the Equilibrium Flask.</u> During the part of Run 9 under consideration, the aluminum pipe surrounding the equilibrium flask was 0.4 to 0.8 degrees (C) above the temperature of the flask. Therefore condensation on the flask wall was not possible, and vaporization was slight.

<u>Source 3. Condensation on the Inner Wall of the Vapor Riser Tube of the Condensate Contactor.</u> Vapor at 91.5 C rose within the tube towards the contacting section and condensate at 82 C lay in a pool around the tube. A temperature drop of 10 degrees (C) or 18 (F) existed across the tube wall. For simplicity of computation, the problem has been turned around to ask: What temperature drop would be necessary to transfer the estimated 42 Btu per min across the tube wall, and how well does the calculated drop compare with the actual 18 degree (F) drop?

<u>Symbols and Their Values</u>

h_1 = coefficient for condensing vapor on the inside wall.

h_2 = coefficient for stagnant liquid with water-ethanol properties.

The thickness of the glass tube is given as 0.1 ± 0.018 cm in the Corning catalogue.

D_2 = outside diameter of the tube = 1.0 cm.

D_1 = inside diameter of the tube = 0.76 to 0.84 cm.

$D_2/D_1 = 1.20$ to 1.31; $\ln(D_2/D_1) = 0.182$ to 0.269

$L = H$ = height of tube immersed in condensate = 1 inch

= 0.083 ft.

$$A_1 = \pi D_1 H = \pi \cdot 0.8\ \text{cm} \cdot \frac{1\ \text{in.}}{2.54\ \text{cm}} \cdot 1\ \text{in.} \cdot \frac{\text{ft}^2}{144\ \text{in.}^2} = 6.88 \times 10^{-3}\ \text{ft}^2.$$

$$A_2 = \pi \cdot 1.0\ \text{cm} \cdot \frac{1\ \text{in.}}{2.54\ \text{cm}} \cdot 1\ \text{in.} \cdot \frac{\text{ft}^2}{144\ \text{in.}^2} = 8.6 \times 10^{-3}\ \text{ft}^2.$$

$A_m = 7.8 \times 10^{-3}\ \text{ft}^2$ average.

k = 0.63 Btu/hr-ft-F for glass.

q = 42 Btu/hr.

For estimation of the inside film properties, the vapor composition may be taken as 0.6 ethanol and 0.4 water. The liquid which condensed to form the inside film was 0.1 ethanol and 0.9 water, all mass fractions. The constants are evaluated at 195 F.

k_f: k = 0.390 Btu/hr-ft-F for water at 195 F (McAdams (47), p. 456).

k for ethanol decreases with increasing temperature.

Use k_f = 0.3 Btu/hr-ft-F.

ρ_f: $\rho_w = 60.1\ \text{lbm/ft}^3$ at 195 F. (Steam Tables)

Use $\rho_f = 60\ \text{lbm/ft}^3$.

$g = 32.2\ \text{ft/sec}^2$.

$$\lambda = \frac{510\ \text{cal}}{\text{gm}} \cdot \frac{\text{Btu}}{252\ \text{cal}} \cdot \frac{454\ \text{gm}}{\text{lbm}} = 920\ \text{Btu/lbm}.$$

μ_f = 0.4 cp (McAdams, p. 466)

A. What ΔT_g must occur through the glass tube to cause the transfer of 42 Btu/hr?

$$\Delta T_g = \frac{q \ln(Do/Di)}{2\pi kL} = \frac{42\ \text{Btu}}{\text{hr}} \left| \ 0.182 \text{ to } 0.269 \ \right| \frac{\text{hr-ft-F}}{0.65\ \text{Btu}} \left| \frac{}{2\pi} \right| \frac{}{0.083\ \text{ft}} = 23.3 \text{ to } 34.3 \text{ degrees (F)}$$

an average of 29 degrees (F). If, as is suspected, the 10 mm tube in the condensate contactor was thinner than the Corning catalog value, then the prediction for ΔT_g would be reduced substantially.

B. What ΔT_{f1} can be calculated for the inside film?

$$h_1 = 0.943 \left[\frac{k_f^3}{\mu_f} \frac{\rho_f^2}{L} \frac{g\ \lambda}{(\Delta T_{f1})} \right]^{1/4} \qquad \text{(McAdams, p. 331)}$$

which is to be used in $q = h_1 A_1 \Delta T_{f1}$. These are combined to give

$$(\Delta T_{f1})^{3/4} = \frac{q}{0.943\ A_1 \left[\frac{k_f^3\ \rho_f^2\ g\ \lambda}{\mu_f\ \ L} \right]^{1/4}}$$

Evaluating the bracketed group gives

$$\left[\frac{0.027\ \text{Btu}^3}{\text{hr}^3\text{-ft}^3\text{-F}^3} \left| \frac{3.6\times10^3\ \ \text{lbm}^2}{\text{ft}^6} \right| \frac{32.2\ \text{ft}}{\text{sec}^2} \left| \frac{920\ \text{Btu}}{\text{lbm}} \right| \frac{}{0.4\ \text{cp}} \right.$$

$$\left. \frac{1488\ \text{cp-ft-sec}}{\text{lbm}} \left| \frac{}{0.083\ \text{ft}} \right| \frac{3600\ \text{sec}}{\text{hr}} \right]^{1/4} = (46.5\times10^{12})^{1/4} \text{ units}$$

$= 2610\ \text{Btu/hr-ft}^2\text{-(F)}^{3/4}$

Substituting,
$$(\Delta T_{f1})^{3/4} = \frac{42\ \text{Btu}}{\text{hr}} \left| \frac{}{0.943} \right| \frac{}{6.88\times10^{-3}\ \text{ft}^2} \left| \frac{\text{hr-ft}^2\text{-(F)}^{3/4}}{2610\ \text{Btu}} \right. = 2.47\ \text{(F)}^{3/4}.$$

$\Delta T_{f1} = 3.34$ degrees (F), the temperature drop through the condensing film.

C. The calculation of a suitable film coefficient for the stagnant liquid is difficult. However, a chart in McAdams, Fig 14-15, p. 383, may be used as a guide.

$\frac{q}{1000A} = \frac{42}{1000} \Big| \frac{}{8.6 \times 10^{-3}} = 4.89.$ A value of $h = 400$ to 800 is indicated. $\Delta T_{f2} = \frac{q}{hA} = \frac{42}{400 \text{ to } 800} \Big| \frac{}{8.6 \times 10^{-3}}$ $= 6$ to 12 degrees (F).

The three temperature drops may be added to get the total estimated drop required to transfer 42 Btu per min.

$$\Delta T_g + \Delta T_{f1} + \Delta T_{f2} = 29 + 3.3 + 9 = 41.3 \text{ degrees (F).}$$

This calculated value of 41.3 degrees (F) must be compared with the value of 18 degrees (F) taken from the experimental data. Although the values do not compare well, it must be remembered that the heat loss is only a rough estimate. The calculation demonstrates that heat transfer through the vapor riser tube caused the major portion of condensation within the region of the equilibrium flask.

EXTRA HEAT SOURCES, RUN 8

Adiabatic Wall Heating

There was a differential of 20 degrees (C) across the lower adiabatic wall in Run 8. From the calculation on the adiabatic enclosure, Appendix, p. 108, a 0.15 degree (C) Δ T produced an exchange of no more than 0.785 cal per min.

$$\frac{20\ (C)}{0.15\ (C)} \Big| \frac{0.785\ \text{cal}}{\text{min}} = 104\ \text{cal/min.}$$

Superheat of Entering Vapor

The vapor temperature was 118 C, at the inlet to the equilibrium flask, the liquid temperature 90.5 C. Superheat amounted to 28 degrees (C). The vapor temperature at the outlet of the equilibrium flask was 90.6 C, showing that all the superheat was removed by contact with the liquid. The approximate specific heat of vapor was 0.5 cal per gm-C. The mass flow rate was about 3 gm per min.

$$\frac{3\ \text{gm}}{\text{min}} \Big| \frac{0.5\ \text{cal}}{\text{gm-C}} \Big| \frac{28\ (C)}{} = 42\ \text{cal/min.}$$

Extra Heat from Both Sources

$104 + 42 = 146$ cal/min $= 35$ Btu/hr.

This value is of the same order as the 42 Btu/hr calculated as the loss for Run 9. Therefore the two extra sources of heat were just sufficient to vaporize enough of the liquid to offset the condensation loss at the vapor riser in the condensate collector.

EXTRA HEAT SOURCES, RUN 8

Adiabatic Wall Heating

There was a differential of 20 degrees (C) across the lower adiabatic wall in Run 8. From the calculation on the adiabatic enclosure, Appendix, p. 108, a 0.15 degree (C) ΔT produced an excess of no more than 0.735 cal per min.

$$\frac{20\ (C)}{0.15\ (C)} \,\Big|\, \frac{0.735\ \text{cal}}{\text{min}} = 104\ \text{cal/min.}$$

Superheat of Entering Vapor

[illegible]

Extra Heat From Both Sources

104 + 42 = 146 cal/min = [illegible]

This value is of the same order as the 42 [illegible] calculated as the loss for Run 8. [illegible] the two extra sources of heat were just sufficient to vaporize enough of the liquid to offset the condensation loss at the vapor riser in the condensate collector.

ADIABATIC ENCLOSURE

How much heat will be transferred across the adiabatic walls as a result of error in matching the temperature of the heated wall with that of the equipment inside?

Assume that thermocouples are calibrated to within 0.1 degree (C), that the aluminum tubes can be maintained to within 0.15 degree (C) of the temperature of the glass. Assume that the insulation has k = 0.03 Btu per hr-ft-F.

At the Contacting Section

The contacting section is 1.13 inches in diameter and 7 inches long. Four inch aluminum pipe with ¼ inch walls was used for the adiabatic wall. How much heat is lost through a cylinder of insulation 1.13 in. ID and 3.5 in. OD, 7 in. long and with 0.15 degrees (C) drop across it?

$$q = \frac{2\pi k l \Delta T}{\ln(r_2/r_1)} = \frac{2\pi\, 0.03\ \text{Btu}}{\text{hr-ft-F}} \,\Big|\, 7\ \text{in} \,\Big|\, \frac{\text{ft}}{12\ \text{in}} \,\Big|\, 0.15\ (C) \,\Big|\, \frac{9\ (F)}{5\ (C)} \,\Big|\, \frac{252\ \text{cal}}{\text{Btu}} \,\Big|\, \frac{\text{hr}}{60\ \text{min}} \,\Big|\, \frac{1}{\ln(3.5/1.13)} = \frac{0.125}{1.13} = 0.11\ \text{cal/min}$$

$$\ln(3.5/1.13) = \ln 3.10 = 1.13$$

At the Equilibrium Flask

How much heat is lost through insulation around

the equilibrium flask kept within 0.15 degrees (C) of the flask temperature? Assume cylindrical insulation 5 in. ID, 6 in. OD, and 8 in. long.

$$q = \frac{0.125}{} \left| \frac{8}{7} \right| \frac{}{\ln(6/5)} = 0.785 \text{ cal/min.}$$

This calculation indicates greater heat transfer than was likely because of the thin cylindrical geometry assumed for the calculation.

ERROR IN FLOW RATE

DUE TO MOVEMENT OF ROTAMETER FLOAT

To calculate the error due to a one mm change in the position in the rotameter float at various float positions, two charts were required. One, the manufacturer's calibration chart, Fig. 19, was used to determine the rate of change in flow rate with the scale reading on the glass tube of the rotameter. Slopes at four scale readings were determined. The second chart, a plot of the scale readings vs. the height in mm of each scale reading, Fig. 20, was used to determine the rate of change in scale reading with height. Slopes at the same four points were taken. The products of slopes at corresponding points gave the errors in flow rate corresponding to a one mm change in float position from the set point.

Example:

Scale reading of 5. Flow rate = 3.7 cu cm/min.

Tangents are shown at the scale reading of 5.

From Fig. 19, $\frac{10.8 - 3.7}{9.0 - 5.0} = \frac{7.1}{4} = 1.77$ cu cm/min per scale reading.

From Fig. 20, $\frac{6.7 - 2.8}{55 - 15} = \frac{3.9}{40} = 0.097$ scale readings per mm.

$$(1.77)(0.097) = 0.173 \text{ cc/min per mm.}$$

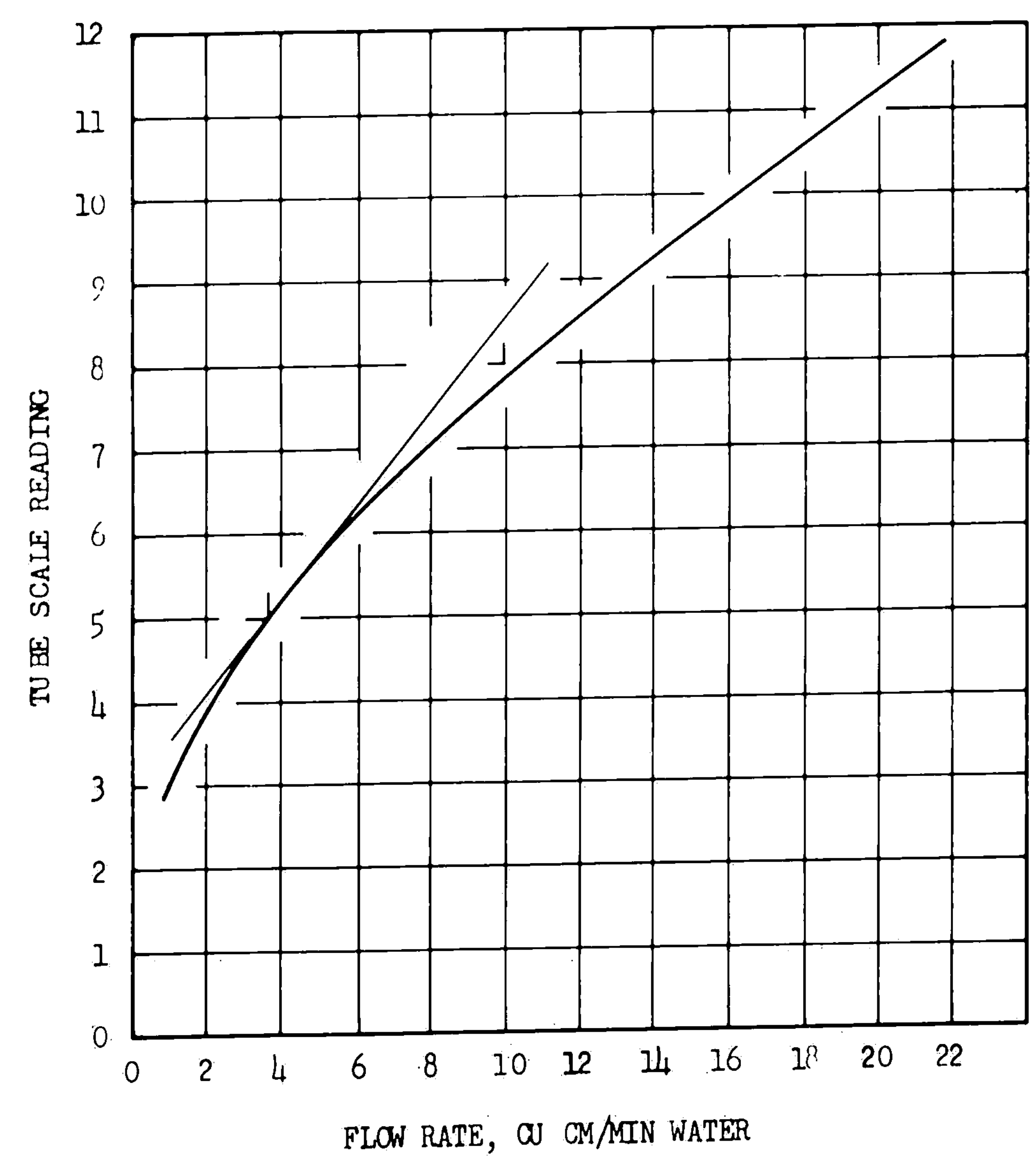
$$\frac{0.173}{3.7}(100) = 4.6\%$$

$$(1.77)(0.097) = 0.173 \text{ cc/min per mm.}$$

$$\frac{0.173}{3.7}(100) = 4.8\%$$

ROTAMETER CALIBRATION CURVE
FROM FISHER AND PORTER CO.
FIG. 19

TUBE - 02F-1/8-12-5
FLOAT - SAPHIRE



PRESSURE CHANGE

FROM TOP OF CONDENSER

TO LIQUID LEVEL IN EQUILIBRIUM FLASK

Pressure Due to Column of Vapor

The height of vapor was not over 20 inches. Vapor density of ethanol at 1 atm. is 0.00165 gm/cm^3, from the International Critical Tables.

$$\frac{0.00165\ \text{gm}}{\text{cm}^3}\ \Bigg|\ \frac{1\ \text{cm}^3\ 10^5}{3.53\ \text{ft}^3}\ \Bigg|\ \frac{\text{lbm}}{454\ \text{gm}} = 0.103\ \text{lbm/ft}^3$$

Pure water at 1 atm has a density of 0.0372 lbm/ft^3.

For computation, use $\rho = 0.1$ lbm/ft^3.

Pressure from the weight of vapor: $\Delta p = \frac{g}{g_0} \rho h$;

$\frac{g}{g_0} = 1$ lbf/lbm.

$$\Delta p = \frac{0.1\ \text{lbm}}{\text{ft}^3}\ \Bigg|\ \frac{1\ \text{lbf}}{\text{lbm}}\ \Bigg|\ 20\ \text{in}\ \Bigg|\ \frac{\text{ft}}{12\ \text{in}}\ \Bigg|\ \frac{1\ \text{mm Hg}}{0.0193\ \text{psi}}\ \Bigg|\ \frac{1\ \text{ft}^2}{144\ \text{in}^2}$$

$\Delta p = 0.06$ mm Hg.

Error in pressure measurement from this source is negligible.

Pressure Drop Due to Flow of Vapor

The only substantial restriction to vapor flow is the inlet to the condensate collector. The shape is cylindrical, 0.8 cm diameter, and 3 in. long. $D = 0.0263$ ft; $L = 0.25$ ft.

$$\text{Area} = \frac{\pi D^2}{4} = \frac{\pi\, 0.0263^2}{4} = 5.44 \times 10^{-4}\ \text{ft}^2.$$

The flow rate was about 2 gm/min. The μ for ethanol vapor is 0.0105 cp, for water vapor is 0.0125 cp. Use $\mu = 0.013$ cp. From the previous calculation, $\rho = 0.1$ lbm/ft^3.

$$G = \frac{W}{A} = \frac{2\ \text{gm}}{\text{min}} \left| \frac{1}{5.44 \times 10^{-4}\ \text{ft}^2} \right| \frac{\text{lbm}}{454\ \text{gm}} \left| \frac{\text{min}}{60\ \text{sec}} \right. = 0.135\ \text{lbm/sec-ft}^2.$$

$$V = \frac{G}{\rho} = \frac{0.135\ \text{lbm}}{\text{sec-ft}^2} \left| \frac{\text{ft}^3}{0.1\ \text{lbm}} \right. = 1.35\ \text{ft/sec.}$$

$$R_e = \frac{DG}{\mu} = \frac{0.0263\ \text{ft}}{0.013\ \text{cp}} \left| \frac{0.135\ \text{lbm}}{\text{sec ft}^2} \right| \frac{1488\ \text{cp ft sec}}{\text{lbm}} = 405$$

Flow was laminar. Therefore, eqn. (12-25), p. 322, of McAdams may be used.

$$-\frac{dp}{dL} = \frac{32 \mu V}{g_c D^2} = \frac{32}{} \left| \frac{0.013\ \text{cp}}{} \right| \frac{1.35\ \text{ft}}{\text{sec}} \left| \frac{\text{sec}^2\text{-lbf}}{32.17\ \text{lbm-ft}} \right.$$

$$\frac{}{0.0263^2\ \text{ft}^2} \left| \frac{\text{lbm}}{1488\ \text{cp-ft-sec}} \right| \frac{\text{in}^2\text{-atm}}{14.7\ \text{lbf}} \left| \frac{\text{ft}^2}{144\ \text{in}^2} \right.$$

$$-\frac{dp}{dL} = 8.03 \times 10^{-6}\ \text{atm/ft.}$$

$$-\Delta p = \frac{0.25\ \text{ft}}{} \left| \frac{8.03 \times 10^{-6}\ \text{atm}}{\text{ft}} \right. = 2 \times 10^{-6}\ \text{atm} = 1.5 \times 10^{-3}\ \text{mm Hg.}$$

The pressure drop from the flowing vapor was negligible. It can be seen that the pressure at the surface of the liquid in the equilibrium flask was essentially the same as the pressure at the top of the condenser.

FILLING AND SETTING

THE THERMOREGULATOR

The stainless steel bulb was firmly attached to the union and completely filled with carbon tetrachloride. With the bulb in the horizontal position shown in Fig. 7, mercury was added through the union, displacing the carbon tetrachloride until the mercury level reached to about one quarter inch from the top of the union. The plugged end of the bulb was lowered a few angular degrees to permit mercury to displace more carbon tetrachloride so that a level would be finally reached as shown in the figure. Additional mercury was used to bring the mercury level to its original position. It was felt that if the bulb were kept level from then on, the plug of mercury would prevent the carbon tetrachloride from escaping. The lucite section with the capillary tube was then attached to the union in the same manner as a section of tubing. Mercury was forced up the capillary and over into the well. The union with both tubes was mounted in the water bath, and the temperature adjusted to within 0.1 degree (C) of the set point. If the capillary remained full of mercury, the temperature was raised a few tenths and the excess mercury knocked into the well. Reduction of the temperature to the set point then brought the mercury level into the capillary. If insufficient mercury was in the regulator, additional could be added either by removing the lucite and refilling the union, or by forcing mercury into the capillary with the use of a small long-nosed plastic syringe. When the mercury level had been brought into range at the set point temperature, the aluminum cap and adjustment screw were placed on the lucite, with the adjustment contact wire running inside the capillary. Air bubbles in the mercury column, introduced when the syringe was used, were removed by running the contact wire up and down the length of the capillary. The set screw on the aluminum cap was used to fit the cap firmly on the lucite. Leads from the two regulator contacts were brought into the jack plug of the controller. Because of polarity in the controller and the fact that one wire was grounded to the water through the regulator bulb, only one of the two possible wiring arrangements worked.

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