A SIMULTANEOUS EXPERIMENTAL INVESTIGATION OF ISOBARIC INTEGRAL HEATS OF VAPORIZATION AND VAPOR-LIQUID EQUILIBRIUM RATIOS FOR CHLOROFORM-BENZENE MIXTURES

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PREFACE

New isobaric integral heats of vaporization data at about 740 mm of Hg pressure have been determined for the binary system chloroform-benzene. Vapor-liquid equilibrium distribution data were simultaneously measured and compared with published data at 760 mm of Hg pressure. A thermodynamic consistency test for the isobaric integral latent heats of vaporization and vapor-liquid equilibrium data was performed. The Redlich-Kwong equation of state was used for the calculation of the partial enthalpy difference and the mixture vapor enthalpy difference from the ideal state gas enthalpies, these enthalpy quantities being required for the thermodynamic consistency test. An IBM 1620 computer was used for the various calculations.

I am indebted to Professor Wayne C. Edmister for his guidance and counseling during this study. Special gratitude is also due to Professor R. N. Maddox and Dr. J. W. Fulton for their suggestions and time as members of the research review committee. The aid of the entire staff of the School of Chemical Engineering and of fellow students is deeply appreciated.

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CHAPTER I

INTRODUCTION

Of the three heats of vaporization of mixtures, namely, the isobaric integral, the isothermal integral and the differential heats of vaporization, the isobaric integral heat of vaporization is most important from practical industrial point of view.

Many chemical processes involve either vaporization or condensation of mixtures, which makes the knowledge of heats of vaporization extremely important. Most calculations involving the enthalpy of mixtures soon lead to the question of heat effects which accompany a vapor-liquid phase change. The isobaric integral heat of vaporization is the difference between enthalpy values of a given mixture at its dew and bubble points at the constant pressure, i.e. with a temperature difference.

The objective of this investigation was to make experimental measurements of isobaric integral heats of vaporization and the simultaneous determination of equilibrium vapor-liquid phase distribution data for the chloroform-benzene system at the local barometric pressure, i.e., approximately 740 mm of Hg pressure. Other objectives included analysis of experimental data and a thermodynamic consistency check. No attempt has been made to evaluate theoretical or empirical heats of vaporization from other thermodynamic properties.

The experimental phase of this work involved the design, construction and operation of an isobaric calorimeter with an equilibrium contact stage, for the simultaneous measurement of isobaric integral heats of vaporization and vapor-liquid compositions. The flow calorimeter-equilibrium stage combination is called a still in the remainder of this thesis. A still meeting the above requirements was available at the beginning of this work. However, extensive modifications were required to insure steady state operation and to reduce the heat leak between the reboiler and the reservoir. The electrical system was completely designed and built.

CHAPTER II

THEORETICAL BACKGROUND

The heats of vaporization of a mixture of liquid are of both practical and theoretical importance. Many industrial designs involve the use of enthalpies for vapor-liquid phase change calculations. The properties of solutions and phase equiliria relations would be better understood with more knowledge about heat quantities. There are many unexplored theoretical and experimental areas in this field because of infinite variety of possible mixture combinations and the nonideality of solutions.

For pure components, the expression "heat of vaporization" stands for a single physical phenomenon. The liquid to vapor phase change for a pure component is both isothermal and isobaric. Also, the composition of the liquid and vapor phases are identical. Thus, the heat effect accompanying the liquid-vapor phase change is a unique quantity, depending upon the system pressure or temperature for each substance.

The expression "heat of vaporization" does not stand for a single quantity for mixtures. There are three possible heats of vaporization for a mixture; the isobaric integral, the isothermal integral and the differential. These quantities are now defined.

The isobaric integral heat of vaporization is the difference between the enthalpy values for a given mixture at its dew and bubble points, taken at the same pressure but at different temperatures.

Similarily, the isothermal integral heat of vaporization is the difference between the enthalpy values of a given mixture at its dew and bubble points with measurements taken at the same temperature. The integral term in both of these definitions indicates that the whole quantity of mixture is fully vaporized from its liquid state to the vapor state.

The differential heat of vaporization of a liquid of composition x is the heat necessary to produce one mole of vapor of composition y, i.e., the composition of vapor in equilibrium with the liquid of composition x, from an amount of liquid so large that its composition is not appreciably altered by the loss of material to the vapor phase. The process takes place at a constant temperature and pressure; also, the liquid and the vapor are at their bubble and dew points, respectively. However, the composition of the resulting liquid and vapor will be different.

In case of isobaric integral and isothermal integral heat effects accompanying vapor-liquid phase change, the heats of vaporization are the same as the heats of condensation, except for the sign. The differential heats of condensation are different quantitatively, as well as in sign, from the differential heats of vaporization.

The differential heat of condensation of a vapor of composition y is the necessary amount of heat removed to produce one mole of liquid of composition x, i.e., the composition of liquid in equilibrium with the vapor of composition y, from an amount of vapor so large that its composition is not appreciably altered by the loss of material to the liquid phase. This topic will not be discussed in detail here.

For a better understanding of these quantities, consider the pressure-temperature diagram for a constant composition mixture shown in Figure 1. Point 1 represents the mixture in its saturated liquid state at a pressure of $P_{1,2}$ and a temperature of $T_{1,3}$. As it is shown in the diagram, the liquid can be fully vaporized, from its saturated bubble point state to saturated dew point state either from point 1 to point 2 or from point 1 to point 3.

The vaporization could proceed from point 1 to 2 at a constant pressure of $P_{1,2}$ but from an initial temperature of $T_{1,3}$ to a final temperature of $T_{2,4}$. The amount of heat required to effect this type of phase change is known as the isobaric integral heat of vaporization.

In case the vaporization proceeds from point 1 to point 3 at a constant temperature of $T_{1,3}$ but from an initial pressure of $P_{1,2}$ to a final pressure of $P_{3,4}$. The heat effect accompanying such a phase change is known as the isothermal integral heat of vaporization.

The third type of heat of vaporization, namely, the differential heat of vaporization, both the temperature and pressure remain constant and as such, the vapor must have a different composition than the liquid, and in particular this composition must be that of the vapor in equilibrium with the liquid. An

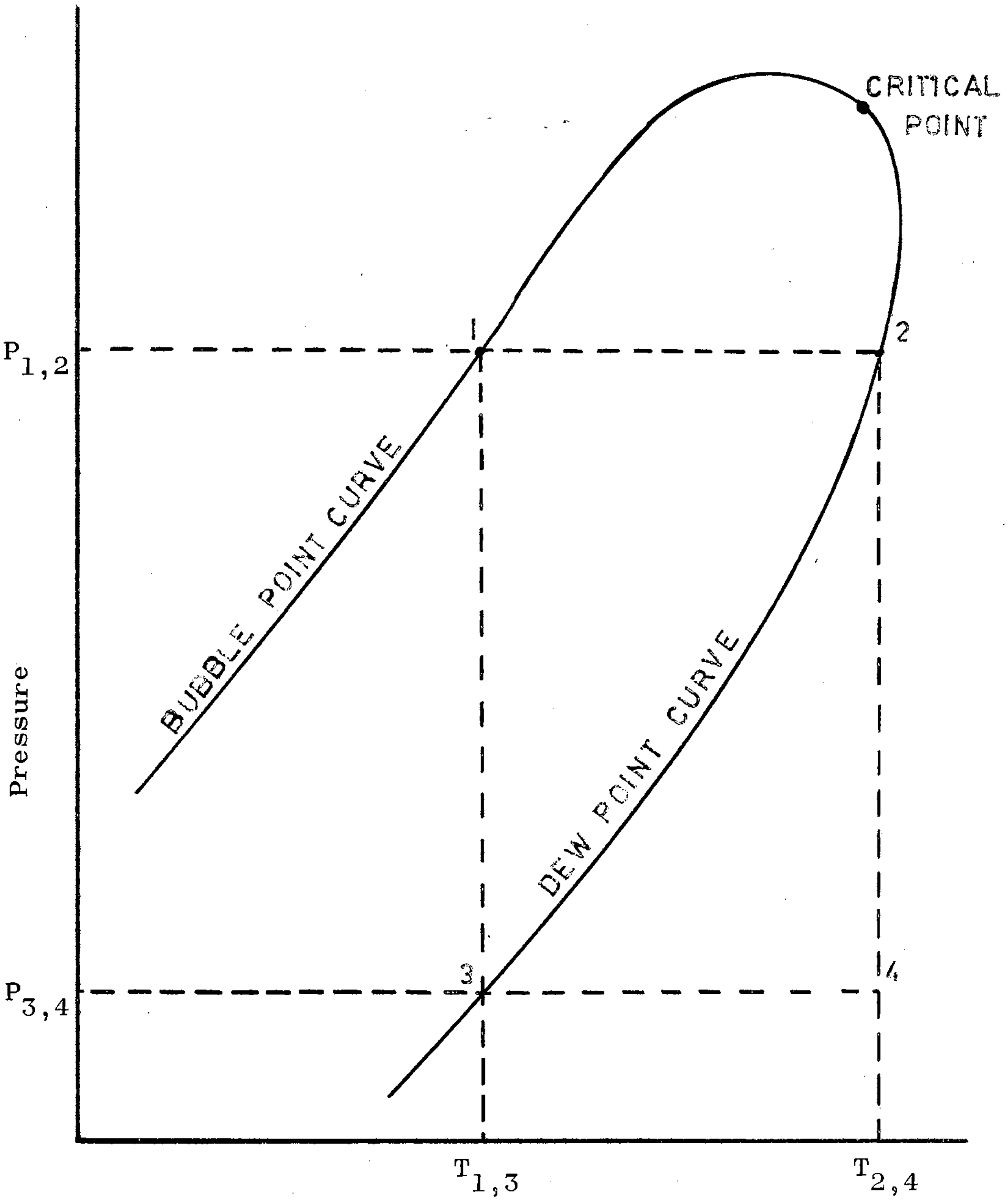


Figure 1

Pressure-Temperature Diagram
for a Constant Composition Mixture

entirely equivalent procedure would be to begin with an essentially infinite quantity of the mixture in the condition described by point 1 and to vaporize from that a unit quantity of vapor in equilibrium with the liquid.

A theoretical survey of various heats of vaporization for binary mixtures has been made by Schroeder and Edmister (25) in a paper that suggested a new and convenient theoretical method for calculating the isobaric integral heats of vaporization quantities. The vapor enthalpy is obtained by adding the enthalpies of the components in the vapor at the dew point temperature, while the liquid enthalpy is obtained by adding the enthalpies of the liquid components and the heat of mixing at the bubble point temperature of the mixture. The construction of an enthalpy-composition diagram is suggested as the most convenient method of determining the isobaric integral heat of vaporization.

Figure 2 gives an enthalpy-composition diagram for a binary at constant pressure. On this plot, the curve L-B-M represents saturated liquid, the curve J-E-C-K represents saturated vapor, and the curve A-B-C-D represents an isotherm. The straight line B-G-E is a constant composition line. The enthalpy difference between point E and B represents the isobaric integral heat of vaporization for a mixture of composition x, for the constituent components and at the pressure of the diagram.

Edmister (4) derived an approximate equation for the calculation of isobaric integral heats of vaporization starting from vapor-liquid equilibrium K-values and ideal gas state specific heats of pure components. The equation is

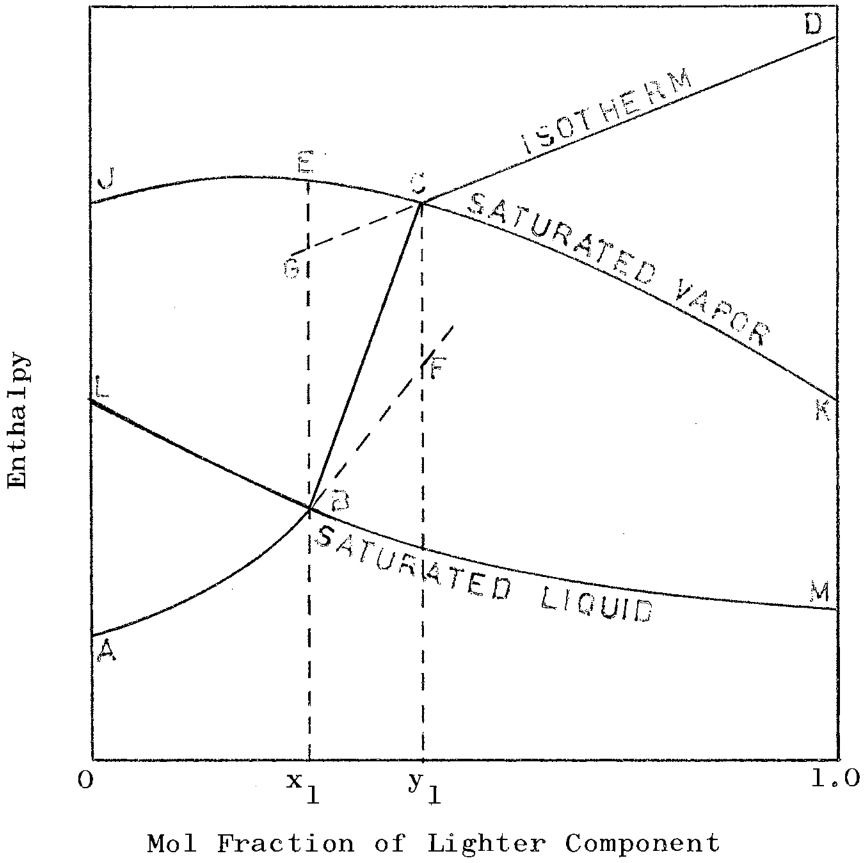


Figure 2

Enthalpy-Composition Diagram
for a Binary Mixture at a Constant Pressure

$$\Delta H = \sum_i z_i \frac{RT_1T_2}{T_2-T_1} \ln \frac{K_{i_2}}{K_{i_1}} + \sum_i z_i \Delta H_i^\circ \qquad \text{(II-1)}$$

where R is the gas constant; T_1 and T_2 are the bubble and the dew point temperatures of the mixture, respectively; z_i is the mole fraction of a component in the mixture; K is the vapor-liquid equilibrium K-value, where first subscript "i" stands for the component and the second subscript "1" or "2" stand for temperature T_1 or T_2 at which the equilibrium K-value is evaluated; ΔH_i° is the ideal gas state enthalpy difference for pure component "i" with the enthalpies being calculated at temperatures T_2 and T_1. For clarification, the term ΔH_i° can be written as

$$\Delta H_i^\circ = H^\circ_{i,2} - H^\circ_{i,1} = Cp_i^\circ \, (T_2-T_1) \qquad \text{(II-2)}$$

where Cp_i° is the specific heat of pure component "i" at ideal gas state and evaluated at average temperature of T_1 and T_2. $H^\circ_{i,1 \text{ or } 2}$ is the ideal gas state enthalpy of the component "i" at the temperature T_1 or T_2.

Though this equation is derived with many simplifying assumptions, as explained by Edmister (4), it gives very good agreement with experimental values for some systems (5).

CHAPTER III

PREVIOUS EXPERIMENTAL INVESTIGATIONS

The latent heats of vaporization for mixtures have been the subject of many experimental works, the earliest dating back to the beginning of the twentieth century. Fenner (10) and Shearer (26) were amongst the earliest investigators in the field. It was not realized by these investigators that the heat of vaporization of a mixture is not a unique quantity as it is for a pure component. Later Tyrer (31, 32, 33) and Fletcher and Tyrer (12) partially conceived the difference between various heat of vaporization quantities. Finally, it was Dana (3) who gave heat of vaporization quantities adequate thermodynamical definition and clarified the subject.

The data collected by these early investigators are of little value today due to the large heat leaks in their experimental apparatus and inadequate theoretical analysis of this heat leak.

Recently, the heat of vaporization for binaries has been the topic of many papers and doctoral dissertations. Recent investigations, which include important modifications over Dana's apparatus were made by Tallmadge, et al., (28, 29) and Plewes, et al., (20, 21, 22). Schnelle (24), Griskey (13), and Stein (27) further modified the apparatus making it especially suitable for mixtures having a large difference in the bubble and the dew point temperatures.

Most of the previous experimental work in the field of isobaric integral heats of vaporization were made in glass apparatus and the data was collected for systems at atmospheric pressure. Recently, Tully (30) designed and successfully operated a highly complicated metallic calorimeter and collected isobaric integral heats of vaporization data for the methane-ethylene system at up to 40 atm pressure.

The binary system formed between the constituents chloroform and benzene is a nonideal mixture. Equilibrium K-values for the system constituents were experimentally determined by Reinders and de Minjer (23) and by Nagata (18). Both of these investigations were made at 760 mm Hg pressure and are in good agreement. The chloroform-benzene system was selected for this work because no previous experimental measurements of the isobaric integral heats of vaporization had been made for this system.

CHAPTER IV

EXPERIMENTAL APPARATUS

An isobaric flow calorimeter with a built-in equilibrium stage was used for this experimental investigation. Heat was supplied to the reboiler electrically and the power input was measured. The rate of vaporization and the heat input data were used to calculate the isobaric integral heats of vaporization. Thermocouples were used for the temperature measurements and the chloroform-benzene mixtures were analyzed by measuring their refractive indices. A detailed description of the apparatus is given below.

The Equilibrium Still System

The equilibrium still system consisted of three main parts, an equilibrium still with a total condenser, a reboiler and a reservoir. Figure 3 gives a schematic diagram of the still system. The fluid flow scheme through these pieces of apparatus will now be described. The chloroform-benzene mixture, in the liquid phase, flows from the reservoir and passes through the capillary to the reboiler where vaporization takes place. The vapor leaving the reboiler then bubbles through the liquid on the equilibrium stage tray and passes on to the main total condenser. By an arrangement of two three-way-values, valves "A"

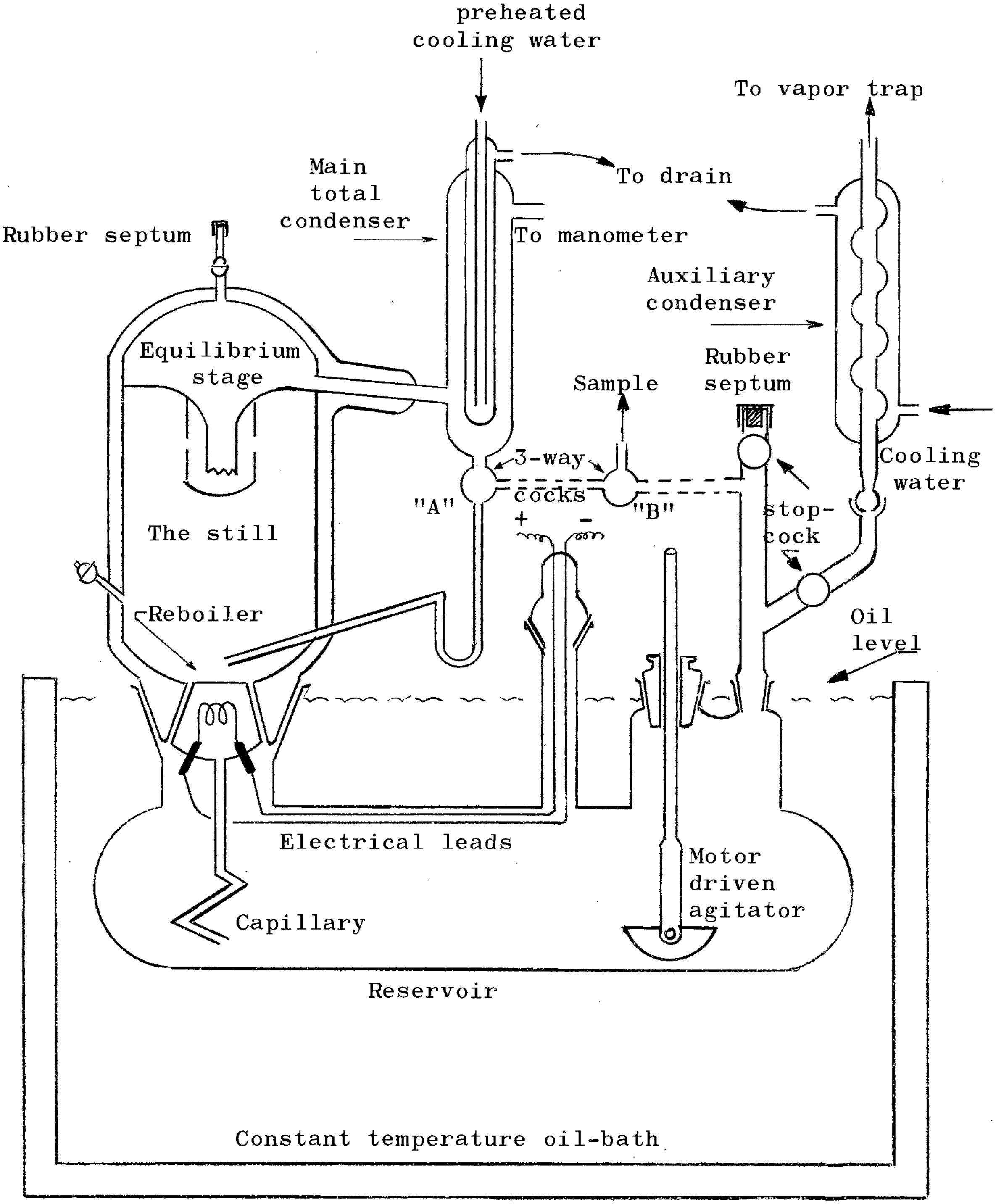


Figure 3

Schematic Diagram of the Still System

and "B" of Figure 3, the condensate could either be returned to the reboiler or to the reservoir or else could be withdrawn out of the system as a sample.

Constructional details of each piece of the apparatus are given below:

The Still

The glass still was cylindrical in shape with an opening in the bottom and an equilibrium stage arrangement in the upper half portion. Figure 3 gives a sketch of the still. The outlet of the equilibrium stage was connected to the main total condenser. At the outlet of the main total condenser, a three-way-valve was provided, one opening of which was connected to the bottom of the still. The still had provision for collecting liquid samples through a rubber septum from the equilibrium tray. Two thermocouple wells, one below the equilibrium tray, i.e., just above the reboiler, and the second above the equilibrium tray were also provided.

The bottom opening of the still had provision to attach the reboiler to the still by means of ground glass, snug-fit, arrangement such that the reboiler could be held in position by the help of Nonaq grease; additional information about the Nonaq grease is given at the end of this chapter.

In addition, the still had provision to connect it to the reservoir. For this purpose, the outside of the still bottom opening was tapered and ground. Thus, the still made a leak proof, ground glass, connection to the reservoir.

The still was double walled, vacuum jacketed and silver coated inside the jacket to minimize heat leak. As the suitability of this particular still for the heat of vaporization work was not established by any previous investigator, no attempt was made to modify the still, to reduce the heat leak to the surroundings, before making these experiments. However, some suggestions for such a modification are given at the end of this thesis.

Two 1/8 inch width strips, opposite each other and along the length of the still, were left unmirrored so that the liquid level inside the still could be observed. One opening at the top of the still and another at the top of the main total condenser were also provided. These openings were for evacuating the system at the beginning of a run. In addition, the opening on the top of the still was also used for collecting samples from the equilibrium tray while the opening at the top of the main total condenser was also the connection for measuring the system pressure. The system pressure was measured with a "U"-tube manometer.

The Reboiler

The reboiler was of the shape of a small cylindrical bowl, made of glass, with a capillary tube attached to the bottom. Figure 3 gives a sketch of the same. The heating element, which was made of 30 gauge nichrome wire, wound around a hollow glass core, was completely inside the bowl. Two tungsten wire electrodes were stuck through the bottom of the reboiler for electrical connections. Inside the reboiler, the ends of the heating elements were silver soldered to the tungsten electrodes. Outside the reboiler, copper electrical leads were connected to the tungsten electrodes. Tungsten electrodes were used to ensure leak proof joints with the glass.

The glass capillary attached to the bottom of the glass bowl of the reboiler had an inside diameter of 2.5 mm and a total length of 15 cm. The purpose of the capillary was to allow the liquid flow from the reservoir to the reboiler and to maintain the desired level in the reboiler. The connection between the reservoir and the reboiler had to be such that the vapors formed in the reboiler do not escape to the reservoir even with sudden surges of high pressure in the reboiler. However, at the same time, the capillary should not offer excessive resistance to the liquid flow from the reservoir to the reboiler as it would tend to make the reboiler run dry. The glass capillary of the above mentioned diameter and length met all of these requirements. The length of the capillary was finalized by trial and error.

The outer surface of the reboiler was grounded and tapered slightly to match exactly the taper of the still where the reboiler was attached. In order to obtain a perfect snug-fit connection between the reboiler and the still, both of these pieces were ground together at the time of construction.

The Reservoir and Its Accessories

The reservoir was a long horizontal cylindrical container with small vertical ends giving it a flat elongated "U" shape appearance. Figure 3 gives a sketch of the same. At one end of the reservoir, the still rested and was connected by a ground glass joint making it leak proof. The only connection for liquid flow between the reservoir and the still was through the glass capillary and there was no direct path for flow between the reservoir and the still. For clarification, refer to assembly drawing, Figure 3. At the other end of the reservoir, there was provision for a thermocouple well, a total condenser and an agitator.

The thermocouple well extended right up to the bottom of the reservoir and thus the thermocouple inserted in this well measured the reservoir liquid temperature. As the liquid in the reservoir was maintained at its bubble point temperature, vapors above the liquid exerted undesired additional pressure in the closed space. Thus, the vapor above the reservoir liquid was led to an auxiliary condenser. The outlet of the condenser was open to the atmosphere through a vapor trap, i.e., uncondensable was allowed to escape to the atmosphere by bubbling through cold water. The cold water condensed and thus trapped any chloroform-benzene vapor escaping to the atmosphere. The depth of water through which vapors must bubble could be adjusted as required.

The agitator was made of a glass shaft with a teflon impeller and was driven by a variable speed, fractional horse power, motor through a flexible rubber coupling. The shaft of the agitator passed through a leak proof glass sleeve in order to avoid any vapor leakage. The sleeve was lubricated by water soluble, Nonaq grease, the viscosity of which was adjusted as required by adding a few drops of water. The glass shaft of the agitator and the electrical motor shaft were connected by means of a flexible rubber coupling in order to avoid vibration carrying over from the motor to the main apparatus as well as to reduce the effect of undesirable strain due to misalignment.

A third vertical branch on the reservoir was provided for copper electrical leads which were connected to the tungsten electrodes of the reboiler at one end. A perfect seal between the copper wires, the procelain insulators and the glass was obtained by coating with "Fisher" sealing compound, Sealzit, and baking the unit at 200°F for two hours. No vapor was allowed to escape through this connection.

Constant Temperature Oil-Bath

The liquid in the reservoir was maintained at its bubble point temperature. For this purpose, a constant temperature oil bath was used. The reservoir was kept fully immersed in oil and the oil temperature was adjusted so as to keep the reservoir liquid at the desired temperature.

The oil-bath, which was a standard one, consists of a fully insulated rectangular metal box, about 2 cubic feet in volume, with an open top. There were two heating coils; the main heating element of 500 watts and an auxiliary heating element of 300 watts. The main heating element was connected through a control thermometer and relay which measured and controled the oil-bath temperature by on-off control of the main heating element. A copper cooling coil was also provided which was to preheat the cooling water to the main total condenser as well as for better temperature control of the oil-bath.

Absorber oil was used in the oil-bath as it is not viscous, its vapor pressure is low even at 80°C and does not have an undesirable odor.

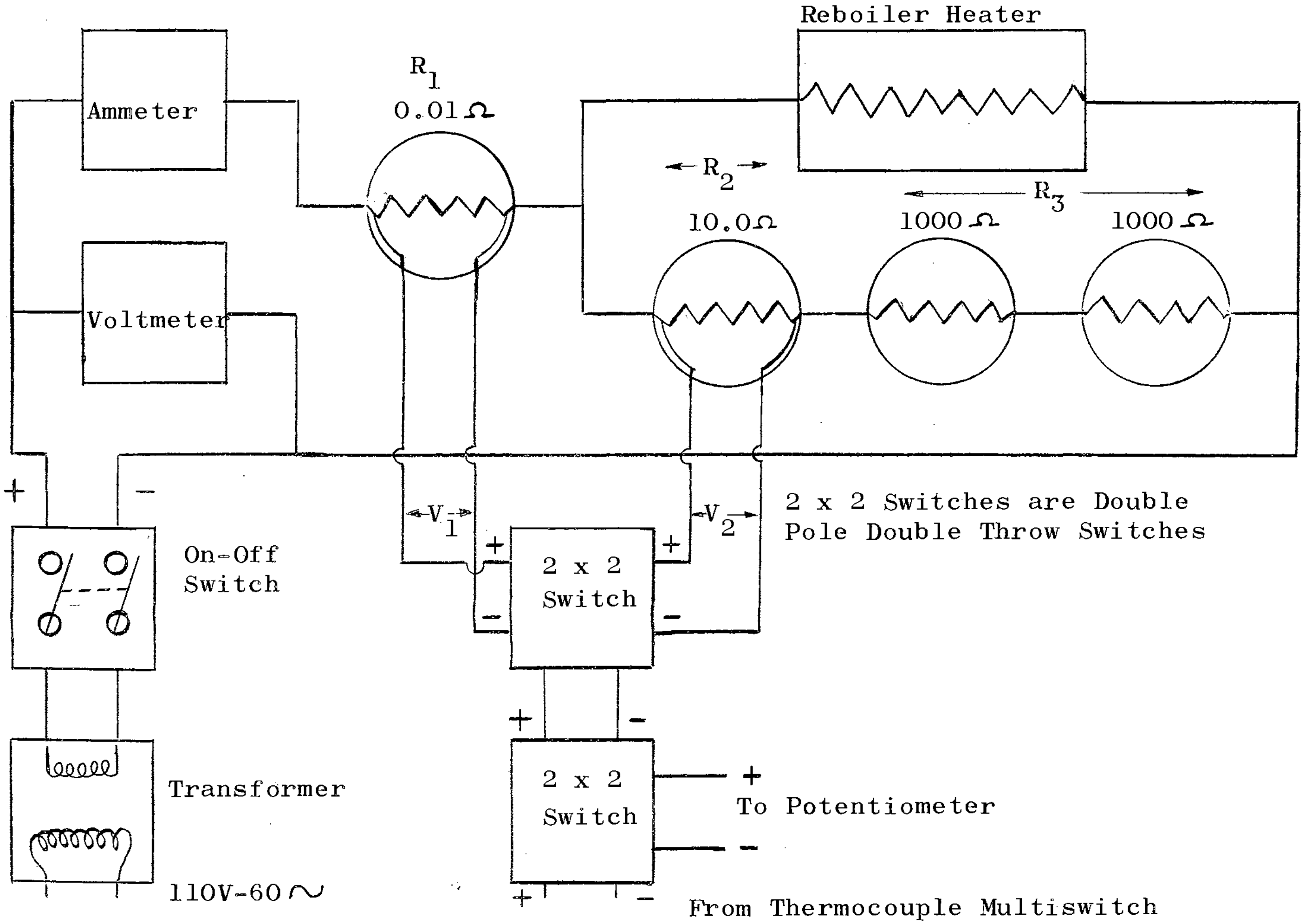
The Electrical Supply and Measuring System

The electrical system consisted of a transformer-rectifier unit, standard resistances, an ammeter, a voltmeter and a switch box with other accessories. A potentiometer was used for the measurement of potential drop across standard resistances. The electrical system was designed to supply electrical energy to the reboiler heater and to measure the energy input accurately. Provision to vary the energy input to the reboiler heater was also included in the design.

Figure 4 gives the schematic electrical circuit diagram. All the electrical units were wired and put together as per this diagram. By an arrangement of two double pole, double throw switches, the potential drop V_1, across standard resistance R_1 or the potential drop V_2, across standard resistance R_2 could be measured. The circuit diagram, Figure 4, also had provision to measure the thermocouple millivolt.

The transformer was a standard one to supply 1.5 amperes maximum at 17 to 25 volts, D. C., from 110/115 volt, 60 cycles A.C. input. The transformer output voltage could be set at any value between 17 to 25 volts and the transformer was designed so as to maintain the output voltage constant at the set value.

Four standard resistances of following capacities were used: one of 0.01 ohm, one of 10.0 ohm and two of 1000.0 ohm each. These standard resistances were of very high accuracy. As per manufacturers recommendation, the standard 0.01 ohm resistance



2 x 2 Switches are Double Pole Double Throw Switches

Figure 4

Schematic Electrical Circuit Diagram

was kept fully immersed in an oil-bath at room temperature and the oil-bath agitator was switched on prior to switching on the current through the circuit. These standard resistances were selected on the basis of maximum current through the circuit.

The ammeter and the voltmeter, mounted on the switch box, were used only for the adjusting the transformer output voltage to its proper value. For the electrical power input calculation, the potential drop across standard resistances were used and calculations carried out as given in Appendix D.

Figure 5 gives a sketch of the switch box which contained the ammeter, the voltmeter and all the switches. The switch box had provision to connect to it electrically the standard resistances, the transformer, the reboiler heater, the thermocouples, and the potentiometer. The electrical wiring of the switch box was such that with all these above mentioned connections, it would correspond exactly to the electrical wiring diagram of the Figure 4.

The Temperature Measuring System

For measurement of temperature, iron-constantan thermocouples were used. These thermocouples are suitable for the entire temperature range of the experiment. For measuring the temperatures at various points inside the still, long thermocouple wells were provided which had many bends. In order to reach the thermocouple junction from the open end of the well to the end of the well, a special glass insulated thermocouple of desired stiffness was selected. These thermocouples could be

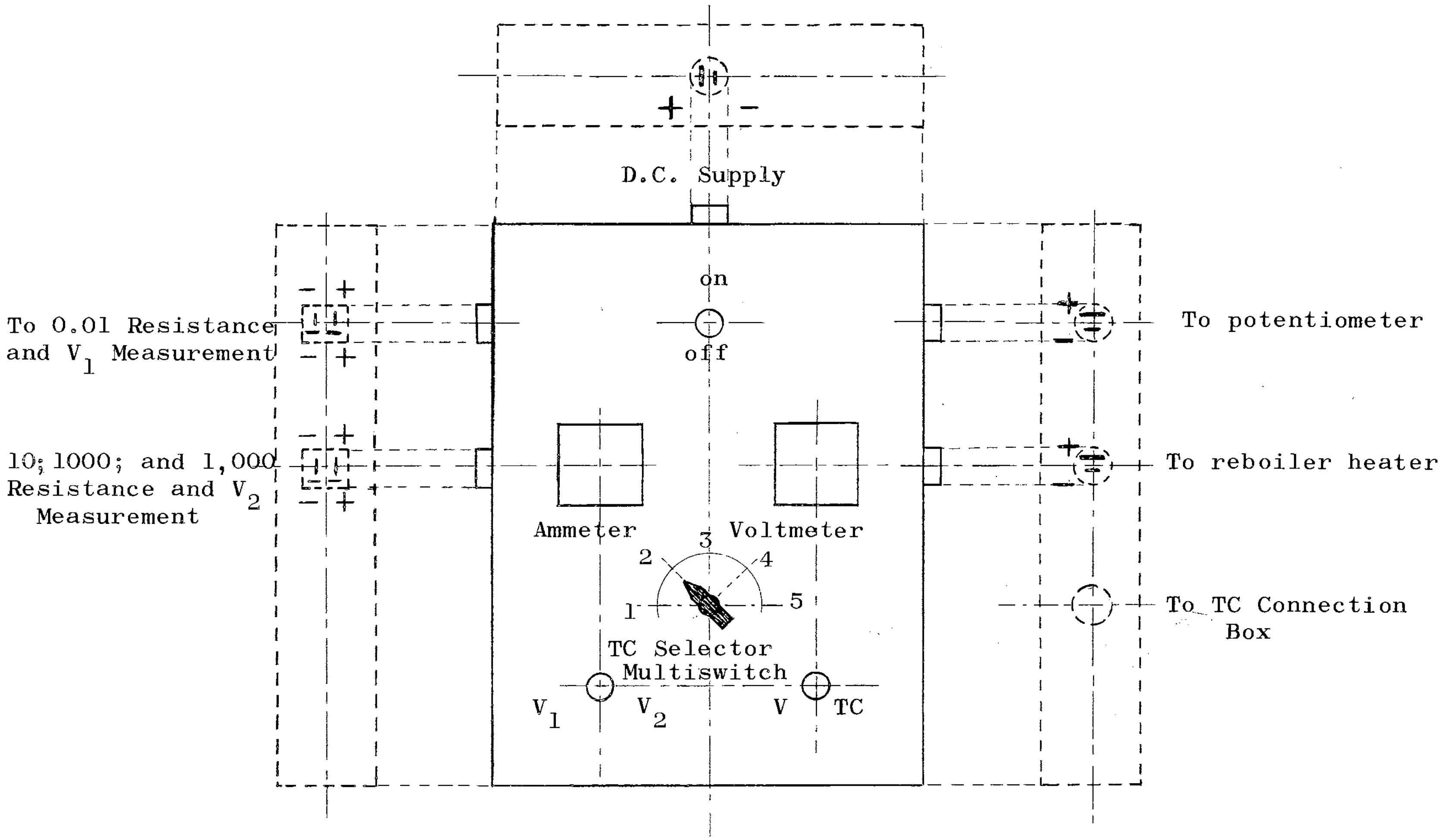


Figure 5

Sketch of the Electrical Switch Box

pushed all the way up to the end of the thermocouple well from the open end.

The cold junction was maintained at 0°C by keeping it immersed in ice made of deionized water. The thermocouple generated e.m.f. was measured as millivolts by the same potentiometer as used for the measurement of the potential drops across the standard resistances of the electrical circuit. A five point multiswitch selected the desired thermocouple for its e.m.f. measurement. Figure 6 gives the schematic wiring diagram for the thermocouple selector multiswitch. Following is a list giving the location of the thermocouples in the apparatus with corresponding reference notation as marked in Figure 6.

TC-1	The constant temperature oil-bath
TC-2	The reservoir
TC-3	The still, below the equilibrium contact stage
TC-4	The still, above the equilibrium contact stage
TC-5	Spare and for room temperature
TC-C	The cold junction

Miscellaneous

Sample Collection

For phase equilibrium data, chloroform-benzene mixture samples were collected from the equilibrium tray and from the reservoir. For this purpose, a hypodermic syringe with a 10" long needle was used. The needle was inserted into the still or the reservoir through a rubber septum, up to the liquid on the tray which was withdrawn. This arrangement permitted sample

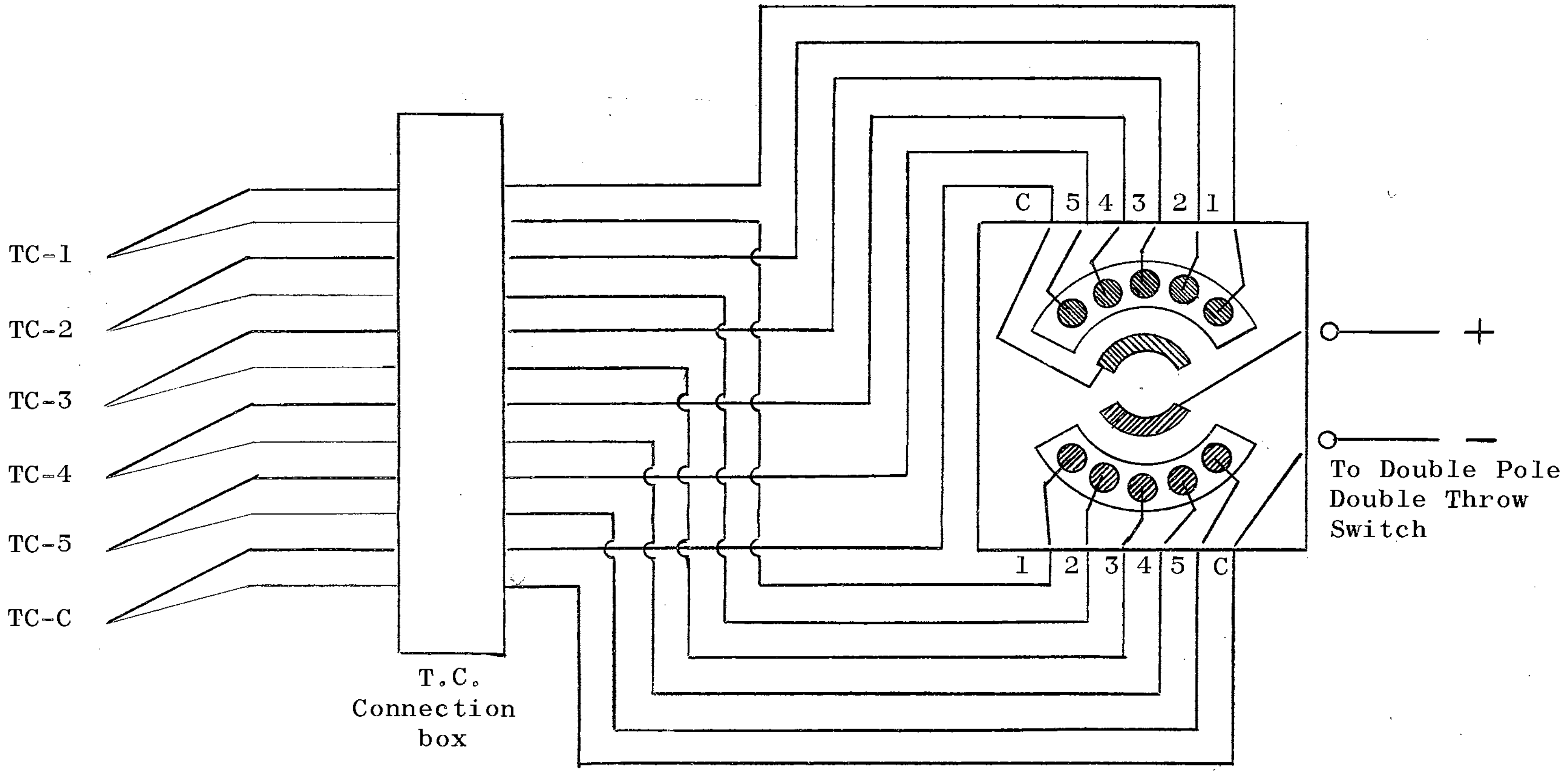


Figure 6

Schematic Wiring Diagram
for Thermocouple Selector Multiswitch

collection without letting atmospheric air into the system.

Refractive Index Measurement

The chloroform -benzene sample composition was determined by measuring its refractive index. For this purpose a Bausch and Lomb refractometer and its accessories, a sodium light source and a constant temperature water-bath were used. The refractometer had a range of 1.32975 to 1.63461 for sodium light and an accuracy of 0.00003 to 0.00006 depending upon the region in which the observations were made. The refractometer was calibrated against a standard prism.

Nonaq Grease

A special water soluble Nonaq grease was used for all the ground glass joints of the apparatus. Though soluble in water, this grease is insoluble in chloroform, benzene and various other hydrocarbons.

Purity of Chemicals

The purity of various chemicals used for the present experimental investigation work is given below:

Chloroform - Fisher Certified Reagent grade chloroform was used for all the experimental work. It contains a minimum of 99.0 mole percent chloroform. Impurities consists of 0.75 mole percent ethyl alcohol, added as preservative, and a maximum of 0.02 mole percent water. It had a specific gravity of 1.474.

Benzene - Phillips Petroleum Company's pure grade benzene was used for all experimental work. It contains a minimum of 99.0 mole percent benzene.

CHAPTER V

EXPERIMENTAL PROCEDURE

The experiment was designed to measure the vapor-liquid phase distribution ratio, i.e., the equilibrium K-value; the bubble point and the dew point temperatures; and the isobaric integral heats of vaporization, for chloroform-benzene mixtures at the local barometric pressure. For the calculation of these above mentioned quantities, directly measured quantities included thermocouple millivolt for temperature measurements; mixture refractive index for composition analysis; time and amount of the condensate for the rate of vaporization calculation; and potential drop across standard resistances for the heat input measurement. The evaporation rate and heat input rate were used in turn to calculate the isobaric integral heats of vaporization for the mixture.

The following procedure was used for conducting the experiment and to measure all the above mentioned quantities.

Composition - Refractive Index Diagram

Prior to starting any experimental vaporization runs, a composition-refractive index diagram for chloroform-benzene system was prepared. The refractive indices were measured at 30°C, using a constant temperature water-bath to maintain the sample at the desired temperature. An electric sodium lamp was used as the source of light rays of approximately 5892 Å wavelength. Standard samples of known compositions were prepared by weighing pure components on a balance, accurate to 0.00001 gram weight. To obtain a smooth and accurate diagram, a graph from eleven data points was made and this was used as reference for all mixture analysis. Calculations and the graph are given in Appendix B.

Assembly of Apparatus

First the oil-bath was installed securely in position and a vertical framework of aluminum rods was made on one side of the oil-bath to hold the glass apparatus. The oil-bath was filled with absorber oil. The reservoir, the still, and the reboiler were next installed as shown in Figure 3 and properly clamped in position from the aluminum framework. Prior to assembly, all the ground glass joints were well greased with Nonaq grease to insure leak-proof joints. At the time of placing the reboiler in position, the electrical leads were clamped to the tungsten electrodes of the reboiler so that power could be supplied to the reboiler.

On the other end of the reservoir, the agitator and the motor were next assembled. The agitator shaft, which passes through a leak-proof sleeve, was well lubricated with water diluted Nonaq grease. The motor and agitator shafts were connected by means of a flexible rubber coupling. The auxiliary condenser and an arrangement to collect reservoir liquid sample through rubber septum was also installed as per Figure 3.

Next, the main condenser outlet was connected to the reservoir through a three-way-valve. Cooling water connections were made by rubber tubing. Cold water was connected to the auxiliary condenser inlet with an outlet to the drain. For a more precise pressure control of the main total condenser, preheated water was used as coolant to the condenser. Preheated water reduces the temperature gradient across the condenser requiring a greater water flow rate for the same amount of heat transfer. A greater condenser water flow rate allowed precise adjustment of water flow and thereby made condenser pressure control easier. For the purpose of heating the water, the cold water line was connected to a copper coil which was fully immersed in the oil-bath. Outlet of the coil was connected to the main condenser and the outlet of the condenser was connected to the drain.

Once the apparatus was thus assembled, the thermocouples were inserted in place and the cold junction inserted in the ice-bath. The electrical connections were completed as per Figure 4 but the electrical switches were kept off. This concluded the assembly of apparatus. Next, the reservoir was filled with chloroform-benzene mixture of desired composition.

Air Evacuation

Before any data could be collected, it was essential to evacuate the system of all the air and to attain a steady state condition. The presence of air makes the system a multicomponent one; any phase equilibria data for binary, measured in presence of air will be of little value.

Air was removed from the system by replacing it with the vapor of the mixture. For this purpose, the highest openings of the still, the main condenser and the auxiliary condenser were opened to the atmosphere through a vapor-trap. Air and vapor escaping through these openings were led through rubber tubings and allowed to bubble through about 1 inch of cold water. This arrangement condenses vapor which collects in the vapor-trap thereby avoiding the contamination of the room with undesirable chloroform vapors. Valve "A" and "B" of Figure 3 were positioned to connect the main condenser outlet to the reservoir. All other openings of the system were kept closed.

The reservoir agitator was started and the oil-bath heaters, both the main and the auxiliary, were switched on. However, the reboiler heater was kept off as the reboiler may be dry at this time. Over-heating of the reboiler may cause many undesirable effects; namely, the Nonaq grease which holds the reboiler in position would become too fluid at high temperature causing the fall of reboiler into the reservoir. The heater elements may burn off due to overheating, or else the still may crack due to expansion of the reboiler. Over heating of the reboiler was, therefore, always avoided.

At the first sign of boiling of the liquid in the reservoir, the oil-bath auxiliary heater was switched off and the temperature controller was set to maintain the oil-bath temperature constant. This was done to keep the reservoir liquid at its bubble point temperature. By increasing the pressure on the auxiliary condenser side of the reservoir, the liquid level on the reboiler side was increased so as to fill the reboiler completely. After filling the reboiler, the reboiler heater was switched on and the transformer output voltage adjusted to keep the total output current at approximately 1.0 ampere. Vapor leaving the reboiler, in due course, replaced all the air from the still which escaped through the vapor trap.

To start with, the still was at room temperature. Thus, vapor leaving the reboiler soon condensed and filled up the tray of the equilibrium tray arrangement.

Once the system was thus free of air, the highest opening of the still was closed with a rubber septum so that liquid samples from the equilibrium tray could be collected without letting air into the system. Samples were collected with the help of a syringe and hypodermic needle inserted through the rubber septum. The highest opening of the main condenser was connected to the "U"-tube manometer.

Phase Equilibria Data

At steady state conditions, the temperature of vapor leaving the reboiler and the temperature of vapor leaving the equilibrium stage became equal as well as constant. Also the composition of liquid on the tray and the composition of liquid leaving the total condenser became constant. In addition, the condensate composition was the same as that of the reservoir liquid. These were ascertained by collecting a set of samples and analyzing them by their refractive indices. This confirmed steady state condition for the entire apparatus and a phase equilibria between the liquid on the tray and the vapor leaving the equilibrium contact stage arrangement.

Under these conditions, the vapor leaving the equilibrium stage was at its dew point and the liquid on the tray was at its bubble point, both temperatures being the same. A sample collected from the tray liquid gave its composition. Whereas the vapor had the same composition as that of the condensate from the total condenser. Thus, a sample of condensate gave the vapor composition. Having thus obtained, both temperature and composition of a mixture, in liquid and vapor phase, the composition-temperature diagram for chloroform-benzene binary at the local barometric pressure was made. The same data points were also used to calculate the equilibrium phase distribution ratio, K-value, for chloroform and benzene, at various temperatures.

Heats of Vaporization Data

The liquid entering the reboiler was at its bubble point, the vapor leaving the still was at its dew point, and both had the same composition. Secondly, the pressure of the entire system was the same and constant. Thus, the heat quantity accompanying the liquid-vapor phase change represented the isobaric integral heat of vaporization.

It was required to maintain the reservoir liquid at its bubble point. For initial experimental work, the liquid was kept at its bubble point by visual observation. However, once data points for the composition-temperature diagram were obtained by a previously mentioned procedure, the bubble point temperature of the reservoir liquid was known. Then the reservoir liquid temperature was accordingly adjusted by varying the oil-bath temperature.

For the heat of vaporization data, the rate of vaporization and the electrical energy input were the two measured quantities. The rate of vaporization was measured by collecting a sample of condensate for two minutes or more and weighing the same. For collecting the condensate sample, three-way-valves "A" and "B" of Figure 3 were positioned to divert all the condensate, from the total condenser, out of the system which was collected as a sample. The repositioning of the valves did not change fluid flow path through the still so as to disturb the steady state conditions, the only difference being that condensate was removed out of the system instead of being returned to the reservoir. This did not make any difference in reservoir liquid composition as both the liquids, the reservoir liquid and the condensate, had the same composition. The reservoir liquid volume was very large compared to the sample size, therefore, the fall in reservoir liquid level was negligible. The reboiler liquid level also remained unaltered.

The electrical energy input was calculated by measuring the potential drops V_1 and V_2 across standard resistances of 0.01 ohm, R_1, and 10.0 ohm, R_2, respectively. Figure 4 gives the electrical circuit diagram which was used for various switch positioning to measure the above mentioned quantities. These data were used to calculate the electrical power input and the heat input rate. This concluded one run of the experiment.

Four runs for the same mixture composition but at different flow rates were made. For this purpose, the system was not re-evacuated as no air had been allowed to enter the system between two runs. To alter the flow rate, the transformer output voltage was adjusted and the experiment repeated. The ammeter reading was not allowed to exceed 1.5 amperes as that was the limiting capacity for which the electrical circuit was designed.

For any run with a liquid of different composition, the system was emptied of all its liquid and the experiment restarted from the very beginning.

CHAPTER VI

RESULTS

Experimental results calculated from original experimental data (Appendix A) are presented and discussed in this chapter. Results include vapor-liquid equilibrium ratios and isobaric integral heats of vaporization for the chloroform-benzene system at 740 mm Hg, which measurement was the main objective of this experimental investigation.

This chapter also includes the chloroform-benzene temperature-composition diagram constructed from the experimental results for 740 mm Hg; the basis for heat calculation; and the effect of flow rate and heat leaks on experimental data.

Vapor-Liquid Equilibrium Ratios

The vapor-liquid equilibrium ratios, i.e., the equilibrium K-values, were calculated from the saturated vapor phase and saturated liquid phase compositions. Thus, a temperature-composition diagram for the chloroform-benzene system was first constructed.

Temperature-Composition Diagram

The bubble and the dew point compositions at the equilibrium temperature were calculated from the original experimental data given in Appendix A. Calculations are given in Appendix C and the results are given in Table I. Figure 7 gives the temperature-composition diagram for the chloroform-benzene system at about 740 mm Hg. The shape of the curve was compared with that of the published data (23) at 760 mm Hg given in Table C-I.

Vapor-Liquid Equilibrium Ratios

The vapor-liquid equilibrium ratios, i.e., equilibrium K-values, were calculated from the data used for the temperature-composition diagram. K-values at various equilibrium temperatures for the chloroform-benzene system at 740 mm Hg are given in Table I. Sample calculations for K-values are given in Appendix C. Figure 8 and 9 give the equilibrium K-value vs. temperature diagrams for chloroform and benzene, respectively. The shape of the curve for experimental values at about 740 mm Hg was compared with the published data (23) at 760 mm Hg, given in Table C-I.

Isobaric Integral Heats of Vaporization

The basis for all heat of vaporization calculation is in the equation

$$\begin{array}{c}\text{Isobaric Integral Heat}\\ \text{of Vaporization}\end{array} = \frac{(\text{Power}) \times (\text{Time})}{(\text{Mass of Condensate})} - \begin{array}{c}\text{Heat Leak}\\ \text{Correction}\end{array} \qquad \text{(VI-1)}$$

The first term on the right hand side of the equation (VI-1) is called the uncorrect heat of vaporization and the second term is the error introduced in the heat of vaporization quantity due to heat leak.

Thus, for the calculation of the isobaric integral heats

TABLE I

VAPOR-LIQUID EQUILIBRIUM DATA FOR THE CHLOROFORM-BENZENE SYSTEM AT ABOUT 740 mm Hg PRESSURE

Reference: Present experimental work

Temp. °C	x_1	y_1	K_1	K_2
60.50	1.000	1.000	1.0000	----
65.45	.683	.807	1.1801	.6088
70.25	.470	.603	1.2830	.7491
73.80	.288	.400	1.3889	.8427
76.30	.140	.205	1.4643	.9244
79.30	.000	.000	------	1.0000

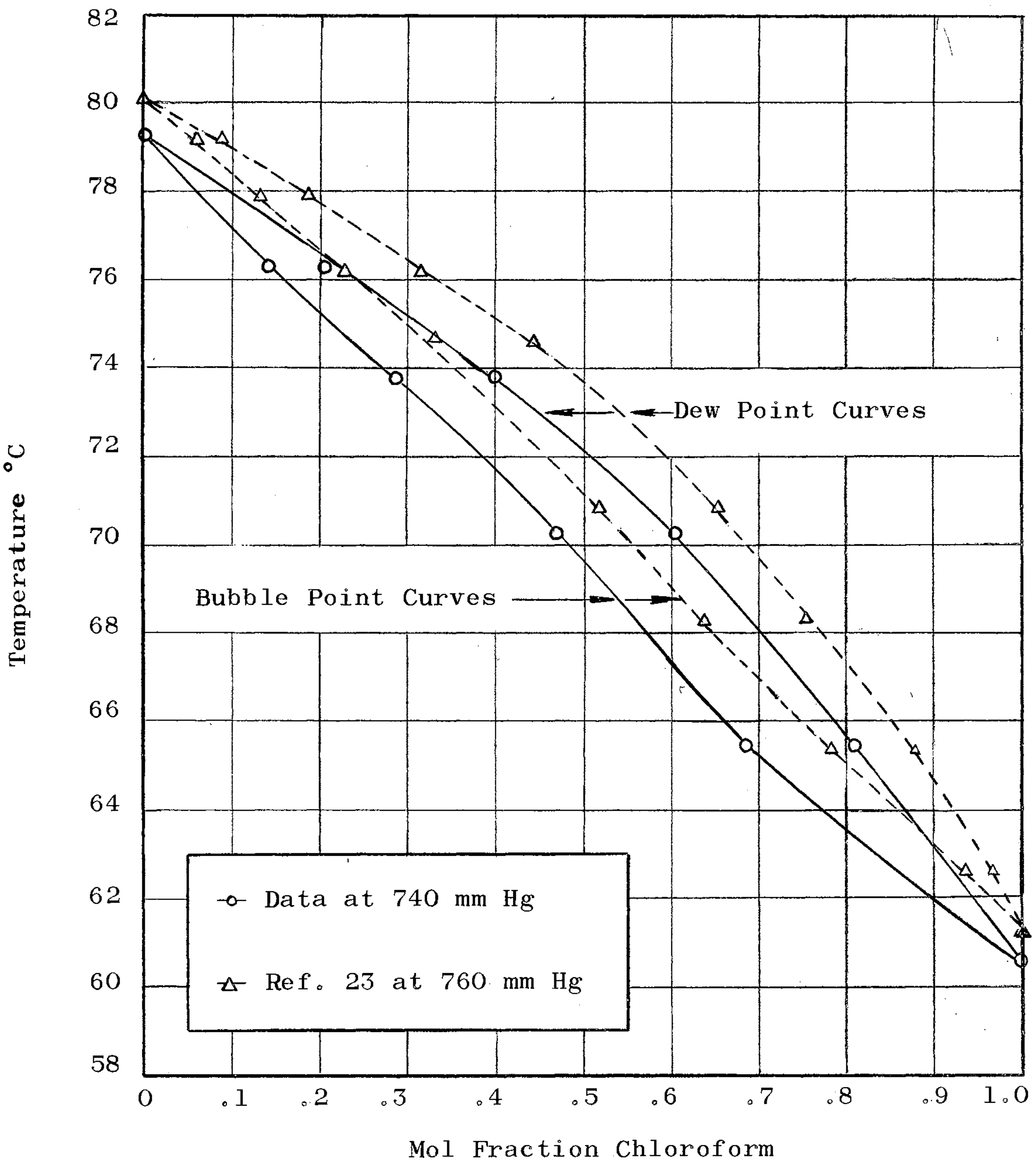


Figure 7

Temperature-Composition Diagram
for Chloroform-Benzene System at 740 and 760 mm Hg

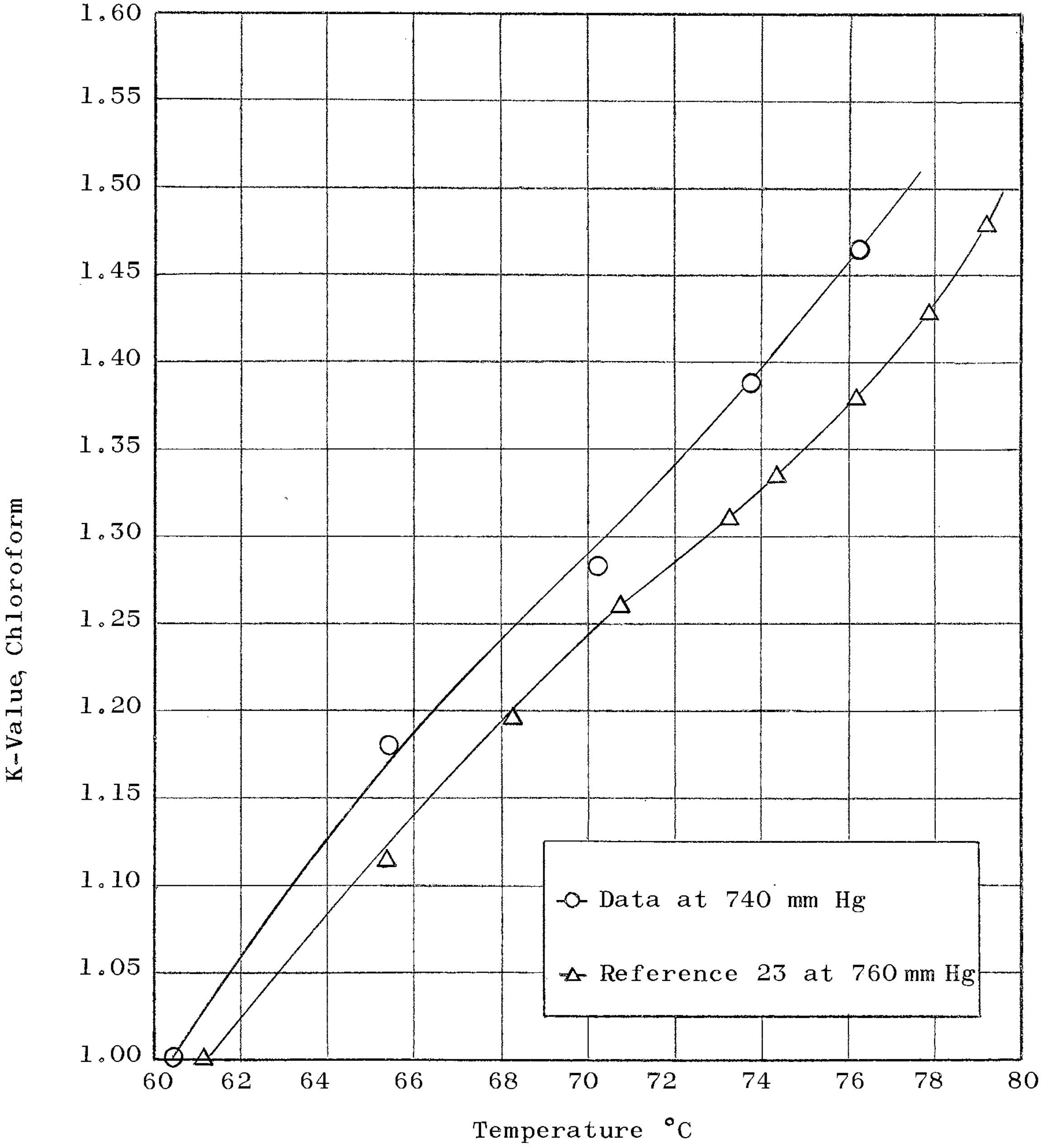


Figure 8

K-Value-Temperature Diagram for Chloroform in Benzene at 740 and 760 mm Hg

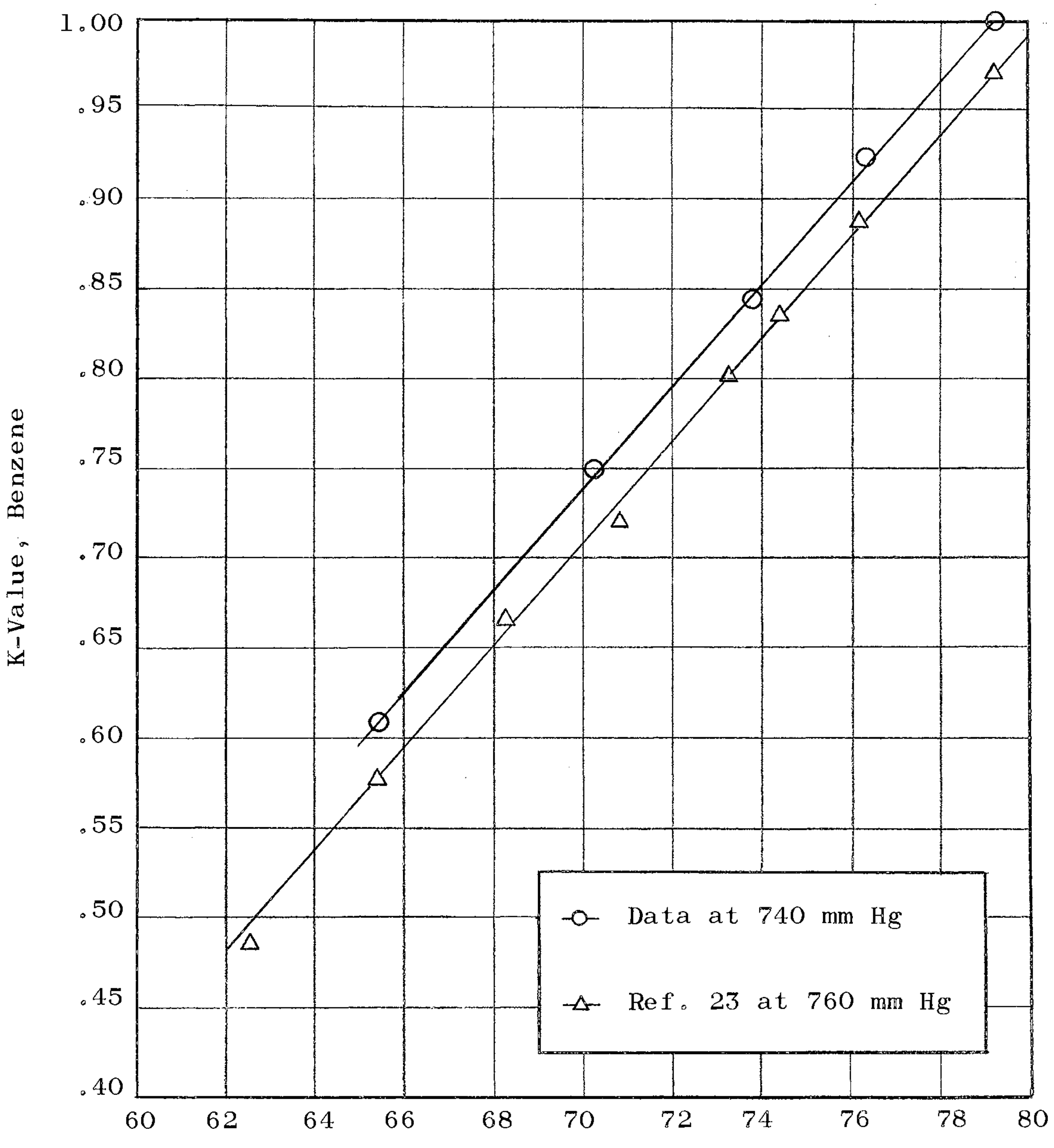


Figure 9

K-Value-Temperature Diagram for Benzene in Chloroform at 740 and 760 mm Hg of vaporization, first the heat calculation and the effect of flow rate and heat leaks are discussed and then the final results, i.e., the isobaric integral heats of vaporization are given.

Heat Calculation

Heat was supplied to the reboiler as electrical power. The electrical power input was calculated from the potential drop V_1 and V_2 across standard resistances R_1 and R_2, respectively. Where R_1 and R_2 refer to the Figure 4, schematic electrical circuit diagram.

Original experimental values of V_1 and V_2 are given in Table A-I. Equations used for the electrical power input calculations are given below.

Total current, $I_1 = V_1/R_1$ amps. (VI-2)

Branch line current, $I_2 = V_2/R_2$ amps. (VI-3)

Reboiler heater current, $I = I_1 - I_2$ amps. (VI-4)

Potential drop across reboiler heater, V

= potential drop in the branch line

$= I_2(R_2 + R_3)$ volts. (VI-5)

Power input to the reboiler

$= V \times I$ watts.

$= I_2(R_2 + R_3) \times (I_1 - I_2)$ watts.

$= (V_2/R_2)(R_2 + R_3)((V_1/R_1)-(V_2/R_2))$ watts.

(VI-6)

In the above equations, the values of R_1, R_2 and R_3 were constant for all the runs and as per Figure 4 they were:

R_1 = 0.01 ohm.

R_2 = 10.0 ohms.

R_3 = (1000.0 + 1000.0) = 2000.0 ohms.

Sample calculation and calculated values of power input are given in Appendix D. The heat input in the units of cal./min. was calculated from the electrical power input in watts, using the following conversion factor.

1 watt = 14.343 cal./min.

Effect of Flow Rate and Heat Leak

For this experimental investigation as well as for other previous investigations concerning the heat of vaporization, the electrical power input, mass of condensate collected and the condensate collection time were the measured quantities. Power input and time were unaffected by the heat leak and the flow rate, i.e., the vaporization rate of the mixture from the reboiler. Thus, the effect of the flow rate and the heat leak will be discussed here. The terms flow rate and vaporization rate have been used interchangeably in this thesis.

Heat leak refers to all the extra heat transferred to the system, in the form of electrical power, that was not utilized for the purpose of evaporating the reservoir liquid. The effect of heat leak must be considered and estimated in calculating the heat of vaporization. As the liquid in the reservoir was at its bubble point and as the vapor entering the main total condenser was at its dew point, because it leaves an equilibrium stage just before entering the condenser, the net heat input per gram mole of the condensate corresponds to the isobaric integral heat of vaporization for the mixture.

The total heat leak is the algebraic sum of two quantities, the external heat leak and the internal heat leak. All the heat which was transferred from the following,

i) reboiler liquid
ii) vapor leaving the reboiler
iii) liquid on the equilibrium stage
iv) vapor leaving the equilibrium stage

to the still and the surrounding, is considered as external heat leak. The heat transferred from the reboiler liquid to the reservoir liquid is called the internal heat leak.

Under steady state conditions, the reboiler liquid temperature, the temperature of the vapor leaving the reboiler, the equilibrium stage temperature and the temperature of the vapor leaving the equilibrium stage were the same and this temperature corresponds to the dew point temperature of the condensate. In further discussion, this temperature is called the still temperature. The still temperature being greater than that of the surroundings causes a positive external heat leak. For a particular mixture composition, the still temperature is a constant, independent of flow rate, a theoretical fact confirmed by experimental observations. Furthermore the resistance to heat flow offered by the vacuum jacket was very large as compared to the inside vapor film coefficient. Thus, any change in vapor film heat transfer coefficient, at different flow rates, had no effect on overall heat transfer coefficient. Thus, it is concluded that the external heat leak was independent of flow rate. It is further concluded that the external heat leak was a constant quantity provided the mixture composition, the atmospheric temperature and the environment around the still, i.e., air velocity etc. remaining constant. Thus, in order to have an accurate heat leak analysis, all the experimental runs for a certain mixture composition were made under identical conditions.

The internal heat leak too was a positive quantity for the system under consideration. The liquid in the reservoir was kept at its bubble point temperature and so was the liquid in the reboiler. Under steady state conditions, the composition of these two liquids was not the same and consequently the temperature of the liquid in the reservoir was not the same as that of the reboiler. As can be shown by material balance and the basic condition for phase equilibria, the reboiler liquid temperature was the same as the dew point temperature of the reservoir liquid. This temperature gradient between two parts of the apparatus provided the necessary driving force for heat transfer from the reboiler liquid to the reservoir thus causing internal heat leak. As can be ascertained from the above discussion, the reboiler was always at a higher temperature than the reservoir and thus the internal heat leak was always a positive quantity.

During the steady state period, the liquid flow from the reservoir to the reboiler was upward through the capillary, whereas heat flow from the reboiler to the reservoir was downward. As the direction of heat and mass flow was opposite to each other, a higher flow rate reduced the internal heat leak.

A common method to correct for the effect of total heat leak from the final results is to plot calculated values of uncorrected heat of vaporization against the reciprocal flow rate and extrapolate to the zero reciprocal flow rate axis. This corresponds to an infinite flow rate, at which heat leak should be negligible. By this method, the Y-axis intercept (i.e. zero reciprocal flow rate) corresponds to the correct heat of vaporization. The procedure has been used by Stein (27). At infinite flow rate, the internal heat leak becomes a minimum and so does the total heat leak. The error introduced in heat of vaporization calculation by a finite heat leak for an infinite vaporization rate automatically approaches zero and thus the effect of heat leak is eliminated from the final result. For the system considered by Stein (27) in his experimental investigation, he observed that the uncorrected heat of vaporization vs. reciprocal flow rate plot is a curve and not a straight line. This dependence of the total heat leak on the flow rate indicates that the internal heat leak was not negligible compared to the external heat leak.

Figure 10, constructed from data given in Appendix D, gives a plot of uncorrected heat of vaporization vs. reciprocal flow rate for a mixture of the chloroform-benzene system, studied in this work. In this plot, data points fall on a straight line. This interesting observation indicates that for the range of the data taken in the present experimental investigation, the total heat leak was independent of the flow rate. In light of previous discussion, this means that for the data

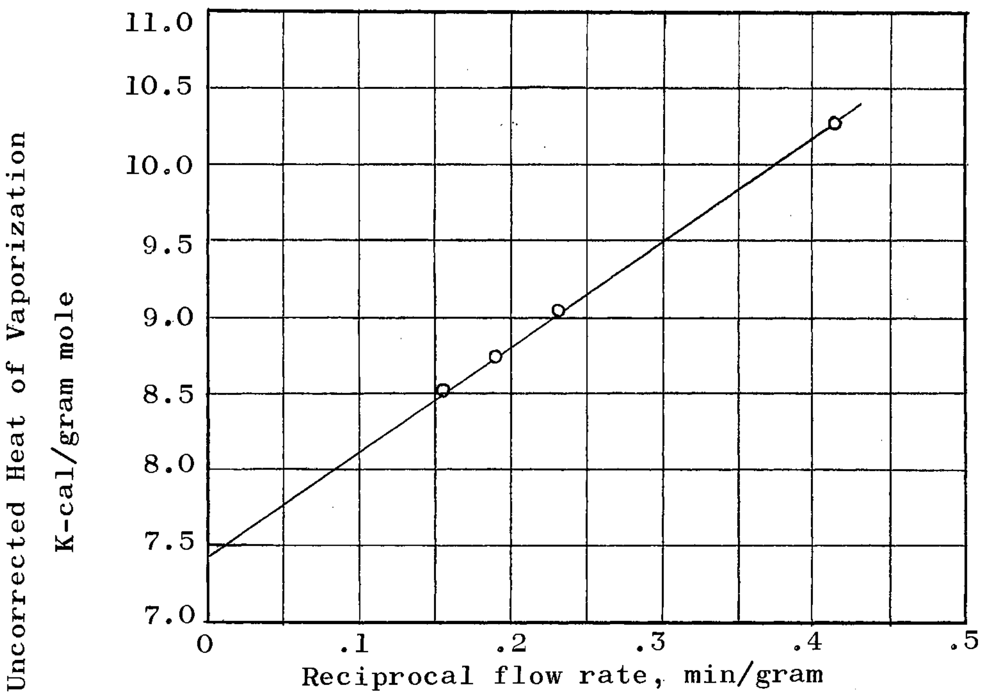


Figure 10

Heat of Vaporization-Reciprocal Flow Rate Diagram for Chloroform-Benzene Mixture, $x_1 = 0.603$

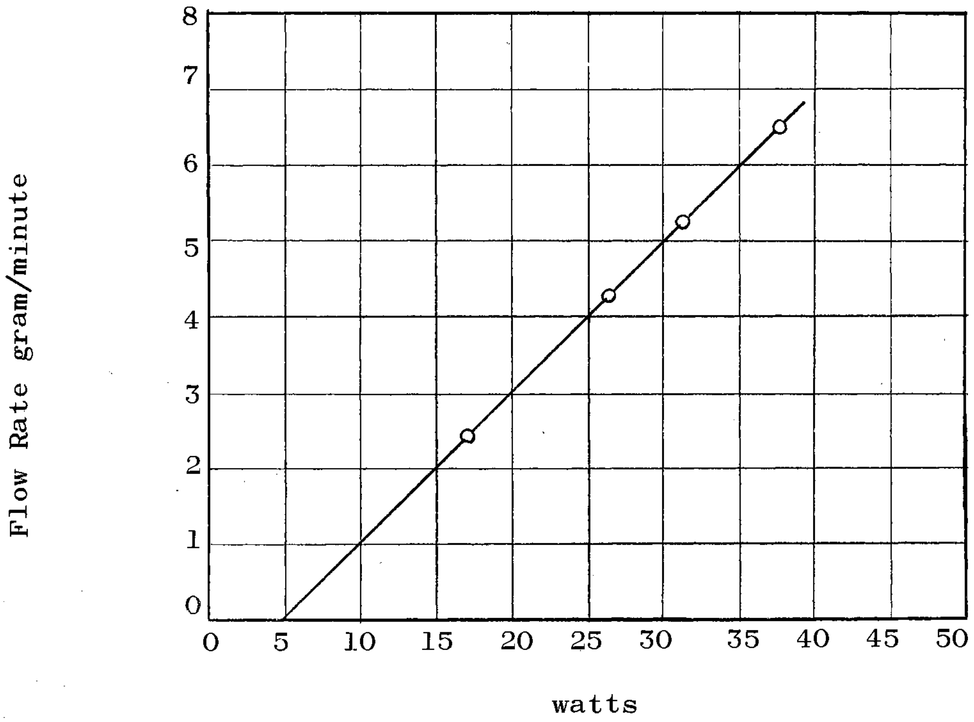


Figure 11

Rate of Vaporization-Heat Input Diagram for Chloroform-Benzene Mixture, $x_1 = 0.603$

under consideration, the internal heat leak was negligible compared to the external heat leak. The following observations are also consistent with the above conclusion.

1. For the chloroform-benzene system at the local barometric pressure, the maximum difference between the dew point and the bubble point temperatures, for a certain mixture composition, was less than 3°C. This reduced the driving force for internal heat leak; whereas in case of the systems investigated by Stein (27), the isopropyl alcohol-water system and the acetone-water system, both at atmospheric pressure, the maximum internal temperature gradient was 15°C and 31°C, respectively.

2. For this work, the range of flow rate was from 1.8564 gram/minute to a maximum of 6.5012 gram/minute for runs made with chloroform-benzene mixtures. These flow rates are higher than those of Canjar and Lonergan (2) and of Stein (27). As discussed earlier, higher flow rate further decreased the magnitude of internal heat leak for this work.

3. For this work, the main still itself was not vapor jacketed and kept at a temperature same as that of the inside of the still. This design reduces the temperature gradient between the still and the surroundings thus reducing the external heat leak. Noninclusion of this feature in the design of the still increased the external heat leak and thus decreased the relative importance of the internal heat leak.

All the above three points had substantial effect on the internal heat leak, making it negligible compared to the external heat leak and thus making the heat leak independent of the flow rate.

Taking into consideration the above factors, the data were analyzed differently for the present work in the calculation of the heats of vaporization and the heat leak. Figure 11, constructed from data given in Appendix D, gives a plot of flow rate vs. power input, which is a straight line. The vaporization rate, i.e., the flow rate in gram/minute is represented on the ordinate and the power input in the unit of watts is represented on the abscissa. In this plot, the reciprocal slope has the units of watt-minute/gram and represents the corrected heat of vaporization for the chloroform-benzene mixture under consideration. The X-axis intercept, corresponding to zero flow rate, represents the total heat leak in the unit of watts.

An "eye-ball" method of curve-fit is dependent upon judgement and prejudices. Therefore, flow rate and power input data were plotted, separately for each mixture composition, as shown in Figure 11 and the equation for the straight line determined by a least-square fit of the data. The correct heats of vaporization and the total heat leaks were subsequently calculated from these data. Appendix D gives detailed sample calculations and the flow rate vs. power input plot for runs made with various different mixture compositions.

Isobaric Integral Heats of Vaporization Results

From the reciprocal slope and the intercept for zero flow rate of the plot of flow rate vs. power input, the heat of vaporization and the heat leak were calculated. Sample calculation for the same is given in Appendix D. Table II gives final corrected

TABLE II

ISOBARIC INTEGRAL HEATS OF VAPORIZATION RESULTS FOR THE CHLOROFORM-BENZENE SYSTEM AT 740 mm Hg.

Composition x_1	Temperature °C	Heat Leak cal/hr	Heats of Vaporization Cal/gram	Cal/gram mol
0.000	79.30	4113.7	92.26	7205.70
0.205	76.30	4424.3	84.94	7349.00
0.400	73.80	4046.3	80.25	7586.75
0.603	70.25	4010.7	72.43	7451.82
0.807	65.45	3672.2	66.55	7405.19
1.000	60.50	3664.2	59.88	7148.70

values of the isobaric integral heats of vaporization for various chloroform-benzene mixture compositions; whereas Figure 12 gives a plot of the same. Figure 13 gives a plot of the heat leak as a function of the still temperature.

As no previous experimental determination of the isobaric integral heats of vaporization has been made for the chloroform-benzene system at atmospheric pressure, results could not be compared. However, for pure chloroform and pure benzene, published heat of vaporization data are available. International Critical Tables (15) gives the heat of vaporization data at normal boiling point, Perry (19) gives the heat of vaporization data at additional temperatures, whereas Hodgman (14) gives the change in boiling point temperature with change in pressure. From these data, the heat of vaporization of chloroform and benzene at 740 mm Hg was calculated and found to be in good agreement with the measured values. Following is a comparison of the same.

Heat of vaporization at 740 mm Hg calories/gram mole.

	Measured value	Published value	Percent off
Chloroform	7148.7	7054.7	+ 1.1%
Benzene	7205.7	7366.5	- 2.0%

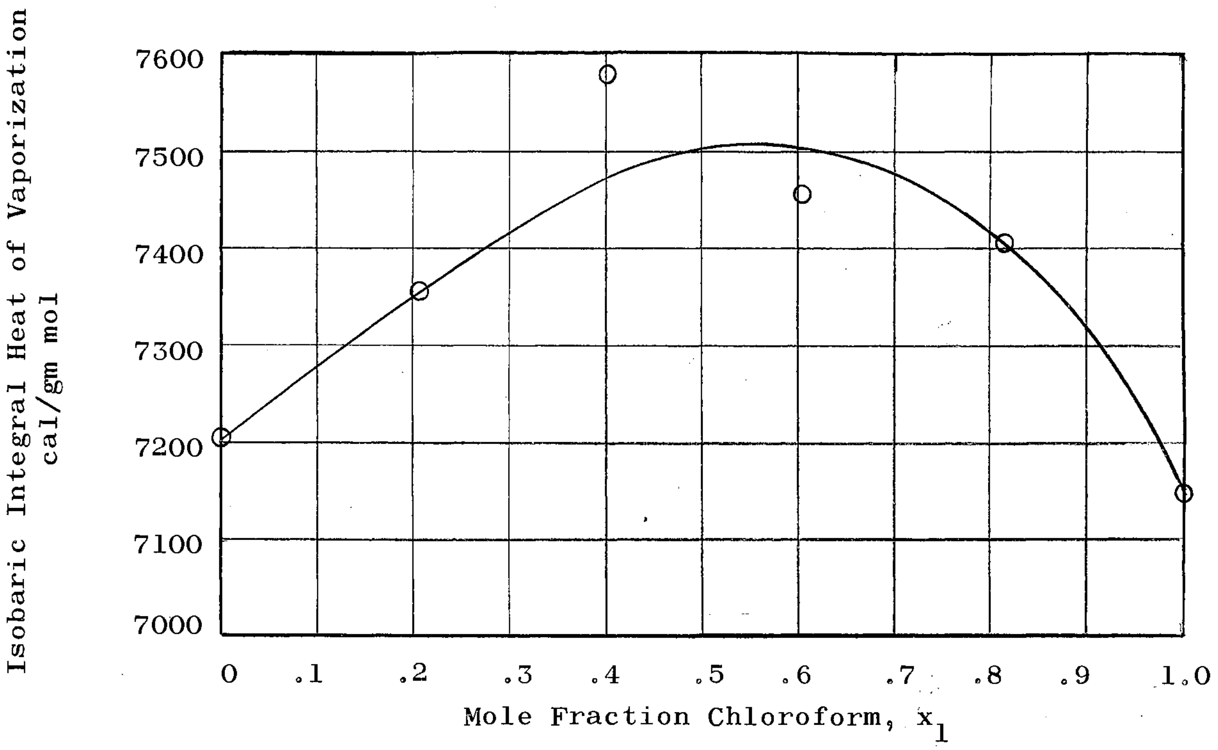


Figure 12

Isobaric Integral Heat of Vaporization-Composition Diagram for the Chloroform-Benzene System at 740 mm Hg

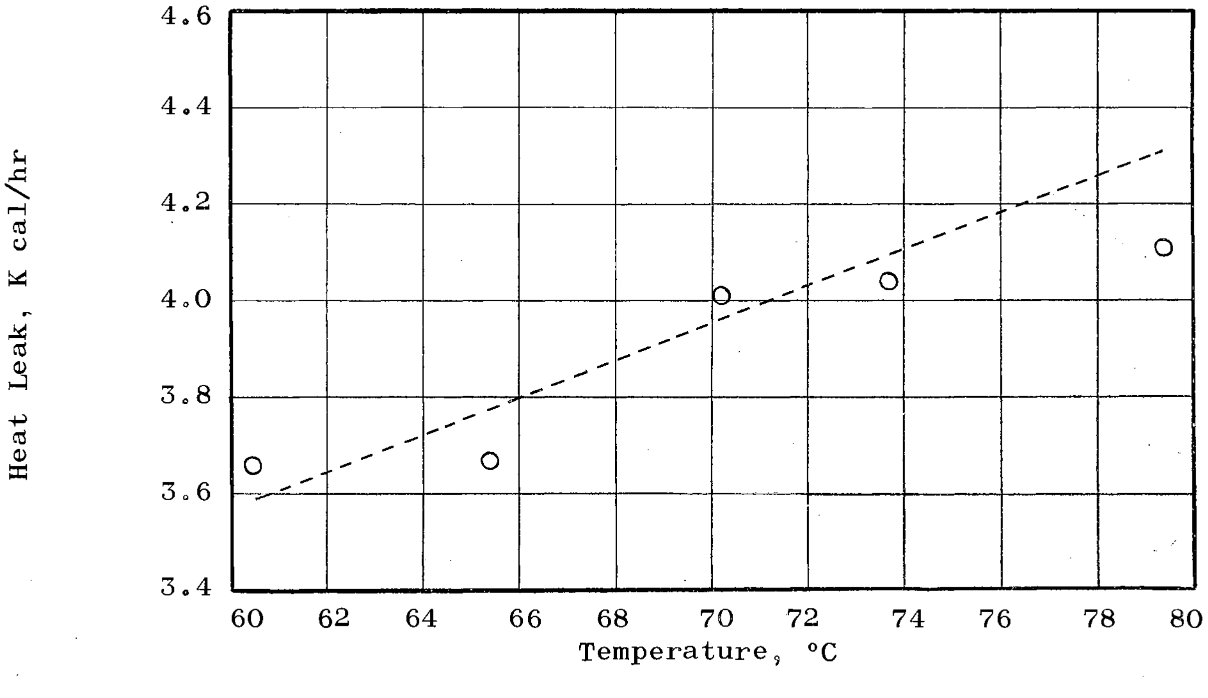


Figure 13

Heat Leak-Still Temperature Diagram

CHAPTER VII

THERMODYNAMIC CONSISTENCY TEST

Theory and Equations

For phase equilibria between two phases, such as vapor and liquid, certain conditions must be satisfied, which are based on basic thermodynamic principles. The pressure and temperature of the vapor phase must be equal to that of the liquid phase; in addition, for each component, the vapor phase chemical potential of a component must be the same as the liquid phase chemical potential of the same component. This forms the very basis of thermodynamic consistency test which all phase equilibria data must pass in order to be consistent with basic chemical engineering thermodynamics.

The thermodynamic consistency test is necessary but not sufficient condition for data to be correct. Such experimental data which fail to pass thermodynamic consistency test must be labelled as inaccurate; however, those data which pass the consistency test may or may not be accurate. There is no method of confidently testing the accuracy of phase equilibria data.

The equation to check the thermodynamic consistency of vapor-liquid phase equilibria data are written in many forms, based on activity coefficients, fugacity coefficients, K-values, and enthalpies. Various tests, both rigorous and approximate, are available in the literature. The subject of thermodynamic consistency has been thoroughly investigated by Edmister and Robinson (8). Details of various tests will not be discussed here.

For the thermodynamic consistency check of the present experimental data, the following rigorous equation was used, which was derived by Edmister (6)

$$\int_{\ln K_1 \text{ at } x_1 = 0.0}^{\ln K_1 \text{ at } x_1 = 1.0} x_1(1 + y_1 \xi_1)\, d \ln K_1 + \int_{\ln K_2 \text{ at } x_1 = 0.0}^{\ln K_2 \text{ at } x_1 = 1.0} x_2(1 + y_1 \xi_1)\, d \ln K_2$$

$$= \int_{T \text{ at } x_1 = 0.0}^{T \text{ at } x_1 = 1.0} \left[\frac{\dfrac{H^V_{mix}}{K_2} + y_1 \bar{H}^V_1 \left(\dfrac{1}{K_1} - \dfrac{1}{K_2} \right) - H^L_{mix}}{RT^2} \right]_T dT \qquad \text{(VII-1)}$$

where

$$\xi_1 = \frac{1}{RT} \int_0^P \left(\frac{\partial \bar{V}}{\partial y_1} \right)_{P,T} dP \qquad \text{(VII-2)}$$

At atmospheric pressure - the pressure for the present experiments - the term ξ_1 becomes negligibly small and thus the left hand side of equation (VII-1) reduces to

$$\int_{\ln K_1 \text{ at } x_1 = 0.0}^{\ln K_1 \text{ at } x_1 = 1.0} x_1\, d \ln K_1 + \int_{\ln K_2 \text{ at } x_1 = 0.0}^{\ln K_2 \text{ at } x_1 = 1.0} x_2\, d \ln K_2 \qquad \text{(VII-1a)}$$

These integrals were evaluated by graphical integration.

The right hand side of equation (VII-1) involves certain additional enthalpy quantities which were not measured experimentally. The saturated vapor enthalpy of the mixture, H^V_{mix}, and the partial vapor enthalpy for chloroform at saturated vapor temperature, $\bar{H}^V_1$, were calculated via Redlich-Kwong equation of state. The saturated liquid enthalpy of the mixture, H^L_{mix}, was calculated by subtracting the experimentally measured value of isobaric integral heat of vaporization from the saturated vapor enthalpy of the mixture. Thus having evaluated all the terms, the integral on the right hand side of the equation (VII-1) was evaluated by graphical integration. Data which satisfy the equation (VII-1) are said to have passed the thermodynamic consistency test.

Enthalpy Calculations

Following equations were used to evaluate saturated vapor enthalpy of the mixture, H^V_{mix}, and the partial vapor enthalpy for chloroform at saturated vapor temperature, $\bar{H}^V_1$.

The Redlich-Kwong equation of state, in terms of the compressibility factor, is written as

$$\frac{PV}{RT} = Z = \frac{1}{1-h} - \left(\frac{A^2}{B}\right) \frac{h}{1+h} \qquad \text{(VII-3)}$$

where

$$h = \frac{BP}{Z} \qquad \text{(VII-4)}$$

$$A = \sum_i y_i A_i \qquad \text{(VII-5)}$$

$$B = \sum_i y_i B_i \tag{VII-6}$$

$$A_i = \left(\frac{0.4278}{P_c T_r^{2.5}} \right)_i^{1/2} \tag{VII-7}$$

$$B_i = \left(\frac{0.0867}{P_c \ T_r} \right)_i \tag{VII-8}$$

And, where P is pressure; V is molal volume; T is temperature; R is gas constant; Z is compressibility factor; P_c is the critical pressure and T_r is the reduced temperature.

Using these relations, terms A, B, h and Z were calculated. Next, the ideal gas state enthalpy of the mixture at saturated vapor temperature was calculated using the relation:

$$H^{\circ}_{mix} = \sum_i y_i H^{\circ}_i \tag{VII-9}$$

where H°_{mix} is the ideal gas state enthalpy of the mixture; y_i is the mole fraction of component "i" and H°_i is the ideal gas enthalpy of component "i" at saturated vapor temperature of the mixture. The ideal gas state enthalpy of chloroform at various temperatures was taken from JANAF Thermochemical Data (16) and the ideal gas state enthalpy for benzene was taken from data published by API Research Project 44 (1).

Next, the vapor mixture enthalpy difference (ΔH^V_{mix}), was calculated, where ΔH^V_{mix} is defined as

$$\Delta H^V_{mix} = H^V_{mix} - H^{\circ}_{mix} \tag{VII-10}$$

The quantity ΔH^V_{mix} was calculated from an expression derived from the Redlich-Kwong equation of state by Edmister, Persyn and Erbar (7).

The expression:

$$-\frac{\Delta H^{V}_{mix}}{RT} = \frac{3}{2}\,\frac{A^{2}}{B}\,\ln\,(1+h) + 1 - Z \qquad \text{(VII-11)}$$

where all the terms have already been defined.

Once H°_{mix} and ΔH^{V}_{mix} were calculated by using equation (VII-9) and equation (VII-11) respectively, the saturated vapor enthalpy of the mixture, H^{V}_{mix}, was then calculated using the equation (VII-10).

The partial vapor enthalpy for chloroform at saturated vapor temperature, $\bar{H}^{V}_{1}$, was claculated from partial vapor enthalpy difference for chloroform at saturated vapor temperature, $\Delta\bar{H}^{V}_{1}$, which is defined as:

$$\Delta\bar{H}^{V}_{1} = \bar{H}^{V}_{1} - H^{\circ}_{1} \qquad \text{(VII-12)}$$

The quantity $\Delta\bar{H}^{V}_{1}$ was calculated from an expression derived from the Redlich-Kwong equation of state by Edmister, Thompson and Yarborough (9). The expression:

$$\begin{aligned}
-\frac{\Delta\bar{H}^{V}_{i}}{RT^{2}} = {} & \frac{B_i}{B}\left(\frac{\partial Z}{\partial T}\right)_{P,y} - \frac{1}{(Z-BP)}\left\{\left(\frac{\partial Z}{\partial T}\right)_{P,y} - P\left(\frac{\partial B}{\partial T}\right)_{P,y}\right\} \\
& - \left\{2\,\frac{A_i}{A} - \frac{B_i}{B}\right\}\left\{\ln\,\left(1+\frac{BP}{Z}\right)\right\}\left\{\frac{\partial\,(A^{2}/B)}{\partial T}\right\}_{P,y} \\
& - \frac{A^{2}}{B}\left\{2\,\frac{A_i}{A} - \frac{B_i}{B}\right\}\left\{\frac{\frac{P}{Z}\left(\frac{\partial B}{\partial T}\right)_{P,y} - \frac{BP}{Z^{2}}\left(\frac{\partial Z}{\partial T}\right)_{P,y}}{1+\frac{BP}{Z}}\right\}
\end{aligned} \qquad \text{(VII-13)}$$

where, using Redlich-Kwong equation

$$\left(\frac{\partial B}{\partial T}\right)_{P,y} = -\,\frac{B}{T} \qquad \text{(VII-14)}$$

$$\frac{\partial(A^2/B)}{\partial T}_{P,y} = -\frac{1.5A^2}{BT} \qquad \text{(VII-15)}$$

In order to be consistent, the term $\left(\frac{\partial Z}{\partial T}\right)_{P,y}$ was also evaluated from the Redlich-Kwong equation of state. The final expression for the term $(\partial Z/\partial T)_{P,y}$ is:

$$\left(\frac{\partial Z}{\partial T}\right)_{P,y} = \frac{1}{T}\left\{\frac{1.5k}{(j+1)} + \frac{j(j(j+1)^3+0.5k(j+1)^2(j-1)-kj(j+1)(j-1)^2-0.5k^2(j-1)^3)}{(j-1)(j+1)(-j^2(j+1)^2+k(j-1)^2(j+1)+kj(j-1)^2)}\right\} \qquad \text{(VII-16)}$$

where

$$j = 1/h = Z/BP \qquad \text{(VII-17)}$$

$$k = A^2/B \qquad \text{(VII-18)}$$

After calculating these differential terms, using equations (VII-14), (VII-15) and (VII-16), they were substituted in equation (VII-13) and the value of $\Delta\bar{H}_i^V$ was evaluated.

The values of the ideal gas state enthalpies of chloroform were taken from the JANAF reference mentioned earlier. Once $\Delta\bar{H}_1^V$ and H_1° were thus evaluated, the partial vapor enthalpy of chloroform, $\bar{H}_1^V$, was calculated, using equation (VII-12).

A computer program for the calculation of compressibility factor, Z; saturated vapor enthalpy for mixture, H_{mix}^V; and partial enthalpy for chloroform vapor at mixture dew point temperature $\bar{H}_1^V$; was written which is given in Appendix E. An IBM 1620 computer was used. Input and output data of the computer are also given in the appendix.

Result and Conclusions for the Consistency Test

After calculating various enthalpy terms and experimentally determining the equilibrium K-values, the consistency test was performed according to equation (VII-1). The value of K_1 at $x_1 = 0.0$ and the value of K_2 at $x_2 = 0.0$ becomes indeterminable, from experimental data. Thus, for the purpose of carrying on the consistency test, extrapolated K-values for above mentioned point were used.

For evaluating the left hand side of the equation (VII-1), the expression marked (VII-1a) was used. Calculations are given in Appendix F and results are given below

$$\int_{K_1 \text{ at } x_1 = 0.0}^{K_1 \text{ at } x_1 = 1.0} x_1 \, d \ln K_1 = -0.21765$$

$$\int_{K_1 \text{ at } x_1 = 0.0}^{K_1 \text{ at } x_1 = 1.0} x_2 \, d \ln K_2 = -0.34920$$

Total left hand side of the equation (VII-1) = -0.56685

Right hand side of equation (VII-1) = -0.59290

Difference = 0.02605

The difference between the right hand side and the left hand side of the equation (VII-1) is less than 5%. Considering the non-ideality of chloroform-benzene mixtures and the theoretical approach for the calculations of saturated vapor mixture enthalpies and partial vapor enthalpies, a 5% error for thermodynamic consistency test can be considered as fairly good. As such, experimental phase equilibria data of this work cannot be labeled as inaccurate. As explained earlier, passage of the consistency test does not necessarily mean that data are accurate beyond any doubt; however, the probability of their being wrong is greatly reduced.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

This study included experimental investigation of the isobaric integral heats of vaporization and simultaneous measurement of vapor-liquid equilibrium ratios for the chloroform-benzene system at the local barometric pressure. The experimental phase was accomplished with a flow calorimeter with a built-in equilibrium contact stage. Thus, the principal portion of the investigation was the design, construction of the apparatus and obtaining experimental data. Main conclusions are given below.

1. The experimental heat of vaporization method used is applicable to mixtures as well as to pure components. The chloroform-benzene system was investigated at the local barometric pressure.
2. The calculation method used for the analysis of heat leaks was applicable to the system and the apparatus as it enabled full accounting of all the heat input to the reboiler.
3. It was possible to analyze mixture samples from their refractive indices, accurate to 0.1 mole percent, or better, in composition.
4. The maximum deviation of the observed value of the isobaric integral heat of vaporization of a mixture

was less than 2% off the smoothed value, taken from the heat of vaporization vs. composition diagram. This indicates that results are consistent among themselves.

5. The heat leak was of the order of 4000 calories/hour which is excessive. The uncorrected heat of vaporization values were as much as 40% off the corrected values. This is very undesirable as it reduces the dgree of confidence on the reliability of the final corrected value.
6. The thermodynamic consistency test indicated that the heats of vaporization and vapor-liquid equilibria results are thermodynamically consistent.

Following are a few recommendations which are necessary for a more accurate set of data.

1. The still should be suitably modified in order to reduce the heat leak. This can be accomplished by vapor jacketing the still in the saturated vapor of a mixture, same in composition to the mixture inside the still. This would make the outside temperature of the still same as inside, thereby reducing the heat leak.
2. Though the reservoir had sufficient volume, the reservoir cross-section at the fluid surface was limited. Thus in order to eliminate liquid level fluctuation, the sample collection time had to be reduced to only two minutes. To eliminate this limitation, the reservoir must be redesigned.

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APPENDIX A

ORIGINAL EXPERIMENTAL DATA

Original experimental heat of vaporization and vapor-liquid phase equilibria data are given in Table A-I. Nomenclature for coded notations is given below.

TC - 1	Oil-Bath Thermocouple
TC - 2	Reservoir Thermocouple
TC - 3	Still-Reboiler Thermocouple
TC - 4	Still Equilibrium Stage Thermocouple
RI - 1	Refractive Index of Reservoir Liquid
RI - 2	Refractive Index of Equilibrium Tray Liquid
RI - 3	Refractive Index of the Condensate
V_1	Potential drop across standard 0.01 ohm resistance
V_2	Potential drop across standard 10.0 ohm resistance

TABLE A-I

ORIGINAL EXPERIMENTAL DATA

Run No.	Thermocouple emf Millivolts TC-1	TC-2	TC-3	TC-4	Refractive Index at 30°C RI-1	RI-2	RI-3	Potential Drop Volts V_1	V_2	Sample Mass Grams	Sample Collection Time
FOR PURE BENZENE, x_1 = 0.000											
5	4.160	4.120	4.110	4.120				0.01425	0.06817	9.79420	4'03.5"
6	4.155	4.120	4.110	4.120				0.01180	0.07920	13.71370	6'00"
7	4.157	4.107	4.110	4.120				0.01440	0.09740	23.34843	7'00"
8	4.170	4.150	4.130	4.150				0.00955	0.06100	13.67815	10'00"
9	4.170	4.150	4.130	4.150				0.01430	0.06600	14.94880	7'00"
10	4.170	4.150	4.130	4.150				0.01433	0.07125	12.00920	5'00"
FOR PURE CHLOROFORM, x_1 = 1.000											
11	3.150	3.130	3.130	3.133				0.01200	0.05582	16.01563	7'17"
12	3.150	3.135	3.130	3.135				0.01220	0.05570	17.31355	7'00"
13	3.150	3.133	3.125	3.135							
14	3.150	3.135	3.135	3.135				0.01305	0.10110	34.0245	6'00"
15	3.150	3.135	3.135	3.135				0.01477	0.11270	38.9643	6'00"
16	3.150	3.137	3.135	3.135				0.01487	0.11365	35.1019	5'00"
17	3.150	3.136	3.125	3.135				0.01296	0.10436	32.3550	6'00"
18	3.150	3.135	3.13	3.135				0.01542	0.11956	23.2013	3'00"
FOR MIXTURE, x_1 = 0.807											
19	3.352	3.286	3.405	3.409	1.449845	1.456708	1.449845	0.01030	0.08110	5.3062	2'00"
20	3.350	3.286	3.405	3.410	1.449845	1.456654	1.449845	0.01287	0.10056	9.3844	2'00"
21	3.357	3.286	3.407	3.409	1.449845	1.456654	1.449845	0.01400	0.11233	11.5905	2'00"
22	3.356	3.286	3.409	3.409	1.449845	1.456654	1.449845	0.014975	0.11607	13.0006	2'00"
FOR MIXTURE, x_1 = 0.603											
23	3.566	3.500	3.667	3.667	1.461126	1.468461	1.461126	0.01048	0.08100	4.8625	2'00"
24	3.566	3.500	3.667	3.667	1.461126	1.468408	1.461126	0.01300	0.10153	8.5712	2'00"
25	3.568	3.500	3.667	3.667	1.461126	1.468408	1.461126	0.01392	0.11213	10.5201	2'00"
26	3.560	3.500	3.665	3.667	1.461126	1.468408	1.461126	0.01552	0.12124	13.0024	2'00"
FOR MIXTURE, x_1 = 0.400											
27	3.817	3.747	3.850	3.852	1.472280	1.478429	1.472280	0.01030	0.08087	4.2615	2'00"
28	3.815	3.747	3.853	3.853	1.472280	1.478480	1.472280	0.01312	0.10295	7.9378	2'00"
29	3.815	3.747	3.852	3.853	1.472280	1.478480	1.472280	0.01407	0.11240	9.5790	2'00"
30	3.815	3.747	3.853	3.853	1.472280	1.478480	1.472280	0.01535	0.12075	11.5431	2'00"
FOR MIXTURE, x_1 = 0.205											
31	4.002	3.932	3.988	3.990	1.483029	1.486610	1.483029	0.01000	0.08085	3.7128	2'00"
32	4.000	3.932	3.990	3.990	1.483029	1.486660	1.483029	0.01280	0.10250	7.1105	2'00"
33	4.000	3.932	3.990	3.991	1.483029	1.486660	1.483029	0.01398	0.11230	8.8036	2'00"
34	4.001	3.932	3.987	3.991	1.483029	1.486660	1.483029	0.01520	0.12146	10.7143	2'00"

APPENDIX B

REFRACTIVE INDEX-COMPOSITION DIAGRAM

The measured quantities were the mass of chloroform and the mass of benzene in the standard mixture and its refractive index at 30°C temperature. For the refractive index-composition diagram, the composition was expressed as mole fraction chloroform in the mixture. Table B-I gives the original data as well as the calculated quantities for the refractive index-composition diagram. The refractive index was directly measured. Calculation for composition expressed as mole fraction chloroform in the mixture is given in the table.

Figure 14 gives the refractive index-composition diagram, for chloroform benzene mixtures at 30°C temperature, constructed from the data of Table B-I. This diagram was used as the standard reference for all the composition analysis of chloroform-benzene mixture samples.

TABLE B-I

ORIGINAL DATA AND CALCULATIONS FOR CONCENTRATION-REFRACTIVE INDEX DIAGRAM

Sample	Mass Chloroform gms.	Mass Benzene gms.	Moles Chloroform gm. moles	Moles Benzene gm. moles	Moles Total gm. moles	Mole Fraction Chloroform	Refractive Index at 30°C
1			Pure Chloroform			1.00000	1.43925
2	39.98810	2.59230	0.33493	0.03318	0.36811	0.90986	1.44428
3	35.42030	5.21150	0.29667	0.06672	0.36339	0.81369	1.44951
4	30.91720	7.84123	0.25895	0.10038	0.35933	0.72064	1.45476
5	26.48425	10.47055	0.22182	0.13404	0.35586	0.62333	1.46011
6	22.11110	13.05040	0.18520	0.16707	0.35227	0.52573	1.46544
7	17.73985	15.75383	0.14858	0.20168	0.35026	0.42419	1.47106
8	13.24270	18.32068	0.11091	0.23454	0.34545	0.32105	1.47668
9	8.82200	21.02660	0.07389	0.36919	0.34308	0.21537	1.48250
10	4.49395	23.48451	0.03764	0.30065	0.33829	0.11126	1.48841
11			Pure Benzene			0.00000	1.49455

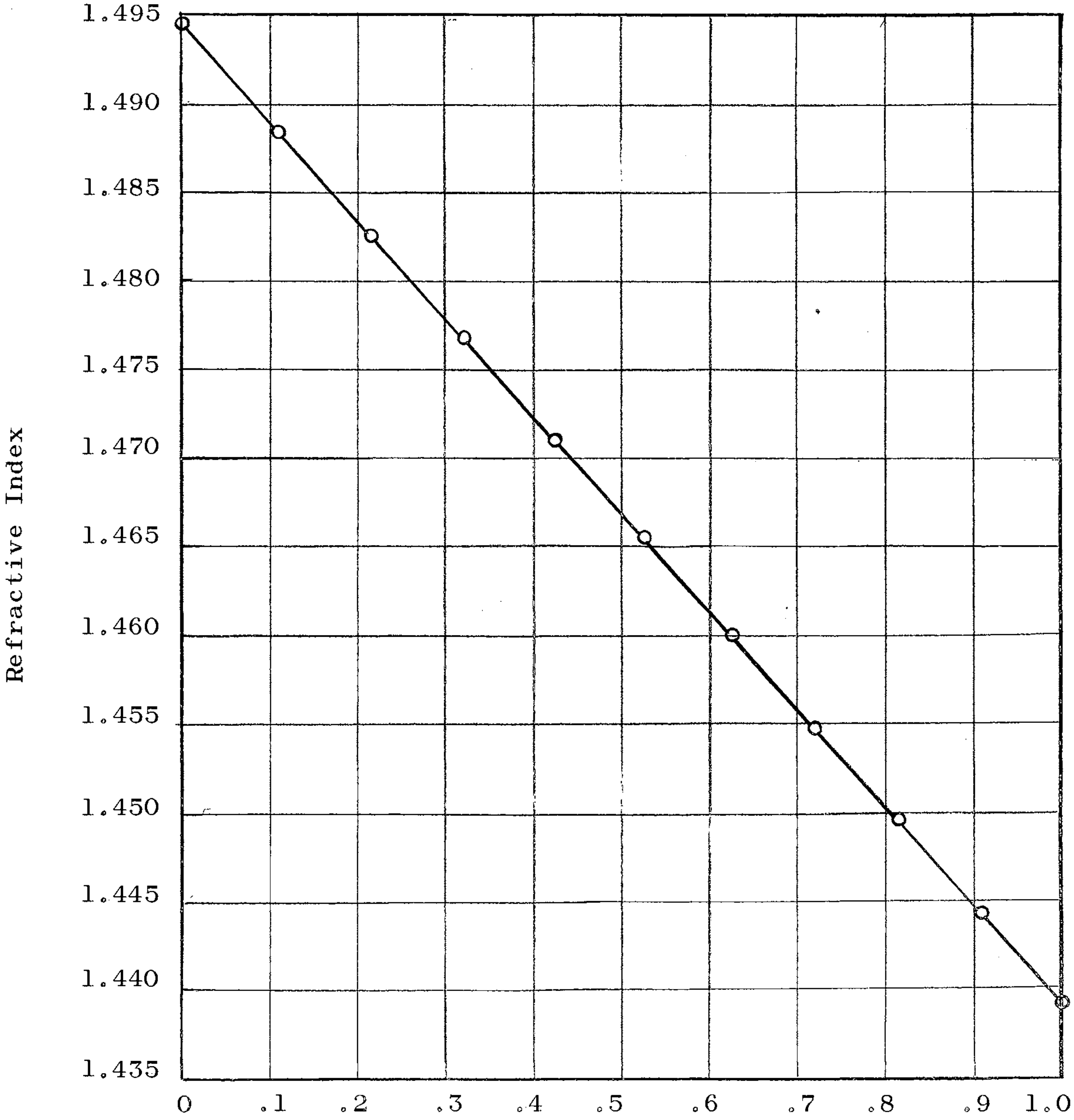

Figure 14

Refractive Index-Concentration Diagram for Chloroform-Benzene Mixtures at 30°C

APPENDIX C

VAPOR-LIQUID PHASE EQUILIBRIA DATA

Original data are given in Table A-I. Equilibrium temperature was calculated from the emf of the equilibrium stage thermocouple, TC - 4, using standard reference tables for iron-constantan thermocouples. The equilibrium liquid composition, x_1, expressed as mole fraction chloroform in the mixture, was calculated from the measured value of its refractive index, RI - 2; and the equilibrium vapor composition, y_1, expressed as mole fraction chloroform in the mixture, was found from the refractive index of the condensate, RI - 3. Both of these compositions were found from the measured refractive indices by using the standard composition-refractive index diagram given in Appendix B, also, where TC - 4, RI - 2, and RI - 3 refer to Table A-I. Values thus calculated, for the equilibrium temperature and compositions, are given in Table I; Figure 7 gives a diagram of the same.

Starting from the temperature and composition data of Table I, the vapor-liquid equilibrium ratios, for chloroform and benzene at the equilibrium temperature, were calculated using the following equations.

Equilibrium K-value for chloroform in benzene, $K_1 = y_1/x_1$

Equilibrium K-value for benzene in chloroform, $K_2 = y_2/x_2$

$= (1-y_1)/(1-x_1)$

Values thus calculated at the various equilibrium temperatures are also included in the Table I; Figure 8 and 9 give K-value vs temperature diagrams for the same. Figure 15 gives the y-x diagram for the chloroform-benzene system at local barometric pressure, about 740 mm Hg.

Table C-I gives published (23) vapor-liquid phase equilibria data for the chloroform-benzene system at 760 mm Hg.

TABLE C-I

VAPOR-LIQUID EQUILIBRIUM DATA
FOR CHLOROFORM-BENZENE SYSTEM AT 760 mm Hg

Temp. °C	x_1	y_1	K_1	K_2
62.6	.934	.968	1.025	.485
64.1	.853	.922	1.080	.530
65.4	.783	.875	1.115	.576
67.0	.700	.814	1.162	.620
68.3	.637	.762	1.197	.655
69.7	.570	.702	1.232	.693
70.8	.517	.652	1.260	.720
71.6	.467	.601	1.287	.749
72.2	.443	.570	1.287	.772
73.3	.388	.508	1.310	.804
74.4	.333	.443	1.330	.835
74.7	.318	.429	1.350	.838
75.7	.266	.361	1.355	.870
76.2	.229	.316	1.380	.887
76.9	.193	.270	1.400	.905
77.9	.133	.190	1.428	.935
78.4	.116	.167	1.440	.943
79.0	.068	.100	1.470	.965
79.2	.060	.089	1.480	.970

Reference: Reinders and Minjer (23)

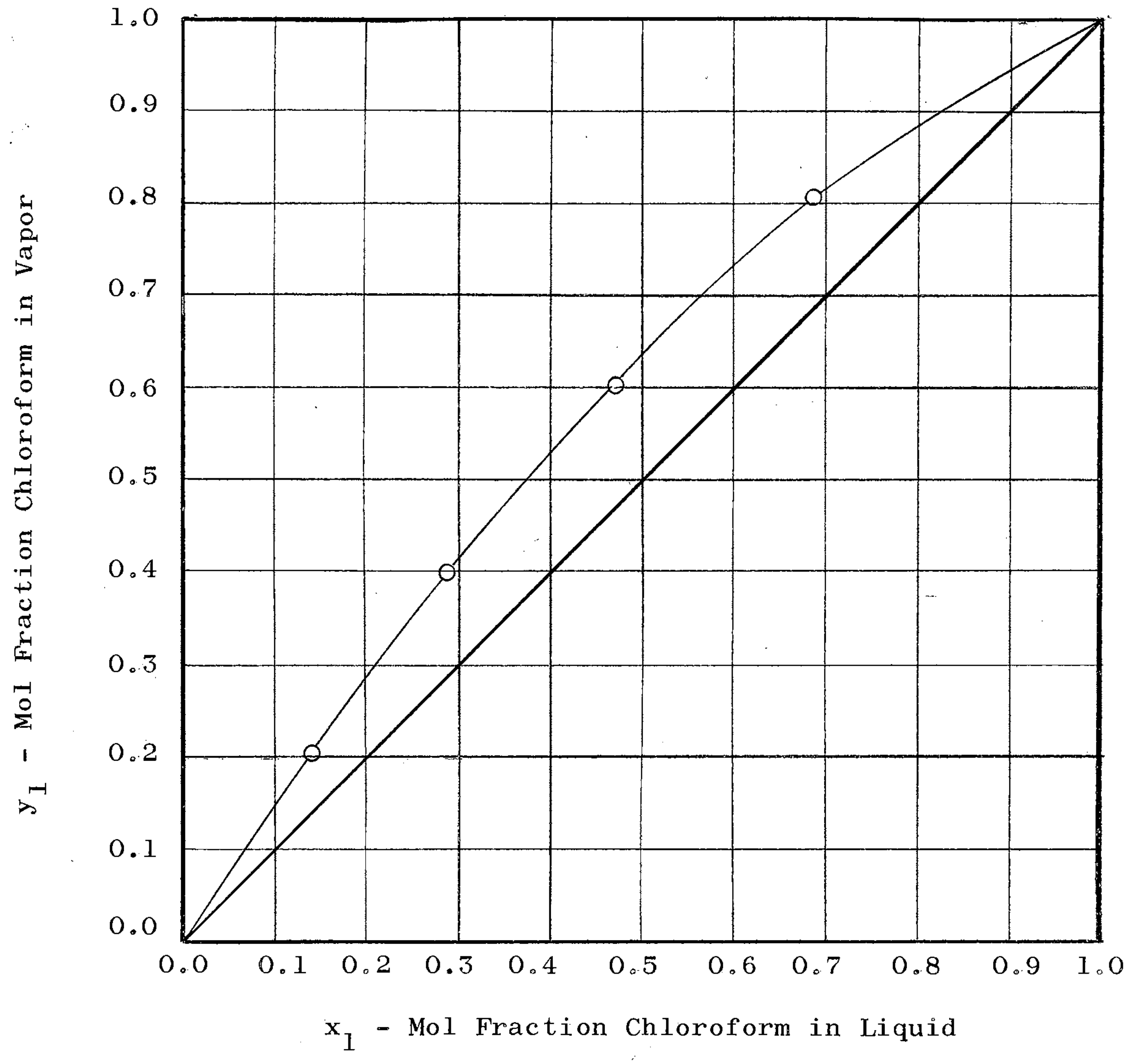

Figure 15

y - x Diagram for Chloroform-Benzene System at 740 mm Hg.

APPENDIX D

CALCULATIONS FOR HEATS OF VAPORIZATION

Original data are given in Table A-I. Table D-I gives electrical energy input in watts, flow rate, i.e., rate of vaporization in gms/min for various runs. Sample calculations for these quantities are given here.

Electrical Energy Input

Run No. 25

Potential drop V_1 = 0.01392 volts

Potential drop V_2 = 0.11213 volts

Total current through the circuit, I_1 = V_1/R_1

= 0.01392/0.01

= 1.392 amps

Current through the branch line containing three standard resistances

I_2 = V_2/R_2

= 0.11213/10.0

= 0.011213 amps

Current through the reboiler heater, I = Total circuit current - current through the branch line

= $I_1 - I_2$ amps

= 1.392000 - 0.011213 amps

= 1.380787 amps

Potential drop across the reboiler, V = Potential drop across the branch line

= I_2 x resistance of the branch line

= I_2 x (10 + 1000 + 1000) volts

= 0.011213 x 2010 volts

= 22.53813 volts

Electrical energy input to the reboiler heater = V x I watts

= 22.53813 x 1.380787

= 21.1052 watts

<u>Flow Rate</u>

Run No. 25

Mass of the Sample = 10.5201 gms

Collection Time = 2'00"

Flow rate = 10.5201/2.00

= 5.26005 gms/min

Figure 16 to 21 gives flow rate vs. power input plots. For each mixture composition, a straight line curve fit between energy input in watts (x - axis) and flow rate in grams/minute (y - axis) was made by the method of least squares. The reciprocal slope in (watt - minute)/gram and intercept for zero flow rate in watts was calculated and results are included in Table D-I.

Isobaric integral heats of vaporization and heat leaks were calculated from the above mentioned reciprocal slope and the intercept, respectively. Sample calculations for both are given here.

TABLE D-I

HEAT OF VAPORIZATION CALCULATIONS

Run No.	$x_1$mole fr. Chloroform	Abscissa Power Input watts	Ordinate Evp.Rate gms/min	Reciprocal Slope watt-min/gr	Intercept watts
5	0.000	19.42	2.4120		
8	0.000	13.88	1.3678		
9	0.000	18.88	2.1355		
10	0.000	20.42	2.4018	6.43182	5.0646
11	1.000	13.40	2.200		
16	1.000	33.87	7.202		
17	1.000	26.98	5.392		
18	1.000	36.80	7.734	4.17026	4.2167
19	0.807	16.66	2.6531		
20	0.807	25.81	4.6922		
21	0.807	31.39	5.7952		
22	0.807	34.37	6.5003	4.64021	4.2670
23	0.603	16.94	2.4312		
24	0.603	26.33	4.2856		
25	0.603	31.11	5.2600		
26	0.603	37.53	6.5012	5.04754	4.6604
27	0.400	16.61	2.1307		
28	0.400	26.91	3.9689		
29	0.400	31.54	4.7895		
30	0.400	36.96	5.7715	5.59482	4.7017
31	0.205	16.21	1.8564		
32	0.205	26.18	3.5552		
33	0.205	31.30	4.4018		
34	0.205	36.81	5.3571	5.92237	5.1410

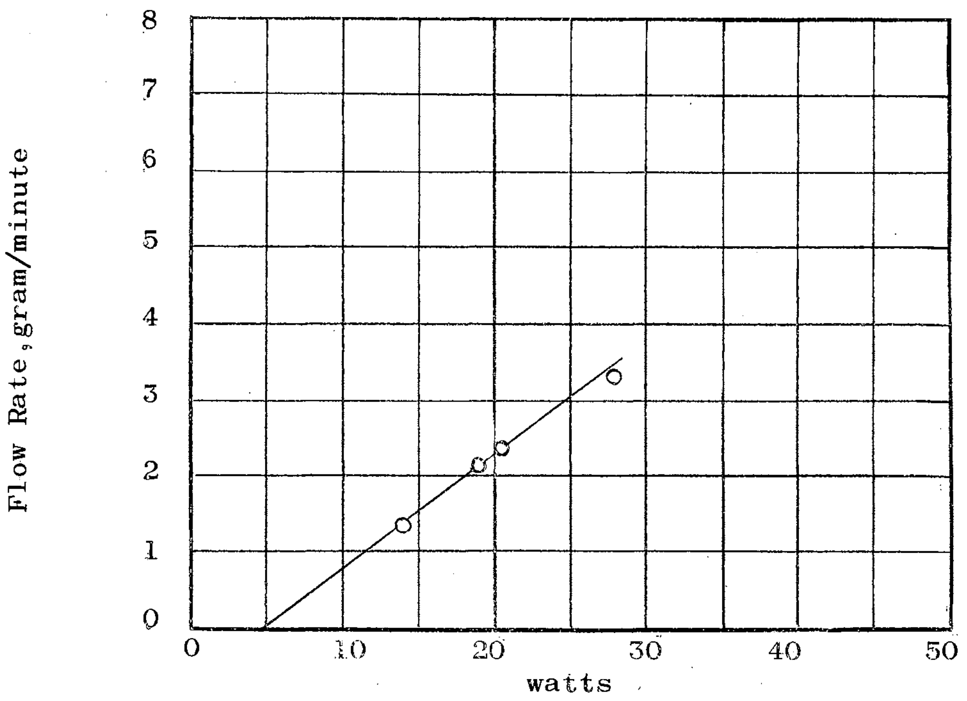

Figure 16

Rate of Vaporization-Heat Input Diagram for Pure Benzene, $x_1 = 0.00$

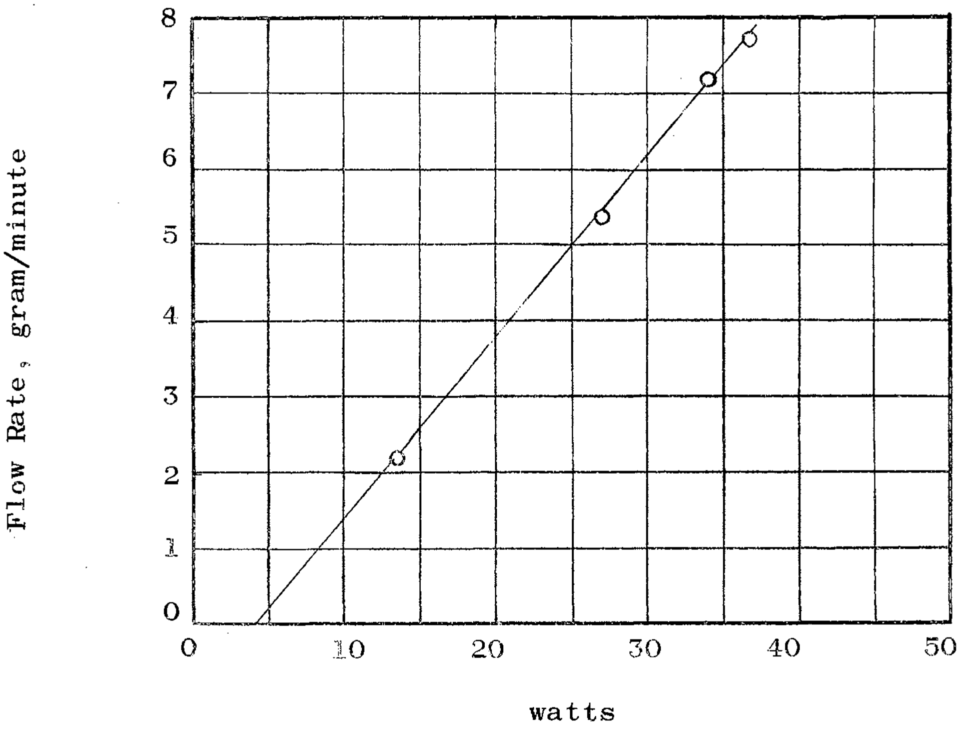

Figure 17

Rate of Vaporization-Heat Input Diagram for Pure Chloroform, $x_1 = 1.00$

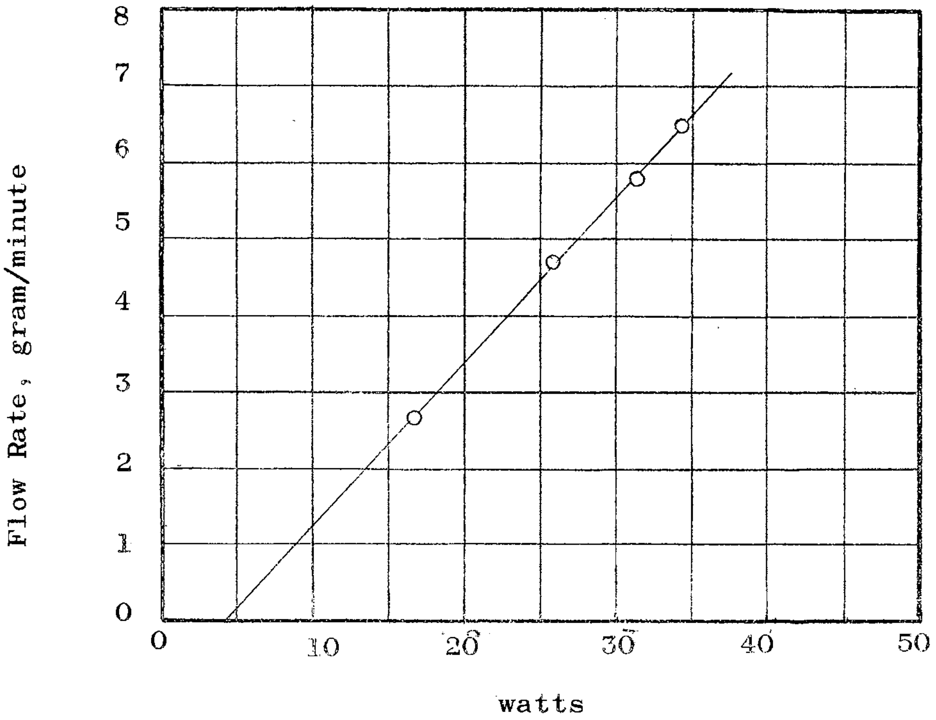

Figure 18

Rate of Vaporization-Heat Input Diagram for Mixture, $x_1 = 0.807$

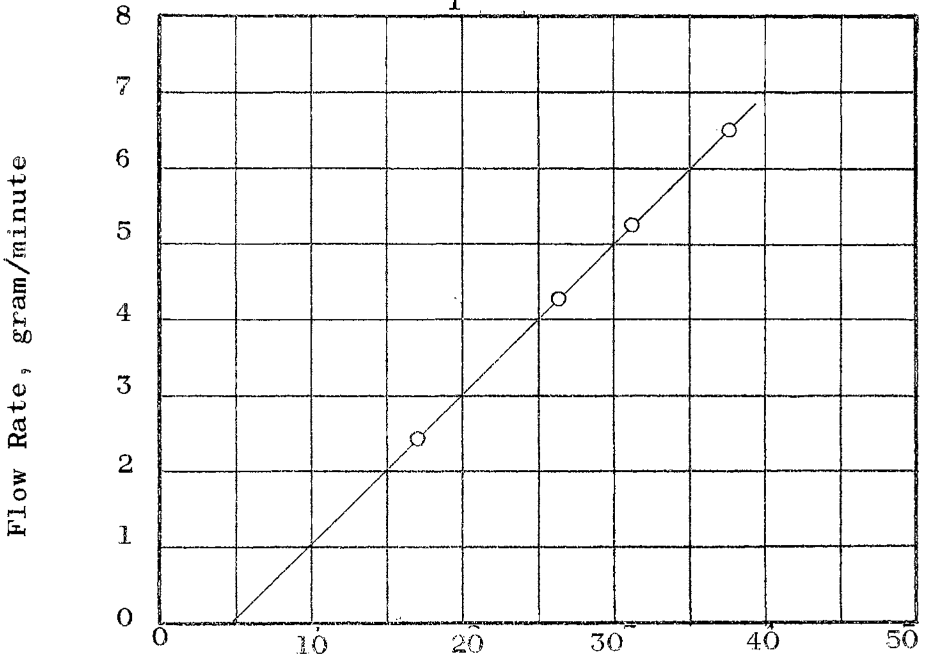

Figure 19

Rate of Vaporization-Heat Input Diagram for Mixture, $x_1 = 0.603$

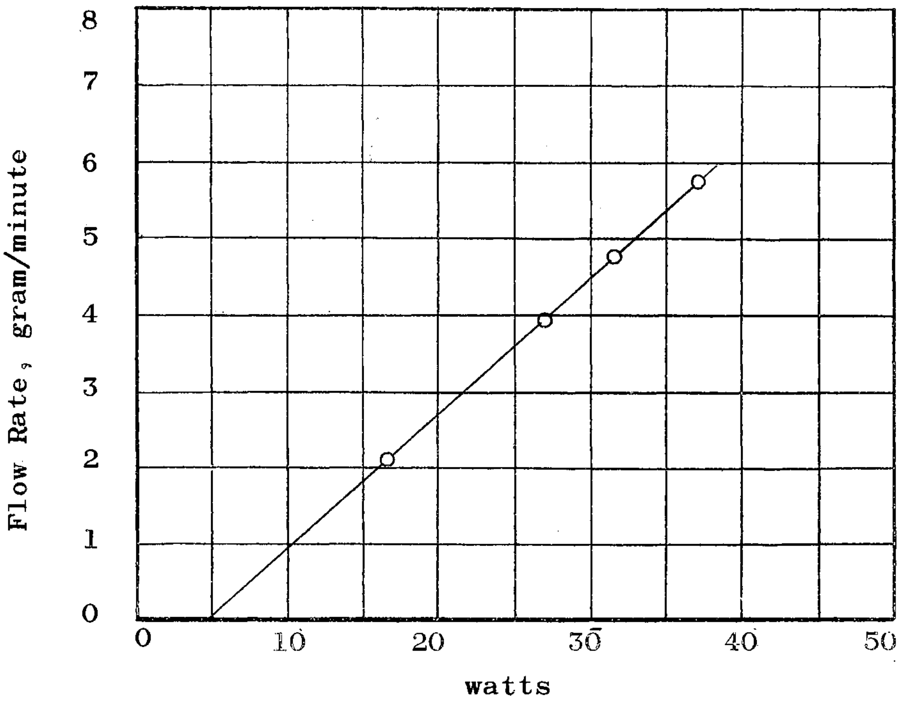

Figure 20

Rate of Vaporization-Heat Input Diagram for Mixture, $x_1 = 0.400$

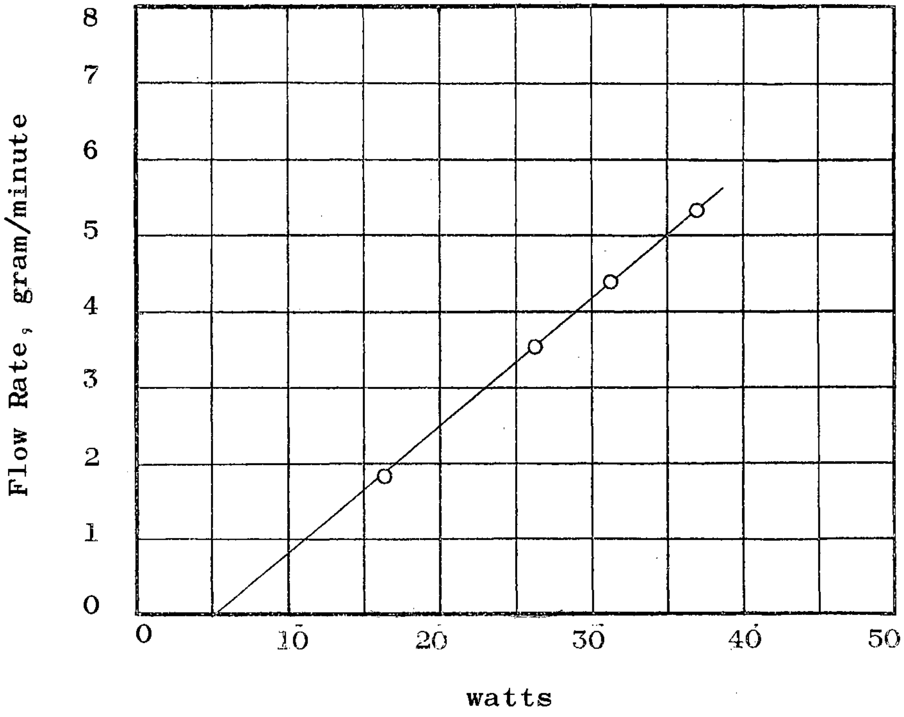

Figure 21

Rate of Vaporization-Heat Input Diagram for Mixture, $x_1 = 0.205$

Isobaric Integral Heat of Vaporization for Mixture, $x_1 = 0.603$

Reciprocal slope = 5.04754 watt-min/gram

= 5.04754 x 14.343

= 72.43215 cal/gram

Molecular weight of the mixture

$= 119.39z_1 + 78.1\ (1-x_1)$

$= 78.1 + 41.29\ x_1$

$= 78.1 + 41.29 \times 0.603$

$= 78.1 + 24.9$

$= 103.0$

Isobaric integral heat of vaporization

= 72.43215 x 103.0

= 8736.25 cal/gram mol.

Heat Leak for Mixture, $x_1 = 0.603$

Intercept = 4.6604 watts

= 4.6604 x 14.343 cal/min

= 4.6604 x 14.343 x 60 cal/hr

Heat leak = 4010.7 cal/hr.

Table II contains calculated values of isobaric integral heats of vaporization and heat leaks.

Uncorrected Heat of Vaporization, $x_1 = 0.603$, Run No. 25

The uncorrected heat of vaporization

$$= \frac{\text{(Power)(Time)}}{\text{(Mass of Condensate)}}\ \text{(watt-minute)/gram}$$

$$= \frac{31.1052 \times 2.00}{10.4201} = 5.91347\ \frac{\text{watt-min}}{\text{gram}}$$

= 14.343 x 5.91347 = 84.8169 cal/gram

= 84.8169 x 103.0 = 8736.25 cal/gram mole

TABLE D-II

CALCULATIONS FOR UNCORRECTED HEAT OF VAPORIZATION

Run No.	Power Input watts	Flow Rate gms/min	Reciprocal Flow Rate min/gm	Uncorrected H cal/gm mol
23	16.94	2.43125	0.4113	10281.46
24	26.33	4.28560	0.2333	9065.85
25	31.11	5.26005	0.1901	8736.25
26	37.53	6.50120	0.1538	8518.40

Heat Leak Comparison with Published Data

For $x_1 = 0.603$

Run No. 23, 24, 25, and 26.

Heat leak, $q = 4010.7$ cal/hr

Temperature gradient, ΔT

= still temperature-room temperature

= 70.25-25.0

= 45.25°C

Area available for heat transfer*, A

$= \pi d\ l + \pi d^2/4$

$= \pi\ (8\ \text{cm})(20\text{cm}) + \pi\ (8 \times 8\ \text{cm}^2)/4$

$= 552\ \text{cm}^2$

*The heat transfer area considered above is the area of the still neglecting the condenser and other connections. Thermocouple wells are also neglected. The heat transfer by conduction through glass is not accounted for. In the above expression d is the diameter and l is the length of the still.

Overall heat transfer coefficient, U

$= q/A\Delta T$

$= 4010.7/552 \times 45.25$ cal/hr cm^2°C

$= 0.16057$ cal/hr cm^2°C

Published literature data taken from a paper by White and Hutchinson (34) for a standard glass dewar with hemispherical bottom are given below:

Diameter, d = 2.8 cm

Length, l = 10 cm

Water content, m = 40 grams

Heat loss $= 0.0078°C/(°C\Delta T)(min)$

Heat loss, $(q/\Delta T) = 40 \times 1 \times 0.0078 \times 60$ cal/hr°C

Heat transfer area, A

$= \pi d\, l + 0.5\, \pi\, d^2$

$= \pi\ (2.8\ cm)(10cm) + 0.5\, \pi\ (2.8 \times 2.8\ cm^2)$

$= 100.23\ cm^2$

Overall heat transfer coefficient, U

$= q/A\Delta T$

$= 40 \times 1 \times 0.0078 \times 60/100.23$ cal/hr cm^2°C

$= 0.20233$ cal/hr cm^2°C

The published value of overall heat transfer coefficient for vacuum jacketed, silver coated glass apparatus compares favorably with the value calculated from data of the present work.

APPENDIX E

ENTHALPY CALCULATIONS

Table E-1 gives ideal gas state enthalpies for chloroform and benzene at various temperatures, source, reference (16) and (1) respectively, Figure 22 gives plots for the same.

An IBM-1620 computer program for the calculation of saturated vapor enthalpy, H^{V}_{mix}, partial vapor enthalpy for chloroform at the dew point temperature, $\bar{H}^{V}_{1}$, and the ideal gas state mixture enthalpy at the dew point temperature is also given here along with input and output data. Critical constants for the components were taken from Kobe (17).

The following codes were used for the computer program. They are listed in the order in which they appear in the program. Immediately following this listing is a listing of the computer program, then input data, and lastly, computer output data.

TC(I)	Critical temperature of component (I), °K.
PC(I)	Critical pressure of component (I), atm.
I = 1	Chloroform.
I = 2	Benzene.
P	System pressure, atm.
T	Dew point temperature of the mixture, °K.
Y	Mole fraction chloroform in the vapor mixture.
HIDL1	Ideal gas state enthalpy of chloroform at temperature T, cal/gram mole.

TABLE E-I

IDEAL GAS STATE ENTHALPIES FOR CHLOROFORM AND BENZENE

Temp. °K	$(H^\circ - H^\circ_o)$ Chloroform k.cal/gm mol	$(H^\circ - H^\circ_o)$ Benzene k.cal/gm mol
Source	Ref. (16)	Ref. (1)
0	0.000	0.000
100	0.836	-----
200	1.975	-----
298.16	3.390	3.401
300	3.419	3.437
400	5.104	5.762
500	6.967	8.750

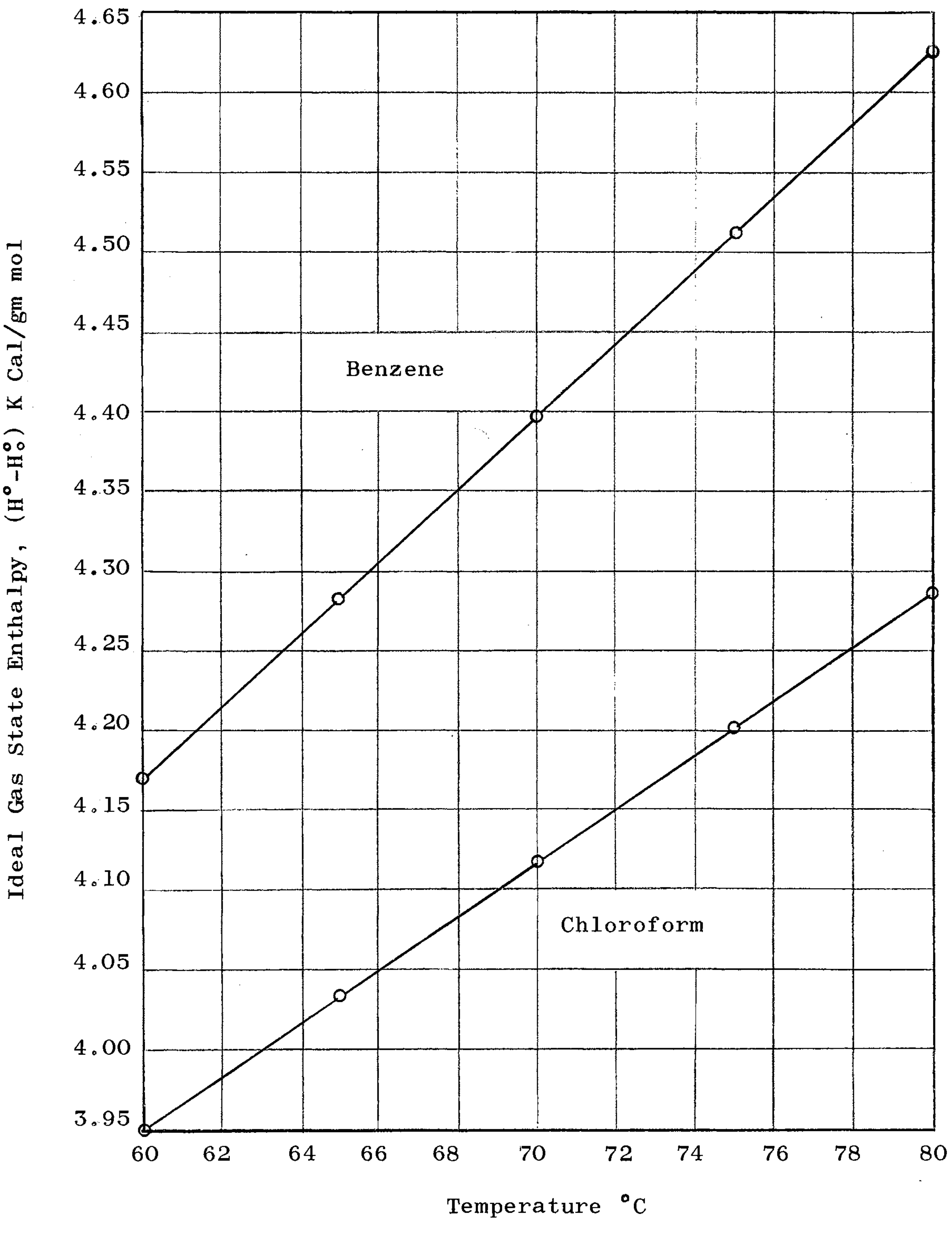

Figure 22

Ideal Gas State Enthalpy - Temperature Diagram
for Chloroform and Benzene

HIDL2	Ideal gas state enthalpy of benzene at temperature T, cal/gram mole.
AA(I)	A^2 of Redlich-Kwong equation for component (I) at T,P.
A(I)	A of Redlich-Kwong equation for component (I) at T, P.
B(I)	B of Redlich-Kwong equation for component (I) at T, P.
AMIX	A of Redlich-Kwong equation for the mixture Y at T, P.
BMIX	B of Redlich-Kwong equation for the mixture Y at T, P.
ZU	Upper limit of the compressibility factor, Z.
ZL	Lower limit of Z.
LOOP	Number of times the calculation repeated for convergence.
ZM	Mean value of Z, also assumed value of Z for further calculations.
HM	h of Redlich-Kwong equation, based on ZM.
AADB	A^2/B.
ZCAL	Calculated value of Z.
ZDEL	Difference between the calculated and assumed value of Z.
Z	Final converged value of Z.
H	Final value of h.
DELHM	Mixture vapor enthalpy difference, $(H^V_{mix} - H^o_{mix})$,cal/gram mole.
ZTPY	Partial of Z with respect to T at constant pressure and composition $(\partial Z/\partial T)_{P,Y}$, $(^\circ K)^{-1}$
DELHP	Partial vapor enthalpy difference for chloroform, $(\bar{H}^V_1 - H^o_1)$ cal/gram mole.
HIDLM	Ideal state gas enthalpy for the mixture Y at temperature T.
HVM	Saturated vapor enthalpy for the mixture, cal/gram mole.
PHV	Partial vapor enthalpy for chloroform at T,P, cal/gram mole.

Codes used for intermediary calculation steps have been omitted from the above listing.

```
C      IBM 1620 PROGRAM FOR THE CALCULATION OF IDEAL GAS STATE ENTHALPY,
C      VAPOR ENTHALPY, PARTIAL VAPOR ENTHALPY AND Z FOR SATURATED VAPOR
C      VIA REDLICH - KWONG EQUATION OF STATE, FOR BINARY MIXTURES ONLY
       DIMENSION TC(10), PC(10), AA(30), A(30), B(30)
       PUNCH 1
    1  FORMAT (7X1HT9X3HPHV8X3HHVM7X5HHIDLM7X1HY8X1HZ5X4HLOOP)
       DO 2 I= 1,2
    2  READ 3, TC(I), PC(I)
    3  FORMAT (F9.3, F6.3)
    4  READ 5, P, T, Y, HIDL1, HIDL2
    5  FORMAT (F10.3, F10.3, F10.3, F10.3, F10.3)
       DO 6 I= 1,2
       AA(I) = 0.4278*(TC(I)**2.5)/(PC(I)*(T**2.5))
       A(I)  = SQRTF(AA(I))
    6  B(I)  = 0.0867*TC(I)/(PC(I)*T)
       AMIX  = A(1)*Y + A(2)*(1.0-Y)
       BMIX  = B(1)*Y + B(2)*(1.0-Y)
       ZU    = (BMIX*P) + 3.0
       ZL    = (BMIX*P)
       LOOP  = 0
    7  LOOP  = LOOP + 1
       ZM    = (ZU + ZL)/2.0
       HM    = (BMIX*P)/ZM
       AADB  = (AMIX*AMIX)/BMIX
       ZCAL  = (1.0/(1.0-HM)) - (AADB*(HM/(1.0+HM)))
       ZDEL  = ZCAL - ZM
       IF (ABSF(ZDEL)-0.0001) 12,12,8
    8  IF (LOOP - 100) 9,9,12
    9  IF (ZDEL) 10,12,11
   10  ZU    = ZM
       GO TO 7
   11  ZL    = ZM
       GO TO 7
   12  Z     = ZM
       H     = (BMIX*P)/Z
       DELHM = -1.9872*T*(1.5*AADB*(LOGF(1.0+H))+1.0-Z)
       R     = AADB
       S     = 1.0/H
       U     = (S+1.0)
       W     = (S-1.0)
       Q1    = (1.5*R)/U
       Q2    = S*((S*U*U*U)+(0.5*R*U*U*W)-(R*S*U*W*W)-(0.5*R*R*W*W*W))
       Q3    = W*U*((R*W*W*U)-(S*S*U*U)+(R*S*W*W))
       ZTPY  = (Q1+(Q2/Q3))/T
       AR    = A(1)/AMIX
       BR    = B(1)/BMIX
       Q4    = BR*ZTPY
       Q5    = (ZTPY+((H*Z)/T))/(Z*(H-1.0))
       Q6    = ((2.0*AR)-BR)*(LOGF(1.0+H))*((1.5*R)/T)
       Q7    = R*((2.0*AR)-BR)*((H/T)+((H*ZTPY)/Z))/(1.0+H)
       DELHP = -1.9872*T*T*(Q4 + Q5 + Q6 + Q7)
       HIDLM = Y*HIDL1 + (1.0-Y)*HIDL2
       HVM   = DELHM + HIDLM
       PHV   = DELHP + HIDL1
       PUNCH 13, T, PHV, HVM, HIDLM, Y, Z, LOOP
   13  FORMAT (F11.3, F11.3, F11.3, F11.3, F9.3, F9.3, I6)
       GO TO 4
       END
```

```
C     INPUT DATA CARDS FOR THE ENTHALPY CALCULATION PROGRAM
C TC(I)  PC(I)
 536.60 54.00
 562.66 48.66
C   P           T           Y          HIDL1      HIDL2
 0.971       333.66      1.000      3957.500   4190.000
 0.971       335.16      0.942      3983.000   4212.000
 0.971       337.16      0.861      4016.500   4257.500
 0.971       339.16      0.787      4050.000   4302.000
 0.971       341.16      0.706      4084.000   4349.000
 0.971       343.16      0.615      4117.000   4394.500
 0.971       345.16      0.518      4151.500   4440.000
 0.971       347.16      0.375      4185.000   4486.000
 0.971       349.16      0.230      4218.500   4532.000
 0.971       351.16      0.077      4252.000   4579.000
 0.971       352.46      0.000      4275.000   4608.000
```

Computer output data

```
    T          PHV         HVM        HIDLM        Y         Z     LOOP
 333.660    3916.467    3916.468    3957.500    1.000      .976    14
 335.160    3942.267    3955.013    3996.282     .942      .976    14
 337.160    3976.169    4008.265    4049.999     .861      .976    11
 339.160    4010.072    4061.645    4103.676     .787      .976    11
 341.160    4044.478    4119.413    4161.910     .706      .976    14
 343.160    4077.891    4180.816    4223.837     .615      .976    13
 345.160    4112.810    4246.975    4290.557     .518      .976    14
 347.160    4146.771    4328.583    4373.125     .375      .975    14
 349.160    4180.752    4414.243    4459.895     .230      .975     8
 351.160    4214.761    4507.004    4553.821     .077      .974    14
 352.460    4238.075    4560.684    4608.000     .000      .974    12
```

Figure 23 gives a plot of mixture ideal gas state enthalpy, vs. composition, for saturated chloroform-benzene vapor at 740 mm Hg. Table E-II gives saturated vapor and saturated mixture enthalpies for chloroform-benzene system at 740 mm Hg. and Figure 24 gives a plot of the same. Figure 25 gives a plot of partial vapor enthalpy for chloroform at dew point vs. concentration, for chloroform-benzene system at 740 mm Hg.

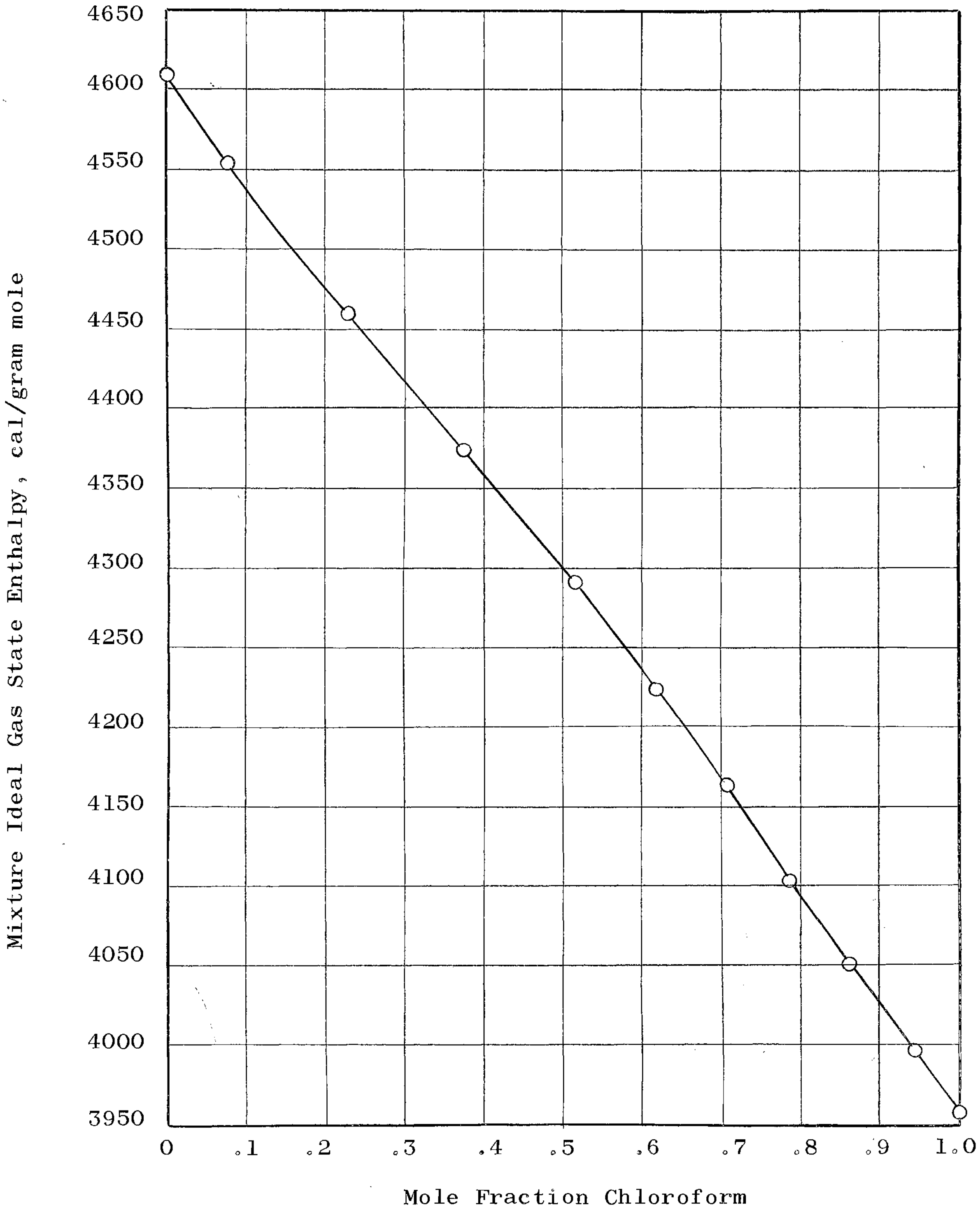

Figure 23

Mixture Ideal Gas State Enthalpy-Composition Diagram for Saturated Chloroform-Benzene Vapor at 740 mm Hg

TABLE E-II

SATURATED ENTHALPIES FOR CHLOROFORM-BENZENE MIXTURES AT 740 mm Hg.

Mol Fraction Chloroform x_1	H^V_{mix} cal/gm mol	ΔH_{mix} Isobaric Integral cal/gm mol	H^L_{mix} cal/gm mol
0.000	4560.7	7205.7	2645.0
0.205	4427.0	7349.0	2922.0
0.400	4315.0	7586.7	3271.7
0.603	4188.0	7451.8	3263.8
0.807	4042.0	7405.2	3363.2
1.000	3916.5	7148.7	3232.2

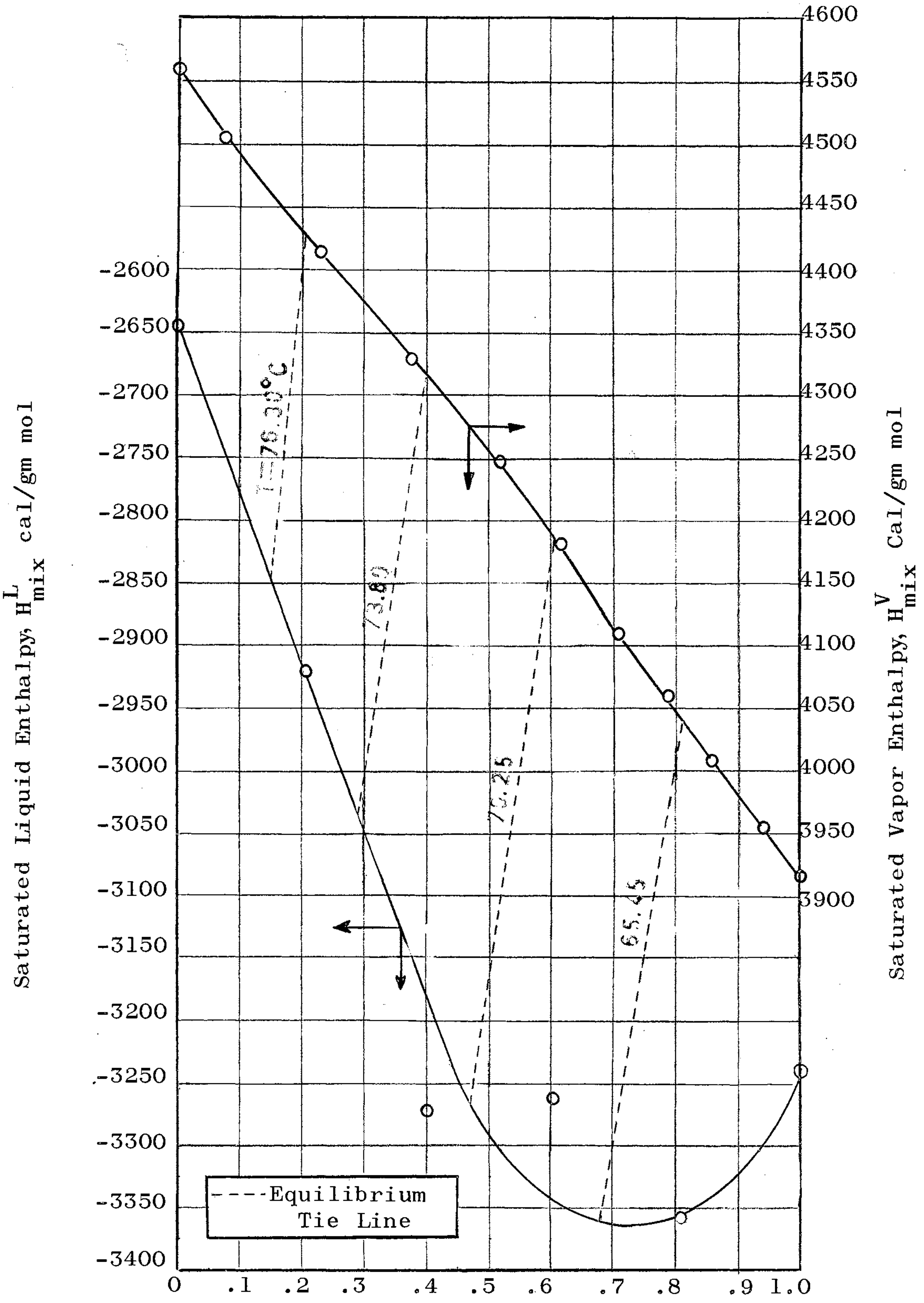

Figure 24

Enthalpy-Concentration Diagram
for Chloroform-Benzene System at 740 mm Hg.

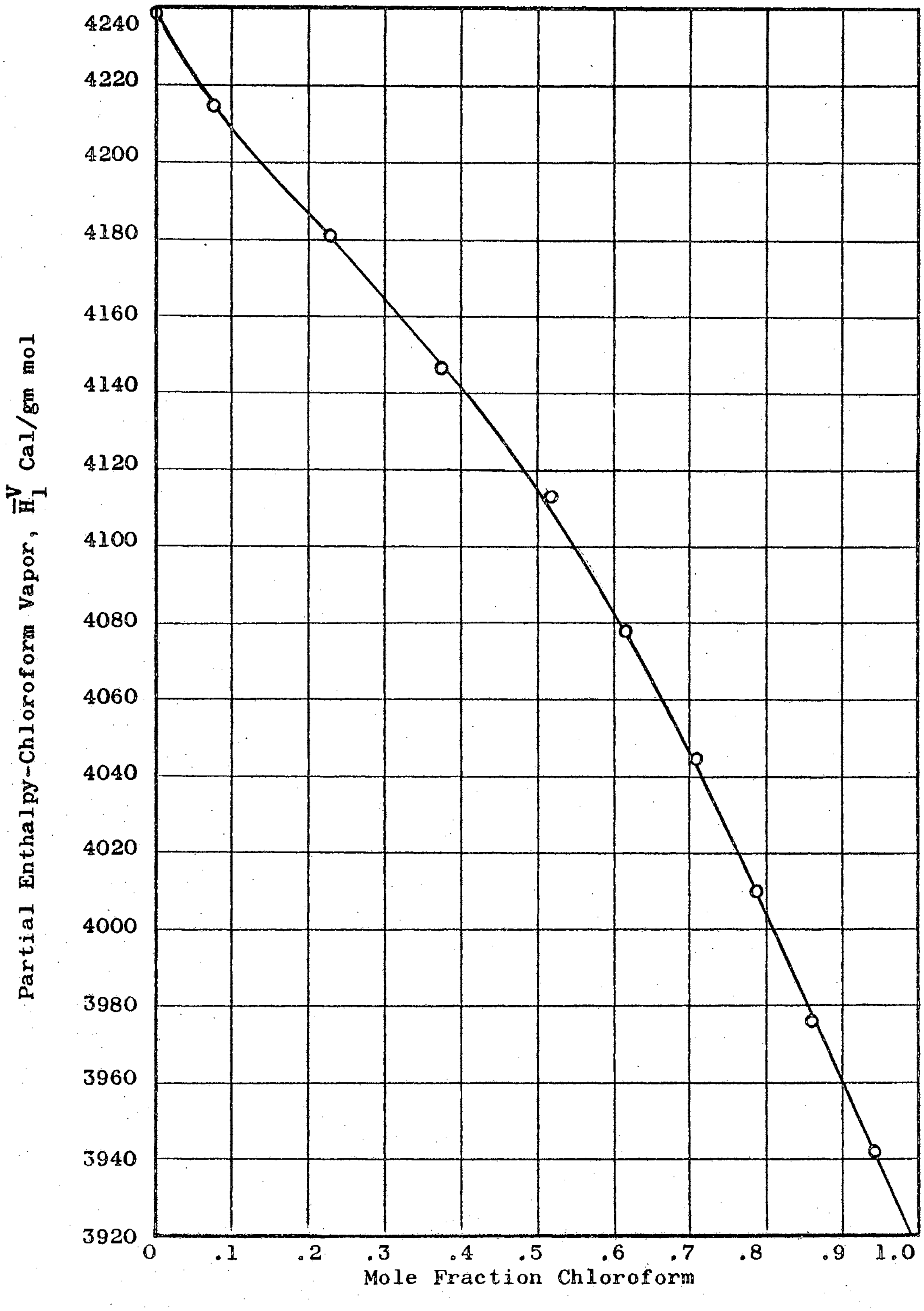

Figure 25

Partial Enthalpy of Chloroform Vapor at Dew Point vs. Concentration of Chloroform in Chloroform-Benzene System at 740 mm Hg

APPENDIX F

CALCULATIONS FOR THE CONSISTENCY TEST

Table F-I gives calculation for

$$\int_{K_1 \text{ at } x_1 = 0.0}^{K_1 \text{ at } x_1 = 1.0} x_1 \, d \ln K_1$$

and

$$\int_{K_2 \text{ at } x_1 = 0.0}^{K_2 \text{ at } x_1 = 1.0} x_2 \, d \ln K_2$$

Both these integrals were calculated graphically. The value of K_1 and K_2 becomes undeterminable at $x_1 = 0.0$ and $x_1 = 1.0$, respectively. Thus for these points, extrapolated values were used. Figure 26 gives x_1 vs $\ln K_1$ diagram and Figure 27 gives x_2 vs $\ln K_2$ diagram, for the graphical integration. Next, the following integral was evaluated.

$$\int_{T \text{ at } x_1 = 0.00}^{T \text{ at } x_1 = 1.00} (\text{RATIO}) \, dT$$

TABLE F-I

CALCULATIONS FOR THE CONSISTENCY TEST

		Chloroform			Benzene	
T°C (B.P.)	x_1	K_1	$\ln K_1$	x_2	K_2	$\ln K_2$
79.3	0.00	---	.415	1.00	1.000	.000
77.0	0.10	1.457	.378	0.90	.947	-.0545
75.3	0.20	1.406	.341	0.80	.989	-.1077
73.45	0.30	1.359	.307	0.70	.843	-.171
71.75	0.40	1.317	.277	0.60	.793	-.232
69.55	0.50	1.270	.239	0.50	.730	-.315
67.3	0.60	1.224	.202	0.40	.663	-.411
65.1	0.70	1.172	.159	0.30	.598	-.514
63.3	0.80	1.117	.111	0.20	.546	-.605
61.8	0.90	1.057	.055	0.10	.502	-.690
60.5	1.00	1.000	.000	0.00	---	-.775

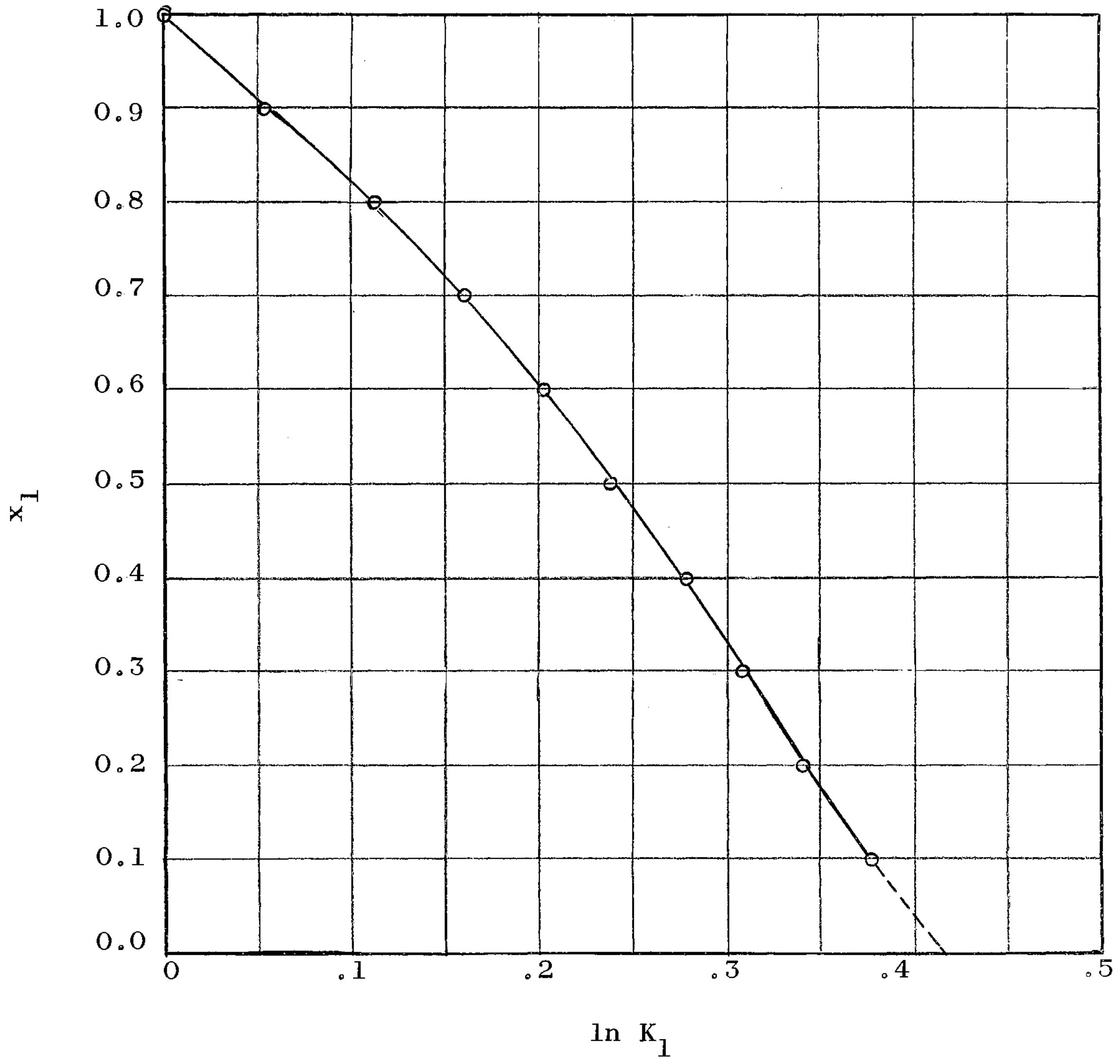

Figure 26

x_1 - ln K_1 Diagram for Thermodynamic Consistency Test

Value of Integral = -0.21768

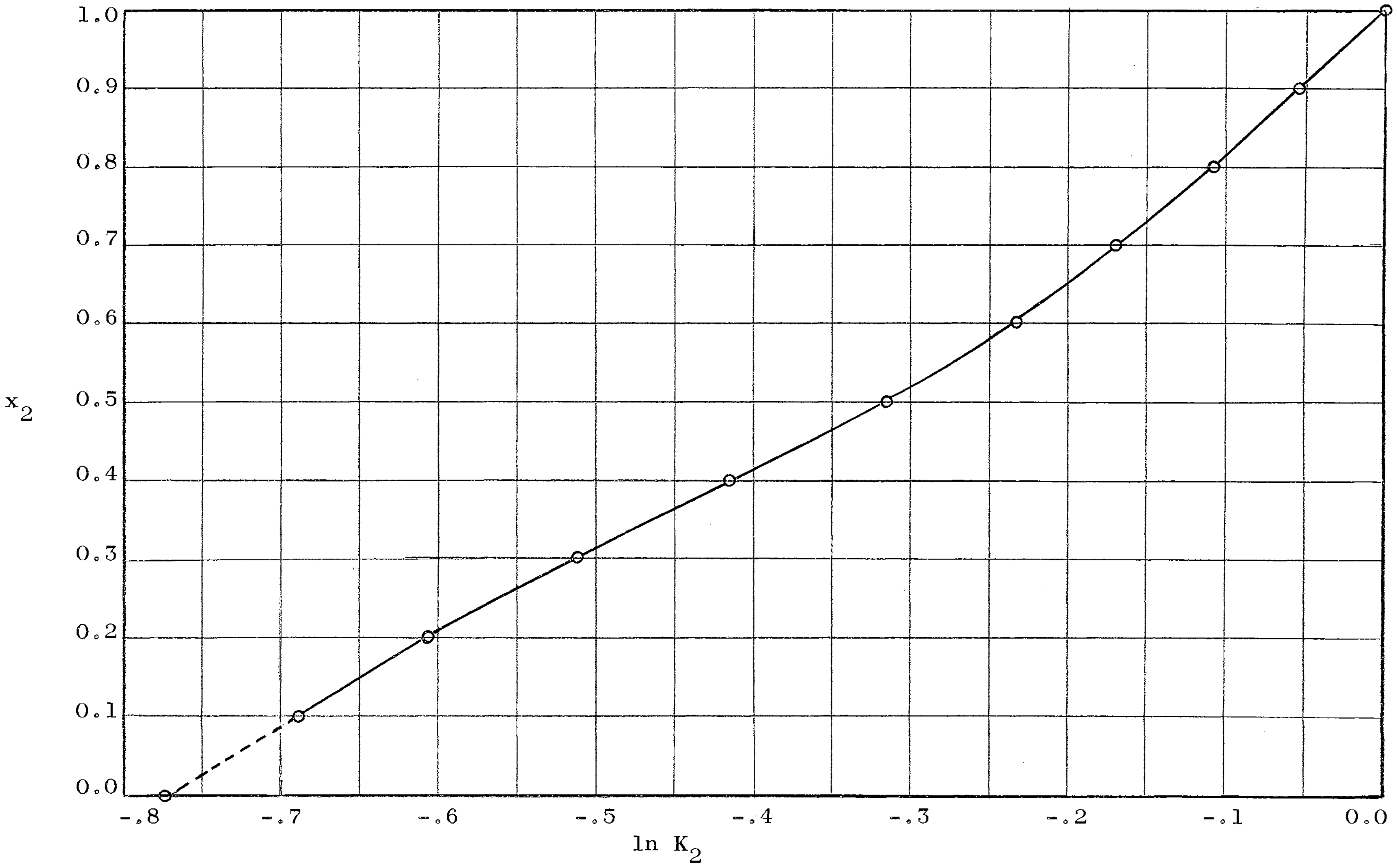

Figure 27

x_2 - ln K_2 Diagram for Thermodynamic Consistency Test

Value of the Integral = - 0.34920

Where

$$(\text{RATIO}) = \left[\frac{\dfrac{H^V_{mix}}{K_2} - \bar{H}^V_1 y_1 \left(\dfrac{1}{K_1} - \dfrac{1}{K_2}\right) - H^L_{mix}}{RT^2}\right]_T$$

$$= \left[\frac{\dfrac{H^V_{mix}}{K_2} - \bar{H}^V_1 \left(\dfrac{1}{K_2} - 1\right) - H^L_{mix}}{RT^2}\right]_T$$

An IBM 1620 computer was used for the above calculation. The following codes were used for the computer program. They are listed in the order in which they appear in the program. Immediately following this listing is a listing of the computer program, then input data, and lastly, computer output data.

T	Equilibrium temperature, °K.
RATIO	Same as defined earlier.
QQ	Value of the integral.
J	Number of the data card.
PHV	Partial vapor enthalpy for chloroform at T,P, cal/gram mole.
HVM	Saturated vapor enthalpy for the mixture, cal/gram mole.
HLM	Saturated liquid enthalpy for the mixture, cal/gram mole.
EK2	Equilibrium K-value for benzene at T°K.

Codes used for intermediary calculation steps have been omitted from the above listing.

```
C     IBM 1620 PROGRAM FOR THE CALCULATION OF RATIO AND FOR EVALUATING
C     INTEGRAL OF RATIO DT. (LIMIT FROM X1=0.0 TO X1=1.0)  WHERE
C     RATIO = ((HVM/EK2)-PHV*((1.0/EK2)-1.0)-HLM)/(1.9872*T*T)
C     INTEGRATION PROGRAM SUITABLE FOR 11 DATA CARDS
C     REQUIRED FOR THE THERMODYNAMIC CONSISTENCY TEST
      DIMENSION RR(30), TT(30), Q(30)
      PUNCH 1
    1 FORMAT (16X1HT10X5HRATIO)
      QQ     = 0.0
      J      = 0
    2 J      = J + 1
      READ 3, T, PHV, HVM, HLM, EK2
    3 FORMAT (F11.3, F11.3, F11.3, F11.3, F11.3)
      RATIO = ((HVM/EK2)-PHV*((1.0/EK2)-1.0)-HLM)/(1.9872*T*T)
      PUNCH 4, T, RATIO
    4 FORMAT (F20.3, F13.7)
      TT(J) = T
      RR(J) = RATIO
      IF (J-1) 8,2,5
    5 Q(J)   = (RR(J)+RR(J-1))*(TT(J-1)-TT(J))/2.0
      QQ     = QQ + Q(J)
      IF (J-11) 2,6,8
    6 PUNCH 7, QQ
    7 FORMAT (6X23HVALUE OF THE INTEGRAL = , F10.7)
      IF (J-11)8,10,8
    8 PRINT 9
    9 FORMAT (6X, 18HMISTAKE IN PROGRAM)
   10 END
```

```
C      INPUT DATA CARDS FOR THE THERMODYNAMIC CONSISTENCY TEST PROGRAM
C        T           PHV          HVM          HLM              EK2
     333.660    3916.467    3916.468    -3232.200           .478
     335.160    3942.267    3955.013    -3325.000           .507
     337.160    3976.169    4008.265    -3365.000           .566
     339.160    4010.072    4061.645    -3360.000           .625
     341.160    4044.478    4119.413    -3330.000           .683
     343.160    4077.891    4180.816    -3280.000           .742
     345.160    4112.810    4246.975    -3160.000           .800
     347.160    4146.771    4328.583    -3010.000           .860
     349.160    4180.752    4414.243    -2865.000           .918
     351.160    4214.761    4507.004    -2720.000           .973
     352.460    4238.075    4560.684    -2645.000          1.000
```

Computer output data

```
             T            RATIO
          333.660       .0327413
          335.160       .0327891
          337.160       .0326911
          339.160       .0325022
          341.160       .0322503
          343.160       .0319071
          345.160       .0313860
          347.160       .0307651
          349.160       .0301327
          351.160       .0295252
          352.460       .0291886
      VALUE OF THE INTEGRAL = -.5928958
```

Figure 28 gives a plot of RATIO vs. temperature which is a smooth curve.

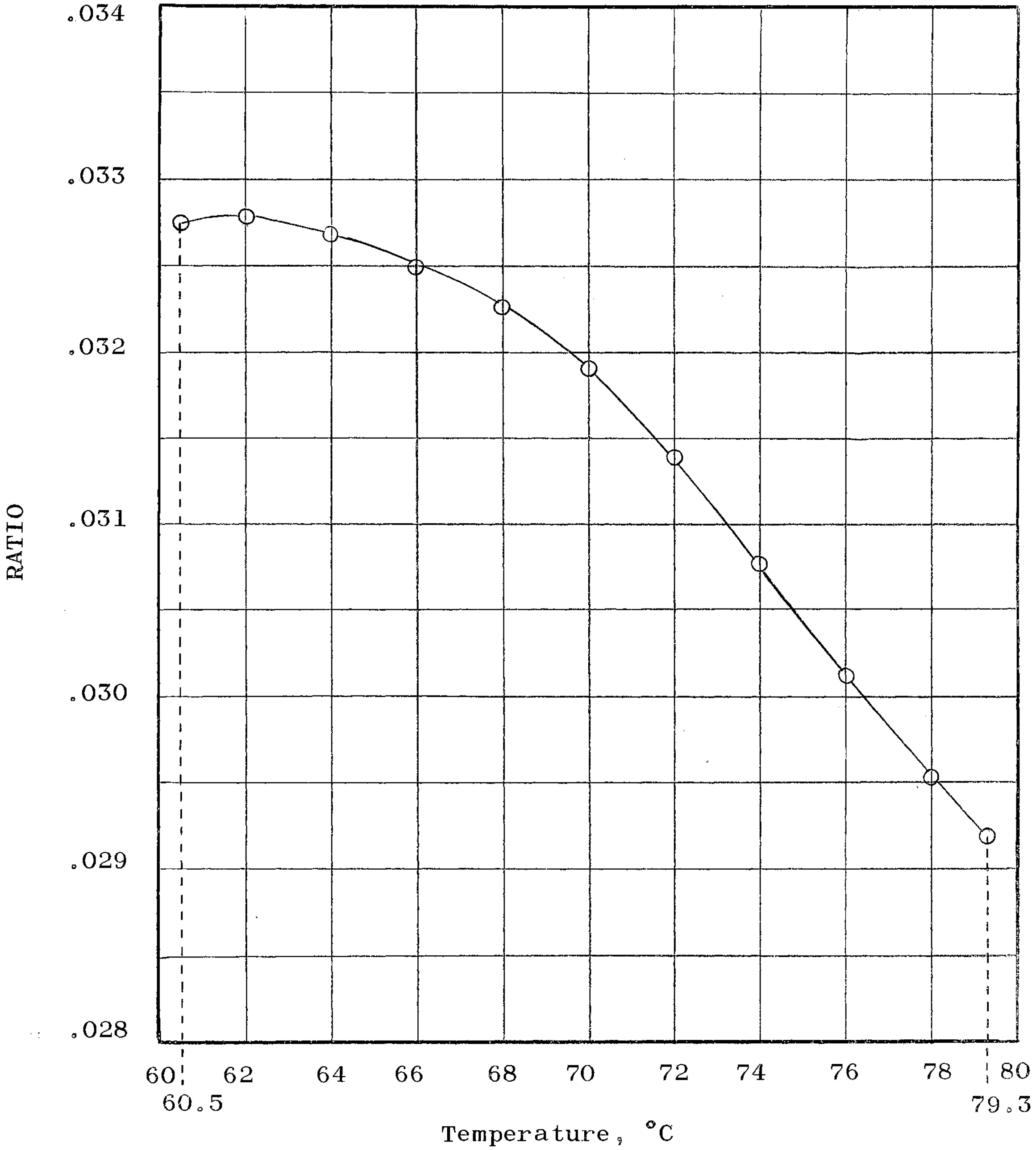

Figure 28

"Ratio"-Temperature Diagram for
Thermodynamic Consistency Test

NOMENCLATURE

A, B	Constants of Redlich-Kwong equation of state
h	Constant of Redlich-Kwong equation of state
H	Molal enthalpy
$H^{\circ}_{i \text{ or } mix}$	Ideal gas state enthalpy of component i or of mixture
H^{V}_{mix}	Saturated vapor enthalpy of mixture
H^{L}_{mix}	Saturated liquid enthalpy of mixture
$\bar{H}^{V}_{1}$	Partial vapor enthalpy of chloroform
ΔH_{mix}	Isobaric integral heat of vaporization of mixture
ΔH^{V}_{mix}	Saturated vapor enthalpy difference of mixture from ideal gas state enthalpy
$\Delta \bar{H}^{V}_{1}$	Partial vapor enthalpy difference of chloroform from ideal gas state enthalpy
K	Vapor-liquid phase distribution ratio
P	System pressure
P_c	Critical pressure
P_r	Reduced pressure
R	Gas constant
R_1, R_2, R_3	Standard electrical resistances
T	Equilibrium temperature
T_1	Bubble point temperature
T_2	Dew point temperature
T_c	Critical temperature

T_r	Reduced temperature
U	Overall heat transfer coefficient
V	Molal volume
V_1, V_2	Potential drop across standard resistances
x_i	Mole fraction of component i, in liquid phase mixture
y_i	Mole fraction of component i, in vapor phase mixture
z_i	Mole fraction of component i, in mixture
Z	Compressibility factor

Subscripts

i	Component "i" where i = 1 is chloroform, i = 2 is benzene
mix	Chloroform-benzene mixture
c	Critical value
r	Reduced value

Superscripts

$^{\circ}$	Ideal gas state
—	Partial molal quantity
L	Liquid phase
V	Vapor phase

VITA

Sanat Kumar

Candidate for the degree of

Master of Science

Thesis: SIMULTANEOUS EXPERIMENTAL INVESTIGATION OF ISOBARIC INTEGRAL HEATS OF VAPORIZATION AND VAPOR-LIQUID EQUILIBRIUM RATIOS FOR CHLOROFORM-BENZENE MIXTURES

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Personal Data: Born in Varanasi, U.P., India, March 3, 1940, son of Rai Satya Vrata and Krishna Mohini.

Education: Attended elementary school in Varanasi, India; graduated from Besant Theosophical High School, Varanasi, India, in 1954; completed Intermediate of Science from Central Hindu College, Varanasi, India, in 1956; received the Bachelor of Science degree in Chemical Engineering from Banaras Hindu University, Varanasi, India, in 1960; completed requirements for the Master of Science degree in Chemical Engineering at Oklahoma State University in July, 1968.

Professional Experience: Employed as an engineering trainee with Mysore Chemicals and Fertilizers Ltd., Belagola, Mysore, India in the summer of 1959. Employed as Project Engineer and later as Deputy Superintendent - Sulfate Recovery Plant with Kesoram Rayon, Calcutta, India from Janyar 1961 to August 1963. Employed as a graduate assistant Oklahoma State University, 1964. Employed as Process Engineer with United Engineers & Constructors Inc., Philadelphia, Pennsylvania since August, 1965.