PHASE DISTRIBUTION RATIOS FOR INTEGRAL TECHNIQUE PETROLEUM DISTILLATION CALCULATIONS

by

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PREFACE

One of the problems in petroleum distillation technology is the accurate determination of vapor-liquid equilibrium constants for heavy hydrocarbon systems. Another problem is the limitation of accuracy caused by the difficulty in identifying the components of a complex petroleum fraction. This study is a step toward the solution of these two problems.

By using the ratio of slopes method to determine vapor-liquid equilibrium constants, pseudo-components may be identified by their boiling point and vapor-liquid distribution ratios derived. These ratios then lend themselves quite handily to the integral technique for design calculations in that this technique does not require knowledge of the components present, but only a distribution ratio vs. feed true boiling point curve relationship. These distribution ratios, which are sometimes called "K ratios" or "K values", are the ratio of mole fractions of any component in the equilibrium vapor and liquid.

This study was an investigation of some of the apparatus and experimental techniques available to obtain K values in this manner. The goal of the study was to select apparatus and develop techniques which would give accurate K values in a minimum of time and with lowest cost. This work is not completed, but definite progress has been made.

I am indebted to Mr. A. Amir-Yeganeh who preceded me, and to C. L. Henderson and R. M. Walston who are continuing the work, for their numerous suggestions and assistance in many areas of this work. Thanks is also due the Phillips Petroleum Company, Continental Oil Company, and the Humble Oil and Refining Company for providing most of the hydrocarbons used in this study and for suggestions regarding experimental techniques.

My deepest gratitude and appreciation is due to my adviser, Professor Wayne C. Edmister, whose door was never closed to me; and to the Esso Research and Engineering Company, whose fellowship made this work possible.

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CHAPTER I

INTRODUCTION

In the petroleum industry today there is need for a fast, reliable, economical method of determining vapor-liquid equilibrium constants for heavy hydrocarbon systems. These data are generally available for the lighter hydrocarbons, and may be used for calculations involving component systems which may be easily analyzed. Calculations for natural gas, for instance, are based upon known amounts of identifiable components present.

But for complex mixtures, sometimes called continua, mixtures which contain an "infinite" number of compounds present in "infinitesimal" quantities, the problem is much more difficult. Distillation calculations are made using empirical relationships or a simplified model in which the oil is divided into hypothetical components. For designing costly full scale refinery distillation equipment, accurate vapor-liquid equilibrium data are very important.

This work is believed to be the beginning of an answer to this problem. Vapor-liquid equilibrium distribution ratios are derived from the ratio of slopes of the assays of the equilibrium vapor and liquid. These values are then used in the integral technique for distillation calculations. In this integral calculation method, point values are used. This makes it well suited for calculations involving complex mixtures.

Scope of the Study

Two areas are investigated in this work: the determination of K ratios, and their use in distillation calculations. In the first area, two analytical distillation columns, an equilibrium still, and other analytical apparatus are investigated in an attempt to find a suitable combination of apparatus and techniques which will yield the desired data quickly and accurately, and at a minimum of cost. The second area of investigation includes use of these data in a calculational technique designed for complex mixtures. The calculations also serve the purpose of checking the accuracy of the experimental data.

The steps in the study are: (1) an equilibrium flash vaporization; (2) analytical distillation of the two equilibrium products to obtain true boiling point (TBP) curves; (3) analysis of the cuts taken during the analytical distillation for weight, specific gravity, and molecular weight to permit conversion of the volumetric TBP curve to a molar basis; (4) determination of the K values from the molar TBP curves; and (5) use of these data in calculations designed to simulate the experimental distillations.

The equilibrium flash vaporization at 177°F and 350 mm. Hg absolute pressure was made in a modified Othmer still, using Hydroformer Feed from the Baytown refinery of the Humble Oil and Refining Company. The analytical distillations were done in both an Oldershaw Fractionator and a Sarnia Mark II Fractionator to determine how the results of these two units compared. Cuts of five volume per cent were collected during these analytical distillations. Molecular weights of these cuts were determined using the cryoscopic method, with benzene as the solvent.

A Fortran program for the IBM 650 computer was used to facilitate calculation of mole fractions for the TBP plots. K ratios were then determined by both the ratio of slopes and ratio of differences methods and used as input data for machine language programs which were written for the digital computer. The equilibrium flash vaporization part of the combined program was used to calculate the vapor-liquid ratio based upon the experimental K values for comparison with the experimental vapor-liquid ratio. The bubble point - dew point and fractional distillation programs were written to illustrate the use of the integral technique in distillation calculations.

CHAPTER II

ANALYTICAL DISTILLATIONS

Component mixtures of petroleum fractions, such as natural gas, may readily be expressed in terms of the mole fraction of each component present. This is not feasible for complex mixtures such as petroleum fractions containing an infinite number of components present in infinitesimal quantities. Chromatographic and mass spectroscopic analyses may be used to identify most of the components, but the excessive amount of time required is prohibitive except in special cases.

The practice of characterizing petroleum fractions by a distillation curve is widely accepted. In 1902 Rayleigh presented a theoretical solution for differential distillation, which is essentially the type of distillation now used for ASTM distillations (43). The American Society for Testing Materials has established rigorous procedures for standarizing this type of distillation (2). The petroleum industry uses the ASTM distillation assays to characterize petroleum fractions and products.

Another type of analytical distillation in wide use is the true boiling point (TBP) distillation, using columns of more than one stage. The curve of boiling point versus volume per cent off which is obtained will vary with column efficiency, and reflux ratio. This method is not standardized as is the ASTM distillation.

Empirical correlations are available for relating ASTM and TBP curves, but these correlations are not sufficiently accurate (12, 19, 23, 37, 44). Additional work is planned in this area (17).

Two TBP apparatus were compared in this work, with all analytical distillations being duplicated in the two columns. Dynamic holdup varied from five to fifteen per cent of the charge; the material which drained back into the boiling flask when the column cooled was distilled in an ASTM-86 apparatus to determine the end point.

Oldershaw Column

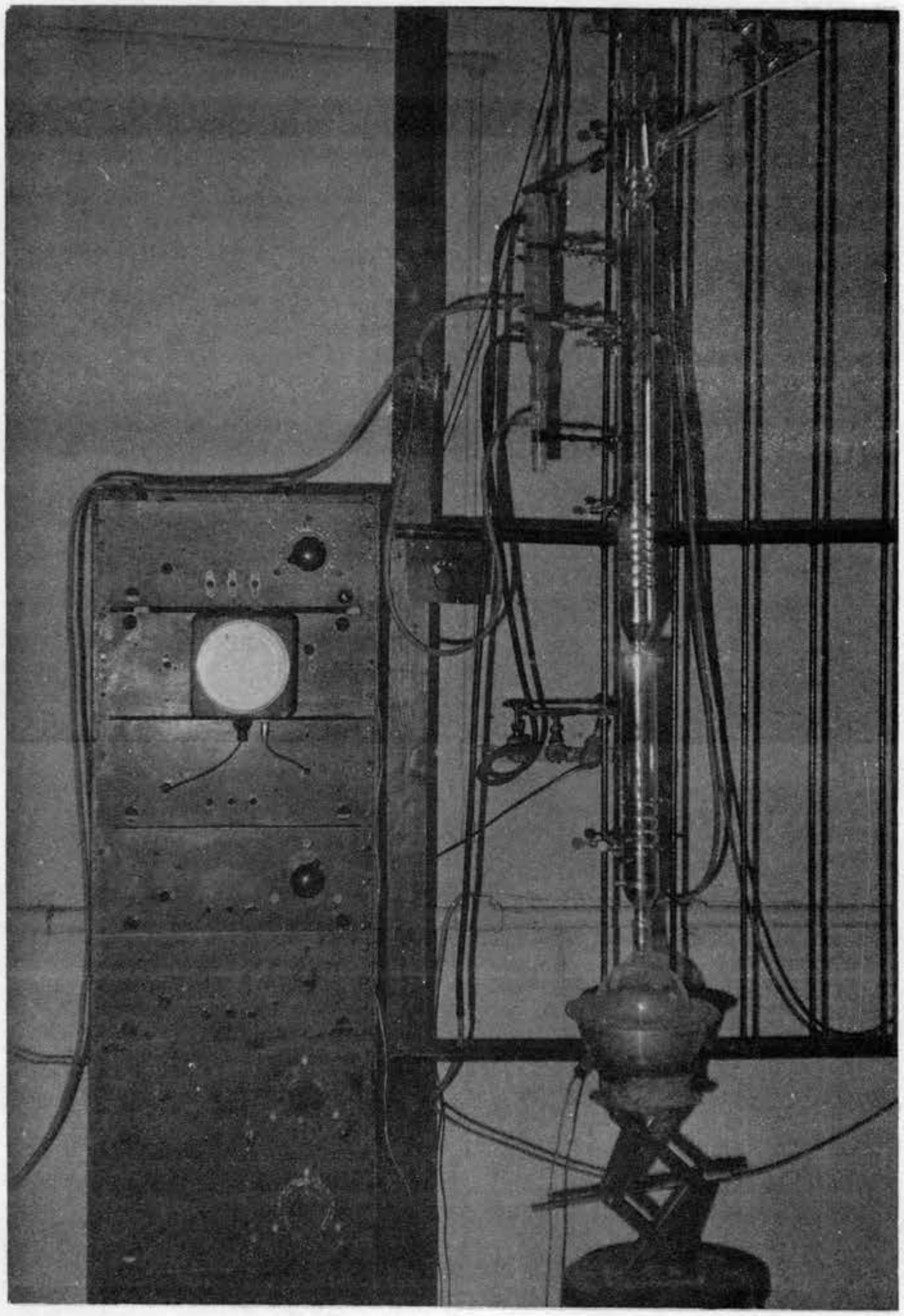
Description of the Apparatus

The Oldershaw column is a vacuum jacketed column which utilizes sieve plates for the separation of hydrocarbons (8, 38). Sections are commercially available in 20, 15, 10, and 5 plate lengths. A 30 plate column composed of an upper 20 plate section and a lower 10 plate section was used in this work. The boiling flask had a capacity of 1000 ml., and was heated by a Glas-col heating mantle. The column is shown in Plate 1.

Reflux was controlled by a vapor dividing head operated by a Flexopulse timer. The "on" cycle of the timer energized a solenoid which attracted a piece of metal imbedded in the upper end of a glass rod attached to the valve ball, causing the ball to be raised from its seat. A take-off tube led from

Plate I

Oldershaw Fractionator



the hollow inner portion of the seat and carried the vapors through the wall of the column to the water-cooled vapor condenser. Condensed vapor flowed out of the condenser and was collected in a graduated cylinder.

During the "off" cycle of the timer, the valve ball was in place upon the seat and the vapors were totally refluxed. An Allihn water cooled overhead condenser at the top of the column condensed the vapors and returned them to the column.

Temperatures were measured by a thermometer which fit into the 10/30 ground glass joint in the vapor dividing head. The bulb of the thermometer was positioned very close to the seat to insure that the temperature indicated was that of the vapor leaving the column.

Operation of the Apparatus

A 1000 ml. flask was selected and inspected to be sure that it was clean and in good condition. The desired volume of sample was measured into a graduated cylinder, weighed, and poured into the flask. The bottom joint of the column was wiped clean and greased with Dow Corning silicone stopcock grease. The flask was fitted into place, the heating mantle positioned around the flask, and the laboratory jack raised until the column began to move upward slightly.

The elevation of the jack was critical. The bottom section of the column was not clamped tightly so it could move upward when pressure was applied. Sufficient force was desired to keep the flask-column and column section joints tight. Excessive pressure could result in a broken column; insufficient pressure resulted in loss of vapor through the joints.

The thermometer was removed, cleaned, greased, and reinserted. The cooling water was turned on to the overhead condenser and the vapor condenser. The Flexopulse timer was checked to be certain that it was not in operation, and the power to the heating mantle turned on. A clean graduated cylinder was placed under the outlet spout from the vapor condenser.

At a setting of 60 on the heating Variac, vapors generally began to reflux in 45 to 50 minutes. The column was kept on total reflux for 15 minutes after vapors started to condense to insure that the top of the column was at the correct temperature. This temperature was then recorded as the initial temperature; the timer was checked for the correct reflux ratio, and turned on.

Temperatures were recorded and samples collected at the desired intervals. Cuts were usually taken every five volume per cent.

Observation of the column showed that the four drops of liquid which fall into the graduated cylinder immediately after the reseating of the valve are from the preceding cycle. The technique for reading the temperatures and collecting the sample was to read the temperature just before the ball was lifted, wait until four drops had been collected after the ball was reseated, and then remove the graduated cylinder and put an empty one in its place. The volume of sample was recorded and the sample poured into a marked two ounce sample bottle.

The run was terminated at 90 to 95 volume per cent off.

At the end of the run the timer and heater power were turned off, but the cooling water was allowed to run until the bottoms had been removed. The column was allowed to cool and drain for four hours before the bottoms (that material remaining in the boiling flask) were removed, measured in a graduated cylinder, and placed in a sample bottle. The cooling water was then turned off.

Data recorded during these distillations were run number, date, charge, time, Variac setting, temperature, volume off, and sample bottle number.

A reflux ratio of ten to one, twenty seconds total reflux to two seconds total take-off, was used. The setting of the Variac was adjusted to maintain a take-off rate of 80 to 100 ml. per hour at this reflux rate.

Sufficient bottles were weighed before the start of the run to permit collection of all the samples without having to weigh bottles during the distillation. All bottles containing samples were reweighed after the run.

Sarnia Mark II Fractionator

Description of the Apparatus

This apparatus was designed in an attempt to give an accurately known and controlled reflux ratio (10). The undesirable effects on heat losses below the reflux dividing head were reduced by providing a heating mantle on the outside of the vacuum jacket of the still, giving nearly adiabatic conditions, and incorporating the reflux divider inside the same vacuum jacket with the column.

The apparatus is sometimes designated as a "15 - 5 unit" which means 15 theoretical plates at total reflux with normal operation at 5:1 reflux ratio. The column is designed to have a dynamic hold up of one to two per cent of the charge. Cannon protruded metal packing is used because it is self-wetting and has a high through-put capacity.

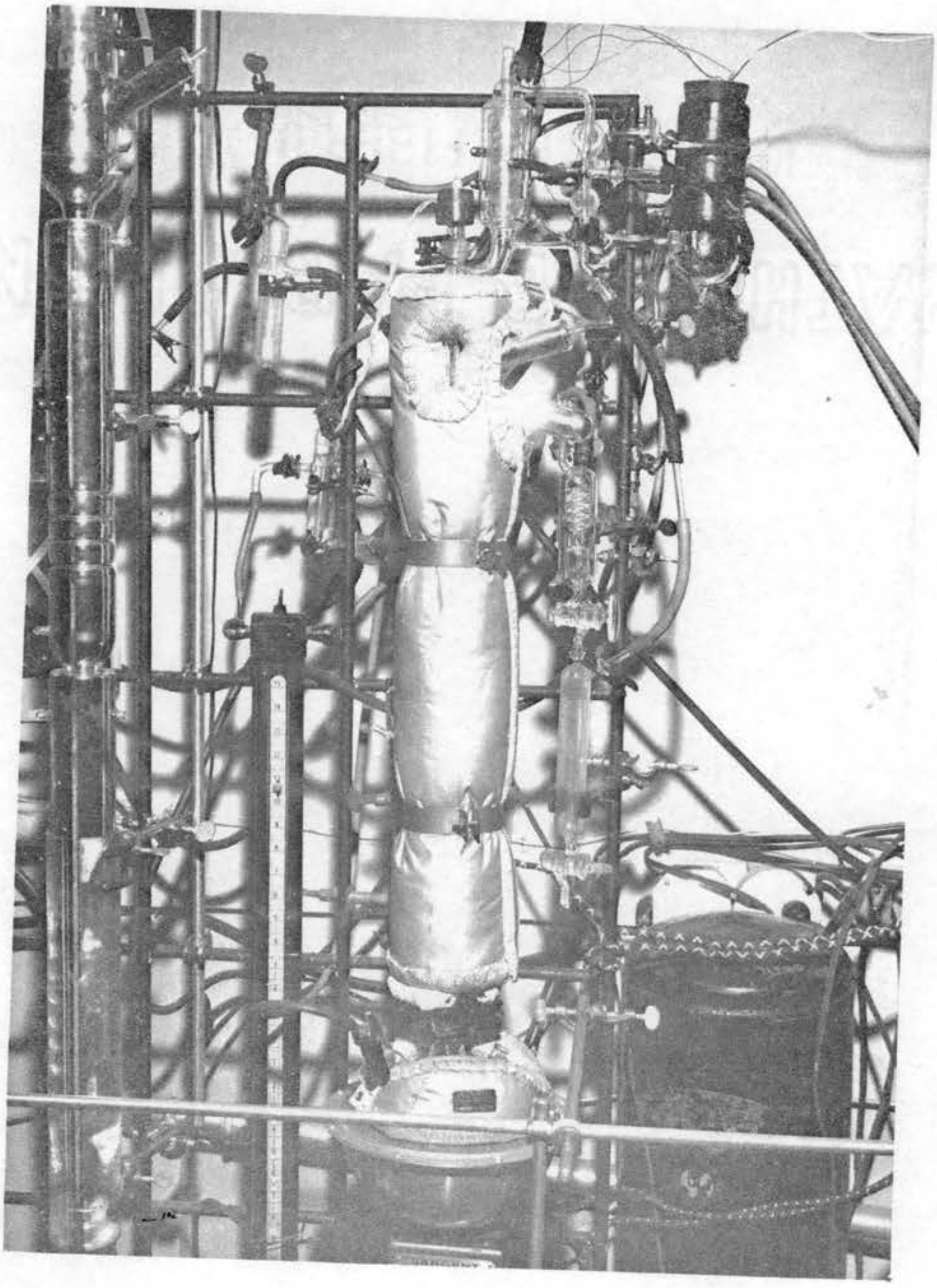
The 11 mm. column used in this study is shown in Plate 2; it consisted of a 1000 ml. boiling flask, an 11 mm. ID vacuum jacketed column, a condenser head, liquid cooler, receiver, and auxiliary equipment. The auxiliary equipment consisted of three heating mantles with controlling Powerstats, a pressure compensating device, a nitrogen system, magnetic stirrer, differential manometer, and a potentiometer and thermocouples for measuring the temperature at the reflux divider.

The reflux rate was controlled by a teflon ball attached to the end of a stainless steel rod. To the upper end of the rod was fastened a larger metal cylinder which could be adjusted by screwing it onto the threaded rod. When properly adjusted, the solenoid would attract the cylinder up into the valve cap just 1/8 inch. This allowed sufficient space for the liquid to flow past the ball and out of the column, but did not raise the valve stem so high that it might not reseat properly. Power to the solenoid was controlled by the Flexopulse timer.

The condenser head is offset so any water which might be present in the charge will fall from the condenser onto the hot neck and flash instead of falling back into the column

Plate II

Sarnia Mark II Fractionator



and upsetting the temperature at the reflux divider.

Liquid from the column flows through the take-off arm into the liquid cooler, and then into the graduated receiver. The receiver is connected to the same pressure system as the condenser head. When removing the sample from the receiver, the rest of the still can be blocked off and the receiver vented to the atmosphere.

The pressure compensating device utilized compressed air from the laboratory main. The pressure in the surge tank was controlled by bubbling air through a long glass tube submerged in water to a depth sufficient to compensate for the difference between 760 mm. Hg absolute and the atmospheric pressure in the laboratory. For vacuum operation, the still can very easily be connected to the vacuum system available in the laboratory, described in connection with the Othmer still.

The three heating mantles provided heat to the bottom of the boiling flask, the top of the flask, and the column, with each mantle controlled by a Powerstat. For light oils, only the bottom mantle was used.

A compact and simple Leeds and Northrup millivolt potentiometer was used with a copper-chromel thermocouple to measure the temperature at the reflux divider. A pair of thermocouples for determining the difference between the temperature inside the column and the temperature of the jacket was used initially, but was later discarded. Voltage input to the tower mantle was then determined from a curve given in Figure 8 of "Instruction Manual B" provided with the equipment.

The pressure drop across the column was measured by a differential manometer connected between the boiling flask and the outlet from the vapor condenser. Nitrogen was bubbled into the line between the manometer and the boiling flask to prevent the escape of vapor from the flask into the manometer.

Operation of the Apparatus

The desired volume of charge was measured into a graduated cylinder and its weight determined. The stopcock on the side of the boiling flask was cleaned and greased, and the charge poured into the flask. Boiling chips and the magnetic stirring bar were then placed in the flask. The ball and socket joint between the flask and the column was cleaned and greased, and the flask was connected to the column and held in place by a screw clamp. The thermometer was inserted into the well in the side of the flask and the level of silicone oil in the thermometer well checked to be sure that it covered the bulb.

The lower flask mantle was held under the flask and the jack elevated until the column began to move slightly upwards. The magnetic stirrer sat on top of the jack with the flask heating mantle resting upon the top of the stirrer. The upper flask mantle was then put into place and laced. The connections were made between the mantles and the power cords.

The line from the manometer was connected to the flask by means of the 18/7 ball and socket joint, and the stopcock checked to be certain that it was open. Failure to open this stopcock will result in the manometer fluid's being forced out of the manometer by the nitrogen which is bubbled into the line between the flask and the manometer.

The nitrogen was then turned on at the rate of one bubble per second. This rate was visually determined by watching the nitrogen bubbler, which was partially filled with ethylene glycol. The cooling water to the vapor condenser and the liquid cooler was turned on.

The Dewar flask which was used for the reference cold junction was filled with crushed ice and distilled water and the thermocouples placed back in it. The thermocouple well and thermocouple at the top of the column were checked to be sure they were properly seated. The amount of silicone oil in the thermocouple well was adjusted so that it just covered the tip of the thermocouple. The ball and socket joints between the side arm, liquid cooler, and receiver were cleaned, greased, and reassembled.

The barometric pressure was determined and the necessary amount of correction calculated. For this calculation the value of standard pressure was taken as 29.98 inches of mercury and the specific gravity of mercury was taken as 13.55. The compressed air regulator was turned on to allow 10 psig. air into the dryer. The valve on the outlet line of the dryer was regulated to allow two or three bubbles of air per second to escape from the tube into the water. The depth of immersion of the glass tube in the water was adjusted to maintain the correct pressure as indicated by a differential manometer connected to the surge tank.

The power to the heating mantles was then turned on and the Powerstats adjusted to their proper settings. The column was operated at total reflux until vapor had been condensing in the vapor condenser for 15 minutes. During the time the column was heating, the thermocouple leads were connected to the potentiometer and the potentiometer properly zeroed and standardized. After the column had operated at total reflux for 15 minutes, the temperature was recorded as the initial boiling point, and the Flexopulse timer checked for the proper reflux ratio and turned on.

The timer was generally operated at a reflux ratio of 20 to 2 seconds, or 10 to 1. The lower flask mantle Powerstat was adjusted to give a take-off rate of 80 to 100 ml. per hour at this condition. For the materials run in this work, this was generally best controlled by maintaining a pressure drop across the column equivalent to 0.9 to 1.2 inches of red oil on the differential manometer.

The temperature was read and samples collected at every five volume per cent. To take a sample, the stopcock between the liquid condenser and the receiver was closed and the stopcock between the receiver and the condenser head pressure manifold turned 180°. This isolated the receiver from the rest of the column and vented it to the atmosphere. The volume of the sample was recorded and the cut drained into a two ounce sample bottle. The receiver stopcock was closed, the stopcock to the pressure manifold turned 180°, and the stopcock to the liquid cooler opened.

Data recorded during the run consisted of run number, date, charge, barometric pressure, still pressure, time, Powerstat settings, temperature, and pressure drop across the column.

The run was generally terminated at 90 to 95 volume per cent. The column was allowed to drain and cool for four hours before the charge remaining in the flask was drained into a graduated cylinder; the volume was recorded and the bottoms poured into a sample bottle.

Sufficient bottles were weighed before the start of the run to permit collection of all cuts taken during the run. After the run all bottles containing cuts were reweighed. The bottoms cut was latter distilled in an ASTM-86 apparatus to obtain the end point.

For both the Oldershaw and Sarnia columns, all analytical distillations were duplicated to check the temperatures. If a disagreement in excess of 3°F was obtained, a third run was made to determine which temperature was correct. Cuts were not taken during the check runs unless disagreement was noted; if the temperatures did not agree, cuts from both runs were saved until the proper value of the temperature was established, then the cuts for the correct run were further analyzed. The cuts from the incorrect run were discarded.

ASTM-86 Apparatus

The ASTM-86 apparatus was used to distill off the bottoms fraction that could not be distilled in the TBP apparatus. The unit is commercially available and is fully described in "ASTM Standards on Petroleum Products and Lubricants" (2). Since its use is widespread and a description and drawing of it are generally available, it is not pictured here.

Description of the Apparatus

The ASTM-86 apparatus consists of a cabinet containing an electrical element controlled by a Variac, with a watt-meter to indicate the power to the heater, and a cooling tube running through a water bath. A 250 ml. Saybolt distillation flask is placed above the heating element, resting upon an asbestos platform which is adjustable in height. A graduated cylinder is placed beneath the exit of the cooling tube, and an ASTM low distillation thermometer is put in the top of the distillation flask.

Operation of the Apparatus

Before beginning the distillation, the cooling tube was wiped clean by pulling a piece of clean dry cloth through it. The cut was poured into a clean distillation flask and a boiling chip added, the side arm of the flask passed through a cork into the cooling tube, and the flask positioned on the platform above the heater. The cork provided a seal to prevent the escape of vapors to the atmosphere.

The thermometer was held in the distillation flask by a one-hole cork so the bottom of the capillary was even with the lowest part of the sidearm-flask joint. Sufficient ice was added to the water bath to bring it to the desired temperature and a 100 ml. graduated cylinder placed beneath the cooling tube spout.

The heater was turned on and the power adjusted so the first drop would come over in about five minutes. As soon as this drop appeared, the power was turned back to maintain a take-off rate of five ml. per minute.

The initial boiling point of the cut was taken as the temperature at the time the first drop came from the spout. Temperature-volume readings were taken for every two volume per cent of the original charge to the TBP apparatus. These cuts were taken by removing the graduated cylinder from beneath the spout and inserting a new one in its place. The cut in the graduated cylinder was poured into a numbered, weighed sample bottle and the bottle and sample reweighed.

The flask was boiled dry, then allowed to cool. All material which drained back into the flask was either taken as a separate cut or added to the last cut, depending upon its size.

CHAPTER III

OTHER ANALYTICAL TESTS

In addition to the equilibrium vaporization and analytical distillations, there were other analyses and tests which were performed in this work. Each of these is presented in this chapter with discussions of the principles, equipment, and technique, where appropriate.

Weighings

All weighings of distillation cuts were performed on Mettler analytical balances. These automatic balances provided a quick and easy means of weighing the empty sample bottles and the bottles containing the cuts from the analytical distillations. A Type H5 balance with a maximum capacity of 150 gm. was used for most of the work; the last few weighings were done on a Type B6. The latter balance could be read to one more place and had a better damping mechanism, but had a capacity of only 100 gm.

Weights were read to the third decimal place with an accuracy of 0.001 gm. This accuracy was superfluous in view of the accuracy of other deteminations, but served to eliminate weighings as one of the sources of error.

Samples exceeding the capacity of the Mettler balance were weighed on an Ohaus double pan beam balance with an accuracy of 0.5 gm.

Molecular Weight Determinations

Molecular weights were determined by the cryoscopic principle. This method was chosen because of its wide use and apparent success (21, 22, 47, 50). The apparatus used was very similar to that commercially available (11). The Beckmann method was used and was essentially the same as that used by commercial laboratories (29, 33). This method is not so accurate as others, but is less time consuming and gives results within an acceptable range of error.

Principle of Operation

The freezing point of a solution is the temperature at which solid solvent begins to separate from the solution. Solutions freeze at lower temperatures than the pure solvent.

The lowering of the freezing point by the addition of solute to a solvent has been known for a long time; but cryoscopy, the study of freezing points of solutions, was first placed on a firm experimental foundation by Beckmann in 1888. The theoretical treatment of freezing point depression is due primarily to J. H. van't Hoff (42).

The freezing point lowering is a consequence of the vapor pressure lowering caused by the addition of a solute. Figure 1 shows a vapor pressure - temperature diagram. The line AB is the sublimation curve of the solid solvent. The line CD is the vapor pressure curve for pure liquid solvent.

At the freezing point, the two phases are in equilibrium with each other and must have the same vapor pressure. This occurs only at B, the intersection of the two lines. The temperature, T_o, corresponding to this point is the freezing point of the pure solvent.

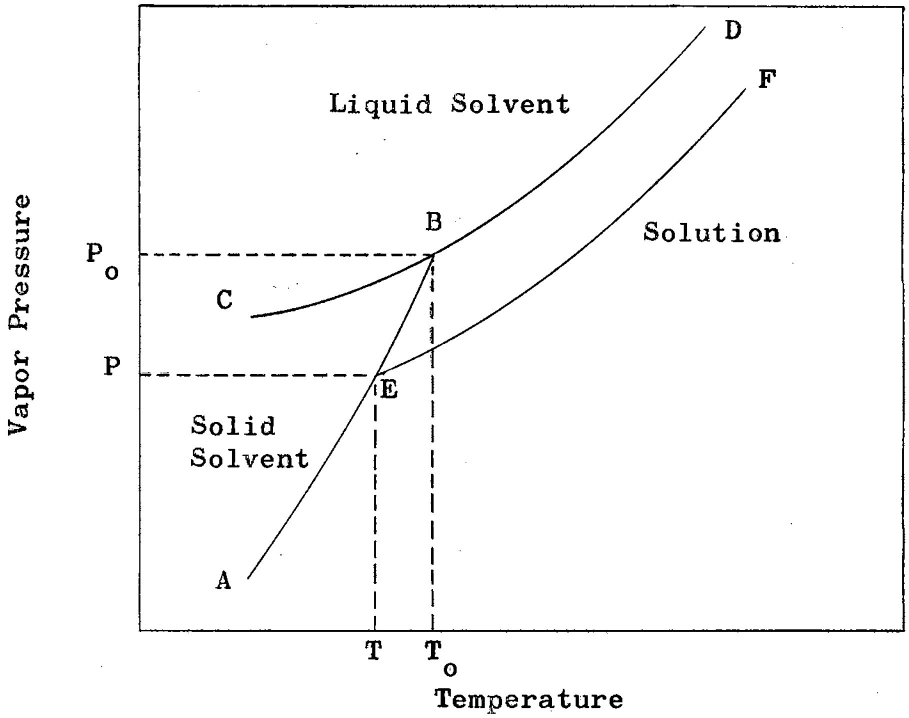


Figure 1. Vapor Pressure - Temperature Diagram

The lowered vapor pressure of the solution is shown by the line EF. Again, the vapor pressure of the two phases must be equal to satisfy the condition for equilibrium. This is satisfied only at E, the point of intersection. The temperature, T, corresponding to this point is the freezing point of the solution. The freezing point depression is thus $T_o - T$.

The dependence of freezing point depression upon concentration has been shown mathematically and experimentally (24). This dependence may be expressed by

$$\Delta T_f = K_f\, m \qquad (1)$$

where: ΔT_f = the freezing point depression, °C

K_f = a constant peculiar to the solvent

m = the molality of the solution, moles per 1000 gm. solvent

But

$$m = \frac{\text{wt. sample/MW}}{\text{wt. solvent}} \times 1000 \qquad (2)$$

and weight = volume x density.

Substituting these equations into equation 1 and rearranging for the molecular weight,

$$MW = K_f \frac{1000\, v_s\, \rho_s}{v_b\, \rho_b\, \Delta T_f} \qquad (3)$$

where: MW = molecular weight of the solute

v = volume, ml.

ρ = density, gm. per ml.

The subscript "s" refers to the solute; "b" refers to the solvent.

Benzene was selected as the solvent; the constant K_f for benzene is 5.12 (42). A ratio of 100 parts benzene to 1 part unknown, by volume, was arbitrarily chosen. Equation 3 then reduced to

$$MW = \frac{51.2\, \rho_s}{\rho_b\, \Delta T_f} \qquad (4)$$

The assumption was made that the volumetric rates of expansion for benzene and the samples were approximately the same over the small changes in room temperature which might occur between the determination of the specific gravities and the determination of moecular weights. Measurement of the specific gravity of benzene at the same time as the measurement of the specific gravities of the samples permitted the use of the volumetric basis instead of necessitating the weighing of every sample during the cryoscopic analyses.

Measurement of the solute by a pipette was not acceptable because of the inability to achieve reproducible results, caused by inaccuracies in the volume of sample delivered into the test tube. For this reason, a 1/4 cc. syringe was used to measure the sample.

Supercooling is frequently experienced in cryoscropic analysis. When working with a solid solute, this effect can be lessened by seeding the solution at the freezing point with a crystal of the solute. This procedure was not practical in this work because of the nature of the solute and the construction of the apparatus. Supercooling was generally limited to not more than 0.5°C, and was not considered to be a serious source of error. Again, this is in keeping with current industrial laboratory practice.

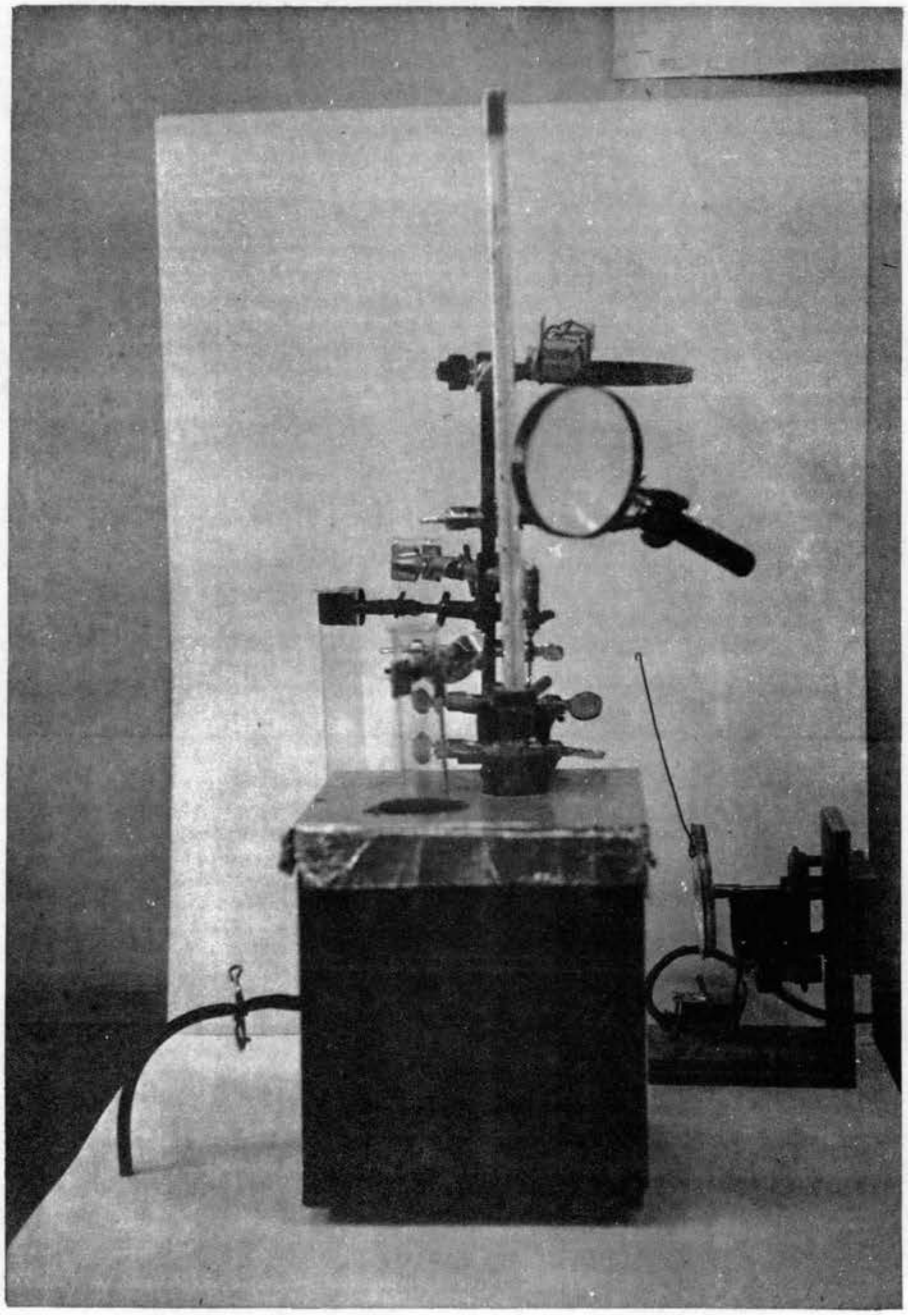
Description of the Apparatus

The apparatus used for the cryoscropic method of determining molecular weights is shown in Plate 3. This equipment is a modification of that commercially available (11). An ice water bath was used as the cooling medium. The bath was enclosed in an insulated box and sat upon the base of a ring stand. A spout was provided near the bottom of the bath to permit draining excess water when adding more ice.

A 38 x 200 mm. test tube was passed through a hole in the

Plate III

Apparatus for Determining Molecular Weights



top of the box to form a cold air bath. When the 28 x 200 mm. sample tube was clamped in place, there was an annular space of about 1/5 inch of air to slow the cooling.

A cork was bored and slotted to provide a means of holding the Beckmann thermometer in place and allowing the stirring wire to move freely up and down in the sample tube.

A small lead weight was fastened to the top of the stirring wire to cause the wire to descend when not being pulled up by the motor. A string ran from the upper end of the stirring wire, over two rollers on a cross arm fastened to the top of the ring stand, and to the motor.

A small 115 v. AC, 40 rpm electric motor was used to operate the stirrer. A metal disk was soldered to the end of the motor shaft and a swivel was placed an inch away from the point of rotation. The string from the end of the stirring rod was attached to this swivel. This transformed the rotational motion into the two-inch vertical motion which was desired for the stirring.

A test tube of benzene at room temperature was clamped to the ring stand to be used to rinse the thermometer and stirring wire when they were removed from a cold sample.

Other equipment included a 1/4 cc. syringe, 48 sample test tubes, a 25 ml. pipette, two test tube racks, a jar containing benzene, and a waste beaker.

Experimental Procedure

Two samples were prepared for each cut, unless more were required to obtain the desired agreement. A test tube was selected and visually inspected to be sure that it was clean and dry. The syringe was rinsed with sample, refilled, and the air bubbles removed; the plunger was depressed to the 1/4 cc. mark, then the sample was ejected from the syringe into the test tube. Care was taken that as little as possible of the sample struck the walls of the tube. The pipette was then used to withdraw 25 ml. of benzene from the bottle and add it to the test tube. The pipette was turned while the benzene was draining into the tube so the benzene would flow down the walls. This served the dual purpose of washing any droplets of sample which might be on the walls into solution and giving an indication of a dirty test tube by uneven or hindered flow down the walls of the tube. If the solvent did not flow freely down the walls of the tube, the sample was discarded, the tube placed aside to be cleaned, and a new sample prepared.

The first sample prepared was shaken by hand and lowered through a hole in the top of the box directly into the cold water bath to be precooled. The second sample was prepared during this time. The sample in the cold bath was clamped so the level of water came even with the level of sample in the tube. This prevented the walls of the tube from becoming cold enough to condense any water vapor out of the air.

Care was taken at all times to leave the sample bottles, the solvent bottle, and the prepared samples exposed to the air a minimum amount of time. Bottles were recapped immediately after use and sample tubes were corked while they remained in the test tube rack.

Samples were precooled sufficiently so crystals would precipitate from solution upon addition of the thermometer and stirring wire. When the sample had cooled long enough, the tube was removed from the water, carefully dried, and placed in the clamp above the cold air tube. The thermometer and stirring wire were then removed from the last sample which was still clamped to the ring stand. The sample had been allowed to remain in the air long enough to commence thawing so a minimum of material would cling to the thermometer and wire. The thermometer bulb and wire were wiped against the lip of the tube and the solution allowed to drain back into the test tube.

The thermometer and wire were then rinsed in the tube of benzene so the warm benzene would dissolve any solid particles which might still be clinging to them. The benzene was carefully drained back into the test tube as the thermometer and wire were removed.

The Beckmann thermometer and stirring wire were placed into the test tube containing the precooled solution and the cork and thermometer adjusted to their proper positions. The insertion of the thermometer and wire caused the crystallization of solid particles out of the solution. The stirring wire was moved up and down by hand until all solid particles dissolved into solution. The test tube was then lowered into the cold air tube. The string on the stirring wire was checked to be sure that it passed over the rollers and the motor was turned on. At this time the temperature of the solution was no more than 1.5°C above the freezing point of the solution.

As soon as the observation was started, the second sample was placed in the cold water bath. This sample cooled while the reading was taken on the first sample.

The thread of mercury was observed to dip below the freezing point, then stop falling and rise to level off at a higher temperature before falling again. The value of the temperature at the constant temperature plateau was recorded as the freezing point.

When the temperature began to fall from the constant temperature plateau, the motor was turned off and the test tube removed from the cold air bath and placed in the clamp to the side of the ring stand. The second sample was then analyzed for the freezing point as just described.

While one sample was being observed, the sample that had just been removed from the cold air tube was allowed to thaw, and then shaken by hand until all crystals had dissolved. It was then placed back into the cold water bath to be precooled for its next observation.

The time for putting the previously determined sample back into the cold water bath was a matter of individual judgement, and was important only in reducing the amount of time necessary for the group of determinations. Depending upon the amount of time it had been out of the cold air tube, the old sample was put into the water bath during the interval between the time when the temperature of the sample being determined was about 0.2°C above its expected freezing point and the time when the thread of mercury began to rise from the lowest sub-cooled temperature.

The freezing point of the second sample was recorded. If the two values were in agreement within one per cent of the freezing point depression, the average value of the two readings was taken as the final value. If the difference was greater than this, additional determinations were made. Conditions for final values were

1. Agreement of two values within one per cent. The average was taken.
2. Agreement of a third value within one-half per cent of a previous value. The average of the two values within agreement was taken.
3. Three or more values approximately equi-spaced within a disagreement of three per cent. The average value was used.
4. Agreement of more samples within one per cent than the number not in agreement. The average value of those in agreement was used.
5. There were a few samples which gave extremely erratic depressions. For these samples, the average value of all readings was used, if there were several values within two per cent of this average value.

Agreement of values for the same sample was not sufficient. If agreement between samples could not be obtained for the two samples, a third sample was prepared and determinations made for it, to get cross agreement.

At the start of every group of determinations, the value of the freezing point of benzene was checked. If the first value obtained was within one-half per cent of the value used previously, the previous value was used for the group to be determined. If disagreement was more than one-half per cent, more determinations were made until agreement was obtained within the limits prescribed above. In all cases, the percentage was on the basis of the approximate freezing point depression, which for this study, was in the range 0.4 - 0.5°C.

At the end of each group of determinations, the last sample was left in the cold air bath so the thermometer would not have to be reset. All glassware used during this time was washed and placed to dry, generally overnight. The bottle containing benzene was refilled, so the check on the freezing point of benzene which would be done first in the next group of determinations would serve the dual purpose of checking the setting of the thermometer and the purity of the new benzene.

The technique as outlined above is essentially the same as that used in research laboratories (29, 33). Rossini, et al., (24, 35, 48) have done extensive research on the correct technique for the cryoscropic method. They have presented apparatus which were developed as a result of this exhaustive study. Included among their publications are correction factors which compensate for the difference between real and ideal solutions. The freezing point is found by constructing the temperature - time curve back to the point before supercooling. In Figure 2 the line ABCDE is the cooling curve. The line DB is the extrapolation of the temperature curve to a pre-supercooled condition. This would be the correct freezing point if the solution were ideal. The curve which compensates for the difference between real and ideal solutions is shown as A'B'DE. The correct temperature of the freezing point is indicated by B'. A table of correction factors is available (35).

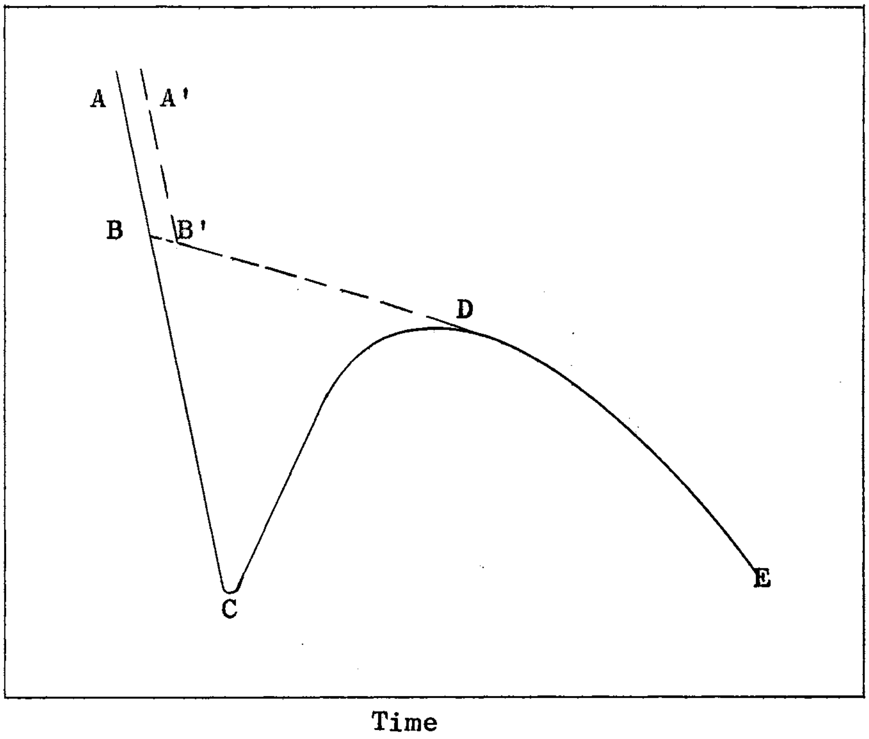


Figure 2. Temperature - Time Diagram

Specific Gravities

There are a number of methods commercially available for determining specific gravities. The Westphal balance was used by Amir-Yeganeh (1), but was not used in this study because of excessive size of sample necessary for the determination. Hydrometers also were not used for this reason. There are hydrometers available which require only 20 ml. sample, but smaller cuts were sometimes taken. Pycnometers were not used because of the tedium and length of time required for the determination.

A Fisher-Davidson Gravitometer was selected for measuring specific gravities because of its wide use in industrial laboratories, its ease of operation, the small size of sample required, and the rapidity and accuracy with which specific gravities can be determined.

Principle of Operation

The Fisher-Davidson Gravitometer operates on the principle of the hydrostatic balance (20). If two U-tube manometers containing liquids of different densities are connected to a common source of vacuum, the heights of the liquids in the connecting manometers are inversely proportional to their densities

$$\frac{h_1}{h_2} = \frac{d_2}{d_1} \tag{5}$$

If a liquid of known specific gravity is placed in one U-tube, the specific gravity of the liquid in the other tube may be measured.

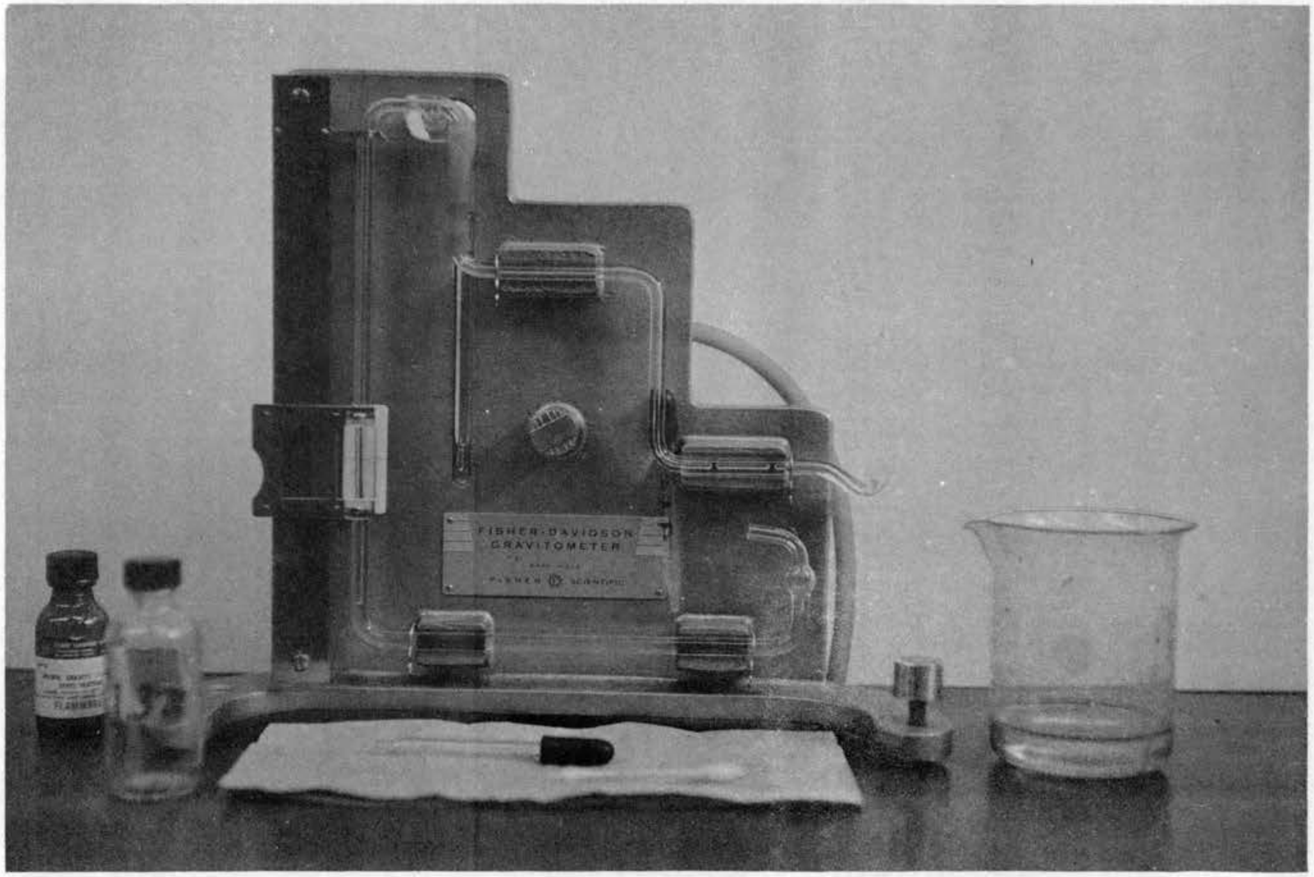
Description of the Equipment

A picture of the Fisher-Davidson Gravitometer is shown in Plate 4. Essentially, the instrument consists of an L-shaped glass tube and a Z-shaped glass tube connected to a common source of vacuum.

The L-tube contains the reference liquid; the sample is placed in the cup at the end of the Z-tube. The upper ends

Plate IV

Fisher-Davidson Gravitometer



of each of these tubes are connected to a rubber tube. The walls of the rubber tube are pressed together by a pair of rollers; as the tube is moved back and forth between these rollers by turning a milled knob, the decreasing and increasing pressure alternately pulls the liquids up into the glass tubes or forces them from the tubes.

The Z-tube containing the sample is made with the upper and lower legs horizontal so the height of the unknown liquid is constant when the two ends of the liquid lie in the horizontal legs. There are then only two unknowns in equation 5: the height of the standard liquid and the specific gravity of the unknown. A scale is provided beside the L-tube which is calibrated for ethylbenzene so the specific gravity of the unknown can be read directly from this scale.

For liquids of specific gravities above 2.0, a heavier reference liquid must be used. The specific gravities as read from the scale are corrected by multiplying by the ratio of the specific gravity of the more dense liquid to the specific gravity of ethylbenzene. Carbon tetrachloride, with a correction factor of 1.84, was provided with the instrument.

Experimental Procedure

The instructions for using the Fisher-Davidson Gravitometer were furnished with the instrument and were followed closely. There were some matters of technique which were of interest because reproducibility was not attainable until they were mastered.

The instrument was leveled, and the level of the standard liquid checked to be sure that it came within the limits inscribed upon the L-tube. A sample of the reference liquid was placed in the Z-tube and the specific gravity determined to check the position of the scale beside the L-tube. The specific gravities of the samples were then determined.

The Z-tube was rinsed with a small amount of the sample, and this portion discarded. Approximately one minute was allowed for the liquid clinging to the walls of the tube to drain down into the lower arm and form a slug of liquid across the tube. This was removed by pinching the rubber tube to move the liquid into the sample cup where it was absorbed by a Johnson Q-tip. A new sample was then placed into the cup and the specific gravity determined.

The hair line was adjusted until the edges of the meniscus just touched each end of the broken hair line, as shown in Figure 3. A second line in back of the broken line eliminated parallax. The specific gravity thus obtained was recorded.

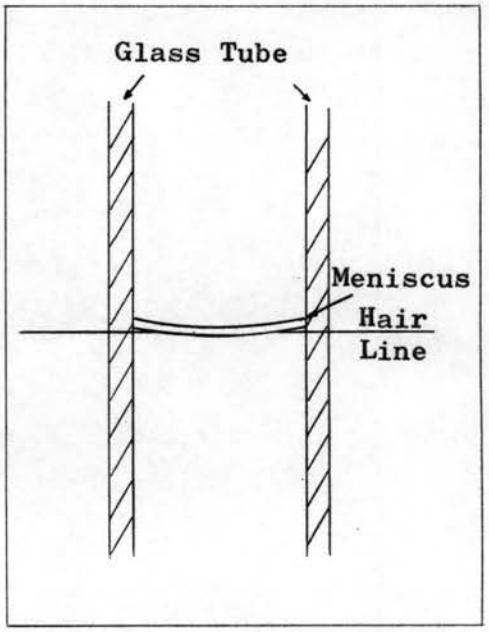


Figure 3. Position of Hair Line

The value could be read to three places. Only one determination was made as experience showed that following this procedure, the results were reproducible within 0.001, which was the accuracy of reading the scale of the instrument.

The third decimal was read from a vernier, which on the particular instrument used in this study, was not accurate. The reading of the vernier did not always agree with the position of the hair line as estimated by eye. For instance, the vernier might give a value of five for the last digit, but an estimate of the position of the index would give a value of three. Since the error seemed to be caused by the markings of the main scale, no corrections were used, and the value as obtained from the vernier was recorded. The vernier was constructed in one piece so adjustments were not possible.

Gas Chromatrograph

A gas chromatograph was used to determine the attainment of steady state in the equilibrium still. Samples were collected from the equilibrium still and injected into the chromatograph. An easily identifiable peak was selected as the reference peak and all other peak heights expressed as the ratio of the two heights. Three successive analyses showing comparative peak height ratios within the limits of reproducibility of the chromatograph was accepted as proof of steady state.

Principles of Operation

The gas chromatograph makes use of the fact that compounds in a mixtures will migrate at differing speeds when carried along by an inert gas through a tube that has been packed or treated in a special way (32). The proper selection of the partitioner - that substance with which the packing is treated - will permit all like molecules to leave the tube in a group, separate from other kinds of molecules.

Molecules flowing through the column establish an equilibrium between the vapor phase and the liquid phase of the partitioner. As the body of the sample is swept along, the absorbed molecules re-enter the gas phase. In this way, the molecules "leap frog" each other through the column.

A heated wire is placed in the exit stream of gas from the column to act as a detector. The resistance of the wire is dependent upon the temperature of the wire. As the gas flows over the wire, the wire is cooled in proportion to the thermal conductivity of the gas. If the gas is pure, the wire stays at one temperature; if other compounds are present in the gas, the temperature, hence, the resistance, changes. The amount of change is a function of the amount of other compounds present; this change was used in this study to establish the attainment of steady state in the equilibrium still.

Description of the Equipment

The vapor-phase chromatograph used in this study is shown schematically in Figure 4. Helium from the cylinder flowed through two pressure regulators and an Ideal-Arrowsmith needle valve before entering the column. The column was enclosed in a constant temperature bath which was controlled by heating pure organic compounds in an annular space around the column.

The organic was boiled in a flask connected beneath the back of the constant temperature bath. Vapors passed through

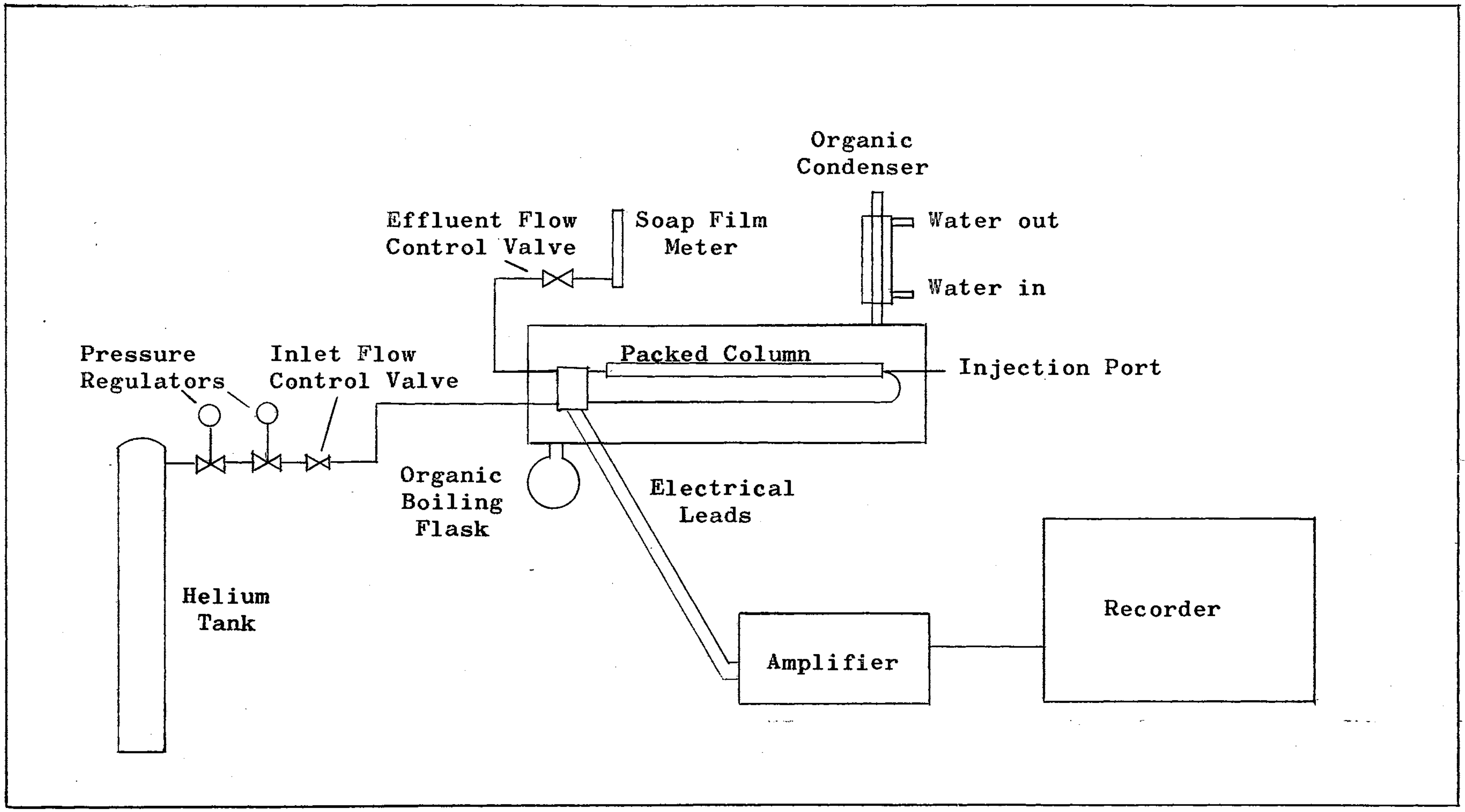


Figure 4. Schematic Diagram of Gas Chromatograph

the annular space and were condensed by a water cooled Allihn condenser mounted on top of the front of the column.

The thermal block containing two matched hot wire elements was located at the back of the constant temperature bath. A 1/16 in. copper tube carried the incoming gas stream from the thermal block to the front of the bath where the injection port was located. From the injection port the carrier stream and sample flowed through a 1/4 in. packed helical copper tube (the column) to the thermal block where the stream passed over the measuring element.

The outlet stream from the column passed through another Ideal-Arrowsmith valve and through a soap film meter, into the atmosphere.

The two hot wire elements were connected to a Wheatstone bridge located in an adjacent cabinet. The electrical ouput from the bridge was fed to a 0.0 to 1.0 mv. Bristol recorder. The fractograms obtained from the recorder were inspected for varying peak height ratios.

Operation of the Apparatus

Benzene was placed in the boiling flask and boiled for at least four hours to bring the column to thermal equilibrium. During the last hour the helium was turned on and allowed to flow through the column to purge the system of air or any other impurities which might be in it. The helium stream left the cylinder at 15 psig. and was further reduced to 10 psig. before entering the column. The flow rate was indicated by the film meter, in which a soap film was carried up a graduated tube by the effluent gas stream; the rate was controlled by the effluent valve, the inlet valve being opened sufficiently far to have no effect. A faster response in flow rate was observed when controlling by the effluent valve.

The Wheatstone bridge and recorder were turned on and allowed to warm up for at least 10 minutes before the sample was injected. The flow rate was determined and controlled to the desired rate, generally 50 to 75 cc. per minute. The flow rate, date, sample number, sample volume, attenuation, and other pertinent information were recorded on the chart and the chart drive motor turned on. The syringe was filled with sample and flushed. The syringe was refilled, the plunger depressed until the desired amount remained in the barrel, and the sample injected through the silicone rubber septum in the injection port. The point of injection was marked on the chart.

For determining equilibrium, several peaks were selected as being easily identifiable. One peak was chosen as the reference, and the heights of the other peaks were expressed as the ratio of the individual peak height to the reference peak height. This compensated for slight changes in the volume injected. The presence of three successive analyses which yielded constant peak height ratios within the reproducibility of the chromatograph was accepted as an indication of equilibrium.

CHAPTER IV

EQUILIBRIUM VAPORIZATION

The first step in this method of experimental determination of vapor-liquid equilibrium constants is the equilibrium flash vaporization of the feed and the collection of the vapor and liquid products. There are many equilibrium stills which are available or can be built for this purpose. The criteria for selection of such an apparatus are: volume of products, ease of operation, and time for reaching equilibrium.

Many vapor-liquid equilibrium constants, K values, in use today are accurate only to within ± 10 per cent (44). One purpose of this work was to develop a technique which could be used in any laboratory to obtain accurate K values with an error of less than 10 per cent. To achieve this, a column was needed which would reliably produce equilibrium and would permit duplication of results. The Othmer vapor-recirculating still seemed to satisfy these requirements (41).

The Othmer still utilizes the concept of vapor recirculation which was first presented in 1913 (51). There were other modifications of equipment using this principle before Othmer presented his first recirculating still in 1928 (39, 45). Today there are many modifications of the original Othmer still in use for various applications (1).

Othmer's later design, of which the equipment used in this study was a modification, has been changed by various workers to fit their particular needs. Othmer has presented a similar still for high pressure work (40).

A more complete study of equilibrium equipment is presented by Amir-Yeganeh (1). He also describes two other equilibrium vaporization stills which proved to be more satisfactory than the Othmer still used in this work.

In presenting his equipment, Othmer claimed a period of 45 minutes to four hours for attaining equilibrium and also simple and adequate control of the recycle by use of a three-way cock. These two features indicated that the still would be highly desirable for this work.

Othmer Vapor-Recirculating Equilibrium Still

Principle of Operation

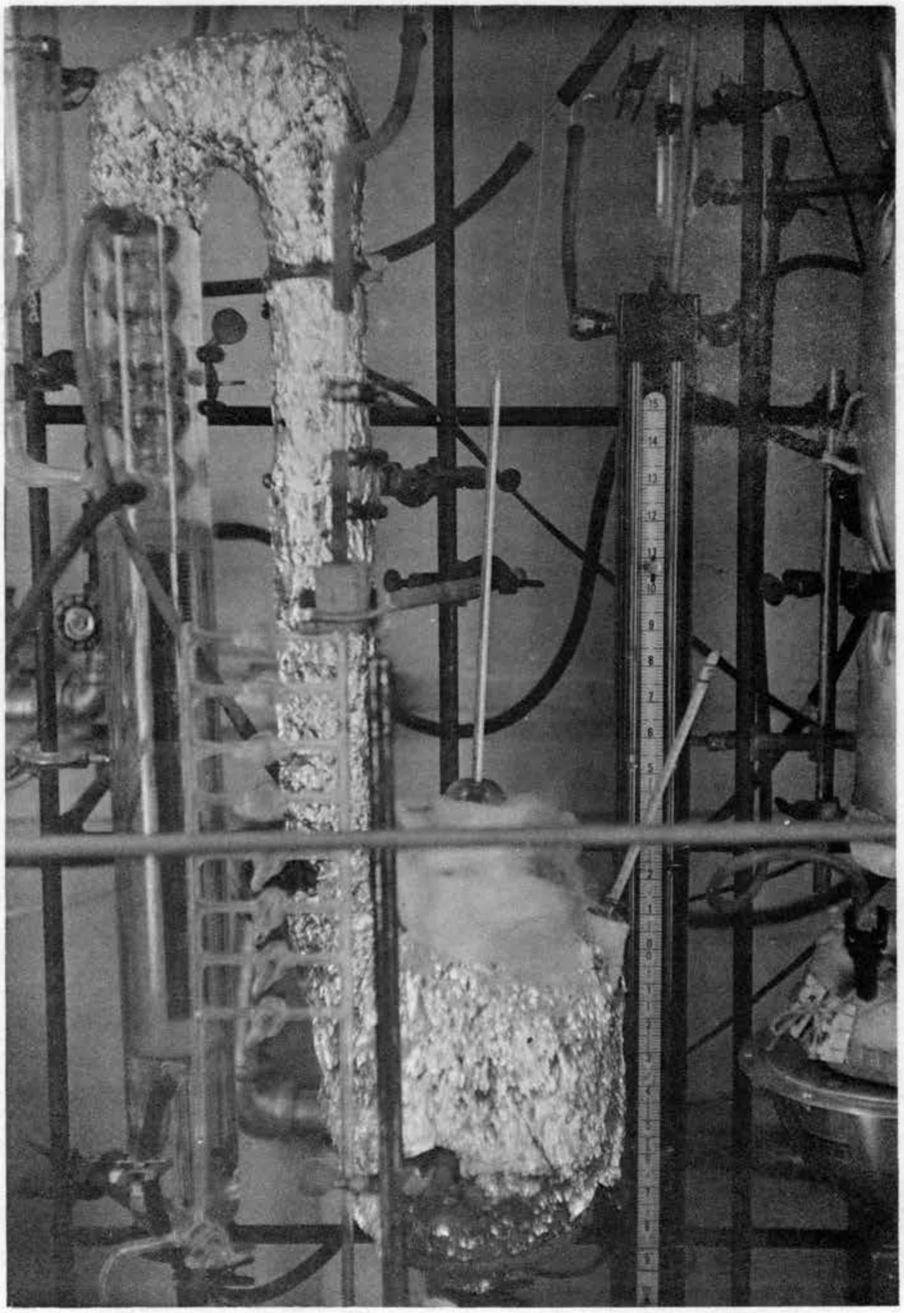
In Othmer's application of vapor recirculation, vapors which are distilled over are condensed and returned to the boiler until the still comes to equilibrium. At this time the composition of the condensed vapor recycled to the boiler is identically the same as the composition of the vapors which are leaving the boiler.

Description of the Apparatus

The modified Othmer still used in this work is shown in Plate 5 and Figures 5 and 6. It differed from the still presented by Othmer in the following respects: larger condensate receiver, larger boiler, no dry ice trap, and no heater on the

Plate V

Othmer Vapor-Recirculating Equilibrium Still



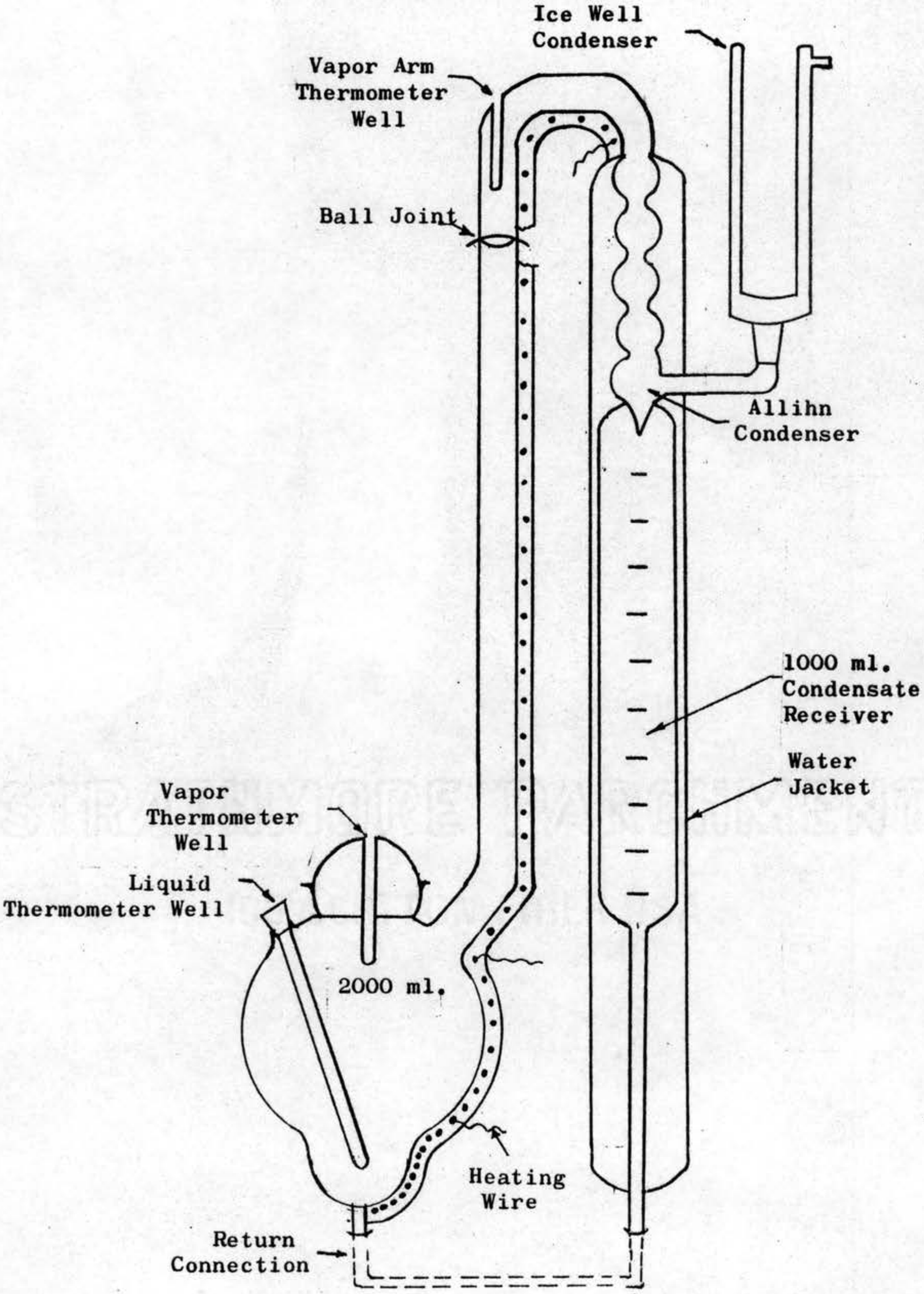


Figure 5. Cross Sectional View of Othmer Vapor-Recirculating Still

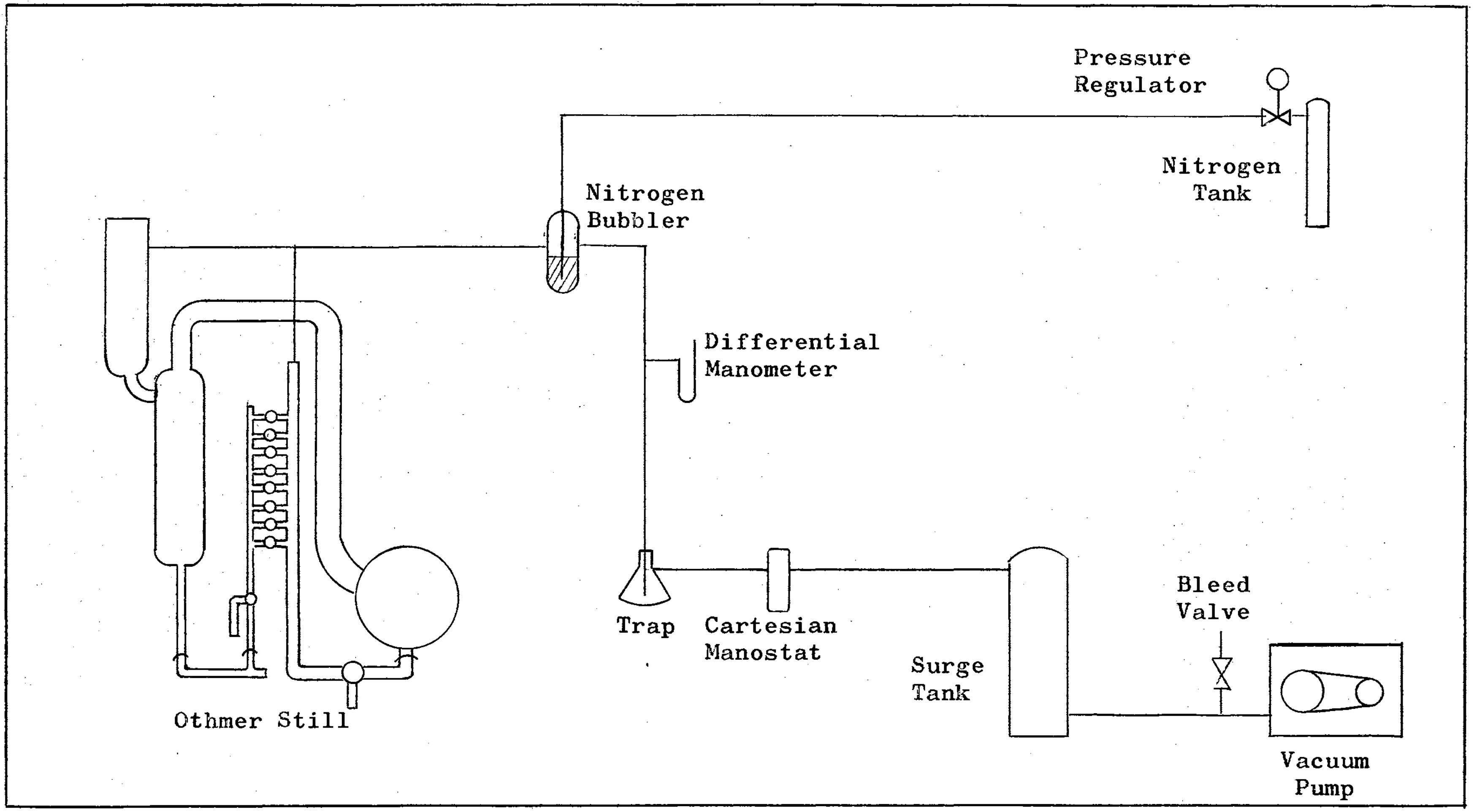


Figure 6. Schematic Diagram of Equilibrium Vaporization System

vapor return line (41).

This apparatus was made in four pieces of glass: the boiler and vapor arm; the condenser and condensate receiver; the return manifold; and the ice well condenser. Auxiliary apparatus included the vacuum system, the cooling water system, thermometers, three electrical heating circuits, and a nitrogen system.

The bottom section of the boiler was fabricated with a smaller bubble so the depth of liquid would be sufficient for heating when most of the charge was in the condensate receiver. A large clean-out opening was provided in the top to permit removal of sludge which may be left in the boiler when working with heavy hydrocarbons. This opening was filled with an evacuated ball stopper in a standard 65/40 socket. The boiler had a capacity of 2000 ml., as compared to Othmer's approximately 1000 ml. capacity.

Two thermometer wells were provided in the boiler. One passed through the top ball stopper and terminated in the vapor space. The other passed through a 19/38 standard taper joint in the wall of the boiler, and was positioned to measure the temperature of the liquid in the center of the boiler, just above the small bubble.

Othmer discovered that the liquid temperature could be held constant and the vapor temperature varied over a range of about $20^{\circ}C$ (41). In operation, the liquid temperature was taken as the equilibrium temperature and the vapor heater controlled so the vapor temperature matched it.

The vapor arm extended upward from the side of the pot a distance of 18 inches. At this point it terminated in a 50/30 socket.

The upper end of the condenser-condensate receiver section was a continuation of the vapor arm. The line extending upward from the Allihn condenser made a 90° turn and projected horizontally for five inches. The other end of the horizontal line was turned 90° downward and terminated in a 50 mm. ball which fitted into the socket on the end of the vapor arm. A thermometer well extended through the upper wall of the horizontal line at the downward bend and was positioned in the center of the vertical vapor arm. The tip of the thermometer well was located 2 1/2 inches below the upper wall of the horizontal section, and three inches above the ball joint.

The bottom end of the Allihn condenser formed a drip spout to facilitate the counting of drops. Droplets of condensed vapor fell from the drip spout into the condensate receiver. The condensate receiver was of 1000 ml. capacity, graduated every 10 ml., from 60 to 990 ml., with every 100 ml. being etched all the way around the receiver to help eliminate parallax in reading the volume. (Othmer's condensate receiver was half this large).

The five ball condenser and condensate receiver were enclosed in a single water jacket. The inlet water connection was located at the top of the condensate receiver, with outlet nozzles at the bottom of the condensate receiver and at the top of the Allihn condenser. A length of three mm. capillary tubing extended downward from the condensate receiver and passed through the bottom of the water jacket.

A side arm extended from the bottom ball of the Allihn condenser, through the wall of the water jacket, and turned upward to terminate in a 24/40 standard taper joint. The ice well condenser fit into this joint. Ice and water were placed in the large central cold finger to condense those light vapors which might pass uncondensed through the water cooled Allihn condenser. An outlet was provided from the annular vapor space for connection to the vacuum system.

The three mm. tube which extended downward from the condensate receiver ended in a 12 mm. ball. A sampling line was fabricated which was connected to this ball by a 12/5 socket. The sampling line is shown in Figure 7. The upper leg of the tee ended in an 18/7 socket which connected to the bottom of the vapor return manifold. The open leg of the tee was plugged with a rubber serum stopper to permit the use of a syringe to withdraw samples which were analyzed in a gas chromatograph to determine the time of equilibrium.

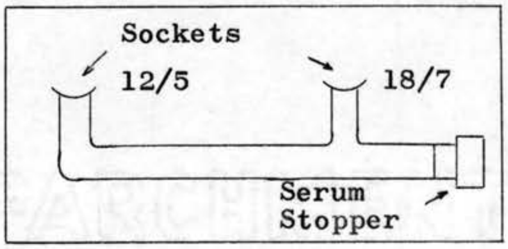


Figure 7. Sampling Line

The vapor return manifold is shown in Figure 8. The lower end of the receiver-side vertical arm ended in an 18/7 ball for connection to the sampling line. A three way cock was located just above the ball to permit draining the receiver. The small amount of liquid left in the line below the cock was drained by removing the rubber serum stopper.

Eight horizontal lines spaced 1 3/8 inches apart connected the two vertical arms of the manifold. Each horizontal line contained a stopcock. These stopcocks were opened or closed to control the level of the liquid in the condensate receiver. The level in the receiver was exactly horizontal with the level of the lowest open stopcock. In this way, positive, reproducible control was maintained of the vapor-liquid ratio. Varying the height of the lowest open stopcock changed the vapor-liquid ratio, for the same size charge, and changed the temperature of the equilibrium flash.

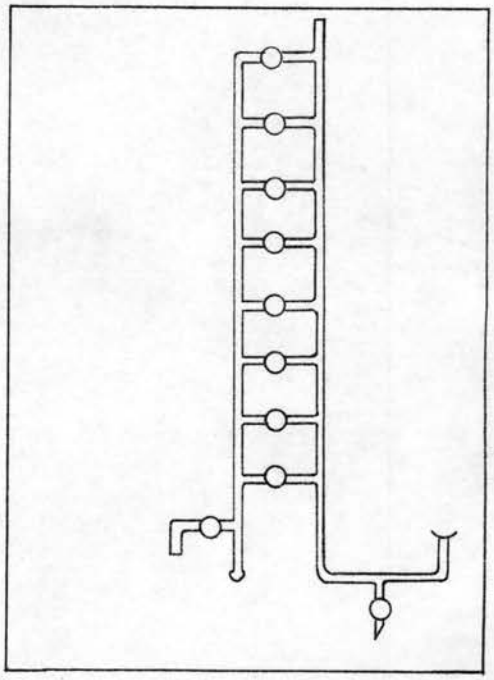


Figure 8. Vapor Return Manifold

The upper end of the boiler-side vertical arm extended past the highest horizontal line and ended in an open line. For atmospheric operation, this served as a siphon breaker. In this study, the line was connected to the vacuum system.

The lower end of the boiler-side vertical arm made a 90° bend and formed a five-inch-long horizontal arm which turned up at the end and terminated in a 12/5 socket. This socket was fastened to a 12 mm. ball on the end of a three mm. line which protruded from the bottom of the boiler. In the center of the horizontal arm was located a three way cock to permit draining the boiler.

Three separate electrical heating circuits of one ohm/ft. Nichrome wire wound about the glass still were provided, each controlled by a Variac. One circuit heated the lower half of the boiler, another the upper half of the boiler, and the third circuit heated the entire vapor arm, past the ball joint, to the beginning of the Allihn condenser. This arrangement permitted control of the liquid, vapor, and vapor arm temperatures.

The vacuum system is shown in Figure 6. It consisted of a vacuum pump, surge tank, manostat, manometer, and nitrogen bubbler. A bleed valve was located between the pump and surge tank. This valve was not sufficiently sensitive to control the pressure of the system, and was used only to release the vacuum when desired. A Cartesian manostat was connected between the surge tank and a wye. One branch of the wye was connected to a trap to protect the manostat from any materials which might be sucked into the line. The other end of the wye was connected to a differential mercury manometer.

A line ran from the trap to the nitrogen bubbler. Nitrogen was bled into the bubbler at a rate of one bubble per second, serving to form a back pressure which hindered the escape of hydrocarbon vapors from the system. The bubbler was partially filled with ethylene glycol to permit visual observation of the rate of injection of the nitrogen.

The line from the nitrogen bubbler went to a wye which led to the two connections on the still; i.e., the line from the ice well condenser annular vapor space and the line from the siphon breaker.

Operation of the Apparatus

Before charging the still, all stopcocks were cleaned and lubricated. The bottom four stopcocks on the vapor return manifold were lubricated with Fisher Nonaq stopcock grease because these cocks were not opened and plugging did not matter. All other cocks and joints were lubricated with Dow Corning High Vacuum grease. A new rubber serum stopper was used for each run.

The desired volume of charge was measured into a graduated cylinder and weighed. The boiler was charged through the liquid thermometer well joint, and the condensate receiver was charged through the ice well condenser joint. The manifold stopcocks were calibrated to determine the volume required to bring the liquid level in the receiver even with each of the cocks. These volumes are listed in Table I. The cocks were numbered from the bottom up.

TABLE I

CALIBRATION OF VAPOR RETURN MANIFOLD

Lowest open cock	Volume in receiver, ml.
1	177
2	270
3	370
4	465
5	560
6	655
7	750
8	845

The first run was made to determine the Variac settings. After the feed was added and the still reassembled, the vacuum pump was started. The nitrogen was turned on and allowed to bubble into the line between the trap and the still. The atmospheric pressure was recorded and sufficient vacuum applied to the system to bring the absolute pressure in the still to 350 mm. Hg. The Cartesian manostat was adjusted to maintain this pressure. The heating circuits were energized and the Variacs turned to the approximate range necessary for equilibrium conditions. For the light oil used in this study, initial settings of 30, 20, and 10 were adequate for the liquid, vapor, and vapor arm Variacs, respectively. The liquid Variac was adjusted to give a boil-up rate of about two drops per second. As the still approached equilibrium these settings were adjusted so the vapor and liquid temperatures would be the same and the vapor arm temperature would be a couple of degrees higher. The vapor temperature was adjusted to the liquid temperature.

When the temperatures became steady, satisfying the stated conditions, the main power switch to the heating circuits was turned off. The settings were left on the Variacs so no adjustments would be necessary during the equilibrium flash. The vacuum pump was turned off and the bleed valve opened to release the vacuum. The liquid was drained from the boiler and condensate receiver and discarded. The rubber serum stopper was removed and discarded so the stopper, which was attacked by the hydrocarbons, would not foul the sides of the tube.

The data that were recorded during every run included: run number, date, charge, barometric pressure, still pressure, time, Variac settings, liquid temperature, vapor temperature, vapor arm temperature, and remarks. Temperatures were recorded every 30 minutes. Each time the temperatures were read, the barometric and still pressures were checked to be sure that the still pressure was 350 mm. Hg absolute. This check was recorded as an "ok" in the column headed "Pressure". If an adjustment was necessary, the amount of error was recorded.

For an equilibrium run, the start up procedures were the same. Usually no adjustment of the Variacs was necessary. Very minor changes were sometimes required.

When the temperatures reached the desired conditions, samples of 0.5 to 1.0 ml. were taken through the rubber serum stopper with a tuberculin syringe. These samples were taken at 30 minute intervals and were immediately analyzed in the gas chromatograph. The attainment of three successive analyses of constant peak height ratios was accepted as proof that the still was at equilibrium.

The shut down procedure previously described was followed except that the liquids drained from the boiler and condensate receiver were weighed and retained. The boiler was allowed to cool before the liquid was drained from it. The liquid was generally cool enough after two hours to be handled safely.

All runs made in this study were at a volumetric vapor - liquid ratio of 560 ml. vapor to 750 ml. liquid, i. e., 42.7 per cent flashed at 177°F and 350 mm. Hg absolute pressure. Additional flashes were made at the same conditions to obtain the quantity of material necessary for analysis. All vapor and liquid products were blended before analytical distillation. This ensured that minor differences in composition which might have occured in the equilibrium flash were not carried over into the analytical distillation, and the evaluation of the two TBP apparatus would be made using identical charges.

Calculation of K Values

In 1960 Edmister (15) proposed the use of the ratio of slopes method to obtain vapor-liquid equilibrium constants. Simply stated,

$$K = \frac{(dT/dm)_L}{(dT/dm)_V} \qquad (6)$$

where $(dT/dm)_L$ is the slope of the molar TBP curve of an equilibrium flash liquid product and $(dT/dm)_V$ is the slope of the molar TBP curve of the vapor product in equilibrium with the liquid, both slopes measured at the same temperature.

This method of computing K values is well suited for complex mixtures, since only point values are needed. For component mixtures which yield plateaus in the TBP curves, the temperatures should be chosen to intersect the steeper portions of the curves between plateaus. This disadvantage may be surmounted by using the ratio of differences method. The coordinates of the curve at mid-points between the selected temperatures are determined and the ratio of the differences between these values used instead of the ratio of the slopes at the point of intersection with the temperature. Then

$$K = \frac{(\Delta T/\Delta m)_L}{(\Delta T/\Delta m)_V} \tag{7}$$

A modification of this equation uses volumetric TBP curves and molar volumes (15).

$$K = \frac{(\Delta T/\Delta \text{ volume per cent})_V}{(\Delta T/\Delta \text{ volume per cent})_L} \; \frac{(m/G)_L}{(m/G)_V} \tag{8}$$

where: m/G is moles per gallon of the fraction.

Computer Program for Processing Data

The first step in the calculation of K values was the conversion of the volumetric TBP curves to molar TBP curves. The calculations involved were sufficiently lengthy and tedious to require a check calculation. A Fortran program was written for the IBM 650 to reduce the amount of time required for these calculations, and to improve the accuracy of the results.

As described in the preceding section, small cuts of five volume per cent were taken during the analytical distillation and analyzed for weight, specific gravity, and freezing point depression. The program calculated the weight of each cut, the molecular weight, and the cumulative mole fraction.

Input data for the program consisted of initial boiling point and the specific gravity of benzene determined at the same time the specific gravities of the samples were measured, and, for each cut, the end point, the weight of the sample bottle, the weight of bottle and sample, the depression in freezing point, and the specific gravity.

Output cards from this program listed the initial boiling point, the total number of moles, and, for each cut, the end point, weight of the cut, the factor 51.2 ρ_s/ρ_b, the molecular weight of the cut, the number of moles in the sample, and the cumulative mole fraction. From this information the molar TBP curve was constructed.

Method of Calculating K Values

The curves for the feed and the equilibrium vapor and liquid products were all drawn on the same graph. The temperatures used to identify the pseudo-components were selected, and the slopes of the vapor and liquid curves determined at the intersection with these temperature values. The ratio of $(dT/dm)_L/(dT/dm)_V$, the vapor-liquid equilibrium constant, so calculated, is valid for the pseudo-component identified by the temperature, at the conditions of the equilibrium flash.

Temperatures for identifying hypothetical components in K value evaluation were selected in 10 degree increments throughout the boiling range of the material. Slopes were determined by the mirror method; a polished metal mirror was placed normal to the curve at the point of intersection with the desired temperature, and the mirror adjusted so the curve and the image formed a smooth, continuous line. The edge of the mirror thus gave the normal to the curve at that point; Δx and Δy were easily found by counting the lines and the slope of the curve then calculated from $\Delta y/\Delta x$.

For comparison, K values were also calculated by the ratio of differences method. The values of the curve were found at midpoints between the identifying temperatures and K ratios found by the ratios of the differences for the values on either side of the identifying temperature.

The values of the mole fractions of the feed TBP curve were found where it intersected the selected temperatures; equilibrium constants and corresponding feed mole fractions were used as input data for the equilibrium flash vaporization computer program described in the next chapter. The vapor-liquid ratio was calculated from this program and compared with that obtained experimentally. The program also computed points for the TBP curves of the products of the equilibrium flash, which were plotted and compared with those curves actually obtained. In this way the accuracy of the calculated results was checked. This method is preferable to comparison with vapor pressure K values because of the presence of many types of compounds which would not necessarily give ideal vapor pressures.

The digital computer was not used to calculate the slopes of the curves and the equilibrium constants because of the difficulty of fitting a curve to the data points. A program was written which attempted to fit a curve to a relatively smooth set of points, but the results of the curve fit were not satisfactory. For this reason the decision was made to determine the slopes by hand; the use of hand calculations also gave the advantage of more freedom in selection of the temperatures used to identify the pseudo-components.

CHAPTER V

APPLICATION OF THE INTEGRAL TECHNIQUE

The principle underlying the integral technique was first published in 1933 (31). Harbert (27, 28) presented modifications of this principle which utilized a differential technique in distillation calculations for complex petroleum fractions. Various applications of the integral technique were presented, but were generally extremely difficult to use (4, 5, 6, 18, 19). In 1955 Edmister (13) presented an application of the integral technique to three types of calculations: equilibrium flash vaporization; bubble and dew points; and fractional distillation. Later, a batch distillation calculation was added (16).

The integral technique is particularly suited to calculations for complex mixtures because it does not require knowledge of the components. It also may be applied to a mixture containing one component or more in sufficient quantity to give a plateau in the distillation curve.

Amir-Yeganeh (1) presented a comprehensive discussion of the integral technique and its theoretical concepts; this work deals with the application of the technique. In this work, programs were written for the IBM 650 computer which do the three types of calculations shown by Edmister in 1955. The same method of calculation was used; the integrated form of the Lagrange interpolation equation was used to integrate the curve (46).

Combined Program

This program combines the equilibrium flash vaporization and the bubble and dew point calculations; the program will do either or both by the use of one of three control cards. A block diagram of the program is given in Figure 9.

A sufficient number of K values at isobaric conditions are required to permit making a quartic curve fit for the bubble point - dew point part of the program. The resulting empirical equation is

$$\log K = A + B\left(\frac{T}{100}\right) + C\left(\frac{T}{100}\right)^2 + D\left(\frac{T}{100}\right)^3 + E\left(\frac{T}{100}\right)^4 \qquad (9)$$

where: T is in ^{o}R.

The five constants thus obtained are input data for the program. The equilibrium flash vaporization program requires only the K value - feed mole fraction relationship and other miscellaneous data to calculate the vapor - liquid ratio and the points for the TBP curves of the equilibrium vapor and liquid products.

The calculations are based upon the integrated form of the Lagrange interpolation equation to find the area under the curve. The accuracy of the results depends on the smoothness of the curve and the selection of sufficient input values to describe the curve accurately.

The equations used in the integral technique are completely analogous to the distillation calculation equations for component mixtures. The equilibrium flash vaporization (EFV) part of the program is a trial and error solution to find the vapor - liquid ratio.

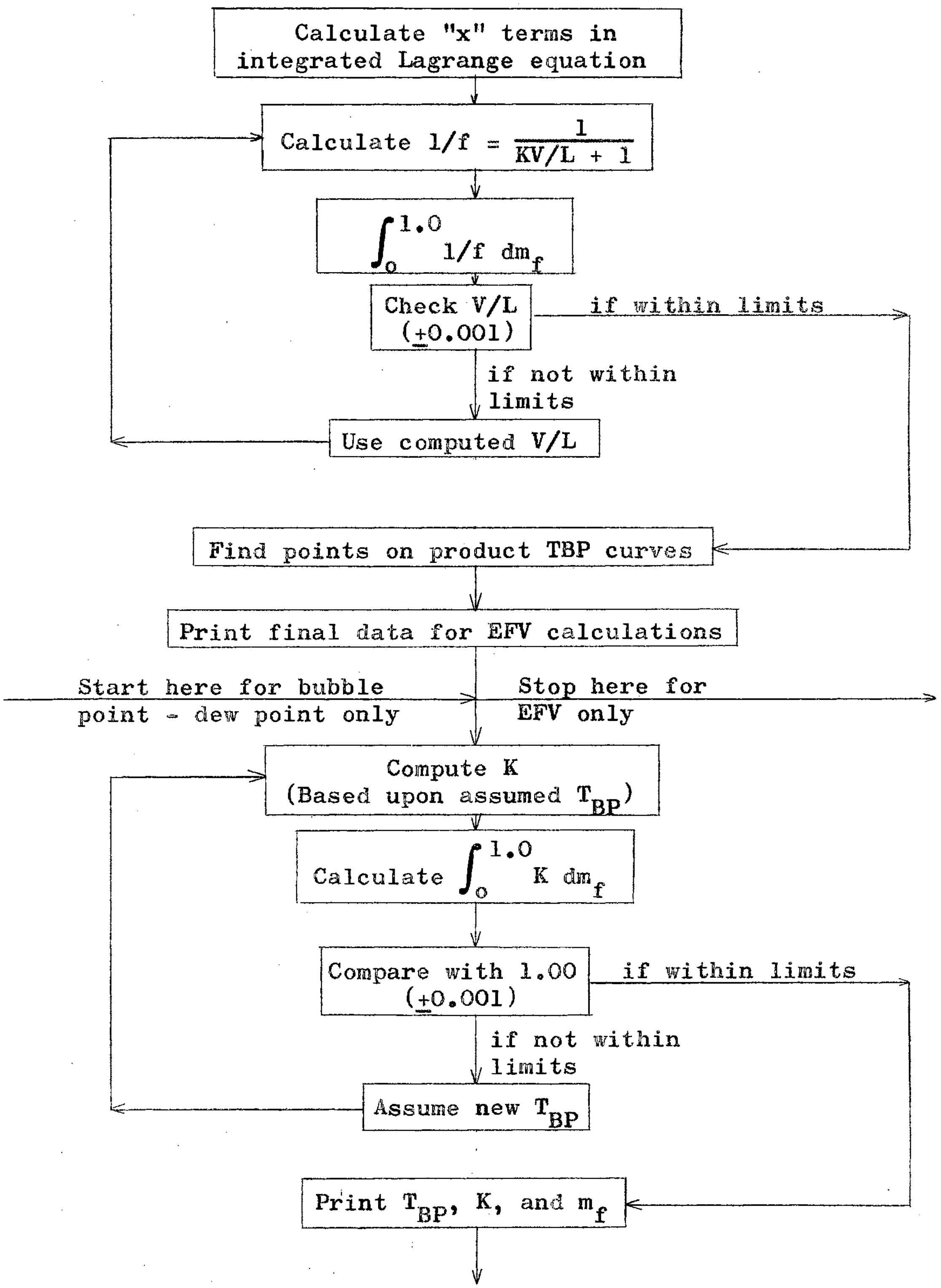


Figure 9. Block Diagram of Combined Program

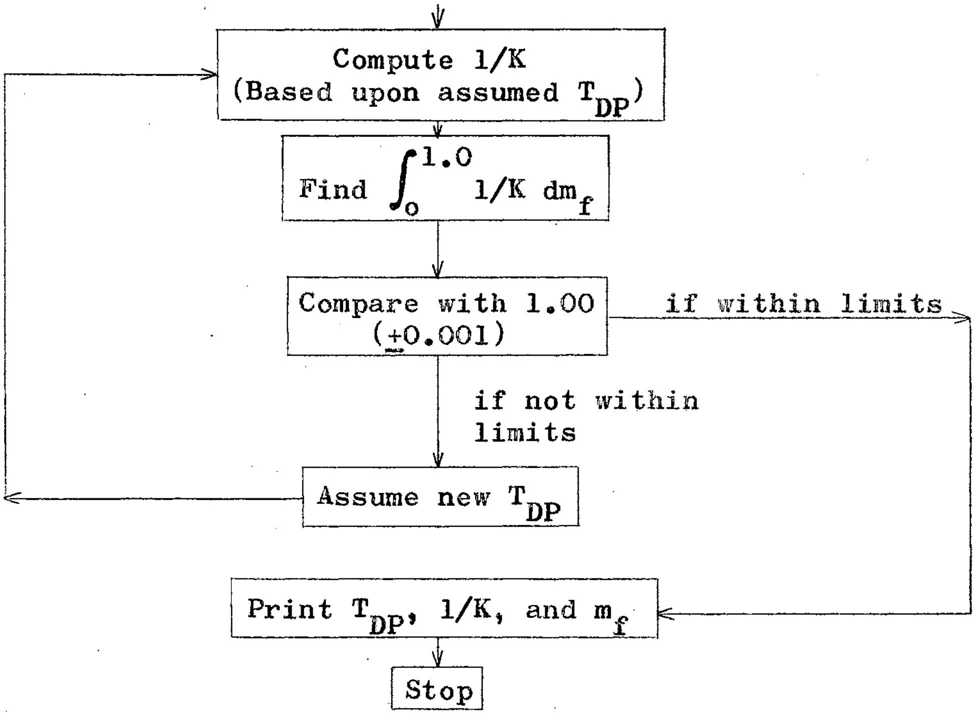


Figure 9. Block Diagram of Combined Program (Cont.)

A value of V/L is assumed, $1/f = \frac{1}{1 + KV/L}$ is calculated, and the curve of 1/f versus m_f integrated to find L/F. V/L is found from the relationship $V/L = \frac{1 - L/F}{L/F}$. If the calculated V/L is not within 0.001 of the assumed V/L, the calculated V/L is used as the new assumed value and the calculation repeated until agreement is reached.

For the bubble point calculation, a temperature is assumed and the values of K found by equation 9; the area under the curve K vs. m_f is calculated to satisfy the condition

$$\int_0^1 K \, dm_f = 1.0 \tag{10}$$

within an agreement of ± 0.001. The value of the assumed temperature is corrected until equation 10 is satisfied. The temperature which satisfies this condition is punched with the K values which were calculated.

For the dew point calculation, a temperature is assumed and values of K calculated as before; the area under the curve 1/K vs. m_f is found to satisfy the condition

$$\int_0^1 1/K \, dm_f = 1.0 \tag{11}$$

within ± 0.001. Again, the temperature and values of 1/K are punched.

Control cards are used to permit the calculation of EFV, dew point - bubble point, or both. The program will take up to 19 input data points, but there must be an odd number.

Input data are mole fraction of the feed curve and corresponding equilibrium constant; the constants for equation 9; the first estimate of the bubble point temperature, ^{o}R, divided by 100; the first estimate of the dew point temperature, ^{o}R, divided by 100; the number of input data points; and the first estimate of the V/L ratio.

Output data from the EFV calculation are

1. V/L
2. Difference between V/L assumed and V/L calculated
3. $\int_o^{m_f} 1/f \, dm_f$
4. $\int_o^{m_f} v/f \, dm_f$
5. $\dfrac{\int_o^{m_f} 1/f \, dm_f}{L/F}$
6. $\dfrac{\int_o^{m_f} v/f \, dm_f}{V/F}$
7. m_f
8. 1/f

Output data from the bubble point - dew point calculation are

1. $T_{BP}/100$
2. Difference between $T_{BP}/100$ assumed and calculated
3. K vs. m_f
4. $T_{DP}/100$
5. Difference between $T_{DP}/100$ assumed and calculated
6. 1/K vs. m_f

Fractional Distillation Program

This program was written to calculate the points necessary to construct TBP curves of the product streams of a simple distillation column with no side streams. The number of trays, and tray temperatures and vapor and liquid loadings must be known. In this respect the program is limited, but the method is demonstrated and a more practical program is feasible. A block diagram of the program is shown in Figure 10.

This program also used the integrated form of the Lagrange interpolation equation to calculate the area under the curves, and requires an odd number of input data points. The calculation is based upon the absorption factor - stripping factor method (14). The program will handle up to 19 pseudo-components and up to 15 plates above and below the feed, including the reboiler and a partial condenser. The use of a total condenser with reflux permits an additional plate above the feed.

Since temperatures and vapor and liquid loadings are known, the program is a straight forward calculation. V/L ratios are calculated, K values found by equation 9, and values of absorption or stripping factors calculated for each pseudo-component on each tray. The absorption factor is $A = L/KV$, and the stripping factor is $S = KV/L$. From these calculations l_k/d and v_h/b may be found where

$$l_k/d = R\, A_k\, A_{k-1} \ldots A_1 + A_k\, A_{k-1} \ldots A_1 + A_{k-1} \ldots A_1 + \ldots + A_1 \qquad (12)$$

and

$$v_h/b = S_h\, S_{h-1} \ldots S_1 + S_{h-1}\, S_{h-2} \ldots S_1 + S_{h-2} \ldots S_1 + \ldots + S_1 \qquad (13)$$

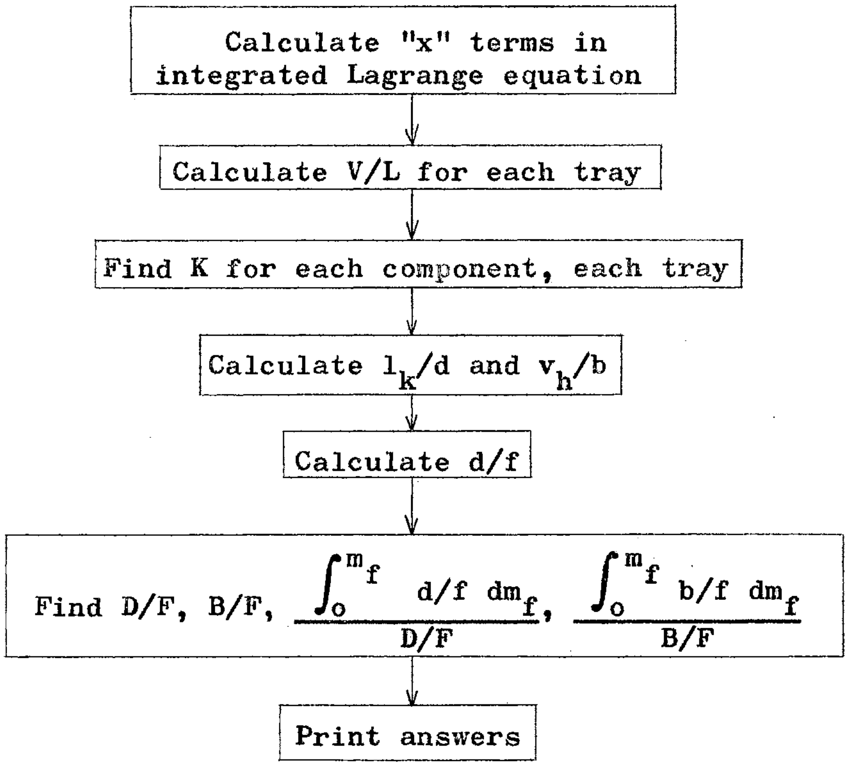


Figure 10. Block Diagram of Fractional Distillation Program

Plates are numbered from the feed zone toward the terminals. Then, by material balance,

$$d/f = \frac{v_h/b + v_f/f}{l_k/d + v_h/b + 1} \qquad (14)$$

The curve d/f vs. m_f is integrated to find D/F, and B/F is found by difference. The points on the product TBP curves are then given by $\frac{\int_0^{m_f} d/f \; dm_f}{D/F}$ and $\frac{\int_0^{m_f} b/f \; dm_f}{B/F}$.

Input data for the program are mole fraction of the feed curve, constants for equation 9, the number of input data points, the number of plates above the feed, the number of plates below the feed, tray temperatures, vapor and liquid loadings, and reflux rate.

Output data for the program are

1. K vs. m_f for each plate
2. D/F
3. B/F
4. $\frac{\int_0^{m_f} d/f \; dm_f}{D/F}$
5. $\frac{\int_0^{m_f} b/f \; dm_f}{B/F}$
6. d/f

CHAPTER VI

EXPERIMENTAL DIFFICULTIES

Some of the laboratory problems encountered in this study are of such unusual and interesting nature that a brief discussion is presented for the benefit of anyone doing a similar work. The particular areas are discussed in the order of their encounter in the experimental procedure.

Equilibrium Flash Vaporization

The Othmer vapor-recirculating equilibrium still was modified for use in this study. The modification permitted close control of the vapor-liquid ratio and the collection of larger sample sizes than Othmer's design yielded (41).

The still, as modified, contained ten stopcocks, five ball and socket joints, and two standard taper joints, exclusive of the vacuum system. The amount of air leakage under conditions of 350 mm. Hg absolute pressure was excessive. The amount of leakage and loss of charge from the still was so bad that close control of the vapor-liquid ratio, which was the reason for eight of the stopcocks, was not achieved, because of inability to control the amount of sample lost in any given run.

Leakage of the two ball joints connecting the sampling line to the still also caused difficulties. A leak in the condensate receiver - sampling line joint permitted the formation of an air bubble in the three mm. capillary line extending downward from the receiver. The presence of a bubble in this line blocked the flow of condensate from the receiver, increasing the level of liquid in the receiver, and upsetting the equilibrium conditions. This bubble could be removed by allowing a pressure build up in the manifold, forcing the liquid and bubble up the tube, until the bubble escaped into the receiver.

A serious leak in any of the joints or cocks below the lowest open stopcock permitted the formation of bubbles in the line, which also upset the equilibrium. As the bubbles flowed up the vertical arm, they raised the liquid level in the arm, causing excessive flow through the stopcock. This caused the level to drop in the condensate receiver, changing the vapor-liquid ratio, and upsetting the equilibrium conditions.

Even though the still was modified to yield larger samples, duplicate runs were still necessary to obtain sufficient sample for the analyses. Two analytical columns were used in this study; the Oldershaw column gave a better separation but required a greater amount of time for the analysis. The Sarnia column did not require so much charge, permitting an analysis in a shorter amount of time, but did not give so sharp a separation. The selection of one of these two stills as yielding data which will produce more accurate K values will eliminate the necessity for duplicate analyses. Use of only the Oldershaw column will reduce the product requirement by 2/5. A further reduction in product amount required may be realized by making one analytical distillation with an accepted degree of error, eliminating the duplicate distillation to check the temperature points.

Analytical Distillations

The Oldershaw column was a piece of equipment which had been used by previous workers and gave no difficulty.

The Sarnia MK II Fractionator, on the other hand, was installed during this study and gave considerable difficulty of the type which is generally associated with any unfamiliar piece of equipment. During installation, the thermocouple well was broken and a new one fabricated locally. Attempts to obtain reproducible volumetric TBP curves were met with disagreement of as high as 14°F. After some time the trouble was found to be in the position of the new thermocouple well. The tip of the well extended too far into the column and a liquid bridge would frequently form between the tip of the well and the stainless steel valve rod, providing a sink for drawing heat away from the thermocouple. The tip was shortened by three mm. and no further liquid bridging was encountered.

The TBP curve from the second run made after shortening the tip of the thermocouple well did not agree with the results of the first run. Investigation revealed the presence of quiescent boiling, an evaporation without nucleation. This caused "bumping" of the liquid in the boiling flask, which gave erratic temperature readings. The presence of a magnetic stirring bar in the still pot did not remove this phenomenon. Thereafter, boiling chips were used in addition to the stirrer and the difficulty was not again encountered.

A sample of the charge, Hydroformer Feed, was distilled in a similar apparatus in the Imperial Oil, Ltd., laboratories in Sarnia, Ontario (9). The phenomenon of quiescent evaporation was again encountered. This had been experienced before, but generally in pure compounds, and not in a petroleum fraction containing so many components.

Molecular Weights

The most time consuming phase of this method of obtaining experimental K values was the determination of molecular weights. Not only was the cryoscopic method long and tedious, but it proved to be inaccurate for the petroleum fraction investigated in this study. Amir-Yeganeh reported generally favorable results except for his Oil D which was Hydroformer Product (1). The other oils studied by Amir-Yeganeh were naphthas and kerosene cuts. The oil used in this study was Hydroformer Feed, a mixture of straight and branch chain saturated and unsaturated hydrocarbons, with some ring sulfur compounds present.

The molecular weights obtained were suspected to be inaccurate from the first set determined, but Mr. Amir-Yeganeh and the writer were not aware of more accurate methods in general use at that time. For this reason the cryoscopic method was used for the remainder of the study.

CHAPTER VII

RESULTS

The purpose of this study was to select apparatus and develop techniques which would yield accurate phase distribution ratios in a short time, to obtain such distribution ratios, and to use them in integral calculational techniques. Each of these three areas will be discussed in turn.

Apparatus and Techniques

Both equilibrium and analytical apparatus were studied. The modified Othmer still was found to be unsatisfactory for this work: the amount of product obtained in one run was not sufficient to permit analysis; excessive leakage through the many joints prohibited reproducibility of the vapor-liquid ratio for successive runs, and allowed too great a loss of charge stock; the equilibrium attainment time was excessive. Modifications of this apparatus have been used successfully by many workers, but the performance of the particular piece of apparatus used in this work left much to be desired.

A choice cannot be made between the two analytical columns because the K values obtained from both columns are not sufficiently accurate to justify a choice. The Oldershaw column gave better resolution, but required more sample and hence longer time than the Sarnia Fractionator. The Sarnia column did not have so many plates and required smaller charge, giving a shorter time for an analysis, but did not yield comparable resolution.

The cryoscopic method used for determining molecular weights of the TBP cuts was not satisfactory. Comparative cryoscopic analyses were made by another laboratory on one set of samples, and showed accurate values of molecular weight for only 50 per cent of the samples tested. These data are shown in Table II.

TABLE II

COMPARISON OF EXPERIMENTAL MOLECULAR WEIGHTS

Cuts from Sarnia analysis of equilibrium liquid produdt.

Sample	Cryoscopic Molecular Weight (This laboratory)	Cryoscopic Molecular Weight (Another laboratory)*	Vapor Density Molecular Weight
B	90.8	112.0	102.3
V_1	91.4	104.7	98.3
L_1	94.3	100.4	106.0
101	86.0	92.6	84.2
109	84.3	92.4	94.7
116	91.3	103.6	105.4
118	88.4	104.4	109.0
144	90.0	110.2	110.1

* Continental Oil Company, Research and Development Laboratory, Ponca City, Oklahoma

Two other methods of molecular weight determination were given cursory examination. The use of an application of the Victor Meyer principle of vapor density gave the most accurate results for the samples analyzed, in the range 85 to 110 MW. This principle is limited by insufficient vapor pressure of samples in the range 180 MW. Above this range the Mechrolab Osmometer may be reliable. Since the Osmometer works on the same principle as cryoscopy, it might not be reliable for highly non-ideal solutions, as were apparently encountered in this work. The Osmometer is limited in the lower range of about 180 MW by the solute vapor pressure to solvent vapor pressure ratio.

The specific gravities and weighings obtained in this work were of sufficient accuracy. Any greater accuracy would require an excessive amount of time.

Phase Distribution Ratios

Phase distribution ratios were obtained from TBP curves from both the Sarnia and Oldershaw analytical columns. The feed and product curves for each column were drawn on one plot and K values obtained by both the ratio of slopes and the ratio of differences methods. The first set of K values was obtained from curves which were drawn directly through the data points. These values are shown in Table III. A second set of K ratios was obtained from smoothed curves which were drawn within ± 3°F of the data points. These values are shown in Table IV.

Each set of phase distribution ratios was plotted as log K vs. T, and the best straight line drawn through the points. K values were obtained from these plots by reading the intersection of the temperature of the data point with this straight line.

TABLE III

COMPARISON OF K VALUES FROM TBP ANALYSES

	Data From Oldershaw Analytical Column		Data From Sarnia Analytical Column	
Temp., °F	Ratio of Slopes Method	Ratio of Differences Method	Ratio of Slopes Method	Ratio of Differences Method
155	6.33	4.07	6.90	7.25
165	1.778	1.81	2.27	3.13
175	2.49	2.74	10.00	8.08
185	1.81	1.96	5.77	6.73
195	0.679	1.306	0.980	0.923
205	1.503	0.918	2.66	1.667
215	1.080	1.665	0.831	0.843
225	1.144	0.947	1.070	1.030
235	0.522	0.555	0.375	0.579
245	1.025	0.707	1.025	0.778
255	0.401	0.402	0.445	0.392
265	0.667	0.698	0.330	0.310
278	0.164	0.231	0.335	0.313

TABLE IV

COMPARISON OF K VALUES FROM SMOOTHED TBP ANALYSES

	Smoothed Data From Oldershaw Analytical Column		Smoothed Data From Sarnia Analytical Column	
Temp., °F	Ratio of Slopes Method	Ratio of Differences Method	Ratio of Slopes Method	Ratio of Differences Method
155	2.325	3.00	9.75	7.00
165	1.706	1.693	5.10	5.60
175	2.770	2.610	10.69	9.78
185	1.904	1.936	5.76	4.10
195	1.250	1.287	0.962	0.992
205	1.228	1.027	2.06	1.576
215	1.335	1.546	0.734	0.880
225	0.603	0.829	1.092	0.934
235	0.748	0.728	0.590	0.653
245	0.710	0.577	0.755	0.699
255	0.584	0.530	0.432	0.415
265	0.404	0.780	0.349	0.340
278	0.168	0.335	0.224	0.285

One line was drawn for the plots of both the ratio of slopes and the ratio of differences methods. Data from Sarnia analyses gave higher K ratios at the lower boiling end, with K decreasing more rapidly with temperature than for the Oldershaw data, to give approximately equal values from both analytical columns at the higher boiling end of the feed.

All sets of K values were used in the equilibrium flash vaporization calculation program to check agreement of calculated and experimental results.

The inaccuracies of determining the K values by the ratio of slopes were investigated. The inaccuracy of $\pm 3^{\circ}F$ which was accepted for the analytical distillations yielded differences in the value of the K ratios ranging from -600 to +600 per cent of the values reported. This was determined by replotting the points with the error of 3° applied, and finding the K values from this plot. This shows that accurate temperature measurement is very critical.

The effect of the inaccurate molecular weights used in calculating mole fraction was investigated by calculating the mole fraction using molecular weights interpolated from a plot of the vapor density molecular weights. TBP curves were drawn using these mole fractions, and K values found from these TBP curves. The resulting K values differed from those reported by -34.1 to +186 per cent.

Integral Calculations

Two equilibrium flash vaporization calculations were made with the computer program when first written to check the results with those obtained by other means. Comparisons of V/L ratios for computer, hand, and planimeter solutions for two sets of input data are shown in Tables V and VI. A sample fractional distillation calculation is shown in Table VII.

Equilibrium flash vaporization calculations were made with the K ratios obtained in this work. The results of all calculations are shown in Appendix B. Vapor-liquid ratios were calculated for comparison with the experimental vapor-liquid ratio; the points for the product TBP curves were calculated and compared with the results obtained experimentally. No good checks were obtained.

A program was written to find the line on the log K vs. T plot that would satisfy the experimental vapor-liquid ratio and simulate the product TBP curves. This program needs minor alterations to perform satisfactorily.

The over all results of this work are not encouraging, but the same approach has yielded successful results in the past (1). Additional work needs to be done in the selection of apparatus, particularly for the determination of molecular weights.

TABLE V

COMPARISON OF HAND AND COMPUTER RESULTS, EFV CALCULATION I

Data from "Applied Hydrocarbon Thermodynamics," Chapter 14 (16)

V/L assumed = 3.23

K	m_f	KV/L + 1	1/f	Mean 1/f	Increment	Cumulative
7.4	0.0	25.0	0.040	0.056	0.0	0.0
4.0	0.14	13.95	0.072	0.0975	0.0078	0.0078
2.2	0.38	8.11	0.123	0.1575	0.0234	0.0312
1.3	0.62	5.20	0.192	0.268	0.0378	0.0690
0.59	0.78	2.91	0.344	0.426	0.0429	0.1119
0.30	0.87	1.969	0.508	0.598	0.0383	0.1502
0.14	0.93	1.452	0.688	0.758	0.0359	0.1861
0.064	0.97	1.207	0.828	0.804	0.0303	0.2164
0.027	1.00	1.087	0.920		0.0241	0.2405

By hand calculation

$$V/L = \frac{1-0.2405}{0.2405} = 3.16$$

By planimeter

$$\int_{o}^{1.0} 1/f \; dm_f = 0.2347$$

V/L = 3.26

By IBM 650

V/L = 3.19

TABLE VI

COMPARISON OF HAND AND COMPUTER RESULTS, EFV CALCULATION II

Data from Thiele and Geddes (49)

V/L assumed = 2.468

K	m_f	KV/L + 1	1/f	Mean 1/f	Increment	Cumulative
217	0.0	536	0.002		0.0	0.0
84.2	0.03	209.3	0.005	0.0035	0.00010	0.00010
42.9	0.054	107.1	0.009	0.007	0.00017	0.00027
40.2	0.113	100.1	0.010	0.0095	0.00047	0.00074
21.7	0.184	54.5	0.018	0.014	0.001	0.00174
9.67	0.271	24.95	0.040	0.029	0.00254	0.00428
4.77	0.378	12.8	0.078	0.059	0.00632	0.0106
2.57	0.481	7.35	0.136	0.107	0.0110	0.0216
1.38	0.566	4.41	0.227	0.1815	0.0154	0.0370
0.760	0.644	2.88	0.347	0.2870	0.0224	0.0594
0.492	0.699	2.22	0.450	0.3985	0.0219	0.0813
0.337	0.751	1.832	0.545	0.4975	0.0259	0.1072
0.238	0.808	1.588	0.630	0.5875	0.0335	0.1407
0.172	0.854	1.425	0.702	0.6660	0.0306	0.1713
0.132	0.898	1.326	0.755	0.7285	0.0321	0.2034
0.095	0.937	1.235	0.810	0.7825	0.0305	0.2339
0.0684	0.968	1.169	0.855	0.8325	0.0258	0.2597
0.0427	0.994	1.105	0.905	0.880	0.0229	0.2882
0.0240	1.000	1.059	0.945	0.925	0.0056	0.2882

By hand calculation

$$V/L = \frac{1-0.2882}{0.2882} = 2.47$$

By planimeter

$$\int_{o}^{1.0} 1/f \; dm_f = 0.285$$

V/L = 2.51

By IBM 650

V/L = 2.51

TABLE VII

COMPARISON OF HAND AND COMPUTER RESULTS, FRACTIONAL DISTILLATION CALCULATION

Data from Thiele and Geddes (49)

Component °R	325	472	492	557	667	714	758	800	829	853	875	895	913	932	957	977	1007
m_f	0.0	0.054	0.113	0.184	0.378	0.481	0.566	0.644	0.699	0.751	0.808	0.854	0.898	0.937	0.968	0.994	1.00
Reboiler T = 435°F L = 196 V = 1079 V/L = 5.5																	
K	341	80.4	71.4	41.3	14.85	8.58	5.18	3.26	2.25	1.70	1.315	1.00	0.79	0.616	0.479	0.329	0.212
K calculated	373.3	80.3	71.0	40.9	15.0	8.45	5.10	3.19	2.19	1.67	1.29	0.985	0.770	0.600	0.468	0.325	0.205
S_o = KV/L	1876	442	393	227	82.8	47.2	28.5	17.9	12.38	9.35	7.09	5.42	4.25	3.39	2.63	1.81	1.166
Plate 1 T = 265°F L = 1275 V = 818 V/L = 0.642																	
K	259	56.2	47.7	27.2	7.63	4.24	2.40	1.395	0.934	0.667	0.486	0.362	0.281	0.210	0.1565	0.102	0.0605
K calculated	261.4	56.1	47.4	27.2	7.56	4.26	2.41	1.41	0.943	0.672	0.489	0.361	0.282	0.211	0.157	0.102	0.0605
S_1 = KV/L	166	36.1	30.6	17.46	4.854	2.72	1.541	0.896	0.60	0.428	0.314	0.232	0.180	0.135	0.1005	0.0655	0.0388
Plate 2 T = 355°F L = 208 V = 822 L/V = 0.253																	
K	251	53.2	44.3	25.5	6.85	3.80	2.14	1.22	0.815	0.575	0.414	0.308	0.235	0.174	0.130	0.084	0.0486
K calculated	250.8	52.9	44.4	25.4	6.74	3.81	2.14	1.23	0.820	0.580	0.418	0.307	0.239	0.178	0.132	0.085	0.050
A_2 = L/KV	0.001	0.0047	0.0057	0.0099	0.0375	0.0666	0.1182	0.207	0.310	0.440	0.605	0.825	1.077	1.454	1.946	3.01	5.21
Plate 3 T = 322°F L = 212 V = 822 L/V = 0.258																	
K	317	42.9	35.0	20.0	4.77	2.57	1.38	0.76	0.492	0.337	0.238	0.172	0.132	0.095	0.068	0.0427	0.024
K calculated	216	42.8	35.1	20.0	4.47	2.55	1.38	0.76	0.500	0.340	0.237	0.170	0.132	0.097	0.070	0.043	0.024
A_3 = L/KV	0.0012	0.0060	0.0074	0.0129	0.0577	0.1004	0.187	0.339	0.524	0.766	1.089	1.518	1.955	2.716	3.77	6.04	10.75
Enriching with reflux R = 0.3475																	
$A_2[1+A_3(1+R)] = l_k/d$	0.0010	0.0048	0.0058	0.0101	0.0404	0.0756	0.1480	0.3016	0.5289	0.894	1.493	2.513	3.91	6.78	11.84	27.51	80.70
$S_1(S_o+1) = v_h/b$	311,600	15,990	12,060	3981	407	131	45.5	16.93	8.03	4.43	2.54	1.489	0.965	0.593	0.365	0.1841	0.084
d/f = $\frac{v_h/b}{v_h/b+l_k/d+1}$	0.99999	0.9999	0.9999	0.9999	0.9975	0.9924	0.976	0.943	0.840	0.701	0.505	0.2977	0.164	0.0708	0.0276	0.0065	0.0010
d/f (computer)	1.000	0.9999	0.9999	0.9997	0.9975	0.9918	0.975	0.930	0.843	0.713	0.529	0.3263	0.1867	0.0861	0.0346	0.0084	0.0014

CHAPTER VIII

CONCLUSIONS

1. The modified Othmer vapor-recirculating equilibrium still used in this work was not satisfactory because of insufficient product yield, excessive equilibrium attainment time, and excessive leakage around the joints under moderate vacuum conditions.
2. There is excessive material loss from both the Oldershaw and Sarnia analytical columns even when operating with Teflon rings in the ball joints and a dry-ice trap on the overhead condenser.
3. The TBP curves and range of values in the K ratios obtained from the Sarnia analyses indicate that this column probably does not give sufficiently good resolution for K value determination.
4. The cryoscopic method of determining molecular weights is not accurate for the oil investigated in this work. Comparison of results obtained in this study with results obtained by another laboratory on the same samples indicate that part of the error is caused by a physical property of the oil.
5. The K values obtained in this investigation are not accurate: the calculated vapor-liquid flash ratio does not check the experimental vapor-liquid ratio and the calculated product

TBP curves points do not agree with the experimental TBP curves.

6. The calculational technique employed in the computer program yields accurate results, compared with hand and planimeter solutions for the same input data.

CHAPTER IX

SUGGESTIONS FOR FUTURE WORK

Toward the conclusion of this work many problems arose which have not been fully solved. Steps have been taken to obtain answers to most of these problems, but others have not yet been studied. This study served the purpose of calling attention to some of these problems, which others are now investigating. Each step in the determination of K values will be considered separately.

Equilibrium Flash Vaporization

As previously mentioned, the modified Othmer still used in this work was not acceptable because of excessive leakage under moderate vacuum, the limitation of product volume, and the amount of time required to come to equilibrium. Amir-Yeganeh presented two equilibrium vaporization stills which proved to be more satisfactory for equilibrium operation than the Othmer still (1). The apparatus he described were flow stills, overcoming the limitation of product size; they were also of simple construction, eliminating many joints. His evaluations were performed using binaries to determine operating conditions to produce equilibrium conditions, then running petroleum fractions through the three apparatus and comparing the results.

The criteria for equilibrium of heavy hydrocarbon systems need to be defined in a more practical manner. Some quick, simple, efficient test must be devised to permit ascertaining with a high degree of certainty the attainment of equilibrium in a system. Previous practice has been to study the equipment using a binary mixture for which experimental data are available, and generalize the results to apply to the heavier, more complex mixtures. This does not always produce accurate results.

Amir-Yeganeh designed his equipment to produce a great amount of contacting between vapor and liquid in the flash chamber. Partially vaporized feed is passed through sintered glass tubes to be dispersed into fine bubbles upon entering the flash chamber. These bubbles must then rise through a controlled head of liquid before the vapor escapes from the flash chamber. The adequacy of this practice is not certain.

There is also the possibility of reflux in his thermostatic apparatus. Vapor must travel a distance of 15 inches upward through a tubular extension of the flash chamber before leaving the still. Any small temperature deviation will permit reflux, giving products which are not in equilibrium. This should be investigated.

Analytical Distillations

One of the purposes of this work was to recommend one of two analytical distillation columns as yielding curves form which more accurate K values could be calculated. Because of the uncertain results obtained in this work, this recommendation cannot be made. Other workers are investigating the problem and should reach a conclusion very shortly. The selection of one of these two columns will give an indication of the degree of compromise possible between speed and accuracy.

The analytical distillation apparatus did not perform so satisfactorily as expected. Weight recovery ran in the order of 98 to 99 per cent; in most laboratories the minimum acceptable recovery is 99.5 weight per cent. The addition of a dry ice trap and the use of teflon rings instead of grease in the ball joints helped increase the recovery, but not appreciably. The source of error in these columns must be located.

Molecular Weights

Perhaps the most challenging area to be investigated is the determination of the proper technique and equipment to give accurate molecular weights. As previously mentioned, this is the most unreliable part of this work.

The existence and satisfactory use of a Mechrolab Model 301 Vapor Pressure Osmometer was made known and investigated (9). Reproducible results were reported for molecular weights in the range of interest for an instrument being used in a physiological application with an aqueous solvent (25). Those instruments which were being used with an organic solvent were not yielding accurate results below the range 180 to 200 MW (3, 26).

The Osmometer operates on the principle of vapor pressure reduction of a solvent by the addition of a small amount of solute. The reduction in vapor pressure causes a change in the rate of evaporation from or condensation upon two matched thermistors in a chamber filled with vapor saturated with solvent. The differential rates of mass transfer, by the heat of vaporization, cause a difference in temperature between the thermistors. This causes an upset of an electrical bridge, in proportion to the molarity of the solution. The instrument may be easily calibrated for the selected solvent, and the molecular weight of the unknown read from the calibration curve, thereafter.

The limitation of accuracy is the ratio of the vapor pressure of the solute to the solvent (36). Thus, if the vapor pressure of the solvent at the conditions of the determination were 100 times as great as the vapor pressure of the solute, the error would be one per cent. The high vapor pressure of the low molecular weight hydrocarbons prohibited accurate determinations with the solvents and under the conditions then being used.

This limitation of the Osmometer is being investigated. Considerable research has been done to find the most effective solvents (30). A lower chamber temperature will be used to permit the use of a more volatile solvent. This will decrease the vapor pressure ratio and should lower the present limit of accuracy. This study will probably be completed in the Fall of 1962.

Another method of determination which is reliable for molecular weights up to approximately 180 is an application of the Victor Meyer principle of vapor densities (7, 11). This method yields results which agree within three to four MW with values obtained by reliable cryoscopic methods in the range 125 MW (7). Table VIII shows a comparison of molecular weights obtained in this manner with those obtained by the cryoscopic method of this study.

In this application of the Victor Meyer principle, a known amount of sample is vaporized in a constant temperature chamber at reduced pressure. The change in pressure is measured and applied to the ideal gas law to determine the number of moles of sample vaporized. The molecular weight can then be determined.

TABLE VIII

COMPARISON OF CRYOSCOPIC AND VAPOR DENSITY MOLECULAR WEIGHTS

Cuts from Sarnia analysis of equilibrium liquid product

Temp., °F	Volume %	Cryoscopic Molecular Weight	Vapor Density Molecular Weight
160	IP		
178	2.0	86.0	84.6
190	4.0	89.8	89.7
191	6.0	82.0	93.8
193	8.0	83.8	91.7
194	10.0	88.6	91.3
198	15.0	86.0	93.1
202	20.0	82.4	94.3
206	25.0	89.9	94.9
211	30.4	84.3	98.1
215	35.4	85.9	97.5
220	40.4	87.7	98.1
227	45.2	87.8	99.5
234	50.2	88.5	102.1
235	55.0	93.9	101.4
242	60.0	92.4	103.7
248	65.0	96.9	105.4
251	70.0	91.3	108.7
255	75.0	88.4	108.2
259	80.4	91.4	110.8
264	85.0	87.8	112.2
269	90.0	90.6	110.4
275	95.0	90.0	111.7

The method is limited by the vapor pressure which can be obtained from the sample at the temperature of the chamber. The upper temperature is limited by the difficulty of constructing a pressure measuring diaphragm which will be linear over the operating pressure encountered at higher temperatures.

The physical properties of the petroleum fraction used in this work need to be studied to isolate the cause of error in the cryoscopic determinations. The occurence of association could be checked by determining molecular weights by the cryoscopic method using two solvents of radically different dielectric constants. This investigation is planned.

K Values

A consideration which may be most promising is the elimination of the necessity for determining the molecular weight of each individual cut. Harbert showed by application of the chain rule that the change of the number of moles with respect to temperature is equal to the change in the volume with temperature times the molar volume (27). Edmister also mentioned this in his presentation of the integral technique (15). Amir-Yeganeh has proposed that the molar volume of each cut is not necessary, but that K values may be obtained by multiplying the ratio of slopes of the volumetric TBP curves by the ratio of the molar volumes of the bulk equilibrium products (1). He presents a mathematical derivation to support this method, based upon the assumption of equal molar volumes in the equilibrium vapor and liquid, for cuts taken over the same temperature range.

If the ratio of the molar volumes of the two bulk equilibrium products is sufficient for the entire boiling range of the products, the ratios of the incremental molar volumes obtained for cuts of the same boiling range must be constant and equal to the bulk ratio. This was checked using the inaccurate cryoscopic data. Table IX shows the results. The deviation was found to be 0.035. This would yield K values which are more accurate than those presently being reported for heavy hydrocarbon systems. This area is being rechecked using molar volumes obtained by the vapor density method.

TABLE IX

COMPARISON OF RATIOS OF MOLAR VOLUMES FOR CUTS FROM OLDERSHAW DISTILLATIONS USING CRYOSCOPIC METHOD

Temp., °F	Ratio of Molar Volumes
165	1.02
185	0.96
190	1.00
196	0.98
201	1.07
206	1.03
210	1.04
214	1.02
219	1.00
234	0.96
243	1.06
246	0.98
253	0.99
257	0.98

Average ratio 1.006
Standard deviation 0.035

Some work has been done to obtain K values from gas chromatography (35). Additional work is planned in this area.

Solution of the problems just delineated will permit the publication of a guide to easy, fast, accurate, low cost K value determinations. When this is accomplished the next step will be the use of these K values in more sophisticated computer programs utilizing the integral technique. Work is now planned which will include the development of computer programs using the integral technique which can be used for design, process control, and process evaluation. The results from these programs will be compared with the streams from an existing column.

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APPENDIX A

EXPERIMENTAL AND CALCULATED DATA

TABLE X

COMPARISON OF VAPOR-LIQUID RATIOS FOR OTHMER EQUILIBRIUM VAPORIZATIONS

T_e = 177°F P_e = 350 mm. Hg absolute

Run No.	Vapor, gm.	Liquid, gm.	V/L	Loss, gm.	Loss, %
29	413	549	0.811	14.7	1.51
31	414	530	0.841	33.0	3.40
32	406	541	0.808	21.0	2.17
33	411	544	0.815	21.0	2.15
Blended Products	1644	2.64	0.819		
Molecular Weight	98.3	106.0			

TABLE XI

REPRODUCIBILITY CHECK FOR GAS CHROMATOGRAPH

Peak, Min.	1	2	3	4	5	6	7	8	Average	Deviation
1.7	0.384	0.392	0.382	0.390	0.391	0.383	0.383	0.382	0.386	0.004
2.0	0.071	0.083	0.079	0.081	0.083	0.085	0.079	0.083	0.083	0.003
2.5	0.538	0.545	0.550	0.542	0.542	0.542	0.539	0.538	0.542	0.003
2.7	0.346	0.362	0.351	0.359	0.357	0.358	0.358	0.359	0.356	0.004
3.3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	---
4.9	0.506	0.505	0.519	0.514	0.508	0.520	0.514	0.520	0.513	0.005
6.4	0.107	0.120	0.115	0.123	0.118	0.122	0.117	0.150	0.122	0.008
7.2	0.103	0.110	0.109	0.113	0.113	0.119	0.112	0.127	0.113	0.005
8.2	0.015	0.025	0.021	0.025	0.025	0.027	0.024	0.032	0.024	0.003
10.6	0.007	0.014	0.013	0.016	0.019	0.020	0.016	0.023	0.016	0.004
15.0	0.041	0.049	0.050	0.054	0.052	0.053	0.052	0.058	0.051	0.003
29.1	---	0.002	0.000	0.002	0.000	0.007	0.002	0.002	0.001	0.001
32.1	---	0.011	0.000	0.011	0.007	0.012	0.011	0.013	0.008	0.003

TABLE XII

COMPARISON OF ANALYTICAL DISTILLATIONS OF HYDROFORMER FEED

Oldershaw 30 Plate Column	
Temp., °F	Volume % Distillate
155	IP
156	1.05
158	2.15
160	3.15
163	4.25
164	5.35
173	6.85
175	7.85
178	9.25
181	10.45
188	14.45
192	17.55
196	22.70
203	28.30
207	33.50
210	40.60
212	45.40
215	50.00
219	55.05
232	59.95
242	65.05
246	70.25
250	75.20
255	80.55
260	85.40
271	90.20

Sarnia Mark II Fractionator	
Temp., °F	Volume % Distillate
155	IP
168	2.0
175	4.0
183	8.2
184	10.0
189	15.4
193	20.0
199	26.0
203	31.2
205	35.8
208	40.0
211	45.0
215	50.0
222	55.0
230	60.0
238	65.0
244	70.0
248	75.0
254	80.0
259	85.0
266	89.0
274	93.0
277	95.0

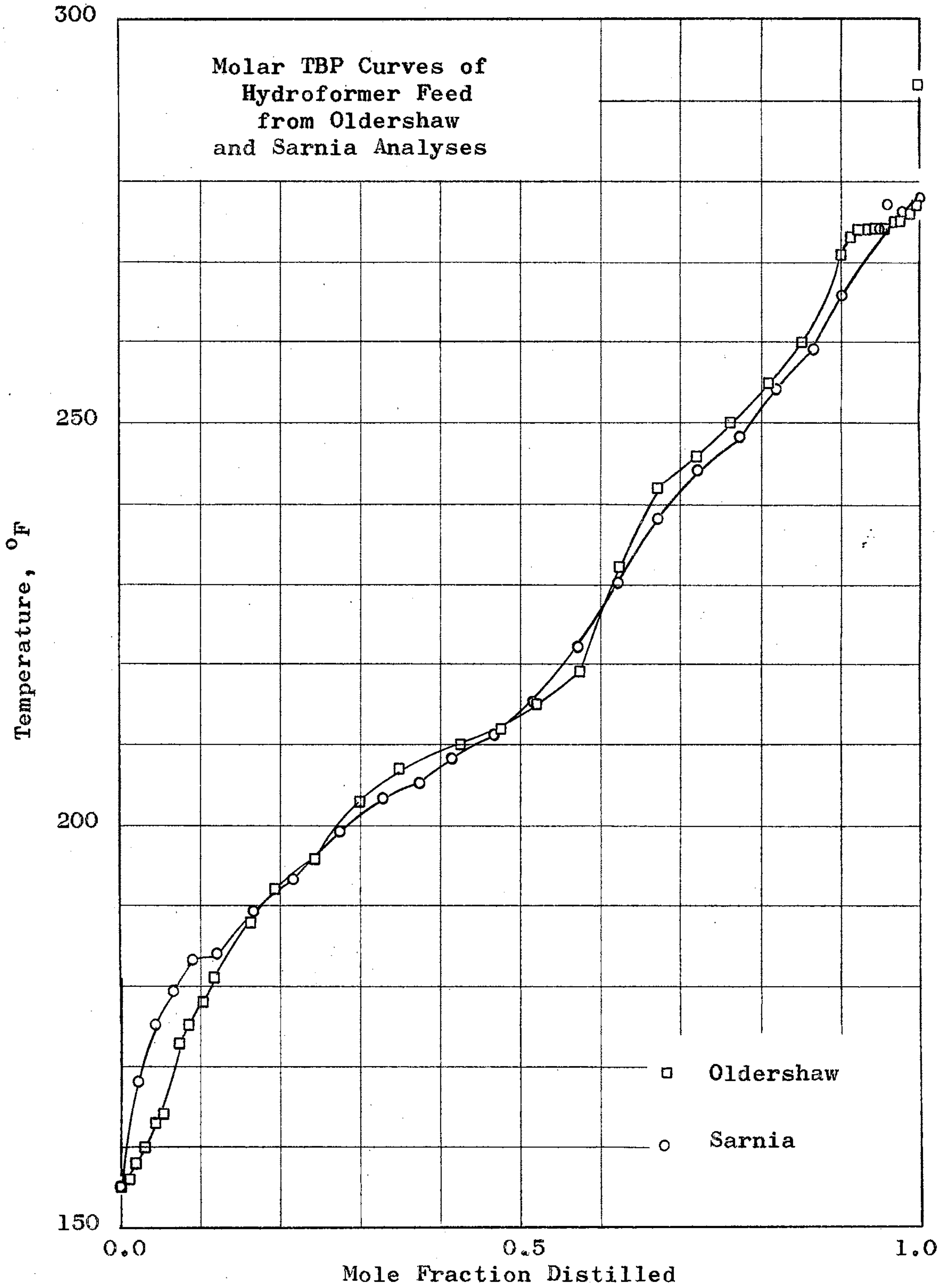

Figure 11. Comparison of Analytical Distillations of Hydroformer Feed

TABLE XIII

OLDERSHAW ANALYSIS OF HYDROFORMER FEED

Temp., °F	Volume % Distillate	Specific Gravity	Molecular Weight	Mole Fraction Distillate
155	TP	0.687	85.0	0.000
156	1.05	0.697	87.4	0.011
158	2.15	0.711	88.0	0.022
160	3.15	0.728	86.1	0.033
163	4.25	0.729	84.4	0.044
164	5.35	0.746	83.5	0.056
173	6.85	0.752	82.1	0.074
175	7.85	0.755	82.6	0.085
178	9.25	0.750	83.2	0.102
181	10.45	0.735	82.1	0.118
188	14.45	0.722	89.8	0.163
192	17.55	0.725	93.5	0.195
196	22.70	0.712	93.1	0.244
203	28.30	0.716	91.4	0.299
207	33.50	0.727	87.8	0.351
210	40.60	0.740	92.8	0.426
212	45.40	0.753	91.9	0.474
215	50.00	0.765	92.0	0.522
219	55.05	0.765	95.3	0.575
232	59.95	0.735	97.4	0.625
242	65.05	0.726	103.0	0.674
246	70.25	0.730	106.1	0.720
250	75.20	0.735	104.3	0.764
255	80.55	0.737	104.6	0.812
260	85.40	0.764	98.3	0.855
271	90.20	0.815	100.5	0.903
273*	91.2	0.815	97.8	0.913
274*	92.2	0.815	96.8	0.925
274*	93.2	0.815	101.1	0.936
274*	94.2	0.818	100.6	0.946
274*	95.2	0.819	104.5	0.957
275*	96.2	0.820	106.3	0.967
275*	97.2	0.820	103.3	0.978
276*	98.2	0.820	101.1	0.988
277*	99.2	0.821	101.9	0.998
292*	99.4			1.000

* ASTM Distillation

TABLE XIV

OLDERSHAW ANALYSIS OF EQUILIBRIUM VAPOR PRODUCT

T_e = 177°F P_e = 350 mm.Hg Absolute

Temp., °F	Volume % Distillate	Specific Gravity	Molecular Weight	Mole Fraction Distillate
152	IP	0.687	83.5	0.000
154	1.4	0.695	84.8	0.015
156	3.4	0.713	88.5	0.035
160	5.6	0.728	86.5	0.056
165	7.6	0.741	84.4	0.078
171	9.9	0.748	81.1	0.103
178	15.1	0.745	82.1	0.164
184	20.3	0.726	85.7	0.221
190	25.4	0.714	87.1	0.275
196	33.1	0.713	88.1	0.352
201	38.6	0.718	92.0	0.406
206	45.0	0.727	91.2	0.467
210	52.6	0.740	89.0	0.542
212	59.9	0.756	88.2	0.616
214	64.9	0.769	91.3	0.670
219	69.9	0.762	93.7	0.721
234	74.9	0.730	102.1	0.772
243	79.9	0.730	102.3	0.816
246	84.9	0.733	99.4	0.860
253	89.9	0.737	100.2	0.905
257	92.0	0.793	100.3	0.926
268*	94.2	0.796	100.9	0.949
270*	96.5	0.805	100.7	0.972
272*	98.4	0.813	98.4	0.992
274*	99.2			1.000

* ASTM Distillation

TABLE XV

OLDERSHAW ANALYSIS OF EQUILIBRIUM LIQUID PRODUCT

T_e = 177°F P_e = 350 mm. Hg Absolute

Temp., °F	Volume % Distillate	Specific Gravity	Molecular Weight	Mole Fraction Distillate
157	IP	0.720	84.2	0.000
165	2.27	0.743	84.5	0.025
174	4.27	0.744	85.6	0.047
180	6.27	0.733	85.0	0.070
186	8.67	0.723	85.4	0.097
190	10.3	0.715	89.7	0.115
196	14.9	0.716	82.9	0.163
201	20.2	0.721	89.7	0.221
206	25.0	0.730	89.3	0.265
209	30.0	0.741	89.8	0.317
210	35.0	0.755	86.7	0.366
214	40.0	0.767	91.1	0.423
220	45.0	0.757	96.6	0.478
234	50.0	0.735	96.3	0.528
241	55.1	0.728	97.8	0.577
243	60.0	0.730	104.1	0.624
246	65.6	0.733	101.5	0.675
250	70.1	0.734	100.7	0.709
253	75.0	0.737	103.1	0.756
258	80.0	0.764	108.9	0.801
268	85.0	0.798	105.3	0.846
273	90.0	0.821	103.0	0.894
276*	92.2	0.823	95.4	0.917
276*	94.4	0.824	95.8	0.942
276*	96.5	0.825	100.7	0.967
277*	98.0	0.827	95.5	0.984
279*	98.6	0.844	99.5	0.998
282*	98.9			1.000

* ASTM Distillation

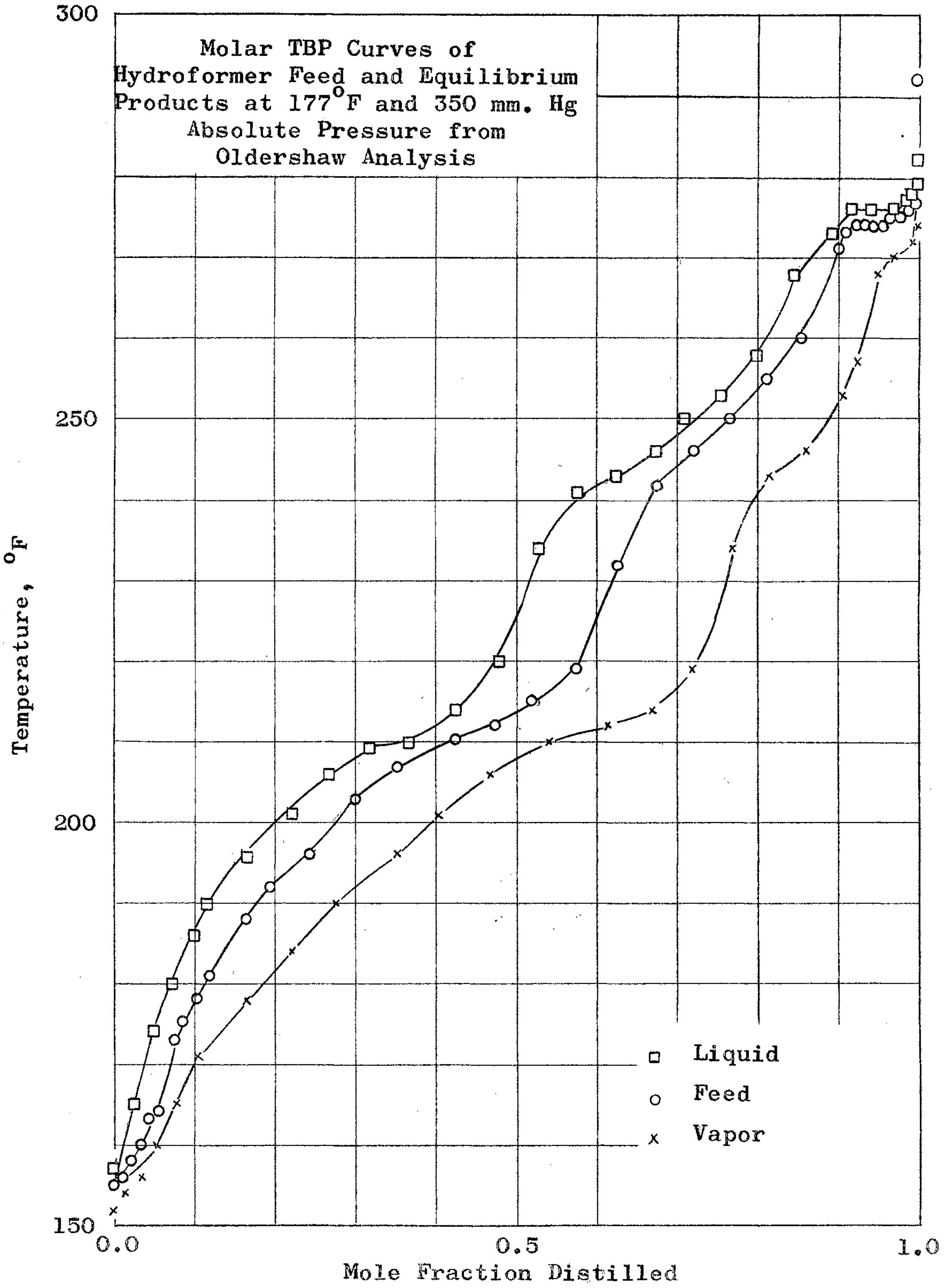

Figure 12. TBP Curves From Oldershaw Analyses

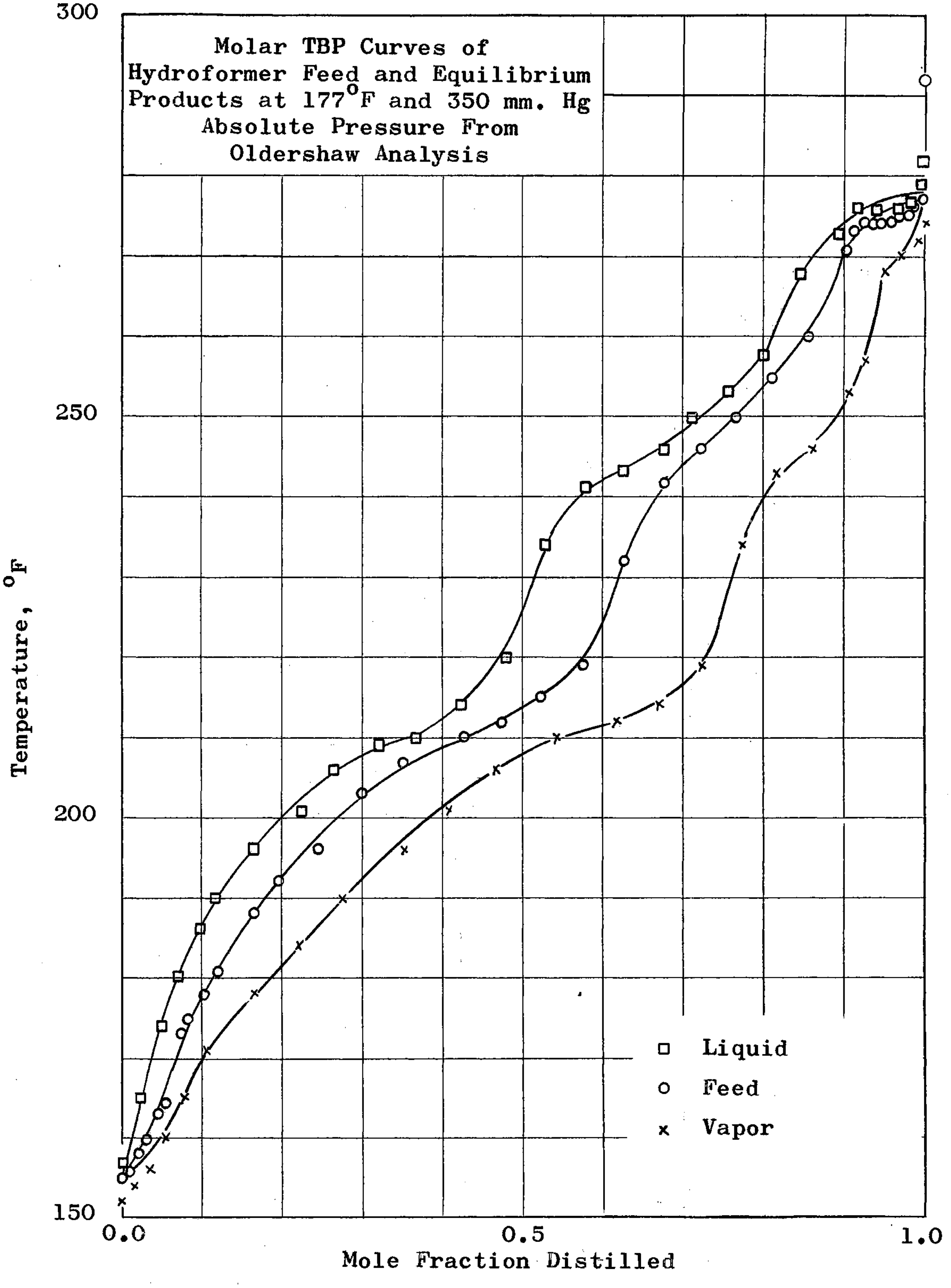

Figure 13. Smoothed TBP Curves From Oldershaw Analyses

TABLE XVI

SARNIA ANALYSIS OF HYDROFORMER FEED

Temp., °F	Volume % Distillate	Specific Gravity	Molecular Weight	Mole Fraction Distillate
155	IP	0.705	85.6	0.000
168	2.0	0.727	85.0	0.024
175	4.0	0.728	85.0	0.045
179	6.2	0.728	82.5	0.068
183	8.2	0.728	84.2	0.090
184	10.0	0.728	86.0	0.113
189	15.4	0.728	87.3	0.168
193	20.0	0.728	89.5	0.216
199	26.0	0.729	89.0	0.277
203	31.2	0.732	90.2	0.329
205	35.8	0.732	91.7	0.375
208	40.0	0.737	88.3	0.416
211	45.0	0.740	89.8	0.468
215	50.0	0.744	84.5	0.518
222	55.0	0.743	89.6	0.573
230	60.0	0.742	93.6	0.623
238	65.0	0.739	90.6	0.672
244	70.0	0.739	91.0	0.722
248	75.0	0.740	100.0	0.774
254	80.0	0.747	101.7	0.819
259	85.0	0.762	98.2	0.864
266	89.0	0.784	102.4	0.903
274	93.0	0.807	100.7	0.950
277	95.0	0.817	100.6	0.960
276*	97.0	0.819	100.4	0.980
278*	99.0			1.000

* ASTM Distillation

TABLE XVII

SARNIA ANALYSIS OF EQUILIBRIUM VAPOR PRODUCT

T_e = 177°F P_e = 350 mm. Hg Absolute

Temp., °F	Volume % Distillate	Specific Gravity	Molecular Weight	Mole Fraction Distillate
155	IP	0.705	81.5	0.000
163	2.05	0.726	78.9	0.021
171	4.1	0.730	80.9	0.044
175	6.15	0.730	80.7	0.066
177	8.2	0.729	88.8	0.089
178	10.0	0.730	81.0	0.107
182	15.1	0.728	79.0	0.163
187	20.0	0.728	81.4	0.218
190	23.8	0.728	85.0	0.258
195	30.0	0.728	87.2	0.323
199	35.1	0.731	82.7	0.374
203	40.2	0.733	80.3	0.428
205	44.9	0.733	83.4	0.480
207	50.0	0.737	86.6	0.536
210	55.1	0.740	86.9	0.589
214	60.3	0.745	87.2	0.642
221	65.2	0.745	88.9	0.693
229	70.8	0.745	93.1	0.750
236	74.9	0.740	87.6	0.797
243	80.0	0.741	98.9	0.844
250	85.1	0.746	101.2	0.889
257	90.0	0.762	99.42	0.932
263	92.0	0.796	97.4	0.953
268*	94.0	0.797	100.3	0.973
271*	96.1	0.815	101.8	0.994
278*	96.7			1.000

* ASTM Distillation

TABLE XVIII

SARNIA ANALYSIS OF EQUILIBRIUM LIQUID PRODUCT

T_e = 177°F P_e = 350 mm. Hg Absolute

Temp., °F	Volume % Distillate	Specific Gravity	Molecular Weight	Mole Fraction Distillate
158	IP	0.728	86.0	0.000
178	2.0	0.729	89.8	0.029
190	4.0	0.729	82.0	0.040
191	6.0	0.729	83.8	0.061
193	8.0	0.730	88.6	0.083
194	10.0	0.732	86.0	0.103
198	15.0	0.734	82.4	0.154
202	20.0	0.736	89.9	0.207
206	25.0	0.737	84.3	0.257
211	30.4	0.737	85.9	0.313
215	35.4	0.739	87.7	0.365
220	40.4	0.743	87.8	0.416
227	45.2	0.743	88.5	0.466
234	50.2	0.740	93.9	0.516
235	55.0	0.744	92.4	0.560
242	60.0	0.745	96.6	0.608
248	65.0	0.757	91.3	0.654
251	70.0	0.751	88.4	0.703
255	75.0	0.758	91.4	0.755
259	80.4	0.767	87.8	0.808
264	85.0	0.778	90.6	0.858
269	90.0	0.796	90.0	0.908
275	95.0	0.808	93.6	0.962
274*	97.0	0.810	94.2	0.982
278*	98.4	0.828	102.8	0.997
280*	98.8			1.000

* ASTM Distillation

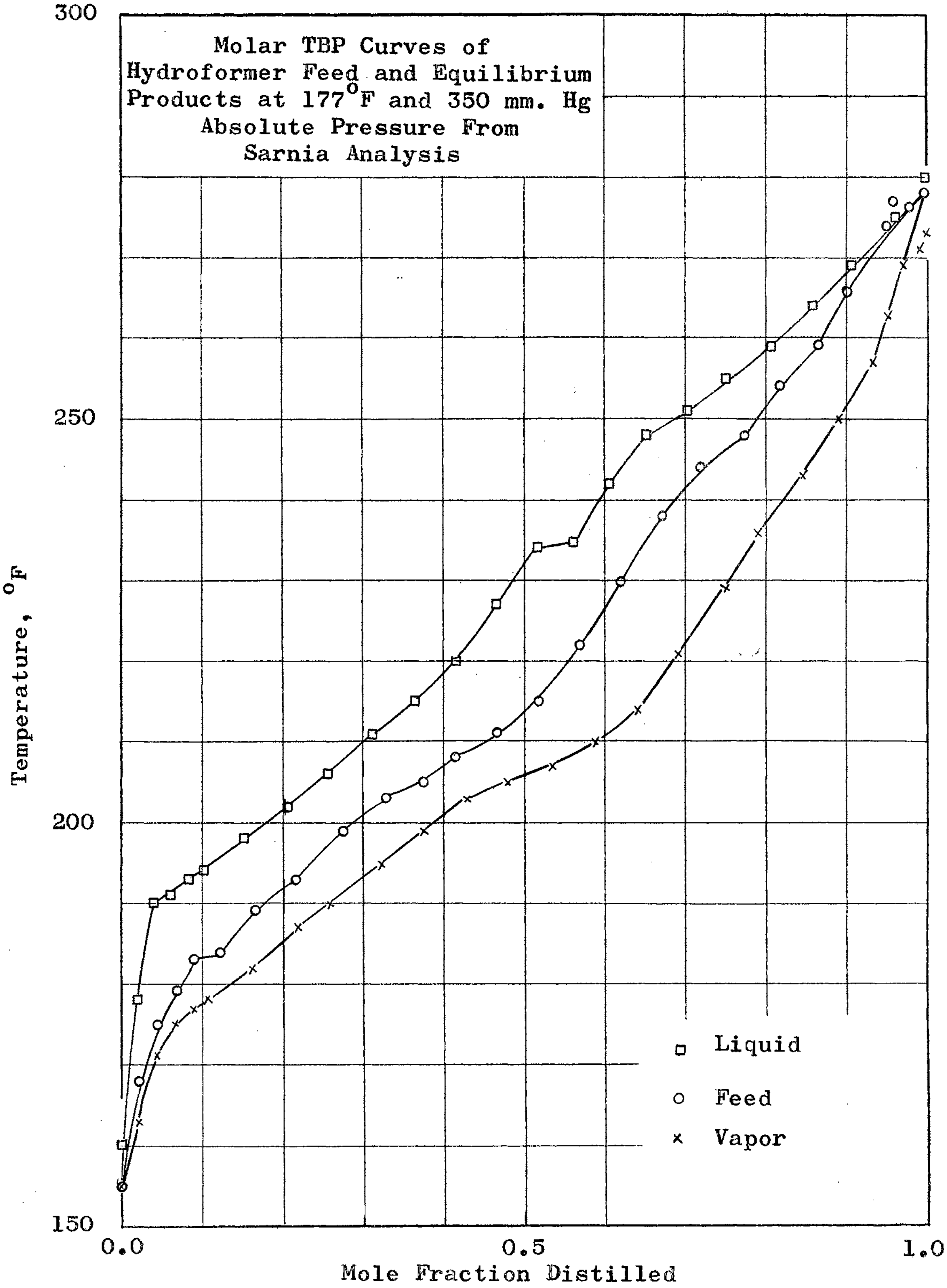

Figure 14. TBP Curves From Sarnia Analyses

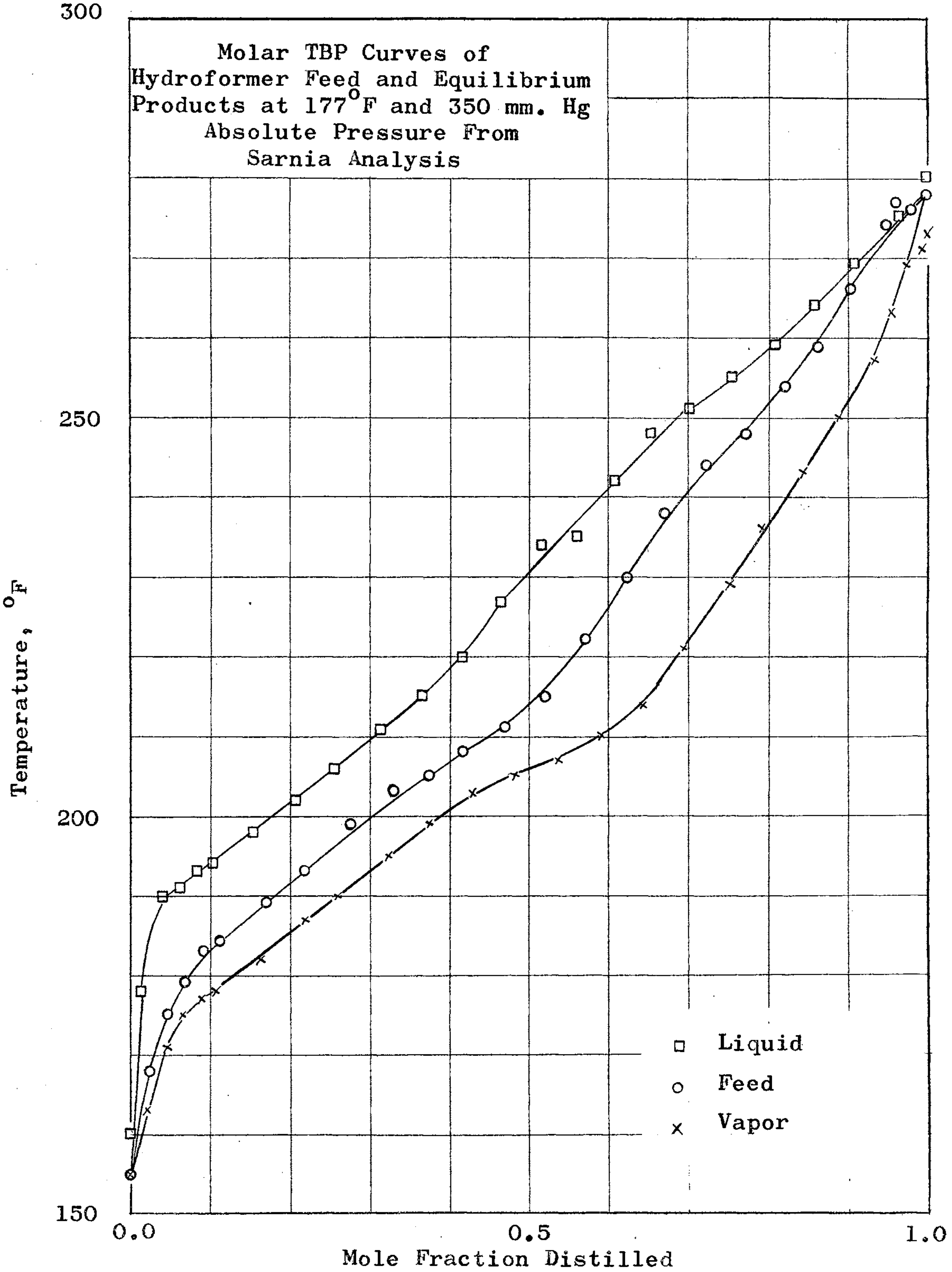

Figure 15. Smoothed TBP Curves From Sarnia Analyses

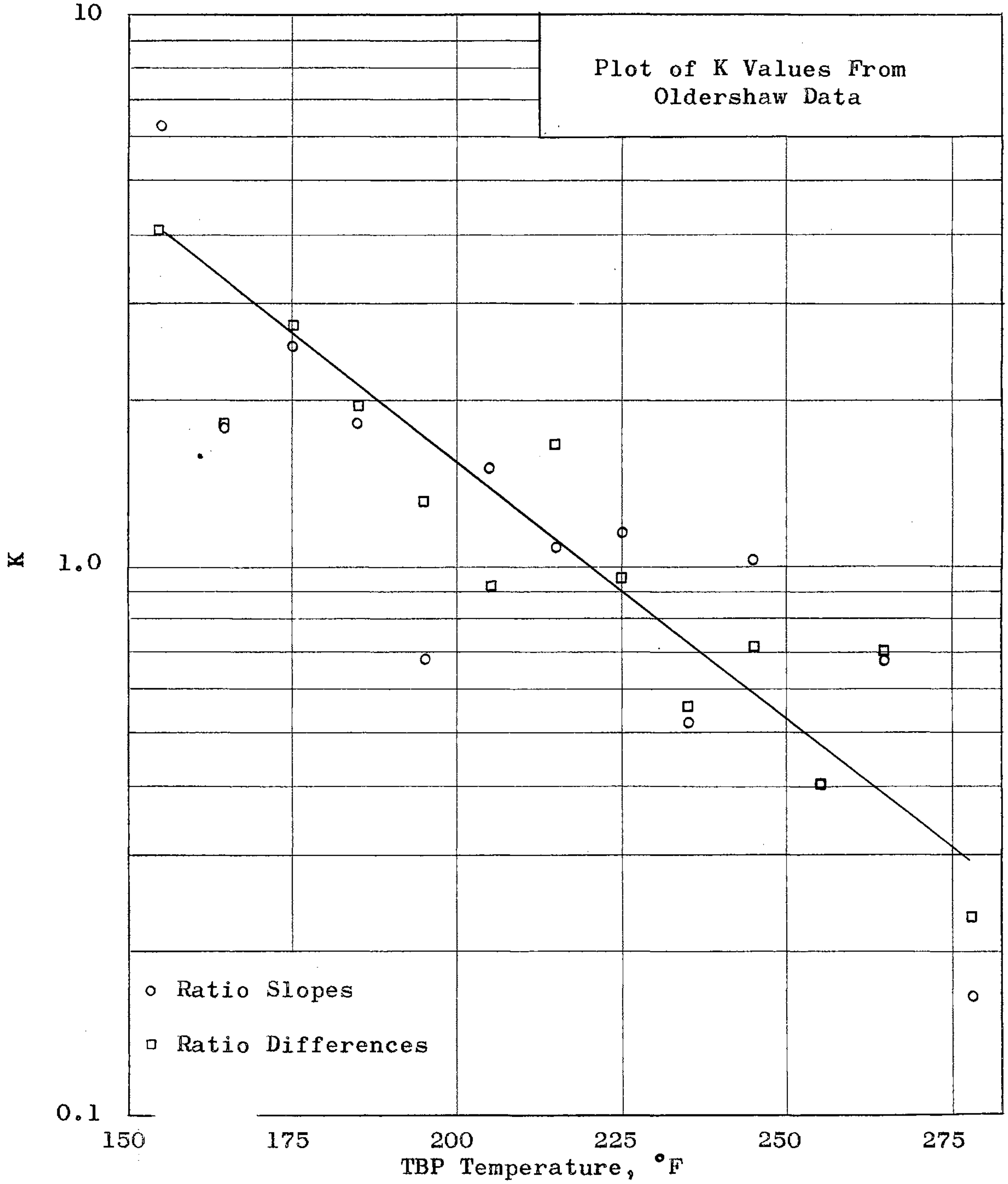

Figure 16. Log K vs. T From Oldershaw Analytical Data

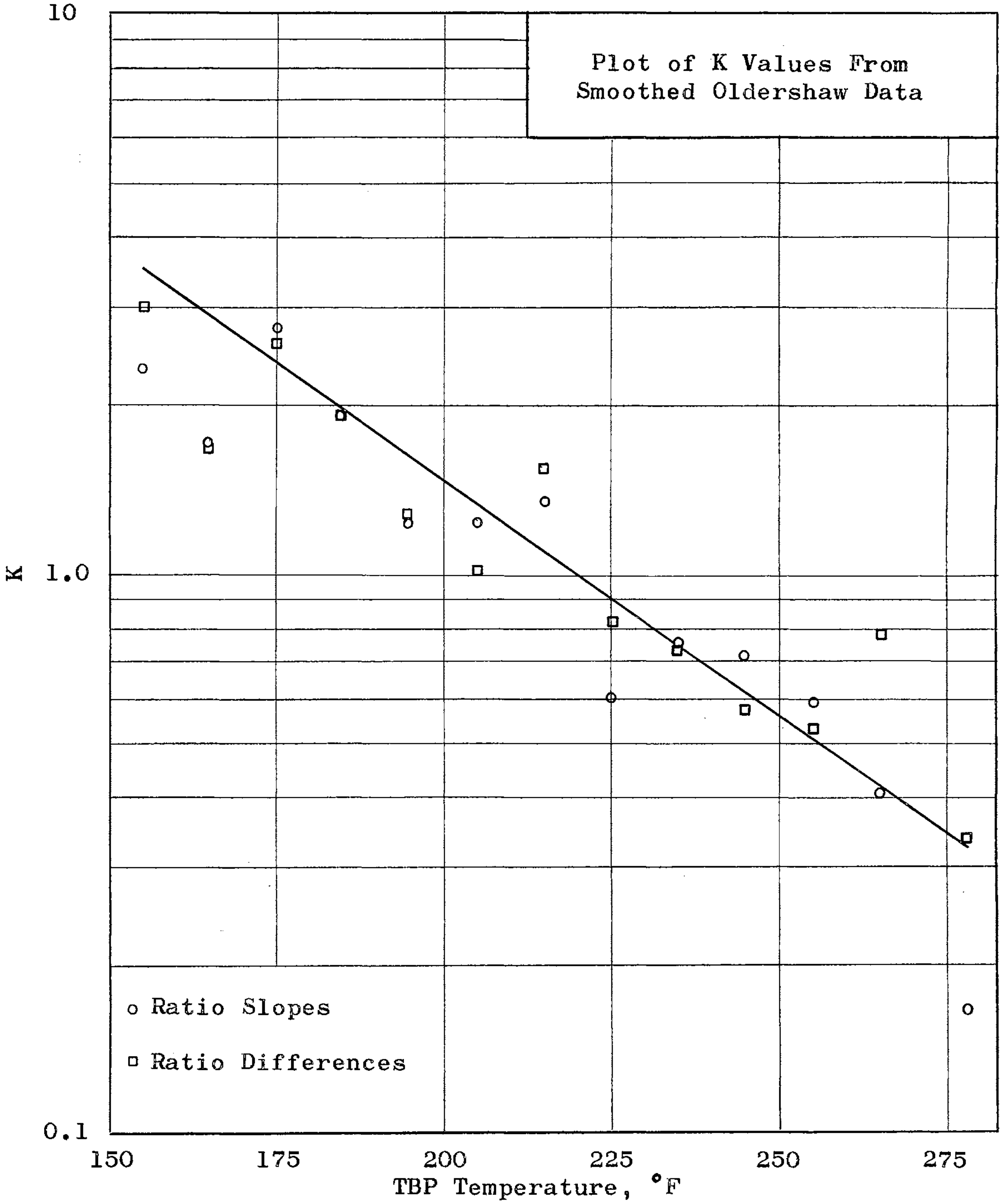

Figure 17. Log K vs. T From Smoothed Oldershaw Analytical Data

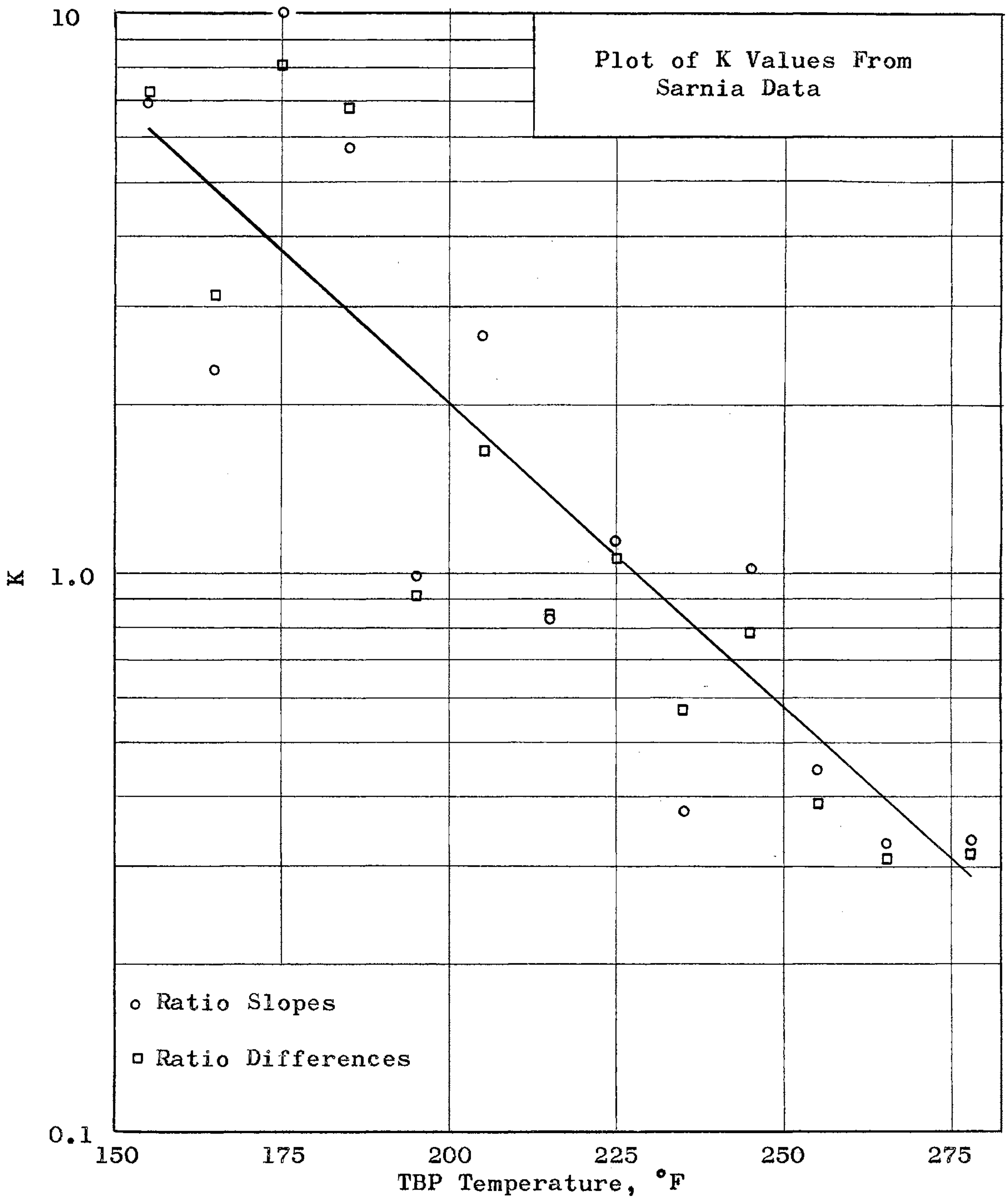

Figure 18. Log K vs. T From Sarnia Analytical Data

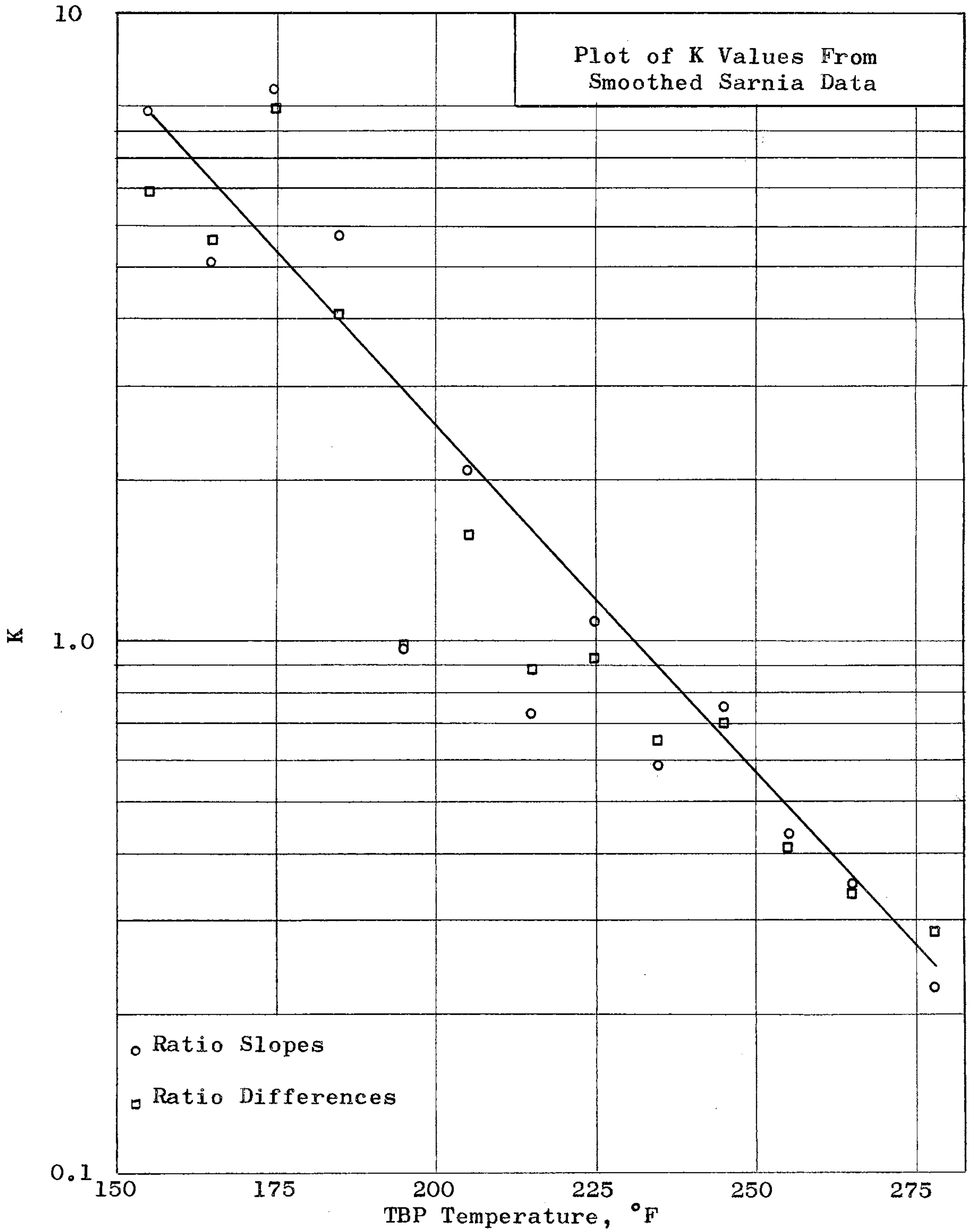

Figure 19. Log K vs. T From Smoothed Sarnia Analytical Data

TABLE XIX

K VALUES FROM PLOT OF LOG K vs. T

Temp., °F	Oldershaw Data	Sarnia Data	Smoothed Oldershaw Data	Smoothed Sarnia Data
155	4.10	6.25	3.53	9.9
165	3.30	4.83	2.90	7.30
175	2.67	3.78	2.40	5.40
185	2.14	2.94	1.97	4.00
195	1.72	2.29	1.62	2.97
205	1.39	1.79	1.33	2.20
215	1.12	1.49	1.10	1.62
225	0.91	1.07	0.91	1.20
235	0.73	0.84	0.75	0.89
245	0.59	0.65	0.62	0.66
255	0.48	0.51	0.51	0.49
265	0.38	0.40	0.42	0.36
275	0.29	0.297	0.327	0.247

TABLE XX

SOURCE OF K VALUES FOR COMPUTER CALCULATIONS

Calculation	Source of K Values
I	TBP curve through data points; inconsistent values not used
II	Smoothed TBP curves, within ± 3°F of data points; inconsistent values not used
III	TBP curve through data points; all values used
IV	Smoothed TBP curves, within ± 3°F of data points; all values used
V	Plot of log K vs. T
VI	Plot of log K vs. T (from smoothed TBP data)

TABLE XXI

COMPARISON OF CALCULATED AND EXPERIMENTAL VAPOR-LIQUID RATIOS

Method for K Values	Calculation					
	I	II	III	IV	V	VI
Sarnia Ratio of Slopes	70.99	8.64	3.55	2.38	2.63	3.74
Sarnia Ratio of Differences	5.45	3.46	1.87	1.60		
Oldershaw Ratio of Slopes	1.11	0.35	2.34	0.32	0.46	0.39
Oldershaw Ratio of Differences	0.35	0.42	0.73	0.96		
Experimental $\frac{V}{L}$	0.819					

TABLE XXII

COMPARISON OF OLDERSHAW EXPERIMENTAL AND CALCULATED TBP CURVES

	Vapor				Liquid			
		Calculation III				Calculation III		
Temp., °F	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. V	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. V
155	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
165	0.077	0.069	0.083	0.114	0.023	0.029	0.038	0.031
175	0.140	0.102	0.124	0.163	0.052	0.046	0.057	0.048
185	0.237	0.169	0.207	0.255	0.091	0.076	0.093	0.089
195	0.336	0.261	0.320	0.380	0.152	0.158	0.164	0.161
205	0.453	0.354	0.416	0.494	0.260	0.250	0.255	0.244
215	0.687	0.580	0.622	0.702	0.440	0.386	0.449	0.439
225	0.746	0.662	0.710	0.774	0.501	0.448	0.516	0.517
235	0.772	0.701	0.745	0.808	0.536	0.497	0.563	0.563
245	0.847	0.766	0.799	0.856	0.662	0.579	0.645	0.643
255	0.916	0.859	0.872	0.916	0.776	0.702	0.768	0.764
265	0.946	0.914	0.920	0.950	0.840	0.800	0.851	0.848
278	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE XXIII

COMPARISON OF OLDERSHAW EXPERIMENTAL AND CALCULATED TBP CURVES (SMOOTHED DATA)

	Vapor				Liquid			
		Calculation IV				Calculation IV		
Temp., °F	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. VI	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. VI
155	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
165	0.078	0.079	0.069	0.103	0.025	0.044	0.035	0.032
175	0.140	0.136	0.116	0.165	0.052	0.071	0.059	0.056
185	0.231	0.231	0.191	0.251	0.093	0.112	0.092	0.098
195	0.325	0.400	0.347	0.426	0.156	0.229	0.195	0.209
205	0.450	0.470	0.411	0.499	0.257	0.285	0.251	0.263
215	0.680	0.698	0.612	0.694	0.435	0.466	0.435	0.454
225	0.745	0.766	0.694	0.769	0.498	0.548	0.510	0.535
235	0.776	0.792	0.726	0.799	0.535	0.589	0.552	0.575
245	0.847	0.849	0.782	0.849	0.660	0.666	0.640	0.655
255	0.917	0.920	0.852	0.910	0.777	0.775	0.769	0.771
265	0.943	0.959	0.909	0.947	0.830	0.855	0.852	0.854
278	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE XXIV

COMPARISON OF SARNIA EXPERIMENTAL AND CALCULATED TBP CURVES

	Vapor				Liquid			
		Calculation III				Calculation III		
Temp., °F	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. V	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. V
155	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
165	0.025	0.020	0.023	0.022	0.005	0.006	0.006	0.004
175	0.066	0.053	0.061	0.057	0.016	0.018	0.016	0.013
185	0.200	0,159	0.184	0.162	0.030	0.028	0.028	0.047
195	0.323	0.276	0.313	0.285	0.117	0.086	0.086	0.100
205	0.480	0.432	0.468	0.445	0.246	0.173	0.201	0.190
215	0.650	0.588	0.623	0.600	0.365	0.271	0.321	0.303
225	0.723	0.661	0.696	0.673	0.456	0.338	0.392	0.371
235	0.787	0.717	0.753	0.733	0.560	0.522	0.463	0.439
245	0.860	0.793	0.827	0.807	0.633	0.534	0.566	0.548
255	0.923	0.879	0.902	0.882	0.756	0.645	0.690	0.686
265	0.960	0.931	0.944	0.934	0.870	0.782	0.812	0.804
278	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE XXV

COMPARISON OF SARNIA EXPERIMENTAL AND CALCULATED TBP CURVES (SMOOTHED DATA)

	Vapor				Liquid			
		Calculation IV				Calculation IV		
Temp., °F	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. VI	Exp.	Ratio of Slopes	Ratio of Diff.	Calc. VI
155	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
165	0.028	0.023	0.025	0.021	0.003	0.004	0.004	0.003
175	0.067	0.060	0.067	0.055	0.010	0.010	0.011	0.008
185	0.194	0.163	0.179	0.145	0.027	0.022	0.028	0.030
195	0.323	0.304	0.325	0.283	0.114	0.089	0.104	0.077
205	0.480	0.454	0.474	0.434	0.246	0.184	0.215	0.148
215	0.647	0.603	0.624	0.584	0.365	0.295	0.333	0.243
225	0.722	0.684	0.704	0.668	0.457	0.376	0.416	0.313
235	0.791	0.745	0.762	0.730	0.550	0.448	0.489	0.382
245	0.858	0.823	0.837	0.809	0.632	0.557	0.595	0.499
255	0.920	0.896	0.905	0.883	0.757	0.697	0.715	0.642
265	0.963	0.942	0.946	0.933	0.870	0.796	0.824	0.770
278	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

APPENDIX B

IBM 650 COMPUTER PROGRAMS

APPENDIX B

IBM 650 COMPUTER PROGRAMS

Data Processing Program

This program was written in Fortran to calculate the mole fraction for each cut of the analytical distillation. The program will handle up to forty cuts.

Input data are

IP	Initial boiling point	
RHOBZ	Specific gravity of benzene	
ANMBR	Number of cuts	
BP	End point	For each cut
WTGR	Weight of bottle and sample	
WTARE	Weight of sample bottle	
DELTA	Freezing point depression	
RHOSA	Specific gravity of the sample	

Output data are

IP	Initial boiling point	
BP	End point	For each cut
WTSAM	Weight of sample	
FACTR	51.2 ρ_s/ρ_b	
WTMOL	Molecular weight	

SAMOL	Number of moles	For each cut
FNMOL	Cumulative mole fraction	
TOTML	Total number of moles	

```
C 0000 0 CALCULATION OF BOILING POINT
C 0000 0 AS FUNCTION OF MOLE-FRACTION
     1 0 DIMENSION BP(40),WTGR(40),
     1 1 WTARE(40),DELTA(40),RHOSA(40),
     1 2 WTSAM(40),FACTR(40),WTMOL(40),
     1 3 SAMOL(40),FNMOL(40)
     2 0 READ,RHOBZ,ANMBR,IP
     3 0 NUMBR=ANMBR
     4 0 DO 5 I=1,NUMBR,1
     5 0 READ,BP(I),WTGR(I),WTARE(I),
     5 1 DELTA(I),RHOSA(I)
    10 0 DO 14 I=1,NUMBR,1
    11 0 WTSAM(I)=WTGR(I)-WTARE(I)
    12 0 FACTR(I)=(51.2*RHOSA(I))/RHOBZ
    13 0 WTMOL(I)=FACTR(I)/DELTA(I)
    14 0 SAMOL(I)=WTSAM(I)/WTMOL(I)
    15 0 TOTML=0.0
    16 0 DO 17 I=1,NUMBR,1
    17 0 TOTML=TOTML+SAMOL(I)
    18 0 SUBTL=0.0
    19 0 PUNCH,IP
    20 0 DO 23 I=1,NUMBR,1
    21 0 SUBTL=SUBTL+SAMOL(I)
    22 0 FNMOL(I)=SUBTL/TOTML
    23 0 PUNCH,BP(I),WTSAM(I),FACTR(I),
    23 1 WTMOL(I),SAMOL(I),FNMOL(I)
    24 0 PUNCH,TOTML
    25 0 END
```

Card Format for Fortran Program

All numbers are in IBM floating point notation

Input Cards

Card 1

Word 1	Specific gravity of benzene, RHOBZ
Word 2	Number of cuts, ANMBR
Word 3	Initial point, IP

Card 2 - (n+1)

Word 1	End point of cut, BP
Word 2	Weight of bottle and sample, WTGR
Word 3	Weight of empty bottle, WTARE
Word 4	Freezing point depression, DELTA
Word 5	Specific gravity of cut, RHOSA

Output Cards

Card 1

Word 1	Initial point, IP

Card 2 - (n+1)

Word 1	End point of cut, BP
Word 2	Weight of sample, WTSAM
Word 3	51.2 ρ_s/ρ_b, FACTR
Word 4	Molecular weight of cut, WTMOL
Word 5	Moles in cut, SAMOL
Word 6	Cumulative mole fraction, FNMOL

Card n + 2 (last card)

Word 1	Total number of moles, TOTML

Combined Program

This program is written in machine language and makes use of the "Drum zero, read, and punch loop" and "Log deck" available at the Computing Center, Oklahoma State University. The instructions in these loops are not listed here; the rest of the program is given below. Each loop of the program is presented separately to facilitate comprehension of the calculation procedure.

Input data are

0001 - 0020	m_f	mole fraction of the feed TBP curve
0051 - 0070	K	corresponding equilibrium constant
0101 - 0120	A	constants in equation 9
0151 - 0170	B	
0201 - 0220	C	
0251 - 0270	D	
0301 - 0320	E	
0042 -	$T_{BP}/100$	estimate of bubble point temperature
0043 -	$T_{DP}/100$	estimate of dew point temperature
0044 -	n	number of input data points
0045 -	n-1	number of data points less one, in fixed point
0047 -	V/L	estimate of V/L ratio

Output data for the EFV calculation are

0793 - V/L

0843 - V/L assumed minus V/L calculated

0721 - 0740 $-\int_0^{m_f} 1/f \; dm_f$

0771 - 0790 $-\int_0^{m_f} v/f \; dm_f$

0821 - 0840 - $\dfrac{\int_o^{m_f} 1/f \; dm_f}{L/F}$

0871 - 0890 - $\dfrac{\int_o^{m_f} v/f \; dm_f}{V/F}$

0921 - 0940 - m_f

0901 - 0920 - $1/f$

Output data for the bubble point - dew point calculation are

0794 - $T_{BP}/100$

0844 - $1 - \int_o^1 K \; dm_f$

0871 - 0890 - K

0921 - 0940 - m_f

0795 - $T_{DP}/100$

0845 - $1 - \int_o^1 1/K \; dm_f$

0871 - 0890 - $1/K$

0921 - 0940 - dm_f

Loop 1. n-1 Instructions   Puts n-1 into all instructions which require it.

From	Loc.	Abbr.	Instruction	Operation
Read and punch loop	- 1000	RAL	65 0045 1001	(n-1) to LA
	1001	RAA	80 0021 1002	21 to A
(1005)	- 1002	LDD	69 2950 1003	Contents of (0950+A) to D
	1003	SDA	22 2950 1004	/xx (n-1) xxxx_/A to 0950+A
	1004	NZA	40 1005 0950	Test A for zero (all instructions modified)
	1005	SXA	51 0001 1002	(-1) in A, recycle

Loop 2. Lagrange terms   Calculates terms for intergrated Lagrange equation.

From	Loc.	Abbr.	Instruction	Operation
1004	- 0950	RAA	80 (n-1) 1006	(n-1) to A
(1014)	- 1006	SXA	51 0001 1007	(-1) in A
	1007	RAU	60 2002 1008	$(m_f)_i$ to UA
	1008	FSB	33 2000 1009	$-(m_f)_{i-2}$ in UA
	1009	STU	21 2352 1010	$(m_f)_i - (m_f)_{i-2}$ to (0352+A)
	1010	RAU	60 2001 1011	$(m_f)_{i-1}$ to UA
	1011	FSB	33 2000 1012	$-(m_f)_{i-2}$ in UA
	1012	STU	21 2351 1013	$(m_f)_{i-1} - (m_f)_{i-2}$ to (0351+A)
	1013	SXA	51 0001 1014	(-1) in A
	1014	NZA	40 1006 0951	Test A for zero (all first degree terms calculated)
	0951	RAA	80 (n-1) 1015	(n-1) to A
(1021)	- 1015	RAU	60 2001 1016	$(m_f)_i$ to UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1015	- 1016	FMP	39 2001 1017	$x(m_f)_i$ in UA
	1017	STU	21 2401 1018	$(m_f)_i^2$ to (0401+A)
	1018	FMP	39 2001 1019	$x(m_f)_i$ in UA
	1019	STU	21 2501 1020	$(m_f)_i^3$ to (0501+A)
	1020	NZA	40 1021 0952	Test A for zero (all m_f squared and cubed)
	1021	SXA	51 0001 1015	(-1) in A
1020	- 0952	RAA	80 (n-1) 1022	(n-1) to A
(1032)	- 1022	SXA	51 0001 1023	(-1) in A
	1023	RAU	60 2402 1024	$(m_f^2)_i$ to UA
	1024	FSB	33 2400 1025	$-(m_f^2)_{i-2}$ in UA
	1025	FDV	34 0092 1026	÷ 2 in UA
	1026	STU	21 2452 1027	$[(m_f^2)_i - (m_f^2)_{i-2}] \div 2$ to (0452+A)
	1027	RAU	60 2401 1028	$(m_f^2)_{i-1}$ to UA
	1028	FSB	33 2400 1029	$-(m_f^2)_{i-2}$ in UA
	1029	FDV	34 0092 1030	÷ 2 in UA
	1030	STU	21 2451 1031	$[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ to (0451+A)
	1031	SXA	51 0001 1032	(-1) in A
	1032	NZA	40 1022 0953	Test A for zero (all second degree terms calculated)

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1032	- 0953	RAA	80 (n-1) 1033	(n-1) to A
(1043)	- 1033	SXA	51 0001 1034	(-1) in A
	1034	RAU	60 2502 1035	$(m_f^3)_i$ to UA
	1035	FSB	33 2500 1036	$-(m_f^3)_{i-2}$ in AU
	1036	FDV	34 0093 1037	÷ 3 in UA
	1037	STU	21 2552 1038	$[(m_f^3)_i - (m_f^3)_{i-2}] \div 3$ to (0552+A)
	1038	RAU	60 2501 1039	$(m_f^3)_{i-1}$ to UA
	1039	FSB	33 2500 1040	$-(m_f^3)_{i-2}$ in UA
	1040	FDV	34 0093 1041	÷ 3 in UA
	1041	STU	21 2551 1042	$[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ to (0551+A)
	1042	SXA	51 0001 1043	(-1) in A
	1043	NZA	40 1033 0954	Test A for zero (all third degree terms calculated)
	0954	RAA	80 (n-1) 1044	(n-1) to A
(1060)	- 1044	SXA	51 0002 1045	(-2) in A
	1045	RAU	60 2001 1046	$(m_f)_{i-2}$ to UA
	1046	FSB	33 2002 1047	$-(m_f)_{i-1}$ in UA
	1047	STU	21 2602 1048	$(m_f)_{i-2} - (m_f)_{i-1}$ to (0602+A)
	1048	RAU	60 2001 1049	$(m_f)_{i-2}$ to UA
	1049	FSB	33 2003 1050	$-(m_f)_i$ in UA
	1050	STU	21 2652 1051	$(m_f)_{i-2} - (m_f)_i$ to (0652+A)
	1051	RAU	60 2002 1052	$(m_f)_{i-1}$ to UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1051 -	1052	FSB	33 2003 1053	$-(m_f)_i$ in UA
	1053	STU	21 2702 1054	$(m_f)_{i-1} - (m_f)_i$ to (0702+A)
	1054	RSU	61 2602 1055	$-[(m_f)_{i-2} - (m_f)_{i-1}]$ to UA
	1055	STU	21 2752 1056	$(m_f)_{i-1} - (m_f)_{i-2}$ to (0752+A)
	1056	RSU	61 2652 1057	$-[(m_f)_{i-2} - (m_f)_i]$ to UA
	1057	STU	21 2802 1058	$(m_f)_i - (m_f)_{i-2}$ to (0802+A)
	1058	RSU	61 2702 1059	$-[(m_f)_{i-1} - (m_f)_i]$ to UA
	1059	STU	21 2852 1060	$(m_f)_i - (m_f)_{i-1}$ to (0852+A)
	1060	NZA	40 1044 0955	Test A for zero (difference and negative of all terms taken)
	0955	RAA	80 (n-1) 1061	(n-1) to A
(1140) -	1061	SXA	51 0002 1062	(-2) in A
	1062	RAU	60 2001 1063	$(m_f)_{i-2}$ to UA
	1063	FAD	32 2002 1064	$+(m_f)_{i-1}$ in UA
	1064	STU	21 2022 1065	$(m_f)_{i-2} + (m_f)_{i-1}$ to (0022+A)
	1065	RAU	60 2002 1066	$(m_f)_{i-1}$ to UA
	1066	FAD	32 2003 1067	$+(m_f)_i$ in UA
	1067	STU	21 2072 1068	$(m_f)_{i-1} + (m_f)_i$ to (0072+A)
	1068	RAU	60 2001 1069	$(m_f)_{i-2}$ to UA
	1069	FAD	32 2003 1070	$+(m_f)_i$ in UA
	1070	STU	21 2122 1071	$(m_f)_{i-2} + (m_f)_i$ to (0122+A)
	1071	RAU	60 2001 1072	$(m_f)_{i-2}$ to UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1071 -	1072	FMP	39 2002 1073	$x(m_f)_{i-1}$ in UA
	1073	STU	21 2172 1074	$(m_f)_{i-2}\ (m_f)_{i-1}$ to (178+A)
	1074	RAU	60 2002 1075	$(m_f)_{i-1}$ to UA
	1075	FMP	39 2003 1076	$x(m_f)_i$ in UA
	1076	STU	21 2222 1077	$(m_f)_{i-1}\ (m_f)_i$ to (0222+A)
	1077	RAU	60 2001 1078	$(m_f)_{i-2}$ to UA
	1078	FMP	39 2003 1079	$x(m_f)_i$ in UA
	1079	STU	21 2272 1080	$(m_f)_{i-2}\ (m_f)_i$ to (0272+A)
	1080	RAU	60 2353 1081	$(m_f)_i - (m_f)_{i-2}$ to UA
	1081	FMP	39 2172 1082	$x[(m_f)_{i-2}\ (m_f)_{i-1}]$ in UA
	1082	STU	21 0600 1083	$[(m_f)_i - (m_f)_{i-2}][(m_f)_{i-2}\ (m_f)_{i-1}]$ to 0600
	1083	RSU	61 2022 1084	$-[(m_f)_{i-2} + (m_f)_{i-1}]$ to UA
	1084	FMP	39 2453 1085	$x[(m_f^2)_i - (m_f^2)_{i-2}] \div 2$ in UA
	1085	FAD	32 0600 1086	$+[(m_f)_i - (m_f)_{i-2}][(m_f)_{i-2}\ (m_f)_{i-1}]$ in UA
	1086	FAD	32 0600 1086	$+[(m_f)_i - (m_f)_{i-2}] \div 3$ in UA
	1087	FDV	34 2852 1088	$\div[(m_f)_i - (m_f)_{i-1}]$ in UA
	1088	FDV	34 2802 1089	$\div[(m_f)_i - (m_f)_{i-2}]$ in UA
	1089	STU	21 2422 1090	$[1-3]_c$ to (0422+A)

Note: The integrated form of the Lagrange equation is

$$\int_{m_{f_0}}^{m_{f_2}} y \, dm_f = \frac{y_0}{(m_{f_0}-m_{f_1})(m_{f_0}-m_{f_2})} \left[\frac{m_{f_2}^3-m_{f_0}^3}{3} - \frac{m_{f_1}+m_{f_2}}{2} (m_{f_2}^2-m_{f_0}^2) + m_{f_1} m_{f_2} (m_{f_2}-m_{f_0}) \right]$$

$$+ \frac{y_1}{(m_{f_1}-m_{f_2})(m_{f_1}-m_{f_0})} \left[\frac{m_{f_2}^3-m_{f_0}^3}{3} - \frac{m_{f_0}+m_{f_2}}{2} (m_{f_2}^2-m_{f_0}^2) + m_{f_0} m_{f_2} (m_{f_2}-m_{f_0}) \right]$$

$$+ \frac{y_2}{(m_{f_2}-m_{f_0})(m_{f_2}-m_{f_1})} \left[\frac{m_{f_2}^3-m_{f_0}^3}{3} - \frac{m_{f_0}+m_{f_1}}{2} (m_{f_2}^2-m_{f_0}^2) + m_{f_0} m_{f_1} (m_{f_2}-m_{f_0}) \right]$$

The bracketed terms are denoted by $[1-3]_a$, $[1-3]_b$, and $[1-3]_c$, respectively. For the integration $\int_{m_{f_0}}^{m_{f_1}} y \, dm_f$, the terms are denoted by $[1-2]_a$, $[1-2]_b$, and $[1-2]_c$.

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1089 -	1090	RAU	60 2353 1091	$(m_f)_i - (m_f)_{i-2}$ to UA
	1091	FMP	39 2272 1092	$\times(m_f)_{i-2}\ (m_f)_i$ in UA
	1092	STU	21 0600 1093	$[(m_f)_i - (m_f)_{i-2}][(m_f)_{i-2}\ (m_f)_i]$ to 0600
	1093	RSU	61 2453 1094	$-[(m_f^2)_i - (m_f^2)_{i-2}] \div 2$ to UA
	1094	FMP	39 2122 1095	$\times[(m_f)_{i-2} + (m_f)_i]$ in UA
	1095	FAD	32 0600 1096	$+[(m_f)_{i-2}\ (m_f)_i][(m_f)_i - (m_f)_{i-2}]$ in UA
	1096	FAD	32 2553 1097	$+[(m_f^3)_i - (m_f^3)_{i-2}] \div 3$ in UA
	1097	FDV	34 2752 1098	$\div[(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1098	FDV	34 2702 1099	$\div[(m_f)_{i-1} - (m_f)_i]$ in UA
	1099	STU	21 2372 1100	$[1-3]_b$ to (0372+A)
	1100	RAU	60 2353 1101	$(m_f)_i - (m_f)_{i-2}$ to UA
	1101	FMP	39 2222 1102	$\times(m_f)_{i-1}\ (m_f)_i$ in UA
	1102	STU	21 0600 1103	$[(m_f)_{i-1}\ (m_f)_i][(m_f)_i - (m_f)_{i-2}]$ to 0600
	1103	RSU	61 2453 1104	$-[(m_f^2)_i - (m_f^2)_{i-2}] \div 2$ to UA
	1104	FMP	39 2072 1105	$\times[(m_f)_{i-1} + (m_f)_i]$ in UA
	1105	FAD	32 0600 1106	$+[(m_f)_{i-1}\ (m_f)_i][(m_f)_i - (m_f)_{i-2}]$ in UA
	1106	FAD	32 2553 1107	$+[(m_f^3)_i - (m_f^3)_{i-2}] \div 3$ in UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1106 -	1107	FDV	34 2652 1108	$\div[(m_f)_{i-2} - (m_f)_i]$ in UA
	1108	FDV	34 2602 1109	$\div[(m_f)_{i-2} - (m_f)_{i-1}]$ in UA
	1109	STU	21 2322 1110	$[1-3]_a$ to (0322+A)
	1110	RAU	60 2352 1111	$(m_f)_{i-1} - (m_f)_{i-2}$ to UA
	1111	FMP	39 2172 1112	$x(m_f)_{i-2}\ (m_f)_{i-1}$ in UA
	1112	STU	21 0600 1113	$[(m_f)_{i-2}\ (m_f)_{i-1}][(m_f)_{i-1} - (m_f)_{i-2}]$ to 0600
	1113	RSU	61 2022 1114	$-[(m_f)_{i-2} + (m_f)_{i-1}]$ to UA
	1114	FMP	39 2452 1115	$x[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ in UA
	1115	FAD	32 0600 1116	$+(m_f)_{i-2}\ (m_f)_{i-1}\ [(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1116	FAD	32 2552 1117	$+[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ in UA
	1117	FDV	34 2852 1118	$\div[(m_f)_i - (m_f)_{i-1}]$ in UA
	1118	FDV	34 2802 1119	$\div[(m_f)_i - (m_f)_{i-2}]$ in UA
	1119	STU	21 2622 1120	$[1-2]_c$ to (0622+A)
	1120	RAU	60 2352 1121	$(m_f)_{i-1} - (m_f)_{i-2}$ to UA
	1121	FMP	39 2272 1122	$x(m_f)_{i-2}\ (m_f)_i$ in UA
	1122	STU	21 0600 1123	$[(m_f)_{i-2}\ (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ to 0600

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1122 -	1123	RSU	61 2452 1124	$-[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ in UA
	1124	FMP	39 2122 1125	$\times[(m_f)_{i-2} + (m_f)_i]$ in UA
	1125	FAD	32 0600 1126	$+[(m_f)_{i-2} (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1126	FAD	32 2552 1127	$+[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ in UA
	1127	FDV	34 2752 1128	$\div[(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1128	FDV	34 2702 1129	$\div[(m_f)_{i-1} - (m_f)_i]$ in UA
	1129	STU	21 2572 1130	$[1-2]_b$ to (0572+A)
	1130	RAU	60 2352 1131	$(m_f)_{i-1} - (m_f)_{i-2}$ to UA
	1131	FMP	39 2222 1132	$\times(m_f)_{i-1} (m_f)_i$ in UA
	1132	STU	21 0600 1133	$[(m_f)_{i-1} (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ to 0600
	1133	RSU	61 2452 1134	$-[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ to UA
	1134	FMP	39 2072 1135	$\times[(m_f)_{i-1} + (m_f)_i]$ in UA
	1135	FAD	32 0600 1136	$+[(m_f)_{i-1} (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1136	FAD	32 2552 1137	$+[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ in UA
	1137	FDV	34 2652 1138	$\div[(m_f)_{i-2} - (m_f)_i]$ in UA
	1138	FDV	34 2602 1139	$\div[(m_f)_{i-2} - (m_f)_{i-1}]$ in UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1138 -	1139	STU	21 2522 1140	$[1-2]_a$ to (0522+A)
	1140	NZA	40 1061 0956	Test A for zero (all Lagrange terms calculated), recycle

Note: Instruction 1140 is modified to produce the desired calculation

40 1061 0956	EFV and bubble point - dew point
40 1061 0956	EFV only
40 1061 0962	Bubble point - dew point only

The combined and EFV programs will be continued here. The bubble point - dew point program skips to Loop 8.

Loop 3. 1/f Calculates 1/f for each value of m_f.

From	Loc.	Abbr.	Instruction	Operation
1140 (1185) -	0956	RAA	80 (n-1) 1145	(n-1) to A
(1153) -	1145	RAU	60 2051 1146	K_i to UA
	1146	FMP	39 0047 1147	x V/L assumed in UA
	1147	FAD	32 0091 1148	+ 1 in UA
	1148	STU	21 0600 1149	$1 + K_i$ V/L to 0600
	1149	RAU	60 0091 1150	1 to UA
	1150	FDV	34 0600 1151	$\div(1 + K_i$ V/L) in UA
	1151	STU	21 2901 1152	$1 \div (1 + K_i$ V/L) (= 1/f) to (0901+A)

Loop 3. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1151	- 1152	NZA	40 1153 0957	Test A for zero (all 1/f calculated)
	1153	SXA	51 0001 1145	(-1) in A, recycle

Loop 4. Area Under Curve Calculates $\int_{i-2}^{i} y \, dm_f$ and $\sum \int_{i-2}^{i} y \, dm_f = Y$

From	Loc.	Abbr.	Instruction	Operation
1152 (1255)	- 0957	RAA	80 (n-1) 1154	(n-1) to A
(1166)	- 1154	SXA	51 0002 1155	(-2) in A
	1155	RAU	60 2422 1156	$[1-3]_c$ to UA
	1156	FMP	39 2903 1157	$x(1/f)_i$ in UA
	1157	STU	21 0600 1158	$(1/f)_i \, [1-3]_c$ to 0600
	1158	RAU	60 2372 1159	$[1-3]_b$ to UA
	1159	FMP	39 2902 1160	$x(1/f)_{i-1}$ in UA
	1160	FAD	32 0600 1161	$+(1/f)_i \, [1-3]_c$ in UA
	1161	STU	21 0600 1162	$(1/f)_i \, [1-3]_c + (1/f)_{i-1} \, [1-3]_b$ to 0600
	1162	RAU	60 2322 1163	$[1-3]_a$ to UA
	1163	FMP	39 2901 1164	$x(1/f)_{i-2}$ in UA
	1164	FAD	32 0600 1165	$+(1/f)_i \, [1-3]_c + (1/f)_{i-1} \, [1-3]_b$ in UA
	1165	STU	21 2472 1166	$\int_{i-2}^{i} 1/f \, dm_f$ to (0472+A)
	1166	NZA	40 1154 0958	Test A for zero (all $\int_{i-2}^{i}$ calculated), recycle

Loop 4. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1166 -	0958	RAA	80 (n-1) 1167	(n-1) to A
	1167	RAU	60 0000 1168	0 to UA
(1170) -	1168	SXA	51 0002 1169	(-2) in A
	1169	FAD	32 2472 1170	$+ \int_{i-2}^{i} 1/f \, dm_f$
	1170	NZA	40 1168 1141	Test A for zero (all $\int_{i-1}^{i}$ summed), recycle
	1141	STU	21 0491 1171	$\int_{0}^{1} 1/f \, dm_f$ to 0491

Note: For bubble point - dew point, instruction 1141 is 21 0491 1271.

Loop 5. Correct V/L Compares V/L calculated to V/L assumed for maximum disagreement of ± 0.001

From	Loc.	Abbr.	Instruction	Operation
1141 -	1171	RAU	60 0091 1172	1 to UA
	1172	FSB	33 0491 1173	- L/F in UA
	1173	STU	21 0492 1174	1 - L/F to 0492
	1174	FDV	34 0491 1175	÷ L/F in UA
	1175	STU	21 0700 1176	V/L calculated to 0700
	1176	RAU	60 0047 1177	V/L assumed to UA
	1177	FSB	33 0700 1178	- V/L calculated in UA
	1178	STU	21 0750 1179	V/L assumed - V/L calculated to 0750
	1179	RAU	60 0000 1180	0 to UA

Loop 5. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1179 -	1180	RAL	65 0000 1181	0 to LA
	1181	FAM	37 0750 1182	+ $\lvert$V/L assumed - V/L calculated$\rvert$ to Accumulator
	1182	FSB	33 0098 1183	- 0.001 in Accumulator
	1183	BMI	46 0959 1184	Test Accumulator for minus (within limits)
	1184	RAU	60 0700 1185	V/L calculated to UA
	1185	STU	21 0047 0956	V/L calculated to 0047 (V/L assumed for next cycle), recycle back to Loop 3

Loop 6. Product Curves Calculates points on product TBP curves.

From	Loc.	Abbr.	Instruction	Operation
1183 -	0959	RAA	80 (n-1) 1186	(n-1) to A
	1186	RAU	60 0000 1187	0 to A
(1199) -	1187	SXA	51 0002 1188	(-2) in A
	1188	RAU	60 2901 1189	$(1/f)_{i-2}$ to UA
	1189	FMP	39 2522 1190	$x[1-2]_a$ in UA
	1190	STU	21 0600 1191	$(1/f)_{i-2}\,[1-2]_a$ to 0600
	1191	RAU	60 2902 1192	$(1/f)_{i-1}$ to UA
	1192	FMP	39 2572 1193	$x[1-2]_b$ in UA
	1193	FAD	32 0600 1194	$+(1/f)_{i-2}\,[1-2]_a$ in UA
	1194	STU	21 0600 1195	$(1/f)_{i-1}\,[1-2]_b + (1/f)_{i-2}\,[1-2]_a$ to 0600
	1195	RAU	60 2903 1196	$(1/f)_i$ to UA
	1196	FMP	39 2622 1197	$x[1-2]_c$ in UA

Loop 6. (Cont.)

From	Loc.	Abbr.	Instruction			Operation
1196 -	1197	FAD	32	0600	1198	$+(1/f)_{i-1}\,[1-2]_b + (1/f)_{i-2}\,[1-2]_a$ in UA
	1198	STU	21	2672	1199	$\int_{i-2}^{i-1} 1/f\ dm_f$ to (0672+A)
	1199	NZA	40	1187	0960	Test A for zero (all $\int_{i-2}^{i-1} 1/f\ dm_f$ calculated), recycle
	0960	RAB	82	(n-1)	1200	(n-1) to B
	1200	RAU	60	0000	1201	0 to UA
	1201	STU	21	0721	1328	0 to 0721
	1328	RAA	80	0000	1329	0 to A
(1209) -	1329	SXB	53	0002	1202	(-2) in B
	1202	RAU	60	2721	1203	$\sum\int_{o}^{i-2} 1/f\ dm_f$ to UA
	1203	RAD	32	2672	1204	$+\int_{i-2}^{i-1} 1/f\ dm_f$ in UA
	1204	STU	21	2722	1205	$\int_{o}^{i-1} 1/f\ dm_f$ to (0722+A)
	1205	FSB	33	2672	1206	$-\int_{i-2}^{i-1} 1/f\ dm_f$ in UA
	1206	FAD	32	2472	1207	$+\int_{i-2}^{i} 1/f\ dm_f$ in UA
	1207	STU	21	2723	1208	$\int_{o}^{i} 1/f\ dm_f$ in (0723+A)
	1208	NZB	42	1209	0961	Test B for zero (all $\int_{o}^{i} 1/f\ dm_f$ calculated)
	1209	AXA	50	0002	1329	+ 2 in A, recycle

Loop 6. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1208 -	0961	RAA	80 (n-1) 1211	(n-1) to A
(1210) -	1211	RAU	60 2001 1224	$(m_f)_i$ to UA
	1224	STU	21 2921 1212	$(m_f)_i$ to (0921+A)
	1212	FSB	33 2721 1213	$-\int_0^i 1/f \, dm_f$ in UA
	1213	STU	21 2771 1214	$\int_0^i v/f \, dm_f$ to (0771+A)
	1214	FDV	34 0492 1215	÷ V/F in UA
	1215	STU	21 2871 1216	$\int_0^i v/f \, dm_f \div V/F$ to (0871+A)
	1216	RAU	60 2721 1217	$\int_0^i 1/f \, dm_f$ in UA
	1217	FDV	34 0491 1218	÷ L/F in UA
	1218	STU	21 2821 1219	$\int_0^i 1/f \, dm_f \div L/F$ to (0821+A)
	1219	NZA	40 1210 1220	Test A for zero (all points calculated)
	1210	SXA	51 0001 1211	(-1) in A, recycle

Loop 7. EFV Punch Stores and punches results from EFV calculations.

From	Loc.	Abbr.	Instruction	Operation
1219 -	1220	RAU	60 0700 1221	V/L to UA
	1221	STU	21 0793 1222	V/L to 0793
	1222	RAU	60 0750 1223	V/L assumed - V/L calculated to UA

Loop 7. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1222 -	1223	STU	21 0843 1225	V/L assumed - V/L calculated to 0843
	1225	LDD	69 0000 1226	0 to D
	1226	STD	24 1894 1227	D to 1894
	1227	RAL	65 1228 1229	Contents of 1228 to LA
	1228		00 0107 9300	
	1229	LDD	69 1230 1950	Punch V/L, error; exit to 1230
	1230	LDD	69 0045 1231	Contents of 0045 to D
	1231	STD	24 1894 1232	D to 1894
	1232	RAL	65 1233 1234	Contents of 1233 to LA
	1233		00 0207 2100	
	1234	LDD	69 1235 1950	Punch $\int 1/f$, $\int v/f$, $\frac{\int 1/f}{L/F}$, $\frac{\int v/f}{V/F}$, m_f; exit to 1235
	1235	LDD	69 0045 1236	Contents of 0045 to D
	1236	STD	24 1894 1237	D to 1894
	1237	RAL	65 1238 1142	Contents of 1238 to LA
	1238		00 3009 0100	
	1142	LDD	69 1260 1950	Punch 1/f; exit to 1260

Note: For EFV only, instruction 1142 is 69 1901 1950 and the program ends here.

Loop 8. BP-DP Instructions Changes instructions from EFV program for BP-DP program.

From	Loc.	Abbr.	Instruction	Operation
1142 -	1260	RAU	60 1141 1261	Contents of 1141 to UA
	1261	AUP	10 0144 1262	+ contents of 0144 in UA
	1262	STU	21 1141 0962	New instruction to 1141

Loop 9. K-Value Calculates K for the assumed temperature.

From	Loc.	Abbr.	Instruction	Operation
1262 (1276) (1309)	- 0962	RAB	82 (n-1) 1240	(n-1) to B
(1256)	- 1240	RAU	60 4301 1241	Constant E_i to UA
	1241	FMP	39 0042 1242	x T/100 in UA
	1242	FAD	32 4251 1243	+ Constant D_i in UA
	1243	FMP	39 0042 1244	x T/100 in UA
	1244	FAD	32 4201 1245	+ Constant C_i in UA
	1245	FMP	39 0042 1246	x T/100 in UA
	1246	FAD	32 4151 1247	+ Constant B_i in UA
	1247	FMP	39 0042 1248	x T/100 in UA
	1248	FAD	32 4101 1249	+ Constant A_i in UA
	1249	STU	21 0600 1250	log K to 0600
	1250	LDD	69 1251 1506	Exit to 1251

Note: 1506 is the entry into the log deck to find x when log x is in the upper accumulator. The log deck is available at the Computing Center, Oklahoma State University

Log Deck	- 1251	STU	21 4901 1252	K_i to (0901+B)
	1252	LDD	69 0141 1253	Contents of 0141 to D
	1253	RAC	88 8001 1254	Data address of D to C
	1254	BMC	49 1257 1255	If positive, to BP calculation, Loop 10 If negative, to DP calculation, Loop 11

Loop 10. T_{BP} Calculates and punches T_{BP}.

Sub-Loop 10a. K Calculates area under curve K vs. m_f.

From	Loc.	Abbr.	Instruction	Operation
1254	- 1255	NZB	42 1256 0957	Test B for zero (all K calculated)
	1256	SXB	53 0001 1240	(-1) in B, recycle to Loop 9
1255	- 0957	Go to Loop 4 to calculate area under curve		
Loop 4	- 1271	LDD	69 0141 1272	Contents of 0141 to D
	1272	RAC	88 8001 1273	Data address of D to C
	1273	BMC	49 1299 1263	To T_{BP} correction, Sub-Loop 10b

Sub-Loop 10b. T_{BP} Correction Corrects T_{BP}.

From	Loc.	Abbr.	Instruction	Operation
1273	- 1263	RAU	60 0091 1264	1 to UA
	1264	FSB	33 0491 1265	$-\int K$ in UA
	1265	STU	21 0750 1266	$1 - \int K$ in 0750
	1266	RAU	60 0098 1267	0.001 to UA
	1267	FSM	38 0750 1268	$- \left\| 1 - \int K \right\|$ in UA
	1268	BMI	46 1269 1277	If negative, error too large If positive, T_{BP} satisfactory; to T_{BP} punch, Sub-Loop 10c
	1269	RAU	60 0750 1270	Error to UA
	1270	FDV	34 0096 1274	÷ 7.5 in UA

Sub-Loop 10b. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1270 -	1274	FAD	32 0091 1275	+ 1 in UA
	1275	FMP	39 0042 1276	x T_{BP} in UA
	1276	STU	21 0042 0962	New T_{BP} to 0042, recycle to Loop 9

Sub-Loop 10c. T_{BP} Punch Punch T_{BP}, error, and K; change program for DP calculations.

From	Loc.	Abbr.	Instruction	Operation
1276 -	1277	RAU	60 0750 1278	Error to UA
	1278	STU	21 0844 1279	Error to 0844
	1279	RAU	60 0042 1280	T_{BP} to UA
	1280	STU	21 0794 0963	T_{BP} to 0794
	0963	RAA	80 (n-1) 1281	(n-1) to A
(1284) -	1281	RAU	60 2901 1282	K_i to UA
	1282	STU	21 2871 1283	K_i to (0871+A)
	1283	NZA	40 1289 1285	Test A for zero (all K stored)
	1284	SXA	51 0001 1281	(-1) in A, recycle
(1283) -	1285	LDD	69 0000 1286	0 to D
	1286	STD	24 1894 1287	D to 1894
	1287	RAL	65 1288 1289	Contents of 1288 to LA
	1288		00 6007 9400	
	1289	LDD	69 1290 1950	Punch T_{BP}; exit to 1290
	1290	LDD	69 0045 1291	(n-1) to D
	1291	STD	24 1894 1292	(n-1) to 1894
	1292	RAL	65 1293 1294	Contents of 1293 to LA
	1293		00 6508 7100	

Loop 10c. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1292	- 1294	LDD	69 1295 1950	Punch K, exit to 1295
	1295	RAU	60 0142 1296	-1 to UA
	1296	STU	21 0141 1299	-1 to 0141
	1297	RAU	60 0043 1298	T_{DP} to UA
	1298	STU	21 0042 0962	T_{DP} to 0042; recycle to Loop 9

Loop 11. T_{DP} Calculates and punches T_{DP}.

Sub-Loop 11a. $\int 1/K$ Calculates area under curve 1/K vs. m_f.

From	Loc.	Abbr.	Instruction	Operation
1254	- 1257	RAU	60 0091 1258	1 to UA
	1258	FDV	34 4901 1259	$\div K_i$ in UA
	1259	STU	21 4901 1255	$1/K_i$ to (0901+B)
	1255	NZB	42 1256 0957	Test B for zero (all 1/K calculated)
	1256	SXB	53 0001 1240	(-1) in B; recycle to Loop 9
1255	- 0957	First instruction in Loop 4 to calculate area under curve		
Loop 4	- 1271	LDD	69 0141 1272	Contents of 0141 to D
	1272	RAC	88 8001 1273	Data address of D to C
	1273	BMC	49 1299 1263	To T_{DP} correction, Sub-Loop 11b

Sub-Loop 11b. T_{DP} Correction Corrects T_{DP}.

From	Loc.	Abbr.	Instruction	Operation
1273	- 1299	RAU	60 0091 1300	1 to UA
	1300	FSB	33 0491 1301	$-\int 1/K$ in UA
	1301	STU	21 0750 1302	$1 - \int 1/K$ to 0750
	1302	RAU	60 0098 1303	0.001 to UA
	1303	FSM	38 0750 1304	$- \left\| 1 - \int 1/K \right\|$ in UA
	1304	BMI	46 1305 1310	If negative, error to large If positive, T_{DP} satisfactory; to T_{DP} punch, Sub-Loop 11c
	1305	RSU	61 0750 1306	- Error to UA
	1306	FDV	34 0096 1307	÷ 7.5 in UA
	1307	FAD	32 0091 1308	+1 in UA
	1308	FMP	39 0042 1309	x T_{DP} in UA
	1309	STU	21 0042 0962	New T_{DP} to 0042; recycle to Loop 9

Sub-Loop 11c. T_{DP} Punch Punch T_{DP}, error, 1/K.

From	Loc.	Abbr.	Instruction	Operation
1304	- 1310	RAU	60 0750 1311	Error to UA
	1311	STU	21 0845 1312	Error to 0845
	1312	RAU	60 0042 1313	T_{DP} to UA
	1313	STU	21 0795 0964	T_{DP} to 0795

Sub-Loop 11c. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1313 -	0964	RAA	80 (n-1) 1314	(n-1) to A
(1317) -	1314	RAU	60 2901 1315	$(1/K)_i$ to UA
	1315	STU	21 2871 1316	$(1/K)_i$ to (0871+A)
	1316	NZA	40 1317 1318	Test A for zero (all 1/K stored)
	1317	SXA	51 0001 1314	(-1) in A; recycle
(1316) -	1318	LDD	69 0000 1319	0 to D
	1319	STD	24 1894 1320	0 to data address of 1894
	1320	RAL	65 1321 1322	Contents of 1321 in LA
	1321		00 9007 9500	
	1322	LDD	69 1323 1950	Punch T_{DP}, error; exit to 1323
	1323	LDD	69 0045 1324	(n-1) to D
	1324	STD	24 1894 1325	(n-1) to data address of 1894
	1325	RAL	65 1326 1327	Contents of 1326 in LA
	1326		00 9508 7100	
	1327	LDD	69 1901 1950	Punch 1/K; stop

Instructions written into program

These are the n-1 instructions which are modified at the start of the program; the proper value of n-1 is put into the data address.

Loc.	Abbr.	Instruction
0950	RAA	80 0000 1006
0951	RAA	80 0000 1015
0952	RAA	80 0000 1022
0953	RAA	80 0000 1033
0954	RAA	80 0000 1044
0955	RAA	80 0000 1061
0956	RAA	80 0000 1145
0957	RAA	80 0000 1154
0958	RAA	80 0000 1167
0959	RAA	80 0000 1186
0960	RAB	82 0000 1200
0961	RAA	80 0000 1211
0962	RAB	82 0000 1240
0963	RAA	80 0000 1281
0964	RAA	80 0000 1314

Constants written into the program

These constants are in IBM 650 floating point notation, except for 0141, 0142, and 0144.

Loc.	Constant			
0091	10	0000	0051	
0092	20	0000	0051	
0093	30	0000	0051	
0094	40	0000	0051	
0095	50	0000	0051	
0096	75	0000	0051	
0098	10	0000	0048	
0141	00	0000	0001	
0142	00	0000	0001	Minus
0144	00	0000	0100	

Control Cards

EFV and BP-DP

Loc.	Instruction
1140	40 1061 0956
1141	21 0491 1171
1142	69 1260 1950
1143	00 0000 0000
1144	00 0000 0000

EFV Only

Loc.	Instruction
1140	40 1061 0956
1141	21 0491 1174
1142	69 1901 1950
1143	00 0000 0000
1144	00 0000 0000

BP-DP Only

Loc.	Instruction
1140	40 1061 0962
1141	21 0491 1271
1142	69 1260 1950
1143	00 0000 0000
1144	00 0000 0000

Card Format for Combined Program

Input Cards

Input data may be inserted in any order, since locations are specified. All values are in floating decimal point except "n-1" in location 0045 which is in fixed point.

Output Cards

Card 1

Word 1 V/L calculated

Word 2 Difference between V/L assumed and V/L calculated for last calculation (≤ 0.001)

Card 2 - (n+1)

Word 1 $\int_0^{m_f} 1/f \; dm_f$

Word 2 $\int_0^{m_f} v/f \; dm_f$

Word 3 $\dfrac{\int_0^{m_f} 1/f \; dm_f}{L/F}$

Word 4 $\dfrac{\int_0^{m_f} v/f \; dm_f}{V/F}$

Word 5 m_f

Card 30 - (n+29)

Word 1 1/f

Card 60

Word 1 $T_{BP}/100$ calculated

Word 2 Difference between $T_{BP}/100$ assumed and $T_{BP}/100$ calculated

Card 65 - (n+64)

Word 1 K calculated at T_{BP}

Word 2 m_f

Card 90

Word 1 $T_{DP}/100$ calculated

Word 2 Difference between $T_{DP}/100$ calculated and $T_{DP}/100$ assumed

Card 95 - (n+94)

Word 1 1/K at T_{DP}

Word 2 m_f

Fractional Distillation Program

This program is written in machine language and makes use of the "Drum zero, read, and punch loop" and "Log deck" available at the Computing Center, Oklahoma State University. The instructions in these loops are not listed here; the rest of the program is given below. Each loop of the program is presented separately to facilitate comprehension of the calculation procedure.

Input data are

0044 - n number of input data points

0045 - n-1 number of data points, less one, in fixed point

0046 - k-1 number of plates above the feed, less one, in fixed point

0047 - h-1 number of plates below the feed, less one, in fixed point

0048 - R reflux rate

0101 - 0120 A
0151 - 0170 B
0201 - 0220 C } constants in equation 9
0251 - 0271 D
0301 - 0320 E

0522 - 0586 vapor loading
} plates above the feed
0572 - 0586 liquid loading

0672 - 0686 vapor loading
} plates below the feed
0722 - 0736 liquid loading

0822 - 0836 temperature on trays above the feed

0872 - 0886 temperature on trays below the feed

Data for the plates are loaded in order from the feed zone toward the terminals.

Output data are

$$\left.\begin{array}{l}\text{0001 - 0020} \quad m_f \\ \text{0051 - 0070} \quad K\end{array}\right\}\text{for each plate}$$

0491 - D/F

0492 - B/F

0351 - 0370 - $\dfrac{\int_o^{m_f} d/f \; dm_f}{D/F}$

0401 - 0420 - $\dfrac{\int_o^{m_f} b/f \; dm_f}{B/F}$

0901 - 0920 - d/f

Loop 1. n-1 Instructions Puts n-1 into all instructions which require it.

From	Loc.	Abbr.	Instruction	Operation
Read and punch loop	- 1000	RAL	65 0045 1001	(n-1) to LA
	1001	RAA	80 0021 1002	21 to A
(1005)	- 1002	LDD	69 2950 1003	Contents of (0950+A) to D
	1003	SDA	22 2950 1004	∠xx (n-1) xxxx_/A to 0950+A
	1004	NZA	40 1005 0950	Test A for zero (all instructions modified)
	1005	SXA	51 0001 1002	(-1) in A, recycle

Loop 2. Lagrange terms Calculates terms for intergrated Lagrange equation.

From	Loc.	Abbr.	Instruction	Operation
1004	- 0950	RAA	80 (n-1) 1006	(n-1) to A
(1014)	- 1006	SXA	51 0001 1007	(-1) in A
	1007	RAU	60 2002 1008	$(m_f)_i$ to UA
	1008	FSB	33 2000 1009	$-(m_f)_{i-2}$ in UA
	1009	STU	21 2352 1010	$(m_f)_i - (m_f)_{i-2}$ to (0352+A)
	1010	RAU	60 2001 1011	$(m_f)_{i-1}$ to UA
	1011	FSB	33 2000 1012	$-(m_f)_{i-2}$ in UA
	1012	STU	21 2351 1013	$(m_f)_{i-1} - (m_f)_{i-2}$ to (0351+A)
	1013	SXA	51 0001 1014	(-1) in A
	1014	NZA	40 1006 0951	Test A for zero (all first degree terms calculated)
	0951	RAA	80 (n-1) 1015	(n-1) to A
(1021)	- 1015	RAU	60 2001 1016	$(m_f)_i$ to UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1015	- 1016	FMP	39 2001 1017	x$(m_f)_i$ in UA
	1017	STU	21 2401 1018	$(m_f)_i^2$ to (0401+A)
	1018	FMP	39 2001 1019	x$(m_f)_i$ in UA
	1019	STU	21 2501 1020	$(m_f)_i^3$ to (0501+A)
	1020	NZA	40 1021 0952	Test A for zero (all m_f squared and cubed)
	1021	SXA	51 0001 1015	(-1) in A
1020	- 0952	RAA	80 (n-1) 1022	(n-1) to A
(1032)	- 1022	SXA	51 0001 1023	(-1) in A
	1023	RAU	60 2402 1024	$(m_f^2)_i$ to UA
	1024	FSB	33 2400 1025	$-(m_f^2)_{i-2}$ in UA
	1025	FDV	34 0092 1026	÷ 2 in UA
	1026	STU	21 2452 1027	$[(m_f^2)_i - (m_f^2)_{i-2}] \div 2$ to (0452+A)
	1027	RAU	60 2401 1028	$(m_f^2)_{i-1}$ to UA
	1028	FSB	33 2400 1029	$-(m_f^2)_{i-2}$ in UA
	1029	FDV	34 0092 1030	÷ 2 in UA
	1030	STU	21 2451 1031	$[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ to (0451+A)
	1031	SXA	51 0001 1032	(-1) in A
	1032	NZA	40 1022 0953	Test A for zero (all second degree terms calculated)

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1032	- 0953	RAA	80 (n-1) 1033	(n-1) to A
(1043)	- 1033	SXA	51 0001 1034	(-1) in A
	1034	RAU	60 2502 1035	$(m_f^3)_i$ to UA
	1035	FSB	33 2500 1036	$-(m_f^3)_{i-2}$ in AU
	1036	FDV	34 0093 1037	$\div$ 3 in UA
	1037	STU	21 2552 1038	$\left[(m_f^3)_i - (m_f^3)_{i-2}\right] \div 3$ to (0552+A)
	1038	RAU	60 2501 1039	$(m_f^3)_{i-1}$ to UA
	1039	FSB	33 2500 1040	$-(m_f^3)_{i-2}$ in UA
	1040	FDV	34 0093 1041	$\div$ 3 in UA
	1041	STU	21 2551 1042	$\left[(m_f^3)_{i-1} - (m_f^3)_{i-2}\right] \div 3$ to (0551+A)
	1042	SXA	51 0001 1043	(-1) in A
	1043	NZA	40 1033 0954	Test A for zero (all third degree terms calculated)
	0954	RAA	80 (n-1) 1044	(n-1) to A
(1060)	- 1044	SXA	51 0002 1045	(-2) in A
	1045	RAU	60 2001 1046	$(m_f)_{i-2}$ to UA
	1046	FSB	33 2002 1047	$-(m_f)_{i-1}$ in UA
	1047	STU	21 2602 1048	$(m_f)_{i-2} - (m_f)_{i-1}$ to (0602+A)
	1048	RAU	60 2001 1049	$(m_f)_{i-2}$ to UA
	1049	FSB	33 2003 1050	$-(m_f)_i$ in UA
	1050	STU	21 2652 1051	$(m_f)_{i-2} - (m_f)_i$ to (0652+A)
	1051	RAU	60 2002 1052	$(m_f)_{i-1}$ to UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1051 -	1052	FSB	33 2003 1053	$-(m_f)_i$ in UA
	1053	STU	21 2702 1054	$(m_f)_{i-1} - (m_f)_i$ to (0702+A)
	1054	RSU	61 2602 1055	$-[(m_f)_{i-2} - (m_f)_{i-1}]$ to UA
	1055	STU	21 2752 1056	$(m_f)_{i-1} - (m_f)_{i-2}$ to (0752+A)
	1056	RSU	61 2652 1057	$-[(m_f)_{i-2} - (m_f)_i]$ to UA
	1057	STU	21 2802 1058	$(m_f)_i - (m_f)_{i-2}$ to (0802+A)
	1058	RSU	61 2702 1059	$-[(m_f)_{i-1} - (m_f)_i]$ to UA
	1059	STU	21 2852 1060	$(m_f)_i - (m_f)_{i-1}$ to (0852+A)
	1060	NZA	40 1044 0955	Test A for zero (difference and negative of all terms taken)
	0955	RAA	80 (n-1) 1061	(n-1) to A
(1140) -	1061	SXA	51 0002 1062	(-2) in A
	1062	RAU	60 2001 1063	$(m_f)_{i-2}$ to UA
	1063	FAD	32 2002 1064	$+(m_f)_{i-1}$ in UA
	1064	STU	21 2022 1065	$(m_f)_{i-2} + (m_f)_{i-1}$ to (0022+A)
	1065	RAU	60 2002 1066	$(m_f)_{i-1}$ to UA
	1066	FAD	32 2003 1067	$+(m_f)_i$ in UA
	1067	STU	21 2072 1068	$(m_f)_{i-1} + (m_f)_i$ to (0072+A)
	1068	RAU	60 2001 1069	$(m_f)_{i-2}$ to UA
	1069	FAD	32 2003 1070	$+(m_f)_i$ in UA
	1070	STU	21 2122 1071	$(m_f)_{i-2} + (m_f)_i$ to (0122+A)
	1071	RAU	60 2001 1072	$(m_f)_{i-2}$ to UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1071	- 1072	FMP	39 2002 1073	$x(m_f)_{i-1}$ in UA
	1073	STU	21 2172 1074	$(m_f)_{i-2}\ (m_f)_{i-1}$ to (178+A)
	1074	RAU	60 2002 1075	$(m_f)_{i-1}$ to UA
	1075	FMP	39 2003 1076	$x(m_f)_i$ in UA
	1076	STU	21 2222 1077	$(m_f)_{i-1}\ (m_f)_i$ to (0222+A)
	1077	RAU	60 2001 1078	$(m_f)_{i-2}$ to UA
	1078	FMP	39 2003 1079	$x(m_f)_i$ in UA
	1079	STU	21 2272 1080	$(m_f)_{i-2}\ (m_f)_i$ to (0272+A)
	1080	RAU	60 2353 1081	$(m_f)_i - (m_f)_{i-2}$ to UA
	1081	FMP	39 2172 1082	$x[(m_f)_{i-2}\ (m_f)_{i-1}]$ in UA
	1082	STU	21 0600 1083	$[(m_f)_i - (m_f)_{i-2}][(m_f)_{i-2}\ (m_f)_{i-1}]$ to 0600
	1083	RSU	61 2022 1084	$-[(m_f)_{i-2} + (m_f)_{i-1}]$ to UA
	1084	FMP	39 2453 1085	$x[(m_f^2)_i - (m_f^2)_{i-2}] \div 2$ in UA
	1085	FAD	32 0600 1086	$+[(m_f)_i - (m_f)_{i-2}][(m_f)_{i-2}\ (m_f)_{i-1}]$ in UA
	1086	FAD	32 0600 1086	$+[(m_f)_i - (m_f)_{i-2}] \div 3$ in UA
	1087	FDV	34 2852 1088	$\div[(m_f)_i - (m_f)_{i-1}]$ in UA
	1088	FDV	34 2802 1089	$\div[(m_f)_i - (m_f)_{i-2}]$ in UA
	1089	STU	21 2422 1090	$[1-3]_c$ to (0422+A)

Note: The integrated form of the Lagrange equation is

$$\int_{m_{f_0}}^{m_{f_2}} y \, dm_f = \frac{y_0}{(m_{f_0}-m_{f_1})(m_{f_0}-m_{f_2})} \left[\frac{m_{f_2}^{3}-m_{f_0}^{3}}{3} - \frac{m_{f_1}+m_{f_2}}{2} (m_{f_2}^{2}-m_{f_0}^{2}) + m_{f_1} m_{f_2} (m_{f_2}-m_{f_0}) \right]$$

$$+ \frac{y_1}{(m_{f_1}-m_{f_2})(m_{f_1}-m_{f_0})} \left[\frac{m_{f_2}^{3}-m_{f_0}^{3}}{3} - \frac{m_{f_0}+m_{f_2}}{2} (m_{f_2}^{2}-m_{f_0}^{2}) + m_{f_0} m_{f_2} (m_{f_2}-m_{f_0}) \right]$$

$$+ \frac{y_2}{(m_{f_2}-m_{f_0})(m_{f_2}-m_{f_1})} \left[\frac{m_{f_2}^{3}-m_{f_0}^{3}}{3} - \frac{m_{f_0}+m_{f_1}}{2} (m_{f_2}^{2}-m_{f_0}^{2}) + m_{f_0} m_{f_1} (m_{f_2}-m_{f_0}) \right]$$

The bracketed terms are denoted by $[1\text{-}3]_a$, $[1\text{-}3]_b$, and $[1\text{-}3]_c$, respectively. For the integration $\int_{m_{f_0}}^{m_{f_1}} y \, dm_f$, the terms are denoted by $[1\text{-}2]_a$, $[1\text{-}2]_b$, and $[1\text{-}2]_c$.

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1089 -	1090	RAU	60 2353 1091	$(m_f)_i - (m_f)_{i-2}$ to UA
	1091	FMP	39 2272 1092	$x(m_f)_{i-2}\ (m_f)_i$ in UA
	1092	STU	21 0600 1093	$[(m_f)_i - (m_f)_{i-2}][(m_f)_{i-2}\ (m_f)_i]$ to 0600
	1093	RSU	61 2453 1094	$-[(m_f{}^2)_i - (m_f{}^2)_{i-2}] \div 2$ to UA
	1094	FMP	39 2122 1095	$x[(m_f)_{i-2} + (m_f)_i]$ in UA
	1095	FAD	32 0600 1096	$+[(m_f)_{i-2}\ (m_f)_i][(m_f)_i - (m_f)_{i-2}]$ in UA
	1096	FAD	32 2553 1097	$+[(m_f{}^3)_i - (m_f{}^3)_{i-2}] \div 3$ in UA
	1097	FDV	34 2752 1098	$\div[(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1098	FDV	34 2702 1099	$\div[(m_f)_{i-1} - (m_f)_i]$ in UA
	1099	STU	21 2372 1100	$[1-3]_b$ to (0372+A)
	1100	RAU	60 2353 1101	$(m_f)_i - (m_f)_{i-2}$ to UA
	1101	FMP	39 2222 1102	$x(m_f)_{i-1}\ (m_f)_i$ in UA
	1102	STU	21 0600 1103	$[(m_f)_{i-1}\ (m_f)_i][(m_f)_i - (m_f)_{i-2}]$ to 0600
	1103	RSU	61 2453 1104	$-[(m_f{}^2)_i - (m_f{}^2)_{i-2}] \div 2$ to UA
	1104	FMP	39 2072 1105	$x[(m_f)_{i-1} + (m_f)_i]$ in UA
	1105	FAD	32 0600 1106	$+[(m_f)_{i-1}\ (m_f)_i][(m_f)_i - (m_f)_{i-2}]$ in UA
	1106	FAD	32 2553 1107	$+[(m_f{}^3)_i - (m_f{}^3)_{i-2}] \div 3$ in UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1106	- 1107	FDV	34 2652 1108	$\div[(m_f)_{i-2} - (m_f)_i]$ in UA
	1108	FDV	34 2602 1109	$\div[(m_f)_{i-2} - (m_f)_{i-1}]$ in UA
	1109	STU	21 2322 1230	$[1-3]_a$ to (0332+A)
	1230	RAU	60 2352 1231	$(m_f)_{i-1} - (m_f)_{i-2}$ to UA
	1231	FMP	39 2172 1232	$x(m_f)_{i-2}\ (m_f)_{i-1}$ in UA
	1232	STU	21 0600 1233	$[(m_f)_{i-2}\ (m_f)_{i-1}][(m_f)_{i-1} - (m_f)_{i-2}]$ to 0600
	1233	RSU	61 2022 1234	$-[(m_f)_{i-2} + (m_f)_{i-1}]$ to UA
	1234	FMP	39 2452 1235	$x[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ in UA
	1235	FAD	32 0600 1236	$+(m_f)_{i-2}\ (m_f)_{i-1}\ [(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1236	FAD	32 2552 1237	$+[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ in UA
	1237	FDV	34 2852 1238	$\div[(m_f)_i - (m_f)_{i-1}]$ in UA
	1238	FDV	34 2802 1239	$\div[(m_f)_i - (m_f)_{i-2}]$ in UA
	1239	STU	21 3300 1240	$[1-2]_c$ to (1300+A)
	1240	RAU	60 2352 1241	$(m_f)_{i-1} - (m_f)_{i-2}$ to UA
	1241	FMP	39 2272 1242	$x(m_f)_{i-2}\ (m_f)_i$ in UA
	1242	STU	21 0600 1243	$[(m_f)_{i-2}\ (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ to 0600

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1242 -	1243	RSU	61 2452 1244	$-[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ in UA
	1244	FMP	39 2122 1245	$\times[(m_f)_{i-2} + (m_f)_i]$ in UA
	1245	FAD	32 0600 1246	$+[(m_f)_{i-2} (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1246	FAD	32 2552 1247	$+[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ in UA
	1247	FDV	34 2752 1248	$\div[(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1248	FDV	34 2702 1249	$\div[(m_f)_{i-1} - (m_f)_i]$ in UA
	1249	STU	21 3325 1250	$[1-2]_b$ to (1325+A)
	1250	RAU	60 2352 1251	$(m_f)_{i-1} - (m_f)_{i-2}$ to UA
	1251	FMP	39 2222 1252	$\times(m_f)_{i-1} (m_f)_i$ in UA
	1252	STU	21 0600 1253	$[(m_f)_{i-1} (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ to 0600
	1253	RSU	61 2452 1254	$-[(m_f^2)_{i-1} - (m_f^2)_{i-2}] \div 2$ to UA
	1254	FMP	39 2072 1255	$\times[(m_f)_{i-1} + (m_f)_i]$ in UA
	1255	FAD	32 0600 1256	$+[(m_f)_{i-1} (m_f)_i][(m_f)_{i-1} - (m_f)_{i-2}]$ in UA
	1256	FAD	32 2552 1257	$+[(m_f^3)_{i-1} - (m_f^3)_{i-2}] \div 3$ in UA
	1257	FDV	34 2652 1258	$\div[(m_f)_{i-2} - (m_f)_i]$ in UA
	1258	FDV	34 2602 1259	$\div[(m_f)_{i-2} - (m_f)_{i-1}]$ in UA

Loop 2. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1258	- 1259	STU	21 3350 1224	$[1-2]_a$ to (1350+A)
	1224	NZA	40 1061 1110	Test A for zero (all Lagrange terms calculated), recycle

Loop 3. k-1 and h-1 Instructions Puts k-1 and h-1 in those instructions requiring it.

From	Loc.	Abbr.	Instruction	Operation
1224	- 1110	RAL	65 0046 1111	(k-1) to LA
	1111	RAA	80 0009 1112	No. of k-1 instructions minus 1 to A
(1115)	- 1112	LDD	69 2538 1113	Contents of (0538+A) to D
	1113	SDA	22 2538 1114	(k-1) to data address of (0538+A)
	1114	NZA	40 1115 1116	Test A for zero (all k-1 instructions modified)
	1115	SXA	51 0001 1112	(-1) in A
	1116	RAL	65 0047 1117	(h-1) to LA
	1117	RAA	80 0009 1118	No. of h-1 instructions minus 1 to A
(1121)	- 1118	LDD	69 2588 1119	Contents of (0588+A) to D
	1119	SDA	22 2588 1120	(h-1) to data address of (0588+A)
	1120	NZA	40 1121 0540	Test A for zero (all h-1 instructions modified)
	1121	SXA	51 0001 1118	(-1) in A

Loop 4. V/L Calculates V/L ratios for all plates.

From	Loc.	Abbr.	Instruction	Operation
1120	- 0540	RAA	80 (k-1) 1215	(k-1) to A

Loop 4. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
0540 -	1215	RAU	60 0048 1216	R to UA
(1218) -	1216	STU	21 2922 1217	R to (0922+A)
	1217	NZA	40 1218 0538	Test A for zero (all R stored)
	1218	SXA	51 0001 1216	(-1) in A
1217 -	0538	RAA	80 (n-1) 1122	(k-1) to A
(1126) -	1122	RAU	60 2522 1123	$(V_k)_i$ to UA
	1123	FDV	34 2572 1124	$\div(L_k)_i$ in UA
	1124	STU	21 2622 1125	$(V/L_k)_i$ to (0622+A)
	1125	NZA	40 1126 0588	Test A for zero (all $(V/L)_k$ calculated)
	1126	SXA	51 0001 1122	(-1) in A
1125 -	0588	RAA	80 (h-1) 1127	(h-1) to A
	1127	RAU	60 2672 1128	$(V_h)_i$ to UA
	1128	FDV	34 2722 1129	$\div(L_h)_i$ in UA
	1129	STU	21 2772 1130	$(V/L_h)_i$ to (0772+A)
	1130	NZA	40 1131 0539	Test A for zero (all $(V/L)_h$ calculated)
	1131	SXA	51 0001 1127	(-1) in A

Loop 5. K-Values Computes K-values.

From	Loc.	Abbr.	Instruction	Operation
1130 -	0539	RAC	88 (k-1) 0956	(k-1) to C
(1166) -	0956	RAB	82 (n-1) 1156	(n-1) to B
(1155) -	1156	RAU	60 0098 1157	1 or 0 to UA
	1157	NZU	44 1132 1180	If zero, take plates below feed If non-zero, take plates above feed

Loop 5. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1157 -	1132	RAU	60 4301 1133	E_i to UA
	1133	FMP	39 6822 1134	x T_k in UA
	1134	FAD	32 4251 1135	+ D_i in UA
	1135	FMP	39 6822 1136	x T_k in UA
	1136	FAD	32 4201 1137	+ C_i in UA
	1137	FMP	39 6822 1138	x T_k in UA
	1138	FAD	32 4151 1139	+ B_i in UA
	1139	FMP	39 6822 1140	x T_k in UA
	1140	FAD	32 4101 1141	+ A_i in UA
	1141	STU	21 4051 1142	log K_i to (0051+B)
	1142	LDD	69 1143 1506	Enter log deck; exit to 1143
Log Deck -	1143	STU	21 4051 1144	K_i to (0051+B)
	1144	RAU	60 0098 1145	1 or 0 to UA
	1145	NZU	44 1146 1158	For zero, calculate stripping factor, Loop 7 For non-zero, calculate absorption factor, Loop 6

Loop 6. Absorption Factor Calculates absorption factor for all components on all plates above the feed.

From	Loc.	Abbr.	Instruction	Operation
1145 -	1146	RAU	60 0091 1147	1 to UA
	1147	FDV	34 6622 1148	÷ $(V/L)_i$ in UA

Loop 6. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1147	- 1148	FDV	34 4051 1149	÷ K_i in UA
	1149	STU	21 0600 1150	$(L/KV)_i$ to 0600
	1150	RAU	60 4922 1151	$\sum_{0}^{i-1}$ L/KV to UA
	1151	FAD	32 0091 1152	+ 1 in UA
	1152	FMP	39 0600 1153	x $(L/KV)_i$ in UA
	1153	STU	21 4922 1154	$\sum_{0}^{i}$ L/KV to (0922+B)
	1154	NZB	42 1155 1295	Test B for zero (A_k calculated for all components); to punch Loop 8
	1155	SXB	53 0001 1156	(-1) in B

Loop 7. Stripping Factors Calculates stripping factors for all components on all plates.

From	Loc.	Abbr.	Instruction	Operation
1170	- 0589	RAC	88 (h-1) 0958	(h-1) to C
	0958	RAB	82 (n-1) 1156	(n-1) to B; to Loop 5

This instruction was changed in Loop 5

1157	- 1180	AXC	58 0050 1132	+ 50 in C
Loop 5	- 1158	RAU	60 6772 1159	$(V/L)_i$ to UA

Loop 7. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1158 -	1159	FMP	39 4051 1160	x K_i in UA
	1160	STU	21 0600 1161	$(KV/L)_i$ to 0600
	1161	RAU	60 4972 1162	$\sum_{0}^{i-1}$ K/VL to UA
	1162	FAD	32 0091 1163	+ 1 in UA
	1163	FMP	39 0600 1164	x $(KV/L)_i$ in UA
	1164	STU	21 4972 1154	$\sum_{0}^{i}$ KV/L to (0972+B)
	1154	NZB	42 1155 1295	Test B for zero (S_h calculated for all components)
	1155	SXB	53 0001 1156	(-1) in B; recycle

Loop 8. Absorption and Stripping Factor Punch Punches K vs. m_f; changes program to do stripping factors.

From	Loc.	Abbr.	Instruction	Operation
1154 -	1295	RAU	60 8007 1296	C to UA
	1296	STU	21 0243 1207	C to 0243
	1207	LDD	69 0045 1208	(n-1) to D
	1208	STD	24 1894 1209	D to 1894
	1209	RAL	65 1210 1211	Contents of 1210 to LA
	1210		00 0100 0100	
	1211	LDD	69 1297 1950	Punch K and m_f for all components; exit to 1297
	1297	LDD	69 0243 1298	Contents of 0243 to D

Loop 8. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1297 -	1298	RAC	88 8001 1165	D to C
	1165	NZC	48 1166 1167	Test C for zero (All plates done)
	1166	SXC	59 0001 0956	(-1) in C; recycle to Loop 5
	1167	RAU	60 0098 1168	1 or 0 to UA
	1168	NZU	44 1169 0957	For zero (All stripping factors done), calculate d/f For non-zero, do stripping factors, Loop 7
	1169	RAU	60 0000 1170	0 to UA
	1170	STU	21 0098 0589	0 to 0098

Loop 9. d/f Calculate d/f for each component.

From	Loc.	Abbr.	Instruction	Operation
1168 -	0957	RAA	80 (n-1) 1171	(n-1) to A
(1179) -	1171	RAU	60 2972 1172	$(v_h/b)_i$ to UA
	1172	FAD	32 2922 1173	$+(l_k/d)_i$ in UA
	1173	FAD	32 0091 1174	+ 1 in UA
	1174	STU	21 2901 1175	$(v_h/b) + l_k/d + 1)_i$ to (0901+A)
	1175	RAU	60 2972 0293	$(v_h/b)_i$ to UA
	0293	FAD	32 3375 1176	$+(v_f/f)_i$ in UA
	1176	FDV	34 2901 1177	$\div(v_h/b + l_k/d + 1)_i$ in UA
	1177	STU	21 2901 1178	$(d/f)_i$ to (0901+A)
	1178	NZA	40 1179 0959	Test A for zero (All d/f calculated)
	1179	SXA	51 0001 1171	(-1) in UA

Loop 10. D/F and B/F Calculate D/F and B/F, punch D/F and B/F.

From	Loc.	Abbr.	Instruction	Operation
1178 -	0959	RAA	80 (n-1) 1189	(n-1) to A
(1201) -	1189	SXA	51 0002 1190	(-2) in A
	1190	RAU	60 2422 1191	$[1-3]_c$ to UA
	1191	FMP	39 2903 1192	$x(d/f)_i$ in UA
	1192	STU	21 0600 1193	$(d/f)_i\ [1-3]_c$ to 0600
	1193	RAU	60 2372 1194	$[1-3]_b$ to UA
	1194	FMP	39 2902 1195	$x(d/f)_{i-1}$ in UA
	1195	FAD	32 0600 1196	$+(d/f)_i\ [1-3]_c$ in UA
	1196	STU	21 0600 1197	$(d/f)_{i-1}\ [1-3]_b + (d/f)_i\ [1-3]_c$ to 0600
	1197	RAU	60 2322 1198	$[1-3]_a$ to UA
	1198	FMP	39 2901 1199	$x(d/f)_{i-2}$ in UA
	1199	FAD	32 0600 1200	$+(d/f)_{i-1}\ [1-3]_b + (d/f)_i\ [1-3]_c$ in UA
	1200	STU	21 2472 1201	$\int_{i-2}^{i} d/f\ dm_f$ to (0472+A)
	1201	NZA	40 1189 0960	Test A for zero (All $\int_{i-2}^{i} d/f\ dm_f$ calculated)
	0960	RAA	80 (n-1) 1202	(n-1) to A
	1202	RAU	60 0000 1203	0 to UA
(1205) -	1203	SXA	51 0002 1204	(-2) in A
	1204	FAD	32 2472 1205	$+\int_{0}^{i-2} d/f\ dm_f$
	1205	NZA	40 1203 1206	Test A for zero (All $\int_{i-2}^{i} d/f\ dm_f$ summed)

Loop 10. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1205	- 1206	STU	21 0491 1212	$\int_o^1 d/f\ dm_f$ (=D/F) to 0491
	1212	RAU	60 0091 1213	1 to UA
	1213	FSB	33 0491 1214	-D/F in UA
	1214	STU	21 0492 1219	B/F to 0492
	1219	LDD	69 0141 1220	2 to D
	1220	STD	24 1894 1221	D to 1894
	1221	RAL	65 1222 1223	Contents of 1222 to LA
	1222		00 3004 9100	
	1223	LDD	69 0961 1950	Punch D/F, B/F, exit to 0961

Loop 11. Product TBP curves Calculates and punches $\dfrac{\int_o^{m_f} d/f\ dm_f}{D/F}$ and $\dfrac{\int_o^{m_f} b/f\ dm_f}{B/F}$

From	Loc.	Abbr.	Instruction	Operation
1223	- 0961	RAA	80 (n-1) 1225	(n-1) to A
(1268)	- 1225	SXA	51 0002 1227	(-2) in A
	1227	RAU	60 2901 1228	$(d/f)_{i-2}$ to UA
	1228	FMP	39 3350 1229	$x[1-2]_a$ in UA
	1229	STU	21 0600 1260	$(d/f)_{i-2}\ [1-2]_a$ to 0600
	1260	RAU	60 2902 1261	$(d/f)_{i-1}$ to UA
	1261	FMP	39 3325 1262	$x[1-2]_b$ in UA
	1262	FAD	32 0600 1263	$+(d/f)_{i-2}\ [1-2]_a$ in UA
	1263	STU	21 0600 1264	$(d/f)_{i-1}\ [1-2]_b + (d/f)_{i-2}\ [1-2]_a$ to 0600
	1264	RAU	60 3300 1265	$[1-2]_c$ to UA

Loop 11. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1264 -	1265	FMP	39 2903 1266	$x(d/f)_i$ in UA
	1266	FAD	32 0600 1267	$+(d/f)_{i-2}\,[1-2]_a + (d/f)_{i-1}\,[1-2]_b$ in UA
	1267	STU	21 2471 1268	$\int_{i-2}^{i-1}$ d/f dm_f to (0471+A)
	1268	NXA	40 1225 0962	Test A for zero (All $\int_{i-2}^{i-1}$ calculated)
	0962	RAA	80 (n-1) 1226	(n-1) to A
	1226	RAU	60 0000 1270	0 to UA
	1270	STU	60 0470 1279	0 to 0470
	1279	RAB	82 0000 1269	0 to B
(1278) -	1269	SXA	51 0002 1271	(-2) in A
	1271	RAU	60 4470 1272	$\int_{o}^{i-2}$ d/f dm_f to UA
	1272	FAD	32 4471 1273	$\int_{i-2}^{i-1}$ d/f in UA
	1273	STU	21 4471 1274	$\int_{o}^{i-1}$ d/f to (0471+B)
	1274	RAU	60 4470 1275	$\int_{o}^{i-2}$ d/f to UA
	1275	FAD	32 4472 1276	$+\int_{i-2}^{i}$ d/f in UA
	1276	STU	21 4472 1277	$\int_{o}^{i}$ d/f to (0472+B)
	1277	NZA	40 1278 0963	Test A for zero (All $\int_{o}^{i}$ d/f calculated)

Loop 11. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1277 -	1278	AXB	52 0002 1269	(+2) in B
1277 -	0963	RAA	80 (n-1) 1280	(n-1) to A
(1288) -	1280	RAU	60 2470 1281	$(\int d/f)_i$ to UA
	1281	FDV	34 0491 1282	÷ D/F
	1282	STU	21 2351 1283	$(\int d/f)_i/(D/F)$ to (0351+A)
	1283	RAU	60 2001 1284	$(m_f)_i$ to UA
	1284	FSB	33 2470 1285	$-(\int d/f)_i$
	1285	FDV	34 0492 1286	÷ B/F
	1286	STU	21 2401 1287	$(\int b/f)_i/(B/F)$ to (0401+A)
	1287	NZA	40 1288 0964	Test A for zero (All terms calculated)
	1288	SXA	51 0001 1280	(-1) in A
1287 -	0964	RAA	80 (n-1) 1299	(n-1) to A
(0292) -	1299	RAU	60 2901 0290	$(\int d/f)_i$ to UA
	0290	STU	21 2451 0291	$(\int d/f)_i$ to (0451+A)
	0291	NZA	40 0292 1289	Test A for zero (All $\int d/f$ stored)
	0292	SXA	51 0001 1299	(-1) in A
0291 -	1289	LDD	69 0045 1290	(n-1) to D
	1290	STD	24 1894 1291	D to 1894
	1291	RAL	65 1292 1293	Contents of 1292 to LA
	1292		01 0003 5100	

Loop 11. (Cont.)

From	Loc.	Abbr.	Instruction	Operation
1291	- 1293	LDD	69 0294 1950	Punch $\frac{\int d/f}{D/F}$, $\frac{\int b/f}{B/F}$; Exit to 0294

Loop 12. Punch d/f

From	Loc.	Abbr.	Instruction	Operation
1293	- 0294	LDD	69 0045 0295	(n-1) to D
	0295	STD	24 1894 0296	(n-1) to 1894
	0296	RAL	65 0297 0298	Contents of 0297 to LA
	0297		01 3009 0100	
	0298	LDD	69 1901 1950	Punch d/f; Stop

Instructions written into program

These are instructions which are written into the program and modified at the start of the program.

Loc.	Abbr.	Instruction	
0950	RAA	80 0000 1006	n-1
0951	RAA	80 0000 1015	
0952	RAA	80 0000 1022	
0953	RAA	80 0000 1033	
0954	RAA	80 0000 1044	
0955	RAA	80 0000 1061	
0956	RAB	82 0000 1156	
0957	RAA	80 0000 1171	
0958	RAB	82 0000 1180	
0959	RAA	80 0000 1189	
0960	RAA	80 0000 1202	
0961	RAA	80 0000 1225	
0962	RAA	80 0000 1226	
0963	RAA	80 0000 1280	
0964	RAA	80 0000 1299	
0538	RAA	80 0000 1122	k-1
0539	RAC	88 0000 0956	
0540	RAA	80 0000 1215	
0588	RAA	80 0000 1127	h-1
0589	RAC	88 0000 0958	

Constants written into the program

Loc.	Constants
0091	10 0000 0051
0092	20 0000 0051
0093	30 0000 0051
0094	40 0000 0051
0095	50 0000 0051
0096	75 0000 0051
0097	10 0000 0048
0098	00 0000 0001
0141	00 0002 0000

These constants are in floating point notation except for 0141.

Card Format for Fractional Distillation Program

Input Cards

Input data may be inserted in any order, since locations are specified. All values are in floating decimal point except "n-1" in location 0045, "k-1" in location 0046, and "h-1" in location 0047.

Output Cards

Cards 1 - n (There are k groups of these, one for each plate above the feed, followed by h more groups, one for each plate below the feed)

Word 1 m_f

Word 2 K calculated at the tray temperature

Card 30

Word 1 D/F

Card 31

Word 1 B/F

Card 100 - (n+99)

Word 1 $\dfrac{\int_o^{m_f} d/f \; dm_f}{D/F}$

Word 2 $\dfrac{\int_o^{m_f} b/f \; dm_f}{B/F}$

Card 130 - (n+129)

Word 1 d/f

APPENDIX C

EXPERIMENTAL AND CALCULATED DATA

APPENDIX C

TABLE OF NOMENCLATURE

A = Constant in equation 9

A = Absorption factor

ASTM = American Society for Testing Materials

b = Mole fraction of the bottoms

B = Constant in equation 9

B = Bottoms stream

C = Constant in equation 9

d = Density

d = Mole fraction in the distillate

dT/dm_f = Slope of the molar TBP curve

D = Constant in equation 9

D = Distillate stream

E = Constant in equation 9

EFV = Equilibrium Flash Vaporization

f = Mole fraction in the feed

F = Feed stream

G = Gallons

h = Height

K = Phase distribution ratio

K_f = Cryoscopic constant

l = Mole fraction of the liquid

L = Liquid

m = Molarity, moles per 1000 grams solvent

m = Moles

mv = Millivolt

MW = Molecular weight

S = Stripping factor

T = Absolute temperature

TBP = True boiling point

ΔT_f = Freezing point depression, °C

$\Delta T/\Delta m$ = Slope of the molar TBP curve by difference

v = Mole fraction of the vapor

V = Vapor

ρ = Specific gravity

<u>Subscripts</u>

b = Solvent

BP = Bubble point

DP = Dew point

f = Feed

h = Plates below the feed zone

i = Any component

k = Plates above the feed zone

l = Liquid

s = Solute

v = Vapor

VITA

Charles Blakey Woodward

Candidate for the Degree of

Master of Science

Thesis: PHASE DISTRIBUTION RATIOS FOR INTEGRAL TECHNIQUE PETROLEUM DISTILLATION CALCULATIONS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Horse Cave, Kentucky, November 11, 1935, the son of Leonard R. and Elizabeth B. Woodward.

Education: Attended grade school in Louisville, Kentucky, and Drumright, Oklahoma; graduated from Drumright High School in 1953; received the Bachelor of Science degree from the Oklahoma State University, with a major in Chemical Engineering, in May 1957; completed requirements for the Master of Science degree in August, 1962.

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