VAPOR-LIQUID K-VALUES FOR APPLICATION OF THE INTEGRAL TECHNIQUE TO PETROLEUM VAPORIZATION CALCULATIONS

By

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PREFACE

With the advance of technology in today's petroleum industry, greater accuracy and reliability are needed in methods for predicting heavy hydrocarbon vapor-liquid phenomena. Equilibrium vapor-liquid distribution ratios, or K-values as they are frequently called, are used in the petroleum industry for making distillation design calculations. This thesis is concerned with improving our knowledge of the vaporization phenomena of petroleum fractions.

I am indebted to all of my fellow graduate students who offered advice and assistance whenever needed. I also wish to thank Dr. A. Amir-Yeganeh and Mr. C. B. Woodward who preceded me and Mr. R. M. Walston who worked with me, for the unselfish sharing of their knowledge and experience.

I owe special thanks to Professor R. N. Maddox for his encouragement throughout my graduate study and to my adviser, Professor Wayne C. Edmister, for his many helpful suggestions and comments without which this work could not have been accomplished. I also wish to express my thanks to Esso Research and Engineering Company for their grant which made this work possible. Thanks should also be given the Continental Oil Company for their help in the development of the molecular weight device, and to the Humble Oil and Refining Company for the oils with which this work was accomplished.

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CHAPTER I

INTRODUCTION

A knowledge of vapor-liquid equilibrium is of great importance to the petroleum industry today. In almost every branch of the industry, accurate vaporization data and calculational methods are needed. Numerical data and the theoretical methods for applying them are most convenient for use on modern high speed computers.

When numbers are to be used to explain physical phenomena, such as flash vaporization of petroleum, some type of physical or mathematical model must be used. There are three main methods or models used today in vaporization calculations, viz., the method of hypothetical (discrete) components, the differential or slope method, and the integral technique wherein the mixture is treated as a continua mixture of an infinite number of infinitesimally small components. The integral method was used in this study because of its closer similarity to the actual physical process of vaporization. It is believed, that with the physical conditions more closely represented in this manner, the vapor-liquid relationships that follow will be of greater utility to the petroleum industry than empirical relationships between the slopes and intercepts of the flash vaporization and analytical assay curves.

One of the first persons to describe hydrocarbons as a continua mixture was Harbert (8). His proposed method was rather complex and awkward to use. Later Edmister (3, 6) refined these calculations into the present integral method which lends itself more easily to computations. In this integral procedure, the K-values of small cuts or hypothetical components and the molar true boiling point assay of the oil must be known.

The main objectives of this study were the calculation of equilibrium ratios and the determination of a rapid and economical procedure for evaluating these ratios.

To fulfill these objectives, several programs were written for the IBM 1620 and IBM 650 digital computers to accomplish the numerous calculations. These include: (1) a program to convert the volumetric true boiling point distillations (TBP's) to molar ones with the aid of the average molecular weights of the fractions or small cuts as determined in the laboratory; (2) a program to calculate the ideal K-values from the imperfection pressure correction and vapor and system pressure; and (3) a program using the integral technique to calculate the equilibrium vapor-liquid ratio, vapor and liquid TBP's, and the activity coefficient correction to the ideal K-values that will give K-values that reproduce the experimental flash vaporization.

Analytical distillations were performed on petroleum fractions with an Oldershaw column to obtain the necessary physical properties for characterizing the oils as functions of normal boiling point. While determining these physical properties, certain deficiencies were noticed in the technique used by previous investigators for obtaining molecular weights. Included in this investigation is the development of a method for determining molecular weights by using vapor density measurements.

In this work, oils provided by Humble Oil and Refining Company were distilled and samples collected to obtain the molar true boiling point assay and the physical properties of the small cuts. Molar true boiling point curves with their respective sample physical properties were also obtained from work by Amir-Yeganeh (1). The hypothetical component vapor-liquid distribution ratios were derived from the petroleum fractions analysed during this study and that of Amir-Yeganeh. The symbol K_{Actual} is used for these ratios.

The vapor-liquid equilibrium K-values for ideal mixtures, i.e., obeying Amagat's Law of Additive Volumes in both coexisting phases, are called K_{Ideal}. K_{Ideal} was taken as the first approimation of the actual vapor-liquid distribution ratios and was calculated from the vapor and system pressures and imperfection pressure correction factors of each small cut or hypothetical component.

These ideal K-values were then used with the integral technique to calculate the liquid-vapor ratio and the true boiling point assays of the equilibrium vapor and liquid products. The calculated liquid-vapor ratios were checked against the experimental ratios obtained for the same oil. If the check was poor, the values were modified by a constant multiplier (liquid activity coefficient) for all hypothetical (infinitesimal)components of a particular petroleum fraction to obtain a check between calculated and experimental V/L within ±0.001. This was done by iterations of the integral vaporization calculations, using different values of the activity coefficient.

Values of K_{Actual} were found in this manner from ideal K-values and experimental data obtained in the laboratory portion of this investigation.

In the integral method of equilibrium vaporization calculations for petroleum, the oil fractions are considered continua mixtures, each hydrocarbon component being present in a infinitesimal amount. In other words, the hydrocarbon components appear as points on the TBP plots rather than as plateaus as in the case for discrete mixtures. The same equilibrium flash vaporization relationships apply in both cases and are based on the K-value definition and the component material balances. With the hydrocarbon components represented as continuous point functions instead of discrete parts, the molar equation, $l/f = 1/(1 + KV/L)$, may be integrated, rather than summed, as $L/F = {}_0^1(l/f)dmf$, where L = bulk equilibrium liquid, F = bulk feed, l = component in equilibrium liquid, f = component in feed, and m_f = mole fraction off.

CHAPTER II

EXPERIMENTAL EQUIPMENT AND PROCEDURES

In applying the integral technique to petroleum vapor-liquid equilibrium calculations, it is necessary to have the true boiling point assay of the petroleum fraction and the K-values of its hypothetical components of very small cuts. In order to characterize these oils for this calculational procedure, the following equipment was used: (1) an equilibrium flash vaporization still of the flow type, (2) a 30-plate Oldershaw sieve-tray column, (3) a gas chromatograph, (4) a molecular weight determining device, and (5) a gravitometer.

Equilibrium Flow Still

Previous work at Oklahoma State University had been conducted with two different equilibrium flow stills and one batch equilibrium still (1, 20). These studies showed that equilibrium products of binary and multicomponent mixtures could be obtained with all equilibrium stills tested. After a study of the advantages and disadvantages of the respective stills, it was decided that the flow still "B" (Figure 1) should be used. Its advantages were: (1) short residence times were possible, while taking samples for assays, (2) products in sufficient quantity for analysis could be obtained without blending products from several

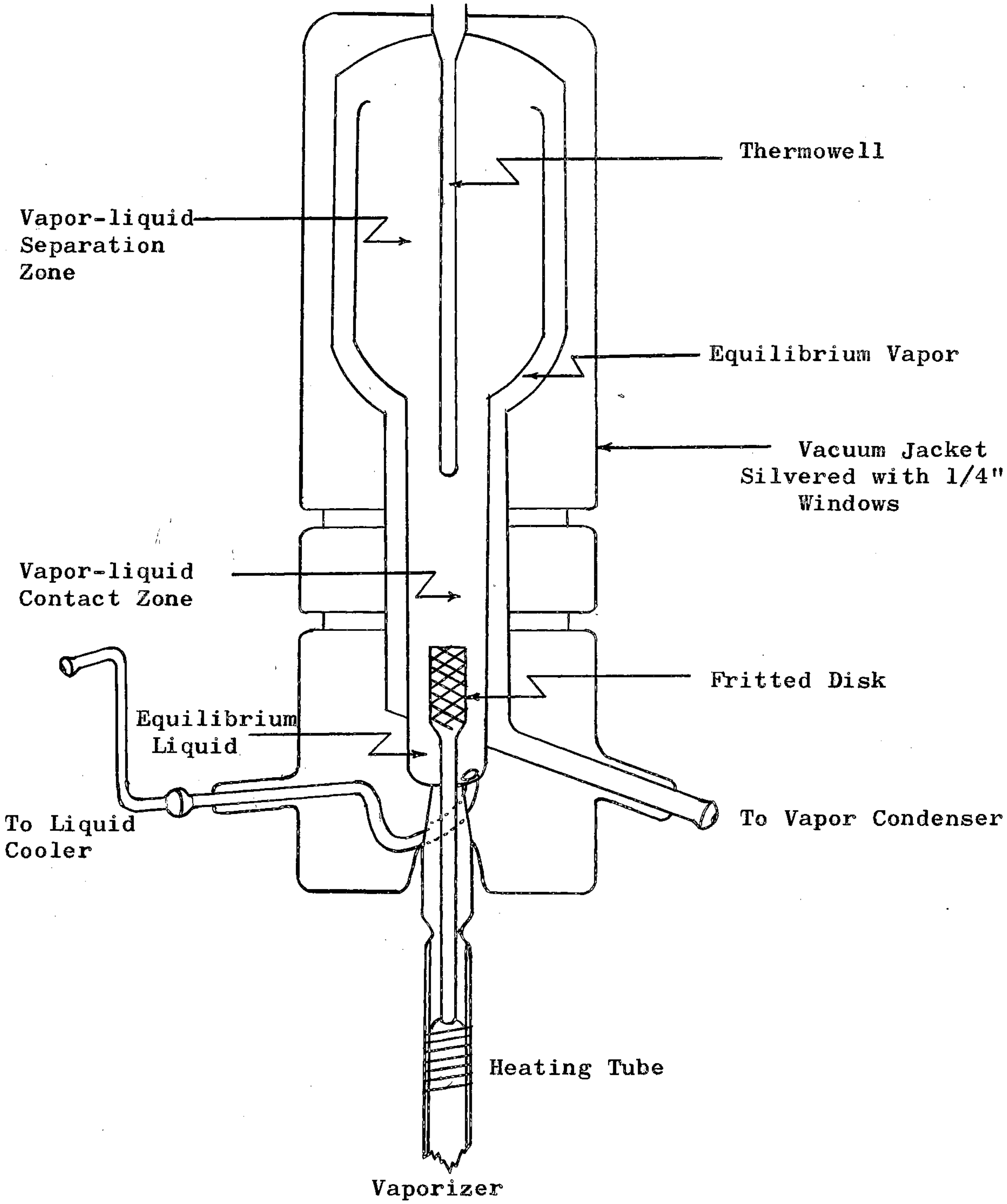

Figure 1. Equilibrium Flow Still "B"

flashes, as was the case in the circulating equilibrium (Othmer type) still, (3) the temperature and pressure could be easily modified when changing the flash conditions.

The flow still had only two apparent disadvantages: (1) during start-up, the flow had to be checked constantly to avoid the possibility of very low flow rates with high heat inputs since there was a possibility of burning out the heating coils if the feed flow and heat input were not balanced properly, and (2) slight cracking of high boiling heavy hydrocarbons made it necessary to clean the fritted disk after completing four or five flashes.

To obtain equilibrium products from still "B", the petroleum fraction flowed to the still from a constant head tank. This tank was constantly filled by a small gear pump at a rate higher than that flowing to the still, with the excess fluid overflowing to a reserve drum (Figure 2). The hydrocarbons flowing into the still were regulated by a Teflon needle valve and metered by a small rotameter.

The feedstock was preheated to temperature by the heating tube prior to entering the still. This tube, located directly below the equilibrium chamber, was heated by a closely wound resistance wire and controlled by a standard 110 volt Variac. The heating tube contained a solid glass rod in the middle of the orifice to accelerate flow through the heated area and to provide greater contact with the outside heated surface. The feedstock, partially vaporized in the heated area, then entered the equilibrium chamber through a fritted disk. The fritted

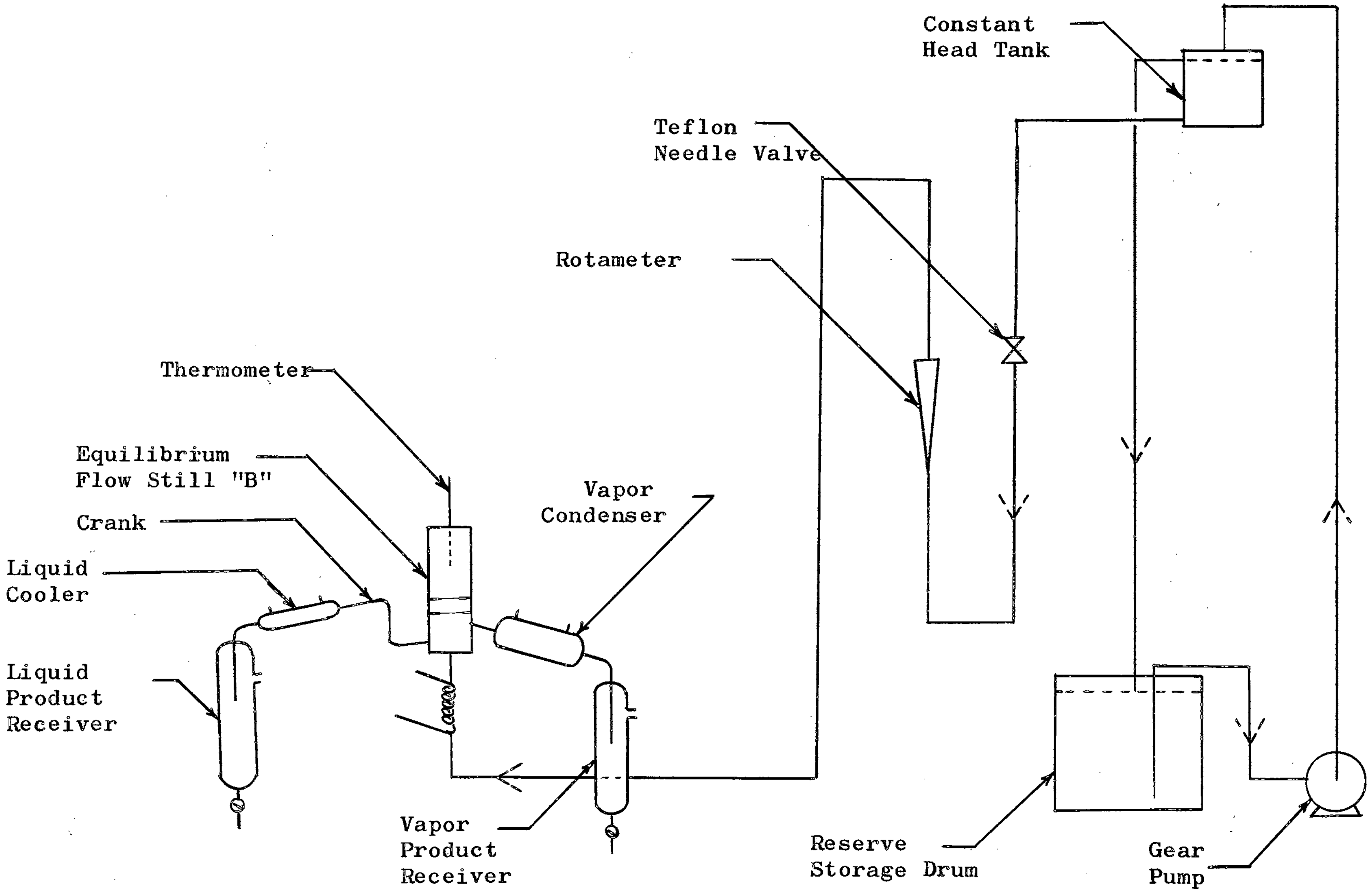

Figure 2. Schematic Flow Diagram of Equilibrium Still "B"

disk was located below the level of the liquid product line, and thus the partially vaporized feedstock bubbled through the equilibrium liquid. The liquid level could be raised or lowered in the still by a "crank" on the liquid product line which was used to change the contacting volume. Both liquid and vapor products from the still passed through water-cooled condensers before entering the receivers. All joints were clamped together so that moderate pressures as well as vacuum could be used. The equilibrium temperature was measured through a thermowell mounted in the top of the still with a high-temperature thermometer.

Most of the equilibrium flashes were conducted at 760 millimeters of mercury, requiring 5 to 30 millimeters of mercury back pressure. The still pressure was controlled in the following manner. The air pressure was reduced from its source pressure of 100 psig to 20 psig by a diaphragm control valve before the air entered the surge tank, drier, and still. A water-filled differential manometer was connected to the surge tank for measuring the pressure. The final pressure was controlled by allowing part of the air to escape through a tube submerged in water.

From the known barometric pressure, the necessary still back pressure could be calculated in inches of water. The tube was then submerged in water to the depth required to produce this back pressure and the resulting pressure drop was shown on the manometer.

The following procedure was used to make the experimental equilibrium flashes. The amount of hydrocarbon sample needed for the flash depended on the vapor-liquid ratio desired. A one to one liquid-vapor split required the minimum feed charge of two liters plus the amount desired for analytical distillations. For vapor-liquid ratios greater or less than unity, larger size charge samples are required. At vapor-liquid ratios other than unity, the smallest product controls the sample requirement.

The sample was placed in the reserve drum and the pump suction and constant head overflow lines connected. Readings on the barometer were made, the back pressure calculated, and the air turned on. The gear pump was started, and as soon as the overflow from the constant head tank could be seen, flow through the still was initiated. This flow should be slightly greater than that desired for the flash, for as soon as the entering fluid starts vaporizing in the heated zone the oil flow slackens. The Variac was turned on and adjusted for the desired flash temperature.

Samples of the equilibrium vapor and liquid products were taken at intervals and the temperatures recorded. These samples were analysed for steady-state by using either the chromatograph or the molecular weight determining device.

When samples were analysed with the chromatograph as a test for steady-state, the important recording chart responses or peaks were the initial and final ones. The initial peaks showed changes occurring in the low boiling components while the final peaks indicated changes in the higher boiling components.

The molecular weight determining device was also used to determine if equilibrium had been reached. In this case, the samples were checked for changes in vapor pressure by reading the micromanometer pressure dial.

When changes in sample properties, as shown by one of the two methods above, and the temperature changes were small in three consecutive samplings, equilibrium conditions were assumed to exist and the products were collected. Care was taken throughout the run not to remove all the sample from the receivers if more product than the receiver capacity was desired. This was done to prevent loss of back pressure through the receiver drain cock. If pressure was lost, the equilibrium conditions would be upset.

Oldershaw Column

The apparatus used in making analytical distillations of the oils was an Oldershaw sieve-plate fractionator (Figure 3) composed of two sections, one having twenty plates and the other having ten, and operating at a pressure of 760 millimeters of mercury. For heavier petroleum fractions (boiling above 500°F), the same column was used with an operating pressure of 100 millimeters of mercury. The product was taken off through a vapor dividing head with a built-in thermowell for measuring the column temperature by a calibrated chromel-copnic thermocouple. A Dewar flask containing an ice-water mixture was used as a cold junction reference for the thermocouple measurement.

Four water condensers are used in this apparatus. The first is the reflux condenser located at the top of the stacked column, the second is on the product line and located as close as possible to the vapor dividing head, and the third and fourth contain the

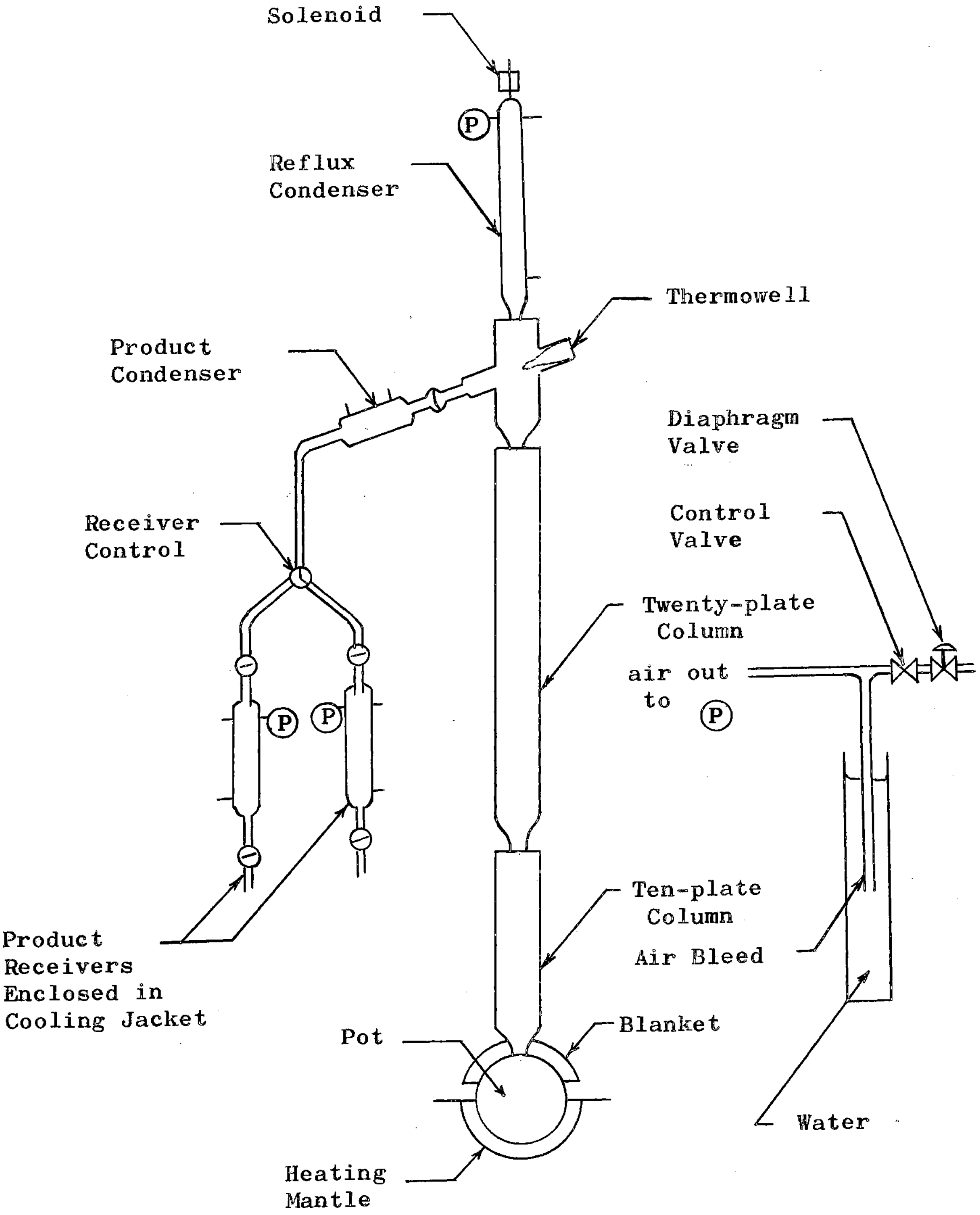

Figure 3. Oldershaw Column

two collecting receivers. Two receivers are used so that the column pressure will not be upset when samples are removed during the run.

The one-liter distillation pot was heated with an electric heating mantle on the bottom and an electric heating blanket on the top. Each heating element was controlled with a separate Variac so that the mantle and blanket could be kept at different temperatures, as required.

The reflux was controlled by a solenoid operated by a Flexopulse. When the solenoid was activated, a metal-topped plunger was raised allowing the vapor to escape to the product receivers. In a closed or down position, the column operated at total reflux. The reflux rate was set on the Flexopulse by setting the on-off cycle of the timing arm. The samples were run in this study at 10/1 reflux. This was accomplished by setting the Flexopulse at a cycle of twenty seconds off and two seconds on.

The column was always operated at a pressure of 760 millimeters of mercury when the feedstock was a lighter petroleum fraction. This was done so that reproducibility from day to day could be achieved, and so that the hypothetical components boiled off at their normal boiling points. The pressure in the still was maintained in the same manner as that in the previously-mentioned equilibrium still. When a heavier hydrocarbon fraction (one boiling above 500°F) was distilled, a pressure of 100 millimeters of mercury was used.

This lower pressure was obtained with the use of a vacuum pump and controlled at the set point of 100 millimeters of mercury by a Cartesian manostat. The pressure was measured with a mercury differential manometer connected to the surge tank. Using the above equipment and pressure controlling methods, the error between two runs on the same stock was never greater than 1°F and usually averaged less than 0.5°F.

Previous work in this laboratory was conducted on both an Oldershaw sieve-plate column and a Sarnia packed column (1, 20). The Sarnia still had the advantage of smaller feed stock requirements and thus shorter operating time. One of the disadvantages was the tendency to flood when too much heat was accidentally applied. Although longer operating times were required, the Oldershaw column did not flood quite as readily and gave very good reproducibility between runs. For this reason, it was used in this work.

The first step in the analytical distillation was the weighing of the sample of 800 milliliters or larger. The sample was weighed so that a material balance could be made at the termination of the run in order to determine the column loss. If the loss was excessive, the run was discarded. The joints were then greased in such a manner that liquid flow through the column and the receivers would not carry an excessive amount of the silicone stopcock grease. If silicone was allowed to permeate the various parts of the column, especially the distillation pot, foaming handicapped operation of the column. The column sections, vapor head, thermocouple, and receiver connections were then put together, and the back pressure or vacuum applied as before.

Two different procedures were used in these analytical distillations. The first two runs with each oil stock were for the purpose of producing small cuts for determination of density and molecular weight as a function of normal boiling point. In these runs, cuts or samples of 16 milliliters size were taken for the first and last ten volume per cent off, and 40 milliliter cuts elsewhere. On the other runs with the same stock, but at different equilibrium conditions, the volumes and temperatures were recorded, but cuts were not taken. At the conclusion of the run, all of the samples and bottoms (residues) were weighed and the losses determined. The bottoms were further distilled and split into samples using an A.S.T.M. - D 86 with the standard procedure. These samples and residues were then weighed and the total losses calculated. All runs having less than 2 per cent loss were considered satisfactory and accepted.

The samples were then ready for specific gravity and molecular weight determinations.

Molecular Weight Determinations

To obtain the average molecular weight of petroleum fractions, a vapor density technique was used in which an accurately known size of liquid sample was introduced into the apparatus through a mercury orifice and allowed to vaporize into a previously evacuated chamber. Molecular weights were computed from the pressure change and the apparatus calibration constant.

In the low pressure and higher temperature conditions of the apparatus, the sample vaporizes and expands as a perfect gas.

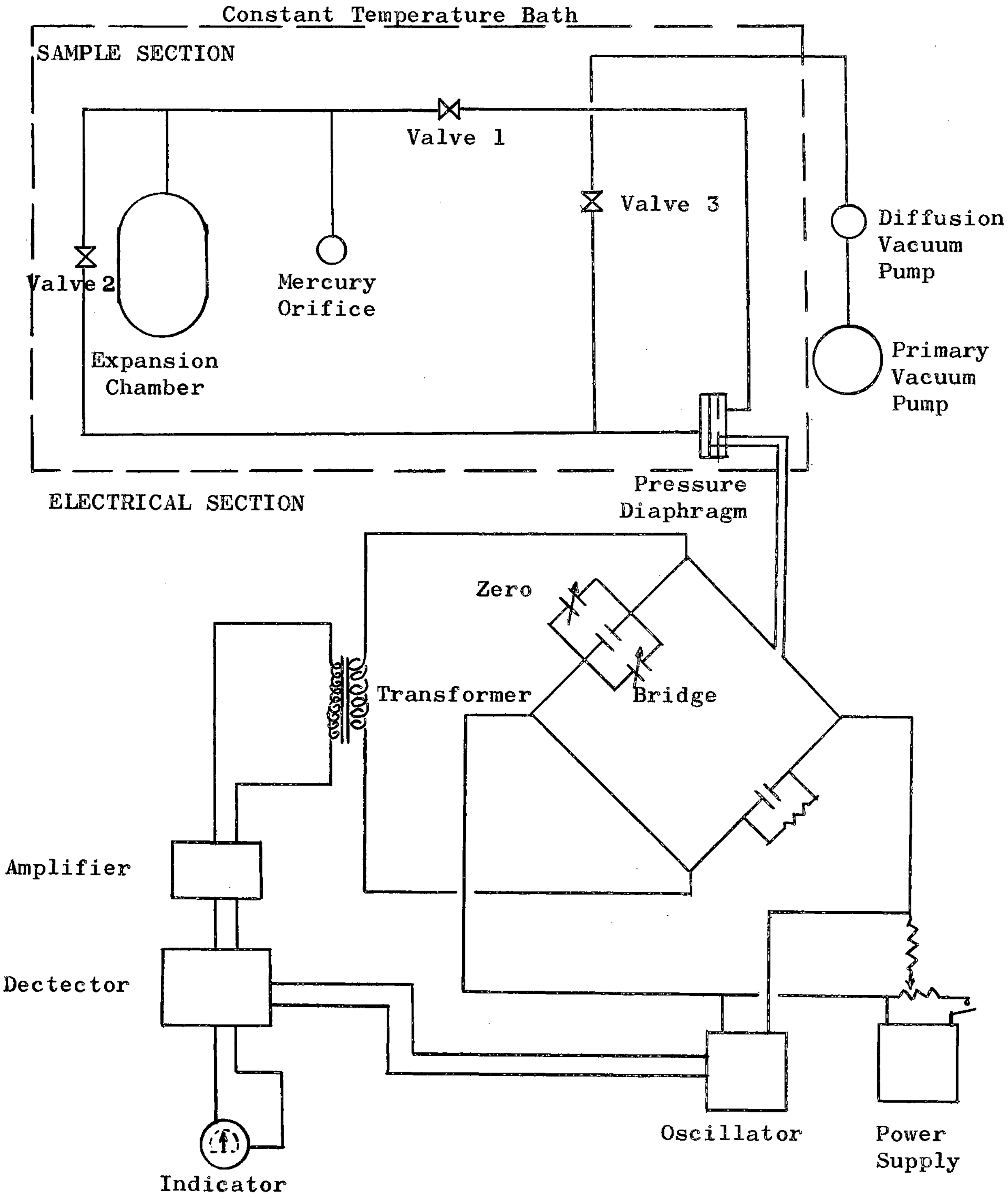

Figure 4. Schematic Diagram of Molecular Weight Device

This expansion of vapor through the system caused a pressure increase on one side of the micromanometer diaphragm which was measured with a capacitance bridge. From the sample size and pressure increase, the molecular weight could be calculated by the following method.

The entire system, with the exclusion of the micromanometer electrical section (Figure 4), was enclosed in a constant temperature air bath and under high vacuum (approximately 10^{-7} mm Hg). At these conditions, it was assumed that the vapor would obey the Perfect Gas Law, PV = nRT. The temperature, T, and the volume, V, are conditions controlled by the equipment while pressure, P, is the force exerted on the micromanometer diaphragm by the expanding vapor.

The pressure, as measured by the micromanometer is related to the apparatus by the equation $P = D^2/k$, where P is the pressure in microns, D is the pressure dial reading, and k is the gage constant. The Perfect Gas Law (or Boyle's Law at constant temperature) may be put in a more convenient form for this purpose, as follows:

$$n = \frac{v\rho}{Mw}$$

Where: v = sample liquid volume

ρ = sample liquid density

Mw = sample molecular weight

Now:

$$PV = RT\left[\frac{v\rho}{Mw}\right]$$

$$P = D^2/k$$

or in terms of molecular weight

$$Mw = \frac{RTv\rho}{PV} = \frac{RkTv\rho}{D^2V}$$

But R, V, k, and all conversion units are constant and may be combined into a single constant, C.

Then:

$$C = \frac{(R)(k)(\text{conversion units})}{V}$$

Therefore:

$$Mw = C\left[\frac{v\rho T}{D^2}\right]$$

The molecular weight was then determined knowing the following:

1. T, the bath temperature, °R.
2. ρ, the sample liquid density, g/cc.
3. v, the sample liquid volume, ml.
4. D, the pressure dial reading.
5. C, the equipment constant, (approximately 0.252×10^8 at T = 658°R)

The constant, C, in this study used the following units and their respective conversion factors to make the equation consistent in units.

P - pressure in microns.

T - temperature in °R.

R - the international gas constant.

V - the equipment volume in ml.

n - the number of gram moles of sample.

k - gage constant as given by the micromanometer manufacturer (1928.6)

The constant, C, may be determined by introducing known pure components and mixtures into the system and backing out the value, or by using the individual constants k (given by the manufacturer), R, V, and unit conversion constants. The first method gave the best results, for the value of C deviates slightly from time to time due to changes in room temperature. It was found that greater accuracy resulted when a pure component was run as the first sample, and the equipment constant determined from its pressure increase.

The apparatus is contained as a compact unit in a cabinet that was 22 inches wide, 27 inches high, and 15 inches deep. The micromanometer is contained in the lower third of the unit with openings on the sides and back to assure adequate ventilation. If ventilation is not provided, the electrical characteristics of the apparatus could change due to the resulting heat, and invalidate the molecular weights obtained.

The upper two thirds of the apparatus was the constant temperature air bath constructed of one-half inch Transite. Four strip heaters were used to heat the bath. Two of these were the source of constant heat, while the remaining two were connected to the temperature-controlling probe. Separate Variacs supplied the voltage to the constant and controlled heaters so that the temperatures could be varied as desired. A heavy duty blower with a four-inch "squirrel cage" was mounted in one end of the bath to circulate the heated air. Enclosed in the bath were the pressure reading diaphragm, expansion chamber, and control valves as shown in Figure 4.

Located outside the bath was the mercury orifice (Figure 5).

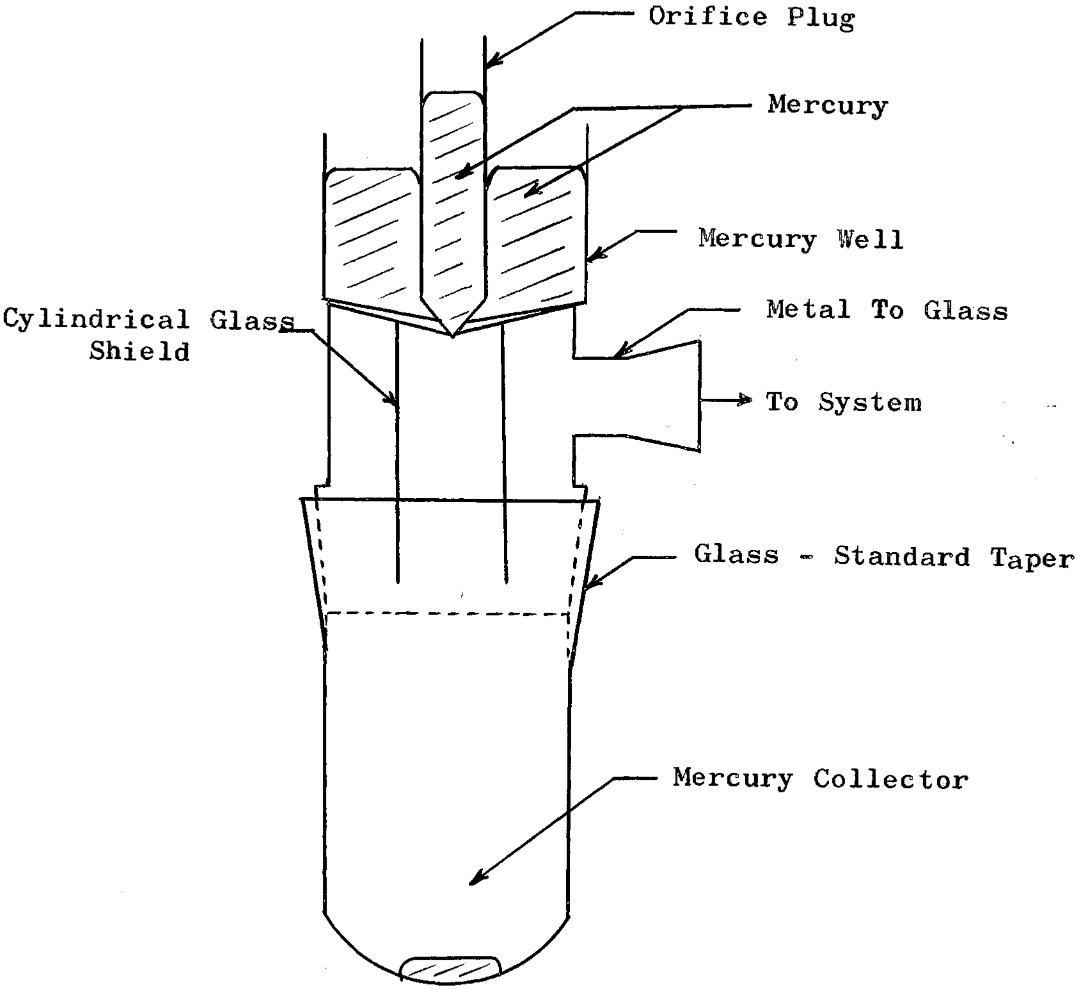

Figure 5. Mercury Orifice

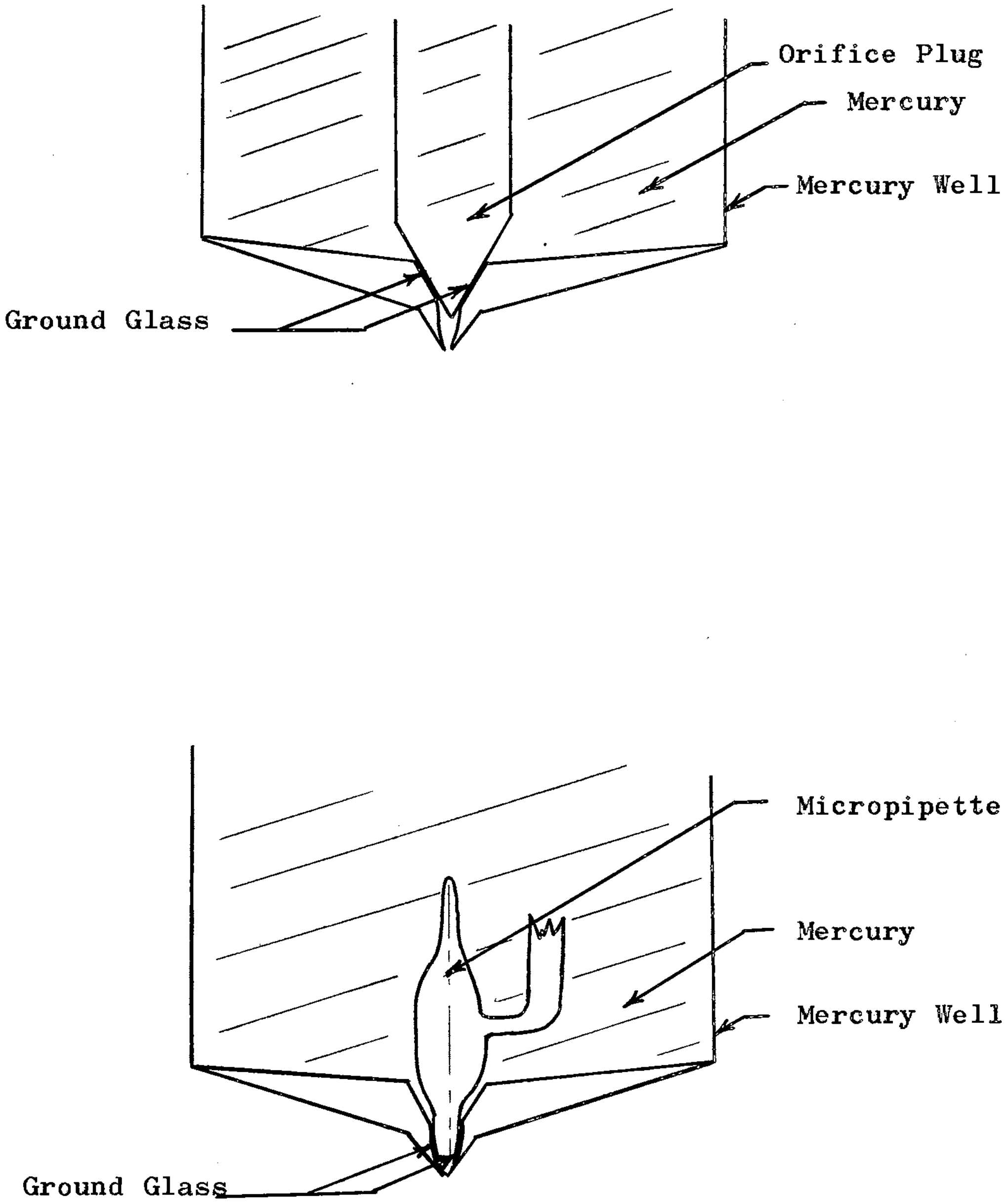

Figure 6. Magnified Mercury Orifice with Ground Glass Sections

The orifice was constructed of 1.5 inch glass tubing with a removable bottom. The injection hole in the orifice should be small enough so that mercury will not pass through the opening when no vacuum is present, but should permit a steady stream of mercury to pass when the protecting plug is removed and the system is under high vacuum.

The orifice should be ground in two places (as shown in Figure 6) to prevent the loss of mercury to the collecting trap at the bottom. The ground sections should match the plug and micropipettes, respectively.

Samples were prepared in the following manner for induction into the system. The system was first heated to the desired operating temperature. This was done slowly to insure even heating of the stainless-steel diaphragm. After the system was degassed and the temperature had reached steady-state (approximately eight hours), the system was ready for use. The auxiliary vacuum pump, for cleaning the micropipettes, was turned on.

The micropipettes were cleaned in a three-step process. The auxiliary vacuum pump was attached to the upper end of the micropipette by a rubber tube. The lower tip of the pipette was then emersed in dilute nitric acid, water, and finally acetone and the solutions sucked through. The pipette was dipped in the sample and filled by capillary action. The mercury level in the orifice was checked to verify that it was high enough to cover the micropipettes when they were inserted into the orifice. The valve to the vacuum pump (valve 2) was closed and the bridge zeroed.

The pipette was then placed in the orifice for approximately three to five seconds to allow all of the sample to enter the system. The balance voltage was then turned on and the pressure balanced. The voltage should not be increased greater than necessary to equalize the pressure. If the voltage is too high there is danger of shorting the diaphragm against the casing. The pressure dial should be read as soon as the sample pressure appears stationary on the pressure indicating meter. If the pressure does not remain stationary when no sample is in the apparatus, there may be a leak or the instrument temperature may not be in steady-state and should be left to reach this condition. A cause of drift after sample induction could be for the same reasons as above, or because the previous sample had not been completely evacuated from the system. Drift is also encountered when running samples of high molecular weights.

There are two main limitations in this method of determining molecular weights, the first being the range of molecular weights that may be determined, and the second the type of components that may not be used with this system.

The molecular weights, for best results, should be less than 150 atomic mass units (amu) but may be higher if the temperature of the bath is increased and the orifice heated. If the molecular weights are higher than 200 amu, an osmometer is recommended.

To date only one type of component has been determined as unsatisfactory for use in this system. This component type is C_6 unsaturated multiples. These particular component types exhibited a lower vapor pressure than necessary for the calculation of physical molecular weights. However, if these multiples constitute a small percentage of the mixture, the error is correspondingly reduced.

If the apparatus is to be used to determine molecular weights greater than 150 amu, the mercury in the orifice should be replaced with gallium and an orifice heater installed. By heating the orifice, the amount of heavy component remaining in the orifice trap would be reduced and the sample more evenly distributed throughout the system. These changes would cause the micromanometer to indicate a higher vapor pressure and result in the calculation of a more accurate molecular weight.

Other Analytical Equipment

Also necessary for the calculation of K-values is the specific gravity of the hydrocarbon fractions. These gravities were taken with a Fisher-Davidson gravitometer. There are several other more common methods of determining specific gravities, but because of the small sample size and desire to incorporate a rapid analytical procedure with the K-value calculations method, this instrument was used.

Work is also being conducted on the chromatograph which will increase the number of analytical distillations that may be accomplished in a given length of time. At present, an analytical distillation on the Oldershaw column requires approximately eight hours to complete. The method now under study would require as little time as three to fifteen minutes.

With the ability to complete analytical distllations in such a short time, at least five times the amount of data could be obtained, with a proportional increase in the number of K-values obtained. This would also be of assistance in on-line operations where it is desirable to have the analytical results as soon as possible so that stream conditions may be changed if necessary.

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results of this investigation are: (1) flash vaporization data on several oils, (2) distillation assays on the feeds and products of the flashes, (3) specific gravities and (4) molecular weights of the feeds and the equilibrium vapors and liquids from flashing.

Equilibrium Flash Vaporizations

A flow type equilibrium flash vaporization still, designed by Amir-Yeganeh, was used to obtain the vapor-liquid distribution data for this investigation. The equilibrium properties, as shown in Tables XVIII through XXII in Appendix D, were determined for five side-streams of the No. 5 Pipe Still at the Humble Baytown refinery and were used in the calculation of vapor-liquid K-values.

The vapor-liquid product ratios obtained from the experimental equilibrium flash vaporization determinations were reproducible to ± 2 per cent.

Other equilibrium flash data used in the calculation of K-values were obtained from Amir-Yeganeh (1).

Volumetric True Boiling Point Distillations

All volumetric true boiling point assays (TBP's) obtained during this study were conducted at 760 or 100 millimeters of mercury depending on the boiling range of the petroleum fraction. If the boiling range was greater than 500°F or included this temperature, the distillation pressure was reduced to 100 millimeters of mercury. The feed to this pipe still and the atmospheric tower bottoms were of too heavy material to be analysed by the present equipment and technique.

The only pipe still side stream analysed completely on the Oldershaw column was that of light crude naphtha (Figure 7). This petroleum fraction and the liquid products from three of its equilibrium flash vaporizations were analysed for physical properties and the true boiling point curves were constructed. These distillation curves were used as a check for the newer and faster technique of chromatographic distillation (18).

The other side streams were analysed on the Oldershaw column to obtain the physical properties of small cuts as a function of normal boiling point for use in converting the chromatographic distillation curves and the Oldershaw assays to molar ones.

The Oldershaw true boiling point assays conducted at 100 millimeters of mercury were converted to a basis of 760 millimeters of mercury by converting the experimental temperatures at 100 mm Hg to equivalent values at 760 mm Hg. This temperature conversion was made with the aid of a vapor pressure chart (3). With the temperatures converted, these low pressure distillations

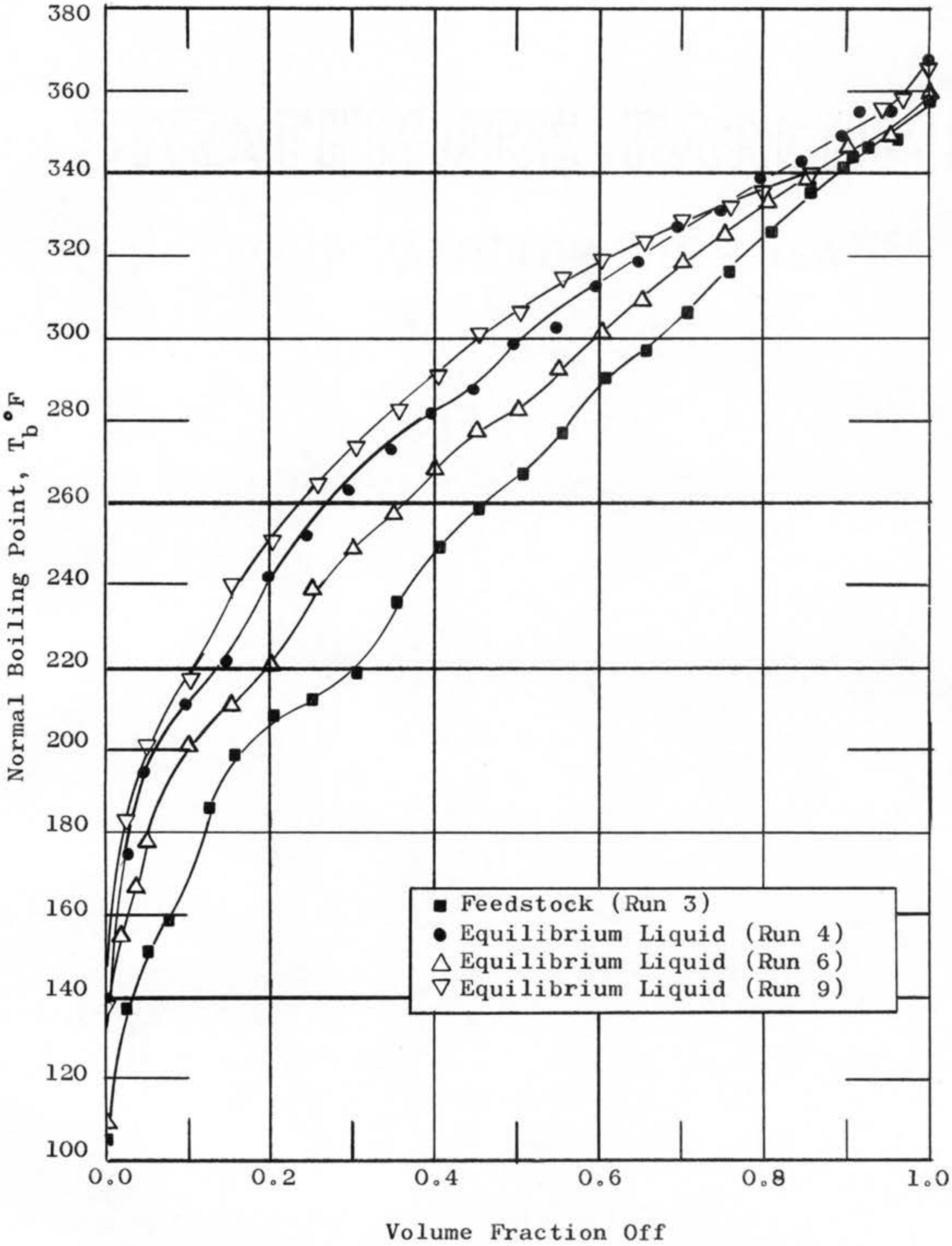

Figure 7. Volumetric True Boiling Point Curves of Light Crude Naphtha and Equilibrium Liquids

were treated in the same manner as those assayed at 760 millimeters of mercury.

Other oils and their respective TBP's studied in this work were those obtained from the thesis of Amir-Yeganeh (1) which were distilled at barometric pressures varying from 730 to 750 millimeters of mercury.

The reproducibility obtained with the Oldershaw column was very good. The TBP curves could be reproduced within ± 1°F even when distillations were run on different days.

Specific Gravities

The densities obtained in this study were determined with a Fisher-Davidson gravitometer, which had a sensitivity of ±0.005 grams per cubic centimeter when tested with 95 mole per cent pure hydrocarbons. The reproducibility between analyses of the same component was ±0.001g/cc.

The specific gravities of small cuts taken during the true boiling point distillations, when taken as a function of the normal boiling point of the oil, were not steadily increasing values but followed the path shown in Figure 8. The frequency of oscillation was not consistent from oil to oil, and was probably a function of the oil constituents and their chemical groupings.

The specific gravities obtained from Amir-Yeganeh (1) on different petroleum fractions had the same tendencies toward oscillation when plotted against boiling point. Amir-Yeganeh's densities were determined with the use of a Westphal balance.

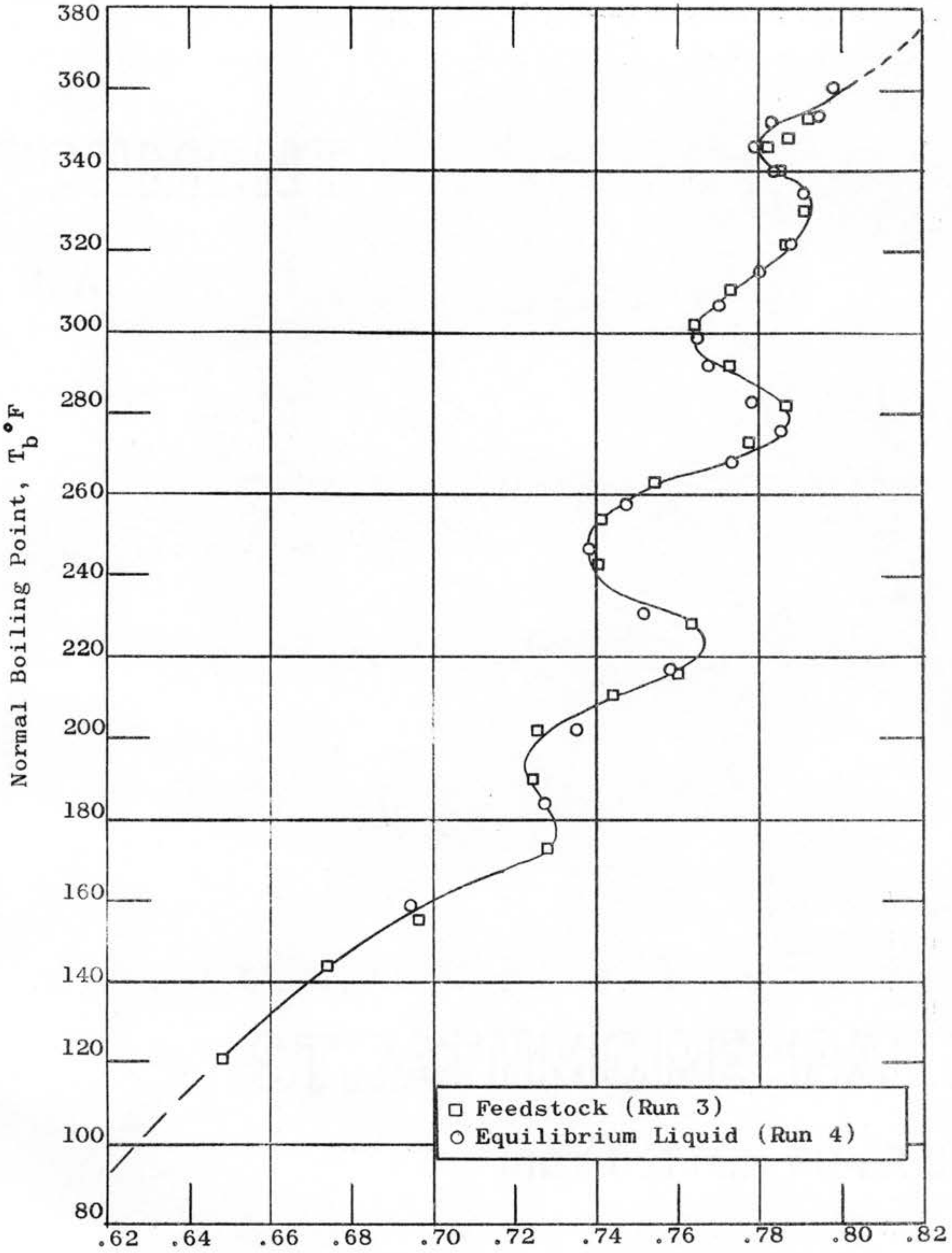

Figure 8. Specific Gravity Versus Normal Boiling Point for Light Crude Naphtha

Molecular Weights

The molecular weight device was checked for reproducibility and accuracy by using both 95 mole per cent pure hydrocarbons and known mixtures of these. The reproducibility of the molecular weights, whether determined on the same day or on a previous one, was within 0.3 per cent. The error between the vapor density calculated molecular weights and the physical molecular weights averaged 4 per cent. It is believed that, if samples of higher purity (greater than 95%) were used, the error could be reduced to ± 2 per cent or less. For the pure hydrocarbons and mixtures shown in Table I, the standard estimate of error was 3.5.

The molecular weights of the samples obtained from the volumetric TBP's were determined by the same methods as above, and that discussed in Chapter II. Figure 9 shows the sample molecular weights as a function of the normal boiling point.

The average molecular weights of the petroleum fractions obtained by Amir-Yeganeh were determined by the slower, less accurate cryoscopic method (1, 20). The molar TBP's calculated by Amir-Yeganeh were, therefore, based on cryoscopic molecular weights rather than vapor density molecular weights.

Molar True Boiling Point Plots

For use in making the integral method of flash vaporization calculations, the experimental volumetric TBP's must be converted to a molar basis. Edmister (6) presented a graphical method for approximating this when actual molecular weights and specific

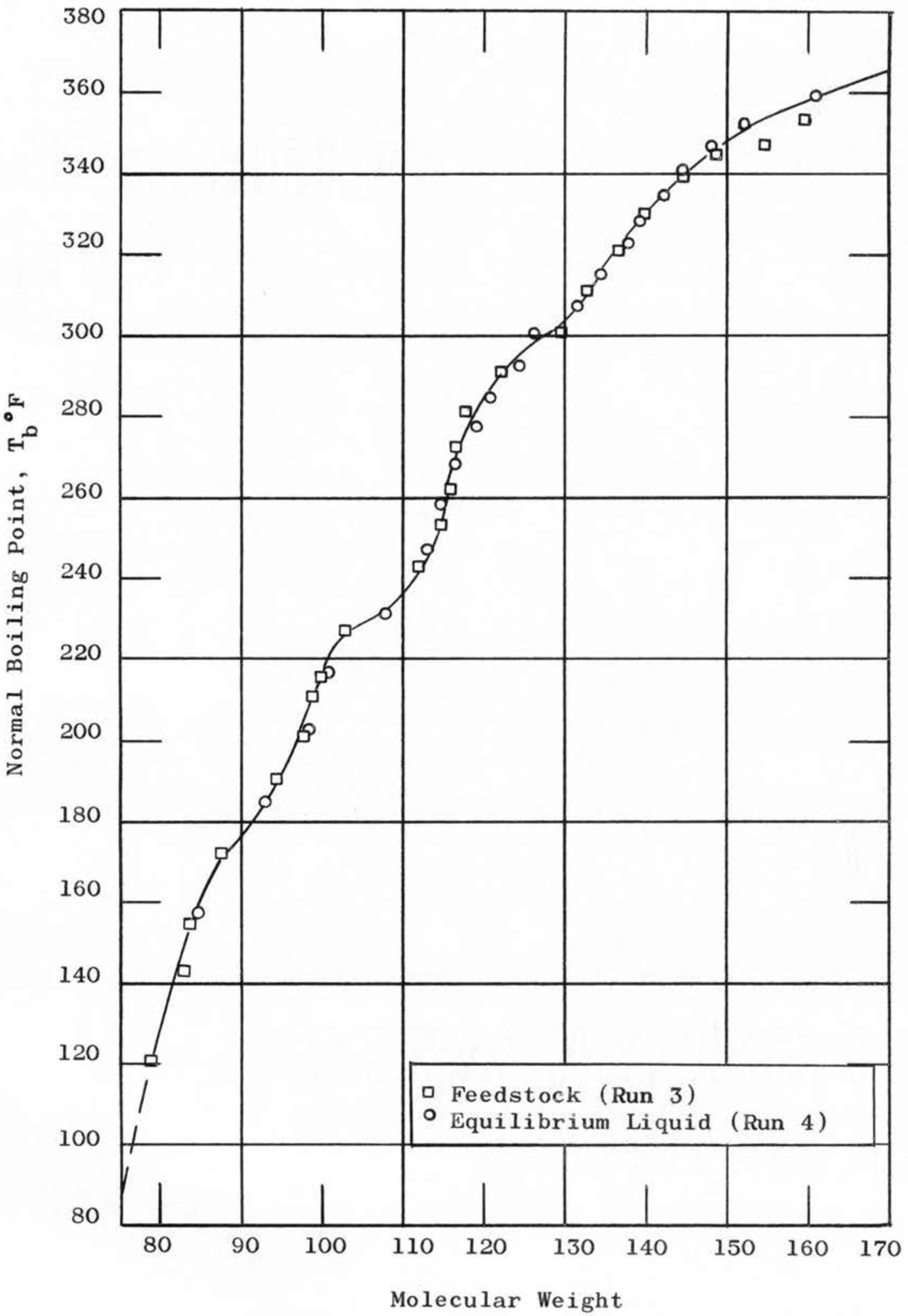

Figure 9. Molecular Weight Versus Normal Boiling Point

1 of 2

TABLE I

Hydrocarbon Molecular Weights Comparing Those Obtained from Vapor Density with Those Known from Atomic Mass

Component or Mixture	Molecular Weight		
	known*	determined[+]	error
Cyclohexene	82.14	84.42	-2.28
Hexene-1	84.16	90.01	-5.85
n-Hexane	86.17	83.50	2.67
Methylcyclohexane	98.18	102.40	-4.22
3-Methylhexane	100.20	100.91	-0.71
2,4 - Dimethylpentane	100.20	101.21	-1.01
n-Heptane	100.20	100.20	0.00
2,3-Dimethylpentane	100.20	100.90	-0.70
Methylcyclohexane n-Octane 2,2,4-Trimethylpentane	104.70	101.75	2.95
n-Heptane n-Octane	105.20	102.67	2.53
Cyclohexene 2,3-Dimethylpentane	106.60	108.64	-2.04
n-Decane n-Heptane n-Hexane	111.00	107.36	3.64
n-Octane	114.23	113.32	0.91
2,2,4-Trimethylpentane	114.23	111.59	2.64
2,3,4-Trimethylpentane	114.23	108.96	5.27

* Handbook of Chemistry and Physics, 37th Edition.

[+] Calculated using vapor density method as described in Chapter II of this thesis.

2 of 2

Table I (continued)

Component or Mixture	Molecular Weight		
	known*	determined$^+$	error
n-Nonane	128.25	127.49	0.76
n-Tridecane n-Nonane n-Undecane	128.60	132.29	-3.69
n-Dodecane 2,2,4-Trimethylpentane	132.80	139.37	-6.57
n-Decane	142.28	136.58	5.70

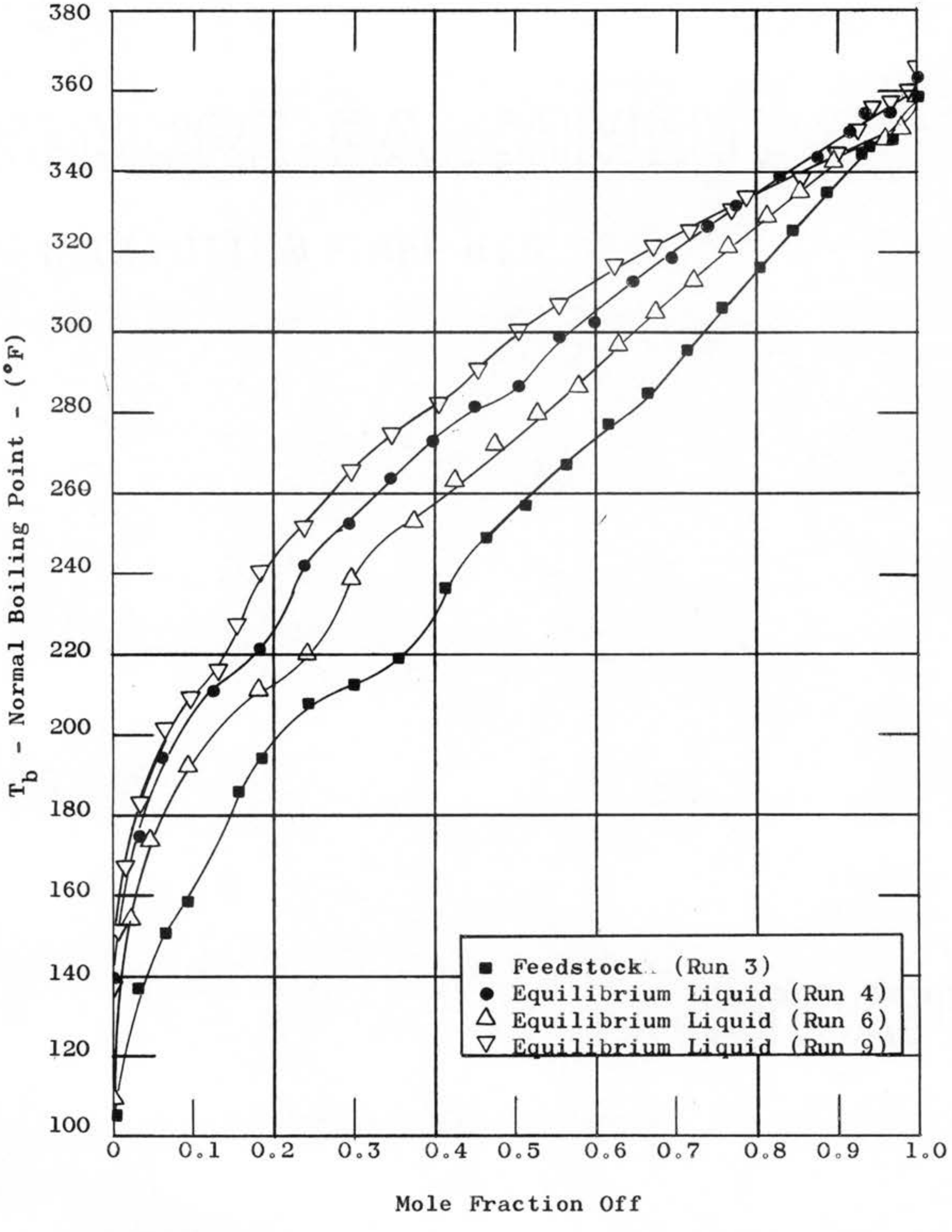

Figure 10. Molar True Boiling Point of Light Crude Naphtha and Equilibrium Liquids from Data Used in Figure 7

gravities were not available.

In this study, both molecular weights and specific gravities were determined experimentally by the aforementioned procedures. To obtain the molar TBP's (Figure 10) from the volumetric (Fig., 7), the volume fraction was multiplied by the ratio of density to molecular weight and normalized to a total of unity. Because of the small error incurred in the determination of specific gravity, the error in the molar TBP is approximately that of the molecular weight, or ± 4 per cent. The volume fraction off, mole fraction off, molecular weight, and specific gravity, may now be presented in the form of the tables in Appendix C.

Other molar TBP's used in the K-value correlation were from Amir-Yeganeh (1). These are defined as the following in this study:

TABLE II

Characteristics of Oils Obtained from Amir-Yeganeh (1)

Oil	Gravity °API	Molecular Weight	TBP Points (°F) 10	50	90	Run No.	Table Reference (1)
A	55	120	230	302	355	101-104	XIV
B	52.5	130	280	324	392	105-107	XVI
C	44.7	158	356	431.6	516.2	110-112	XXI

CHAPTER IV

EVALUATION OF VAPOR-LIQUID EQUILIBRIUM FUNCTIONS

The calculational results are: (1) vapor-liquid K-values for the hypothetical components of the oils and (2) the liquid activity coefficients for the petroleum fractions themselves.

Previously, K-values for use in the integral technique had been determined directly from the molar true boiling point assay by either the ratio of differences or the ratio of slopes method. The K-values determined by these methods were found to have a larger error than could be tolerated (20). In an effort to eliminate this error another method of calculation has been used here.

Liquid Activity Coefficient From Regular Solution Theory

Initially in this study, the K-values were calculated using the equation of Scatchard-Hildebrand for liquid activity coefficient and using these to estimate K's. These calculated K-values were then used in an iterative procedure, in which the activity coefficients were revised until the experimental flash vaporization results were approximated by the integral calculational technique. The iteration technique was that of modifying the K-values of all hypothetical components of a single equilibrium flash by a constant factor.

When this method of calculation was applied, it was noticed that the values of the liquid activity coefficient calculated by the Scatchard-Hildebrand equation, varied in a random manner (Table III) and were actually a minor correction when compared with that required to check the observed iteration. For this reason, the Scatchard-Hildebrand liquid activity coefficient was abandoned and a single overall correction was used with K_{Ideal} to generate the final K-values.

The calculation of K_{Ideal} is discussed in Appendix B.

TABLE III

Liquid Activity Coefficient as Calculated
by the Scatchard-Hildebrand Equation as a
Function of Normal Boiling Point

T_e = 286.0°F		T_e = 323.6°F		T_e = 258.2°F	
P_e = 760.0 mm Hg		P_e = 760.0 mm Hg		P_e = 760.0 mm Hg	
Oil A Run 101		Oil B Run 105		Light Crude Naphtha Run 34	
T_b, °F	γ	T_b, °F	γ	T_b, °F	γ
204.00	1.00310	140.00	1.03953	104.99	1.08342
222.00	1.06179	295.20	1.00998	180.00	1.00000
243.50	1.00073	325.80	1.00054	195.00	1.00100
287.59	1.00001	354.20	1.00004	240.00	1.00050
300.00	1.00008	392.00	1.00379	279.00	1.00923
352.40	1.00009	415.40	1.06583	310.00	1.00000
374.90	1.00059	527.00	1.00593	362.00	1.01980

Derived Liquid Activity Coefficients

The value of the overall liquid activity coefficient, γ, for a particular equilibrium flash was calculated from experimental data using computer programs 1 and 2 (Appendix B), where K_{Ideal} was the starting value of K.

When the flash vaporization calculations were completed, the calculated V/L ratio was tested against the experimental V/L for agreement within ±0.001. If the first comparison of V/L was within the test limits, the value of the liquid activity coefficient was 1.0. If the difference in ratios was not within these limits and the calculated V/L ratio was high or low, the correction was decreased or increased, respectively, and the calculations repeated with the newly corrected K-values. This was continued until the V/L agreement test was passed.

This same calculation method was used on petroleum fractions analysed with the gas chromatography by Walston (18). His values of the activity coefficient tended to be closer to one than those calculated in this work. At this time, the reason for the difference is not known. A comparison of Walston's (18) equilibrium functions with those determined in this study will be given in Appendix F.

A plot of the liquid activity coefficient (calculated from both assays) versus reciprocal equilibrium temperature is given in Figure 11.

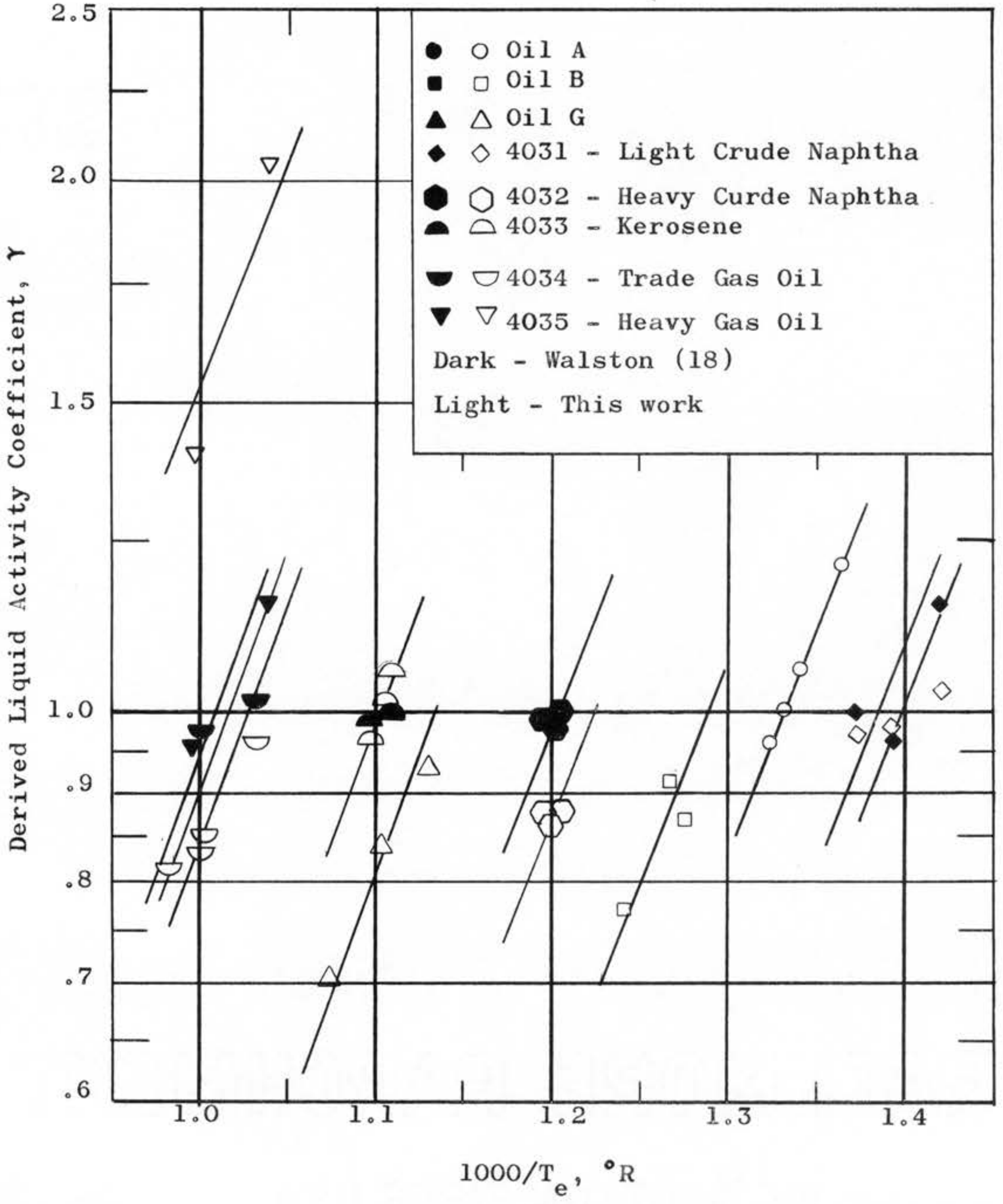

Figure 11. Log γ Versus Reciprocal Equilibrium Temperature

Comparison of Vapor-Liquid Distribution Ratios

Very few sources of K-values for narrow boiling range petroleum fractions are available in the literature, and most of these references are inadequate for the temperature range considered in this investigation.

The comparisons made in Table IV show the relation between K-values as determined by (1) the ratio of vapor pressure to system pressure, (2) the ratio of slopes method, and (3) the method proposed in this work.

Correlation of K-values

There are two principal methods of presenting the K-values as derived in Chapter IV. The first method is the direct correlation of the final K-values as functions of the normal boiling point and the equilibrium temperature, while the second method is a combination of the activity coefficient (derived by comparing calculated and experimental flashes) and calculated K_{Ideal}. Figure 12 shows the typical form of the values of K_{Ideal} and K_{Actual} (the final derived K-value) with the difference between the two represented by the activity coefficient.

The first method of presenting the data was chosen for this study because of discontinuities in the values of the activity coefficient.

K-values for each equilibrium flash vaporization on a single petroleum fraction were curve-fit as quadratic functions of log K versus reciprocal normal boiling point.

TABLE IV

1 of 4

K = y/x for Hypothetical Components
by Different Methods

Run 101
Oil A

$T_e = 286.0°F$

$P_e = 760.0$ mm Hg

°F Temp.	Raoult's Law K Values Ideal Solutions and Perfect Gases	K Value by Ratio of Slopes	K Value for Ideal Solutions	Derived K Values for Experimental Conditions
T_b	$K = \frac{p^\circ}{P}$	$K = \frac{dy}{dx}$	$K = \frac{p^\circ}{P}\left[\frac{1}{\theta}\right]$	$K = \frac{p^\circ}{P}\left[\frac{\gamma}{\theta}\right]$
204.0	3.286	2.71	3.035	3.232
222.0	2.553	2.16	2.404	2.561
243.5	1.877	1.78	1.806	1.923
257.9	1.520	1.46	1.483	1.579
272.3	1.226	1.20	1.212	1.291
287.6	.974	1.04	.976	1.039
300.2	.805	.84	.814	.867
311.0	.681	.66	.694	.739
323.6	.559	.56	.576	.613

TABLE IV (continued)

Run 101 (continued)

°F Temp. T_b	Raoult's Law K Values Ideal Solutions and Perfect Gases $K = \frac{p^\circ}{P}$	K Value by Ratio of Slopes $K = \frac{dy}{dx}$	K Value for Ideal Solutions $K = \frac{p^\circ}{P}\left[\frac{1}{\Theta}\right]$	Derived K Values for Experimental Conditions $K = \frac{p^\circ}{P}\left[\frac{\gamma}{\Theta}\right]$
352.4	.355	.42	.374	.399
360.5	.312	.38	.334	.352
374.9	.246	.31	.262	.280

Run 107

Oil B

$T_e = 346.0°F$

$P_e = 760.0$ mm Hg

140.0	14.232	---	11.190	8.712
261.5	3.207	4.66	2.956	2.301
278.2	2.558	3.02	2.401	1.869
304.7	1.796	2.40	1.953	1.520
316.4	1.528	1.86	1.731	1.347
325.8	1.340	1.22	1.316	1.025
335.3	1.174	1.06	1.163	.905
342.1	1.069	1.36	1.064	.829

TABLE IV (continued)

3 of 4

Run 107 (continued)

°F Temp.	Raoult's Law K Values Ideal Solutions and Perfect Gases	K Value by Ratio of Slopes	K Value for Ideal Solutions	Derived K Values for Experimental Conditions
T_b	$K = \frac{p^\circ}{P}$	$K = \frac{dy}{dx}$	$K = \frac{p^\circ}{P}\left[\frac{1}{\theta}\right]$	$K = \frac{p^\circ}{P}\left[\frac{\gamma}{\theta}\right]$
354.2	.899	.91	.905	.704
392.0	.519	.35	.538	.419
415.4	.367	.24	.387	.302
527.0	.065	---	.076	.059

Run 111

Oil G

$T_e = 446.0°F$

$P_e = 760.0$ mm Hg

239.0	11.890	---	9.391	7.907
331.7	4.195	---	3.727	3.138
356.0	3.139	3.94	2.874	2.420
381.2	2.314	3.52	2.175	1.831
398.3	1.870	1.64	1.790	1.507
417.2	1.479	1.16	1.439	1.212

TABLE IV (continued)

Run 111 (continued)

°F Temp.	Raoult's Law K Values Ideal Solutions and Perfect Gases	K Value by Ratio by Slopes	K Values for Ideal Solutions	Derived K Values for Experimental Conditions
T_b	$K = \frac{p^\circ}{P}$	$K = \frac{dy}{dx}$	$K = \frac{p^\circ}{P}\left[\frac{1}{\theta}\right]$	$K = \frac{p^\circ}{P}\left[\frac{\gamma}{\theta}\right]$
431.6	1.234	.97	1.216	1.024
450.5	.967	.65	.969	.816
473.9	.714	.38	.729	.614
509.0	.448	---	.470	.396
516.2	.407	---	.429	.362
525.2	.361	---	.383	.323
552.2	.250		.272	.229

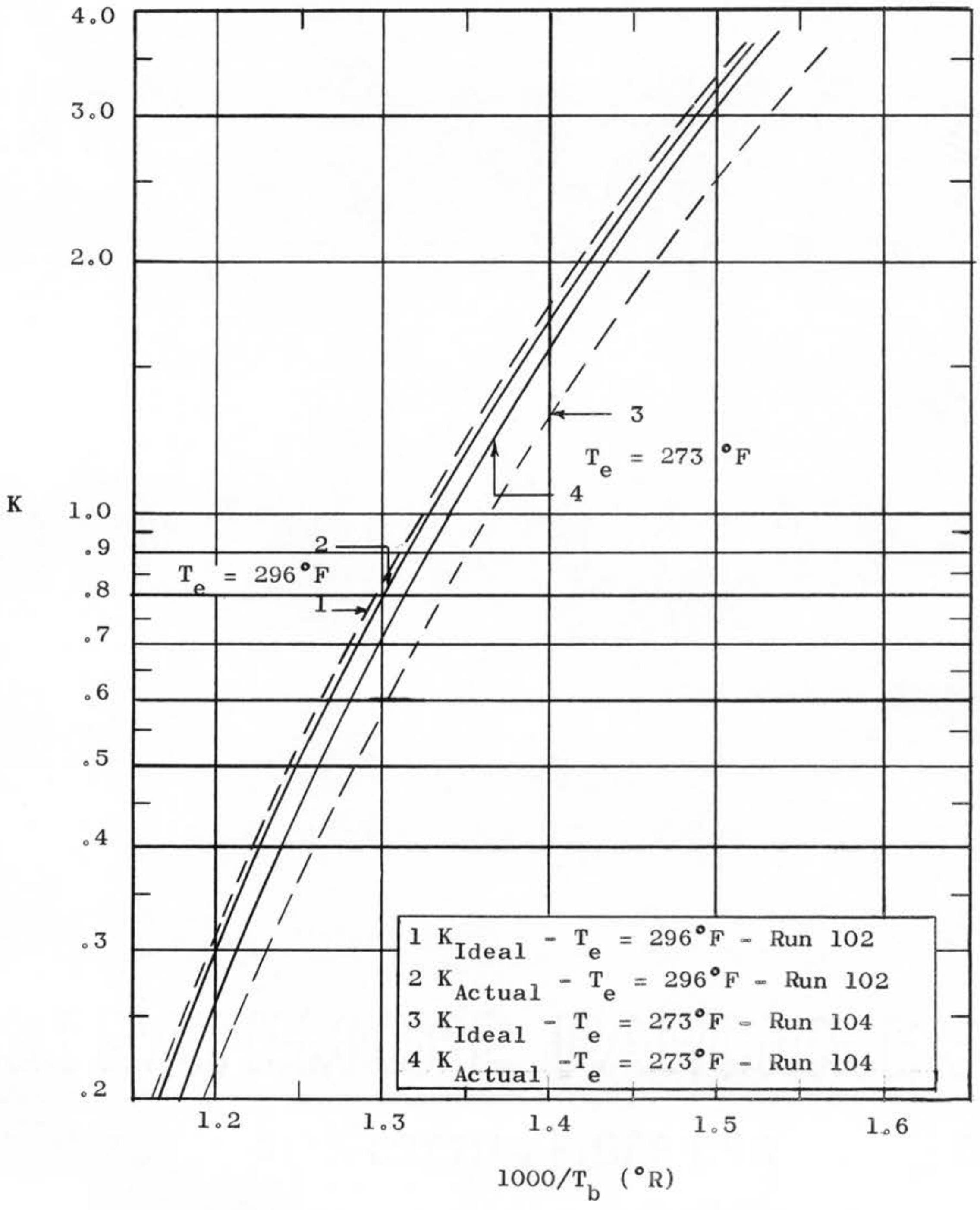

Figure 12. K_{Ideal} and K_{Actual} Versus Reciprocal Normal Boiling Point

$$\log K = A + B/T_b + C/T_b^2 \qquad \text{(IV-1)}$$

Where:

A, B, C, are constants for each equilibrium flash

T_b is the normal boiling temperature in °R

The average deviation between the derived K-values and those predicted from the curve-fit constants was 2 per cent or less. The curve-fit constants, shown in Table V as a function of equilibrium temperature for each oil studied, were then linearly correlated as a function of equilibrium temperature (Figures 13, 14, 15) with an average deviation from a linear relation of 1 per cent. The equations used for this correlation are as follows:

$$\begin{aligned} A &= A_1 + A_2\,(1000/T_e) \\ B &= B_1 + B_2\,(1000/T_e) \qquad \text{(IV-2)} \\ C &= C_1 + C_2\,(1000/T_e) \end{aligned}$$

Where:

A_1 and A_2, B_1 and B_2, and C_1 and C_2 are constants for each petroleum fraction.

T_e is the equilibrium temperature in °R.

Equations (IV-1) and (IV-2) may now be combined in the form:

$$\log K = A_1 + A_2\left[\frac{1000}{T_e}\right] + \left[B_1 + B_2\left[\frac{1000}{T_e}\right]\right]\frac{1}{T_b} + \left[C_1 + C_2\left[\frac{1000}{T_e}\right]\right]\frac{1}{T_b{}^2} \qquad \text{(IV-3)}$$

The values of K for a particular petroleum fraction, at any equilibrium temperature and boiling point desired, may be calculated from equation IV-3.

TABLE V

Constants for Equation (IV-1)

$$\log K = A + B/T_b + C/T_b^2$$

Oil	Run	T_e °F	$-A(10^{-2})$	$B(10^{-5})$	$-C(10^{-7})$
A	101	286.0	.25652	.30286	.82868
	102	273.0	.26343	.30980	.84544
	103	292.0	.25338	.29967	.82089
	104	296.2	.25122	.29749	.81559
B	105	323.6	.25448	.30675	.85005
	106	329.0	.25081	.30395	.84302
	107	346.1	.24254	.29514	.82072
G	110	424.4	.23936	.32381	.99681
	111	446.0	.22902	.31236	.96415
	112	471.2	.21797	.29925	.92619
Light Crude Naphtha	34	258.2	.23796	.26323	.66544
	36	243.86	.24654	.27032	.68123
	39	268.9	.23152	.25806	.65384
Heavy Crude Naphtha	4032-1	375.9	.23386	.29846	.86993
	4032-2	373.5	.23532	.29977	.87344
	4032-3	370.0	.23718	.30153	.87811
Trade Gas Oil	4034-1	546.8	.20446	.30109	.97735
	4034-2	539.6	.20749	.30450	.98765
	4034-3	532.0	.21060	.30813	.99860
	4034-4	509.0	.21995	.31932	1.03200
Kerosene	4033-1	451.4	.24046	.33855	1.09030
	4033-2	446.0	.24280	.34166	1.09970
	4033-3	442.2	.24421	.34341	1.10450
Heavy Gas Oil	4035-1	545.0	.23832	.36904	1.26590
	4035-2	501.8	.25618	.39332	1.34270

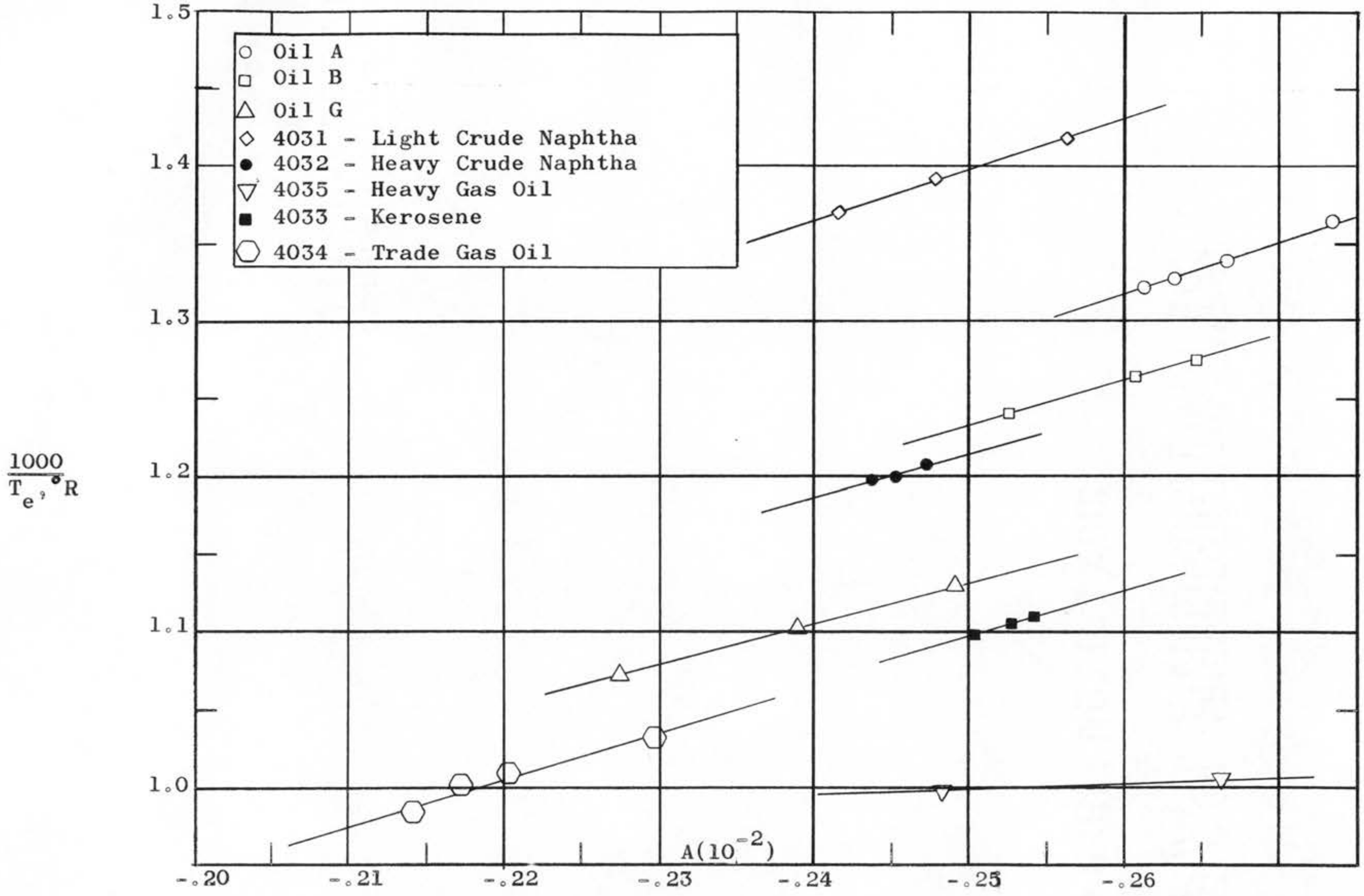

Figure 13. Constant A From Equation (IV-1) Versus Reciprocal Equilibrium Temperature

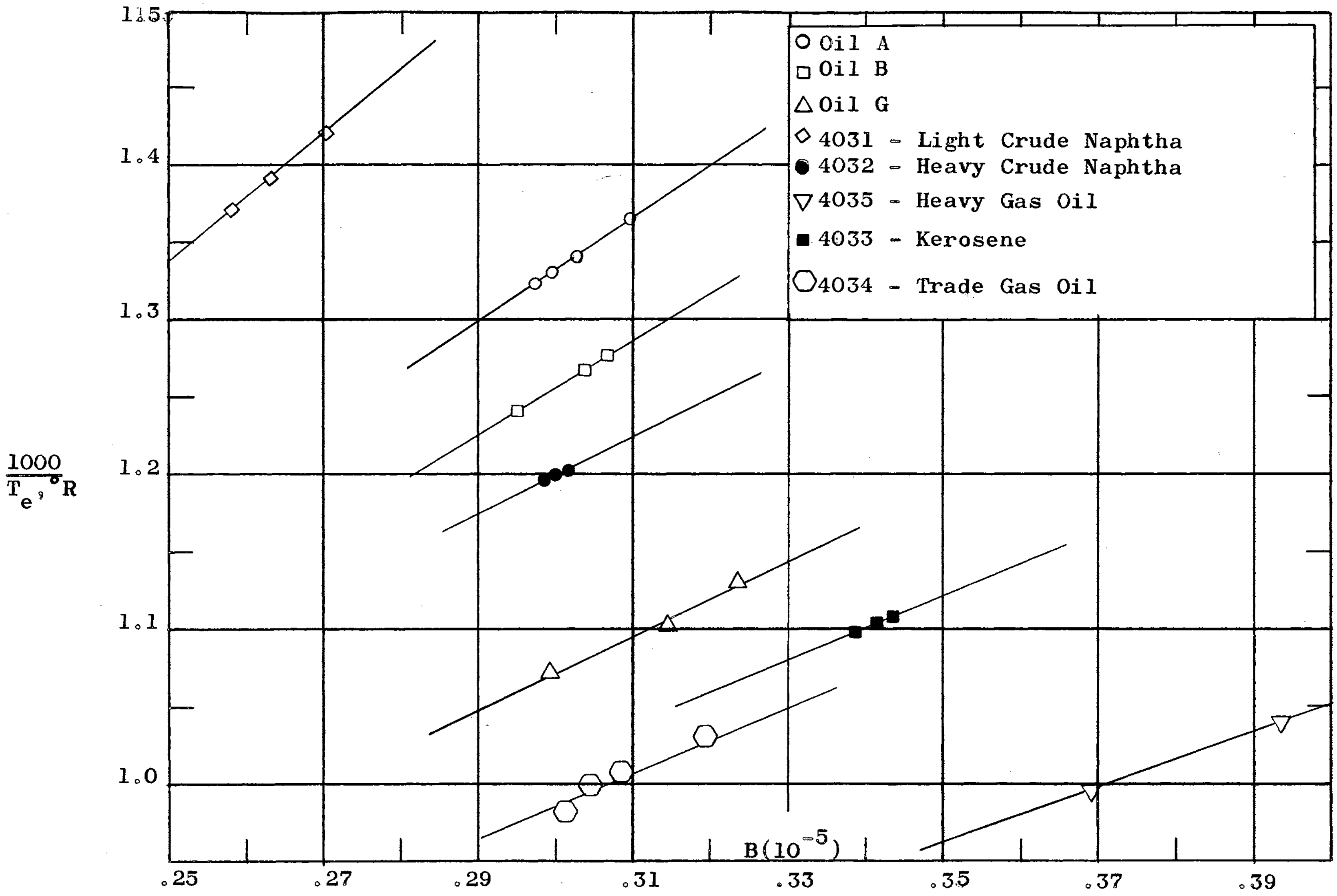

Figure 14. Constant B From Equation (IV-1) Versus Reciprocal Equilibrium Temperature

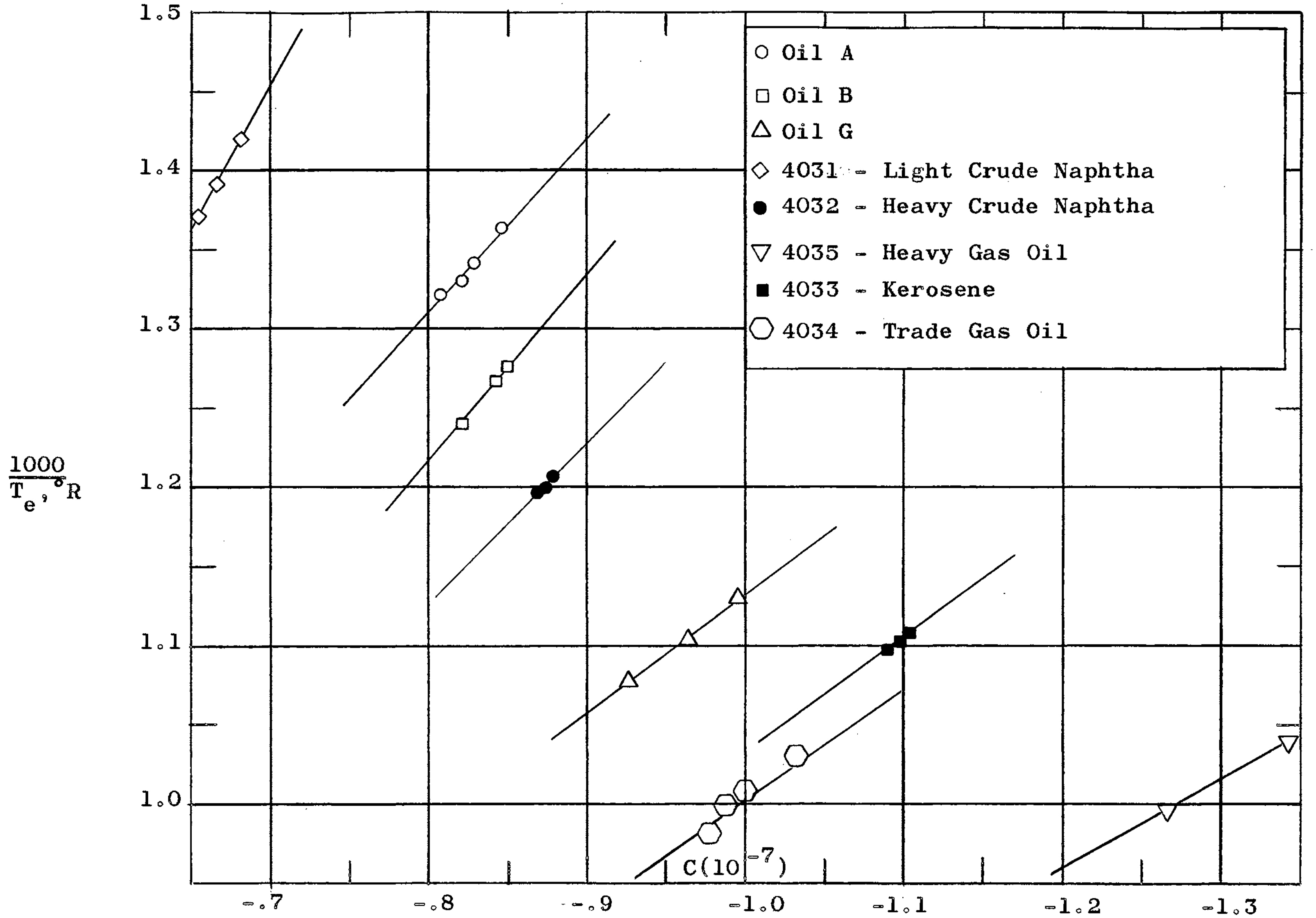

Figure 15. Constant C from Equation (IV-1) Versus Reciprocal Equilibrium Temperature

If the values of A_1, A_2, B_1, B_2, C_1, and C_2 could be generalized as a function of the petroleum fractions characteristics, the K-values of any petroleum fraction could be determined with the same equation for all oils. An equation of this form would be of great value for computer calculations.

Equation IV-3 and the constants listed in Table VI can be used only for the petroleum fractions from which they were derived. If the constants in Table VI can be generalized as a function of oil characteristic, Equation IV-3 could be made more general and useful.

TABLE VI

Constants for Equation (IV-2)

$A = A_1 + A_2 \ (1000/T_e)$ $B = B_1 + B_2 \ (1000/T_e)$ $C = C_1 + C_2 \ (1000/T_e)$

Oil	$A_1(10^{-2})$	$A_2(10^{-2})$	$B_1(10^{-5})$	$B_2(10^{-5})$	$C_1(10^{-7})$	$C_2(10^{-8})$
A	.13413670	-.29130	-.09116350	.29380	.12678790	-.07124
B	.16461558	-.32800	-.10904329	.32570	.20046000	-.08229
G	.18576313	-.37579	-.16449320	.43177	.40715660	-.12415
Light Crude Naphtha Sx-4031	.18538106	-.30388	-.08249876	.24821	.10681002	-.05544
Heavy Crude Naphtha Sx-4032	.10942498	-.28700	-.01852164	.26500	-.02545005	-.07060
Kerosene Sx-4033	.13363300	-.34100	-.14521634	.44100	.33793940	-.13020
Trade Gas Oil Sx-4034	.11489601	-.32366	-.07523243	.38130	.15057150	-.11429
Heavy Gas Oil Sx-4035	.16591543	-.40586	-.18044036	.55169	.47221160	-.17451

CHAPTER V

RECOMMENDATIONS AND CONCLUSIONS

Several of the analytical procedures and items of apparatus were changed or modified to improve the accuracy and reproducibility of the determinations. Previous investigators (20) had noted problems with the reproducibility of TBP assays, and with the molecular weight and equilibrium flash vaporization equipment. All of these problems were studied and improved wherever possible.

The TBP assay equipment (the Sarnia still) was exchanged for an Oldershaw column and modified so that a slight back pressure or vacuum could be applied and distillations completed at 760 or 100 millimeters of mercury. This increased the reproducibility of the determinations to ± 1 °F.

The equilibrium flash vaporization still of the Othmer type was replaced with a new equilibrium flash still of the flow type (Still "B") designed by Amir-Yeganeh (1). This still had the advantage that products could be produced in large enough quantity for analysis without the necessity of blending the products of two or more flashes. The reproducibility obtained between two flashes at identical conditions was approximately ± 2 per cent.

The cryoscopic method of determining molecular weights was abandoned completely and a vapor density apparatus developed as a replacement. The accuracy, when tested against known hydrocarbons, was ± 4 per cent.

The experimental procedure now used is believed to be within the allowable accuracy for the determination of K-values. A reasonable error to be expected in these K-values is ± 6 per cent. With further refinement of the molecular weight determination method, it is believed that the error in the derived K-values could be reduced to 3 or 4 per cent.

The Scatchard-Hildebrand liquid activity coefficient was not used in calculating the final K-values because of oscillations in these activity coefficients between hypothetical components of an equilibrium flash vaporization and because this correction of K_{Ideal} was actually minor when compared with the derived liquid activity coefficient, γ. In this work, only the derived activity coefficient was used to modify K_{Ideal}.

The derived K-values were curve-fitted as a quadratic function of log K versus the reciprocal normal boiling point. A deviation of 2 per cent or less between the K-values determined by the curve-fit and the derived K-values was obtained.

The curve-fit constants of the above functions were then linearly correlated as a function of equilibrium temperature with a standard deviation of 1 per cent.

Further investigations should be conducted on these oils to obtain a parameter which is a function of the oils' bulk properties and which can be used to correlate the constants in Equation IV-2. The equations presented here are for use only with the petroleum fractions from which they were derived and may not be applied to other oil fractions.

If another molecular weight device is to be built, the diaphragm should be moved further from the heat source and surrounded with baffles to prevent direct hot currents of air from changing the diaphgram temperature over long determination periods. Also, results might be improved if a more sensitive probe were used as the heat controller and a cold sink included for closer temperature control. If hydrocarbons with molecular weights higher than 150 amu are to be investigated, the mercury in the orifice should be replaced with gallium and the orifice heated.

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APPENDIX A

NOMENCLATURE

A - constant in equation (IV-1)
A_1 - constant in equation (IV-2)
A_2 - constant in equation (IV-2)
B - constant in equation (IV-1)
B_1 - constant in equation (IV-2)
B_2 - constant in equation (IV-2)
C - constant in equation (IV-1)
C_1 - constant in equation (IV-2)
C_2 - constant in equation (IV-2)
D - pressure dial reading (micromanometer)
E - energy
EFV - equilibrium flash vaporization
H - heat of vaporization
i - "i" th component
K - K-value or equilibrium vapor-liquid distribution ratio
K_A - K-value (Actual)
K_I - K-value (Ideal)
MF,mf - mole fraction off
Mw - molecular weight
n - number of gram moles
P - pressure

P_e - equilibrium pressure
p^o - vapor pressure
P_c - critical pressure
P_r - reduced pressure, P/P_c
p_r^o - reduced vapor pressure
P_{r_k} - convergence pressure
R - universal gas constant
T - temperature
TBP - true boiling point assay
T_e - equilibrium temperature
T_c - critical temperature
T_r - reduced temperature
T_b - normal boiling point from TBP
v,V - volume
V_r - reduced volume
VF - volume fraction off
V/L - equilibrium product molar ratio
x - liquid mole fraction

Greek Letters

β - reduced second virial coefficient
γ - liquid activity coefficient
δ - solubility parameter
$\bar{\delta}$ - average solubility parameter
Δ - change in property
Θ - imperfection pressure correction factor
ρ - density

ψ - semi-empirical third virial coefficient

ω - acentric factor

APPENDIX B

COMPUTER PROGRAMS

All of the computer programs presented in this appendix were written for use on the IBM 1620 digital computer. These programs were compiled with UTO Fortran and, therefore, require UTO subroutines for correct data output.

Program 1

This program was written to calculate the hypothetical component K-values of various petroleum fractions. The vapor-liquid distribution ratios calculated were: p^o/P, $p^o/P\Theta$, and $p^o\gamma/P\Theta$; where p^o is the vapor pressure, P is the system pressure, Θ is the imperfection pressure correction coefficient, and γ is the Scatchard-Hildebrand liquid activity coefficient.

Critical Values

Critical values of temperature and pressure may be read into the program as input data or may be calculated with an included correlation derived by Cavett (2). The equations used to obtain the critical temperature and pressure are as follows:

$$T_c = a_0 + a_1T + a_2T^2 + a_3AT + a_4T^3 + a_5AT^2 + a_6A^2T^2$$

Where: T_c is the critical temperature in °R.
A is the density in °API.
T is the molar average boiling point in °F.

(See Table VII for the equation constants)

TABLE VII

Constants for Equations of T_c and P_c

Subscript	a	b
0	768.07121	2.8290406
1	(0.17133693)(10^{1})	(0.94120109)(10^{-3})
2	(-0.10834003)(10^{-2})	(-0.30474749)(10^{-5})
3	(-0.89212579)(10^{-2})	(-0.20876110)(10^{-4})
4	(0.38890584)(10^{-6})	(0.15184103)(10^{-8})
5	(0.53094920)(10^{-5})	(0.11047899)(10^{-7})
6	(0.32711600)(10^{-7})	(-0.48271599)(10^{-7})
7	.	(0.13949619)(10^{-9})

$$P_c = b_0 + b_1T + b_2T^2 + b_3AT + b_4T^3 + b_5AT^2 + b_6A^2T + b_7A^2T^2$$

Where: P_c is the critical pressure in lbs/in^2.
A is the density in °API.
T is the molar average boiling point in °F.

(See Table VII for the equation constants)

Acentric Factor

The acentric factor (3) was calculated using the following equation:

$$\omega = \frac{3}{7}\left[\frac{\log P_c\text{, atm}}{T_c/T_b - 1}\right] - 1$$

Vapor Pressure

Also available in the program is the option of reading in vapor pressure as input data or using a correlation as presented by Stuckey (16), which is :

$$\ln p_r^o = (\ln p_r^o)^o + \left[\frac{\partial \ln p_r^o}{\partial \omega}\right]_T$$

For $T_r < 1.0$

$$(\ln p_r^o)^o = 5.365525 - (5.365525/T_r)$$

$$\left[\frac{\partial \ln p_r^o}{\partial \omega}\right]_T = 2.4154214 - (0.7115813/T_r) - (1.1791156/T_r^2) - (0.707157/T_r^3) + (0.18243243/T_r^4)$$

For $T_r > 1.0$

$$\left[\frac{\partial \ln p_r^o}{\partial \omega}\right]_T = 5.1788022 - (5.13314/T_r) - (0.0456619/T_r^2)$$

For $T_r = 0.0$

$$\left[\frac{\partial \ln p_r^o}{\partial \omega}\right]_T = 0.0$$

Where: p_r^o is the reduced vapor pressure.
ω is the acentric factor.
T_r is the reduced temperature.

The correlated vapor pressures of the small cuts or hypothetical components are compared with literature values in Table VIII.

Imperfection Pressure Correction Factor

The imperfection pressure correction coefficient was calculated using a semi-empirical equation the form of which is:

$$\ln \theta_i = \beta_i (P_r - p^o_{r_i}) + \psi_i (P_r^2 - p^{o2}_{r_i})$$

$$\beta_i = \frac{1}{T_{r_i}} \left[\frac{BP_{c_i}}{RT_{c_i}} - \frac{V^L P_{c_i}}{RT_{c_i}} \right]$$

$$\psi_i = \frac{\ln p^o_{r_i} - \ln P_{r_k} - (P_{r_k} - p^o_{r_i})}{(P^2_{r_k} - p^{o2}_{r_i})}$$

where the convergence pressure, $P_{r_k} = 6.29$

$$\left[\frac{BP_c}{RT_c}\right]_i = (0.1445 + 0.073\omega_i) - (0.330 - 0.46\omega_i)T_{r_i}^{-1}$$
$$- (0.1385 + 0.50\omega_i)T_{r_i}^{-2} - (0.0121 + 0.097\omega_i)T_{r_i}^{-3}$$
$$- (0.0073\omega_i)T_{r_i}^{-8}$$

The above is a generalized equation giving a reduced second virial coefficient as a function of reduced temperature and acentric factor (13,17). The second term in the calculation of β is the reduced volume ($V_{r_i} = V^L P_c/RT_c$) which may be calculated using an equation of the form of the Watson equation (17),

$$V_{r_i} = v_i'(5.7 + 3.0T_{r_i}).$$

where $v_i' = 0.0135439 + 0.00436516\omega_i$

TABLE VIII

Comparison of Vapor Pressure by Correlation and by Maxwell and Bonnell (12)

Oil A Run 101 T_e = 286.0°F P_e = 760 mm Hg			Oil B Run 105 T_e = 323.6°F P_e = 760 mm Hg		
Temp.-°F	$(p^o)^*$	$(p^o)^{**}$	Temp.-°F	$(p^o)^*$	$(p^o)^{**}$
204.0	3.147	3.100	140.0	9.787	11.000
222.0	2.484	2.400	261.5	2.355	2.390
243.5	1.852	1.800	278.6	1.881	2.000
257.9	1.511	1.600	295.2	1.502	1.500
272.3	1.224	1.200	304.7	1.315	1.250
287.6	.974	1.000	316.4	1.114	1.100
300.2	.804	.800	325.8	.971	.980
311.0	.678	.670	335.3	.846	.850
323.6	.554	.550	342.1	.766	.760
336.2	.452	.470	354.2	.638	.610
352.4	.345	.360	392.0	.351	.370
360.5	.300	.313	415.4	.238	.255
374.9	.233	.259	527.0	.029	.045

$(p^o)^*$ - vapor pressure by correlation

$(p^o)^{**}$ - vapor pressure by Maxwell and Bonnell

Scatchard-Hildebrand Liquid Activity Coefficient

In the calculation of the liquid activity coefficient, the following steps were completed.

The Kistyakowsky equation was first used to determine the normal heat of vaporization and Watson's 0.38 exponential correction (9) to convert this value to 25°C. At temperatures well below the critical, the energy of a liquid may be calculated by subtracing RT from the heat of vaporization. This is then used to determine the energy density when divided by the molar volume at 25°C. The molar volume is equal to the molecular weight divided by the density at 25°C.

The solubility parameter, the square root of the energy density, is now used to calculate the volume fraction average solubility parameter. Since these values are used only as differences, they are always calculated at 25°C. The molar volume is then converted to the system temperature and the liquid activity coefficient may be calculated. These steps in equation form are:

$$\Delta H_{@T_{b_i}} = T_{b_i}(8.75 + 4.571(\log T_{b_i}))$$

$$\Delta H_{@25^\circ C} = \Delta H_{@T_{b_i}} \left[\frac{1 - \frac{536.688}{T_{c_i}}}{1 - \frac{T_{b_i}}{T_{c_i}}} \right]^{0.38}$$

$$\Delta E_{i@25^\circ C} = \Delta H_{@25^\circ C} - 529.444$$

$$V_{i@25^\circ C} = \frac{Mw_i}{\rho_i}$$

$$\delta_{@25^\circ C} = \left[\frac{\Delta E_i}{V_i} \right]^{0.5}$$

$$\bar{\delta} = \sum \frac{x_i V_i \delta_i}{x_i V_i}$$

$$V_{o_i} = \frac{V_{i@25^\circ C}}{(5.7 + 3.0(536.69/T_{c_i}))}$$

$$V_i = V_{o_i}(5.7 + 3.0 T_{r_i})$$

then:

$$\ln \Upsilon = \frac{V_i(\delta_i - \bar{\delta})^2}{RT_i}$$

The final output of this program is shown for one petroleum fraction in Table IX. The K-values used for the first assumption in the equilibrium flash calculations were those of K_I, $p^o/P\Theta$. These K-values were then iterated until the experimental V/L ratio was reproduced within $\pm$ .001.

Data Input For Program 1

If the critical properties and vapor pressures are to be calculated by the program, the operator must have sense switch 1 in an on position. The critical values and vapor pressures are read into the program as input data with sense switch 1 turned off.

The data card input is as follows:

CARD	COLUMN	EXPLANATION
1	1 - 10	System or Equilibrium pressure, (mm Hg)
1	11 - 20	System temperature, (°F)
1	21 - 30	Number or data points, (FIXED POINT)
2	1 - 10	Liquid mole fraction off
2	11 - 20	Density, (g/cc)
2	21 - 30	Molecular weight
2	31 - 40	TBP boiling point, (°F)
2	41 - 50	Critical pressure, (lbs/in^2)
2	51 - 60	Critical temperature, (°R)
2	61 - 70	Vapor pressure, (atm.)

All of the words on Card 2 and Card 1 are in floating point except where it is mentioned otherwise. There will be as many of these second cards as there are data points. The maximum number of data points for any one calculation is 30.

Program 2

This program calculates the V/L ratio and the vapor and liquid molar TBP's for an equilibrium flash vaporization using the integral technique. The integral, $\int_0^1 (1/f)dm_f = L/F$, in this program is approximated by the integrated Lagrange interpolation equation and is derived for three points. A more complete discussion of this integration method is given by Woodward (20). There are two main functions to this program, (1) the determination of the liquid activity coefficient, γ , and (2) the calculation of K_{Actual} or the final K-values.

These functions are accomplished by typing the second approximation of γ on the typewriter. If this correction was not valid, the error will be typed. A positive error indicates that γ should be increased for the next approximation, while a negative error means the opposite. This procedure is continued until γ is correct and the flash conditions are printed. The last column of the output is the tabulation of K_A.

The data input is in the following form:

CARD	COLUMN	EXPLANATION
1	1 - 10	Number of data points, (FIXED POINT)
1	11 - 20	Experimental V/L ratio
1	21 - 30	Equilibrium temperature, (°F)
1	31 - 40	Equilibrium pressure, (mm Hg)
1	41 - 50	Initial activity coefficient
2	1 - 10	Mole fraction feedstock
2	11 - 20	K_I-value
2	21 - 30	TBP (feedstock) boiling point, (°F)

All of the words are in floating point except where mentioned otherwise. Card 2 will be repeated for as many components as desired. With this program, the maximum number of data points is 30 with the number of components always being odd.

The sense switch options for this program are as follows:

SENSE SWITCH	OPTION	EXPLANATION
1	on	do not print trial V/L ratio
1	off	print trial V/L ratio
2	on	print complete output
2	off	print only equilibrium conditions and γ
3	on	go to start
3	off	punch data for curve-fit of log K versus reciprocal normal boiling point
4	on	slow convergence (accurate) V/L calculated = V/L assumed
	off	fast convergence (used for estimation)

TABLE IX

Output From Program 1

Light Crude Naphtha (Sx - 4031)

T_e = 258.2°F P_e = 760.0 mm Hg

T_b, °F	p^o/P	$p^o/P\theta$	$p^o\gamma/P\theta$	θ	γ	δ	ω
105	8.92479	7.41487	8.03348	1.20363	1.08342	7.02612	.24093
140	5.61488	4.92766	5.02951	1.13946	1.02066	7.37155	.27892
160	4.25556	3.84795	3.85935	1.10593	1.00296	7.58712	.29279
180	3.19660	2.97059	2.97060	1.07608	1.00000	7.71493	.30148
195	2.58072	2.43253	2.43497	1.06092	1.00100	7.64534	.32625
210	2.06348	1.97869	1.98087	1.04285	1.00110	7.79729	.33062
220	1.77338	1.71829	1.72634	1.03206	1.00468	7.87952	.33270
230	1.52621	1.49167	1.49479	1.02315	1.00209	7.82454	.34467
240	1.31614	1.29631	1.29696	1.01529	1.00050	7.66982	.36793
250	1.12989	1.12236	1.12369	1.00671	1.00119	7.64420	.38154
260	.96561	.96740	.96741	.99815	1.00001	7.71227	.38580
270	.82178	.82983	.83340	.99030	1.00431	7.86386	.38215
280	.70013	.71221	.71879	.98303	1.00923	7.93018	.38647
290	.59816	.61325	.61592	.97540	1.00435	7.86128	.40348
300	.54012	.52574	.52678	.96755	1.00025	7.75318	.42078
310	.43333	.45109	.45109	.96062	1.00000	7.72223	.42733
320	.36673	.38420	.38438	.94541	1.00045	7.76316	.42908
330	.31047	.32750	.32766	.94801	1.00050	7.76506	.43574
340	.26336	.28016	.28021	.94006	1.00019	7.69195	.45148
350	.22240	.23825	.23915	.93346	1.00376	7.59986	.45852
362	.18095	.19532	.19919	.92644	1.01980	7.45432	.46280

$\bar{\delta}$ = 7.71940

FORTRAN STATEMENTS FOR PROGRAM 1

CALCULATION OF K_{IDEAL}

```
   DIMENSION FRAC(30),RHO(30),WTMOL(30),TB(30),PC(30),TC(30),
   DIMENSION DELTA(30),VP(30)
14 READ 100,P,T,N
   DO 2 I=1,N
 2 READ 101,FRAC(I),RHO(I),WTMOL(I),TB(I),PC(I),TC(I),VP(I)
   IF(SENSE SWITCH 1) 3,1
 3 A0=768.07121
   A1=1.7133693
   A2=-0.10834003*(10.**(-2.))
   A3=-0.89212579*(10.**(-2.))
   A4=0.38890584*(10.**(-6.))
   A5=0.53094920*(10.**(-5.))
   A6=0.32711600*(10.**(-7.))
   B0=2.8290406
   B1=0.94120109*(10.**(-3.))
   B2=-0.30474749*(10.**(-5.))
   B3=-0.20876110*(10.**(-4.))
   B4=0.15184103*(10.**(-8.))
   B5=0.11047899*(10.**(-7.))
   B6=-0.48271599*(10.**(-7.))
   B7=0.13949619*(10.**(-9.))
   DO 4 I=1,N
   AP = 141.5/RHO(I)-131.5
   TC(I)=A0+A1*TB(I)+A2*TB(I)**2.+A3*AP*TB(I)+A4*TB(I)**3.
   TC(I)=TC(I)+A5*AP*(TB(I)**2.)+A6*(AP**2.)*(TB(I)**2.)
   TM = TB(I)
   PCL=B0+B1*TM+B2*(TM**2.)+B3*AP*TM+B4*(TM**3.)+B5*AP*(TM**2.)
   PCL=PCL+B6*(AP**2.)*TM+B7*(AP**2.)*(TM**2.)
 4 PC(I)=10.**PCL
 1 Z=0.0
   D=0.0
   SDELB=0.0
   DO 5 I=1,N
   A0=536.688/TC(I)
   TB(I)=(TB(I)+459.69)/1.8
   A1=(TB(I)*1.8)/TC(I)
   A2=TB(I)*(8.75+4.571*(LOG(TB(I))/2.30259))
   A2=A2*((1.-A0)/(1.-A1))**0.38
   A3=A2-529.444
   RHO(I) = RHO(I)*0.98907
   A4=WTMOL(I)/RHO(I)
   DELTA(I)=(A3/A4)**0.5
   FRAC(I)=FRAC(I)-Z
   Z=Z+FRAC(I)
   A5=FRAC(I)*A4
```

```
      D=D+A5
      A6=A5*DELTA(I)
    5 SDELB=SDELB+A6
      B0=SDELB/D
      PRINT 102,B0,T,P
      PRINT 104
      DO 6 I=1,N
      B6=(T+459.69)/TC(I)
      B7=(WTMOL(I)/RHO(I))/(5.7+3.*(536.69/TC(I)))
      A4=B7*(5.7+3.*B6)
      A5=A4*((DELTA(I)-B0)**2.)/(1.987*(T+459.69)/1.8)
      A6=EXP(A5)
      PC(I)=PC(I)/14.696
      A1=LOG(PC(I))/2.30259
      A2=TC(I)/(TB(I)*1.8)-1.
      A3=(3./7.)*(A1/A2)-1.
      A4=6.29
      B7=LOG(A4)
      A5=1./B6
      B1=0.1445+(0.073*A3)
      B2=(0.330-(0.460*A3))*A5
      B3=(0.1385+(0.50*A3))*(A5**2.)
      B4=(0.0121+(0.097*A3))*(A5**3.)
      B5=(0.0073*A3)*(A5**8.)
      B5=B1-B2-B3-B4-B5
      A1=0.0135439-(0.00436516*A3)
      A2=A1*(5.7+(3.*B6))
      B3=(B5-A2)/B6
      IF(SENSE SWITCH 1) 8,7
    8 B1=5.365525-(5.365525*(1./B6))
      IF(B6-1.) 9,10,11
    9 B2=2.4154214-(0.71158130*A5)-(1.1791156*(A5**2.))
      B2=B2-(0.7071570*(A5**3.))+(0.18243243*(A5**4.))
      GO TO 12
   11 B2=5.1788022-(5.1331403*A5)-(0.0456619*(A5**2.))
      GO TO 12
   10 B2=0.0
   12 B4=B1+(A3*B2)
      B5=EXP(B4)
      VP(I)=B5*PC(I)
      GO TO 13
    7 A1=VP(I)/PC(I)
      B4=LOG(A1)
      B5=A1
   13 A2=B4
      A5=A2-B7-(B3*(A4-B5))
      B7=B5*B5
      A2=(A4*A4)-(B7)
      A4=A5/A2
      B3=B3
      B2=A4
      B1=P/760.
```

```
      A1=B1/PC(I)
      A5=LOG(A1)
      A2=A1-B5
      B5=(A1**2.)-B7
      B7=B3*A2
      A4=B2*B5
      B2=B7+A4
      B5=B4-A5-B7-A4
      A2=EXP(B5)
      A5 = A2*A6
      B2=EXP(B2)
      B3=VP(I)/B1
    6 PRINT 101,B3,A2,A5,B2,A6,DELTA(I),A3
      GO TO 14

  100 FORMAT (F10.5, F10.5, I10)
  101 FORMAT(F10.5,F10.5,F10.5,F10.5,F10.5,F10.5,F10.5)
  102 FORMAT(1X10HDEL BAR = ,F8.4,5X7HTEMP = ,F8.2,5X8HPRESS = ,F8.2/)
  104 FORMAT(5X4HP*/P5X5HP*/P05X6HP*G/P07X1H010X1HG8X3HDEL8X4HACEN/)

  350 END
```

FORTRAN STATEMENTS FOR PROGRAM 2

EQUILIBRIUM FLASH VAPORIZATION CALCULATIONS

```
      DIMENSION FM(30),Y(30),TB(30)
    1 READ 30,N,VLO,TE,PE,COR
      ROC = COR
      DO18 I=1,N
      READ 31,FM(I),Y(I),TB(I)
   18 TB(I)=TB(I)*1.8-459.69
  104 DO 50 I=1,N
   50 Y(I)=COR*Y(I)
      COR = ROC
      VL=VLO
      M=(N-1)/2
      AREA=0.0
      AERA=0.0
      NONE=0
      WONE=0.0
    2 ONE=0.0
   20 T=0.0
      U=0.0
      I=1
      J=0
    3 A=FM(I)-FM(I+1)
      B=FM(I)-FM(I+2)
      C=(FM(I+2)**3.-FM(I)**3.)/3.
      D=(FM(I+1)+FM(I+2))/2.
      E=FM(I+2)**2.-FM(I)**2.
      F=FM(I+1)*FM(I+2)
      G=FM(I+2)-FM(I)
      H=FM(I+1)-FM(I+2)
      P=(FM(I)+FM(I+2))/2.
      Q=FM(I)*FM(I+2)
      R=(FM(I)+FM(I+1))/2.
      S=FM(I)*FM(I+1)
      FL1=1./(1.+Y(I)*VL)
      FL2=1./(1.+Y(I+1)*VL)
      FL3=1./(1.+Y(I+2)*VL)
      VF1=1.-FL1
      VF2=1.-FL2
      VF3=1.-FL3
      W=B
      J=J+1
      IF(ONE) 4,5,6
    4 I=I+1
    6 C=(FM(I+1)**3.-FM(I)**3.)/3.
      B=FM(I)-FM(I+1)
      E=FM(I+1)**2.-FM(I)**2.
```

```
      ONE=-ONE
    5 AA=(1./(A*W))*(C-D*E+F*(-B))
      BB=(1./(H*(-A)))*(C-P*E+Q*(-B))
      CC=(1./(W*H))*(C-R*E+S*(-B))
      D=FL1*AA
      E=FL2*BB
      F=FL3*CC
      G=VF1*AA
      H=VF2*BB
      P=VF3*CC
      T=T+D+E+F
      U=U+G+H+P
      IF(ONE) 17,7,17
    7 I=I+2
      GO TO 11
   17 IF(NONE) 8,14,8
   14 PRINT 34,NONE,TB(I),WONE,WONE,FL1,VF1,FM(I),Y(I)
      NONE=1
    8 TBP=T/AREA
      TVP=U/AERA
      IF(ONE) 9,11,10
    9 PRINT 34,I,TB(I+1),TBP,TVP,FL2,VF2,FM(I+1),Y(I+1)
      GO TO 3
   10 PRINT 34,I,TB(I+1),TBP,TVP,FL3,VF3,FM(I+1),Y(I+1)
      I=I+1
      J=J-1
      GO TO 11
   11 IF(M-J) 12,12,3
   12 IF(ONE) 16,15,16
   15 IF(SENSE SWITCH 4) 52,53
   52 VL1=VL
      VL5=(1./T)-1.
      VL4=ABSF(VL5-VL1)
      VL=VL5
      IF(VL4-.001) 13,13,64
   53 IF(NONE) 350,22,23
   22 VL1=VL
      VL5=(1./T)-1.
      FX1=T-1./(1.+VL1)
      VL2=0.98*VL
      VL=VL2
      NONE=1
      GO TO 2
   23 FX2=T-1./(1.+VL2)
      NONE=0
      VL3=VL2-(FX2*(VL1-VL2))/(FX1-FX2)
      VL4=ABSF(VL5-VL1)
      VL =ABSF(VL3)
      IF(VL4-.0001) 13,13,64
   64 IF(SENSE SWITCH 1) 2,351
  351 PRINT 51,VL5,VL1
      GO TO 2
```

```
 13 ERROR =VLO-VL
    PRINT 200,ERROR
200 FORMAT(5HERROR,F10.5)
    ERR=ABSF(ERROR)
    IF(ERR-.01) 54,54,103
103 ACCEPT 201,ROC
201 FORMAT(F9.6)
    COR=ROC/COR
    GO TO 104
 54 PRINT 32
    PRINT 41,COR
    PRINT 36,VLO,VL
    PRINT 40,VL4
    PRINT 37,TE,PE
    IF(SENSE SWITCH 2) 25,1
 25 PRINT 38
    NONE=0
    ONE=1.0
    AERA=U
    AREA=T
    GO TO 20
 16 IF(SENSE SWITCH 3) 1,60
 60 DO 67 I=1,N
    TB(I)=(TB(I)+459.69)/1.8
 67 PUNCH 61,TB(I),Y(I)
    GO TO 1
 61 FORMAT(F10.5,F10.5)
 30 FORMAT(I3,7X,F10.5,F10.5,F10.5,F10.5)
 31 FORMAT(F10.5,F10.5,F10.5)
 32 FORMAT(24X30HEQUILIBRIUM FLASH CALCULATIONS//)
 36 FORMAT(10X11HV/L(EXP) =  ,F8.3,15X12HV/L(CALC) =  ,F8.3/)
 37 FORMAT(10X26HEQUILIBRIUM TEMP(DEG F) =  ,F7.2,5X7HPRESS=  ,F8.2/)
 38 FORMAT(1X4HCOMP8X4HTEMP9X2HML7X2HMV7X3HL/F6X3HV/F7X2HMF8X1HK/)
 34 FORMAT(I4,6X,F7.2,5X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,F9.4)
 40 FORMAT(10X7HERROR=  ,F7.4/)
 41 FORMAT(1X7HGAMMA=(,F7.4,1X1H)/)
 51 FORMAT(4X10HV/L(CALC)=,F10.5,4X13HV/L(ASSUMED)=,F10.5)

350 END
```

APPENDIX C

PHYSICAL PROPERTIES OF OILS

The following tables contain the experimental properties of the hydrocarbon stocks as determined from samples taken from distillations with the Oldershaw column. These samples were taken at approximately 2% (volume) intervals for the first and last 10% volume off and 5% (volume) samples elsewhere.

These samples were then analysed for specific gravity and molecular weights with a Fisher-Davidson gravitometer and molecular weight device, respectively.

By using these physical properties, the volumetric true boiling point assay was converted to a molar one.

The physical properties of other petroleum fractions used in the determination of K-values were obtained from Amir-Yeganeh (1).

TABLE X

Physical Properties of Light Crude Naphtha

(Humble Oil Sx-4031)

Run No. 3 - Feedstock

Temp. T_b, °F	Fraction volume	Fraction mole	Density (g/cc)	Molecular Weight	Average Temp. (°F)
105.760	.0000	.0000	.6480	78.797	121.430
137.100	.0252	.0312	.6740	82.924	143.825
150.550	.0505	.0622	.6960	83.556	154.715
158.880	.0757	.0939	.7280	87.499	172.445
186.010	.1262	.1572	.7240	94.266	190.200
194.390	.1515	.1864	.7250	97.795	201.235
208.080	.2020	.2428	.7440	98.953	210.345
212.610	.2525	.3000	.7600	99.735	215.930
219.250	.3030	.3580	.7630	102.605	227.815
236.380	.3535	.4146	.7400	111.867	242.905
249.430	.4040	.4649	.7410	114.617	253.320
257.210	.4545	.5141	.7540	115.863	262.370
267.530	.5050	.5636	.7770	116.472	272.530
277.530	.5555	.6144	.7860	117.668	281.355
285.180	.6060	.6652	.7730	122.536	291.140
297.100	.6565	.7132	.7640	129.612	301.770
306.440	.7070	.7581	.7730	132.691	311.335
316.230	.7575	.8024	.7860	136.433	321.105
325.980	.8080	.8462	.7910	139.729	330.585
335.190	.8585	.8893	.7850	144.408	339.900
344.610	.9090	.9307	.7820	148.624	345.600
346.590	.9229	.9417	.7870	154.844	347.545
348.500	.9608	.9707	.7920	159.721	353.750
359.000	1.0000	1.0000			

TABLE XI

Physical Properties of Light Crude Naphtha

(Humble Oil Sx-4031)

Run No. 4 - Equilibrium Liquid

T_e = 258.2°F P_e = 760.0 mm Hg

Temp.	Fraction		Density	Molecular	Average
T_b, °F	volume	mole	(g/cc)	Weight	Temp. (°F)
140.000	.0000	.0000			
			.6940	84.925	157.555
175.110	.0248	.0326			
			.7270	92.957	184.750
194.390	.0496	.0639			
			.7350	98.414	202.695
211.000	.0992	.1236			
			.7580	100.821	216.320
221.640	.1488	.1837			
			.7510	107.741	231.890
242.140	.1985	.2395			
			.7380	112.694	247.215
252.290	.2481	.2918			
			.7470	114.587	257.850
263.410	.2977	.3440			
			.7730	116.302	268.290
273.170	.3473	.3971			
			.7850	119.099	277.520
281.870	.3970	.4498			
			.7780	120.826	284.415
286.960	.4466	.5013			
			.7670	124.250	292.790
298.620	.4962	.5507			
			.7650	126.101	300.510
302.400	.5459	.5992			
			.7700	131.211	307.560
312.720	.5955	.6461			
			.7800	134.472	315.605
318.490	.6451	.6925			
			.7870	137.849	322.360
326.230	.6947	.7382			
			.7910	139.224	328.845
331.460	.7444	.7836			
			.7910	142.171	335.230
339.000	.7952	.8292			
			.7840	144.439	341.435
343.870	.8436	.8715			
			.7790	148.111	346.935
350.000	.8945	.9146			
			.7830	152.148	352.250
354.500	.9193	.9352			
			.7950	159.208	354.500
354.500	.9565	.9651			
			.7980	160.402	359.250
364.000	1.0000	1.0000			

TABLE XII

1 of 2

Physical Properties of Light Crude Naphtha

(Humble Oil Sx-4031)

Run No. 6 - Equilibrium Liquid

T_e = 243.86°F P_e = 760.0 mm Hg

Temp. T_b, °F	Fraction volume	Fraction mole	Density (g/cc)	Molecular Weight	Average Temp. (°F)
109.790	.0000	.0000	.6585	80.500	132.115
154.440	.0187	.0240	.6915	84.900	157.765
161.090	.0250	.0320	.7030	85.700	163.985
166.880	.0312	.0401	.7132	88.100	170.450
174.020	.0375	.0480	.7300	90.000	176.660
197.300	.0500	.0639	.7260	91.700	186.035
192.770	.0750	.0950	.7200	96.400	197.345
201.920	.1001	.1243	.7336	98.500	205.000
208.080	.1251	.1535	.7421	99.000	209.815
211.550	.1501	.1829	.7529	100.000	213.410
215.270	.1752	.2125	.7605	100.900	217.790
220.310	.2002	.2420	.7630	102.500	224.935
229.560	.2252	.2712	.7525	108.900	234.410
239.260	.2503	.2983	.7405	111.600	242.265
245.270	.2753	.3244	.7381	112.900	247.350
249.430	.3003	.3500	.7390	113.800	251.510
253.590	.3254	.3755	.7418	114.600	255.660
257.730	.3504	.4009	.7500	115.600	260.765
263.800	.3754	.4264	.7625	116.400	266.305
268.810	.4005	.4521	.7778	117.300	270.865
272.920	.4255	.4781	.7820	118.100	274.840
276.760	.4505	.5041	.7850	119.000	278.420
280.080	.4755	.5299	.7845	119.700	281.740
283.400	.5006	.5557	.7809	121.000	285.250
287.100	.5256	.5810	.7760	122.500	289.820
292.540	.5506	.6058	.7659	125.000	295.075
297.610	.5757	.6299	.7650	127.100	299.800
301.990	.6007	.6535	.7659	130.000	303.965
305.940	.6257	.6766	.7699	131.700	307.825
309.710	.6508	.6995	.7740	133.100	311.595
313.480	.6758	.7224	.7800	134.600	315.860
318.240	.7008	.7451	.7839	135.800	320.115
321.990	.7259	.7677	.7886	137.900	323.985
325.980	.7509	.7902	.7905	139.100	327.600
329.220	.7759	.8125	.7911	140.000	330.965
332.710	.8010	.8347	.7906	141.500	334.325
335.940	.8260	.8566			

TABLE XII (continued) 2 of 2

Temp. T_b, °F	Fraction		Density (g/cc)	Molecular Weight	Average Temp. (°F)
	volume	mole			
335.940	.8260	.8566			
			.7879	143.500	337.675
339.410	.8510	.8781			
			.7830	145.000	341.145
342.880	.8760	.8993			
			.7790	148.000	344.615
346.350	.9011	.9200			
			.7801	149.000	346.675
347.000	.9261	.9405			
			.7812	150.000	348.000
349.000	.9511	.9609			
			.7851	152.100	350.250
351.500	.9762	.9812			
			.7955	158.000	355.750
360.000	1.0000	1.0000			

TABLE XIII

1 of 2

Physical Properties of Light Crude Naphtha

(Humble Oil Sx-4031)

Run No. 9 - Equilibrium Liquid

T_e = 268.9°F P_e = 760.0 mm Hg

Temp. T_b, °F	Fraction volume	Fraction mole	Density (g/cc)	Molecular Weight	Average Temp. (°F)
137.600	.0000	.0000	.6840	83.800	144.630
151.660	.0062	.0084	.7089	86.700	159.630
167.600	.0125	.0169	.7288	93.700	175.445
183.290	.0251	.0330	.7250	97.200	192.340
201.390	.0503	.0638	.7424	98.900	205.420
209.450	.0755	.0949	.7603	100.800	213.555
217.660	.1045	.1308	.7628	103.900	222.555
227.450	.1259	.1566	.7410	111.300	233.750
240.050	.1511	.1842	.7381	112.500	242.790
245.530	.1763	.2113	.7392	113.900	248.565
251.600	.2015	.2382	.7449	115.100	254.405
257.210	.2267	.2650	.7609	116.400	261.340
265.470	.2581	.2988	.7761	117.000	268.040
270.610	.2770	.3194	.7814	117.900	272.660
274.710	.3022	.3468	.7850	118.800	276.500
278.290	.3274	.3742	.7848	120.000	280.205
282.120	.3551	.4040	.7767	122.600	285.175
288.230	.3841	.4341	.7715	123.600	289.625
291.020	.4030	.4535	.7650	125.800	293.810
296.600	.4282	.4787	.7650	128.500	298.370
300.140	.4534	.5033	.7652	129.100	301.720
303.300	.4785	.5278	.7681	131.100	305.120
306.940	.5037	.5521	.7722	132.700	309.080
311.220	.5289	.5762	.7777	134.000	312.725
314.230	.5541	.6002	.7810	135.000	315.480
316.730	.5793	.6241	.7839	135.800	317.860
318.990	.6045	.6480	.7863	136.800	320.240
321.490	.6297	.6718	.7880	137.600	322.615
323.740	.6549	.6955	.7898	138.200	324.610
325.480	.6801	.7192	.7911	139.500	326.855
328.230	.7052	.7426	.7911	140.100	329.225
330.220	.7304	.7660	.7910	141.100	331.215
332.210	.7556	.7892	.7891	143.000	334.200
336.190	.8060	.8349	.7869	143.800	337.180
338.170	.8312	.8575			

TABLE XIII (continued)

2 of 2

Temp. T_b, °F	Fraction volume	Fraction mole	Density (g/cc)	Molecular Weight	Average Temp. (°F)
338.170	.8312	.8575			
			.7809	145.200	339.535
340.900	.8602	.8831			
			.7794	147.400	342.510
344.120	.8816	.9017			
			.7818	149.200	345.355
346.590	.9068	.9234			
			.7878	152.100	348.295
350.000	.9118	.9277			
			.7935	155.900	352.250
354.500	.9244	.9382			
			.7946	157.600	355.250
356.000	.9370	.9487			
			.7952	157.800	356.100
356.200	.9496	.9591			
			.7968	158.600	356.850
357.500	.9622	.9695			
			.7978	159.900	358.000
358.500	.9748	.9798			
			.7990	161.500	359.250
360.000	.9874	.9901			
			.8020	168.000	363.000
366.00	1.0000	1.0000			

TABLE XIV

Physical Properties of Heavy Crude Naphtha

(Humble Oil Sx-4032)

Run No. 4032 - Feedstock

Temp.	Fraction		Density	Molecular	Average
T_b, °F	volume	mole	(g/cc)	Weight	Temp. (°F)
232.710	.0000	.0000			
			.7650	111.310	262.500
292.290	.0247	.0348			
			.7780	128.316	308.760
325.230	.0741	.0963			
			.7860	134.168	329.340
333.450	.0988	.1259			
			.7850	138.313	337.670
341.890	.1483	.1835			
			.7850	141.152	345.355
348.820	.1977	.2399			
			.7870	146.880	350.920
353.020	.2472	.2942			
			.7900	149.641	356.345
359.670	.2966	.3477			
			.7930	156.278	361.880
364.090	.3461	.3991			
			.7950	162.218	366.425
368.760	.3955	.4488			
			.7950	161.650	370.600
372.440	.4449	.4987			
			.7940	165.596	374.275
376.110	.4944	.5473			
			.7940	167.015	376.965
377.820	.5438	.5955			
			.7900	164.645	379.165
380.510	.5933	.6441			
			.7880	172.696	383.200
385.890	.6427	.6904			
			.7910	167.217	385.155
384.420	.6922	.7383			
			.7920	156.081	385.765
387.110	.7416	.7898			
			.7910	173.353	388.940
390.770	.7911	.8360			
			.8040	188.327	393.690
396.610	.8405	.8793			
			.8170	189.232	400.380
404.150	.8899	.9231			
			.8150	201.363	405.550
406.950	.9035	.9344			
			.8090	242.792	407.975
409.000	.9530	.9681			
			.8150	246.687	418.500
428.000	1.0000	1.0000			

TABLE XV

Physical Properties of Kerosene

(Humble Oil Sx-4033)

Run No. 4033 - Feedstock

Temp. T_b, °F	Fraction		Density (g/cc)	Molecular Weight	Average Temp. (°F)
	volume	mole			
370.0	.0000	.0000			
			.8100	149.0	372.5
375.0	.0052	.0059			
			.8120	151.2	377.5
380.0	.0093	.0106			
			.8140	153.0	285.0
390.0	.0104	.0118			
			.8180	156.6	395.0
400.0	.0519	.0575			
			.8220	160.5	405.0
410.0	.0933	.1013			
			.8240	163.9	415.0
420.0	.1470	.1588			
			.8240	168.2	422.5
425.0	.1815	.1954			
			.8250	171.3	427.5
430.0	.2278	.2422			
			.8270	172.7	435.0
440.0	.3541	.3695			
			.8350	175.9	442.5
445.0	.4190	.4351			
			.8380	177.5	447.5
450.0	.5036	.5197			
			.8360	180.0	452.5
455.0	.5880	.6036			
			.8380	181.6	457.5
460.0	.6774	.6914			
			.8410	183.7	462.5
465.0	.7417	.7542			
			.8450	185.5	467.5
470.0	.7813	.7926			
			.8480	187.0	475.0
480.0	.8851	.8919			
			.8540	189.5	482.5
485.0	.9802	.9822			
			.8570	190.6	485.7
486.5	1.0000	1.0000			

TABLE XVI

Physical Properties of Trade Gas Oil

(Humble Oil Sx-4034)

Run No. 4034 - Feedstock

Temp. T_b, °F	Fraction volume	Fraction mole	Density (g/cc)	Molecular Weight	Average Temp. (°F)
250.0	.0000	.0000			
			.800	165.0	325.0
400.0	.0262	.0332			
			.815	169.0	407.0
414.0	.0499	.0630			
			.834	177.0	428.0
442.0	.0788	.0986			
			.837	181.0	447.0
452.0	.1024	.1271			
			.846	195.0	469.0
486.0	.1537	.1852			
			.852	196.0	492.0
498.0	.2049	.2433			
			.853	202.0	504.0
510.0	.2404	.2825			
			.858	205.0	511.0
513.0	.2904	.3370			
			.847	210.0	516.0
519.0	.3403	.3896			
			.855	211.0	520.0
521.0	.3810	.4327			
			.860	214.0	525.5
530.0	.4296	.4837			
			.866	215.0	532.5
535.0	.4783	.5349			
			.857	219.0	537.5
540.0	.5335	.5913			
			.846	231.0	550.0
560.0	.6189	.6729			
			.853	241.0	567.5
575.0	.6727	.7227			
			.835	250.0	576.0
577.0	.7227	.7663			
			.828	260.0	578.0
579.0	.7621	.7990			
			.858	252.0	587.0
595.0	.8383	.8668			
			.849	265.0	598.5
602.0	.8646	.8888			
			.847	270.0	604.5
607.0	.8909	.9103			
			.866	265.0	610.0
613.0	.9145	.9305			
			.872	280.0	629.0
645.0	1.0000	1.0000			

TABLE XVII

Physical Properties of Heavy Gas Oil

(Humble Oil Sx-4035)

Run No. 4035 - Feedstock

Temp. T_b, °F	Fraction volume	Fraction mole	Density (g/cc)	Molecular Weight	Average Temp. (°F)
250.0	.0000	.0000	.784	159.0	315.0
380.0	.0202	.0318	.809	179.0	406.0
432.0	.0362	.0547	.828	192.0	451.5
471.0	.0652	.0944	.847	195.0	480.0
489.0	.0869	.1245	.867	205.0	504.5
520.0	.1231	.1732	.863	222.0	535.0
550.0	.1797	.2431	.857	240.0	564.0
578.0	.2376	.3089	.870	258.0	590.0
602.0	.2956	.3711	.857	265.0	607.0
612.0	.3478	.4247	.865	272.0	619.0
626.0	.4014	.4790	.864	279.0	631.0
636.0	.4652	.5418	.870	290.0	647.5
659.0	.5202	.5943	.876	300.0	667.0
675.0	.5753	.6455	.875	310.0	680.0
686.0	.6289	.6936	.867	320.0	692.0
698.0	.6797	.7373	.878	325.0	703.5
709.0	.7231	.7747	.868	350.0	717.0
725.0	.7695	.8112	.897	335.0	730.0
736.0	.8304	.8631	.960	330.0	755.5
775.0	.8942	.9221	.905	375.0	776.5
778.0	.9144	.9376	.905	395.0	791.0
804.0	1.0000	1.0000			

APPENDIX D

EXPERIMENTAL FLASH VAPORIZATION DATA AND EQUILIBRIUM FLASH VAPORIZATION CALCULATIONS

The experimental flash vaporization data taken for five side streams of the No. 5 pipe still at the Humble Oil and Refining Company Baytown refinery are presented in tables 18 to 22. Additional experimental flash vaporization data for other petroleum fractions were obtained from Amir-Yeganeh (1) and appear in his work.

The experimental flash vaporization data together with the true boiling point assay of the petroleum fractions were then used in flash vaporization calculations in the manner proposed in this study.

The remainder of the tables in this appendix give these flash vaporization calculations as determined by computer program 2 and discussed in Appendix B.

TABLE XVIII

Equilibrium Flash Vaporization Data

Petroleum Fraction - Light Crude Naphtha (Sx-4031)

Run No.	34	36	39
Equilibrium Flash Conditions			
Temperature (°F)	258.2	243.86	268.9
Pressure (mm Hg)	760.0	760.0	760.0
Products			
Vapor (ml.)	901.0	379.0	2091.0
Liquid (ml.)	900.0	900.0	900.0
Molar V/L Ratio	1.140	.481	2.714
Bulk Density - .756 g/cc or 55.5°API			
Vapor (g/cc)	.746	.735	.750
Liquid (g/cc)	.769	.764	.771
Bulk Molecular Weight - 108.2			
Vapor	105.9	101.5	108.3
Liquid	124.8	120.6	130.5

TABLE XIX

Equilibrium Flash Vaporization Data

Petroleum Fraction - Heavy Crude Naphtha (Sx-4032)

Run No.	4032-1	4032-2	4032-3
Equilibrium Flash Conditions			
Temperature (°F)	375.9	373.5	370.0
Pressure (mm Hg)	760.0	760.0	760.0
Products			
Vapor (ml.)	663.3	275.0	151.0
Liquid (ml.)	201.0	250.0	302.0
Molar V/L Ratio	3.510	1.176	.531
Bulk Density - .797 g/cc or 45.6°API			
Vapor (g/cc)	.796	.797	.796
Liquid (g/cc)	.802	.801	.800
Bulk Molecular Weight - 146.8			
Vapor	146.0	145.0	145.0
Liquid	155.0	156.0	155.0

TABLE XX

Equilibrium Flash Vaporization Data

Petroleum Fraction - Kerosene (Sx-4033)

Run No.	4033-1	4033-2	4033-3
Equilibrium Flash Conditions			
Temperature (°F)	451.4	446.0	442.4
Pressure (mm Hg)	760.0	760.0	760.0
Products			
Vapor (ml.)	72.6	78.0	113.0
Liquid (ml.)	38.0	73.0	195.0
Molar V/L Ratio	2.020	1.201	.614
Bulk Density - .829 g/cc or 38.8°API			
Vapor (g/cc)	.827	.823	.821
Liquid (g/cc)	.836	.827	.832
Bulk Molecular Weight - 173.2			
Vapor	176.8	170.7	170.0
Liquid	189.0	192.5	182.4

TABLE XXI

Equilibrium Flash Vaporization Data

Petroleum Fraction - Trade Gas Oil (Sx-4034)

Run No.	4034-1	4034-2	4034-3	4034-4
Equilibrium Flash Conditions				
Temperature (°F)	546.8	539.6	532.0	509.0
Pressure (mm Hg)	760.0	760.0	760.0	760.0
Products				
Vapor (ml.)	130.0	345.0	171.0	76.0
Liquid (ml.)	60.0	325.0	270.0	330.0
Molar V/L Ratio	2.218	1.137	.702	.246
Bulk Density - .858 g/cc or 34.0°API				
Vapor (g/cc)	.851	.851	.843	.837
Liquid (g/cc)	.857	.863	.860	.859
Bulk Molecular Weight - 218.5				
Vapor	216.0	210.0	202.0	184.5
Liquid	222.3	228.0	228.1	213.0

TABLE XXII

Equilibrium Flash Vaporization Data

Petroleum Fraction - Heavy Gas Oil (Sx-4035)

Run No.	4035-1	4035-2
Equilibrium Flash Conditions		
Temperature (°F)	545.0	501.8
Pressure (mm Hg)	760.0	760.0
Products		
Vapor (ml.)	150.0	18.0
Liquid (ml.)	635.0	113.0
Molar V/L Ratio	.262	.176
Bulk Density - .873 g/cc or 30.1°API		
Vapor (g/cc)	.846	.835
Liquid (g/cc)	.885	.882
Bulk Molecular Weight - 221.0		
Vapor	189.6	179.0
Liquid	220.0	215.0

TABLE XXIII

EQUILIBRIUM FLASH CALCULATIONS

Oil A

Run 101

γ = 1.065

V/L = .945

T_e = 286.0°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
204.0	.0000	.0000	.2466	.7533	.0000	3.2320
222.0	.0596	.1801	.2923	.7076	.1182	2.5607
243.5	.0943	.2576	.3548	.6451	.1737	1.9232
257.9	.1722	.3966	.4011	.5988	.2813	1.5794
272.3	.2167	.4604	.4504	.5495	.3352	1.2908
287.6	.3126	.5712	.5045	.4954	.4383	1.0390
300.2	.4147	.6679	.5495	.4504	.5378	.8572
311.2	.5235	.7552	.5886	.4113	.6361	.7394
323.6	.6379	.8325	.6329	.3670	.7325	.6135
336.2	.7547	.8978	.6751	.3248	.8243	.5089
352.4	.9262	.9750	.7262	.2737	.9500	.3988
360.5	.9549	.9858	.7502	.2497	.9700	.3521
374.9	.0000	1.0000	.7909	.2090	1.0000	.2795

TABLE XXIV

EQUILIBRIUM FLASH CALCULATIONS

Oil A

Run 102

γ = 1.213

V/L = .506

T_e = 273.0°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
204.0	.0000	.0000	.3852	.6147	.0000	3.1482
222.0	.0718	.2097	.4435	.5564	.1182	2.4750
243.5	.1117	.2958	.5171	.4828	.1737	1.8417
257.9	.1988	.4439	.5676	.4323	.2813	1.5028
272.3	.2468	.5094	.6178	.3821	.3352	1.2203
287.6	.3469	.6185	.6690	.3309	.4383	.9757
330.2	.4503	.7102	.7089	.2910	.5378	.8100
311.0	.5577	.7906	.7416	.2583	.6361	.6873
323.6	.6680	.8597	.7767	.2232	.7325	.5671
336.2	.7776	.9162	.8082	.1917	.8243	.4680
352.4	.9343	.9809	.8441	.1558	.9500	.3643
360.5	.9600	.9897	.8602	.1397	.9700	.3205
374.9	.9994	1.0010	.8864	.1135	1.0000	.2527

TABLE XXV

EQUILIBRIUM FLASH CALCULATIONS

Oil A

Run 103

γ = 1.003 T_e = 292.0°F

V/L = .004 P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	1/f	v/f	mole fraction feed	K_A
204.0	.0000	.0000	.1980	.8019	.0000	3.2636
222.0	.0552	.1689	.2370	.7629	.1182	2.5947
243.5	.0879	.2428	.2917	.7082	.1737	1.9570
257.9	.1619	.3775	.3334	.6665	.2813	1.6117
272.3	.2048	.4403	.3789	.6210	.3352	1.3211
287.6	.2983	.5510	.4304	.5695	.4383	1.0666
300.2	.3993	.6493	.4746	.5253	.5378	.8924
311.0	.5080	.7392	.5138	.4861	.6361	.7625
323.6	.6238	.8200	.5596	.4403	.7325	.6343
336.2	.7436	.8893	.6044	.3955	.8243	.5275
352.4	.9219	.9726	.6603	.3396	.9500	.4146
360.5	.9520	.9844	.6873	.3126	.9700	.3666
374.9	.9998	1.0001	.7341	.2658	1.0000	.2919

TABLE XXVI

EQUILIBRIUM FLASH CALCULATIONS

Oil A

Run 104

γ = .963

V/L =1.530

T_e = 296.2°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
204.0	.0000	.0000	.1657	.8342	.0000	3.2872
222.0	.0523	.1612	.1995	.8004	.1182	2.6198
243.5	.0834	.2326	.2479	.7520	.1737	1.9816
257.9	.1547	.3639	.2854	.7145	.2813	1.6352
272.3	.1963	.4259	.3272	.6727	.3352	1.3431
287.6	.2881	.5364	.3754	.6245	.4383	1.0866
300.2	.3880	.6356	.4177	.5822	.5378	.9106
311.0	.4965	.7272	.4560	.5439	.6361	.7794
323.6	.6131	.8104	.5015	.4984	.7325	.6493
336.2	.7350	.8826	.5470	.4529	.8243	.5409
352.4	.9184	.9706	.6052	.3947	.9500	.4261
360.5	.9497	.9832	.6339	.3660	.9700	.3772
374.9	.9997	1.0001	.6845	.3154	1.0000	.3010

TABLE XXVII

EQUILIBRIUM FLASH CALCULATIONS

Oil B

Run 105

$\Upsilon = .870$ $T_e = 323.6$ °F

$V/L = .232$ $P_e = 760.0$ mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	l/f	v/f	mole fraction feed	K_A
140.0	.0000	.0000	.3476	.6523	.0000	8.0982
261.5	.0417	.1529	.6850	.3149	.0627	1.9841
278.6	.0951	.2380	.7303	.2696	.1220	1.5936
295.2	.2006	.3881	.7710	.2289	.2359	1.2820
304.7	.3060	.5140	.7926	.2073	.3452	1.1290
316.4	.4112	.6236	.8175	.1824	.4512	.9633
325.8	.5153	.7175	.8360	.1639	.5534	.8464
335.3	.6189	.7994	.8531	.1468	.6529	.7432
324.1	.7209	.8716	.8643	.1356	.7493	.6775
354.2	.8317	.9361	.8831	.1168	.8433	.5712
392.0	.9186	.9806	.9286	.0713	.9303	.3315
415.4	.9611	.9932	.9483	.0516	.9672	.2349
527.0	1.0002	.9989	.9901	.0098	1.0000	.0430

TABLE XXVIII

EQUILIBRIUM FLASH CALCULATIONS

Oil B

Run 106

γ = .914

V/L = 1.130

T_e = 329.0°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
140.0	.0000	.0000	.0903	.9096	.0000	8.9045
261.5	.0267	.0945	.2846	.7153	.0627	2.2224
278.6	.0670	.1706	.3306	.6693	.1220	1.7899
295.2	.1535	.3086	.3798	.6201	.2359	1.4438
304.7	.2458	.4330	.4098	.5901	.3452	1.2735
316.4	.3428	.5469	.4481	.5518	.4512	1.0887
325.8	.4440	.6501	.4799	.5200	.5534	.9582
335.3	.5493	.7444	.5120	.4879	.6529	.8426
342.1	.6570	.8309	.5349	.4650	.7493	.7689
354.2	.7667	.9110	.5765	.4234	.8433	.6495
392.0	.8837	.9714	.6998	.3001	.9303	.3792
415.4	.9404	.9908	.7662	.2337	.9672	.2697
527.0	.9996	1.0003	.9462	.0537	1.0000	.0502

TABLE XXIX

EQUILIBRIUM FLASH CALCULATIONS

Oil B

Run 107

Υ = .7735

V/L = 2.630

T_e = 346.1°F

P_e = 760.0 mm Hg

	mole fraction				mole	
Temp. (°F)	liquid	vapor	l/f	v/f	fraction feed	K_A
140.0	.0000	.0000	.0418	.9581	.0000	8.7117
261.5	.0222	.0780	.1417	.8582	.0627	2.3011
278.6	.0569	.1467	.1690	.8309	.1220	1.8689
295.2	.1335	.2748	.2000	.7999	.2359	1.5201
304.7	.2172	.3928	.2200	.7799	.3452	1.3474
316.4	.3072	.5059	.2470	.7529	.4512	1.1589
325.8	.4032	.6104	.2705	.7294	.5534	1.0249
335.3	.5057	.7088	.2957	.7042	.6529	.9054
324.1	.6126	.8012	.3144	.6855	.7493	.8287
354.2	.7232	.8889	.3505	.6494	.8433	.7044
392.0	.8513	.9603	.4756	.5243	.9303	.4191
415.4	.9174	.9861	.5576	.4423	.9672	.3015
527.0	.9999	1.0000	.8653	.1346	1.0000	.0591

TABLE XXX

EQUILIBRIUM FLASH CALCULATIONS

Oil G

Run 110

γ = .933

V/L = .400

T_e = 424.4°F

P_e = 760.0 mm Hg

	mole fraction				mole	
Temp. (°F)	liquid	vapor	l/f	v/f	fraction feed	K_A
239.0	.0000	.0000	.2519	.7480	.0000	7.4106
331.7	.0324	.1360	.4699	.5300	.0621	2.8147
356.0	.0753	.2366	.5381	.4618	.1215	2.1422
381.2	.1655	.4026	.6092	.3907	.2334	1.6006
298.3	.2619	.5410	.6566	.3433	.3418	1.3049
417.2	.3610	.6562	.7059	.2940	.4455	1.0396
431.6	.4631	.7530	.7410	.2589	.5461	.8720
450.5	.5668	.8338	.7838	.2161	.6432	.6880
473.9	.6722	.8969	.8298	.1701	.7365	.5115
509.0	.7815	.9408	.8851	.1148	.8271	.3239
516.2	.8907	.9734	.8943	.1056	.9144	.2948
525.2	.9447	.9886	.9050	.0949	.9573	.2619
552.2	.9995	1.0010	.9315	.0684	1.0000	.1834

TABLE XXXI

EQUILIBRIUM FLASH CALCULATIONS

Oil G

Run 111

γ = .842

V/L = 1.320

T_e = 446.0°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	l/f	v/f	mole fraction feed	K_A
239.0	.0000	.0000	.0874	.9125	.0000	7.9072
331.7	.0210	.0931	.1944	.8055	.0621	3.1383
356.0	.0515	.1745	.2384	.7615	.1215	2.4197
381.2	.1207	.3187	.2926	.7073	.2334	1.8310
398.3	.1998	.4493	.3345	.6654	.3418	1.5072
417.2	.2864	.5659	.3846	.6153	.4455	1.2120
431.6	.3811	.6710	.4252	.5747	.5461	1.0239
450.5	.4829	.7646	.4814	.5185	.6432	.8161
473.9	.5944	.8440	.5523	.4476	.7365	.6140
509.0	.7230	.9059	.6568	.3431	.8271	.3958
516.2	.8594	.9560	.6769	.3230	.9144	.3616
525.2	.9276	.9797	.7013	.2986	.9576	.3227
552.2	1.0000	.9999	.7679	.2320	1.0000	.2288

TABLE XXXII

EQUILIBRIUM FLASH CALCULATIONS

Oil G

Run 112

Υ = .7065

V/L = 3.900

T_e = 471.2°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	1/f	v/f	mole fraction feed	K_A
239.0	.0000	.0000	.0312	.9687	.0000	7.9493
331.7	.0162	.0738	.0718	.9281	.0621	3.3101
356.0	.0403	.1423	.0901	.9098	.1215	2.5890
381.2	.0965	.2684	.1143	.8856	.2334	1.9870
398.2	.1626	.3877	.1342	.8657	.3418	1.6532
417.2	.2376	.4988	.1602	.8397	.4455	1.3433
431.6	.3223	.6034	.1831	.8168	.5461	1.1440
450.0	.4169	.7012	.2175	.7824	.6432	.9221
473.9	.5271	.7901	.2672	.7327	.7365	.7031
509.0	.6682	.8678	.3566	.6433	.8271	.4626
516.2	.8273	.9367	.3767	.6232	.9144	.4242
525.2	.9083	.9698	.4026	.5973	.9573	.3804
552.2	1.0000	.9999	.4836	.5163	1.0000	.2738

TABLE XXXIII

EQUILIBRIUM FLASH CALCULATIONS

Light Crude Naphtha (Sx-4031)

Run 34

Υ = .982

V/L = 1.140

T_e = 258.2°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
105.0	.0000	.0000	.1074	.8925	.0000	7.2814
140.0	.0112	.0651	.1534	.8465	.0400	4.8389
160.0	.0340	.1596	.1883	.8116	.1010	3.7786
180.0	.0529	.2219	.2311	.7688	.1430	2.1971
195.0	.0776	.2866	.2685	.7314	.1890	2.3887
210.0	.1256	.3891	.3109	.6890	.2660	1.9430
220.0	.1924	.5088	.3419	.6580	.3610	1.6873
230.0	.2222	.5558	.3744	.6255	.4000	1.4648
240.0	.2490	.5924	.4079	.5920	.4320	1.2729
250.0	.2845	.6344	.4431	.5568	.4710	1.1021
260.0	.3430	.6939	.4800	.5199	.5300	.9499
270.0	.3965	.7409	.5183	.4816	.5800	.8148
280.0	.4598	.7886	.5563	.4436	.6350	.6993
290.0	.5261	.8318	.5928	.4071	.6890	.6022
300.0	.5836	.8639	.6286	.3713	.7330	.5180
310.0	.6445	.8931	.6644	.3355	.7770	.4429
320.0	.7087	.9194	.6992	.3007	.8210	.3772
330.0	.7715	.9413	.7316	.2683	.8620	.3216
340.0	.8467	.9636	.7612	.2387	.9090	.2751
350.0	.9345	.9861	.7894	.2105	.9620	.2339
362.0	.9999	1.0000	.8205	.1794	1.0000	.1918

TABLE XXXIV

EQUILIBRIUM FLASH CALCULATIONS

Light Crude Naphtha (Sx-4031)

Run 36

$\gamma = 1.026$ $T_e = 243.86°F$

V/L = .481 $P_e = 760.0$ mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	1/f	v/f	mole fraction feed	K_A
105.0	.0000	.0000	.2394	.7605	.0000	6.6091
140.0	.0169	.0880	.3252	.6747	.0400	4.3163
160.0	.0496	.2079	.3842	.6157	.1010	3.3350
180.0	.0756	.2832	.4496	.5503	.1430	2.5467
195.0	.1081	.3573	.5012	.4987	.1890	2.0705
210.0	.1685	.4688	.5547	.4452	.2660	1.6703
220.0	.2494	.5931	.5905	.4094	.3610	1.4425
230.0	.2845	.6402	.6254	.3745	.4000	1.2460
240.0	.3149	.6756	.6587	.3412	.4320	1.0779
250.0	.3539	.7145	.6914	.3085	.4710	.9286
260.0	.4159	.7674	.7233	.2766	.5300	.7960
270.0	.4706	.8076	.7539	.2460	.5800	.6790
280.0	.5332	.8468	.7821	.2178	.6350	.5797
290.0	.5967	.8810	.8073	.1926	.6890	.4967
300.0	.6500	.9056	.8303	.1696	.7330	.4252
310.0	.7048	.9271	.8519	.1480	.7770	.3617
320.0	.7609	.9458	.8716	.1283	.8210	.3064
330.0	.8144	.9609	.8889	.1110	.8620	.2598
340.0	.8768	.9758	.9038	.0961	.9090	.2212
350.0	.9482	.9905	.9174	.0825	.9620	.1872
362.0	1.0002	.9994	.9317	.0682	1.0000	.1525

TABLE XXXV

EQUILIBRIUM FLASH CALCULATIONS

Light Crude Naphtha (Sx-4031)

Run 39

γ = .973

V/L = 2.714

T_e = 268.9°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	1/f	v/f	mole fraction feed	K_A
105.0	.0000	.0000	.0441	.9558	.0000	7.9728
140.0	.0081	.0517	.0642	.9357	.0400	5.3649
160.0	.0248	.1290	.0802	.9197	.1010	4.2216
180.0	.0390	.1813	.1008	.8991	.1430	3.2848
195.0	.0579	.2372	.1199	.8800	.1890	2.7037
210.0	.0956	.3287	.1427	.8572	.2660	2.2124
220.0	.1494	.4389	.1603	.8396	.3610	1.9290
230.0	.1740	.4832	.1797	.8202	.4000	1.6807
240.0	.1966	.5187	.2008	.7991	.4320	1.4653
250.0	.2274	.5607	.2244	.7755	.4710	1.2732
260.0	.2797	.6221	.2505	.7494	.5300	1.1018
270.0	.3289	.6724	.2796	.7203	.5800	.9490
280.0	.3893	.7255	.3106	.6893	.6350	.8176
290.0	.4546	.7753	.3427	.6572	.6890	.7065
300.0	.5133	.8139	.3765	.6234	.7330	.6098
310.0	.5778	.8503	.4130	.5869	.7770	.5234
320.0	.6484	.8845	.4514	.5485	.8210	.4475
330.0	.7202	.9142	.4903	.5096	.8620	.3829
340.0	.8092	.9457	.5284	.4715	.9090	.3287
350.0	.9166	.9787	.5676	.4323	.9620	.2806
362.0	.9998	1.0000	.6145	.3854	1.0000	.2310

TABLE XXXVI

EQUILIBRIUM FLASH CALCULATIONS

Heavy Crude Naphtha (Sx-4032)

Run 4032-1

γ = .873

V/L = 3.510

T_e = 375.93°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	1/f	v/f	mole fraction feed	K_A
232.71	.0000	.0000	.0554	.9445	.0000	4.8579
262.50	.0101	.0418	.0753	.9246	.0348	3.4979
303.76	.0372	.1131	.1224	.8775	.0963	2.0413
329.34	.0557	.1458	.1520	.8479	.1259	1.5890
337.67	.0892	.2077	.1657	.8342	.1835	1.4340
345.36	.1422	.2677	.1793	.8206	.2399	1.3032
350.92	.1875	.3245	.1899	.8100	.2942	1.3151
356.34	.2346	.3799	.2007	.7992	.3477	1.1343
361.33	.2824	.4323	.2123	.7876	.3991	1.0569
366.42	.3311	.4823	.2222	.7777	.4488	.9971
370.60	.3822	.5318	.2315	.7684	.4987	.9453
374.28	.4339	.5795	.2400	.7599	.5473	.9019
376.96	.4868	.6264	.2467	.7535	.5955	.8712
379.16	.5413	.6733	.2515	.7484	.6441	.8476
383.20	.5948	.7176	.2614	.7385	.6904	.8050
385.16	.6519	.7629	.2664	.7335	.7383	.7843
385.76	.7140	.8113	.2680	.7319	.7898	.7779
388.94	.7706	.8546	.2761	.7238	.8360	.7467
393.69	.8257	.8945	.2894	.7105	.8793	.6995
400.38	.8838	.9342	.3085	.6914	.9231	.6385
405.55	.8999	.9442	.3231	.6768	.9344	.5967
407.98	.9488	.9736	.3298	.6701	.9681	.5788
423.00	1.0000	.9999	.3918	.6081	1.0000	.4422

TABLE XXXVII

EQUILIBRIUM FLASH CALCULATIONS

Heavy Crude Naphtha (Sx-4032)

Run 4032-2

γ = .867

V/L = 1.176

T_e = 373.46°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	l/f	v/f	mole fraction feed	K_A
232.71	.0000	.0000	.1528	.8471	.0000	4.7144
262.50	.0133	.0530	.2006	.7993	.0348	3.3881
303.76	.0466	.1384	.3013	.6986	.0963	1.9712
329.34	.0680	.1750	.3569	.6430	.1259	1.5324
337.67	.1154	.2413	.3809	.6190	.1835	1.3821
345.36	.1636	.3047	.4038	.5961	.2399	1.2554
350.92	.2124	.3637	.4208	.5791	.2942	1.1701
356.34	.2623	.4202	.4378	.5621	.3477	1.0919
361.33	.3123	.4729	.4553	.5446	.3991	1.0170
366.42	.3623	.5223	.4699	.5300	.4488	.9592
370.60	.4141	.5706	.4833	.5166	.4987	.9091
374.28	.4658	.6165	.4951	.5048	.5473	.8672
376.96	.5182	.6611	.5038	.4961	.5955	.8375
379.16	.5718	.7055	.5107	.4892	.6441	.8147
383.20	.6239	.7469	.5236	.4763	.6904	.7735
385.16	.6788	.7888	.5301	.4698	.7383	.7536
385.76	.7384	.8334	.5322	.4677	.7898	.7474
388.94	.7924	.8730	.5424	.4575	.8360	.7173
393.69	.8442	.9091	.5587	.4412	.8793	.6717
400.38	.8980	.9444	.5812	.4187	.9231	.6128
405.55	.9125	.9530	.5976	.4023	.9344	.5724
407.98	.9562	.9781	.6049	.3950	.9681	.5552
423.00	1.0000	.9999	.6674	.3325	1.0000	.4236

TABLE XXXVIII

EQUILIBRIUM FLASH CALCULATIONS

Heavy Crude Naphtha (Sx-4032)

Run 4032-3

γ = .870

V/L = .531

T_e = 370.04°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction		1/f	v/f	mole fraction feed	K_A
	liquid	vapor				
232.71	.0000	.0000	.2917	.7082	.0000	4.5804
262.50	.0175	.0676	.3649	.6350	.0349	3.2830
303.76	.0580	.1685	.4979	.5020	.0963	1.9020
329.34	.0821	.2084	.5610	.4389	.1259	1.4757
337.67	.1336	.2775	.5864	.4135	.1835	1.3300
345.36	.1852	.3429	.6097	.3902	.2399	1.2073
350.92	.2366	.4026	.6264	.3735	.2942	1.1247
356.34	.2886	.4591	.6426	.3573	.3477	1.0490
361.33	.3398	.5109	.6588	.3411	.3991	.9765
366.42	.3904	.5589	.6720	.3279	.4488	.9206
370.60	.4421	.6053	.6838	.3161	.4987	.8722
374.28	.4934	.6489	.6940	.3059	.5473	.8317
376.96	.5449	.6909	.7013	.2986	.5955	.8031
379.16	.5972	.7324	.7071	.2928	.6441	.7811
383.20	.6476	.7709	.7178	.2821	.6904	.7413
385.16	.7005	.8095	.7231	.2768	.7383	.7220
385.76	.7576	.8505	.7248	.2751	.7898	.7161
388.94	.8091	.8867	.7330	.2669	.8360	.6870
393.69	.8580	.9193	.7457	.2542	.8793	.6430
400.38	.9083	.9509	.7629	.2370	.9231	.5862
405.55	.9216	.9584	.7750	.2249	.9344	.5474
407.98	.9615	.9804	.7803	.2196	.9681	.5308
423.00	1.0005	.9989	.8234	.1765	1.0000	.4043

TABLE XXXIX

EQUILIBRIUM FLASH CALCULATIONS

Kerosene (Sx-4033)

Run 4033-1

γ = .962

V/L = 2.020

T_e = 451.4°F

P_e = 760.0 mm Hg

	mole fraction				mole	
Temp. (°F)	liquid	vapor	l/f	v/f	fraction feed	K_A
370.0	.0000	.0000	.1650	.8349	.0000	2.5057
375.0	.0030	.0073	.1727	.8272	.0059	2.3709
379.0	.0055	.0131	.1808	.8191	.0106	2.2426
390.0	.0061	.0145	.1981	.8018	.0118	2.0045
400.0	.0491	.0616	.2167	.7832	.0575	1.7894
410.0	.0791	.1122	.2368	.7631	.1013	1.5957
420.0	.1221	.1769	.2583	.7416	.1588	1.4218
425.0	.1513	.2171	.2696	.7303	.1954	1.3413
430.0	.1903	.2678	.2813	.7186	.2422	1.2650
440.0	.3032	.4023	.3059	.6940	.3695	1.1233
445.0	.3650	.4697	.3187	.6812	.4351	1.0582
450.0	.4481	.5551	.3317	.6682	.5197	.9975
455.0	.5338	.6381	.3451	.6548	.6036	.9394
460.0	.6270	.7232	.3589	.6410	.6914	.8842
465.0	.6964	.7828	.3731	.6268	.7542	.8319
470.0	.7405	.8183	.3875	.6124	.7926	.7826
480.0	.8614	.9069	.4171	.5828	.8918	.6920
485.0	.9768	.9848	.4322	.5677	.9822	.6504
486.5	1.0002	.9998	.4368	.5631	1.0000	.6384

TABLE XL

EQUILIBRIUM FLASH CALCULATIONS

Kerosene (Sx-4033)

Run 4033-2

γ = 1.021

V/L = 1.201

T_e = 446.0°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	1/f	v/f	mole fraction feed	K_A
370.0	.0000	.0000	.2487	.7512	.0000	2.5148
375.0	.0032	.0080	.2593	.7406	.0059	2.3780
380.0	.0060	.0144	.2702	.7297	.0106	2.2479
390.0	.0067	.0159	.2932	.7067	.0118	2.0067
400.0	.0513	.0625	.3175	.6824	.0575	1.7891
410.0	.0832	.1163	.3431	.6568	.1013	1.5935
420.0	.1284	.1840	.3699	.6300	.1588	1.4181
425.0	.1588	.2258	.3837	.6162	.1954	1.3371
430.0	.1991	.2780	.3978	.6021	.2422	1.2602
440.0	.3146	.4151	.4269	.5730	.3695	1.1175
445.0	.3774	.4831	.4417	.5582	.4351	1.0521
450.0	.4610	.5685	.4564	.5435	.5197	.9912
455.0	.5467	.6509	.4715	.5284	.6036	.9329
460.0	.6392	.7348	.4868	.5131	.6914	.8775
465.0	.7075	.7930	.5022	.4977	.7542	.8250
470.0	.7506	.8275	.5176	.4823	.7926	.7756
480.0	.8674	.9122	.5486	.4513	.8619	.6850
485.0	.9777	.9858	.5640	.4359	.9822	.6434
486.5	.9999	1.0000	.5686	.4313	1.0000	.6314

TABLE XLI

EQUILIBRIUM FLASH CALCULATIONS

Kerosene (Sx-4033)

Run 4033-3

γ = 1.060

V/L = .614

T_e = 442.4°F

P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
370.0	.0000	.0000	.3928	.6071	.0000	2.5141
375.0	.0038	.0093	.4063	.5936	.0059	2.3763
380.0	.0069	.0165	.4200	.5799	.0106	2.2453
390.0	.0077	.0183	.4481	.5518	.0118	2.0027
400.0	.0543	.0625	.4769	.5230	.0575	1.7840
410.0	.0891	.1210	.5060	.4939	.1013	1.5877
420.0	.1376	.1932	.5353	.4646	.1588	1.4118
425.0	.1696	.2372	.5000	.4499	.1954	1.3306
430.0	.2118	.2915	.5647	.4352	.2422	1.2535
440.0	.3309	.4321	.5942	.4057	.3695	1.1100
445.0	.3947	.5007	.6088	.3911	.4351	1.0451
450.0	.4788	.5861	.6229	.3770	.5197	.9843
455.0	.5642	.6676	.6372	.3627	.6036	.9260
460.0	.6554	.7498	.6513	.3486	.6914	.8707
465.0	.7222	.8062	.6653	.3346	.7542	.8182
470.0	.7639	.8392	.6790	.3209	.7926	.7689
480.0	.8750	.9192	.7056	.2943	.8919	.6784
485.0	.9788	.9877	.7185	.2814	.9822	.6370
486.5	.9995	1.0007	.7223	.2776	1.0000	.6250

TABLE XLII

EQUILIBRIUM FLASH CALCULATIONS

Trade Gas Oil (Sx-4034)

Run 4034-1

Υ = .8187

V/L = 2.218

T_e = 546.8°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	l/f	v/f	mole fraction feed	K_A
250.0	.0000	.0000	.0318	.9681	.0000	13.6813
325.0	.0044	.0461	.0573	.9426	.0332	7.4053
366.0	.0077	.0661	.0803	.9196	.0480	5.1605
407.0	.0124	.0857	.1132	.8867	.0630	3.5288
428.0	.0274	.1306	.1349	.8650	.0986	2.8895
447.0	.0408	.1659	.1583	.8416	.1271	2.3962
469.0	.0738	.2354	.1900	.8099	.1852	1.9210
492.0	.1130	.3019	.2291	.7708	.2433	1.5167
504.0	.1434	.3451	.2519	.7480	.2825	1.3383
511.5	.1890	.4036	.2671	.7328	.3370	1.2364
516.0	.2351	.4592	.2763	.7236	.3896	1.1084
520.0	.2740	.5041	.2850	.7149	.4327	1.1306
525.5	.3218	.5566	.2972	.7027	.4837	1.0658
532.5	.3722	.6082	.3132	.6867	.5349	.9882
537.5	.4302	.6639	.3245	.6754	.5913	.9379
550.0	.5181	.7426	.3543	.6456	.6729	.8214
567.5	.5782	.7877	.3992	.6007	.7007	.6782
576.0	.6360	.8250	.4206	.5793	.7663	.6207
578.0	.6806	.8523	.4255	.5744	.7990	.6083
587.0	.7744	.9084	.4519	.5480	.8668	.5466
598.5	.8074	.9254	.4830	.5169	.8888	.4823
610.0	.8745	.9558	.5165	.4834	.9306	.4218
645.0	.9998	1.0000	.6145	.3854	1.0000	.2827

TABLE XLIII

EQUILIBRIUM FLASH CALCULATIONS

Trade Gas Oil (Sx-4034)

Run 4034-2

γ = .830

V/L = 1.137

T_e = 539.6°F

P_e = 760.0 mm Hg

	mole fraction				mole	
Temp. (°F)	liquid	vapor	l/f	v/f	fraction feed	K_A
250.0	.0000	.0000	.0619	.9380	.0000	13.3113
325.0	.0057	.0573	.1096	.8903	.0332	7.1422
366.0	.0098	.0815	.1508	.8491	.0480	4.9511
407.-	.0156	.1046	.2070	.7929	.0630	3.3672
428.0	.0335	.1557	.2423	.7576	.0986	2.7486
447.0	.0495	.1953	.2789	.7210	.1271	2.2735
469.0	.0874	.2711	.3261	.6738	.1852	1.8170
492.0	.1314	.3416	.3807	.6192	.2433	1.4300
504.0	.1646	.3861	.4110	.5889	.2825	1.2598
511.5	.2137	.4453	.4306	.5693	.3370	1.1626
516.0	.2628	.5010	.4421	.5578	.3896	1.1095
520.0	.3040	.5457	.4529	.5470	.4327	1.0619
525.5	.3542	.5975	.4678	.5321	.4837	1.0002
532.5	.4065	.6477	.4869	.5130	.5349	.9264
537.5	.4661	.7013	.5001	.4998	.5913	.8788
550.0	.5554	.7761	.5335	.4664	.6729	.7686
567.5	.6146	.8177	.5814	.4185	.7227	.6331
576.0	.6699	.8510	.6029	.3970	.7663	.5789
578.0	.7122	.8752	.6078	.3921	.7990	.5673
587.0	.8010	.9245	.6334	.3665	.8668	.5088
598.5	.8314	.9391	.6622	.3377	.8888	.4484
610.0	.8918	.9646	.6919	.3080	.9306	.3914
645.0	.9999	1.0000	.7710	.2289	1.0000	.2611

TABLE XLIV

EQUILIBRIUM FLASH CALCULATIONS

Trade Gas Oil (Sx-4034)

Run 4034-3

γ = .853

V/L = .702

T_e = 532.0°F

P_e = 760.0 mm Hg

	mole fraction				mole	
Temp. (°F)	liquid	vapor	l/f	v/f	fraction feed	K_A
250.0	.0000	.0000	.0981	.9018	.0000	13.0857
325.0	.0071	.0702	.1699	.8300	.0332	6.9551
366.0	.0121	.0990	.2290	.7709	.0480	4.7942
407.0	.0190	.1255	.3052	.6947	.0630	3.2416
428.0	.0398	.1821	.3506	.6493	.0986	2.6371
447.0	.0580	.2254	.3956	.6043	.1271	2.1753
469.0	.1003	.3060	.4511	.5488	.1852	1.7328
492.0	.1480	.3789	.5116	.4883	.2433	1.3591
504.0	.1833	.4237	.5436	.4563	.2825	1.1953
511.5	.2347	.4826	.5638	.4361	.3370	1.1017
516.0	.2857	.5374	.5753	.4246	.3896	1.0510
520.0	.3283	.5812	.5862	.4137	.4327	1.0052
525.5	.3799	.6315	.6008	.3991	.4837	.9459
532.5	.4331	.6798	.6193	.3806	.5349	.8752
537.5	.4932	.7309	.6318	.3681	.5913	.8298
550.0	.5826	.8014	.6627	.3372	.6729	.7245
567.5	.6404	.8398	.7052	.2947	.7227	.5952
576.0	.6935	.8698	.7236	.2763	.7663	.5439
578.0	.7340	.8915	.7276	.2723	.7990	.5329
587.0	.8184	.9355	.7490	.2509	.8668	.4770
598.5	.8469	.9483	.7723	.2276	.8888	.4198
610.0	.9026	.9703	.7956	.2043	.9306	.3657
645.0	.9999	1.0001	.8543	.1456	1.0000	.2427

TABLE XLV

EQUILIBRIUM FLASH CALCULATIONS

Trade Gas Oil (Sx-4034)

Run 4034-4

γ = .960 T_e = 509.0°F

V/L = .246 P_e = 760.0 mm Hg

	mole fraction					
Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
250.0	.0000	.0000	.2413	.7586	.0000	12.7895
325.0	.0125	.1173	.3814	.6185	.0332	6.5969
366.0	.0204	.1602	.4766	.5233	.0480	4.4671
407.0	.0303	.1958	.5784	.4215	.0630	2.9655
428.0	.0581	.2632	.6302	.3697	.0986	2.3873
447.0	.0813	.3132	.6757	.3242	.1271	1.9524
469.0	.1324	.3999	.7255	.2744	.1852	1.5393
492.0	.1867	.4743	.7730	.2269	.2433	1.1946
504.0	.2250	.5161	.7956	.2043	.2825	1.0450
511.5	.2795	.5705	.8091	.1908	.3370	.9597
516.0	.3328	.6203	.8165	.1834	.3896	.9143
520.5	.3769	.6597	.8234	.1765	.4327	.8725
525.5	.4295	.7042	.8324	.1675	.4827	.8188
532.5	.4829	.7461	.8434	.1565	.5349	.7549
537.5	.5425	.7897	.8506	.1493	.5913	.7146
550.0	.6296	.8488	.8675	.1324	.6729	.6209
567.5	.6841	.8796	.8893	.1106	.7227	.5060
576.0	.7326	.9030	.8982	.1017	.7663	.4611
578.0	.7693	.9196	.9000	.0999	.7990	.4516
587.0	.8455	.9532	.9101	.0898	.8668	.4019
598.5	.8706	.9672	.9203	.0796	.8888	.3521
610.0	.9188	.9786	.9302	.0697	.9306	.3048
645.0	1.0001	.9993	.9533	.0466	1.0000	.1991

TABLE XLVI

EQUILIBRIUM FLASH CALCULATIONS

Heavy Gas Oil (Sx-4035)

Run 4035-1

γ = 1.410

V/L = .262

T_e = 545.0°F

P_e = 760.0 mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	l/f	v/f	mole fraction feed	K_A
250.0	.0000	.0000	.1417	.8582	.0000	23.0936
315.0	.0066	.1278	.2185	.7814	.0318	13.6382
406.0	.0151	.2055	.3871	.6128	.0547	6.0375
451.5	.0373	.3120	.4957	.5042	.0944	3.8788
480.0	.0575	.3798	.5676	.4323	.1245	2.9053
535.0	.1528	.5871	.7011	.2988	.2431	1.6257
564.0	.2137	.6718	.7624	.2375	.3089	1.1880
590.0	.2756	.7352	.8110	.1889	.3711	.8883
607.0	.3314	.7802	.8379	.1620	.4247	.7373
619.0	.3896	.8202	.8558	.1441	.4791	.6422
631.0	.4580	.8611	.8718	.1281	.5418	.5604
647.5	.5164	.8910	.8918	.1081	.5943	.4626
667.0	.5747	.9152	.9120	.0879	.6455	.3679
680.5	.6305	.9342	.9238	.0761	.6936	.3141
692.0	.6817	.9492	.9326	.0673	.7373	.2753
703.5	.7259	.9606	.9410	.0589	.7747	.2387
717.0	.7694	.9702	.9491	.0508	.8112	.2041
730.5	.8319	.9820	.9572	.0427	.8631	.1702
755.5	.9036	.9924	.9695	.0304	.9221	.1198
776.5	.9226	.9945	.9755	.0244	.9376	.0954
791.0	.9998	1.0004	.9796	.0203	1.0000	.0793

TABLE XLVII

EQUILIBRIUM FLASH CALCULATIONS

Heavy Gas Oil (Sx-4035)

Run 4035-2

$\gamma = 2.050$ $T_e = 501.8$°F

$V/L = .176$ $P_e = 760.0$ mm Hg

Temp. (°F)	mole fraction liquid	mole fraction vapor	l/f	v/f	mole fraction feed	K_A
250.0	.0000	.0000	.1797	.8202	.0000	25.8738
315.0	.0079	.1671	.2802	.7197	.0318	14.5607
406.0	.0180	.2627	.4868	.5131	.0547	5.9769
451.5	.0436	.3822	.6057	.3942	.0944	3.6898
480.0	.0664	.4539	.6779	.3220	.1245	2.6931
535.0	.1698	.6586	.7977	.2022	.2431	1.4371
564.0	.2335	.7361	.8467	.1532	.3089	1.0261
590.0	.2969	.7916	.8831	.1168	.3711	.7498
607.0	.3532	.8296	.9021	.0978	.4247	.6146
619.0	.4113	.8627	.9145	.0854	.4790	.5295
631.0	.4793	.8961	.9253	.0746	.5418	.4577
647.5	.5368	.9200	.9383	.0616	.5943	.3724
667.0	.5937	.9388	.9511	.0488	.6455	.2912
680.5	.6477	.9533	.9584	.0415	.6936	.2459
692.0	.6971	.9646	.9636	.0363	.7373	.2137
703.5	.7397	.9731	.9686	.0313	.7747	.1833
717.0	.7814	.9801	.9733	.0266	.8112	.1551
730.5	.8409	.9886	.9779	.0220	.8631	.1275
755.5	.9090	.9959	.9848	.0151	.9221	.0872
776.5	.9270	.9973	.9880	.0119	.9376	.0687
791.0	.9997	1.0013	.9901	.0098	1.0000	.0563

APPENDIX E

SMOOTHED K_A-VALUES

The smoothed K-values for each oil investigated are presented here as a function of normal boiling point, T_b, and at constant equilibrium temperature, T_e.

The vapor-liquid distribution ratios for various petroleum fractions were smoothed by fitting the derived K-values to a quadratic function of log K versus the reciprocal of the normal boiling point. The function was:

$$\log K = A + B/T_b + C/T_b^2$$

where A, B, and C were the regression coefficients.

Using the above equation, smoothed K-values were calculated at even increments of boiling temperature and are presented in the following tables.

TABLE XLVIII

SMOOTHED K_A-VALUES DERIVED FOR OIL A

P_e = 760 mm Hg

T_b, °F	T_e = 286.0°F	T_e = 273.0°F	T_e = 292.0°F	T_e = 296.2°F
	Run 101	Run 102	Run 103	Run 104
180.00	4.22805	4.16229	4.25218	4.27234
190.00	3.78715	3.71267	3.81586	3.38390
200.00	3.37259	3.29225	3.40458	3.42962
210.00	2.98787	2.90420	3.02200	3.04826
220.00	2.63506	2.55020	2.67031	2.69712
230.00	2.31460	2.23031	2.35014	2.37694
240.00	2.02596	1.94365	2.06112	2.08744
250.00	1.76790	1.68863	1.80213	1.82764
260.00	1.53862	1.46318	1.57152	1.59593
270.00	1.33600	1.26491	1.36727	1.39041
280.00	1.15782	1.09139	1.18727	1.20901
290.00	1.00174	.94012	1.02926	1.04954
300.00	.86552	.80873	.89105	.90985
310.00	.74700	.69493	.77055	.78787
320.00	.64413	.59663	.66575	.68163
330.00	.55505	.51190	.57480	.58931
340.00	.47807	.43900	.49604	.50925
350.00	.41162	.37637	.42793	.43990
360.00	.35436	.32264	.36911	.37994
370.00	.30506	.27658	.31836	.32814
380.00	.26264	.23713	.27462	.28342
390.00	.22618	.20336	.23594	.24485
400.00	.19484	.17446	.20449	.21159
410.00	.16792	.14973	.17656	.18293

TABLE XLIX

1 of 2

SMOOTHED K_A-VALUES DERIVED FOR OIL B

P_e = 760 mm Hg

	K_A-Values		
T_b, °F	T_e = 323.6°F Run 105	T_e = 329.0°F Run 106	T_e = 346.1°F Run 107
140.00	7.89707	8.68906	8.49992
150.00	7.36357	8.11258	7.96717
160.00	6.79866	7.50038	7.39631
170.00	6.22214	6.87401	6.80770
180.00	5.64976	6.25073	6.21789
190.00	5.09408	5.64434	5.64030
200.00	4.56448	5.06523	5.08524
210.00	4.06712	4.52031	4.55979
220.00	3.60618	4.01432	4.06899
230.00	3.18355	3.54951	3.61552
240.00	2.79965	3.12650	3.20045
250.00	2.45377	2.74468	2.82367
260.00	2.14431	2.40244	2.48404
270.00	1.86906	2.09749	2.17973
280.00	1.62557	1.82725	1.90855
290.00	1.41114	1.58882	1.66798
300.00	1.22305	1.37932	1.45543
310.00	1.05864	1.19586	1.26829
320.00	.91534	1.03568	1.10401
330.00	.79075	.89618	.96017
340.00	.68268	.77497	.83452
350.00	.58909	.66981	.72493
360.00	.50818	.57875	.62953
370.00	.43831	.49998	.54658
380.00	.37803	.43192	.47453
390.00	.32608	.37316	.41200
400.00	.28133	.32245	.35777
410.00	.24280	.27872	.31077
420.00	.20963	.24102	.27004
430.00	.18108	.20852	.23476
440.00	.15651	.18050	.20419
450.00	.13526	.15635	.17770
460.00	.11715	.13552	.15475
470.00	.10146	.11755	.13486
480.00	.08795	.10205	.11762
490.00	.07630	.08866	.10266
500.00	.06626	.07710	.08968

TABLE XLIX (continued) 2 of 2

K_A-Values

T_b, °F	T_e = 323.6°F Run 105	T_e = 329.0°F Run 106	T_e = 346.1°F Run 107
510.00	.05759	.06711	.07841
520.00	.05010	.05847	.06862
530.00	.04363	.05099	.06010
540.00	.03803	.04451	.05269
550.00	.03318	.03889	.04625

TABLE L

SMOOTHED K_A-VALUES DERIVED FOR OIL G

P_e = 760 mm Hg

	K_A-Values		
T_b, °F	T_e = 424.4°F Run 110	T_e = 446.0°F Run 111	T_e = 471.2°F Run 112
220.00	8.39675	8.88365	8.86469
230.00	7.83230	8.32028	8.33840
240.00	7.25695	7.74186	7.79386
250.00	6.68336	7.16133	7.24341
260.00	6.12160	6.58912	6.69717
270.00	5.57942	6.03345	6.16323
280.00	5.06284	5.50085	5.64815
290.00	4.57581	4.99575	5.15655
300.00	4.12090	4.52122	4.69180
310.00	3.69943	4.07904	4.25604
320.00	3.31163	3.66986	3.85027
330.00	2.95702	3.29356	3.47480
340.00	2.63452	2.94940	3.12928
350.00	2.34254	2.62607	2.81276
360.00	2.07939	2.35207	2.52410
370.00	1.84305	2.09558	2.26179
380.00	1.63145	1.86467	2.02420
390.00	1.44259	1.65742	1.80964
400.00	1.27440	1.47184	1.61634
410.00	1.12498	1.30605	1.44261
420.00	.99248	1.15823	1.28676
430.00	.87516	1.02664	1.14719
440.00	.77143	.90967	1.02237
450.00	.67984	.80582	.91089
460.00	.59905	.71372	.81144
470.00	.52784	.63212	.72279
480.00	.46512	.55986	.64383
490.00	.40991	.49591	.57354
500.00	.36132	.43935	.51101
510.00	.31858	.38933	.45539
520.00	.28100	.34512	.40594
530.00	.24794	.30604	.36198
540.00	.21887	.27149	.32291
550.00	.19331	.24096	.28817
560.00	.17082	.21397	.25729
570.00	.15103	.19010	.22984

TABLE LI

SMOOTHED K_A-VALUES DERIVED FOR LIGHT CRUDE NAPHTHA (Sx-4031)

P_e = 760 mm Hg

T_b, °F	T_e = 258.2°F Run 34	T_e = 243.8°F Run 36	T_e = 268.9°F Run 39
	K_A-Values		
100.00	7.33377	6.66718	8.02909
110.00	6.72708	6.08698	7.38944
120.00	6.11263	5.50436	6.73756
130.00	5.50821	4.93564	6.09272
140.00	4.92720	4.39287	5.46965
150.00	4.37909	3.88431	4.87894
160.00	3.86986	3.41493	4.32755
170.00	3.40299	2.98733	3.81969
180.00	3.97954	2.60191	3.35698
190.00	2.59904	2.25770	2.93937
200.00	2.25988	1.95273	2.56551
210.00	1.95955	1.68428	2.23304
220.00	1.69521	1.44938	1.93916
230.00	1.46367	1.24483	1.68069
240.00	1.26174	1.06744	1.45431
250.00	1.08626	.91417	1.25680
260.00	.93424	.78214	1.08500
270.00	.80288	.66867	.93594
280.00	.68963	.57139	.80692
290.00	.59215	.48811	.69543
300.00	.50837	.41692	.59924
310.00	.43646	.35614	.51636
320.00	.37478	.30428	.44500
330.00	.32192	.26006	.38361
340.00	.27663	.22237	.33082
350.00	.23783	.19025	.28543
360.00	.20461	.16289	.24642
370.00	.17615	.13956	.21288
380.00	.15177	.11968	.18405

TABLE LII

SMOOTHED K_A-VALUES DERIVED FOR HEAVY CRUDE NAPHTHA (Sx-4032)

P_e = 760 mm Hg

	K_A-Values		
T_b, °F	T_e = 375.9°F Run 4032-1	T_e = 373.4°F Run 4032-2	T_e = 370.0°F Run 4032-3
200.00	6.46784	6.28877	6.12420
210.00	5.95230	5.78418	5.62830
220.00	5.44475	5.28784	5.14108
230.00	4.95340	4.80773	4.67035
240.00	4.48443	4.34984	4.22192
250.00	4.04224	3.91846	3.79989
260.00	3.62957	3.51616	3.40674
270.00	3.24776	3.14424	3.04366
280.00	2.89730	2.80311	2.71099
290.00	2.57770	2.49224	2.40814
300.00	2.28794	2.21062	2.13406
310.00	2.02660	1.95680	1.88729
320.00	1.79190	1.72902	1.66607
330.00	1.58196	1.52541	1.46851
340.00	1.39481	1.34405	1.29272
350.00	1.22844	1.18293	1.13670
360.00	1.08095	1.04021	.99863
370.00	.95048	.91403	.87669
380.00	.83528	.80271	.76921
390.00	.73374	.70466	.67463
400.00	.64436	.61840	.59151
410.00	.56577	.54262	.51855
420.00	.49675	.47611	.45458
430.00	.43617	.41777	.39852
440.00	.38303	.36663	.34942
450.00	.33644	.32182	.30645
460.00	.29561	.28259	.26885

TABLE LIII

SMOOTHED K_A-VALUES DERIVED FOR KEROSENE (Sx-4033)

P_e = 760 mm Hg

		K_A-Values	
T_b, °F	T_e = 451.4°F Run 4033-1	T_e = 446.0°F Run 4033-2	T_e = 442.4°F Run 4033-3
300.00	5.08563	5.14961	5.18156
310.00	4.64197	4.69514	4.72027
320.00	4.22094	4.26443	4.28362
330.00	3.82501	3.85994	3.87399
340.00	3.45561	3.48306	3.49275
350.00	3.11323	3.13421	3.14022
360.00	2.79791	2.81336	2.81633
370.00	2.50899	2.51977	2.52026
380.00	2.24551	2.25238	2.25088
390.00	2.00625	2.00990	2.00683
400.00	1.78975	1.79077	1.78651
410.00	1.59452	1.59343	1.58828
420.00	1.41897	1.41622	1.41044
430.00	1.26150	1.25748	1.25128
440.00	1.12058	1.11560	1.10916
450.00	.99471	.98905	.98251
460.00	.88250	.87637	.86985
470.00	.78260	.77618	.76976
480.00	.69378	.68722	.68098
490.00	.61489	.60832	.60229
500.00	.54490	.53840	.53263
510.00	.48285	.47649	.47101

TABLE LIV

SMOOTHED K_A-VALUES DERIVED FOR TRADE GAS OIL
(Sx-4034)

P_e = 760 mm Hg

T_b, °F	T_e = 546.8°F Run 4034-1	T_e = 539.6°F Run 4034-2	T_e = 532.0°F Run 4034-3	T_e = 509.0°F Run 4034-4
200.00	15.44326	15.09561	14.90125	14.81767
220.00	14.82590	14.47064	14.27006	14.10493
240.00	13.76739	13.41362	13.20248	12.96751
260.00	12.43629	12.09236	11.87635	11.58301
280.00	10.97958	10.65246	10.43751	10.10222
300.00	9.51209	9.20697	8.99848	8.63909
320.00	8.11385	7.83416	7.63651	7.26965
340.00	6.83392	6.59142	6.39777	6.03734
360.00	5.69694	5.47198	5.30431	4.96079
380.00	4.71010	4.51195	4.36113	4.04167
400.00	3.86891	3.69604	3.56209	3.27087
420.00	3.16195	3.01237	2.89468	2.63348
440.00	2.57435	2.44579	2.34331	2.11213
460.00	2.09023	1.98035	1.89177	1.68936
480.00	1.69404	1.60056	1.52447	1.34880
500.00	1.37147	1.29223	1.22719	1.07582
520.00	1.10988	1.04290	.98752	.85783
540.00	.89831	.84182	.79481	.68420
560.00	.72752	.67994	.64013	.54612
580.00	.58981	.54976	.51612	.43643
600.00	.47881	.44513	.41672	.34930
620.00	.38933	.36101	.33703	.28008
640.00	.31717	.29335	.27312	.22504
660.00	.25892	.23887	.22180	.18122

TABLE LV

SMOOTH K_A-VALUES DERIVED FOR HEAVY GAS OIL (Sx-4035)

P_e = 760 mm Hg

	K_A-Values	
T_b, °F	T_e = 545.0°F Run 4035-1	T_e = 501.8°F Run 4035-2
220.00	21.36202	24.17734
240.00	21.19461	23.78649
260.00	20.19069	22.42416
280.00	18.58849	20.39600
300.00	16.63066	18.00342
320.00	14.52732	15.49869
340.00	12.43917	13.06707
360.00	10.47547	10.82771
380.00	8.70182	8.84487
400.00	7.14729	7.14104
420.00	5.81689	5.71101
440.00	4.69923	4.53263
460.00	3.77420	3.57593
480.00	3.01757	2.80818
500.00	2.40441	2.19771
520.00	1.91122	1.71584
540.00	1.51677	1.33758
560.00	1.20267	1.04188
580.00	.95337	.81145
600.00	.75594	.63225
620.00	.59983	.49305
640.00	.47647	.38500
660.00	.37902	.30111
680.00	.30202	.23595
700.00	.24112	.18529
720.00	.19291	.14584
740.00	.15470	.11509
760.00	.12436	.09106
780.00	.10022	.07225
800.00	.08098	.05749
820.00	.06561	.04588

APPENDIX F

COMPARISON OF EQUILIBRIUM FUNCTIONS DERIVED FROM PETROLEUM FRACTIONS ANALYSED BY THE CHROMATOGRAPH AND THE OLDERSHAW COLUMN

There are three major differences in the calculational procedure used for deriving K-values from the chromatographic assays of Walston (18) and the Oldershaw assays obtained in this work. These differences appear in: (1) initial analytical data, (2) critical temperature and pressure, and (3) vapor pressure.

The initial analytical assays from the chromatographic distillations were obtained as weight fraction off versus boiling point. The only physical property necessary to convert these assays to a molar basis was molecular weight. The initial Oldershaw assay was obtained as volume fraction off versus normal boiling point. For this assay the physical properties of specific gravity and molecular weight were needed to convert from a volumetric basis to a molar one. A comparison of the molar true boiling point curves determined by these two methods is given in the work of Walston (18).

The second difference in calculation procedure was that of obtaining the critical values for the calculation of the imperfection pressure correction coefficient, Θ. The correlations used in computer program 1 for calculating these critical properties are based on specific gravity and boiling point. Specific gravities were not necessary with the chromatographic distillations and, therefore, the critical properties were found by other means as described by Walston (18). The critical properties used in this work were obtained by using the correlations mentioned in Appendix B. The differences in critical values are shown in the final calculations by differences in the imperfection pressure correction and are compared in the following table.

The third calculation procedure difference was the method used to determine the vapor pressure. The correlation offered in computer program 1 for the determination of vapor pressures was a function of the critical temperature.

This vapor pressure correlation could have been used in both calculation methods but was used only with those analyses completed on the Oldershaw column. The vapor pressures for the other method were obtained from Maxwell and Bonnell (12). A comparison of vapor pressures is given in Table VIII, Appendix B.

TABLE LVI

Comparison of Imperfection Pressure Correction

Feedstock (Sx-4032)

$T_e = 369.5$°F

$P_e = 760.0$ mm Hg

Temp. (°F)	θ^*	θ^{**}
232.0	1.12	1.15
262.0	1.10	1.11
308.0	1.06	1.06
337.0	1.03	1.03
362.0	1.01	1.02
370.0	1.00	1.00
383.0	0.99	0.99

Feedstock (Sx-4034)

$T_e = 359.6$°F

$P_e = 760.0$ mm Hg

Temp. (°F)	θ^*	θ^{**}
325.0	1.04	1.00
407.0	0.96	0.97
428.0	0.95	0.94
447.0	0.93	0.93
469.0	0.92	0.92
492.0	0.90	0.90

θ^* Walston

θ^{**} This work

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