EVALUATION OF VAPORIZATION CHARACTERISTICS
OF PETROLEUM FRACTIONS

By

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PREFACE

One of the problems process design engineers encounter today is the shortage of accurate vapor-liquid equilibrium data. This investigation is directed at this problem.

The procedure was to derive first ideal vapor-liquid equilibrium ratios for heavy hydrocarbon oils from their vapor pressures, the system pressure, and the imperfection pressure correction. The calculated ideal K-values were then corrected with an activity coefficient derived from experimental flash vaporizations by applying the integral technique.

The author is grateful to Professor W. C. Edmister, his adviser, for his aid and guidance during this work.

I also extend my appreciation to the School of Chemical Engineering and to Esso Research and Engineering Company for the financial support and fellowship that made this work possible.

I am indebted to Dr. Amir-Yeganeh, Mr. C. B. Woodward and Mr. C. L. Henderson for their numerous suggestions and assistance in many areas of this work.

My deepest appreciation and gratitude go to my parents and my wife, Sue, whose continuous encouragement, aid and patience made my graduate work possible.

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CHAPTER I

INTRODUCTION

Experimental and calculated phase equilibrium ratios or K-values of heavy hydrocarbons have extensive industrial use in the design of process equipment, such as fractionators, strippers and all types of vapor-liquid contacting devices.

The petroleum industry is always in need of methods to obtain faster and more accurate equilibrium data. To obtain faster and more accurate K-values, the methods described in this thesis were developed.

This work presents a solution to part of the problems encountered in evaluating hydrocarbon systems and proposes a gas chromatographic technique for acquiring molar TBP (True Boiling Point) assays.

Conventional assay methods, such as the Oldershaw and Sarnia Mark II analytical distillation units, were also used to fractionate the oils, thus allowing a comparison to be made between the standard and new techniques for generating equilibrium data.

A new method for determining average molecular weights of multicomponent mixtures in the 20 to 200 atomic mass unit range was needed. As part of this work an instrument was developed, tested and put into routine laboratory use that allows these measurements to be made, applying a vapor density technique.

It was apparent during the design, testing and periods of operation of the molecular weight instrument that a manual or record of the operating procedure and characteristics should be available to future operators of the instrument. A section of the thesis is devoted to the operation and "trouble shooting" of the new molecular weight apparatus.

Equilibrium vaporization ratios were derived, applying the integral technique, from data obtained using the new laboratory methods and were compared to the K values calculated from conventional methods.

Recommendations for better and faster techniques are discussed.

CHAPTER II

DISTILLATION ASSAYS

In this chapter both chromatographic and batch fractional distillation assays are discussed. These are the methods that were used to separate the pseudo (hypothetical or discrete) components of petroleum fractions according to their boiling points.

Fractionations performed using a sieve plate column (Oldershaw) and a packed column (Sarnia Mark II) are compared with the results obtained from programmed temperature gas chromatography. The speed and small sample requirements of the gas chromatograph make it a good analytical tool. However, like many analytical methods for separation it is dependent on several system variables that are discussed in this section. The chromatograph was used to establish a method of preparing precision distillation curves.

The ASTM D-86 distillation was used to distill the bottoms fraction that could not be distilled in the Sarnia and Oldershaw columns. The unit is available commercially and described in the "ASTM Standards Handbook" (1). Since its use and operation is general knowledge in the petroleum industry, a description is not given here.

Sarnia Fractionator

The Sarnia Mark II Fractionator is called a "15-5" distillation unit signifying: 15 theoretical plates at total reflux but operated at a 5:1 reflux ratio (10). Cannon protruded metal packing (8) is used as packing because of its high throughput capacity.

The reflux device, (Figure 1), is compact and is built immediately above the packed section. There is little heat leak below the reflux divider and most of the reflux is produced above this point.

Condensate runs down the walls from the condenser and is collected in a ring device that is built into the wall of the tower. Here, the total condensate is taken off or returned to the tower as reflux. The take-off vapor comes from opposite sides of the collector ring at the center of the tower and is passed through the liquid cooler, then into a graduated receiver.

A thermocouple together with a Leeds and Northrup potentiometer is used for temperature measurement. If this method of temperature measurement is to be continued it is recommended that an automatic instrument be used for recording the temperature variable.

Tower pressure was controlled using a back pressure system,

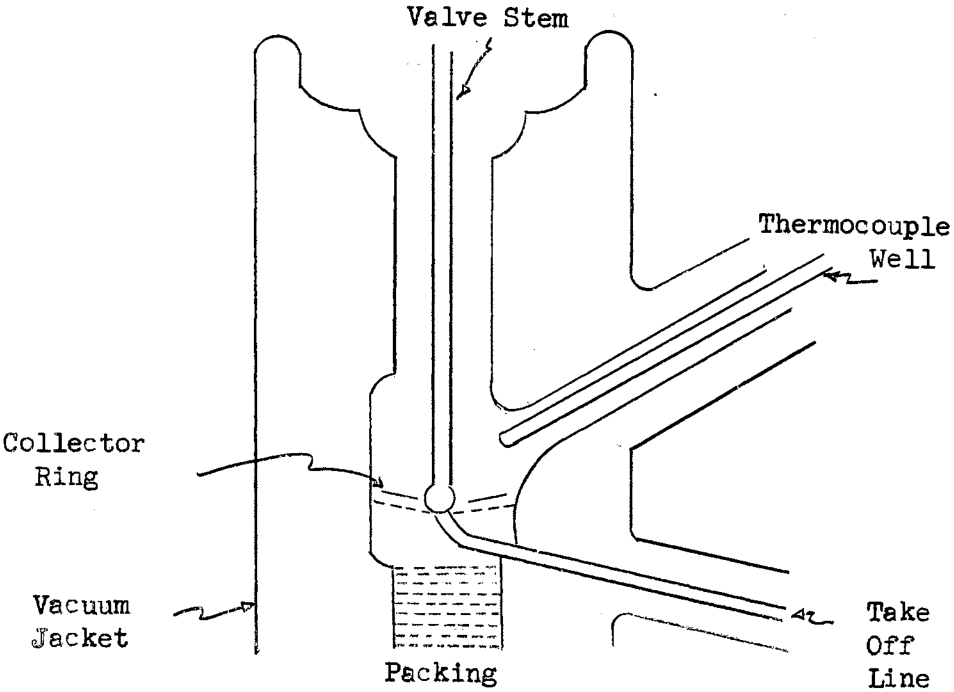


Figure 1

Sarnia Reflux Head

that consisted of a surge tank, necessary tubing and compressed air, where air is bubbled through a tube submerged in water to a depth sufficient to compensate for the difference between 760 mm Hg and local atmospheric pressure.

The liquid receiver was connected to the same pressure system as the column, thus allowing the removal of collected liquid without disrupting the system pressure.

The Sarnia Fractionator, which was recommended by Esso Research and Engineering Company and purchased for this work, gave difficulty in attempts to obtain reproducible volumetric TBP curves. Previous work, using this piece of apparatus, reported disagreement between consecutive assays as high as 14°F (39). To aid in solving the difficulty of operating the Mark II Fractionator, Mr. G. M. Cooke of Imperial Oil Limited, Sarnia Ontario, Canada, came for a one week visit to our laboratories, at our request. Mr. Cooke's recommendations for operating the Sarnia Fractionator and a summary of his visit are given in the Appendix. By following his suggestions and recommendations, reproducible TBP data were obtained from the Sarnia still; however, the accuracy of the apparatus was not satisfactory for our work.

Oldershaw Column

The Oldershaw column uses sieve plates for the separation of hydrocarbons. Five, 10, 15, and 20 plate sections are commercially available, each with a silvered vacuum jacket for insulation. The 30 plate column, 10 and 20 plate sections combined, used in this study was made of Pyrex glass with expansion bellows to allow operation up to 500°F.

The Oldershaw column was selected for this work because of its high plate efficiency (approximately 60%) and reproducibility. Its normal reproducibility for consecutive assays on the same feed stock was ± 1°F.

The Oldershaw column gave no difficulty in operation. A full description and operating characteristics of the column have been given previously by Amir-Yeganeh (2) and Woodward (39). Henderson also included a description (22).

Programmed Temperature Gas Chromatography

The technique of using programmed temperature gas chromatography was investigated to obtain information on hydrocarbons analogous to that obtained from conventional analytical distillation.

The general literature (16) method was used with modifications to make an extensive study of the variable effects for n-paraffins and to a limited extent for condensed aromatics. The purpose of the study was to establish a method for determining true boiling point assays for petroleum fractions at optimum conditions regardless of boiling range or molecular species.

The normal boiling points of the pseudo-components were correlated with the emergence temperatures for hydrocarbons of varied species and molecular weights.

The value of this technique lies in the ability to separate mixtures with a wide boiling range in short periods of time. Separation of wide boiling mixtures can sometimes be achieved isothermally in a column, but only at the expense of long waiting times for the high boiling components. The increased waiting time often results in a very high dilution which leads to indeterminate peaks.

In programmed temperature analysis of a wide boiling mixture the ideal temperature of each narrow boiling fraction is obtained in succession. Therefore, each group of substances or pseudo-component selects its own temperature at which to migrate within the column. Prior to reaching this migration or boiling temperature, the component is frozen or condensed in the first of the column waiting its time or temperature while the lower boiling components are in the process of separation.

Programmed temperature gas chromatography then obtains its success by automatically selecting the appropriate temperature range for each component.

Since comparisons are beginning to be made between gas chromatography and fractional distillation there has been some confusion. Therefore, a very brief review of distillation theory will be presented. For a more complete discussion the author recommends the text by Robinson and Gilliland (29).

Distillation is a method of separating the components of a mixture. The separation depends upon the distribution of the substances between a gas and liquid phase, where all components are present in both phases. The process of separating a mixture of two or more volatile substances is accomplished by causing the mixture to vaporize and to condense the vapors in such a manner so that components of varying boiling points are obtained. The separation of the mixture is only possible when the composition of the vapor coming from the liquid phase is different from the composition of the liquid itself. The Oldershaw column and Sarnia Fractionator perform this type of separation.

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases. One is a stationary bed of liquid (i.e. silicone polymer) and the other a gas (helium) that flows through the bed. In order to distribute the liquid over a large area, it is coated onto an inert solid support (such as crushed fire brick) and packed into a 1/4 inch column. In capillary columns the walls are coated with the liquid substrate. The petroleum fraction or mixture is then introduced into the carrier gas stream, just before the packed column, (Figure 2), and carried through the column by the helium. When the mixture enters the column it will condense and/or equilibrate between the liquid and vapor phases. That is, some of the sample will dissolve in the liquid and some still remain in the vapor.

According to Porter, Deal, and Stross (29) the separation is directly related to the relative volatility of the components comprising the mixture. This observation was also noted in this work. As mixtures were used where the components exerted very similar vapor pressures, separation was difficult. However, in determining the distillation characteristics of petroleum fractions we were not interested in fractionation of the sample into isolated pure components, rather to produce precision analytical distillation curves to characterize the oils.

Eggertsen (16) reported data from a chromatograph for this

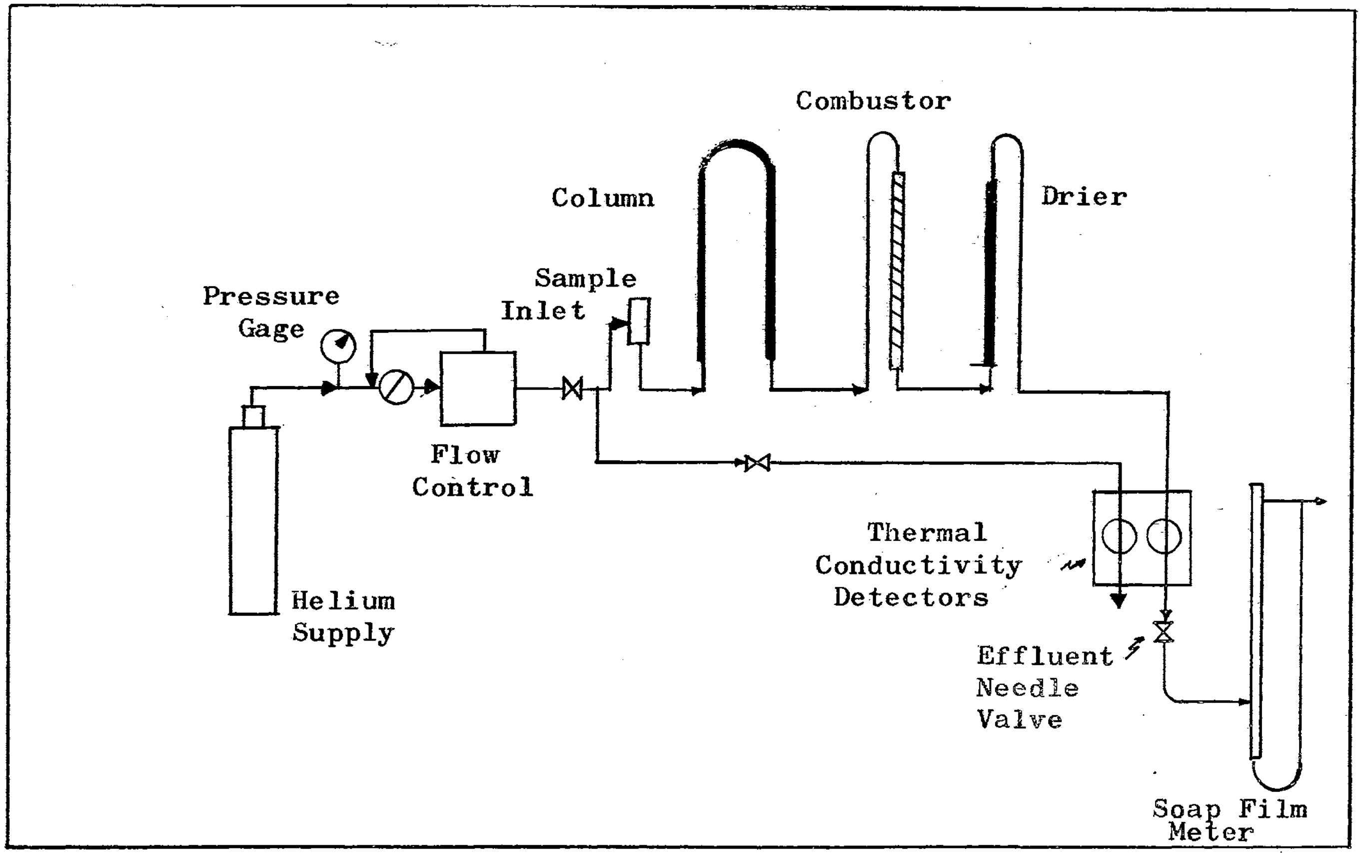


Figure 2

Gas Chromatograph Flow Scheme

type operation. His work was duplicated and boiling point separations of varied petroleum fractions studied using some additional modifications.

Definitions

Before discussing the theory applied in developing this technique, relevant terms will be defined. Indicating column temperature is the column temperature indicated by the instrument. Actual column temperature is the temperature of the column as determined by welding a thermocouple (chromel-copnic) to the column and correlating the emf generated to a temperature scale. Emergence temperature or time will designate the actual column temperature at the maximum detector-signal for an eluting component. Injection temperature is considered the temperature of the column at the time the sample is injected into the vaporization chamber.

One of the main problems of programmed temperature chromatography is to find column packings capable of withstanding the higher temperatures. The high temperatures affect the column stationary liquid phase in three ways: thermal decomposition, interaction with components of the samples, and by "bleeding", which is the simple vaporization and carrying away of the column liquid phase by the carrier gas. "Bleeding" results in the shortening of retention time , broadening of peaks, loss of resolution and changes in relative retention times of different peaks within the sample.

Elution is the continuous passing of a carrier fluid, helium in this work, through the chromatographic system. A gaseous or volatile liquid sample is injected into this gas stream and carried into the column of adsorbent. Theoretically, the mixture distributes itself between the gaseous phase and fixed phase (solid or liquid) in a manner that is characteristic of its normal boiling point. That portion remaining in the gas phase moves with the carrier gas stream. In the favorable case the components are separated and pass from the column in the elution stream at different temperatures. Figure 3 shows an ideal elution curve for one component. The emergence temperature is the means of qualitative identification and the area of the peak is proportional to the amount of the component in the stream. Ideally, a separate peak is produced for each component in the mixture; however, in multicomponent mixtures such as petroleum fractions, pseudo-components are obtained.

Since this thesis is primarily concerned with characterizing petroleum fractions, when the word component is used it will be understood that the author is referring to a pseudo-component of some petroleum fraction.

Unless there is distortion due to instrumental or operational factors, the shape of the elution peak for a component is directly related to its sorption isotherm. Three common types of isotherms and corresponding elution peaks are shown in Figure 4. The symmetrical peak, of course, is the most desirable for analytical distillations. Unfortunately for chromatographic distillation, the adsorption isotherms for most petroleum fractions are not completely linear. Nevertheless, elution of petroleum fractions produces usable chromatograms and in many cases

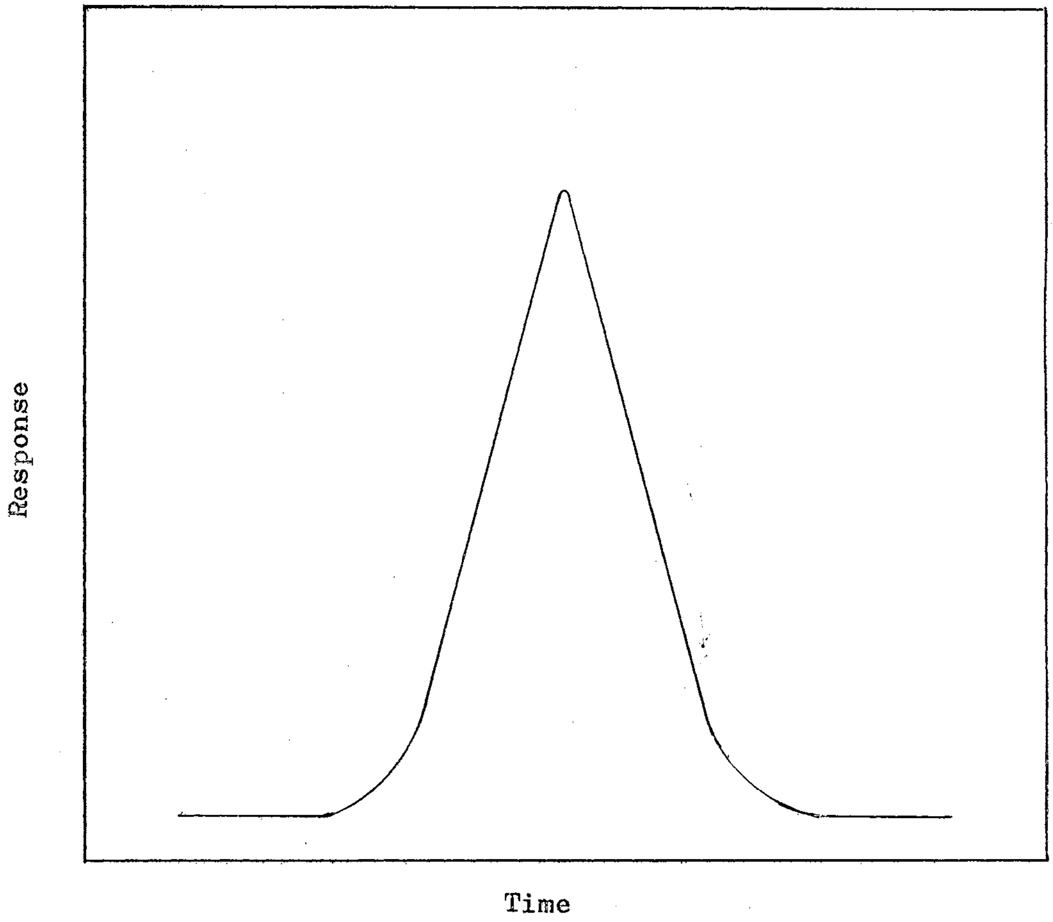


Figure 3

Typical Chromatographic Elution Curve

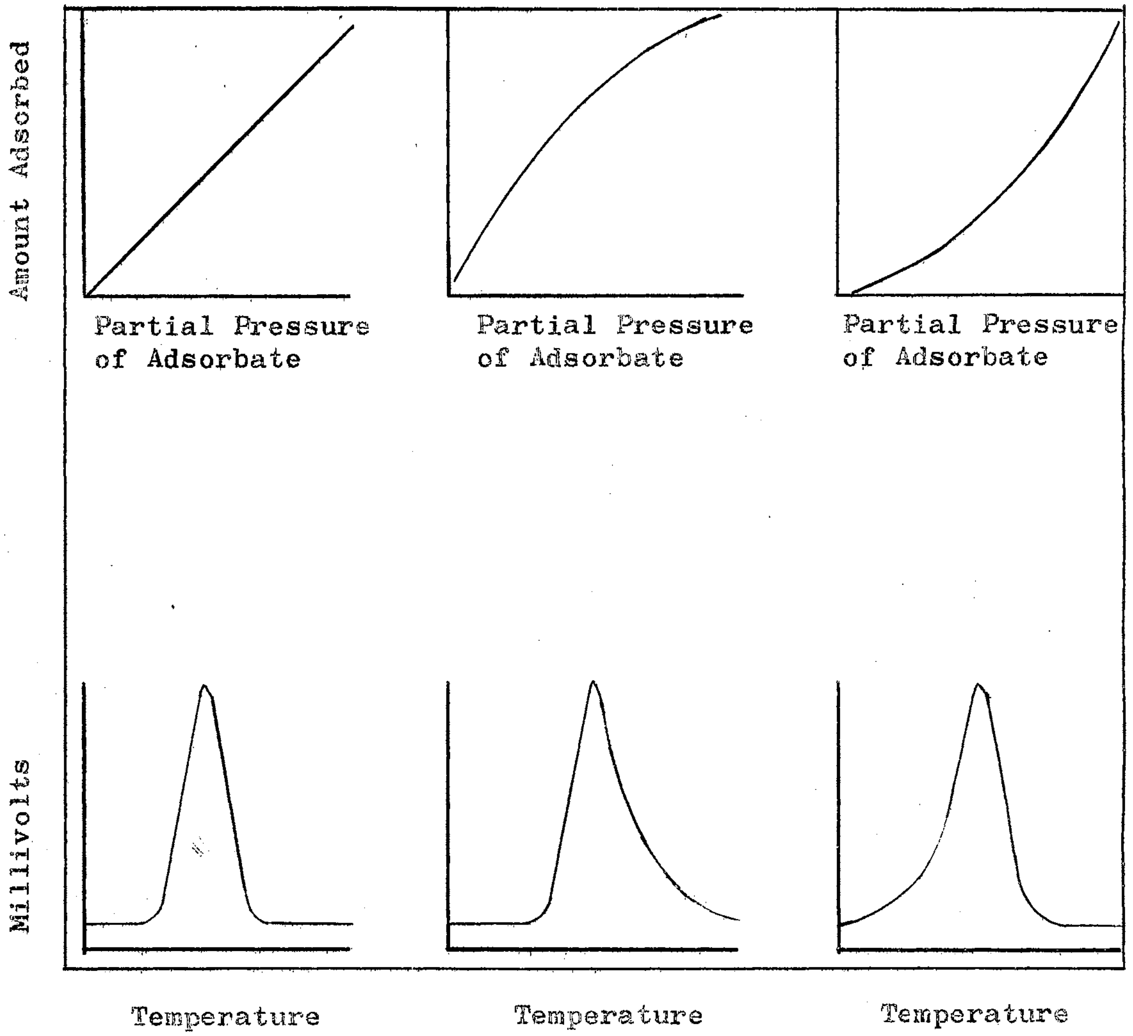


Figure 4

Elution Curves and Related Isotherms

there are a few examples of pseudo-components that produce highly symmetrical peaks. Peak distortions are discussed in more detail later.

Theoretical Considerations

A large amount of theoretical work has been done to establish a background for isothermal gas chromatography, i.e., the work of Van Deemter (35), Golay (19), and more recently, Giddings (18). There have been such a large number of contributions that it would be impossible to mention all of them here. Recently, attempts have been made to include programmed chromatography in the general theory of gas chromatography. A number of papers have been published by Hodgood (23) and Giddings (18) describing the theory of chromatography. Details of these theoretical treatments will not be given here; however, a summary of the highlights from the above papers follows.

In isothermal chromatography, the characteristic parameters of an analysis are: retention volume of a component and resolution between two neighboring components. The retention volume is a function of column temperature, column length, carrier gas flow rate, and affinity between the sample and the stationary phase, and the amount of stationary phase in the column.

The resolution between two components is a function of the retention volume and peak width. It, therefore, is influenced by all of the above variables, including the quality of the separating column which is the controlling factor affecting the peak width.

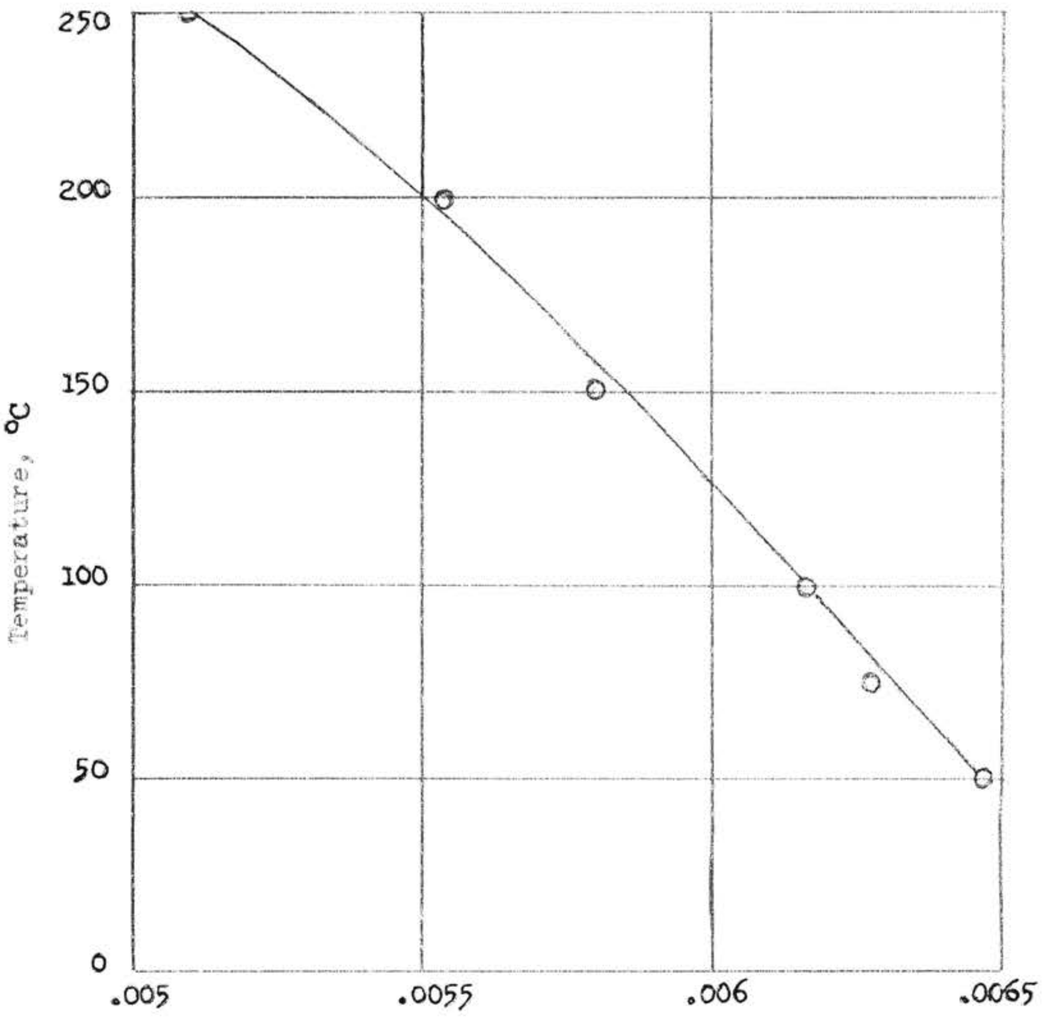
The characteristic parameters of programmed temperature gas chromatography are also the retention volume and resolution. In addition, a new variable has been introduced, the retention temperature. The retention volume is dependent on the initial column temperature and the heating rate. In fact, if these two variables are not kept constant, reproducible results cannot be obtained, and comparison of results from different sources is meaningless. It has been proposed to replace the volume by the temperature as the characteristic parameter of a peak (23). It has also been shown that temperature is more linearly dependent on the above variables than on retention volume (23). Thus, it is better to use temperature instead of volume to characterize a component in programmed temperature chromatography.

The height equivalent to a theoretical plate (HETP) of a chromatographic column is obtained by dividing the column length by the theoretical number of plates, N. N is used to characterize the column efficiency, and is given by the equation

$$N = 16 \left(\frac{V_{TR}}{\Delta V} \right)^2 \qquad \text{(III-1)}$$

V_{TR} is the retention volume of a component obtained at T_R. ΔV is the change in carrier gas velocity resulting from the programmed temperature increase.

The HETP may be assumed to be independent of the emergence temperature, however, it was observed in this work that the HETP generally decreases with increasing temperature, (Figure 5), and increases with column length, (Figure 6). Low values of HETP indicate an efficient column operation.



HETP (inches)

Figure 5

HETP as a Function of Temperature

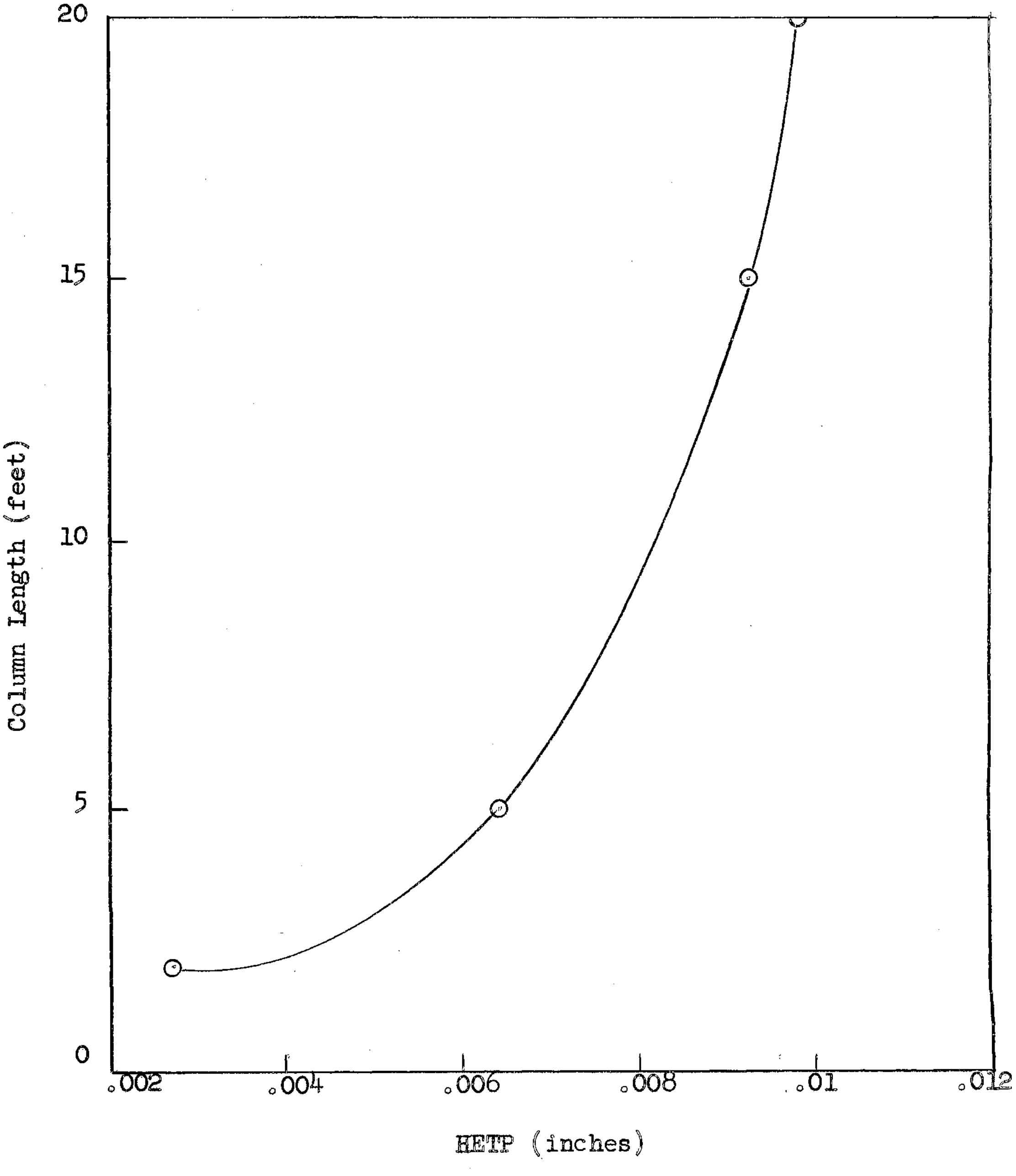


Figure 6

Plot of HETP as a Function of Column Length

Apparatus

A programmed temperature gas chromatograph is similar to an isothermal unit. The main difference is that a method is provided for linearly increasing the column temperature. This may be done by any number of mechanical or electrical methods, such as a motor driven autotransformer.

The basic equipment used for this chromatographic distillation study was a Model 500 F & M Scientific Corporation Programmed Temperature Gas Chromatograph. Three primary modifications were made on the instrument for this applications.

1. **Column Temperature.** A thermocouple was silver soldered to the midsection of each column, (Figure 7), and the EMF generated was measured with an L & N Model 8690 millivolt potentiometer. A conversion chart was used to convert the millivolt readings to a temperature scale. These temperature values were used in making a correlation between the actual column temperature and the indicating column temperature, (Figure 8). This correlation allows the operator to characterize each component for any particular set of operating conditions.

2. **Effluent Valve.** A valve, ideal-aerosmith needle type, was added to the effluent gas terminal, (Figure 2). The purpose of the valve is to move the principal pressure drop of the system to the end of the flow scheme, thus allowing the entire system to remain isobaric. This permits the operator to predetermine the pressure of the column at which the analysis is to be performed. The column pressure adds one more system variable to aid

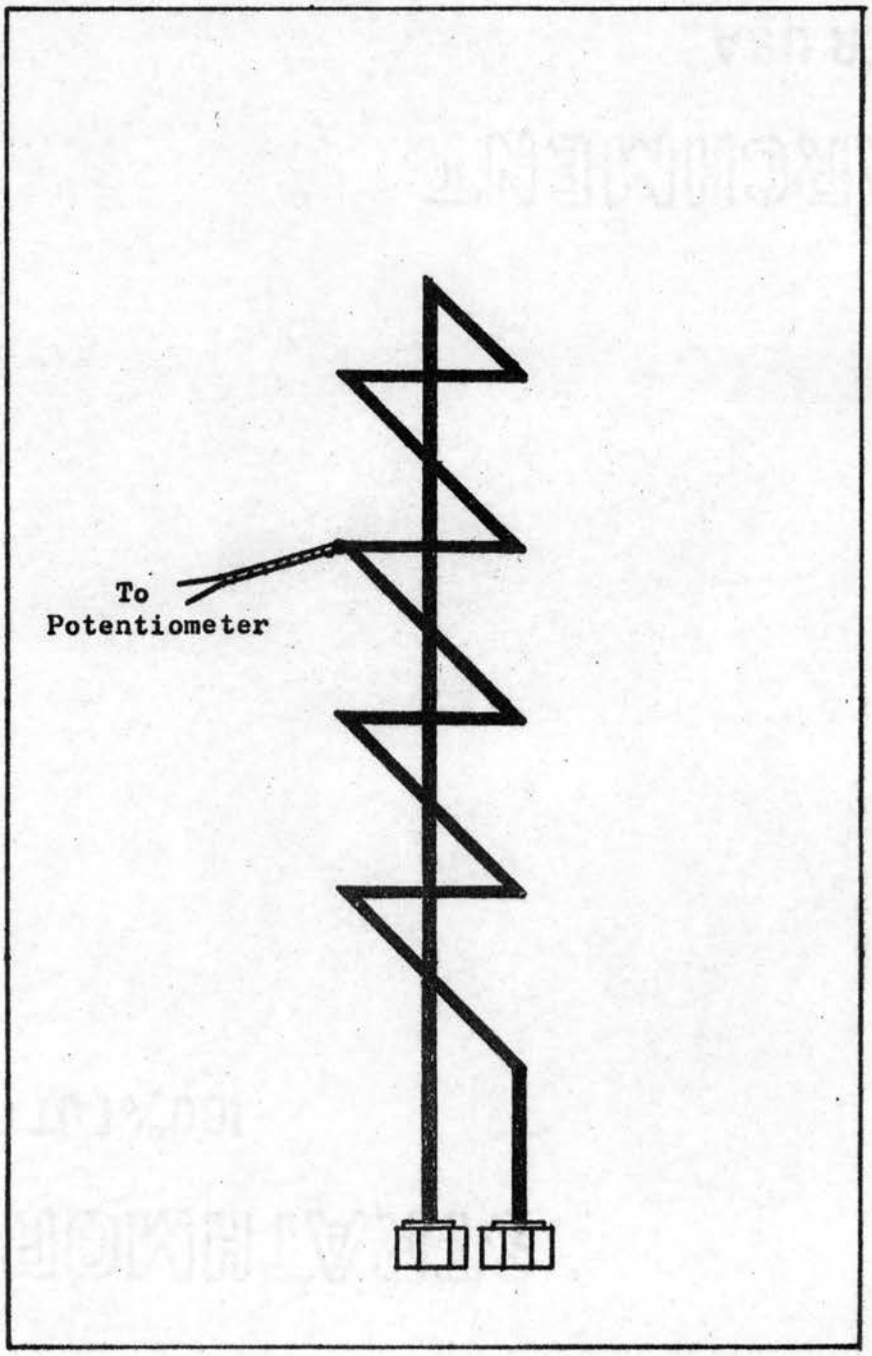


Figure 7

Chromatographic Column and Thermocouple

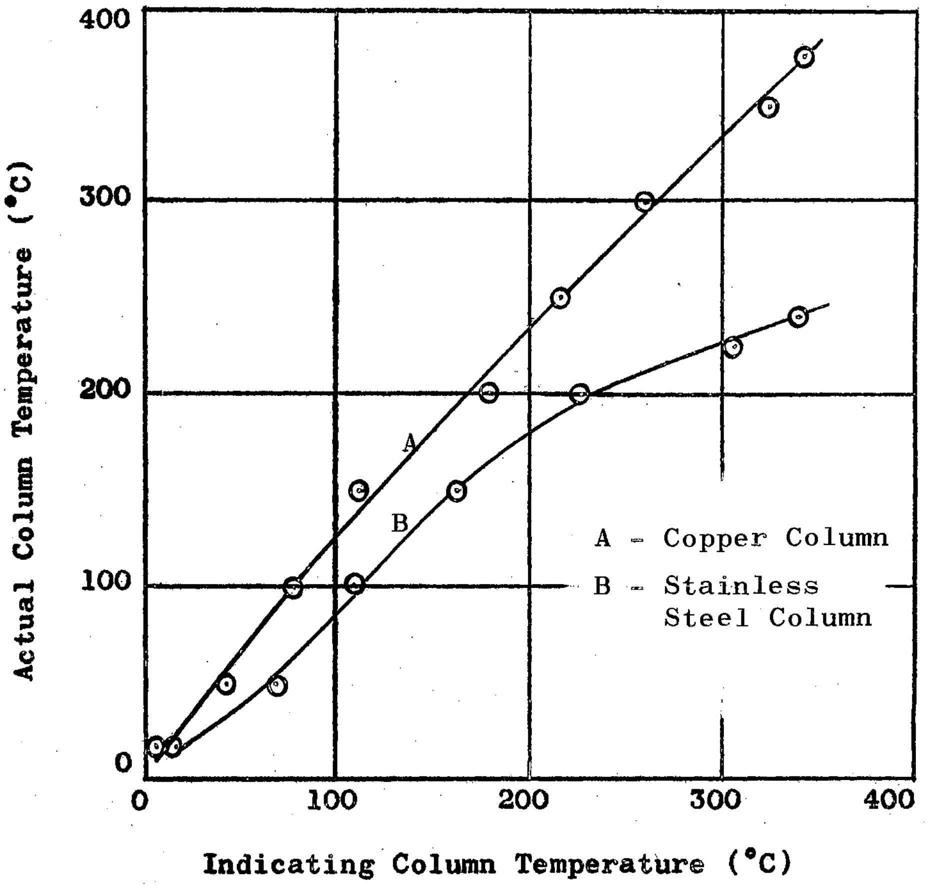


Figure 8

Actual Column Temperature as a Function of Indicating Column Temperature in the characterization of the oils. The system pressure was measured with a mercury manometer for several pressure gage settings and a plot constructed, (Figure 9), of gage pressure as a function of pressure (inches Hg) so that the system gage pressure could be converted to inches of Hg for each assay.

3. Combustor Attachment. For the third modification, a copper oxide combustor, similar to the one described by Eggertsen and Worker (17), was used to convert the hydrocarbons to carbon dioxide and water. The use of combustion chromatography was introduced by Martin and Smart (26) and has several advantages: It allows use of thermistors, if desired; sensitivity is increased for high molecular weight hydrocarbons; it allows a material balance to be made around the system, and the difference in thermal conductivity of each pseudo-component does not have to be taken into consideration.

This method described by Eggertsen (16), gives the resulting data in more fundamental units than usual for distillation, per cent carbon rather than volume per cent off. However, this is no difficulty because of the reasons discussed in Chapter V.

The combustor for this work was constructed from a stainless steel tube, ¼ inch O.D. x 12 inches in length, was covered with a fiberglass sleeve for insulation and then resistance wire wound around the insulation, (Figure 10). A total of 40 ohms of resistance was used, thus, allowing a maximum heat output, at 110 volts potential, from the wire of 1500 watts. This was sufficient to heat the combustor to the desired operating temperature of

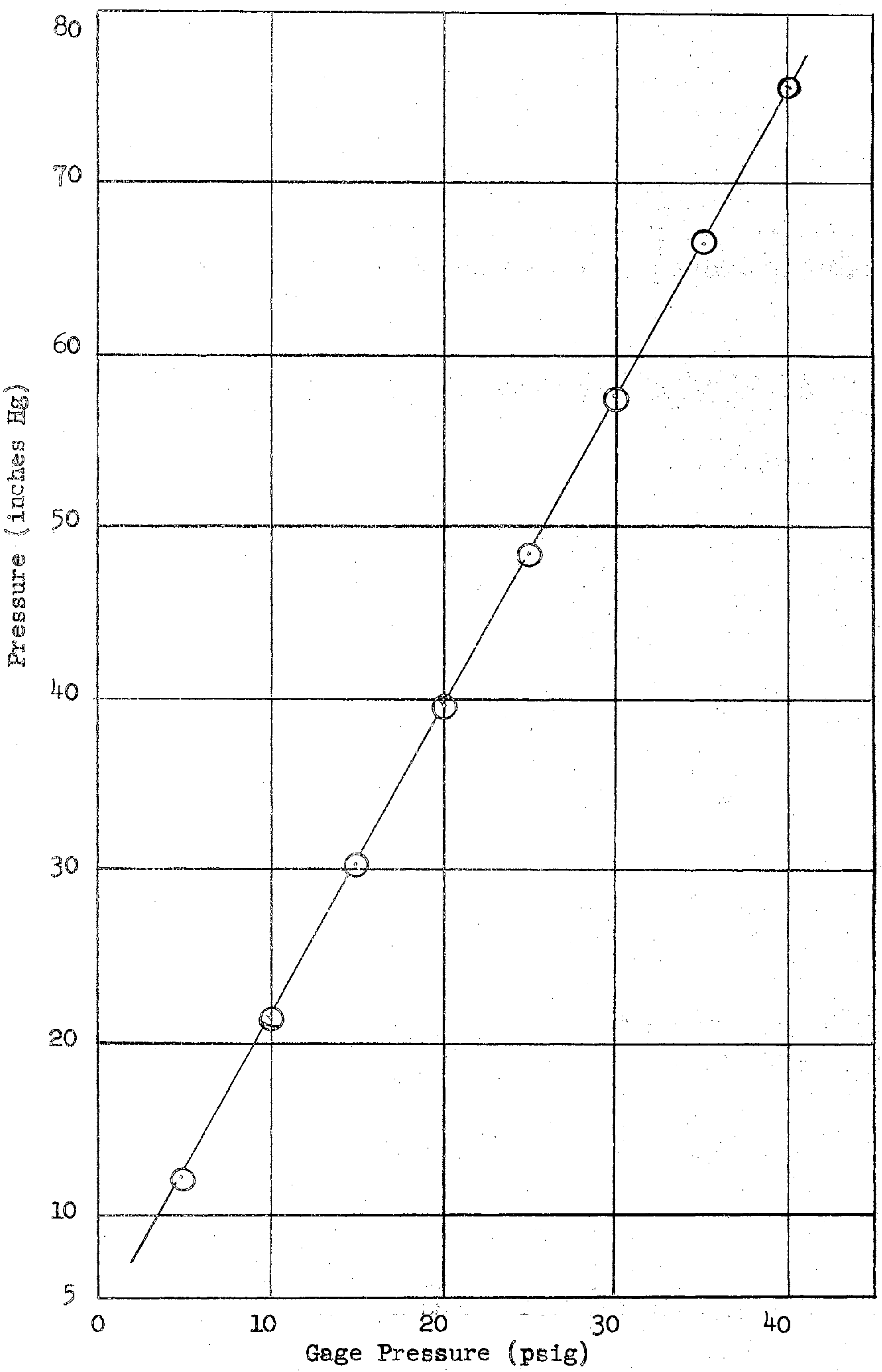


Figure 9

Pressure as a Function of System Gage Pressure

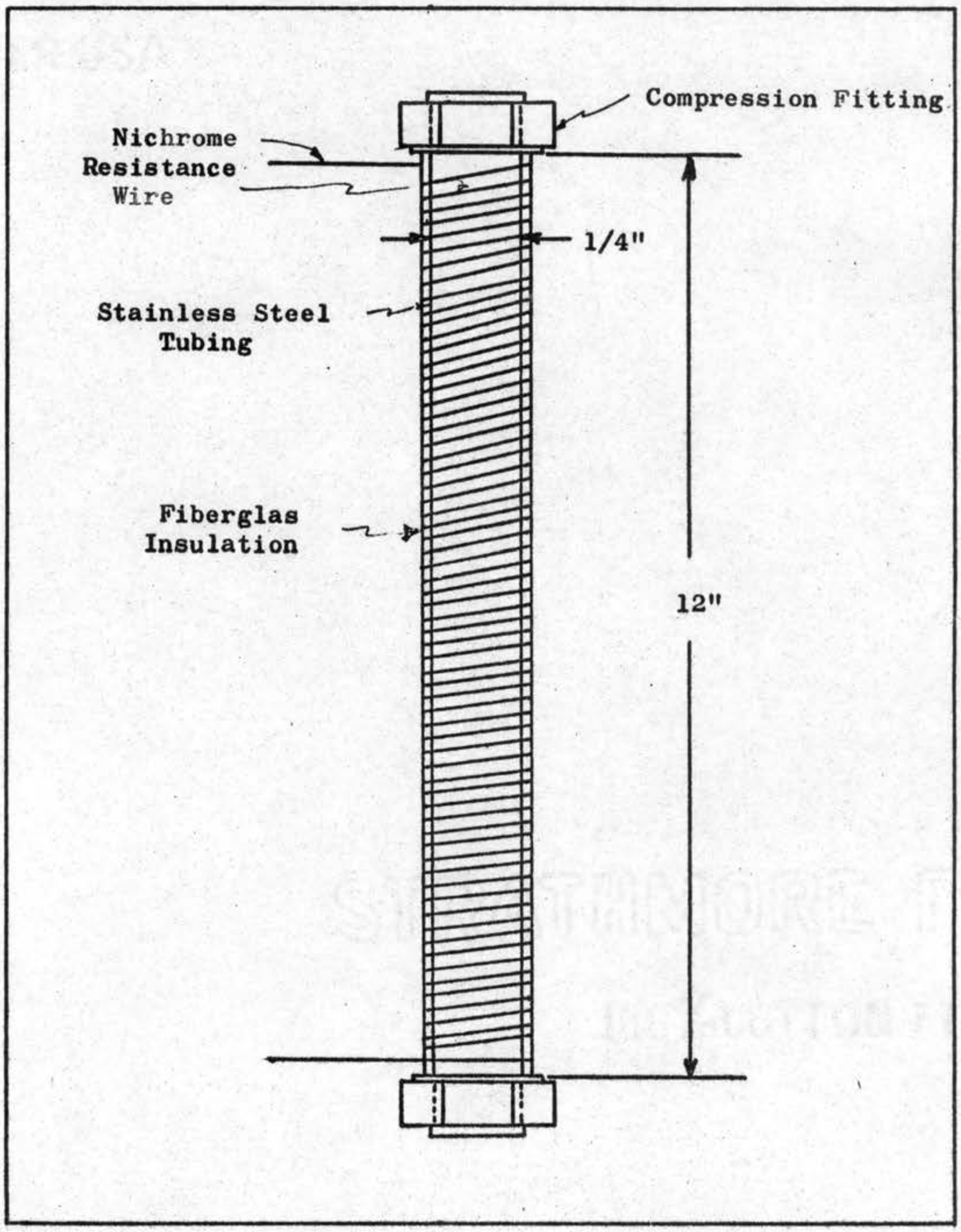


Figure 10

Copper Oxide Combustor

750°C. A variable transformer, Superior Powerstat 7.5 amp, supplied the necessary current for heating.

To remove the water produced from combustion of the hydrocarbons a 12 inch by ¼ inch O.D. stainless steel tube was packed with activated silica gel and put in series with the combustor in the chromatographic flow system, (Figure 2).

Columns and Packings

The stationary liquid phase and its support for the packed columns were contained in ¼ inch stainless steel tubes. However, the diameter of the chromatographic column does not enter into any of the theoretical equations, since it is assumed that the packing is completely uniform. Realizing that this is not always true and that any void spaces or uneven packing will result in loss of efficiency, the standard principles of column preparation was closely followed (33).

Five principal columns were used for assays (Table I). All were made of ¼ inch stainless steel and coiled on a 4 inch mandrel. Each time before a column was used it was "baked-out" or heated in the gas chromatograph at a temperature near its maximum limit with a flow of carrier gas (He) passing through it until the "bleeding" had stopped, indicated by a stable base line on the recording potentiometer.

Most of the assays were made using the 2 foot silicone gum rubber column as it provided sufficient distribution of the petroleum fractions over a large temperature range. Also, the gum rubber has less tendency to vaporize at the higher temperatures,

TABLE I

CHROMATOGRAPHIC DISTILLATION COLUMNS

Length	Stationary Phase	Solid Support
2 ft.	Silicone Gum Rubber	
5 ft.	Methyl-Silicone Polymer*	Chromosorb-P**
10 ft.	Methyl-Silicone Polymer*	Chromosorb-P**
10 ft.	Apiezon L	Chromosorb-P**
5 ft.	DYLT Polyethylene	Crushed Firebrick

* Dimethyl-Polysiloxane

** 40-60 Mesh

producing less recorder base line drift on the fractogram.

DISCUSSION OF RESULTS

Applying the combustion technique, four separate blends of high purity hydrocarbons were used to establish the feasibility of chromatographic distillation. The analyses of these synthetic blends are listed in (Tables II, III, IV, and V) with their respective boiling points and weight percentages.

The vaporization chamber and detector block were maintained at a constant temperature of 350°C through out each analysis. Injection temperatures, multiples of two, 30°C, 60°C, and 120°C were used; 30°C was the lowest allowable injection temperature without special cooling. The heating rates were programmed at 5.6, 11.0, and 21.0°C per minute. These are approximately related by a factor of two. Carrier gas flow rates of 30, 60, and 120 milliliters per minute and system pressures of 10, 20, and 40 pounds per square inch were used. Again, these are related by a factor of two.

The emergence temperature of each component was reproducible within a deviation of slightly more than 9°C, (Table VI).

Small changes in the size of the sample charge produced no effect in the emerging temperatures. In fact, the emergence temperature was completely insensitive to volume changes of sample within the loading capacity of the columns used.

It was apparent that precision in reproducing the emergence temperatures decreases as the vapor pressure decreases or as the molecular weight increases. This attributed to the longer period of time that the higher boiling components remain in the

TABLE II

CHROMATOGRAPHIC ANALYSIS OF SYNTHETIC BLEND 1

Boiling Point	Component	WT. % Carbon	Peak Area (% Carbon) Trial 1	2	3	4	Ave.
60°C	n-Hexane	24.4	24.5	24.2	24.8	25.3	24.7
89.8°C	2,3-Dimethylpentane	11.2	10.8	10.6	10.7	10.2	10.58
126°C	n-Octane	20.75	21.2	20.8	21.1	21.2	21.08
194.5°C	n-Hendecane	30.35	29.9	29.9	29.6	30.2	29.9
234°C	n-Tridecane	13.3	12.8	12.4	12.5	12.5	12.55
	Total	100.0%	99.2	97.9	98.7	99.4	98.81

TABLE III

CHROMATOGRAPHIC ANALYSIS OF SYNTHETIC BLEND 2

Boiling Point	Component	Wt. % Carbon	Peak Area (% Carbon) Trial		Ave.
			1	2	
80.1°C	Benzene	15.45	15.1	15.15	15.125
125.8°C	Octane	43.06	42.62	42.58	42.6
176°C	Decane	31.39	31.1	31.18	31.14
252.5°C	Tetradecane	10.1	9.92	9.95	9.94
	Total	100.0%	98.74	98.86	98.81

TABLE IV

CHROMATOGRAPHIC ANALYSIS OF SYNTHETIC BLEND 3

Boiling Point	Component	Wt. % Carbon	Peak Area (% Carbon) Trial			Ave.
			1	2	3	
83°C	Cyclohexane	12.3	12.17	12.3	12.29	12.25
100.3°C	Methylcyclohexane	22.01	22.1	22.07	22.04	22.07
151°C	Nonane	17.66	17.62	17.65	17.63	17.63
218	Naphthalene	31.09	31.11	31.12	31.08	31.10
234°C	Tridecane	16.94	16.95	16.95	16.93	16.94
	Total	100.0%	99.95	100.0	99.97	99.99

TABLE V

CHROMATOGRAPHIC ANALYSIS OF SYNTHETIC BLEND 4

Boiling Point	Component	Wt. % Carbon	Peak Area (% Carbon) Trial 1	2	Ave.
64°C	1-Hexene	21.7	21.5	21.41	21.46
99°C	2,2,4-Trimethylpentane	36.21	36.21	36.21	36.19
114°C	2,3,4-Trimethylpentane	23.18	23.2	23.21	23.21
151°C	Nonane	8.64	8.64	8.66	8.64
176°C	Decane	10.27	10.34	10.29	10.32
	Total	100.0%	99.85	99.78	99.82

instrument and to the relative volatility between the higher molecular components and the stationary liquid phase.

Experience has shown that after completing an assay, more time is required for the column to return to the initial "steady state" condition than is indicated by the temperature. This may be due to a readjustment of the column because some "bleeding" of the liquid phase occurs at the higher temperatures. The effect of the higher injection temperature is to increase the emergence temperature of the lower boiling components, (Figure 11). This, however, is to be anticipated as a component injected into the instrument at 100°C could not be expected to emerge at some lower temperature, regardless of its normal boiling point.

Emergence temperatures were not affected greatly by column length changes (Figure 12). The data in Table VI compares identically packed 5 and 10 foot methyl-silicone columns. It will be noted that for the 10 foot column the emergence temperatures are higher, particularly for the lower boiling components. This effect is probably due to the longer retention time of the 10 foot column.

The rate of change of emergence temperatures with the change in boiling point was found to be independent of the carrier gas flow rate. It is postulated that this consistency of slope will permit estimation of boiling points of unknown components in mixtures, (Figure 13). However, due to the change in partial pressures, a slope change does occur when the system pressure is varied, (Figure 14). As is expected, the pressure variations tend to have a greater effect on lighter components. It is believed that this fluctuation with pressure will permit characterizing the

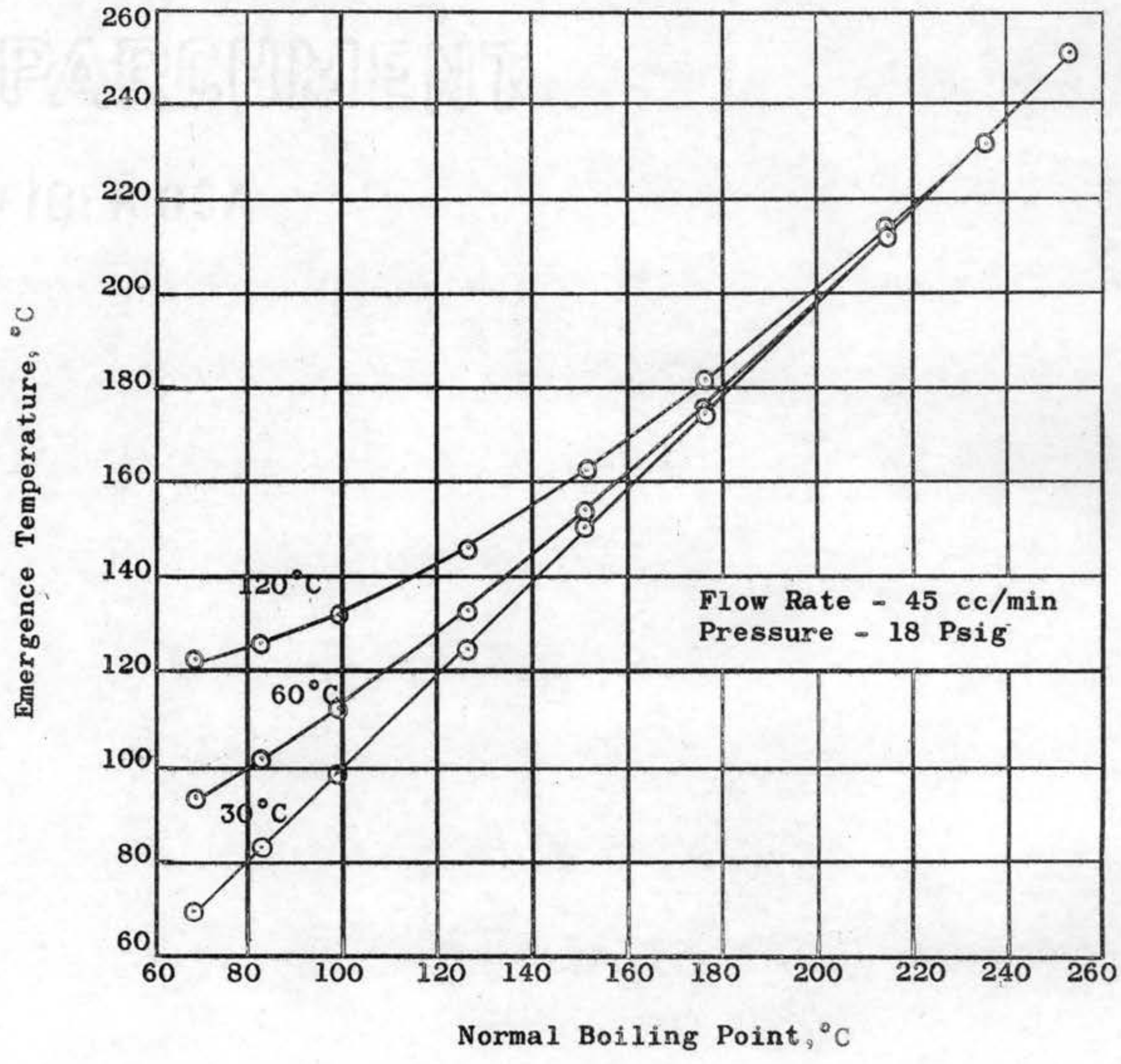


Figure 11

Effect of Injection Temperature

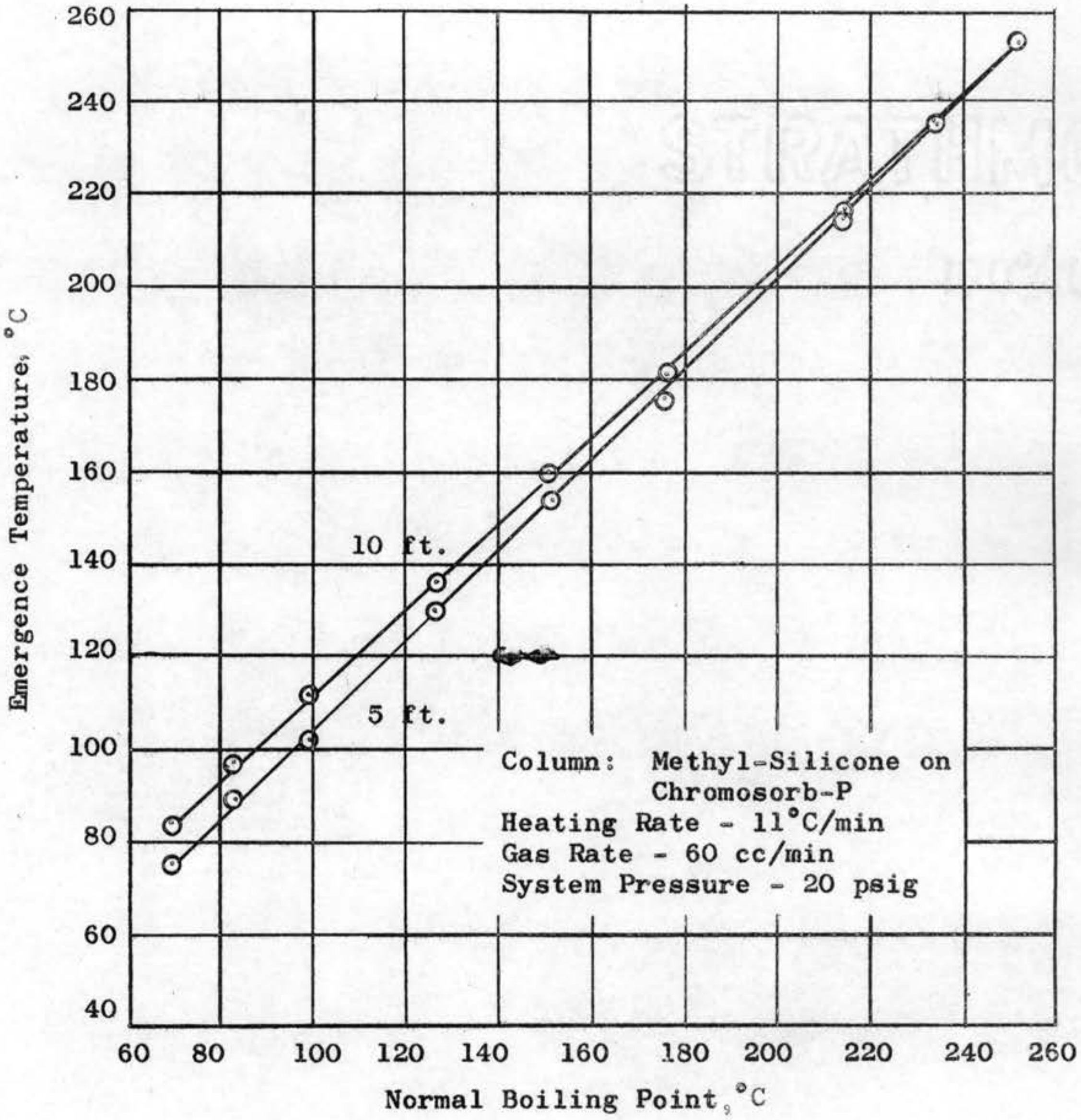


Figure 12

Effect of Column Length

TABLE VI

EFFECT OF COLUMN LENGTH ON EMERGENCE TEMPERATURE

Column: 5' Methyl Silicone

Heating Rate: 11°C/min
Carrier Gas Flow Rate: 45cc/min
System Pressure: 20 psig

Component	Emergence Temperature °C	Literature Boiling Point °C
n-Hexane	75	69
Cyclohexane	89	83
2,2,4-Trimethylpentane	102	99
n-Octane	130	126
n-Nonane	153	151
n-Decane	176	176
n-Dodecane	215	214.5
n-Tridecane	235	234

Column: 10' Methyl Silicone (at same conditions as above)

Component	Emergence Temperature °C	Literature Boiling Point °C
n-Hexane	84	69
Cyclohexane	97	83
2,2,4-Trimethylpentane	112	99
n-Octane	137	126
n-Nonane	160	151
n-Decane	181	176
n-Dodecane	216	214.5
n-Tridecane	236	234
n-Tetradecane	253	252.5

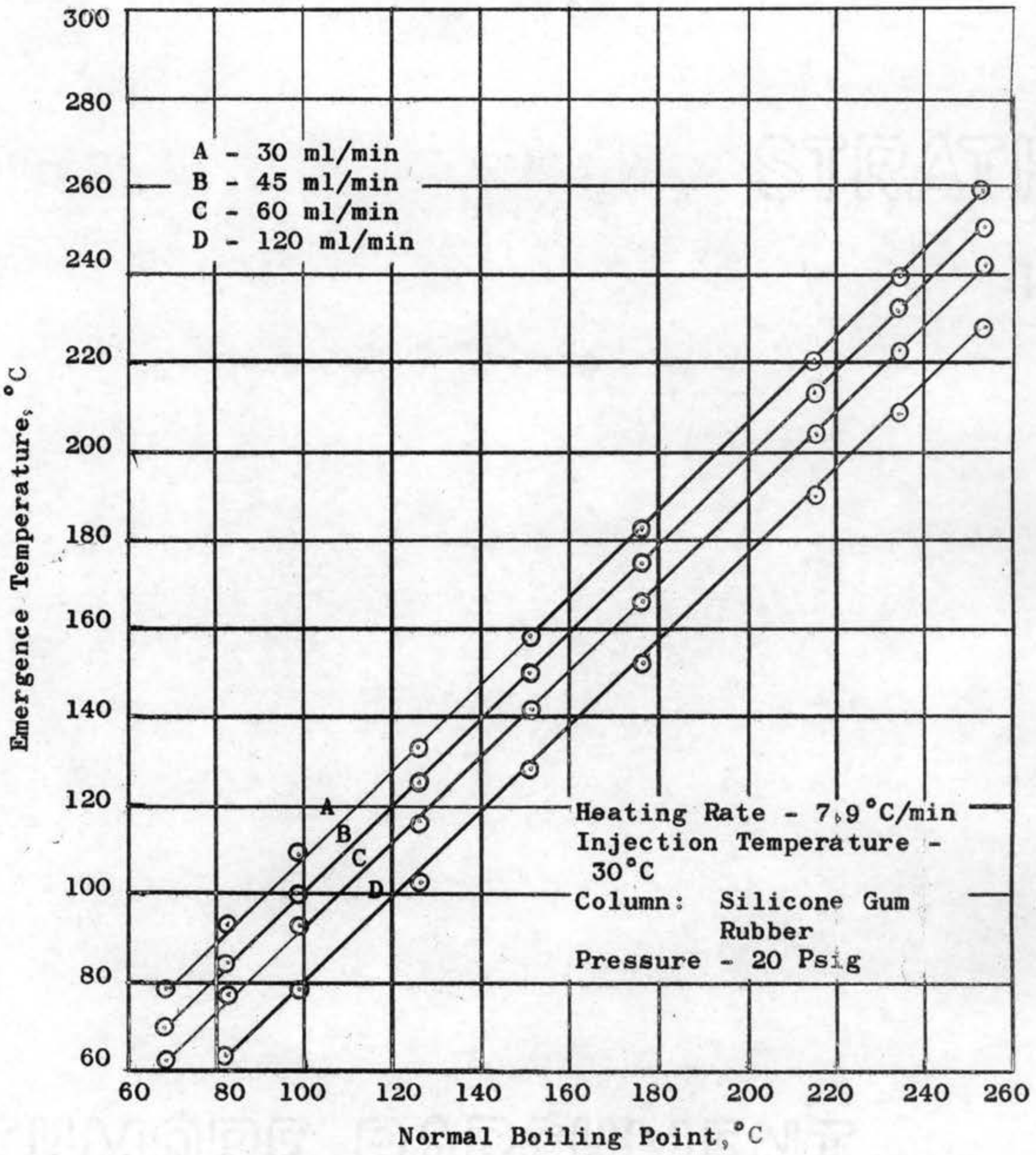


Figure 13

Effect of Carrier Gas Flow Rate

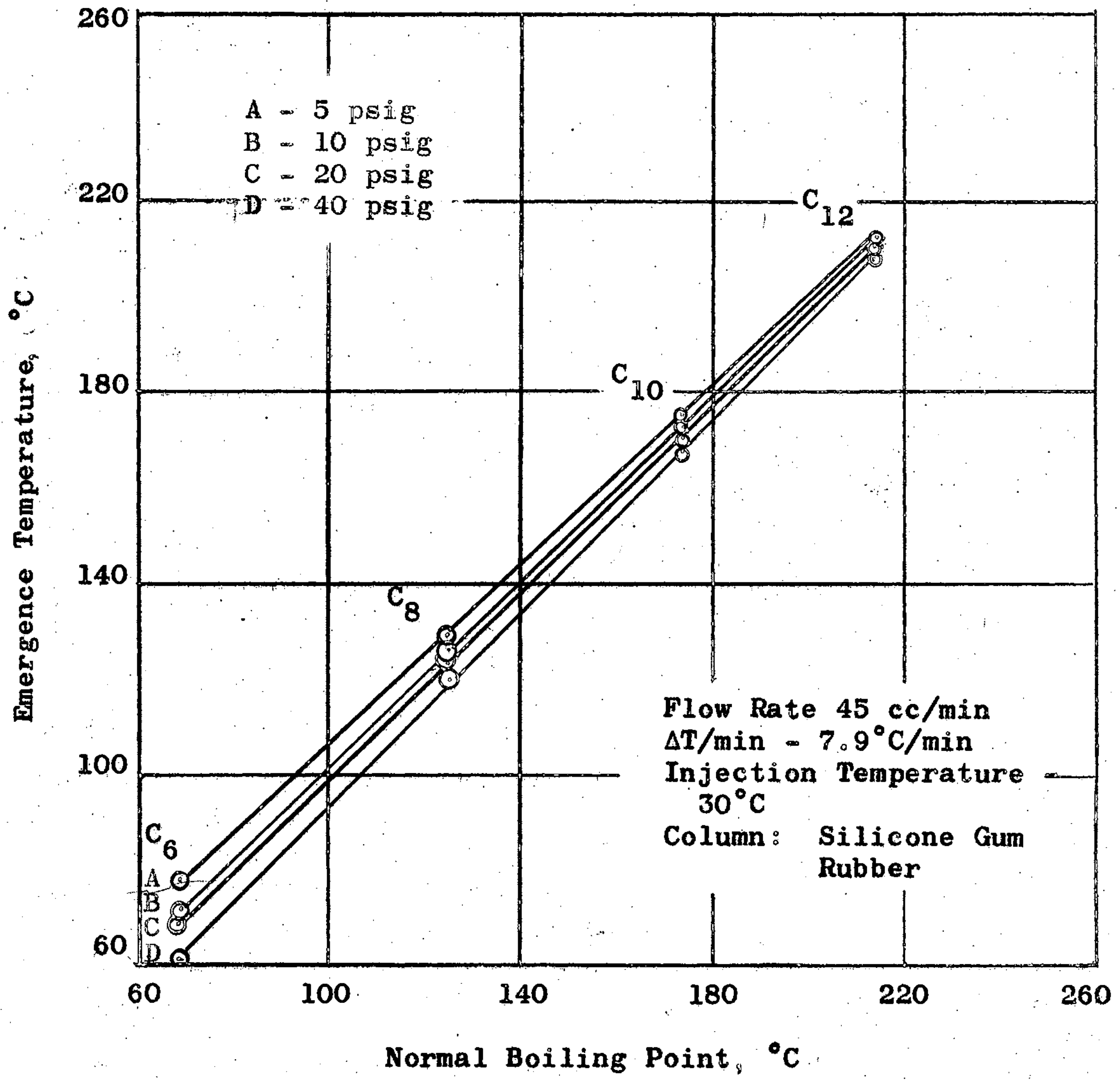


Figure 14

Effect of System Pressure

pseudo-components of an "infinite" mixture by an interpolation method using a set of known or internal standards. The slopes of the heating rate curves were also constant, (Figure 14).

About a 20°C change in the emergence temperatures occurs when the carrier flow rate is doubled, from 30 to 60 ml per minute, (Figure 13), while the increase from 60 to 120 ml per minute causes only a 12°C change in temperature. Thus, a 10 per cent error in flow rate control would result in an error of only 1-2°C in the emergence temperature or indicated boiling point. However, with the effluent needle valve flow rates are easily controlled within 2 per cent. Heating rate introduces a linear error of about 2°C in emergence temperature for each 3°C per minute change, (Figure 15).

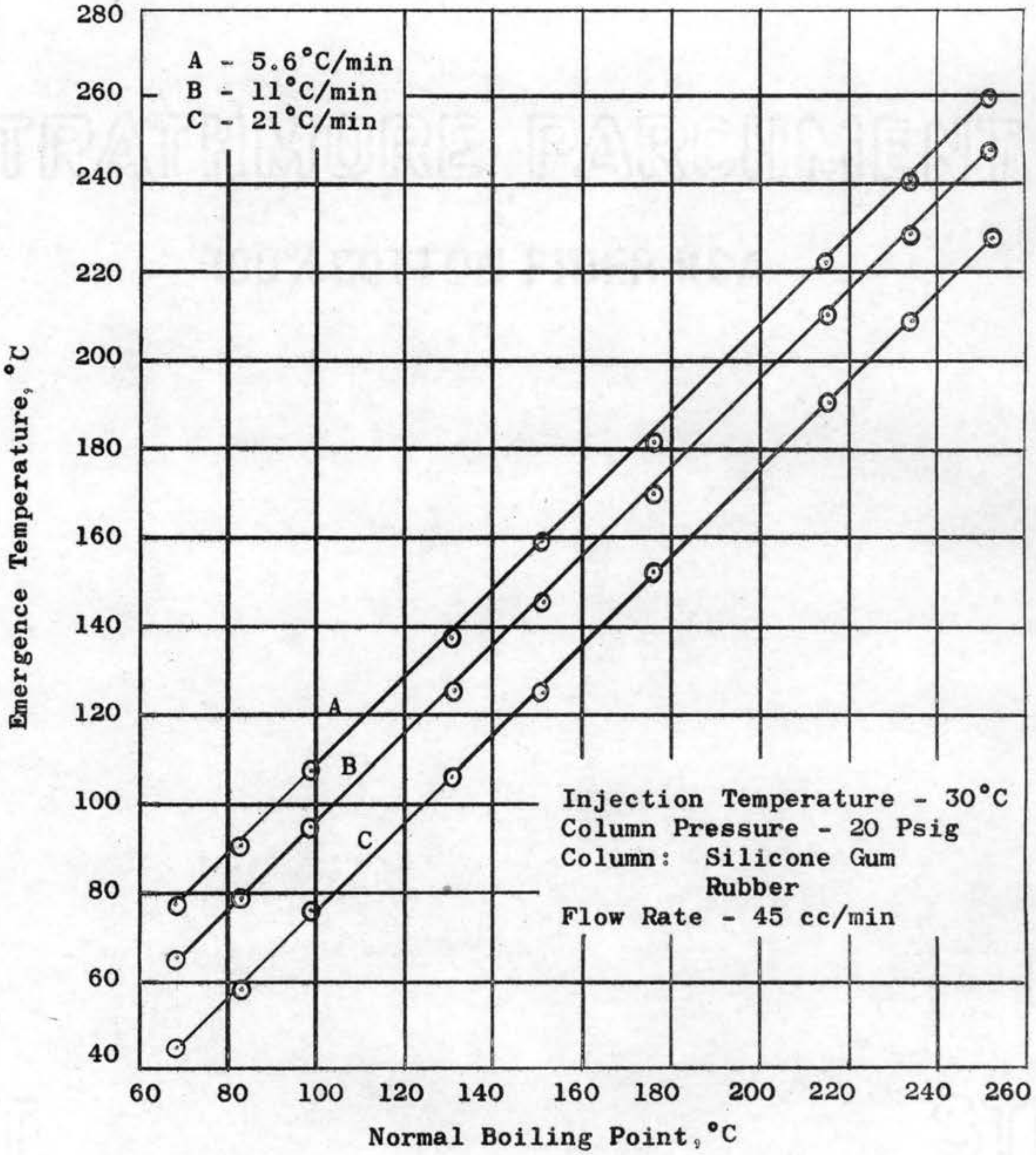


Figure 15

Effect of Heating Rate

CHAPTER III

MEASUREMENT OF MOLECULAR WEIGHTS

Conversion of weight per cent TBP data to molar TBP data requires a knowledge of the molecular weight of an oil. Measurement of molecular weights is presented in this chapter with discussions of the principles, apparatus, techniques, and results.

A vapor density method and apparatus was developed for measuring the average molecular weights of petroleum fractions. The molecular weights measured by this method, for specially prepared mixtures, were found to be in good agreement with the calculated average molecular weights of the synthetic blends.

The apparatus and procedure proved successful and are discussed in detail in the Appendix. The Appendix also includes a section devoted to maintenance and "trouble-shooting" of the instrument.

A new method for determining average molecular weights of multicomponent mixtures in the 20-200 amu (atomic mass units) range has been needed by the petroleum industry. From this work a new reliable technique was developed to make accurate measurements in the desired molecular weight range.

Previously Available Methods

Laboratory methods available for determining molecular weights are the cryoscopic, the vapor pressure osmometer, and boiling point elevation determinations.

The cryoscopic method is based on the freezing point depression of a solution caused by addition of a small quantity of unknown solute to a solvent. The depression is usually detected by a highly sensitive differential thermometer. A description of the apparatus and exact procedure is given by Wilson and Wylde (35). This method has proven inaccurate for petroleum fractions (36).

The osmometer applies the principle of the vapor pressure reduction of a solution by the addition of small amounts of unknown solute. The reduction in vapor pressure causes a change in the rate of evaporation of a solution from two matched thermistors in a chamber filled with vapor saturated with the solvent. The difference in the heats of vaporization between the pure solvent and the solution containing the solute cause a change in the temperature of the thermistors. This causes an unbalance in the resistance of an electrical bridge, in proportion to the molarity of the solution. Molecular weights determined with this instrument do not yield accurate results below the range of 200 amu (3,4).

Solutions containing nonvolatile solutes boil at temperatures higher than the boiling point of the pure solvents. This fact is shown in Figure 16, where the curve for the vapor pressure of

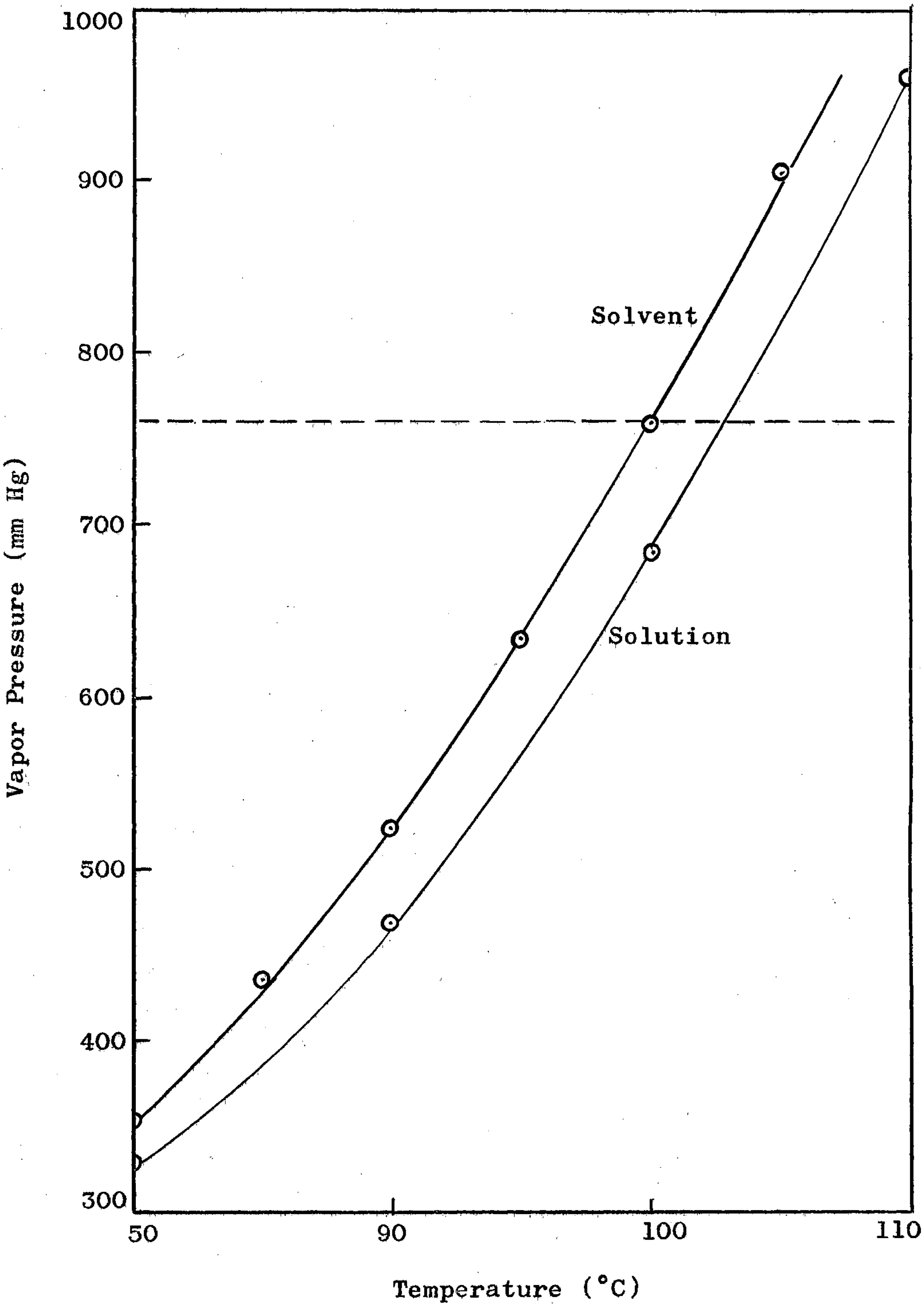


Figure 16

Vapor Pressure as a Function of Temperature the solution cuts the line of barometric pressure at a higher temperature than the curve of the vapor pressure of the solvent. As the temperature is raised the solvent or solution will boil when its vapor pressure is equal to the atmospheric or system pressure (760 mm in this figure). Since the organics of interest in this work are volatile, little consderation was given to this method in seeking a method of determining accurate molecular weights.

Previous workers (2, 29) used the cryoscopic technique for measuring molecular weights of petroleum mixtures and found the method to be inaccurate as determined by a mass spectrometer analysis. However, before discarding the method, several analyses were made of synthetic blends prepared of n-paraffins and saturated and unsaturated branched chain hydrocarbons. These analyses are compared to the calculated values in Table VII.

A plot of this data, (Figure 17), shows the inconsistency of the results from the method. Inaccuracies in the measurement of molecular weights of this magnitude will result in more than a ten percent deviation in the calculation of K values (39). Therefore, a search began for a new method or technique that could be used to measure the average molecular weights of multicomponent mixtures to a greater degree of accuracy.

Vapor Density Method

In visiting several of the research facilities in the surrounding area we discovered that the sample introductory system

TABLE VII

MOLECULAR WEIGHTS OF SYNTHETIC BLENDS BY CRYOSCOPIC METHOD

Components	Molecular Weight	Average Mol. Wt.	Cryoscopic Mol. Wt.
Blend I			
n-Heptane	100.2	100.2	88.6
2,3-Dimethylpentane	100.2		
Blend II			
1-Hexane	84.16	125.2	137.4
n-Tetradecane	198.38		
Blend III			
n-Octane	114.23		
Methylcyclohexane	98.18	127.8	115.3
n-Dodecane	170.33		
Blend IV			
3 Methylhexane	100.2		
n-Undecane	156.3	109.4	81.2
Benzene	78.11		
2,4-Dimethylpentane	100.2		
Blend V			
n-Tridecane	184.36		
2,2,4-Trimethylpentane	114.23		
n-Hexane	86.17	117.4	86.6
Cyclohexane	84.16		
Blend VI			
n-Nonane	128.25		
2,3,4-Trimethylpentane	114.23	115.8	93.6
n-Decane	142.28		
Benzene	78.11		

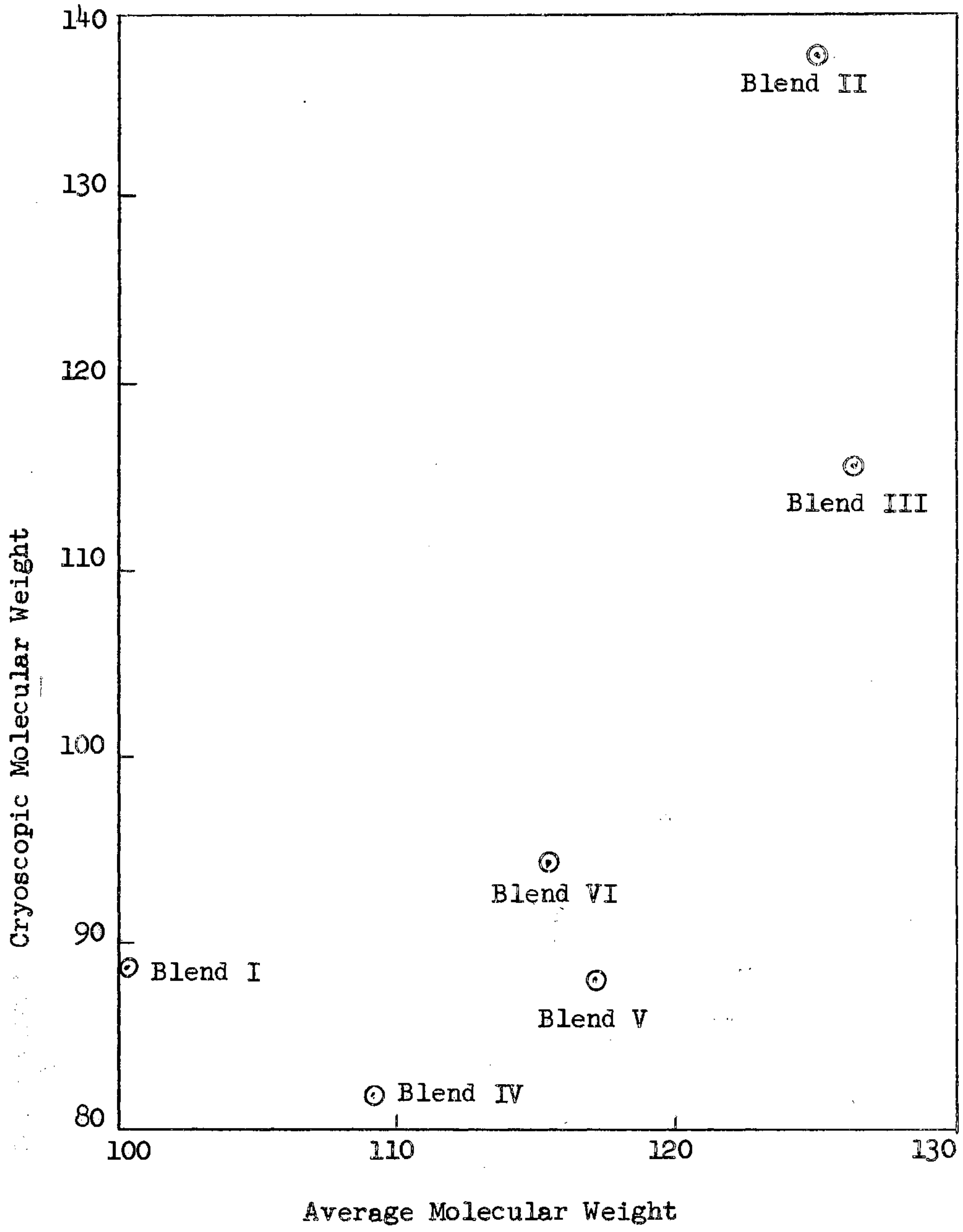


Figure 17

Cryoscopic Molecular Weights of Synthetic Blends of a Consolidated Electrodynamics Corporation mass spectrometer was being used to measure the vapor pressure of petroleum mixtures (4). In discussing this technique the fact was pointed out that these vapor pressure measurements could be used with the perfect gas law to calculate molecular weights (7).

Theory

To obtain the average molecular weights of multicomponent mixtures (i.e., petroleum fractions), a vapor density apparatus was designed, built and the operating procedure developed.

In the vapor density method a liquid sample of known volume and density is vaporized and expanded into a controlled temperautre, high vacuum system. The pressure exerted by the sample is measured by a micromanometer that is composed of a pressure sensing diaphragm and a capacitance bridge. Using the known sample volume and density, the measured vapor pressure, and the ideal gas law, the molecular weight is calculated as follows.

The sample section, (Figure 18), with the exception of the vacuum pumps, is enclosed in a controlled temperature air bath and is subjected to a high vacuum (approximately 10^{-7} mm Hg). It is assumed that at these conditions the vapor will obey the perfect gas law:

$$PV = nRT \qquad \text{(III -1)}$$

R is the commonly known gas constant, V is a constant as fixed by the actual volume of the system, and T is the controlled variable. P is the pressure, as determined by the pressure diaphram, of the expanded sample volume. By definition:

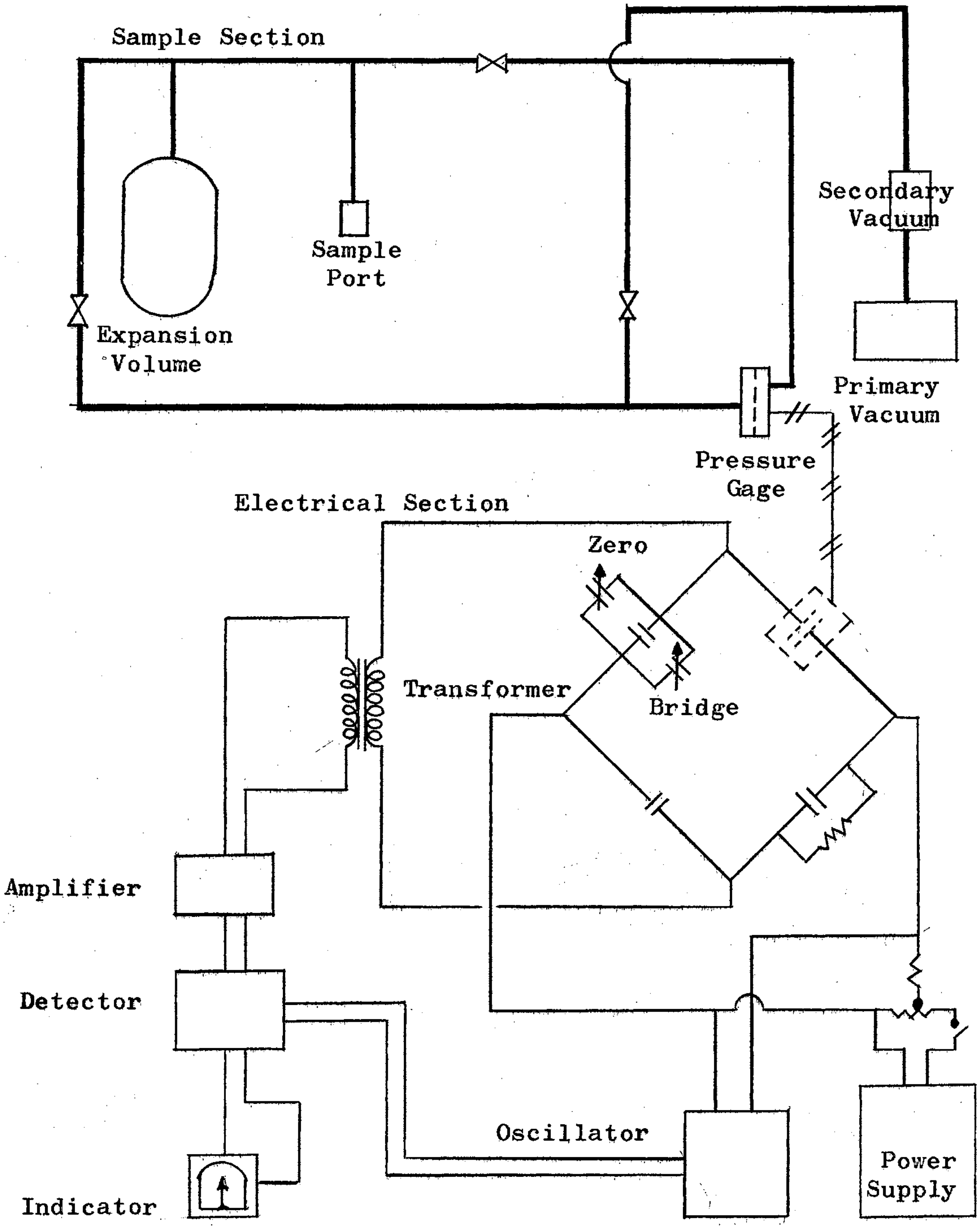


Figure 18

Schematic Diagram of Molecular Weight Apparatus

$$n = (\rho v)_{\text{liquid}}/MW \qquad \text{(III-2)}$$

Therefore, by substitution of Equation 2 into Equation 1:

$$MW = RT\ (\rho v)_{\text{liquid}}/PV \qquad \text{(III-3)}$$

The experimental value obtained from the instrument is a numerical dial reading, indicative of the electrical force equal to the pressure exerted by the sample vapor. The dial reading, D, is converted to pressure, in microns, by the relation

$$P = D^2/\underline{k} \qquad \text{(III-4)}$$

where k is a predetermined gage constant (gage constant = 1852).

The liquid volume, v, of the sample is measured by part of the sample introduction apparatus. Therefore, once the liquid density or specific gravity, ρ, of the sample is known, the pressure value obtained from Equation III-4 can be used in Equation III-3 to calculate the molecular weight.

Apparatus

The apparatus is in a "self-contained" metal cabinet with removable top and back doors that allow easy access to all parts of the instrument. The lower section of the panel contains a micromanometer that is an electronic instrument, composed of a pressure sensing gage, capacitance bridge and a bridge amplifier, (Figure 18; electrical section), for directly and accurately measuring gas pressure in the range from 1.0 to 150 microns. The unique design of the instrument allows the pressure measurements to be independent of gas composition, therefore eliminating the need for special calibrations of individual gases.

The sample handling section is contained in the controlled temperature air bath which is constructed of one-half inch Transite (concrete asbestos board). Heat is provided by four 250 watt strip heaters, two of which are wired in series with a variable temperature probe. Separate Variacs are used to supply current to the constant temperature and controlling heaters to allow selection of any desired operating temperature. A "squirrel cage" type blower fan connected to an extension shaft of a continuous duty motor is used to circulate the heated air at about 60 cfm (cubic feet per minute).

The sample receiver, (Figure 19), is located on the front panel. It is constructed of one and one-half inch diameter glass tubing with a 40/30 § (standard taper) fitting that permits removal of the lower section, a mercury collecting trap. The small hole or orifice is only large enough to permit a steady stream of mercury droplets to pass through when a high vacuum (0.1 microns) exist in the closed section. The sample receiver is connected to the system by the use of a metal to glass § fitting. The receiver orifice requires two lapped surfaces, (Figure 20). The upper surface is lapped or ground to match the mercury restraining plug and the lower surface lapped to match the sampling micro-pipette, (Figure 20).

The key part of the system is the pressure gage, which is a pressure-sensitive capacitor having a stainless steel diaphragm and a fixed plate with metalized coating, (Figure 21). The gage is part of the capacitance bridge circuit. If a high vacuum or equal pressure exists on both sides of the diaphragm, it remains

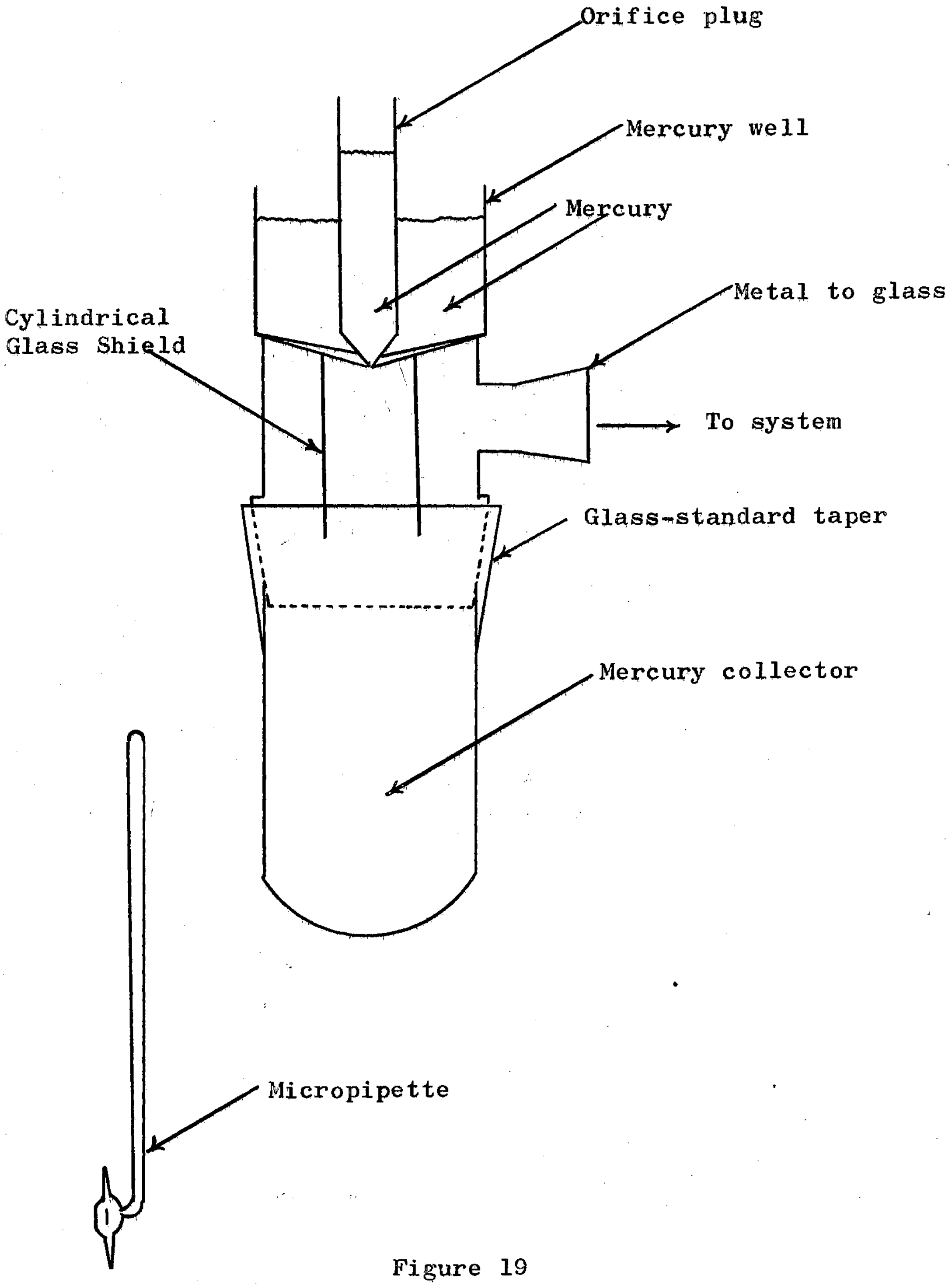


Figure 19

Molecular Weight Sample Receiver and Micropipette

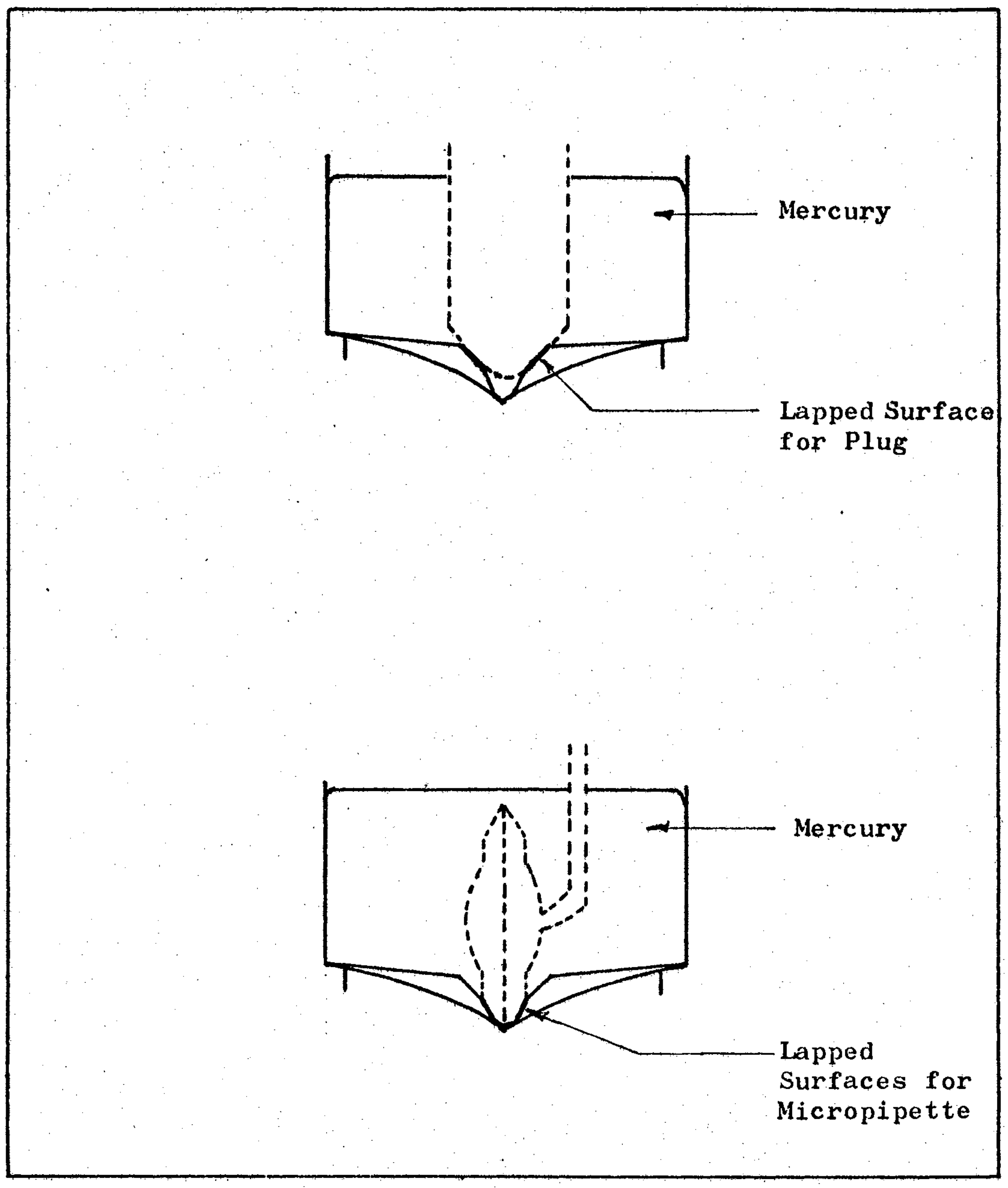


Figure 20

Lapped Surfaces of Sample Receiver

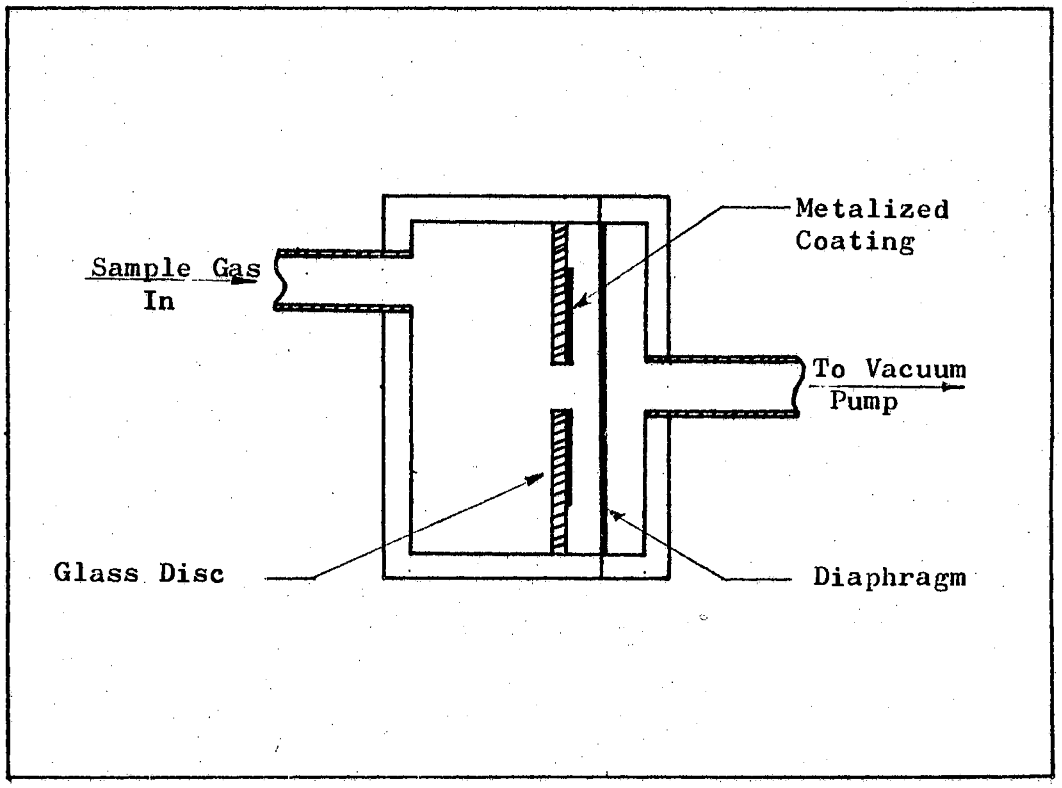


Figure 21

Diagram of Pressure Sensing Gage

at rest, and the bridge is balanced and the null meter on the instrument panel indicates zero, (Figure 22).

When a sample is introduced into the system one side of the diaphragm is exposed to a high vacuum while the other side is exposed to the sample gas. The sample pressure displaces the steel diaphragm and the capacitance between the diaphragm and metallized surface is changed, (Figure 23). This produces an unbalance in the bridge and a null no longer exists.

To regain the null, the bridge voltage is turned on and the correct amount of d-c balancing voltage, an electro-static force equal and opposite to the force of the sample gas, exerted on the diaphragm. This returns the diaphragm to its original position and capacitance, (Figure 24), and thus restores the null. The reading of the balancing dial can, as discussed previously, be converted to the actual sample pressure.

The bridge amplifier consists of two sections; the first of which is the capacitance bridge, (Figure 18), one arm formed by the gage head, and the second a single stage amplifier which amplifies the unbalanced voltage produced by the bridge.

The sample handling section, (Figure 18), is composed of primary and secondary vacuum pumps, sample receiver (already discussed), expansion volume, and teflon packed vacuum tight valves.

The expansion volume, a three liter stainless steel container, is connected to the system by a one-half inch stainless steel tube that is silver-soldered to the container and to a one and one-half inch flange that serves as a coupler with the system.

The valves are of a "ball" type that were designed to allow

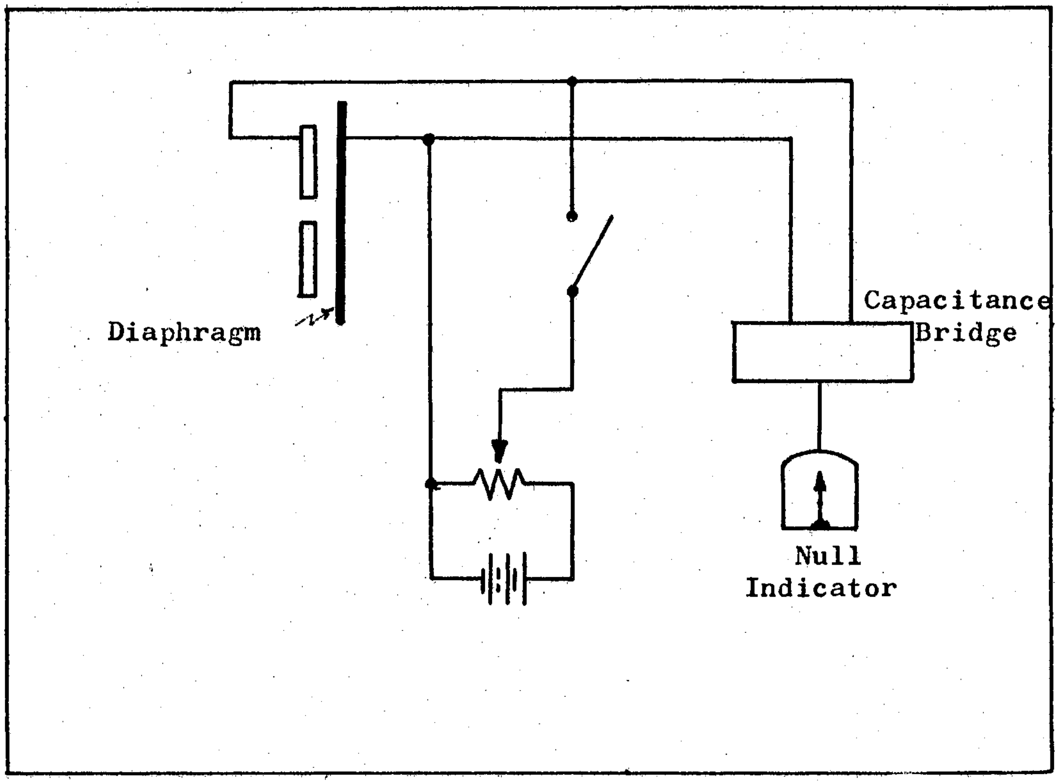


Figure 22

Pressure Diaphragm Before Sample Is Introduced

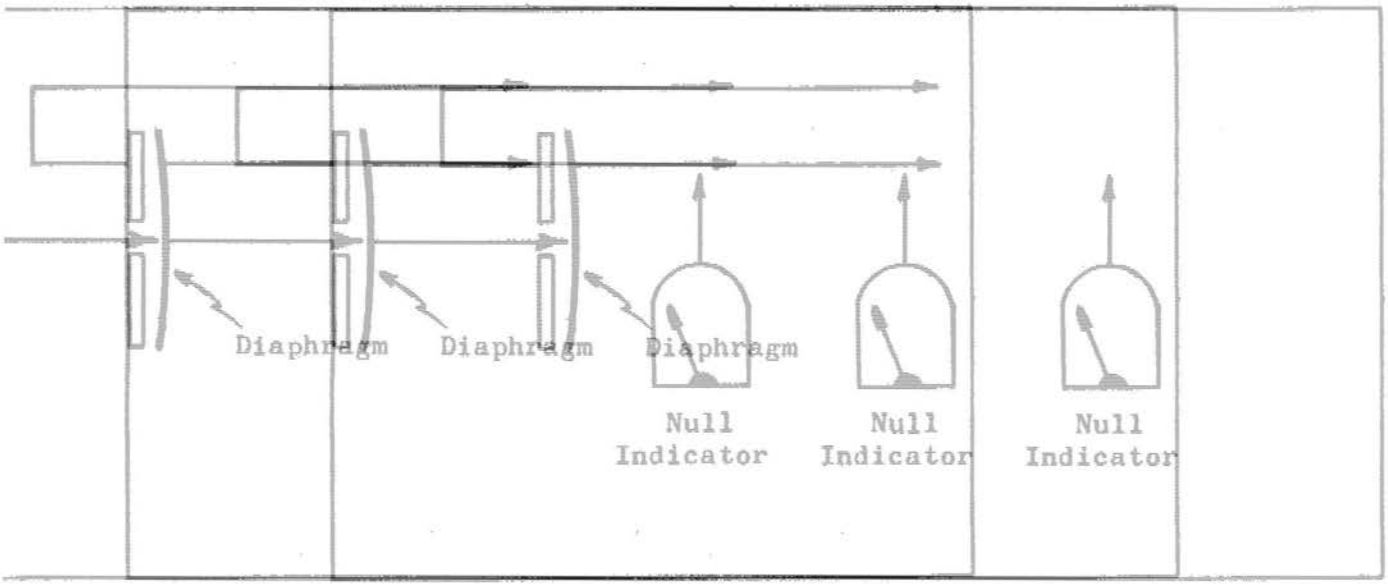


Figure 23

Pressure Diaphragm After Sample Is Introduced

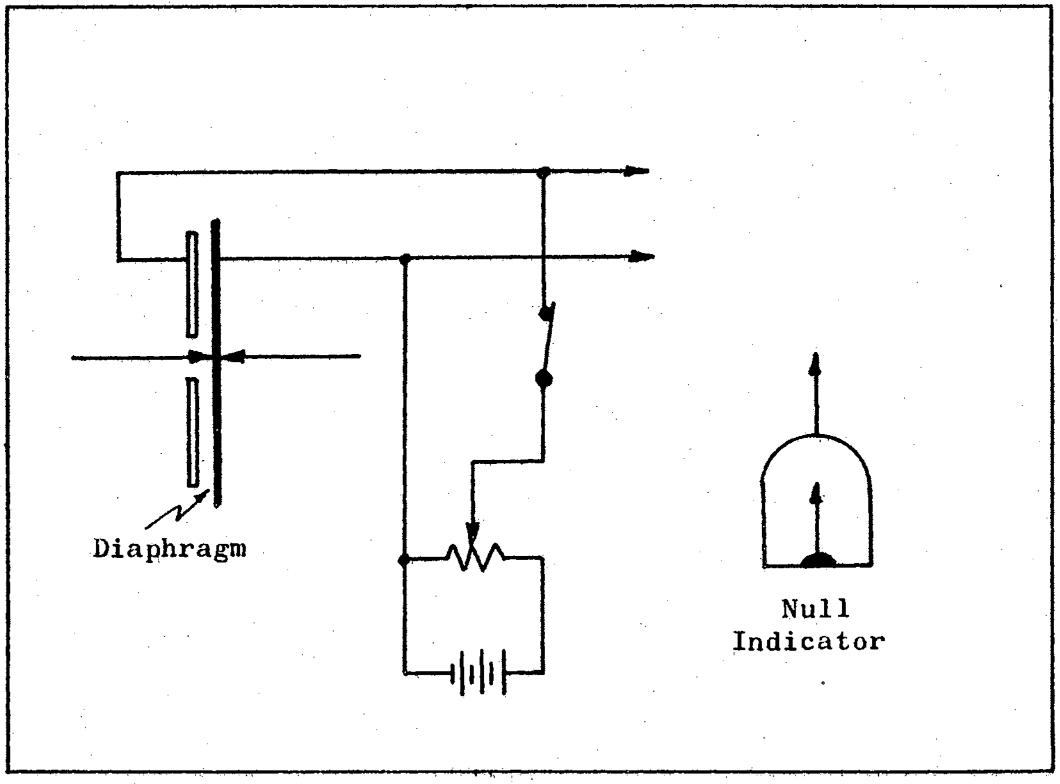


Figure 24

Pressure Diaphragm After Null Is Restored full flow. Ball type valves are necessary because any restriction in the system will greatly increase the time required to evacuate the system after each sampling. Teflon packing is required to withstand the desired operating temperature of 150°C +.

A roughing pump, capacity of 250 liters per minute, is used for the primary vacuum, and a diffusion pump (oil) is connected in series with the roughing pump to reduce the system pressure below one micron (the required operating pressure).

Discussion of Results

The first samples to be tested were essentially pure hydrocarbons, n-paraffins. A comparison between the actual molecular weights of this group of hydrocarbons and the molecular weights as determined with the vapor density instrument is given in Table VIII. From these measurements the observation was made that R, K, V and necessary conversion units could be combined into an instrument constant, $\underline{k}$; thus the equation for calculating the molecular weights from the instrument dial reading became:

$$MW = \underline{k}T\ (\rho v)\ /D^2P \tag{III-5}$$

Several synthetic blends of n-paraffins, branched chain, saturated and unsaturated hydrocarbons were prepared and their molecular weights determined, (Table IX). The error of the results obtained (weight per cent basis) was approximately +0.5 to +3.0 per cent.

The method has several limitations. One, the determinable molecular weight range is between 4.0 and 180 amu. The heavier

TABLE VIII

MOLECULAR WEIGHT OF PURE COMPONENTS BY THE VAPOR DENSITY METHOD

Component	Literature Molecular Weight	Vapor Density Molecular Weight
Benzene	78.11	78.50
1-Hexane	84.16	84.58
Cyclohexane	84.16	84.66
n-Hexane	86.16	86.56
Methylcyclohexane	98.18	98.98
2,3-Dimethylpentane	100.2	101.02
2,4-Dimethylpentane	100.2	101.08
3-Methylhexane	100.2	101.22
n-Heptane	100.2	101.32
2,2,4-Trimethylpentane	114.23	115.49
2,3,4-Trimethylpentane	114.23	115.59
n-Octane	114.23	115.71
n-Nonane	128.25	130.04
n-Decane	142.28	144.66
n-Undecane	156.3	159.12
n-Dodecane	170.33	173.40
n-Tridecane	184.36	188.04
n-Tetradecane	198.38	202.74

TABLE IX

MOLECULAR WEIGHTS OF SYNTHETIC BLENDS BY THE VAPOR DENSITY METHOD

Components	Molecular Weight	Average Mol. Wt.	Vapor density Mol. Wt.
Blend I			
n-Heptane	100.2	100.2	101.04
2, 3-Dimethylpentane	100.2		
Blend II			
1-Hexane	84.16	125.2	127.83
n-Tetradecane	198.38		
Blend III			
n-Octane	114.23	127.8	130.61
Methylcyclohexane	98.18		
n-Dodecane	170.33		
Blend IV			
3-Methylhexane	100.2	109.4	111.9
n-Undecane	156.3		
Benzene	78.11		
2, 4-Dimethylpentane	100.2		
Blend V			
n-Tridecane	184.36	119.4	120.22
2,2,4-Trimethylpentane	114.23		
n-Hexane	86.17		
Cyclohexane	84.16		
Blend VI			
n-Nonane	128.25	115.8	118.69
2,3,4-Trimethylpentane	114.23		
n-Decane	142.28		
Benzene	78.11		

components exert vapor pressures that are almost indeterminate. Since the method depends on the measurement of the vapor pressure of the sample, as the pressure becomes immeasurable the method fails. Two, the upper temperature limit is approximately 150°C. The temperature is limited by the difficulty of constructing a pressure measuring diaphragm that is linear over the desired operating pressure range. Three, the C_6 hydrocarbons exert a changing pressure in the system. It was postulated that these components may tend to dimerize when subjected to a low pressure system; this could cause the material to exert a lower vapor pressure. For best results with these type hydrocarbons, the dial reading should be made immediately after sample introduction.

The reproducibility of the molecular weights determined using the vapor density method was within 1.0 per cent.

It will be noted that the results from the vapor density method were consistently high. A reason for this deviation is not known at this time.

CHAPTER IV

EQUILIBRIUM FLASH VAPORIZATIONS

Only flow type vapor-liquid equilibrium devices were used in this study. In this apparatus the feed is partially vaporized in a pre-heater. The mixture of the two phases then passes into a contacting area and then to a disengaging chamber, where the equilibrium temperature and pressure are measured. This type of unit is commonly used in characterization studies of petroleum oils (31, 25, 12).

Thermostatic Flow Still

This constant temperature flow appratus has a limited operating flow range. When the flow rate is higher than the allowable rate, it will exceed the capacity of the heat exchanger, resulting in less vaporization than the actual amount possible at the temperature. The vapor velocity can become high enough to cause entrainment, thus enriching the vapor with the less volatile components. A complete description and schematic is not given here as this still has been described previously (2).

New EFV Flow Still

This new type flow still (2) produces a great amount of contacting between the vapor and liquid in the flash chamber,

(Figure 25). Partially vaporized feed is passed through a sintered glass tube and dispersed into fine bubbles upon entering the flash chamber. These bubbles then rise through a controlled head of liquid before the vapor escapes the chamber.

The apparatus consists of a heater-vaporizer, a flash chamber, a vapor condenser, and a liquid cooler with a small "crank" attachment, (Figure 25).

The heater-vaporizer is made of 50 cm. x 7 mm. glass tubing with a ball joint at the inlet end. The heater is attached to the flash chamber by a (24/40) ₸ glass joint which holds the fritted disc. A thin layer of asbestos paper coated with graphite impregnated with cement is molded over the glass heater. A nichrome resistance wire (1.65 ohm/ft.) is uniformly wound around the heater section. The heating wire is covered with asbestos cement, three layers of asbestos paper, one layer of glass tape, and one layer of reflective aluminum foil. A 2 mm. glass rod is placed inside the heater to increase the heating surface area to volume ratio.

The flash chamber is isothermally insulated by the vapor, and the entire internal section is adiabatically insulated by a vacuum jacket. The vacuum jacket is completely silvered with the exception of two narrow observation windows. A thermometer well extends from the top of the jacket down to the flash chamber. A water-cooled condenser is connected to the vapor outlet by means of a ball joint. As the feed flows from the heater to the flash chamber (Figure 25), the vapor portion of it is divided into a large number of very small bubbles (by the dispersing action of

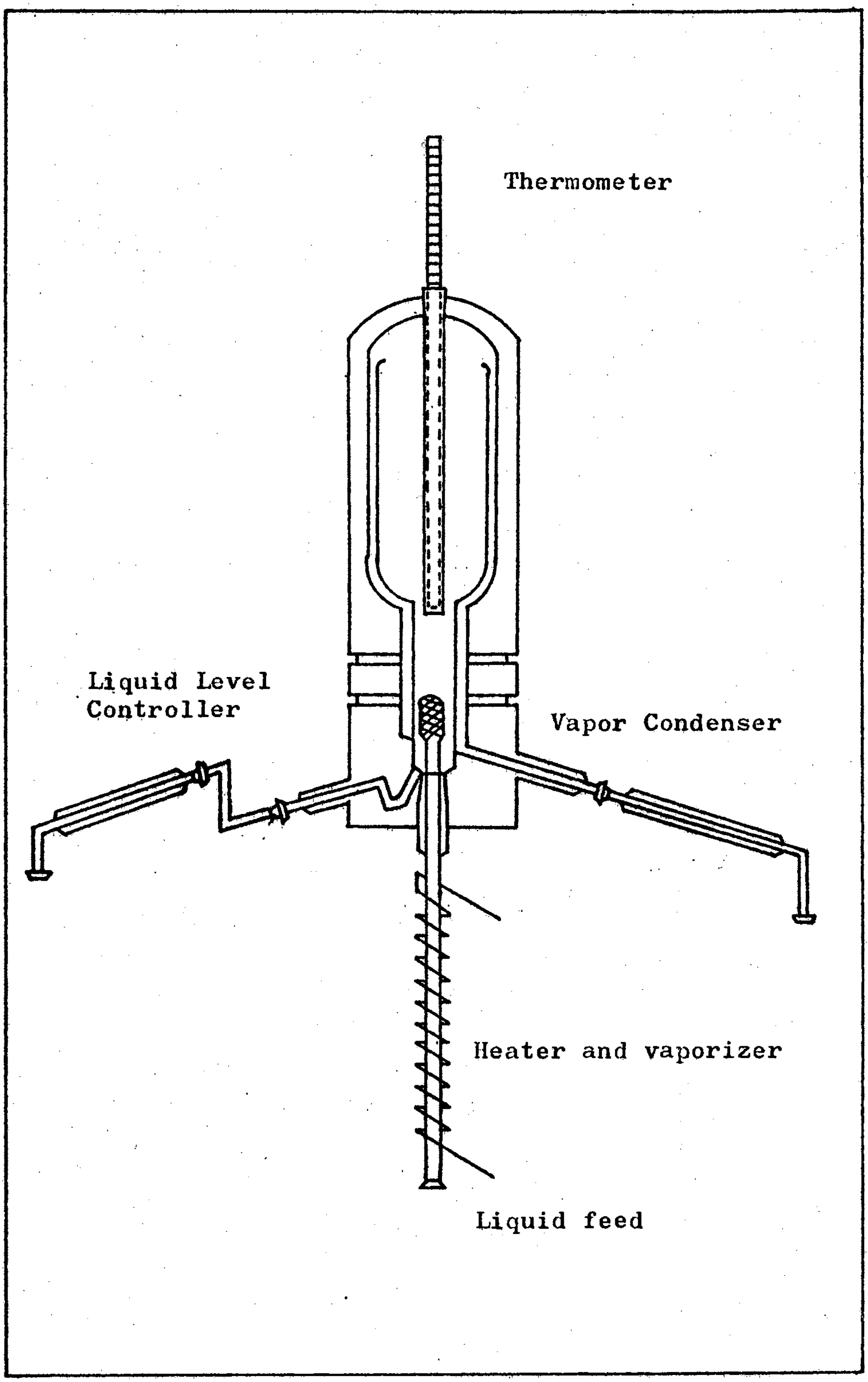


Figure 25

Equilibrium Flow Apparatus

the sintered disc) in the lower section of the flash chamber. The vapor then passes through the upper section with a much lower velocity, where it loses its liquid droplets, and finally flows downward around the flash chamber between the composite walls to the condenser. The position of the crank controls the amount of liquid hold-up and in effect governs the extent of contact area between the two phases.

A well-controlled feed flow is essential for equilibrium flow apparatus. Figure 26 shows a successful flow system that can be used for accurately (±2cc/min) controlled flow rates from 1cc/min to 50cc/min. Liquid feed is transported by a small gear pump from the bottom of a large supply tank to a constant head tank, located 10-20 ft. above the pump. The constant head tank has an overflow line which returns the excess liquid to the supply tank. Flow control from the bottom of the constant head tank, is accomplished by a Teflon needle valve on each side of a rotameter. All the connecting lines are of 3/16 inch thin wall polyethylene tubing.

An accurate pressure compensator was designed to eliminate the variations in the atmospheric pressure (Figure 27). Air from a high pressure line is reduced by a pressure regulator and dried as it passes through a silica gel bed. The air pressure is then further reduced by a needle valve, before it enters into a surge tank. Pressure in the surge tank is controlled and regulated by a sensitive gas-bubbler. The bubbler is 30 inches of 5 mm I.D. glass tubing, partially submerged in a 1 1/2 inch glass pipe filled with water. The other end of the small glass

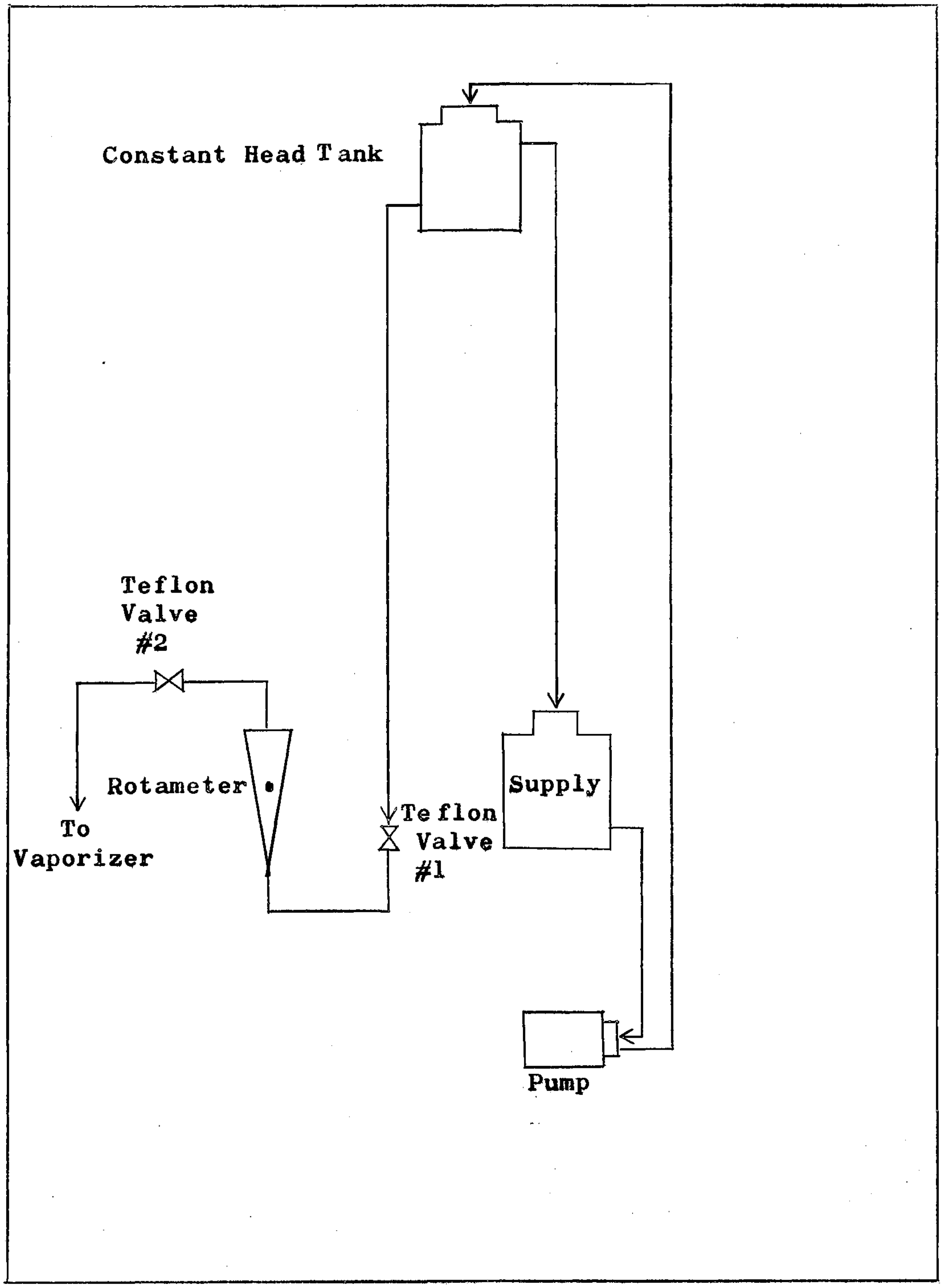


Figure 26

Feed Flow System for Flow Still

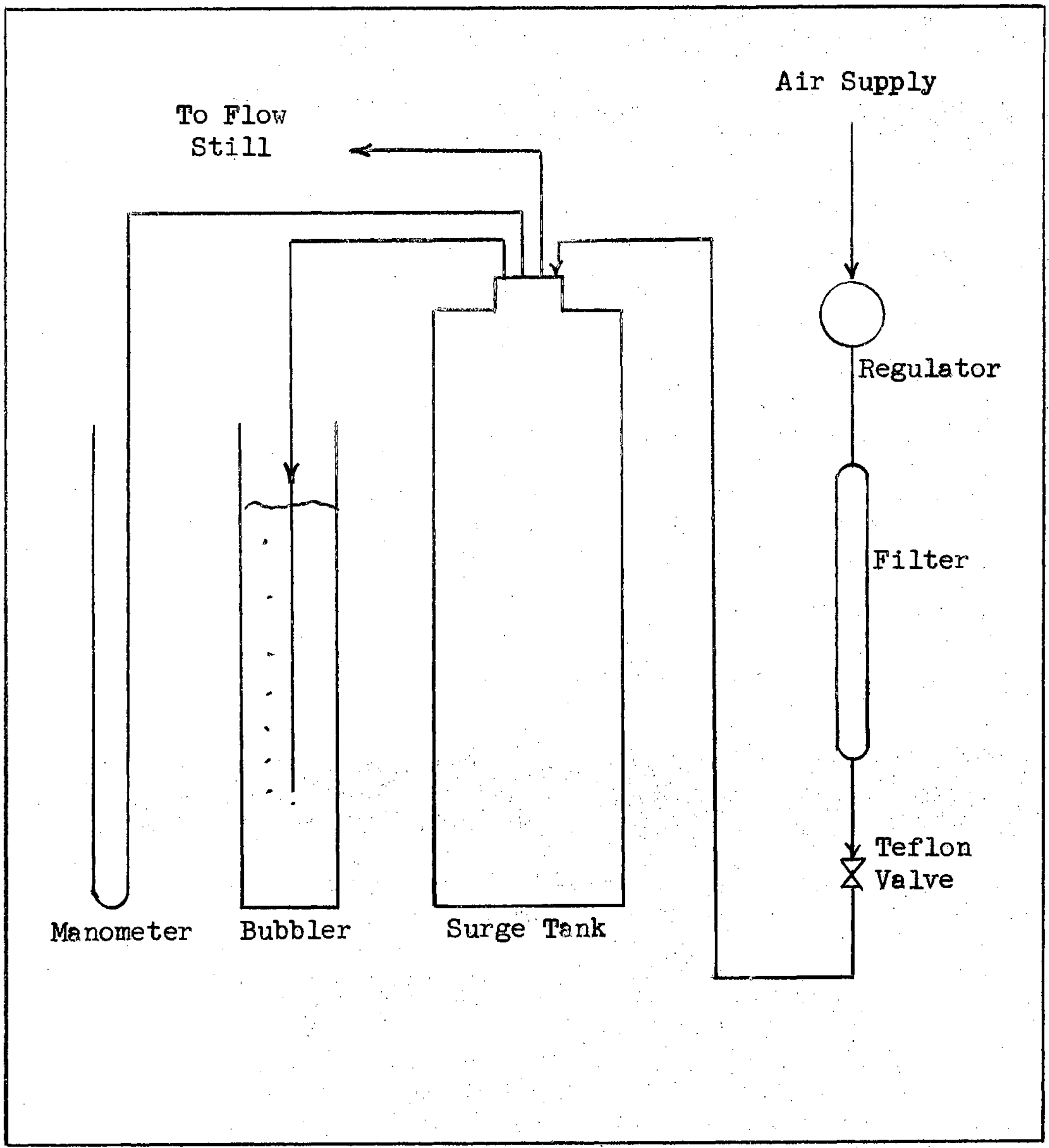


Figure 27

Pressure Regulating System for Flow Still tubing, not in the water, is connected to the surge tank. The air pressure is regulated to permit a very low flow rate (one to two bubbles/sec.) through the glass tubing into and through the water to the atmosphere. The glass tubing can be moved up or down to change the static head of water at the point where air is released. The immersion depth of the glass tubing in the H_2O is proportional to the pressure in the surge tank because the pressure drop due to the small flow of air through the bubbler is small.

Temperature measurements can be made with calibrated thermocouples or thermometers. If thermocouples are to be used, Chromel-Copnic is recommended. The wires should be flash welded together and cold baths provided.

Steady State Operation

To check for steady state operation three indications were used. One, the volume of the equilibrium products (vapor and liquid) was measured at a constant time interval (i.e., every 15 minutes) and the operating temperature of the still recorded. From the liquid volumes of the products the volumetric V/L was calculated. When three successive V/L (volumetric) ratios were the same within $\pm .01$ the products were collected for assaying. Two, samples of the products were analyzed, using the gas chromatograph, every time the liquid volumes of the products were collected. The attainment of successive Fractograms of constant peak area was accepted as proof that the still was at steady state. For the third check, the bulk molecular weights of the product streams were checked periodically. If the molecular weight of the stream remained constant during the operation, it was assumed the still was at steady state operation.

CHAPTER V

ANALYSIS OF PETROLEUM FRACTIONS

The true boiling point distribution for the oils from an atmospheric pipe still, (Figure 48), was determined using the technique described herein.

The chromatogram of a typical feed oil is shown in Figure 28. With the heavier oils the base line drift, as indicated by the dotted line, is due to column "bleeding". The methods of chromatogram analysis are discussed in Appendix E.

Figures 29 through 33 show assays obtained from the chromatographic method compared to the analyses from a 30 plate Oldershaw column. As previously discussed, because the effluent hydrocarbons are oxidized, the yields from the chromatograph are plotted in weight per cent carbon. The Oldershaw TBP volume per cent data were converted to weight per cent hydrocarbon by using the specific gravities of the hypothetical cuts of the oil fractions (22).

It should be noted that a difference exists in weight per cent hydrocarbon and weight per cent carbon. The change in carbon content within a small cut of a petroleum fraction may be assumed negligible if the components of the cut are similar (see Tables XXXII and XXXIII). However, for extreme cases, e.g., a mixture of methane and decane, the difference is not negligible. As the boiling range of the fraction increases there is a greater possibility for difference between weight per cent hydrocarbon and weight per cent carbon.

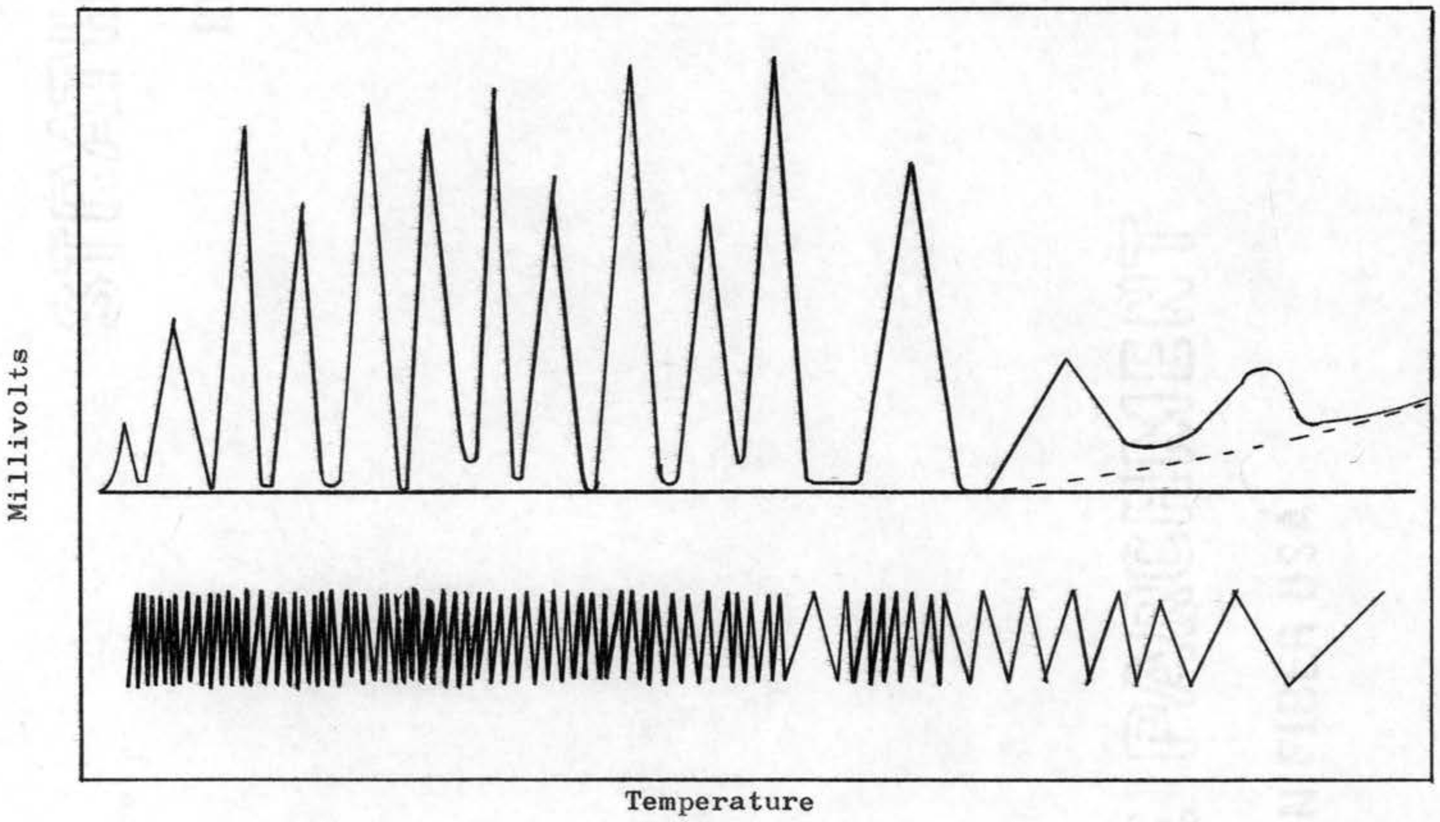


Figure 28

Typical Fractogram of Petroleum Fraction

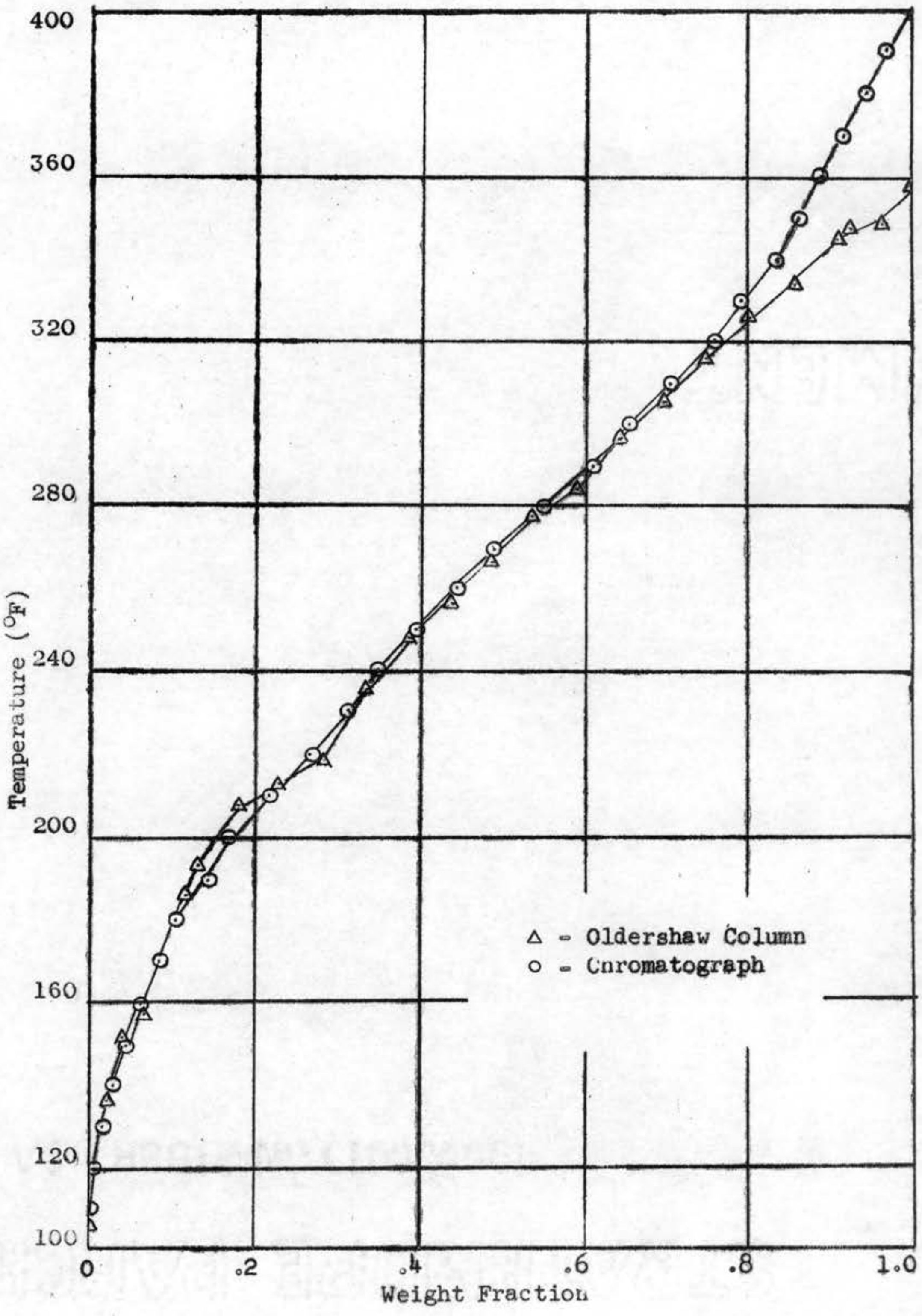


Figure 29

Analysis of Feed Oil (Sx-4031)

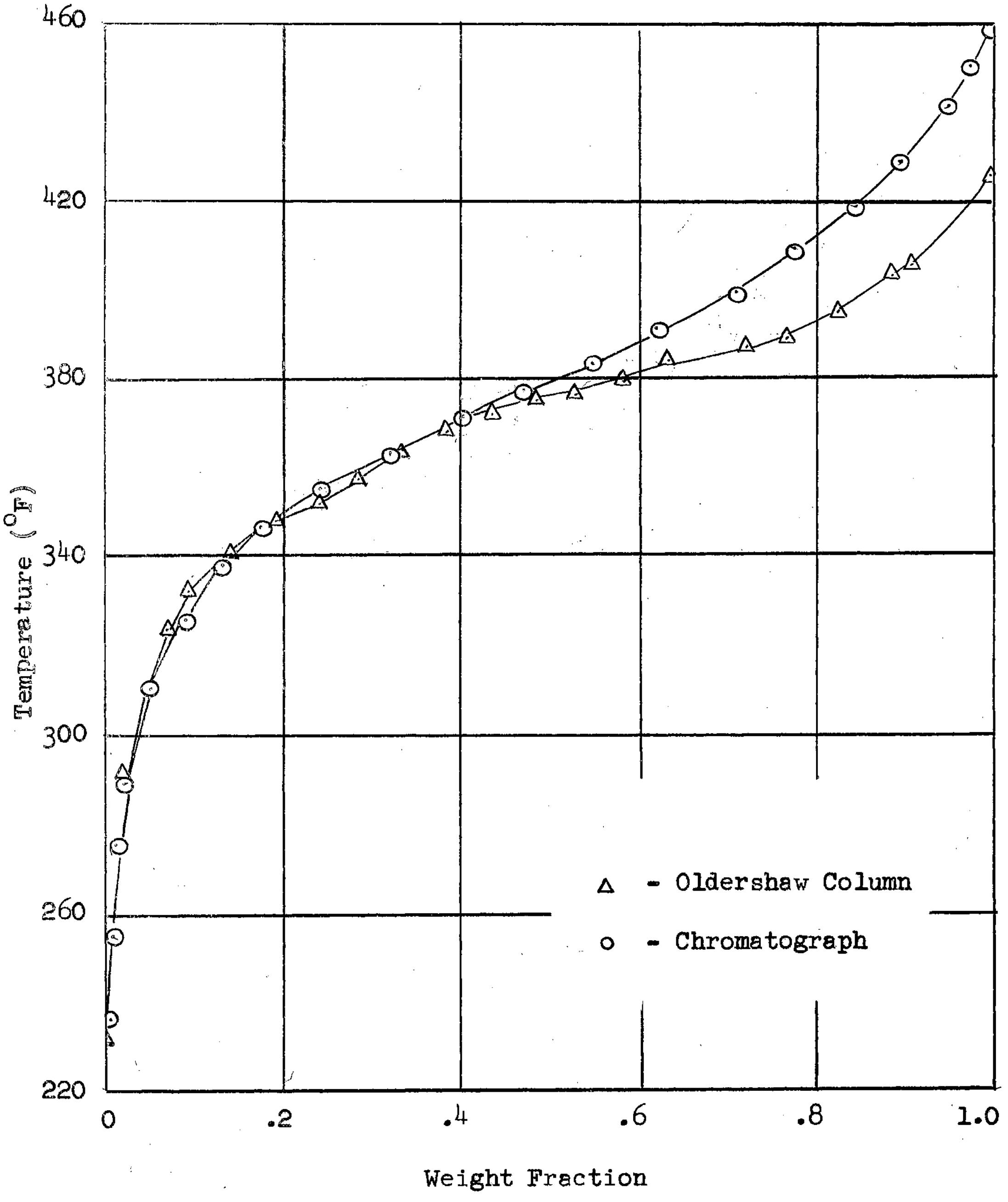


Figure 30

Analysis of Feed Oil (Sx-4032)

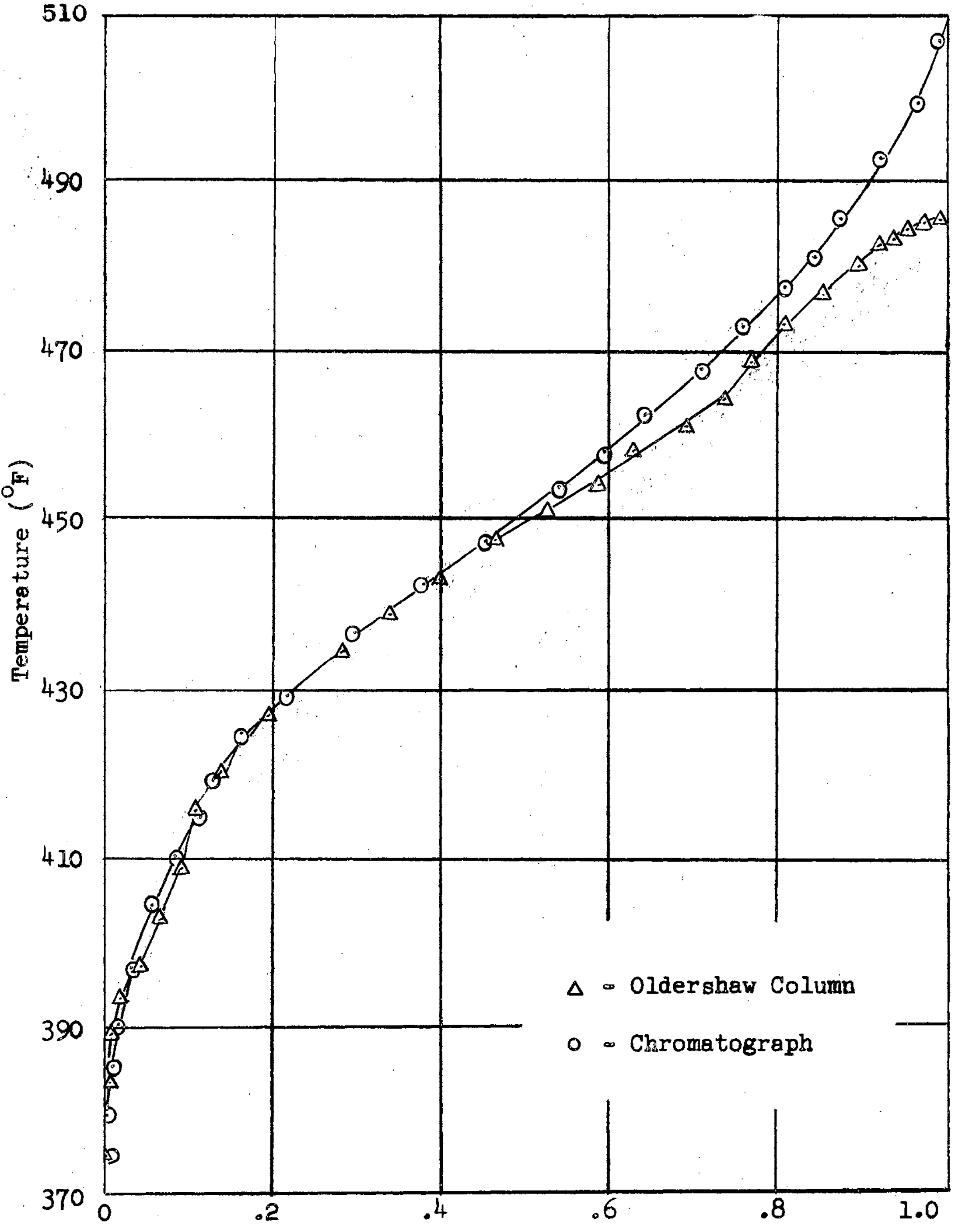


Figure 31

Analysis of Feed Oil (Sx-4033)

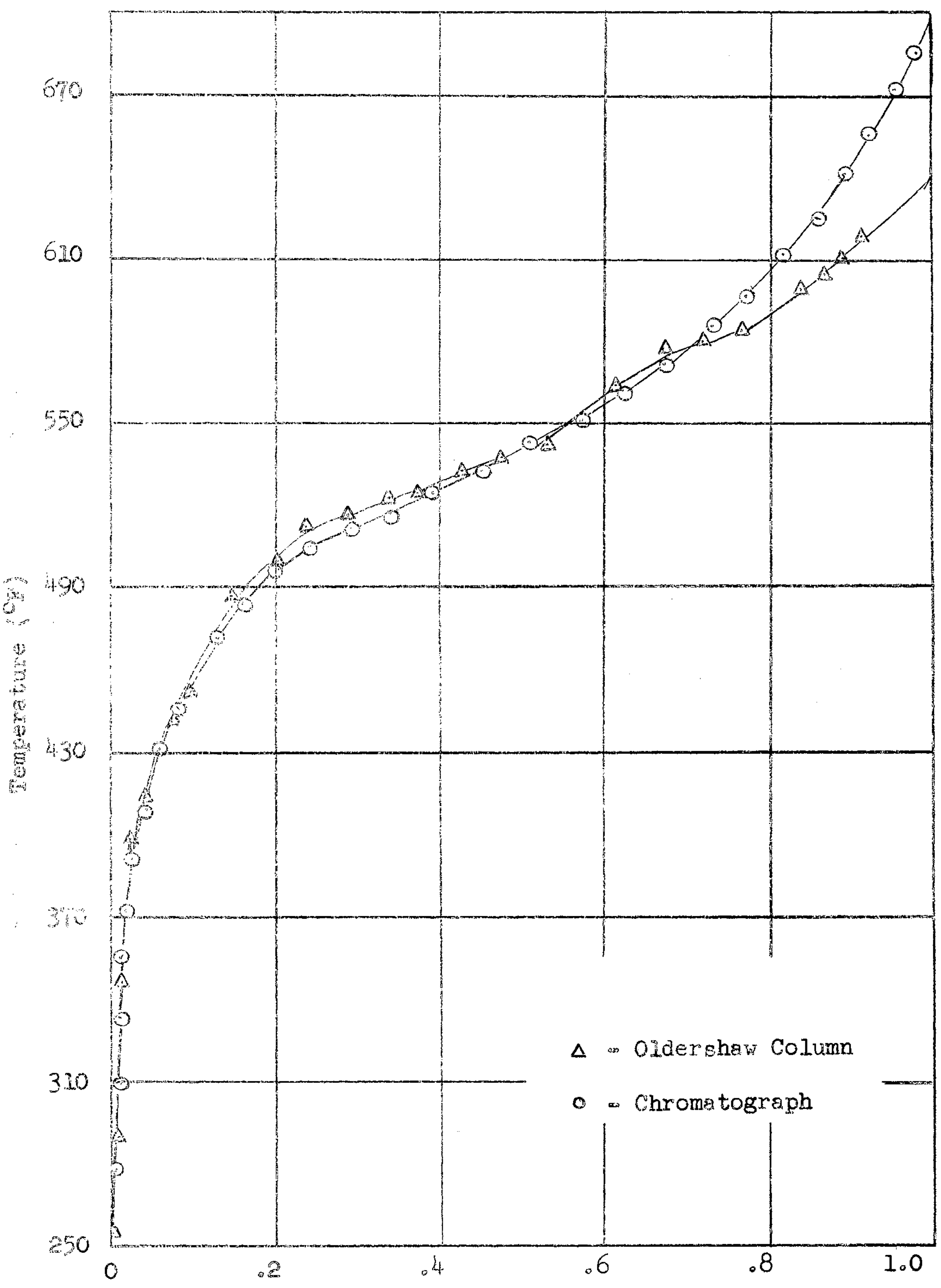


Figure 32

Analysis of Feed Oil (Sx-4034)

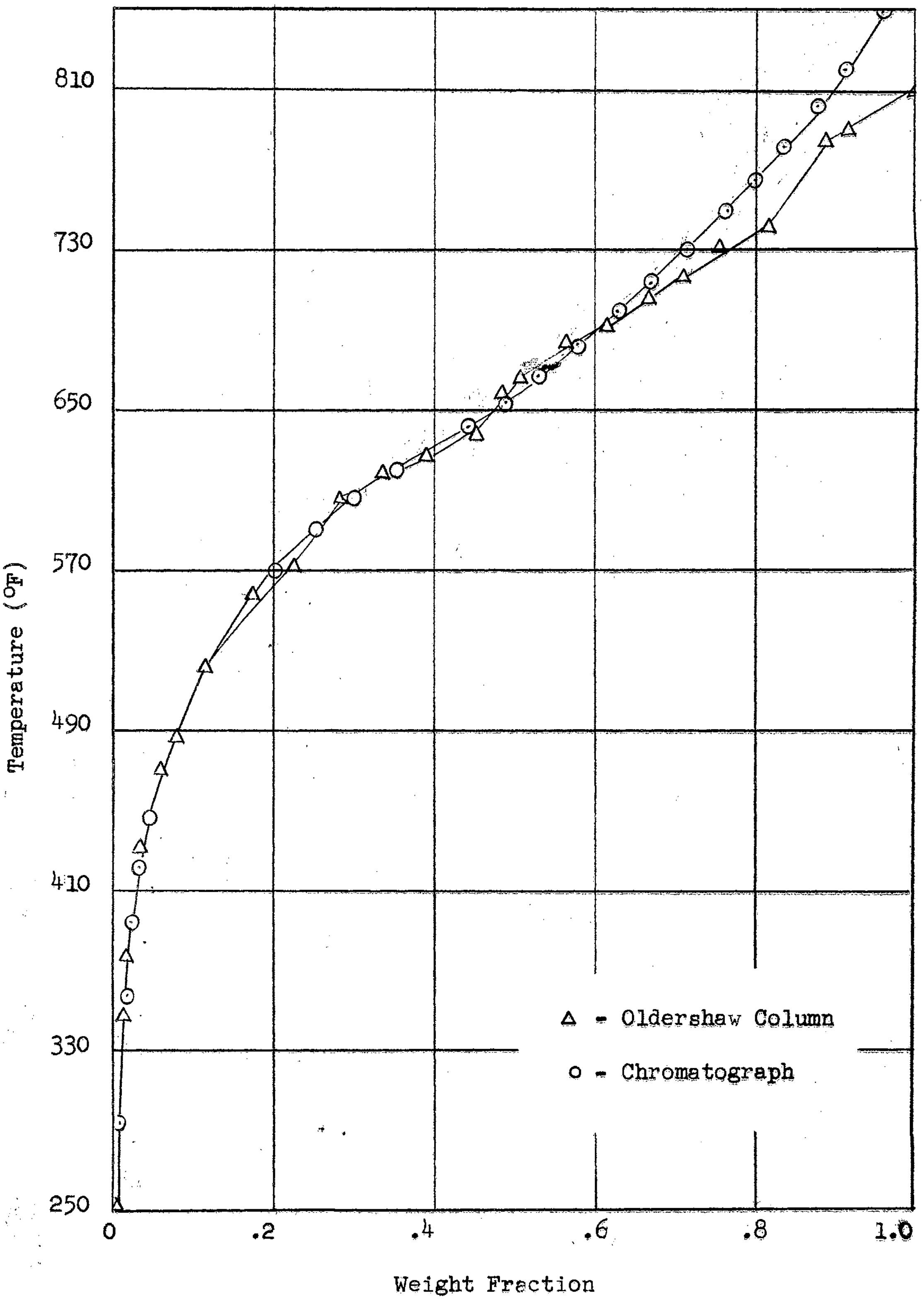


Figure 33

Analysis of Feed Oil (Sx-4035)

CHAPTER VI

DERIVED EQUILIBRIUM VAPOR-LIQUID RATIOS (K VALUES)

Engineers utilize vapor-liquid phase distribution coefficients for design purposes. The subject for the case of complex hydrocarbon systems is fully discussed by Edmister (10).

In the preceding chapters the apparatus and experimental methods of obtaining the equilibrium products, TBP distillation curves, and molecular weights of petroleum fractions were discussed. This chapter deals with the calculation of K values of petroleum fractions.

Application of the Integral Technique

The integral technique is ideal for calculations of complex mixtures (i.e., petroleum fractions) because it does not require complete knowledge of the components. The principles of the method were introduced by Katz and Brown (24) and several variations have been published (5, 6, 7, 13, 14). Edmister (10) has presented an application of the technique to four types of calculations; equilibrium flash vaporizations, bubble and dew points, fractional distillations, and batch distillations. Amir-Yeganeh (2) presented a comprehensive discussion of the theoretical concepts of the integral technique, therefore, only a brief discussion of these comcepts is given here.

Applying the integral technique to flash vaporization calculations for an infinite mixture (i.e., petroleum fractions) requires finding the molar ratio of the equilibrium products, L/V, by trial and error. The following equations are used for this calculation

$$v_i/f_i = \frac{1}{1 + L/K_iV} \qquad \text{(VI-1)}$$

$$l_i/f_i = \frac{1}{1 + K_iV/L} \qquad \text{(VI-2)}$$

where L and V are the moles of liquid and vapor mixtures; and v, l, and f are the moles of small increments or cuts of the vapor, liquid, and feed respectively.

Equations VI-1 and VI-2 are based on component material balances and the definition of K, where K is defined as

$$K_i = y/x = \frac{v_i/\sum v_i}{l_i/\sum l_i} \qquad \text{(VI-3)}$$

The summation of v and l are defined as V and L respectively, Therefore, by substitution into Equation VI-3

$$K_i = \frac{v_i L}{l_i V} \qquad \text{(VI-4)}$$

The following outline is a stepwise procedure that was used in applying the above technique.

1. Weight fraction TBP data of the feedstock were obtained from a gas chromatographic assay.
2. The feedstock was fractionated using the Oldershaw column and the pseudo-components collected for measuring their average molecular weights. (This step can be eliminated if a fraction collector is used with the

chromatograph, see recommendation.)

3. Average molecular weights of the fractions obtained from the Oldershaw assay were determined using the method described in Chapter III.
4. Knowledge of the molecular weights of the individual cuts permits the chromatographic weight fraction TBP data to be converted to a molar TBP curve.
5. Vapor pressures were then obtained from a Maxwell and Bonnell (28) correlation, for each component at its normal boiling point, T_b, and the equilibrium flash temperature, T_e.
6. The critical constants, P_c and T_c, necessary to calculate θ were obtained from Figures 34, 35, and 36. These correlations of P_c and T_c as a function of molecular weight and boiling point were made using data from Edmister (15). The critical constants from these correlations agree well with values from vapor pressure data.
7. Ideal K-values were then calculated using the vapor pressure, system pressure and imperfection pressure correction.
8. The activity coefficient, γ, was derived, using an iteration procedure that corrects V/L (calculated) equal to V/L (experimental) (22).
9. K_A-values were then calculated as the product of K_I and the activity coefficient or correction factor from Step 8.
10. Applying the integral technique (equations VI-1 and VI-2) the equilibrium TBP product curves were generated (10).

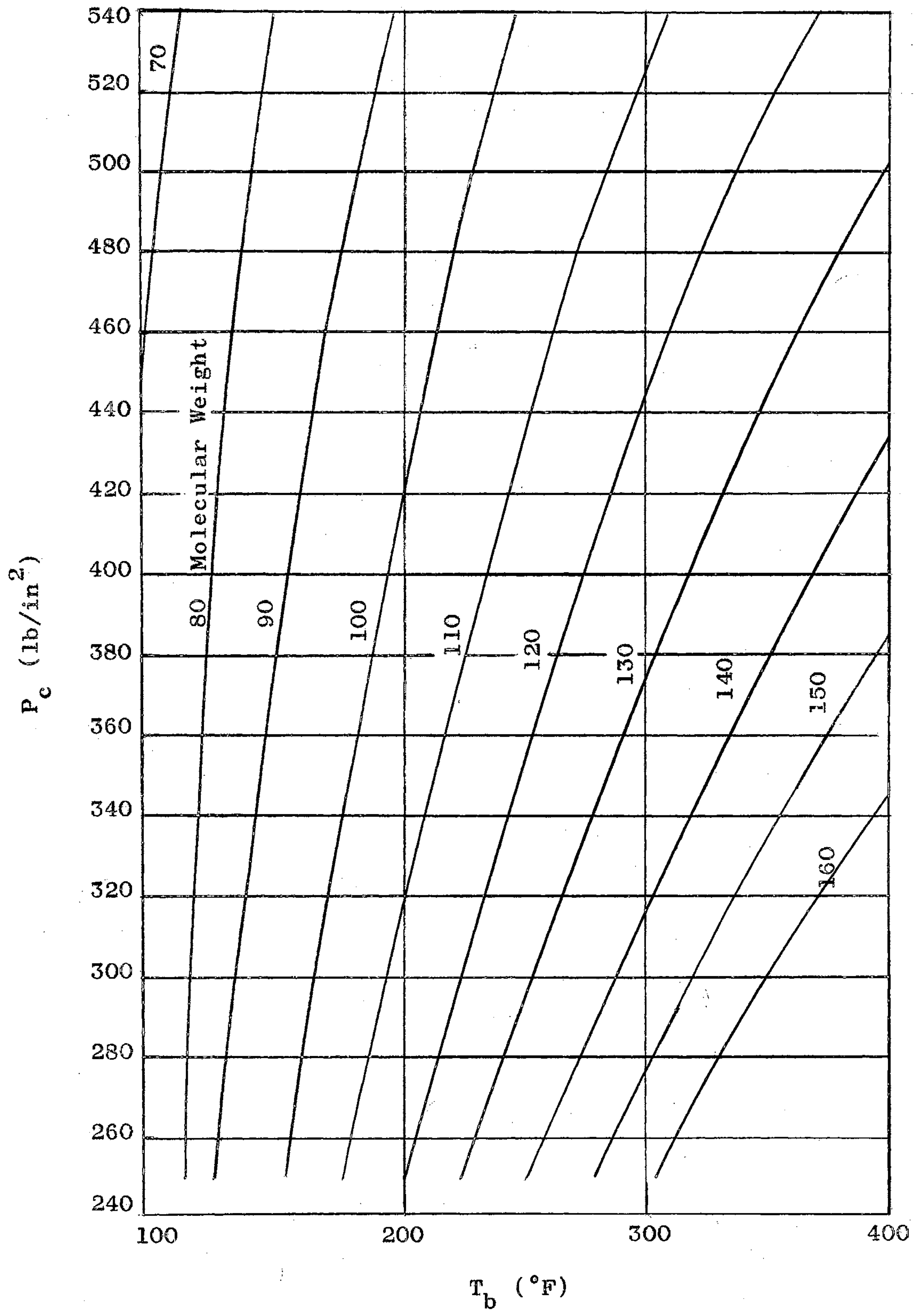


Figure 34

P_c as a Function of T_b and Molecular Weight

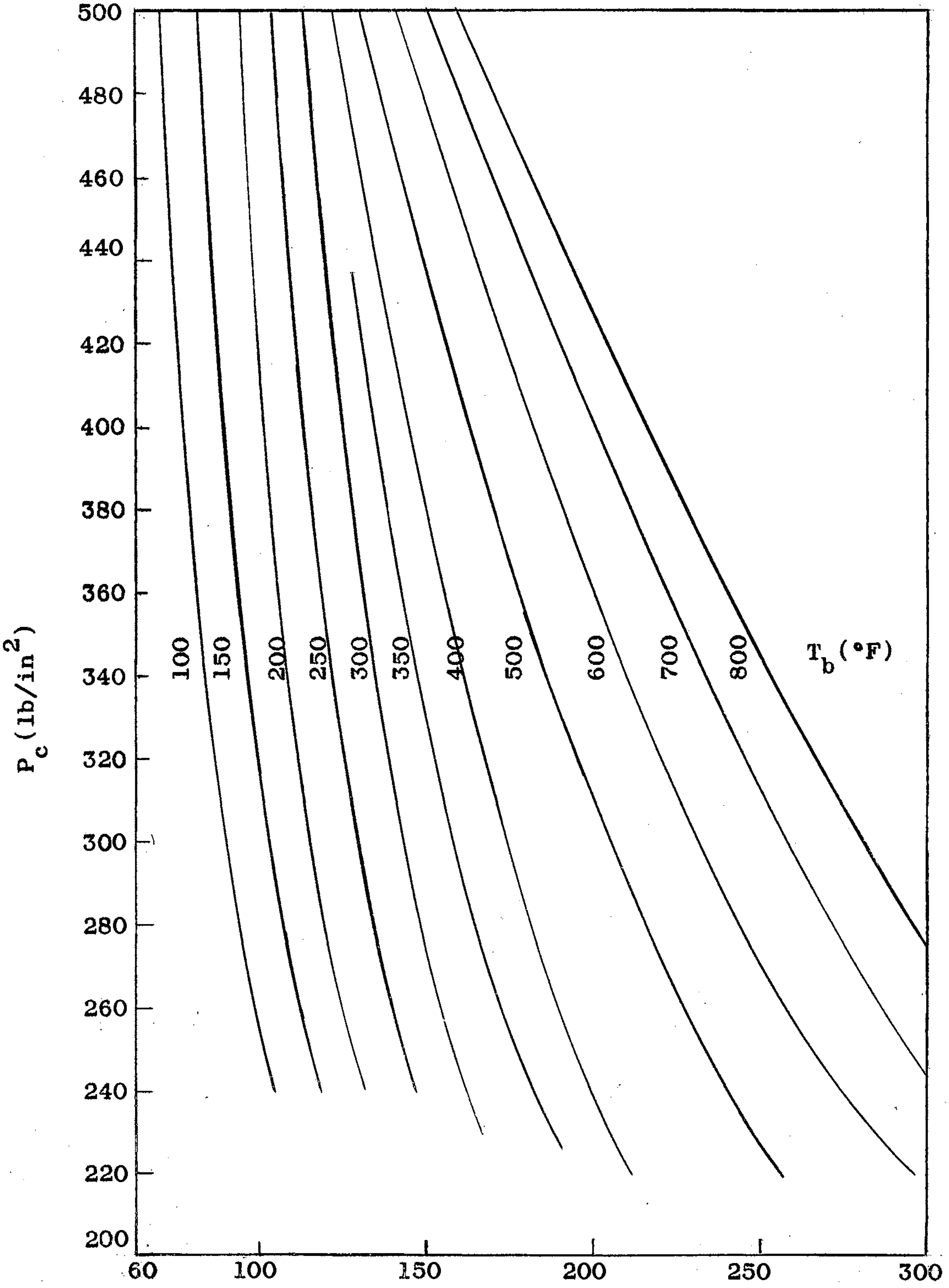
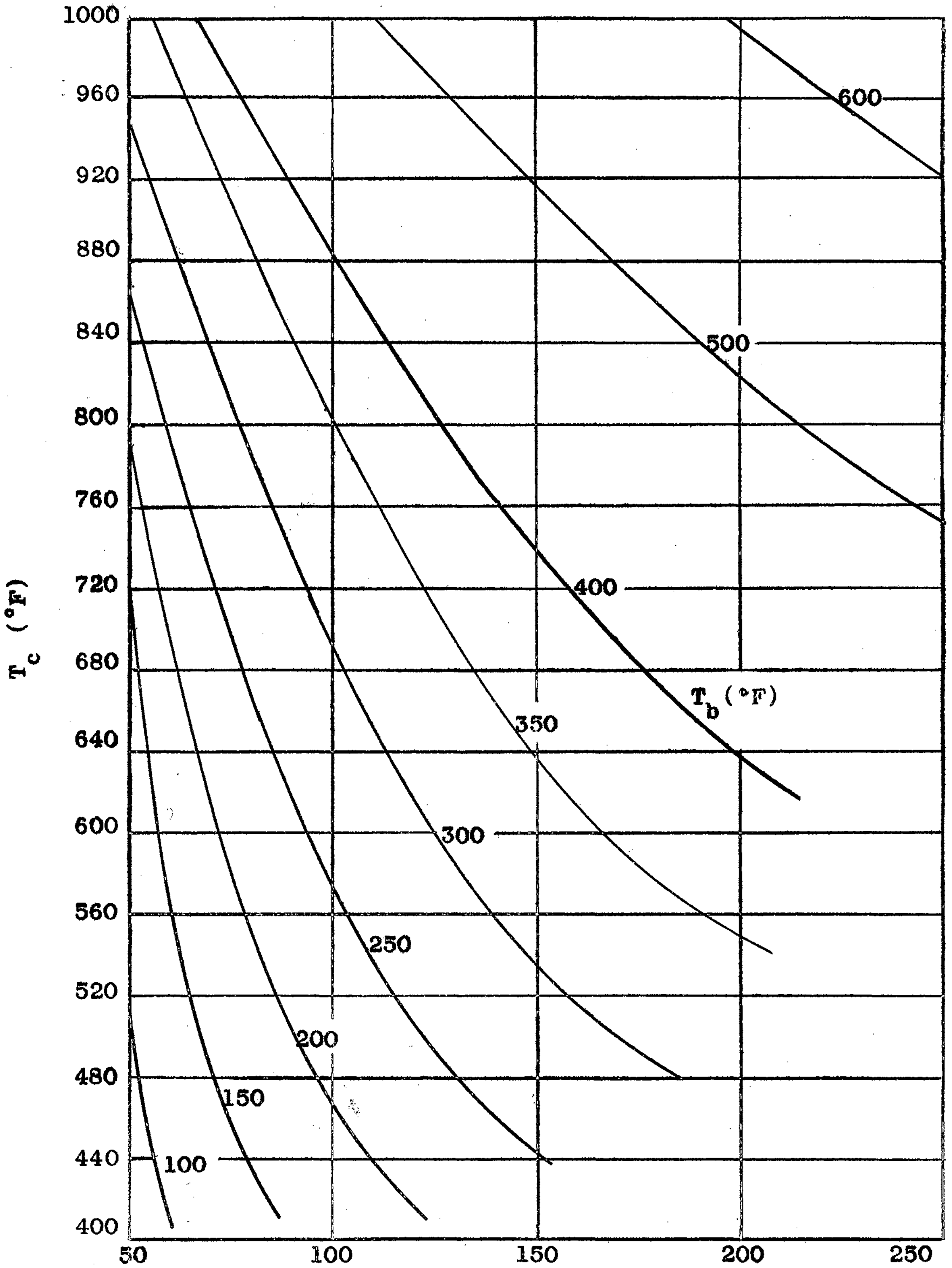


Figure 35

P_c as a Function of Molecular Weight and T_b



Molecular Weight

Figure 36

T_c as a Function of Molecular Weight and T_b

CHAPTER VII

RESULTS, CONCLUSIONS AND RECOMMENDATIONS

The primary objective of this study was to develop and improve techniques of evaluating vapor-liquid equilibrium ratios (K-values) of petroleum fractions.

K-values were calculated using vapor pressures, system pressure, and the imperfection pressure correction, the latter calculated from a virial equation of state. The normal boiling points of the pseudo-components were obtained from both conventional (Oldershaw column) and chromatographic assays.

The first set of K-data, (Tables X, XI, XII) are K_{Ideal} obtained directly from the vapor pressure, system pressure, and imperfection pressure correction for a light naphtha fraction. The second set of K-values, (Table XIII, XIV, XV), are K_{Actual} that were calculated from the product of K_I and the derived activity coefficient, γ, the correction necessary to adjust V/L (calculated) equal to V/L (experimental).

A comparison of the K_A values, where the normal boiling points of the components were determined from both analytical methods, is shown in Figures 37, 38, and 39. These figures, in which log K is plotted as a function of $1/T_b$, indicate good agreement between the two methods. The largest deviation between the two analytical methods occurs at the higher temperatures

TABLE X

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4031

T_e = 243.8°F P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	Θ
105.00	7.400	6.18225	1.19697
140.00	4.600	4.11683	1.11736
160.00	3.450	3.18744	1.08237
180.00	2.500	2.36315	1.05790
195.00	2.050	1.96548	1.04299
210.00	1.650	1.60384	1.02877
220.00	1.400	1.37436	1.01865
230.00	1.220	1.20672	1.01100
240.00	1.050	1.04719	1.00267
250.00	.900	.90510	.99435
260.00	.770	.78051	.98653
270.00	.670	.68334	.98046
280.00	.560	.57572	.97267
290.00	.480	.49740	.96500
300.00	.400	.41811	.95667
310.00	.340	.35841	.94861
320.00	.290	.30764	.94263
340.00	.205	.22111	.92713
362.00	.138	.15260	.90427
400.00	.135	.15339	.88009
412.00	.085	.09867	.86142

TABLE XI

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4031

T_e = 258.2°F P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	Θ
105.00	8.80000	7.15652	1.22964
140.00	5.60000	4.90037	1.14276
160.00	4.20000	3.80944	1.10252
180.00	3.20000	2.96134	1.08059
195.00	2.60000	2.44835	1.06193
210.00	2.10000	2.00763	1.04600
220.00	1.80000	1.73876	1.03521
230.00	1.55000	1.51080	1.02594
240.00	1.31000	1.28983	1.01563
250.00	1.16000	1.15022	1.00849
260.00	.99000	.99054	.99944
270.00	.84000	.84755	.99108
280.00	.72000	.73194	.98368
290.00	.62000	.63523	.97601
300.00	.53000	.54741	.96818
310.00	.45000	.46879	.95990
320.00	.38000	.39867	.95316
340.00	.27500	.29319	.93793
362.00	.18700	.20419	.91578
400.00	.13500	.15189	.88874
412.00	.08500	.09753	.87145

TABLE XII

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4031

T_e = 268.9°F　　　　P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	Θ
105.00	9.70000	7.77581	1.24745
140.00	6.20000	5.36630	1.15535
160.00	4.70000	4.21935	1.11391
180.00	3.60000	3.29832	1.09146
195.00	2.85000	2.66717	1.06854
210.00	2.35000	2.22945	1.05406
220.00	2.00000	1.91916	1.04212
230.00	1.75000	1.69268	1.03385
240.00	1.50000	1.46466	1.02412
250.00	1.28000	1.26208	1.01419
260.00	1.12000	1.11297	1.00631
270.00	.98000	.98104	.99893
280.00	.83000	.83792	.99054
290.00	.70000	.71287	.98193
300.00	.61000	.62574	.97483
310.00	.52000	.53793	.96665
320.00	.44000	.45846	.95972
340.00	.32000	.33875	.94462
362.00	.21500	.23300	.92272
400.00	.13500	.15090	.89461
421.00	.08500	.09678	.87827

TABLE XIII

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4031

$\gamma = 1.015$

$V/L = .481$

$T_e = 243.86°F$

$P_e = 760.00$ mm Hg

	temp.(°F)	liquid	vapor	l/f	v/f	Mole fraction feed	K_A
0	105.00	.0000	.0000	.2488	.7511	.0000	6.2749
1	140.00	.0190	.0957	.3322	.6677	.0439	4.1785
2	160.00	.0424	.1810	.3911	.6088	.0874	3.2352
3	180.00	.0793	.2823	.4642	.5357	.1452	2.3985
4	195.00	.1266	.3846	.5102	.4897	.2104	1.9949
5	210.00	.1873	.4939	.5608	.4391	.2869	1.6278
6	220.00	.2381	.5705	.5984	.4015	.3461	1.3949
7	230.00	.2846	.6316	.6292	.3707	.3973	1.2248
8	240.00	.3211	.6734	.6616	.3383	.4355	1.0628
9	250.00	.3690	.7207	.6935	.3064	.4833	.9186
10	260.00	.4236	.7673	.7240	.2759	.5353	.7922
11	270.00	.4752	.8056	.7498	.2501	.5825	.6935
12	280.00	.5427	.8485	.7805	.2194	.6420	.5843
13	290.00	.6115	.8863	.8045	.1954	.7008	.5048
14	300.00	.6627	.9101	.8304	.1695	.7431	.4243
15	310.00	.2842	.7349	.8510	.1489	.4306	.3637
16	320.00	.7635	.9475	.8694	.1305	.8233	.3122
17	340.00	.8464	.9699	.9025	.0974	.8865	.2244
18	362.00	.9050	.9810	.9306	.0693	.9297	.1548
19	400.00	.9870	.9983	.9303	.0696	.9907	.1556
20	412.00	.9999	1.0000	.9540	.0459	1.0000	.1001

TABLE XIV

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4031

γ = .965 T_e = 258.20°F

V/L = 1.140 P_e = 760.00 mm Hg

Temp.(°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
105.00	.0000	.0000	.1127	.8872	.0000	6.9060
140.00	.0125	.0706	.1565	.8434	.0435	4.7288
160.00	.0287	.1374	.1926	.8073	.0866	3.6761
180.00	.0550	.2218	.2349	.7650	.1439	2.8576
195.00	.0901	.3123	.2707	.7292	.2085	2.3626
210.00	.1373	.4132	.3117	.6882	.2843	1.9373
220.00	.1784	.4872	.3433	.6566	.3429	1.6779
230.00	.2173	.5884	.3757	.6242	.3936	1.4579
240.00	.2492	.5915	.4134	.5865	.4315	1.2446
250.00	.2924	.6424	.4414	.5585	.4788	1.1099
260.00	.3430	.6946	.4785	.5214	.5303	.9558
270.00	.3930	.7387	.5175	.4824	.5771	.8178
280.00	.4607	.7900	.5540	.4459	.6361	.7063
290.00	.5317	.8369	.5887	.4112	.6943	.6129
300.00	.5861	.8680	.6241	.3758	.7362	.5282
310.00	.6538	.9012	.6598	.3401	.7856	.4523
320.00	.7108	.9251	.6951	.3048	.8249	.3847
340.00	.8076	.9576	.7561	.2438	.8875	.2829
362.00	.8795	.9749	.8166	.1833	.9303	.1970
400.00	.9828	.9978	.8568	.1431	.9908	.1465
412.00	1.0000	.9999	.9031	.0968	1.0000	.0941

TABLE XV

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4031

γ = 1.000

V/L = 2.714

T_e = 268.90°F

P_e = 760.0 mm Hg

	temp.(°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
0	105.00	.0000	.0000	.0452	.9547	.0000	7.7758
1	140.00	.0089	.0568	.0643	.9356	.0439	5.3663
2	160.00	.0207	.1121	.0804	.9195	.0874	4.2193
3	180.00	.0401	.1840	.1005	.8994	.1452	3.2983
4	195.00	.0670	.2633	.1215	.8784	.2104	2.6671
5	210.00	.1043	.3543	.1419	.8580	.2869	2.2294
6	220.00	.1375	.4320	.1612	.8387	.3461	1.9191
7	230.00	.1696	.4813	.1789	.8210	.3973	1.6926
8	240.00	.1965	.5237	.2012	.7987	.4355	1.4646
9	250.00	.2344	.5751	.2261	.7738	.4833	1.2620
10	260.00	.2803	.6293	.2489	.7510	.5353	1.1129
11	270.00	.3261	.6771	.2732	.7267	.5825	.9810
12	280.00	.3900	.7350	.3056	.6943	.6420	.8379
13	290.00	.4603	.7895	.3410	.6589	.7008	.7128
14	300.00	.5163	.8269	.3708	.6291	.7432	.6257
15	320.00	.6369	.8921	.4458	.5541	.8233	.4584
16	340.00	.7489	.9373	.5213	.4786	.8865	.3387
17	362.00	.8394	.9630	.6129	.3870	.9297	.2330
18	400.00	.9744	.9967	.7097	.2902	.9907	.1509
19	412.00	1.0002	.9999	.7921	.2078	1.0000	.0967

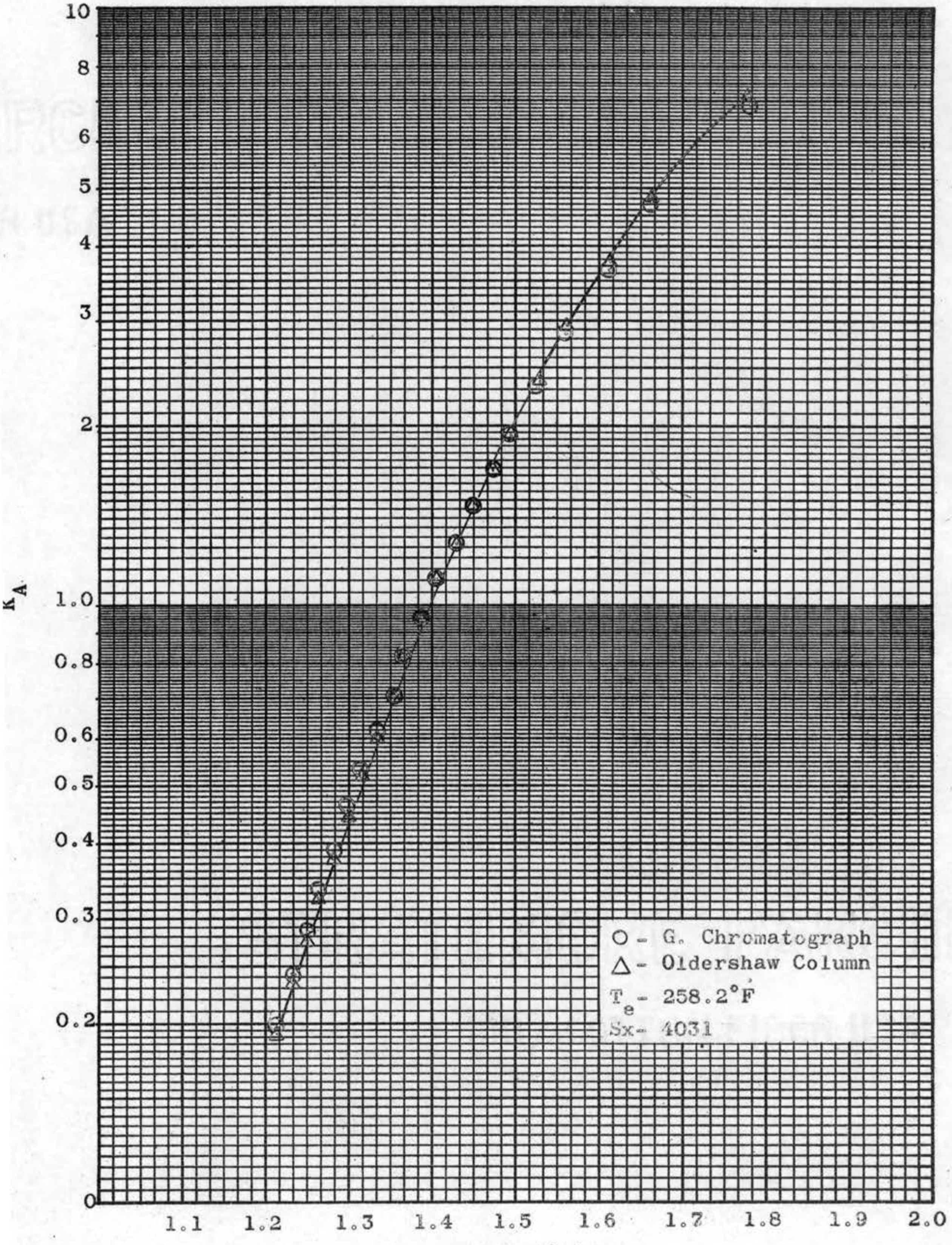


Figure 37

Comparison of Log K_A as a Function of $1/T_h$

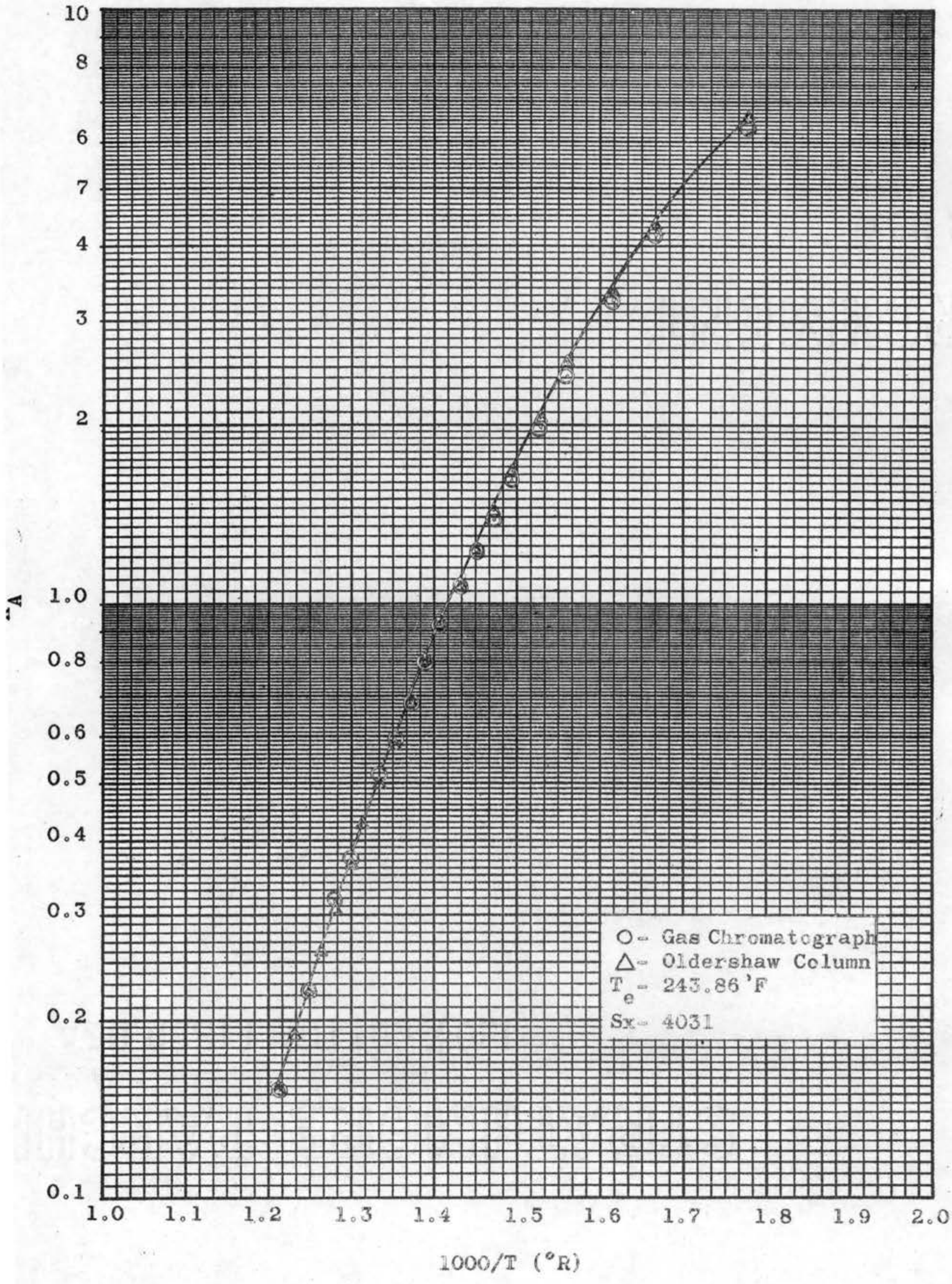


Figure 38

Comparison of Log K_A as a Function of $1/T_b$

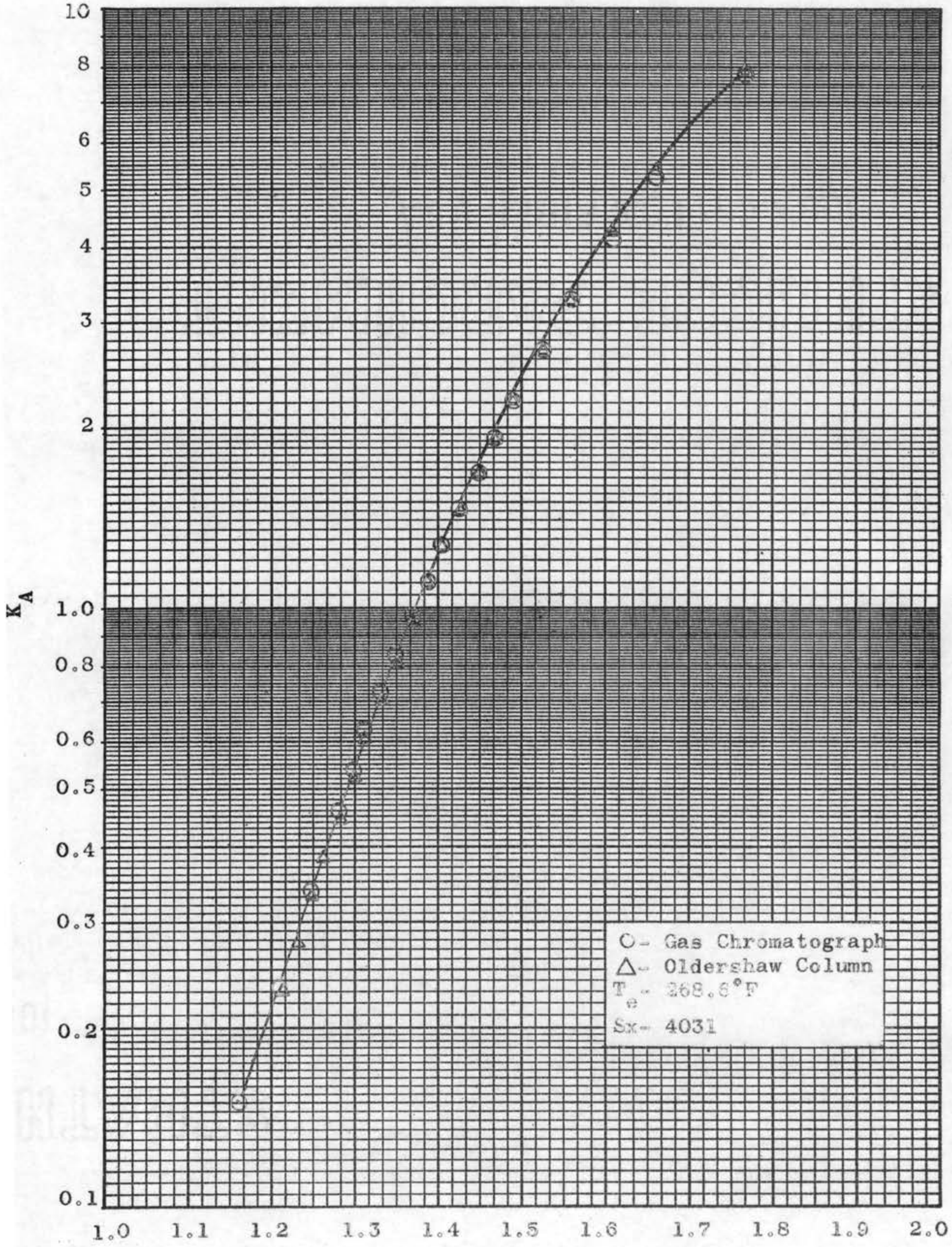


Figure 39

Comparison of Log K_A as a Function of $1/T_b$

(Figure 40). This indicates better separation by the chromatographic method of the heavier components.

The derived values of the activity coefficient were calculated for each equilibrium flash using the computer programs written by Henderson (22). In these equilibrium flash vaporization calculations, V/L (calculated) was compared with V/L (experimental). If V/L (calculated) was not equal to V/L (experimental) the activity coefficient, γ, was increased or decreased, depending if the difference between V/L (calculated) and V/L (experimental) was high or low, and the calculation repeated until V/L (calculated) equaled V/L (experimental).

The derived values of the activity coefficient when plotted against reciprocal equilibrium temperature, (Figure 41), suggest that more correction is needed to make V/L (calculated) equal to V/L (experimental) as the values of V/L increase and/or as the flash temperature increases.

Conclusions

1. The method and apparatus developed to measure molecular weights of multicomponent mixtures is accurate to ± three per cent (within the range of 4 to 180 amu).

2. Precision TBP curves obtained from chromatographic assays agree with the conventional batch distillation assays, except for the heavier components. Chromatographic assays of the heavier components were as much as 45°F higher than the batch distillations. TBP curves obtained from the Sarnia Fractionator did not give sufficient resolution for calculation of good K data.

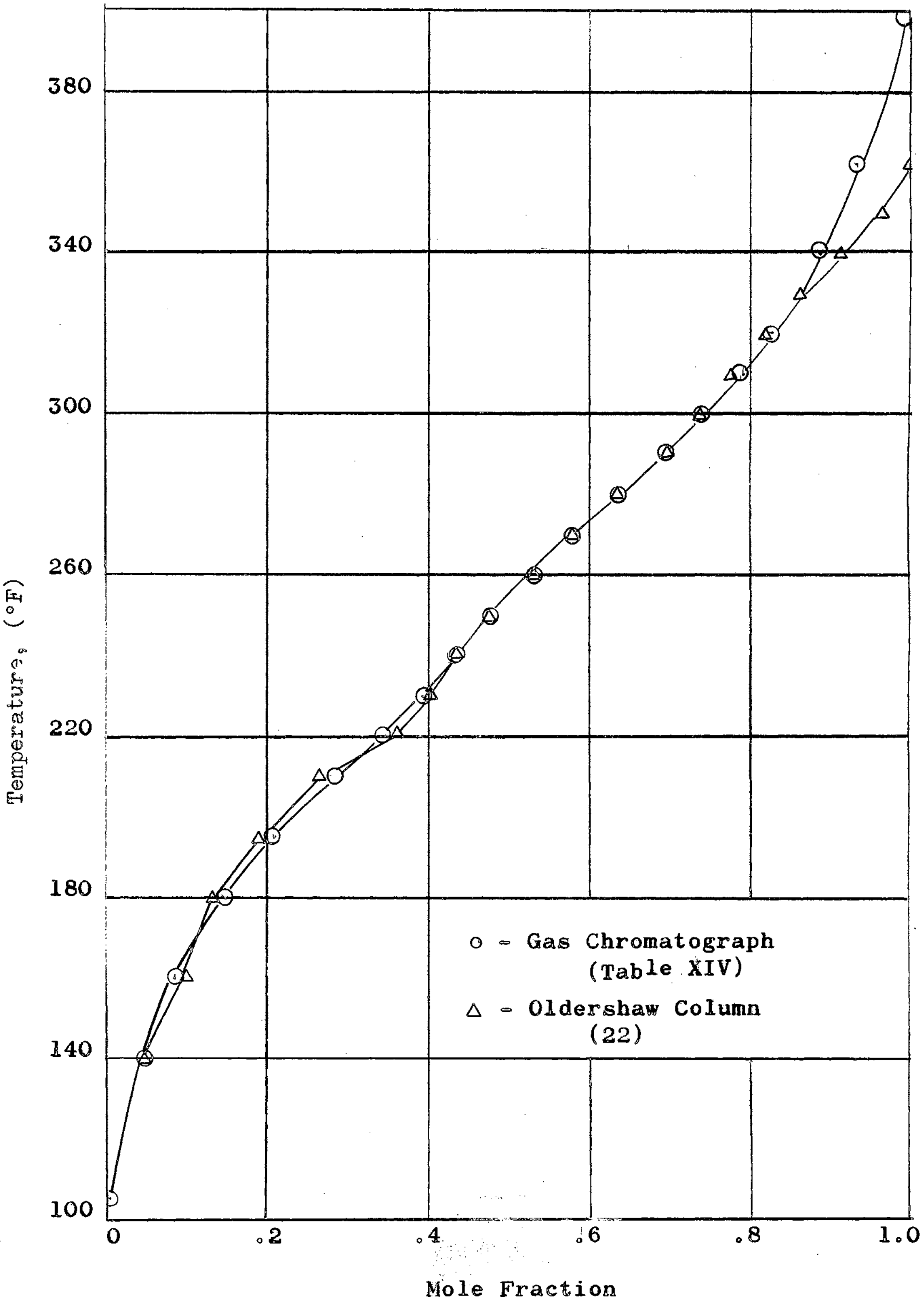


Figure 40

Comparison of Calculated Molar TBP Data From Oldershaw Column and Gas Chromatograph for Feed Oil Sx-4031

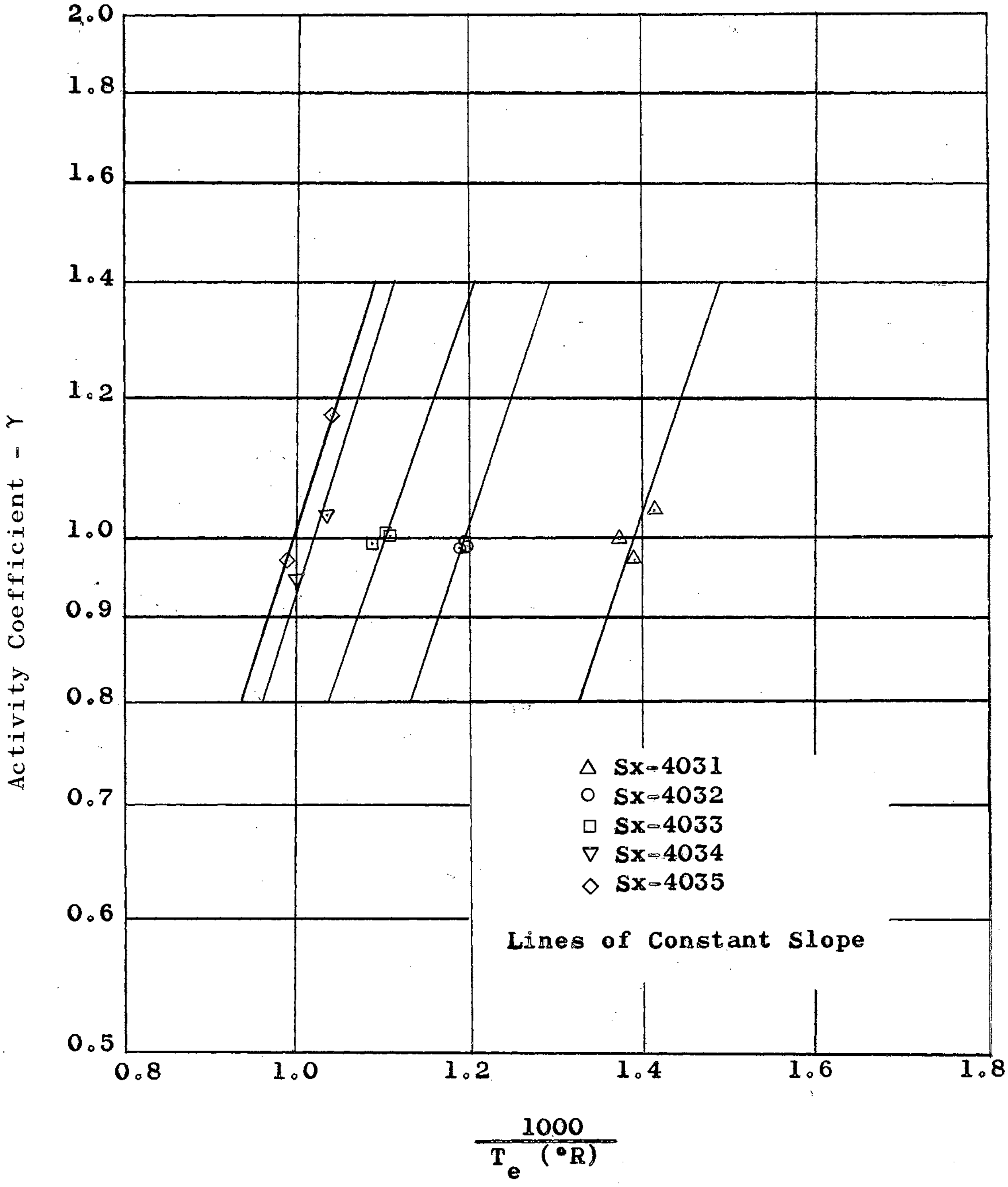


Figure 41

Derived Activity Coefficients as a Function of Reciprocal Equilibrium Temperature

3. Ideal K-values, based on vapor pressure, system pressure, and the imperfection pressure correction, between the two assay methods were within ±four per cent. The critical constants used in calculating θ were obtained from a correlation where P_c and T_c were plotted as a function of molecular weight and normal boiling point.

4. The correction necessary to adjust V/L (calculated) equal to V/L(experimental) increases as V/L and T_e increases.

5. Actual K-values obtained from the product of K_I and the derived activity coefficient are considered accurate to ±six per cent.

6. The calculated equilibrium product TBP curves do not agree well with the experimental product TBP curves.

Recommendations

1. Assaying the feed stocks with the Oldershaw column, to obtain the molecular weights of the pseudo-components, can be eliminated. A fraction collection device (available commercially) attached to the chromatograph will "trap" sufficient quantity of each component for a molecular weight determination using the vapor density instrument. To apply this technique a semi-preparative chromatographic column (approximately 1/2 inch O.D.) will need to be developed that will handle an 0.5ml sample charge without overloading.

2. More information is need to validate the postulation that the C_6 hydrocarbons are dimerizing in the molecular weight apparatus. Perhaps a plot of pressure (exerted by the C_6's in the instrument) as a function of time would give an indication

of the mechanism that takes place when these type hydrocarbons are subjected to reduced pressure.

3. The upper limit of the molecular weight instrument can be extended by using gallium, instead of mercury, in the sample receiver and heating the receiver. Heating the mercury causes it to vaporize and migrate into the system. The diaphragm pressure gage has gold foil for gaskets, thus, mercury in the gage would amalgamate with the gold and damage the pressure gage.

4. An accurate method for correlating K-values to higher temperatures for heavy hydrocarbons is needed. Knowledge of an empirical relationship for the higher temperatures would permit accurate and inexpensive K-value determinations that could aid the engineer in design, evaluation and operation of process equipment.

K-values obtained from generalized methods are usually less accurate than the values evaluated from experimental data. However, a correlation may be developed by characterizing a broader range of petroleum fractions using the steps outlined in Chapter VI. In this technique the Ideal K-values, generated from the vapor pressure, system pressure and imperfection pressure correction, are adjusted by a derived activity coefficient that is a function of the equilibrium flash temperature.

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APPENDIX A

NOMENCLATURE

amu - atomic mass unit

°C - degree Centigrade

cc - cubic centimeter

D - molecular weight instrument dial reading

ΔT - temperature increment

ΔV - volume increment

d-c - direct current

EFV - equilibrium flash vaporization

emf - electromotive force

f - moles of any small increment of the feed

°F - degree Fahrenheit

He - helium

HETP - height equivalent to a theoretical plate

I.D. - inside diameter

in. - inches

K - vapor-liquid equilibrium phase distribution ratio

k - pressure sensing gage constant

K_A - actual K-value

K_I - ideal K-value

L - moles of liquid mixture

l - moles of any small increment of the liquid lb. - pounds

ml - milliliter

mm - millimeter

mmfd - micromicrofarad

mm Hg - millimeters of mercury (pressure)

MW - molecular weight

N - number of theoretical plates

n - total number of moles

O.D. - outside diameter

P - pressure

P_c - critical pressure

P_e - equilibrium pressure

psig - pounds per square inch gage

R - gas constant

°R - Rankine

Σl - L, moles of liquid mixture

Σv - V, moles of vapor mixture

Sx - identification of petroleum assays

T - temperature

T_b - normal boiling point

T_c - critical temperature

T_e - equilibrium temperature

T.C. - thermal conductivity

₮ - standard taper

TBP - true boiling point

V - volume

V - moles of vapor mixture

v - moles of small increment of the vapor

Greek Letters

γ - derived activity coefficient

ρ - density

$\sum$ - summation

θ - imperfection pressure correction

Subscript

i - pseudo-component

APPENDIX B

EXPERIMENTAL AND CALCULATED DATA

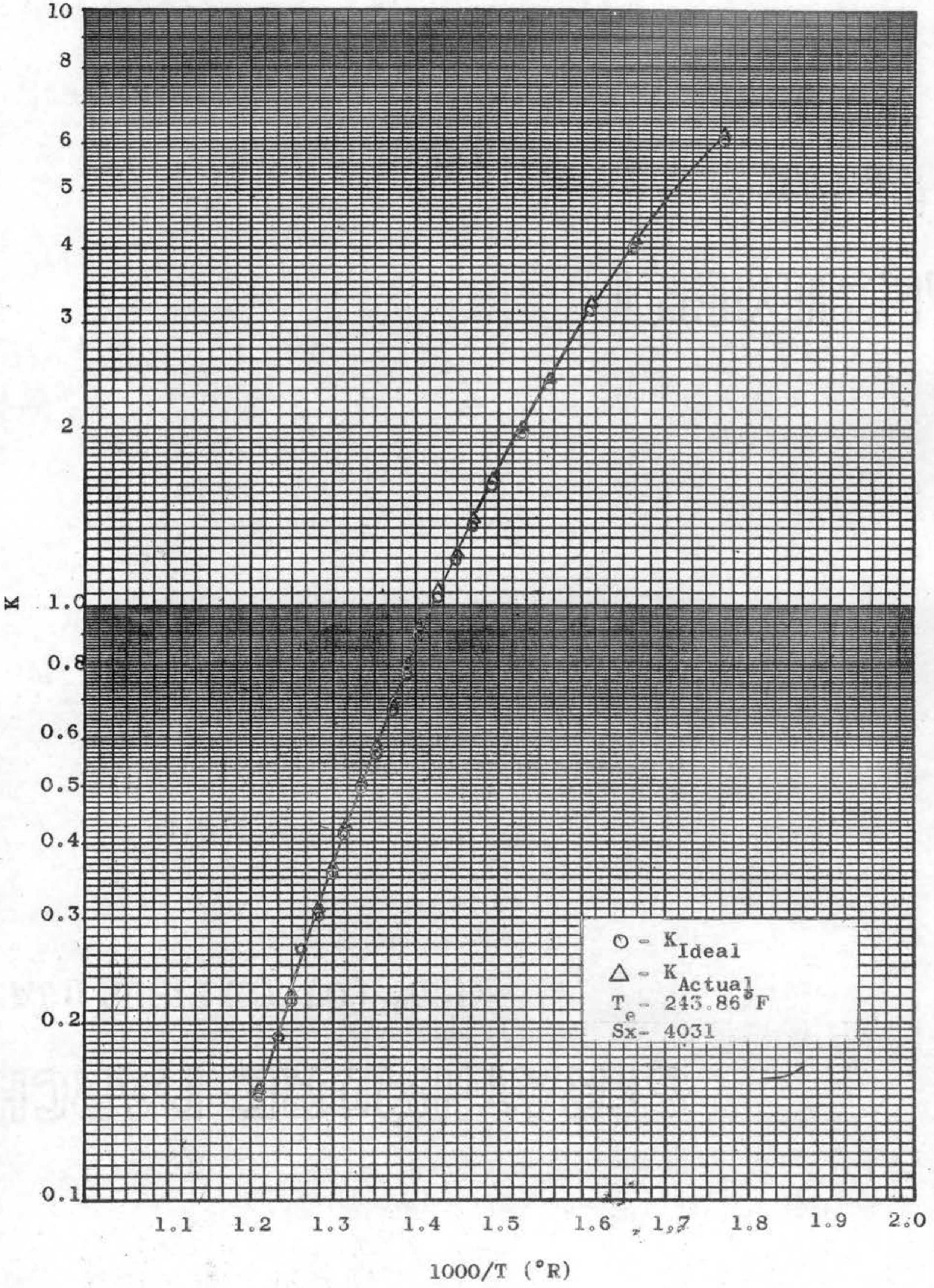

Figure 42

Comparison of Ideal and Actual K-Values

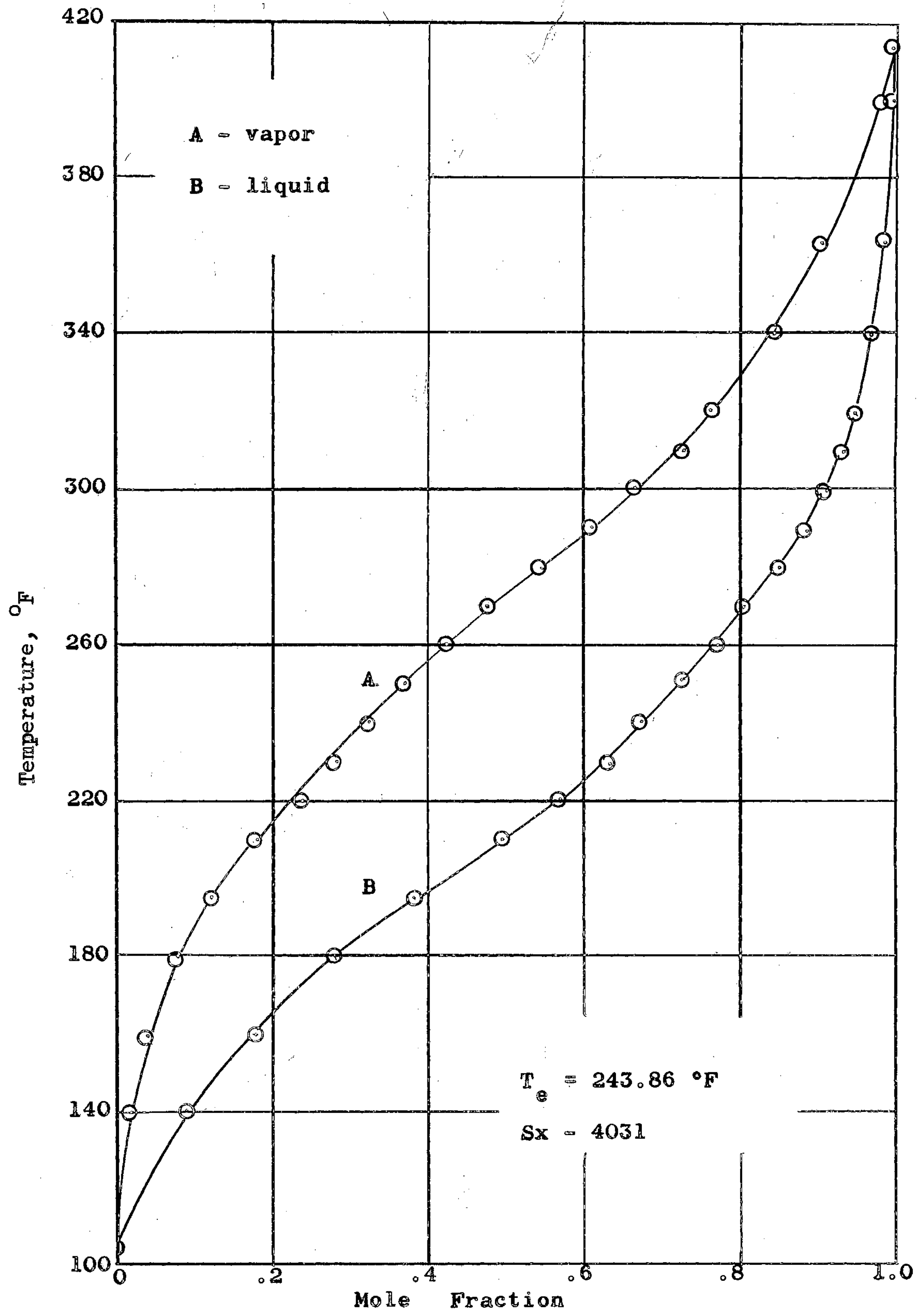

Figure 43
Calculated Vapor-Liquid Equilibrium Products

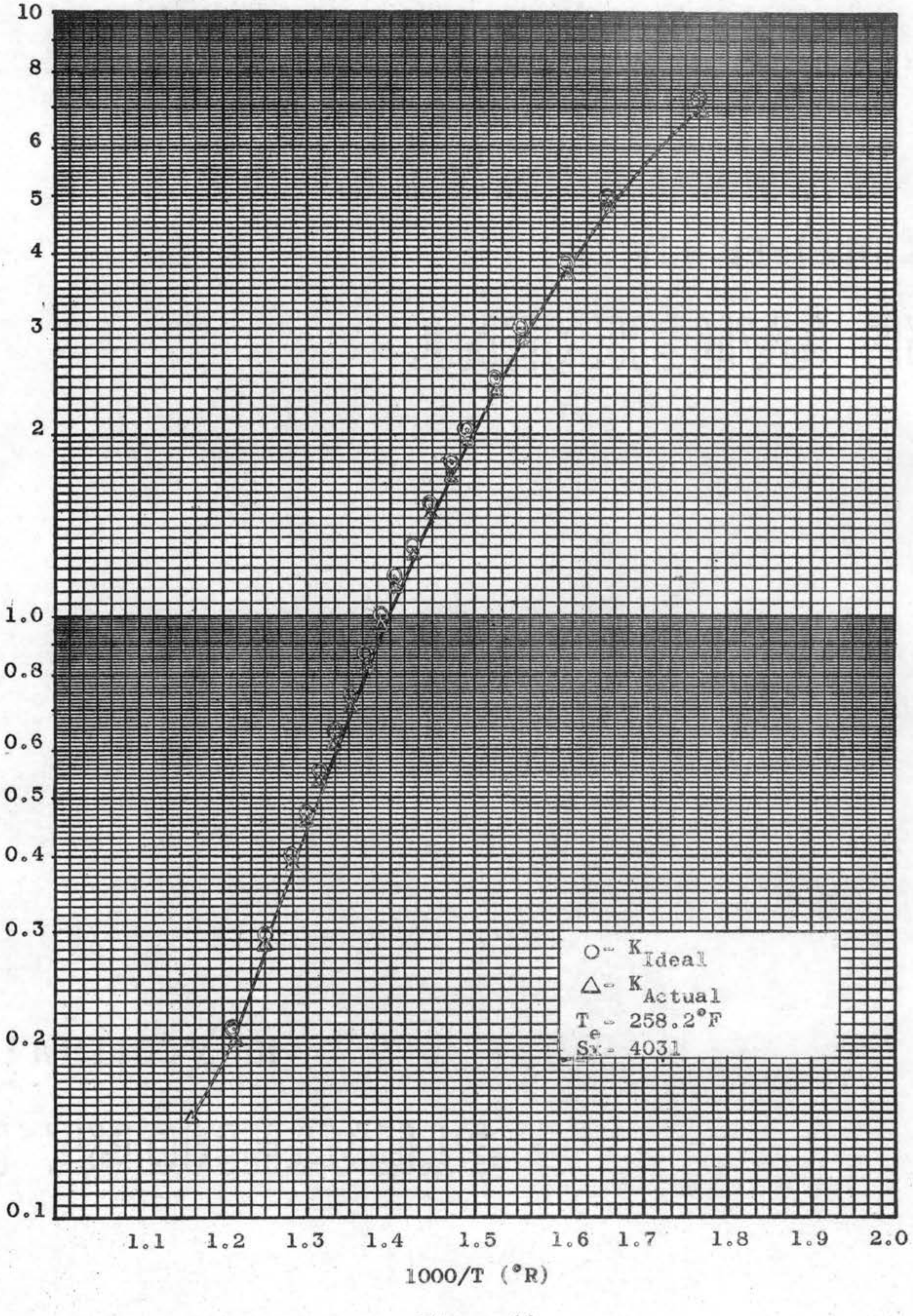

Figure 44

Comparison of Calculated K-Values

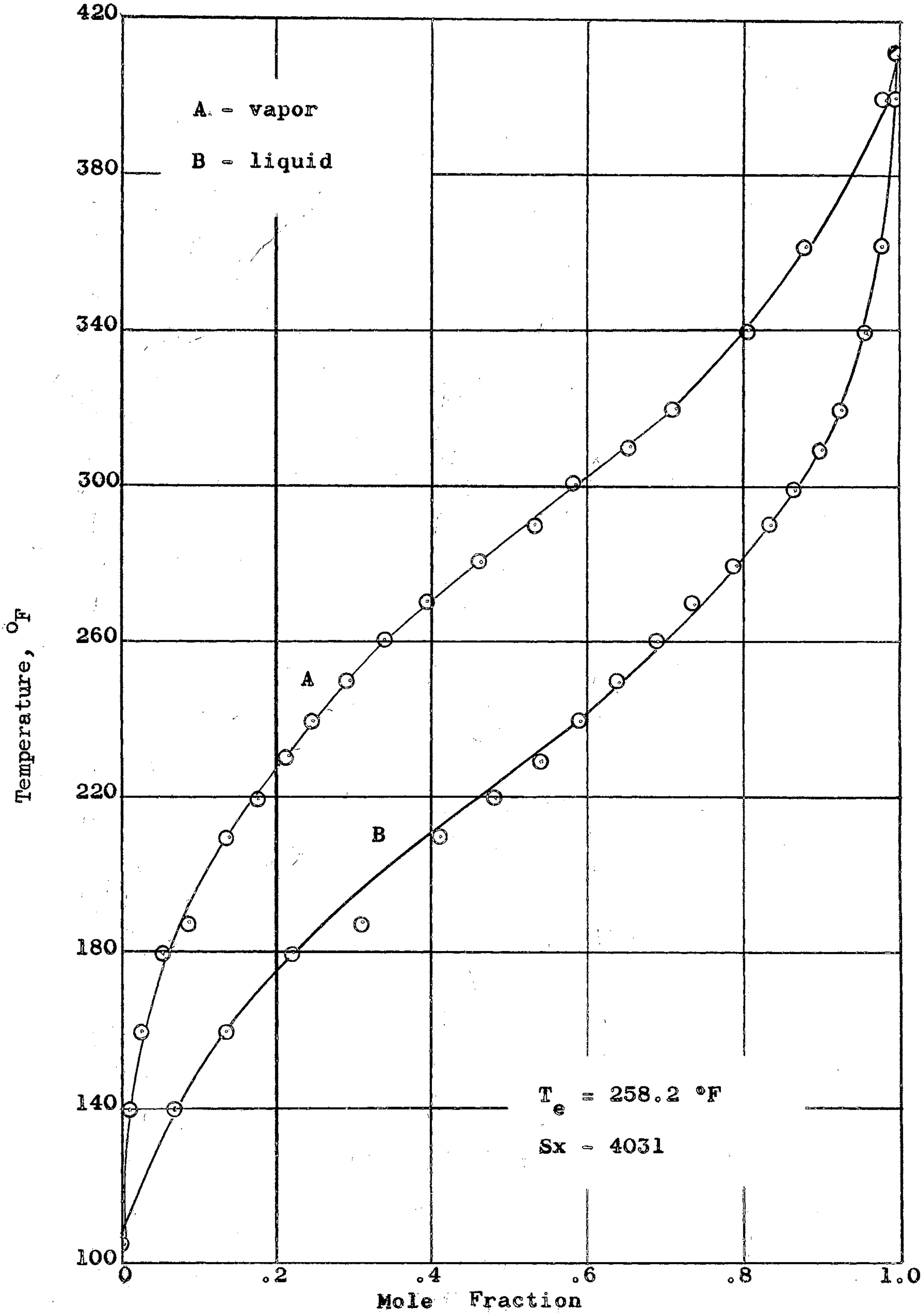

Figure 45

Calculated Vapor-Liquid Equilibrium Products

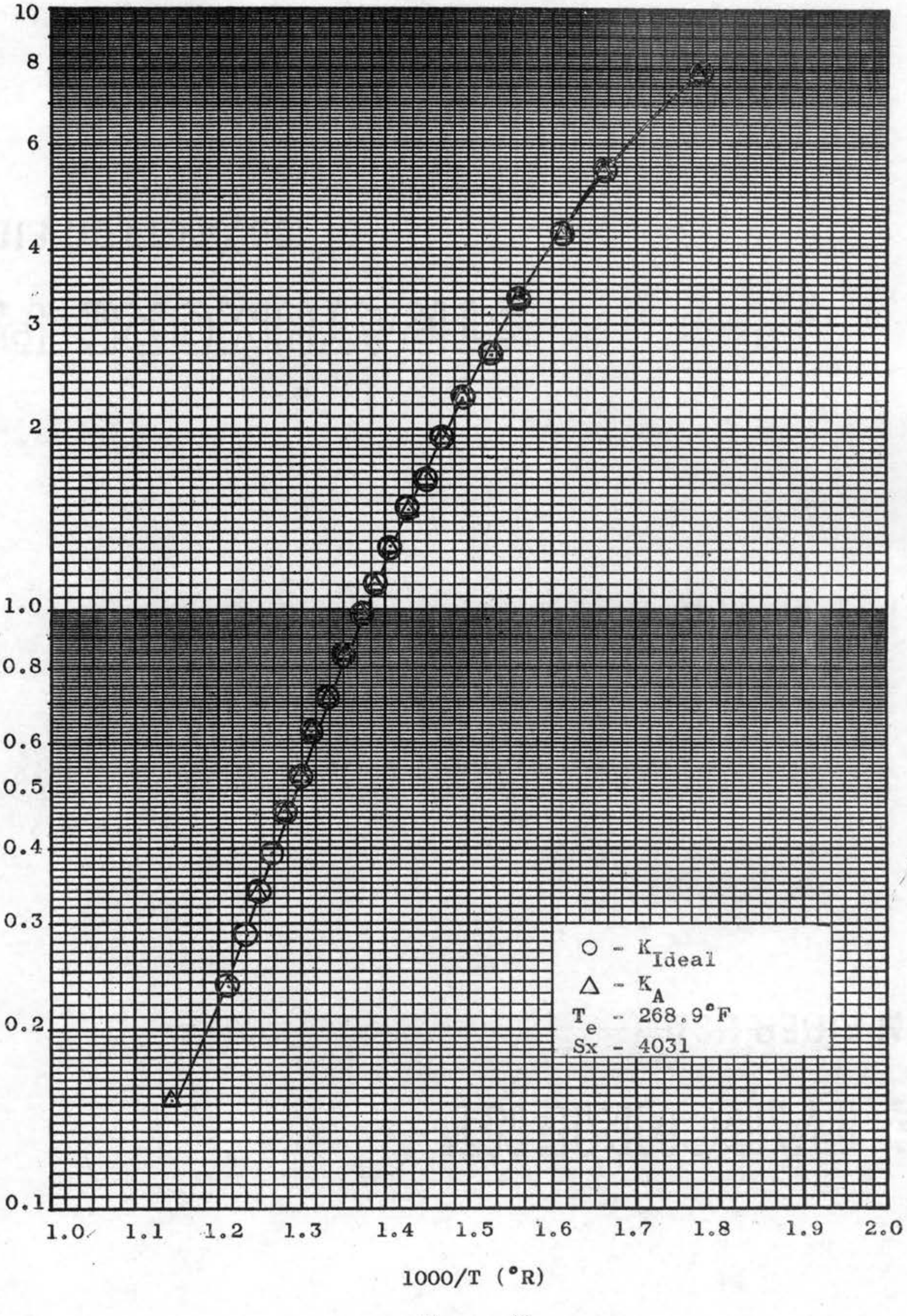

Figure 46

Comparison of Calculated K-Values

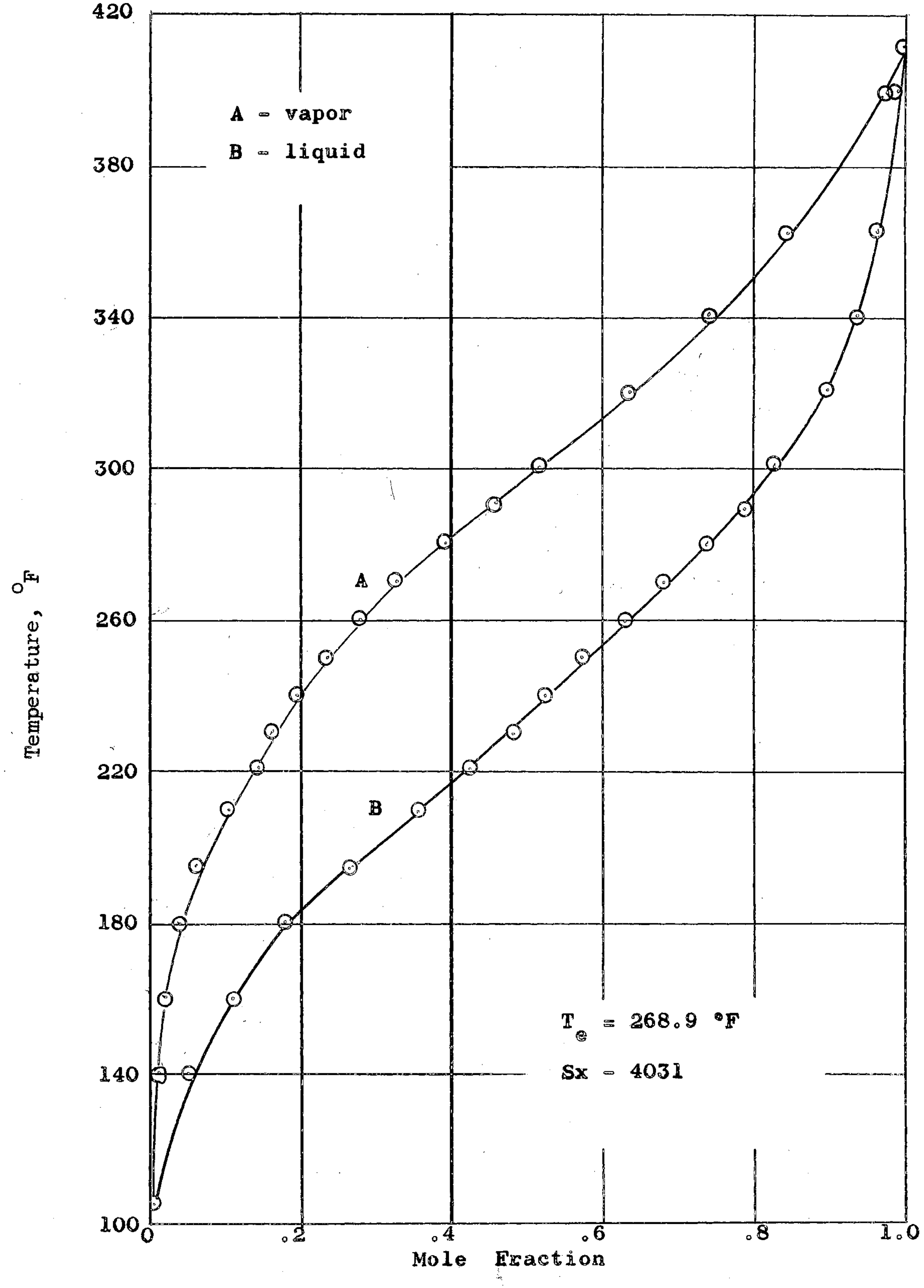

Figure 47

Calculated Vapor-Liquid Equilibrium Products

TABLE XVI

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4032

T_e = 369.5°F

P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	Θ
230.00	6.300	5.58979	1.12705
245.00	5.200	4.64858	1.11861
260.00	4.400	3.97737	1.10625
275.00	3.700	3.38372	1.09347
290.00	2.950	2.74692	1.07392
305.00	2.500	2.35766	1.06037
320.00	2.050	1.96067	1.04555
335.00	1.680	1.62820	1.03180
350.00	1.3700	1.34333	1.01985
358.00	1.2400	1.22340	1.01356
365.00	1.1100	1.10274	1.00658
373.00	1.0100	1.00937	1.00062
380.00	.9200	.92479	.99481
388.00	.8200	.83005	.98788
395.00	.7400	.75516	.97992
410.00	.6000	.61660	.97307
425.00	.4700	.48963	.95988
440.00	.3850	.40430	.95224
453.00	.3300	.34942	.94440

TABLE XVII

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4032

T_e = 376°F P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	Θ
230.00	6.400	5.67161	1.12842
245.00	5.300	4.72972	1.12057
260.00	4.500	4.05915	1.10860
275.00	3.800	3.46631	1.09626
290.00	2.550	2.40133	1.07719
305.00	2.550	2.40133	1.06190
320.00	2.100	2.00503	1.04736
335.00	1.700	1.64652	1.03247
350.00	1.400	1.37080	1.02129
358.00	1.290	1.26935	1.01626
365.00	1.150	1.13984	1.00890
373.00	1.0300	1.02890	1.00184
380.00	.9500	.95306	.99678
388.00	.8300	.83952	.98864
395.00	.770	.78381	.98237
410.00	.620	.63614	.97462
425.00	.490	.50950	.96170
440.00	.410	.42952	.95454
453.00	.340	.35952	.94569

TABLE XVIII

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4032

T_e = 374.0°F

P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	Θ
230.00	6.300	5.58979	1.12705
245.00	5.200	4.64858	1.11861
260.00	4.400	3.97737	1.10625
275.00	3.700	3.38372	1.09347
290.00	2.950	2.74692	1.07392
305.00	2.500	2.35766	1.06037
320.00	2.050	1.96067	1.04555
335.00	1.680	1.62820	1.03180
350.00	1.370	1.34333	1.01985
358.00	1.240	1.22340	1.01356
365.00	1.110	1.10274	1.00658
373.00	1.010	1.00937	1.00062
380.00	.920	.92479	.99481
388.00	.820	.83005	.98788
395.00	.740	.75516	.97992
410.00	.600	.61660	.97307
425.00	.470	.48963	.95988
440.00	.385	.40430	.95224
453.00	.330	.34942	.94440

TABLE XIX

EQUILIBRIUM FLASH CALCULATIONS

γ = 1.007 Feedstock Sx-4032 T_e = 376.0°F

V/L = 3.300 P_e = 760 mm Hg

Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
230.00	.0000	.0000	.0504	.9495	.0000	5.7056
245.00	.0014	.0073	.0598	.9401	.0060	4.7580
260.00	.0034	.0160	.0690	.9309	.0131	4.0835
275.00	.0060	.0258	.0799	.9200	.0212	3.4871
290.00	.0190	.0412	.0961	.9038	.0341	2.8483
305.00	.0214	.0687	.1114	.8885	.0577	2.4157
320.00	.0435	.1169	.1306	.8693	.0998	2.0170
335.00	.0870	.1958	.1546	.8453	.1705	1.6563
350.00	.1807	.3351	.1801	.8198	.2992	1.3790
358.00	.2395	.4132	.1918	.8081	.3728	1.2769
365.00	.3017	.4887	.2090	.7909	.4453	1.1466
373.00	.3774	.5710	.2266	.7733	.5260	1.0342
380.00	.4465	.6397	.2401	.7598	.5948	.9587
388.00	.5225	.7078	.2640	.7359	.6647	.8445
395.00	.5860	.7596	.2776	.7223	.7192	.7885
410.00	.7307	.8634	.3213	.6786	.8325	.6499
425.00	.8517	.9329	.3715	.6284	.9140	.5125
440.00	.9476	.9791	.4122	.5877	.9718	.4320
453.00	1.0001	.9999	.4559	.5440	1.0000	.3610

TABLE XX

EQUILIBRIUM FLASH CALCULATIONS

γ = .976 Feedstock Sx-4032 T_e = 374.0°F

V/L = 1.110 P_e = 760 mm Hg

Temp. (°F)	liquid	vapor	1/f	v/f	mole fraction feed	K_A
230.00	.0000	.0000	.1416	.8583	.0000	5.4556
245.00	.0019	.0096	.1656	.8384	.0060	4.5370
260.00	.0046	.0207	.1883	.8116	.0131	3.8819
275.00	.0080	.0331	.2142	.7858	.0212	3.3035
290.00	.0144	.0519	.2514	.7485	.0341	2.6809
305.00	.0277	.0848	.2813	.7186	.0577	2.3010
320.00	.0545	.1406	.3200	.6799	.0998	1.9136
335.00	.1055	.2290	.3617	.6382	.1705	1.5891
350.00	.2108	.3788	.4072	.5927	.2992	1.3110
358.00	.2758	.4602	.4299	.5700	.3728	1.1940
365.00	.3435	.5369	.4555	.5444	.4453	1.0762
373.00	.4229	.6188	.4775	.5224	.5260	.9851
380.00	.4938	.6857	.4994	.5005	.5948	.9025
388.00	.5695	.7507	.5264	.4735	.6647	.8101
395.00	.6313	.7984	.5499	.4500	.7192	.7370
410.00	.7681	.8905	.5994	.4005	.8325	.6018
425.00	.8757	.9486	.6533	.3466	.9140	.4770
440.00	.9576	.9845	.6953	.3046	.9718	.3945
453.00	.998	1.0001	.7253	.2746	1.0000	.3410

TABLE XXI

EQUILIBRIUM FLASH CALCULATIONS

γ = .97 Feedstock Sx-4032 T_e = 369.5°F

V/L = .502 P_e = 760 mm Hg

Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
230.00	.0000	.0000	.2737	.7262	.0000	5.2781
245.00	.0026	.0126	.3094	.6905	.0060	4.4391
260.00	.0061	.0269	.3467	.6532	.0131	3.7480
275.00	.0106	.0423	.3885	.6114	.0212	3.1302
290.00	.0186	.0650	.4307	.5692	.0341	2.6288
305.00	.0347	.1034	.4757	.5242	.0577	.21918
320.00	.0665	.1661	.5220	.4779	.0998	1.8209
335.00	.1244	.2623	.5650	.4349	.1705	.15310
350.00	.2390	.4188	.6151	.3848	.2992	1.2445
358.00	.3080	.5017	.6327	.3672	.3728	1.1543
365.00	.3782	.5785	.6593	.3406	.4453	1.0276
373.00	.4594	.6584	.6799	.3200	.5260	.9364
380.00	.5308	.7220	.7019	.2980	.5948	.8445
388.00	.6059	.7817	.7256	.2743	.6647	.7518
395.00	.6659	.8253	.7377	.2622	.7192	.7069
410.00	.7947	.9077	.7768	.2231	.8325	.5714
425.00	.8919	.9581	.8090	.1901	.9140	.4670
440.00	.9634	.9884	.8417	.1582	.9718	.3739
453.00	.9995	1.0009	.8612	.1387	1.0000	.3203

TABLE XXII

CALCULATED VALUES OF K_I AND θ

Feedstock Sx-4034

T_e = 312 °F

P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	θ
250.00	2.40000	2.25356	1.06497
280.00	1.6800	1.62312	1.03503
310.00	1.02000	1.01878	1.00118
340.00	.65000	.66517	.97718
370.00	.41000	.43053	.95230
400.00	.26000	.27856	.93335
430.00	.16000	.17513	.91356
460.00	.09470	.10636	.89029
490.00	.05570	.06408	.86913
505.00	.04210	.04897	.85958
520.00	.03160	.03727	.84771
535.00	.02470	.02955	.83579
550.00	.01690	.02088	.80928
565.00	.01320	.01674	.78849
580.00	.00948	.01218	.77789
610.00	.00500	.00657	.75991
640.00	.00264	.00363	.72714
670.00	.00132	.00189	.69800
703.00	.00068	.00104	.65146

TABLE XXIII

CALCULATED VALUES OF K_I AND θ

Feedstock Sx-4034

T_e = 359.6°F P_e = 760 mm Hg

Temp. (°F)	P*/P	K_I	θ
250.00	4.20000	3.72253	1.12826
280.00	2.90000	2.67941	1.08232
310.00	1.95000	1.86335	1.04649
340.00	1.60000	1.54979	1.03239
370.00	.85000	.85848	.99011
400.00	.56000	.57861	.96783
430.00	.38000	.40062	.94851
460.00	.24000	.25920	.92592
490.00	.17000	.18725	.90784
505.00	.10900	.12167	.89581
520.00	.07380	.18348	.88395
535.00	.06450	.07372	.87482
550.00	.05000	.05856	.85373
565.00	.03690	.04411	.83637
580.00	.02900	.03503	.82782
610.00	.01580	.01947	.81134
640.00	.00920	.01170	.78575
670.00	.00474	.00620	.76362
703.00	.00237	.00325	.72789

TABLE XXIV

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4034

$\gamma = 1.017$

$V/L = 0.246$

T_e = 509.0°F

P_e = 760 mm Hg

Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
250.00	.0000	.0000	.0943	.9050	.0000	4.5200
280.00	.0012	.0466	.1263	.8740	.0090	3.1160
340.00	.0024	.0790	.1872	.8127	.0162	1.9589
370.00	.0034	.0936	.2608	.7391	.0195	1.2771
400.00	.0174	.1977	.4572	.5427	.0492	.8266
430.00	.0412	.2972	.5726	.4273	.0871	.5346
460.00	.1269	.5874	.6881	.3118	.2094	.3363
490.00	.1477	.6218	.7855	.2144	.2327	.2042
505.00	.2200	.7007	.8273	.1726	.3062	.1230
520.00	.3478	.7801	.8629	.1370	.4298	.0940
535.00	.4715	.8292	.8881	.1118	.5458	.0716
550.00	.5692	.8622	.9183	.0816	.6347	.0567
565.00	.6457	.8925	.9334	.0665	.7026	.0401
580.00	.7171	.9215	.9506	.0493	.7648	.0322
610.00	.8204	.9620	.9727	.0272	.8529	.0234
640.00	.8924	.9845	.9847	.0152	.9133	.0126
670.00	.9481	.9910	.9920	.0079	.9595	.0070
703.00	.9971	1.0000	.9955	.0044	1.0000	.0017

TABLE XXV

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4034

$\Upsilon = 0.976$ $T_e = 539.6°F$

$V/L = 1.137$ $P_e = 760$ mm Hg

Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
250.00	.0000	.0000	.0195	.9804	.0000	4.8021
280.00	.0004	.0180	.0269	.9730	.0093	3.4564
340.00	.0008	.0311	.0383	.9616	.0162	2.4037
370.00	.0011	.0375	.0457	.9542	.0195	1.9992
400.00	.0022	.0538	.0795	.9204	.0284	1.1024
430.00	.0064	.0918	.1136	.8863	.0497	.7464
460.00	.0168	.1554	.1563	.4836	.0871	.5168
490.00	.0549	.3594	.2226	.7773	.2094	.3344
505.00	.0668	.3940	.2838	.7161	.2327	.2416
520.00	.1166	.4095	.3788	.6211	.3062	.1570
535.00	.2248	.6290	.4706	.5293	.4298	.1077
550.00	.4335	.8303	.5589	.4983	.6347	.0964
565.00	.5153	.8846	.6272	.4410	.7026	.0755
580.00	.5979	.9271	.6793	.3206	.7648	.0582
610.00	.7295	.9728	.7921	.2078	.8529	.0452
640.00	.8310	.9829	.8638	.1361	.9133	.0251
670.00	.9149	.9910	.9229	.0770	.9595	.0151
703.00	.9922	.9956	.9580	.0419	1.0000	.0080

TABLE XXVI

CALCULATED VALUES OF K_I AND Θ

Feedstock Sx-4035

$T_e = 502°F$ $P_e = 760$ mm Hg

Temp. (°F)	P*/P	K_I	Θ
250.00	17.00000	11.66714	1.45708
290.00	11.00000	8.57211	1.28323
330.00	6.70000	5.68815	1.17788
370.00	5.75000	4.84541	1.18668
410.00	2.95000	2.72020	1.08447
450.00	1.95000	1.85622	1.05051
490.00	1.20000	1.18535	1.01235
530.00	.75000	.76376	.98197
570.00	.42100	.44405	.94807
610.00	.24400	.26558	.91871
630.00	.18500	.20428	.90559
650.00	.13700	.15350	.89246
670.00	.11500	.13101	.87777
690.00	.07400	.08663	.85411
710.00	.05400	.06424	.84052
730.00	.04000	.04880	.81966
770.00	.01580	.01960	.80596
810.00	.00920	.01226	.75018
850.00	.00435	.00622	.69918
880.00	.00244	.00367	.66362

TABLE XXVII

CALCULATED VALUES OF K_I AND θ

Feedstock Sx-4031

$T_e = 545$°F $P_e = 760$ mm Hg

Temp. (°F)	P*/P	K_I	θ
250.00	22.00000	14.28691	1.53987
290.00	15.50000	11.36203	1.36419
330.00	10.50000	8.31120	1.26335
370.00	6.70000	5.61466	1.19330
410.00	4.00000	3.59322	1.11320
450.00	2.97000	2.72195	1.09112
490.00	1.85000	1.76951	1.04548
530.00	1.15000	1.13935	1.00934
570.00	.70000	.71655	.97689
610.00	.39000	.41344	.94328
630.00	.34200	.36610	.93414
650.00	.26400	.28670	.92079
670.00	.19800	.21888	.90459
690.00	.15800	.17841	.88557
710.00	.10600	.12181	.87014
730.00	.08200	.09629	.85155
770.00	.04300	.05122	.83941
810.00	.02100	.02660	.78939
850.00	.01070	.01435	.74525
880.00	.00575	.00803	.71521

TABLE XXVIII

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4035

$\Upsilon = 1.185$ T_e = 502°F

V/L = .176 P_e = 760 mm Hg

Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
250.00	.0000	.0000	.2515	.7484	.0000	16.9299
290.00	.0035	.0675	.2970	.7029	.0111	13.4640
330.00	.0076	.1262	.3662	.6337	.0216	9.8487
370.00	.0139	.1904	.4610	.5389	.0347	6.6533
410.00	.0228	.2949	.5720	.4279	.0493	4.2579
450.00	.0454	.3542	.6382	.3617	.0811	3.2255
490.00	.0811	.4711	.7307	.2692	.1254	2.0968
530.00	.1438	.6028	.8082	.1917	.1946	1.3501
570.00	.2373	.7260	.8701	.1298	.2888	.8491
610.00	.3667	.8289	.9207	.0792	.4112	.4899
630.00	.4447	.8730	.9291	.0708	.4828	.4338
650.00	.5366	.9175	.9436	.0563	.5664	.3397
670.00	.6060	.9435	.9564	.0435	.6285	.2593
690.00	.6696	.9624	.9641	.0358	.6848	.2114
710.00	.7233	.9744	.9752	.0247	.7319	.1443
730.00	.7753	.9828	.9803	.0196	.7771	.1141
770.00	.8687	.9930	.9894	.0105	.8578	.0606
810.00	.9430	.9971	.9944	.0055	.9215	.0315
850.00	1.0000	.9988	.9970	.0029	.9703	.0170

TABLE XXIX

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4035

$\Upsilon = 0.976$ $T_e = 545°F$

$V/L = 0.262$ $P_e = 760$ mm Hg

Temp. (°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
250.00	.0000	.0000	.0000	1.0000	.0000	23.1448
290.00	.0011	.0464	.1399	.8600	.0111	18.4064
330.00	.0035	.0859	.1819	.8180	.0216	13.4641
370.00	.0072	.1326	.2477	.7522	.0347	9.0957
410.00	.0129	.1795	.3397	.6602	.0493	5.8210
450.00	.0286	.2701	.4044	.5955	.0811	4.4095
490.00	.0556	.3795	.5109	.4890	.1254	2.8666
530.00	.1079	.5150	.6187	.3812	.1946	1.8457
570.00	.1927	.6543	.7206	.2793	.2888	1.1608
610.00	.3193	.7785	.8172	.1827	.4112	.6697
630.00	.3985	.8343	.8347	.1652	.4828	.5930
650.00	.4931	.8912	.8657	.1342	.5664	.4644
670.00	.5660	.9251	.8941	.1058	.6285	.3545
690.00	.6337	.9502	.9119	.0880	.6848	.2890
710.00	.6919	.9664	.9381	.0618	.7319	.1973
730.00	.7488	.9778	.9504	.0495	.7771	.1559
770.00	.8523	.9918	.9730	.0269	.8578	.0829
810.00	.9356	.9976	.9858	.0141	.9215	.0430
850.00	1.0000	1.0000	.9922	.0077	.9703	.0232

TABLE XXX

PHYSICAL PROPERTIES OF FEED OILS

Feed Oil Sx-4031		
Light Crude Naphtha		
Bulk Density (g/cc)	.756	55.5 °API
Bulk Molecular Weight	108.2	
Feed Oil Sx-4032		
Heavy Crude Naphtha		
Bulk Density (g/cc)	.797	45.6 °API
Bulk Molecular Weight	146.8	
Feed Oil Sx-4033		
Kerosene		
Bulk Density (g/cc)	.829	38.8 °API
Bulk Molecular Weight	173.2	
Feed Oil Sx-4034		
Trade Gas Oil		
Bulk Density (g/cc)	.858	34.0 °API
Bulk Molecular Weight	218.5	
Feed Oil Sx-4035		
Heavy Gas Oil		
Bulk Density (g/cc)	.873	30.1 °API
Bulk Molecular Weight	221.0	

TABLE XXXI

EQUILIBRIUM FLASH VAPORIZATION DATA

		Flash Number	
	1	2	3
Feed Oil Sx-4031			
Pe (mm Hg)	760.0	760.0	760.0
Te (°F)	243.8	258.2	268.9
V/L	.481	1.140	2.714
γ	1.015	.965	1.000
Equilibrium Vapor			
Molecular Weight	101.6	105.9	108.3
Bulk Density (g/cc)	.764	.769	.771
Equilibrium Liquid			
Molecular Weight	120.5	124.8	130.5
Bulk Density (g/cc)	.764	.769	.771
Feed Oil Sx-4032			
Pe (mm Hg)	760.0	760.0	760.0
Te (°F)	376.0	374.0	369.5
V/L	3.30	1.110	.502
γ	1.007	.976	.972
Equilibrium Vapor			
Molecular Weight	146.0	145.0	145.0
Bulk Density (g/cc)	.796	.797	.796
Equilibrium Liquid			
Molecular Weight	155.0	156.0	155.0
Bulk Density (g/cc)	.802	.801	.800
Feed Oil Sx-4033			
Pe (mm Hg)	760.0	760.0	760.0
Te (°F)	451.4	446.0	442.4
V/L	2.02	1.20	.614
γ	.989	1.012	1.003
Equilibrium Vapor			
Molecular Weight	176.8	170.7	170.0
Bulk Density (g/cc)	.827	.823	.821

Equilibrium Liquid			
Molecular Weight	189.0	192.5	182.4
Bulk Density (g/cc)	.836	.827	.832
Feed Oil Sx-4034			
Pe (mm Hg)	760.0	760.0	760.0
Te (°F)	509.0	539.8	546.0
V/L	.246	1.137	2.218
γ	1.017	.976	
Equilibrium Vapor			
Molecular Weight	184.5	210.0	216.0
Bulk Density (g/cc)	.837	.851	.851
Equilibrium Liquid			
Molecular Weight	213.0	228.0	222.3
Bulk Density (g/cc)	.859	.863	.857
Feed Oil Sx-4035			
Pe (mm Hg)	760.0	760.0	
Te (°F)	502.0	545.0	
V/L	.176	.262	
γ	1.185	.976	
Equilibrium Vapor			
Molecular Weight	179.0	189.6	
Bulk Density (g/cc)	.882	.846	
Equilibrium Liquid			
Molecular Weight	215.0	220.0	
Bulk Density (g/cc)	.835	.885	

TABLE XXXII

SYNTHETIC PETROLEUM FRACTION

Component	Weight grams	Weight Carbon grams	Weight %	% Carbon
Cyclohexane	4.66	3.98	12.47	12.30
Methy-Cyclohexane	8.34	7.14	22.32	22.01
Nonane	6.81	5.72	18.23	17.66
Napthalene	11.04	10.34	29.55	31.09
Tridecane	6.51	5.49	17.42	16.94

TABLE XXXIII

SYNTHETIC PETROLEUM FRACTION

Component	Weight grams	Weight Carbon grams	Weight %	% Carbon
Hexane	7.59	6.32	24.50	24.40
2,3-Dimethylpentane	3.47	2.90	11.19	11.20
Octane	6.41	5.37	20.68	20.75
Hendecane	9.40	7.86	30.32	30.35
Tridecane	4.13	3.45	13.32	13.30

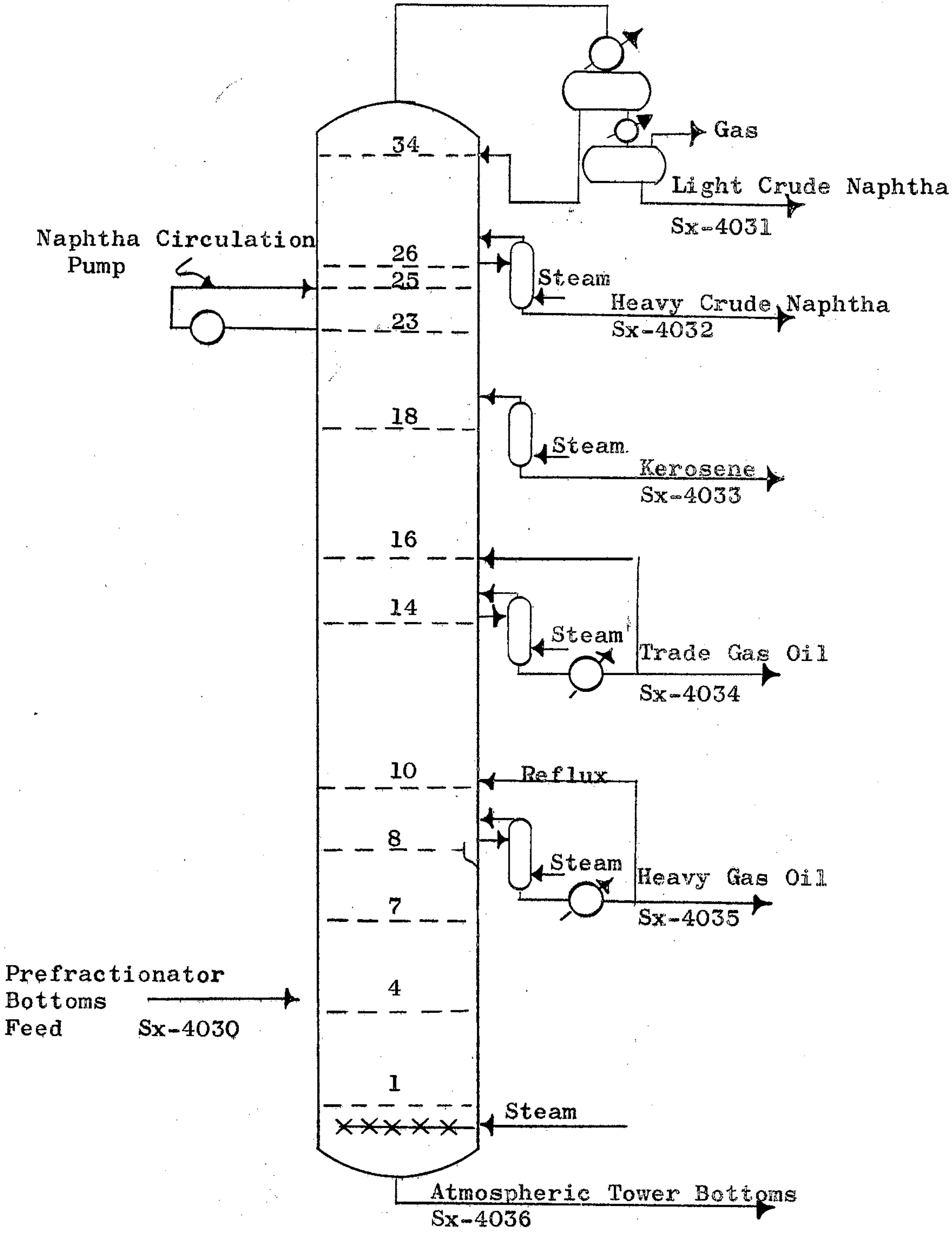

Figure 48

Diagram of Atmospheric Pipe Still

TABLE XXXIV

CHROMATOGRAPHIC ANALYSIS OF FEED OIL Sx-4031

Temperature T_b, °F	Weight Fraction
110	0.000
120	0.005
130	0.015
140	0.025
150	0.042
160	0.060
170	0.082
180	0.110
190	0.141
200	0.169
210	0.218
220	0.268
230	0.312
240	0.350
250	0.395
260	0.444
270	0.490
280	0.550
290	0.609
300	0.652
310	0.702
320	0.757
330	0.795
340	0.838
350	0.862
360	0.890
370	0.918
380	0.944
390	0.970
400	0.998
412	1.000

TABLE XXXV

CHROMATOGRAPHIC ANALYSIS OF FEED OIL Sx-4032

Temperature T_b, °F	Weight Fraction
220	0.000
235	0.001
255	0.005
275	0.011
290	0.020
310	0.052
325	0.090
340	0.130
345	0.172
355	0.241
360	0.321
370	0.405
380	0.475
385	0.550
390	0.621
400	0.714
410	0.778
420	0.848
430	0.895
440	0.951
450	0.972
453	1.000

TABLE XXXVI

CHROMATOGRAPHIC ANALYSIS OF FEED OIL Sx-4033

Temperature T_b, °F	Weight Fraction
370	0.000
375	0.001
380	0.002
385	0.010
390	0.015
400	0.031
405	0.056
410	0.084
415	0.112
420	0.131
425	0.160
430	0.220
435	0.299
440	0.380
445	0.451
450	0.541
455	0.596
460	0.645
465	0.711
470	0.758
475	0.810
480	0.841
485	0.875
490	0.921
500	0.966
505	0.991
510	1.000

TABLE XXXVII

CHROMATOGRAPHIC ANALYSIS OF FEED OIL Sx-4034

Temperature T_b, °F	Weight Fraction
250	0.000
280	0.004
310	0.009
325	0.011
355	0.013
370	0.018
390	0.030
410	0.041
430	0.056
445	0.081
460	0.131
485	0.162
500	0.200
505	0.242
510	0.291
515	0.338
520	0.387
530	0.452
540	0.510
550	0.575
560	0.625
570	0.672
580	0.734
590	0.775
610	0.821
625	0.860
640	0.894
655	0.922
670	0.955
685	0.981
703	1.000

TABLE XXXVIII

CHROMATOGRAPHIC ANALYSIS OF FEED OIL Sx-4035

Temperature T_b, °F	Weight Fraction
250	0.000
290	0.009
360	0.018
395	0.020
420	0.032
450	0.048
530	0.132
570	0.201
590	0.256
610	0.304
620	0.358
640	0.446
655	0.490
670	0.535
690	0.587
710	0.668
730	0.715
750	0.760
770	0.801
780	0.835
800	0.879
820	0.913
840	0.961
860	1.000

TABLE XXXIX

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4033

γ = .989 T_e = 451.4°F

V/L = 2.02 P_e = 760.0 mm Hg

Temp.(°F)	liquid	vapor	l/f	v/f	mole fraction feed	K_A
365	.0000	.0000	.3539	.6460	.0000	1.6042
370	.0047	.0938	.4271	.5728	.0012	1.1786
375	.0103	.1697	.5291	.4708	.0029	.7821
380	.0182	.2524	.5687	.4312	.0097	.6662
385	.0284	.3274	.7014	.2985	.0126	.3740
395	.0546	.4415	.7749	.2250	.0285	.2552
405	.0948	.5563	.8435	.1564	.0501	.1629
415	.1617	.6804	.8932	.1067	.1010	.1050
425	.2580	.7888	.9350	.0649	.1982	.0610
435	.3873	.8755	.9601	.0398	.3005	.0365
445	.4643	.9102	.9690	.0309	.4280	.0280
455	.5548	.9412	.9765	.0234	.5603	.0211
465	.6225	.9597	.9799	.0200	.6842	.0180
475	.6842	.9725	.9866	.0133	.7867	.0119
480	.7361	.9800	.9900	.0099	.8341	.0088
485	.7860	.9855	.9924	.0075	.8756	.0067
490	.8753	.9914	.9969	.0030	.9223	.0026
495	.9461	.9936	.9980	.0019	.9640	.0016
499	1.0000	.9946	.9990	.0009	1.0000	.0008

TABLE XXXX

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4033

γ = 1.012
V/L = 1.20

T_e = 446.0°F
P_e = 760.0mm Hg

Temp. °F	liquid	vapor	l/f	v/f	mole fraction feed	K_A
365	.0000	.0000	.1342	.8657	.0000	1.9214
370	.0019	.0094	.1571	.8428	.0012	1.3956
375	.0045	.0203	.1789	.8210	.0029	1.3164
380	.0079	.0325	.2039	.7960	.0097	1.1989
385	.0141	.0511	.2399	.7600	.0126	1.0806
395	.0272	.0836	.2688	.7311	.0285	.9891
405	.0537	.1390	.3066	.6933	.0501	.9062
415	.1042	.2269	.3474	.6525	.1010	.8134
425	.2087	.3761	.3922	.6077	.1982	.7400
435	.2733	.4573	.4147	.5852	.3005	.6042
445	.3407	.5341	.4401	.5598	.4280	.4798
455	.4199	.6161	.4620	.5379	.5603	.3962
465	.4907	.6832	.4838	.5161	.6842	.3424
475	.5664	.7483	.5108	.4891	.7867	.3068
480	.6284	.7964	.5344	.4655	.8341	.2761
485	.7657	.8892	.5843	.4156	.8756	.2259
490	.8741	.9480	.6390	.3609	.9223	.1823
495	.9568	.9845	.6819	.3180	.9640	.1206
499	.9995	1.0000	.7127	.2872	1.0000	.0908

TABLE XXXXI

EQUILIBRIUM FLASH CALCULATIONS

Feedstock Sx-4033

Υ = 1.003
V/L = 0.614

T_e = 442.4 °F
P_e = 760.0mm Hg

Temp. °F	liquid	vapor	l/f	v/f	mole fraction feed	K_A
365	.0000	.0000	.2394	.7605	.0000	2.0642
370	.0169	.0880	.3252	.6747	.0012	1.9628
375	.0496	.2079	.3842	.6157	.0029	1.7203
380	.0756	.3573	.4496	.5503	.0097	1.6870
385	.1081	.4688	.5012	.4987	.0126	1.3220
395	.1685	.5931	.5547	.4452	.0285	1.1328
405	.2494	.6402	.5905	.4094	.0501	.9090
415	.2845	.6756	.6254	.3745	.1010	.8167
425	.3149	.7145	.6587	.3412	.1982	.7863
435	.3539	.7674	.6914	.3085	.3005	.7421
445	.4159	.8468	.7233	.2766	.4280	.7085
455	.4706	.8810	.7821	.2178	.5603	.6863
465	.5332	.9056	.8073	.1926	.6842	.6412
475	.5967	.9458	.8303	.1696	.7867	.5908
480	.6500	.9609	.87.6	.1283	.8341	.5233
485	.7048	.9709	.8889	.1110	.8756	.4791
490	.8768	.9821	.9038	.0961	.9223	.3228
495	.9482	.9905	.9174	.0825	.9640	.2809
499	1.0000	.9994	.9317	.0682	1.0000	.1163

APPENDIX C

COLUMN PREPARATION FOR GAS CHROMATOGRAHY

The column should be only as long as necessary to accomplish the desired separation, and no longer if time is a factor. With modern plate efficiencies on the order of one thousand plates per foot most analysis can be made with columns less than ten feet long. However, the longer columns do have an increased sample capacity, in proportion to the square root of the length. For gas analysis the long columns will continue to be more desirable.

Many types of tubing are available for packing, such as copper, aluminum, stainless steel, and glass. For all around utility stainless steel is preferable. Most commercial equipment has stainless detector assemblies and columns, especially those used for high temperature work.

This work does not include a comprehensive study of column diameter. Probably the efficiency of 3/8 inch standard tubing is a little worse than 1/4 inch tubing, with larger sizes falling off in efficiency.

Straight and u-shaped columns are less likely to permit channeling than coiled columns, as they settle. They also have the advantage of being easily repacked if desired. The author has no evidence that coiled columns are less efficient, and coils will continue to be used for convenience and compactness.

The following technique is general and is probably used by a great majority of investigators with but minor variations.

The support is weighed into an evaporating dish, the non-volatile solvent weighed in a suitable container and dissolved in enough volatile solvent to completely wet the support. If two non-volatile solvents are to be used it is often preferable to blend them at this point. The solution is added to the support and the mixture stirred on a steam bath (a hot plate is useable if the temperature is raised slowly) until the packing is dry. Fine packing will tend to splatter during this operation. Continue the drying with frequent stirring until the odor of the volatile solvent is gone.

Place a plug of glass wool in one end of the tubing and pour the packing into the other end through a funnel, vibrating the column with a massage vibrator, or tapping it with a metal rod and tapping it vigorously on the floor. If the column is long it may be bent into a u-shape and packed from each end. When it is full to within one to one-half inches from the top, pack the remaining space with glass wool.

A record is kept of the packing weight so that the data can be reported in the conventional methods.

Before putting the column into use it should be "baked-out" at a temperature near its maximum limit for one-half hour or until the "bleeding" stops, as is indicated by a constant base line on the recorder.

APPENDIX D

COPPER OXIDE COMBUSTOR FOR CHROMATOGRAPHIC ANALYSIS

The use of a copper oxide combustor to convert chromatographic hydrocarbons to carbon dioxide and water was first suggested by Martin and Smart (25). They used such a device in connection with an infrared detector sensitive to carbon dioxide. Such a device is not limited to this application, however, and would appear to be useful in several ways: One, as a "gas amplifier" for trace and/or high boiling hydrocarbons. The combustor, placed at the outlet of the chromatographic column, converts the effluent peaks to carbon dioxide and water, with a corresponding increase in number of molecules reaching the detector. Thus, each mole, for example toluene, is converted to seven molecules of carbon dioxide and four molecules of water.

Two, as a method for analysis of hydrocarbon samples. The combustor is placed in series with a column which is capable of separating hydrocarbons according to their boiling points. This sort of arrangement, properly calibrated, yields quantitive information such as the carbon weight per cent of pseudo-components, or the identity of pure samples.

The apparatus used consisted of a piece of 1/4 inch stainless steel tubing about 14 inches in length, wrapped with fiberglass cloth and a nichrome heater wire. A chromel-alumel thermocouple was silver soldered to the outside of the tube. As the tube was separated from the heater wire by a layer of glass cloth, this was capable of giving a reasonably good indication of the temperature of the tube. The combustor tube was filled with various grades of copper oxide wire and copper oxide powder mixes. Temperature was adjusted by means of a powerstat.

Three tube fillings were tried: One, a short (about six inches) length of tube was filled with fine, powdered copper oxide. This was an effective combustor, but had the disadvantage of restricting the flow considerably, particularly at combustion temperature.

Two, the entire length of the tube was filled with copper oxide wire (Baker Chemical Company). About 11 gm was required to fill a 14 inch tube. This had desirably low flow impedance, but insufficient active area to completely convert stable compounds such as methane at normal (60 cc/min) flow rates.

Three, a mixture of copper oxide wire and fine copper oxide was used as a compromise. About 50 per cent by weight copper oxide wire appeared to be the upper limit consistent with a reasonably uniform mixture. This mix converted methane satisfactorily at normal flow rates.

The obvious filling would be the proper particle size of pure copper oxide. This does not seem to be as readily available as one would expect. Another possibility might be a blend of fine copper oxide and Celite.

The operating temperature of the combustor was determined by observing the degree of conversion of methane with gradual temperature increases. Virtually no conversion occurs very much below 600°C. At 700°C, the conversion is complete. An operating temperature of 750°C (nominal) was used to avoid the consequences of temperature measurement errors. This agrees with references in the literature. Regeneration of the combustor was accomplised by passing an air carrier through the instrument with the copper oxide at 750°C.

It was apparent from the outset that the theoretical "gain" was not being realized. For example, methane (theoretical gain of 3) was a gain of 2.23; pentane, (theoretical gain of 11) a gain of only 2.24. This shortcoming was at first attributed to the combustor. The combustor was then placed ahead of a molecular sieve column and methane was introduced. Since a molecular sieve column will retain water and carbon dioxide indefinitely but will pass methane, the almost complete disappearance of 5 cc of methane was accepted as proof that the conversion was complete.

The combustor was then placed ahead of a 12 inch silica gel column which will separate carbon dioxide and water. A sample of toluene was introduced and converted. Since toluene has a longer retention time than water, complete conversion was verified by the absence of any trace of toluene. Samples of carbon dioxide and water in the same amount as the expected yield from the converted toluene were introduced and checked within the limits of sample reproducibility. The failure to achieve the expected gain was due to three facts; One, the thermal conductivity of carbon dioxide is higher than that of most samples. Two, the response of the detector is not linear over the wide range involved in converting a large sample of a heavier hydrocarbon. Three, the water vapor resulting from the combustion does not emerge as a clean peak but tails noticeably as a result of sorption upon the metal surfaces.

APPENDIX E

METHODS OF FRACTOGRAM ANALYSIS

The only data obtained from the chromatograph is a recording of detector signal versus time or from a programmed temperature unit detector signal versus temperature can be used. For many purposes, such as chromatographic distillation, the temperature is a convenient variable.

The amount of additional information required varies with the instrument, the method obtaining analytical results, and the nature and accuracy of the results expected. It may be necessary to obtain any or all the following information: nature of column packing, type and amount of liquid phase, flow rate of carrier gas, system pressure, temperature programming rate, and perhaps the history of the particular column.

Since identification of the separated components was not required for this study, qualitative methods are not included as part of this discussion.

Quantitative Methods

Peak Height. The height of the peak measured from the base line is the simplest method of quantitative analysis. For routine or control methods where only a few components must be determined, measurements at pre-set times may supply the necessary information without taking the entire chromatogram. The method is extremely rapid and calibration can be programmed after each analysis.

Peak Area. For chromatographic distillation, the peak area is proportional to the amount of substance present. The proportionality constant depends on the nature of the substance, the type of detector, and whether the amount is expressed on a weight or molar basis. For thermal conductivity detectors, peak areas are functions of the system pressure, heating rate, and flow rate, but are otherwise independent of the operating conditions providing that the detector signal is a simple function of concentration expressed either in weight per cent or mole per cent.

If weight per cent is used, it is possible to obtain accurate results by applying a correction factor which is closely related to the thermal conductivity of the particular component. An extensive study is reported by Rosie (28), who found that the relative response (area per mole of component/area per mole of standard substance) of thermal conductivity detectors can be predicted from the molecular weight and class of the compound. They claim that the relative response is independent of the individual sensing unit (filament or thermistor), carrier gas flow rate, or column length. Extensive tables are given.

From the above discussion, it should be clear that indiscriminate use of peak areas as a measure of concentration is subject to errors. Calibration or correction factors must be applied according to the expected accuracy of results.

Internal Normalization of Peak Area. In this method it is assumed that the total area under a chromatogram represents all of the sample components. The area under each peak is multiplied by the proper correction factor to convert it to grams or moles. The corrected area of a component is divided by the total of the corrected areas for all components, and this yields the fraction of each component present in the sample. The accuracy of the analysis does not depend on accurate knowledge of the sample size. On the other hand the method does require a complete chromatogram and correction factors. For rough analysis, the correction factors can be assumed equal to unity, however, an error will exist in the results of about 10-12 per cent.

Internal Standardization. In this method a known amount of a standard substance is added to a known volume of sample before it is analyzed. Therefore, the concentration of the standard is known. The selection of the standard is important. It should be one that is inert toward all sample components, and its peak should be readily and completely resolved from all others. It should have an emergence temperature between the lowest and highest boiling components. To obtain the concentration of a component it is only necessary to multiply the concentration of the standard by the corrected area for the component and divide by the corrected area for the standard. This method is not limited to peak areas; peak heights may also be used.

In this work the internal normalization method was used, except the area under each peak was not converted to grams or moles. Instead, the area for each hypothetical component was divided by the total area for all the components to obtain the individual data points in weight per cent carbon. This method does not require correction factors because all the eluting hydrocarbons have been converted to CO_2 and water and only the CO_2 is measured. However, the method does require a complete chromatogram.

Measurement of Peak Areas

In most cases, the physical measurement of the peak area is the limiting factor in the accuracy of the results. Several methods exist. However, for this study only a ball and disc type automatic integrator was used, but a brief discussion is also given for the other methods.

The peak can be cut out and the paper weighed. This is an inexpensive but tedious method. The accuracy is limited by the patience of the operator and the uniformity of the paper.

The area can be measured with a planimeter. This is a more elegant method than cutting and weighing the peak and is also relatively inexpensive. It is impractical for routine analysis where miles of chart paper may be involved.

The peak height can be multiplied by the peak width at half height. For symmetrical peaks this simple method is equally as accurate as some of the more tedious methods of measuring areas. However, peaks with leading or tailing edges are not suitable.

One of the best methods is to use an automatic integrator. The area enclosed by the chromatographic trace is given by a secondary pipping pen or a digital read-out device. An electronic integrator amplifies the detector output with a chopper stabilizer D.C. linear amplifier and feeds the signal to the condenser whose charge build-up can continue until it reaches a potential sufficient to fire a tube. When the tube becomes conducting it discharges the condenser. The rate of tube firing depends upon the detector output emf and each tube pulse trips an electronic counter circuit. A device zeros the count rate at the base line and clears the counter between peaks. The advantage of this instrument is that it is not dependent upon the recorder span, and thus eliminates the necessity for keeping larger peaks within the recorder scale.

In this work a ball and disc type integrator was used which has a variable drive output that is attached to the recorder slide wire so that at the base line the output shaft has zero rotation. The shaft rotation increases in direct linear relation to the amount of deflection above the base line. This shaft then drives a pipping pen that records along the edge of the chart. The number of pips observed during the passage of a peak is the integrated area.

APPENDIX F

PROCEDURE FOR OPERATING THE MOLECULAR WEIGHT INSTRUMENT

Operation of the molecular weight apparatus entails the following steps. Figure 33, shows the arrangement of the vacuum system and panel controls. The instrument should have an initial warm up period of 30 minutes before any measurements are made.

Warning

Do not turn on the balancing voltage switch unless a pressure equal to or exceeding the pressure dial setting exists on the sample side of the gage

The gage diaphragm is pulled toward the metallized surface of the glass disc when the balancing voltage is on. Therefore, when no sample or pressure is present, the diaphragm will short to the surface and damage the gage.

Procedure

1. With all valves open obtain the highest possible vacuum in the system. (Make sure the sample receiver "plug" is in position and mercury is in the receiver, see maintenance appendix for operational procedure of vacuum system.)

2. Turn the instrument on (allowing for the warm up period) and adjust the null meter to zero.

3. Close valve 2. If the null meter does not change, the lowest obtainable pressure has been reached.

4. Open valve 2 and recheck the null adjustment, then reclose valve 2.

5. Set the pressure dial to zero.

6. Close valve 1, recheck the null adjustment. (The meter should not change; if it does the system is completely evacuated.)

7. Introduce the sample into the sample receiver.

8. Open valve 1 (null meter needle should move off scale to the left side of the meter.)

9. Set pressure dial to zero.

10. Turn balancing voltage switch on.

11. Adjust the pressure dial for a zero reading on the null meter, lock the dial.

12. Turn off balancing voltage.

13. Open valve 2. This evacuates the sample from the system.

14. Convert the dial reading to pressure in microns by means of the formula $P = d^2/\underline{k}$, where d is the dial reading and $\underline{k}$ is the gage constant (gage constant value = 1852).

To eliminate time-consuming calculations, a set of conversion tables for each value of the dial reading were made and are in the laboratory.

Note: If frequent measurements are to be made, valve 3 should be open to the pump to maintain the reference pressure as low as possible at all times.

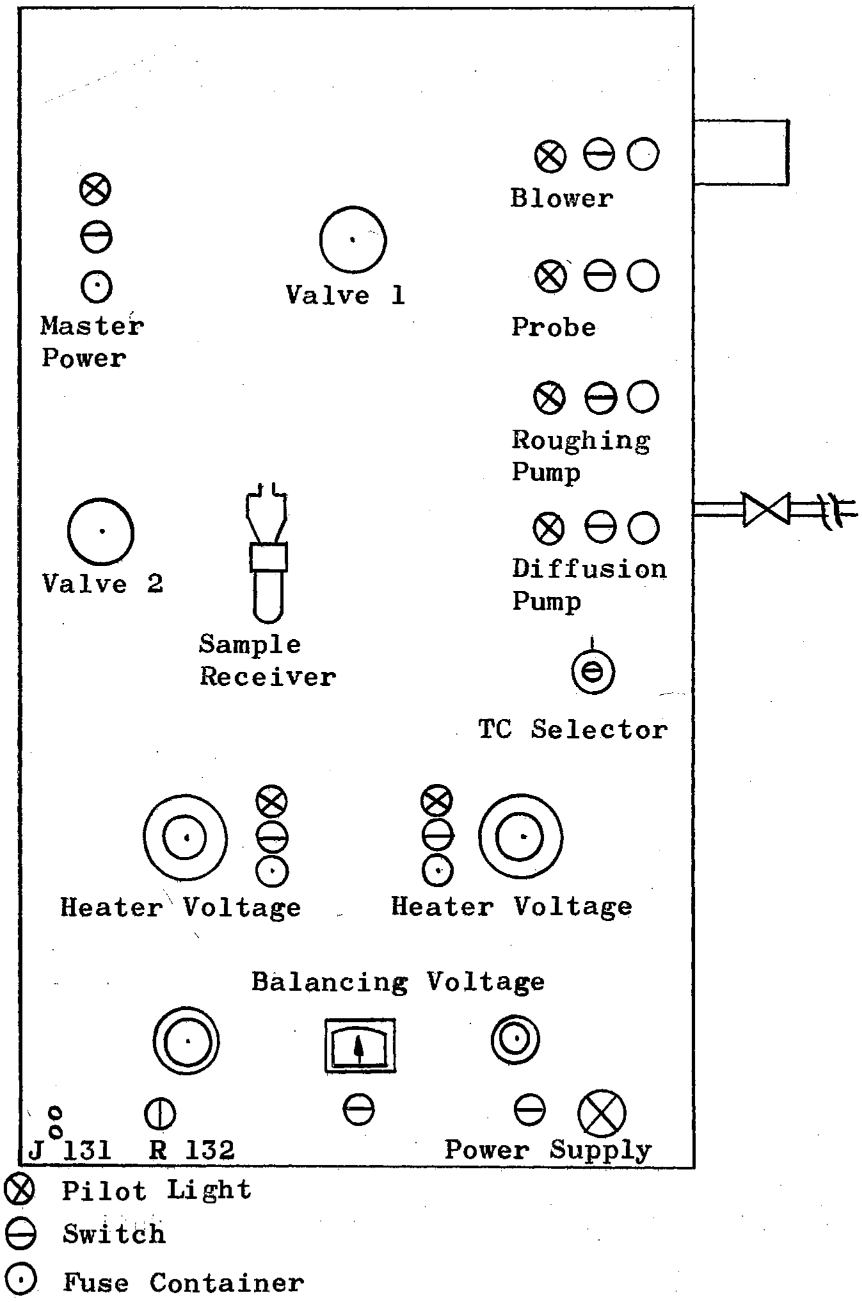

Figure 48

Front Panel of Molecular Weight Instrument

APPENDIX G

MAINTENANCE AND TROUBLE SHOOTING OF THE MOLECULAR WEIGHT INSTRUMENT

This section consists of routine maintenance to assure proper operation and trouble shooting to correct for improper operation of the mole weight apparatus.

Routine Maintenance

A. Daily check of the d-c balancing voltage should be made. To check the d-c current connect a senstitive potentiometer (i.e., Leeds & Northrup Model No. 8690) across the calibrating jacks (lower left corner of front panel). Adjust the variable resistor (set screw on left corner of front panel) to a reading of 1.0 volt ± 0.0015 volt on the potentiometer.

B. A 100 hour check of the voltages indicated on figure 50. If improper voltages exist, replace the associated vacuum tube and check the remainder of the components.

C. Operation and maintenance of vacuum system.

   1. Starting procedure

      (a) Turn on mechanical pump. (with valve 3 off.)

      (b) When system pressure reaches 500 microns Hg or less, (approximately 20 minutes) turn on diffusion pump and cooling water.

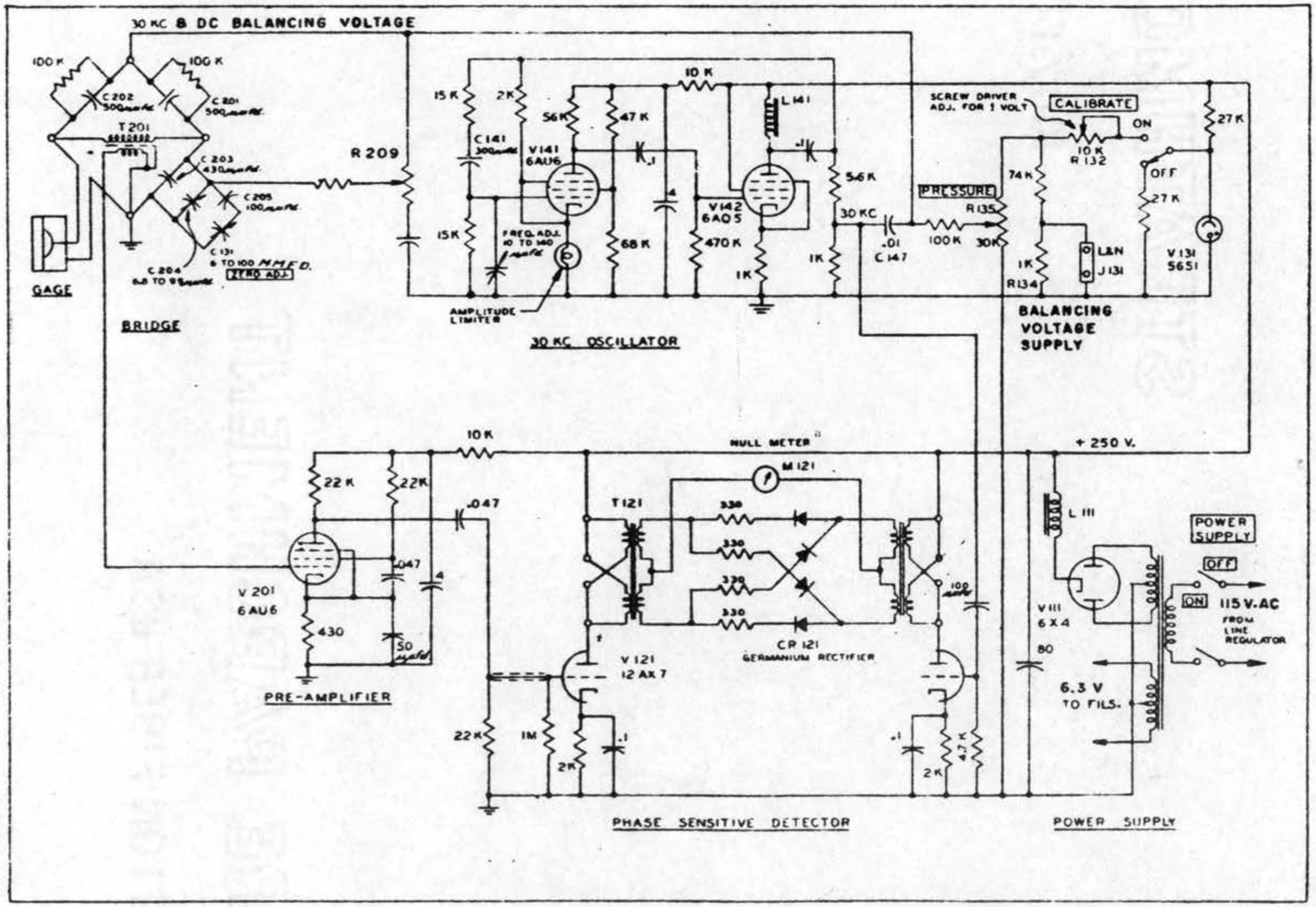

Figure 50

Schematic Diagram of Molecular Weight Instrument

2. Shut down procedure
    (a) Close valve 3.
    (b) Turn off diffusion pump heater. (Leaving cooling water on until pump boiler is cool enough to touch.)
    (c) When pump boiler is cool, turn off mechanical pump.
3. Maintenance

Note: The performance of the system depends primarily on the condition of the diffusion pump fluid. Exposure of the hot organic pump fluid to the atmosphere for even a short period of time will result in the decomposition of the fluid. If the exposure has been very slight, the fluid may purify itself after a few hours of pumping. However, if the pressure in the system remains high after considerable pumping, then the fluid must be changed. For complete maintenance see the operating instructions for type VMF pumps (9).

Trouble-Shooting

A. Symptom:

The micromanometer cannot be balanced.

Fault:

A change in the gage resistance or capacitance.

Correction:

Measure the gage resistance and capacitance. The gage resistance should be in excess of 100 Megohms and the capacitance from 300 to 700 mmfd.

1. The gage resistance measurement is made by disconnecting

the bridge/amplifier (located immediately under the heated air bath) from the gage head and connecting the leads from a vacuum tube volt meter to the gage connector. Do not apply more than 50 volts to the gage in making this measurement. The Triplett Model 630A meter is recommended. The Simpson Model 260 meter and R. C. A. Voltohmyst are also satisfactory.

2. If the gage resistance is less than 100 ohms, the diaphragm may be stuck to the metallized surface of the glass spacer, or a paricle of foreign matter may be lodged between the two. The short may be eliminated by admitting a few centimeters of pressure to the sample side of the system to push the diaphragm away from the spacer. This can be done by injecting into the system a few cubic centimeters of air. To do this remove enough mercury from the sample receiver so that when a micropipette is placed in the orifice the upper tip is above the mercury level.

3. Measurement of the gage capacitance is made with a calibrated variable air condenser with a range of 100 to 1000 mmfd. First make sure the bridge/amplifier is working correctly by observing the following procedure.
   (a) Remove the bridge amplifier from the gage.
   (b) Replace the gage with an air condenser.
   (c) Adjust the air condenser until a null is obtained on the meter.

   Again connect the bridge/amplifier to the gage. Disconnect capacitance 203 (each capacitor is labeled on the chassis) in the bridge/amplifier and remove it from the circuit. Adjust the coarse balance control, C-204, to a minimum. Disconnect cable J-202 and connect a variable air condenser for a null on the meter. The value of the variable condenser should be approximately (30 mmfd.) equal to the gage capacitance.

4. If in step 3 (above), it was found that the bridge would not balance a capacitance equal to that of the gage, the following circuit check should be performed.

   Using a variable air condenser in place of the gage, find the range of capacitance that can be balanced with the coarse balance control, C-204. If the gage capacitance is outside the range of the bridge, change C-203 to bring the gage within range.

B. Symptom:

Mercury will not flow through orifice.

Fault:

Foreign matter lodged in orifice.

Correction:

1. Close valves 1 and 2, and turn off diffusion pump.
2. Slowly remove the glass sample receiver at the metal-to-glass standard tapered joint. (This will release the vacuum in this section of the system.)
3. Carefully, pour the mercury in the upper section into a container, then remove the lower section and pour its mercury into the same vessel.

4. Clean the silicone stopcock grease from the tapered joints with a soft cloth and acetone.
5. Air pressure may then be applied to the bottom part of the orifice. If this does not remove the lodged particle, the orifice may be "soaked" in cleaning solution, acid, water or acetone. (Whatever is necessary to remove the object from the orifice.)
6. To replace the sample receiver, apply a thin coat of silicone high vacuum stopcock grease to the male ends of standard tapered joints.
7. Then slip the male end of the upper section into the female fitting of the lower section and rotate slowly at the same time applying pressure forcing the two sections together. (Continue to rotate until all air bubbles are forced out.)
8. Replace the sample receiver on the instrument (using same procedure as described in step 7).
9. Open valve 1 slowly (after diffusion pump has cooled enough to touch) and allow the roughing pump to remove the trapped air.
10. Turn on diffusion pump after the trapped air has been removed (about 15 minutes) and open valve 2.

APPENDIX H

SUMMARY AND RECOMMENDATIONS FROM G. M. COOKE'S VISIT ON THE SARNIA FRACTIONATOR

The following notes describe the salient points of Mr. Cooke's help in getting the Sarnia Mark II Fractionator in operation.

Mr. Cooke accredited part of the trouble of the unsteady distillation TBP curves to the fact that the thermowell tip was not correctly located. The original thermowell had been broken and replaced incorrectly. Most of the rest of the trouble was due to the peculiar nature of the reformer feedstock that was being assayed. It was refusing to boil smoothly. It frequently superheated and then released its vapor in spurts; i.e., bumping was excessive. Mr. Cooke noted that the new smooth flask probably encouraged this bumping effect, and preceded to nick and scratch the interior of the glass flask bottom. He suggested using a bare stirring bar and several boiling stones. This reduced the excessive bumping to an acceptable level.

Our unfamiliarity with the new still accounted for some of the mal-operation of the unit. Thus Mr. Cooke made the following recommendations that aid in successful operation of the Sarnia Fractionator:

1. Keep thermowell tip in the space between collector ring and valve stem; do not touch stem or any part of wall or ring with tip.
2. Use silicone or similar heat stable liquid in the tip of thermowell for good contact to T. C. bead. Use one drop only.
3. Keep T. C. wire and insulation in good condition.
4. Calibrate T. C. and use calibration. Check calibration weekly, at least at one point. (Use freezing point plateaus rather than at boiling points.)
5. Inspect and regrease all ball and taper joints every run. Do not use excessive grease. Dow silicone is good, compound #11. Even better are O-rings which can stand temperatures up to 600°F and eliminate the need for grease. They seal perfectly and for an indefinite time when properly used. The O-rings can be obtained from H. S. Martin Glass Company, specify ball joint size.
6. Replace valve stem and ball when necessary, see parts list. (Part No. n-9221-11)
7. If expected initial vapor temperature is below 150°F, use a dry ice trap to quarantee no vapor losses.
8. Do a material balance (to nearest gram) as an over-all check for accidental errors.
9. Use mantle heat on jacket of tower if distillation temperature exceeds 400°F, especially if vacuum is used. Check glass jacket for conductivity once in a while when

vapor temperature is 300°F +, and tower mantel is off. It should feel cool or barely warm (except at ends).

10. When charge refuses to boil smoothly use bare stirring bar to promote smooth boiling. Also the inside of the glass flask should be scratched or marred to facilitate nucleation of bubbles.

11. Products of cracking operation, among others, tend to produce stable foams at times. This prevents startup of a distillation. The only solution we have is to put the still on total "take off" for sufficient time to remove the offending liquids. Usually the foaming clears up in 5-10 per cent over.

APPENDIX I

CALCULATIONAL PROCEDURES

In this section calculational procedures for the imperfection pressure correction, Θ; K-Ideal, K_I; and K-Actual, K_A; are discussed. All of the actual calculations applying these methods were made using the computer programs written by Henderson(22).

Imperfection Pressure Correction

The imperfection pressure correction factor, Θ, was calculated using equation (I-1). A complete discussion of this equation is given by Henderson(22).

$$\ln \Theta_i = \beta_i (P_r - p^\circ_{r_i}) + \psi_i (P_r^2 - p^{\circ 2}_{r_i}) \qquad \text{(I-1)}$$

$$\beta_i = \frac{1}{T_{r_i}} \left[\frac{BP_{c_i}}{RT_{c_i}} - \frac{V^L P_{c_i}}{RT_{c_i}} \right] \qquad \text{(I-2)}$$

$$\psi_i = \frac{\ln p^\circ_{r_i} - \ln P_{r_k} - (P_{r_k} - p^\circ_{r_i})}{(P^2_{r_k} - p^{\circ 2}_{r_i})} \qquad \text{(I-3)}$$

where: P_r is the reduced pressure

p°_r is the reduced vapor pressure

T_r is the reduced temperature

The critical values, P_c and T_c, for the above equations were obtained by cross plotting data from Edmister (15). The plots of this data are shown in Figures 34, 35, and 36. The convergence pressure, $P_{r_k} = 6.29$.

K-Ideal

The ideal vapor-liquid distribution ratio, K_I, was calculated using equation (I-4).

$$K_I = \frac{p^\circ}{P\theta} \quad \text{(I-4)}$$

Where the vapor pressure of each hypothetical component, p°, was obtained from Maxwell and Bonnell (28). The imperfection pressure correction, θ, was calculated from equations (I-1) through (I-3). The system pressure, P, was equal to 760.0 mm Hg for this work.

K-Actual

K-Actual, K_A, was determined as the product of K-Ideal and the derived activity coefficient, γ, equation (I-5).

$$K_A = \frac{p^\circ \gamma}{P\theta} \quad \text{(I-5)}$$

The derived values of the activity coefficient, γ, were calculated for each equilibrium flash using the computer programs written by Henderson (22). In these equilibrium flash vaporization calculations, V/L (calculated) was compared with V/L (experimental). If V/L (calculated) was not equal to V/L (experimental) the activity coefficient, γ, was increased or decreased, depending if the difference between V/L (calculated) and V/L (experimental) was high or low, and the calculation repeated until V/L (calculated) equaled V/L (experimental).

VITA

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