PRINCIPLES AND PROPERTIES OF GAS CHROMATOGRAPHY

By

JAMES LANG WEBSTER

Bachelor of Science
Oklahoma State University
Stillwater, Oklahoma
1958

Submitted to the faculty of the Graduate School of the
Oklahoma State University in partial fulfillment
of the requirements for the degree of
MASTER OF SCIENCE
August, 1960

PRINCIPLES AND PROPERTIES OF

GAS CHROMATOGRAPHY

Thesis Approved:

J M Marchello
Thesis Adviser

R. N. Maddox

Robert Nesbitt
Dean of the Graduate School

PREFACE

During the past eight years, gas chromatography has come into its own as a fundamental technique for analyzing vapor and liquid mixtures. In 1959 over 1000 technical papers were written on gas chromatography and its applications. It has rapidly become a basic analytical tool, almost as common and as simple as titration.

A method utilizing gas chromatography in the analysis of samples from a high pressure equilibrium cell is presented in this thesis. In conducting these experiments, the factors affecting the reproducibility and accuracy of the results were noted and analyzed. Data were taken to help develop theoretical correlations of some of the parameters of chromatography.

I would like to express my gratitude to Dr. R. N. Maddox and members of the Chemical Engineering Staff who aided in my work with their helpful suggestions, and particularly I appreciate the advice and guidance given by Dr. J. M. Marchello.

I wish to thank the Dow Chemical Company for a Fellowship which made this work possible.

I am indebted to my wife, Virginia, for her encouragement and continued interest in my graduate studies.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

In the Spring of 1959 the School of Chemical Engineering at Oklahoma State University, with the purchase of precision high pressure equilibrium apparatus, initiated a long range study of the thermodynamic properties of vapors and liquids. This equipment had three main functions: the control and measurement of temperature, the control and measurement of pressure, and the intimate mixing of the vapor and liquid in the equilibrium cell. One major step was still needed. This was the quantitative analysis of samples taken from the equilibrium cell.

After careful consideration of the various methods of analysis, Professor Wayne C. Edmister, the director of the high pressure work, decided to use gas chromatography.[1] His decision was based on the availability and cost of the equipment and on the expected accuracy of the chromatograph.

Objectives

The work of this thesis was to be generally directed toward a method of analysis for the high pressure equilibrium samples. The following objectives were set up:

1. Assembly and construction of the necessary gas chromatography equipment.

---

[1] The term "chromatography," in keeping with common practice, will be used interchangeably with "gas chromatography."

2. Development of a high pressure gas and liquid sampling system.
3. Determination of the accuracy of gas chromatography.
4. Development of theoretical correlations to aid in the use of chromatographic columns.

Basic Principles of Gas Chromatography

An overly simplified picture of gas chromatography may be explained as follows. Take a length of pipe and fill it with loose gravel which has a thin coat of some type of oil on it. Place the pipe in a vertical position and pour a mixture of two liquids (acetone and alcohol, for example) into the pipe. As gravity pulls the mixture through the pipe, the two liquids begin to separate. If conditions are right when the liquids reach the bottom of the pipe, first one component will flow out and then the other. In practice, the pipe is usually replaced by a length of metal tubing and the gravel by a quantity of crushed fire brick. The fire brick is coated with a thin layer of some oil or a high boiling-point liquid. A constant flow of some inert gas is kept moving through the column in place of using gravity to move the sample through the column. Usually the unit is placed in a constant temperature bath in order to obtain greater accuracy and reproducibility.

Once a sample has been injected onto the top of the column the inert gas carries the components through the column. A small syringe is used to inject the samples. As the sample moves through the column the various components are separated from each other. The separated components emerge from the column and pass through a detector which is part of a balanced electrical bridge system. The

detector used is a thermal conductivity cell. The presence and amount of each component is indicated by the degree of unbalance of the bridge system. The bridge system is commonly connected to a strip recorder upon which the unbalance of the bridge is recorded as a peaked curve. (Figure 1) The time required for a given component to elute from the column is a characteristic of the component which permits its identification.

The quantity of a given component in a sample can be directly related to the height of its unbalance voltage curve or to the area under this curve. The area under the curve is most often used to determine the amount of a component present since it is less dependent upon injection rate than is peak height.

Components are separated on a chromatograph because of differences in their partition functions. Partition functions indicate the length of time a given component will spend in the carrier gas phase and how long it will reside in the liquid coating phase.

Mixture separation in a column is dependent, in part, upon column temperature, flow rate of carrier gas, length of column, ratio of inert solid to liquid phase, size of the sample used, type of liquid phase used, column operating pressure, and the vapor pressure of the components in the mixture to be separated. To simplify repeated analysis and to assure reproducibility, as many of these variables as possible are held constant. In this manner, fairly exact relationships can be determined for the length of time (retention time) that a given component takes to elute from the column. Conversely, retention time may be used to calculate approximate vapor pressures which aid in identification of unknown components.

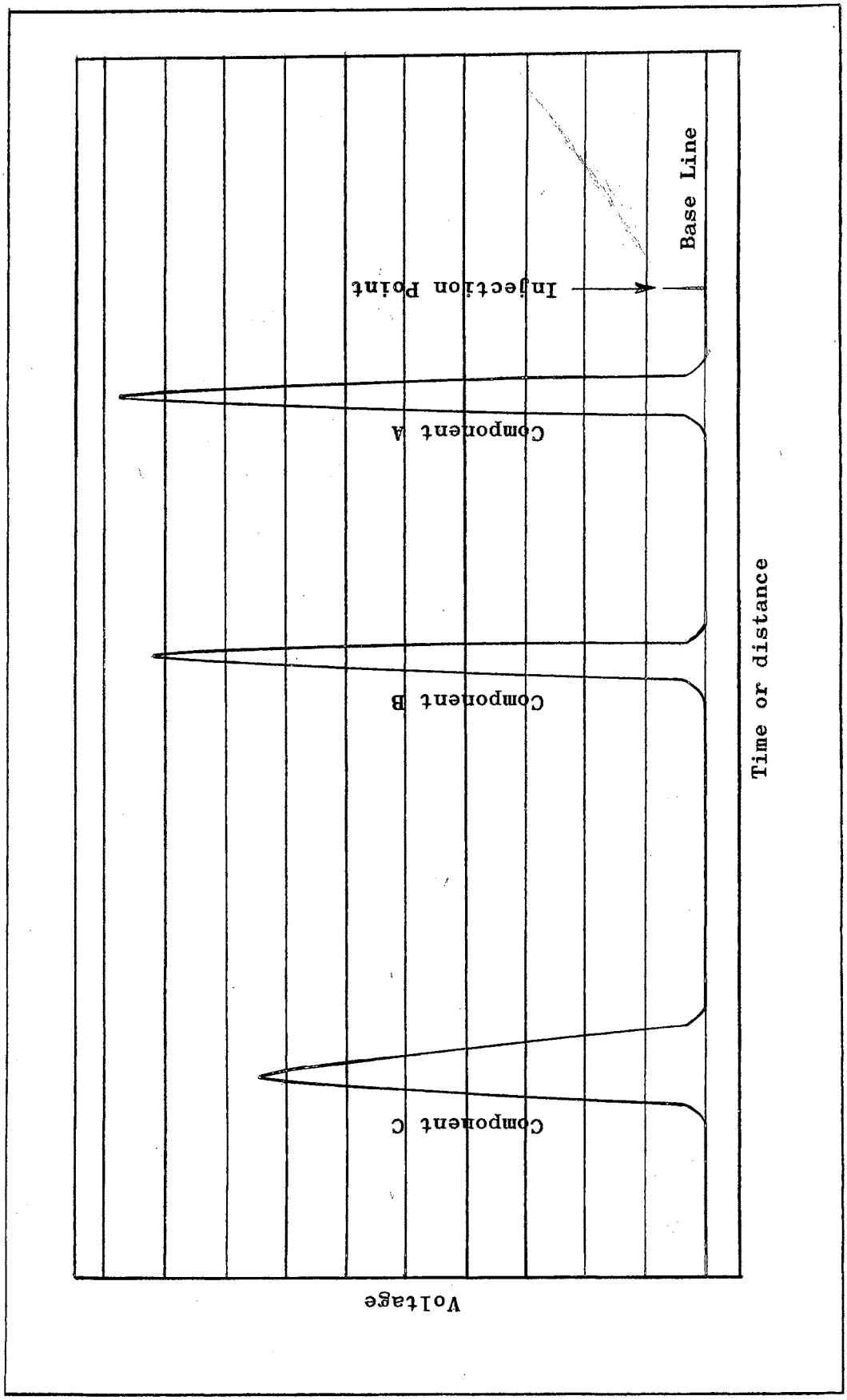


Figure 1. Typical Chromatogram Curve

For the most part, in chromatographic analysis the components are known, but the amount of each component in the mixture is not known. When an analysis is made by a gas chromatograph with a strip recorder attached, the component emerging from the column will produce a curve of the type shown in Figure 1. The amount of a given component in a mixture is quite often related to the area under the voltage-time curve. To calibrate the unit for a given component, varying sizes of samples of that component are run through the machine. In this manner a relationship, usually in the form of a plot, is obtained for the variation of characteristic area with sample size. As long as the conditions under which the chromatograph is operating remain the same, the amount of the known component in a mixture can be found by comparing the area under its curve with the correlation of sample size and area.

CHAPTER II

SURVEY OF GAS CHROMATOGRAPHY LITERATURE

Chromatography, in many different forms, has been known for years. Gas chromatography, so-called because a gas is used to elute the sample from the column, was first set forth as a possibility by Martin and Synge (25) in an article in 1942. The paper was concerned with the separation of liquid mixtures and the following classical statement was made.

> "The mobile phase need not be a liquid but may be a vapour. --- Very refined separations of volatile substances should therefore be possible in a column in which permanent gas is made to flow over gel impregnated with a non-volatile solvent in which the substances to be separated approximately obey Raoult's Law."

The first actual experimental work reported using a liquid film on the inert column packing was by James and Martin (17) in 1952. Since then, many thousand articles have been written about gas chromatography. The wide acceptance and rapid development of gas chromatography is due primarily to the fact that it is a relatively simple, efficient method for the separation and analysis of gas and liquid samples.

By 1958, gas chromatography had grown so rapidly that a "Journal of Chromatography" was initiated and published six times yearly. Because of the increasing number of articles being written, the Journal was made a monthly publication in 1959. Recently a number of excellent books on gas chromatography have become available (20,

27, 28) which present the fundamentals of operation, theory, and application of gas chromatography.

The Bureau of Mines has published two fairly comprehensive bibliographies of Gas Chromatography. The first, in 1956 (19) was a series of over 140 abstracts on the subject. The second (33), covering up to 1958, lists over 500 references. A recent article by Hardy and Pollard (16) gives a comprehensive review of chromatography up to January, 1959. The authors present both a review of the "ins and outs" of chromatography and an excellent bibliography of over 600 articles. Another article by Dal Norgare (9) covers chromatography from January, 1959 to January, 1960.

Several International Symposiums have been held on gas chromatography, and from these, many outstanding sets of notes have been published. (6, 11, 12). Because of these symposiums, many recommendations have come about for the standardization of terms, methods of analysis and the reporting of results for chromatography.

Operating Characteristics

Of major importance in this thesis work was the degree of accuracy that could be obtained from the chromatograph. The literature on gas chromatography shows that, in general, the reported accuracy is in the range of ± 1 per cent (16,24). It was seldom found that anyone was willing to report accuracy as high as ± 0.1 per cent. The usual repeatability given for various types of sampling valves and syringes alone is ± 0.1 per cent or poorer (7).

In order to insure the best possible reproducibility and accuracy, the literature of chromatography was checked to ascertain

what degree of control must be exercised over condition variables. The conditions listed below were generally recommended:

Temperature control ±0.2°C to ±0.1°C.

Flow control ±0.1 cc/min.

Other variables were usually such that they were expected to be fairly exact. These variables included voltage, and inlet and outlet pressure.

Many authors feel that there is another very important factor in utilizing chromatography accurately. This is the quantitative interpretation of the curve or chromatogram obtained from the recorder for a given component. This interpretation is usually based either on peak height or the area under the peak. Many investigators feel that for routine analysis, peak height is satisfactory but for accurate analysis, peak area must be used. Peak areas may be determined by any of the following methods: (1) by cutting the curves from the chart and weighing them, (2) by means of a planimeter, (3) by employing some automatic integrating device in the recording equipment, (4) by one of several methods of geometric approximation. The most commonly used of the apprximation methods consists of multiplying the peak height by the width at half the height. One article (18), recommended that the width product be taken at 45.4 per cent peak height for more accurate area measurement. The present tendency would seem to favor the automatic integrating devices (5,10), but many claim that the planimeter gives the most satisfactory results (29). One chromatography authority (33) prefers the geometric approximation. It seems that the important factor is not whether the results obtained are the actual

area under the curve, but whether the results can be reproduced from run to run.

Since the conception of gas chromatography, there have been many advances in design and use of equipment. A basic consideration in the choice of equipment for this proposed research was the possible use of equipment already available. Would this equipment be satisfactory? Two parts of the chromatograph are of interest in this respect. They are the type detector used and the type column used.

There are two major styles of columns now in use. The first is the packed column. In its usual form the column will be 1/4 inch metal tubing packed with an inert material which has been coated with some particular heavy liquid. The second type of column is a capillary column. This is usually a metal or glass capillary tube without inert material as in the common packed column. The heavy liquid is placed on the wall of the capillary. Large numbers of theoretical plates are obtained using capillary columns. As many as 3/4 million theoretical plates have been reported (31). Serious question has been raised as to whether the numbers of plates reported actually indicate improved results. In comparing capillary columns with packed columns giving 1/100 to 1/300 fewer theoretical plates, it was found that, in many instances, there was only a relatively small improvement in the actual separation obtained (4). The capillary columns bring into focus the other component of primary interest, the detector.

The detector used with the capillary column must be able to detect very minute amounts of a component. This can be done with radiation detectors or with hydrogen flame detectors. The packed

columns, since much larger samples are used in them, cannot generally use detectors of this type. A sample 1/1000 as large as that used in the packed columns is usually satisfactory for the capillary columns.

Since, in this research work, as large a sample as possible was desirable in order to reduce error, the capillary columns were not considered further.

The detector commonly used with packed columns in this country is the thermal conductivity cell. There are two modifications of this cell. One uses very small coils of fine wire as the sensing elements, and the other uses thermistors. Because of the availability and the high signal to noise ratio (3), thermistors were selected for use. Thermistors are inexpensive, readily available, and useable at temperatures up to 150°C.

The use of gas chromatography for the analysis of high pressure vapor-liquid equilibrium mixtures has been found to be a difficult problem. In most studies of this type the pressure is taken off of the sample obtained and only part of the sample is used for analysis. This method presents the possibility of transfer losses and losses due to condensation.

Price and Kobayashi (29) describe in fairly complete detail how they used gas chromatography to assist them in the analysis of their vapor-liquid equilibrium samples. A small high pressure equilibrium sample was trapped in a piece of tubing between two valves. The tubing was wrapped with a heating element and the entire sample was vaporized. One valve was then cracked and the pressure was allowed to bleed down to atmospheric pressure.

The valve was then closed and connected to the chromatography unit. Helium was used to force the remaining sample from the tube into the chromatography unit.

Price and Kobayashi used a series of correction factors to determine the composition. They felt that this was necessary since the chromatography parameters they were using were not held constant. Their final equation for the amount of a given component in a sample had the form:

$$m_i = (A_i/A_r)(Q_s/Q_r)(Z_s/Z_r)(P_r/P_s) \qquad (1)$$

where: m_i = mole fraction of component i present in the sample.

A_i = area under curve for component i.

A_r = reference area of component i.

Q_s = flow rate of carrier gas during sample analysis.

Q_r = flow rate of carrier gas during reference run.

Z_s = compressibility factor of the unknown sample.

Z_r = compressibility factor of the reference sample.

P_r = barometric pressure during reference run.

P_s = barometric pressure during sample run.

If Price and Kobayashi had kept the column outlet always corrected to 760 mm of mercury and had kept the flow rate through the column constant, the "P" and "Q" terms each could have been reduced to unity. This would have given them an equation of the form:

$$m_i = (A_i/A_r)(Z_s/Z_r) \qquad (2)$$

In essence, all that the remaining terms show is that the calibration curve for a given component is not a completely straight

line. They used compressibility factors to estimate the true calibration curve in place of calculating the curves. Their analysis was constantly off for one component, with an average error of almost two per cent.

Theoretical Background

Explanations of the theory behind gas chromatography have been advanced by many authorities in the field. Some of the theoretical developments have been well accepted; many have been passed over and forgotten in the expansion of this relatively new field of analysis.

Two international symposiums on gas chromatography (6,12) have recommended the following equation for standardization as the method of determining the number of theoretical plates in a gas chromatography column:

$$n = 16\,(d/w)^2 \qquad (3)$$

where: n = number of theoretical plates

d = distance from the injection point to the middle of the component peak

w = width of the component peak measured at the base between the intersection of the tangents of the inflection points of the curve.

This equation was chosen primarily because it was felt that it would be easy for all investigators to use.

Possibly one of the best known and most discussed equations for gas chromatography is the van Deemter, Zuiderweg and Klinkenberg equation (32). This equation was developed to explain the mechanisms of peak broadening and to derive an expression for the

"Height Equivalent to a Theoretical Plate," (HETP).

The basic equation is:

$$HETP = 2\lambda d_p + \gamma D_g/u + (8/\pi^2)\ (k'/1+k')^2\ (d_f^2/D_l)(u) \qquad (4)$$

where: λ = a quantity characteristic of the packing

d_p = average particle diameter

γ = a correction factor accounting for the tortuosity of the gas channels

D_g, D_l = diffusivity in the gas and liquid phases, respectively

u = linear gas velocity in the packed column

d_f = "effective" thickness of the liquid film with which the particles of the support are coated

$k' = K(F_l/F_g)$ where: K is the partition coefficient of the solute expressed as the ratio of moles per unit volume of gas phase; and F_l and F_g are the fraction of cross section occupied by the liquid and gas phases, respectively.

This equation is of the form $H = A + B/u + Cu$. The "A" portion of this equation is the contribution of eddy diffusion due to packing. The "B/u" term is the contribution of molecular diffusion and the "Cu" term is the contribution of the resistance to mass transfer.

The van Deemter equation has been discussed and criticized by many writers, but most agree that it is a good attempt to explain the complex phenomena occurring in a gas chromatography column (8, 13,23).

CHAPTER III

EXPERIMENTAL APPARATUS

The main components of the experimental equipment that were used for this research are shown in Plate I and Plate II. The basic unit was a model 119 gas chromatography purchased from the F & M Scientific Corporation, Wilmington, Delaware. A one millivolt Bristol Recorder, model 560, with a one second scale sweep was used with the chromatograph.

Items of Chromatographic Equipment

The equipment described below was used to obtain the best possible constancy for the gas chromatography parameters of operation. The parameters of each individual component are noted.

Constant Temperature Bath

A reflux vapor bath, 28 inches long was provided for controlling the temperature of the chromatography unit. (Plate I and Figure 2). This unit was similar in design to a straight-through jacketed reflux condenser. Temperature control was obtained by boiling a pure liquid in a distillation flask connected to the reflux vapor bath. By boiling various materials in the flask, a wide range of operating temperature levels could be obtained. Heat to the flask was controlled by a Variac on the right of the electrical control panel (Plate II). A condenser was provided to keep

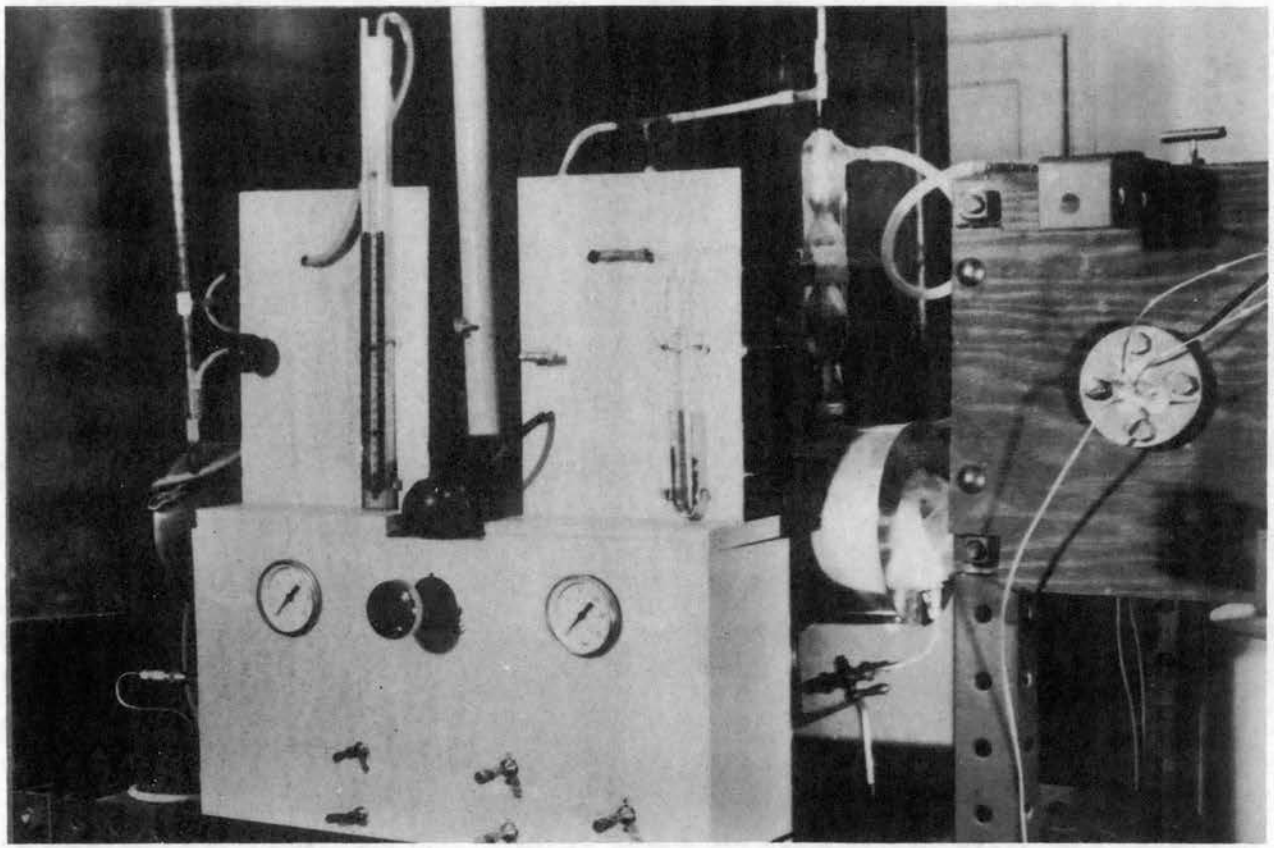


Plate I

Flow Control Panel and Constant Temperature Bath

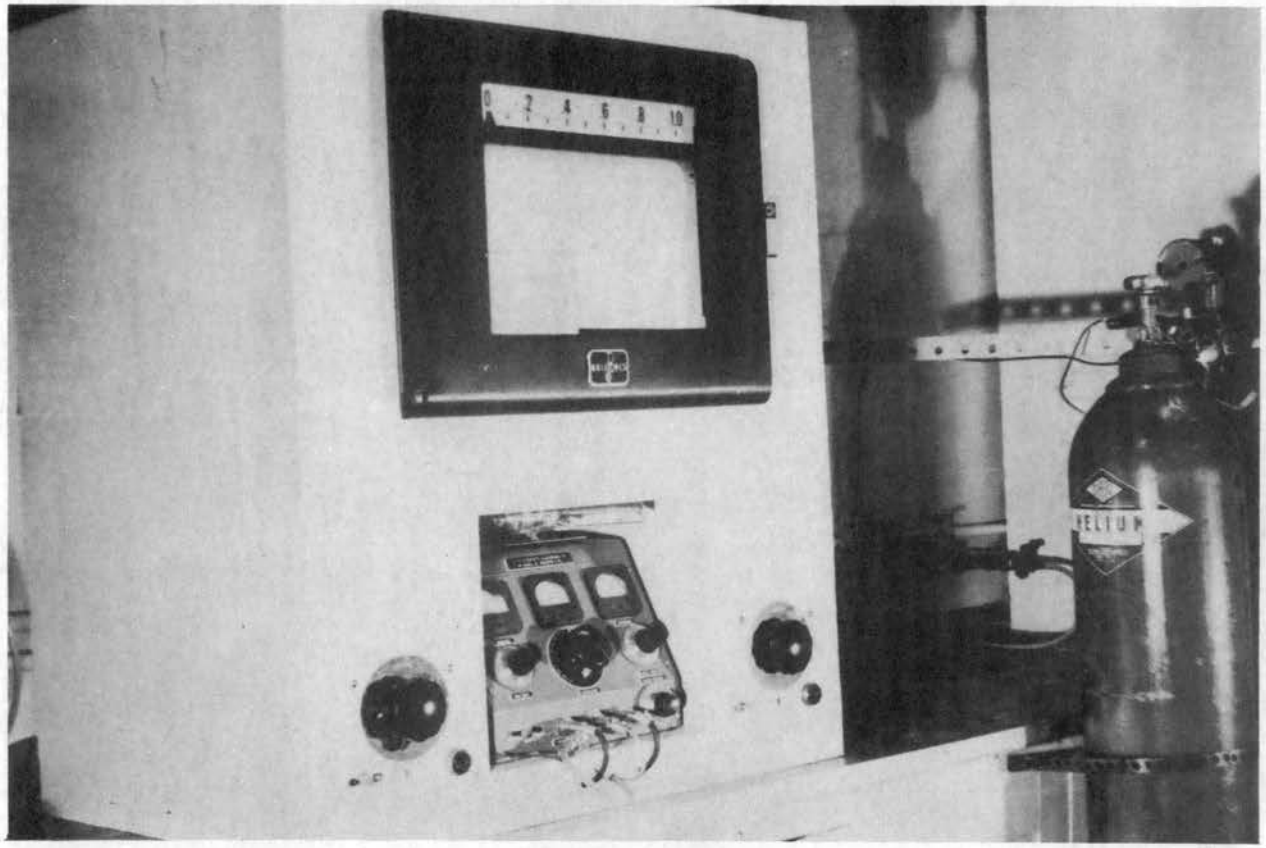
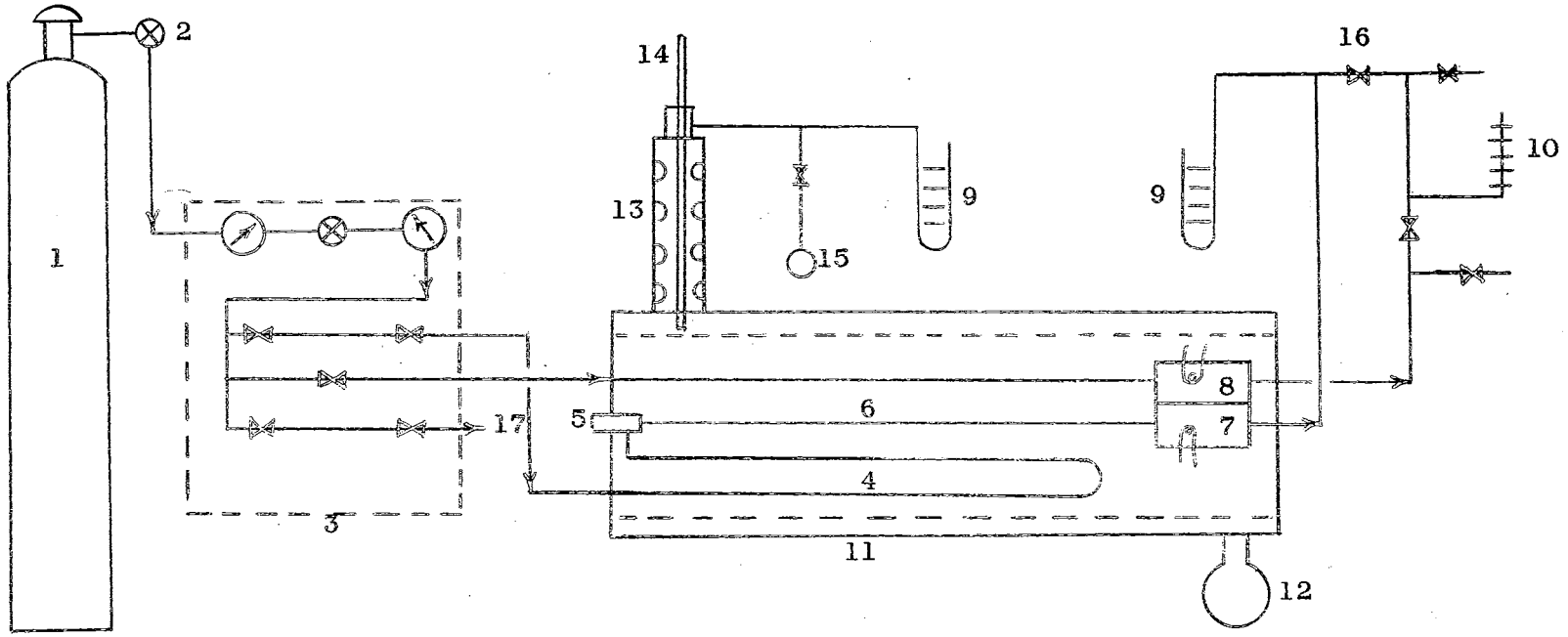


Plate II

Electrical Control Panel and Recorder



1. Gas source
2. Pressure regulator
3. Flow control panel
4. Preheat loop
5. Sample injection port
6. Packed column
7. Measuring thermistor
8. Reference thermistor
9. Manometer
10. Soap film meter
11. Constant temperature vapor bath
12. Heated flask
13. Condenser
14. Thermometer
15. Squeeze bulb
16. Outlet control valve
17. Sampling valve

Figure 2. Flow Diagram of Gas Chromatograph

the boiling vapor in the bath. Connected to the condenser were a thermometer and a pressure control system which served to maintain a constant temperature. Pressure on the system was controlled at exactly 760 mm mercury.

Pressure was maintained on the system at 760 mm of mercury by manually adjusting the mercury level of a manometer. The required manometer adjustment was determined from barometric readings. After the pressure correction was made, the system was then closed off from the atmosphere.

The temperature bath was provided with end plugs to reduce heat losses and maintain a constant temperature along the bath. Glass wool insulation was also used at the ends of the unit.

Gas Source

A cylinder of helium was used as the inert carrier gas source. A double diaphragm pressure regulator was placed on the cylinder to bring the pressure down to the operating pressure which was not more than 10 psig. Pressure was maintained by the use of this pressure regulator.

Flow Control Panel

The gas flowed from the pressure regulator on the helium cylinder to the inlet pressure gage and then on to a flow controller on the control panel (Plate I).

The flow controller was difficult to operate and did not give satisfactory pressure control. The controller was bypassed and the flow was controlled only by the downstream needle valves. At a later date, the flow controller was removed entirely from the control panel and a sensitive pressure regulator installed in its place.

This regulator gave very satisfactory results.

The gas flow was divided into three streams on the control panel. The main flow stream went to the preheat coil. The secondary flow stream went to the reference side of the column detector block. An auxiliary stream was provided so that the flow could be routed through an exterior sampling valve. Toggle valves were provided to control this switching. Each of the above streams had its own flow-control needle valve.

Preheat Coil (Figure 2)

The gas flowed from the control panel into the constant temperature bath and through a four foot copper tube 1/8-inch in diameter. This tube was used to bring the temperature of the inlet gas up to the bath temperature.

Sample Injection Port and Packed Column (Figure 2)

The gas flowed from the preheat coil into the packed column. This column was from 2 to 6 feet long and was made of 1/4-inch copper tubing. It was connected to the injection port and the detector block by compression fittings. To change a column, the lead wires on the detector block and the outlet and inlet gas lines were disconnected; and the injection port, front plug, column, and detector block, as a unit, were pulled gently from the bath. The column was removed by loosening the nuts on each end. The nuts and sealing "O" ring could be placed on a new column and the unit reassembled in reverse order.

The columns were packed with 35-80 mesh chromosorb. The chromosorb was coated with the desired weight per cent of stationary liquid to be used (usually 20 % by weight). The column packing

was made by first weighing accurately the chromosorb and the stationary liquid. The stationary liquid was then dissolved in a suitable solvent (acetone or ether). This provided a large volume which was thoroughly mixed with the chromosorb. The volatile solvent was driven off by placing the mixture on a steam plate. This mixture was continuously stirred until all noticeable traces of the solvent were removed.

Accurate lengths of 1/4-inch copper tubing were cut to the desired size. A small plug of glass wool was placed in one end of the tubing and the prepared packing was poured into the other end. The sides of the column were tapped gently as the packing was poured in so there would be no dead spaces and so that the packing would assume a fairly uniform density. The other end was sealed with another plug of glass wool and the column was bent so that it could be placed in the constant temperature bath.

Detector Block (Figure 2)

The detector block contained two thermistors which were connected to the bridge system. One thermistor was in the column stream and was called the measuring thermistor. The other was the reference thermistor which was supplied with helium by the secondary flow stream.

Outlet Control System (Figure 2)

The gas flowed from the column through the detector block and then through the outlet pressure control. The outlet pressure was controlled by closing the valve on the outlet panel until the sum of the manometer pressure and the atmospheric pressure were equal to 760 mm Hg. Down stream from the valve was a soap bubble flow

meter. For flow measurements, the liquid level of a soap solution was raised above the gas inlet so that soap bubbles would travel up the calibrated tube. The gas flow rate was determined at room temperature by measuring the time required for the soap bubble to pass between two given points. By changing connections, either the measuring flow or the reference flow could be checked.

Electrical Control Panel (Plate II)

This unit housed the electronic recorder and the electrical bridge system. The 12 volt supply battery for the bridge system was located behind the control panel. The control Variacs were on the left and the right of the panel. The Variac on the right controlled current to the vapor bath and the one on the left was used for auxiliary control. The controls for the electrical bridge system were located in the center of this unit.

Electrical Bridge System (Figure 3)

A Wheatstone bridge was the measuring portion of the chromatograph. The input voltage from the battery was regulated by the bridge voltage control. The recorder pen was zeroed on the left side of the recorder chart by the coarse and fine zero controls. If the peak of a curve on the recorder was about to go off the chart paper, the peak height was attenuated. A peak would be one-third as high, with an attenuator setting of three, as it would at a setting of one. There were 20 settings on the attenuator ranging from 1 to 1000.

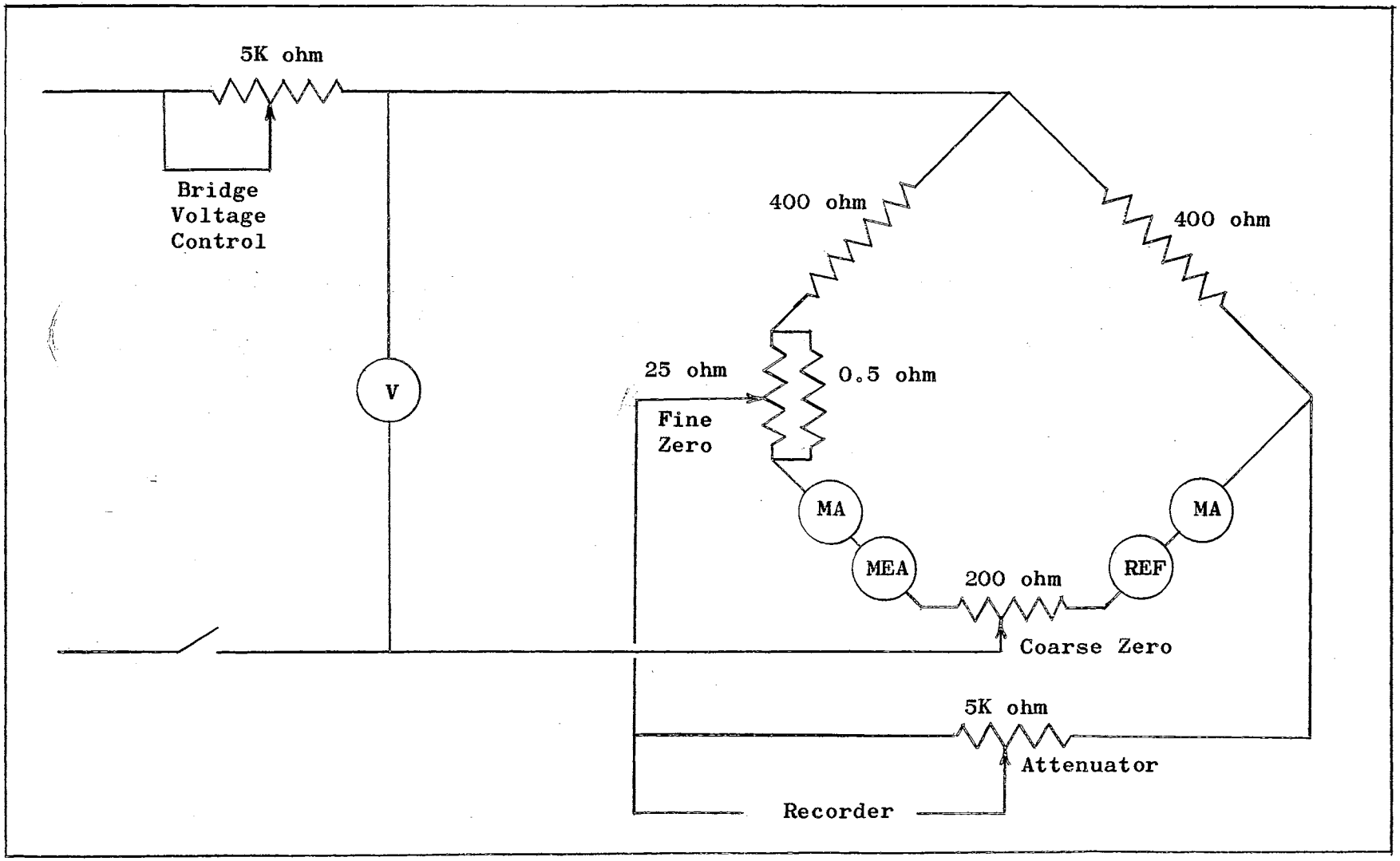


Figure 3. Electrical Bridge Circuit For Chromatograph

Choice of Operating Conditions

Most operating conditions depend upon the materials to be separated. The operating conditions of the gas chromatograph are interrelated; thus it is difficult to speak of them individually. The conditions shown below were typical of those used in this experimental work but would hold for many other chromatographic separations.

1. Stationary Liquid Packing. Choice of column packing was generally based on what was to be separated. The liquids used to separate a given class of chemicals were found in literature on this subject (1,2,15,26) or from manufacturers' specifications on the liquid phases (34,35). The separation obtained for a given stationary liquid was a function of the amount of stationary liquid present on the chromosorb. The stationary liquids used were all purchased from suppliers of chromatographic equipment and supplies.

2. Column Length. If two peaks were found to run together on a chromatographic curve, one method of improving the separation would be to lengthen the column. The length to which the column could be increased was limited by the size of the constant temperature bath and, of more importance, by the pressure drop across column. For most work, the shortest column length that would achieve the desired separation would be used.

3. Temperature. As a rule of thumb, the temperature at which the column and detector are maintained should not be less than one-half the boiling point of the highest boiling component in the sample. The temperature of the unit must be sufficiently low so

the liquid phase on the column packing will not be lost by vaporization. The vapor pressure of the stationary liquid should be no more than 0.1 mm of mercury for the temperature of operation.

4. Gas Flow Rate. Flow rates from 25 - 100 ml per minute are commonly used with 1/4-inch diameter columns. The higher the flow rate, the more rapidly the samples elute from the column, but this may reduce the component separation.

5. Column Pressure. Though supposedly a chromatographic column could be operated at any pressure, the unit used was limited to 15 psig. This limitation was imposed by the seals used in the detector block. All experiments were run with a column inlet pressure of 10 psig and a column outlet pressure of one atmosphere.

6. Bridge Voltage. Maximum response for the 8000 ohm thermistors used in the chromatograph was obtained between 7 and 8 volts. (See Figure 7.)

7. Sample Size. For liquids, the smallest size sample that could be injected with any appreciable accuracy was 0.001 ml. The largest size sample was approximately 0.1 ml, being limited by a condition resembling flooding in a distillation column. The peak would become very broad and would emerge from the column more rapidly than normal since equilibrium was not obtained. Thus, smaller size samples are more desirable. For gases, the range in sample size is from 0.1 ml to 1.5 ml. This limitation on the sample size is primarily due to the attenuator capacity which is limited to 1000 divisions.

Operating Procedure

The vapor bath was left on at all times. This allowed the warm-up time for operation to be approximately 30 minutes. Only enough heat was used to make the unit reflux.

To begin operation, the helium cylinder pressure regulator was turned up so that there was 20 psig available. The column pressure was then adjusted to 10 psig. A flow of 25 ml per minute was set on the reference side of the detector block. The flow which passed the measuring thermistor was set at the value to be used for the run. At the same time the outlet pressure control was adjusted to bring the total pressure at the column outlet to 760 mm of mercury. The constant temperature bath pressure control system was also adjusted to 760 mm of mercury. After the helium flows had been adjusted, the voltage on the bridge system was turned on and set at 8 volts. The recorder was then turned on. The bridge system was balanced with first the coarse zero control and then the fine zero control. This placed the recorder pen on the zero setting on the left hand side of the recorder. The unit was then allowed to warm up for at least 15 minutes. After the warm-up period, all variables (pressure, flow, temperature, etc.) were rechecked and corrected if necessary.

The sample to be run was injected into the chromatograph and the attenuator was adjusted so that the largest possible peak would be produced on the chart. The column variables were continually checked while running samples through the chromatograph unit.

When the unit was to be shut down, the bridge current was turned off; then the recorder and finally the helium cylinder was

closed. The constant temperature bath was left on to be ready for the next run.

Use and Calibration of Syringes for Liquid Analysis

The general accuracy of the syringes used in this work is indicated by the calibration data in Appendix C. The syringes were manufactured by the Hamilton Syringe Company of California and were of 0.01 ml, 0.05 ml, and 0.1 ml maximum volume, respectively. The 0.05 ml syringe was equipped with an adapter which the manufacturer claimed could achieve a routine accuracy of 0.01 per cent. Difficulty in operating the 0.05 ml syringe in this manner raised serious questions as to this accuracy, and after several attempts it was no longer used.

In order to obtain the highest possible degree of accuracy, the following procedure and precautions were followed in using the syringes. Because of the very small clearance between the syringe plunger and barrel, the only lubrication used was the liquid being sampled. Pieces of rubber tubing were placed over the syringes for two purposes: first, to protect the syringe if it were dropped and second, to keep hand heat from affecting the volume of the syringe.

Before a liquid sample was drawn, the syringe was cleaned and dried with acetone and air. The syringe was rinsed twice with portions of the sample to be analyzed. The syringe was then filled well past the calibration mark to be used and turned vertically so that any air bubbles present would rise to the top. The air bubbles were then pushed out and the syringe was placed under a

magnifying glass. The magnifying glass had a cross hair on it and the table to which the magnifying glass was attached had a fine line drawn on it. By placing the syringe under the magnifying glass and aligning the line on the table, the line on the plunger, and the cross hair, a high degree of accuracy could be obtained. All calibrations were made using the above procedure.

The syringes were calibrated by filling them with triple distilled mercury and then weighing the syringe on an analytical balance to 0.1 of a milligram. One difficulty was encountered in using this procedure. It was difficult to determine where the mercury stopped and where the syringe plunger started. Great patience was required for this calibration.

Another problem was encountered when injecting the samples into the chromatograph. The needle could be inserted so far into the column that it could shorten the effective length of the column. Precautions were taken to assure that the samples were injected into the area above the inlet helium stream. No trouble was encountered using this method.

When injecting a sample, the needle was pushed through a rubber cap covering the top of the column, emptied quickly and removed. It was noted at an analytical laboratory of a leading oil company that the syringe was often left sticking in the rubber injection cap for several minutes. It would seem that as the syringe needel was heated to the temperature of the unit, part of the liquid left in the needle would have been vaporized and forced out at a later time. This practice was not followed in this research work.

Gas Injection Systems

Several systems are used for the analysis of gases with the chromatograph. The easiest system was again the use of a syringe. Many authors reported satisfactory results using a micro syringe for gas analysis (22,30). Another, more precise method would be to trap a definite volume of gas in a tube between two stopcocks and then force the gas into the column by the carrier gas (22). A modification of this procedure would be to vary the volume of the sample trapped (14). This could be done by using a gas burette filled with mercury to measure the volume of sample to be injected. A system of this type was built.

Another procedure that could be used would be to vary the pressure of a sample of gas in a known volume. Thus using compressibility data for the pure gas, different volume samples could be injected into the chromatography unit.

High Pressure Gas and Liquid Sampling Valve

One of the major problems of analyzing vapor-liquid equilibrium samples is taking the sample. To overcome this problem, the sampling valve shown in Figures 4, 5, and 6 was designed and built for high pressure operation.

The valve had three major parts: the top plate, the rotating cylinder, and the bottom plate. The top and bottom plates each had three holes drilled through them for inlet and outlet lines. Each plate had a gas sample line, a liquid sample line, and a helium line attached to it. The rotating cylinder had a single, small

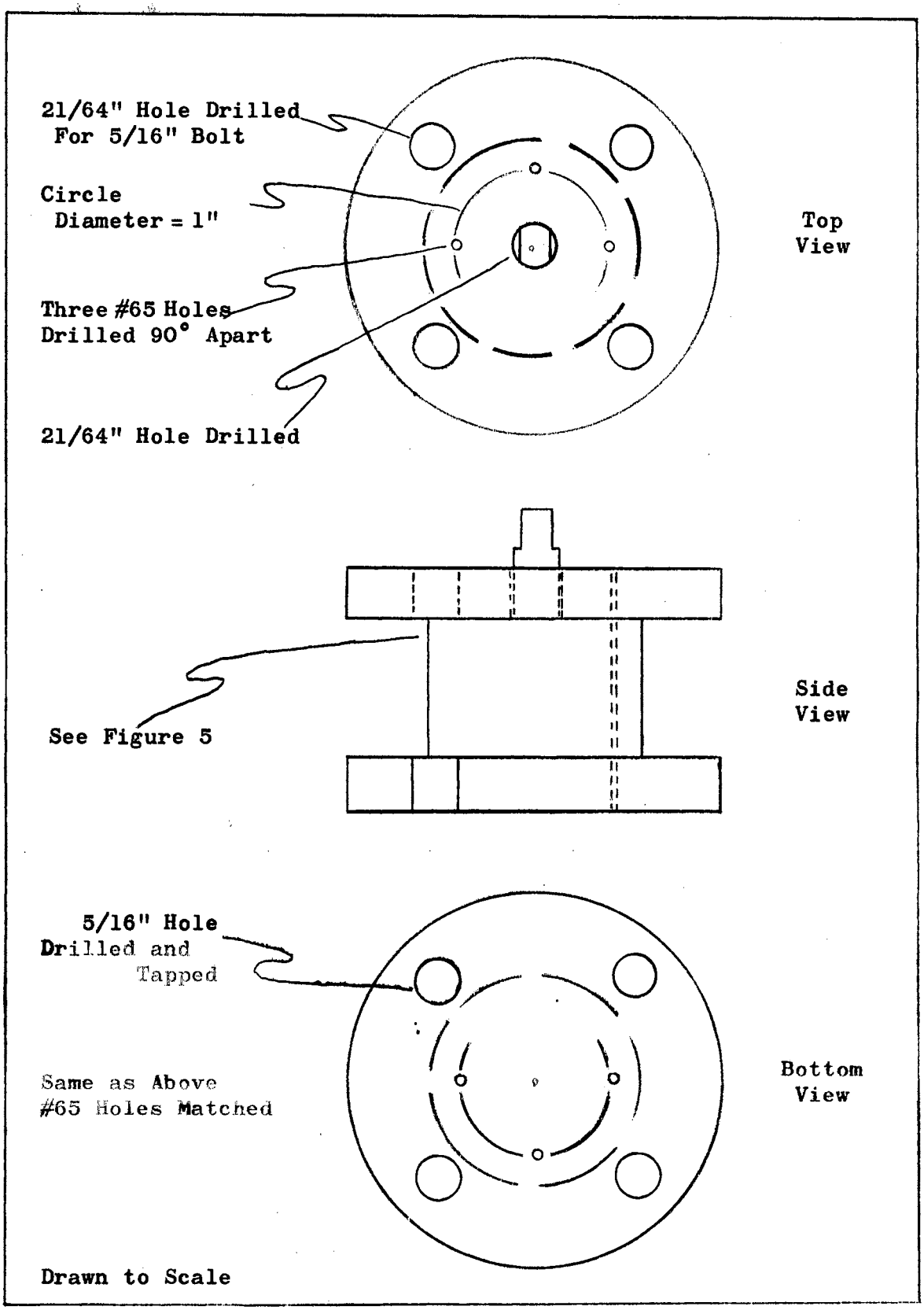


Figure 4. High Pressure Sampling Valve

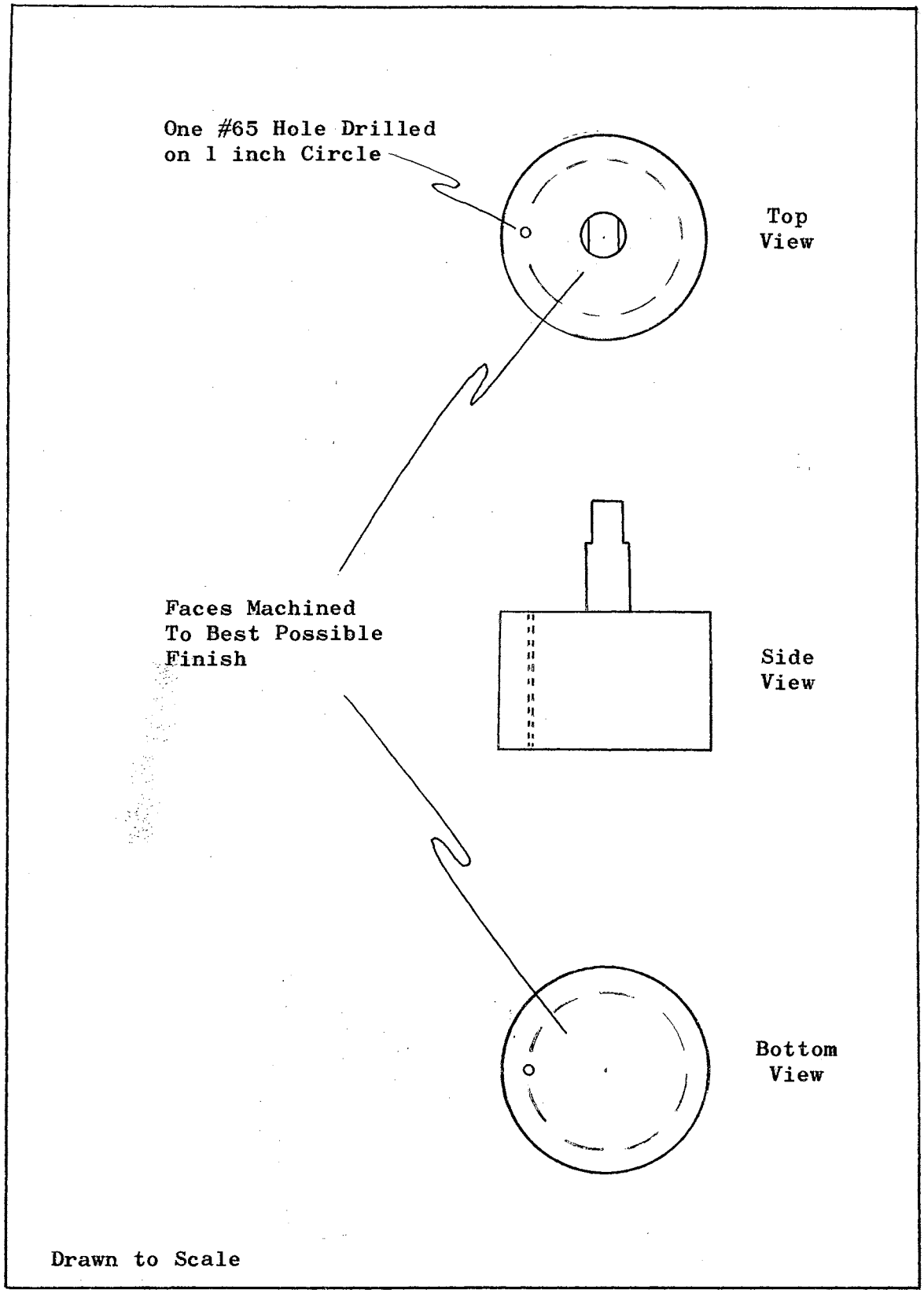


Figure 5. Rotating Cylinder For Sampling Valve

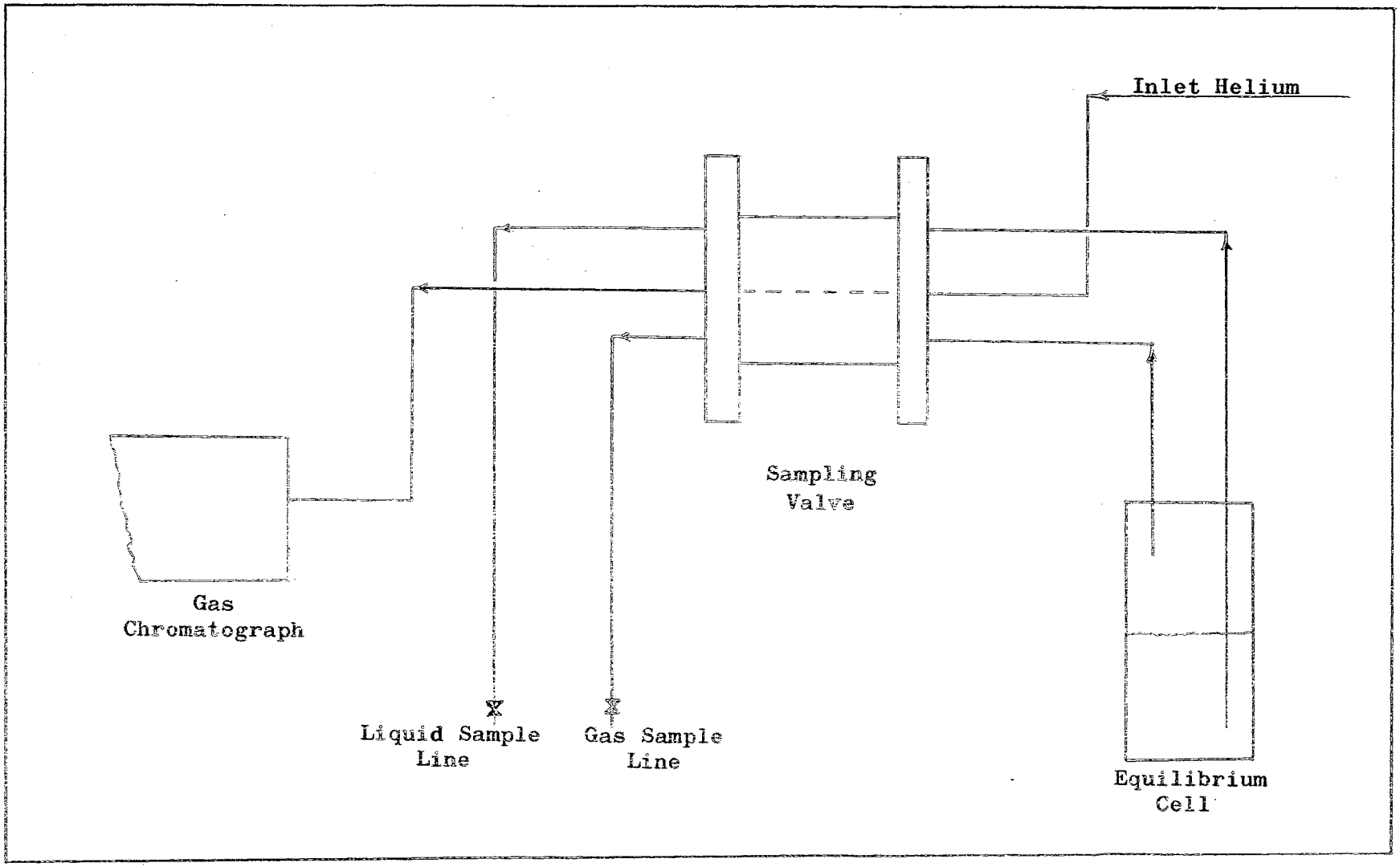


Figure 6. Sampling Valve Flow Sheet

diameter, hole through it. This small hole could be rotated so there would be flow in any given line. If the cylinder had been turned to allow flow in the liquid line, the hole could be rotated to the helium line and the small volume of liquid sample trapped in the cylinder would be placed in the helium flow stream. The helium flow would carry the sample directly to the chromatograph. To aid in lubricating the cylinder and to form a seal, pieces of teflon, with holes for each stream, were placed in the top and bottom plates. The line carrying the helium stream to the chromatograph was heated so there would be less chance of hold-up for the liquid portion of the samples. This line was made of copper capillary tubing.

Quantitative Measurement of Samples

For each unknown to be determined in a sample, there has to be a calibration curve. To make a calibration curve for a pure component, different size samples were plotted against some output variable such as area under a peak curve. This gave a smooth curve. As long as the conditions of operation of the chromatograph remained the same, a given component emerged each time at the same distance from the point of injection. Unless there was overlapping of two components, the area under a peak was easily calibrated. By calculating the area of a known component in an unknown sample, the size of pure sample required to give the known peak was found from the calibration curve.

Dividing the unknown sample volume by the volume of the known component gave the volume per cent of the known component.

Chemicals

The pure chemicals used as standards for the gas chromatograph were obtained from the Phillips Petroleum Company of Bartlesville, Oklahoma.

CHAPTER IV

OPERATING CHARACTERISTICS OF THE EQUIPMENT

These runs were made so that the ultimate accuracy and factors affecting the accuracy of the gas chromatograph could be studied. In this way it was hoped to find just how successful gas chromatography would be for analysis of high pressure vapor-liquid equilibrium samples. Where average run results are listed, the data were within ± 3 per cent of the value given.

Effect of Voltage

For every pair of thermistors used in a chromatograph, there is an optimum operating voltage (23). For maximum sensitivity, the chromatography unit should be run near this optimum voltage.

In order to determine the optimum voltage, a series of runs were made with all conditions constant, except the voltage. Since the runs were not highly critical, 1 ml samples of air were injected with a gas syringe. The peak heights were used for the calibration (23). The peak heights were multiplied by the attenuator setting to give a height-attenuator product. The results are given in Table I and are shown in Figure 7. For each value of voltage three runs were made and averaged. The three runs agreed within ± 2 per cent maximum error.

From Figure 7, the value of 8 volts was chosen to be used in the remainder of the experimental work.

TABLE I

EFFECT OF VOLTAGE ON PEAK HEIGHT

Run Number	Voltage (Volts)	Average Peak Height (Chart Units)	Attenuation Factor	Attenuator Height Product
2-1-1	4	71.2	300	21,400
2-1-2	5	65.4	500	32,700
2-1-3	6	80.5	500	40,300
2-1-4	7	89.5	500	44,700
2-1-6	8	95.1	500	47,500
2-1-8	9	94.6	500	47,300
2-1-10	10	94.2	500	47,100
2-1-11	11	93.7	500	46,800

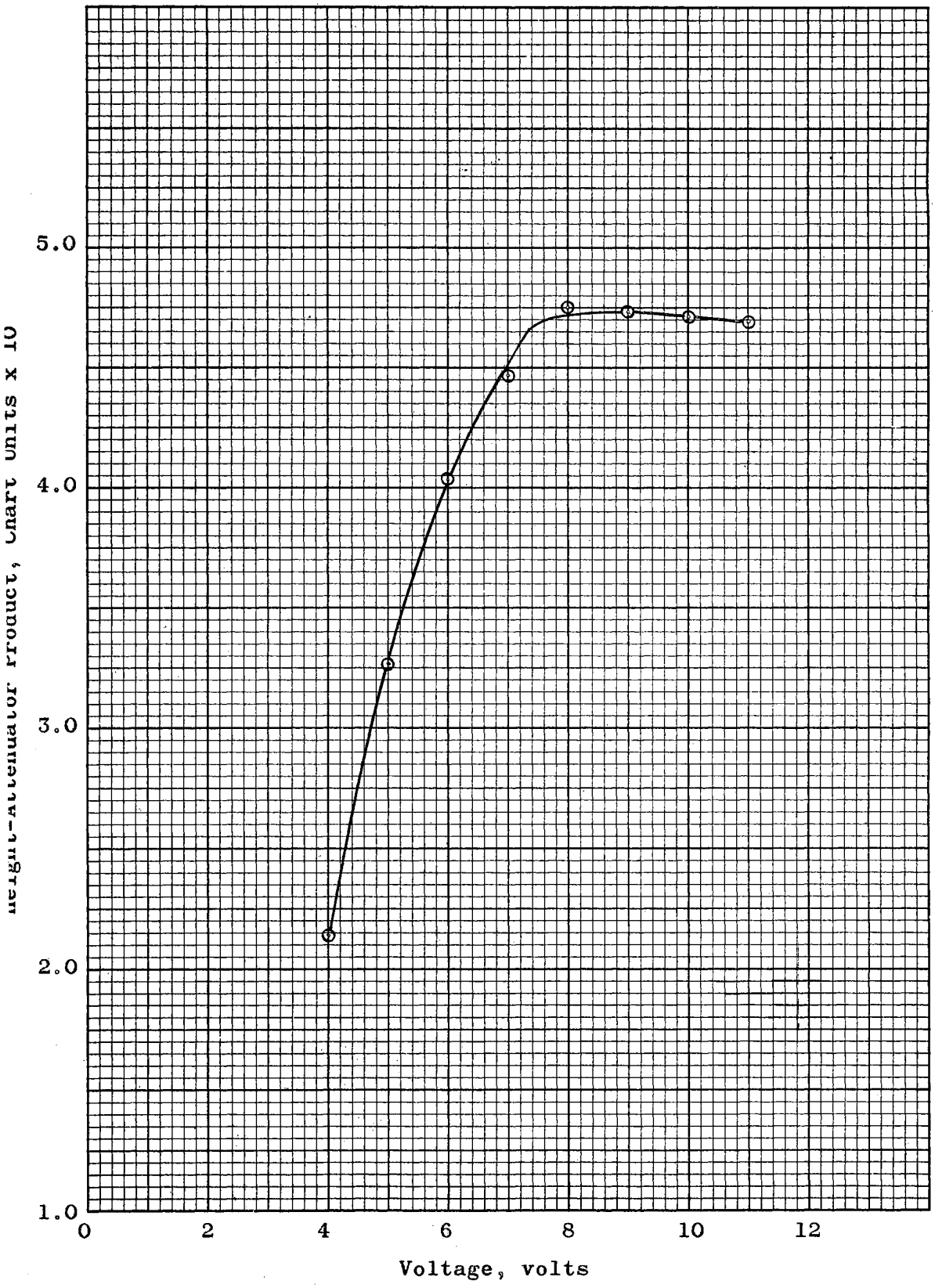


Figure 7. Variation of Peak Height With Voltage

Attenuator Calibration

The attenuator is made from a group of resistors and its accuracy is dependent upon the tolerance of the resistors. The belief was that for the utmost precision the attenuator must be calibrated. To do this, at least two different methods could be employed. First, a deflection of the recorder pen could be made with the attenuator at some setting. This could be done using the zero adjustments. The attenuator could then be turned to the next lower scale and the change in height compared with the two different attenuator readings.

A second method of calibrating the attenuator would be to inject a sample of known volume into the chromatograph. This could be done at a particular attenuator setting and then, using the same size sample, repeated for some other attenuation.

An interesting factor was noted after making a few preliminary runs. In comparing such setting changes as 1000 to 700, 100 to 70, and 10 to 7, approximately the same ratio of heights was obtained for each pair. This could mean possibly that another factor was involved in the scale readings. The recorder slide wire might not be completely linear and the attenuator could be essentially correct.

It was not difficult to find a solution to the problem. When running a sample through the chromatography unit, the highest possible peak is always the most desirable. Thus for a particular size sample of a given component, the attenuation factor should always be the same. This would mean that a calibration curve for

a given component would have its correction factors built into it. This eliminated the necessity of obtaining correction factors for the attenuator and the recorder slide wire.

Syringe Reproducibility

Possibly the only method of telling actual syringe reproducibility would be to look at the calibration tables in Appendix C. To determine the reproducibility of a syringe volume by injecting a sample into the gas chromatograph would be nearly impossible. It could be done only if there were no other variables involved. The syringe calibration tables indicate that the syringes are fairly accurate with a maximum difference between two readings of approximately 0.2%. The calibration data seem to follow a definite trend, showing that the glass syringes must have a highly precise bore in them.

Gas Injector

Several difficulties were encountered in the operation of the gas injector. The chromatograph was always operated at 10 psig. This meant that the mercury resorvoir had to be almost 2 feet above the top of the injector to force the gas from the burette. Because of the capillary tubing used in the injector, the rate at which the gas was forced into the helium line caused the peaks to be broadened. Another problem was found in that the mercury became easily contaminated, thus making the burette hard to read. The gas injector was calibrated, but because of the broadening peak effect, it was not used.

Injection Delay

The question arises as to what the effect would be if not all of a sample reached the head of the chromatograph column at essentially the same time. Obviously, the peak height of the sample would be shortened and the width broadened. But would the area under the curve be changed? To test this, a series of runs were made injecting the samples at slower and slower rates. Obviously, the information obtained would only indicate a general trend since it would be very difficult to delay the sample injection exactly the proper time.

The operating conditions were kept constant and 0.05 ml samples of nC_7 were injected at different rates. The results are shown in Figure 8. The areas were determined by a planimeter. It was assumed that the time for injection of the quickly injected sample was 0.5 of a second.

TABLE II

EFFECT OF INJECTION DELAY ON PEAK AREA

Run Number	Injection Delay, Sec.	Attenuator Setting	Planimeter Area, Sq. Units
3-8-21	0.5	700	6.203
3-8-22	0.5	700	6.217
3-8-23	0.5	700	6.227
3-8-25	5.0	700	6.270
3-8-26	15.0	700	6.303
3-8-27	20.0	700	6.443
3-8-28	30.0	700	6.577

The results show that the area increases with injection delay. For best results the samples should be injected with some constant

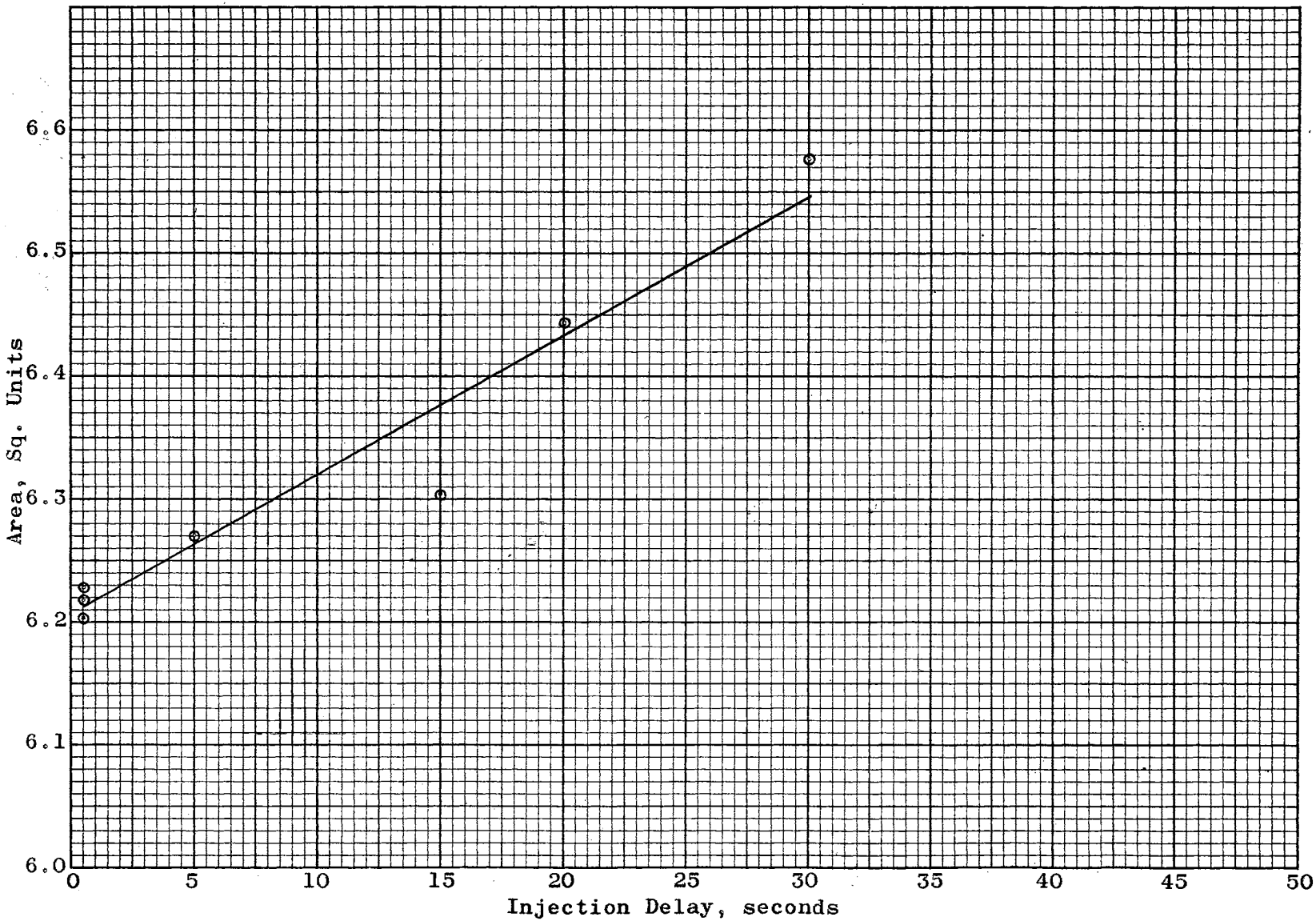


Figure 8. Effect of Injection Delay on Peak Area

factor of delay. This can best be obtained by making the injection as rapidly as possible and thus approximating a "plug" type injection.

A similar test was run on gases and it was found that they were even more sensitive to injection speeds than were the liquids.

Gas and liquid samples were injected into the preheat coil to determine if there would be any changes in the curve area. The gas samples showed little or no effect but the liquid samples were almost impossible to calculate due to excessive tailing of the curves.

Another series of runs was made to test the effect of a large amount of gas passing through a small liquid sample while in the column. No change was noted in the area or shape of the liquid curve.

Trace Analysis

The determination of the minimum amount of a hydrocarbon that could be detected in a sample was believed desirable. To do this, three samples of normal hexane in normal heptane were prepared. The three samples were as follows: 100 ppm, 10 ppm and 1 ppm (by volume). Each was made by injecting 0.001 ml of hexane from a syringe into a measured volume of heptane. A 0.1 ml sample of mixture was used with the attenuator setting of 1. The following operating conditions were used: temperature, 210°F; reference flow, 25 ml/min; measuring flow, 50 ml/min; chart speed, 4 1/2 inches/min; and a 4 foot-20% tricresyl phosphate (TCP) column.

TABLE III

TRACE ANALYSIS

Run Number	PPM nC_6 By Volume	Mol nC_6 In Sample	Peak Height mm	Peak Width mm	Peak Area mm^2
3-21-1	100	0.767×10^{-7}	98.1	4.0	392
3-21-2	10	0.767×10^{-8}	10.5	3.9	40.9
3-21-3	1	0.767×10^{-9}	1	4.0	4

For the 1 ppm sample, the peak was very small, as can be seen from the peak height and the width data. The 10 ppm and 100 ppm samples showed up clearly. The 10 ppm sample used 4% of the possible scale deflection while the 100 ppm sample used 38%.

Effect of Flow Changes

If the flow of helium should decrease during a run, it would affect the shape of the component curve in some manner. Samples of normal hexane were injected into the chromatograph at three slightly different flow rates. All other conditions were held as constant as possible. The results of these three runs are shown in Figure 9. The following operating conditions were used: temperature, 209°F; reference flow, 24.8 ml/min; chart speed, 1/2 inch/min; sample size, 0.007 ml; attenuator setting, 500; and a 6 foot - 20% TCP column.

Three runs were made for each flow rate. The average values are reported here.

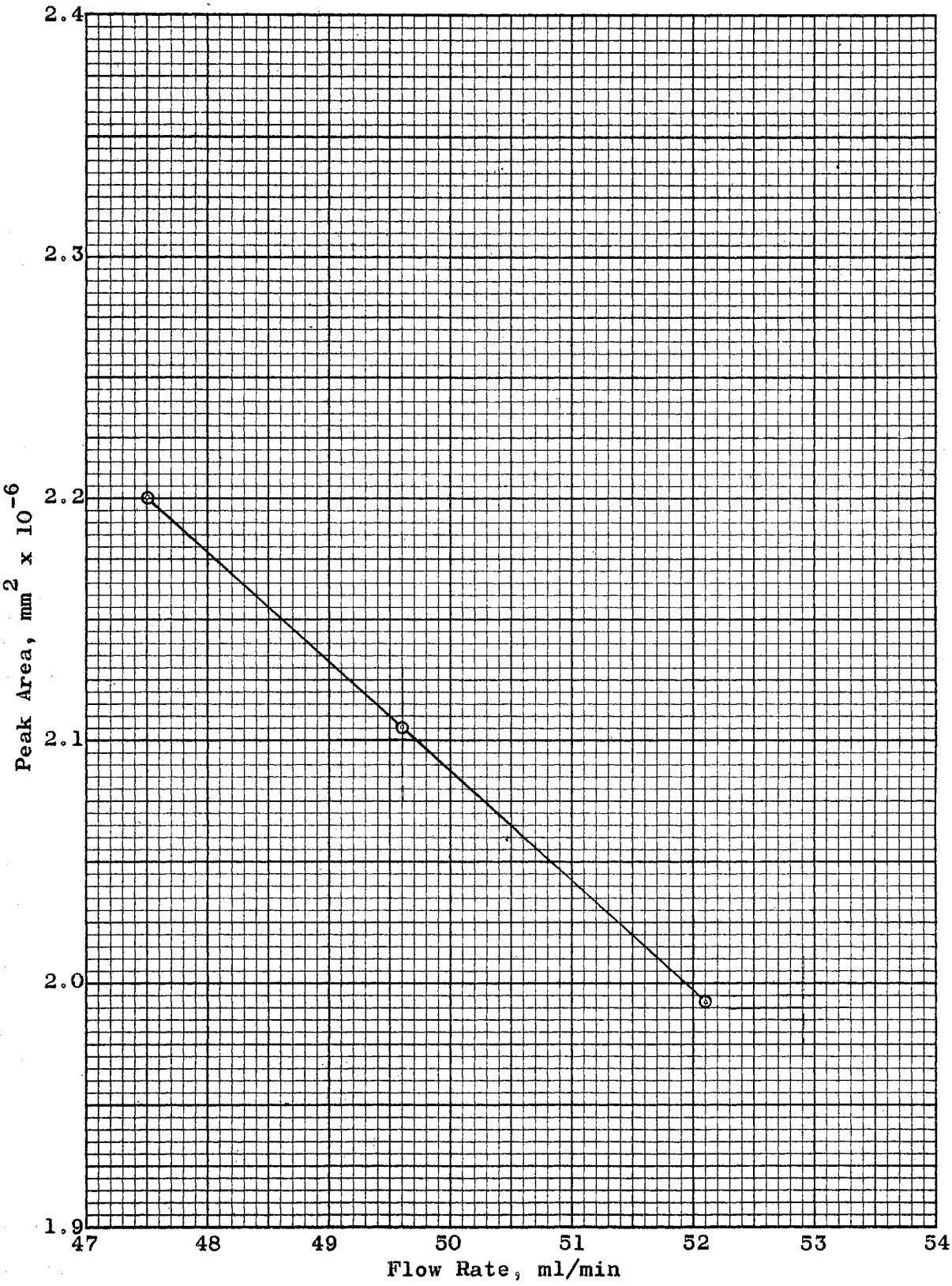


Figure 9. Effect of Flow Rate Variations on Peak Area

TABLE IV

EFFECT OF FLOW CHANGES ON PEAK AREA

Run Number	Column Flow ml/min	Peak Height mm	Peak Width mm	Peak Area $mm^2 \times 10^{-6}$
4-2-2	52.1 cc/min	190.1	20.99	1.993
4-2-5	47.5 cc/min	190.2	23.13	2.20
4-2-8	49.6 cc/min	188.0	22.33	2.105

The following data are taken from Figure 9.

Area at 49.5 ml/min. 2.108×10^{-6}

Area at 50.5 ml/min. 2.064×10^{-6}

Area at 50 ml/min. 2.088×10^{-6}

A one ml/min. change in flow at 50 ml/min. will cause error of:

$$\frac{2.108 \times 10^{-6} - 2.064 \times 10^{-6}}{2.088 \times 10^{-6}} \times 100 = 2.1\% \text{ error}$$

The conclusion can be drawn that the flow rate is a critical value.

Effect of Temperature Fluctuations

The same column and conditions which were used in the experimentation on flow changes were used to study the effect of temperature changes. For this group of runs, the measuring flow was held constant at 50 ml/min. and the temperature was varied. The results are presented in Figure 10. The point on the graph representing 209°F was taken from Fig. 9 at 50 ml/min. The results shown are the averages of three runs at each condition.

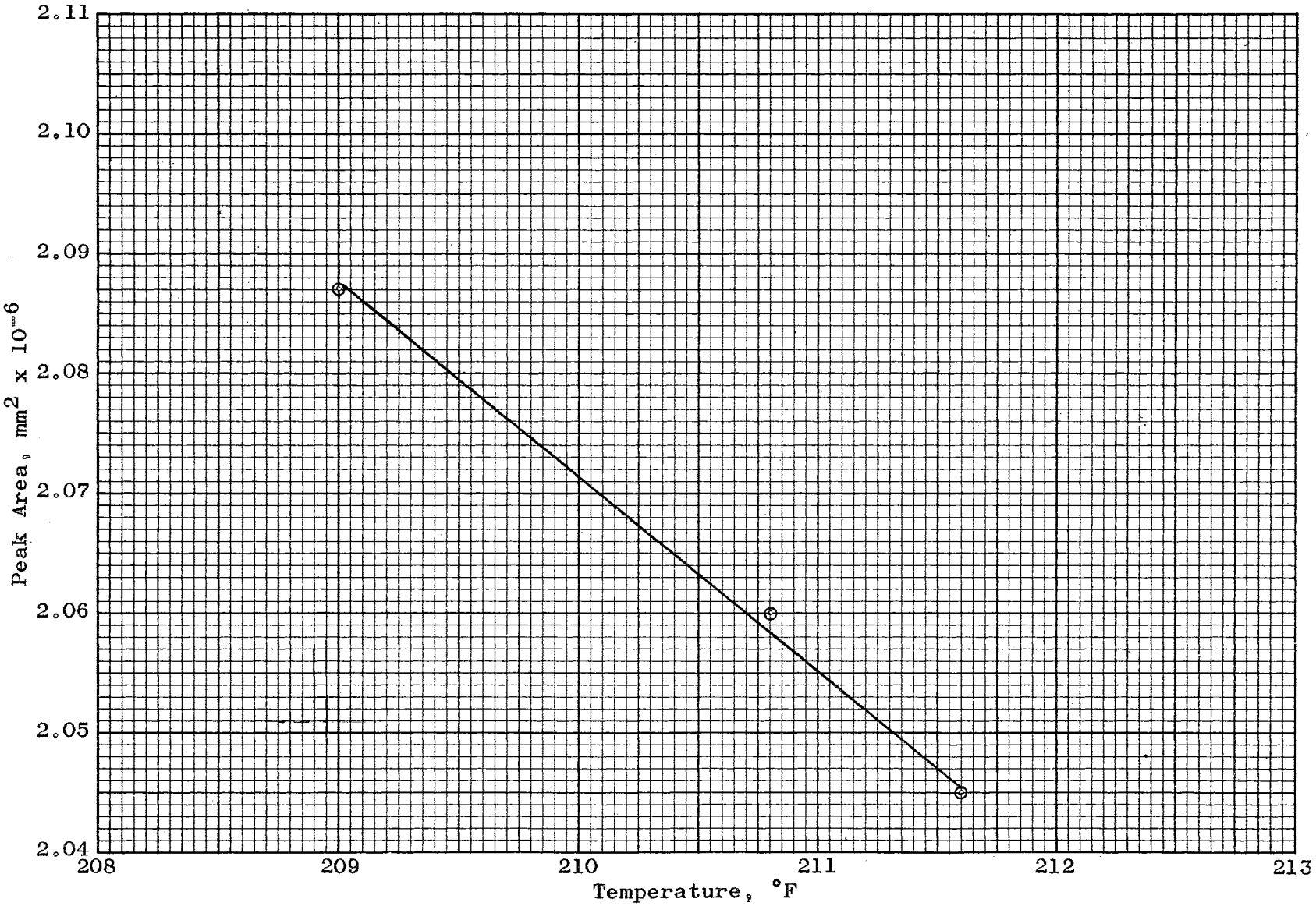


Figure 10. Effect of Temperature Variations on Peak Area

TABLE V

EFFECT OF TEMPERATURE FLUCTUATIONS ON PEAK AREA

Run Number	Temperature °F	Peak Width mm	Peak Height mm	Area $mm^2 \times 10^{-6}$
4-4-2	211.6	21.6	189.1	2.045
4-4-5	210.8	21.9	188.1	2.060

Figure 10 would indicate that 1°F variation during a run would change the calculated area by 0.7 per cent.

Effect of Outlet Pressure Variations

Most commercial gas chromatography units control the inlet pressure but let the outlet of the column be at the prevailing barometric pressure. The inlet pressure is easily controlled and has slight, if any, noticeable variations if proper regulating equipment is used. The effect of variation of outlet pressure was tested by closing the valve on the outlet control panel until the desired pressure was obtained. All variables were kept constant and were the same as in the two preceding series of runs. The temperature was 209.8°F and the measuring flow was maintained at 50.3 ml per minute. The results given are the average values of several runs made at each condition. (Table VI and Figure 11).

Important conclusions can be drawn from Figure 11. If a chromatography unit were run on a day when the barometric pressure was 750 mm of mercury and the same runs were made the next day when the barometric pressure was 760 mm of mercury, there would be approximately 3.9% difference between the two sets of data. Because

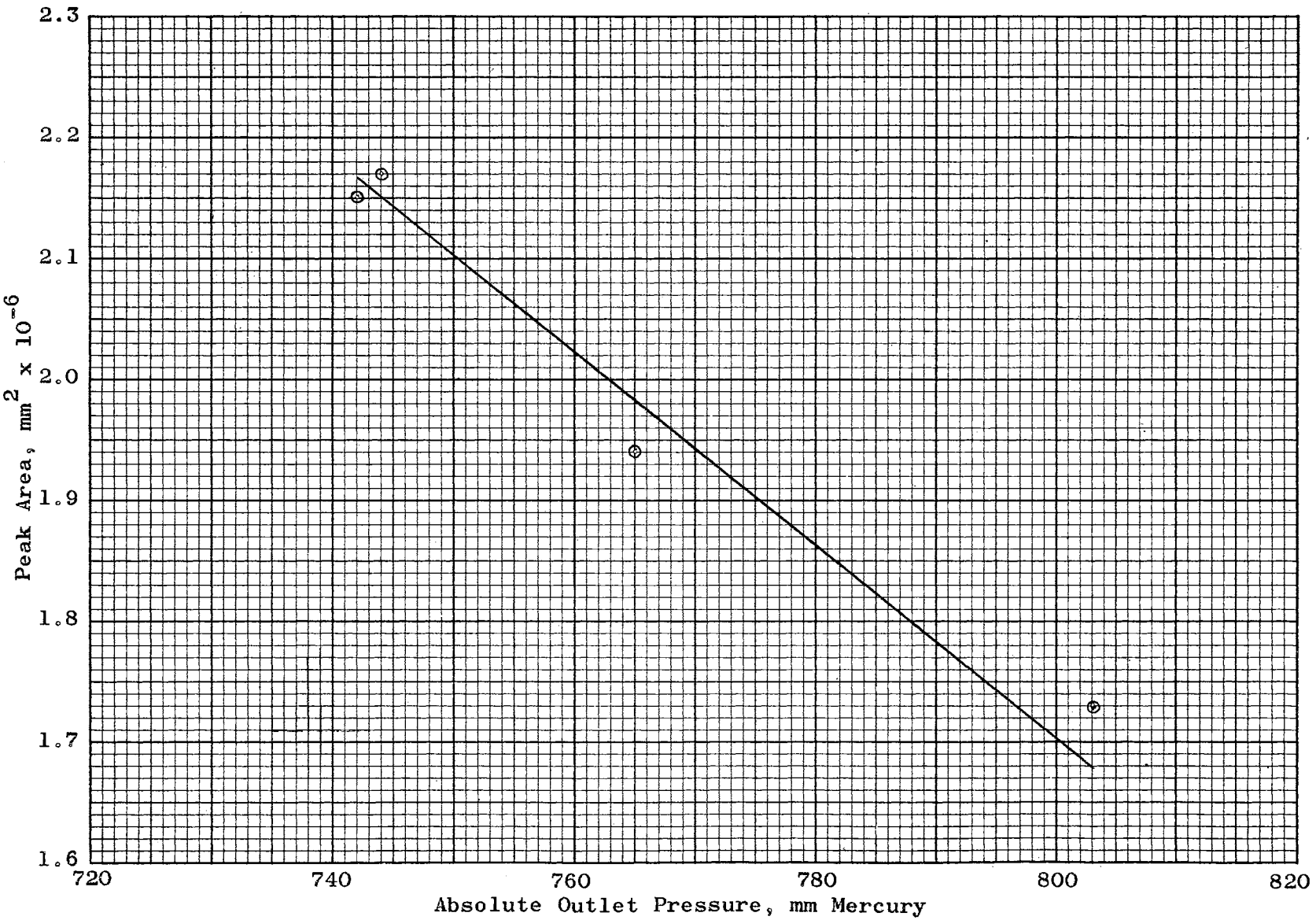


Figure 11. Effect of Barometric Pressure on Peak Area

TABLE VI

EFFECT OF OUTLET PRESSURE ON PEAK AREA

Run Number	Absolute Outlet Pressure mm Mercury	Peak Height mm	Peak Width mm	Peak Area $mm^2 \times 10^{-6}$
4-10-21A	765	210.9	18.4	1.94
4-10-22A	744	218.0	19.9	2.17
4-10-23A	803	205.5	16.8	1.73
4-10-24A	742	217.5	19.8	2.15

of this sensitivity, the mercury manometer on the column outlet was replaced by one filled with red oil (specific gravity = 1).

Method of Calibration

One advantage in applying gas chromatography to vapor-liquid equilibrium samples is that the composition of the sample can be known approximately. To obtain the best results, the chromatography unit should be calibrated just before use. Knowing the approximate composition, the calibration points required can be kept to a minimum. A mixture of normal hexane and normal heptane was analyzed to show three things: first, the method used in the calibration and analysis of a sample; second, a comparison of two curve area calculation methods; and third, the over-all accuracy obtainable with the equipment.

Pure samples of n-hexane and n-heptane were injected into the chromatograph with all operational parameters kept constant. The sample sizes and operating conditions are given in Tables VII and VIII. Each size sample was run twice and each curve was measured

TABLE VII

CALIBRATION DATA FOR n HEXANE

Operating Conditions:

Temperature - 210.0°F Measuring flow - 50 ml/min Column - 4 feet, 20% TCP
Reference flow - 25 ml/min Chart speed - 4 1/2 inches/min Outlet pressure - 760.0 mm Hg

Run Number	Sample Size, ml	Attenuator Setting	Peak Height mm	Peak Width mm	Triangulation Area, $mm^2 \times 10^{-6}$	Planimeter Area $mm \times 10^{-6}$ Trial 1	Trial 2
5-22-3	0.00290	300	231.4	14.2	0.986	1.005	1.010
5-22-4	0.00290	300	230.4	13.9	0.964	0.989	0.989
5-22-5	0.00339	300	252.6	14.9	1.128	1.159	1.161
5-22-6	0.00339	300	253.8	14.9	1.133	1.165	1.163
5-22-7	0.00388	500	164.0	15.4	1.262	1.279	1.281
5-22-8	0.00388	500	163.4	15.5	1.268	1.296	1.300

TABLE VIII

CALIBRATION DATA FOR n HEPTANE

Operating Conditions: (Same as for n Hexane)

Run Number	Sample Size, ml	Attenuator Setting	Peak Height mm	Peak Width mm	Triangulation Area, $mm^2 \times 10^{-6}$	Planimeter Area $mm \times 10^{-6}$ Trial 1	Trial 2
5-22-9	0.00290	300	172.6	18.8	0.973	1.030	1.030
5-22-10	0.00290	300	172.8	18.9	0.980	1.036	1.036
5-22-11	0.00339	300	194.4	19.3	1.122	1.195	1.195
5-22-12	0.00339	300	195.9	19.2	1.129	1.208	1.204
5-22-13	0.00388	300	212.7	19.6	1.250	1.313	1.310
5-22-14	0.00388	300	213.0	19.8	1.265	1.329	1.323

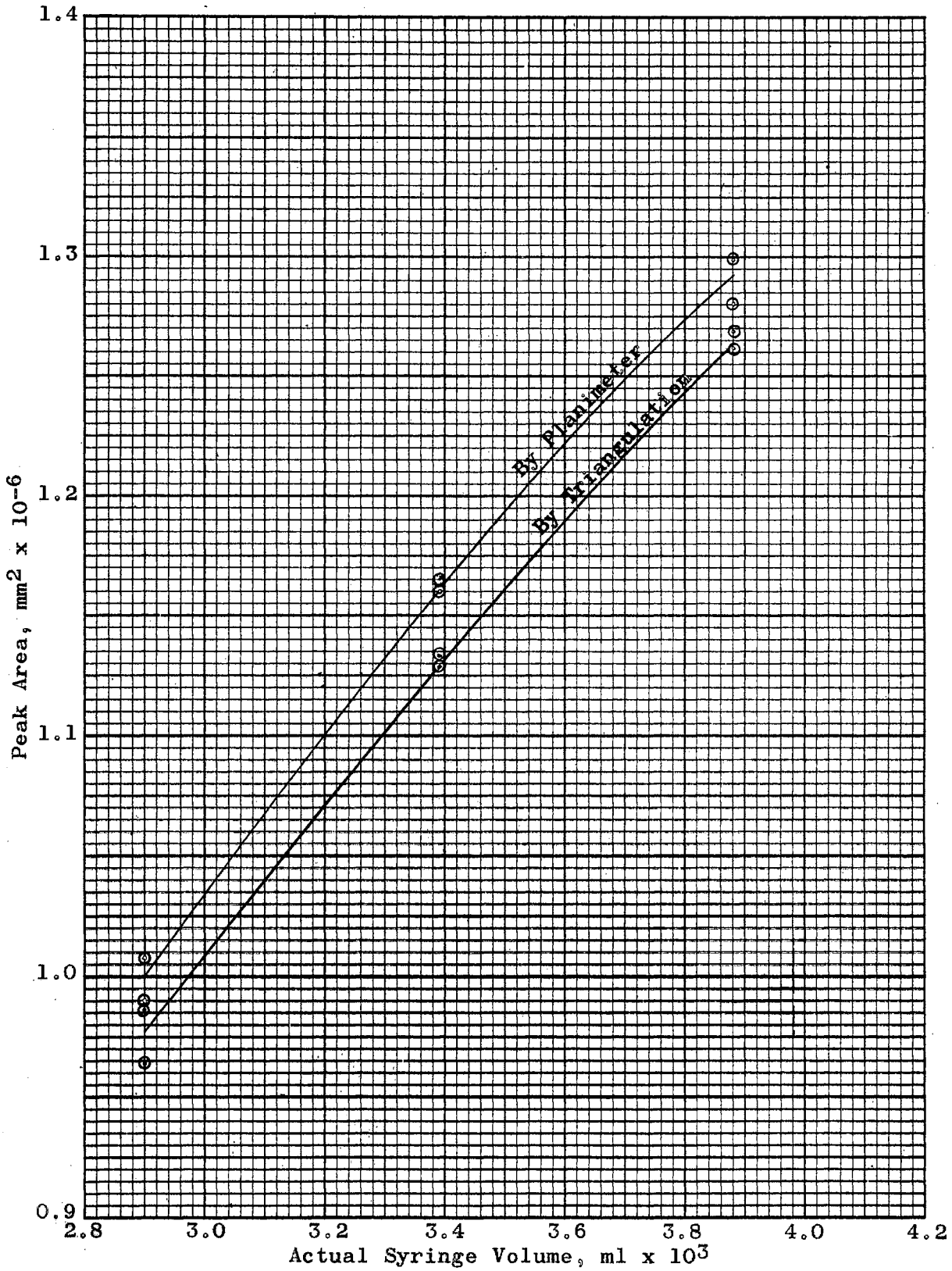


Figure 12. Calibration Curve For nC_6

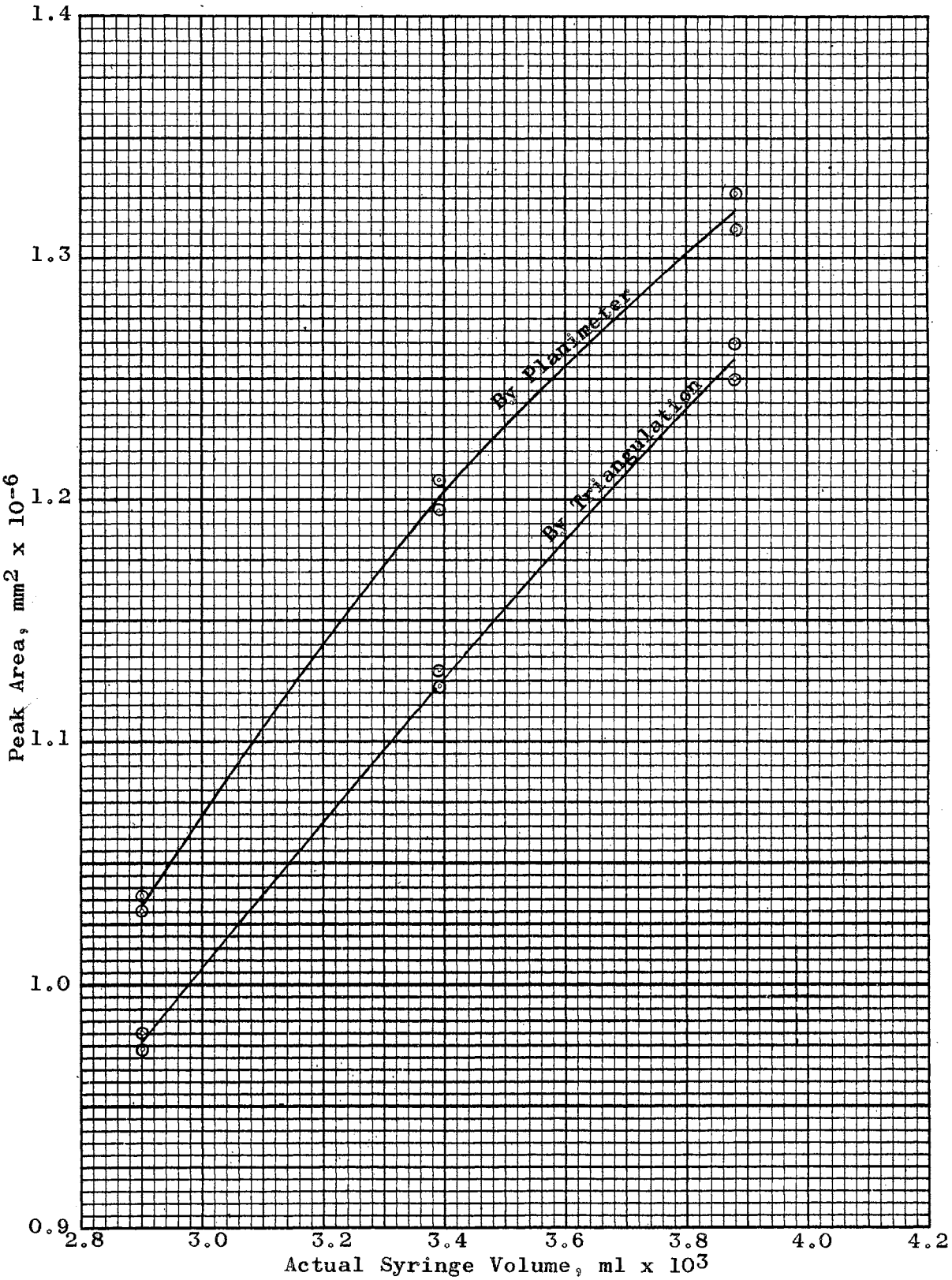


Figure 13. Calibration Curve For nC_7

twice with a polar compensating planimeter. The area was also calculated by the triangular estimation method of the peak height times the peak width at one half the peak height. The data obtained for each component were plotted in Figures 12 and 13.

A mixture of 50 per cent each by volume of n-hexane and n-heptane was made and two 0.007 ml samples were run through the column at the same conditions as the calibration curve. The results of these runs are given in Tables IX and X. The 50 per cent mixture was made by measuring and pipetting a one milliliter sample of each component. At the time this was done, the room temperature was 86°F. This and the possible error of the pipettes may explain the fact that the results are low in n-hexane. The mixture was placed in a vial, stoppered and allowed to stand overnight to reach equilibrium.

The relative merits of triangulation area and the planimeter area can be seen from the calibration and mixture data. Not only do the planimeter areas vary more between the two runs of each sample size than the triangulation areas, but they vary up to 0.5% on the same curve. The average planimeter area varies approximately 0.2%. The triangulation method suffers from the fact that it is difficult, if not impossible, to calculate accurately the width of a peak. The data presented are given with four significant figures but cannot be justified because the peak width can be found only to three significant figures.

The data shows that for the systems run, the planimeter is not as consistent as the triangulation method. This may be due to the fact that there is a slight tailing off of the curves with the TCP column.

TABLE IX

TEST OF 50% MIXTURE OF n HEXANE AND n HEPTANE

Operating Conditions:

Temperature = 210.0°F
Reference flow = 25 ml/min
Measuring flow = 50 ml/min
Attenuator setting = 300

Chart speed = 4 1/2 inches/min
Column = 4 feet, 20% TCP
Outlet pressure = 760.0 mm Hg

Run Number	Peak	Peak Height mm	Peak Width mm	Triangulation Area, $mm^2 \times 10^{-6}$	Planimeter Area, $mm^2 \times 10^{-6}$ Trial 1	Trial 2	Average
5-22-1	nC_6	246.9	14.8	1.095	1.112	1.115	1.114
5-22-1	nC_7	190.5	20.0	1.142	1.203	1.203	1.203
5-22-2	nC_6	247.7	14.8	1.098	1.118	1.122	1.120
5-22-5	nC_7	192.5	19.7	1.138	1.188	1.188	1.188

TABLE X

RESULTS OF MIXTURE TEST

Operating Conditions:

Temperature - 210.0°F
Reference flow - 25 ml/min
Measuring flow - 50 ml/min
Attenuator setting - 300
Chart speed - 4 1/2 inches/min
Column - 4 feet, 20% TCP
Outlet pressure - 760.0 mm Hg

Run Number	Peak	Triangulation		Planimeter	
		Volume %	Corrected Volume %	Volume %	Corrected Volume %
5-22-1	nC_6	48.3	48.7	47.8	48.8
5-22-1	nC_7	50.8	51.3	50.2	51.2
		99.1	100.0	98.0	100.0
5-22-2	nC_6	48.5	48.9	47.7	49.1
5-22-2	nC_7	50.7	51.1	49.4	50.9
		99.2	100.0	97.1	100.0

The results (Table X) show that the corrected volume compositions have a maximum deviation of ± 0.4 per cent. The triangulation value varies approximately ± 0.2 per cent. The fact remains that the composition did not agree with the value which had been expected, but a possible source of this error has been explained earlier. It is believed that the corrected results give a true indication of the actual composition.

Vapor-Liquid Equilibrium Analysis

In the proposed vapor-liquid equilibrium studies, a gas such as methane, and a heavier liquid such as heptane, will be used. This presents a problem of slowing the gas down so that it can be successfully analyzed and yet letting the liquid pass through the column in a relatively short time (less than 15 minutes). Four different column liquids that were suggested by manufacturers were tried on both gases and hydrocarbon mixtures. The four were tricresyl phosphate, dinonyl phthalate, Aprezon L., and polyethylene glycol. From these, tricresyl phosphate was selected as the best choice; although the over-all difference between the column liquids was not great.

The next problem arose in taking the sample and transferring it to the chromatograph. The sampling valve (Figure 6) described earlier was used to do this. A heated copper capillary tube one meter long was used to transfer the samples from the valve to the chromatograph. The capillary tubing (0.031 inches diameter) had a small volume so that its entire length could be swept by the helium stream in less than 1/2 second. This was to keep injection

delay at a minimum.

The valve has been tested with little or no leakage up to a pressure of 400 psig. As long as corrected volumes are used in the calculations the exact sample size taken is not important.

It was found that when the flow to the chromatograph was interrupted to use the sampling valve, the flow fluctuations caused a peak on the recorder chart. Though it did not directly interfere with the samples taken, it is deemed advisable that the valve have a second hole drilled in it so that the flow fluctuations will be kept as small as possible. Further testing and development of the high pressure sampling valve will be carried out when the equilibrium equipment has been readied for service.

CHAPTER V

THEORETICAL CHARACTERISTICS OF THE EQUIPMENT

The van Deemter equation (32), as pointed out earlier, is considered by many to have given an adequate explanation of what takes place in a chromatography column. This equation is handicapped by the fact that it is difficult to use.

The distance-width equation

$$n = 16(d/w)^2$$

is easily used but the only information given by it is the number of theoretical plates. This number is not a universal number for the entire column. Thus with one component, a given number of plates will be obtained, while another component of the same sample can give an entirely different number of plates. Changing the sample size will also affect the number of plates. Doubling the length of column will not necessarily double the number of plates. As an aid to understanding the distance-width equation, the number of theoretical plates was calculated for a group of runs made to test the effect of changing column length. The results of these runs are given in Table XI and Figure 14. The runs were for air, toluene, methylcyclohexane, normal hexane, normal heptane, and normal octane.

The data from the above runs plotted exceptionally well. Note that if the lines for each component were extended they would all

TABLE XI

THEORETICAL PLATE-COLUMN LENGTH CORRELATION

Operating conditions:

Temperature - 210.2°F
Measuring flow - 50 ml/min
Column packing - 20% TCP
Outlet pressure - 760 mm Hg
Reference flow - 25 ml/min

Run Number	Sample	Chart Speed in/min	Size, ml	Column Length, ft.	Distance, mm	Width, mm	Theoretical Plates
4-1-11	nC_6	1/2	0.02	2	5.6	3.6	39
3-30-21	nC_6	1/2	0.02	4	12.3	4.6	115
4-5-21	nC_6	1/2	0.02	6	19.0	5.4	198
4-1-11	nC_7	1/2	0.02	2	10.6	5.4	61.5
3-30-21	nC_7	1/2	0.02	4	23.5	6.2	230
4-5-21	nC_7	1/2	0.02	6	32.5	6.6	388
4-1-11	nC_8	1/2	0.02	2	20.8	8.4	108
3-30-21	nC_8	1/2	0.02	4	45.8	9.8	349
4-5-21	nC_8	1/2	0.02	6	68.0	11.2	590
4-1-13	MCH	1/2	0.02	2	15.2	6.4	90
3-30-23	MCH	1/2	0.02	4	34.0	7.4	338
4-5-23	MCH	1/2	0.02	6	51.6	8.8	550
4-1-13	TOL	1/2	0.02	2	45.4	16.4	123
3-30-23	TOL	1/2	0.02	4	99.1	18.4	465
4-5-23	TOL	1/2	0.02	6	148.0	22.2	712
4-1-19	AIR	4 1/2	1.00	2	17.1	8.2	69.5
3-30-29	AIR	4 1/2	1.00	4	37.5	10.4	208
4-5-29	AIR	4 1/2	1.00	6	55.0	11.6	359

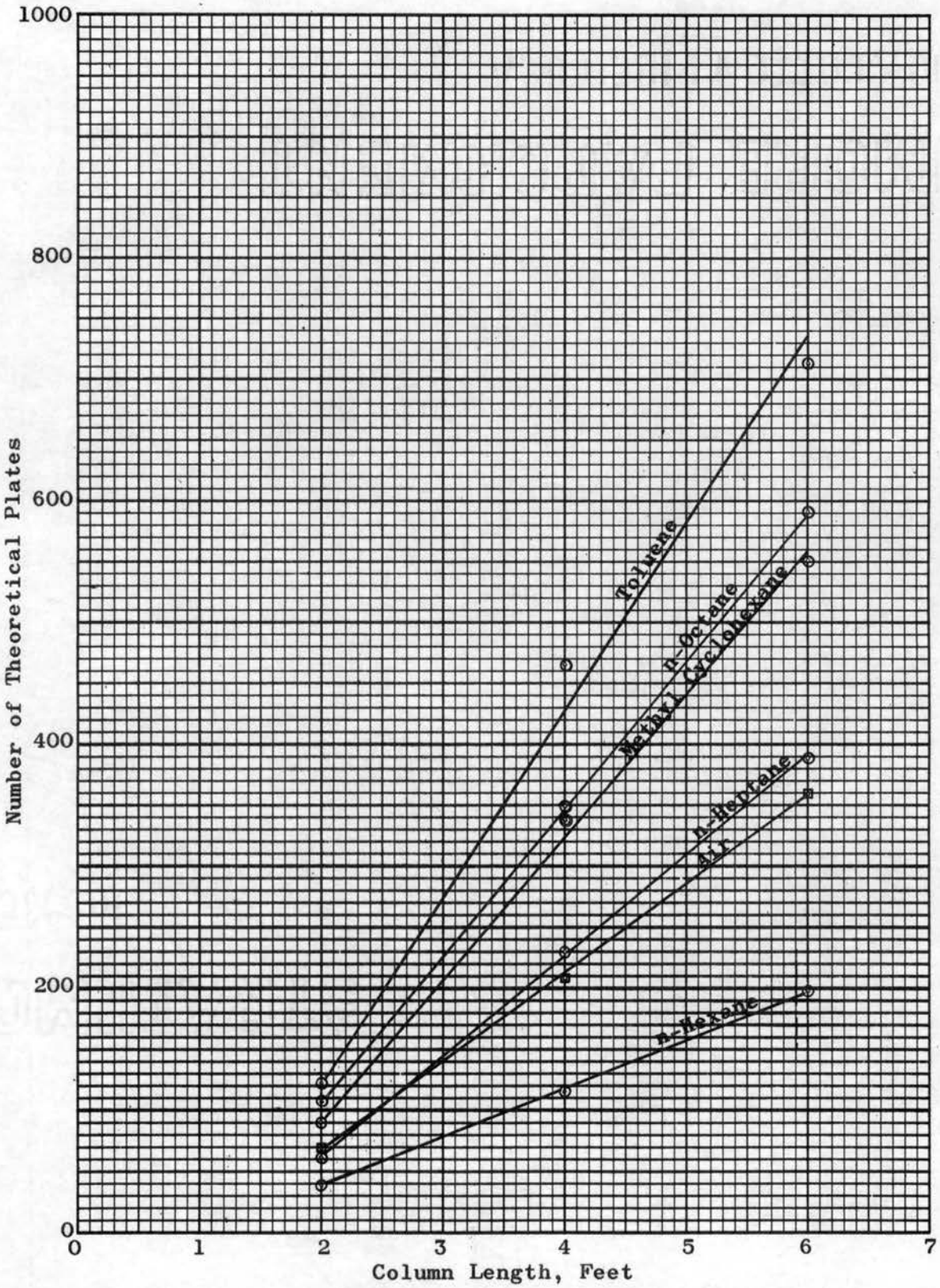


Figure 14. Correlation of Theoretical Plates and Column Length

roughly intersect in a point. This would mean that the ratio of plates between any two components will be approximately the same for different column lengths. The possible value of this relationship will be shown later.

Figure 14 also indicates that the variation of the number of stages with column length may be represented by an expression of the form

$$n = a + bL$$

where a and b are constants determined by the properties of the system. It appears that a depends primarily upon column characteristics, while b depends primarily upon sample characteristics.

In the distance-width equation, both "d" and "w" can be expressed in time units rather than distance units. The conversion factor is the chart drive speed.

The time, Θ_{He}, for helium to flow through a column of length L, will be given by:

$$\Theta_{He} = L/V_{He} \qquad (5)$$

where: V_{He} = linear velocity of helium, cm/min

$$V_{He} = F/A$$

where: F = volumetric flow rate, cc/min

A = cross sectional area of tube, cm^2

For an empty tube,

$$\Theta_{He} = \frac{LA}{F} = \frac{\text{tube volume}}{\text{volumetric flow}}$$

Since the tube volume will be decreased by the column packing, the actual volume will be given by (L)(A)(P), where P = porosity = $\frac{\text{volume of void space}}{\text{total tube volume}}$; therefore

$$\Theta_{He} = (L)(A)(P)/F \qquad (6)$$

Let ϕ_A be the fraction of component "A" in the helium stream at any time. Thus the time, Θ_A, for component "A" to flow through the column will be:

$$\Theta_A = \Theta_{He}/\phi_A = (L)(A)(P)/(F)(\phi_A) \qquad (7)$$

All of the values necessary to calculate ϕ_A are readily available, with the exception of the porosity term. This term was found with the aid of a vacuum pump and a soap film flowmeter. The procedure listed below was used to find the column porosity.

A section of quarter inch copper tubing was plugged at one end. The tubing was then cut to leave one foot of open length beyond the plug. The tube was then filled with packing and butted against another short piece of tubing connected to a valve. The two pieces of tubing were connected by a short piece of rubber tubing. The volume of the valve and short piece of copper tubing were determined by sealing the copper tubing, pulling a vacuum on the valve, closing the valve, and then connecting the valve to the soap film flowmeter. A bubble was placed in the flowmeter and the valve was slowly opened. The change in the position of the bubble in the calibration flowmeter was taken as the volume of the valve and short piece of tubing. The effective volume of the void space was found in the same manner for the one-foot sections of copper tubing filled with various packings. The pressure was always taken down to 0.2 mm of mercury. In each case the volume of the valve and short section of tubing were subtracted from the values obtained. The final results are given in Table XII and are plotted in Figure 15.

TABLE XII

POROSITY CALCULATIONS

Operating Conditions:

Volume of value - 2.8 ml
Volume of void 1 foot tube - 5.8 ml
Inert packing - 35 to 80 mesh, Chromosorb Red

Run Number	% Liquid On Packing	Type of Liquid	Volume of Filled Tube	Porosity, P
5-3-3A	0	-	4.90	.845
5-3-3B	0	-	4.90	.845
5-3-4A	5	TCP	4.60	.793
5-3-4B	5	TCP	4.55	.785
5-3-5A	10	TCP	4.50	.776
5-3-5B	10	TCP	4.50	.776
5-3-6A	20	TCP	4.25	.733
5-3-6B	20	TCP	4.30	.742
5-3-7A	30	TCP	4.00	.690
5-3-7B	30	TCP	4.05	.698
5-3-8A	20	DNP	4.15	.715
5-3-8B	20	DNP	4.15	.715

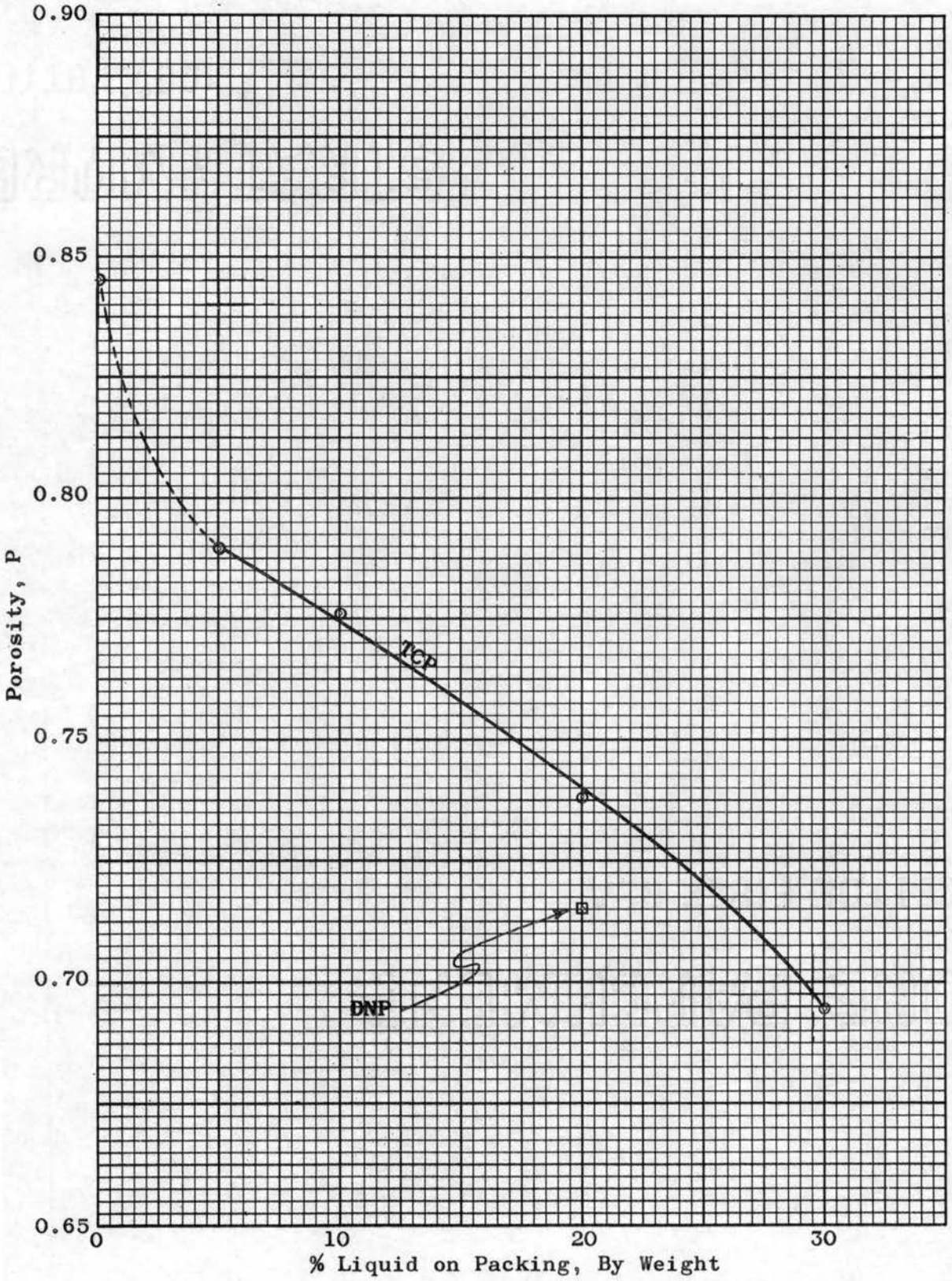


Figure 15. Porosity as a Function of Amount of Column Liquid

Effect of Parameters

A series of tests were made to observe how ϕ changes with various parameters. The first test was made to determine what would be the effect of different column lengths on ϕ. All variables other than length were kept constant. The data for this test are given in Table XIII and are shown in Figure 16. The method used in calculating the values of ϕ is outlined as an example in Appendix B.

The results tend to show what would be expected. Column length should have little or no effect on ϕ once "equilibrium" has been obtained. On a very short column there would be some end effects, but as longer and longer columns are used the end effects should be less and less. One end effect factor would be the plugs of glass wool in the ends of the columns.

A second test was made to determine what would be the effect of changing the concentration of the liquid phase on the packing. Again, all other variables except the one in question were held constant. The data are given in Table XIV and presented in Figure 17.

It would be expected that as the amount of stationary liquid phase in the column increases, the time that the components reside in the liquid would increase. The normal hexane curve in Figure 17 brings this out. The air curve, since it goes through the column almost unaffected by the liquid, has a ϕ of approximately 1.0. No apparent reason can be seen for $\pm 8\%$ variance in the ϕ for air. The value of ϕ, approximately equal to 1.0, for air would tend to show that the porosity valves are in the right range.

TABLE XIII

EFFECT OF LENGTH ON Ø

Operating Conditions:

Reference flow = 25 ml/min
Outlet pressure = 760 mm Hg
% liquid on packing = 20%

Measuring flow = 50 ml/min
Chart speed = 4 1/2 in/min
Temperature = 210.2°F

Run Number	Column Packing	Sample	Column Length, ft.	Distance, mm	Peak Width mm	P/Ø	Porosity P	Ø
4-1-18	TCP	nC_6	2	44	28.4	1.73	0.745	0.430
3-30-28	TCP	nC_6	4	101	37.8	1.98	0.745	0.376
4-5-28	TCP	nC_6	6	158	44.8	2.07	0.745	0.360
5-10-8	DNP	nC_6	2	82	19.0	3.20	0.735	0.230
5-9-8	DNP	nC_6	4	177	24.9	3.46	0.735	0.212
3-31-8	DNP	nC_6	6	291	60.0	3.80	0.735	0.192
4-1-11	TCP	nC_8	2	175	37.8	6.88	0.745	0.108
3-30-21	TCP	nC_8	4	412	44.2	8.12	0.745	0.092
4-5-21	TCP	nC_8	6	612	50.4	8.01	0.745	0.093
4-1-12	TCP	MCH	2	137	29.7	5.38	0.745	0.138
3-30-22	TCP	MCH	4	306	33.3	6.00	0.745	0.124
4-5-22	TCP	MCH	6	464	39.6	6.08	0.745	0.122

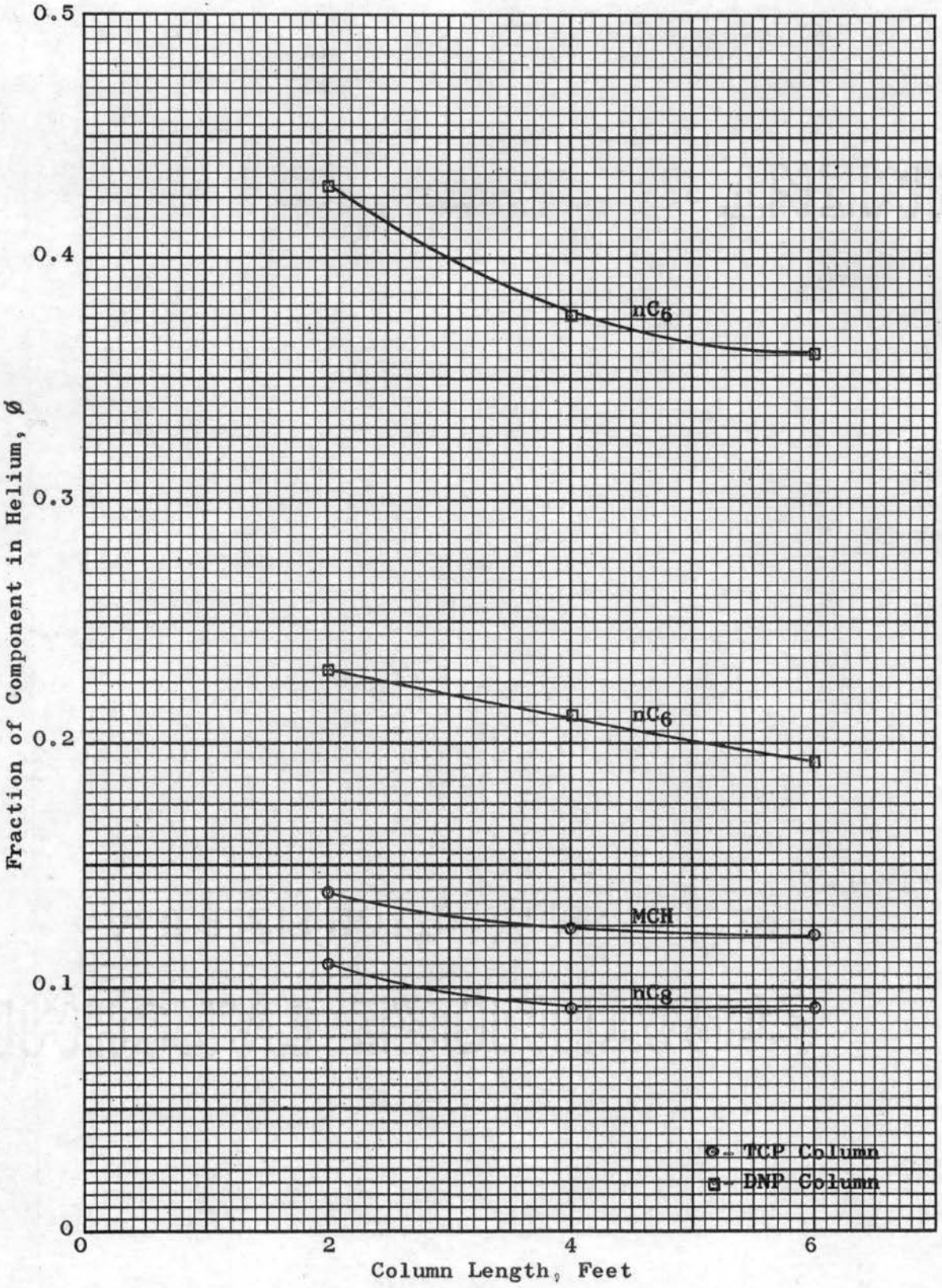


Figure 16. Effect of Column Length on Ø

TABLE XIV

VARIATION OF Ø WITH AMOUNT OF LIQUID PHASE

Operating Conditions:

Temperature - 210.2°F
Measuring flow - 50 ml/min
Outlet pressure - 760 mm Hg
Column length - 4 feet
Air sample - 1.0 ml

Chart speed - 4 1/2 in/min
Reference flow - 25 ml/min
Column packing - TCP
nC_6 sample - 0.007 ml

Run Number	% Liquid By Weight	Sample	Distance mm	Peak Width, mm	P/Ø	Porosity P	Ø
4-4-18	5	nC_6	49.0	23.8	0.961	0.789	0.820
4-5-8	10	nC_6	62.0	30.0	1.220	0.776	0.636
3-30-28	20	nC_6	101.0	37.8	1.980	0.738	0.373
4-5-18	30	nC_6	138.0	49.8	2.710	0.684	0.256
4-4-19	5	AIR	404.0	10.4	0.784	0.789	1.007
4-5-9	10	AIR	38.0	10.6	0.745	0.776	0.959
3-30-29	20	AIR	37.2	10.4	0.735	0.738	1.003
4-5-19	30	AIR	32.8	10.2	0.643	0.694	1.080

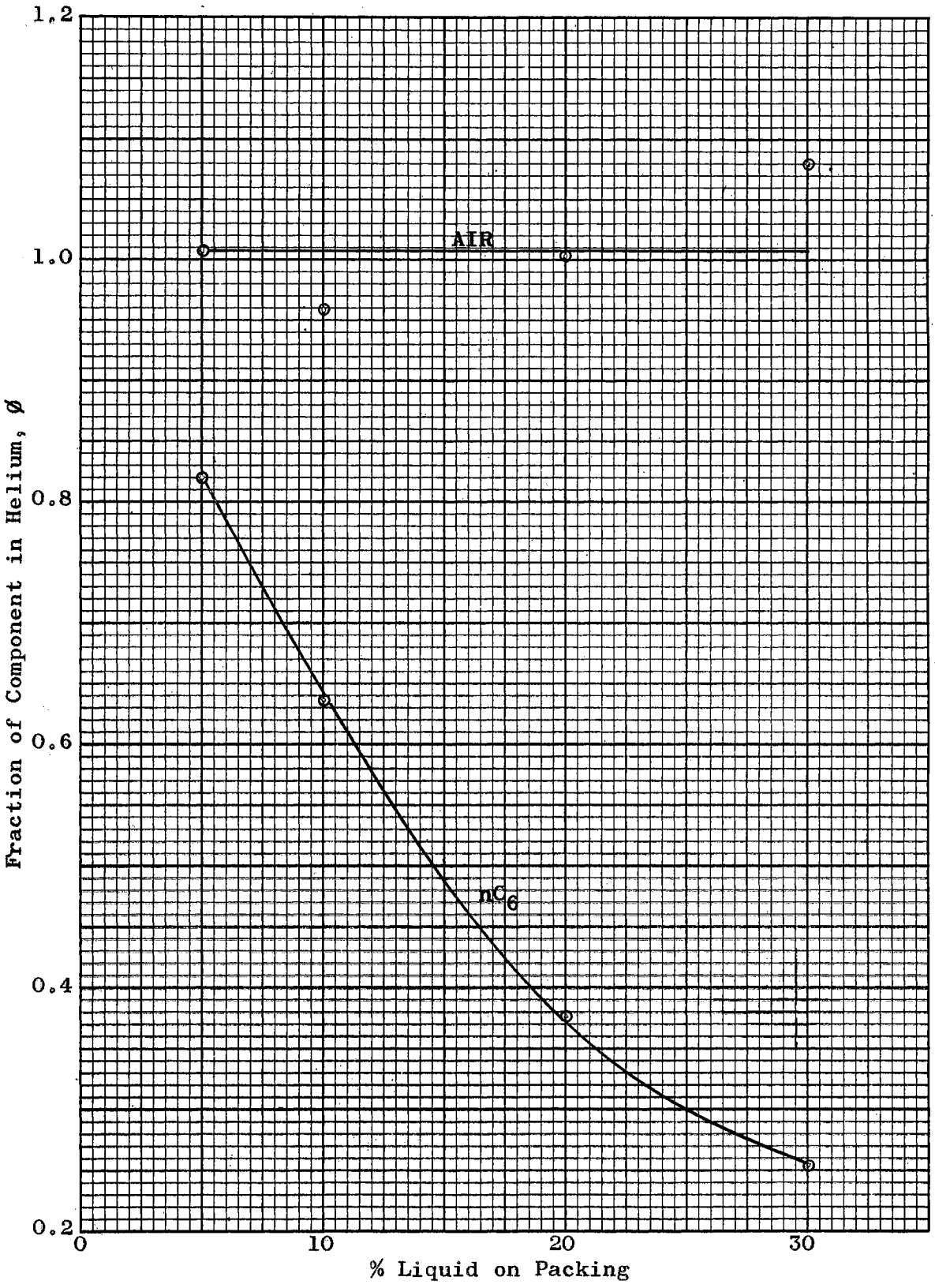


Figure 17. Variation of Ø With Amount of Liquid Phase

A final group of test runs were made which correlated three variables. These variables were flow rate, type of liquid phase, and column temperature. The conditions and data are given in Table XV and the results are plotted in Figure 18.

Noting first the results of flow variation, it would seem strange that as the flow increased, the amount of sample residing in the liquid would increase. It may be possible to explain this by saying the turbulence would be greater and the interfacial mass transfer rate would be increased. At high flow rates, the rate at which the sample enters and leaves the liquid is greater so that a truer value may be reached for the equilibrium saturation between the liquid phase and sample.

The change in temperature in Figure 18 shows that as the column temperature is increased, the time a given component resides in the helium will be increased. Figure 18 also shows that by changing the liquid phase, different values of $\emptyset$ may be obtained for a given flow rate and temperature.

Application

Rewriting the distance-width equation,

$$w^2 = 16d^2/n \text{ or } w = 4d/\sqrt{n} \tag{8}$$

but $d_A/(\text{chart speed}) = \Theta_A = LAP/F\emptyset_A$, or

$$d_A = (LAP)(c.s.)/F\emptyset_A \tag{9}$$

Substituting in (8)

$$w = 4(L/\sqrt{n})(AP/F)(1/\emptyset_A)(c.s.) \tag{10}$$

TABLE XV

EFFECT OF FLOW, TEMPERATURE, AND LIQUID PHASE ON Ø

Operating Conditions:

Reference flow - 25 ml/min
Per cent liquid on packings - 20%
Sample - 0.007 ml nC_6
Outlet pressure - 760 mm Hg
Column length - 4 feet
Chart speed - 4 1/2 in/min

Run Number	Column Packing	Measuring Flow, ml/min	Temperature °F	Distance, mm	Width, mm	P/Ø	Porosity P	Ø
3-29-8	DNP	25	210.2	269	85.4	2.64	0.735	0.278
3-28-8	DNP	50	210.2	147	46.2	2.88	0.735	0.255
3-29-18	DNP	75	210.2	109	33.4	3.21	0.735	0.229
3-29-28	DNP	100	210.2	87	25.4	3.41	0.735	0.215
3-30-38	TCP	25	210.2	188	72.6	1.84	0.745	0.404
3-30-28	TCP	50	210.2	101	37.8	1.98	0.745	0.376
3-30-18	TCP	75	210.2	70	25.6	2.06	0.745	0.362
3-30-8	TCP	100	210.2	59	20.4	2.31	0.745	0.322
4-6-38	TCP	25	164.0	279	81.0	2.74	0.745	0.272
4-6-28	TCP	50	164.0	161	45.6	3.16	0.745	0.236
4-6-18	TCP	75	164.0	119	31.8	3.50	0.745	0.212
4-6-8	TCP	100	164.0	164	26.0	3.69	0.745	0.202

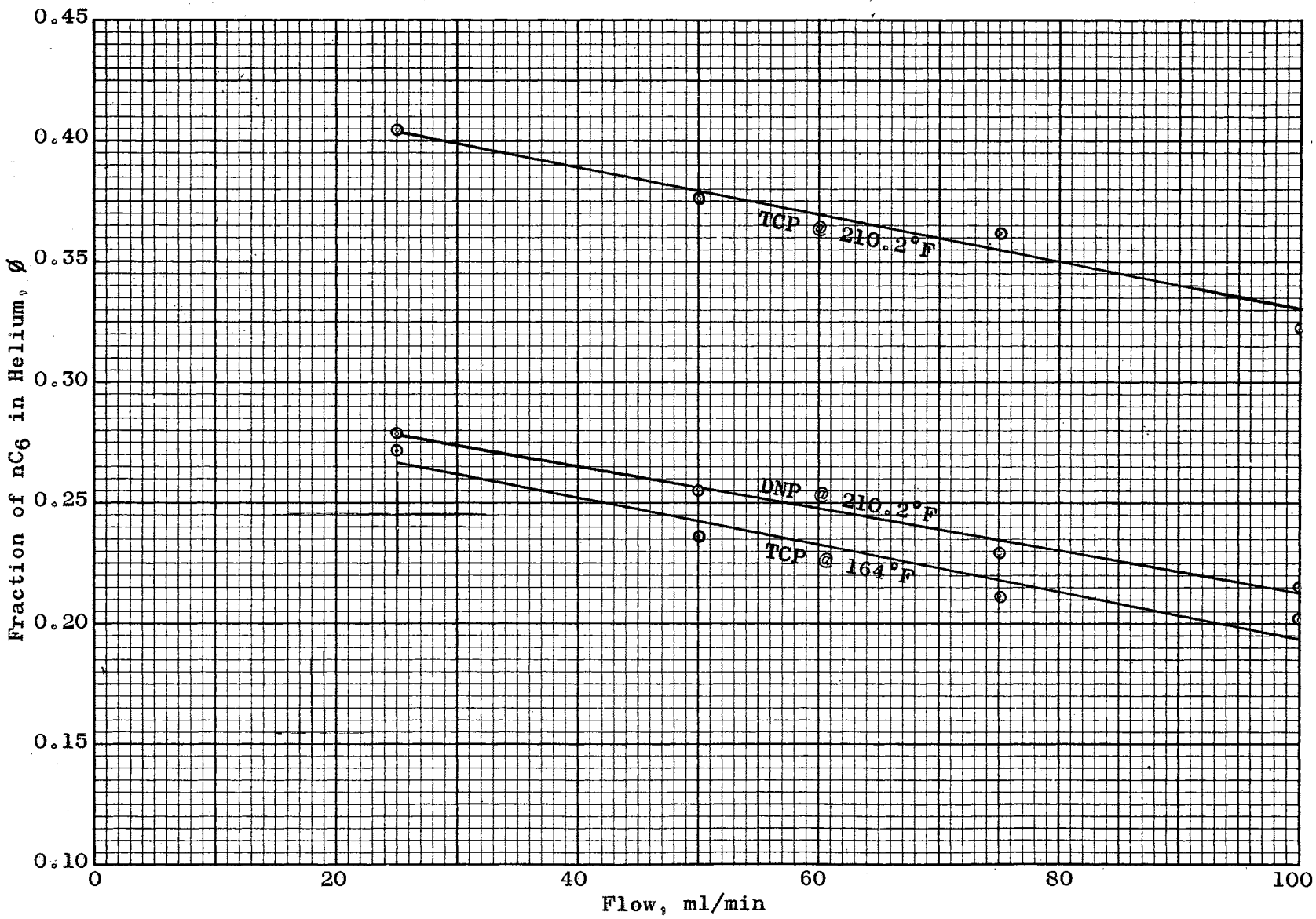


Figure 18. Effect of Flow, Temperature, and Liquid Phase on Ø

This equation gives what may be a satisfactory solution to a problem in modern gas chromatography. Many times in doing routine analyses, it is found: (1) that components are well separated but take a great length of time to pass through a column, and (2) the components in question are barely separated and for calculational purposes must be farther apart. This problem is pointed up by the use of automatic integrators. Distinct and separate curves must be available to use the integrators. On the other hand, time is important and too long a column will involve wasted time and effort. The example shown below will be used to illustrate a possible use of equation (10) in the solution of this problem.

Example

Assume that the 20% TCP column is to be used under the conditions shown in Table XI. A large number of samples containing normal hexane and normal heptane need to be analyzed. To conserve time, the shortest column that will give complete separation will be used. The only information available is the relationship, for air, of column length to number of theoretical plates.

As a first attempt, a six foot TCP column was tried. The components were well separated and using the distance-width equation, one point for normal hexane and one for normal heptane were obtained at six feet for the column length-plate correlation. The following ratios were obtained.

$$\frac{nC_6}{AIR} = \frac{198}{359} = 0.552 \qquad \frac{nC_7}{AIR} = \frac{388}{359} = 1.08$$

The number of plates for air at two feet is 69.5. Therefore,

$$nC_6 = (69.5)(0.552) = 38.4 \text{ plates at two feet}$$

$$nC_7 = (69.5)(1.08) = 75 \text{ plates at two feet.}$$

The value of $\emptyset$ for each of the components is calculated as shown in Appendix B and based on the results of Figure 14. The values obtained were:

$$\emptyset_{nC_6} = 0.33 \qquad \emptyset_{nC_7} = 0.193$$

Using the value of the number of plates obtained at two feet for nC_6 and nC_7 and the method shown in Appendix B,

$$d_{nC_6} = 6.3 \text{ mm} \qquad d_{nC_7} = 10.8 \text{ mm}$$

Using equation (10),

$$w_{nC_6} = 4.1 \text{ mm} \qquad w_{nC_7} = 5.0 \text{ mm}$$

If these peaks do not overlap, then $d_{nC_6} + 1/2\, w_{nC_6}$ must be less than $d_{nC_7} - 1/2\, w_{nC_7}$.

For nC_6, $6.3 + 2.05 = 8.35$

For nC_7, $10.8 - 2.5 = 8.3$

Thus a two foot column could almost be used.

An experimental run was made to check the solution of this problem and it was found that for a two-foot column, the two curves intersected just before the baseline. A four-foot column gave wide separation of the two components. The actual length needed would seem to be between 2 and 2 1/2 feet.

The preceding correlation would possibly be more useful in calculating in the opposite direction, that is, two peaks are only

slightly separated. How long must the column be to achieve complete separation between the peaks?

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Restatement of Thesis Goals

1. Assembly and construction of the necessary gas chromatography equipment.
2. Development of a high pressure gas and liquid sampling system.
3. Determination of the accuracy of gas chromatography.
4. Development of theoretical correlations to aid in the use of chromatographic columns.

Conclusions

Equipment

The assembled equipment performed satisfactorily. The most difficult operation was the control of the gas flow rate. The earlier runs were troubled by slight fluctuations from the helium cylinder pressure regulator. These fluctuations were removed by the installation of a more sensitive regulator down stream from the cylinder regulator.

It was also necessary to accurately control the outlet pressure of the chromatography column.

Sampling Valve

A valve was constructed and tested up to 400 psig. The valve has not been used in sampling since the high pressure equilibrium

equipment is not yet in use.

Over-all Accuracy

It appears that the best results that can be obtained with the present gas chromatography equipment are no better than ± 0.2 per cent. Though all variables are important in the over-all accuracy, the greatest source of error lies in the measurement of the curve areas.

Theoretical Correlations

The development of ϕ, the fraction of a component in the gas stream, as a correlating parameter looks very promising. This value may be used effectively in calculating the proper column lengths and operating conditions required to give a separation between two components.

Recommendations

Equipment Alterations

Since it was found very difficult to accurately calculate the area of the component curves, the installation of an automatic integrator may give better results.

Future Studies

The ϕ values present a good possibility for further work. One possible study would be the determination of ϕ values from system properties rather than from experimental results.

A SELECTED BIBLIOGRAPHY

1. Anderson, J. R. and K. H. Napier, Australian Journ. Chem. 9, 541 (1956).

2. Andronikashvili, T. G. and L. P. Kuz'mina, Zavodskaya Lab. 22, 1403 (1956).

3. Bennett, C. E., et al., Anal. Chem. 30, 898 (1958).

4. Bradt, W. W., Anal. Chem. 32, 339 (1960).

5. Claudy, H. N., et al. Paper presented at Pittsburgh Conference on Anal. Chem. and Appl. Spectroscopy, March 2-6, 1959.

6. Coates, V. J., ed., Gas Chromatography, International Gas Chromatography Symposium. New York: Academic Press, Inc. (1958) p. 323.

7. Ibid, pp. 67-72.

8. Ibid, pp. 41-50.

9. Dal Nogare, S., Anal. Chem. 32, 19R (1960).

10. Davis, J. J. Paper presented at I.S.A. Symposium on Gas Chromatography, Michigan State Univ., June 10-12, 1959.

11. Desty, D. H., ed., Gas Chromatography, 1958. Institute of Petroleum. New York: Academic Press, Inc. (1958) p. 383.

12. Desty, D. H., ed., Vapor Phase Chromatography. Institute of Petroleum. New York: Academic Press, Inc. (1958) p. 436.

13. Ibid, pp. 18-34.

14. Ibid, pp. 388.

15. Fredericks, E. M. and F. R. Brooks, Anal. Chem. 28, 297 (1956).

16. Hardy, C. J. and F. H. Pollard, Journ. of Chrom. 2, No. 1, 1 (1959).

17. James, A. T. and A. J. P. Martin, Biochem. Journ. 50, 679 (1952).

18. Jaulmes, P. and R. Mestres, Compt. rend. 248, 2752 (1959).

19. Juneau, J. Bibliography on Gas Chromatography and Some Related Methods. Bureau of Mines Petroleum Experiment Station, Bartlesville, Oklahoma. (1956) p. 70.

20. Keulemans, A. I. M. Gas Chromatography, Second Edition. New York: Reinhold Publishing Corp. (1959) p. 234.

21. Ibid, p. 33.

22. Ibid, pp. 67-68

23. Ibid, pp. 134-139.

24. Lichtenfels, D. H., S. A. Fleck, and F. H. Burow, Anal. Chem. 27, 1510 (1955).

25. Martin, A. J. P. and R. L. M. Synge, Biochem. Journ. 35, 1358 (1941).

26. Nunez, L. J., W. H. Armstrong, and H. W. Cogswell, Anal. Chem. 29, 1164 (1957).

27. Pecsok, R. L., Principles and Practice of Gas Chromatography. New York: John Wiley and Sons, Inc. (1959) p. 226.

28. Phillips, C. S. G. Gas Chromatography. New York: Academic Press, Inc. (1956).

29. Price, A. R. and R. Kobayashi, Journ. of Chem. and Engr. Data 4, 40 (1959).

30. Ray, N. H., Journ. of Appl. Chem. 4, 82 (1954).

31. Scott, R. P. W., Nature 183, 1783 (1959).

32. van Deempter, J. J., F. J. Zuiderweg, and A. Klinkengerg, Chem. Eng. Sci. 5, 271 (1956).

33. Zahn, C. and S. H. Langer. Bibliography on Gas Chromatography. Bureau of Mines Information Circular 7856, 40, Pittsburgh, Pa. (1958).

34. _____ Burrell Corporation, Instruments for Gas and Vapor Chromatography, Catalog 84, Pittsburgh, Pa. n.d.

35. _____ Podbielniak, Inc. Chromacon Series 9580, Bulletin a-15-859, Chicago, Ill. n.d.

APPENDIX A

LIST OF NOMENCLATURE

A - area under a curve, mm^2
cross sectional area, cm^2

c.s. - chart speed

D - diffusivity

d - distance from injection point to middle of component peak

d_f - film thickness

d_p - average particle diameter

F - volumetric flow rate, cc/min

F_l - fraction of cross section occupied by liquid

F_g - fraction of cross section occupied by gas

HETP - height equivalent to a theoretical plate

K - partition coefficient of the solute

k' - $K(F_l/F_g)$

L - length, feet

MA - milliamp. meter

MES - measuring detector

m - mole fraction

n - number of theoretical plates

P - barometric pressure
porosity

Q - flow rate of carrier gas

REF - reference detector

u - linear gas velocity

V - voltmeter
linear gas velocity, cm/sec

w - width of component peak

Z - compressibility factor

γ - a correction factor accounting for the tortuosity of the gas channels

θ - time

λ - a quantity characteristic of the packing

ϕ - fraction of a component in the gas stream at any time

Subscripts

A - component designation

g - gas phase

He - helium stream

i - individual component

l - liquid phase

r - reference run

s - sample run

APPENDIX B

SAMPLE CALCULATION

Determination of Ø Values and Component Peak Widths For a 2 Foot Column

Operating Conditions: Same as Table XI

Theoretical Plates: AIR - 6 ft = 359
AIR - 7 ft = 69.5
nC_6 - 6 ft = 198
nC_7 - 6 ft = 388

Distance, mm: nC_6 - 6 ft = 19.0
nC_7 - 6 ft = 32.5

Step 1. Determination of $\emptyset_{nC_6}$ and $\emptyset_{nC_7}$ using a 6 foot column.

$$d_A = (LAP)(c.s.)/F\emptyset_A$$

$$P = 0.738$$

$$LA = \text{Volume} = 33{,}400 \text{ mm}^3$$

$$c.s. = 1/2 \text{ in/min} = 0.212 \text{ mm/sec}$$

$$F = 50 \text{ cc/min} = 833.3 \text{ mm}^3/\text{sec}$$

$$\emptyset_A = \frac{(33.400\text{mm}^3)(0.738)(0.212 \text{ mm/sec})}{(833.3\text{mm}^3/\text{sec}) \qquad (d_A)}$$

$$\emptyset_A = 6.28 \text{ mm}/d_A$$

$$\emptyset_{nC_6} = 6.28/19 = 0.33$$

$$\emptyset_{nC_7} = 6.28/32.5 = 0.193$$

Step 2. For the 6 foot column, the following plate ratios are obtained.

$$\frac{nC_6}{AIR} = \frac{198}{356} = 0.552 \qquad \frac{nC_7}{AIR} = \frac{388}{359} = 1.08$$

Step 3. The number of plates for air for a two foot column is 69.5; therefore

$$nC_6 = (0.552)(69.5) = 38.4 \text{ plates}$$

$$nC_7 = (1.08)(69.5) = 75 \text{ plates}$$

Step 4. For the two foot column, solve:

$$d_A = (LAP)(c.s.)/F\phi_A$$

Step 5. Solve for peak width by using

$$w_A = 4(1/\sqrt{n})(LAP/F)(1/\phi_A)(c.s.)$$

$$w_A = \frac{(4)(11{,}100 \text{ mm}^3)(0.738)(0.212 \text{ mm/sec})}{(833.3 \text{ mm}^3/\text{sec}) \quad (\sqrt{n})(\phi_A)}$$

$$w_A = 8.35/(\sqrt{n})(\phi_A)$$

$$w_{nC_6} = 8.35/(\sqrt{38.4})(0.33) = 4.1 \text{ mm}$$

$$w_{nC_7} = 8.35/(\sqrt{75})(0.193) = 5.0 \text{ mm}$$

Step 6. Check to see if curves overlap:

$d_{nC_6} + 1/2\ w_{nC_6}$ must be less than $d_{nC_7} - 1/2\ W_{nC_7}$

for $nC_6 = 6.3 + 2.05 = 8.35$

for $nC_7 = 10.8 - 2.5 = 8.30$

Thus the peaks should just touch.

APPENDIX C

SYRINGE CALIBRATION DATA

TABLE XVI

10 MICROLITER SYRINGE CALIBRATION

Maximum Syringe Volume - 0.01 ml

Temperature - 25.8°C Mercury Density - 13.5335 g/ml

Syringe Reading	Syringe Weight, grams	Difference from Zero Volume Reading, grams	Calculated Volume, ml
0.010	10.8475	0.1305	0.0096420
0.008	10.8219	0.1049	0.0077511
0.006	10.7955	0.0785	0.0058004
0.004	10.7694	0.0524	0.0038719
0.002	10.7430	0.0260	0.0019212
0.000	10.7170	0.0000	0.0000000
0.010	10.8480	0.1307	0.0096575
0.000	10.7173	0.0000	0.0000000

TABLE XVII

50 MICROLITER SYRINGE CALIBRATION

Maximum Syringe Volume - 0.05 ml

Temperature - 26.2°C Mercury Density 13.531 g/ml

Syringe Reading	Syringe Weight, grams	Difference from Zero Volume Reading, grams	Calculated Volume, ml
0.05	15.9617	0.6857	0.5067
0.04	15.8251	0.5491	0.4058
0.03	15.6874	0.4114	0.3040
0.03	15.5510	0.2750	0.2032
0.01	15.4130	0.1370	0.1012
0.00	15.2760	0.0000	0.0000
0.05	15.9610	0.6854	0.5065
0.04	15.8226	0.5470	0.4042
0.03	15.6860	0.4104	0.3033
0.02	15.5485	0.2729	0.2017
0.00	15.2756	0.0000	0.0000

TABLE XVIII

100 MICROLITER SYRINGE CALIBRATION

Maximum Syringe Volume - 0.1 ml

Temperature - 26.2°C Mercury Density - 13.531 g/ml

Syringe Reading	Syringe Weight, grams	Difference from Zero Volume Reading grams	Calculated Volume, ml
.10	14.6933	1.3468	0.99534
.09	14.5586	1.2121	0.89579
.08	14.4231	1.0766	0.79565
.07	14.2885	0.9420	0.69617
.06	14.1498	0.8033	0.59367
.05	14.0138	0.6673	0.49310
.00	14.3465	0.0000	0.00000
Temperature - 25.6°C		Mercury Density - 13.533 g/ml	
.10	14.6959	1.3476	0.99579
.07	14.2880	0.9397	0.69438
.05	14.0147	0.6664	0.49243
.00	13.3483	0.0000	0.00000
Temperature - 25.6°C		Mercury Density - 13.5330 g/ml	
.10	14.6933	1.3463	0.99483
.02	13.6130	0.2660	0.19656
.00	13.3470	0.0000	0.00000

VITA

James Lang Webster

Candidate for the Degree of

Master of Science

Thesis: PRINCIPLES AND PROPERTIES OF GAS CHROMATOGRAPHY

Major Field: Chemical Engineering

Biographical:

Personal data: Born in Stillwater, Oklahoma, March 20, 1935, the son of James E. and Verna I. Webster; married to Virginia G. Batchelor, Lake Jackson, Texas, in November, 1958.

Education: Attended grade school and high school in Stillwater, Oklahoma; graduated from Stillwater High School in May, 1953; attended Oklahoma State University, 1953 to 1958; received the degree of Bachelor of Science in Chemical Engineering, May 1, 1958; completed the requirements for the Master of Science degree in August, 1960.

Professional experience: Employed as a Chemical Engineer with the Dow Chemical Company, Organic Process Development Department, 1958; served six months as a Chemical Corps officer, United States Army, April, 1959 to October, 1959.

Professional societies: Associate member of the American Institute of Chemical Engineers; associate member of the American Chemical Society.