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GAS CHROMATOGRAPHY AS A RECOVERY PROCESS

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NOMENCLATURE

a	cross section area of empty column (cm^2)
a_v	cross section area of void volume (cm^2)
A	sample size (cc @ 1 atm and 70°F)
b	band width (cm)
B	sample size (cc)
A, B, C	van Deemter constants
c', c''	constants
C_0	sample concentration (g-mol/cc)
d	distance from sample injection to point under consideration on chromatogram (cm)
d_0	distance from sample injection to oxygen peak (cm)
d_R	distance from sample injection to peak maximum (cm)
d_f	liquid film thickness (cm)
d_p	particle diameter (cm)
D	diffusivity in gas phase (cm^2/sec)
D_l, D_g	diffusivity in liquid or gas (cm^2/sec)
f	fraction of gas passing through conductivity cell
F	factor defined by Equation (30)
F	total sample size (cc)
F_l, F_g	fraction of liquid or gas in the column
g	$(1 - V/V_R)$
G	gas phase
G^E	excess free energy of solution
h	height of a peak (cm)
H	height equivalent to a theoretical plate (cm)

NOMENCLATURE (CONT'D)

J	factor defined by Equation (124)
k	partition coefficient, concentration of solute in liquid phase/ concentration of solute in gas phase
k'	$k(F_l/F_g)$
k_1, k_2	constants
K	permeability (cm^2)
K	a constant
L	column length (cm)
L	liquid phase
M	concentration of sample (g-mol/cc)
M_m	mols carries gas/cc
M_s	mols liquid phase/cc
n	number of theoretical plates in column
n	mols of gas
p	plate number
P	pressure ("Hg or psia)
\bar{P}	average pressure
P^0	vapor pressure
P_s	pressure at soap film meter
q_0	sample size (g-mol)
Q	factor defined in Equation (h), Appendix B
r	(P_i/P_0)
R	resolution (cc)
R	gas constant

NOMENCLATURE (CONT'D)

S	chart speed (cm/min)
S	sample volume (cc)
S ₀	total sample volume (cc)
t	time (sec)
t _R	retention time (min)
t ₀	residence time for carrier gas (min)
T	temperature (°R)
T _s	temperature at soap film meter (°R)
u	gas velocity (cm/min)
\bar{u}	average velocity (cm/min)
u ₀	outlet velocity (cm/min)
\bar{v}	average flow rate (cc/min)
v ₀	outlet flow rate (cc/min)
v _a	flow rate of gas passing through conductivity cell (cc/min)
V _V	void volume (cc)
V*	volume as shown in Figure 9 (cc)
V ⁺	volume as shown in Figure 9 (cc)
V _T	V _V + V ₁ + V ₂ in Figure 10 (cc)
V ₁	volume of valve (cc)
V ₂	volume of pinch clamp (cc)
V _R	retention volume (cc)
V _g	gas in one theoretical plate (cc)
V _ℓ	liquid in one theoretical plate (cc)
V _s	liquid in the column (cc)
V	volume of gas which has passed thru the column (cc)

NOMENCLATURE (CONT'D)

W	band width (cm)
W'	band width (cc)
x	mol fraction in the liquid phase
X_p	concentration in the liquid phase on the p-th plate (mol/cc)
X_0	defined by Equation (31)
X_1	defined by Equation (32)
y	mol fraction in the gas phase
Y_p	concentration in the gas phase on the p-th plate (mol/cc)
z	distance through the column (cm)

Subscripts

f	final
G,g	gas
i	initial, inlet
L, l	liquid
o	oxygen or outlet
p	plate number

Greek Letters

α	relative volatility
α	mass transfer coefficient
β	van Deemter constant, Equation (45)
μ	viscosity (gm/cm-sec)
λ	heat of vaporization
λ	packing factor

NOMENCLATURE (CONT'D)

γ	activity coefficient
γ	tortuosity factors
$\varphi(r)$	function of pressure ratio, Equation (62)
v	number of plate volume, Equation (10)
σ_1, σ_2	van Deemter constants, Equation (46), and (47)
η	a constant
δ	a constant

I. INTRODUCTION

A. General

In recent years there has been possibly as much information published about the subject of gas chromatography as about almost any other in the scientific field. Chromatography has been described in varied and poetic language. It has been glorified as the "poor man's mass spectrometer." It has been criticized as being nothing more than a fancy name given to an ordinary absorption process. It has received some criticism and much praise as a valuable addition to the ever growing arsenal of analytical tools.

A number of definitions have been given for chromatography. The word was coined by Tswett⁽⁵⁵⁾ in 1906. It means "color writing" and suggested itself because the materials which he separated were pigments and formed discrete bands of varying color. It is clear that the name is no longer appropriate, but long usage prevents the substitution of another in its place.⁽²⁹⁾

Cassidy⁽⁵⁾ defines it in the following manner: "Chromatography comprises a group of methods for separating molecular mixtures that depend on distribution between a bulk, usually mobile phase, and a thin, usually stationary phase. These are brought into contact in a differential, counter-current manner." Keulemans⁽³⁰⁾ gives us the following definition: "Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through the stationary bed." It is

felt that both of these definitions give a fairly accurate picture of the chromatographic process. To elaborate somewhat, chromatography is a process for separating a sample, usually of small size, into its various components. This separation takes place when these components are repeatedly distributed between two phases which are in contact with each other. A general definition of chromatography makes no specification of the nature of these phases. They may be liquid, solid, or gaseous. It is specified, however, that one phase is stationary and should have a large surface area. Large, in this sense, is a relative term, but in general it may be taken to be of the order of 10 square meters per gram.⁽³¹⁾ The second phase is designated as the mobile phase. It is this phase which acts as the carrier, transporting the sample through the stationary phase. It is apparent from such a definition that many different forms of chromatography are possible. Both phases may be liquids for example, or one phase liquid and the other gas, or any of a number of other combinations. Cassidy enumerates these possibilities and discusses some of those which have been investigated. In this work the term chromatography will be taken to mean gas-liquid partition chromatography, with gas referring to the mobile phase and liquid referring to the stationary phase. This particular type of chromatography, first introduced by Martin and James⁽²⁴⁾, has received by far the most attention in a still new and growing field.

It is not our purpose here to present an outline of the history of chromatography. The interested reader is referred to almost any good text on the subject.^(28, 47) It should be noted, however, that the rapid advance of the theory of chromatography has been due primarily to

its great versatility as an analytical tool. It fills a need left by such well known methods as infra-red analysis, mass spectroscopy, electron microscopy, distillation, etc. There are a number of features which chromatography possesses from which it derives its value as an analytical tool. The speed with which an analysis may be performed is one of the primary assets. Whereas a separation by distillation may take several hours or even days to perform, a chromatographic analysis may be completed in a matter of minutes.⁽⁴⁸⁾ This speed, especially in the analysis of complex systems, enables chromatography to perform as routine analyses certain separations which would be out of the question by older methods. A second feature of chromatography, which in many instances is just as important as the speed of analysis, is that a very small amount of sample is needed to perform an analysis.⁽⁴⁸⁾ This is of great importance both in dealing with very costly materials and in performing analyses for certain experiments where extraction of a large sample would alter the course of the experiment. It is also of great value when only a small amount of material is available due to the very nature of the sample. Other important features of chromatography which lend to its value as an analytical tool are the purity of the separation attained, the ease of detection of the separated components, and the low cost per analysis. These, while perhaps not as important as the features mentioned above, nevertheless add to the attractiveness of chromatography as an analytical tool.

Up to this point a good deal has been said about chromatography, and yet a reader completely unfamiliar with the subject may still be in the dark about what is going on in a chromatographic separation. An

idea of the physical set-up for a chromatographic analysis is given in the photograph of the author's equipment in Figure 1. Integral parts of the system are the coiled column (A) packed with the granular support which is coated with the absorbent liquid, the constant temperature bath (B), the thermal conductivity detection device (C), the recorder (D), the pressure gages (E), and the flow meter (F). An idea of the manner in which separation occurs may be obtained from the following analogy.

Let us consider ourselves an observer riding on a molecule of gas A in the sample to be separated. This sample is injected by some suitable means into the stream of carrier gas just before it enters the packed section of the column. What happens? The first thing is that the molecule we are riding comes in contact with the liquid film covering the inert packing and is absorbed in that liquid. All of our molecule's companions are likewise absorbed, so that the whole sample has gone from the gas phase into the liquid phase in the first small section of the column. Now once molecule A is absorbed it is stationary. Thus the carrier gas which carried it into the column leaves it behind, and fresh gas continually passes over the site in the column where our molecule is sitting. This fresh gas picks up the molecule and begins to carry it down the column once more. However, soon we reach a fresh section of packing, and once again we are grabbed by the liquid phase. Thus, as we sit on our molecule, we travel through the column by a series of short leaps from one liquid site to another.

While we are making this bouncy trip, the other molecules of component A are doing the same thing at much the same rate of speed.

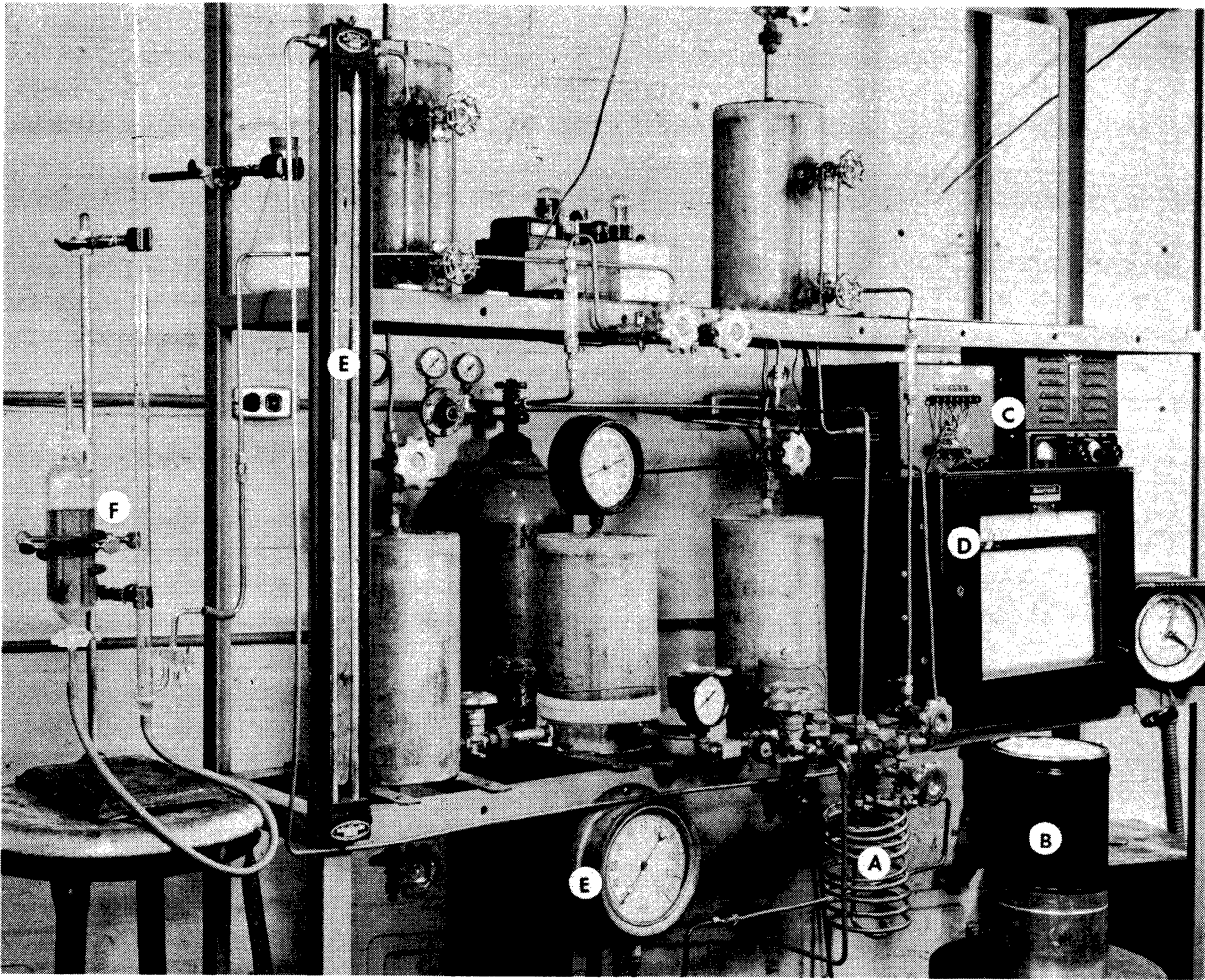


Figure 1. Equipment Photograph Showing: (A) Column, (B) Constant Temperature Bath, (C) Conductivity Cell and Power Supply, (D) Brown Recorder, (E) Pressure Gage and Manometer, (F) Soap Film Meter.

Therefore, all the molecules of component A emerge from the column at about the same time. Molecules of component B also go leap-frogging through the column, but since B is less volatile than A (let us suppose), the B molecules stay in the liquid longer at each hop, and so component B leaves the column at a later time than component A. Thus the separation between A and B is effected. And the same would hold true for any number of additional components. Looking at it in a slightly different way, the molecules of components A, B, C, etc. may be considered frogs which are to race. All the frogs can jump the same distance, say three inches, but frog A can jump faster than frog B who likes to pause after each jump to catch his breath. Frog B in turn can jump faster than C, etc. It is immediately clear that frog A will win the race, and the longer the distance raced, the greater the separation between A and B will become. This is analogous to what occurs in a chromatographic separation.

One thing further should be noted. Our molecule of A has a great many brothers who we have said are traveling at much the same speed as we. The speed is not exactly the same since all the molecules of A are not exactly alike. Some possess more energy than others and these tend to travel faster. The shape of the curve representing the number of molecules with a given energy is the well-known Maxwellian or Gaussian distribution curve.⁽⁴¹⁾ Since this energy distribution controls the relative speeds of the molecules of A, it follows that a plot of the number of molecules of A emerging as a function of time will also be Gaussian in shape. A typical chromatogram for the separation of a binary mixture is shown in Figure 2. It will be shown later that the

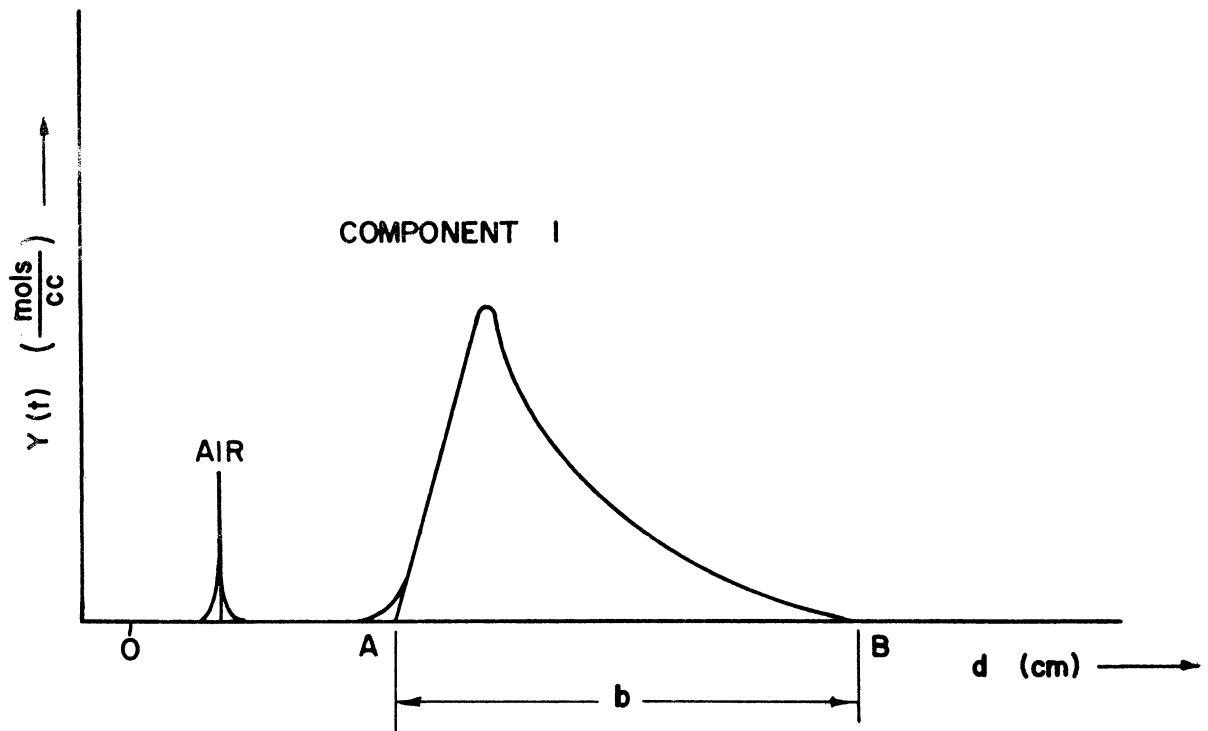
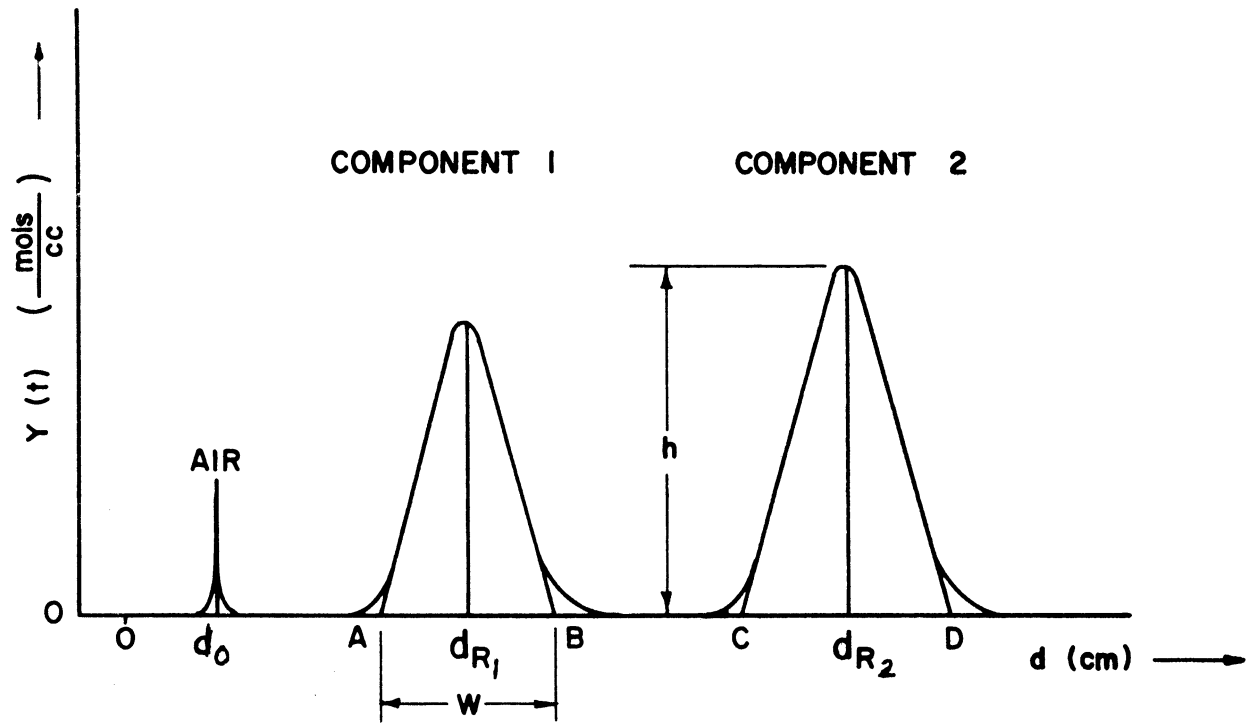


Figure 2. Typical Chromatograms Showing Symmetric and Asymmetric Peaks.

longer the chromatographic column is, the wider the band of component A will be on emerging from this column. Thus in the analogy of the jumping frogs, if we look at frog A (representing all the molecules of A in the sample) as he travels down the column, we will observe that he starts out tall and thin but becomes progressively shorter and fatter as he goes along.

While a great deal of work has been done studying chromatography from the analytical point of view, little consideration has been given to its use as a process for separating and recovering gases.^(1,23) It is true that certain investigators have used chromatography as a method of preparing small samples for further analysis, but little work has been done by way of attempting to adapt chromatography for use as a recovery process. The reason for this is fairly obvious to anyone familiar with even the most general principles of chromatography. From its definition it is seen that chromatography is a transient process. A given sample enters the separation column and is transported by a moving stream of carrier gas. The sample passes through the column and is separated as it does so. Examining any section in the column, one observes that its state changes continually with time, going from a condition of zero sample concentration through a period of maximum concentration and finally returning to its initial state. It is easy to see that such a process by its very nature can never be made continuous in the usual sense of the word, and lack of continuous operation is a serious drawback in a proposed process of separation.

It might be noted at this point that it is not quite correct to say that such a process can never be made continuous. By allowing the liquid phase to move through the column it might be possible under certain conditions to operate continuously.⁽¹⁷⁾ In this circumstance the chromatographic column would actually be operating as a counter-current absorber, and continuous operation would be possible provided a suitable stripping operation were performed on the liquid phase leaving the column. However, it may be seen by referring to the definition that once we cause the liquid phase to move, we are deserting the whole realm of chromatography. Thus for all practical purposes it may be reiterated that chromatography as a result of its definition can never be a continuous process. In spite of this difficulty, however, it is the purpose of this thesis to conduct a study of chromatography as a process for the separation and recovery of gaseous mixtures.

B. Objectives

The specific objectives of this research were two-fold. The first was to study the variables in chromatography which are important in the design of a system which could be used to separate gases effectively. Not all the variables in chromatography have been considered. For instance the effect of the absorbent liquid on the separation has not been studied. One particular liquid was chosen and used throughout the research. In like manner a particular packing was used as the solid support in all experimentation. No consideration was made of the effect of particle diameter on separation efficiency. The effect of temperature, flow rate, sample size, pressure, and column length have been

considered.. Correlations are provided showing the effect of these variables on retention volume and band width. It is felt that from these correlations it is possible to determine with a small amount of physical data whether a desired separation is feasible.

The second objective of this research was to design a system for automatically separating a binary mixture of gases in a semi-continuous or cyclic manner. A system has been proposed to accomplish this. In this system samples of an arbitrary size may be automatically injected into the column at fixed intervals of time. The separated components, which are detected by a thermal conductivity cell described later in this paper, are shunted to appropriate storage tanks by an automatic switching system connected to the recorder.

II. THEORETICAL BACKGROUND

A. Theories of Chromatography

A number of investigators have presented derivations of chromatographic equations. These derivations may be divided into two main groups: (1) those adopting the "theoretical plate" approach, and (2) those adopting the "rate" approach. In the first group, Martin and Synge⁽⁴⁴⁾; Porter, Deal, and Stross⁽⁵²⁾; and Keulemans⁽³²⁾ have been prominent. Van Deemter, Klinkenberg, and Sjenitzer⁽⁵⁶⁾; Lapidus and Amundson⁽⁴²⁾; and Houston⁽²³⁾ have done work from the rate approach. Van Deemter⁽⁵⁶⁾ has related these two theories with his derivation of an equation for the Height Equivalent to a Theoretical Plate (H).

Within these main groups, the derivations differ according to the simplifying assumptions which are made. These assumptions concern the size of the sample and the method of injecting it, the gas flow rate, and the form of the distribution isotherm.

1. Plate Theory of Chromatography

The concept of the theoretical plate is one which has proved as useful in chromatography as in the many other fields such as distillation and extraction where it finds extensive use. Martin and Synge⁽⁴⁴⁾ developed the original theory for liquid-liquid chromatography. James and Martin⁽²⁴⁾ later modified it to cover the case of a compressible mobile phase. This derivation has since been extended by Porter⁽⁵²⁾ to include the injection of finite samples by several methods.

Figure 3 shows a schematic representation of a section of a column which has been divided into a number of theoretical plates or

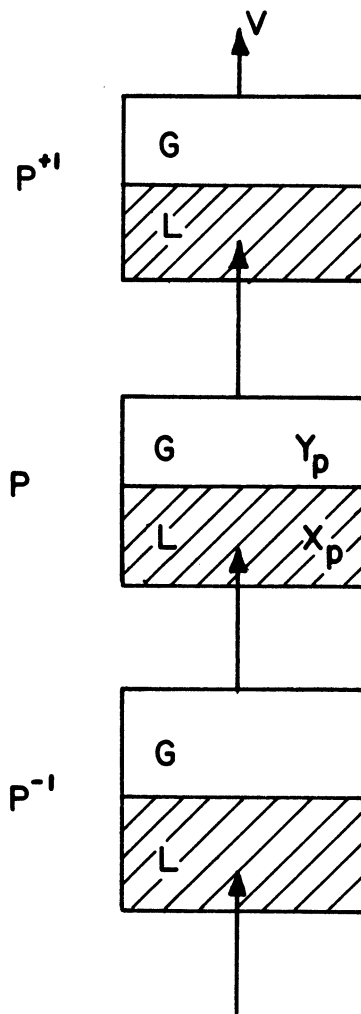


Figure 3. Schematic Diagram of a Theoretical Plate in a Chromatographic Column.

vessels. It should be noted that the flow in this system is continuous, just as it is in the rate theory.^(18,41) The distinguishing characteristics are the separation of the column into a series of discrete segments and the assumptions about the conditions which exist in each of these compartments. The derivation given here follows Keulemans.⁽³²⁾ The assumptions which have been made are the standard ones for gas-liquid partition chromatography. The first of these is that the liquid and gas volumes are constant in each theoretical plate and do not change throughout any given run. The second assumption is that complete equilibrium exists between phases in all plates at all times. This is where the term "theoretical" or "ideal" plate comes from. The third assumption is that the equilibrium between the liquid and gas phases may be represented by an equation of the form

$$X_p = k Y_p, \quad (1)$$

where k is a constant, X_p is the concentration of solute in the liquid phase, and Y_p is the concentration of solute in the gas phase of the p -th plate. This is the assumption of a linear distribution isotherm. It will be discussed briefly in a later section. The last assumption is that the sample is all injected on the first plate of the column.

Let us now make a material balance around the p -th plate shown in Figure 3. The quantity V is the total amount of gas which has passed through the column. Entering the vessel shown is a volume of gas, dV . This gas contains solute with a concentration of Y_{p-1} . The same volume of gas leaves the p -th plate carrying with it solute with a concentration of Y_p . The accumulation of solute in the p -th vessel is the

sum of the change in the amount of solute in the liquid phase and that in the gas phase. The material balance then reads:

$$\Sigma_{p-1} dV - \Sigma_p dV = V_g d\Sigma_p + V_l d\Sigma_p. \quad (2)$$

Or,

$$(\Sigma_{p-1} - \Sigma_p) dV = V_g d\Sigma_p + V_l d\Sigma_p. \quad (3)$$

Now combining this equation with our expression for X_p we find:

$$(\Sigma_{p-1} - \Sigma_p) dV = (V_g + kV_l) d\Sigma_p, \quad (4)$$

or

$$\frac{d\Sigma_p}{dV} = \frac{\Sigma_{p-1} - \Sigma_p}{V_g + kV_l}. \quad (5)$$

The boundary condition for this equation is that the concentration on each plate at $V = 0$ is zero. Thus,

$$\Sigma_1(0) = \Sigma_2(0) = \dots = \Sigma_n(0) = 0. \quad (6)$$

For the first plate in the column (plate 0) we have both a new material balance and a new boundary condition. In the material balance, we have no solute entering the column after the sample injection. Thus, $Y_{-1} = 0$, and the material balance reduces to:

$$-\Sigma_0(V) dV = (V_g + kV_l) d\Sigma_0(V). \quad (7)$$

The initial condition is as follows:

$$\Sigma_0(0) = M \text{ (g-md/cc)}. \quad (8)$$

The method for solving these equations is simple. First we solve for $Y_0(V)$. This may be done directly using Equations (7) and (8). Then we use Y_0 in Equation (2) along with the boundary condition in Equation (6) to solve for Y_1 . Then Y_1 is used to find Y_2 , Y_2 to find Y_3 , etc. This derivation is carried out in Appendix A. The result is shown below.

$$\Sigma_n(z) = M \frac{e^z z^n}{n!}, \quad (9)$$

where

$$z = V/(V_g + kV_l). \quad (10)$$

If we now let n be the last plate in the column, Equation (9) expresses the concentration of solute in the gas leaving the column as a function of the amount of gas which has passed through the column up to any given time.

We can, by simple calculus, determine that the peak maximum will occur at

$$z = n, \quad (11)$$

and that the inflection points intersect the horizontal axis at

$$z = n+1 \pm 2\sqrt{n}. \quad (12)$$

Equation (11) gives us the retention volume since

$$z_{max.} = V_{max.}/(V_g + kV_l) = n, \quad (13)$$

or

$$V_{max.} = n(V_g + kV_l). \quad (14)$$

V_{\max} is by definition the retention volume, V_R . Therefore, Equation (14) is an important statement of the relationship between retention volume and partition coefficient.

Equation (12) is of great value in determining an expression for band width, defined as the distance between the two intersection points mentioned above. Thus, if we call this spread ω , we have

$$\omega = 4\sqrt{n'}. \quad (15)$$

And if V_i and V_f represent the initial and final points of the band, we have:

$$(V_f - V_i) = 4\sqrt{n'}(V_g + kV_e). \quad (16)$$

This equation expresses the width of a peak in volumetric terms. We shall return to it again in a later section.

It should be remembered that Equation (9) is valid only for a very small sample. Porter⁽⁵²⁾ has modified this result to account for large samples. We begin by modifying Equation (9) in the following manner:

$$\frac{\Sigma_n(z)}{M} = \frac{e^{-z} z^n}{n!} = \frac{e^{-n} n^n}{n!} e^{n-z} \left(\frac{z}{n}\right)^n. \quad (17)$$

The following approximation is justified for large n :

$$\frac{e^n n^n}{n!} \sim \frac{1}{\sqrt{2\pi n'}} \quad (18)$$

$$\therefore \Sigma_n(z) = \frac{M}{\sqrt{2\pi n'}} e^{n-z} \left(\frac{z}{n}\right)^n. \quad (19)$$

A further approximation is possible when $(n-v)$ is small with respect to n , which is the case in chromatography.

$$\left(\frac{v}{n}\right)^n \sim e^{-\frac{(n-v)^2}{2n}} \cdot e^{-(n-v)} \quad (20)$$

$$\therefore \Sigma_n(v) = \frac{M}{\sqrt{2\pi n}} e^{-\frac{(n-v)^2}{2n}} \quad (21)$$

And from Equations (10) and (14) we see that

$$v = \frac{nV}{V_R}, \quad (22)$$

so Equation (21) becomes

$$\Sigma_n(v) = \frac{M}{\sqrt{2\pi n}} e^{-\frac{n}{2}\left(1 - \frac{V}{V_R}\right)^2} \quad (23)$$

Since

$$M = \frac{q_0}{V_g + kV_R} = \frac{q_0 n}{V_R}, \quad (24)$$

where q_0 is the amount of solute injected, we get

$$\Sigma_n(v) = \frac{n}{V_R} \frac{q_0}{\sqrt{2\pi n}} e^{-\frac{n}{2}\left(1 - \frac{V}{V_R}\right)^2} \quad (25)$$

Now suppose that the sample injected has a volume S_0 . We can consider the injection to take place incrementally with $Y(S)$ the concentration of the increment dS which is injected at S . We assume that each portion of sample is developed independently of the rest of the sample. Then the infinitesimal sample injected at S is developed by $(V-S)$ cc. when V cc. of gas have passed through the column. For this segment of sample, Equation (25) becomes:

$$d\Sigma_n(v) = \frac{n}{V_R} \frac{Y(S)dS}{\sqrt{2\pi n}} e^{-\frac{n}{2}\left(1 - \frac{V-S}{V_R}\right)^2} \quad (26)$$

Since the effects of each segment of sample are additive⁽²⁴⁾, the concentration at the column outlet may be obtained by integration.

$$\therefore \Sigma_n(V) = \frac{n}{V_R} \frac{1}{\sqrt{2\pi n}} \int_0^{S_0} \bar{Y}(S) e^{-\frac{n}{2} \left(1 - \frac{V-S}{V_R}\right)^2} dS. \quad (27)$$

This equation makes it possible to calculate the shape of a chromatogram provided the concentration profile of the sample is postulated. For the so-called "perfect mixing" case, the sample concentration is given by the expression

$$\bar{Y}(S) = M e^{-S/B}, \quad (28)$$

where M is the initial concentration in mols/cc. and B is the size of the total sample.

Upon performing the integration, we obtain the following result:

$$\Sigma_n(V) = \frac{M}{2} e^F [\text{erf } X_1 - \text{erf } X_0], \quad (29)$$

where

$$F = \frac{V_R^2}{2nB^2} + \frac{V_R - V}{B}, \quad (30)$$

$$X_0 = \sqrt{\frac{n}{2}} \left(1 - \frac{V}{V_R} + \frac{V_R}{nB}\right), \quad (31)$$

and

$$X_1 = \sqrt{\frac{n}{2}} \left(1 - \frac{V_R}{nB}\right). \quad (32)$$

The term erf α refers to the error function which is defined as:

$$\text{erf } \alpha = \frac{2}{\sqrt{\pi}} \int_0^{\alpha} e^{-x^2} dx. \quad (33)$$

The result given in Equation (29) is derived in Appendix B. This equation will be used in evaluating the effect of sample size on band width.

2. Rate Theory of Chromatography

Let us consider a differential section of a chromatographic column. Figure 4 shows a schematic representation of this section. A material balance may be written around this portion of the column. Houston⁽²³⁾ chooses to write his material balance around the whole section. Van Deemter⁽⁵⁶⁾ writes two balances, one around the gas phase, and one around the liquid phase. This procedure permits one to see clearly the mass transfer between phases while the overall balance does not.

For the gas phase the material balance may be written

$$\text{Accumulation} = \text{In} - \text{Out}. \quad (34)$$

$$\text{Accumulation} = F_g a \Delta Y \Delta z. \quad (35)$$

$$\begin{aligned} \text{In} = F_g a [uY - D \frac{\partial Y}{\partial z}] \Delta t + \\ + \alpha \left[\frac{x}{k} - Y \right] a \Delta z \Delta t. \end{aligned} \quad (36)$$

$$\text{Out} = F_g a \left[u(Y + \Delta Y) - D \left(\frac{\partial Y}{\partial z} + \Delta \frac{\partial Y}{\partial z} \right) \right] \Delta t. \quad (37)$$

\therefore

$$F_g \frac{\partial Y}{\partial t} = -F_g u \frac{\partial Y}{\partial z} + F_g D \frac{\partial^2 Y}{\partial z^2} + \alpha \left(\frac{x}{k} - Y \right), \quad (38)$$

or

$$\frac{\partial Y}{\partial t} = D \frac{\partial^2 Y}{\partial z^2} - u \frac{\partial Y}{\partial z} - \frac{\alpha}{F_g} (Y - x/k). \quad (39)$$

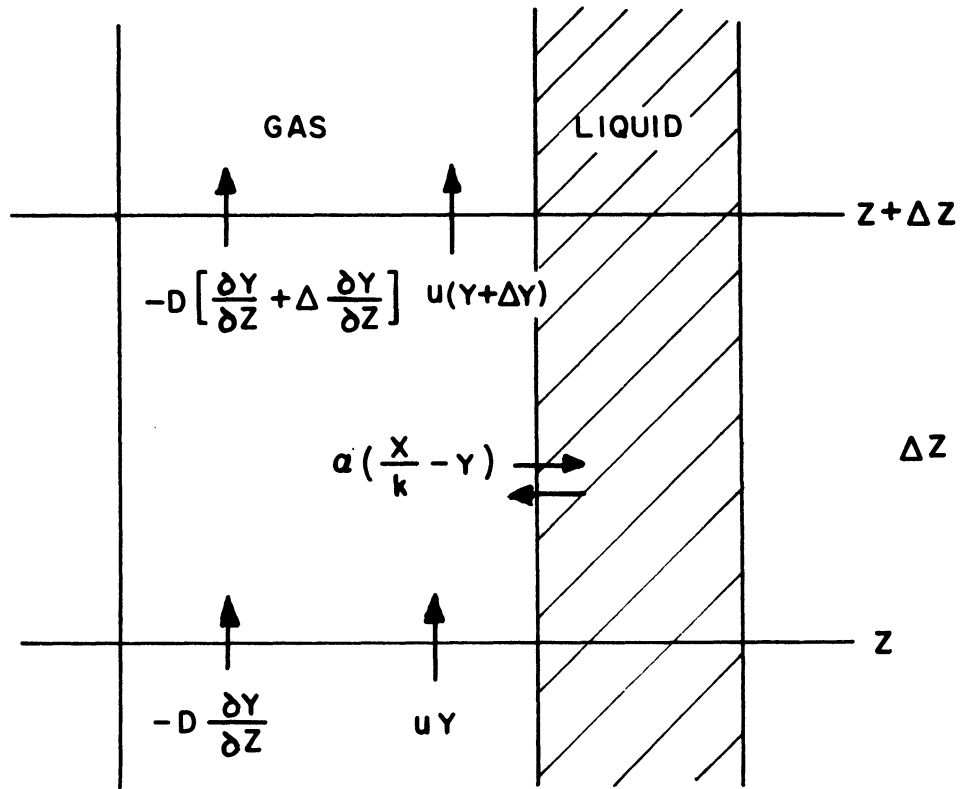


Figure 4. Schematic Diagram Showing Material Balance for the Rate Theory of Chromatography.

In like manner, a material balance for the liquid phase gives:

$$\frac{\partial X}{\partial t} = \frac{\alpha}{F_l} (Y - X/k). \quad (40)$$

Equations (39) and (40) comprise the basic equations of chromatography from the "rate" viewpoint. Solutions are dependent upon the boundary conditions chosen. It is universally assumed that the initial concentration in the column is zero, thus

$$X(0, z) = Y(0, z) = 0. \quad (41)$$

Another common boundary condition is that at the exit of the column, there is no concentration gradient, then

$$\frac{\partial Y(z, L)}{\partial z} = 0. \quad (42)$$

Greater latitude is available in choosing the boundary condition to represent the method of sample injection. Houston uses an impulse function to represent his injection system. Van Deemter uses plug flow:

$$Y(0, t) = \begin{cases} M, & t < t_0 \\ 0, & t > t_0 \end{cases}. \quad (43)$$

His solution to the rate equation is given in the Appendix. The result is:

$$Y(z, t) = \frac{MBt_0}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}} \exp\left\{-\frac{(\frac{z}{\beta} - \beta t)^2}{2(\sigma_1^2 + \sigma_2^2)}\right\}, \quad (44)$$

where

$$\frac{1}{\beta} = 1 + k \frac{F_l}{F_g}, \quad (45)$$

$$\sigma_1^2 = \frac{2Dz}{u^3}, \quad (46)$$

and

$$\sigma_2^2 = 2\beta^2 \frac{k^2 F_l^2 z}{\alpha F_g u}. \quad (47)$$

Van Deemter compares this expression with the one obtained from the plate theory, Equation (21). The result is the well-known van Deemter equation for the Height Equivalent to a Theoretical Plate (H). This derivation is also shown in the Appendix. It is found that:

$$H = A + \frac{B}{v} + C v, \quad (48)$$

where

$$A = 2 \lambda d_p, \quad (49)$$

$$B = 2 \gamma D_{gas} a_v, \quad (50)$$

$$C = \frac{8}{\pi^2} \frac{k'}{(1+k')^2} \frac{d_f^2}{D_{lg} a_v}. \quad (51)$$

The first two terms in the van Deemter equation are a measure of longitudinal diffusion in the gas phase. The first term, A, is the so-called "eddy" diffusion term. It arises from the fact that paths of different lengths are available for use by the gas molecules, so the retention times vary according to the path lengths and band broadening results. As may be seen by examining Equation (49), this "eddy" diffusion term is a function of particle size and λ , a dimensionless parameter which is a measure of packing irregularities⁽⁴⁰⁾, ranging in magnitude from 1 to ~ 10 . The higher λ is, the more irregular the packing.

The second term is a measure of molecular diffusion in the gas phase, which is the second cause of band broadening. It is a function, as Equation (50) will show, of the diffusivity of the solute in the carrier gas and of γ , the "tortuosity" factor. This factor lies between 0.5 and 1 and increases with particle size.

The third term in the equation is the mass transfer term. More correctly, it measures the resistance to mass transfer. With an infinite mass transfer coefficient, this term becomes zero. It is a function of the partition coefficient, the thickness of the liquid coating on the inert support, and the diffusivity of the solute in the liquid phase. (33)

B. Resolution

When we consider a proposed system to be separated, we are interested in the resolution which we can expect to attain under a given set of conditions. Resolution has been defined as the gap or separation between the trailing edge of one peak and the leading edge of the next. (2) If we are dealing with symmetric peaks so that the peak maximum bisects the peak, then we may write:

$$(V_{R_2} - V_{R_1}) = \frac{W_1'}{2} + R + \frac{W_2'}{2}, \quad (52)$$

or

$$R = (V_{R_2} - V_{R_1}) - \frac{1}{2}(W_1' + W_2'), \quad (53)$$

where W' is the volumetric band width expressed in cc's.

When R is zero, the edges of the peaks just touch and the separation is essentially complete. A negative resolution factor indicates overlapping of peaks, while a positive R indicates a finite distance between the edges. It is easy to see that the two factors in resolution are the retention volume and the band width. We shall now define each of these factors, and then consider the variables which affect them.

1. Retention Volume or Partition Coefficient

In most investigations into scientific phenomena it is desirable to seek out the most fundamental of the variables affecting the system. It is also true that as we delve deeper into the study of any phenomenon, the quantities which once seemed to be fundamental are discovered to be only special forms of more basic quantities.⁽¹⁴⁾ Thus in a case familiar to most readers the relationship between current and voltage passing through a wire is given by the formula $E/I = R$. This law of nature is of course Ohms law, and the quantity R , which at the time of its discovery was considered to be a fundamental variable, is known as the resistance of the wire.

However, further investigation has shown that one may replace this "fundamental" quantity by one which takes both the shape of the wire and its temperature into account. The more general expression reads

$$\frac{E}{I} = \frac{\rho_0(1+\alpha T)L}{a_x} ,$$

where L is the length of the wire, a_x its cross-sectional area, T the absolute temperature, and ρ_0 the "specific resistance at zero degrees." Thus it is clear that what started out as a quantity of fundamental importance is in actuality only a highly specialized case of a more fundamental concept. Nevertheless, it should be noted that while the resistance of an object is not the fundamental variable, it is undoubtedly the one which finds the greatest use in problems of a practical nature.

In the field of chromatography it has been pointed out^(51,52) that the fundamental variable is not retention volume as has been often claimed, but the partition coefficient k , which is related

to the retention volume by the equation

$$k = \frac{V_R - V_V}{V_S} . \quad (54)$$

While this is undoubtedly true, it does not affect the general usefulness of the retention volume concept in practical chromatography; and retention volume rather than the partition coefficient will be given primary consideration throughout this dissertation.

a. Partition Coefficient

The partition coefficient as normally defined in gas-liquid partition chromatography is the amount of solute per unit volume of stationary liquid phase divided by the amount of solute per unit volume of mobile phase:

$$k = \frac{x M_s}{y M_m} . \quad (55)$$

It has been shown by Porter to be expressed by the following equation:

$$k = \frac{M_s RT}{\gamma P^0} . \quad (56)$$

From this it may be seen that it is a function of the liquid phase, the activity coefficient, the vapor pressure, and the temperature.

A term often used in discussing chromatography is distribution isotherm or distribution coefficient. The term distribution coefficient is synonymous with the term partition coefficient. The term distribution isotherm refers to a distribution coefficient at a given fixed temperature. This is generally implied in the other two terms also. The distribution coefficient in a general case is dependent on the concentration of solute in the liquid phase.⁽¹¹⁾ In a very specialized

case, however, the partition coefficient is independent of concentration and in this case we see that the isotherm is linear. Linear and non-linear isotherms are pictured in Figure 5. It can be shown that the statement that a distribution isotherm is linear is equivalent to the statement that Henry's law is valid in the region considered. This has generally been found to be the case in gas-liquid partition chromatography.

It is possible to show the effect of temperature upon the partition coefficient. However, there are certain advantages in deriving this relationship for retention volume. This derivation will be given in the following section. It should be noted before leaving the partition coefficient that it is different in nature from the ordinary equilibrium coefficient familiar to many engineers. This is due to the fact that the partition coefficient depends not only upon the vapor pressure of the component under consideration but also upon the nature of the liquid which is the absorbent. Whereas in ordinary distillation two components with equal equilibrium coefficients (i.e., with a relative volatility = 1) can never be separated, it is quite possible to separate such components chromatographically by making a judicious choice of liquid phase; for it may be seen that in chromatography the relative volatility may be expressed by the following equation:

$$\alpha_{A,B} = \frac{k_A}{k_B} = \frac{Y_B P_B^{\circ}}{Y_A P_A^{\circ}}. \quad (57)$$

All that is necessary to obtain a separation is to find an absorbent liquid which leads to differing values of activity coefficients for the two components.

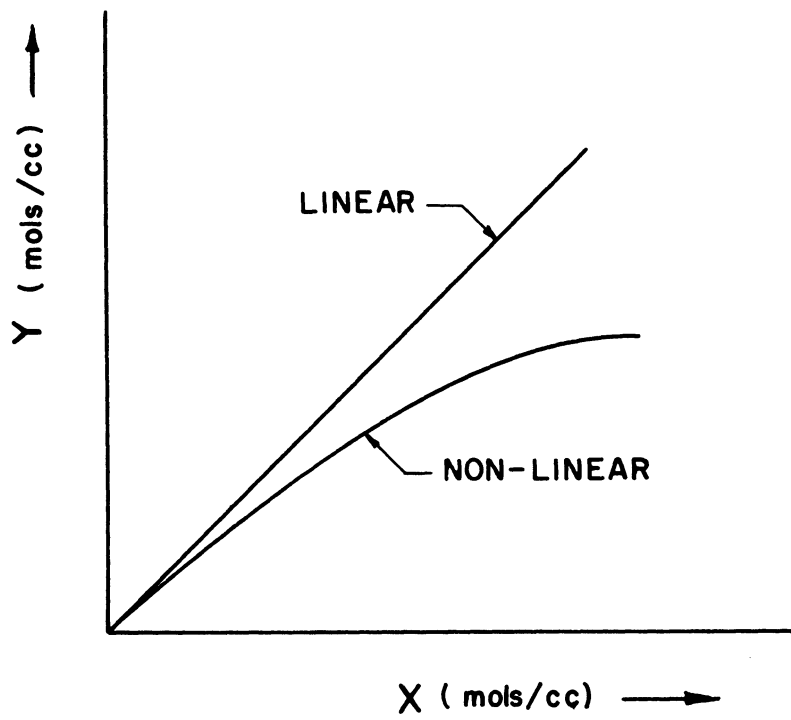


Figure 5. Linear and Non-Linear Distribution Isotherms.

b. Retention Volume

Since retention volume is one of the prime factors considered in this research, it is well to begin the discussion with a careful definition of the term. The retention volume as used here will be taken to be the volume of gas, measured at the average pressure of the column, which has emerged from the column at the time the peak maximum appears, with the starting time taken as the instant of sample injection. Retention volume is related to retention time by the following equation:

$$V_R = \bar{v} t_R, \quad (58)$$

where

$$t = d_r/S \text{ in Figure 2.}$$

In this equation \bar{v} is the average flow rate. It will be shown that the average flow rate is given by the equation:

$$\bar{v} = \frac{3}{2} \phi(r) v_0, \quad (59)$$

where $\phi(r)$ is a function of inlet and outlet pressures.

The use of retention volume has been objected to because to some it seems a rather unreal quantity. While this will not be debated, the advantage of using retention volume instead of retention time cannot be denied since retention time is a function of the flow rate used by each investigator, whereas retention volume is not. Certain investigators have used a quantity referred to as "apparent" retention volume in their investigations. It is defined by the following equation:

$$V_{R(\text{apparent})} = v_0 t_R, \quad (60)$$

where v_o is the flow rate measured at the outlet conditions of the column. For negligible pressure drops through the column the apparent retention volume coincides with the true retention volume. However, since the correction of apparent retention volume is simple to make, there is little advantage to be gained in reporting apparent retention volume as such. For a perfect gas at a constant temperature and under flow conditions where Darcy's law is found to be valid, the following expression for retention volume may be derived:

$$V_R = V_V + \frac{3}{2} \phi(r) \frac{V_o}{S} (d_R - d_o). \quad (61)$$

In this expression V_V is the void volume of the chromatographic column, v_o is the flow rate at the outlet condition of the column, d_R is the distance on the chromatogram from the point of injection to the point of maximum concentration (see Figure 2), d_o is the distance from the point of injection to the maximum point of an oxygen peak, S is the chart speed, and

$$\phi(r) = \frac{r^2 - 1}{r^3 - 1}, \quad (62)$$

where

$$r = (P_i/P_o). \quad (63)$$

It is easy to see from Equation (61) that retention volume is a sum of two quantities--the first being the void space in the column, and the second being the volume which is proportional to the time that an average molecule is held up in the liquid phase as it passes through the column.⁽⁴³⁾ This hold-up is measured in the chromatogram as the lag between the emergence of the sample peak and the oxygen peak. It is converted to a

volume by first dividing by the chart speed and then multiplying by the average flow rate as expressed in Equation (61). The derivation of this retention volume formula may be found in Appendix C.

2. Band Width

In discussing the plate theory of chromatography, we saw that under certain conditions we could express the width of a chromatographic peak as a function of the number of theoretical plates in the column:

$$\omega = 4\sqrt{n'}, \quad (15)$$

and we also observed that ω is given in dimensionless units. Substituting the definition for ω into Equation (15), we arrived at the following result:

$$(V_f - V_i) = 4\sqrt{n'}(V_g + kV_d). \quad (16)$$

$(V_f - V_i)$ expresses the band width as the volume of gas which has passed through the column during the time that the peak is emerging. We would like to express band width as a length since that is the quantity which is actually measured on a chromatogram. We are now in a position to do this. It has been shown that V_R may be expressed by the equation:

$$V_R = V_V + \frac{V}{S}(d_R - d_0). \quad (64)$$

It may be shown that any volume of gas, V , may be expressed by a similar equation where d_R is replaced by the d which corresponds to the desired V . Thus:

$$V = V_V + \frac{V}{S}(d - d_0). \quad (65)$$

Then for $(V_f - V_i)$ we have:

$$(V_f - V_i) = \left[V_v + \frac{\bar{v}}{S}(d_f - d_o) \right] - \left[V_v + \frac{\bar{v}}{S}(d_i - d_o) \right]. \quad (66)$$

And simplifying:

$$(V_f - V_i) = \frac{\bar{v}}{S}(d_f - d_i) = \frac{\bar{v}W}{S}, \quad (67)$$

where W is the band width in cm.

Inserting this expression in Equation (16) we find:

$$W = 4 \frac{S}{\bar{v}} \sqrt{n'} (V_g + kV_b). \quad (68)$$

And since by Equation (14), $V_R = n(V_g + kV_b)$,

we have

$$W = \frac{4SV_R}{\bar{v}} \frac{1}{\sqrt{n'}}. \quad (69)$$

C. Variables Affecting Resolution

Space prohibits a lengthy discussion of all the variables which affect a chromatographic separation. I shall attempt, however, to present briefly some of the more important ones and the effects which they have upon the chromatographic processes.

1. Nature of the Carrier Gas

In general chromatographic work only two or three gases have found widespread uses as the mobile phase. In this country where helium is available, it is the most frequently used. The prime reason for this choice is that the thermal conductivity of helium differs so

much from that of most materials that detection by thermal conductivity devices is simplified. The detection device operates linearly⁽⁵⁷⁾ or nearly so, and thus in many cases it is not necessary to calibrate the thermal conductivity cell to obtain correct results. In addition, helium, being inert, does not react with the other components in the system. In areas where helium is unavailable, nitrogen, hydrogen, and carbon dioxide have been widely used. Hydrogen, with a thermal conductivity even higher than that of helium^(9,46), is acceptable except in cases where it reacts with the material to be analyzed. Nitrogen normally does not have this drawback, but its conductivity is quite similar to certain materials which makes their detection difficult. It has the advantage, however, of having a higher molecular weight; and, as DeWet and Pretorius⁽¹²⁾ have shown, column efficiency is directly proportional to the square root of the density of the gas. Thus nitrogen is actually better than either hydrogen or helium if suitable identification can be made of the components to be separated.⁽⁵⁸⁾ In this research nitrogen was used exclusively with quite satisfactory results. The conductivity cell was calibrated in a manner to be described later, and the calibration curves for the components separated were found to be linear although with differing slopes. Thus any attempt to measure composition by the comparison of areas under the curves would have led to error. Requiring conductivity cell calibration is not a severe deterrent, however, for in any repeated operation it is undoubtedly wise to calibrate anyway.

2. Column Packing

The primary considerations in the choice of a solid support are strength, surface, and particle size. Johns-Manville C-22 fire-brick has proved to be a superior material in these respects.⁽¹⁶⁾ This material packs easily and is much stronger than celite, another commonly used packing. DeWet and Praetorius⁽¹²⁾ have studied the effect of particle size and packing density on column efficiency. Their conclusion was that a particle diameter of approximately .1 mm. led to the highest efficiency. However, the maximum point is not sharply defined since the curve is a rather gradual one. Thus particle size is not of prime importance. In their study of packing densities, however, the curve shows a very sharp break at a density of between .2 and .3 grams/cc. Below a density of .2 grams/cc the curve of HETP vs ρ is almost vertical, while above .3 grams/cc it is horizontal. Therefore, as long as one takes care to stay above this critical density, packing is not a factor. The packing density in this research has been about 0.27 grams/cc.

Care must be taken in packing a column to avoid leaving any gaps or channels in the bed. Description of the author's packing procedure is given in Section III. Johns-Manville Columpak has been the only support used in this research.

3. Absorbent Liquid

The selection of the proper liquid to be used as a fixed phase in a given chromatographic separation remains more an art than a science at the present time. Certain authors give hints as to ways for

making intelligent guesses in choosing liquids. (4,26,34,51,53) However, any final decision must be made on a trail and error basis. We are slightly better off when we come to the matter of the amount of liquid which should be used in the chromatographic column. However, there seems to be a good deal of disagreement in this field as to the exact amount of liquid which should be used to obtain optimum results. (6,12,13,17) The trouble seems to be that each investigator determines the optimum amount of liquid to be used in the particular separation or separations which he has considered. However, this figure does not hold up too well when it is transported to another set of separations. Cheshire and Scott (6) reported that a liquid to solid ratio of 0.05 grams/gram yielded the optimum results in their investigation. DeWet and Praetorius (12), on the other hand, found a ratio of approximately .30 to be the optimum. The amount of liquid which can be used also seems to depend to some degree upon the inert support used. Dimbat (13) reports that Columpak is able to hold a larger amount of liquid than other supports.

In this investigation no study has been made of the effect of liquid phase upon the separation. Diisodecylphthalate (DIDP) has been used as the liquid phase. For the majority of the work a liquid-to-solid ratio of 0.50 grams/gram was employed.

4. Column Diameter

Under ideal conditions the diameter of the chromatographic column should not enter into consideration at all; and if care is taken in packing the column, this is found to be the case [see, however Mellor (45)]. The only reason that column diameter would ever be an important factor would be that above a certain diameter the column could

not be packed uniformly thus leaving channels of low resistance through which the gas could flow freely. If channelling occurs, of course, certain portions of the mobile phase travel at a much greater speed than other portions and the result is a chromatogram in which the peaks are diffuse with rather pronounced tails. With uniform packing the gas travels through a cross-section of the column at a uniform velocity with a much more symmetric peak resulting. All the data presented in this research were collected on columns made out of 1/4 inch copper tubing with an ID of 0.19 inches. A column was prepared using 1/2 inch copper tubing and was used to analyze several samples. The results obtained from this column were compared with the results of a similar analysis using the 1/4 inch column and they were found to be identical. No further work was carried out using the larger column.

5. Column Pressure

The effect of inlet and outlet pressure upon separation is discussed by Keulemans.⁽³⁵⁾ He demonstrates the error in the belief that low pressures tend to increase the speed with which a component of low volatility travels through the column. As he points out, the rate of transportation depends more upon the pressure difference across the column than on the absolute values of the pressures at inlet and outlet. The effect of pressure on separation efficiency is essentially derived from the effect of gas velocity upon separation and this effect will be discussed in the following section.

It will be useful in future derivations to have an expression for the average pressure in a packed bed. Average pressure \bar{P}

is defined by the following equation:

$$\bar{P} = \frac{\int_0^L P dz}{\int_0^L dz}, \quad (70)$$

where P is the pressure at any point in the column and L is the total length of the column. Darcy's law is a statement of the velocity of a gas flowing through a packed bed as a function of pressure gradient and viscosity:

$$v = - \frac{Ka}{\mu} \frac{dP}{dz}. \quad (71)$$

K is the permeability of the bed, a the cross-sectional area, and μ the viscosity of the gas.

If we assume isothermal operation and further assume that the perfect gas law is valid, we may write

$$Pv = P_0 v_0. \quad (72)$$

Combining this with Darcy's law we get:

$$\frac{P_0 v_0}{P} = \frac{-Ka}{\mu} \frac{dP}{dz}, \quad (73)$$

or

$$dz = - \frac{Ka}{P_0 v_0 \mu} P dP. \quad (74)$$

Inserting this expression for dz into Equation (70) we see that

$$\bar{P} = \frac{\int_{P_1}^{P_0} P^2 dP}{\int_{P_1}^{P_0} P dP} = \frac{2}{3} \frac{P_0}{\phi(r)}, \quad (75)$$

where $\phi(r)$ and r are defined in Equations (62) and (63).

It is easy to see by application of l'Hospital's rule to Equation (75) that \bar{P} approaches P_0 as the ratio of pressures approximates one. This result is not completely surprising but is reassuring nevertheless. For low pressure ratios it may be shown that \bar{P} can be approximated by $\frac{P_i + P_0}{2}$ with only a small error.

As we have already seen from Darcy's law, pressure drop through the column provides an approximate measure of the gas flow rate. A curve showing flow rate as a function of pressure for a 20 ft. column at 70°F is shown in Figure 25 in the Appendix. This figure may also be used to calculate flow rates at temperatures other than 70° by making a suitable correction. In practice, however, flow rates were measured directly using a soap film meter, and Figure 25 was used only as an aid in setting the flow rate at a given value.

In this research the outlet pressure of the column has been atmospheric pressure, and the inlet pressure has been varied according to the flow rate desired.

6. Temperature

The effect of temperature on retention volume has been studied by many authors. (19,21,36,43,52) The treatment given here follows Porter. We begin by recalling that the partition coefficient is defined as

$$k = \frac{x M_s}{y M_m} . \quad (55)$$

Once again assuming an ideal gas and in addition assuming Dalton's law we have:

$$P_y = y P^0 , \quad (76)$$

where γ is the activity coefficient, and P° is the vapor pressure of the solute at the given temperature. Then from Equation (76) we see that

$$(x/y) = P/YP^\circ, \quad (77)$$

and so

$$k = \frac{PM_s}{YP^\circ M_m}. \quad (78)$$

Now once again turning to the ideal gas law, we know that:

$$P = M_m RT, \quad (79)$$

so that

$$k = \frac{M_s RT}{YP^\circ}. \quad (80)$$

And since from Equation (54) we have the relationship between V_R and k , we may write

$$\frac{V_R - V_v}{V_s} = \frac{M_s RT}{YP^\circ}, \quad (81)$$

or

$$\frac{V_R - V_v}{T} = \frac{V_s M_s R}{YP^\circ}. \quad (82)$$

We will take the logarithm of both sides of this equation.

$$\ln \left[\frac{V_R - V_v}{T} \right] = \ln(V_s M_s R) - \ln Y - \ln P^\circ. \quad (83)$$

Now from the Clausius-Clapeyron equation:

$$\ln P^\circ = \frac{\lambda}{RT} + \text{constant}, \quad (84)$$

where λ is the latent heat of vaporization.

It may also be shown from thermodynamics⁽²²⁾ that

$$\ln \gamma = \frac{1}{RT} \frac{\partial G^E}{\partial n}, \quad (85)$$

where $\frac{\partial G^E}{\partial n}$ is the partial excess free energy of solution.

When we insert Equations (84) and (85) into Equation (83) the result is:

$$\ln \left[\frac{V_E - V_V}{T} \right] = \ln(V_S M_S R) - \frac{1}{RT} \left[\frac{\partial G^E}{\partial n} + \lambda \right] - \text{constant}, \quad (86)$$

or

$$\ln \left[\frac{V_E - V_V}{T} \right] = \frac{C'}{RT} - C'' \quad (87)$$

7. Gas Flow Rate

The velocity with which the carrier gas moves through the column is a prime factor in determining the separation obtained. In almost all mathematical theories of chromatography it is assumed that the gas passes through the column at a uniform velocity.^(32,42,43,44) This, of course, in any real situation is not the case due to the compressibility of the gas. For this reason in attempting to adapt theory to practice an average velocity or flow rate must be used.⁽²⁴⁾ What this average flow rate is may be seen in the following way: Let t_0 = residence time of a molecule of carrier gas in the column. Then since

$$u = \frac{dz}{dt}, \quad (88)$$

$$t_0 = \int_{z=0}^{z=L} \frac{dz}{u}, \quad (89)$$

or

$$t_0 = \int_0^L \frac{a_v dz}{v}, \quad (90)$$

where a_v is the cross-sectional area of the empty space in the column.

Now for a perfect gas at constant temperature we know that

$$Pv = P_0 v_0 \quad (72)$$

Therefore substituting in Equation (90) for v we see that

$$t_0 = \frac{a_v}{P_0 v_0} \int_0^L P dz, \quad (91)$$

but

$$\int_0^L P dz = \bar{P} L. \quad (92)$$

In a preceding section we saw that

$$\bar{P} = \frac{2}{3} \frac{P_0}{\varphi(r)}. \quad (75)$$

Substituting this in Equation (91) we obtain the result that

$$t_0 = \frac{2}{3} \frac{V_v}{v_0 \varphi(r)}, \quad (93)$$

or rearranging

$$\frac{V_v}{t_0} = \frac{3}{2} v_0 \varphi(r). \quad (94)$$

But by definition the average velocity

$$\bar{v} = \frac{V_v}{t_0}. \quad (95)$$

Thus we see that

$$\bar{v} = \frac{3}{2} \varphi(r) v_0, \quad (96)$$

where

$$\varphi(r) = \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} . \quad (97)$$

This is the result which was given in the discussion of retention volume. Once again it is comforting to note that as the inlet and outlet pressures approach each other, $\varphi(r)$ approaches $2/3$ and \bar{v} approaches v_o .

The effect of gas flow rate on column efficiency may best be seen by considering the van Deemter equation for the Height Equivalent to a Theoretical Plate.

This equation has been presented in the section on the rate theory of chromatography. Repeating it here for reference we write:

$$H = A + \frac{B}{\bar{v}} + C\bar{v}, \quad (48)$$

where \bar{v} is the average flow rate as expressed in Equation (96), and A, B, and C are constants for a given system.

Since the HETP is a measure of column efficiency, we may determine the effect of gas flow rate on column efficiency by studying this equation. To be more specific, column efficiency is directly proportional to $1/H$. Thus we seek to minimize the value of H in the van Deemter equation. This minimum value occurs when $\bar{v} = \sqrt{B/C}$ at which point $H = A + 2\sqrt{BC}$. Due to the velocity gradient in the column, there can only be one point in the column which is operating at optimum efficiency. However, it should be safe to say that choosing the average velocity close to the optimum value would provide close to the best efficiency obtainable. The effect of gas flow rate on efficiency may be demonstrated in another way. Let us consider the relationship between

band width and flow rate. It has been shown that band width is given by the formula:

$$W = \frac{4SV_R}{\bar{v}} \frac{1}{\sqrt{n}}, \quad (69)$$

where n = number of theoretical plates, V_R is the retention volume, S the chart speed, and \bar{v} the average flow rate. In expressing band width in this form we have assumed that the gas flow through the column is constant, that complete equilibrium is obtained on each theoretical plate, that the sample is injected in such a narrow band that it occupies only the first theoretical plate, and that the distribution isotherm is linear.

We may relate band width to the van Deemter equation by noting that the definition of HETP is:

$$H = \frac{L}{n}. \quad (98)$$

Therefore:

$$W = \frac{4SV_R}{\bar{v}} \sqrt{\frac{H}{L}}, \quad (99)$$

or

$$W^2 = \frac{16S^2V_R^2}{L\bar{v}^2} H = \frac{16S^2V_R^2}{L\bar{v}^2} \left(A + \frac{B}{\bar{v}} + C\bar{v} \right). \quad (100)$$

In its final form then we see that W^2 is a rather complicated function of average velocity as expressed in Equation (100). Further discussion of this equation will be deferred until the data are presented and discussed.

8. Sample Injection

A number of different methods of sample injection have been studied by various investigators.^(8,23,52,56) The ideal method of sample injection is one which would cause the sample to enter the column in an infinitesimally small volume and consequently with an infinitely higher concentration. The mathematics for this case have been worked out by Houston⁽²³⁾, who expressed the injection as an impulse function. Houston's derivation is based on the Lapidus-Amundson rate theory of chromatography.⁽⁴²⁾ Porter, Deal, and Stross⁽⁵²⁾ derive equations starting with a plate theory and using both plug flow injection and exponential decay injection. They show that for plug flow the resulting chromatogram is symmetric. In the case of perfect mixing a chromatogram is unsymmetric, having a long tailing edge.

Sample size, as well as the method of sample injection, is a factor affecting chromatographic separation. Porter's equation takes sample size into account. No analytical expression can be derived showing the effect of sample size on bandwidth, but by calculating a series of chromatograms the effects may be shown graphically. Results of calculations of this type will be presented along with the data for the effect of sample size on bandwidth.

III. EXPERIMENTAL APPARATUS AND MATERIALS

A. Apparatus

The experimental apparatus is shown in Figures 1, 6, 7, 8, and 9. The main components in the system are the following.

1. Column

The column is made from standard 1/4" copper tubing with 0.03" walls. It is packed with crushed firebrick coated with diisodecylphthlate (DIDP). The packing is accomplished in the following manner: First, a small piece of glass wool is inserted in the end of the tube to hold the packing in place. Then, the column is suspended in a vertical manner so that the packing may be poured in. The coated firebrick is poured into the column until it fills about the bottom six inches. The column is then vibrated vigorously in order to pack the firebrick in place. More firebrick is added and the process is repeated until the column is filled. Finally, another portion of glass wool is placed in the inlet of the column, completing the packing. The packing density is approximately 0.3 gm/cc, and the percent voids is approximately 73.5%. The column may then be coiled by wrapping it around a cylinder of appropriate diameter. This coiling is of course not necessary, but for long columns it is quite convenient; and it in no way affects the operation of the column as long as care is taken not to crimp the tube while bending it.

2. Temperature Bath

The column is placed in a constant temperature bath in order to assure isothermal operation. The bath is composed simply of a

large Dewar flask filled with water and covered by a slab of styrafoam. This was found to hold the temperature to $\pm 0.1^{\circ}\text{F}$ for the temperature range considered.

3. Thermal Conductivity Cell

The cell used was a Gow-Mac, model TR2B thermal conductivity cell with a Gow-Mac Power Pack, Model 9293-B as the constant current source. This cell is the heart of the detection system. It is a balanced Wheatstone bridge type, depending on changes in thermal conductivity for its source of EMF. It is shown schematically in Figure 6. Many authors have discussed the factors affecting the sensitivity of a thermal conductivity cell. (9,20,45) A partial bibliography on this subject is given by Juneau. (27)

4. Recorder

A Brown Recorder was used to plot the output of the conductivity cell as well as to operate the switching system to be described later. The instrument used is a 7.9 mv recorder with mercury switch controllers. The output of the conductivity cell was fed directly into the recorder, thus giving a direct reading at all times of the voltage generated by the cell.

5. Flow Rate Meter

A soap film meter was used to measure volumetric flow rates at the column outlet conditions. (24,37,49) This apparatus, shown in Figure 7, consists of a 100 ml. buret adapted so that a film of soap may be placed across it. By raising or lowering the soap reservoir, the

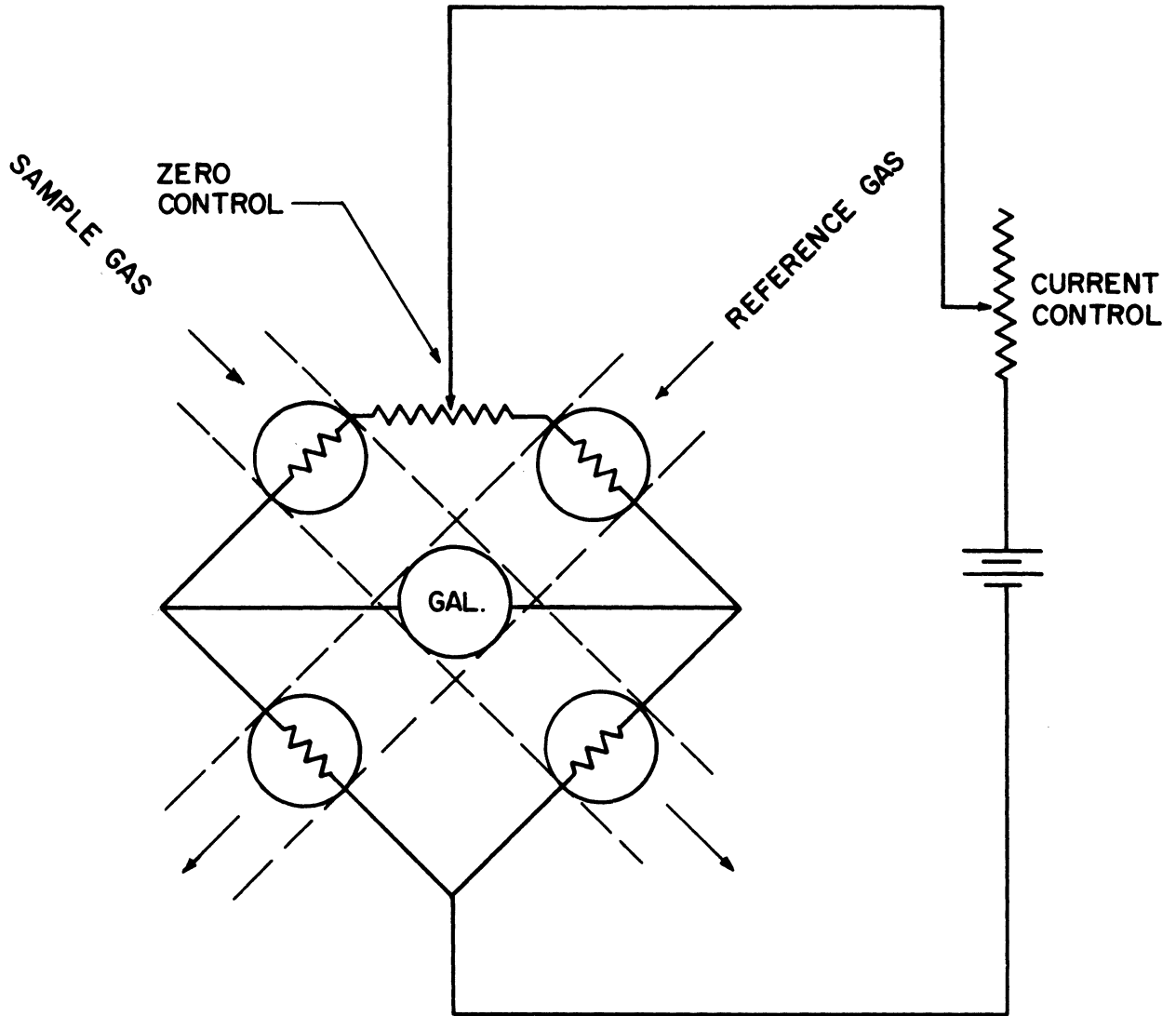


Figure 6. Schematic Diagram of Thermal Conductivity Cell.

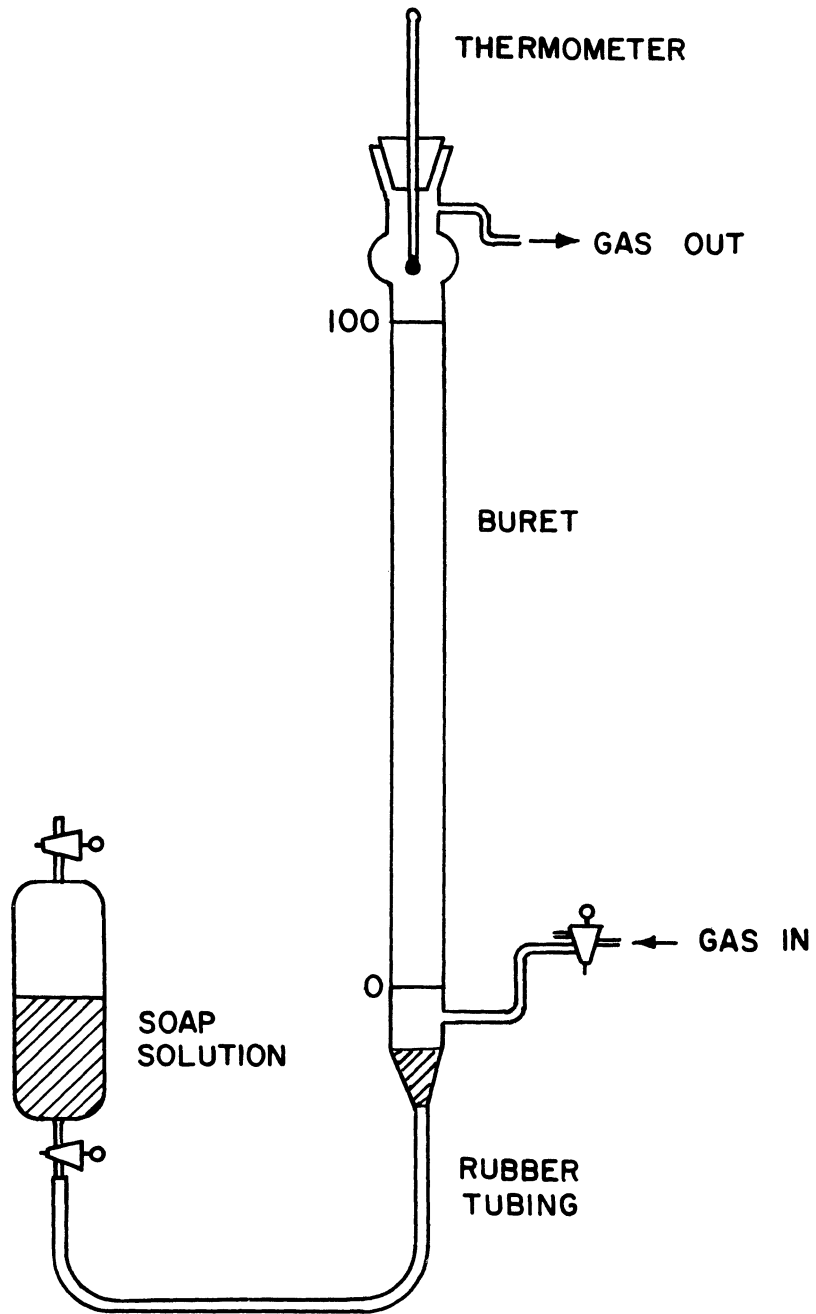


Figure 7. Schematic Diagram of Soap Film Meter.

level of liquid soap may be adjusted so that it is just below the gas inlet opening. Then by squeezing the rubber tubing, the level may be raised enough to cover the opening causing a soap bubble to form. The gas stream carries the bubble up the buret. Measuring the time taken for the bubble to move a given volume gives a very accurate measure of flow rate. Rates accurate to within $\pm 0.5\%$ are easily obtainable. The device is equipped with a thermometer in the top so that a temperature correction may be made. Ordinary liquid soap of the type normally found in public washrooms was quite satisfactory in this service. Once the walls of the equipment were wetted, no difficulty in bubble breakage was encountered.

6. Solenoid Valves

Two three-way solenoid valves, model 8300, were obtained from the Automatic Switch Company. The first valve, used to introduce sample into the column, was equipped with two inlets and a single outlet. When sensitized, the gas flowed in one inlet; when desensitized, in the other. In both cases the gas exited in the same place. The second valve was used as part of the automatic switching system. It was equipped with a single inlet and two outlets. The maximum operating pressure for each of these valves was 40 psig.

7. Timer

A Flexopulse repeat cycle timer was obtained from the Eagle Signal Corporation. The timer has independently adjustable off and on times which may be varied from 0 to 5 minutes continuously.

8. Switching System

The switching system is used to activate the three-way solenoid valve which shunts the column effluent to the appropriate condenser. The author wishes to acknowledge the tremendous assistance given him by Mr. Eric Aupperle in the design and construction of this switching system. The design is solely his. He also checked the completed system and offered valuable advice on its most efficient use.

The circuit is commonly called a Flip-Flop circuit. It is activated by the impulse generated by the closing of a mercury switch. A circuit diagram is shown in Figure 9. The apparatus causes the relay leading to the solenoid valve to close every other time the mercury switch changes state. This gives the type of switching desired.

The equipment includes a neon bulb which switches with the relay to indicate which state the system is in.

B. Materials

1. Column Packing

Johns-Manville Columpak was used as the solid phase in all experimentation. This material is crushed firebrick with a particle size of from 30 to 60 mesh. In some instances the Columpak was screened further to reduce the number of fines in the packing. When this second screening was done the particle size was from 35 to 40 mesh with an average particle diameter of 0.046 cm.

2. Absorbent Liquid

Diisodecylphthalate (DIDP), generously supplied by the Monsanto Chemical Company, was used as the liquid phase in this research. It has a molecular weight of 414 and a density of 0.961 gm/cc at 26°C.

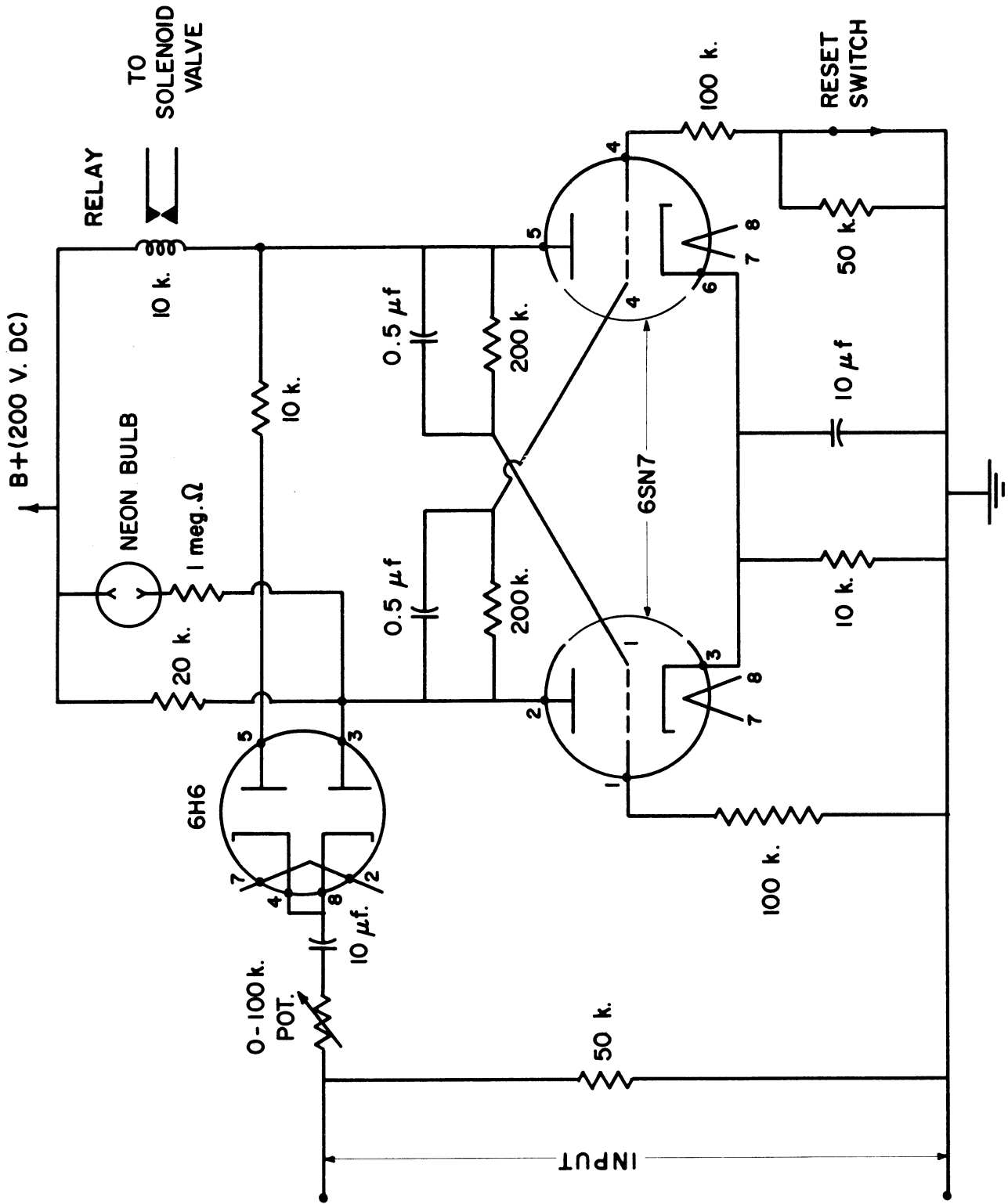


Figure 8. Schematic Wiring Diagram for Automatic Switching System.

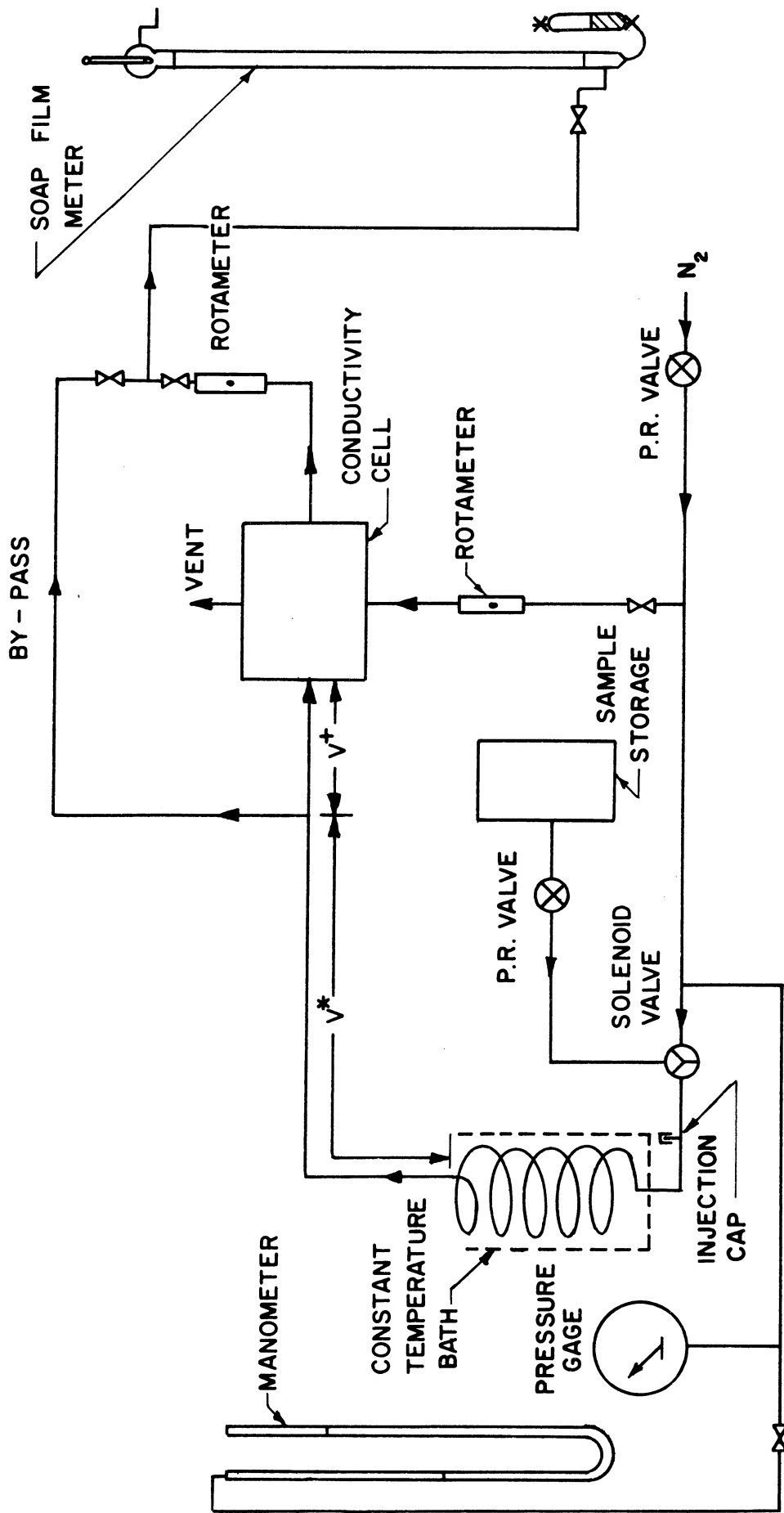


Figure 9. Schematic Diagram of Equipment with Gas Flow Indicated.

The DIDP was coated on the firebrick in the following manner. The liquid-to-solid ratio to be used was selected. Then the Columpak to be used was weighed, and from this weight and the (L/S) ratio, the weight of DIDP to be used was determined. From this number and the known density of DIDP, the volume of DIDP to be used was calculated. This volume of DIDP was poured into a beaker together with enough acetone to give an initial (L/S) of about 2.4 cc/gm. The Columpak was poured into the mixture of acetone and DIDP. The slurry was thoroughly mixed to make sure that all the firebrick had been contacted by the DIDP. It was then placed on a hot plate where the excess acetone was boiled off. After this preliminary drying, the beaker was placed in an oven at 150°C to drive off the last traces of acetone. The dried firebrick was finally screened to remove any fines and lumps which might have been formed during the coating process. It was then ready for use.

The coated firebrick still poured freely, and to all outward appearances was dry. It could be distinguished from the uncoated Columpak only by its slightly darker color.

3. Carrier Gas

The inert gas used in this research was water-pumped nitrogen with a minimum purity of 99.6 mol percent. Its thermal conductivity, as reported by Perry⁽⁴⁶⁾, is 0.0180 Btu/hr-ft²-(°F/ft) at 212°F. The reported values for normal and isobutane at this same temperature are 0.0135 and 0.0139 respectively.

4. Sample Gases

Commercial grade iso and normal butane, obtained from the Phillips Petroleum Company, was used in this research. The purity of

these samples was reported as 95 mol percent minimum purity. The impurities in the normal butane are isobutane and propane. In the isobutane the impurities are normal butane and propane.

IV. EXPERIMENTAL PROCEDURE

A. General Description

For all experimental runs the procedure outlined below was followed. The conductivity cell was allowed to reach its equilibrium temperature before any run was made. This temperature was measured by a thermocouple in the heating block of the cell and was recorded by the Brown Recorder. This equilibrium temperature was 225°F, and it was found that from one to two hours were required to reach this temperature. The rate of carrier gas flow was also allowed to come to equilibrium before any data were taken. Normally five minutes was sufficient to accomplish this. Flow rates varied from 12 to 780 cc/min at outlet conditions. When changing flow rates, care was taken to allow the column and conductivity cell to adjust to the new rate before a run was started.

While the conductivity cell temperature and the flow rate were coming to equilibrium, the constant temperature bath was regulated to the chosen value. When changing bath temperatures a short period of time was allowed to permit the column to adjust to the new temperature in the bath. Before each run the following data were recorded: flow rate at the outlet conditions of the column, column temperature, inlet pressure of the carrier gas, and atmospheric pressure.

The normal flow of gas during a run is shown in Figure 9. Nitrogen controlled to a constant pressure by a two-stage pressure reducing valve enters the system where it is divided into two streams. The first stream passes through a control valve and a rotameter and into

the reference side of the conductivity cell. This flow is controlled as close as possible to 50 cc/min unless the flow through the sample side of the conductivity cell is less than 50, in which case the reference gas flow is adjusted to match the sample flow rate. The remaining portion of the nitrogen stream enters the solenoid valve. A side tap immediately in front of this valve leads to both a manometer and a pressure gage. For high flow rate operation (i.e., pressure greater than 12 psig) the manometer is valved off and the pressure gage used for all pressure measurements. For low pressures, the valve is opened, and the manometer furnishes the inlet pressure measurement. The nitrogen passes through the solenoid valve in its normal (desensitized) state and enters the column which is submerged in the constant temperature bath. After passing through the column, the nitrogen passes up to the sample inlet of the conductivity cell, where it is split again. The flow through the conductivity cell is regulated to 50 cc/min in order to balance the flow of reference gas. The excess flow by-passes the conductivity cell. After the gas containing the sample passes through the conductivity cell it goes through a rotameter where it is metered and then is reunited with the gas which had by-passed the conductivity cell. This combined flow is sent to the gas film meter where the total flow rate is measured.

B. Injection Technique

Two methods of injection were used in this research. The first, injection using a hypodermic syringe, was used to obtain data on retention volume and effect of flow rate on band width. The second, injection using the three-way solenoid valve, was used to study the effect of sample size on band width.

1. Hypodermic Injection

Injection with a hypodermic needle was made through a serum cap situated at a position approximately two inches above the packed section of the column. The hypodermic needle was inserted to a point roughly in the center of the stream of carrier gas. The injection was made by rapidly depressing the plunger over a period of time not exceeding one second. This method of injection is felt to be highly reproducible and approaches plug injection as closely as possible. Elution peaks resulting from this type injection are quite symmetric and hence are highly suited for retention volume measurements. No alteration in the flow system outline above was made by these hypodermic injections.

2. Solenoid Valve Injection

For the study of the effect of sample size on band width, larger samples were required than could easily be obtained by using a hypodermic. For this reason injection was made using a three-way solenoid valve. The normal flow through this solenoid valve was such that when desensitized, the carrier gas passed through the valve into the column. The valve was activated by the Eagle timer described in the previous section. When this took place, the flow of carrier gas was shut off and the sample flowed from the tank containing it into the column. The pressure of the sample gas was regulated by a pressure reducing valve to a value slightly higher than the inlet pressure of the column. This prevented the possibility of a back flow when the solenoid was activated. When once again the solenoid was desensitized, the sample

flow was cut off and the flow of carrier gas resumed. This type injection tends to give elution peaks which are highly unsymmetric, having rather pronounced tails.

C. Cyclic Separation System Operation

It has been pointed out in the introduction that from its very nature a chromatographic separation process cannot be made to operate continuously. The next best thing to continuous operation is a cyclic process. This offers no special difficulties. Two problems must be solved. The first is the spacing of sample injections so as to prevent overlapping between successive samples. The second is isolating the separated products that emerge from the column. The proposed solutions to these two problems will now be discussed. A similar solution is given by Ambrose and Collerson.⁽¹⁾

1. Sample Injection

This problem is relatively simple. The parameter of interest is the time from the beginning of the first peak to the end of the last one. This time may be calculated, knowing retention volumes, band widths, and flow rates; or it may be experimentally determined. Once it is known, it gives the length of time between injections necessary to just prevent overlapping. A longer time would leave a gap between the final peak of one injection and the initial peak of the following one. This, of course, would lower the amount of sample separated.

The timing of the injections was done by the Eagle timer described in Section III. The setting of the on arm of the timer determined the sample size. The off setting fixed the length of time between injections.

2. Separated Products Channelling

The components of the sample are separated when they emerge from the column. It is necessary, however, to isolate each component and remove it from the carrier gas stream. The switching system used to isolate the components is operated, naturally enough, by a mercury switch on the Brown recorder plotting the elution history. The switching system which was used was designed to separate a binary mixture, but it is easy to see the manner in which it could be extended to an n-component system.

The Brown recorder used was equipped with a variable mercury switch which could be set to make contact when the recorder pen passed any given point of the graph. This controller was set just above the base line which the pen drew when no sample was being eluted. Thus when a component began to emerge from the column, the pen rose causing the mercury switch to make contact. The contact was maintained until the pen returned to a point below the controller setting at which time the contact was broken. This was repeated for each successive peak that emerged.

When the mercury switch made contact, it sent a small electrical impulse to the input of the switching system described in Section III. This impulse caused the switching system to activate the relay, causing it to close the circuit which operated the three-way solenoid valve. The solenoid valve, being activated, shunted the carrier gas containing the first component into condenser 1 where the sample was separated from the carrier gas by condensation. The flow to this condenser continued until the second peak started to emerge from the column,

at which time the new impulse caused the relay to open, breaking the circuit and desensitizing the solenoid valve. The carrier gas then passed into condenser 2 where the second component was removed from the carrier gas.

V. EXPERIMENTAL MEASUREMENTS

A. Flow Rate Measurements

Flow rate was normally measured by the soap film meter previously described. In a typical measurement a stop watch was used to determine the time necessary for a soap bubble to travel the length equivalent to 100 cc. The temperature of the gas passing through the soap film meter was measured by the thermometer located near the top of the meter. The flow rate at the outlet conditions of the column could then be calculated using the following formula:

$$v_o = \frac{6000}{t} \left(\frac{T_c}{T_s} \right) \left(\frac{P_s}{P_o} \right), \quad (101)$$

where T_c is the column temperature, T_s is the temperature measured at the soap bubbler, P_s is the pressure of the gas at the soap bubbler (atmospheric), P_o is the pressure at the outlet of the column, and t is the time required for a bubble to move 100 cc. Flow rates varied from 12 to 778 cc/min measured with an accuracy of $\pm 0.5\%$.

B. Column Temperature Measurements

The temperature of the column was assumed to be essentially the same as that of the constant temperature bath. This temperature was recorded by a standard total immersion mercury thermometer. Bath temperature was held constant to $\pm 0.1^\circ\text{F}$ over a temperature range from 59 to 157°F.

C. Pressure Measurements

Outlet pressure of the column in all instances was atmospheric pressure and this pressure was measured by a Cenco Scientific barometer.

Inlet pressures under 12 psig were measured by a 30 inch mercury manometer. Inlet pressures greater than 12 psig were measured by a Marsh 0-100 psig pressure gage which was calibrated against a dead weight tester. A calibration curve for this gage is shown in Figure 26 in the Appendix.

D. Void Volume Measurement

The measurement of void volume, i.e., the void space in the column, was accomplished in the following manner. The column to be measured was removed from the apparatus and fitted with a valve on one end and a piece of rubber tubing with a pinch clamp on the other end. Closing the pinch clamp and opening the valve, the column was filled to a given pressure with nitrogen, after which the column was connected to the mercury manometer and the valve opened. When the mercury in the manometer came to rest, the valve was once again closed and the mercury level read, affording an accurate measure of the nitrogen pressure in the column. The column was then connected through the rubber tubing to the soap film meter, in which a soap bubble had been previously positioned. Upon opening the pinch clamp, the nitrogen gradually escaped from the column forcing the soap bubble to rise. The difference in the soap bubble's initial and final positions gave an accurate measurement of the volume of nitrogen leaving the column. The pressure in the column was allowed to drop to atmospheric conditions. Thus the pressure of the gas leaving the column, the volume of gas leaving the column, and the initial and final pressures in the column were all known. From these data the total volume of the column plus the attached valve could be calculated.

The derivation of the equation for void volume is short and will be given here. In this derivation nitrogen is assumed to be an ideal gas under the prevailing conditions. Figure 10 shows a schematic diagram of the experimental arrangement.

The total volume of the apparatus, V_T , may be written:

$$V_T = V_V + V_1 + V_2. \quad (102)$$

From the perfect gas law:

$$P_i V_T = n_i RT, \quad (103)$$

and,

$$P_f V_T = n_f RT. \quad (104)$$

Subtracting Equation (104) from (103):

$$(P_i - P_f) V_T = (n_i - n_f) RT = n_{out} RT, \quad (105)$$

where n_{out} is the amount of gas leaving the column.

Now for this gas leaving we know:

$$P_{out} V_{out} = n_{out} RT. \quad (106)$$

Combining (106) and (105) we get:

$$P_{out} V_{out} = (P_i - P_f) V_T, \quad (107)$$

or

$$V_T = \frac{P_{out} V_{out}}{P_i - P_f}. \quad (108)$$

And finally from the definition of V_T :

$$V_V = \frac{P_{out} V_{out}}{P_i - P_f} - V_1 - V_2. \quad (109)$$

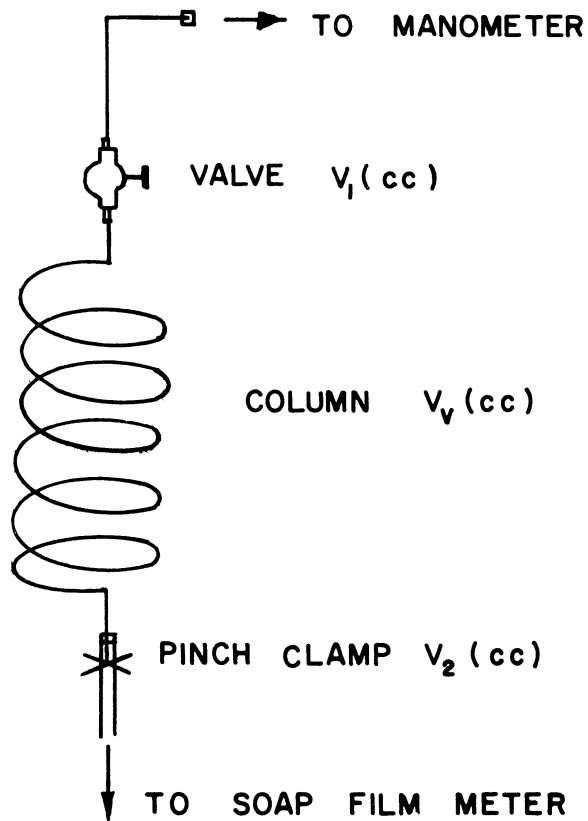


Figure 10. Schematic Diagram of Column During Void Volume Measurement Showing Volumes Involved.

The volume contained by the valve and its connections (V_1) was measured by removing the valve from the column, closing it, and injecting a measured amount of water from a hypodermic syringe into the valve. This volume was then subtracted from the total volume measured to obtain the void volume of the column. The volume occupied by the pinch clamp (V_2) was assumed to be negligible. This procedure resulted in an accuracy of $\pm .4\%$. The data for the void volume calculations are presented in Table I.

E. Sample Size

1. Hypodermic Injection

When using a hypodermic syringe to make the sample injection, the sample volume was simply taken to be the volume read on the syringe. The pressure was atmospheric, and the temperature was room temperature. Upon injection, the pressure was essentially the inlet pressure of the carrier gas.

2. Solenoid Valve Injection

When the sample was injected by this means, there was no direct method for measuring the sample size. However, assuming the conservation of mass, we can determine the sample size from the size of the elution peaks, if suitable calibration is made. The calibration of the conductivity cell is described in a later section.

In order to determine the size of the sample from the calibration curves, it is necessary to know the fraction of the carrier gas which passes through the conductivity cell (f). Knowing this number, the total sample may be determined as follows:

$$F = A/f, \quad (110)$$

TABLE I
VOID VOLUME DATA

<u>Column No. 6 (L ~ 20 Ft.)</u>						
Run No.	P _i ("Hg)	P _f ("Hg)	P _{out} ("Hg)	V _{out} (cc)	V _T (cc)	V _V (cc)
1	21.21	0	28.63	61.2	82.6	81.7
2	26.00	0	28.63	75.8	83.5	82.6
3	23.36	0	28.86	67.2	83.1	82.2
4	19.56	0	28.86	56.2	83.0	82.1

<u>Column No. 6' (L ~ 10 Ft.)</u>						
1	8.06	0	29.25	11.8	42.8	41.9
2	10.15	0	29.25	14.1	40.6	39.7
3	8.02	0	29.25	11.05	40.3	39.4
4	12.28	0	29.55	16.9	40.7	39.8
5	20.80	0	29.55	29.4	41.7	40.8
6	22.30	0	29.55	31.5	41.7	40.8

<u>Column No. 6" (L ~ 5 Ft.)</u>						
1	26.41	0	29.55	19.55	21.8	20.9
2	22.94	0	29.55	16.9	21.8	20.9
3	18.68	0	29.55	14.05	22.2	21.3
4	24.59	0	29.55	18.4	22.1	21.2
5	12.64	0	29.55	9.3	21.7	20.8

where F is the total sample size, and A is the size of the sample passing through the conductivity cell as measured on the calibration curve.

It is possible to find f in two ways. The first is the simplest. A measured sample of air is injected into the column using a hypodermic. The amount of air which passes through the conductivity cell may be determined from the air calibration curve, Figure 27. Knowing F and A we can calculate f from Equation (110).

The second method for determining f depends upon a knowledge of the volumetric capacity of two sections in the system. By examining Figure 10, it may be seen that the volume of the tubing from the column outlet to the by-pass around the conductivity cell is V^* . The volume from this by-pass to the sensing elements of the cell is V^+ . If we call the gas flow rate through the cell v_a , and assume that the pressure drop from the outlet of the column to the cell is negligible, then we may write the following expression for the carrier gas residence time:

$$\tau_o = \frac{d_o}{S} - \left(\frac{V^*}{v_o} + \frac{V^+}{v_a} \right), \quad (111)$$

where the quantity in parentheses represents the time taken by the gas in going from the column outlet to the conductivity cell. We also know from Equation (93) that

$$\tau_o = \frac{2}{3} \frac{V_v}{\phi(r) v_o}. \quad (93)$$

Then equating these two results, we have

$$\frac{d_0}{S} - \left(\frac{V^*}{v_0} + \frac{V^+}{v_a} \right) = \frac{2}{3} \frac{V_V}{\phi(r) v_0} \quad (112)$$

or

$$V^+ (v_0/v_a) = \frac{v_0 d_0}{S} - \frac{2}{3} \frac{V_V}{\phi(r)} - V^* \quad (113)$$

But

$$(v_a/v_0) = f \quad (114)$$

Therefore,

$$f = V^+ / \left[\frac{v_0 d_0}{S} - \left(\frac{2}{3} \frac{V_V}{\phi(r)} + V^* \right) \right] \quad (115)$$

Using Equation (115) we have an independent check on the f obtained by the air injection method. Notice that in both cases, though, an air injection must be made. While the two methods are in essential agreement, it is felt that the first method is the more accurate.

F. Quantities on the Chromatogram

A number of measurements are made directly from the elution diagram. These include band width, retention time, peak height, and sample size in some cases. Referring now to the typical chromatogram shown in Figure 2, we shall describe these and other quantities.

The elution diagram is a plot of the concentration of a sample in the column effluent vs time (or distance along the chart which is proportional to time). When using a thermal conductivity cell as a detection device, it should be understood that the quantity measured is not concentration as such, but rather millivolts generated by the conductivity cell. This out-of-balance bridge voltage is directly proportional

to the change in thermal conductivity⁽⁹⁾ which in turn is directly proportional to concentration⁽³⁸⁾ in the low concentration range of gas chromatography.

The first quantity of interest on the elution diagram is the distance from the injection point 0 to the air peak, d_0 . This distance gives the residence time of the carrier gas in the column. Multiplying this number by the average flow rate gives the gas hold-up or void volume of the column.

The retention time is given by the distance d_{R1} for component 1 and d_{R2} for component 2. The points d_{R1} and d_{R2} are located by dropping a perpendicular from the peak maximum. The intersection of this line with the base line gives the point d_R . Once again, multiplying the retention time by the average flow rate gives the retention volume, V_R .

The quantity $(d_R - d_0)$ is found to be a useful one. It is called by some authors⁽⁴³⁾ the "apparent retention time." It is a measure of the time which the sample spends in the liquid phase of the column.

There are two different "band widths" used in this paper. The first, W , is used when the chromatographic peaks are roughly symmetric like those shown in Figure 2. For component 1, $W_1 = B - A$; and for component 2, $W_2 = D - C$. To find the values of A, B, C, and D the following procedure is used. The approximate inflection points on the peaks are located. The exact location is not necessary since for these peaks the sides are steep and almost straight. Tangents are constructed at these inflection points.⁽¹⁰⁾ The intersections of the tangents and the baseline give the points A, B, C, and D.

The second band width, b , is used when the peaks are asymmetric. In this case, while the initial edge is quite steep, the tailing edge is much shallower and usually curved. This makes the location of the inflection point quite important and it also means that a considerable portion of the peak will lie outside this tangent. For these reasons, it is felt that a more accurate picture of band width is given by defining it as the distance AB' where A is the same as before and B' is the point of intersection of the tailing edge and the baseline.

The last measurement of interest is peak height. This is simply the perpendicular distance from the peak maximum to the base line.

As a final remark, the author is aware that he has sometimes used the term "distance" and sometimes the term "time" in referring to the quantities discussed. This should not be confusing to the reader. Since the chart moves at a constant speed, S , distances on the graph are related to times by the expression $t = d/S$.

General practice is followed in selecting the term used. Thus it seems more natural to refer to retention time than to retention distance, though the latter would be wholly acceptable. In like manner band width is spoken of rather than band time, and peak height rather than peak concentration maximum.

G. Retention Volume

From the theoretical background it has been shown that calculation of retention volume involves the knowledge of pressure, speed, flow rate, void volume of the column, and the difference in peak maximum location and air elution peak. The Brown Recorder chart speed was

measured over a 15 minute interval and was found to be 1.02 cm/min \pm 0.004. The measurements of the location of the peak maximum and the location of the air peak were made by dropping a vertical line from the point of maximum height to the base line of the curve. The distance of this line from the point of injection was then measured and recorded in centimeters. This measurement may be taken to be accurate to \pm .1 cm.

H. Band Width Measurement

1. Band Widths Resulting from Hypodermic Injections

When injection was made using a hypodermic syringe, highly symmetric peaks resulted. Reproducible results could thus be obtained for band widths by locating approximate inflection points on the elution peak and constructing tangents at these points which extended to the base line of the chromatogram. The intersection of tangent and base line gives an outer limit to the band width, and the difference between these two intersections is a measure of the band width. This number was measured and recorded in centimeters. It should be pointed out that this procedure is feasible only with symmetrical peaks and with peaks whose sides are fairly straight so that an accurate tangent might be obtained.

2. Band Widths Obtained from Solenoid Valve Injection

When injection was made using the solenoid valve, it has already been pointed out that the resulting peaks were highly unsymmetrical. While the initial edge of the peak was fairly straight, the tailing edge was quite curved and no accurate placing of a tangent line could be made. For this reason, the procedure outlined above could not be

followed for obtaining band width, and an alternate procedure was used. The width of the band was taken to be the distance from the intersection of the leading edge tangent with the base line to the point at which the tailing edge of the curve intersects with the base line. This method, while not so accurate as that outlined under 1, has been found, nevertheless, to be reproducible and to give relatively accurate results.

I. Conductivity Cell Calibration

In order to calibrate the conductivity cell response, samples of known volume were injected into the column which was operated at 70°F and at flow rates low enough for all the gas to pass through the cell. Then the areas under the curves of the resulting peaks were plotted against the known sample size.

This process is completely straightforward if pure samples are injected. However, since the samples used were commercial grade normal and isobutane, a slight complication was added to the computation of the calibration curve. The samples were approximately 96% pure with the remaining 4% composed mostly of the other component plus a little propane. In addition to these impurities, there was normally a small amount of air injected with each component. Thus, any sample injected resulted in four distinct peaks, although sometimes some of them were too small to measure.

The method followed in the calculation was essentially one of trial and error. An air calibration curve had been made so the volume of air in the sample could be subtracted from the total sample size. This air calibration resulted in a straight line plot given by the equation:

$$A_{air} (cc) = 0.33 h_{air} (cm). \quad (116)$$

After the air volume had been removed from the total sample size, a rough calibration curve was drawn for the normal butane, assuming that the isobutane in the sample gave essentially the same response as the normal. This assumption is not correct, but it gives a good first approximation to the normal butane curve.

This calibration curve for normal butane was used to determine the amount of that component in the isobutane samples. Then for the initial isobutane approximation the volumes of air and normal butane were subtracted. This gave a fairly accurate calibration curve for the isobutane. This curve was then used to determine the amount of isobutane in the normal butane samples and that permitted a corrected sample size to be determined. Then a new calibration curve for normal butane was drawn. This process was repeated until no further change resulted in the calibration curves. The final curves are shown in Figure 27 in the Appendix. The data are presented in Table VIII.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A. Retention Volume as a Function of Temperature

Data showing the effect of temperature on retention volume is presented in Table II. These data were taken on a 20 foot column over a temperature range of from 59 to 157°F. Additional data for a number of runs at 70°F are presented in Table III. In all runs the size of the sample was held at a constant value of approximately 1 cc of each component at atmospheric pressure and at 70°F. Thus the effect of sample size was eliminated from this study. As has been shown in the theoretical background, retention volume should plot roughly as a straight line against reciprocal temperature on semi-logarithmic paper. Figure 11 shows the data plotted in this manner. The equations for these curves are as follows:

$$I-C_4 \quad \log_{10} V_R = \frac{688}{T} + 1.129 \quad (117)$$

$$N-C_4 \quad \log_{10} V_R = \frac{925}{T} + 0.838 \quad (118)$$

Actually, as the theory shows, what should be plotted is $\log\left[\frac{V_R - V_V}{T}\right]$ vs $1/T$. This has been done in Figure 12. The equations for these curves are:

$$I-C_4 \quad \log_{10} \left[\frac{V_R - V_V}{T} \right] = \frac{1320}{T} - 2.949 \quad (119)$$

$$N-C_4 \quad \log_{10} \left[\frac{V_R - V_V}{T} \right] = \frac{1489}{T} - 3.069 \quad (120)$$

The maximum error in these data is 2.7% for isobutane and 4.3% for normal butane.

TABLE II

RETENTION VOLUME AS A FUNCTION OF TEMPERATURE

Run No.	P _i (psig)	P _i (corr) (psia)	φ(r)	v ₀ (cc/min)	T (°F)	$\frac{1}{T} \times 10^3$ (°R ⁻¹)	d ₀ (cm)	d _I (cm)	d _N (cm)	V _{RI} (cc)	V _{RN} (cc)	$\frac{V_{RI}-V_V}{(cc/°R)}$	$\frac{V_{RN}-V_V}{(cc/°R)}$
Column No. 6 L = 20 Ft. V _V = 82.15cc Injection: = Hypodermic													
103	32.5	46.2	.295	252	144.0	1.658	1.10	2.10	2.55	191.3	240.7	.1810	.2625
104	32.5	46.2	.295	252	143.8	1.659	1.10	2.05	2.52	185.9	237.1	.1720	.2575
105	32.5	46.2	.295	246.5	131.0	1.690	1.05	2.10	2.60	194.4	248.0	.1898	.280
106	27.0	40.7	.328	195.8	157.4	1.620	1.30	2.34	2.75	180.3	219.1	.1590	.222
107	27.0	40.7	.328	195.6	156.8	1.620	1.20	2.20	2.62	176.6	216.1	.1530	.217
108	27.0	40.7	.328	190	140.0	1.666	1.18	2.30	2.80	184.8	230.7	.1709	.2475
109	27.0	40.7	.328	183	116.9	1.731	1.18	2.58	3.28	205.9	267.7	.214	.321
110	27.0	40.7	.328	177	99.0	1.790	1.15	2.85	3.71	227.3	300.6	.260	.391
111	27.0	40.7	.328	171	80.2	1.850	1.15	3.18	4.15	249.9	330.1	.310	.459
112	27.0	40.7	.328	168	71.0	1.880	1.10	3.40	4.75	268.5	378.1	.3505	.556
113	27.0	40.7	.328	164.3	59.0	1.930	1.08	3.63	5.28	284.1	415.6	.390	.644
*	-	-	-	-	70.0	1.888	-	-	-	269.3	380.2	.3535	.563

* Average value for Runs 201-210 and 501-511, all at 70°F.

TABLE III

RETENTION VOLUME MEASUREMENTS AT 70.0°F

Column No. 6 $T_c = 70.0^\circ\text{F}$ Injection: Hypodermic $V_V = 82.15\text{cc}$										
Run No.	P_o ("Hg)	P_i ("Hg)	P_i (corr) or psia)	$\phi(r)$	v_o (cc/min)	d_o (cm)	d_I (cm)	d_N (cm)	V_{RI} (cc)	V_{RN} (cc)
201	29.00	-	82.2	.175	675	.60	1.775	2.54	286	420
202	29.00	-	72.3	.197	545	.675	2.02	2.785	288	404
203	29.00	-	62.5	.225	415	.80	2.34	3.24	288	409
204	29.00	-	52.4	.265	288	.95	2.805	3.895	285	405
205	29.04	-	43.2	.312	190	1.13	3.455	4.85	280	409
206	29.04	-	32.8	.394	95.0	1.68	5.17	7.27	271	384
207	29.04	-	25.5	.466	47.0	3.10	9.12	12.62	249	345
208	29.04	-	25.3	.480	46.0	3.20	9.47	13.12	280	395
209	29.04	9.50	-	.565	17.1	6.78	19.63	27.25	265	373
210	29.04	9.25	-	.568	16.3	7.00	20.32	28.12	265	374
501	29.01	-	28.3	.440	70.7	2.27	6.64	9.27	277	396
502	29.01	-	37.7	.350	141.2	1.44	4.21	5.91	279	398
503	29.01	-	47.6	.288	236	1.00	3.21	4.37	290	411
504	29.01	-	56.8	.246	337	.86	2.56	3.58	284	405
505	29.01	-	77.4	.185	616	.60	1.89	2.53	283	383
506	29.01	13.92	-	.530	25.2	4.60	13.61	18.92	259	364
507	29.01	13.65	-	.530	24.8	4.56	13.53	18.83	256	358
508	29.01	8.67	-	.574	12.4	7.59	21.11	29.20	223	308
509	29.20	14.29	-	.525	25.9	4.39	12.95	18.06	254	357
510	29.20	13.97	-	.530	25.6	4.55	13.30	18.46	256	359
511	29.20	10.95	-	.550	18.3	5.81	16.74	23.23	244	340

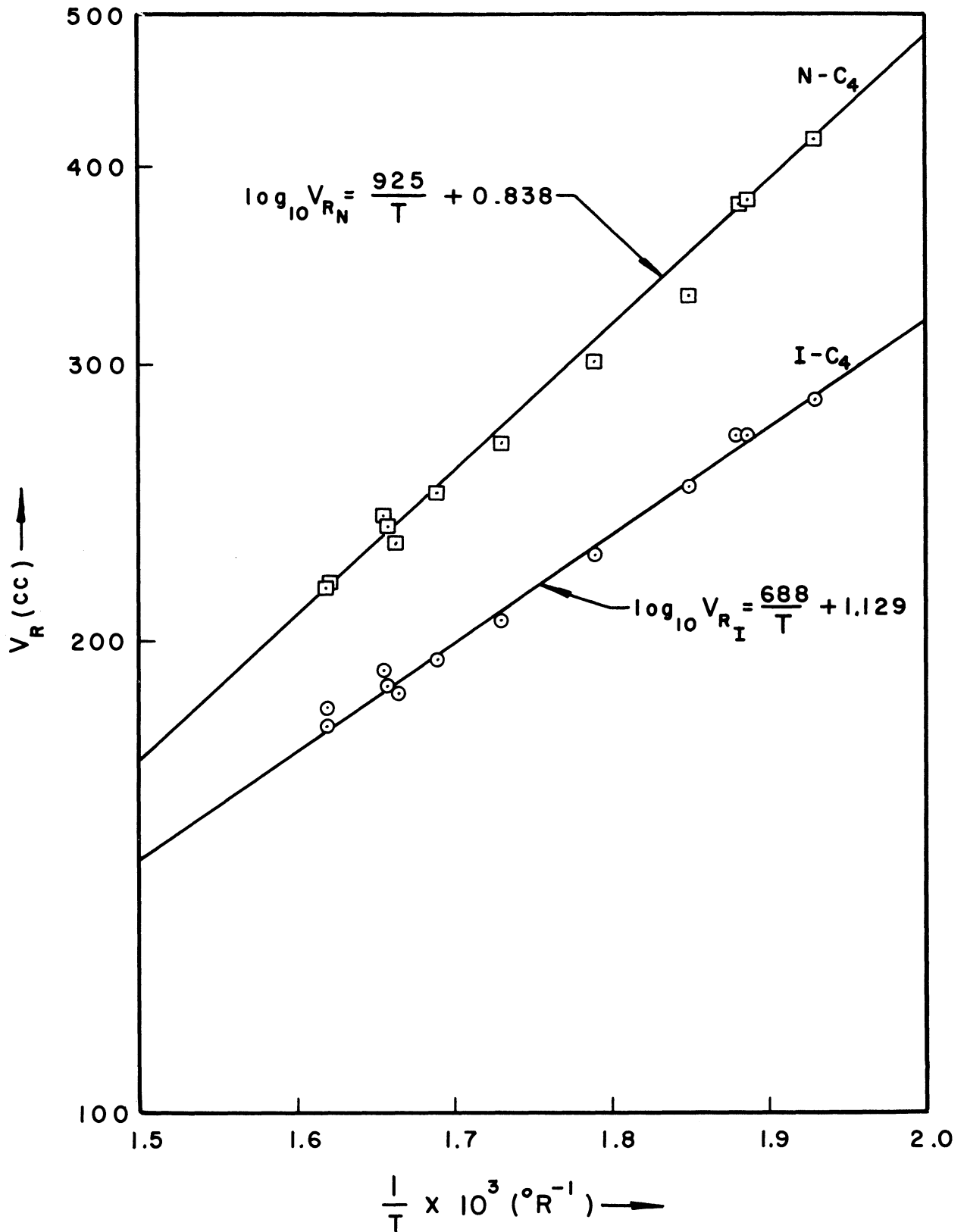


Figure 11. Retention Volume as a Function of Temperature Showing Convergence of Retention Volumes at High Temperatures.

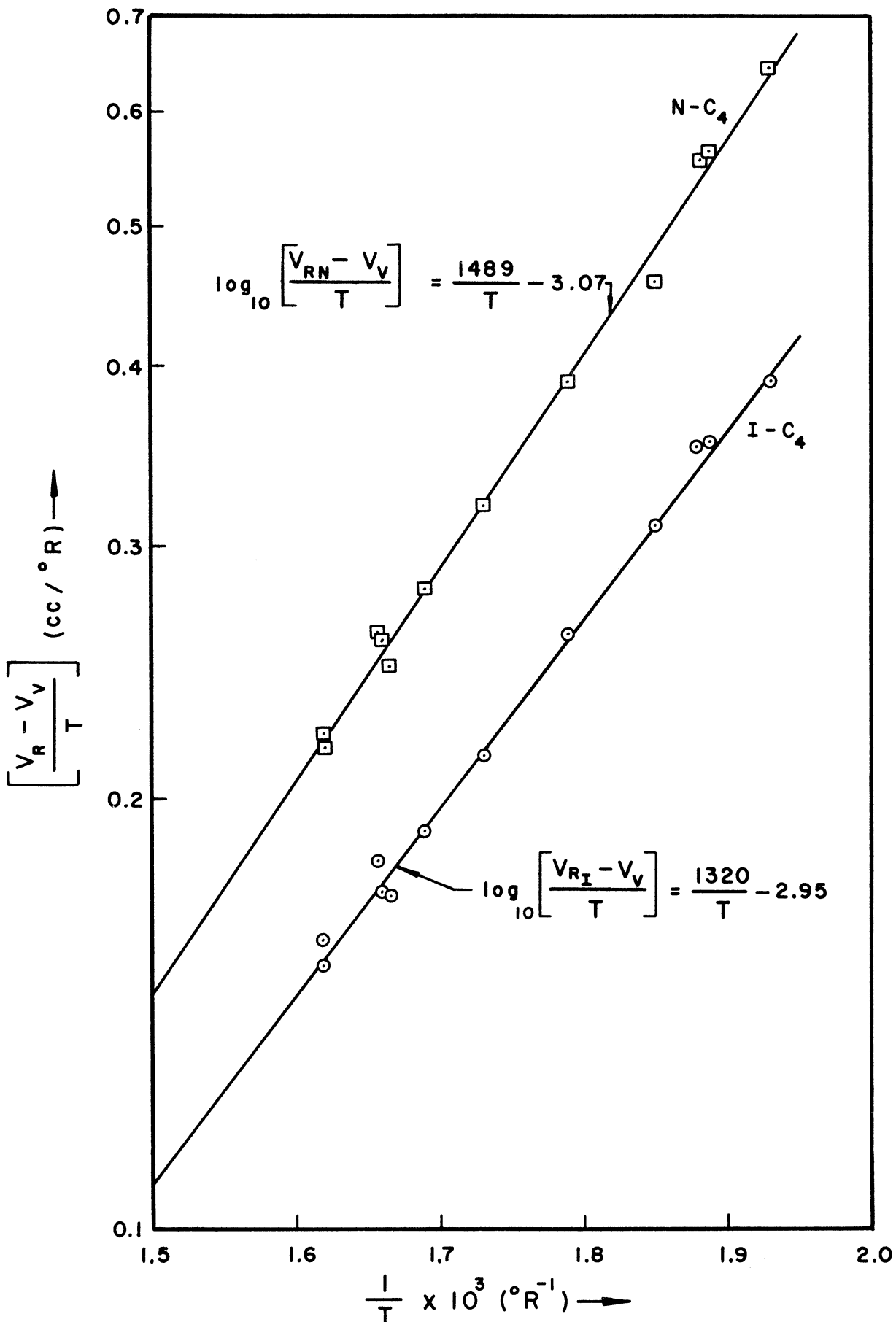


Figure 12. Theoretical Relationship Between Retention Volume and Temperature.

It is clear from Figures 11 and 12 that retention volumes diverge as temperature decreases. And by extrapolation it can be seen that the retention volumes of iso and normal butane coincide at a temperature of 953°F. This extrapolation is probably too great to be valid, however. In any analytical work the largest separation possible is desired, and hence the column should be operated at as low a temperature as is possible. This statement must be modified, of course, by the fact that as temperature decreases the retention time increases, and there is a certain point beyond which it is impractical to cool the column. In considering chromatographic separation as a recovery process, however, it is desired to have the retention volumes as close to one another as possible and still attain the required degree of separation. This degree of separation depends not only on the retention volume but also on the band widths of the components in the sample to be separated, as has been pointed out in the section on resolution. However, using Figure 12 in conjunction with band width correlations one may determine the correct operating temperature for his column.

B. Retention Volume as a Function of Column Length

The relationship between retention volume and length is so obvious that it brings a blush to the author's cheek to mention it. However, at the risk of insulting the intelligence of the reader, the results of retention volume measurements on three columns are presented in Figure 13. These data were not taken for this purpose, but rather to study the effect of length on band width. The retention volume data are merely a natural by-product. The two shorter columns were obtained by

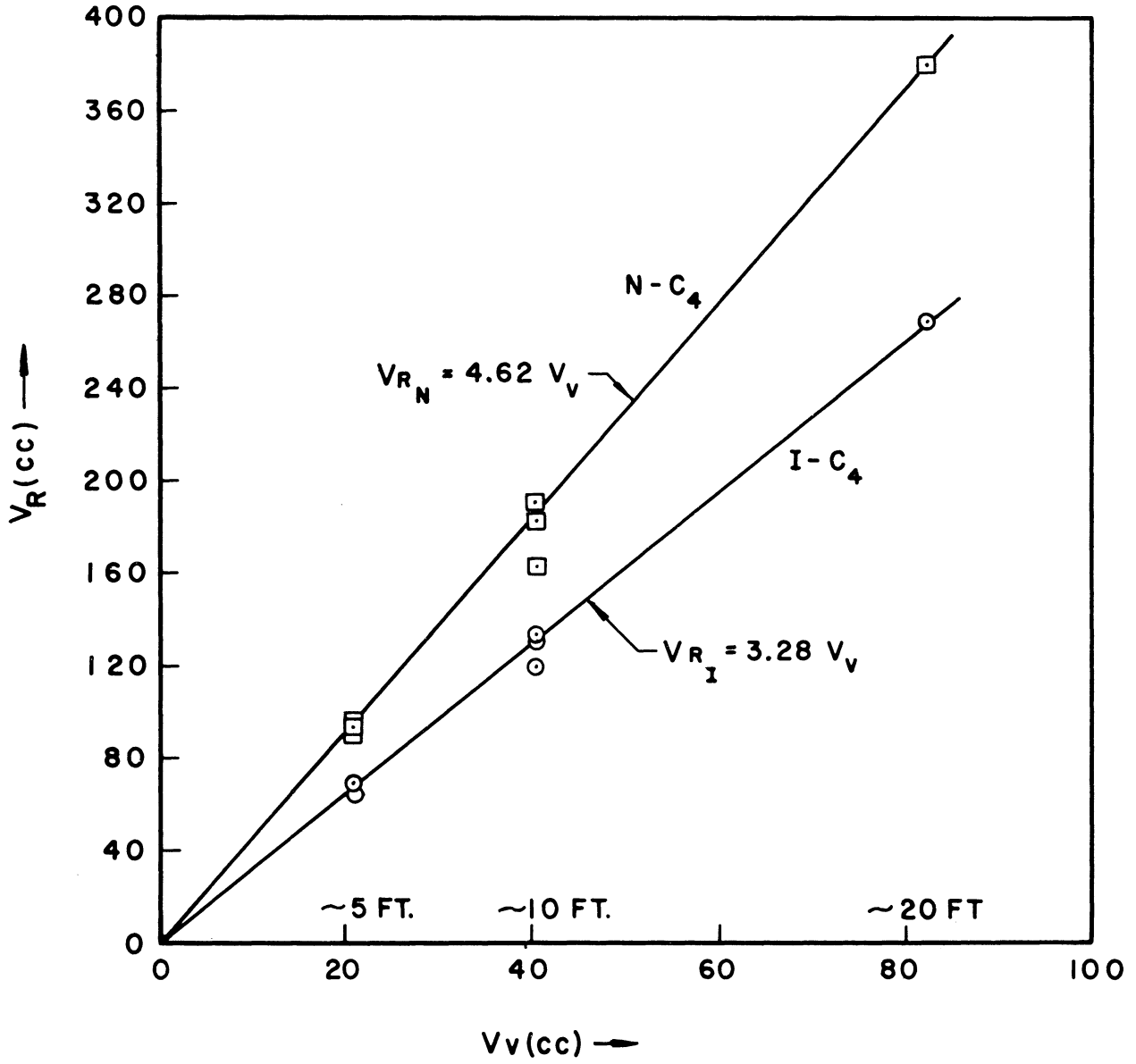


Figure 13. Retention Volume is a Linear Function of Void Volume or Column Length.

cutting the 20 foot column into segments. Thus the three columns are identical in all particulars except length. Since the 20 foot column was coiled when it was cut, it was almost impossible to accurately measure the lengths of the shorter columns. Therefore the void volume of each column was measured, and this quantity was used instead of length in Figure 13. This is a valid substitution since void volume is directly proportional to length as long as uniform packing is assumed. Figure 13 shows, of course, that retention volume is directly proportional to void volume (or length). The equations are:

$$I-C_4 \quad V_R = 3.28 V_v. \quad (121)$$

$$N-C_4 \quad V_R = 4.62 V_v. \quad (122)$$

The data are presented in Table IV.

C. Band Width as a Function of Flow Rate

Data showing the effect of flow rate on band width are presented in Table V. These data were taken on a 20 foot column at a constant temperature of 70°F. Flow rates varied from 12 to 780 cc/min. Samples were injected with a hypodermic needle. In all cases, sample size was approximately 1 cc at atmospheric conditions.

According to the theoretical development, band width should be correlated by the three term power series given in Equation (100). Modified slightly it reads:

$$W^2 = J \left[\frac{A}{v^2} + \frac{B}{v^3} + \frac{C}{v} \right], \quad (123)$$

where

$$J = \frac{16S^2 V_R^2}{L}. \quad (124)$$

TABLE IV
RETENTION VOLUME AS A FUNCTION OF COLUMN LENGTH

Columns No. 6, 6', and 6" T _c = 70.0°F Injection: Hypodermic										
<u>Isobutane</u>										
Run No.	P ₀ ("Hg)	P ₁ ("Hg)	P ₁ (corr) or psia)	φ(r)	v ₀ (cc/min)	d ₀ (cm)	d _I (cm)	V _{RI} (cc)	L (ft)	V _V (cc)
930	29.38	16.18	-	.511	76.6	1.10	2.72	133.6	10	40.4
932	.	-	64.1	.219	782	.34	.69	128.6	10	40.4
934	.	6.73	-	.592	23.7	2.79	6.60	119.0	10	40.4
936	29.56	12.35	-	.540	106.3	.67	1.25	70.0	5	21.0
938	.	-	43.7	.308	698	.276	.408	63.6	5	21.0
940	29.57	3.75	-	.625	26.8	1.963	3.67	63.0	5	21.0
*	-	-	-	-	-	-	-	269.3	20	82.15
<u>Normal Butane</u>										
Run No.	P ₀ ("Hg)	P ₁ ("Hg)	P ₁ (corr) or psia)	φ(r)	v ₀ (cc/min)	d ₀ (cm)	d _I (cm)	V _{RN} (cc)	L (ft)	V _V (cc)
931	29.38	15.97	-	.513	76.2	1.11	3.74	191.5	10	40.4
933	.	-	64.1	.219	782	.34	.91	183.2	10	40.4
935	.	6.57	-	.598	23.7	2.885	9.03	163.6	10	40.4
937	29.56	12.35	-	.540	106.3	.67	1.603	99.8	5	21.0
939	.	-	43.6	.310	698	.276	.50	93.7	5	21.0
941	29.57	3.73	-	.625	26.4	1.963	4.81	90.1	5	21.0
*	-	-	-	-	-	-	-	380.2	20	82.15

* Average values for Runs 201-210 and 501-511.

TABLE V
BAND WIDTH AS A FUNCTION OF FLOW RATE

Columns No. 6, 6', and 6'' T_c = 70.0°F Injection: Hypodermic Sample Size: sec @ 70°F and 1 atm

Run No.	P ₁ (Hg)	P ₂ (Hg)	P ₁ (corr) (Hg or psia)	φ(τ)	Y ₀ (cc/min)	V̄ (cc/min)	V̄ ² (cc/min) ²	V _V (cc)	W _T (cm)	W _H (cm)	$\frac{(28.15)W_T^2}{(cm^2)}$	$\frac{(28.15)W_H^2}{(cm^2)}$	$\frac{(28.15)W_T^2}{(cm^2)(min)^2}$	$\frac{(28.15)W_H^2}{(cm^2)(min)^2}$	$\frac{(28.15)W_T^2}{(cm^2)(min)^2}$	$\frac{(28.15)W_H^2}{(cm^2)(min)^2}$	$\frac{(28.15)W_T^2}{(cm^2)(min)^2}$	$\frac{(28.15)W_H^2}{(cm^2)(min)^2}$	$\frac{(28.15)W_T^2}{(cm^2)(min)^2} - \frac{1504}{V}$	$\frac{(28.15)W_H^2}{(cm^2)(min)^2} - \frac{2180}{V}$	
201	29.00	-	82.2	.175	675	177	31,300	82.15	.445	.55	1.98	.502	6,200	9,460	1,097,400	1,674,000	6,191	9,442			
202	29.00	-	72.3	.157	545	161	25,900	82.15	.475	.655	.226	.404	5,850	10,480	942,000	1,687,000	5,840	10,460			
203	29.00	-	62.5	.225	415	140	19,600	82.15	.49	.655	.240	.404	4,700	7,900	658,000	1,106,000	4,689	7,877			
204	29.00	-	52.4	.265	288	115	13,220	82.15	.555	.76	.308	.578	4,080	7,650	469,000	860,000	4,066	7,622			
205	29.04	-	43.2	.312	190	89.0	7,910	82.15	.65	.85	.423	.723	3,350	5,730	298,000	510,000	3,332	5,694			
206	29.04	-	32.8	.394	95.0	56.1	3,150	82.15	.855	1.15	.697	1.322	2,200	4,160	123,000	233,000	2,172	4,103			
207	29.04	-	25.5	.466	47.0	32.9	1,080	82.15	1.10	1.70	1.21	2.89	1,310	3,130	43,100	103,000	1,262	3,033			
208	29.04	-	25.3	.480	46.0	33.2	1,100	82.15	1.20	1.62	1.44	2.625	1,590	2,900	52,800	96,300	1,542	2,804			
209	29.04	9.50	-	.565	17.1	14.6	213	82.15	2.05	2.94	4.20	8.64	895	1,840	13,100	26,900	786	1,622			
210	29.04	9.25	-	.568	16.3	13.9	193	82.15	2.00	2.88	4.00	8.29	772	1,600	10,700	22,200	657	1,372			
501	29.01	-	28.3	.440	70.7	46.6	2,170	82.15	.90	1.30	.81	1.69	1,610	3,360	75,000	156,600	1,576	3,292			
502	29.01	-	37.7	.350	141.2	74.2	5,500	82.15	.76	1.00	.578	1.00	3,190	5,500	236,700	408,000	3,169	5,457			
503	29.01	-	47.6	.288	236	102.0	10,400	82.15	.65	.82	.423	.672	4,400	7,000	449,000	714,000	4,384	6,969			
504	29.01	-	56.8	.246	337	124	15,400	82.15	.55	.77	.302	.594	4,650	9,120	576,600	1,131,000	4,637	9,094			
505	29.01	-	77.4	.185	616	171	29,200	82.15	.50	.63	.250	.397	7,310	11,600	1,250,000	1,984,000	7,301	11,281			
506	29.01	13.92	-	.530	25.2	20.0	400	82.15	1.42	1.85	2.02	3.42	809	1,369	16,200	27,400	729	1,253			
507	29.01	13.65	-	.530	24.8	19.7	388	82.15	1.59	2.02	2.53	4.08	981	1,583	19,300	31,200	900	1,567			
508	29.01	8.67	-	.574	12.4	10.7	114	82.15	2.53	3.46	6.40	11.96	734	1,372	7,800	14,700	585	1,342			
509	29.20	14.29	-	.525	25.9	20.4	416	82.15	1.57	2.09	2.46	4.37	1,025	1,820	20,900	37,100	947	1,804			
510	29.20	13.97	-	.530	25.6	20.4	416	82.15	1.52	2.06	2.31	4.25	961	1,770	19,600	36,100	885	1,754			
511	29.20	10.95	-	.550	18.3	15.1	228	82.15	2.00	2.72	4.00	7.40	912	1,688	13,800	25,500	807	1,667			
930	29.38	16.18	-	.511	76.6	58.7	3,440	40.4	.587	-	.700	-	2,420	-	142,000	-	2,393	-	-		
932	29.38	-	64.1	.219	782	257	66,000	40.4	.265	-	.1428	-	9,450	-	2,429,000	-	9,444	-	-		
934	29.38	6.73	-	.592	23.7	21.1	445	40.4	1.143	-	2.665	-	1,186	-	25,200	-	1,110	-	-		
936	29.56	12.35	-	.540	106.3	86.2	7,440	21.0	.37	-	.532	-	3,985	-	343,500	-	3,967	-	-		
938	29.56	-	43.7	.308	698	322.5	104,100	21.0	.19	-	.1412	-	14,300	-	4,611,800	-	14,295	-	-		
940	29.57	3.75	-	.625	26.8	25.2	635	21.0	.83	-	2.70	-	1,712	-	43,100	-	1,649	-	-		
931	29.38	15.97	-	.513	76.2	58.6	3,440	40.4	-	.815	-	1.348	-	4,620	-	270,700	-	-			4,566
933	29.38	-	64.1	.219	778	255	65,000	40.4	-	.342	-	.238	-	15,200	-	3,957,600	-	-			15,308
935	29.38	6.37	-	.598	22.8	20.4	416	40.4	-	1.50	-	4.59	-	1,907	-	38,900	-	-			1,891
937	29.56	12.35	-	.540	106.3	86.2	7,440	21.0	-	.46	-	.83	-	6,160	-	531,000	-	-			6,123
939	29.56	-	43.6	.310	698	324.5	105,300	21.0	-	.23	-	.207	-	21,500	-	7,074,000	-	-			21,790
941	29.57	3.73	-	.625	26.4	24.8	615	21.0	-	1.013	-	4.02	-	2,475	-	61,400	-	-			2,462

As we showed in the last section, V_R is directly proportional to void volume. Thus we may express J in the following manner:

$$J = \frac{16S^2(\lambda V_v)^2}{(V_v/a_v)} = (16S^2 a_v \lambda^2) V_v = K V_v, \quad (125)$$

where λ and K are constants.

Then it is obvious from Equations (123) and (125) that W^2 is directly proportional to V_v . This makes it possible to use data taken on columns of different lengths. All that is necessary is to scale the data to a chosen length by use of the formula:

$$\frac{W_L^2}{W_L^2} = \frac{(V_v)_L}{(V_v)_L}. \quad (126)$$

A small amount of additional data have been taken using shorter columns. These data are presented in Table VI. They have been modified as suggested above, and used in conjunction with the data from the 20 foot column. Experimental verification of Equation (126) will be given in the following section.

In order to test the validity of Equation (123), the data may be plotted in several different ways. By rewriting Equation (123) we see that

$$W^2 \bar{v}^2 = J \left[A + \frac{B}{\bar{v}} + C \bar{v} \right] \quad (127)$$

If B is approximately zero, then $W^2 \bar{v}^2$ will plot linearly against \bar{v} .

Writing Equation (123) still another way gives:

$$W^2 \bar{v}^3 = J [A \bar{v} + B + C \bar{v}^2]. \quad (128)$$

TABLE VI
BAND WIDTH AS A FUNCTION OF COLUMN LENGTH

Columns No. 6' and 6" $T_c = 70.0^\circ\text{F}$ Injection: Hypodermic					
<u>Isobutane</u>					
Run No.	\bar{v} (cc/min)	W_I (cm)	$\frac{W_I^2}{\bar{v}^2}$ (cm^8/min^2)	L (Ft)	V_V (cc)
930	58.7	.587	1,189	10	40.4
932	257	.265	4,645	10	40.4
934	21.1	1.143	582	10	40.4
936	86.2	.37	1,019	5	21.0
938	322.5	.19	3,755	5	21.0
940	25.2	.83	438	5	21.0
<u>Normal Butane</u>					
Run No.	\bar{v} (cc/min)	W_N (cm)	$\frac{W_N^2}{\bar{v}^2}$ (cm^8/min^2)	L (Ft)	V_V (cc)
931	58.6	.815	2,270	10	40.4
933	255	.342	7,620	10	40.4
935	20.4	1.50	936	10	40.4
937	86.2	.46	1,575	5	21.0
939	324.5	.23	5,570	5	21.0
941	24.8	1.013	632	5	21.0

If A were negligible, then $W^2\bar{v}^3$ vs \bar{v}^2 would be linear. The data have been plotted in both these ways. The results are shown in Figures 14 and 15. Both of these methods of plotting result in straight lines. This rather surprising result would seem to indicate that the dominant term in the expression is the last term, involving C, and that while both other terms are present, their effects are small.

It should be pointed out that these methods of plotting the data tend to be deceiving since the quantity \bar{v} appears in both the ordinate and abscissa. Any time this is done it tends to smooth the data. The same thing is done, by the way, by authors who show plots of H versus \bar{v} . This is true since H is calculated from an expression which contains the factor \bar{v}^2 .

It is felt that the data are not precise enough to verify or disprove the theory. However, the data are in essential agreement with it. Figure 15 shows that the intercept, representing the term B, is very small. Calculating the theoretical values for B from Equation (50) we find that

$$B = 1.073 \gamma. \quad (129)$$

The factor γ lies between 0.5 and 1.0 depending on the packing of the column. Thus we have an upper and lower bound on the theoretical B values.

$$0.536 < B < 1.073 \quad (130)$$

If we assume $\gamma \sim 0.75$,

we find $B \sim 0.805$. (131)

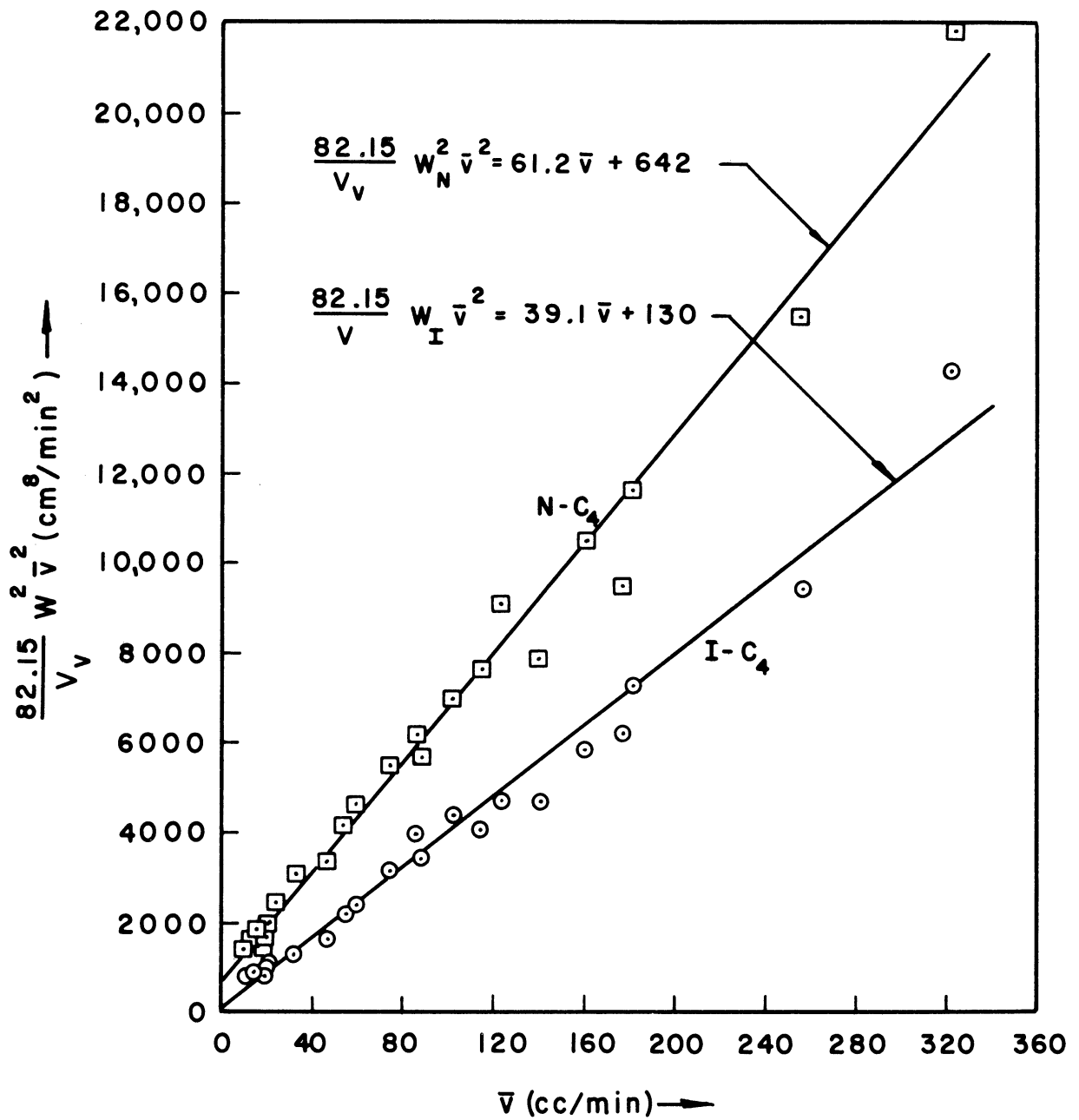


Figure 14. Relationship Between Band Width and Average Flow Rate: $(W^2 \bar{v}^2)$ vs. \bar{v} is Linear Provided Little Molecular Diffusion Takes Place in the Gas Phase.

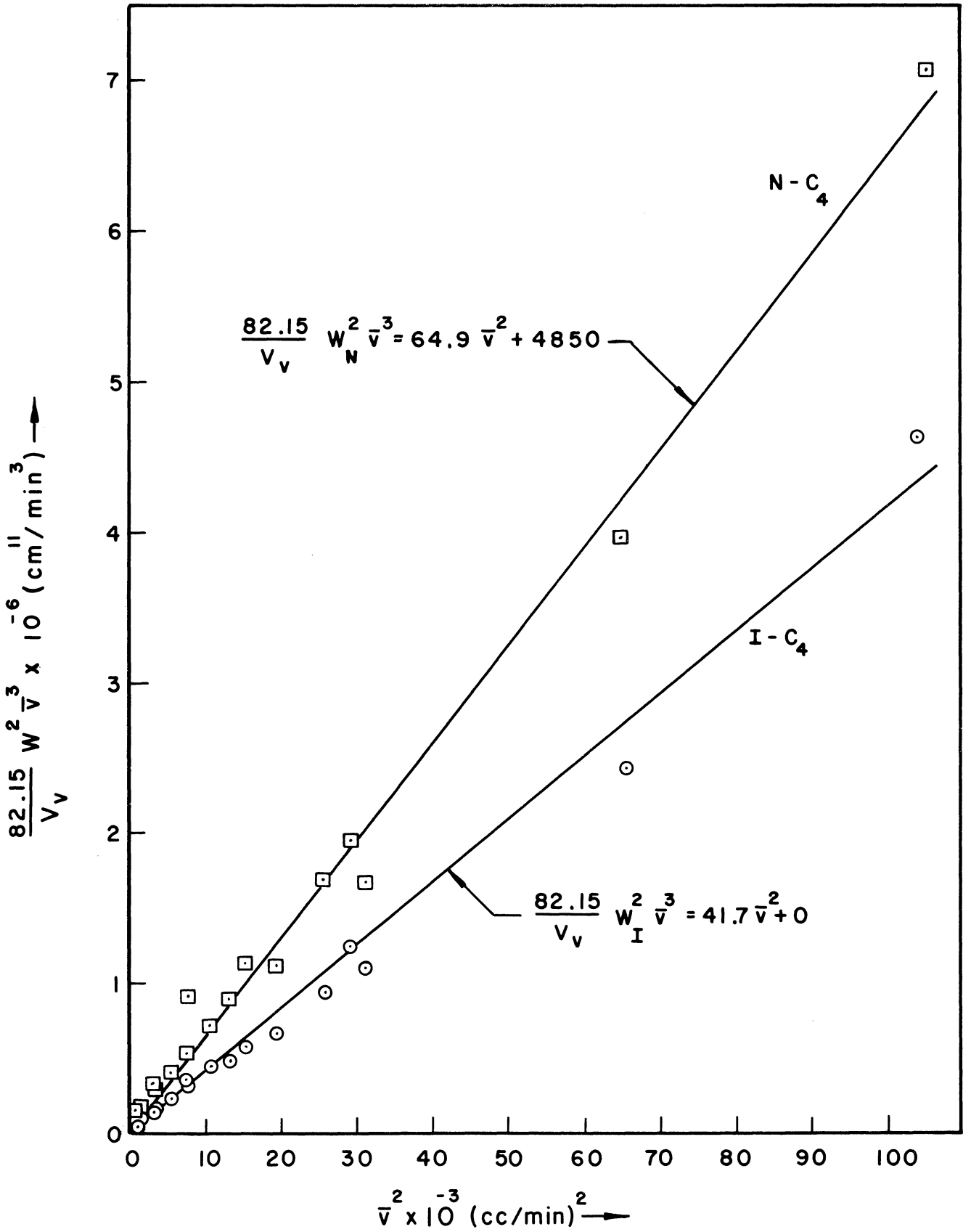


Figure 15. Relationship Between Band Width and Average Flow Rate: $(W^2 \bar{v}^{-3})$ vs. \bar{v}^2 is Linear Provided the "Eddy" Diffusion Effect is Small.

Using this value of B, we may now modify Equation (123) once more:

$$[W^2 \bar{v}^2 - \frac{JB}{\bar{v}}] = J[A + C\bar{v}]. \quad (132)$$

The quantity on the left is plotted vs \bar{v} in Figure 16. The resulting equations are:

$$I-C_4 \quad W^2 = \frac{63.2}{\bar{v}^2} + \frac{1594}{\bar{v}^3} + \frac{39.37}{\bar{v}}. \quad (133)$$

$$N-C_4 \quad W^2 = \frac{744}{\bar{v}^2} + \frac{3180}{\bar{v}^3} + \frac{59.8}{\bar{v}}. \quad (134)$$

And extracting J:

$$I-C_4 \quad W^2 = 24.1 V_V \left[\frac{.032}{\bar{v}^2} + \frac{.805}{\bar{v}^3} + \frac{.01986}{\bar{v}} \right]. \quad (135)$$

$$N-C_4 \quad W^2 = 48.0 V_V \left[\frac{.188}{\bar{v}^2} + \frac{.805}{\bar{v}^3} + \frac{.01512}{\bar{v}} \right]. \quad (136)$$

That these equations satisfactorily fit the data may be seen by examining Figure 17, where W^2 is plotted against \bar{v} on log-log paper. The curves are calculated from Equations (135) and (136).

From Equations (135) and (136) it is possible to calculate an approximate value for the packing parameter λ , in the first term of the Van Deemter equation. By definition,

$$\lambda = A/2d_p. \quad (137)$$

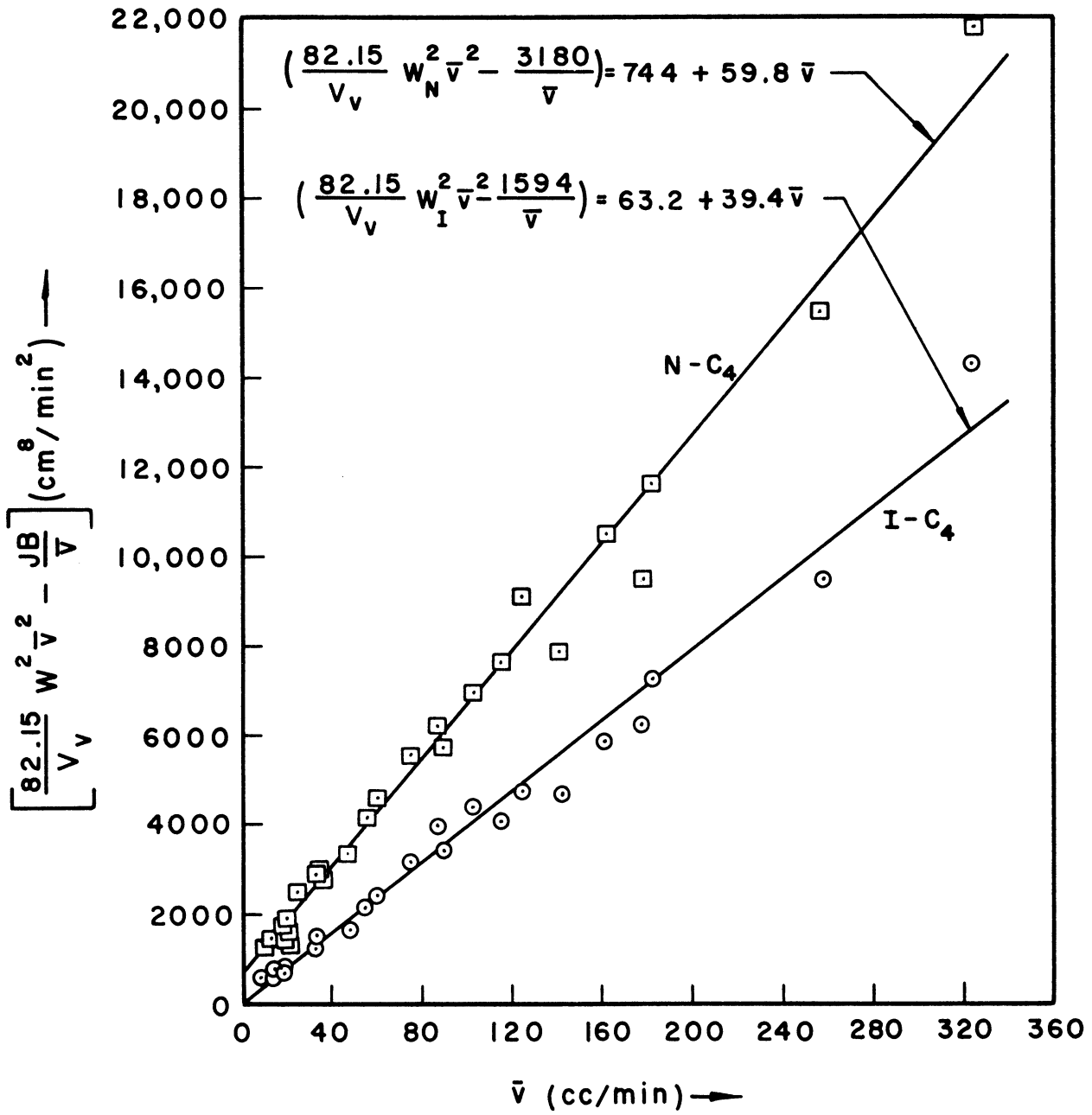


Figure 16. Final Plot for Determination of van Deemter Constants.

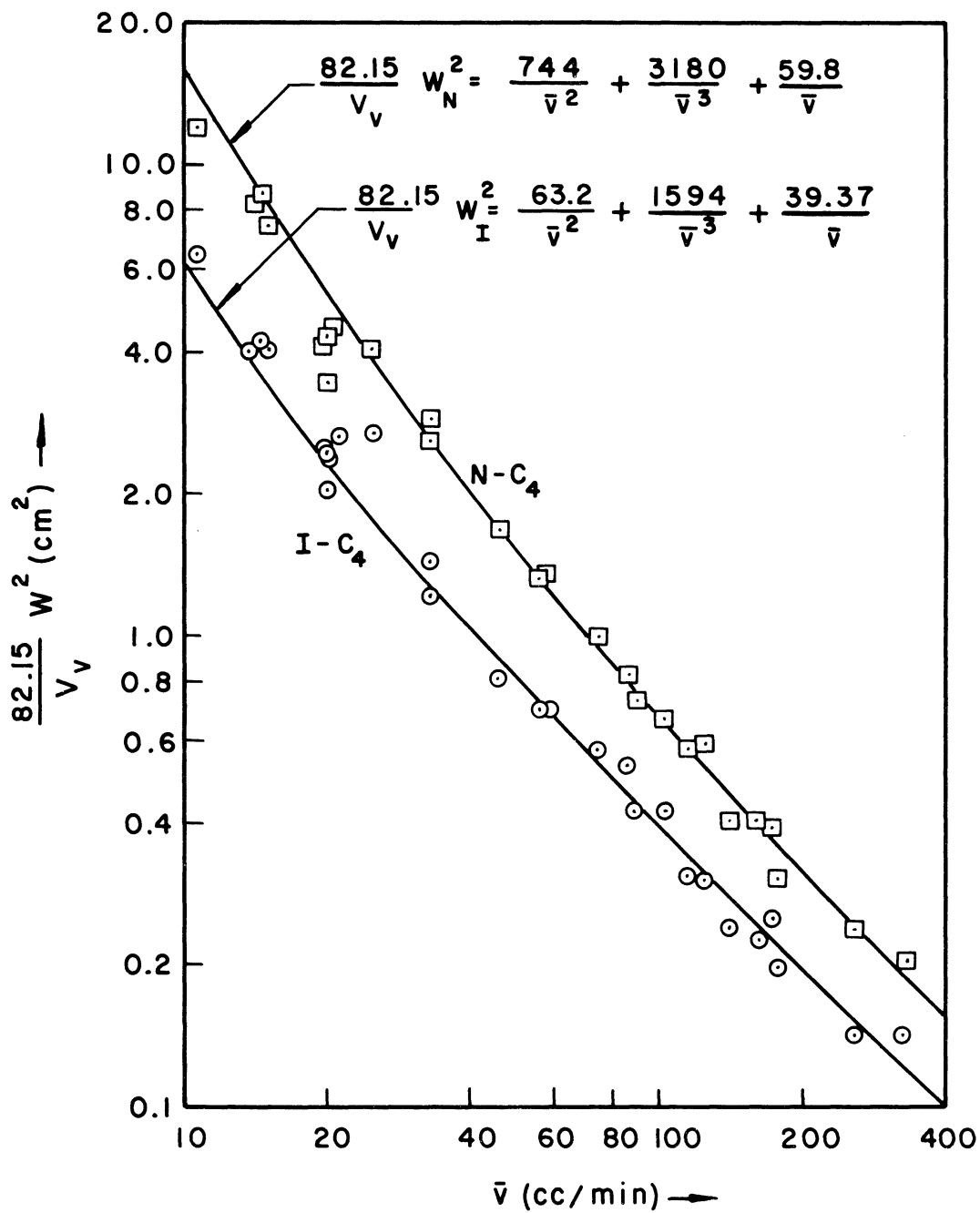


Figure 17. Band Width as a Function of Flow Rate.

Estimating the average particle diameter as 0.046 cm, we calculate that λ lies between 0.35 and 2.04, the former figure obtained from the isobutane data, and the latter from the normal butane data. Thus,

$$0.35 < \lambda < 2.04 \quad (138)$$

This is in agreement with the values of λ reported by van Deemter⁽⁵⁶⁾ and Keulemans.⁽³⁹⁾

While it is not possible to calculate theoretical values of the C constant without knowing a value for both d_f and D_{liq} , it is possible to calculate the ratio of two C's, provided we assume that d_f and D_{liq} are the same for each component. It is clear that d_f will be exactly the same in all cases. It is also reasonable to assume that for similar molecules such as normal and isobutane, their D_{liq} 's will be equal. Then from the definition of C, we have:

$$(C_I/C_N) = \frac{k_I / (1+k_I)^2}{k_N / (1+k_N)^2} . \quad (139)$$

This ratio has been found to be 1.23 at a temperature of 70°F. The experimental value for (C_I/C_N) is 1.31. This is felt to be a satisfactory agreement with the theory.

Figure 17 shows that increasing the flow rate decreases the spread of the elution bands. Using this fact alone, the indication would seem to be that a chromatographic separation should be performed at as high a flow rate as possible. However, this conclusion is not valid for the simple fact that the retention volumes approach each other so closely at high flow rates that no separation will occur. Indeed it is easy to see that at an infinite flow rate retention volumes of all components

become equal and zero separation is obtained. It is found in practice that the slower the flow rate, the better the separation obtained. It is for this reason primarily that most analytical separations are performed with carrier gas flow rates in the neighborhood of 50 to 100 cc/min. In considering chromatography as a separation process, however, higher flow rates are essential to increasing the amount of material recovered. Thus it is clear that a balance must be struck between the separation obtainable and the amount of material separated.

D. Band Width as a Function of Column Length

For this study three columns were used: the 20 foot column previously used, a 10 foot section of this column, and a 5 foot section of the same column. Injections in all cases were made with a hypodermic, and column temperature was maintained at 70°F. The data relating column length (or void volume) to band width is shown in Tables V and VI. The correlations were obtained in the following manner. From the theoretical derivation, it was clear that W^2 would be proportional to L (or V_V). The problem was to verify this from data which also showed the effect of flow rate of W^2 . First, the data for each column were plotted in separate figures. These three plots are shown in Figures 18, 19, and 20. All of these data are expressible in the form:

$$W^2 \bar{v}^2 = A' + C' \bar{v}. \quad (140)$$

Now if the assumption is made that $W^2 \propto V_V$, Equation (140) may be written

$$W^2 \bar{v}^2 = V_V (a + c \bar{v}). \quad (141)$$

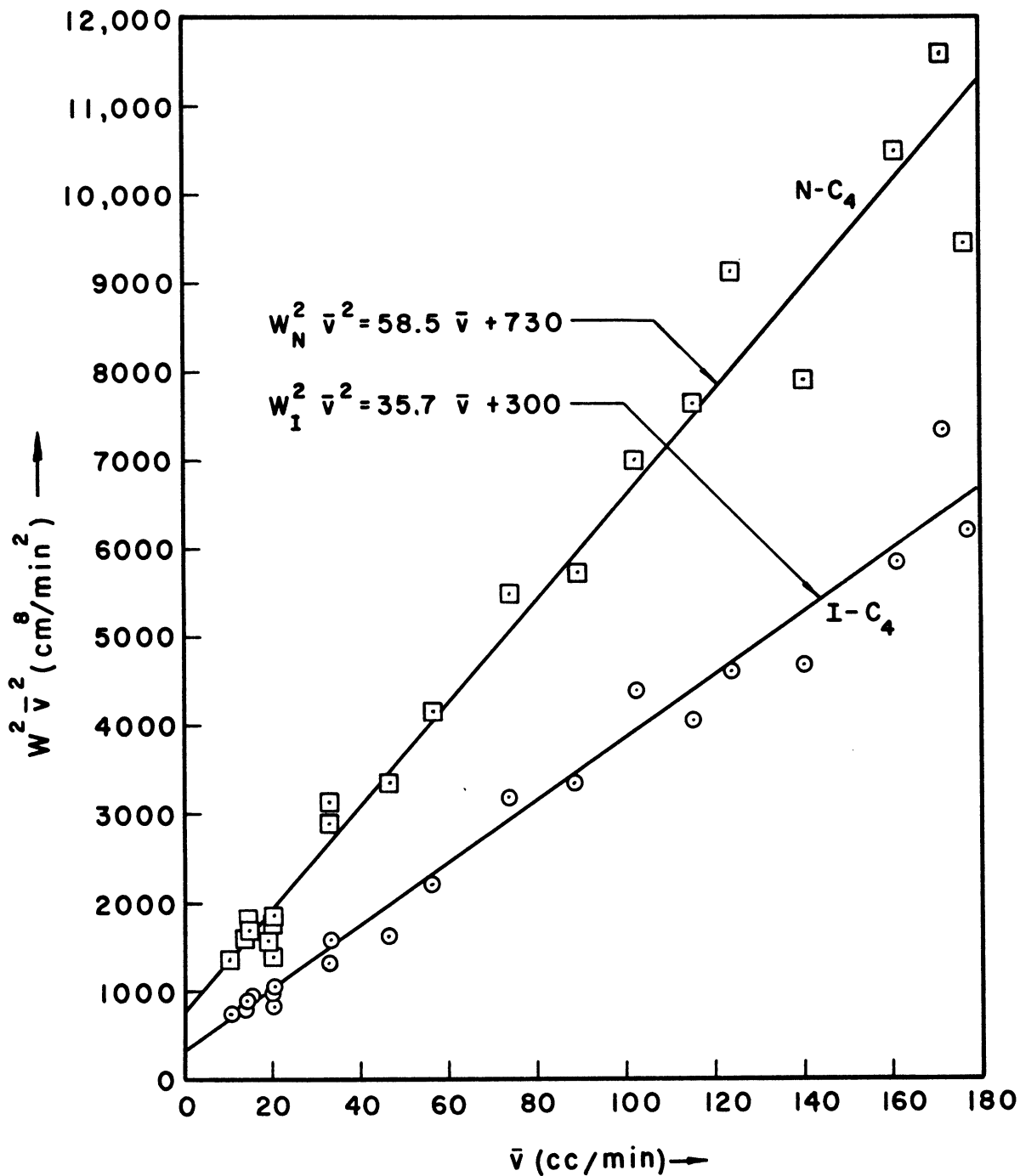


Figure 18. Band Width as a Function of Flow Rate for a 20 ft. Column.

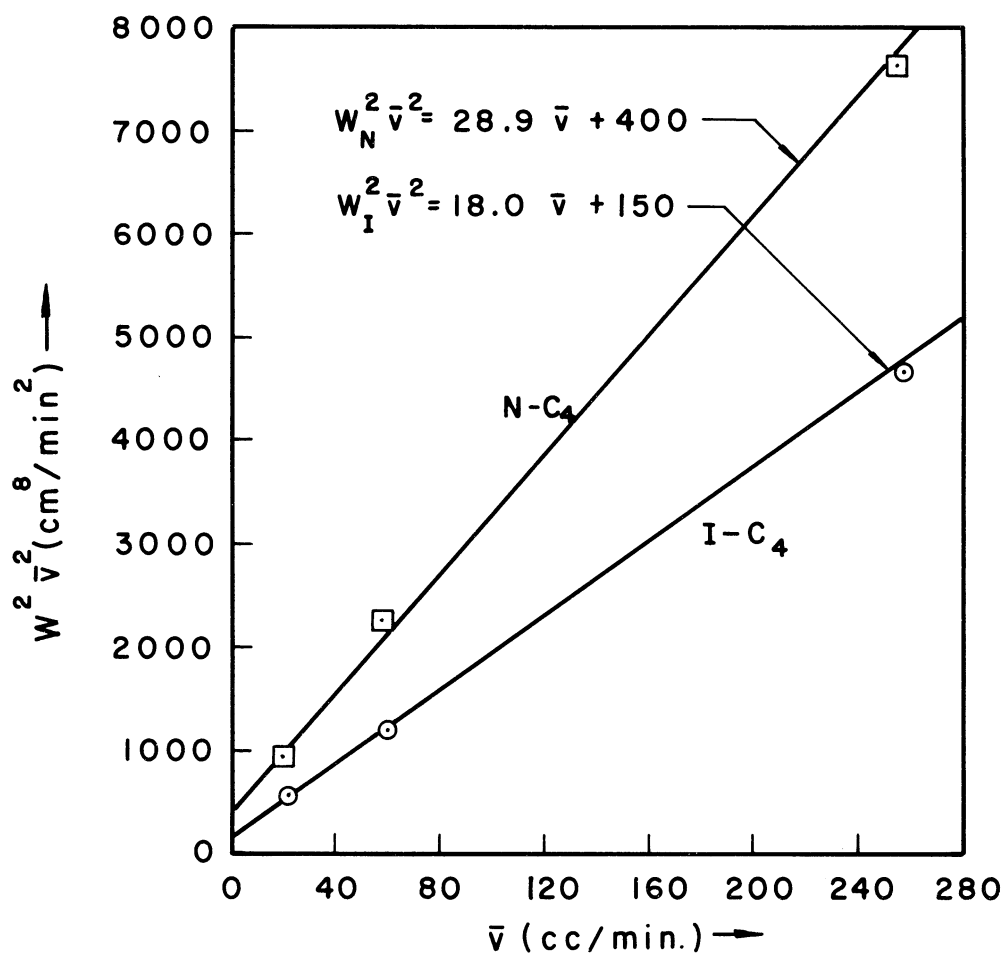


Figure 19. Band Width as a Function of Flow Rate for a 10 ft. Column.

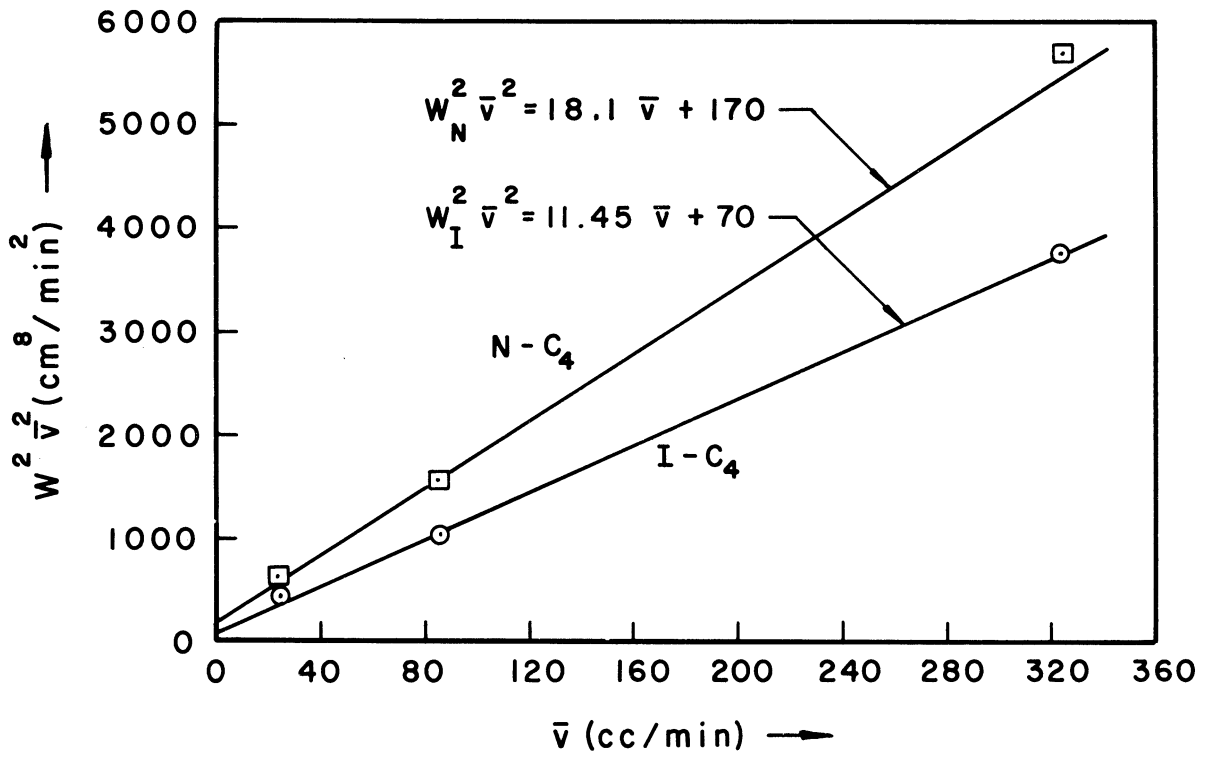


Figure 20. Band Width as a Function of Flow Rate for a 5 ft. Column.

From this it is apparent that $A' = aV_V$ and $C' = cV_V$. We now have a check on whether W^2 is proportional to V_V or not. We can plot A' and C' vs V_V and examine the results. If our assumption is correct, then both of these plots will give straight lines. If they do not, then the assumption is false. Figure 21 shows these plots. In both cases, it is felt that the agreement between the theory and the data is satisfactory.

E. Band Width as a Function of Sample Size

These data were collected in a 20 foot column at a constant temperature of 70°F, and at a constant flow rate of ~ 50 cc/min. Samples were injected using the three-way solenoid valve at a pressure approximating the inlet pressure of the carrier gas. Sample size was measured from the area of the elution peaks using the calibration curves previously described. In contrast to previous experiments, a pure sample of each component was injected instead of a mixture. The data showing the relationship of band width to size of sample are presented in Table VII. The data are plotted in Figure 22.

This figure clearly indicates that band width increases with sample size. This well known fact is the reason that in analytical work small samples are used. However, in a separation process it is equally clear that larger samples mean larger column through-puts. Therefore, once again a balance must be made between sample size and the amount of material to be separated. It should be pointed out that theoretical plots of band width vs. sample size, while having the same general shape as the experimental results, differ by a factor of 5.7 for I-C₄ and 8.0 for N-C₄. The theoretical curves are plotted along with the experimental results

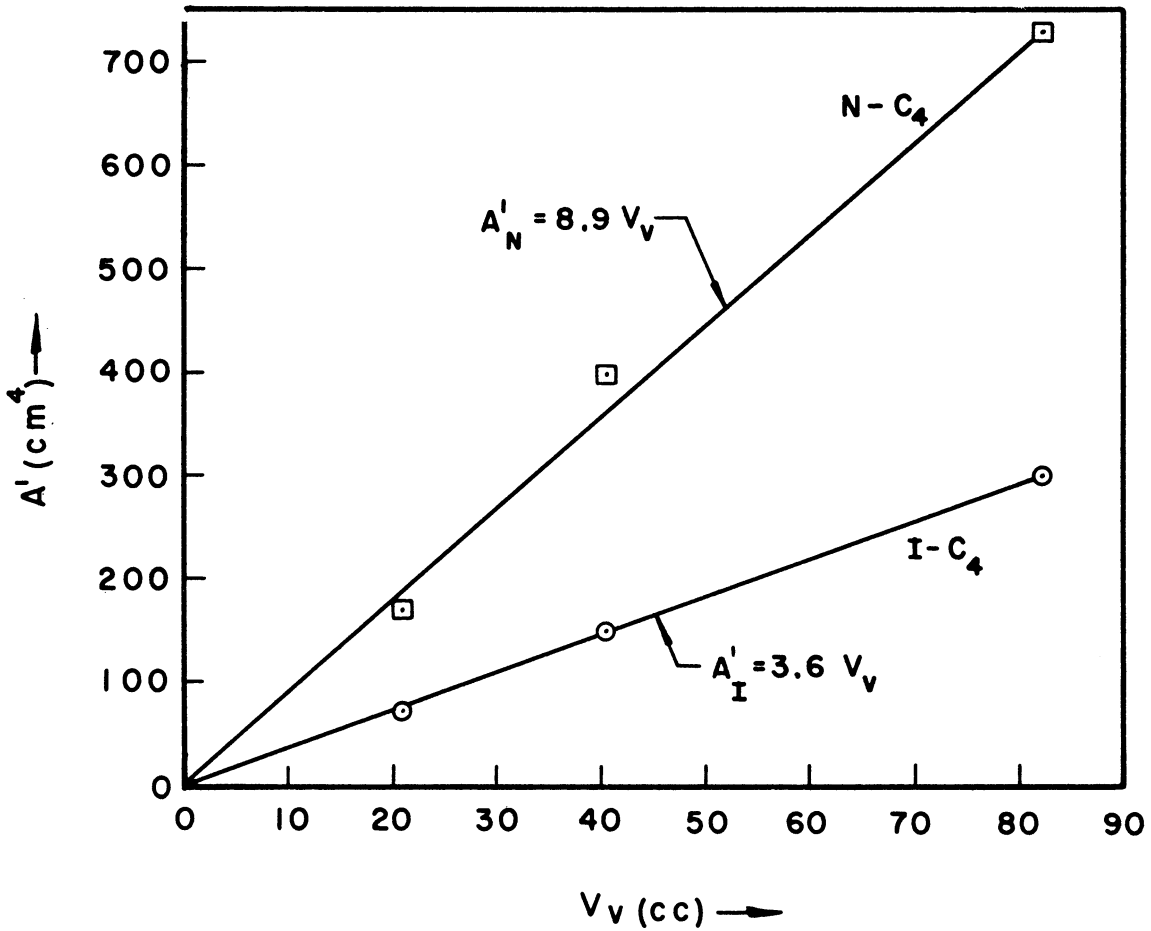
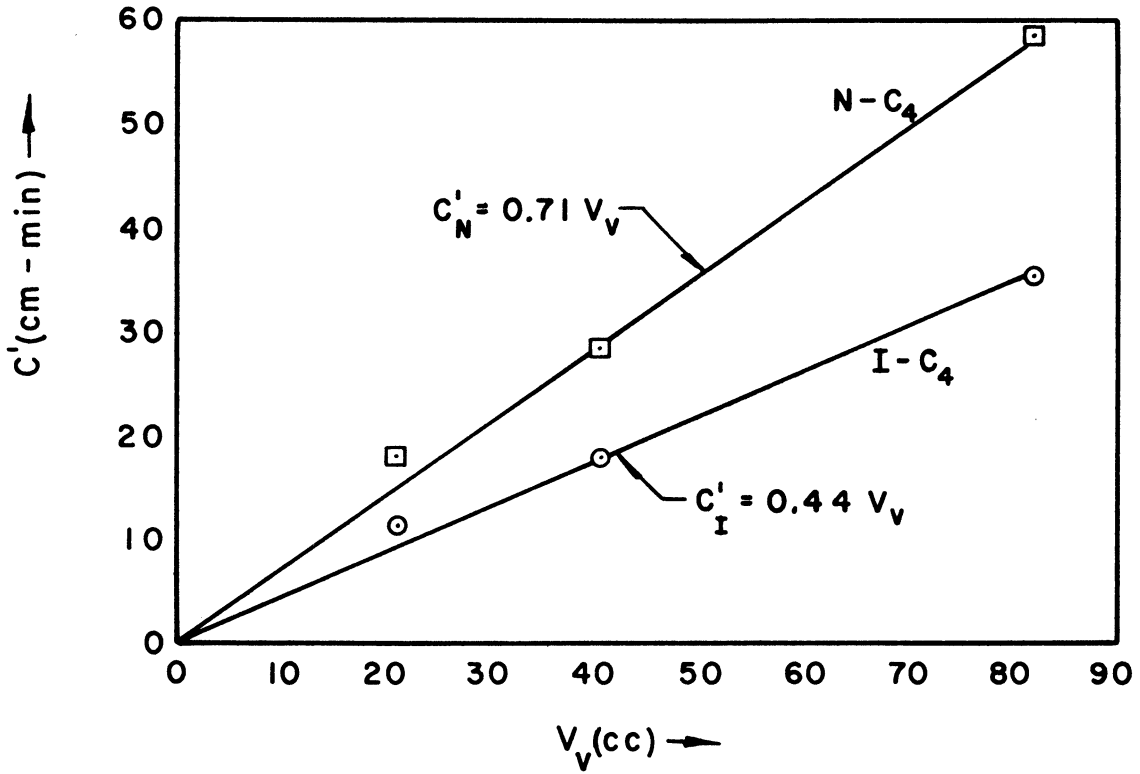


Figure 21. Band Width Constants Plotted vs. Void Volume Demonstrates the Linear Relationship Between W^2 and V_v .

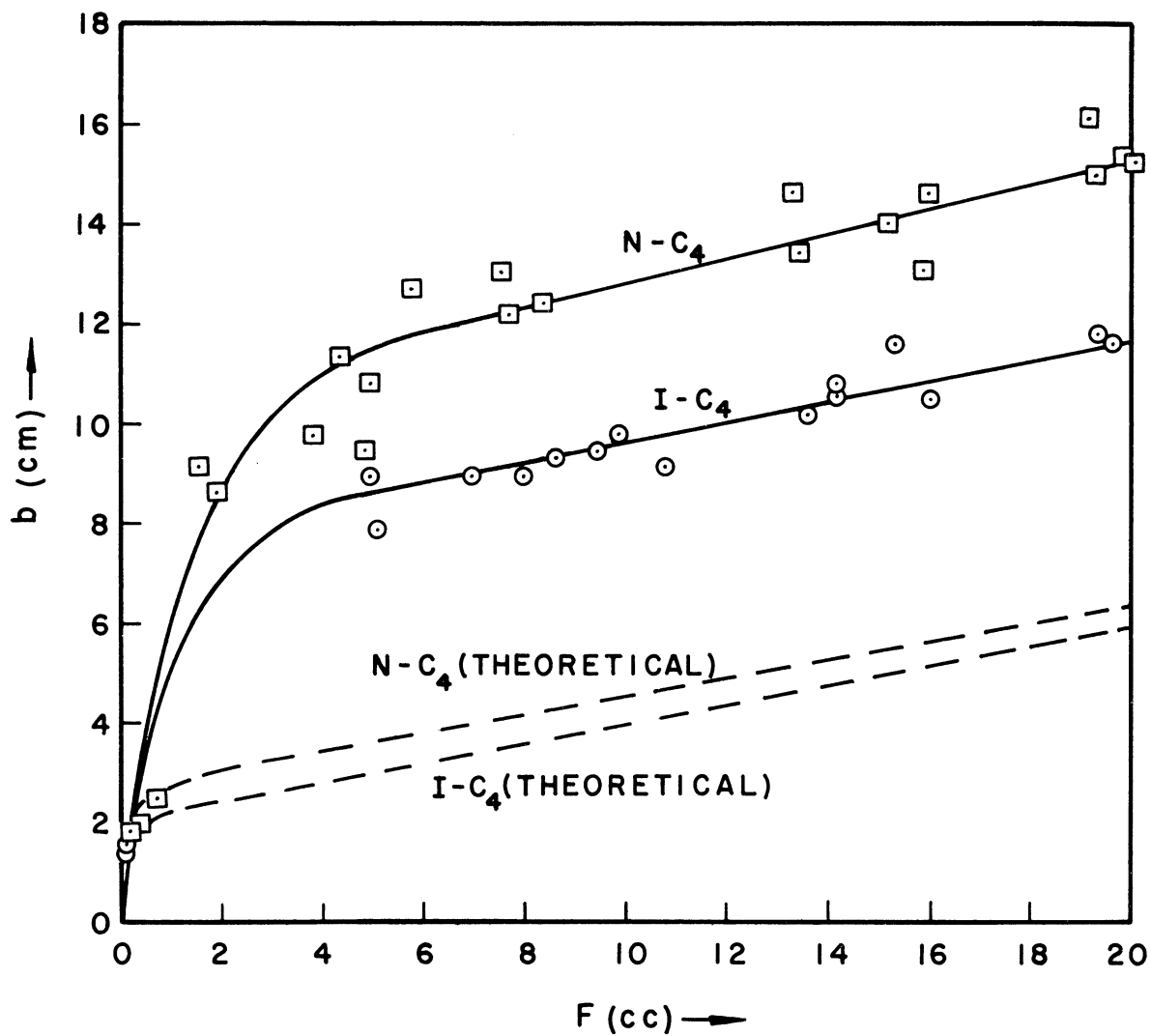


Figure 22. Band Width as a Function of Sample Size Showing Theoretical Curves as Calculated.

TABLE VII
BAND WIDTH AS A FUNCTION OF SAMPLE SIZE

Column No. 6 $T_c = 70.0^\circ\text{F}$ Injection: Solenoid Valve $P_{inj.} \sim P_1$											
Isobutane											
Run No.	Injection Time (sec)	P_1 (corr) (psig)	v_o (cc/min)	b_I (cm)	b_I (corr) (cm)	Area (cm ²)	A_I (cc)	h_o (cm)	A_o (cc)	f	F_I (cc)
814*	15.0	9.90	50	1.31	1.31	.616	.05	5.91	2.0	1.0	.05
815*	20.9	9.90	50	1.50	1.50	1.11	.11	5.91	2.0	1.0	.11
816*	20.9	9.90	50	1.37	1.37	.958	.09	5.91	2.0	1.0	.09
835	3.5	9.95	50	8.96	8.96	18.0	4.98	5.91	2.0	1.0	4.98
836	3.5	9.95	50	7.82	7.82	18.3	5.06	5.91	2.0	1.0	5.06
837	6.5	9.95	50	9.32	9.32	30.4	8.65	5.91	2.0	1.0	8.65
838	6.3	9.95	50	8.94	8.94	24.8	7.00	5.91	2.0	1.0	7.00
839	9.1	9.95	50	9.40	9.40	33.1	9.44	5.91	2.0	1.0	9.44
840	9.1	9.95	50	9.78	9.78	34.5	9.86	5.91	2.0	1.0	9.86
841	15.3	9.95	50	10.50	10.50	49.0	14.15	5.91	2.0	1.0	14.15
842	15.3	9.95	50	11.60	11.60	53.0	15.35	5.91	2.0	1.0	15.35
843	21.0	9.95	50	11.78	11.78	66.6	19.37	5.91	2.0	1.0	19.37
844	21.0	9.95	50	11.65	11.65	67.6	19.65	5.91	2.0	1.0	19.65
864	0.9	29.0	224	5.17	8.95	12.8	3.43	2.60	.86	.430	7.98
865	2.0	29.0	224	5.30	9.16	16.84	4.63	2.60	.86	.430	10.75
866	3.0	29.0	224	5.86	10.13	21.0	5.86	2.60	.86	.430	13.62
867	3.8	29.0	224	6.20	10.70	20.0	5.57	2.38	.79	.394	14.17
868	4.7	29.0	224	6.03	10.40	23.55	6.62	2.50	.83	.413	16.05

* In these runs the sample valve was only cracked slightly, giving very small samples.

TABLE VII (CONT'D)
BAND WIDTH AS A FUNCTION OF SAMPLE SIZE

Column No. 6 $T_c = 70.0^\circ\text{F}$ Injection: Solenoid Valve $P_{inj.} \sim P_1$											
<u>Normal Butane</u>											
Run No.	Injection Time (sec)	P_1 (corr) (psig)	v_o (cc/min)	b_N (cm)	b_N (corr) (cm)	Area (cm ²)	A_N (cc)	h_o (cm)	A_o (cc)	f	F_N (cc)
814*	15.0	9.90	50	1.80	1.80	1.179	.20	5.91	2.0	1.0	.20
815*	20.9	9.90	50	2.49	2.49	2.74	.73	5.91	2.0	1.0	.73
816*	20.9	9.90	50	2.00	2.00	1.94	.47	5.91	2.0	1.0	.47
845	3.0	9.92	50	9.78	9.78	15.11	3.82	5.91	2.0	1.0	3.82
846	3.2	9.92	50	11.37	11.37	17.24	4.38	5.91	2.0	1.0	4.38
847	6.1	9.92	50	9.42	9.42	18.88	4.82	5.91	2.0	1.0	4.82
848	6.1	9.92	50	10.80	10.80	19.28	4.92	5.91	2.0	1.0	4.92
849	9.2	9.92	50	12.74	12.74	22.40	5.76	5.91	2.0	1.0	5.76
850	15.2	9.92	50	12.42	12.42	32.15	8.33	5.91	2.0	1.0	8.33
851	15.0	9.92	50	12.20	12.20	29.80	7.72	5.91	2.0	1.0	7.72
852	20.6	9.92	50	13.04	13.04	60.5	15.84	5.91	2.0	1.0	15.84
853	20.6	9.92	50	13.41	13.41	51.2	13.40	5.91	2.0	1.0	13.40
854	26.9	9.92	50	15.24	15.24	76.5	20.1	5.91	2.0	1.0	20.1
855	26.6	9.92	50	14.98	14.98	73.6	19.34	5.91	2.0	1.0	19.34
856	18.2	9.92	50	14.02	14.02	58.0	15.2	5.91	2.0	1.0	15.2
857	17.8	9.92	50	14.62	14.62	61.1	16.0	5.91	2.0	1.0	16.0
858	24.0	9.92	50	16.15	16.15	73.1	19.2	5.91	2.0	1.0	19.2
859	23.9	9.92	50	15.31	15.31	75.0	19.7	5.91	2.0	1.0	19.7
860	1.0	29.4	221	4.26	8.60	3.96	0.87	2.80	.94	.463	1.88
861	1.0	29.4	221	4.52	9.14	3.35	0.71	2.80	.94	.463	1.53
862	3.0	29.4	221	6.42	13.0	13.91	3.50	2.80	.94	.463	7.56
863	5.9	29.4	221	7.21	14.6	24.0	6.17	2.80	.94	.463	13.33

* In these runs the sample valve was only cracked slightly, giving very small samples.

NOTE: $B(\text{corr})$ is the band width corrected to a flow rate of 50 cc/min at column outlet.

Equations (133) and (134) are used to determine the correction factors.

in Figure 22. The theoretical curves with the correction factors added are plotted in Figure 23 along with the experimental data. While no detailed study of the cause of this discrepancy has been conducted, it is felt that the most likely explanation is that the sample injection profile differed from that postulated by the theoretical model (exponential decay). Two alternative injection profiles are illustrated in Figure 24. The first is a combination of plug flow and exponential decay, while the second shows an exponential decay in front of the sample injection as well as behind it. This second behavior might result if the sample injection pressure were higher than the column pressure. It is postulated that this higher pressure would cause the sample on injection to be propagated down the column to an extent greater than that anticipated in the perfect mixing case. The mathematics have not been carried out for either of these cases. However, it is clear that both will result in larger band widths for a given sample size.

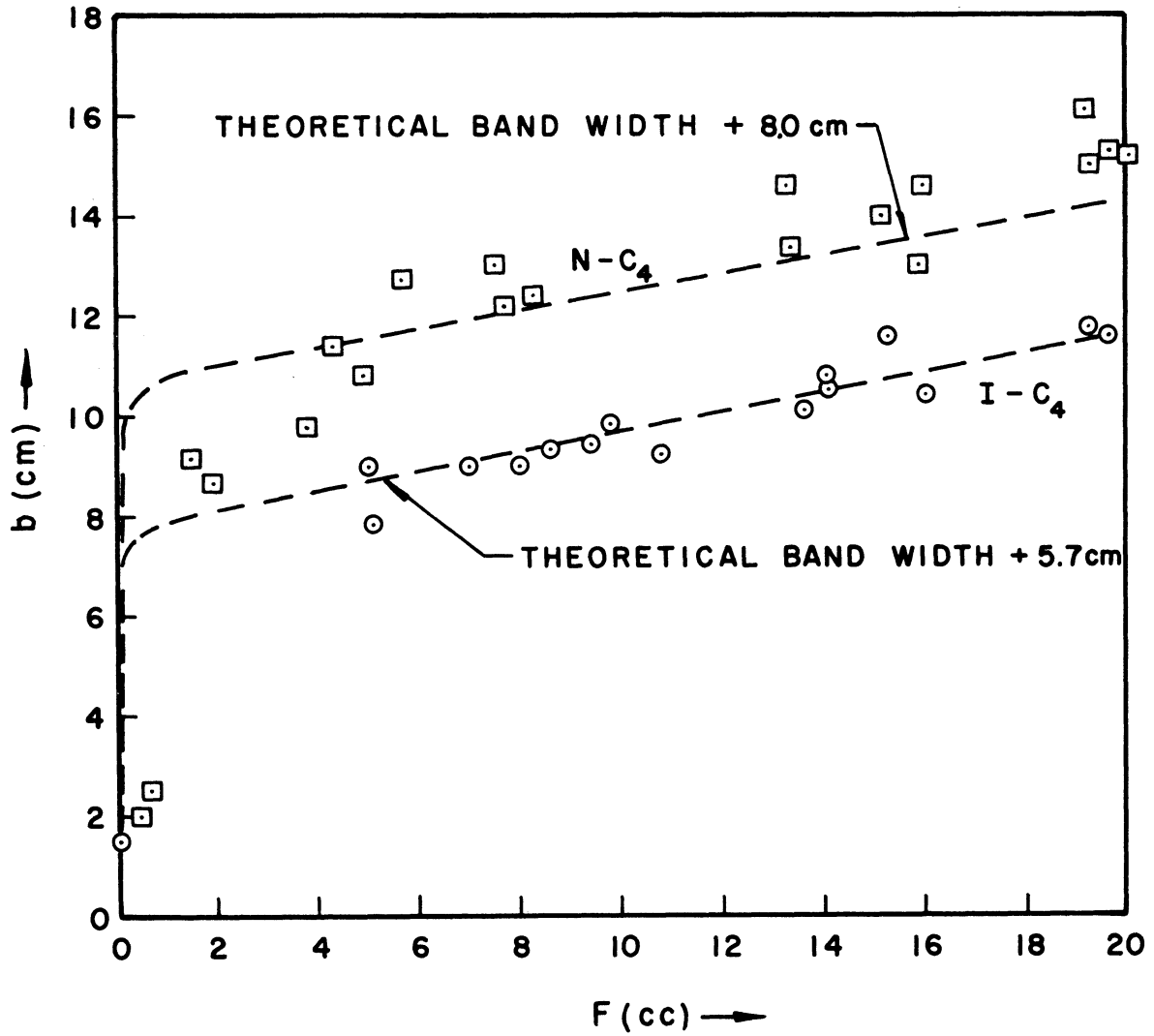


Figure 23. Band Width as a Function of Sample Size Showing Theoretical Curves Translated by the Constants Shown.

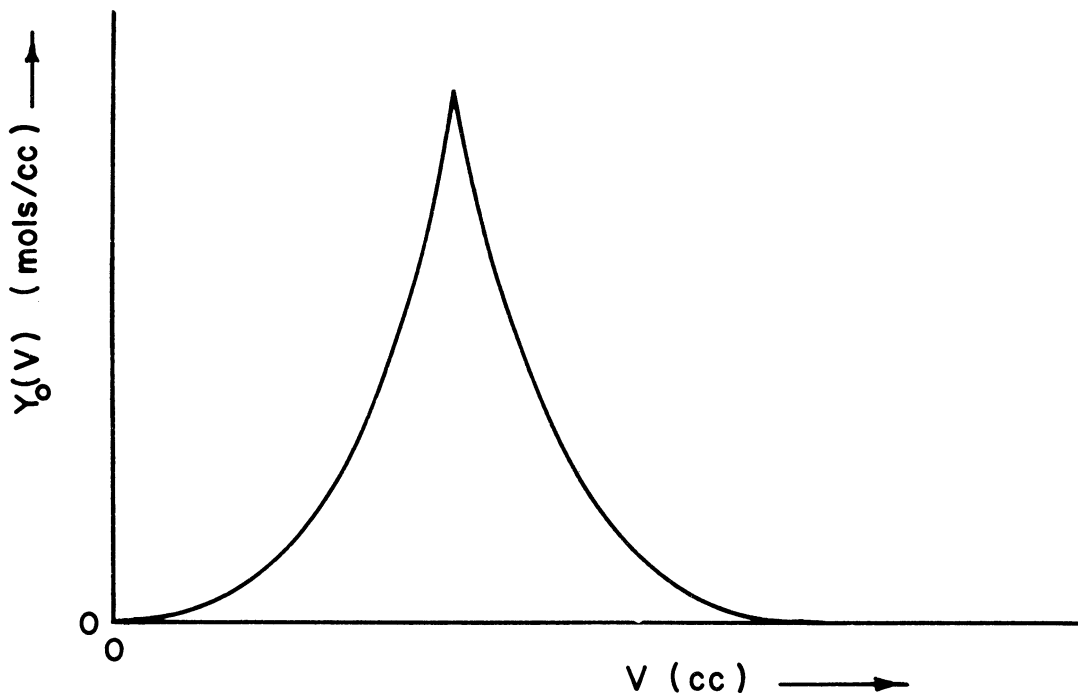
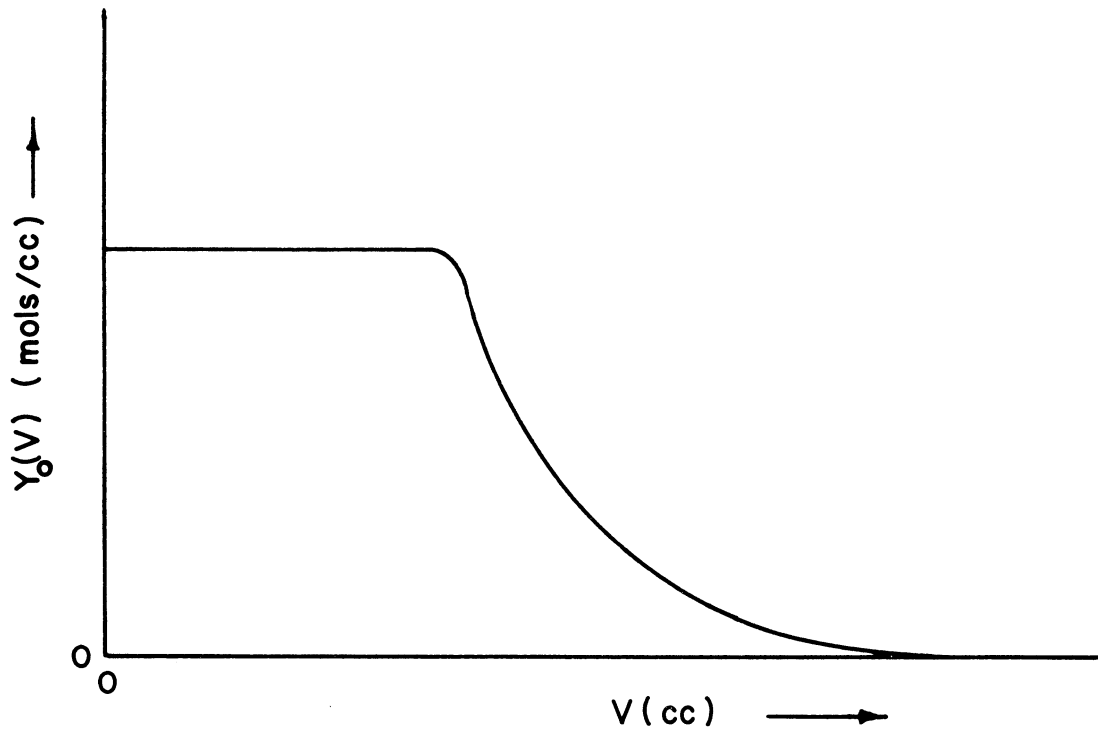


Figure 24. Two Possible Sample Injection Profiles Leading to Larger Band Widths.

VII. SUMMARY AND CONCLUSIONS

Chromatography has been widely used as an instrument for the analysis of gaseous mixtures for a number of years. However, it has received only scant attention as a process for the separation and recovery of quantities of materials. The object of this research was to show what variables in chromatography are important in the design of a column for use in recovery processes. The effects of temperature, flow rate, sample size, and column length have been shown on retention volume and band width; and these in turn have been related to resolution in a chromatographic separation.

A. Resolution

It has been shown that the success of a chromatographic separation may be measured in terms of the resolution attained. Resolution has been defined as the distance between successive elution bands in a chromatogram. It may be expressed in terms of the retention volumes of the components under consideration and their band widths:

$$R = (V_{R2} - V_{R1}) - \frac{1}{2}(W_1' + W_2') \quad (53)$$

It is easy to see from Equation (53) that the conditions for good separation are narrow elution bands and widely separated retention volumes.

B. Retention Volume

1. Effect of Temperature

Studies have been made showing the effects of temperature and column length on the retention volumes of iso and normal butane. The

data show that decreasing the operating temperature of the chromatographic column increases the retention volume as predicted by theory, and also increases the difference in the retention volumes. It has been demonstrated that the data may be fitted by a curve of the form:

$$\log_{10} V_R = \frac{k_1}{T} + k_2, \quad (142)$$

or of the form:

$$\log_{10} \left[\frac{V_R - V_V}{T} \right] = \frac{c'}{T} - c''. \quad (87)$$

This latter form is the one predicted by the theoretical expression.

Figure 12 shows the data plotted in this manner.

2. Effect of Column Length

The relationship between column length and retention volume has been studied briefly and shown to be linear over the range considered. The expressions are

$$V_{R_I} = 3.28 V_V, \quad (121)$$

and

$$V_{R_N} = 4.62 V_V. \quad (122)$$

It should be noted, however, that it is quite possible that extrapolation of these results over a wide range could lead to very grave errors.

C. Band Width

1. Effect of Flow Rate

It has been shown that, for the systems studied, the band width may be estimated from the van Deemter equation. The agreement of

the constants predicted by the van Deemter equation with those calculated from the data is felt to fall within the accuracy of the experiment. As Figure 17 illustrates, band width is a decreasing function of average flow rate of velocity. The major factor leading to band broadening has been shown to be the resistance to mass transfer between the liquid and gas phases.

2. Effect of Column Length

The effect of column length on band width has also been shown to be in substantial agreement with the theory as proposed by van Deemter. It has been demonstrated that the square of the band width is directly proportional to length. This fact has been used to incorporate data taken on columns of different lengths into a single correlation of band width versus flow rate. The results of this correlation are presented in Equations (135) and (136). They are of the form

$$W^2 = (\text{CONSTANT}) V_V \left[\frac{A}{V^2} + \frac{B}{V^3} + \frac{C}{V} \right]. \quad (143)$$

3. Effect of Sample Size

Size of sample is an important factor in determining the band width of a component. In general band width increases as sample size increases. This effect has been shown in Figure 22. These correlations agree in general shape with the theoretical derivation of Porter; but, as has been pointed out, they differ from the theoretical curve by factors of approximately 5.7 and 8.0. No satisfactory explanation has been found for the difference.

D. Conclusion

Using the correlations mentioned above, it is possible to calculate resolution for a given sample. It is also possible to determine the span of an elution diagram and from this to determine the amount of sample which it is possible to separate per unit time. From these factors one may design a chromatographic column to perform a specified separation on a given amount of material.

E. Suggestions for Future Investigations

There are at least three areas in which opportunities for future work present themselves. The first of these is in studying the effect of temperature on the retention volume. As has been pointed out, over the temperature range considered it is impossible to say whether the data are fitted better by an equation of the form of Equation (142) or of Equation (87). An extension of the temperature range should clarify this issue.

Secondly, the effect of column diameter upon resolution presents itself as a fertile area of study. Although theoretically, column diameter should have no effect upon the operation of a column, it has been pointed out by certain authors that this is not the case.⁽⁴⁵⁾ These effects would prove vital in any attempt to scale up a chromatographic operation to a commercial basis.

Thirdly, it is clear that more work needs to be done in the study of sample size as a factor affecting resolution. In such a study the method of injecting the sample would undoubtedly be of great importance and should be given careful consideration. The theoretical treatments of the large sample phenomenon do not seem to agree adequately with the data and any amplification of these treatments would be a valuable addition.

APPENDICES

APPENDIX A

DERIVATION OF THEORETICAL PLATE EQUATION FOR SMALL SAMPLE

The differential equation for the material balance around the first plate is given by Equation (7):

$$\bar{Y}_0(V) dV = (V_g + kV_l) d\bar{Y}_0(V), \quad (7)$$

and the initial condition is:

$$\bar{Y}_0(0) = M. \quad (8)$$

Let

$$z = \frac{V}{V_g + kV_l} \quad (a)$$

Then (7) becomes:

$$\frac{d\bar{Y}_0(z)}{dz} = -\bar{Y}_0(z). \quad (b)$$

Solving (b) by separation of variables we get:

$$\bar{Y}_0(z) = ce^{-z}, \quad (c)$$

and from Equation (8) we find that $C = M$, so that

$$\bar{Y}_0(z) = Me^{-z}. \quad (d)$$

Now the general equation for the material balance is:

$$\frac{d\bar{Y}_P(V)}{dV} = \frac{\bar{Y}_{P-1} - \bar{Y}_P}{V_g + kV_l}, \quad (5)$$

and the initial conditions are:

$$\bar{Y}_1(0) = \bar{Y}_2(0) = \dots = \bar{Y}_n(0) = 0. \quad (6)$$

Equation (5) becomes

$$\frac{d\bar{Y}_p(z)}{dz} = \bar{Y}_{p,1} - \bar{Y}_p. \quad (e)$$

For $p = 1$ we have:

$$\frac{d\bar{Y}_1}{dz} = \bar{Y}_0 - \bar{Y}_1, \quad (f)$$

or

$$\bar{Y}_1' + \bar{Y}_1 = M e^{-z}. \quad (g)$$

The complementary solution of Equation (g) is

$$\bar{Y}_1(z) = c e^{-z}. \quad (h)$$

A particular solution of (g) is

$$\bar{Y}_1(z) = M z e^{-z}. \quad (i)$$

Therefore,

$$\bar{Y}_1(z) = M z e^{-z} + c e^{-z}, \quad (j)$$

and

$$\bar{Y}_1(0) = 0. \quad (k)$$

From (j) and (k) we see that $C = 0$. Thus,

$$\bar{Y}_1 = M e^{-z}(z). \quad (l)$$

Having determined Y_1 we now move on to Y_2 :

$$\bar{Y}_2' + \bar{Y}_2 = \bar{Y}_1 = M z e^{-z}. \quad (m)$$

Notice that in this, and all subsequent equations, the complementary solution is always the same:

$$\bar{Y}_{comp.} = c e^{-z}. \quad (n)$$

To find the particular solution we may use the exponential shift⁽⁵⁴⁾:

$$e^{ax} f(D)y = f(D-A)[e^{ax}y]. \quad (o)$$

Then for Equation (m):

$$e^{2(D+1)}Y_2 = Mz', \quad (p)$$

and with the exponential shift:

$$D(e^2Y_2) = Mz'. \quad (q)$$

Integrating:

$$Y_2(z) = Me^{-2} \int z dz = Me^{-2} \left(\frac{z^2}{2} \right). \quad (r)$$

From this we see that

$$Y_2(z) = ce^{-2} + Me^{-2} \frac{z^2}{2}, \quad (s)$$

and

$$Y_2(0) = 0. \quad (t)$$

As before $C = 0$ so

$$Y_2(z) = Me^{-2} \left(\frac{z^2}{2} \right). \quad (u)$$

For $Y_3(v)$ we find

$$Y_3(z) = Me^{-2} \int \frac{z^2}{2} dz = Me^{-2} \left(\frac{z^3}{3 \cdot 2} \right). \quad (v)$$

In like manner

$$Y_4(z) = Me^{-2} \left(\frac{z^4}{4!} \right), \quad (w)$$

and finally

$$\vdots \\ Y_n(z) = Me^{-2} \left(\frac{z^n}{n!} \right). \quad (9)$$

APPENDIX B

INTEGRATION OF THE THEORETICAL PLATE EQUATION
FOR A LARGE SAMPLE INTRODUCED EXPONENTIALLY

Equation (27) states:

$$\bar{Y}_n(V) = \frac{n}{V_R} \frac{1}{\sqrt{2\pi n}} \int_0^{S_0} Y(S) e^{-\frac{n}{2} \left[1 - \frac{V-S}{V_R} \right]^2} dS. \quad (27)$$

The form of $Y(S)$ is given as:

$$Y(S) = M e^{-S/B}. \quad (28)$$

Inserting this we obtain:

$$\bar{Y}_n(V) = \frac{n}{V_R} \frac{M}{\sqrt{2\pi n}} \int_0^V e^{-S/B - \frac{n}{2} \left(1 - \frac{V-S}{V_R} \right)^2} dS. \quad (a)$$

It is greatly to be desired that the part of the exponent in Equation (a) which contains S be made into a perfect square. The reason for this will be apparent later. Calling the exponent P , we have

$$P = - \left\{ \frac{S}{B} + \frac{n}{2} \left[\left(1 - \frac{V}{V_R} \right) + \frac{S}{V_R} \right]^2 \right\}. \quad (b)$$

Let

$$g = \left(1 - \frac{V}{V_R} \right), \quad (c)$$

and let us add and subtract

$$F = \frac{V_R}{2B} \left(\frac{V_R}{nB} + 2g \right). \quad (30)$$

Then we have:

$$P = F - \left\{ \frac{V_R}{2B} \left(\frac{V_R}{nB} + 2g \right) + \frac{S}{B} + \frac{n}{2} \left(g + \frac{S}{V_R} \right)^2 \right\}. \quad (d)$$

$$= F - \frac{n}{2} \left\{ \frac{2S}{nB} + \left(g + \frac{S}{V_R} \right)^2 + \frac{V_R}{nB} \left(\frac{V_R}{nB} + 2g \right) \right\}. \quad (e)$$

$$= F - \frac{n}{2} \left\{ \frac{2S}{nB} + \underline{g^2} + \underline{2g \left(\frac{S}{V_R} \right)} + \left(\frac{S}{V_R} \right)^2 + \left(\frac{V_R}{nB} \right)^2 + \underline{2g \left(\frac{V_R}{nB} \right)} \right\}$$

$$= F - \frac{n}{2} \left\{ \left(g + \frac{V_R}{nB} \right)^2 + 2 \left(\frac{S}{V_R} \right) \left(g + \frac{V_R}{nB} \right) + \left(\frac{S}{V_R} \right)^2 \right\}.$$

$$= F - \frac{n}{2} \left\{ \left(g + \frac{V_R}{nB} \right) + \left(\frac{S}{V_R} \right) \right\}^2.$$

$$P = F - \frac{n}{2} \left\{ \frac{S}{V_R} + \left(1 - \frac{1}{V_R} \right) + \frac{V_R}{nB} \right\}^2. \quad (f)$$

Inserting this expression for P into Equation (a) we get:

$$\Sigma_n(V) = \frac{n}{V_R} \frac{M}{\sqrt{2\pi n}} e^F \int_0^V e^{-\frac{n}{2} \left\{ \frac{S}{V_R} + g + \frac{V_R}{nB} \right\}^2} dS. \quad (g)$$

Now if we let

$$Q(S) = \sqrt{\frac{n}{2}} \left(\frac{S}{V_R} + g + \frac{V_R}{nB} \right), \quad (h)$$

then

$$dQ = \sqrt{\frac{n}{2}} \left(\frac{1}{V_R} \right) dS, \quad (i)$$

and Equation (g) becomes

$$\Sigma_n(V) = \frac{n}{V_R} \frac{M}{\sqrt{2\pi n}} e^F \int_{X_0}^{X_1} e^{-Q^2} \frac{V_R}{\sqrt{n/2}} dQ, \quad (j)$$

or

$$Y_n(V) = \frac{M}{2} e^F \cdot \frac{2}{\sqrt{\pi}} \int_{X_0}^{X_1} e^{-Q^2} dQ, \quad (k)$$

where

$$X_0 = \sqrt{\frac{n'}{2}} \left(\frac{S}{V_R} + \frac{V_R}{nB} \right), \quad (31)$$

and

$$X_1 = \sqrt{\frac{n'}{2}} \left(1 + \frac{V_R}{nB} \right). \quad (32)$$

Recalling that the definition of the error function is

$$\text{erf } \alpha = \frac{2}{\sqrt{\pi}} \int_0^\alpha e^{-x^2} dx, \quad (l)$$

we see that

$$\frac{2}{\sqrt{\pi}} \int_{X_0}^{X_1} e^{-Q^2} dQ = \text{erf } X_1 - \text{erf } X_0. \quad (m)$$

Then finally:

$$Y_n(V) = \frac{M}{2} e^F [\text{erf } X_1 - \text{erf } X_0]. \quad (29)$$

It should be noted that in Porter's article⁽⁵²⁾, there are three typographical errors in his result. His expression for F is given as

$$F = \frac{V_R}{nB} \left[\frac{1}{nB} + 2g \right],$$

omitting the second V_R in his Equation(XIII). In that same equation the square root sign is omitted from the π . In his definition of X_1 , the square root sign is omitted from the r (number of plates).

APPENDIX C

DERIVATION OF RETENTION VOLUME EXPRESSION

From the definition of retention volume given in Equation (58):

$$V_R = \bar{v} t_R, \quad (58)$$

where $t_R = d_R/S$ in Figure 2. Now also by definition:

$$\bar{v} = V_V/t_0, \quad (95)$$

so

$$V_R = V_V \frac{t_R}{t_0}. \quad (a)$$

The difference in emergence times between the air and sample peaks is given by the equation:

$$t_R - t_0 = \frac{d_R - d_0}{S}. \quad (b)$$

Thus Equation (a) may be written:

$$V_R = V_V \left[\frac{t_0 + \frac{d_R - d_0}{S}}{t_0} \right], \quad (c)$$

or

$$V_R = V_V + \frac{V_V}{S t_0} (d_R - d_0). \quad (d)$$

In discussing the gas flow rate, it is shown that the residence time for the gas is given by the expression:

$$t_0 = \frac{2}{3} \frac{V_V}{v_0 \phi(r)}. \quad (93)$$

Using Equation (93) in Equation (d) we have:

$$V_R = V_V + \frac{3}{2} \phi(r) \frac{V_0}{S} (d_R - d_0), \quad (61)$$

where

$$\varphi(r) = \frac{r^2 - 1}{r^3 - 1}, \quad (62)$$

and

$$r = (P_i/P_o). \quad (63)$$

APPENDIX D

DERIVATION OF THE RATE THEORY EQUATION
FOR PLUG FLOW SAMPLE INJECTION

We begin this derivation by slightly re-writing the material balance given in Equation (39):

$$D \underline{Y}_{zz}(z,t) = u \underline{Y}_z(z,t) + \underline{Y}_t(z,t) + \frac{F_2}{F_1} \underline{X}_t(z,t). \quad (39)$$

The liquid phase material balance is given in Equation (40):

$$F_2 \underline{X}_t(z,t) = \alpha \left[Y(z,t) - \frac{X(z,t)}{k} \right]. \quad (40)$$

The initial conditions in the column may be expressed as:

$$\underline{Y}(z,0) = \underline{X}(z,0) = 0. \quad (a)$$

And the boundary conditions are:

$$\underline{Y}(0,t) = \underline{Y}_0(t) = \begin{cases} M, & t < t_0 \\ 0 & t > t_0 \end{cases}, \quad (b)$$

and

$$\lim_{z \rightarrow \infty} \underline{Y}(z,t) < M' \text{ (some constant)}. \quad (c)$$

The five equations presented above constitute the boundary value problem.

These may be solved by means of the Laplace transform. We define the transform of $Y(z,t)$ as

$$\mathcal{L}\{\underline{Y}(z,t)\} = h(z,s) = \int_0^{\infty} e^{-st} \underline{Y}(z,t) dt,$$

and the transform of $X(z, t)$ as

$$\mathcal{L}\{X(z, t)\} = \chi(z, s) = \int_0^{\infty} e^{-st} X(z, t) dt.$$

Taking the transform of Equation (39) we get:

$$D h''(z, s) = u h'(z, s) + s h(z, s) + \frac{F_2}{F_1} s \chi(z, s). \quad (d)$$

The transform of Equation (40) gives:

$$s \chi(z, s) = \frac{\alpha}{F_2} \left(h(z, s) - \frac{\chi(z, s)}{k} \right). \quad (e)$$

Eliminating $\chi(z, s)$ from these two equations we get:

$$D h'' - u h' - s h \left[1 + \frac{\alpha/F_2}{s + \alpha/kF_2} \right] = 0. \quad (f)$$

Transforming Equations (b) and (c) we see,

$$\mathcal{L}\{Y_0(A)\} = h_0(s) = \frac{M}{z} [1 - e^{-st_0}], \quad (g)$$

and

$$\lim_{z \rightarrow \infty} h(z, s) < \frac{M'}{s}, \quad (s > 0). \quad (h)$$

Now a simplifying substitution will be made. Let

$$y(z, s) = h(z, s) e^{-\frac{uz}{2D}}. \quad (i)$$

Then Equation (f) reduces to

$$y''(z, s) - g y(z, s) = 0, \quad (j)$$

where $g(s) = \frac{1}{D} \left[\frac{s^2 + As + B}{s + m} \right], \quad (k)$

$$m = \frac{\alpha}{k F_g} \quad (l)$$

$$A = \frac{u^2}{4D} + \frac{\alpha}{F_g} + m, \quad (m)$$

and

$$B = \frac{u^2 m}{4D}. \quad (n)$$

Equation (g) becomes

$$y_0(s) = \frac{M}{s} [1 - e^{-st_0}], \quad (o)$$

and Equation (h) becomes

$$\lim_{z \rightarrow \infty} y(z, s) = 0. \quad (p)$$

We may now solve this ordinary differential equation. The general solution is:

$$y(z, s) = c_1 e^{z\sqrt{g'}} + c_2 e^{-z\sqrt{g'}}. \quad (q)$$

At $z = \infty$, we find $y(\infty, s) = 0 = c_1 e^{\infty}$, or $c_1 = 0$.

At $z = 0$, we find $y(0, s) = y_0(s) = c_2 e^{(0)}$. Therefore $c_2 = y_0(s)$.

Thus

$$y(z, s) = y_0(s) e^{-z\sqrt{g'}}. \quad (r)$$

We may re-write this

$$y(z, s) = y_0(s) \left[m \frac{e^{-z\sqrt{g'}}}{s+m} + s \frac{e^{-z\sqrt{g'}}}{s+m} \right],$$

or letting

$$Q(s) = \frac{e^{-z\sqrt{g'}}}{s+m} \quad (s)$$

$$y(z, s) = y_0(s) [mQ + sQ]. \quad (t)$$

Now let us find the inverse of $Q(s)$.

It can be shown that:

$$\mathcal{L}\left\{\int_0^t J_0[2\sqrt{ax(t-x)}]f(x)dx\right\} = \frac{1}{s} \varphi\left(s + \frac{a}{s}\right), \quad (u)$$

where

$$\varphi(s) = \mathcal{L}\{f(t)\}. \quad (v)$$

Then we know that:

$$\mathcal{L}\left\{e^{-mt} \int_0^t J_0[2\sqrt{ax(t-x)}]f(x)dx\right\} = \frac{1}{s+m} \varphi\left(s+m + \frac{a}{s+m}\right),$$

or

$$\mathcal{L}\left\{e^{-mt} \int_0^t J_0[2\sqrt{ax(t-x)}]f(x)dx\right\} = \frac{1}{s+m} \varphi\left[\frac{s^2 + 2ms + m^2 + a}{s+m}\right]. \quad (w)$$

Now $\varphi\left[\frac{s^2 + 2ms + m^2 + a}{s+m}\right]$ will be squeezed into the form of Equation (s).

Let

$$\varphi(s) = e^{-\frac{z}{\sqrt{D}}\sqrt{s+d}}. \quad (x)$$

Thus in Equation (w):

$$\varphi\left(\frac{s^2 + 2ms + m^2 + a}{s+m}\right) = \exp\left\{-\frac{z}{\sqrt{D}}\sqrt{\frac{s^2 + s(2m+d) + (m^2 + a + md)}{D(s+m)}}\right\}.$$

Now if we let $A = 2m + d$, (y)

and $B = m^2 + a + md$, (z)

then the quantity under the square root sign will be g .

Equations (y) and (z) mean that we are assigning values to d and a .

These values are:

$$a = -\frac{\alpha M}{F_g}, \quad (aa)$$

$$d = \frac{u^2}{4D} + \frac{\alpha}{F_g} - M. \quad (bb)$$

Now Equation (w) reads

$$\mathcal{L}\left\{e^{-mt} \int_0^t I_0\left[2\sqrt{\frac{\alpha m}{Fg}} x(t-x)\right] f(x) dx\right\} = \frac{e^{-z/g}}{s+m} = Q(s), \quad (\text{cc})$$

where

$$f(t) = \mathcal{L}^{-1}\left\{e^{-\frac{z}{D}\sqrt{s+d}}\right\}. \quad (\text{dd})$$

From Churchill⁽⁷⁾:

$$\mathcal{L}^{-1}\left\{e^{-k\sqrt{s}}\right\} = \frac{k}{2\sqrt{\pi t^3}} e^{-k^2/4t}. \quad (\text{ee})$$

Therefore:

$$\mathcal{L}^{-1}\left\{e^{-\frac{z}{D}\sqrt{s+d}}\right\} = \frac{z}{2\sqrt{\pi D t^3}} e^{-\frac{z^2}{4Dt}} e^{-dt}.$$

Then

$$f(t) = \frac{z}{2\sqrt{\pi D t^3}} e^{-\left[\frac{z^2}{4Dt} + \frac{ut^2}{4Dt} + \frac{\alpha t}{Fg} - mt\right]},$$

or

$$f(t) = \frac{z}{2\sqrt{\pi D t^3}} e^{-\left[\frac{(z-ut)^2}{4Dt} + \frac{uz}{2D} + \frac{\alpha t}{Fg} - mt\right]}. \quad (\text{ff})$$

Now we know the inverse of $Q(s)$ from Equations (cc) and (ff). Notice however that

$$J_0(ix) = I_0(x).$$

Therefore

$$\mathcal{L}^{-1}\{Q(s)\} = e^{-mt} \int_0^t I_0(\xi) f(x) dx = G(t), \quad (\text{gg})$$

where

$$\xi = 2\sqrt{\frac{\alpha m}{Fg}} x(t-x). \quad (\text{hh})$$

Now going back to Equation (t):

$$L\{F'(t)\} = sL\{F(t)\} - F(0).$$

Therefore

$$G'(t) = L^{-1}\{sQ(s)\}. \quad (\text{ii})$$

So

$$L^{-1}\{mQ + sQ\} = mG(t) + G'(t). \quad (\text{jj})$$

And

$$\nabla(z, t) e^{\frac{uz}{2D}} = \nabla_0(t) * [mG(t) + G'(t)]. \quad (\text{kk})$$

The convolution form used in Equation (kk) is by definition:

$$\nabla(z, t) = e^{-\frac{uz}{2D}} \int_0^t \nabla_0(t-\tau) [mG(\tau) + G'(\tau)] d\tau. \quad (\text{ll})$$

Now

$$\nabla_0(t-\tau) = \begin{cases} 0, & \tau < t-t_0 \\ M, & \tau > t-t_0 \end{cases}. \quad (\text{mm})$$

Thus

$$\nabla(z, t) = Me^{-\frac{uz}{2D}} \int_{t-t_0}^t [mG(x) + G'(x)] dx. \quad (\text{nn})$$

And if $t_0 \ll t$, then the interval over which we integrate (t_0) will be small, and we can assume that $[mG(t) + G'(t)]$ is approximately constant.

With this assumption we have:

$$\nabla(z, t) \cong Me^{-\frac{uz}{2D}} [mG(t) + G'(t)]. \quad (\text{oo})$$

Now we need to evaluate $G'(t)$. Leibnitz's rule states:

$$\frac{d}{dt} \int_{u(t)}^{v(t)} f(t,x) dx = \int_{u(t)}^{v(t)} \frac{\partial f}{\partial t} dx + f[v(t),t]v'(t) - f[u(t),t]u'(t).$$

Thus,

$$G'(t) = e^{-mt} \left\{ \frac{d}{dt} \int_0^t I_0(\xi) f(x) dx - m \int_0^t I_0(\xi) f(x) dx \right\}.$$

$$G'(t) = e^{-mt} \left\{ \int_0^t I_1(\xi) \sqrt{\frac{\alpha m}{F_g} \frac{x}{t-x}} f(x) dx + I_0(0) f(t) \right\} - mG(t). \quad (pp)$$

Therefore

$$\mathcal{V}(z,t) = Mt_0 e^{-\frac{uz}{2D} - mt} \left\{ f(t) + \int_0^t I_1(\xi) \sqrt{\frac{\alpha m}{F_g} \frac{x}{t-x}} f(x) dx \right\}$$

or

$$\frac{\mathcal{V}(z,t)}{M} = \frac{zt_0}{2\sqrt{\pi D t^3}} e^{-\left[\frac{(z-ut)^2}{4Dt} + \frac{\alpha t}{F_g}\right]} + \int_0^t \sqrt{\frac{\alpha m}{F_g} \frac{x}{t-x}} I_1(\xi) \frac{zt_0}{2\sqrt{\pi D x^3}} e^{-\left[\frac{(z-ux)^2}{4Dx} + \frac{\alpha x}{F_g} + m(t-x)\right]} dx.$$

And letting $F(x) = \sqrt{\frac{\alpha m}{F_g} \frac{x}{t-x}} I_1(\xi) \exp\left\{-\left[\frac{\alpha x}{F_g} + m(t-x)\right]\right\}$, (qq)

we have:

$$\frac{\mathcal{V}(z,t)}{M} = \frac{zt_0}{2\sqrt{\pi D t^3}} e^{-\left[\frac{(z-ut)^2}{4Dt} + \frac{\alpha t}{F_g}\right]} + \int_0^t \frac{zt_0 F(x)}{2\sqrt{\pi D x^3}} e^{-\frac{(z-ux)^2}{4Dx}} dx. \quad (rr)$$

Now if ξ is large,

$$I_1(\xi) \sim \frac{e^\xi}{\sqrt{2\pi\xi}} \quad (ss)$$

Making this approximation the expression for $F(x)$ reduces to:

$$F(x) = \frac{1}{2\sqrt{\pi}} \sqrt{\frac{\alpha m}{F_g} \frac{x}{(t-x)^3}} \exp\left\{-\frac{\alpha}{kk'} \left[\frac{(t-\frac{x}{\beta})}{\sqrt{\frac{F_g}{k}(t-x)} + \sqrt{x F_g}} \right]^2\right\}, \quad (tt)$$

where

$$\frac{1}{\beta} = 1+k', \quad (45)$$

and

$$k' = k\left(\frac{F_D}{F_g}\right).$$

Now in Equation (tt), the exponential term has a maximum value when $x = \beta t$. In Equation (rr) the exponential term's maximum occurs when $x = z/u$. Then if we assume a fairly close approach to ideal chromatography (i.e., not much diffusion and a close approach to equilibrium), we can say that almost all of the peak lies near

$$x \sim \frac{z}{u} \sim \beta t. \quad (uu)$$

Therefore, we may substitute either z/u or βt for x any place except in the numerator of an exponent. This further reduces the expression for $F(x)$ to:

$$F(x) = \frac{1}{2} \sqrt{\frac{\alpha u}{\pi F_g k'^2 z}} \exp\left\{-\frac{\alpha u}{4z k'^2 F_g} \left[t - \frac{x}{\beta}\right]^2\right\}. \quad (vv)$$

We may also simplify Equation (rr) by neglecting the first term. This is justified since $(z-ut) \sim ut(\beta-1) = k'ut$, and the exponent may be written $\exp\left\{-\frac{k'u}{4D} - \frac{\alpha t}{F_g}\right\}$. Then Equation (rr) reads:

$$\frac{Y(z,t)}{M} = \int_0^t \frac{z t_0}{2\sqrt{\pi D x^3}} e^{-\frac{(z-ux)^2}{4Dx}} \cdot \frac{1}{2} \sqrt{\frac{\alpha u}{\pi F_g k'^2 z}} e^{-\frac{\alpha u}{4z F_g k'^2} \left[t - \frac{x}{\beta}\right]^2} dx,$$

or once again making the substitutions of Equation (uu):

$$\frac{Y(z,t)}{M} = \frac{\beta t_0}{2\pi} \int_0^t \frac{1}{\sigma_1 \sigma_2} e^{-\left\{\frac{(\frac{z}{\beta} - x)^2}{2\sigma_1^2} + \frac{(\beta t - x)^2}{2\sigma_2^2}\right\}} dx, \quad (ww)$$

where

$$\sigma_1^2 = \frac{2Dz}{u^3}, \quad (46)$$

and

$$\sigma_2^2 = \frac{F_g k'^2 z}{\alpha u} (2\beta^2). \quad (47)$$

This integral may be re-written:

$$\frac{Y(z,t)}{M} = \frac{\beta t_0}{2\pi} e^{-\frac{(\beta t - z/u)^2}{2(\sigma_1^2 + \sigma_2^2)}} \int_0^t \frac{1}{\sigma_1 \sigma_2} e^{-\frac{\sigma_1^2 + \sigma_2^2}{2\sigma_1^2 \sigma_2^2} \left[x - \frac{\beta \sigma_1^2 + \frac{z \sigma_2^2}{u}}{\sigma_1^2 + \sigma_2^2} \right]^2} dx. \quad (xx)$$

It may now be seen that the integral in Equation (xx) is the difference of two error functions. Calling the integral I, we have:

$$I = \frac{\sqrt{\pi/2}}{\sqrt{\sigma_1^2 + \sigma_2^2}} \left[\text{erf } N_t - \text{erf } N_0 \right],$$

where

$$N_0 = -\sqrt{\frac{\sigma_1^2 + \sigma_2^2}{2\sigma_1^2 \sigma_2^2}} \left(\frac{\beta t \sigma_1^2 + \frac{z \sigma_2^2}{u}}{\sigma_1^2 + \sigma_2^2} \right), \quad (yy)$$

and

$$N_t = \sqrt{\frac{\sigma_1^2 + \sigma_2^2}{2\sigma_1^2 \sigma_2^2}} \left(t - \frac{\beta t \sigma_1^2 + \frac{z \sigma_2^2}{u}}{\sigma_1^2 + \sigma_2^2} \right). \quad (zz)$$

It may be shown that both N_t and N_0 will be large if $\left(\frac{zu}{2D}\right)$ and $\left(\frac{Fg zu}{\alpha}\right)$ are large. Since this is generally the case in chromatography we may say that:

$$\text{erf } N_t - \text{erf } N_0 = \text{erf } N_t + \text{erf } |N_0| \sim 2,$$

and

$$I \sim \frac{\sqrt{2\pi}}{\sqrt{\sigma_1^2 + \sigma_2^2}}.$$

Thus,

$$Y(z,t) = \frac{M \beta t_0}{\sqrt{2\pi} (\sigma_1^2 + \sigma_2^2)} e^{-\frac{(\frac{z}{u} - \beta t)^2}{2(\sigma_1^2 + \sigma_2^2)}}. \quad (44)$$

APPENDIX E

DERIVATION OF THE VAN DEEMTER EQUATION FOR
THE HEIGHT EQUIVALENT TO A THEORETICAL PLATE

We want to compare the rate equation with the plate equation in order to determine the Height Equivalent to a Theoretical Plate.

The rate equation derived in Appendix D is given as:

$$Y(z,t) = \frac{M\beta t_0}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}} e^{-\frac{(z/\mu - \beta t)^2}{2(\sigma_1^2 + \sigma_2^2)}} \quad (44)$$

The plate theory equation we shall use is presented in Equation (25):

$$\Sigma_n(V) = \frac{n}{V_R} \frac{g_0}{\sqrt{2\pi n}} e^{-\frac{(n - \frac{nV}{V_R})^2}{2n}} \quad (25)$$

Now in Equation 25,

$$V_R = n(V_g + kV_l) \quad (a)$$

But

$$V_g = (Ha)F_g \quad (b)$$

and

$$V_l = (Ha)F_l \quad (c)$$

so

$$V_R = nHa(F_g + kF_l) = \frac{nHaF_g}{\beta} \quad (d)$$

where

$$H = HETP = \frac{z}{n} \quad (e)$$

Also in Equation (25):

$$g_0 = MF_g \text{ auto}, \quad (f)$$

and

$$V = F_g \text{ aut}. \quad (g)$$

Therefore, Equation (25) becomes

$$\bar{Y}_n(V) = \left(\frac{B}{HaF_g} \right) \frac{M F_a u_0}{\sqrt{2\pi n}} e^{-\frac{\left(\frac{\beta u_0}{H} - n\right)^2}{2n}} \quad (h)$$

or

$$\frac{\bar{Y}_n(V)}{M} = \frac{\beta u_0}{H} \frac{1}{\sqrt{2\pi n}} e^{-\frac{\left(\frac{\beta u_0}{H} - n\right)^2}{2n}} \quad (i)$$

Looking now at Equation (44), and making the substitutions for σ_1^2 and σ_2^2 , and letting $z = nH$, we get:

$$\frac{\bar{Y}(z,t)}{M} = \frac{\beta t_0}{\sqrt{2\pi}} \frac{1}{\sqrt{\frac{2Dz}{u^3} + \frac{2\beta^2 F_g K^2 z}{\alpha u}}} \exp\left\{-\frac{\left(\frac{z}{u} - \beta t\right)^2}{\frac{4z}{u}\left(\frac{D}{u^2} + \frac{\beta^2 F_g K^2}{\alpha}\right)}\right\},$$

or

$$\frac{\bar{Y}(z,t)}{M} = \frac{\beta t_0}{\sqrt{2\pi}} \frac{u}{H} \frac{1}{\sqrt{\frac{2n}{H}\left[\frac{D}{u} + \frac{u F_g}{\alpha}(\beta K)^2\right]}} \exp\left\{-\frac{\left(n - \frac{\beta u_0}{H}\right)^2}{\frac{4n}{H}\left[\frac{D}{u} + \frac{u F_g}{\alpha}(\beta K)^2\right]}\right\} \quad (j)$$

$$\text{Now we will let } H' = 2\left[\frac{D}{u} + \frac{u F_g}{\alpha}(\beta K)^2\right], \quad (k)$$

and we will show that $H' = H$.

In Equation (j) with this substitution we get:

$$\frac{\bar{Y}(z,t)}{M} = \frac{\beta u_0}{H\sqrt{2\pi}} \frac{1}{\sqrt{\frac{nH'}{H}}} e^{-\frac{\left(n - \frac{\beta u_0}{H}\right)^2}{\left(\frac{2nH'}{H}\right)}} \quad (l)$$

or

$$\frac{\bar{Y}}{M} = \frac{\beta u_0}{H} \frac{1}{\sqrt{2\pi n}} \sqrt{\frac{H}{H'}} \exp\left\{-\frac{\left(\frac{\beta u_0}{H} - n\right)^2}{2n} \frac{H}{H'}\right\} \quad (l)$$

Equating this with Equation (i) we find:

$$\sqrt{\frac{H'}{H}} e^{-P\left(\frac{H}{H'}\right)} = e^{-P}, \quad (m)$$

where

$$P = \frac{\left(\frac{\beta u t}{H} - n\right)^2}{2n}. \quad (n)$$

Rearranging Equation (m) we have:

$$\sqrt{\frac{H'}{H}} e^{P(1-H/H')} - 1 = 0. \quad (o)$$

If $P = 0$, then $\sqrt{H/H'} = 1$ or $H = H'$.

If $P \neq 0$, then let $H/H' = \lambda$. (p)

Equation (o) becomes:

$$\sqrt{\lambda} e^{P(1-\lambda)} - 1 = 0. \quad (q)$$

The solution to this equation is also $\lambda = 1$ or $H = H'$.

Thus we have shown that

$$H = \frac{2D}{u} + \frac{2uFg}{\alpha} \left[\frac{k'}{1+k'} \right]^2, \quad (r)$$

and if we split the gas diffusion coefficient into its component parts we get the expression for H shown in Equation (48).

$$D = \lambda d_p u + \gamma D_{gas}, \quad (s)$$

and

$$\alpha = \frac{\pi^2}{4} \frac{F_0 D_{ig} k}{d_f^2}, \quad (t)$$

so

$$H = 2\lambda d_p + \frac{2\gamma D_{gas}}{u} + \frac{8}{\pi^2} \frac{d_f^2}{D_{ig}} \frac{k'}{(1+k')^2} u. \quad (u)$$

APPENDIX F

DATA ON COLUMN CONSTANTS

Column 6.

Column: 1/4" Cu tubing (ID = 0.19") Length = 20 ft.

Packing: Johns-Manville Columpak, 35-40 mesh

$$\rho_{F.B.} = 1.52 \text{ gm/cc}$$

Liquid Phase: Diisodecylphthalate.

$$M.W. = 414 \quad \rho_s = 0.961 \text{ gm/cc @ } 26^\circ\text{C.}$$

$$\text{Liquid/Solid} = 0.50 \text{ gm/gm}$$

$$\text{Total Volume} = 111.8 \text{ cc}$$

$$\text{Void Volume, } V_V = 82.15 \text{ cc}$$

$$\text{Liquid Volume, } V_S = 13.1 \text{ cc}$$

$$\text{Solid Volume} = 16.55 \text{ cc}$$

Column 6'.

This column is Column 6 cut approximately in half. The measured void volume is: $V_V = 40.4 \text{ cc}$.

Column 6".

This column is the top quarter of Column 6. The measured void volume is: $V_V = 21.0 \text{ cc}$.

Flow Rate Estimation.

For a constant outlet pressure, the flow rate through a packed bed may be estimated from the inlet pressure. A calibration curve for Column 6 is shown in Figure 25. The correction curve for the pressure gage used is given in Figure 26.

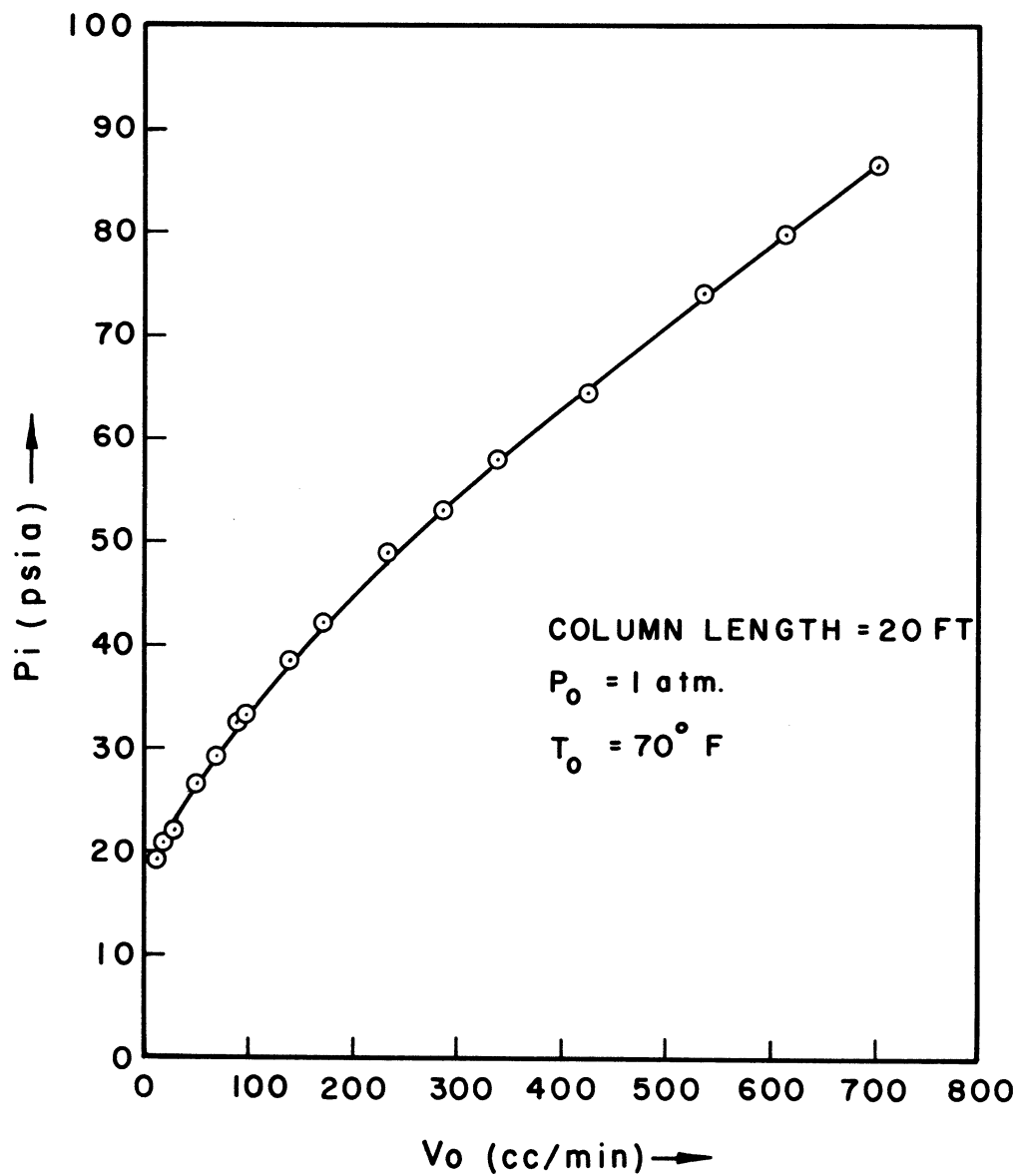


Figure 25. Approximate Flow Rate Determined From Inlet Pressure.

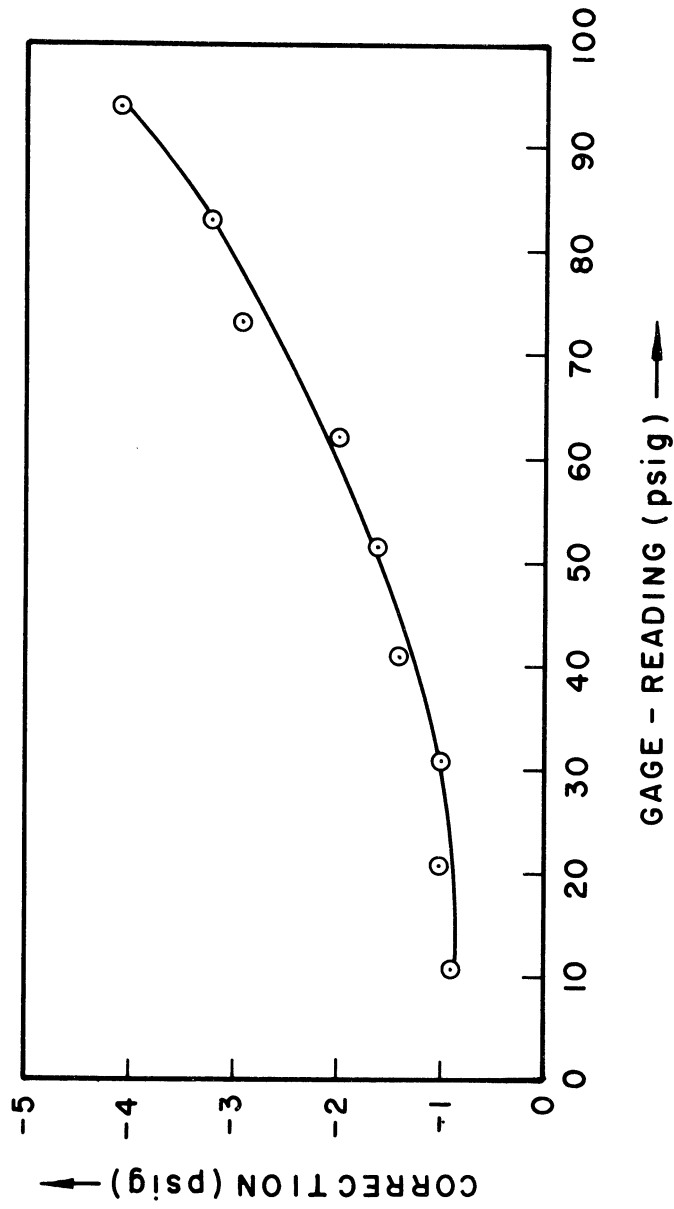


Figure 26. Corrections to be Subtracted from Pressure Gage Reading.

APPENDIX G

THERMAL CONDUCTIVITY CELL CALIBRATION DATA

The data for calibrating the conductivity cell response for air, normal butane, and isobutane are presented in Table VIII. Injections were made with a hypodermic syringe, and areas were measured with a planimeter. The calibration curves are shown in Figure 27.

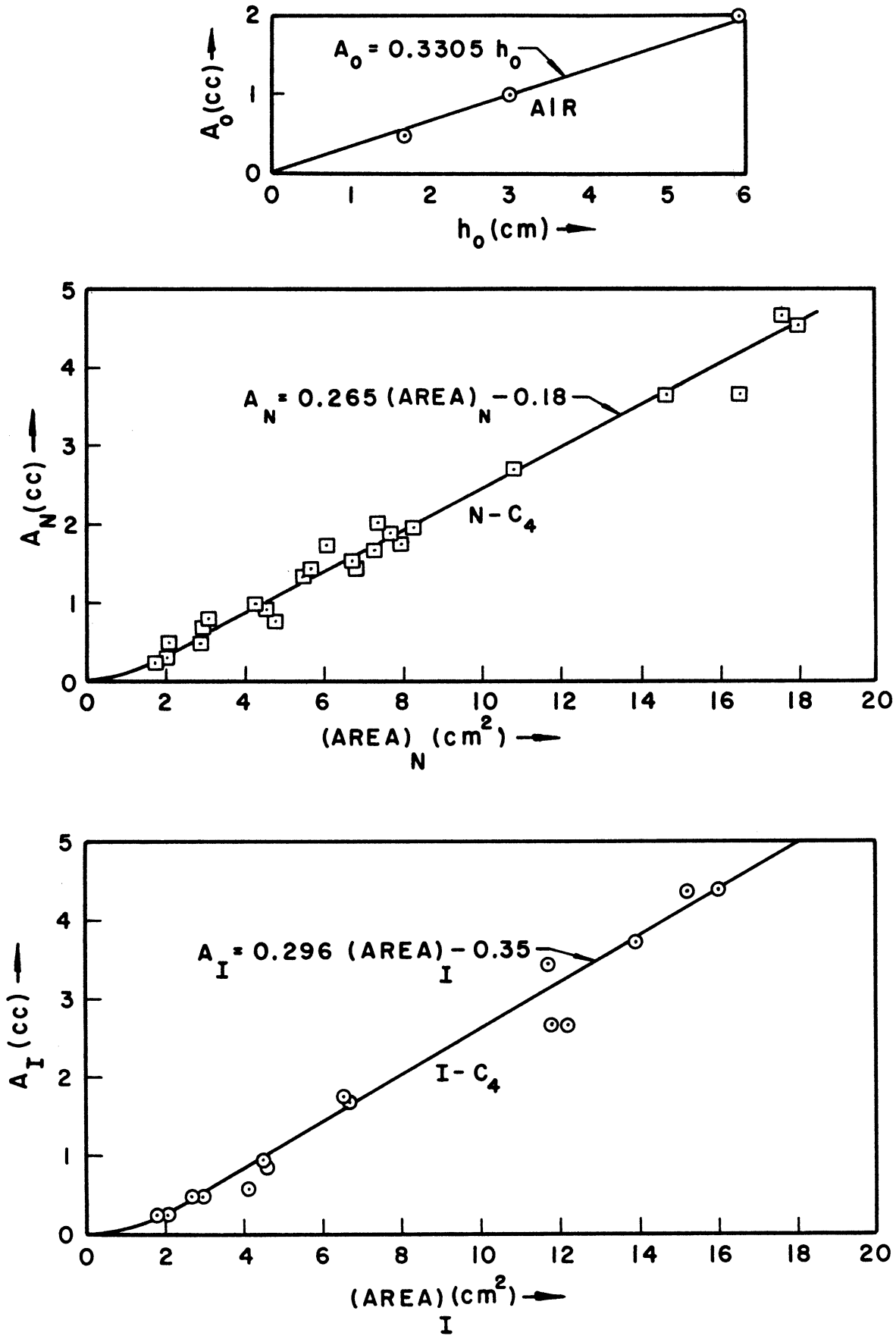


Figure 27. Thermal Conductivity Cell Calibration Curves.

TABLE VIII
CONDUCTIVITY CELL CALIBRATION

Column No. 6 $T_c = 70.0^\circ\text{F}$ $v_o(\text{avg}) = 58 \text{ cc/min}$ $p_o(\text{avg}) = 29.3''\text{Hg}$ $p_i(\text{avg}) = 22''\text{Hg}$

Air			
Run No.	A_{Total} (cc)	h_o (cm)	A_o (cc)
601	2.0	5.90	2.0
602	1.0	3.00	1.0
603	0.5	1.69	0.5

Normal Butane									
Run No.	A_{Total} (cc)	h_o (cm)	A_o (cc)	(Area) _P (cm ²)	A_P (cc)	(Area) _I (cm ²)	A_I (cc)	(Area) _N (cm ²)	A_N (cc)
604	2.0	.70	.23	.08	.02	.182	.03	6.1	1.72
605	2.0	.90	.29	.07	.02	.16	.03	7.3	1.66
606	1.5	0	0	.07	.02	.18	.03	5.7	1.45
607	1.5	.35	.11	.06	.01	.12	.02	5.5	1.36
608	1.0	.25	.08	.04	.01	.06	.01	4.6	.90
609	1.0	0	0	.02	.00	.055	.01	4.3	.99
610	0.8	.10	.03	.03	.01	.06	.01	4.8	.75
611	0.8	.35	.11	.02	0	.025	0	2.9	.69
612	0.5	0	0	0	0	0	0	2.1	.50
613	0.5	0	0	.02	0	.07	.01	2.9	.49
614	0.25	0	0	0	0	0	0	1.8	.25
615	0.25	0	0	0	0	0	0	2.0	.25
616	2.0	1.17	.38	.18	.04	.21	.04	6.7	1.54
617	2.0	0	0	.22	.05	.29	.05	7.7	1.90
618	3.0	4.33	1.41	.24	.05	.33	.06	6.8	1.48
619	3.0	.38	.12	.40	.09	.52	.09	10.8	2.70
620	3.0	3.08	1.00	.25	.06	.35	.06	8.3	1.88
621	4.0	.40	.13	.52	.12	.56	.10	14.7	3.65
622	4.0	.35	.11	.54	.12	.59	.10	16.5	3.67
623	5.0	.20	.07	.66	.15	.70	.12	17.6	4.66
624	5.0	.55	.18	.62	.14	.68	.12	18.0	4.56
625	2.3	.45	.15	.31	.07	.32	.06	7.4	2.02
626	2.3	4.50	1.46	.07	.02	.15	.03	3.1	0.79
627	2.3	1.40	.46	.26	.06	.26	.04	8.0	1.74

TABLE VIII (CONT'D)
 CONDUCTIVITY CELL CALIBRATION

Column No. 6 $T_c = 70.0^\circ\text{F}$ $v_o(\text{avg}) = 58 \text{ cc/min}$ $p_o(\text{avg}) = 29.3''\text{Hg}$ $p_i(\text{avg}) = 22''\text{Hg}$

Isobutane

Run No.	A_{Total} (cc)	h_o (cm)	A_o (cc)	(Area) _P (cm^2)	A_P (cc)	(Area) _N (cm^2)	A_N (cc)	(Area) _I (cm^2)	A_I (cc)
628	0.5	0	0	0	0	.21	.02	3.0	.48
629	0.5	0	0	0	0	.20	.02	2.7	.48
630	1.0	0	0	0	0	.34	.04	4.5	.96
631	1.0	1.16	.38	0	0	.29	.03	4.1	.59
633	2.0	.44	.14	.04	.01	.69	.10	6.5	1.75
634	3.0	.55	.18	.06	.01	.96	.15	12.2	2.66
635	4.0	0	0	.10	.02	1.39	.26	13.9	3.72
636	5.0	1.00	.33	.08	.01	1.48	.29	15.2	4.37
637	5.0	.96	.31	.10	.02	1.47	.29	16.0	4.38
638	4.0	.90	.29	.06	.01	1.43	.28	11.7	3.42
639	3.0	.40	.13	.06	.01	1.20	.20	11.8	2.66
640	2.0	.60	.20	.03	.01	.73	.11	6.7	1.68
641	1.0	.40	.13	.02	0	.43	.05	4.6	.82
642	0.5	0	0	0	0	.30	.04	2.9	.46
643	0.25	0	0	0	0	.14	.02	1.8	.23
644	0.25	0	0	0	0	.13	.02	2.1	.23

APPENDIX H

SAMPLE CALCULATIONS

1. Void Volume Determination, Run 4, Column 6.

$$V_V = \frac{P_{out} V_{out}}{P_i - P_f} - V_1, \quad (109)$$

$$= \frac{(28.86)(56.2)}{(19.56)} - 0.93 = 82.1 \text{ cc.} \quad (a)$$

2. Retention Volume, Isobutane, Run 201.

$$\text{Average flow rate: } \bar{v} = \frac{\bar{v}}{2} \phi(r) v_0, \quad (59)$$

$$= 1.5 \left[\frac{(82.2/14.7)^2 - 1}{(82.2/14.7)^2 - 1} \right] (675) = 177 \text{ cc/min.} \quad (b)$$

$$\text{Retention volume: } V_{R_I} = V_V + \frac{\bar{v}}{S} (d_{R_I} - d_0), \quad (64)$$

$$= 82.1 + \frac{177}{1.02} (1.775 - 0.60) = 286.1 \text{ cc.} \quad (c)$$

$$\left[\frac{V_{R_I} - V_V}{T} \right] = \frac{286.1 - 82.1}{460 + 70.0} = 0.385. \quad (d)$$

3. Partition Coefficient, Isobutane, Run 201.

$$\text{Liquid volume: } V_S = \frac{\left(\frac{L}{S}\right)(V_T - V_V) \left(\frac{P_{FB}}{P_S}\right)}{1 + \left(\frac{L}{S}\right) \left(\frac{P_{FB}}{P_S}\right)}, \quad (e)$$

From the data in Appendix F we find:

$$V_S = \frac{(0.50)(111.8 - 82.15) \left(\frac{1.52}{0.961}\right)}{1 + (0.50) \left(\frac{1.52}{0.961}\right)} = 13.1 \text{ cc.} \quad (f)$$

$$k = \frac{V_R - V_V}{V_S} \quad (54)$$

$$= \frac{286.1 - 82.1}{13.1} = 15.56. \quad (g)$$

$$\frac{F_D}{F_j} = \frac{V_S}{V_V} = \frac{13.1}{82.15} = .1595 \quad (h)$$

$$k' = k \frac{F_D}{F_j} \quad (i)$$

$$= 15.56(.1595) = 2.48. \quad (j)$$

4. Number of Theoretical Plates, Isobutane, Run 207.

$$n = \left[\frac{4.5 V_R}{\bar{v} W} \right]^2 \quad (69)$$

$$= \left[\frac{4(1.02)(249)}{(32.9)(1.10)} \right]^2 = 789 \text{ plates.} \quad (k)$$

5. Theoretical Band Width, I-C₄.

Assume the average number of plates, $n = 450$ plates.

$V_{RI} = 270$ cc @ 70°F.

$v_0 = 50$ cc/min.

$\bar{v} = 34.2$ cc/min.

$B = 20$ cc.

$$\frac{Y_b(V)}{M} = \frac{1}{2} e^F [\text{erf } X_1 - \text{erf } X_0], \quad (29)$$

where

$$F = \frac{V_R^2}{2nB^2} + \frac{V_R - V_i}{B}, \quad (30)$$

$$X_0 = \sqrt{\frac{n}{2}} \left(1 - \frac{V}{V_R} + \frac{V_R}{nB} \right), \quad (31)$$

and

$$X_1 = \sqrt{\frac{n}{2}} \left(1 - \frac{V_R}{nB} \right). \quad (32)$$

∴

$$F = \frac{(270)^2}{2(450)(20)^2} + \frac{270 - V}{20} = 0.2025 + \frac{270 - V}{20}. \quad (l)$$

$$X_0 = \sqrt{\frac{450}{2}} \left(1 - \frac{V}{270} + \frac{270}{(450)(20)} \right) = 0.0555(278.1 - V). \quad (m)$$

$$X_1 = \sqrt{\frac{450}{2}} \left(1 - \frac{270}{(450)(20)} \right) = 14.6. \quad (n)$$

$$\text{erf } X_1 \sim 1.000000 \quad (o)$$

∴

$$\frac{Y(V)}{M} = \frac{1}{2} e^{0.2025 + \frac{270 - V}{20}} \left[1 - \text{erf} \{ 0.0555(278.1 - V) \} \right]. \quad (p)$$

We assume that the band limits occur at the points where $\frac{Y(V)}{M} = 0.0005$.

These points may be determined from Equation (p).

They are $V_i = 228.7$ cc, and $V_f = 426.1$ cc .

Theoretical Band Width:

$$W = \frac{S}{V} (V_f - V_i), \quad (67)$$

$$= \frac{(1.02)}{34.2} (426.1 - 228.7) = 5.9 \text{ cm.} \quad (q)$$

6. Corrected Band Width, Isobutane, Run 864.

$$b_I(\text{corr.}) = b_I \left(\frac{W_{v_0=50}}{W_v} \right), \quad (\text{r})$$

$$W_I^2 = \frac{63.2}{\bar{v}^2} + \frac{1594}{\bar{v}^3} + \frac{39.37}{\bar{v}}. \quad (133)$$

For $v_0 = 50$ cc/min, $\bar{v} = 35$ cc/min.

$$W_{v_0=50} = \sqrt{\frac{63.2}{(35)^2} + \frac{1594}{(35)^3} + \frac{39.37}{(35)}} = 1.1015 \quad (\text{s})$$

For $v_0 = 224$ cc/min, $\bar{v} = 100$ cc/min.

$$W_{v_0=224} = \sqrt{\frac{63.2}{(100)^2} + \frac{1594}{(100)^3} + \frac{39.37}{(100)}} = 0.634 \quad (\text{t})$$

$$b_I(\text{corr.}) = 5.17 \left(\frac{1.1015}{0.634} \right) = 8.95 \text{ cm.} \quad (\text{u})$$

7. Total Sample Size, Isobutane, Run 864.

Air injected = 2 cc.

$$h_0 = 2.60 \text{ cm.}$$

$$A_0 = .33(2.60) = 0.86.$$

$$f = \frac{0.86}{2.00} = 0.43. \quad (\text{v})$$

$$F_I = A_I / f = \frac{3.43}{0.43} = 7.98 \text{ cc.} \quad (110)$$

8. J Calculation, Isobutane

$$J_I = \frac{16S^2 V_{PI}^2}{L} \quad (124)$$

$$= \frac{16(1.02)^2 (269.3)^2}{(610)} = 1980. \quad (125)$$

BIBLIOGRAPHY

1. Ambrose, D. and Collerson, R.R. Nature, 177, (1956), 84.
2. Brennan, D. and Kemball, C. J. Inst. Pet., 44, (1958), 14.
3. Brooks, F.R. Anal. Chem., 21, (1949), 1105.
4. Butler, J.A.V. J. Chem. Soc., 1935, (1935), 280.
5. Cassidy, H.G. J. Chem. Ed., 33, (1956), 483.
6. Cheshire, J.D. and Scott, R.P.W. J. Inst. Pet., 44, (1958), 74.
7. Chruchill, R.V. Modern Operational Mathematics in Engineering. New York: McGraw Hill, (1944), 299.
8. Danckwerts, P.V. Ch. E. Sci., 2, (1953), 1.
9. Daynes, H.A. Gas Analysis by Measurement of Thermal Conductivity. London: Cambridge Univ. Press, 1933.
10. Desty, D.H. Vapor Phase Chromatography. London: Butterworths Scientific Publications, (1957), xiii.
11. De Vault, D. J. Am. Chem. Soc., 65, (1943) 532.
12. De Wet, W.J. and Pretorius, V. Anal. Chem., 30, (1958), 325.
13. Dimbat, M., Stross, F.H., and Porter, P.E. Anal. Chem., 28, (1956), 290.
14. Dingle, H. The Special Theory of Relativity. New York: Wiley, 1940.
15. Eggertsen, F.T. and Knight, H.S. Anal. Chem., 30, (1958), 15.
16. Fredericks, E.M. and Brooks, F.R. Anal. Chem., 28, (1956), 298.
17. Freund, M., Benedek, P., and Szepesy, L. Vapor Phase Chromatography. London: Butterworths Scientific Publications, 1957.
18. Glueckauf, E. Trans. Faraday Soc., 51, (1955), 34.
19. Grant, D.W. and Vaughan, G.A. J. App. Chem., 6, (1956), 145.
20. Harvey, D. and Morgan, G.O. Vapor Phase Chromatography. London: Butterworths Scientific Publications, 1957.
21. Hoare, M.R. and Furnell, J.H. Trans. Faraday Soc., 52, (1956), 222-9.

22. Hougan, O.A. and Watson, K.M. Chemical Process Principles, Part II. New York: Wiley, (1943), 649.
23. Houston, R.H. A Theory for Industrial Gas-Liquid Chromatographic Columns. Master's Thesis, University of California Radiation Laboratory, Berkeley, California, 1958.
24. James, A.T. and Martin, A.J.P. Biochem. J., 50, (1952), 679.
25. James, A.T. and Martin, A.J.P. Biochem. J., 52, (1952), 238.
26. James, A.T. Biochem. J., 52, (1952), 242.
27. Juneau, Joan Bibliography of Gas Chromatography and Some Related Methods, Bureau of Mines, Department of the Interior, 1956.
28. Keulemans, A.I.M. Gas Chromatography. New York: Reinhold, 1957.
29. Ibid., 9.
30. Ibid., 2.
31. Ibid., 145.
32. Ibid., 110-113.
33. Ibid., 127.
34. Ibid., 200-205.
35. Ibid., 139-142.
36. Ibid., 28.
37. Ibid., 56-57.
38. Ibid., 83-84.
39. Ibid., 146.
40. Keulemans, A.I.M. and Kwantes, A. Vapor Phase Chromatography. London: Butterworths Scientific Publications, 1957.
41. Klinkenberg, A. and Sjenitzer, F. Chem. Eng. Sci., 5, (1956), 258.
42. Lapidus, L. and Amundson, N.R. J. Phys. Chem., 56, (1952), 984.
43. Littlewood, A.B., Phillips, C.G.S., and Price, D.T. J. Chem. Soc., 1955, (1955), 1480.
44. Martin, A.J.P. and Synge, R.L.M. Biochem. J., 35, (1941), 1358.

45. Mellor, N. Vapor Phase Chromatography. London: Butterworths Scientific Publications, 1957.
46. Perry, J.H. Chemical Engineers' Handbook, Third Edition. New York: McGraw-Hill, (1950), 461.
47. Phillips, Courtenay. Gas Chromatography. New York: Academic Press Inc., 1956.
48. Ibid., 7.
49. Ibid., 26.
50. Ibid., 59-60.
51. Pierotti, G.J., Deal, C.H., Jr., Derr, E.L., and Porter, P.E. J. Am. Chem. Soc., 78, (1956) 2989.
52. Porter, P.E., Deal, C.H., Jr., and Stross, F.H. J. Am. Chem. Soc., 78, (1956), 2999.
53. Purnell, J.H. Vapor Phase Chromatography. London: Butterworths Scientific Publications, 1957.
54. Rainville, E.D. Elementary Differential Equations. New York: MacMillan, (1952), 118.
55. Tswett, M. Ber. deut. botan. Ges., 24, (1906), 316, 384.
56. van Deemter, J.J., Zuiderweg, F.J., and Klinkenberg, A. Chem. Eng. Sci., 5, (1956), 271.
57. van de Craats, F. Anal. Chim. Acta., 14, (1956), 136.
58. Wiseman, W.A. Chemistry and Industry, 1956, (1956), 127-129.

