Diffusion of short chain n-alkanes was found to be faster in the polydimethylsilicone elastomer SE-30 than in the polydimethylsilicone oil SF-96-2000. The opposite was true for the longer chain n-alkanes suggesting that choice of stationary phase for gas chromatography would depend on the chain length of sample components. The dependence of diffusion on chain length is explained as being the result of competition between the effects of free volume and viscosity for dominance in the diffusion process. Peak skewing was not found to be a problem in SE-30 down to 50°C contrary to previous findings. The equation \[ \ln K = -1.805 - 0.590C + (950+905C)/1.987T \] was found to be excellent for determining partition coefficients of n-alkanes in SE-30. The entropy and enthalpy for evaporation of n-alkane from SE-30 were determined to be \[ \Delta S = 1.987(1.805+0.590C) \text{ cal/deg-mole} \] and \[ \Delta H = 950 + 905C \text{ cal/mole}. \] The friction coefficient for n-pentane was found to be approximately equal to the reported friction coefficient for a monomer unit of polydimethylsiloxane at 100°C.
While friction coefficients for n-alkanes in other polymers have been reported as being linear with carbon number, this was not true for n-alkanes in SE-30 and SF-96-2000.
Diffusion of n-Alkanes in Polydimethylsilicones

by

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. POLYDIMETHYLSILICONE STATIONARY PHASES</td>
<td>3</td>
</tr>
<tr>
<td>III. DIFFUSION IN POLYMERS</td>
<td>5</td>
</tr>
<tr>
<td>A. Definition of the Diffusion Constant</td>
<td>5</td>
</tr>
<tr>
<td>B. Viscosity Effects</td>
<td>5</td>
</tr>
<tr>
<td>C. Diffusion in Polydimethylsilicones</td>
<td>6</td>
</tr>
<tr>
<td>IV. CHROMATOGRAPHIC THEORY</td>
<td>9</td>
</tr>
<tr>
<td>A. The General Plate Height Equation</td>
<td>9</td>
</tr>
<tr>
<td>B. Sources of Peak Spreading</td>
<td>10</td>
</tr>
<tr>
<td>Simple Gaseous Diffusion</td>
<td>11</td>
</tr>
<tr>
<td>Mobile Phase Mass Transfer</td>
<td>12</td>
</tr>
<tr>
<td>Stationary Phase Mass Transfer</td>
<td>13</td>
</tr>
<tr>
<td>Pressure Corrections</td>
<td>14</td>
</tr>
<tr>
<td>C. The Full Theoretical Plate Height Equation</td>
<td>15</td>
</tr>
<tr>
<td>D. Partition Coefficients</td>
<td>16</td>
</tr>
<tr>
<td>V. EXPERIMENTAL</td>
<td>19</td>
</tr>
<tr>
<td>A. Apparatus</td>
<td>19</td>
</tr>
<tr>
<td>B. Plate Height Calculations</td>
<td>20</td>
</tr>
<tr>
<td>C. Effect of Sample Size on Skewing</td>
<td>21</td>
</tr>
<tr>
<td>D. Gas Phase Mass Transfer Calculations</td>
<td>27</td>
</tr>
<tr>
<td>E. D_g Calculations</td>
<td>30</td>
</tr>
<tr>
<td>F. Partition Coefficient Calculations</td>
<td>31</td>
</tr>
<tr>
<td>VI. RESULTS AND DISCUSSION</td>
<td>35</td>
</tr>
<tr>
<td>A. Tabulation of Data</td>
<td>35</td>
</tr>
<tr>
<td>B. Partition Coefficients</td>
<td>35</td>
</tr>
<tr>
<td>C. Diffusion in SE-30 and SF-96-2000</td>
<td>39</td>
</tr>
<tr>
<td>D. Friction Coefficients</td>
<td>43</td>
</tr>
<tr>
<td>VII. CONCLUSIONS</td>
<td>49</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>51</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>53</td>
</tr>
<tr>
<td>Appendix I: Fortran Program for Calculation of Sample Peak Statistics</td>
<td>53</td>
</tr>
<tr>
<td>Appendix II: Fortran Program for Calculation of D_g and Plate Height Parameters</td>
<td>56</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Log $D_f$ for benzene against log $M$ for polydimethylsilicones.</td>
<td>8</td>
</tr>
<tr>
<td>2.</td>
<td>Effect of sample size on peak position and skewing for $n$-decane on SE-30.</td>
<td>25</td>
</tr>
<tr>
<td>3.</td>
<td>Effect of sample size on peak position and skewing for $n$-decane on SF-96-2000.</td>
<td>26</td>
</tr>
<tr>
<td>4.</td>
<td>Van Deemter plots of $n$-decane on SE-30 at 100°C.</td>
<td>28</td>
</tr>
<tr>
<td>5.</td>
<td>Log partition coefficient against carbon number for $n$-alkanes on SE-30 at 50°, 100°, 150° and 200°C.</td>
<td>37</td>
</tr>
<tr>
<td>6.</td>
<td>Log $D_f$ against carbon number for $n$-alkanes on SE-30 at 50°, 100°, 150° and 200°C.</td>
<td>41</td>
</tr>
<tr>
<td>7.</td>
<td>Log $D_f$ against $1/T$ for $n$-alkanes on SE-30.</td>
<td>42</td>
</tr>
<tr>
<td>8.</td>
<td>Log $D_f$ against carbon number for $n$-alkanes at 50°C.</td>
<td>44</td>
</tr>
<tr>
<td>9.</td>
<td>Log $D_f$ against carbon number for $n$-alkanes at 100°C.</td>
<td>45</td>
</tr>
<tr>
<td>10.</td>
<td>Friction coefficient against carbon number for $n$-alkanes at 50°, 100°, 150° and 200°C.</td>
<td>48</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Effect of sample size on mean, skewness and standard deviation.</td>
<td>24</td>
</tr>
<tr>
<td>II. Density of SE-30 at selected temperatures.</td>
<td>33</td>
</tr>
<tr>
<td>III. Diffusion and partition coefficients of n-alkanes in SE-30 and SF-96-2000.</td>
<td>36</td>
</tr>
<tr>
<td>IV. Diffusion and partition coefficients of n-alkanes in SE-30 at 150 and 200°C.</td>
<td>38</td>
</tr>
<tr>
<td>V. Friction coefficients for n-alkanes in SE-30 and SF-96-2000.</td>
<td>47</td>
</tr>
</tbody>
</table>
DIFFUSION OF n-ALKANES IN POLYDIMETHYLSILICONES

I. INTRODUCTION

The elucidation of the mechanism for diffusion of molecules through polymers has been the subject of hundreds of papers by polymer chemists. These studies of diffusion reach into many disciplines. The drying rate and breathability of paints, dyeing of synthetic fibers and the production of moisture impermeable plastic packaging are but a few of many examples for which the study of the diffusion process has importance. Much of this literature has been drawn into a book edited by Crank and Park (1) and places the various theories and methods of measurement into a well defined format.

This work was primarily undertaken as a means of measuring the diffusion constant of sample molecules through polymeric chromatographic stationary phases but may eventually find its way into work done by polymer chemists. The diffusion constant of a sample in the stationary phase may greatly affect the spreading of chromatographic peaks. This peak spreading affects the resolution between neighboring peaks and eventually any analytical calculations which may be attempted.

By measuring their various diffusion constants, stationary phases can be characterized as having or not having those properties which make high resolution separations possible.
The chromatographic method for determining diffusion constants was developed by Hawkes and Carpenter (2), Butler and Hawkes (3) and Kong and Hawkes (4). Some of their work with the polydimethylsilicone oil SF-96-2000 and polydimethylsilicone gum SE-30 is repeated here and extended to include some of the higher molecular weight n-alkanes that they had found impossible to work with. The theoretical equation has also been improved so that the final results show more continuity and are probably more accurate.
II. POLYDIMETHYLSILICONE STATIONARY PHASES

Silicone polymers with a variety of molecular weights and branching groups have found a permanent home in gas chromatography. One of their main advantages lies in the large dynamic temperature range of these compounds. Their stability and low vapor pressure make them ideal stationary phases for programmed temperature work.

Some of the most commonly used silicone stationary phases are the polydimethylsilicones

\[
\left[ \begin{array}{c}
CH_3 \\
- Si - O - \\
CH_3
\end{array} \right]_n
\]

which have trimethylsilyl groups terminating the polymer chains. The polydimethylsilicones made by General Electric Company are marketed under such designations as SF-96-200, SF-96-2000 and Viscasil 100,000 where the "SF" stands for silicone fluid and the terminating number stands for the viscosity of the polymer in centistokes at 25°C. General Electric also makes a series of elastomers under the "SE" series label, however, the only one to gain wide use in gas chromatography is SE-30 with a viscosity of \(9.5 \times 10^6\) centistokes at 25°C.

The molecular weights of the SF-96-2000 and SE-30 used in this work are \(3.5 \times 10^4\) and \(4.0 \times 10^5\) g/mole respectively (5). The
advantage in using these two polymers in a study of this type is that the chemical composition of the two polymers is essentially identical. Any differences observed in diffusivity can then be attributed to or correlated with the various physical properties of the polymers, such as viscosity and density, and not to differences in their chemical structure.

There are many other silicones used in chromatography with various amounts of phenyl, trifluoropropyl or cyanopropyl substituted in place of one or more methyl groups on the silicone chain. An excellent overview of these other silicone polymers and some of their diffusion characteristics is provided in the paper by Kong and Hawkes (4).
III. DIFFUSION IN POLYMERS

A. Definition of the Diffusion Constant

The diffusion constant for solute molecules in a solvent has long been defined using Fick's first

\[ F = -D \frac{\partial c}{\partial x} \quad \text{Eq. 1} \]

and second

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Eq. 2} \]

laws of diffusion where \( F \) is the rate of transfer of solute molecules across a unit area, \( c \) is the concentration of the solute, \( x \) is a coordinate normal to the unit area, \( t \) is the time unit and \( D \) is the diffusion constant. Extensive treatments of these two laws can be found in a book by Crank (6) or in physical chemistry texts and will not be pursued here. What is important is that we should be able to characterize those properties of a polymer which help or hinder diffusion.

B. Viscosity Effects

In attempting to characterize the diffusion constants for molecules in liquids, Reid and Sherwood (7) reviewed the various equations of Eyring, Stokes-Einstein and Wilke-Chang. What is
typical of all these equations is that they show an inverse relationship between the diffusion constant for a solute and the viscosity of the solvent. Since the viscosity of a polymer increases as its molecular weight increases, the diffusion constant could also be thought to be a function of the molecular weight of the solvent. As the molecular weight and viscosity increase, a point is reached where the viscosity suddenly increases sharply with molecular weight. It is at this point that the chains of a polymer are believed to have become so tangled and wrapped around each other that there is much more resistance to any movements which would pull the molecules apart (8, p. 271). The molecular weight at which this sharp increase in viscosity occurs is called the critical weight of entanglement and is seen at molecular weights between 10,000 and 30,000 for most polymers. The classical equations for diffusivity do not hold for these high polymers even though the trend of increasing viscosity and decreasing diffusivity is still generally true.

C. Diffusion in Polydimethylsilicones

More recently it was discovered by Butler and Hawkes (3) and confirmed by Kong and Hawkes (4) that the highly viscous polydimethylsilicone elastomer SE-30 \(9.5 \times 10^6\) centistokes at 25°C) showed two to four times higher diffusivities for n-alkanes than the less viscous polydimethylsilicone fluid SF-96-200 \(200\) centistokes at 25°C). The
work by Kong and Hawkes (4) also showed that the diffusivities for n-alkanes also increased with increasing viscosity for SF-96-2000 and Viscasil 100,000 but were still lower than those for SE-30.

Though the chromatographic method for determining diffusion constants was unproved, Kong and Hawkes (9) showed that data for the diffusivity of benzene in their series of polydimethysilicones overlapped and extended data determined by Tanner (10), who used an entirely different technique. Figure 1 shows these two sets of data on one graph and shows that the diffusion constant for benzene did not level off at high molecular weights, as proposed by Tanner, but instead has reached a minimum. Clearly, the relationship between viscosity and diffusivity has completely broken down.

At least part of the answer to the mechanism involved in diffusion through these polymers may lie in one of the various "free volume" theories correlated and reviewed by Kumins and Kwei (1, Ch. 4). The basis of these theories lies in relating diffusivity to the volume of holes created in a polymer matrix due to the movements of the polymer chains. The size distribution of these holes is related to the polymer's density, rotational freedom of the chain units and the ability of the chains to cooperate in forming a hole large enough for a solute to move into.

These theories would help explain the higher diffusivities observed in SE-30 since it has a lower density than the other polydimethysilicones which implies a higher free volume.
Figure 1. Log $D_2$ for benzene against log $M$ for polydimethylsilicones.  
- Tanner (10), □ Kong and Hawkes (9).
IV. CHROMATOGRAPHIC THEORY

A. The General Plate Height Equation

Even though liquid column chromatography has been in use since the early 1900's, it was not until 1941 that Martin and Synge (11) suggested that a gas could be used in place of the liquid as the mobile carrier and it was not until 1952 that James and Martin (12) developed gas chromatography into a workable analytical tool. From here on only gas chromatography will be discussed even though many of the equations may also be applicable to liquid systems.

Both of these early papers used the concept of the height equivalent to a theoretical plate (HETP or H) as a measure of a particular column's efficiency. The HETP for a column is defined as

\[ H = \frac{\sigma^2}{L} \]  

Eq. 3

where \( \sigma^2 \) is the variance of an eluting sample peak and \( L \) is the length of the column. The plate height for a column can therefore be thought of as the average variance generated per unit length of column. This use of HETP is important in that it gives workers a measure of the separation efficiency for a column. Given any one length of column, a small HETP would indicate a small \( \sigma^2 \) and thus better separation of two adjacent peaks.
Attempts to describe HETP based on theoretical calculations was begun by van Deemter, Zuiderweg and Klinkenberg (13). The abbreviated equation

\[ H = A + \frac{B}{v} + Cv \]  
Eq. 4

which bears van Deemter's name was actually proposed by Keulemans and Kwantes (14). The \( \frac{B}{v} \) term refers to simple gaseous diffusion along the length of the column, the \( Cv \) term refers to the effects of the rate of mass transfer and the \( A \) term refers to extra column or flow independent effects. The \( A \) term tends to be a catch-all term and should be negligible if a column and instrument are well designed. The \( v \) in Equation 4 is the velocity of the carrier gas.

B. Sources of Peak Spreading

In identifying the sources of peak spreading, Giddings (15) was able to produce a series of theoretical equations which describe the plate heights for most types of chromatographic columns. As a basis for these equations one must assume that each of the sources of peak spreading is independent of the others. The plate height for any column can then be described as the sum of four major parameters

\[ H = H_d + H_m + H_s + H_{ee} \]  
Eq. 5
where $H_d$ is that plate height due to longitudinal diffusion of a solute in the mobile phase, $H_m$ is due to the mass transfer of solute between stream paths in the mobile phase, $H_s$ is due to mass transfer of solute between the stationary and mobile phase and $H_{ee}$ is due to extraneous spreading at either end of a column and is called "end effects". In a well designed instrument $H_{ee}$ should be negligible while the other three are usually important in most uses of gas chromatography.

**Simple Gaseous Diffusion**

For columns used in analytical applications, peak spreading is limited to a longitudinal process. As in any system where a solute finds itself in an area of high solute concentration, the solute will diffuse away from this area according to Einstein's equation (16)

$$
\frac{\sigma^2}{g} = 2D_g t \quad \text{Eq. 6}
$$

where $D_g$ is the diffusion constant for the solute in the gas and $t$ is the time over which diffusion is allowed to occur.

Combining Equations 3 and 6

$$
H_d = \frac{\frac{\sigma^2}{d}}{L} = \frac{2D_g t}{L} = \frac{2D_g}{v} \quad \text{Eq. 7}
$$

we obtain an equation which relates the plate height for gaseous
diffusion to the diffusion constant of the solute and the average linear velocity of the mobile gas. The equation is not entirely accurate in that it describes an unobstructed diffusion process. Other authors (17-19) have shown that for packed columns, the solid particles hinder diffusion by a factor, \( \gamma \), so that the equation is modified to

\[
H_d = \frac{2\gamma D}{v} \quad \text{Eq. 8}
\]

The value of \( \gamma \) varies from about 0.60 for very low velocities to a maximum of about 0.73 for average linear velocities above 6 cm/sec (20).

**Mobile Phase Mass Transfer**

The second major source of peak spreading is expressed by \( H_m \) or the mobile phase mass transfer term. Within any packed column, flow channels exist where the flow of gas is unobstructed relative to neighboring areas where the particles may be more tightly packed. Since the gas will move preferentially through the less restricted channels, the solute zone will spread as a result of some solute molecules moving ahead and others lagging behind the center of the sample zone. The final width of the eluting peak will therefore depend on how quickly solute molecules can diffuse into and out of these various flow paths so that, on the average, no molecules get too far ahead
or lag too far behind the center of the peak. The equation quantifying this and extensively developed by Giddings (15) is

\[ H_m = \frac{\omega d_v^2}{D} \]

where \( \omega \) is a geometric factor which appears to express the average number of particle diameters a molecule must diffuse in order to move from one flow path to another and \( d_p \) is the average diameter of the solid support particles.

**Stationary Phase Mass Transfer**

The last major source of peak spreading is \( H_s \) or the stationary phase mass transfer term. This term is particularly important in this work as it is the largest contributor to the plate height for the experimental conditions used and is the basis for the determination of \( D_f \). The basic premise is that as the solute molecules move across the surface of a stationary liquid, they will be absorbed into the liquid. The solute can then either return to the mobile gas or diffuse deeper into the stationary liquid before returning to the surface and then into the mobile phase. The range of residence times in the stationary liquid is what affects the width of the solute peak and the diffusion constant of the solute in the liquid as well as the shape or distribution of the liquid on the solid support are major factors.
A complex equation was developed by Giddings, Mallik and Eikelberger (21) describing the stationary phase mass transfer term for a stationary liquid on solid glass beads

\[ H_s = \frac{d^2 \text{k} \nu}{12D_f (1+k)^2 \rho_g} \left( \frac{\% \rho_g}{100(3m)\rho_f} \right)^{1/2} \quad \text{Eq. 10} \]

where \( m \) is the average number of contact points per bead (about 6.25), \( \rho_g \) and \( \rho_f \) are the densities of the glass beads and stationary liquid respectively, \( \% \) is the percent loading of liquid on the stationary support, \( k \) is called the column capacity ratio or partition ratio and \( D_f \) is the diffusion constant for the solute in the stationary liquid. The factor of \( 1/12 \) is a geometric term relating the fact that the liquid does not spread itself evenly over the surface but instead collects at the contact points (21) in an unusual geometry where the depth of the liquid below most of the surface is much less than the maximum depth represented by the term in parentheses. The use of glass beads as the support is necessary because it is the only support for which the distribution of liquid on its surface has been well characterized.

**Pressure Corrections**

Additional adjustments must be made to Equations 8 and 9 due to the compressibility of the mobile gas. As the sample zone moves
down a column the pressure begins to drop and the gas expands, increasing the width of the zone. Likewise the velocity of the gas increases slowly in the beginning of the column and then more quickly as the outlet of the column is reached. The factors used to correct for the effects of compressibility and uneven velocity were formulated by James and Martin (7) and by Giddings (22).

\[
j = \frac{2}{3} \left( \frac{P_i^2/P_0^2 - 1}{P_i^3/P_0^3 - 1} \right) \quad \text{Eq. 11}
\]

\[
f = j \left( \frac{P_i^2/P_0^2 + 1}{2} \right) \quad \text{Eq. 12}
\]

where \( j \) and \( f \) are called the James-Martin and Giddings compressibility factors respectively.

C. The Full Theoretical Plate Height Equation

Combining Equations 8-12, we obtain an equation which can be used to evaluate the total theoretical plate height

\[
H = \frac{2 \gamma D_j f}{v P_o g} + \frac{\omega_d^2 j v}{D f g} + \frac{d^2 k v}{120 D f (1+k)} \left( \frac{\% \rho}{18.75 \rho_f} \right)^{1/2}
\]

Eq. 13

This is the equation that is used to determine the value of \( D_f \) for a particular solute. All of the other terms in the equation are either
readily calculated from known values or are determined during the experiment.

In order to maximize the stationary phase mass transfer term so that an accurate determination of $D_f$ can be made, there are two things that can be done:

1) operate at high carrier gas velocities so that the $B/v$ term is kept at a minimum and

2) use a heavy stationary phase loading (about 0.3% for glass bead supports) so that the $H_s$ term will be greater than the $H_m$ term.

**D. Partition Coefficients**

One of the useful parameters obtained from gas chromatographic data is called the partition coefficient and is defined as

$$K = \frac{\text{concentration of solute in stationary phase}}{\text{concentration of solute in mobile phase}}$$

Eq. 14

This parameter is important in that it can be used in any laboratory to predict the elution time for a known solute-stationary phase pair.

In order to determine the partition coefficient, the time the solute spends in the stationary and mobile phases must be determined. As a solute moves down a column, the molecules partition themselves between the stationary and mobile phases and their ratio is called the
column capacity ratio

\[ k = \frac{\text{wt. sorbed}}{\text{wt. mobile}} = \frac{w_s}{w_m} \quad \text{Eq. 15} \]

This value corresponds directly to the time a molecule spends in the stationary and mobile phases

\[ k = \frac{w_s}{w_m} = \frac{t_s}{t_m} \quad \text{Eq. 16} \]

where \( t_m \) is equal to the elution time for an unretained sample and \( t_s \) is the difference between the total elution time for the sample and \( t_m \).

To make the conversion between partition coefficient and column capacity ratio, one only needs to know the volume of stationary phase and the total mobile phase volume of the column

\[ K = \frac{\text{conc. sorbed}}{\text{conc. mobile}} = \frac{w_s/v_s}{w_m/v_m} = \frac{w_s}{w_m} \frac{v_m}{v_s} \]

\[ = k \frac{v_m}{v_s} \quad \text{Eq. 17} \]

which is sometimes written

\[ K = \beta k \quad \text{Eq. 18} \]

where \( \beta \) is the ratio of the mobile phase to stationary phase
volumes. By using Equations 16 and 17, the retention time for a solute at any mobile phase velocity can easily be determined.

In addition to retention time calculations, the partition coefficient can be used to provide thermodynamic information about a solute-stationary phase pair (23)

\[ K = e^{\frac{\Delta G}{RT}} \tag{Eq. 19} \]

where \( \Delta G \) is the free energy for the transfer (or evaporation) of the solute from the stationary to the mobile phase and \( R \) is the gas constant (1.987 cal/deg-mole).
V. EXPERIMENTAL

A. Apparatus

The experimental data was collected on a Perkin-Elmer 3920 gas chromatograph equipped with flame ionization detectors. The oven has a maximum temperature of 400°C, is stable within 0.1% of the set point and has an absolute accuracy of ±1% of the set temperature in °K.

Two columns were constructed of 6 ft x 0.25 in o.d. x 0.18 in i.d. stainless steel tubing. These columns were packed with 0.291% SE-30 or 0.345% SF-96-2000 on solid 60-80 mesh glass beads using a tap-fill method. The columns were closed with 200 mesh stainless steel screens and were then coiled to approximately 8 in. in diameter.

The carrier gases were prepurified nitrogen and helium and were passed through 8 ft of 0.25 in o.d. copper tubing filled with 5A molecular sieve before entering the gas chromatograph.

The output of the gas chromatograph was recorded on an Esterline Angus Model E1101s, one millivolt recorder. The recorder had a full scale response time of 0.15 second and had a maximum chart speed of 8 in/sec.

A small amount of n-alkane, usually less than 0.05 μl, was injected into the gas chromatograph using a 1.0 μl Hamilton model 7001 syringe. The chart speed was adjusted so that the width of the
peak at half its maximum height \((W_{1/2})\) was at least one and one-half inches wide so that measuring errors would be kept to a minimum.

B. Plate Height Calculations

If one assumes that the eluting peak has a Gaussian profile, the half-width of the recorded peak has a very definite relationship to the time-based standard deviation \((\tau)\) of the peak

\[
W_{1/2} = \sqrt{8} \ln 2 \tau \quad \text{Eq. 20}
\]

The definition of \(H\) in Equation 3 is described in terms of a length-based standard deviation for the eluting zone so that a conversion must be made as follows

\[
\tau = \frac{\sigma}{\nu} = \frac{\sigma t}{L} \quad \text{Eq. 21}
\]

where \(L\) is the length of the column, \(t\) is the total elution time for the peak and \(\nu\) is the zone velocity of the peak. Rearranging Equations 20 and 21

\[
\sigma = \frac{W_{1/2} L}{t \sqrt{8 \ln 2}} \quad \text{Eq. 22}
\]

and combining this with Equation 3

\[
H = \frac{\sigma^2}{L} = \frac{W_{1/2}^2 L}{t^2 (8 \ln 2)} \quad \text{Eq. 23}
\]
Of course the relationship between $W_{1/2}$ and $\tau$ in Equation 20 assumes that the eluting peak has a Gaussian profile and this may not be true. Some of the previous work done with methyl silicones (3, 4) reported severe peak skewing for most n-alkanes on SE-30 and for the higher n-alkanes when the lower molecular weight polydimethylsilicones were used as stationary phases.

C. Effect of Sample Size on Skewing

In order to test the validity of the half-width method used to calculate peak variance, a test was conducted where samples of different sizes were injected into a column and the eluting peaks analyzed by both computer and graphical means. Both the SE-30 and SF-96-2000 columns were tested using helium as the carrier gas at an average linear velocity of 15 cm/sec. The oven temperature was 100°C and n-decane was chosen as the sample.

In taking data points from the gas chromatograph for computer analysis, the voltage output was stored in a computer interface every 0.05 sec so that for a peak width of 15 sec, 300 sample points would be stored for subsequent analysis.

For the actual treatment of this data, one has to consider the eluting peak as the frequency distribution over each of the sample points. By summing the voltages $(V_j)$ and dividing the voltage at each sample point by this sum, the frequency distribution becomes a
probability distribution

\[ f(t) = \frac{V}{n} \sum_{j=1}^{\Sigma V_j} \]

Eq. 24

for each data point. The mean elution time can then be calculated as

\[ \bar{t}_p = \frac{1}{n} \sum_{i=1}^{n} t_i f(t) \quad \text{Eq. 25} \]

and each of the moments about the mean

\[ m_k = \frac{1}{n} \sum_{i=1}^{n} (t_i - \bar{t}_p)^k f(t) \quad \text{Eq. 26} \]

where the second moment, \( m_2 \), is just the time based variance for the peak, \( \tau^2 \).

The skewness of each peak is defined as

\[ g_1 = \frac{m_3}{\tau^3/2} = \frac{m_3}{\tau^3} \quad \text{Eq. 27} \]

where negative values indicate peak fronting and positive values indicate peak tailing.

The actual program used to make the statistical analysis is listed in Appendix I and the results of the computer analysis for over
200 points per peak, along with \( \tau \) values computed by the half-width method, are shown in Table I. A comparison of the peak shapes that produced these data can be seen in Figures 2 and 3.

In none of the cases tested does the computer standard deviation differ from the half-width determined value by more than 4%. While it appears that sample sizes less than about 0.2 µl have little effect on the standard deviation, it would be best to keep sample sizes less than 0.1 µl in order to maintain proper elution times.

The fronting of the peaks, evidenced by negative \( g_1 \) values, is due to overloading the column and is what causes the shift of the peak maximums to longer elution times. The smaller samples show slight tailing in their eluting peaks. This is the problem most often encountered in all forms of chromatography and in this case is most likely caused by small pockets of dead volume at the ends of the column or possibly by samples that do not evaporate instantly on injection.

One of the unexpected results of this study was that the sample size which caused excessive skewing of the eluting peak appeared to be about the same for both SE-30 and SF-96-2000. It had been assumed that the reported skewing problems (3, 4) for SE-30 was a sample size effect. In the actual experimental work done to determine \( D_f \) values, sample sizes were kept below 0.05 µl and in no case were the peaks fronted or tailed excessively.
Table I. Effect of sample size on mean, skewness and standard deviation.

<table>
<thead>
<tr>
<th>Sample (µl)</th>
<th>Mean (sec)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Sample (µl)</th>
<th>Mean (sec)</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>75.2</td>
<td>-0.481</td>
<td>2.85</td>
<td>2.80</td>
<td>0.5</td>
<td>89.6</td>
<td>-0.453</td>
<td>3.46</td>
<td>3.44</td>
</tr>
<tr>
<td>0.3</td>
<td>74.9</td>
<td>-0.431</td>
<td>2.79</td>
<td>2.69</td>
<td>0.4</td>
<td>89.2</td>
<td>-0.416</td>
<td>3.47</td>
<td>3.34</td>
</tr>
<tr>
<td>0.15</td>
<td>73.2</td>
<td>-0.204</td>
<td>2.49</td>
<td>2.44</td>
<td>0.23</td>
<td>87.2</td>
<td>-0.200</td>
<td>3.05</td>
<td>3.03</td>
</tr>
<tr>
<td>0.09</td>
<td>72.5</td>
<td>-0.026</td>
<td>2.40</td>
<td>2.38</td>
<td>0.15</td>
<td>85.8</td>
<td>0.041</td>
<td>2.99</td>
<td>2.96</td>
</tr>
<tr>
<td>0.045</td>
<td>71.9</td>
<td>0.133</td>
<td>2.38</td>
<td>2.42</td>
<td>0.10</td>
<td>85.2</td>
<td>0.133</td>
<td>3.04</td>
<td>3.01</td>
</tr>
<tr>
<td>0.03</td>
<td>71.6</td>
<td>0.174</td>
<td>2.48</td>
<td>2.46</td>
<td>0.04</td>
<td>84.7</td>
<td>0.184</td>
<td>3.02</td>
<td>3.07</td>
</tr>
</tbody>
</table>
Figure 2. Effect of sample size on peak position and skewing for n-decane on SE-30.
Figure 3. Effect of sample size on peak position and skewing for \textit{n}-decane on SF-96-2000.
Equation 13 can be written in the abbreviated form

\[ H = \frac{B}{v} + C \frac{v}{g} + C_f v \]  

Eq. 28

where all the various parameters except velocity are lumped together in the constants \( B \), \( C_g \) and \( C_f \).

The gas phase mass transfer term, \( C \frac{v}{g} \), had been assumed to be negligible in previous determinations of \( D_f \) (3, 4) using the chromatographic method. The fallacy of this assumption is demonstrated by making plots of \( H \) against carrier gas velocity (van Deemter plots) using one column, two different carrier gases and then observing the divergence of the curve at high velocities. A typical set of van Deemter plots is shown in Figure 4. By noting the velocity dependence of each of the terms in Equation 28, one can see that the \( B/v \) term becomes small at high velocity and in fact is less than 10% of the total \( H \) above 20 cm/sec. Referring back to Equation 13, one can see that there is no change in the \( C_f v \) term when two different carrier gases are used so that the entire difference between the two curves in Figure 4 at high velocity is a result of a change in the \( C_g v \) term.

The evaluation of this term would be simple if it was not for the indeterminate factor, \( \omega \). The value of \( \omega \) has been approximated
Figure 4. Van Deemter plots of n-decane on SE-30 at 100°C. ● helium carrier gas, □ nitrogen carrier gas.
(24) as being about 0.4 for glass beads but may vary somewhat from column to column.

The term \( \omega d_p^2 \) in Equation 9 is sometimes combined and given the symbol \( C'_g \) and may be determined experimentally by obtaining HETP data using two different carrier gases at equal temperature and velocity. If \( H \) is determined for the same sample in two gases, we will produce a system of two equations with one unknown

\[
\begin{align*}
H_1 - \frac{B_1}{v} &= C_{g1} v + C_{f1} v \\
H_2 - \frac{B_2}{v} &= C_{g2} v + C_{f2} v \\
\frac{H_1 - \frac{B_1}{v} - H_2 - \frac{B_2}{v}}{v} &= C_{g1} v - C_{g2} v + 0
\end{align*}
\]

Eq. 29

where the \( C_{fV} \) terms cancel because they are equal. If we call the left hand side of the equation \( x \) and expand the right hand side

\[
x = \frac{C'_{f1}}{D_{g1} v} - \frac{C'_{f2}}{D_{g2} v} \]

Eq. 30

and

\[
C'_g = \frac{x D_{j1} D_{j2}}{v(D_{22} - D_{11})}
\]

Eq. 31

In the actual experimental work, data was taken for each \( n \)-alkane at each temperature and velocity using helium and nitrogen as the two carrier gases. By assuming a particle diameter of 0.021 cm,
the value of \( w \) varied between about 0.5 and 1.1 and the \( C_v \) term was found to be 5 to 40% of the total plate height, depending on what carrier gas, temperature, gas velocity and n-alkane sample was being used. The value of \( w \) could then be put into Equation 13 for eventual use in determining \( D_f \).

**E. D \(_g\) Calculations**

One of the drawbacks in the use of Equation 13 is that the diffusivities of the higher n-alkanes in nitrogen and helium have never been determined experimentally. The diffusion constants have been measured in helium up to n-octane and in nitrogen only up to n-hexane (25).

An empirical equation for determining the diffusion constants of many organic molecules in a variety of gases was developed by Fuller, Schettler and Giddings (26). The equation was developed from measurements of 340 data points on 153 different binary gas mixtures which were then fitted to various temperature, molecular weight, pressure and atomic cross section parameters. The resulting empirical equation was able to predict the diffusion constants for each of these 340 cases with an average error of only 4.32%.

The diffusion constants obtained for the higher n-alkanes appear to be reasonable even though the use of this equation for their determination must be viewed with some reservation. The equation used is
\[ D_{AB} = \frac{10^{-3} T^{1.75} (1/M_A + 1/M_B)^{1/2}}{p[(\Sigma \nu_i)^{1/3}_A + (\Sigma \nu_i)^{1/3}_B]^2} \]  

Eq. 32

where the \( A \) and \( B \) subscripts refer to each component of a binary gas mixture, \( D_{AB} \) is their diffusion constant, \( M_A \) and \( M_B \) are their molecular weights, \( T \) is the temperature in °K, \( p \) is the pressure in atmospheres and \( \nu_i \) is an empirical summing parameter for each atom in a particular molecule.

Only four summing parameters need to be known for this work

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>( \nu_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>1.98</td>
</tr>
<tr>
<td>N(_2)</td>
<td></td>
<td>17.9</td>
</tr>
<tr>
<td>He</td>
<td></td>
<td>2.88</td>
</tr>
</tbody>
</table>

As an example, the diffusivity for n-octane in helium at one atm. and 373°K was determined by Maynard and Grushka (25) to be 0.3161 cm\(^2\)/sec. Equation 32 predicts a value of 0.3346 cm\(^2\)/sec, an error of 5.9% (assuming the literature value is accurate).

F. Partition Coefficient Calculations

Before the partition coefficients for the n-alkanes could be determined, the value of \( \beta \) in Equation 16 had to be calculated. The volume of mobile phase in a column is
\[ V_m = 0.38V_c \]  \hspace{1cm} \text{Eq. 33}

where \( V_c \) is the volume of the empty column and 0.38 is the fraction of the column not filled by glass beads.

The volume of stationary phase in a column is

\[ V_s = \frac{w_s}{\rho_s} \]  \hspace{1cm} \text{Eq. 34}

where \( \rho_s \) is the density of the stationary phase. The actual weight of stationary phase in a particular column is not always reported, but the percent loading of the stationary phase on the support usually is. In this case the volume of stationary phase must then be determined by

\[ V_s = 0.62V_c \frac{\% \rho_g}{100 \rho_s} \]  \hspace{1cm} \text{Eq. 35}

where 0.62 is the fraction of column volume occupied by glass beads, \( \% \) is the percent loading and \( \rho_g \) is the density of the glass beads.

The value of \( \rho_g \) has been determined to be 2.936 g/cc \((2, 3)\) and the glass has a negligible thermal expansion coefficient.

The unusual diffusion characteristics of n-alkanes in SE-30 have been noted \((3, 4)\) and linked at least tentatively to the unusually lower density of SE-30 relative to the other polydimethylsilicones \((4)\). Even
though the densities and expansion coefficients have been determined for these compounds (5), the values of their thermal expansion coefficients appear to be approximate and the resulting $\rho_s$ used in Equations 34 and 35 could be in error. Accordingly, a study of the density and thermal expansion coefficient for SE-30 was undertaken to determine any difference between published and experimental values.

The density of SE-30 was determined between 30°C and 230°C in 20°C steps and are listed in Table II. The literature value for the density of SE-30 at 28°C was 0.966 g/cc (3) and the experimental value at 30°C was 0.964 g/cc, which is a 0.2% error before thermal expansion is allowed for.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\rho$ (g/cc)</th>
<th>T (°C)</th>
<th>$\rho$ (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.9687</td>
<td>151</td>
<td>0.8702</td>
</tr>
<tr>
<td>50</td>
<td>0.9506</td>
<td>154</td>
<td>0.8654</td>
</tr>
<tr>
<td>70</td>
<td>0.9333</td>
<td>171</td>
<td>0.8581</td>
</tr>
<tr>
<td>90</td>
<td>0.9185</td>
<td>190</td>
<td>0.8379</td>
</tr>
<tr>
<td>110</td>
<td>0.8967</td>
<td>210</td>
<td>0.8275</td>
</tr>
<tr>
<td>130</td>
<td>0.8837</td>
<td>231</td>
<td>0.8119</td>
</tr>
<tr>
<td>133</td>
<td>0.8815</td>
<td>250</td>
<td>0.7985</td>
</tr>
</tbody>
</table>

The thermal expansion coefficient was experimentally determined to be $9.99 \times 10^{-4}$ cc/cc-°C while the literature value for high molecular weight polydimethylsilicones is $9.25 \times 10^{-4}$ cc/cc-°C which is an 8% difference.
While the experimental and literature densities at 30°C agree closely, the thermal expansion coefficients appear to differ, probably because of the anomalous morphology of SE-30. The experimental \( \rho_s \) values were used in determining the \( \beta \) values needed for subsequent calculation of partition coefficients from Equation 16.
VI. RESULTS AND DISCUSSION

A. Tabulation of Data

The evaluation of the terms in Equation 13 was carried out using the Oregon State University OS-3 computer system and the program listed in Appendix II. The $D_f$ and $K$ values calculated by this program for a series of n-alkanes in SE-30 and SF-96-2000 at 50° and 100°C are listed in Table III. Additional data for n-alkanes in SE-30 at 150° and 200°C are in Table IV.

B. Partition Coefficients

As can be seen in Figure 5, plots of $\ln K$ against carbon number are linear. Following the procedure of Roberts and Hawkes (27) the partition coefficient data for SE-30 was fitted to the regression model

$$\ln K = K_0 + K_1 C + \frac{(K_2 + K_3 C)}{RT} \quad \text{Eq. 36}$$

where the $K_i$ values represent the regression coefficients and $C$ represents the number of carbon atoms in a particular n-alkane molecule. The values of the regression coefficients were determined using the SIPS computer statistics program available on the OS-3 computer system. These regression coefficients may also be
Table III. Diffusion and partition coefficients of n-alkanes in SE-30 and SF-96-2000.

<table>
<thead>
<tr>
<th></th>
<th>SE-30 50°C</th>
<th>SF-96-2000 50°C</th>
<th>SE-30 100°C</th>
<th>SF-96-2000 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_f \times 10^7$ cm²/sec</td>
<td>$D_f \times 10^7$ cm²/sec</td>
<td>$D_f \times 10^7$ cm²/sec</td>
<td>$D_f \times 10^7$ cm²/sec</td>
</tr>
<tr>
<td>n-heptane</td>
<td>73.2</td>
<td>55.3</td>
<td>125</td>
<td>104</td>
</tr>
<tr>
<td>n-octane</td>
<td>59.3</td>
<td>47.2</td>
<td>82.4</td>
<td>89.6</td>
</tr>
<tr>
<td>n-nonane</td>
<td>44.0</td>
<td>39.6</td>
<td>115</td>
<td>116</td>
</tr>
<tr>
<td>n-decane</td>
<td>31.2</td>
<td>31.2</td>
<td>94.2</td>
<td>90.3</td>
</tr>
<tr>
<td>n-undecane</td>
<td>18.9</td>
<td>23.0</td>
<td>79.6</td>
<td>69.4</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>9.62</td>
<td>14.5</td>
<td>54.3</td>
<td>57.0</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>4.83</td>
<td>8.33</td>
<td>32.9</td>
<td>46.6</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>20.3</td>
<td>20.3</td>
<td>32.9</td>
<td>46.6</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>7.66</td>
<td>35.5</td>
<td>14.0</td>
<td>14.700</td>
</tr>
<tr>
<td>n-octadecane</td>
<td>2.01</td>
<td>46.500</td>
<td>4.51</td>
<td>51.600</td>
</tr>
</tbody>
</table>
Figure 5. Log partition coefficient against carbon number for n-alkanes on SE-30 at 50°, 100°, 150° and 200°C.
determined tediously by hand using methods developed in a good
statistics text. A good reference for a variety of linear regression
models is a book written by Neter and Wasserman (28).

Table IV. Diffusion and partition coefficients of n-alkanes in
SE-30 at 150 and 200°C.

<table>
<thead>
<tr>
<th></th>
<th>150°C</th>
<th>200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D_f \times 10^7 )</td>
<td>( D_f \times 10^7 )</td>
</tr>
<tr>
<td></td>
<td>( \text{cm}^2/\text{sec} )</td>
<td>( \text{cm}^2/\text{sec} )</td>
</tr>
<tr>
<td>n-undecane</td>
<td>179</td>
<td>107</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>148</td>
<td>174</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>122</td>
<td>285</td>
</tr>
<tr>
<td>n-tetradeane</td>
<td>95.5</td>
<td>462</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>58.3</td>
<td>1,200</td>
</tr>
<tr>
<td>n-octadecane</td>
<td>25.0</td>
<td>3,100</td>
</tr>
<tr>
<td>n-docosane</td>
<td>4.52</td>
<td>20,000</td>
</tr>
<tr>
<td>n-tetracosane</td>
<td>24.9</td>
<td>3,530</td>
</tr>
<tr>
<td>n-octacosane</td>
<td>4.42</td>
<td>14,100</td>
</tr>
</tbody>
</table>

The regression model in Equation 36 is based on Equation 19
and can be rearranged into the equation

\[
\ln K = \frac{\Delta G}{RT} = \frac{-T \Delta S + \Delta H}{RT}
\]

Eq. 37

which describes the energy relationship between the partition coeffi-
cient and the various thermodynamic parameters for evaporation of the
solute from the stationary phase. By comparing Equations 36 and 37
it becomes apparent that \( K_2 + K_3 C \) is \( \Delta H \), the enthalpy change
for the solute's evaporation, and that \( K_0 + K_1 C \) is \( -\Delta S/R \) where
ΔS is the entropy change in the evaporation process.

Fitting the SE-30 data in Tables III and IV to Equation 36 yields the following regression coefficients

<table>
<thead>
<tr>
<th>i</th>
<th>K_i</th>
<th>Std. Error</th>
<th>t-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1.805</td>
<td>0.366</td>
<td>- 4.93</td>
</tr>
<tr>
<td>1</td>
<td>-0.590</td>
<td>0.026</td>
<td>-22.9</td>
</tr>
<tr>
<td>2</td>
<td>950</td>
<td>282</td>
<td>3.37</td>
</tr>
<tr>
<td>3</td>
<td>905</td>
<td>21.7</td>
<td>41.7</td>
</tr>
</tbody>
</table>

The regression model has a correlation coefficient, R, of 0.9992 which represents an excellent fit to the data. The complete equation is

\[ \ln K = -1.805 - 0.590C + (950+905C)/RT \]

Eq. 38

The ΔH for evaporation of an n-alkane solute from SE-30 is 950 + 905 C cal/mole and has a standard deviation of

\[ [282^2+(21.7C)^2+2C(-5500)]^{1/2} \] cal/mole where -5500 is the covariance of K_2 and K_3. The entropy change, ΔS, is 1.987(1.805+0.590C) cal/mole-°K and has a standard deviation of

\[ 1.987[0.366^2+(0.026C)^2+2C(-0.0084)]^{1/2} \] cal/mole-°K where 1.987 is the gas constant and -0.0084 is the covariance of K_0 and K_1.

C. Diffusion in SE-30 and SF-96-2000

A concerted effort to fit D_f to a similar regression model, as has been done previously (3, 4), was not attempted here as plots of
In $D_f$ against carbon number, Figure 6, are obviously curved. A new regression model which might fit these data points could be made but it would be empirical in nature and any thermodynamic significance would be lost.

The diffusivity of simple gases in polymers has been shown to be part of an activated process (1, Ch. 2)

$$D_f = D_0 e^{-\frac{E_d}{RT}}$$

Eq. 39

where $D_0$ is a pre-exponential constant and $E_d$ is the activation energy for diffusion. In plotting $\ln D_f$ against $1/T$, Figure 7, one can see that $E_d$ increases with carbon number and decreases with increasing temperature, as would be expected, but that accurate determinations of $D_0$ and $E_d$ cannot be made as their values depend on a long extrapolation of lines with unknown curvature.

The $D_f$ values for SE-30 in Tables III and IV are substantially lower than those found by Kong and Hawkes (4) while those for SF-96-2000 are slightly higher. A part of the reason for this difference lies in the use of the gas phase mass transfer term in the theoretical equation and a part may also be the result of the use of a better gas chromatograph and equipment design with subsequent improvement in results.
Figure 6. Log $D_t$ against carbon number for n-alkanes on SE-30 at 50°, 100°, 150° and 200°C.
Figure 7. Log $D_f$ against $1/T$ for n-alkanes on SE-30.
One of the most important observations to be made about the data in Table III is that in plots of $\ln D_{f}$ against carbon number, Figures 8 and 9, the curves for SE-30 and SF-96-2000 actually cross each other. Extrapolation of the data of Butler and Hawkes (3) and Kong and Hawkes (4) may have resulted in a similar observation, however the data obtained for SE-30 was so limited that such an extrapolation would have been presumptuous.

The crossing of the curves in Figures 8 and 9 implies some rather complex diffusion mechanisms. In the first portion of the curves where n-alkanes have higher diffusivities in SE-30 than in SF-96-2000, diffusion may have been enhanced by the higher free volume of the SE-30. As the molecular weight of the n-alkanes increases, their longer chains may become more tangled in the strands of the polymer matrix. This would slow diffusion much more quickly in the extremely viscous SE-30 than in the less viscous SF-96-2000.

D. Friction Coefficients

One of the quantities popularly used by polymer chemists is the friction coefficient. This quantity is used as a measure of the resistance a molecule experiences as it attempts to move through the bulk of a polymer and may be applied to the movement of monomer
Figure 8. Log $D_A$ against carbon number for n-alkanes at 50°C.
Figure 9. Log $D_1$ against carbon number for n-alkanes at 100°C.
units of the polymer itself or to solute molecules diffusing through the polymer matrix.

The calculation of the friction coefficient for a solute molecule, \( \xi_1 \), can be accomplished by using the equation

\[
\xi_1 = \frac{kT}{D_g}
\]

where \( k \) is Boltzmann's constant in ergs/°K. Values of \( \xi_1 \) for n-alkanes in SE-30 and SF-96-2000 are listed in Table V and those for SE-30 have been plotted against carbon number in Figure 10.

There has been some evidence to indicate that \( \xi_1 \) is proportional to the chain length of diffusing n-alkanes (8, p. 371). This has been refuted by Kong and Hawkes (9) for silicone polymers and their report is clearly supported by Figure 10.

The friction coefficient for a polymer's monomer unit, \( \xi_0 \), has been shown by Ferry (8, p. 372) to be approximately the same as \( \xi_1 \) for a molecule of the same size. This proposal is consistent with data calculated here

<table>
<thead>
<tr>
<th>Mol. Wt.</th>
<th>( \xi ) (dyne-sec/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>72</td>
</tr>
<tr>
<td>monomer unit</td>
<td>74</td>
</tr>
</tbody>
</table>

where \( \xi_1 \) for n-pentane was obtained by extrapolation of the SE-30 data at 100°C and \( \xi_0 \) for the monomer unit was the value noted by Ferry (8, p. 363) for a polydimethylsilicone at 100°C.
Table V. Friction coefficients for n-alkanes in SE-30 and SF-96-2000.

<table>
<thead>
<tr>
<th></th>
<th>$\zeta_1 \times 10^9$ dyne-sec/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50°C</td>
</tr>
<tr>
<td></td>
<td>SE-30</td>
</tr>
<tr>
<td>n-heptane</td>
<td>6.09</td>
</tr>
<tr>
<td>n-octane</td>
<td>7.52</td>
</tr>
<tr>
<td>n-nonane</td>
<td>10.1</td>
</tr>
<tr>
<td>n-decane</td>
<td>14.3</td>
</tr>
<tr>
<td>n-undecane</td>
<td>23.6</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>46.4</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>92.4</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>25.4</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>67.2</td>
</tr>
<tr>
<td>n-octadecane</td>
<td>256</td>
</tr>
<tr>
<td>n-docosane</td>
<td>129</td>
</tr>
<tr>
<td>n-tetracosane</td>
<td>26.2</td>
</tr>
<tr>
<td>n-octacosane</td>
<td></td>
</tr>
</tbody>
</table>
Figure 10. Friction coefficient against carbon number for n-alkanes at 50°, 100°, 150° and 200°C.
VII. CONCLUSIONS

The problems with excessive peak skewing encountered by previous authors (3, 4) were not encountered here at temperatures down to 50°C. This observation is supported by work done by Baughman et al. (29) who found that SE-30 produced symmetric peaks down to 0°C. The reasons for the reported peak skewing have not been established but may have been the result of inferior instrument design.

The partition coefficients for n-alkanes in SE-30 and SF-96-2000 are linear with carbon number and those for SE-30 can be predicted by the equation

\[ \ln K = -1.805 - 0.590C + \frac{(950+905C)}{RT} \]

Based on this equation, the enthalpy change for evaporation of an n-alkane from SE-30 is \( 950 + 905C \text{ cal/mole} \) and the entropy change is \( 1.987(1.805+0.590C) \text{ cal/mole} \cdot ^\circ \text{K}. \)

The mechanism for the diffusion of n-alkanes through SE-30 and SF-96-2000 appears to be affected differently by density and viscosity. The higher free volume of SE-30 (lower density) allows faster diffusion of lower molecular weight n-alkanes than does the more dense SF-96-2000. On the other hand, the high viscosity of SE-30 appears to slow diffusion of n-alkanes much faster than
SF-96-2000 so that diffusion of the longer chain n-alkanes is faster in the SF-96-2000.

In applying this to the use of these polymers as stationary phases for gas chromatography, it appears that SE-30 would provide better separations of lower molecular weight compounds while SF-96-2000 would be superior when the heavier compounds need to be resolved.

The friction coefficients for n-alkanes in SE-30 and SF-96-2000 are not linear with carbon number but instead rise very sharply with the increase in carbon number. This would seem to support the contention that the longer n-alkanes are hindered more by the viscosity of the polymer than the smaller molecules. In addition, the fact that the friction coefficient for n-pentane is close to the reported friction coefficient for a dimethylsilicone monomer unit, would seem to lend support to the overall validity of the chromatographic method for determining diffusivities of compounds in polymers.


APPENDICES
APPENDIX I

Fortran Program for Calculation of

Sample Peak Statistics
PROGRAM MYSTAT

DIMENSION T(1000), V(1000), F(1000), KDAT(1000), NONE(6)

M = TTYIN(4HM=)
N = TTYIN(4HN=)
IPT = TTYIN(4HIP=)
LPT = TTYIN(4HLPT=)

M IS THE M PARAMETER ON COMPUTER INTERFACE
N IS THE N PARAMETER - NUMBER OF DATA PTS
IPT IS THE > OF THE FIRST DATA PT TO BE USED IN THE CALCULATION OF THE STATISTICS
LPT IS THE > OF THE LAST PT TO BE USED

TB = TTYIN(4HTB=)

TB IS THE TIME BASE - TIME INCREMENT

INB = TTYIN(4HINB=)
IN3 = TTYIN(4HIN3=)

INB IS THE > OF THE FIRST DATA PT TO BE USED TO DETERMINE THE BASELINE VOLTAGE
IN3 IS THE > OF THE FIRST DATA PT TO BE USED TO

LAB = TTYIN(4HLAB=)

LAB IS THE LAST PT FOR BASELINE VOLTAGE CALCULATION

WRITE(61,7)
FFORMAT(# CORRECT*)
J = TTYIN(4HA=)
IF (J.EQ.0) GO TO 5
IF (J.NE.1) GO TO 6
WRITE(61,20)

WRITE(61,30)
FFORMAT(# WHAT LUN IS THE DATA STORED IN*)

LUN = TTYIN(4HLUN=)

WRITE(61,40)
FFORMAT(# CORRECT*)
J = TTYIN(4HA=)
IF (J.EQ.0) GO TO 10
IF (J.NE.1) GO TO 25

BUFFER IN(LUN,1)(NONE(1),NONE(6))

GC TO(40,45,185,187),UNITSTF(LUN)

BUFFER IN(LUN,1)(KDAT(0),KDAT(N))

GC TO(46,47,185,187),UNITSTF(LUN)

DC 50 T=1:N

V(I)=FLOAT(KDAT(I))

BASAV=0

DC 100 I=INB,LAB
BASAV=V(I)+BASAV

BASAV=3BASAV/(LAB-INQ)

DC 110 I=1:N

V(I)=V(I)-BASAV
SUMV=0

T=(T+IOT)*TB
DO 120 I = IPT, LPT
SUMV = SUMV + V(I)
T(I) = T
T = T + T
DC 130 I = IPT, LPT
F(I) = V(I) / SUMV
EMU = 0
DO 140 I = IPT, LPT
EMU = EMU + T(I) * F(I)
VAR = 0
EM3 = 0
FM4 = 0
DC 150 I = IPT, LPT
PR = F(I)
VAR = VAR + (T(I) - EMU) * (T(I) - EMU) * PR
EM3 = EM3 + (T(I) - EMU) * (T(I) - EMU) * PR
FM4 = FM4 + (T(I) - EMU) * (T(I) - EMU) * PR
CONTINUE
SD = SORT(VAR)
SKEW = EM3 / (VAR * SD)
SKURT = FM4 / (VAR * VAR)
WRITE (61, 160) EMU, VAR, SD, EM3, EM4, SKEW, SKURT
FORMAT (F, E 14.6, /) VAR, 7(3X, E 14.6, /)
1 X STD DEVIATION... E 14.6, /
3RD MOMENT... E 14.6, /
SKWNESS... E 14.6, /
KURTOSIS... E 14.6, /)
WRITE (61, 170)
FORMAT (F, DO YOU WANT TO RERUN? = )
J = TTYIN (4 HA = )
IF (J .EQ. 0) GO TO 190
IF (J .NE. 0) GO TO 165
WRITE (61, 180)
FORMAT (F, DO YOU WANT TO CHANGE VARIABLES? = )
J = TTYIN (4 HA = )
IF (J .EQ. 0) GO TO 10
IF (J .NE. 0) GO TO 175
GO TO 5
WRITE (61, 186)
FORMAT (F, EOF ENCOUNTERED - CHECK REWIND < > OF PTS? = )
GO TO 5
WRITE (61, 186)
FORMAT (F, PARITY ERROR - RESTART? = )
GO TO 5
STOP
END
APPENDIX II

Fortran Program for Calculation of $D_f$ and Plate Height Parameters
PROGRAM OSUBL

CONST = 1.013256 * 27/16 * 2.73 = (DYNES-CM**-2)

CONSTANTS IN <J>*?*GAMMA

IFTEST=0

ITEST IS USED TO SAVE TIME BY ELIMINATING

UNNECESSARY OUTPUT OF TELETYPE VARIABLE DESCRIPTION

WHEN SYMBOLS ARE UNDERSTOOD BY USER

FORMAT(1 PARAMETER DESCRIPTION 1=YES C=NO*//)

J=TTYIN(4HA=)

IF(J.EQ.1)GO TO 3

IF(J.NE.0)GO TO 1

ITEST=1

GO TO 6

WRITE(51,4)

FORMAT(P = % STATIONARY PHASE*,//)

RG=TTYIN(4HRE=)

PL=TTYIN(4HL)=

CL=TTYIN(4HCL=)

T=TTYIN(4HT=)

T=T+273.16

C T IS NOW IN DEGREES KELVIN

CP=TTYIN(4HCP=)

CF=TTYIN(4HCS=)

TFT=C

IF(ITEST.EQ.1)GO TO 7

WRITE(51,6)

FORMAT(2 ENTER THE CORRECT > FOR CARRIER GAS*,//)

J=TTYIN(4HGAS=)

IF(J.EQ.1)GO TO 9

IF (J.EQ.2) GO TO 9
IF(J.EQ.3)GO TO 10
00047
GO TO 55
00049
8 VIS=4.92E-6*T**.647
00051
9 VIS=2.39E-6*T**.756
00053
10 VIS=2.07E-6*T**.827
00055
105 IF(ITEST.EQ.1)GO TO 125
00056
11 WRITE(61,12)
00057
12 FORMAT('DO YOU WANT TO USE PHI OR PRESS INPUT 1,2',/)
00058
13 TYPE 1 FOR PHI AND 2 FOR PT/
00059
C USE PHI ONLY IF PO AND PIN ARE NOT KNOWN
00062
125 J=TTYIN(4HPI)
00065
IF(J.EQ.1)GO TO 13
00066
IF(J.NE.2)GO TO 11
00067
PIN=TTYIN(4HPIN=)
00068
PIN=PIN*1337
00069
PT=1
00070
C PIN NOW IN CYMES PER CM**2
00071
GO TO 14
00072
PHI=TTYIN(4HPI=)
00073
C PHI NOW IN CYMES PER CM**2
00074
PC=TTYIN(4HPD=)
00075
C PC IS NOW IN CYMES PER CM SQUARED
00076
WRITE(61,15)
00077
15 FORMAT('NOW ENTER VARIABLES',/)
00078
1 IF TEST.EQ.1)GO TO 16
00079
WRITE(61,15)
00081
15 FORMAT('NOW ENTER VARIABLES',/)
00082
1 IF(Test.EQ.1)GO TO 16
00083
WRITE(61,15)
00085
15 TA=TTYIN(4HTA=)
00087
TH=TTYIN(4HTH=)
00089
WH=TTYIN(4HWH=)
00091
WD=TTYIN(4HWD=)
00093
C=TTYIN(4HCC=)
00095
C BETA = 0.35**100*RL/0.62/RG -1. (1 ASSUMED INSIGN.)
00097
C
00099
6 IF(IPIT.EQ.1)GO TO 17
00100
S=VIS*1.33*CL*CLS/TA/PHI/PO
THE FOLLOWING IS AN EMPIRICAL FITTING EQUATION TO DERIVE \( \frac{\text{PM}}{\text{PO}} = \text{PT} \) FROM VELOCITY

\[
\text{PT} = 1.0 + 0.75 \times (9.92519 \times 10^{-14} \text{S} + 3.62541 \times 10^{-7} \text{S}^4) \tilde{\text{PT}}^2
\]

\[
\tilde{\text{PT}}^2 = \frac{\text{PT}^2 - \text{PT} \times \text{PT}^2}{\text{PT}^4}
\]

\[
\text{FCP} = \text{FC} \times \left( (\text{PT}^4 - 1) \times (\text{PT}^2 - 1) \times (\text{PT}^2 - 1) \times (\text{PT}^3 - 1) \times \text{PO} \right)
\]

\[
\text{OL} = \text{H} - \text{FO} \times \text{PL} \times \text{CS}
\]

\[
\text{OL} = \text{OL} \times \sqrt{\text{PT}^4 \times \text{PG} / 1.75 / \text{RL}}
\]

\[
\text{ALIL} = \text{ALOG} \times 110
\]

\[
\text{WQTTF} = \left( \text{ALDLOK} \times \text{ALIL} \times \text{BVF} \times \text{CGV} \times \text{111} \times \text{114} \times \text{117} \times \text{113} \times \text{116} \times \text{119} \times \text{122} \times \text{125} \right)
\]

\[
\text{OL} = \text{OL} \times \sqrt{\text{PT}^4 \times \text{PG} / 1.75 / \text{RL}}
\]

\[
\text{ALIL} = \text{ALOG} \times 110
\]

\[
\text{WQTTF} = \left( \text{ALDLOK} \times \text{ALIL} \times \text{BVF} \times \text{CGV} \times \text{111} \times \text{114} \times \text{117} \times \text{113} \times \text{116} \times \text{119} \times \text{122} \times \text{125} \right)
\]

\[
\text{OL} = \text{OL} \times \sqrt{\text{PT}^4 \times \text{PG} / 1.75 / \text{RL}}
\]

\[
\text{ALIL} = \text{ALOG} \times 110
\]

\[
\text{WQTTF} = \left( \text{ALDLOK} \times \text{ALIL} \times \text{BVF} \times \text{CGV} \times \text{111} \times \text{114} \times \text{117} \times \text{113} \times \text{116} \times \text{119} \times \text{122} \times \text{125} \right)
\]

\[
\text{OL} = \text{OL} \times \sqrt{\text{PT}^4 \times \text{PG} / 1.75 / \text{RL}}
\]

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\[
\text{WQTTF} = \left( \text{ALDLOK} \times \text{ALIL} \times \text{BVF} \times \text{CGV} \times \text{111} \times \text{114} \times \text{117} \times \text{113} \times \text{116} \times \text{119} \times \text{122} \times \text{125} \right)
\]