FACTORS AFFECTING THE SEPARATION OF ORGANIC COMPOUNDS
BY GAS LIQUID CHROMATOGRAPHY

by

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The objects of this thesis have been threefold. In the first place it has been an investigation of the factors which influence retention time in an attempt to predict the retentions of new compounds. Secondly it has been an investigation into the conditions for the best separation of diastereoisomers, and thirdly it has been an application of gas chromatography in the study of the forces of intermolecular interaction in solution.

To carry out these investigations, the retention times of twenty five monofunctional and bifunctional compounds have been determined on four stationary liquids at 130°C.

It was found that by dividing the retention time of a solute by that of a hypothetical normal hydrocarbon of the same molar volume of the solute, a functional group constant was obtained. By means of this constant, termed the Group Retention Factor, it was found that it is possible to predict the retention of bifunctional compounds.

The separation of diastereoisomeric pairs is discussed in terms of the Group Retention Factors of the functional groups on the diastereomers.

The molar volume is also utilized in order to develop an equation by means of which the ratio of retention times on two solvents can be related to the forces of interaction between solute and solvent.
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SECTION 1

INTRODUCTION AND THEORY

1.1 INTRODUCTION

In the comparatively short time since its inception, Gas Liquid Chromatography (GLC) has proved to be a technique of great versatility and application.

It is used in the analysis of complex volatile mixtures, in the separation of very closely related substances, in the preparation of ultra pure samples, and in the investigation of thermodynamics at infinite dilution.

In this study it is hoped to extend the application in three of these areas.

(i) Retention times

In the analysis of a complex mixture, the components present are usually identified according to the time they spend in the column. Analysis is simplified if this retention time is known beforehand. In this thesis a method is presented for the estimation of the retention times of various chemical types from a knowledge of their basic molecular features.

(ii) Diastereoisomers

Gas chromatography is a powerful tool for the separation/
separation of close boiling liquids. A number of pairs of diastereoisomers have been chosen to investigate the way upon which the resolution of these very similar chemical species may be improved.

(iii) Solution theory

As a technique of simplicity and accuracy, GLC is pre-eminent in the study of thermodynamic properties at infinite dilution. Gas chromatographic retentions lead to values of enthalpies, entropies and free energies of solution. Equations are developed below which lead to values of the intermolecular forces of interaction between the liquid in the column and the vapour being chromatographed.

SECTION 1.2

OUTLINE OF THEORY

Gas chromatography is a technique for separation in which the component, a vapour, is partitioned between a gas (the mobile phase), and a solid or a liquid (the stationary phase).

The first case is known as gas-solid chromatography, and the second, the only type dealt with here, as gas liquid chromatography.

In the procedure the components to be chromatographed, which are also known as solutes, are injected as a liquid mixture into a heated inert gas stream. Instantly vaporised, they pass through a column/....
column containing the stationary phase.

The liquid phase, or solvent, is present as a thin layer coated either on an inert packing material (the support), or on the wall of the column. The first case is known as packed column chromatography, which is the technique used exclusively in this study. The second case is capillary chromatography. In capillary chromatography column diameters of the order of 0.1 mm are used, while in packed column chromatography the column diameter is usually of the order of 4 to 6 mm.

The solutes, eluted from the column by the continuous passage of the carrier gas, are detected by a physical method at the column outlet. The detection signal after having been amplified, is recorded on chart paper.

The parameter which is measured, and which may be related to the physico-chemical properties of the system is the retention volume. The retention volume is defined as the volume of carrier gas in cubic centimeters required to elute the solute. This quantity is independent of the flow rate of the carrier gas. This must however be known to enable the calculation of retention volume from the retention time, which is the time the solute spends in the column. This latter quantity is the parameter most conveniently measured and utilized. The retention time is always measured from the point on the chart where air injected with the solutes emerges, or would emerge. This position is termed /....
termed the air peak, and the reason for its importance will be understood when the basic gas chromatographic equations are derived below.

There are now two approaches to the derivation of equations relating retention volume to physical constants. Littlewood (1) relates them from a basic consideration of the partition coefficients of the solutes between the mobile and stationary phases, while Purnell (2), with most other authors presents a more readily understood derivation of the equation from a consideration of the vapour pressures of the pure solutes. Both pathways lead to identical relationships, and the derivation given by Purnell is presented below.

The retention volume per gram of solvent at the column temperature $T_1$, $V_{T_1}^g$ is given by

$$V_{T_1}^g = \frac{RT}{\gamma^0 P^0 M_1}$$  \hspace{1cm} 1.1

where $R$ is the gas constant, $T$ the temperature in degrees Kelvin, $\gamma^0$ the activity coefficient at infinite dilution, $P^0$ the vapour pressure of the pure solute and $M_1$ the molecular weight of the solvent.

By eliminating $T$ from the equation, the retention volume per gram of solvent at $0^\circ C$, known as the specific retention volume, $V_g$, is obtained

$$V_g = \frac{273}{T} V_{T_1}^g$$  \hspace{1cm} 1.2

$$= \frac{273}{T} \frac{RT}{\gamma^0 P^0 M_1}$$  \hspace{1cm} 1.3
From a knowledge of the molecular weight of the solvent and the vapour pressure of the pure solute at that temperature, it is then possible to determine the activity coefficient of the solute in the solvent at infinite dilution.

Since the excess partial molar free energy of mixing at infinite dilution is related to the activity coefficient by

$$\Delta G^\circ_E = RT \ln \gamma^0$$

it is seen that the retention volume may be related to various other thermodynamic quantities. This has in fact been verified, and utilized, by a number of authors (3 - 9).
The accurate determination of the specific retention volume is, however, not always a simple procedure. In addition to a precise knowledge of the flow rate and the weight of solvent on the column, it is necessary to apply a carrier gas compressibility correction factor (see 2, eqn. 5.21). More often than not specific retentions are not measured, and published data are presented in the form of relative retention times, or volumes. To do this, some solute is arbitrarily chosen as having unit retention time, and those of all others are measured relative to this. Provided that all measurements are made under identical column pressure conditions, it is unnecessary to apply the compressibility equation, or to know the weight of the solvent in the column. Furthermore, retention may be measured in any units, such as centimeters of chart.

For these reasons, and also for the reason that in gas chromatography one is primarily concerned with the separation of components, relative retentions are used throughout this work.

The relative retention time is obtained by dividing the specific retention of the solute, 1, by that of a reference solute, 2.

It may be written

\[ r_{12} = \frac{V_g(1)}{V_g(2)} = \frac{\gamma_2^{0P_2^0}}{\gamma_1^{0P_1^0}} \]

Equation/....
Equation 1.6 illustrates that the relative retention of two solutes depends both on the ratio of their vapour pressures, and upon the ratio of their activity coefficients at infinite dilution. The phenomenon which enables GLC to effect separations far more efficiently than distillation, is the ability of gas chromatographic liquids to change the activity coefficient ratio.

It is felt, however, that for theoretical treatment, the relative retention of two solutes is better described in terms of the heats of solution. Retention volume equations in these terms have been developed for this thesis to help understand the forces which operate in solution, and are derived below.

If we consider solutes 1 and 2 to have vapour pressures \( P_1^0 \) and \( P_2^0 \) in mm of Hg at temperature \( T_1 \) in degrees Kelvin, then from the Clapeyron–Clausius equation,

\[
\ln \left( \frac{P_1^0}{760} \right) = \frac{\Delta H_V}{R} \left( \frac{1}{T_{b_1}} - \frac{1}{T_1} \right) \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots 
\]

where \( T_{b_1} \) is the boiling point of the solute, \( x \), and \( \Delta H_V^x \) the molar heat of evaporation of the pure solute.

Then

\[
\ln \left( \frac{P_2^0}{P_1^0} \right) = \frac{1}{R} \left( \frac{\Delta H_V^1}{T_{b_2}} - \frac{\Delta H_V^1}{T_{b_1}} \right) + \frac{\Delta H_V^1}{RT} - \frac{\Delta H_V^2}{RT} \approx \frac{1}{RT} (\Delta H_V^1 - \Delta H_V^2) / \ldots \ldots
\]
\[ \Delta S_E^0 = \frac{1}{RT} (\Delta H_1^V - \Delta H_2^V) \]

if 1 and 2 have similar Trouton constants.

From 1.5 we see that

\[ \ln \gamma_2^o/\gamma_1^o = \frac{1}{RT} \left\{ \Delta G_E^0(2) - \Delta G_E^0(1) \right\} \]

Since

\[ \Delta G_E^0 = \Delta H_E^0 - T \Delta S_E^0 \]

and \( \Delta H_E^S = \Delta H^V - \Delta H_E^0 \)

where \( \Delta H_E^0 \) is the partial molar enthalpy and \( \Delta S_E^0 \) the partial molar entropy of solution, and \( \Delta H_E^S \) is the molar heat of evaporation of solute from solution (see 9),

\[ \ln \gamma_2^o/\gamma_1^o = \frac{1}{RT} \left( \Delta H_E^0(2) - T \Delta S_E^0(2) - \Delta H_2^V \right) \]

\[ - \Delta H_E^0(1) + T \Delta S_E^0(1) + \Delta H_1^V \]

\[ = \frac{1}{RT} (\Delta H_E^S(1) - \Delta H_E^S(2)) + \frac{(\Delta S_E^0(1) - \Delta S_E^0(2))}{R} \]

The entropy term is small and may be represented * by

\[ \Delta S_E^0 = \ln \frac{1}{r^1} + (1 - \frac{1}{r^1}) \]

where \( r^1 \) is the molecular volume ratio of the solute and solvent molecules.

* See discussion on activity coefficients below.
If solutes 1 and 2 are of similar size, and in a common solvent,

\[ \Delta S^o_{E(1)} - \Delta S^o_{E(2)} = \ln \frac{V_S}{V_1} \cdot \frac{V_2}{V_S} + \left(1 - \frac{V_S}{V_1}\right) - \left(1 - \frac{V_S}{V_2}\right) \]

\[ = 0 \]

1.16

where \( V_S \) represents the molar volume of the solvent molecules, \( V_X \) the molar volume of solute X.

Relative retentions are seen to be determined only by the difference between the heats of evaporation from solution of the two solutes, and by the absolute temperature.

\[ \ln r_{12} = \frac{1}{RT} (\Delta H^S_{E(1)} - \Delta H^S_{E(2)}) \]  

1.17

This is considered a particularly lucid presentation of the relative retention time as a function of thermodynamic variables, and this equation will be used in preference to others, such as 1.6.

One of the earliest relationships established in gas chromatography is that there is a linear relationship between the logarithm of the retention volume of members of an homologous series and their carbon number.

This may be explained in a number of ways.

From equation 1.4 it is seen that

\[ \log V_g = \text{constant} - \log \gamma^\circ \]  

1.18

and the increase in \( \log V_g \) with carbon number can be thought of as being caused /....
caused by the linear decrease in the logarithms of vapour pressure as carbon number increases. Since \( \log P^0 \) is directly proportional to the boiling point, \( \log V \) is also linearly related to the boiling point of members of an homologous series. This is a relationship of very wide application.

Equation 1.17 explains the logarithmic increases in retention volume with chain length in terms of the linear increase of \( \Delta H^S_\infty \) with chain length.

The heat of evaporation of the solute from solution increases with carbon number for the same reason that the heats of vaporisation of the pure liquids increase. Increasing molecular complexity makes it more difficult for molecules to break free from the liquid.

A different aspect of the relative retention is brought out when it is written in the form 1.6

\[
r_{12} = \frac{\gamma_2^o P_2^o}{\gamma_1^o P_1^o}
\]

In this equation, \( r_{12} \) is seen to be determined by the vapour pressure ratio and by the activity coefficient ratio of solutes 1 and 2.

The activity coefficient is a measure of the non-ideality of solution. In a solution which is ideal, the activity coefficient is unity, and partition between two solutes is determined solely by the vapour pressure ratio of the solutes.
Gas chromatographic solvents very seldom give rise to ideal solutions. The few that do are the hydrocarbon solvents, such as squalane, and separations on these liquids are determined only by the vapour pressures of the solutes. In most solvents the activity coefficient is not equal to unity, and it is this property which enables gas chromatographic resolution of compounds of very similar boiling point, yet different chemical character, which cannot be separated by distillation.

Because of the importance of the activity coefficient, a considerable body of work has been carried out to relate the activity coefficient to molecular parameters. Purnell (2, pp25ff) has treated this in some detail, giving an expression for the activity coefficient which may be developed from the Flory-Huggins treatment. A summary of Purnell's derivation of the expression will now be presented.

From equations 1.5 and 1.11, we may write

\[ \ln \gamma^o = \frac{\Delta H^o}{RT} - \frac{\Delta S^o}{R} \]  

1.19

and the activity coefficient may be considered as the product of a thermal and of an athermal factor,

\[ \ln \gamma^o = \ln \gamma_t^0 \gamma_a^o \]  

1.20

By development of the Flory-Huggins theory, these factors can be evaluated individually in terms of molecular parameters, (2, p.29). In the gas chromatographic column, the solutes,
because of the small quantities injected, may be considered to be at infinite dilution. The activity coefficient at infinite dilution of solute $1$ in solvent $S$ is then written

$$\ln \gamma_1^0 = \frac{Z_1}{2RT} \left( U_{11} + U_{SS} - 2U_{1S} \right) + \ln \frac{1}{r_1} + \left( 1 - \frac{1}{r_1} \right) \ldots 1.21$$

$Z_1$ is the co-ordination number of $1$ in the solvent. It is a function of the number of nearest neighbour sites to a given segment of solvent molecule, but is difficult to define precisely.

$U_{11}$, $U_{SS}$ and $U_{1S}$ are the forces of interaction between molecules of solute, molecules of solvent, and between solute and solvent, respectively.

$r_1$ is the molecular volume ratio of solute to solvent molecules, as before.

The relation made between entropy and molecular size in equation 1.15 will now be understood.

As in the case of retention volumes, it is more convenient to work with relative activity coefficients.

If the two solute molecules $1$ and $2$ are of similar size, then the athermal factor can be eliminated, and the co-ordination numbers equated,

$$Z_1 = Z_2 = Z \quad \ldots \quad 1.22$$

Then the relative activity coefficient of solute $2$ to solute $1$, a quantity/....
quantity which is obtained by eliminating the vapour pressure from the relative retention of 1 to 2 (equation 1.6), becomes

\[ \ln \left( \frac{\gamma_2^0}{\gamma_1^0} \right) = \frac{Z}{2RT} \left\{ (u_{22} - u_{11}) - 2(u_{2S} - u_{1S}) \right\} \] ........................ 1.23

It will be noticed that the solvent - solvent interaction factor has been removed. \((u_{22} - u_{11})\) is often equated with the difference in the heat of vaporisation of solutes 2 and 1, while \((u_{2S} - u_{1S})\) is the difference in interaction energies of solutes 2 and 1 with the solvent. It is thus apparent that even in a solvent which shows no preferential interaction with either of the solutes, the activity coefficient ratio will still have a value, dependant on the heats of vaporisation of the solutes and their size.

SECTION 1.3

OUTLINE OF WORK

The fundamental objects of this thesis have been presented in the introduction.

These are presented again below.

1) To investigate the factors which influence retention time in an attempt to predict the retentions of new compounds.

2) To investigate the resolution of diastereoisomers, solute pairs which are particularly difficult to separate.

3) To apply gas chromatography to study the forces of intermolecular interaction in solution.
To carry out these investigations, the retention times of twenty-five monofunctional and bifunctional solutes have been measured relative to normal heptane on four stationary liquids at 130°C.

The compounds studied include five chemical classes and four structural types. The monofunctional compounds were normal butyl bromide, n-butyl methyl ether and n-butyl cyanide. The bifunctional compounds chosen were 1,2 disubstituted ethanes, 2,3 and 1,4 disubstituted butanes. Both substituents on the disubstituted butanes were in each case the same, while 1,2 disubstituted ethanes with different functional groups have also been studied.

The four gas chromatographic liquids chosen are all well-known solvents of general applicability. They are squalane (SQ), dinonyl phthalate (DNP), tricresyl phosphate (TCP) and polyethylene glycol 600 (PEG).

The temperature employed throughout was 130°C, and in addition the acetates and bromides were chromatographed at 100°C.

The retention times so obtained are manipulated to obtain functional group constants, and values for the forces of interaction, in the discussions which follow. From the retention times of the monofunctional compounds it has been found that it is possible to predict the retentions of the bifunctional compounds. The diastereoisomeric pairs have all been separated, and the ease
with which the various pairs separate is discussed. Finally, an equation is derived which relates the activity coefficient to the forces of interaction between solute and solvent.
APPARATUS AND EXPERIMENTAL TECHNIQUE

2.1 APPARATUS

The gas chromatograph was purchased from the Department of Physical Chemistry, University of Pretoria.

The oven consisted of a 12" x 14" x 8" hollow-walled container fitted with a 1/2" asbestos top, and heated by means of resistances wound close to the walls inside the container.

The chromatographic columns were 1 metre in length, and made from 1/4", 18 gauge copper tubing. Coiled, they were secured within the oven by means of flange nuts.

The oven temperature was measured by means of a thermometer guaranteed to within ± 1°C, and immersed in the oven top to within a few inches of the mercury level. The oven temperature was kept constant at 130°C or 100°C to within 0.5°C. The column preheater temperature, at the injection port was maintained at 180°C, the temperature being measured by a thermocouple built into the apparatus.

A Hamilton 10 µl syringe was used to inject the solute mixture into the gas stream through a silicone injection cap. The carrier gas used, nitrogen, was not treated in any way before entering the column, except when it was pretreated for one particular experiment.
thiocyanate), then with 5% sodium hydroxide, followed by repeated washing with water until neutral. Thoroughly dried, it was thereafter treated with 5% dichlorodimethyl silane in redistilled toluene for seven days, followed by washing with anhydrous methanol and then repeatedly with ether. Finally it was dried at 120°C for two hours.

Various authors (see for example 2 and 58) have described this treatment to inactivate a support. The dichlorodimethyl silane acts by silizing the hydroxyl groups on the support. The support after this treatment produces far less tailing due, it is believed, to the silization of these groups.

The slurry technique was used to coat the support. The stationary liquids weighed accurately to 0.001g, were dissolved in a suitable volatile solvent, and added to a slurry of the support with the same solvent. The support was weighed to an accuracy of 0.1g beforehand. The solvent used for squalene was chloroform, and the solvent used for the other three liquids was acetone. The solvents were evaporated over a water bath, and in a draught, with constant stirring of the slurry until dry. The coated support was finally heated at 120°C for two to three hours.

Loadings prepared were: squalene 20% w/w, and the others 5% w/w. The reasons for the particular choice of these figures are given in the last section.

The columns were not usually matured in the chromatograph for any length of time, though the carrier gas was passed through the columns while they were being heated. No variation in column behaviour was observed over any length of time. The reference solute used in...
all cases has been normal heptane, this hydrocarbon being chosen because of its suitable boiling point (98°C), and availability. In each case it was mixed with the component to be chromatographed prior to injection.

Since it is well established (10, 11) that the sample volume injected does influence the retention time, particularly if the samples are large, volumes were injected such that the quantity of each component injected was of the order of 0.05 µl per % liquid loading. Thus 0.25 µl of each component could be tolerated on the 5% column. Retentions were not found to change with volume injected within these limits. Comparisons with pure samples chromatographed were also made, and it was confirmed that the injection of a mixture does not alter the retention times of any of the components.

The flame ionisation detector does not respond to air, and hence with this detector, the "dead volume" must be determined by alternative methods. Two techniques have been used here:

1. A saturated solution of coal gas in a relatively high boiling solvent (heptane to decane) was chromatographed. The first peak appearing was assumed to be methane which can be considered as having a retention time identical to air at these temperatures.

2. The dead volume was estimated by the method described by Peterson and Hirsh (12), and extended by Gold (13). Since a plot of the logarithmic retention time, corrected by subtracting the column dead volume, of normal alkanes against carbon number is linear, the dead volume may be estimated from uncorrected retentions by the relationship

\[ v_{n3} \]
\[
\left( \frac{V_{n_3} - V_d}{V_{n_2} - V_d} \right)^{n_2 - n_1} = \left( \frac{V_{n_2} - V_d}{V_{n_1} - V_d} \right)^{n_3 - n_2}
\]

where \( V_d \) is the dead volume of the apparatus, and \( V_{n_1}, V_{n_2}, \) and \( V_{n_3} \) the uncorrected retention times of normal hydrocarbons, or any members of an homologous series, \( n_1, n_2, \) and \( n_3 \). In practice the hydrocarbons normal hexane, octane and decane were used, and equation 2.1 reduces to

\[
V_d = \frac{V_{n_1} V_{n_3} - V_{n_2}^2}{V_{n_1} + V_{n_3} - 2V_{n_2}}
\]

The first method suggested for determining the air peak is a new technique, and it was verified by comparison with the second, established method. The coal gas technique was however employed only in a few measurements during the early part of the work. These appear in the last section of the thesis.

It was frequently necessary to alter the flow rate of the carrier gas. It was either increased to elute high boiling components within a reasonable time, or it was decreased to allow an accurate measurement of the retentions of low boiling components. When this was done new determinations of the dead volume by Peterson's method were not usually made, but the retention of n-heptane was used as a measure of the flow rate. The new dead volume, \( V_{d(2)} \), was calculated from the dead volume at the first rate, \( V_{d(1)} \), by direct proportion using the retentions of n-heptane \( V_{nC_7(2)} \) and \( V_{nC_7(1)} \):

\[
V_{d(2)} = \ldots
\]
The validity of this relationship was established by making direct comparison with dead volumes calculated from 2.2 at different flow rates. Corrected retention times were then established for the various compounds by measuring the distance from the point of injection to the height of the peak, and subtracting the calculated dead volume. Retentions of less than 10 cm were measured to 0.1 mm, those greater than 10 cm to 1 mm.

Injection Procedure;

1. The column was allowed to equilibrate at 130°C with the carrier gas flowing through the packing to remove any volatile impurities or products of decomposition which might be present.

2. 1µl of a blend of n-hexane, n-heptane, n-octane and n-decane was injected from seven to ten times at a suitable flow rate. The retention times recorded on chart paper were measured later, the mean values being used to calculate the dead volume.

3. The component to be chromatographed was dissolved in, or mixed with n-heptane and injected between five and ten times. Sometimes the other hydrocarbons were added to the mix if a simultaneous estimation of the dead volume was required. In the case of very high boiling compounds, n-decane was used as reference solute. The retention relative to n-heptane can be calculated...
calculated from a knowledge of the retention of decane relative to heptane, \( r_{10,7} \)

\[
\frac{r_{x,7}}{r_{x,10}} = r_{10,7}
\]

\section{2.3}

\textbf{ERRORS}

There are three main causes of errors in gas chromatographic measurements:

(1) Variation in retention time produced by irregularities in evaporation and mixing in the preheater; these vary from one injection to another and account for the fact that two retentions seldom agree to better than 0.2 mm, a quantity which can be highly significant, particularly when the retention time of the reference solute is very much smaller than the compound being eluted. This problem is overcome by taking the average of multiple retentions.

(2) Variation in the retentions of asymmetric peaks with peak height; it is found that if a particular peak is asymmetrical, by virtue of tailing caused by interaction with the support, there is a shift in the position of the peak depending on its height. Sharp peaks have smaller retentions while low peaks usually take longer to emerge. The differences involved, which may be large (of the order of a centimeter), do not, however, introduce significant/...
significant errors since this phenomenon is only observed in peaks which have relatively long retention times, and the retention time is always the numerator in the ratio taken. Any variation due to this effect in the retention of the reference solute, which is usually a small figure in the denominator of the ratio, would be of significance, but fortunately alkanes were not found to give assymetric peaks.

(3) Errors introduced in the calculation of $V_d$: this is the most serious source of faulty results. The relationship used to calculate $V_d$, equation 2.2, frequently involves the difference and ratio of small numbers, which can only be measured to 0.1 mm. A small error in the dead volume can introduce a large percentage error in the retention of the reference solute when the subtraction is made to obtain its corrected retention volume.

For these reasons the greatest care has been taken in the injection and measurement of the retentions of the normal hydrocarbons, and the flow has been kept as low as possible, since the longer the retention time the smaller is the percentage error introduced by fluctuation in retentions.

SECTION 2.4

PREPARATION AND IDENTIFICATION OF CHEMICALS

Of the four stationary liquids used in the study, squalane, dinonyl phthalate and tricresyl phosphate were all supplied as gas chromatographic solvents, and were used directly without purification.
The polyethylene glycol was however treated for the removal of volatile impurities by heating at 100°C and 0.5 mm pressure for 8 hours.

Table 2.1 gives a list of the chemicals chromatographed. Postscripts indicate whether the chemical was bought (b) or prepared in the laboratory (p). The chemicals bought were all obtained from British Drug Houses.

**TABLE 2.1**

**Chemicals obtained for chromatography**

<table>
<thead>
<tr>
<th>Substituted Hydrocarbon</th>
<th>Bromide</th>
<th>Acetate</th>
<th>Alcohol</th>
<th>Methyl ether</th>
<th>Cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butyl</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>p(^4)</td>
</tr>
<tr>
<td>1,2-disubstituted ethane</td>
<td>b(^1)</td>
<td>b</td>
<td>b(^2)</td>
<td>p</td>
<td>p(^5)</td>
</tr>
<tr>
<td>1,4-disubstituted butane</td>
<td>p</td>
<td>p</td>
<td>b</td>
<td>p</td>
<td>p(^6)</td>
</tr>
<tr>
<td>2,3-disubstituted butane</td>
<td>p</td>
<td>p</td>
<td>b(^3)</td>
<td>p</td>
<td>p(^7)</td>
</tr>
</tbody>
</table>

1-bromo-2-cyanoethane  b\(^8\)
2-bromo ethyl alcohol   b\(^9\)
2-methoxy ethyl alcohol b\(^10\)
2-methoxy ethyl acetate p
ethylene glycol monoacetate b

Alternative names:
1, ethylene bromide; 2, ethylene glycol;
3, \(\gamma\)-butylene glycol; 4, valeronitrile;
5, succinonitrile; 6, adiponitrile;
7, 2,3-dimethyl succinonitrile; 8, \(\beta\)-bromopropionitrile;
9, ethylene bromohydrin; 10, methyl cellosolve.
For convenience, the following abbreviations are used for the different solute types:

n-butyl is abbreviated to Bu
1,2-disubstituted ethane is abbreviated to \((\text{CH}_2\text{CH}_2\text{)}_2\)
1,4-disubstituted butane is abbreviated to \((\text{CH}_2\text{CH}_2\text{)}_2\)
2,3-disubstituted butane is abbreviated to \((\text{CH}_3\text{CH}_2\text{)}_2\)

Preparation, Identity and Purity of Chemicals

One of the most useful features of GLC is the fact that the retention volume of a solute is independent of the impurities which might be injected with it (2, 10). Thus an impure solution of a particular chemical may be used for accurate studies of the thermodynamic constants at infinite dilution of that chemical in the chromatographic solvent, provided that the correct peak can be identified. For this reason none of the chemicals procured was purified in any way, unless ambiguity arose from the presence of an unidentified peak in the chromatogram.

In only one case did this problem arise. Ethylene glycol monoacetate, technical grade, was found to give two peaks of equal size. Fortunately the second peak was readily identified from its retention time as being ethylene glycol diacetate.

Production of the di-ester in the monoacetate is very difficult to prevent, and the two esters having very similar boiling points are extremely difficult to separate by distillation.
One important chemical which did give more than one peak, but
is not listed in the table, was n-heptane. On chromatography it was
found to give three peaks, presumably due to close boiling isomers
present in the original petroleum distillate. The hexane was also
seen to be contaminated, but in this case the accompanying peak was
very much smaller. Fortunately n-pentane, octane and decane each
gave only one peak, and the true n-heptane and hexane peaks were
identified from a plot of the log retention volume against carbon
number. Redistillation of the heptane increased the relative size
of the normal isomer peak.

2,3-Butanediol

All the 2,3 disubstituted butane derivatives, with the
exception of 2,3-dimethyl succinonitrile, were prepared from commercial
2,3-butanediol. The relative proportions of the diastereoisomers in
these samples therefore were determined by the original composition
of the butanediol. For these reasons some time has been spent
ascertaining the purity and chemical composition of this compound.
From a knowledge of the composition of the butanediol it is possible
to identify the diastereomeric peaks of the daughter compounds.

The following procedure was adopted to analyse the 2,3-butane-
diol:

Four samples of the diol obtained were chromatographed on
polyethylene glycol, the chromatographic solvent known to have the
best/...
best selectivity for alcohols. In each case two peaks were observed, but only in one case were they of equal size. In the other cases one large peak appeared accompanied by a much smaller peak. After distillation (b 180-20°C/750 mm), the latter samples were observed to crystallize after standing for some weeks.

Wilson and Lucas (14) have published the melting point curve for the meso-dl 2,3-butanediol system, and the melting point, 26°C of the crystals obtained here corresponds to a sample composition of 95% of the meso form.

This agrees with the measurement of the gas chromatographic peak areas. Since the diastereoisomers are compounds of almost identical nature, it seems likely that the response of the detector will be very similar for each of them, and hence the relative peak areas a measure of the relative amounts of each in the mixture. This assumption is justified by comparison of the percentage meso form in the various samples as deduced from chromatographic data and from the melting point:

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Meso from GC</th>
<th>M.P.</th>
<th>% Meso from M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>&lt;17°C</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>20-22°C</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>87</td>
<td>25-26°C</td>
<td>92</td>
</tr>
</tbody>
</table>

The first sample did not crystallise even on seeding at -17°C, and it was tentatively suggested that the large peak in the other samples be the meso isomer.

This /.....
This was finally confirmed by recrystallisation of the high melting samples from isopropanol to obtain crystals melting at \(30 - 32^\circ\text{C}\), (lit. m.p. pure meso form \(34^\circ\text{C}\)), and by the preparation of a mixture of the isomers by the reduction of dimethyl glyoxal. The product so obtained showed an absorption peak due to the hydroxyl band in the infra-red spectrum at \(3380\ \text{cm}^{-1}\), as did the other samples, and gave two peaks when chromatographed on PEG. These peaks corresponded exactly to those obtained from the "50%" sample of 2,3-butanediol. Since the dimethyl glyoxal was pure before starting, and since it has a retention time quite different from butanediol, it may be accepted that the two peaks observed in the commercial sample are indeed the diastereoisomers of 2,3-butanediol, and not due to some impurity.

The relative proportions of isomers in the butanediol now known, the amount of meso and dl forms in any compound prepared from the diol will also be known, providing that the mechanism of the preparation is understood.

**Preparation of chemicals**

1,4-Dibromobutane.

This was prepared from 1,4-butanediol, procured from British Drug Houses (BDH), and tested for purity by GLC. The preparation was that given by Vogel (15). The product boiling at \(107-8^\circ/47-49\text{mm}\) (lit. \(110^\circ/58\text{mm}\)), gave only one peak on chromatography/...
chromatography. The infra-red spectrum was free of peaks in the region of hydroxyl absorption (3500 - 3600 cm\(^{-1}\)). Analysis figures are:

<table>
<thead>
<tr>
<th></th>
<th>theoretical</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>22.2%</td>
<td>21.9%</td>
</tr>
<tr>
<td>H</td>
<td>3.73%</td>
<td>3.60%</td>
</tr>
<tr>
<td>Br</td>
<td>74.0%</td>
<td>73.6%</td>
</tr>
</tbody>
</table>

2,3-Dibromobutane.

A sample of this was bought from BDH, but was found to give only one peak. Two samples of 2,3-dibromobutane, 50% meso and 5% meso were then prepared from 50% meso and 95% meso 2,3-butanediol diacetate (preparation below), according to the method of Wilson and Lucas (14). Bromination of meso 2,3-butanediol diacetate gives rise only to dl-2,3-dibromobutane as these authors show.

1,4-Butanediol diacetate.

This was prepared from 1,4-butanediol and acetic acid. The reaction was conducted in benzene solution, catalysed by p-toluene sulphonic acid, the water being azeotropically removed. The product boiling at 126-8°/26mm (lit. 130°/40 mm) gave only one peak on chromatography, an infra-red spectrum with a peak at 1750 cm\(^{-1}\) (ester position), and no absorption in the hydroxyl region.

2,3-Butanediol diacetate.

This was prepared in a similar way from the different samples of 2,3-butanediol. Since acetylation does not involve inversion at the /...
the asymmetric carbons, a knowledge of the composition of the diol samples allows identification of the acetate peaks. The diester distilled at 93-4°/23mm (lit. 100°/25mm) and showed an infra-red peak at 1746 cm⁻¹, with no absorption in the hydroxyl region. The "50% meso" sample gave two peaks of equal size on chromatography and the "95% meso" sample only one. Saponification furnished further proof that the sample was pure 2,3-butanediol diacetate.

Methoxybutane.

Methoxybutane was prepared from n-butanol by treatment with sodium and methyl iodide (Williamson synthesis). The product boiling at 70-71°C (lit. 70°C) was distilled over sodium and was found to be pure by chromatography.

1,2-Dimethoxyethane.

This was prepared from methyl cellosolve by a Williamson synthesis in the same way. The product distilled over sodium boiled at 80-82°C (lit. 82-3°C) and was tested for purity by gas chromatography.

1,4-Dimethoxybutane.

This was prepared from 1,4 dibromobutane and sodium methoxide, after direct synthesis from 1,4-butanediol had been found to be cumbersome and lengthy due to incomplete methylation of the diol. The product distilled over sodium at 130-132°C (lit. 132-3°) and on chromatography gave only one peak.

2,3-dimethoxy butane/...
2,3-Dimethoxybutane.

Some difficulty was experienced in the preparation of this compound due to the instability of the sodium salt of 2,3-butanediol. At temperatures above 90°, the solution of sodium in the glycol darkened appreciably, and after treatment with methyl iodide gave products which distilled over a wide range of temperatures, giving multiple peaks on chromatography. The pure diether was finally prepared from a dilute solution of the sodium salt of butanediol in butanediol at a temperature below 80°C. The monomethylether, the product of the first treatment with sodium and methyl iodide, was separated by repeated distillation until a constant boiling liquid was obtained (b. 41-46°/22mm; lit. 40°/20mm) and was then dissolved in anhydrous ether and treated with sodium and methyl iodide. The final product after two distillations boiled at 110°C (lit. 108-111°C), distilled over sodium, and gave only one peak on chromatography. 50% Meso and 75% meso samples were prepared but each sample showed only one peak.

n-Butyl cyanide.

This was prepared from n-butyl bromide and sodium cyanide according to the method outlined in Vogel (15 p.408). The product boiling at 140-1°C (lit. 141°C) showed only one peak on chromatography.

1,2-Dicyanoethane.

1,2-Dicyanoethane was prepared in a similar way from ethylene dibromide. The waxy, deliquescent crystals obtained melted at /....
at 45 - 50°C (lit. 57°C). The infra-red spectrum showed a strong band in the nitrile position (2250 cm⁻¹), and the sample gave a single peak on chromatography. The sample was analysed for C, H and N.

Theoretical  C 60.0%  H 5.0%  N 35.0%

found         C 60.0%  H 5.0%  N 34.2%

1,4-Dicyanobutane.

This was prepared from 1,4-dibromobutane and sodium cyanide. The product boiled at 180-2°/30 mm (lit. 180-2°/20 mm). On chromatographing the nitrile, a tiny leading peak was observed in addition to the main peak. This was identified by comparison of retention times as 1,4 dibromobutane. The cyanide showed infra-red absorption at 2260 cm⁻¹.

2,3-Dicyanobutane.

This compound was prepared according to the method of Beech and Piggott (16). The product boiled at 120-137°/17 mm (lit. 120-135°/15 mm) forming white crystals in the condenser. These melted at 43 - 44°C (lit. 44 - 45°C). The infra-red spectrum showed a peak in the nitrile position at 2280 cm⁻¹.

Linstead and Whalley (17) describe the separation of the racemic isomer by crystallisation from light petroleum-ethanol.

The/...
The diastereomer so obtained should melt at $58^\circ\text{C}$. A number of carefully controlled crystallisations were performed from these solvents, but in all cases crystals melting between 40 and $42^\circ\text{C}$ were obtained. On chromatography two peaks well separated and of equal size appeared. This indicates that the crystals are 50% meso and 50% racemic, and since they could not be resolved by crystallisation, it is assumed that the later peak is of the high melting racemic isomer.

2-Methoxy ethyl acetate.

This was prepared from methyl cellosolve and acetic anhydride, the reaction being catalysed by conc. sulphuric acid. The product was distilled twice b.140-142^\circ\text{(lit.143^\circ)}$ and tested for purity by GLC.

Amines.

It was intended to study the gas chromatographic behaviour of some amines, and the diastereomeric pair of 2,3 diaminobutanes were prepared by hydrogenation of dimethyl glyoxime. The diastereomers were resolved by crystallisation of the dihydrochlorides, and obtained free by treatment with sodium hydroxide. It was, however, not possible to elute the free amines from any of the gas chromatographic columns. Even low boiling n-butylamine could be eluted only with difficulty, producing peaks with severe tailing. For this reason the study of amine behaviour was abandoned.
SECTION 2.5

PHYSICAL PROPERTIES OF THE SOLUTES

The boiling points, vapour pressures at 130°C (and 100°C in the case of bromides and acetates, molar volumes, dipole moments, refractive indices and "volume reduced boiling points" of the twenty five solutes studied are presented in Table 2.2. The molar volumes are calculated from the densities at 20°C relative to water at 4°C. The refractive indices, also at 20°C, are the values for the sodium-D line.

The "volume reduced boiling point", Δ*Tb, is the difference in boiling point between the solute in question and a hypothetical hydrocarbon of the same molar volume. The significance of such a quantity will be explained in the text below.

Table 2.2/....
<table>
<thead>
<tr>
<th>Solute</th>
<th>$T_b$ °C</th>
<th>$P^0_{130^\circ}$ (mm)</th>
<th>$P^0_{100^\circ}$ (mm)</th>
<th>$\nu_4$ c.c. / mole</th>
<th>$n_0$</th>
<th>$\mu$</th>
<th>$\Delta^*T_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuBr</td>
<td>100</td>
<td>1626</td>
<td>745</td>
<td>107</td>
<td>1.4398</td>
<td>2.15</td>
<td>73</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{Br})_2$</td>
<td>132</td>
<td>727.8</td>
<td>296</td>
<td>86</td>
<td>1.5379</td>
<td></td>
<td>147</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{Br})_2$</td>
<td>198</td>
<td>103.3</td>
<td>33</td>
<td>119</td>
<td>1.5190</td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>Meso-$(\text{CH}_3\text{CHBr})_2$</td>
<td>157</td>
<td>368</td>
<td>134</td>
<td>121</td>
<td>1.5147</td>
<td></td>
<td>117</td>
</tr>
<tr>
<td>dl-$(\text{CH}_3\text{CHBr})_2$</td>
<td>160</td>
<td>347</td>
<td>123</td>
<td>122</td>
<td>1.5147</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>BuOAc</td>
<td>124</td>
<td>862.2</td>
<td>347</td>
<td>132</td>
<td>1.3943</td>
<td>1.84</td>
<td>52</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{OAc})_2$</td>
<td>187</td>
<td>107.2</td>
<td>24</td>
<td>132</td>
<td>1.415</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{OAc})_2$</td>
<td>230</td>
<td>39.8</td>
<td>5.9</td>
<td>166</td>
<td>1.4229</td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>Meso-$(\text{CH}_3\text{CHOAc})_2$</td>
<td>190</td>
<td>90</td>
<td>26</td>
<td>170</td>
<td>1.4134</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>dl-$(\text{CH}_3\text{CHOAc})_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BuOH</td>
<td>117</td>
<td>1154</td>
<td>102</td>
<td>1.3993</td>
<td>1.63</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{OH})_2$</td>
<td>197</td>
<td>61.8</td>
<td>64</td>
<td>1.4318</td>
<td></td>
<td>229</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{OH})_2$</td>
<td>235</td>
<td>16</td>
<td>104</td>
<td>1.4467</td>
<td></td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>Meso-$(\text{CH}_3\text{CHOH})_2$</td>
<td>182</td>
<td>117.5</td>
<td></td>
<td>107</td>
<td>1.4308</td>
<td></td>
<td>155</td>
</tr>
<tr>
<td>dl-$(\text{CH}_3\text{CHOH})_2$</td>
<td>181</td>
<td>113</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2 continued /.../
### Table 2.2 continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>( T_b ) (^{\circ} \text{C} )</th>
<th>( P_{130}^{\circ} \text{O} ) (mm)</th>
<th>( P_{100}^{\circ} \text{O} ) (mm)</th>
<th>( V_{40}^{20} ) c. s. / mole</th>
<th>( r_{D}^{20} )</th>
<th>( \mu )</th>
<th>( \Delta_{b-T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuOCH(_3)</td>
<td>71</td>
<td>4000</td>
<td></td>
<td>118</td>
<td>1.374</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>((\text{CH}_2\text{OCH}_3)_2)</td>
<td>82</td>
<td>1780</td>
<td></td>
<td>96</td>
<td>1.3722</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_2\text{CH}_2\text{OCH}_3)_2)</td>
<td>130</td>
<td>760</td>
<td></td>
<td>136</td>
<td>1.4031 (^4)</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Meso-(\text{CH}_3\text{CHOCH}_3)_2</td>
<td>108</td>
<td></td>
<td>1073</td>
<td>139</td>
<td>1.3935</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>dl-(\text{CH}_3\text{CHOCH}_3)_2</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>BuCN</td>
<td>141</td>
<td>545</td>
<td></td>
<td>104</td>
<td>1.3949</td>
<td>4.09</td>
<td>119</td>
</tr>
<tr>
<td>((\text{CH}_2\text{CN})_2)</td>
<td>266</td>
<td>5.62</td>
<td></td>
<td>81(^1) \</td>
<td>1.4173</td>
<td>(^1)</td>
<td>284</td>
</tr>
<tr>
<td>((\text{CH}_2\text{CH}_2\text{CN})_2)</td>
<td>295</td>
<td>4.40</td>
<td></td>
<td>111</td>
<td>1.4597</td>
<td></td>
<td>261</td>
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<tr>
<td>Meso-(\text{CH}_3\text{CHCN})_2</td>
<td>265</td>
<td></td>
<td>15</td>
<td>113(^2) \</td>
<td></td>
<td>-</td>
<td>229</td>
</tr>
<tr>
<td>dl-(\text{CH}_3\text{CHCN})_2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>BrCH(_2)\text{CH}_2\text{CN}</td>
<td>180</td>
<td>135</td>
<td></td>
<td>81</td>
<td>1.4750</td>
<td></td>
<td>198</td>
</tr>
<tr>
<td>BrCH(_2)\text{CH}_2\text{OH}</td>
<td>149</td>
<td>389</td>
<td></td>
<td>71</td>
<td>1.4969</td>
<td></td>
<td>185</td>
</tr>
<tr>
<td>\text{CH}_3\text{OCH}_2\text{OH}</td>
<td>124</td>
<td>910</td>
<td></td>
<td>79</td>
<td>1.4024</td>
<td></td>
<td>144</td>
</tr>
<tr>
<td>\text{CH}_3\text{OCH}_2\text{OAc}</td>
<td>143</td>
<td>511</td>
<td></td>
<td>118</td>
<td></td>
<td>-</td>
<td>97</td>
</tr>
<tr>
<td>\text{HOCH}_2\text{CH}_2\text{OAc}</td>
<td>188</td>
<td>100</td>
<td></td>
<td>94</td>
<td></td>
<td>-</td>
<td>184</td>
</tr>
</tbody>
</table>

1 at 60\(^\circ\)C
2 estimated; see below
3 at 25\(^\circ\)C
4 at 15\(^\circ\)C

Origin/....
Origin of the data in Table 2.2

All the data tabulated above, with the exception of the density of \((\text{CH}_3\text{CHCN})_2\), were obtained from the literature, usually from Chemical Abstracts or from Beilstein. Because of the large amount of literature covered, only the most important references are quoted.

Vapour pressures

The vapour pressures at 130°C and 100°C are given in millimeters of mercury in the table. Those which are underlined have been derived either from an Antoine equation or from accurate data of vapour pressures at a range of temperatures. The remainder were either determined from boiling point data at reduced pressures from various sources, or by other methods.

Estimation of the vapour pressure at 130°C from boiling point data is obtained by extrapolation of the linear plot of the logarithms of \(P\) against \(1/T\), where \(T\) is the boiling point of the solute, in degrees Kelvin, at pressure \(P\). When insufficient data could be found in the literature to make such a plot, other methods of estimation had to be used. Fortunately, such cases were few. The vapour pressures of 1,4-dimethoxybutane and methoxybutane were estimated using the Trouton constant of 1,2-dimethoxyethane. This constant gives the slope of the log \(P\) versus \(1/T\) plot from which, knowing the boiling point, the vapour pressure at another temperature can be determined.

The
The vapour pressure of 2-methoxy ethyl acetate was determined from the evaporation rate (23). A relationship between the evaporation rate and the vapour pressure at 20°C is given in the abstract quoted. Using the boiling point, the logarithms of pressure may be plotted against the reciprocal of temperature, and the vapour pressure at 130°C estimated.

The sources of the vapour pressure data used for the different solutes are given in Table 2.3 below.

**TABLE 2.3**

**Origins of vapour pressure data**

1. | Antoine equation | Source | Solutes |
   | | | |
   | | Othmer (18) | BuBr, (CH₂Br)₂, (CH₂CH₂Br)₂, (CH₂OAc)₂, BuOH, (CH₂OH)₂ |
   | | Woodman (19) | (CH₂CN)₂, (CH₂CH₂CN)₂ |
   | | Schiopu (20) | BuOAc |
   | | Piek (21) | CH₃·O·CH₂CH₂·OH |
   | | Jordan (22) | (CH₃CHBr), (CH₃CHOH)₂, (CH₂OCH₃)₂, BuCN |

2. | From boiling points in the literature |
   | | |
   | | (CH₂CH₂OH)₂, (CH₂CH₂OAc)₂, (CH₂CHOAc)₂, (CH₂CHCN)₂, Br CH₂CH₂CN |
   | | HO CH₂CH₂OAc, Br CH₂ CH₂ OH, (CH₂CH₂OCH₃)₂ |

From/...
3. From Trouton constants

$$\text{BuOCH}_3, (\text{CH}_3\text{CHOCH}_3)_2$$

4. From evaporation rate

$$\text{CH}_2\text{O CH}_2\text{ CH}_2\text{ OAc}$$

The vapour pressures determined via the Trouton constants cannot be expected to be very accurate, but fortunately this is not of great significance since the vapour pressures are required for only a small section of the work, in the verification of one equation, and it is felt that the values so obtained are acceptable.

Densities

With the exception of the alcohols, molar volumes have been obtained by dividing the molecular weight of the compound by the density. For convenience, the density at 20°C relative to water at 4°C has been used in all cases but succinonitrile. The density at 60°C is given for this compound which is solid at 20°C.

Molar volumes cannot be estimated from densities in the case of alcohols since high association in the liquid state gives alcohols abnormally high densities. The increment in molar volume with carbon number in an homologous series is 17, and the molar volumes of the alcohols have been estimated by subtracting a value of 17 from the related methyl ether where the alcoholic hydrogen is replaced by a methyl group.
Density values, where used, have been obtained from the literature.

In some cases, more than one value for the density appears. In these cases the choice of a particular value has not been arbitrary, but has been determined by the nature of the paper concerned, the accuracy to which the density was given, and from a knowledge of the purity of the material handled.

The density of 2,3-dimethyl succinonitrile was not available, but it was observed that in all the other cases the molar volumes of the 2,3 disubstituted butanes are two or three units larger than the isomeric 1,4 disubstituted butanes. From the molar volume of 1,4-dicyanobutane, therefore, which is 111, the approximate volume of the 2,3-dicyanobutane isomers is estimated as being 113.

**Dipole moments**

The dipole moments of the n-butyl derivatives have been tabulated above. These are all taken from Smith's "Electric Dipole Moments"(24).

**Refractive indices**

These have been obtained, as were the densities, from the literature. In all cases, except those indicated, the refractive index at 20°C using the sodium-D line, is given. The same criteria as were used to govern the choice of density were used to choose the best value of refractive index when there was ambiguity in the literature.

Section /....
SECTION 3

THE BEHAVIOUR OF GAS CHROMATOGRAPHIC STATIONARY LIQUIDS

The retention time of any compound, and hence the separation achieved between any two compounds in a gas chromatograph is determined by the stationary liquid in the column. The choice of column liquid for a particular separation must therefore be based on a knowledge of the way in which different liquids retain particular solutes. To this end a number of methods have been presented of "classifying" gas chromatographic liquids, and a review on this subject will now be given.

3.1 REVIEW: THE CLASSIFICATION OF STATIONARY LIQUIDS

From the point of view of gas chromatography, any pair of volatile compounds may be placed into one of four categories.

These are:

(1) Solutes of different vapour pressures and different chemical character.

(2) Solutes of different vapour pressures but similar chemical character.

(3) Solutes of the same vapour pressure and different chemical character.

(4) Solutes /...
(4) Solutes of the same vapour pressure and the same chemical character.

Gas chromatographic solvents are classified according to the way they separate different solutes. Solutes in classes (1) and (2) present no difficulty for resolution because retentions are always determined primarily by the vapour pressure of the solute, and separations due to differences in chemical character are only a modifying effect. It is in the separation of solutes in classes (3) and (4) that the classification of liquids becomes of importance since an understanding of the way in which a particular column liquid retains a particular solute can lead to a choice of the best possible column.

The classification is generally approached from one of two points of view.

Either a study is made of the way in which solutes of different chemical type and different vapour pressure are separated, and the separation is directly related to their molecular characteristics, or the vapour pressures of the solutes are eliminated from equation 1.6, and a more fundamental understanding of the forces operating is sought by considering these hypothetical solutes of the same vapour pressure. The first method is termed 'classification according to retention volume' and the second, 'classification according to activity coefficients'.

1. Classification/...
1. Classification according to retention volume

The first classification of GC solvents to be presented was that of Rohrschneider, and in some modified form the graphical procedure which he used has been employed by a number of authors subsequently.

Rohrschneider (25) compared a number of liquids on the basis of one parameter "polarity". By assuming that a more polar liquid will have greater retention for a polarisable solute than for a solute which is not polarisable, he assigned values of polarity to the different liquids on the basis of the separation of polarisable butadiene and non-polarisable normal butane on the different liquids. Squalane was arbitrarily given a polarity of 0, and the solvent β,β’-oxydipropionitrile, which produced the largest relative retention of butadiene, was given a polarity of 100. The logarithms of the relative retentions on these liquids were then plotted on the ordinate of the diagram as shown in figure 1. The log r values on squalane and oxydipropionitrile were then connected by straight lines, and all other liquids were positioned between 0 and 100 according to their relative retention of butadiene to n-butane. It was found that the liquids kept the same position whatever hydrocarbon retentions ratio was used. This classification facilitates the choice of a stationary phase for the separation of hydrocarbons.

Figure 1 /.....
More recently Chovin (26, 27) has used a similar approach to classify stationary liquids. A polar liquid, which in Rohrschneider's treatment is defined as a liquid which gives the greatest separation of a polarisable and a non-polarisable solute, has the additional property of producing a small relative retention of consecutive members of an homologous series. A non-polar liquid, on the other hand, provides a greater separation of homologues. Chovin uses this phenomenon to define polarity. Polarity, $P$, is defined as being proportional to the negative slope of the plot of the logarithm of $V_g$ against carbon number in an homologous series

$$\log r_{z+1,z} = n-mP$$

Where/...
where \( z \) and \( z + 1 \) are consecutive members of the series and \( n \) and \( m \) are constants.

This slope is constant for all homologous series, and depends only on the stationary liquid.

Littlewood (28) has published the most comprehensive treatment to date on the comparison of gas chromatographic solvents. This author points out that in systems with the complexity of interaction found in GLC columns, a comparison of all columns on the basis of one parameter, such as 'polarity' is bound to be inadequate. In point of fact, the term 'polarity' is misleading, for the polarity value given to a liquid by Rohrschneider's treatment has little, if any, relationship to its dipole moment or dielectric constant (see 10). It is felt here that a better term for the column behaviour described by Rohrschneider and Chovin would be 'alkane affinity'. The more 'polar' a liquid, the lower the alkane affinity.

Littlewood discusses the merits of classification methods such as those of Rohrschneider and Chovin, and presents a new method of comparison. Once again squalane is arbitrarily assigned value of zero, and other liquids are classified according to the specific retentions of normal hexane. He shows that by this method the retentions of various hydrocarbons on particular liquids can be predicted from knowledge of the retentions of \( n \)-hexane. Such methods cannot, however, be used for predicting the retentions of \( / \ldots \).
of polar compounds. The only possibility of predicting the behaviour of polar solutes on different columns is to classify the columns according to the behaviour of the individual types on these columns. This he does, showing that the retentions of alcohols and halides can be predicted when the columns are classified according to the specific retention of n-propyl acetate, or n-propyl bromide respectively. He concludes that every stationary liquid requires several parameters to predict the way in which it will retain any particular solute. The classification according to the retention of n-hexane is of the most general application, however, and gives a good idea of the way in which a liquid will retain different hydrocarbons.

By giving, as Littlewood does, a value of zero to squalane, the comparison of the retention of a solute on two liquids is in fact virtually a comparison of the activity coefficient ratio of this solute in the two liquids. On squalane

\[ V_{g(s)} = \frac{RT}{\gamma^o_{P} M_s} \]

where \( M_s \) is the molecular weight of squalane, \( \gamma^o_s \) the activity coefficient at infinite dilution of the solute in squalane and \( P^o \) is as before the vapour pressure of the pure solute at that temperature, while on the polar liquid,

\[ V_{g(P)} = \frac{RT}{\gamma^o_{P} M_P} \]

Then/****
Then
\[ \frac{V_g(P)}{V_g(s)} = \frac{\gamma_{g,s}^0}{\gamma_{P,P}^0} \] 3.2

By classifying liquids relative to squalane, a value is given to the liquid which is the activity coefficient ratio of the reference solute in those liquids modified by the molecular weight ratio of the liquids.

2. **Classification according to activity coefficient**

A number of authors have attempted to predict activity coefficients theoretically from molecular parameters in order to enable to calculate retention times by using equation 1.6. Pierotti and others (29, 30) have developed an empirical equation for the activity coefficient in a non-ideal hydrocarbon system, and have correlated \( \gamma^0 \) for a wide range of solutes and solvents. Their treatment, which is summarised in most of the standard texts (see for example (2) p.25 ff) is useful for the prediction of the behaviour of non-polar gas chromatographic solutes on non-polar solvents. McNair (31) attempted to correlate Hildebrand's solubility parameter and retention volume, but found such a correlation to be limited to a system of non-polar solutes and solvents. The only theoretical approach which has been extended to polar compounds, is that of Martire (32). This author derived an expression relating activity coefficient and molecular /...
molecular structure via the Hildebrand – Scatchard treatment of solubility. From a knowledge of the physical constants of liquid and vapour, he demonstrates a method for choosing the best solvent for a particular separation. While he illustrates the validity of his equation convincingly, its application is difficult. A detailed knowledge of the physical constants of the components must be known before the calculation can be carried out. Moreover, the calculation is itself a lengthy procedure.

For obvious reasons, the fundamental approaches have never proved popular. In practice it is far easier to try one or two likely columns than to solve complicated equations which require detailed information about the components, and which are often of doubtful value.

An activity coefficient classification must, it is decided, be empirical to be useful.

Tenney (33) and Bayer (34) have independently presented a method of comparison which, if developed, could lead to a general classification by activity coefficient.

A plot of the logarithm of \( V_g \) against boiling point is linear for an homologous series (see p.10). The slope of this plot is constant for all series on one particular liquid. Bayer compares the behaviour of various solute types on different solvents by taking the relative retention of hypothetical members of different homologous series/...
series which have a constant boiling point. Such ratios at different temperatures are almost constant, since the lines are parallel. This ratio between two compounds is very nearly equal to the activity coefficient ratio of these compounds in the solvent, which will be a measure of the way in which the functional groups of the series interact with the liquid. In a later paper (35), Bayer incorrectly equates this ratio with the activity coefficient ratio. In fact this is not so, unless the heats of vaporisation of the solutes are the same, as the following treatment shows.

From equation 1.6
\[
r_{12} = \frac{\gamma_{2}^{o}P_{2}^{o}}{\gamma_{1}^{o}P_{1}^{o}}
\]
and for each of the components at temperature \(T\),
\[
\ln \frac{P_{2}^{o}}{760} = \frac{\Delta H_{2}^{V}}{R} \left( \frac{1}{T_{b_{2}}} - \frac{1}{T} \right)
\]
and
\[
\ln \frac{P_{1}^{o}}{760} = \frac{\Delta H_{1}^{V}}{R} \left( \frac{1}{T_{b_{1}}} - \frac{1}{T} \right)
\]

Now the criterion is that the solutes have equal boiling points
\[
T_{b_{2}} = T_{b_{1}}
\]
\[
\therefore \ln \frac{P_{2}^{o}/P_{1}^{o}}{760} = \frac{1}{RT} (\Delta H_{1}^{V} - \Delta H_{2}^{V})
\]
The relative retention of these compounds will be equal to the activity coefficient ratio only if the vapour pressure ratio is unity. This occurs only if the temperature \(T\) is close to the common boiling point.
It is seen from the discussion that classification according to activity coefficient is merely a special case of classification according to retention volume. It is the case when two solutes have similar vapour pressures. It is felt that the special case must be inferior to any general treatment which will enable direct prediction of the retention times directly and not via its activity coefficient.

3.2 The prediction of retention times

Littlewood criticises Rohrschneider's concept of polarity and his conclusion is that no ubiquitous classification can ever be made. The best that can be hoped for is to compare the behaviour of solutes of similar chemical type.

In this thesis his thoughts are taken a step further. Gas chromatographic solvents are not classified according to any general characteristics, but the retention behaviour of particular groups on the liquid are compared. From a knowledge of the way in which a particular functional group is retained on the liquid the retention of other molecules containing the same functional group can be predicted. The older idea of trying to predict how one type of compound will be retained, from a knowledge of the retention of another type of compound, is abandoned. To enable the prediction of retention times of new compounds, some characteristics of the retentions of the particular functional groups in the chromatographic...
chromatographic liquid had to be found. The problem of finding some characteristics of functional groups, and hence predicting the retentions of new compounds which contain those functional groups has been approached on a number of previous occasions. Borer (36) investigated the increment made to the retention volume of aromatic hydrocarbons on the addition of functional groups to the nucleus, but found no general trend to emerge. Clayton (37) however, showed that by direct multiplication of 'Group Retention Factors', with the retention time of the hydrocarbon skeleton, the retention times of substituted steroids may be estimated. Later this technique was employed by Knights and Thomas (38, 39) with success. Kovats, in an approach which is discussed in detail below, has used the difference in a function called the Retention Index on a polar and a non-polar phase to predict the retentions of polyfunctional compounds.

Evans and Smith (40) point out that direct predictions (such as Clayton's) are limited to a few favourable cases, and these authors propose a method for the estimation of the retentions of large numbers of different compounds from a knowledge of the retention times of structurally related molecules. To estimate the retention of a structurally complex solute, Evans and Smith require to know only the retentions of two different molecules each of which contains components of the original solute molecules.

The /...
The relationship

$$\log R_{12} = \frac{1}{2} (\log R_{11} + \log R_{22})$$

is used,

where $R_{12}$, $R_{11}$ and $R_{22}$ are the retention times of solutes $R - X - R^1$, $R-X-R$ and $R^1-X-R^1$ respectively.

They state that agreement between observed and calculated values may be expected to be good provided that

1. there is no conjugation across $X$,
2. none of the molecules is structurally hindered,
3. neither $R$ nor $R^1$ is strongly polar,
4. the bonds linking $R$ and $X$, and $R^1$ and $X$ are symmetrical in polar character, or that these bonds are separated by a number of non-conjugated atoms in group $X$
5. the retention times of the two symmetrical compounds can be measured accurately.

Kovat's Retention Index, $I$, is defined (41) by

$$I = 200 \left( \frac{\log R_{12}}{\log R_{Z + 2}} \right) + 100Z$$

where $Z$ and $Z + 2$ are normal hydrocarbons of carbon number $Z$ and $Z + 2$ respectively. By making use of the difference in retention index on a polar and a non-polar solvent, Kovats (42) developed an intricate method of predicting retentions.
The retention index has gained general acceptance in gas chromatography as a method of presentation of retention data, since it is a retention function related to two standards.

Kovats method, requiring as it does retention data on two columns will not be discussed here. It is more desirable to be able to predict the retentions of compounds from a knowledge of the behaviour of their functional groups on only one column.

In this chapter a method of doing this is developed which uses lines of thought similar to those of Clayton.

It will be remembered from equation 1.17 that the logarithm of the relative retention of two solutes can be expressed in terms of the difference of their heats of evaporation from solution:

\[ \ln r_{12} = \frac{1}{RT} (\Delta H^S_{E(1)} - \Delta H^S_{E(2)}) \] .................... 1.17

In terms of this equation, the linear increase in the logarithm of retention time with carbon number in an homologous series can be described as being produced by the linear increase of \( \Delta H^S_{E(1)} \) with chain length, where 1 is an homologue member, and 2 a constant reference solute.

A prediction can be made of the retention times of polyfunctional compounds if it is found that each functional group makes a specific contribution to the retention. The contribution made by the functional group can be found by eliminating the part/...
part played by the carbon chain in the retention of an homologous series.

If we consider the heat of evaporation from solution as the sum of a polar and an apolar contribution:

\[ \Delta H^S_E(1) = \Delta H^S_E(1)(P) + \Delta H^S_E(1)(A) \]

and then if the reference solute is a non-polar hydrocarbon,

\[ \Delta H^S_E(2) = \Delta H^S_E(2)(A) \]

then the polar contribution of 1 to the retention is obtained by choosing 2 such that

\[ \Delta H^S_E(1)(A) = \Delta H^S_E(2)(A) \]

If we call the reference solute so chosen, *, equation 1.17 becomes

\[ \ln r_{1*} = \frac{\Delta H^S_E(1)(P)}{RT} \]

A prediction of the retentions of polyfunctional compounds will be based upon the assumption that interaction with the stationary phase is proportional to the number of functional groups. Or, since the energy of interaction determines the heat of evaporation from solution,

\[ \Delta H^S_E(\text{polyfunctional})(P) = n \Delta H^S_E(\text{monofunctional})(P) \]

where \( n \) is the number of functional groups.

By/...
By eliminating $\Delta H_E^S(A)$ from the retentions of members of an homologous series, a constant will be obtained for that series. Different constants for homologous series have already been found by a number of authors. Evans and Smith (43) proposed the "Effective Molecular Weight", while Littlewood (1, p.103) has shown that retentions taken relative to a constant homologue number are constant in a series. But it is obvious that the apolar contribution to the retention has not been eliminated by either of these methods, since the constants for monofunctional compounds are not simply related to the retentions of polyfunctional compounds.

3.3 The volume reduced retention time

In this thesis a new series constant with this property has been sought. Molar volume is known to be an important parameter determining vapour pressure and other physical constants and it was considered that by eliminating the relative volumes of members of an homologous series, the part played by the carbon chain, that which has been called the "apolar contribution", might be eliminated.

The way of doing this appeared to be by taking retentions of different solutes relative not to any particular hydrocarbon, but to a hypothetical hydrocarbon of the same size as the solute molecule. This is readily accomplished since both the logarithmic retention volume, and molecular volume are linearly related to carbon number, and the retention of any solute relative to a hypothetical hydrocarbon
of the same size as that solute can be determined by reading the retention of such a hydrocarbon off a plot of the logarithmic retention volumes of hydrocarbons against their molecular volumes. From the data of Littlewood (44) such a plot was made of the logarithmic retentions of the normal alkanes against the molar volumes.

This is illustrated in Figure 2.

FIGURE 2

![Graph](image)

Retention volumes of homologue members were taken from this same paper to ascertain whether such a ratio is constant in a series. The results are presented in Table 3.1. The retentions are given at 80°C, on two liquids: squalane (SQ) and polyethylene glycol 400 (PEG 400) for homologous series of bromides, formates and alcohols. These ratios are for convenience called the "Volume Reduced Retentions".

Table 3.1/...
### TABLE 3.1

Volume reduced retentions of some homologous series

<table>
<thead>
<tr>
<th>Solute</th>
<th>$v_4$ (c.c./mole)</th>
<th>SQ.</th>
<th>FEG 400</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtBr</td>
<td>75.5</td>
<td>1.01</td>
<td>1.67</td>
</tr>
<tr>
<td>PrBr</td>
<td>91.5</td>
<td>0.99</td>
<td>1.61</td>
</tr>
<tr>
<td>BuBr</td>
<td>107.5</td>
<td>0.97</td>
<td>1.57</td>
</tr>
<tr>
<td>MeOOCH</td>
<td>63.2</td>
<td>0.73</td>
<td>1.92</td>
</tr>
<tr>
<td>EtOOCH</td>
<td>80.2</td>
<td>0.68</td>
<td>1.77</td>
</tr>
<tr>
<td>PrOOCH</td>
<td>97.5</td>
<td>0.68</td>
<td>1.72</td>
</tr>
<tr>
<td>BuOOCH</td>
<td>114.5</td>
<td>0.66</td>
<td>1.66</td>
</tr>
<tr>
<td>MeOH</td>
<td>46</td>
<td>0.88</td>
<td>2.74</td>
</tr>
<tr>
<td>EtOH</td>
<td>63</td>
<td>0.77</td>
<td>2.48</td>
</tr>
<tr>
<td>PrOH</td>
<td>80</td>
<td>0.80</td>
<td>2.45</td>
</tr>
<tr>
<td>BuOH</td>
<td>97</td>
<td>0.77</td>
<td>2.46</td>
</tr>
<tr>
<td>AmOH</td>
<td>117</td>
<td>0.74</td>
<td>2.39</td>
</tr>
</tbody>
</table>

The molar volumes of the bromides and formates have been calculated as before from the densities of the compounds and those of the alcohols by subtracting 17 from the volumes of the related methyl ethers. With due allowance for error introduced in the estimation, the volume reduced retention may be accepted as a constant in a series after the first two members. In fact this is not unexpected since molar volume and carbon number are linearly related...
related, and since Littlewood (1, p.163) has shown that retentions relative to a constant homologue are constant in a series. Whether the volume reduced retention does give a better measure of the contribution made by the polar factor to the retention can only be ascertained by considering the retentions of bifunctional compounds.
RESULTS

4.1 Retentions of hydrocarbons

In Table 4.1 the molar volumes and retentions relative to n-heptane \( r_7 \) of the five hydrocarbons used in this study are presented on the four stationary liquids. These retentions were of course obtained when determining the dead volume of the apparatus.

In addition, since they were not included in Table 2.2 with the other solutes, the vapour pressures of the hydrocarbons at 100\(^\circ\)C and 130\(^\circ\)C are tabulated.

### TABLE 4.1

Retentions of hydrocarbons relative to heptane

<table>
<thead>
<tr>
<th>Solute</th>
<th>( v_4 ) c.c./mole</th>
<th>( r_7 )</th>
<th>( \log r_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
<td>TCP</td>
</tr>
<tr>
<td>n-C(<em>5)H(</em>{12})</td>
<td>114</td>
<td>0.276</td>
<td>0.294</td>
</tr>
<tr>
<td>n-C(<em>6)H(</em>{14})</td>
<td>130</td>
<td>0.530</td>
<td>0.544</td>
</tr>
<tr>
<td>n-C(<em>7)H(</em>{16})</td>
<td>146</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>n-C(<em>8)H(</em>{18})</td>
<td>162</td>
<td>1.87</td>
<td>1.83</td>
</tr>
<tr>
<td>n-C(<em>{10})H(</em>{22})</td>
<td>195</td>
<td>6.59</td>
<td>6.24</td>
</tr>
</tbody>
</table>

The /.../
Graph 1

The Retentions of Hydrocarbons

Legend

I. Squalane
II. Dinonyl Phthalate
III. Tricresyl Phosphate
IV. Polystyrene Glycol

Log $r_7$

<table>
<thead>
<tr>
<th>$r_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
</tr>
<tr>
<td>1.00</td>
</tr>
<tr>
<td>0.50</td>
</tr>
<tr>
<td>0.00</td>
</tr>
<tr>
<td>0.50</td>
</tr>
<tr>
<td>1.00</td>
</tr>
<tr>
<td>1.50</td>
</tr>
</tbody>
</table>

$\text{Molecular Volume}$

$\text{nC}_5\text{H}_{12}$ $\text{nC}_6\text{H}_{14}$ $\text{nC}_8\text{H}_{16}$ $\text{nC}_{10}\text{H}_{22}$
### TABLE 4.2

<table>
<thead>
<tr>
<th></th>
<th>log $r_x$</th>
<th>log $r_x^*$</th>
<th>log $r_x^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
<td>TCP</td>
</tr>
<tr>
<td>BuBr</td>
<td>0.065</td>
<td>0.270</td>
<td>0.448</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{Br})_2$</td>
<td>0.351</td>
<td>0.613</td>
<td>0.900</td>
</tr>
<tr>
<td>$(\text{CH}<em>2\text{CH}</em>{2}\text{Br})_2$</td>
<td>1.092</td>
<td>1.374</td>
<td>1.682</td>
</tr>
<tr>
<td>Meso-$(\text{CH}_2\text{CHBr})_2$</td>
<td>0.688</td>
<td>0.894</td>
<td>1.124</td>
</tr>
</tbody>
</table>

### TABLE 4.3

<table>
<thead>
<tr>
<th></th>
<th>log $r_x$</th>
<th>log $r_x^*$</th>
<th>log $r_x^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
<td>TCP</td>
</tr>
<tr>
<td>BuOAc</td>
<td>0.226</td>
<td>0.436</td>
<td>0.650</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{OAc})_2$</td>
<td>0.663</td>
<td>1.069</td>
<td>1.456</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{OAc})_2$</td>
<td>1.312</td>
<td>1.665</td>
<td>2.026</td>
</tr>
<tr>
<td>Meso-$(\text{CH}_2\text{CHOAc})_2$</td>
<td>0.847</td>
<td>1.137</td>
<td>1.446</td>
</tr>
</tbody>
</table>

Table 4.4/...
### TABLE 4.4

<table>
<thead>
<tr>
<th></th>
<th>log $r_x$</th>
<th>log $r_{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
</tr>
<tr>
<td>BuOH</td>
<td>-0.108</td>
<td>0.192</td>
</tr>
<tr>
<td>(CH$_2$OH)$_2$</td>
<td>0.322</td>
<td>0.600</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OH)$_2$</td>
<td>0.955</td>
<td>1.336</td>
</tr>
<tr>
<td>Meso-(CH$_2$CHOH)$_2$</td>
<td>0.448</td>
<td>0.818</td>
</tr>
</tbody>
</table>

### TABLE 4.5

<table>
<thead>
<tr>
<th></th>
<th>log $r_x$</th>
<th>log $r_{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
</tr>
<tr>
<td>BuOCH$_3$</td>
<td>-0.245</td>
<td>-0.156</td>
</tr>
<tr>
<td>(CH$_2$OCH$_3$)$_2$</td>
<td>-0.44</td>
<td>-0.24</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OCH$_3$)$_2$</td>
<td>0.351</td>
<td>0.558</td>
</tr>
<tr>
<td>Meso-(CH$_2$CHOCH$_3$)$_2$</td>
<td>0.094</td>
<td>0.282</td>
</tr>
</tbody>
</table>
### TABLE 4.6

<table>
<thead>
<tr>
<th></th>
<th>log $r_{x7}$</th>
<th>log $r_{*7}$</th>
<th>log $r_{x*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
<td>TCP</td>
</tr>
<tr>
<td>BuCN</td>
<td>0.162</td>
<td>0.626</td>
<td>0.916</td>
</tr>
<tr>
<td></td>
<td>SQ DNP TCP PEG</td>
<td>SQ DNP TCP PEG</td>
<td>SQ DNP TCP PEG</td>
</tr>
<tr>
<td></td>
<td>0.93 1.35 1.60 1.68</td>
<td>2.15 2.93 3.43 3.99</td>
<td></td>
</tr>
<tr>
<td>(CH$_2$CN)$_2$</td>
<td>1.005</td>
<td>1.816</td>
<td>2.394</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$CN)$_2$</td>
<td>1.458</td>
<td>2.240</td>
<td>2.80</td>
</tr>
<tr>
<td>Meso-(CH$_2$CHCN)$_2$</td>
<td>0.816</td>
<td>1.488</td>
<td>1.892</td>
</tr>
</tbody>
</table>

### TABLE 4.7

<table>
<thead>
<tr>
<th></th>
<th>log $r_{x7}$</th>
<th>log $r_{*7}$</th>
<th>log $r_{x*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SQ</td>
<td>DNP</td>
<td>TCP</td>
</tr>
<tr>
<td>BrCH$_2$CH$_2$CN</td>
<td>0.613</td>
<td>(0.636)</td>
<td>1.660</td>
</tr>
<tr>
<td>BrCH$_2$CH$_2$OH</td>
<td>0.288</td>
<td>0.740</td>
<td>1.220</td>
</tr>
<tr>
<td>CH$_3$O.CH$_2$CH$_2$OH</td>
<td>-0.103</td>
<td>0.301</td>
<td>0.630</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$OAc</td>
<td>0.281</td>
<td>0.655</td>
<td>0.906</td>
</tr>
<tr>
<td>HOCH$_2$CH$_2$OAc</td>
<td>0.486</td>
<td>1.114</td>
<td>1.502</td>
</tr>
</tbody>
</table>

In /...
In the case of the diastereoisomers, only the meso form is given.

4.3 Discussion - Group Retention Factors

Examination of the tables immediately shows that on all four liquids the volume reduced retentions of the linear compounds are very nearly twice those of the monofunctional compounds. This suggests that the volume reduced retention has eliminated the non-polar contribution to the retention, and has provided a factor which increases proportionally with the number of functional groups in the molecule. Similar in nature to Claytor's factor, this too may be called a Group Retention Factor. The choice of butyl derivatives for the study of the monofunctional compounds has been a happy one since the volume reduced retention is not a constant for lower members of a series.

In table 4.8 the ratios of the volume reduced retentions of the bifunctional compounds (for molecules containing similar functional groups) to the group retention factors of the functional groups are given. The nearer this ratio approximates to 2, the more perfect the technique. The volume reduced retentions of the bifunctional compounds are represented as \( \log r_{xx} \).

It is observed that the volumed reduced retentions of the linear bifunctional compounds are readily calculable from the group retention/....
### Table 4.8

**Comparison of Volume Reduced Retentions of Bifunctional Compounds with the Group Retention Factor**

\[
\log r_{xx,*/}\log r_{x*}
\]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>SQ</th>
<th>DNP</th>
<th>TCP</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₂Br)₂</td>
<td>1.80</td>
<td>1.74</td>
<td>1.72</td>
<td>1.88</td>
</tr>
<tr>
<td>(CH₂CH₂Br)₂</td>
<td>2.01</td>
<td>1.96</td>
<td>1.97</td>
<td>2.01</td>
</tr>
<tr>
<td>Meso-(CH₃CHBr)₂</td>
<td>1.47</td>
<td>1.42</td>
<td>1.42</td>
<td>1.48</td>
</tr>
<tr>
<td>(CH₂OAc)₂</td>
<td>1.88</td>
<td>1.92</td>
<td>1.91</td>
<td>2.00</td>
</tr>
<tr>
<td>(CH₂CH₂OAc)₂</td>
<td>2.02</td>
<td>1.97</td>
<td>1.95</td>
<td>2.03</td>
</tr>
<tr>
<td>Meso-(CH₂CHOAc)₂</td>
<td>0.94</td>
<td>1.10</td>
<td>1.22</td>
<td>1.33</td>
</tr>
<tr>
<td>(CH₂OH)₂</td>
<td>2.20</td>
<td>1.86</td>
<td>1.92</td>
<td>1.95</td>
</tr>
<tr>
<td>(CH₂CH₂OH)₂</td>
<td>2.50</td>
<td>2.18</td>
<td>2.12</td>
<td>2.11</td>
</tr>
<tr>
<td>Meso-(CH₂CHOH)₂</td>
<td>1.87</td>
<td>1.71</td>
<td>1.68</td>
<td>1.68</td>
</tr>
<tr>
<td>(CH₂OCH₃)₂</td>
<td>1.73</td>
<td>1.83</td>
<td>1.81</td>
<td>1.63</td>
</tr>
<tr>
<td>(CH₂CH₂OCH₃)₂</td>
<td>2.12</td>
<td>2.21</td>
<td>2.26</td>
<td>2.40</td>
</tr>
<tr>
<td>Meso-(CH₃CHOCH₃)₂</td>
<td>0.89</td>
<td>1.21</td>
<td>1.36</td>
<td>1.37</td>
</tr>
<tr>
<td>(CH₂CN)₂</td>
<td>2.32</td>
<td>2.17</td>
<td>2.14</td>
<td>2.38</td>
</tr>
<tr>
<td>(CH₂CH₂CN)₂</td>
<td>2.25</td>
<td>2.10</td>
<td>2.10</td>
<td>1.94</td>
</tr>
<tr>
<td>Meso-(CH₂CH CN)₂</td>
<td>1.54</td>
<td>1.54</td>
<td>1.53</td>
<td>1.68</td>
</tr>
</tbody>
</table>
retention factors of the functional groups contained. This is particularly striking in the case of the solutes substituted with different functional groups. In these cases predicted retentions compare remarkably well with the retentions obtained. (At this point comment may be made about the retention of \( \beta \)-bromopropionitrile on dinonylphthalate. At no time could this solute be chromatographed on the DNP column. A sharp, tailing peak, such as is often associated with decompositions, was observed close to the air peak. Its volume reduced retention is very different from that predicted and it is not believed to be that of the nitrile).

The obvious advantage of this technique is the ability to predict the retentions of unknown compounds. The retention of any solute relative to any normal hydrocarbon is readily accomplished by rearranging equation 4.2

\[
\log r_x \approx \log r_x^* + \log r^* \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots 4.2
\]

and using Graph 1.

The advantage of such a procedure over that of Evans and Smith (40) (p.51 above) is that two special solutes do not have to be chromatographed to calculate the retention of a new solute, rather, group retention factors can be tabulated in the literature, and the retentions of new solutes can be calculated from these.

Consideration of the non-linear 2,3-disubstituted butanes, however/...
however, shows that simple prediction of the retentions of all solutes is not possible. Moreover examination of table 4.8 reveals that there are quite large deviations from 2 in the case of some solute types. In particular the ethers, alcohols and cyanides show a number of examples with values rather larger than 2.

In general it is found that the 1,4-disubstituted butane derivatives show higher values in table 4.8 than do the 1,2-disubstituted ethanes. This may be understood by considering again the nature of the volume reduced retention. It is believed, as illustrated in equation 3.9, to be a measure of the polar contribution to the force of interaction between the solute and the solvent.

A higher value for the 1,4-derivatives suggests that, being separated, the two functional groups are more capable of individually interacting with the stationary liquid.
In Table 4.9, the volume reduced retentions of the bifunctional compounds containing different functional groups are compared with the retentions predicted by addition of group retention factors.

The volume reduced retentions are represented by $r_{xy}^{*}$, and the calculated values are obtained using the relationship

$$\log r_{xy}^{*} = \log r_x^{*} + \log r_y^{*}$$


\[\text{TABLE 4.9}\]

**PREDICTION OF VOLUME REDUCED RETENTIONS OF SOLUTES CONTAINING DIFFERENT FUNCTIONAL GROUPS**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>SQ</th>
<th>DNP</th>
<th>TOP</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pred.</td>
<td>Found</td>
<td>Pred.</td>
<td>Found</td>
</tr>
<tr>
<td>BrCH$_2$CH$_2$CN</td>
<td>1.71</td>
<td>1.76</td>
<td>2.29 (1.65)</td>
<td>2.68</td>
</tr>
<tr>
<td>BrCH$_2$CH$_2$OH</td>
<td>1.64</td>
<td>1.61</td>
<td>2.04</td>
<td>1.02</td>
</tr>
<tr>
<td>CH$_3$O.CH$_2$CH$_2$OH</td>
<td>1.12</td>
<td>1.08</td>
<td>1.48</td>
<td>1.45</td>
</tr>
<tr>
<td>CH$_3$O.CH$_2$CH$_2$OAc</td>
<td>0.75</td>
<td>0.79</td>
<td>1.03</td>
<td>1.16</td>
</tr>
<tr>
<td>HO.CH$_2$CH$_2$OAc</td>
<td>1.35</td>
<td>1.41</td>
<td>1.83</td>
<td>2.01</td>
</tr>
</tbody>
</table>

These two tables bring out clearly the successes, and failures of the treatment. Regrettably, the errors involved in determining molar volumes, and the reading of points off the graph make it impossible to make a precise comparison of the results.

Nevertheless/...
Nevertheless it appears that some trends certainly do exist. The 1,2 disubstituted compounds apparently hinder each other and are not capable of interacting as efficiently as do the 1,4 derivatives. The data on table 4.9, however, show that even if this be the case, the retentions of the 1,2 derivatives are still accurately predictable from the group retention factors.

The prediction of the retentions of the 2,3 disubstituted butanes presents a problem which has yet to be overcome. In all cases the volume reduced retentions of these compounds are well below those predicted by simple addition. The reason is not difficult to understand. The functional groups are pushed by the methyl groups into close proximity producing interference (hydrogen bonding in the case of the alcohol), thereby reducing the affinity of the groups for the solvent. Furthermore the functional groups are sterically hindered. Both these points are mentioned by Evans and Smith (p.52 above) as being deleterious to the predictability of retentions. A method for the prediction of the retentions of non-linear compounds is not immediately apparent. A possible answer might be the use of an empirical factor, or it might be possible to use a method similar to that of Evans and Smith. With more data available, it should be possible to tabulate group retention factors not only of functional groups, but of segments such as the substituted isopropyl radical. These could then be added in a similar way.
In spite of the shortcomings of this technique at the moment, it is remarkable that such a correlation does exist, particularly when the wide variations in retention relative to heptane of the different solutes, (tabulated in the first columns of table 4.2 to 4.7) are considered.

A comparison of the work of Clayton, and of Evans and Smith, can now be made.

The validity of Clayton's multiplicative group retention factor when applied to steroids, and its failure when applied to smaller molecules is understood. The large steroid nucleus does not change appreciably in size on substitution, but in small molecules the introduction of a substituent can change the volume, and hence affect the volume reduced retention. Evans and Smith's technique involves the addition of molecular fragments; a process which itself includes size factors.

In the case of linear compounds, the group retention factor approach appears to be superior to the treatment of Evans and Smith, since in the former case, group retention factors can be tabulated. It is inferior to the work of these authors in the prediction of the retention of branched molecules, however.

The prediction of the retention of any solute should be possible from a knowledge of the molecular formula and structure of the molecule. Although inadequate at the moment, the group retention /...
retention factor is perhaps a start in the right direction. It remains for further study to prove whether this approach will in the future be one of any general applicability.

4.4 The prediction of boiling points

The observations made in the above section are also of interest from a theoretical point of view.

The retention volume, it will be remembered from equation 1.6 can be thought of as determined largely by the vapour pressure of the pure solute. By combining equations 1.12 and 1.17, it may also be written.

\[ \ln r_{12} = \frac{1}{RT} \left\{ (\Delta H^V_{1} - \Delta H^V_{2}) - (\Delta H^o_E(1) - \Delta H^o_E(2)) \right\} \] ...... 4.4

Let us now, as in the case of evaporation of solute from solution (equation 3.6) write the enthalpy of vaporisation of pure solute as the sum of polar and apolar contributions,

\[ \Delta H^V_{1} = \Delta H^V_{1}(P) + \Delta H^V_{1}(A) \] ......................... 4.5

The heat of vaporisation, and hence the boiling point of a bifunctional compound \((xy)\) should be given by

\[ \Delta H^V_{xy}(P) = \Delta H^V_{x*}(P) + \Delta H^V_{y*}(P) \] ......................... 4.7

where /....
where, as in the case of retention volumes, $\Delta H^V_{x^*}(P)$ and $\Delta H^V_{x y}(P)$ are functional group constants of $x$ and $y$ for molecules of that particular size.

Then from 4.5, 4.7 becomes

$$\Delta H^V_{x y}(P) =$$

$$= \Delta H^V_{x^*} - \Delta H^V_*(P) + \Delta H^V_{y^*} - \Delta H^V_* \quad \cdots \cdots \quad 4.8$$

the letters $x$ and $y$ being dropped from the athermal contributions, since in these cases the enthalpy is that of an hypothetical hydrocarbon of the same size as $x$, $y$ and $xy$, all of which are the same size.

$$\Delta H^V_{x y}(A) = \Delta H^V_{x^*}(A) = \Delta H^V_{y^*}(A) = \Delta H^V_* \quad \cdots \cdots \quad 4.9$$

$$\therefore \Delta H^V_{x y} = \Delta H^V_{x y}(P) + \Delta H^V_*$$

$$= \Delta H^V_{x^*} + \Delta H^V_{y^*} - \Delta H^V_*$$

Since boiling point and heat of vaporisation are related by Trouton's constant, the boiling point of $xy$ is given by

$$T_b(xy) = T_b(x^*) + T_b(y^*) - T_b(*) \quad \cdots \cdots \quad 4.10$$

In words, the boiling point of a bifunctional compound should be expected to be equal to the sum of the boiling points of hypothetical members of homologous series of that molar volume, containing those functional groups, minus the boiling point of a hypothetical hydrocarbon of the same molar volume.

Such /...
Boiling point °C

BOILING POINTS OF HOMOLOGOUS

LEGEND
I Hydrocarbons
II Methyl ethers
III Acetates
IV Bromides
V Alcohols
VI Nitriles

Molecular volume
Such a relationship is tested by means of a plot of boiling point against molar volume for as many homologous series as there are functional groups. This is shown in Graph 2, the data for the graph all being obtained from Vogel (15).

In Table 4.10, the boiling points of the same liquids as were studied before are compared with values calculated by equation 4.10. An example of one of these calculations is presented:

The molar volume of $\beta$-brompropionitrile is 81. From the graph the boiling points of a hypothetical bromide and a hypothetical cyanide of this volume are read off. They are 64°C and 110°C respectively. The boiling point of a normal hydrocarbon of the same size would be -48°C. The predicted boiling point is therefore $110 + 64 + 18 = 192^\circ$. This is exactly the true boiling point.

**TABLE 4.10**

**THE PREDICTION OF BOILING POINTS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling point</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>True</td>
</tr>
<tr>
<td>(CH$_2$Br)$_2$</td>
<td>154</td>
<td>132</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$Br)$_2$</td>
<td>208</td>
<td>198</td>
</tr>
<tr>
<td>Meso (CH$_3$CHBr)$_2$</td>
<td>210</td>
<td>169</td>
</tr>
<tr>
<td>(CH$_2$OAc)$_2$</td>
<td>177</td>
<td>187</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OAc)$_2$</td>
<td>208</td>
<td>230</td>
</tr>
<tr>
<td>Meso (CH$_2$CHOAc)$_2$</td>
<td>212</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 4.10 contd./...
Table 4.10 continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling point</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>True</td>
</tr>
<tr>
<td>(CH₂OH)₂</td>
<td>186</td>
<td>197</td>
</tr>
<tr>
<td>(CH₂CH₂OH)₂</td>
<td>218</td>
<td>235</td>
</tr>
<tr>
<td>Meso (CH₃CHOH)₂</td>
<td>220</td>
<td>182</td>
</tr>
<tr>
<td>(CH₂OCH)₃</td>
<td>80</td>
<td>82</td>
</tr>
<tr>
<td>(CH₂CH₂OCH₃)₂</td>
<td>131</td>
<td>130</td>
</tr>
<tr>
<td>Meso (CH₃CHOCH₃)₂</td>
<td>136</td>
<td>108</td>
</tr>
<tr>
<td>(CH₂CN)₂</td>
<td>240</td>
<td>266</td>
</tr>
<tr>
<td>(CH₂CH₂CN)₂</td>
<td>264</td>
<td>295</td>
</tr>
<tr>
<td>Meso (CH₃CHCN)₂</td>
<td>264</td>
<td>265</td>
</tr>
<tr>
<td>BrCH₂CH₂CN</td>
<td>192</td>
<td>192</td>
</tr>
<tr>
<td>BrCH₂CH₂OH</td>
<td>151</td>
<td>149</td>
</tr>
<tr>
<td>CH₃O·CH₂CH₂OH</td>
<td>120</td>
<td>124</td>
</tr>
<tr>
<td>CH₃OCH₂CH₂OAc</td>
<td>137</td>
<td>143</td>
</tr>
<tr>
<td>HOCH₂CH₂OAc</td>
<td>176</td>
<td>188</td>
</tr>
</tbody>
</table>

The validity of the relationship is adequately demonstrated in the table.

As expected the boiling points of the 2,3-disubstituted butanes are higher than predicted. The reason for this is the same as before. Sterically hindered, the two functional groups in these molecules are not as free to interact with surrounding molecules as...
as are the other types.

The relationship between the boiling point and retention time is brought out again by reference to equation 4.4. The relative retention time is determined largely by the difference of heats of vaporisation of the two solutes. The excess partial molar enthalpy of mixing, $\Delta H^\circ_{E}$, is a lesser term.

This, it will be remembered, is equal to the activity coefficient ratio:

\[
\ln r_{12} = \frac{1}{RT} (\Delta H^V_1 - \Delta H^V_2) + \frac{1}{RT} (\Delta H^\circ_{E(2)} - \Delta H^\circ_{E(1)}) \quad \ldots \ldots \ldots \ldots 4.4
\]

\[
r_{12} = \frac{P_2^o}{P_1^o} \cdot \frac{\gamma_2^o}{\gamma_1^o}, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 1.6
\]

and since \[
\ln \left( \frac{P_2^o}{P_1^o} \right) = \frac{1}{RT} (\Delta H^V_1 - \Delta H^V_2). \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 1.9
\]

\[
\therefore \ln \frac{\gamma_2^o}{\gamma_1^o} = \frac{1}{RT} (\Delta H^\circ_{E(2)} - \Delta H^\circ_{E(1)}) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 4.11
\]

when 1 and 2 are of similar size.

4.5 The Activity Coefficient - Intermolecular Interaction in Solution

The excess partial molar enthalpy of mixing, and hence the activity coefficient, is a measure of the forces of interaction between solute and solvent.

An expression has already been derived for the relative activity /...
activity coefficient of two solutes of similar size in a common solvent, in terms of such interaction forces. It is written

\[
\ln \left( \frac{\gamma_2^0}{\gamma_1^0} \right) = \frac{z}{2RT} \left\{ (U_{22} - U_{11}) - 2 (U_s - U_{1s}) \right\} \quad \text{............... 1.23}
\]

To study the forces of interaction between solute and solvent it is necessary to isolate the latter term, \((U_{2s} - U_{1s})\).

The term \((U_{22} - U_{11})\) is often equated with the difference in heats of vaporisation of pure liquids 2 and 1 (see 2, p.29), but it is difficult to estimate and eliminate this term directly due to the presence of the imprecise \(z\) factor. It was then realized that if the ratio of relative activity coefficients on two liquids is taken, the solute - solute interaction term is eliminated.

If the two liquids are called \((P)\) and \((A)\), from 1.23 we obtain

\[
\ln \frac{(\gamma_2^0/\gamma_1^0)_P}{(\gamma_2^0/\gamma_1^0)_A} = \frac{z}{RT} \left\{ (U_{1P} - U_{2P}) - (U_{1A} - U_{2A}) \right\} \quad \text{............... 4.12}
\]

provided that the molar volumes of \(P\) and \(A\) are similar, and \(z\) remains constant.

By doing this, not only have the solute - solute terms been removed, but a function has been derived which is dependant directly on the energy of interaction between solute and solvent, and which is easily obtained from gas chromatographic retentions. Moreover, it is not necessary to know the vapour pressures of the solutes, and then to calculate/...
calculate activity coefficients since by taking this ratio, vapour pressures are eliminated

\[
\ln \left( \frac{\gamma_2^o/\gamma_1^o}{\gamma_2^o/\gamma_1^o} \right)_P = \ln \left( \frac{r_{12}^o}{r_{12}^o} \right)_P \left( \frac{r_{12}^o}{r_{12}^o} \right)_A \quad \cdots \cdots \cdots \cdots \quad 4.13
\]

It should now be possible to use similar reasoning to that used in the prediction of retention times to study the interaction of particular functional groups with the stationary liquid. If, as before, solute z is non-polar reference solute, and liquid A is apolar, while \( 1 \) and \( P \) are polar solute and solvent respectively, then in the same way as before we can write

\[
U_{1P} = U_{1P}(P) + U_{1P}(A) \quad \cdots \cdots \cdots \cdots \quad 4.14
\]

i.e. that the energy of interaction of \( 1 \) with \( P \) is made up of a polar and an apolar contribution, while

\[
U_{2P} = U_{2P}(A) \quad \text{only} \quad \cdots \cdots \cdots \cdots \quad 4.15
\]

On the non-polar liquid only dispersion forces are operative

\[
U_{1A} = U_{1A}(A) \quad \cdots \cdots \cdots \cdots \quad 4.16
\]

and

\[
U_{2A} = U_{2A}(A) \quad \cdots \cdots \cdots \cdots \quad 4.17
\]

Then by substituting 4.14 to 4.17 into 4.12, and using 4.13, the relative retention ratio on two solvents can be written

\[
\ln \left( \frac{r_{12}^o}{r_{12}^o} \right)_P = \frac{z}{RT} \left\{ U_{1P}(P) + U_{1P}(A) - U_{2P}(A) - U_{1A}(A) + U_{2A}(A) \right\}
\]

\cdots \cdots \cdots \cdots \quad 4.18

If/...
If 2 is chosen so that the apolar forces of both solutes on the two solvents are equal, i.e. that

\[ U_{1P}(A) = U_{2P}(A) \] \hspace{1cm} 4.19

and \[ U_{1A}(A) = U_{2A}(A) \] \hspace{1cm} 4.20

these terms will cancel, and 4.18 will become

\[ \ln \left( \frac{r_{12}}{r_{12}} \right)_P / \left( \frac{r_{12}}{r_{12}} \right)_A = \frac{z}{RT} \left( U_{1P}(P) \right) \] \hspace{1cm} 4.21

The ratio of the relative retention of 1 and 2 on polar solvent P to the relative retention on apolar solvent A will be directly proportional to the polar interaction of solute 1 with P.

It will be remembered that Littlewood has used the ratio of retentions on two liquids, but the theoretical aspects were not given consideration. Consequently it is not clear that his treatment gives a direct measure of the forces of interaction in solution since he has used the ratio of specific retention volumes.

For equation 4.21, relative retentions must be used, with the reference solute being specifically chosen to satisfy equations 4.19 and 4.20.

4.6 Relative Activity Coefficient on a Single Liquid

The proof that such a reference solute has been found can be made by reference to equation 1.23, by considering the relative activity/...
activity coefficients of a variety of polar solutes on a non-polar liquid.

In all cases the polar interactions with this solvent will be zero; equation 4.14 reduces to

\[ U_{1P} = U_{1P(A)} \]  
4.22

The relative activity coefficients will be determined only by the difference in solute - solute interaction between the polar and the reference solutes. A plot of the logarithmic relative activity coefficient of 1 and 2 in a non-polar liquid, such as squalane, against the difference in heats of vaporisation of the two solutes should show a trend. It will not be linear, since \( z \) itself is not constant but a function of the size of the molecules.

From previous experience, it appeared likely that by choosing 2 so that it is of the same size as 1, the dispersion forces might cancel out.

The logarithms of the relative activity coefficients of polar solutes to non-polar hydrocarbons of the same molar volume should therefore be plotted against the difference in heats of vaporisation of these components to test this assumption.
The method of obtaining activity coefficients relative to hydrocarbons of the same size ("Volume Reduced Activity Coefficients") is similar to that used for retention times, but is more lengthy. By means of a graph of the logarithmic relative activity coefficients of the normal hydrocarbons plotted against molar volume, and the relationship,

\[ \log \frac{\gamma_x^0}{\gamma_*^0} = \log \frac{\gamma_x^0}{\gamma_7^0} - \log \frac{\gamma_*^0}{\gamma_7^0} \]

this quantity can be determined. Activity coefficients relative to heptane are obtained from gas chromatographic retentions relative to heptane by elimination of vapour pressure.

In this case the graph is simpler than Graph 1, since only the values on squalane are required. Activity ratios on polyethylene glycol will be included, however, to ascertain that equation 4.22 does not hold on this polar liquid.

The data required to plot Graph 3 are presented in Table 4.11. They are calculated from the retentions and vapour pressures of the hydrocarbons in Table 4.10 above.

Table 4.11/....
Graph 3

Relative Activity Coefficient of Normal Hydrocarbons on Squalane and Polyethylene Glycol at 120°C

Legend

I Squalane
II Polyethylene glycol
### Table 4.11

**Relative Activity Coefficients of the Hydrocarbons**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>SQ</th>
<th>log (\gamma_T/\gamma_X)</th>
<th>PEG</th>
<th>log (\gamma_T/\gamma_X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon, (x)</td>
<td>(\gamma_T/\gamma_X)</td>
<td></td>
<td>(\gamma_T/\gamma_X)</td>
<td></td>
</tr>
<tr>
<td>(n-C_5H_{12})</td>
<td>1.175</td>
<td>0.069</td>
<td>1.606</td>
<td>0.205</td>
</tr>
<tr>
<td>(n-C_6H_{14})</td>
<td>1.120</td>
<td>0.048</td>
<td>1.189</td>
<td>0.074</td>
</tr>
<tr>
<td>(n-C_7H_{16})</td>
<td>1.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
</tr>
<tr>
<td>(n-C_8H_{18})</td>
<td>0.894</td>
<td>-0.048</td>
<td>0.765</td>
<td>-0.115</td>
</tr>
<tr>
<td>(n-C_{10}H_{22})</td>
<td>0.722</td>
<td>-0.140</td>
<td>0.542</td>
<td>-0.265</td>
</tr>
</tbody>
</table>

To test equation 4.22, the energies of solute interaction are equated with the heats of vaporisation. It is more convenient, however, to use the boiling point which is related to the heat of vaporisation by Trouton's constant. Although this "constant" varies from about 22 to 28, it will be sufficiently precise for the verification of the equation. The term \((r u_{11} - r u_{22})\) is therefore replaced by the difference in boiling point between the polar solute, and a hypothetical hydrocarbon of the same molar volume. This function is calculated by means of the hydrocarbon curve on Graph 2, and is termed the volume reduced boiling point, \(\Delta V_{TB}\). The volume reduced boiling points of the twenty solutes studied are presented in Table 2.2.
Table 4.12 contains the volume reduced activity ratios, in the logarithmic form, of these same solutes on squalane at 130°C.

**TABLE 4.12**

**LOG VOLUME REDUCED ACTIVITY RATIOS ON SQUALANE AT 130°C**

<table>
<thead>
<tr>
<th>Solute</th>
<th>log $\gamma_x/\gamma_*$</th>
<th>Solute</th>
<th>log $\gamma_x/\gamma_*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuBr</td>
<td>0.074</td>
<td>BuOCH$_3$</td>
<td>-0.023</td>
</tr>
<tr>
<td>(CH$_2$Br)$_2$</td>
<td>0.220</td>
<td>(CH$_2$OCH$_3$)$_2$</td>
<td>0.376</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$Br)$_2$</td>
<td>0.228</td>
<td>(CH$_2$CH$_2$OCH)$_2$</td>
<td>0.050</td>
</tr>
<tr>
<td>Meso(CH$_3$CHBr)$_2$</td>
<td>0.107</td>
<td>Meso(CH$_3$CHOCH$_3$)$_2$</td>
<td>0.059</td>
</tr>
<tr>
<td>BuOAc</td>
<td>0.132</td>
<td>BuCN</td>
<td>0.481</td>
</tr>
<tr>
<td>(CH$_2$OAc)$_2$</td>
<td>0.598</td>
<td>(CH$_2$CN)$_2$</td>
<td>1.692</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OAc)$_2$</td>
<td>0.280</td>
<td>(CH$_2$CH$_2$CN)$_2$</td>
<td>1.260</td>
</tr>
<tr>
<td>Meso(CH$_3$CHOAc)$_2$</td>
<td>0.375</td>
<td>Meso(CH$_3$CHCN)$_2$</td>
<td>1.357</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.316</td>
<td>Br.CH$_2$CH$_2$CN</td>
<td>0.698</td>
</tr>
<tr>
<td>(CH$_2$OH)$_2$</td>
<td>1.368</td>
<td>Br.CH$_2$CH$_2$OH</td>
<td>0.595</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OH)$_2$</td>
<td>1.222</td>
<td>AcO.CH$_2$CH$_2$OH</td>
<td>0.979</td>
</tr>
<tr>
<td>Meso(CH$_3$CHOH)$_2$</td>
<td>0.844</td>
<td>AcO.CH$_2$CH$_2$OCH$_3$</td>
<td>0.474</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOCH$_2$CH$_2$OCH$_3$</td>
<td>0.412</td>
</tr>
</tbody>
</table>

These are plotted against $\Delta_\ast T_b$ on graph 4.
GRAPH 4
VOLUME REDUCED ACTIVITY COEFFICIENTS ON SQUALANE
AT 150°C

LEGEND

- Normal hydrocarbons
- Bromides
- Acetates
- Alcohols
- Methyl ethers
- Cyanides
- Mixed Groupings
- Mixed Groupings with bromides

Log $\frac{\gamma}{\gamma^0}$

$0$ $50$ $100$ $150$ $200$ $250$ $300$ $\Delta^{Pb}$
Graph 4 demonstrates that there is a real trend when the activity coefficients are treated in this way. In examining the results it must be remembered that errors can be introduced in the calculation of vapour pressures, in the estimation of molar volumes and in the use of boiling point instead of heat of vaporisation. It must also be taken into account that an extremely diverse group of chemicals have been compared. In view of these facts, it is extremely significant that such a trend should emerge.

The trend is not linear, and it will be remembered that the $z$ factor is itself size dependent. It increases in size as the solute's volume increases.

The bromides, it will be noticed, all lie below the general trend. Littlewood (28) has made a comment about the behaviour of halogenated compounds in non-polar chromatographic solvents. Having high ionisation constants, the interaction with non-polar liquids is not negligible. This interaction with the liquid accounts for their low values. Indeed the fact that chloroform was used in this study to dissolve squalane for coating on the support further illustrates the affinity of halogenated derivatives for hydrocarbons. The points have not been connected by a line since this makes it more difficult to compare the position of the different functional types, but in Graph 5, the bromides have been omitted, and a line more clearly demonstrates the trend.
GRAPH 5

VOLUME REDUCED ACTIVITY COEFFICIENTS ON SQUALANE AT 130°C.
BROMIDES EXCLUDED

$log \frac{\gamma_x^0}{\gamma_s^0}$ vs $\Delta_x^T_b$
Graph 6

Volume Reduced Activity Coefficients on Squalane at 100°C

Legend
- Normal hydrocarbons
- Bromides
- Acetates
- Alcohols

Log $\gamma_x/\gamma*$ vs $\Delta_x T_b$
In table 4.13, the retentions and activity coefficients of some of the solutes at 100°C are given.

**TABLE 4.13**

<table>
<thead>
<tr>
<th>Solute</th>
<th>log $r_x/7$</th>
<th>log $r_{*7}$</th>
<th>log $r_x/7^*$</th>
<th>log $\gamma_x/\gamma_7$</th>
<th>log $\gamma_x/\gamma_7^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuBr</td>
<td>0.06</td>
<td>-0.79</td>
<td>0.85</td>
<td>+0.030</td>
<td>-0.066</td>
</tr>
<tr>
<td>(CH$_2$Br)$_2$</td>
<td>0.31</td>
<td>-1.20</td>
<td>1.51</td>
<td>+0.116</td>
<td>-0.077</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$Br)</td>
<td>1.11</td>
<td>-0.55</td>
<td>1.66</td>
<td>+0.271</td>
<td>-0.055</td>
</tr>
<tr>
<td>Meso(CH$_3$CHBr)$_2$</td>
<td>0.72</td>
<td>-0.50</td>
<td>1.22</td>
<td>+0.074</td>
<td>-0.052</td>
</tr>
<tr>
<td>BuOAc</td>
<td>0.20</td>
<td>-0.30</td>
<td>0.50</td>
<td>+0.164</td>
<td>-0.013</td>
</tr>
<tr>
<td>(CH$_2$OAc)$_2$</td>
<td>0.65</td>
<td>-0.30</td>
<td>0.95</td>
<td>+0.874</td>
<td>-0.013</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OAc)$_2$</td>
<td>1.37</td>
<td>0.40</td>
<td>0.97</td>
<td>+0.756</td>
<td>+0.044</td>
</tr>
<tr>
<td>Meso(CH$_2$CH$_2$OAc)$_2$</td>
<td>0.82</td>
<td>0.49</td>
<td>0.33</td>
<td>+0.662</td>
<td>+0.050</td>
</tr>
<tr>
<td>BuOH</td>
<td>-0.25</td>
<td>-0.90</td>
<td>0.65</td>
<td>+0.560</td>
<td>-0.070</td>
</tr>
<tr>
<td>(CH$_2$OH)$_2$</td>
<td>0.36</td>
<td>-1.62</td>
<td>1.98</td>
<td>1.374</td>
<td>-0.085</td>
</tr>
<tr>
<td>(CH$_2$CH$_2$OH)$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Meso (CH$_3$CHOH)$_2$</td>
<td>0.29</td>
<td>-0.79</td>
<td>1.08</td>
<td>1.107</td>
<td>-0.066</td>
</tr>
</tbody>
</table>

Volume reduced retention times and activity coefficients are calculated from graphs similar to 1 and 3 from hydrocarbon retentions at 100°C. These are not included, but the graphs may be reconstructed if required from the log $r_{*7}$ and log $\gamma_{x}/\gamma_7$ data tabulated above.
The volume reduced activity coefficients at 100°C are plotted against $\Delta_x T_b$ in the same way on graph 6.

Although the trend is less obvious due to the paucity of results, it is again observed that the bromides lie well below the others, and that the alcohols and acetates can approximately be related by a straight line. In this case the slope is $6.5 \times 10^{-3}$/°C, from which $Z$ is calculated to be 0.96 at that temperature. It seems likely therefore, if the assumptions employed have been valid, that the value of $z$ is about unity.

Volume reduced activity coefficients of all twenty-five solutes on polyethylene glycol at 130°C are plotted against $\Delta x T_b$ on graph 7. This is to illustrate that the trends observed in the previous graphs do not occur when a polar solvent is used. This is a further verification that equation 4.22 does hold when the reference solutes are chosen according to the molecular volumes.

Another interesting relationship is brought out by expanding equation 1.17 and combining it with 1.23. This treatment leads to,

$$\ln r_{12} = \frac{1}{RT} (\Delta H_1^V - \Delta H_2^V) - \frac{z}{2RT} (U_{11} - U_{22}) + \frac{z}{RT} (U_{1P} - U_{2P})$$

\[4.24\]

for the retention of 1 relative to 2 on solvent $P$. It/...
Graph 7

Volume Reduced Activity Coefficient on Polyethylene Glycol at 130°C

- Normal hydrocarbons
- Aromides
- Acetates
- Alcohols
- Methyl ether
- Cyanides
- Mixed groupings
Graph 8

Volume Reduced Retentions on Squalane at 130°C

Legend:
- Normal hydrocarbons
- Bromides
- Acetates
- Alcohols
- Methyl ether
- Cyanides
- Mixed groupings
GRAPH 9

VOLUME REDUCED RETENTIONS OF POLYETHYLENE GLYCOL AT 130°C

LEGEND

* Normal hydrocarbons
• Bromides
○ Acetates
× Alcohols
○ Methyl ethers
□ Cyanides
△ Mixed groupings
4.7 Relative activity coefficients on two different liquids

From the treatment in the foregoing section, it can be accepted that the ratio of volume reduced retentions on a polar and a non-polar liquid is a measure of the forces of interaction between the polar portion of the solute and the polar solvent (equation 4.21).

In Tables 4.14 - 4.16, the volume reduced retentions of the twenty five solutes on dinonyl phthalate, tricresyl phosphate and polyethylene glycol relative to the volume reduced retentions on squalane, at 130°C are presented.

In Table 4.15, the ratios of the retentions relative to squalane of the bifunctional to monofunctional compounds are compared, while in Table 4.16 volume reduced retentions relative to squalane of the derivative with different functional groups are compared with the retentions calculated by addition of monofunctional constants by means of equation 4.25:

\[ \log \left( \frac{r_{xy,*}}{r_{xy,*}} \right)_p \left/ \frac{r_{xy,*}}{r_{xy,*}} \right)_s = \log \left( \frac{r_{x,*}}{r_{x,*}} \right)_p + \log \left( \frac{r_{y,*}}{r_{y,*}} \right)_p \]

4.25

Table 4.14/...
### Table 4.14

**Volume Reduced Activity Coefficients Relative to Squalane**

<table>
<thead>
<tr>
<th>Solvent Solute</th>
<th>DNP</th>
<th>TCP</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuBr</td>
<td>0.15</td>
<td>0.29</td>
<td>0.35</td>
</tr>
<tr>
<td>((CH_2Br))_2</td>
<td>0.22</td>
<td>0.45</td>
<td>0.73</td>
</tr>
<tr>
<td>((CH_2CH_2Br))_2</td>
<td>0.26</td>
<td>0.55</td>
<td>0.71</td>
</tr>
<tr>
<td>Meso((CH_3CHBr))_2</td>
<td>0.18</td>
<td>0.38</td>
<td>0.53</td>
</tr>
<tr>
<td>BuOAc</td>
<td>0.20</td>
<td>0.40</td>
<td>0.52</td>
</tr>
<tr>
<td>((CH_2OAc))_2</td>
<td>0.40</td>
<td>0.78</td>
<td>1.10</td>
</tr>
<tr>
<td>((CH_2CH_2OAc))_2</td>
<td>0.40</td>
<td>0.74</td>
<td>1.05</td>
</tr>
<tr>
<td>Meso((CH_2CHOAc))_2</td>
<td>0.30</td>
<td>0.62</td>
<td>0.88</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.28</td>
<td>0.56</td>
<td>0.84</td>
</tr>
<tr>
<td>((CH_2OH))_2</td>
<td>0.23</td>
<td>0.83</td>
<td>1.42</td>
</tr>
<tr>
<td>((CH_2CH_2OH))_2</td>
<td>0.34</td>
<td>0.87</td>
<td>1.44</td>
</tr>
<tr>
<td>Meso((CH_3CHOH))_2</td>
<td>0.34</td>
<td>0.78</td>
<td>1.25</td>
</tr>
<tr>
<td>BuOCH_3</td>
<td>0.03</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>((CH_2OCH_3))_2</td>
<td>0.17</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>((CH_2CH_2OCH_3))_2</td>
<td>0.20</td>
<td>0.40</td>
<td>0.48</td>
</tr>
<tr>
<td>Meso((CH_3CHOCH_3))_2</td>
<td>0.18</td>
<td>0.24</td>
<td>0.44</td>
</tr>
<tr>
<td>BuCN</td>
<td>0.42</td>
<td>0.67</td>
<td>0.75</td>
</tr>
<tr>
<td>((CH_2CN))_2</td>
<td>0.78</td>
<td>1.28</td>
<td>1.84</td>
</tr>
<tr>
<td>((CH_2CH_2CN))_2</td>
<td>0.75</td>
<td>1.28</td>
<td>1.15</td>
</tr>
<tr>
<td>Meso((CH_3CHCN))_2</td>
<td>0.65</td>
<td>1.01</td>
<td>1.38</td>
</tr>
</tbody>
</table>

*Table 4.15/....*
TABLE 4.15
VOLUME REDUCED RETENTIONS RELATIVE TO SQUALANE:
THE RATIO OF BIFUNCTIONAL TO MONOFUNCTIONAL DERIVATIVES

<table>
<thead>
<tr>
<th>Solvent Solute</th>
<th>DNP</th>
<th>TCP</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_2\text{Br})_2$</td>
<td>1.47</td>
<td>1.55</td>
<td>2.09</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{Br})_2$</td>
<td>1.73</td>
<td>1.90</td>
<td>2.03</td>
</tr>
<tr>
<td>Meso$(\text{CH}_3\text{CHBr})_2$</td>
<td>1.28</td>
<td>1.31</td>
<td>1.52</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{OAc})_2$</td>
<td>2.00</td>
<td>1.95</td>
<td>2.12</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{OAc})_2$</td>
<td>2.00</td>
<td>1.85</td>
<td>2.02</td>
</tr>
<tr>
<td>Meso$(\text{CH}_3\text{CHOAc})_2$</td>
<td>1.50</td>
<td>1.55</td>
<td>1.69</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{OH})_2$</td>
<td>0.81</td>
<td>1.48</td>
<td>1.69</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{OH})_2$</td>
<td>1.21</td>
<td>1.55</td>
<td>1.71</td>
</tr>
<tr>
<td>Meso$(\text{CH}_3\text{CHOH})_2$</td>
<td>1.21</td>
<td>1.40</td>
<td>1.49</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{OCH}_3)_2$</td>
<td>2.12</td>
<td>2.00</td>
<td>1.52</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{OCH}_3)_2$</td>
<td>2.50</td>
<td>2.50</td>
<td>2.08</td>
</tr>
<tr>
<td>Meso$(\text{CH}_3\text{CHOCH}_3)_2$</td>
<td>2.25</td>
<td>1.50</td>
<td>1.83</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CN})_2$</td>
<td>1.86</td>
<td>1.91</td>
<td>2.46</td>
</tr>
<tr>
<td>$(\text{CH}_2\text{CH}_2\text{CN})_2$</td>
<td>1.79</td>
<td>1.91</td>
<td>1.53</td>
</tr>
<tr>
<td>Meso$(\text{CH}_3\text{CHCN})_2$</td>
<td>1.55</td>
<td>1.51</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Table 4.16/...
Since it is now believed that the above treatment gives an understanding of the forces of interaction between solute and solvent, the tables can be examined in this light.

Table 4.15 shows that usually forces of interaction between solute and solvent increase with the number of functional groups in the linear compounds, in the same way as solute-solute forces increase, as is discussed in the section on volume reduced retentions.

The most striking exceptions are the alcohols. In this case, the retentions of the diol are much less than the monosubstituted derivatives. The argument to explain this is that once again intramolecular hydrogen bonding reduces the ability of the diol to interact/...
interact with the solvent.

Again the predicted values of the compounds substituted with different functional groups compare well with the values actually found.

It is also observed again, that the 2,3-disubstituted butanes have much lower retentions than predicted. This may be due to the proximity of the groups, or to shielding by methyl groups. The question of steric effects in solution is a highly complex one, which may be illustrated by the fact that it is not yet possible to relate the boiling points of hydrocarbon isomers to their structure (see 1 p.62).

At this stage, mention must be made of Kovats (42) who has used his retention index (equation 3.5) to predict retentions. By taking the difference between the retention index on a polar and a non-polar solvent, he too has obtained a function which shows proportional increase with functional groups. Predictions of the retentions of structurally complex solutes were attained by means of additive functional increments termed 'haftzones', and the use of complicated rules for steric addition.

The retention index has gained wide acceptance in gas chromatography. Kaiser (45) gives tables of retention indices of large numbers of compounds, and Dhont (46) shows it to be a function of greater dependability than log r by virtue of the use of two reference/....
reference solutes. This method of prediction may yet prove popular. Although Kovats' technique has the disadvantage of requiring retention data on two columns, this is not difficult to obtain. The use of retention data on two columns has been employed by other authors too in the identification of solutes. Merritt and Watson (47) and Connell (48) discuss the use of the ratio of retentions of unknown solutes on different column liquids for identification.

It will be clear that if the method of predicting retentions from data on a single column can be developed, however, this technique will be superior to any method which requires retentions on two columns.

A second disadvantage of Kovats retention index is that it contains complicating factors which make it a difficult approach to use in the study of solute – solvent interactions.

Furthermore, it is not altogether clear whether Kovats' theoretical treatment is valid.

It will be realised from equation 3.5, that the retention index on column P may be written

$$I^P = \frac{\log r_{12}}{b_P} + 100z \quad \ldots \ldots \ldots \ldots \ldots \ldots 3.5$$

where $b_P$ is the slope of the plot of retention of any homologous series against carbon number on $P$. In any one solvent this slope
is constant, but it varies from one solvent to another (see equation 3.1). In the justification of his use of the difference in retention index between a polar and a non-polar liquid, what he terms ΔI, Kovats reasons that for a solute i in polar solvent P,

$$RT \ln \left( \frac{P}{x} \right)_i = \mu_D^i + \mu_P^i + \mu_\rho^i$$  \hspace{1cm} 4.26

and, since $P = P^0 \gamma^0 x$

$$RT \ln \left( \frac{\gamma^0 P^0}{\gamma^0 P^0} \right)_i = \mu_D^i + \mu_P^i + \mu_\rho^i$$  \hspace{1cm} 4.27

where $\mu_D^i$, $\mu_P^i$ and $\mu_\rho^i$ are the contributions made by dispersion, polar and structural factors to the chemical potential of solute i.

The relative retention of solute 1 (polar) to solute 2 (non-polar) on solvent P can be written

$$RT \ln r_{12}(P) = RT \ln \frac{\gamma_2^0 P_2^0}{\gamma_1^0 P_1^0}$$  \hspace{1cm} 4.28

$$= \mu_D^2 + \mu_P^2 + \mu_\rho^2 - \mu_D^1 - \mu_P^1 - \mu_\rho^1$$  \hspace{1cm} 4.29

which, if 1 and 2 are assumed to be the same size, $\mu_P^2$ zero and $\mu_D^2 = \mu_D^1$ reduces to

$$RT \ln r_{12x}(P) = \mu_D^2(P) - \mu_D^1(P) - \mu_P^1(A)$$  \hspace{1cm} 4.30

By similar reasoning, on a non-polar phase where now $\mu_P^1 = 0$,

$$RT \ln r_{12}(A) = \mu_D^2(A) - \mu_D^1(A)$$  \hspace{1cm} 4.31

(cf equation 1.17)

Since /....
Since
\[ I = \frac{RT \ln r_{12}}{b} + 100z \] ................................. 3.5

where \( z \) is the carbon number of 2, \( I \) is proportional to the chemical potential of the liquid phase. Kovats now subtracts 4.31 from 4.30 to yield

\[ \Delta I = I^P - I^A = \mu_{p_1}(p), \] ................................. 4.32

a statement that \( \Delta I \) is proportional to the forces of interaction between the polar component of the solute and the stationary phase.

Whether this indeed is so is in doubt, however, since

1. he assumes the molecules have similar molar volumes in deriving 4.30, without taking special precaution. The work of this thesis on the other hand suggests that molar volume is an important factor.

2. he makes the subtraction

\[
\frac{RT \ln r_{12}(p)}{b_p} - \frac{RT \ln r_{12}(A)}{b_A}
\]

to obtain equation 4.32.

The validity of this may also be questioned since \( b_p \) and \( b_A \) are not equal, being the slopes of the logarithms of \( V_g \) plotted against carbon number on different liquids.

In spite of these criticisms, however, it is obvious from his results that his treatment has validity in the prediction of retentions.

4.8/...
4.8 Correlation of forces of interaction with functional type

The interaction energies of the different functional groups with the polar liquids, $U_{tp}(P)$, are summarised in Table 4.17. Included are other properties of the functional types which might be important: the dipole moment of the butyl derivatives, $\mu_{BuX}$, and an energy function which Littlewood (28) has developed, $M(n^2 - 1)/(n^2 + 2)$.

**Table 4.17**

<table>
<thead>
<tr>
<th>Functional type</th>
<th>Solvent</th>
<th>$\mu_{BuX}$</th>
<th>$M(n^2 - 1)/(n^2 + 2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DNP</td>
<td>TCP</td>
<td>PEG</td>
</tr>
<tr>
<td>Br</td>
<td>0.15</td>
<td>0.29</td>
<td>0.35</td>
</tr>
<tr>
<td>OAc</td>
<td>0.20</td>
<td>0.40</td>
<td>0.52</td>
</tr>
<tr>
<td>OH</td>
<td>0.28</td>
<td>0.56</td>
<td>0.84</td>
</tr>
<tr>
<td>CN</td>
<td>0.42</td>
<td>0.67</td>
<td>0.75</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>0.08</td>
<td>0.16</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The dipole moment of methoxybutane has not been found, but ethers all have fairly low polarity and so its dipole moment may be expected to be in the region of 1.00 - 1.10.

The last function is stated by Littlewood to be a measure of the force of interaction between a polar solute and a non-polar solvent/...
Graph 10

Volume Reduced Retention Relative to Squalane
Against Dipole Moments

Log \((r_x*)^{2.9}/(r_x^*)^{0.9}\) vs.

Dipole Moments
GRAPH 1
VOLUME REDUCED RETENTIONS RELATIVE TO SQUALANE AGAINST ALKANE AFFINITY
solvent. In the expression, $M$ is the molecular weight of the solute, and $n$ its refractive index. The data above have been calculated from the refractive indices tabulated in Table 2.2.

A plot of the energy of interaction of the various groups with dinonyl phthalate against dipole moment is presented on Graph 10. It is observed that, with the alcohol excluded, the dipole moment is related to the energy of interaction.

There is no correlation, on the other hand, between Littlewood's factor and interaction energy, as comparison of the columns readily shows.

Beyond the observation that dipole moment is a factor in determining the interaction forces, it is difficult, if not impossible, to make any contribution to an understanding of the forces in solution. The alcohols give abnormally high values due to the formation of hydrogen bonds.

An interesting comparison of behaviours is shown in Graph 11, where the behaviour of the different solute types are compared on the stationary liquids classified according to hydrocarbon retention. It will be remembered that the classification of solvents according to the retention of hexane has been made by Littlewood (28), and has been called here classification according to alkane affinity.

In Graph 9 the liquids are classified according to retentions taken from Littlewood, the only difference being the polyethylene/...
polyethylene glycol which has a molecular weight of 400. As expected, as the alkane affinity of the solvent increases, the force of interaction with a polar solute decreases.

The values of the logarithmic retentions of normal hexane on the liquids are

PEG 400, 0.71; TCP, 1.23; DNP, 1.57; SQ, 1.80.

These values determine the abscissae of the graph, the data in Table 4.17 the ordinates.

This graph illustrates that the general behaviour pattern of hydrocarbons on the solvents holds for polar substances. One interesting reversal in behaviour is the retention of the cyanide and alcohol on PEG. The high retention of the alcohol on PEG is known to be due to hydrogen bonding between the alcohol and ether linkage in the polyethylene glycol.

4.9 The behaviour of diastereoisomers

The work for this thesis began with a study of the separation of diastereoisomers. These are solute pairs in which the members are very similar in chemical and physical properties. Their separation by chemical methods, e.g. distillation, has proved extremely difficult, but GLC is now known as a technique capable of resolving these pairs fairly readily.

The work on the separation of diastereoisomers, in particular the diastereomeric pairs of 2,3 disubstituted butanes, was commenced
because the separation of different 2,3 disubstituted butanes is being studied by Mr. D. Nurok in the same department. The other solutes studied in this thesis were chosen because of their similarity with the 2,3 butanediol derivatives, in the hope that information obtained from their behaviour might facilitate an understanding of the best conditions for the separation of a diastereomeric pair. With the concept of group retention factor now developed it can be hoped to obtain a better understanding of the processes at this stage. A large number of reports on the separation of diastereomeric pairs has already appeared (49 - 52) while Stern et al (53) describe a gas chromatographic method for the preparation of the pure diastereomers of 2,3-dichlorobutane.

In this work, five diastereomeric pairs have been studied and it will be attempted to relate their separation, presented as the separation factor, with their functional types. The five diastereomeric pairs have already been presented in Table 2.2. They are all 2,3-disubstituted butanes with the functional groupings bromide, acetate, alcohol, methyl ether and cyanide. The separation factor, $\alpha$, is defined as the retention of the racemic or dl, isomer relative to that of the meso isomer.

RESULTS

Of the solute pairs chosen, the only ones which could be separated with ease were the bromides, acetates and cyanides.
Meso- and dl- 2,3-dimethoxybutane were partially resolved on the squalane columns at 70°C. The retentions relative to n-heptane at that temperature are:

\[
\begin{align*}
\text{meso} & : 1.43 \\
\text{dl} & : 1.53 \quad \alpha = 1.07
\end{align*}
\]

The two diastereoisomers of 2,3-butanediol, however, could be separated only on polyethylene glycol. At 130°C, the retentions of these isomers relative to heptane are

\[
\begin{align*}
\text{meso} & : 77.6 \\
\text{dl} & : 68.6 \quad \alpha = 0.88(5)
\end{align*}
\]

The other diastereomeric pairs were all resolved without difficulty. The isomers of 2,3-dimethyl succinonitrile in particular were always well separated. As mentioned in Section 2.4, identification of the peaks could not be made with absolute certainty, but in view of the large difference in melting points (meso 45 - 46°C, dl 57 - 59°C) it may reasonably be supposed that the first isomer eluted is the meso form.

On this assumption, the retentions of the three pairs of diastereomers which could be resolved are presented, relative to heptane, in Table 4.18.
TABLE 4.18

RETENTIONS OF DIASTEREOSOMERS RELATIVE TO HEPTANE

<table>
<thead>
<tr>
<th>Solvent</th>
<th>SQ</th>
<th>DNP</th>
<th>TCP</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meso ((\text{CH}_3\text{CHBr})_2)</td>
<td>4.88</td>
<td>7.84</td>
<td>13.3</td>
<td>20.0</td>
</tr>
<tr>
<td>dl((\text{CH}_3\text{CHBr})_2)</td>
<td>5.25</td>
<td>8.50</td>
<td>14.3</td>
<td>21.5</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>1.07(5)</td>
<td>1.08(5)</td>
<td>1.07(5)</td>
<td>1.07(5)</td>
</tr>
<tr>
<td>Meso((\text{CH}_3\text{CHOAc})_2)</td>
<td>7.02</td>
<td>13.7</td>
<td>27.8</td>
<td>46.5</td>
</tr>
<tr>
<td>dl((\text{CH}_3\text{CHOAc})_2)</td>
<td>7.80</td>
<td>15.6</td>
<td>32.2</td>
<td>55.0</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>1.11</td>
<td>1.14</td>
<td>1.16</td>
<td>1.18(5)</td>
</tr>
<tr>
<td>Meso((\text{CH}_3\text{CHCN})_2)</td>
<td>6.55</td>
<td>30.8</td>
<td>78.0</td>
<td>200</td>
</tr>
<tr>
<td>dl((\text{CH}_3\text{CHCN})_2)</td>
<td>9.09</td>
<td>47.2</td>
<td>128</td>
<td>340</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>1.39</td>
<td>1.53(5)</td>
<td>1.64</td>
<td>1.70</td>
</tr>
</tbody>
</table>

From the data in Table 4.18, two graphs can be constructed which illustrate the way in which the different stationary liquids separate diastereoisomers. In Graph 12, the logarithm of the separation factor of the diastereomeric pairs is plotted against the alkane affinity of the stationary liquids. This graph demonstrates that the separation of diastereoisomers increases as the "polarity" of the stationary liquids increases, although in the case of dibromobutane, the separation factor remains constant.

In Graph 13, a plot of \(\log \alpha\) against the group retention factors/...
GROUP RETENTION FACTORS

LEGEND
I 2,3-dicyan butane
II 2,3-butanediol diacetate
III 2,3-dibromobutane

GRAPH 43
SEPARATION FACTORS OF DIASTEROISOMERS
factors is constructed. In this case it is interesting to observe that in the cases of the acetates and cyanides the logarithmic separation factor increases linearly with the group retention factor of the functional groups concerned. The group retention factor thus appears clearly to be the best parameter to consider when choosing a liquid for the separation of diastereoisomers. The liquid with the highest group retention factor for the particular functional groups may be expected to give the best resolution. Once again the bromides are the exceptions and the fact that the separation remains constant in this case suggests that there is no interaction of the functional groups with the liquids; separation being achieved entirely by difference in physical properties, such as molecular structure and vapour pressure. It is unfortunate that the diol and the diether isomers are so similar as to preclude a quantitative comparison of the same sort.

4.10 Variation of group retention factors with temperature

The group retention factor, and volume reduced retentions, it will be remembered from equation 3.9, are inversely proportional to the absolute temperature

\[ \ln r_1 = \frac{1}{RT} \Delta H_E^S(1)(P) \]

The difference in heats of evaporation from solution of the bromides and the acetates have been calculated from the retention data at 100 and 130°C by eliminating R and T, and are presented as Kilo/...
Kilocalories per mole in table 4.19.

### TABLE 4.19

**HEATS OF EVAPORATION FROM SOLUTION AT 100°C AND 130°C, Kcal/mole**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>SQ</th>
<th>DNP</th>
<th>TCP</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°</td>
<td>130°</td>
<td>100°</td>
<td>130°</td>
</tr>
<tr>
<td>BuBr</td>
<td>1.45</td>
<td>1.46</td>
<td>1.71</td>
<td>1.73</td>
</tr>
<tr>
<td>(CH₂Br)₂</td>
<td>2.58</td>
<td>2.61</td>
<td>3.00</td>
<td>3.02</td>
</tr>
<tr>
<td>(CH₃CH₂Br)₂</td>
<td>2.84</td>
<td>2.92</td>
<td>3.46</td>
<td>3.40</td>
</tr>
<tr>
<td>Meso(CH₃CHBr)₂</td>
<td>2.08</td>
<td>2.13</td>
<td>2.48</td>
<td>2.46</td>
</tr>
<tr>
<td>BuOAc</td>
<td>0.85</td>
<td>0.91</td>
<td>1.40</td>
<td>1.27</td>
</tr>
<tr>
<td>(CH₂OAc)₂</td>
<td>1.62</td>
<td>1.69</td>
<td>2.64</td>
<td>2.43</td>
</tr>
<tr>
<td>(CH₂CH₂OAc)₂</td>
<td>1.66</td>
<td>1.82</td>
<td>2.70</td>
<td>2.50</td>
</tr>
<tr>
<td>Meso(CH₃CHOAc)₂</td>
<td>0.55</td>
<td>0.85</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

It was hoped from such a manipulation to detect differences in energies of interaction with the solvent at the different temperatures. Unfortunately, however, the scatter in results is too high to allow this. The use of a temperature-independent term might however be useful in the prediction of retentions at different temperatures. From published energy constants such as those...
those in table 4.19, group retention factors at any desired temperature could be calculated by introducing the RT term.

With more precise measurements it might also be possible to detect the variation of $\Delta H_E^S(P)$ with temperature which would lead to a better understanding of the processes of solution.
SECTION 5

THE SUPPORT

5.1 PART PLAYED BY THE SUPPORT IN GAS LIQUID CHROMATOGRAPHY

It is well known that the support in the gas chromatograph is not inactive, but very often acts as a solvent modifier producing tailing in chromatographic peaks and altering retention times.

A number of authors (11, 54 - 57) have given considerable attention to this problem. Sawyer and Barr (54) have advocated the use of lightly loaded columns. It will be remembered (equation 1.1) that the retention volume is proportional to the volume of stationary liquid on the column, and the main advantage in using a small loading of liquid is that high boiling solutes can be eluted within a reasonable time. For the elution of such high boiling compounds as were used in this study, for example 1,4-butanediol and 1,4-dicyanobutane, on polar liquids it was decided to employ lightly loaded columns in this work.

From the work of Ottenstein (56) who has published a very comprehensive review on gas chromatographic supports, it was realised that even after acid-alkali washing and treatment with dichlorodimethyl silane, chromasorb P is still capable of influencing the retention times of polar solutes.

That the support was not inactive was apparent from the severe /.../
severe tailing shown by some of the chromatographic peaks obtained. Polar solvents, such as polyethylene glycol, are known to be capable of inactivating the support to some extent. The explanation is that a polar liquid of this type interacts with the active sites on the solid which consequently loses the ability of absorbing the solute. PEG 400 has in fact often been used in the past in very small quantities as a subcoating for this purpose.

Non-polar liquids, such as squalane, do not have this property, however, and it is necessary to use heavy loadings in these cases. With more liquid on the support, the active sites are supposed to be effectively covered, and interaction reduced.

To ensure that interaction of the support was not producing incorrect retentions, it was necessary for this work to ensure that the support was inactivated.

5.2 Variation in liquid loading

To determine the smallest percentage of liquid which could safely be used, the variation of retention of a number of small polar molecules with percentage loading of two liquids was studied.

The liquids chosen were polar polyethylene glycol 6000, and slightly polar dinonyl phthalate. The retentions were all obtained relative to n-pentane at 110°C. The use of a normal hydrocarbon as reference solute in such a study is valid, since it is known from the above mentioned references, that non-polar hydrocarbons are not affected/...
affected by the chromatographic support.

The solutes studied were n-butyl bromide, ethyl acetate, ethyl alcohol and acetonitrile, and their retentions on different percentage loadings of dinonyl phthalate are recorded in Table 5.1.

**TABLE 5.1**

**RETENTIONS OF POLAR SOLUTES RELATIVE TO N-PENTANE AS A FUNCTION OF PERCENTAGE LOADING AT 110°C ON DINONYL PHTHALATE**

<table>
<thead>
<tr>
<th>% loading</th>
<th>0</th>
<th>0.58</th>
<th>4.75</th>
<th>10.0</th>
<th>20.0</th>
<th>35.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BuBr</td>
<td>6.55</td>
<td>7.06</td>
<td>8.03</td>
<td>8.43</td>
<td>-</td>
<td>7.80</td>
</tr>
<tr>
<td>EtOAc</td>
<td>29.9</td>
<td>7.70</td>
<td>3.86</td>
<td>3.73</td>
<td>3.28</td>
<td>3.35</td>
</tr>
<tr>
<td>EtOH</td>
<td></td>
<td>12.00</td>
<td>3.34</td>
<td>2.73</td>
<td>1.75</td>
<td>1.77</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>25.4</td>
<td>9.60</td>
<td>3.49</td>
<td>3.12</td>
<td>2.66</td>
<td>2.78</td>
</tr>
</tbody>
</table>

* not eluted

In Table 5.2, retentions are studied as a function of percentage loading of PEG 6000.
GRAPH 14.

RETENTIONS OF POLAR SOLUTES RELATIVE TO PENTANE
AT 110°C ON DIMETHYL PHthalate.

LEGEND

I  Bu Br
II  Et OAc
III  CH₃CN
IV  Et OH

Log r₅

PERCENTAGE DNP
GRAPH 15

RETENTIONS OF POLAR SOLUTES RELATIVE TO PENTANE
AT 110°C ON POLYSTYRENE GLYCOL

LEGEND
I CH₃CN
II BuBr
III EtOH
IV EtOAc

PERCENTAGE PEG 6000
TABLE 5.2

RETENTIONS OF POLAR SOLUTES RELATIVE TO N-PENTANE AS A
FUNCTION OF PERCENTAGE LOADING AT 110°C ON PEG 6000.

<table>
<thead>
<tr>
<th>% loading</th>
<th>0</th>
<th>2</th>
<th>5</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BuBr</td>
<td>6.55</td>
<td>5.08</td>
<td>7.23</td>
<td>7.72</td>
</tr>
<tr>
<td>EtOAc</td>
<td>29.9</td>
<td>5.33</td>
<td>4.63</td>
<td>5.06</td>
</tr>
<tr>
<td>EtOH</td>
<td>*</td>
<td>9.98</td>
<td>5.50</td>
<td>5.84</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>25.4</td>
<td>9.20</td>
<td>8.53</td>
<td>9.87</td>
</tr>
</tbody>
</table>

* not eluted

The same procedure was employed to obtain these retentions as previously, except that the column dead volume was estimated by the "coal gas" technique.

These retentions are plotted in the logarithmic form against percentage loading in graphs 14 and 15.

With the exception of butyl bromide, which exhibits slightly smaller retention times on the more lightly loaded columns, a sharp increase in the retentions of polar compounds is observed as the percentage loading approaches zero. The increase appears to begin at about 5% on the DNP Column, and
at about 2 - 3\% on PEG.

These curves have been the basis of the choice of loading used for the columns in this work. A 5\% w/w loading was considered a safe weight for the liquids DNP, TCP and PEG. For less polar squalane, a 20\% loading was employed. Fortunately the use of a lightly loaded column is not required in this latter case, since on a non-polar column polar liquids have small retentions and no difficulty is experienced in eluting even high boilers.

5.3 Inactivation of the support

(i) Precoating with polyethylene glycol

As has been mentioned, PEG 400 in small amounts has been used in the past to inactivate the support, and reduce tailing. The possibility of using this technique was considered, and a column containing 0.5\% PEG 400 and 5\% DNP was prepared. Although tailing was reduced, this method could not be used since the PEG altered the retentions of the solutes, as comparison with a pure DNP column in table 5.3 shows.
Table 5.3

**Effect on Retention Times of Precoating with PEG 400**

(retentions relative to heptane at 130°C)

<table>
<thead>
<tr>
<th>Solute</th>
<th>Column</th>
<th>5% DNP</th>
<th>5% DNP + 0.5% PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuBr</td>
<td>1.86</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>(CH₂Br)₂</td>
<td>4.10</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>(CH₂CH₂Br)₂</td>
<td>23.6</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td>Meso(CH₃CHBr)₂</td>
<td>7.84</td>
<td>8.64</td>
<td></td>
</tr>
<tr>
<td>BuOAc</td>
<td>2.60</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>(CH₂OAc)₂</td>
<td>11.7</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>(CH₂CH₂OAc)₂</td>
<td>46.2</td>
<td>48.3</td>
<td></td>
</tr>
<tr>
<td>Meso(CH₃CHOAc)₂</td>
<td>13.6</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>BuOH</td>
<td>1.56</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>(CH₂OH)₂</td>
<td>3.98</td>
<td>33.1</td>
<td></td>
</tr>
<tr>
<td>(CH₂CH₂OH)₂</td>
<td>21.6</td>
<td>36.6</td>
<td></td>
</tr>
<tr>
<td>Meso(CH₃CHOH)₂</td>
<td>6.57</td>
<td>11.1</td>
<td></td>
</tr>
</tbody>
</table>

The effect is particularly pronounced in the case of the alcohols.

(ii) **Prior injection of water**

Some authors (see 56) have advocated saturation of the carrier gas with amines or water to reduce tailing effects. To
test these suggestions, 50μl water samples were injected into the carrier stream immediately prior to injection of a compound which normally gives tailing, on the TCP column. Since a flame ionisation detector was employed, no interference with the solute peak occurred. This method was not successful, however, and no reduction in tailing was obtained.

5.4 Tailing chart

Table 5.4 is a semi-quantitative representation of the peak shapes of the various solutes when chromatographed on the different columns at 130°C. This is presented here only as a guide to anyone who may wish to chromatograph the same solutes on the same or similar columns, and also as an indication of the cases in which the column was inactive, and when the column itself may have influenced the retentions recorded in the preceding tables.

The numbers assigned to each case describe the peak shape.

1 : An asymmetric peak with a leading slope, a "tail" coming before rather than after the peak.

2 : A symmetrical peak. This is the desired case. Hydrocarbons, which are not included on the chart all give symmetrical peaks on all the columns.

3/...
3: A symmetrical peak with a very slight tail.

4: In this case the tailing is quite pronounced, but the peak is still sharp and well defined.

5: Very severe tailing, the peak position is uncertain.

**TABLE 5.4**

**TAILING CHART**

<table>
<thead>
<tr>
<th>Solute columns</th>
<th>BuBr</th>
<th>(CH₂Br₂)₂</th>
<th>(CH₂CH₂Br)₂</th>
<th>BiOAc</th>
<th>(CH₂CH₂OAc)₂</th>
<th>BuOH</th>
<th>(CH₂CH₂OH)₂</th>
<th>(CH₂COH)₂</th>
<th>BuOCH₃</th>
<th>(CH₂COH₂)₂</th>
<th>(CH₃CHOH₂)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% SQ</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5% DNP</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5% DNP + 0.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5% TCP</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>5% PEG</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

The table shows that most tailing is observed with the alcohol peaks, while with the others there is little or no tailing on the columns employed.

References/...
REFERENCES

42. Kovats E.; ibid 1959, 42, 2709.
44. Littlewood A.B., J. Gas Chromatog. May 1963, 1, 8.