THE DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION USING GAS LIQUID CHROMATOGRAPHY

Submitted in partial fulfilment of the requirements for the degree of Master in Science in the department of Chemistry, University of Natal.

by

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I hereby certify that this research is the result of my own investigation, which has not already been accepted in substance for any degree, and is not being concurrently submitted for any other degree.

I hereby certify that the above statement is correct.

signed: ........................................

Prof. T.M. Letcher
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ABSTRACT

The aim of this investigation was to develop and test a theory that allowed for the calculation of the activity coefficients at infinite dilutions \( (\gamma^\infty) \) from G.L.C. measurements using moderately volatile solvents. The solvents chosen for study were straight chained \((C_5 \text{ to } C_7)\) and cyclic \((C_5, C_6 \text{ and benzene})\) liquid hydrocarbons using cis- and trans-decahydronaphthalene (decalin) as the stationary liquid phase (solvent). The systems were studied at two different temperatures, 283.15 K and 298.15 K. The solutes were n-pentane, n-hexane, n-heptane, cyclopentane, cyclohexane and benzene. This method for the determination of activity coefficients has the advantage of being able to work at infinite dilution, whereas in other techniques, extrapolation to infinite dilution of finite-concentration data is necessary. In addition solutes are separated from impurities when chromatographed so that only very small quantities of moderately pure material need be used. However the technique is also limited since the solute studied (injected reagent) needs to be volatile, while the solvent (liquid stationary phase) should be involatile. The solvents chosen in this experiment (cis- and trans-decalin) are moderately volatile which introduces many limitations since the theory developed for the determination of activity coefficients at infinite dilution is restricted to involatile solvents. However a novel method for working with moderately volatile solvents is developed by relating the loss of solvent to its partial pressure and modifying the existing theory. In the past the use of precolumns and/or saturators, coarse packing, small pressure gradients, and internal standards were used when working with volatile solvents. However employing this new method excludes the use of precolumns, saturators, or internal standards, and allows any type of packing and pressure gradient to be used.

The calculated activity coefficients are compared with literature values, where the workers employed G.L.C. techniques, and with predicted values. The activity coefficients calculated at both temperatures are used in the calculation of excess partial molar enthalpies. These results are compared with values obtained from finite concentration data by other workers.
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APPENDIX I
1. INTRODUCTION

The aim of this investigation is to develop and test a theory that allowed for the calculation of activity coefficients at infinite dilution ($\gamma_{13}^\infty$), from gas liquid chromatography measurements using moderately volatile solvents (liquid stationary phase).

Activity coefficients at infinite dilution are macroscopic quantities related to interaction between molecules and are a measure of solution non-ideality. They are useful in analytical chemistry for the selection of suitable stationary phases for difficult separations and in chemical engineering for the design of separation processes.

Gas chromatography is an analytical method based on differences in free energy of the solute distributed between a static phase (usually of great surface area), and a moving gas phase. Simple physico-chemical considerations can be applied to the technique resulting in an equation from which the activity coefficient of the solute at infinite dilution ($\gamma_{13}^\infty$), can be calculated. However the theory developed by Everett(1) and Cruickshank(2) can only be used to calculate $\gamma_{13}^\infty$ for systems that have volatile solutes and involatile solvents, and that do not show a Gibbs adsorption effect at the solvent surface. Their equation is (see chapter 2)

$$\ln \gamma_{13}^\infty = \ln \frac{n_3RT}{V_N P_1^*} - \frac{(B_{11} - V_1^*)}{RT} P_1^* + \frac{(2B_{12} - V_1^*)}{RT} J_3 P_O^2$$  \hspace{1cm} (1.1)

where $V_N$ is the net retention volume, $P_O$ the outlet pressure, $J_3 P_O$ the mean column pressure, $n_3$ is the amount of liquid solvent on the column, $T$ the column temperature, $P_1^*$ the saturated vapour pressure of the solute at temperature $T$, $B_{11}$ the second virial
coefficient of the pure solute, $V_1^*$ the molar volume of the solute as a liquid, $V_1^{\infty}$ the partial molar volume of the solute at infinite dilution in the solvent, and $B_{12}$ the mixed second virial coefficient of the solute and carrier gas. In this thesis the subscripts 1, 2 and 3 refer to the solute, carrier gas and solvent respectively.

Much work has been conducted using this technique to determine $\gamma_{13}^{\infty}$ by Cruickshank(3), Letcher(4), Young(5), Everett(1), and other researchers. The method has the obvious advantage of speed and also producing an accurate activity coefficient at infinite dilution using only moderately pure solutes. However the technique does suffer from several limitations. The most important being that the solvent must be sufficiently involatile to prevent it from evaporating off the column.

In this work the range of systems which can be studied have been extended to include solvents of moderate volatility. The theory has been modified to take this into account. Simple physico-chemical considerations result in a new equation(6) that relates the amount of solvent lost to its partial pressure ($P_3^*$). (see chapter 2)

\[
\frac{V_N}{n_3 e^c} = \frac{RT}{\gamma_{13}^{\infty} P_1^*} - \frac{U_{ij}^*}{n_3} \left[ \frac{P_3^*}{\gamma_{13}^{\infty} P_1^*} \right]
\]  

(1.2)

where

\[
C = - \left[ \frac{B_{11}}{RT} \right] P_1^* + \left[ \frac{2B_{12}}{RT} \right] P_3^* J^2
\]  

(1.3)
1. INTRODUCTION

$U_0$ is the volumetric flow rate corrected for temperature and the presence of water
vapour and $t$ is the time of the injection of the solute on to the column.
The activity coefficient at infinite dilution was determined at two temperatures,
283.15 K and 298.15 K for solutes n-pentane, cyclopentane, n-hexane, cyclohexane,
benzene and n-heptane using cis- and trans-decahydronaphthalene as the solvents. The
isomers cis- and trans-decahydronaphthalene were chosen because of their moderate
volatility. Also they provided a change from previous systems studied by replacing the
normally straight chain stationary phase with a planar, bicyclic nonlinear hydrocarbon.

In order to calculate $\gamma^\circ_{13}$, a gas liquid chromatograph was built along the lines of
that described by the Bristol group\cite{7-9}. A detailed theory of gas liquid chromatography
and the modifications to accommodate moderately volatile solvents is given in chapter
2. The apparatus used, the experimental procedure and the measurements obtained
from them are described in chapters 3 and 4. Finally in chapter 5 the results obtained
are discussed and compared with results obtained by other workers using similar
methods. The activity coefficients at the two temperatures were then used to calculate
the partial molar excess enthalpies of the solutes, and the results compared with data
obtained from enthalpy measurements by other workers.
2. THEORY OF GAS LIQUID CHROMATOGRAPHY

2.1. Gas Chromatography Principles

The chromatographic process involves the distribution of a solute component between two phases, a mobile phase and a stationary phase. The two phases are mutually well dispersed with a large area of contact. In G.L.C. the liquid stationary phase (e.g. hexadecane) is dispersed on an inert solid support, such as celite, which is packed into the column. The liquid is held on the surface and in the pores of the support, while the a stream of inert gas, the mobile phase, flows continuously through the spaces between the particles.\(^{(10)}\)

In the elution process a small quantity of solute is introduced into the column at the inlet. The solute zone or peak is carried through the column by the mobile phase and its emergence at the other end is observed by a suitable detector, in this case a thermal conductivity detector. The velocity with which the peak travels through the column is less than that of the mobile phase and depends on the distribution coefficient of solute between the two phases.\(^{(10)}\)

When the solute reaches the column, an equilibrium is set up between the liquid phase and the carrier gas phase so that a proportion of the sample always remains in the gas phase. This portion moves a little further along the column in the carrier gas stream, where it again equilibrates with the stationary phase. At the same time, material already dissolved in the stationary phase re-enters the gas phase so as to restore equilibrium with the clean carrier gas, which follows the zone of vapour.\(^{(11)}\)

This process in which carrier gas containing the vapour is stripped by the solvent in front of the zone, while vapour enters carrier gas at the rear of the zone, goes on
continuously with the result that the zone of vapour moves along the column more or less compactly.

The speed at which the zone moves depends mainly on two factors, the rate of flow of the carrier gas and the partition coefficient of the solute between carrier gas and liquid phase. The faster the flow of carrier gas the faster the zone moves; and the more strongly the vapour is adsorbed on to the solvent, the more slowly the zone moves. When two or more components are present in the sample, each usually behaves independently of the other, so that for a given carrier gas flow rate, the speed of the zone of each component will depend on the extent to which it is adsorbed. Since different substances differ in their adsorption, they may therefore be separated by making use of their different speeds of progress through the column. When eluted the solutes will appear one after the other in the gas stream, the fastest first and the slowest last.

2.1.1. Assumptions

The theory for the determination of activity coefficients at infinite dilution rests on the following assumptions.\(^{(12)}\)

(i) The column can be divided into a large number of theoretical plates.

(ii) The partition coefficient is constant throughout the range of concentration encountered, that is, Henry's Law is obeyed. This is only true for very low solute concentration.

(iii) The solute volume upon introduction into the column occupies only a small portion of the column length.

(iv) There is negligible resistance to mass transfer from gas to solvent i.e. the rate at which equilibrium is reached is very much greater than the rate of travel of solute down the column.
2.2. Summary of the G.L.C. Theory for $\gamma_{13}^\infty$

In 1941 Martin and Purnell\(^{(13)}\) related the equilibrium partition coefficient, $K_R$, to retardation properties using a plate theory, whereby they related the retention volume of the solute, $V_R$, to the gas hold up volume, $V_G$, and the solvent volume, $V_3$ (for zero pressure difference across the column).

$$V_R = V_G + K_R V_3$$  \hspace{1cm} (2.1)

In 1952 James and Martin\(^{(14)}\) took into account the compressibility of the mobile phase by using a correction factor which according to Everett's notation can be generalized as

$$J_n^m = \frac{n (P_i/P_o)^m - 1}{m (P_i/P_o)^n - 1}$$  \hspace{1cm} (2.2)

where $P_i$ is the inlet pressure and $P_O$ the outlet pressure.

In 1956 Porter\(^{(15)}\) related the net retention volume, $V_N$, to the activity coefficient of the solute at infinite dilution, $\gamma_{13}^\infty$, by

$$V_N = \frac{n_3RT}{\gamma_{13}^\infty P_1^*}$$  \hspace{1cm} (2.3)

where $n_3$ is the amount of solvent on the column and $P_1^*$ the vapour pressure of the solute. The net retention volume is obtained from the outlet flow rate $U_O$ using
2. THEORY OF G.L.C.

2.2. Summary of the Theory of G.L.C.

where \( t_R \) and \( t_D \) are the retention times for the solute and an unretained gas respectively, and \( V_D \) is the dead space volume. By taking into account imperfections of the solute vapour and the solute carrier gas, the net retention volume \( (V_N) \) can be calculated by extrapolating \( \ln V_N \) to \( P_O = 0 \) using (16)

\[
\ln V_N = \ln V_N^0 + \beta P_O J_3^2
\]  \hspace{1cm} (2.5)

where

\[
\beta = \frac{2B_{12} - V_1^\infty}{RT}
\]  \hspace{1cm} (2.6)

in which \( B_{12} \) is the mixed second virial coefficient of the solute vapour in the carrier gas and \( V_1^\infty \) is the partial molar volume of the solute at infinite dilution in the solvent. The activity coefficient of the solute at infinite dilution in the solvent \( \gamma_{13}^\infty \) is related to \( V_N^0 \) by the equation (7)

\[
\ln V_N^0 = \frac{n_3RT}{\gamma_{13}^\infty P_1^*} - \frac{B_{11} - V_1^*}{RT} P_1^*
\]  \hspace{1cm} (2.7)

where \( V_1^* \) is the molar volume of the pure solute, and \( B_{11} \) is the second virial coefficient of the pure solute vapour.
2. THEORY OF G.L.C.

2.2. Summary of the Theory of G.L.C.

The Bristol group\(^{(7-9)}\) took into account carrier gas imperfection and suggested a different extrapolation technique for ideal gases

\[ \ln V_N = \ln V_N^0 + \beta P_1 J_3^4 \]  

(2.8)

2.3. Detailed Theory of G.L.C.

2.3.1. The Theoretical Plate Concept

In the theoretical plate model, the column is regarded as divided up into large number of theoretical plates small enough so that the concentration of sample in both mobile and stationary phases can be regarded as uniform. Each plate consists of two volumes, i.e. the volume of free gas \((\Delta V_G)\) and of liquid \((\Delta V_L)\); the sum of the volumes being the total plate volume \(\Delta x\), thus

\[ \Delta x = \Delta V_G + \Delta V_L \]  

(2.9)

The solute sample in the first theoretical plate is distributed between the stationary and mobile phases according to a partition coefficient, such that at equilibrium a fraction \(z\) of solute exists in the gas phase and a fraction \(y\) in the liquid phase.\(^{(17)}\)

If \(r\) volumes of carrier gas is passed through the column and we designate the number of any plate by \(N\), the quantity of solute in the \((N + 1)\)th plate can be shown to be: (APPENDIX 2)
2. THEORY OF G.L.C.
2.2.1. The Theoretical Plate Model

\[ Q_{N+1} = \frac{r! (y)^{r-N} (z)^N}{N! (r-N)!} \]  (2.10)

In order to have some measure of the rate of movement of a solute through a column, the maximum of the distribution curve is chosen as a reference point. Assuming that the \((N + 1)^{th}\) plate contains more solute than any other plate after \(r\) volumes of \(\Delta V_G\) have passed, this would mean that this plate contains more solute than when \((r-1)\) or \((r+1)\) volumes have passed.\(^{(18)}\)

Thus we require

\[ Q(r) > Q(r - 1) \]  (2.11)

and

\[ Q(r) > Q(r + 1) \]  (2.12)

simultaneously

If \(Q(r) > Q(r-1)\) then

\[ \frac{r! y^{(r-N)} z^N}{N! (r-N)!} > \frac{(r-1)! y^{(r-N-1)} z^N}{N! (r-N-1)!} \]  (2.13)

ie

\[ \frac{ry}{r - N} > y^{-1} \]  (2.14)

But

\[ y = 1 - z \]  (2.15)

Hence (2.14) becomes

\[ r (1 - z) > r - N \]  (2.16)
2. THEORY OF G.L.C.

2.2.1. The Theoretical Plate Model

Similarly

\[ Q(r) > Q(r+1) \rightarrow N < (r + 1)z \]  \hspace{1cm} (2.18)

Therefore to all intents and purposes for \( Q_{\text{max}} \)

\[ N = rz \]  \hspace{1cm} (2.19)

The fraction of solute in the gas phase in any plate is given by

\[ z = \frac{C_G \Delta V_G}{C_G \Delta V_G + C_L \Delta V_L} \]  \hspace{1cm} (2.20)

where \( C_G \) is the solute concentration in the gas and \( C_L \) is the solute concentration in the liquid. If the solute partition coefficient \( K_R \) is given by

\[ K_R = \frac{C_L}{C_G} \]  \hspace{1cm} (2.21)

\[ \rightarrow z = \frac{\Delta V_G}{\Delta V_G + K_R \Delta V_L} \]  \hspace{1cm} (2.22)

Equation 2.19 states that the maximum of an elution curve is found in the \((N+1)^{\text{th}}\)
2. THEORY OF G.L.C.
2.2.1. The Theoretical Plate Model

plate, where \( N = rz \), hence if the \((N+1)\)th plate is taken to be the detector system, \( N \) is therefore the total number of plates in the column and \( r \Delta V_G \) is the peak retention volume of the solute.

\[ \Rightarrow \quad V'_R = r \Delta V_G \quad (2.23) \]

Hence

\[ \Rightarrow \quad V'_R = N(\Delta V_G + K_R \Delta V_L) \quad (2.24) \]

where \( V'_R \) is the apparent retention volume.

If \( N \Delta V_G = V'_D \), the total free, or dead space in the column, and \( N \Delta V_L \) the total volume of solute we get the retention volume equation

\[ V_R = V'_R - V'_D \quad (2.25) \]

where \( V_R \) is the true retention volume.

This is the basic equation of gas chromatography and is of considerable theoretical importance since it connects the thermodynamic quantity \( K_R \) with column parameters.

2.3.2. Relation of the Net Retention Volume and the Activity Coefficient to the Partition Coefficient

The distribution of a solute between stationary phase \((L)\) and mobile phase, at constant temperature and pressure corresponds to equilibrium when the solute free energy is a minimum.\(^{19}\) Its chemical potential in one phase is then equal to that in the other phase.
Thus

\[ \mu_L = \mu_G \]  \hspace{1cm} (2.26)

where

\[ \mu_i = \mu_i^0 + RT \ln a_i \]  \hspace{1cm} (2.27)

\( a_i \) being the solute activity in the \( i \)th phase and \( \mu_i^0 \) is the solute chemical potential at some unit activity.

Approximating for the moment that activities can be replaced by concentration

\[ \mu_i^0 + RT \ln C_L = \mu_G^0 + RT \ln C_G \]  \hspace{1cm} (2.28)

\[ \frac{C_L}{C_G} = \exp\left(\frac{\Delta \mu^0}{RT}\right) = K_R \]  \hspace{1cm} (2.29)

\( K_R \) being the solute partition coefficient.

When the solute is dissolved in or adsorbed on the stationary phase, it is assumed to be immobile; movement occurs only when the solute vaporizes and is carried down the column by the mobile phase. (19)

The linear rate of travel is therefore equal to the average carrier velocity \( \bar{u} \) multiplied by the fraction of time the solute spends in the mobile phase.
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2.2.2. Relation of $V_N$ and $V_{13}$ to $K_R$

\[
rate\ of\ travel = \bar{u} \left[ \frac{C_G V_G}{C_G V_G + C_L V_L} \right] \quad (2.30)
\]

$V_G$ being the mobile phase volume and $V_L$ being the stationary phase volume.

\[
rate\ of\ travel = \bar{u} \ [1 + \frac{C_L V_L}{C_G V_G}]^{-1} \quad (2.31)
\]

\[
= \bar{u} \ [1 + K_R \frac{V_L}{V_G}]^{-1} \quad (2.32)
\]

since $C_L/C_G = K_R$

Alternatively

\[
rate\ of\ travel = \frac{L}{u} \ [1 + K_R \frac{V_L}{V_G}] \quad (2.33)\]

\[
t_R = \frac{L}{u} \ [1 + K_R \frac{V_L}{V_G}] \quad (2.34)
\]

The quantity $L/\bar{u}$ is just $t_D$, the (dead) time a nonsorbed ($K_R = 0$) solute requires to pass through the column.

\[
t_R = t_D \ (1 + K_R \frac{V_L}{V_G}) \quad (2.35)
\]

To convert retention times to gas volumes the flow rate of the mobile phase generally measured at the column outlet, must be known. The measured flow rate ($U_C$) must
therefore be corrected to the conditions prevailing in the column; that is

\[ U_O = U_C \left( \frac{T}{T_{fm}} \right) \left( \frac{P_{fm} - P_w}{P_{fm}} \right) \]  \hspace{1cm} (2.36)

where \( T \) is the column temperature, \( T_{fm} \) is the flowmeter temperature, \( P_{fm} \) is the flowmeter vapour pressure at \( T_{fm} \), \( P_w \) is the water vapour pressure at \( T_{fm} \). The dead (\( V_D' \)) and retention (\( V_R \)) volumes are now given by

\[ V_D' = t_D U_O \]  \hspace{1cm} (2.37)

\[ V_R' = t_R U_O \]  \hspace{1cm} (2.38)

\[ \Rightarrow V_R' = V_D' \left( 1 + K_R \frac{V_L}{V_G} \right) \]  \hspace{1cm} (2.39)

by substituting eq.2.37 and 2.38 into eq.2.35

From eq.2.25

\[ V_R = V_R' - V_D' = U_O (t_R - t_D) \]  \hspace{1cm} (2.40)

In order for a mobile phase to flow through a column a pressure gradient must exist. This necessitates the introduction of a gas compression factor, as first recognized by James and Martin \(^{(14)}\) in 1952.

Consider a carrier gas flowing through a packed column of uniform cross section \( A \) at a pressure \( P \), and velocity \( u \). The volume throughout must be constant within the
column so that by Boyles law, \(^{20}\)

\[ Pu = P_o \bar{u} = \bar{P} \bar{u} \quad (2.41) \]

where \( \bar{P} \) is the average pressure, \( P_o \) the outlet pressure, \( \bar{u} \) the average velocity and \( u_o \) the outlet velocity. The velocity at any given point is given by

\[ u = \frac{P_o \bar{u}}{P} \quad (2.42) \]

The velocity can also be related to the pressure gradient \( dp \) within a length \( dx \) along the column, the column specific permeability coefficient \( K \), porosity \( e \) and gas viscosity, through Darcy’s law\(^{20}\)

\[ u = \frac{K dP}{\eta dx} \quad (2.43) \]

\[ \Rightarrow \frac{P_o \bar{u}}{P} = \frac{K dP}{e \eta dx} \quad (2.44) \]

\[ \Rightarrow dx = \left[ -\frac{K}{e \eta u_o P_o} \right] P dP \quad (2.45) \]

Multiplying by \( P \)

\[ P dx = \left[ -\frac{K}{e \eta u_o P_o} \right] P^2 dP \quad (2.46) \]
The average value of a continuous function $F(x)$ is

$$
\bar{F}(x) = \frac{\int F(x)dx}{\int dx}
$$

(2.47)

$$
\bar{P} = \frac{\int (-\frac{K}{e\eta u_o P_o})P^2dP}{\int (-\frac{K}{e\eta u_o P_o})PdP}
$$

(2.48)

$\bar{P}$ being the average pressure over the column. Integrating over the column pressure gradient, which is bounded by the inlet $(P_i)$ and outlet $(P_o)$ pressure

$$
\bar{P} = \frac{2}{3} \frac{(P_i^3 - P_o^3)}{(P_i^2 - P_o^2)}
$$

(2.49)

$$
\frac{\bar{P}}{P_o} = \frac{2}{3} \frac{\left(\frac{P_i}{P_o}\right)^3 - 1}{\left(\frac{P_i}{P_o}\right)^2 - 1}
$$

(2.50)

Since $\frac{\bar{P}}{P_o} = \bar{V}/V_o$
2. THE THEORY OF G.L.C.

2.2.2. Relation of $V_N$ and $\gamma_{13}$ to $K_R$

\[ \bar{V} = \frac{3}{2} V_O \left[ \frac{\frac{P}{P_O}}{\frac{P}{P_O}} - 1 \right] = J V_O \quad (2.51) \]

\[ J = \frac{3}{2} \left[ \frac{\frac{P}{P_O}}{\frac{P}{P_O}} - 1 \right] \quad (2.52) \]

Gas volumes measured at the column outlet can therefore be corrected to the average column pressure by multiplying by the fraction $\bar{V}/V_O$ which is given by the symbol $J$. Everett (1) suggested that the compressibility correction can be represented as

\[ J_n^m = \frac{n}{m} \left[ \frac{\frac{P}{P_O}}{\frac{P}{P_O}} - 1 \right] \quad (2.53) \]

The fully corrected dead volume is given by $V_D = J_3^2 V'_D$

Therefore from eq.2.39

\[ J_3^2 V'_R = V_D (1 + K_R \frac{V_L}{V_G}) \quad (2.54) \]

The term $J_3^2 V'_R$ is given the symbol $V'_R$ and is referred to as the corrected retention
2. THE THEORY OF G.L.C.

2.2.2. Relation of $V_N$ and $\gamma_{13}^\infty$ to $K_R$

volume\(^1\).

Since $V_D = V_G$

$$V_R^o = V_D + K_R V_L$$  \hspace{1cm} (2.55)

The product $K_R V_L = V_N$, the net retention volume. Therefore

$$V_N = J_2^2 V_R^l = V_R^o - V_D = K_R V_L$$

$$= U (t_G - t_R)$$  \hspace{1cm} (2.56)

The solute partial pressure over its infinitely dilute solution (Henry law region) in the liquid phase is

$$P_1 = \gamma_{13}^\infty x_1^L P_1^*$$  \hspace{1cm} (2.57)

where $\gamma_{13}^\infty$ is the activity coefficient at infinite dilution and $P_1^*$ is the saturated vapour pressure of the solute.

Recognizing that $x_1^L = n_1^L/n_3$\(^{19}\)

where $x_1^L$ is the solute mole fraction in the liquid phase, $n_1^L$ is the solute molar amount, and $n_3$ is the liquid phase molar amount.

$$\Rightarrow \quad P_1 = \gamma_{13}^\infty P_1^* \frac{n_1^L}{n_3}$$  \hspace{1cm} (2.58)

Dividing by $V_L$
2. THE THEORY OF G.L.C.

2.2.2. Relation of \( V_{13} \) and \( \gamma_{13}^\infty \) to \( K_R \)

\[
\frac{P_1}{V_L} = \frac{\gamma_{13}^\infty P_1^* n_1}{n_3} \quad \text{(2.59)}
\]

\[
= \frac{n_1^L}{V_L} = \frac{n_3 P_1}{\gamma_{13}^\infty P_1^* V_L} \quad \text{(2.60)}
\]

where \( P_1 \) is the solute partial vapour pressure and \( P_1^* \) is the solute saturation vapour pressure.

For ideal gases

\[
\frac{n_1^G}{V_G} = \frac{P_1}{RT} \quad \text{(2.62)}
\]

and

\[
K_R = \frac{(n_1^L V_G)}{(n_1^G V_L)} \quad \text{(2.62)}
\]

From eq.(2.60)

\[
\frac{n_1^L}{V_L} = \frac{n_3 P_1}{\gamma_{13}^\infty P_1^* V_L} \quad \text{(2.63)}
\]

and from eq.(2.61)
2. THE THEORY OF G.L.C.  

2.2.2. Relation of $V_N$ and $\gamma_{13}^\infty$ to $K_R$

Substituting into eq. (2.62)

$$K_R = \frac{n_3 P_1}{\gamma_{13}^\infty P_1^*} \frac{V_G}{V_L} / \left[ \frac{P_1 V_G}{RT} V_L \right] \quad (2.65)$$

$$K_R = \frac{n_L P_1}{\gamma_{13}^\infty P_1^*} \frac{RT}{P_1 V_G V_L} \quad (2.66)$$

$$\therefore K_R = \frac{RT}{\gamma_{13}^\infty P_1^* \bar{V}_L} \quad \text{since} \quad \frac{n_3}{V_L} = \bar{V}_L \quad (2.67)$$

where $\bar{V}_L$ is the molar volume of the liquid stationary phase

Mass of stationary phase ($W_L$)

$$n_3 = \frac{W_L}{M_L \bar{V}_L} \quad (2.68)$$

Molar mass of stationary phase ($M_L$)

$$K_R = \frac{W_L RT}{\gamma_{13}^\infty P_1^* M_L \bar{V}_L} \quad (2.69)$$
2. THE THEORY OF G.L.C.
2.2.2. Relation of $V_N$ and $\gamma_{13}^\infty$ to $K_R$

\[ K_R = \frac{n_3 RT}{V_L \gamma_{13}^\infty P_1^*} \quad (2.70) \]

\[ K_R V_L = \frac{n_3 RT}{\gamma_{13}^\infty P_1^*} \quad (2.71) \]

But

\[ K_R V_L = V_N \quad (2.72) \]

\[ V_N = \frac{n_3 RT}{\gamma_{13}^\infty P_1^*} \quad (2.73) \]
2. THEORY OF G.L.C.

2.3.3. The Pressure Dependence of $K_R$

2.3.3. The Pressure Dependence of the Partition Coefficient

The partition coefficient at infinite dilution, $K_R$, in a static system can be defined as

$$K_R = \lim_{x_i \to 0} \frac{n_i^L V_G}{V_L n_i^G}$$  \hspace{1cm} (2.74)

where $n_i^L$ is the number of mols of 1 in volume $V_L$ of liquid and $n_i^G$ is the number of mols of 1 in volume $V_G$ of gas. But $n^G = y_i n^G$ and $n_i^L = x_i n_i^L$ where $n^G$ is the total number of mols of gas (solute + carrier gas) in volume, $V_G$, of carrier gas, $n^L$ is the total number of mols of liquid (solute + solvent) in $V_L$, $y_i$ is the mole fraction of 1 in the gas, and $x_i$ is the mole fraction of 1 in liquid.

$$K_R = \lim_{x_i \to 0} \frac{x_i n_i^L}{V_L} \cdot \frac{V_G}{y_i n_i^G}$$  \hspace{1cm} (2.75)

$$K_R = \lim_{x_i \to 0} \frac{x_i n_i^L}{V_L y_i} V_G^n$$  \hspace{1cm} (2.76)

where $V_G^n$ is the molar volume in the gas phase.

In the limit of infinite dilution of the solute (1) in gas phase (2)
2. THEORY OF G.L.C.

2.3.3. The Pressure Dependence of \( K_R \)

\[
V_G^m = \frac{RT}{P} + B_{22} + \frac{C_{222} - B_{22}^2}{RT} P \tag{2.77}
\]

where \( P \) is the carrier gas pressure, \( B_{22} \) is the second virial coefficient of carrier gas and \( C_{222} \) is the third virial coefficient of the carrier gas.

\[
\Rightarrow K_R = \lim_{x \to 0} \frac{x_1 n_3}{V_L y_1} \frac{RT}{P} \left[ 1 + \frac{B_{22} P}{RT} + \frac{(C_{222} - B_{22}^2)}{(RT)^2} P^2 + \ldots \right] \tag{2.78}
\]

where \( n_3 = n^L \)

Now since \( y_1 P = P_1 \) (partial pressure),

\[
K_R = \lim_{x \to 0} \frac{x_1 n_3 RT}{V_L P_1} \left[ 1 + \frac{B_{22} P}{RT} + \frac{(C_{222} + B_{22}^2)}{(RT)^2} P^2 + \ldots \right] \tag{2.79}
\]

\[
\Rightarrow \lim_{x \to 0} \frac{P_1}{x_1} = \frac{n_3 RT}{V_L K_R} \left[ 1 + \frac{B_{22} P}{RT} + \frac{C_{222} - B_{22}^2}{(RT)^2} P^2 + \ldots \right] \tag{2.81}
\]

multiplying by \( 1/P_1^2 \)
2. THEORY OF G.L.C.

2.3.3. The Pressure Dependence of $K_R$

\[
\lim_{x \to 0} \frac{P_1}{x_1P_i} = \frac{n_3RT}{V_LK_RP_L} \left[ 1 + \frac{B_{22}P}{RT} + \frac{(C_{222} - B_{22}^2)P^2}{(RT)^2} + \ldots \right] \quad (2.82)
\]

But

\[
\gamma_{13}^\infty(T,P) = \lim_{x \to 0} \frac{P_1}{P_i^*x_i} \quad (2.83)
\]

\[
\therefore \gamma_{13}^\infty(T,P) = \frac{n_3RT}{V_LK_RP_L^*} \left[ 1 + \frac{B_{22}P}{RT} \right] + \frac{(C_{222} - B_{22}^2)P^2}{(RT)^2} + \ldots \quad (2.84)
\]

It can be shown that $\gamma_{13}^\infty(T,P)$ is related to the activity coefficient at zero pressure and infinite dilution $\gamma_{13}^\infty(T,0)$ by

\[
\ln \gamma_{13}^\infty(T,0) = \ln \gamma_{13}^\infty(T,P) - \frac{B_{11} - V_1^\infty}{RT}P + \frac{2C_{222} - 3B_{11}^2}{2RT}P_1^{*2}
\]

\[
+ \frac{2B_{12} - B_{22} - V_1^*}{RT}P + \frac{(2C_{222} - 3B_{122} - 3B_{22}^2 + 4B_{12}B_{22})}{2(RT)}P^2 \quad (2.85)
\]

Substituting into the equation for $\gamma_{13}^\infty(T,P)$

\[
\ln \gamma_{13}^\infty(T,0) = \ln \frac{n_3RT}{V_LK_RP_L^*} \left[ 1 - \frac{(2B_{12} - V_1^\infty)}{RT}P \right] + \frac{(2B_{12} - V_1^\infty)}{RT}
\]

\[
+ (3C_{122} - 4B_{12}B_{22}) \frac{P^2}{2RT} \quad (2.86)
\]
2. THEORY OF G.L.C.

2.3.3. The Pressure Dependence of $K_R$

where

$$\ln \left[ 1 + \frac{B_{22}P}{RT} + \frac{B_{22}^2P^2}{(RT)^2} + \frac{C_{222}P^2}{(RT)^2} + \ldots \right]$$

has been approximated by

$$\left[ \frac{B_{22}P}{RT} - \frac{3}{2} \frac{B_{22}^2P^2}{(RT)^2} + \frac{C_{222}P^2}{(RT)^2} + \ldots \right]$$

Solving for $K_R$ in eq. 2.86

$$\ln K_R = \ln \frac{n_2RT}{P_1^*V_L\gamma_{13}(T,0)} - \frac{(B_{11} - V_1^*)}{RT} P_1^* + \frac{(2B_{12} - V_1^*)}{RT} P$$

$$+ (3C_{122} - 4B_{12}B_{22}) \frac{P^2}{2RT}$$

(2.87)

$$\Rightarrow \ln K_R = \ln K_R(0) + \beta P + \zeta P^2$$

(2.88)

where

$$\ln K_R(0) = \ln \left[ \frac{n_2RT}{\gamma_{13}(T,0) P_1^* V_L} \right] - \left[ \frac{B_{11} - V_1^*}{RT} \right] P_1^*$$

(2.89)
2. THEORY OF G.L.C.

2.3.3. The Pressure Dependence of $K_R$

$$\beta = \frac{(2B_{12} - V_1^*)}{RT}$$

(2.90)

$$\zeta = \frac{(3C_{122} - 4B_{12}B_{22})}{2(RT)^2}$$

(2.91)

The term $P^2$ is negligible at pressures below 15 atms. From equation 2.87

$$\ln[K_R(0)V_L] = \ln \left[ \frac{n_2RT}{\gamma_{13}(T,0)P_1^*} \right] - \left[ \frac{B_{11} - V_1^*}{RT} \right] P_1^*$$

(2.92)

From eq.2.72

$$K_R V_L = V_N \quad \Rightarrow \quad K_R(0)V_L = V_N^o$$

(2.93)

where $V_N^o$ is the retention volume at zero mean column pressure

$$\ln V_N^o = \ln \left[ \frac{n_2RT}{\gamma_{13}(T,0)P_1^*} \right] - \left[ \frac{B_{11} - V_1^*}{RT} \right] P_1^*$$

(2.94)

Equation 2.92 expresses the pressure dependence of the partition coefficient $K_R$.

2.3.4. The Elution Process

When the distribution coefficient is defined as (22)
2. THEORY OF G.L.C.

2.3.4. The Elution Process

The peak velocity \( W \) is given by

\[
W = \frac{uV_G}{V_G + K_R V_L}
\]  \hspace{1cm} (2.96)

Equation 2.96 can be written as

\[
\frac{l}{W} = \frac{V_G + K_R V_L}{uV_G}
\]  \hspace{1cm} (2.97)

where \( l \) is the distance from the column inlet.

Also

\[
\frac{l}{w} = \frac{dt}{dl} = \frac{V_G + K_R V_L}{uV_G}
\]  \hspace{1cm} (2.98)

where \( t \) is the retention time i.e. the time taken for the peak to travel a distance \( l \).

Now \( \bar{u} \) is the volumetric flow rate of the carrier gas therefore \( \bar{u}V_G \) can be replaced by \( U \)

\[
U dt = (K_R V_L + V_G) dl
\]  \hspace{1cm} (2.99)
Since \( U \) varies along the column in proportion to the carrier gas molar flow, it is convenient to express this variation in terms of local pressure, using the approximate equation of state.

\[
P V_2 = RT + B_{22}P \quad (2.100)
\]

\[
\Rightarrow U = \frac{P_o(1 + bP)}{P(1 + bP_o)} U_o \quad (2.101)
\]

where \( b = B_{22}/RT \)

\( U_o \) is the carrier gas flowrate at the column outlet and \( P_o \) is the pressure at the column outlet.

Equation 2.101 is derived as follows

\[
\frac{P V_2}{RT} = 1 + \frac{B_{22}P}{RT} \quad (2.102)
\]

Dividing eq. 2.100 by \( RT \)

since \( b = B_{22}/RT \)

\[
V_2 = \frac{1 + \frac{B_{22}P}{RT}}{P \frac{RT}{RT}} \quad (2.103)
\]

At the outlet of the column
2. THEORY OF G.L.C.
2.3.4. The Elution Process

\[ v = \frac{1 + bP}{P}\ \frac{RT}{P} \]  \quad (2.104)

\[ V_2^o = \frac{1 + bP_o}{P_o\ \frac{RT}{P}} \]  \quad (2.105)

\[ \Rightarrow \quad \frac{V_2}{V_2^o} = \frac{\frac{1 + bP}{P}\ RT}{\frac{1 + bP_o}{P_o\ RT}} \]  \quad (2.106)

\[ \Rightarrow \quad \frac{V_2}{V_2^o} = \frac{P_o(1 + bP)}{P(1 + bP_o)} \]  \quad (2.107)

but \( V_2/V_2^o \) = ratio of molar volumes = \( U/U_o \) = ratio of volumetric flow rates

\[ \Rightarrow \quad U = \frac{P_o(1 + bP)}{P(1 + bP_o)}\ U_o \]  \quad (2.108)

substituting for \( U \) in eq.2.97

\( U_o\ dt \) is the volume of gas leaving the column outlet as the elution peak advances a
2. THEORY OF G.L.C.

2.3.4. The Elution Process

\[ U_o \frac{dt}{dl} = \frac{(K R V_L + V_G)(1 + bP_o)}{P_o(1 + bP)} Pdl \]  \hspace{1cm} (2.109)

distance \( dl \). Because of the difficulty of defining \( V_o \) accurately it is more convenient to consider instead \( U_o \frac{dt}{dl} \), the volume of carrier gas measured at the column outlet which passes the elution peak during its progress from \( l \) to \( l + dl \).

This is obtained by allowing \( V_L = 0 \) (value corresponding to no liquid phase). This is simply

\[ dV_R = K R V_L \frac{1 + bP_o}{P_o} P \frac{dl}{1 + bP} \]  \hspace{1cm} (2.110)

The retention volume \( V_R \) is the same given in equation 2.25 ie. the observed (apparent) retention volume minus the gas holdup at the column outlet. Since \( K_R \) is a function of pressure, the most direct way to integrate the equation is to change the variable from \( l \) to \( P \) by means of Darcy’s law.

\[ \frac{dP}{dl} = \frac{-uen}{K} \]  \hspace{1cm} (2.111)

\[ dl = dx \Rightarrow \frac{dP}{dx} = \frac{-u}{A} \]  \hspace{1cm} (2.112)

where \( A \) takes into account the column packing permeability. If the pressure < 50 atms the Chapman-Enskog\(^{(23)}\) relation in approximation form can be used ie.
2. THEORY OF G.L.C.

2.3.4. The Elution Process

where

\[ a = 0.175 \frac{B_{22}}{RT} \]  \hspace{1cm} (2.113)

Combining with Darcy's law

\[ dl = -\frac{a}{u_o(1 + aP_0)\eta}dP \]  \hspace{1cm} (2.114)

But carrier gas pressure varies according to

\[ U = \frac{P_o(1 + bP)}{P(1 + P_0b)}U_o \]  \hspace{1cm} (2.115)

\[ \Rightarrow U_o = \frac{UP(1 + bP_0)}{P_0(1 + bP)} \]  \hspace{1cm} (2.116)

but

\[ U_o = \frac{dP A}{dl \eta} \]  \hspace{1cm} (2.117)

also

\[ \eta = \eta_o(1 + aP) \]  \hspace{1cm} (2.118)
2. THEORY OF G.L.C.
2.3.4. The Elution Process

substituting eqs. 2.115 and 1.118 into eq. 2.117

\[
\frac{UP(1 + bP)_{o}}{P_{o}(1 + bP)} = \frac{AP}{dL \eta_{o}(1 + aP)} \quad (2.119)
\]

\[
= \frac{dL}{AP(1 + bP)_{o}dP} = \frac{AP(1 + bP)_{o}dP}{P_{o}(1 + bP)U\eta_{o}(1 + aP)} \quad (2.120)
\]

Integrating

\[
L = \frac{A(1 + bP)}{U(\eta_{o})P} \int_{P_{o}}^{P} \frac{P}{(1 + bP_{o})(1 + aP)} \, dP \quad (2.121)
\]

Dividing eq. 2.120 by 2.121

\[
\frac{dl}{L} = \frac{AP(1 + bP)_{o}dP}{P_{o}(1 + bP) U\eta_{o}(1 + aP)} \quad (2.122)
\]

\[
dl = \frac{L PdP}{(1 + aP)(1 + bP)} \int_{P_{o}}^{P} \frac{PdP}{(1 + aP)(1 + bP)} \quad (2.123)
\]

\[
\ln K_{R} = \ln K_{R}(0) + \beta P + \zeta P^{2} \quad (2.124)
\]
\[ K_R = K_R(0) + e^{\beta P} + e^{\zeta P^2} \quad (2.125) \]

Eq. (2.110) states that

\[ dV_R = K_R V_L \frac{1 + bP_O}{P_O} \frac{P}{1 + bP} dP \]

Substituting eqs. 2.123 and 2.125 into eq. 2.110

\[ dV_R = \frac{K_R + e^{\beta P} + e^{\zeta P^2} V_L (1 + bP_O)}{P_O} \frac{P}{(1 + bP)} \frac{LPdP}{(1 + aP)(1 + bP)} \]

Also by substituting eqs. 2.125 and 2.120 into eq. 2.110

\[ dV_R = [K_R(0) + e^{\beta P} + e^{\zeta P^2}] [V_L \frac{1 + bP_O}{P_O} \frac{P}{1 + bP} \frac{AP(1 + bP_O)bP}{P_O(1 + bP)U_1(1 + aP)}] \quad (2.127) \]

By integration

\[ V_R = K_R(0)V_L \left[ \frac{1 + bP_O}{P_O} \int_{P_*}^{P_i} \frac{P^2 e^{\beta P} e^{\zeta P^2}}{(1 + aP)(1 + bP)^2} dP \right] \quad (2.128) \]

The above equation gives the required relationship between the retention volume \( V_R \) and the partition coefficient.
2.3.5. The Net Retention Volume of an Ideal Carrier Gas

In the case of an ideal carrier gas \( a \) and \( b \) in equation 2.128 and \( B_{22} \) (second virial coefficient of the carrier gas) are all zero.

\[
V_R = \frac{K_R(0)V_L \int_{P_o}^{P_1} P^2 e^{\beta P} e^{xP^2} dP}{P_o \int_{P_o}^{P_1} P dP} \quad (2.129)
\]

By integration

\[
\ln \left( \frac{V_R}{J_3^2} \right) = \ln V_N = \ln V_N(0) + \beta P_o J_3^4 + \zeta (P_o J_3^4)^2 \quad (2.130)
\]

where

\[
V_N(0) = K_R(0) \cdot V_L \quad (2.131)
\]

since \( (P_o J_3^4)^2 \) is negligible at pressures below 15 atms eq.2.130 approximates to

\[
\ln V_N = \ln V_N(0) + \beta P_o J_3^4 \quad (2.132)
\]

But

\[
\ln V_N(0) = \ln \left[ \frac{n_2^{RT}}{\gamma_{13}(T,0) P_1^*} \right] - \left[ \frac{B_{11} - V_1^*}{RT} \right] P_1^* \quad (2.133)
\]
2. THEORY OF G.L.C.

2.3.5. The Net Retention Volume...

Therefore substituting for $\ln V_N(T, 0)$ and $\beta$

$$\ln V_N = \ln \left[ \frac{n_3RT}{\gamma_{13}(T, 0)P_1} \right] - \left[ \frac{B_{11} - V^{*}_{1}}{RT} \right]P_1^* + \left[ \frac{2B_{12} - V^{*}_{1}}{RT} \right]P_1^* \sigma \beta$$

This is identical to eq. (1.1) for pressures $P_0$ and $P_i$ less than 1 atm since under these conditions $\gamma_{13}(T, 0) = \gamma_{13}^{*}$ and $f_3^{*} = f_3^{*}$

The above equation was developed by Everett(1) and Cruickshank(2) for the determination of activity coefficients at infinite dilution.

2.3.6. Treatment of a Volatile Solvent

The usual method for determining activity coefficients at infinite dilution developed by Everett(1) and Cruickshank(2) is restricted to volatile solutes (eg. n-pentane, n-hexane and n-heptane) and involatile solvents (eg. dotricontane, squalane, and dinonylphthalate).

2.3.6.1. Review of Work using Volatile Stationary Phases

Previously evaporation off the column by the stationary phase was avoided by presaturating the carrier gas with vapour of the volatile phase before it enters the column. The presaturator involved bubbling the carrier gas through the liquid or passing the carrier gas through a short precolumn which, like the main column, contained a stationary phase coated on a solid support. This technique was introduced by Kwantes and Rijnders.(23) However, even though the carrier gas was saturated with vapour it still removed stationary phase as it expanded along the column. Since a smaller pressure drop led to less evaporation of the stationary phase, a coarse packing was used which reduced the pressure drop considerably. While the use of a precolumn and coarse packing kept the bleed rate very low, the loss cannot be eliminated completely.
Kurkchi and Iogansen\(^{(24)}\) proposed weighing the column before and after use, assuming that the solvent loss was constant with time. Langer et al\(^{(25)}\) monitored the loss of solvent by measuring the retention time of a solute at intervals, taking the first reading as soon as the column reached its operating temperature. A graph of retention time against elapsed time of operation was plotted. The graph was then extrapolated to zero time and the correct retention time obtained. Letcher\(^{(26)}\) successfully used this method for the determination of the activity of various hydrocarbons with decahydronaphthalene as the volatile stationary phase.

In the present work Everett’s and Cruickshank’s method has been extended to accommodate a solvent of low volatility. During its passage through the column the carrier gas becomes charged with solvent vapour. The total amount of solvent lost from the column, \(n_3'\), may be expressed in terms of the total volume of gas which has passed through the column, the partial pressure, \(P_3'\), of the solvent in the gas at the column outlet and the time \(t\) elapsed from the start of the carrier gas passing through the column. We assume that the observed retention times are negligible compared with the total flow time through the column. The gas flow rate, \(U_o\), measured at the outlet is maintained constant during the whole experiment. The expression for \(n_3'\) is given by

\[
n_3' = \frac{U_o t P_3'}{RT} \tag{2.135}
\]

In this work we found the partial pressure of the solvent in the carrier gas to be very much less than 1 per cent of the total. It is probably further reduced in the flowmeter.
2. THEORY OF G.L.C.

2.3.6. Treatment of a Volatile Solvent

Therefore no correction was applied to the flowrate for the presence of the solvent. Equation (2.134) becomes

\[
\ln V_N = \ln \left( \frac{n_3 RT - P_3^l U_{of}}{\gamma_{13} P_1^*} \right) + C \tag{2.136}
\]

where

\[
C = - \left[ \frac{B_{11} - V_1^*}{RT} \right] P_1^* + \left[ \frac{2B_{12} - V_1^\infty}{RT} \right] P_{\sigma f}^3 \tag{2.137}
\]

Hence

\[
\frac{V_N}{e^{C n_3}} = \frac{RT}{\gamma_{13} P_1^*} + \left[ \frac{U_{of}^*}{n_3} \right] \frac{P_3^l}{\gamma_{13} P_1^*} = a + \frac{U_{of}}{n_3} \tag{2.138}
\]

By plotting \( V_N/n_3 e^C \) against \( U_{of}/n_3 \) a straight line is obtained, giving an intercept of \( RT/\gamma_{13} P_1^* \ (a) \) and a slope of \( P_3^l/RT \ (b) \).

The values of \( \gamma_{13} \) and \( P_3^l \) are obtained graphically from this linear relationship.
3. APPARATUS AND EXPERIMENTAL PROCEDURE

The gas-liquid chromatograph used for the determination of the activity coefficients at infinite dilutions was similar to that used by Cruickshank(2) and also by Letcher and Marsicano(27).

3.1 The Design of the Gas-Liquid Chromatograph

The basic plan of the gas chromatograph is shown in figure 3.1. This type of chromatograph is suitable for physico-chemical measurements. The scheme is similar to that of a commercial analytical chromatograph except for the addition of a manometer to register the column inlet pressure and an accurate flowmeter to measure the flowrate (0.01 s) and accurate temperature control of the column (± 0.01 K). Two thermal conductivity detector chromatographs were used differing only in the make and design of the detector. The advantage of using a thermal conductivity detector (T.C.D.) or a katharometer is that the flow-meter can be placed downstream of the column exit. The flow and pressure control unit was constructed mainly of 6.35 mm o.d. (1/4 inch) copper tubing and Swagelock couplings. The flow-meter and manometer were constructed of thick-walled glass tubing.

3.1.1. Flow Control

Good flow control was achieved by using a two-stage pressure regulator, attached to the cylinder head, in conjunction with a Negretti and Zambra precision pressure regulating valve which controlled the pressure to better than 0.1 torr. The column outlet in the experiment was open to the atmosphere. It was necessary to monitor the outlet pressure since variations in atmospheric pressure would have negligible effects on the flow-rate only if the column impedance was unusually high.(28) A buffer vessel was placed at the column outlet to minimise the effect of pressure changes due to slight disturbances in the laboratory atmosphere.

§ 1 torr = 1 mm Hg
FIGURE 3.1. FLOW DIAGRAM OF G.L.C.
3.1.2. Pressure Measurement

The outlet pressure was considered to be atmospheric and was measured on a normal Fortin barometer. The column inlet pressure was measured by a mercury manometer using a kathetometer (± 0.01 mm Hg). A trap was attached to one end of the manometer to retain mercury in case of an accidental pressure surge.

3.1.3. Flow Rate Measurements

The measurement of the gas flow-rate is carried out with a soap bubble meter (figure 3.2), constructed from a graduated 100 ml burette, which was situated downstream of the column. Since helium was used as the carrier gas, it was necessary to ensure that air did not enter the burette during flow measurements since light gases, such as helium, diffuse more rapidly through soap films than air and this would cause the actual flow-rate to be different from the rate of film movement. To prevent back diffusion of air a rubber bung with a tiny hole was placed at the flowmeter outlet. The hole was not narrow enough to cause a significant pressure rise in the flow tubes.

3.1.4. Column Temperature Control

Good temperature control was essential since the vapour pressure (of the solute and the solvent) is temperature dependent. This was achieved by immersing the column in a well-stirred waterbath. The temperature at 298.15 K (using a single waterbath) was controlled by a Tronac temperature controller in conjunction with a simple on-off relay using a light bulb as a low thermal capacity heater (figure 3.3).

The temperature was measured using an accurate quartz thermometer: The bath temperature was always known to an accuracy of better than 0.01 K. For the control of the temperature at 283.15 K two water baths were used (figure 3.4). The temperature of the first bath was kept at approximately 280.15 K using a large cooling unit and an immersion heater. The bath was kept well stirred using two high speed mechanical stirrers. The temperature in the second bath (containing the column) was
TO THE ATMOSPHERE

100 ml BURETTE TUBE

FROM GAS CHROMATOGRAPH OUTLET

RUBBER BULB CONTAINING SOAP SOLUTION

FIGURE 3.2. THE SOAP BUBBLE FLOW METER
FIGURE 3.3. WATER BATH FOR TEMPERATURE CONTROL AT 298.15 K
FIGURE 3.4. TWO WATER BATH SYSTEM FOR TEMPERATURE CONTROL AT 283.15 K
lowered to 283.15 K by pumping water from the first bath through a 6 m coil of copper tubing placed on the floor of the second bath. As with temperature control at 298.15 K the temperature in the second bath was controlled by a Tronac temperature controller and a light bulb and the temperature was monitored using a quartz thermometer.

3.1.5 Sample Injection and the Injection System

The solutes used were usually of the purest grade available although this was not necessary. Samples were injected using a microsyringe and sample sizes varied from 0.1 µl to 1.0 µl. It is shown later that this yields infinite dilute conditions in the column. The injection system for both the Gow-Mac and Shandon detectors was the same and was specially designed to minimise back diffusion, dead volume, multiple septum perforation and damage to the syringe. It consisted of an inner tube located concentrically inside an outer tube (figure 3.5). Carrier gas entering at the one end of the annulus between the tubes is deflected into the inner tube by the septum at the other end. The entry of the gas at the one end of the narrow annulus in conjunction with the high velocity purge of the gas through it, ensured that there was no upswept dead volume, back diffusion of the sample, or its retention on the underside of the septum. The diaphragm injection system was mounted in a tapered bore. It was retained under compression by a funnel shaped needle guide, which was screwed down on its upper surface. This needle guide ensures that the needle penetration was always at the same spot in the septum.

3.1.6. G.L.C. Columns

The packed columns used were all stainless steel which are inert to the solutes and does not cause adsorption or react with the solutes in any way. The columns were all 6.35 mm o.d. (1/4 inch) and 1 to 1.5 m in length.
FIGURE 3.5. THE INJECTION SYSTEM
3.1.7. Detectors

Two types of thermal conductivity detectors were used, a Shandon U.K.3 gas chromatograph and a Gow-Mac gas chromatograph.

*The Shandon U.K.3 Detector.* - A circuit diagram of the detector system is shown in figure 3.6. The detector consists of two matched, electrically heated, helically coiled, tungsten filaments. These are mounted in the brass detector body by means of mechanical seal tube-nuts. In this way the two filaments are inserted directly into the gas stream, one (reference) in the pure carrier gas before it enters the column, and the other (measuring) in the column effluent. The geometrical configuration of each filament was identical. The filament forms two arms of an electrical Wheatstone bridge circuit. This bridge is unbalanced by a change in the temperature (and hence the resistance) of the filament in the effluent, which is caused by a change in the composition of the gas stream as a component is eluted. The signals are recorded on a Phillips recorder.

*The Gow-Mac Detector.* - A circuit diagram of the four filament Gow-Mac detector cell is shown in figure 3.7. In this detector four tungsten filaments lie in the gas path. It is a semi-diffusion cell of a flow-through design with a response time less than 1.0 seconds. The stream of pure gas is split so that half of the pure gas enters the reference chamber and passes over the two reference filaments and the other half of the gas enters the column. The gas emerging from the column flows over the measuring filaments. The filaments used are of the same design as those used in the Shandon detector.
FIGURE 3.6. CIRCUIT DIAGRAM OF SHANNDON UK3 T.C.D. DETECTOR
FIGURE 3.7. CIRCUIT DIAGRAM OF GOW-MAC T.C.D. DETECTOR
3.2. Experimental Procedure

3.2.1. Preparation of the Stationary Phase

The stationary phase was prepared following the procedure used by Marsicano. The columns were cleaned with hot soap solution, rinsed with distilled water, and dried with nitrogen. Celite was used as the solid support for the stationary phase. The column loading (mass solute/total mass coated solid support) ranged between 3 to 15 mass per cent. The packing was prepared by adding a known mass of solvent to a known mass of celite. The combined mass was noted. A solvent in which the stationary phase is soluble (diethyl ether) was added (approx. 50 ml) and the contents were swirled gently in order to dissolve the stationary phase and distribute it throughout the celite. The ether was slowly removed by the application of a vacuum using a Buchi rotary evaporator without heating. The flask was rotated slowly to minimise disintegration of the fragile celite. The last trace of ether was removed by allowing the flask to stand in a fume hood. The coated celite was weighed and reweighed on completion to check that all the ether had been removed and that no stationary phase had been lost. The column was then straightened. It was packed using a plastic funnel and rubber tubing of known mass. The funnel was attached to the column by the tubing and the coated celite was poured into the funnel. The other end of the column was plugged with glass wool. A rubber stopper was attached to this end which was lightly tapped on the floor during packing. The column was also lightly tapped with a rubber-covered metal rod. On completion the funnel and tubing were weighed and the amount of stationary phase added was determined by difference. The column was plugged with glass wool at the open end and coiled. The small amount of compression produced on coiling does not significantly change the properties of the packing, nor its adsorptive properties.

3.2.2. Measurement Procedure

Measurements of flow-rate (which was kept constant), retention times of solute and
unretained gas (nitrogen), and temperature were made for each column. The flowrate was set, depending on the length of the column and the amount of solvent on the column, so that the column would have a life of about 3-4 hours. The system was allowed to equilibrate for about 10-15 min before the first injection was made. When several solutes are studied on a single column, the solutes are injected simultaneously as a mixture. Solutes chosen for such measurements must have significantly different retention times to allow each component to be fully resolved at the detector. Incorporation of air to determine the gas holdup was accomplished by first taking up the desired volume of solute into the syringe and withdrawing the plunger further to admit a suitable volume of air before making an injection.

Retention times were calculated from distance measurements on the chart from the point of injection to the point at which the tangents to the peak intersect (figure 3.8). These are then converted to retention times using the chart speed which was accurately measured using a stopwatch.

The carrier gas flow-rate was measured regularly throughout each run using an accurate stopwatch. Prior to measuring the flow-rate a stream of bubbles were sent through the flowmeter to allow the interior walls of the burette to be thoroughly wetted by the soap solution to avoid errors arising from uneven movement of the bubble film due to surface tension effects and the possibility that the burette was not fully saturated with water vapour.

3.3. Calculation of Results

From the experimental readings, values of \( V_N \) were calculated using the programme GAMMA (see Appendix 1) which uses the following equation.
FIGURE 3.8. A Typical Chromatogram Showing the Determination of the Retention Time of a Solute Using the Tangents to The Peak Method
3.4. Disadvantage of Conventional Methods

The values of $\frac{V_n}{n_3e^c}$ and $\frac{U_0}{n_3}$ are fitted to the best straight line (eq. 3.2) using a regression analysis.

$$\ln\gamma_{13}^\infty = \ln\frac{n_3RT}{V_nP_1^c} - \left(\frac{B_{11} - V_1^*}{RT}\right)P_1^c + \left(\frac{2B_{12} - V_1^*}{RT}\right)P_0^3$$

From the intercept of that line the value of the quantity $\frac{RT}{\gamma_{13}^\infty P_1^c}$ was obtained and the activity coefficient at infinite dilution ($\gamma_{13}^\infty$) was calculated. From the ratio of the slope to the intercept the quantity $\frac{RT}{P_3^f}$ was obtained and consequently, $P_3^f$, the partial pressure of the solvent at the temperature of the experiment was calculated.

3.4. Disadvantages of Conventional methods of Determining $\gamma_{13}^\infty$

Conventional methods of studying solution phenomena, which depend on the measurement of vapour pressure, suffer from the disadvantage that the percentage experimental error of measurement at low concentration is usually much greater than at higher concentration.\(^{(29)}\) Great errors are incurred if properties at infinite dilution are calculated from finite concentration data.\(^{(30)}\) Another disadvantage of conventional vapour pressure measurements on systems of the type volatile solute + involatile solvent is that the measurements are usually very time consuming and require both solvent and solute in a state of high purity.
3.5. Advantages and Disadvantages of Physico-chemical Methods by G.L.C.

3.5.1 Advantages

**Speed.** A gas chromatographic experiment is relatively rapid taking no more than a few minutes. Such speed is possible since the stationary phase is highly dispersive and has a large area of interface with the gas. Path lengths for mass transport are small and so phase equilibrium is rapidly attained. Another time saving feature is that several solutes can often be studied in one run. The components can be injected as a mixture provided that their retention times differ.\(^{(31)}\)

**Quantity of material.** In the normal elution mode the amount of solute injected onto the column is such a small quantity that they are effectively at infinite dilution in the solvent.\(^{(31)}\) In addition the amount of stationary phase required is usually small.\(^{(31)}\)

**Purity of Material.** A chromatographic column can separate and purify the components of a mixed sample at the same time as it measures their properties. Hence small quantities of moderately pure material can be used without preliminary purification.\(^{(32)}\)

**Temperature Variation.** Since a chromatographic column is normally made into a compact shape, such as a coil, and housed in a small thermostated enclosure, it is a simple matter to operate it at any temperature within the capacity of the equipment. Thus a wide temperature range is available.

**Solubility of Solutes.** Non-chromatographic methods are often unsuitable for highly unstable solutes. Reaction of the solute with the reaction vessel or trace impurities can lead to pressure changes and false experimental values. Chromatographic methods of
measurement are often preferred for reactive solutes since quantities are small and the contact time is short.

3.5.2. Disadvantages

Gas chromatography, although well established as a means of studying interactions in solutions however has certain limitations that may necessitate the choice of another technique. The technique is simplest to operate if the solute is at infinite dilution, the solvent is involatile, and the solute does not show a Gibbs adsorption effect at the liquid surface.\(^{[33]}\)

**Interferences.** It is characteristic of chromatography that the column may contain more components or phases than those being studied. For example the gas liquid chromatographic system contains a total of five or more phases: three bulk phases and two interfacial phases. The measurements may reflect equilibrium interactions in more than one phase. A study of one interaction may be subject to interferences from other interactions present in the system. An example being the adsorption on the solid support particularly prevalent with polar solutes. Such adsorption, if not the subject of study, interferes with measurements concerning the stationary phase held on the support.\(^{[34]}\)

**Solvent Volatility.** Another problem, associated with solute volatility, is the temperature limit of the stationary phase. Liquid phases are limited normally to operation at temperatures at which their vapour pressure is less than about 0.01 torr, i.e. 1.2 Pa,\(^{[33]}\) if one is to ensure that the amount of stationary phase in the column remains virtually constant over a reasonable period.

If there exists a finite pressure drop across the column, a volatile or moderately volatile solvent will be gradually stripped off. This is partially offset by employing coarse packing, internal standards, saturators and/or precolumns.\(^{[34]}\) The main
objective of this work was to overcome the problem associated with the loss of solvent from the column without employing the use of saturators, precolumns or an internal standard. In this work a theory has been developed (chapter 2) that not only enables the determination of activity coefficients using a moderately volatile solvent, but also relates the amount of solvent lost to its vapour pressure.
4. Results

Data was collected for 19 columns (12 trans-decalin and 7 cis-decalin columns) at two different temperatures, 298.15 K and 283.15 K. The solutes used were n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and n-heptane and solvents cis- and trans-decalin. Helium was used as the carrier gas and the retention time $t_0$ was determined using nitrogen. Two thermal conductivity detectors were used (a Gow-Mac T.C.D. and a Shandon U.K.3 T.C.D.). For each experiment the retention time was kept constant.

The effect of the type of packing used (silanized or unsilanized) is also investigated by running eight columns (three cis- and five trans-decalin columns) with silanized chromasorb as the packing. The amount of solute injected (to determine the solute volume required for infinite dilution conditions) is also investigated by varying the injection size between 1.0 $\mu$l and 0.1 $\mu$l.

The column loading ranged from three to fifteen mass per cent.

The mixed virial coefficients, $B_{12}$, were calculated from McGlashan and Potter's equation\(^{(35)}\) and Hudson and McCoubrey's combining rules\(^{(36)}\) following Letcher et al\(^{(37)}\).

\[
B_{12}/V_{C,12} = 0.43 - 0.886(T_{C,12}/T) - 0.694(T_{C,12}/T)^2 \\
- 0.0375(n_{12} - 1)(T_{C,12}/T)^{4.5} \tag{4.1}
\]
where

\[ T_{c,12} = 128(T_{c,1} T_{c,2})^{1/2}(I_{c,1} I_{c,2})^{1/2} V_{c,11} V_{c,22}/I_{c,12} \]  \( (4.2) \)

\[ V_{c,12} = (V_{c,11}^{1/3} + V_{c,22}^{1/3})^3/8 \]  \( (4.3) \)

\[ I_{c,12} = (I_{11} + I_{22})(V_{c,11}^{1/3} + V_{c,22}^{1/3})^6 \]  \( (4.4) \)

and

\[ n_{12} = (n_1 + n_2)/2 \]  \( (4.5) \)

The critical data and ionization energies used in the calculation of \( B_{12} \) are given in table 26 using \( n_1 = 5 \) (n-pentane and cyclopentane), \( n_1 = 6 \) (n-hexane, cyclohexane and benzene), \( n_1 = 7 \) (n-heptane) and \( n_2 = 1 \) (helium). The values for \( B_{12} \) was found to be 2.429x10^{-6} m^3 mol^{-1} (n-pentane), 18.0477x10^{-6} m^3 mol^{-1} (cyclopentane), 29x10^{-6} m^3 mol^{-1} (n-hexane), 21.579x10^{-6} m^3 mol^{-1} (cyclohexane), 17.6579x10^{-6} m^3 mol^{-1} (benzene) and 31.532x10^{-6} m^3 mol^{-1} (heptane).
TABLE 4.1. Definition of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_3 )</td>
<td>Moles of decalin (trans or cis) on the column</td>
</tr>
<tr>
<td>( P_i )</td>
<td>Inlet pressure</td>
</tr>
<tr>
<td>( P_o )</td>
<td>Outlet pressure (atmospheric)</td>
</tr>
<tr>
<td>( J_3^2 )</td>
<td>Correction factor for the compressibility of the mobile phase</td>
</tr>
<tr>
<td>( U_0 )</td>
<td>Flow rate corrected for temperature and water-vapour pressure</td>
</tr>
<tr>
<td>( t_G )</td>
<td>Retention time of an unretained gas (nitrogen)</td>
</tr>
<tr>
<td>( t_R )</td>
<td>Retention time of the solute studied</td>
</tr>
<tr>
<td>( t )</td>
<td>Time of injection of the solute</td>
</tr>
</tbody>
</table>
### TABLE 4.2. Column Specifications

<table>
<thead>
<tr>
<th>Column number</th>
<th>Solvent isomer</th>
<th>$U_0 \times 10^6$ m$^3$ s$^{-1}$</th>
<th>$n_3$ mmols</th>
<th>percentage loading mass per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>decalin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>trans§</td>
<td>0.8872</td>
<td>3.393</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>trans§</td>
<td>0.9541</td>
<td>2.124</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>trans§</td>
<td>0.8370</td>
<td>2.329</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>trans§</td>
<td>0.9542</td>
<td>3.684</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>cis§</td>
<td>0.9828</td>
<td>1.790</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>cis§</td>
<td>0.5715</td>
<td>1.786</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>trans</td>
<td>1.7177</td>
<td>4.086</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>trans</td>
<td>1.9916</td>
<td>6.350</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>cis</td>
<td>1.8935</td>
<td>6.082</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>trans</td>
<td>1.0702</td>
<td>2.615</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>trans</td>
<td>2.3727</td>
<td>2.233</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>cis</td>
<td>1.2387</td>
<td>2.310</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>cis</td>
<td>2.6964</td>
<td>2.217</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>trans§</td>
<td>1.2542</td>
<td>5.991</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>cis§</td>
<td>2.9239</td>
<td>2.512</td>
<td>5</td>
</tr>
<tr>
<td>16</td>
<td>trans§</td>
<td>1.8196</td>
<td>1.091</td>
<td>5</td>
</tr>
<tr>
<td>17</td>
<td>trans§</td>
<td>2.1629</td>
<td>2.527</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>cis§</td>
<td>1.9212</td>
<td>5.812</td>
<td>10</td>
</tr>
<tr>
<td>19</td>
<td>cis§</td>
<td>2.8041</td>
<td>3.911</td>
<td>5</td>
</tr>
</tbody>
</table>

§: silanized Chromasorb

£: Columns run at 283.15 K
Experiment 1. n-Hexane in trans-decalin (15%) on Column 1 (Gow-Mac T.C.D. Detector) at 298.15 K.

\[ n_{\text{mol}} = 3.3935 \times 10^{-3} \]

\[ P_{i}/Pa = 119652.72 \]

\[ P_{o}/Pa = 100633.50 \]

\[ J_{3} = 0.914 \]

\[ U_{o}/m^{3} s^{-1} = 8.872 \times 10^{-7} \]

\[ t_{o}/s = 20.31 \]

TABLE 4.3. Results obtained from column 1 (trans-decalin 15%) with n-hexane as solute.

<table>
<thead>
<tr>
<th>Time</th>
<th>( t_{R} )</th>
<th>( V_{N} \times 10^{4} )</th>
<th>( V_{N}/n_{s}e^{c} )</th>
<th>( U_{o}t/n_{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
<td>m(^{3})</td>
<td>m(^{3}) mol(^{-1})</td>
<td>m(^{3}) mol(^{-1})</td>
</tr>
<tr>
<td>1200</td>
<td>428.82</td>
<td>3.312</td>
<td>0.0975</td>
<td>0.313</td>
</tr>
<tr>
<td>2400</td>
<td>419.22</td>
<td>3.234</td>
<td>0.0953</td>
<td>0.627</td>
</tr>
<tr>
<td>4800</td>
<td>413.88</td>
<td>3.191</td>
<td>0.0904</td>
<td>1.255</td>
</tr>
<tr>
<td>5700</td>
<td>413.28</td>
<td>3.182</td>
<td>0.0937</td>
<td>1.490</td>
</tr>
<tr>
<td>6600</td>
<td>401.22</td>
<td>3.088</td>
<td>0.0910</td>
<td>1.725</td>
</tr>
<tr>
<td>7200</td>
<td>401.10</td>
<td>3.087</td>
<td>0.0909</td>
<td>1.882</td>
</tr>
<tr>
<td>9000</td>
<td>399.66</td>
<td>3.076</td>
<td>0.0906</td>
<td>2.353</td>
</tr>
<tr>
<td>9600</td>
<td>396.06</td>
<td>3.046</td>
<td>0.0897</td>
<td>2.509</td>
</tr>
</tbody>
</table>
4. RESULTS

Experiment 2. n-Hexane in trans-decalin (10%) on column 2 (Gow-Mac T.C.D. detector) at 298.15 K.

\[ n_3/\text{mol} \quad 2.124 \times 10^{-3} \]
\[ P_f/\text{Pa} \quad 120035.45 \]
\[ P_o/\text{Pa} \quad 99967.10 \]

\[ J_3 \quad 0.901 \quad t_o/s \quad 19.68 \text{ s} \]

TABLE 4.4. Results obtained from column 2 (trans-decalin 10%) with n-hexane as the solute.

<table>
<thead>
<tr>
<th>Time s</th>
<th>( t_R \text{ s} )</th>
<th>( V_N \times 10^4 \text{ m}^3 )</th>
<th>( V_N/n_3e^c \text{ m}^3 \text{ mol}^{-1} )</th>
<th>( U_Ot/n_3 \text{ m}^3 \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3900</td>
<td>228.57</td>
<td>1.936</td>
<td>0.0901</td>
<td>1.752</td>
</tr>
<tr>
<td>4200</td>
<td>228.49</td>
<td>1.935</td>
<td>0.0900</td>
<td>1.889</td>
</tr>
<tr>
<td>4800</td>
<td>224.44</td>
<td>1.894</td>
<td>0.0881</td>
<td>2.156</td>
</tr>
<tr>
<td>5100</td>
<td>223.51</td>
<td>1.884</td>
<td>0.0876</td>
<td>2.291</td>
</tr>
<tr>
<td>5700</td>
<td>219.03</td>
<td>1.838</td>
<td>0.0855</td>
<td>2.560</td>
</tr>
<tr>
<td>6300</td>
<td>218.53</td>
<td>1.833</td>
<td>0.0852</td>
<td>2.850</td>
</tr>
</tbody>
</table>
4. RESULTS

Experiment 3. n-Hexane in trans-decalin (8%) on column 3 (Gow-Mac T.C.D. detector) at 298.15 K.

\[ n_0/\text{mol} = 2.329 \times 10^{-3} \]
\[ P/P_0 = 121099.81 \]
\[ P_0/P_0 = 102233.01 \]
\[ t_c/s = 23.7 \]

**TABLE 4.5.** Results obtained from column 3 (trans-decalin 10%) with hexane as the solute

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>( t_R ) (s)</th>
<th>( V_N \times 10^4 ) (m(^3))</th>
<th>( V_N/n_0 e^C ) (m(^3) mol(^{-1}))</th>
<th>( U_0 t/n_0 ) (m(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>312.88</td>
<td>2.211</td>
<td>0.0937</td>
<td>0.431</td>
</tr>
<tr>
<td>2100</td>
<td>311.49</td>
<td>2.200</td>
<td>0.0934</td>
<td>0.754</td>
</tr>
<tr>
<td>3000</td>
<td>310.37</td>
<td>2.192</td>
<td>0.0930</td>
<td>1.078</td>
</tr>
<tr>
<td>4200</td>
<td>309.17</td>
<td>2.182</td>
<td>0.0926</td>
<td>1.509</td>
</tr>
<tr>
<td>6000</td>
<td>297.31</td>
<td>2.091</td>
<td>0.0887</td>
<td>2.156</td>
</tr>
</tbody>
</table>
4. RESULTS

Experiment 4. n-Hexane in trans-decalin (10%) on column 4 (Gow-Mac T.C.D. detector) at 298.15 K.

\[
\begin{align*}
n_n & \text{/mol} \quad 3.682 \times 10^3 \\
P_l & \text{/Pa} \quad 141016.73 \\
P_o/\text{Pa} & \quad 101758.29
\end{align*}
\]

\[
\begin{align*}
J_3 & \quad 0.888 \\
U_o/\text{m}^3 \text{ s}^{-1} & \quad 9.542 \times 10^{-7} \\
t_c/\text{s} & \quad 22.08
\end{align*}
\]

TABLE 4.6. Results obtained from column 4 (trans-decalin 10%) with n-hexane as the solute.

<table>
<thead>
<tr>
<th>Time</th>
<th>( t_R )</th>
<th>( V_N \times 10^4 )</th>
<th>( V_N/n_3 e^c )</th>
<th>( U_o/n_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
<td>m³</td>
<td>m³ mol⁻¹</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>2100</td>
<td>335.94</td>
<td>2.659</td>
<td>0.0939</td>
<td>0.921</td>
</tr>
<tr>
<td>3300</td>
<td>334.98</td>
<td>2.651</td>
<td>0.0936</td>
<td>1.125</td>
</tr>
<tr>
<td>3900</td>
<td>330.30</td>
<td>2.611</td>
<td>0.0923</td>
<td>1.330</td>
</tr>
<tr>
<td>4500</td>
<td>328.14</td>
<td>2.593</td>
<td>0.0916</td>
<td>1.535</td>
</tr>
<tr>
<td>5160</td>
<td>326.16</td>
<td>2.576</td>
<td>0.0910</td>
<td>1.760</td>
</tr>
<tr>
<td>6300</td>
<td>315.78</td>
<td>2.488</td>
<td>0.0879</td>
<td>2.149</td>
</tr>
</tbody>
</table>
4. RESULTS

Experiment 5. n-Hexane in cis-decalin (10%) on column 5 (Gow-Mac T.C.D. detector) at 298.15 K.

\[ n_\text{mol} = 1.790 \times 10^{-3} \]
\[ P_1/\text{Pa} = 116166.31 \]
\[ P_0/\text{Pa} = 99967.11 \]

\[ J_3 = 0.923 \]
\[ U_0/\text{m}^3 \text{ s}^{-1} = 9.828 \times 10^{-7} \]
\[ t_0/\text{s} = 30.99 \]

**TABLE 4.7.** Results obtained from column 5 (cis-decalin 10%) with n-hexane as the solute.

<table>
<thead>
<tr>
<th>Time</th>
<th>( t_\text{R} )</th>
<th>( V_N \times 10^4 )</th>
<th>( V_N/n_\text{mol}^\text{c} )</th>
<th>( U_0t/n_\text{mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
<td>m(^3)</td>
<td>m(^3) mol(^{-1})</td>
<td>m(^3) mol(^{-1})</td>
</tr>
<tr>
<td>1800</td>
<td>204.72</td>
<td>1.708</td>
<td>0.0942</td>
<td>0.882</td>
</tr>
<tr>
<td>3300</td>
<td>200.94</td>
<td>1.967</td>
<td>0.0924</td>
<td>1.811</td>
</tr>
<tr>
<td>4200</td>
<td>196.56</td>
<td>1.633</td>
<td>0.0901</td>
<td>2.305</td>
</tr>
<tr>
<td>5400</td>
<td>194.58</td>
<td>1.615</td>
<td>0.0891</td>
<td>2.946</td>
</tr>
<tr>
<td>9300</td>
<td>173.34</td>
<td>1.422</td>
<td>0.0785</td>
<td>5.105</td>
</tr>
</tbody>
</table>
Experiment 6. n-Hexane in cis-decalin (3%) on column 6 (Gow-Mac T.C.D. detector) at 298.15 K.

\[
\begin{align*}
n_3/\text{mol} & \quad 1.786 \times 10^{-3} \\
P_1/\text{Pa} & \quad 121099.48 \\
P_0/\text{Pa} & \quad 100731.71
\end{align*}
\]

\[J_3 = 0.913\]

\[U_0/\text{m}^3 \text{ s}^{-1} = 5.715 \times 10^{-7}\]

\[t_0/\text{s} = 90.12\]

**TABLE 4.8.** Results obtained from column 6 (cis-decalin 3%) with n-hexane as the solute.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>(t_R) (s)</th>
<th>(V_N \times 10^4) (m³)</th>
<th>(V_N/n_3e^c) (m³ mol⁻¹)</th>
<th>(U_0/n_3) (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>630</td>
<td>406.79</td>
<td>1.646</td>
<td>0.0922</td>
<td>2.016</td>
</tr>
<tr>
<td>1330</td>
<td>391.87</td>
<td>1.569</td>
<td>0.0879</td>
<td>4.257</td>
</tr>
<tr>
<td>1459</td>
<td>390.95</td>
<td>1.564</td>
<td>0.0876</td>
<td>4.671</td>
</tr>
<tr>
<td>1519</td>
<td>388.19</td>
<td>1.550</td>
<td>0.0868</td>
<td>4.862</td>
</tr>
<tr>
<td>1787</td>
<td>383.95</td>
<td>1.528</td>
<td>0.0856</td>
<td>5.718</td>
</tr>
<tr>
<td>2000</td>
<td>372.95</td>
<td>1.470</td>
<td>0.0824</td>
<td>6.403</td>
</tr>
<tr>
<td>2150</td>
<td>358.28</td>
<td>1.394</td>
<td>0.0781</td>
<td>6.881</td>
</tr>
</tbody>
</table>
Experiment 7. 5% trans-decalin column 7 (Shandon UK3 T.C.D. detector) at 298.15 K

\[
\begin{align*}
n_0/\text{mol} & \quad 4.0865 \times 10^{-3} & \quad J_3^2 & \quad 0.789 \\
P_0/\text{Pa} & \quad 148758.02 & \quad U_0/\text{m}^3\text{s}^{-1} & \quad 1.7177 \times 10^{-6} \\
P_o/\text{Pa} & \quad 100831.71 & \quad t_c/\text{s} & \quad 13.89
\end{align*}
\]

TABLE 4.9. Results obtained from column 7 (a 5% trans-decalin column) with solutes cyclohexane and benzene run separately.

<table>
<thead>
<tr>
<th>Time $t_R$ s</th>
<th>$t_R$ s</th>
<th>$V_N \times 10^{-4}$ m$^3$</th>
<th>$V_N/n_3 e^c$ m$^3$ mol$^{-1}$</th>
<th>$U_0/t/n_3$ m$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>solute: Cyclohexane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1205</td>
<td>541.23</td>
<td>7.232</td>
<td>0.176</td>
<td>0.506</td>
</tr>
<tr>
<td>2904</td>
<td>520.30</td>
<td>6.942</td>
<td>0.169</td>
<td>1.221</td>
</tr>
<tr>
<td>4396</td>
<td>494.69</td>
<td>6.594</td>
<td>0.161</td>
<td>1.847</td>
</tr>
<tr>
<td>4954</td>
<td>485.15</td>
<td>6.463</td>
<td>0.157</td>
<td>2.083</td>
</tr>
<tr>
<td>5512</td>
<td>461.64</td>
<td>6.141</td>
<td>0.149</td>
<td>2.318</td>
</tr>
<tr>
<td>6043</td>
<td>462.45</td>
<td>5.152</td>
<td>0.150</td>
<td>2.541</td>
</tr>
<tr>
<td>7167</td>
<td>443.61</td>
<td>5.893</td>
<td>0.1430</td>
<td>3.013</td>
</tr>
<tr>
<td>7780</td>
<td>433.21</td>
<td>5.751</td>
<td>0.1399</td>
<td>3.270</td>
</tr>
<tr>
<td><strong>solute: Benzene</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>690</td>
<td>429.88</td>
<td>5.568</td>
<td>0.135</td>
<td>0.290</td>
</tr>
<tr>
<td>960</td>
<td>399.11</td>
<td>5.428</td>
<td>0.1285</td>
<td>1.2213</td>
</tr>
<tr>
<td>4395</td>
<td>378.89</td>
<td>5.006</td>
<td>0.1218</td>
<td>1.847</td>
</tr>
<tr>
<td>4956</td>
<td>371.15</td>
<td>4.900</td>
<td>0.1192</td>
<td>2.083</td>
</tr>
</tbody>
</table>
4. RESULTS

TABLE 4.9 cont.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>( t_r ) (s)</th>
<th>( V_N \times 10^4 ) (m³)</th>
<th>( V_N / n_{S} e^{C} ) (m³ mol⁻¹)</th>
<th>( U_{G} t / n_{3} ) (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5515</td>
<td>356.04</td>
<td>4.692</td>
<td>0.1142</td>
<td>2.318</td>
</tr>
<tr>
<td>6571</td>
<td>347.98</td>
<td>4.582</td>
<td>0.1115</td>
<td>2.762</td>
</tr>
<tr>
<td>7144</td>
<td>340.41</td>
<td>4.478</td>
<td>0.1089</td>
<td>3.003</td>
</tr>
<tr>
<td>7749</td>
<td>332.41</td>
<td>4.368</td>
<td>0.1063</td>
<td>3.257</td>
</tr>
</tbody>
</table>
Experiment 8. 10% trans-decalin on column 8 (Shandon UK3 T.C.D. detector) at 298.15 K.

\[ n_3/\text{mol} = 6.3501 \times 10^{-3} \quad J_3 = 0.769 \]

\[ P_i/\text{Pa} = 158051.25 \quad U_0/\text{m}^3 \text{s}^{-1} = 1.9916 \times 10^{-6} \]

\[ P_0/\text{Pa} = 101351.66 \quad t_0/\text{s} = 14.38 \]

**TABLE 4.10.** Results obtained from column 8 (a 10% trans-decalin column) with solutes n-pentane, cyclopentane, benzene, and n-hexane run as a mixture.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>( t_\text{R} ) (s)</th>
<th>( V_\text{N} \times 10^4 ) (m³)</th>
<th>( V_\text{N}/n_3 \text{e}^c ) (m³ mol⁻¹)</th>
<th>( U_0t/n_3 ) (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3857</td>
<td>121.94</td>
<td>1.647</td>
<td>0.02525</td>
<td>1.209</td>
</tr>
<tr>
<td>4950</td>
<td>118.30</td>
<td>1.592</td>
<td>0.02439</td>
<td>1.553</td>
</tr>
<tr>
<td>5657</td>
<td>114.29</td>
<td>1.530</td>
<td>0.02346</td>
<td>1.7798</td>
</tr>
<tr>
<td>6394</td>
<td>112.20</td>
<td>1.498</td>
<td>0.02296</td>
<td>2.005</td>
</tr>
<tr>
<td>7016</td>
<td>113.71</td>
<td>1.521</td>
<td>0.02332</td>
<td>2.193</td>
</tr>
<tr>
<td>8418</td>
<td>108.87</td>
<td>1.447</td>
<td>0.02218</td>
<td>2.640</td>
</tr>
<tr>
<td>9192</td>
<td>103.00</td>
<td>1.357</td>
<td>0.02080</td>
<td>2.883</td>
</tr>
</tbody>
</table>

Solute: Cyclopentane

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>( t_\text{R} ) (s)</th>
<th>( V_\text{N} \times 10^4 ) (m³)</th>
<th>( V_\text{N}/n_3 \text{e}^c ) (m³ mol⁻¹)</th>
<th>( U_0t/n_3 ) (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>315</td>
<td>259.81</td>
<td>3.759</td>
<td>0.0577</td>
<td>0.122</td>
</tr>
<tr>
<td>3857</td>
<td>247.94</td>
<td>3.577</td>
<td>0.0549</td>
<td>1.209</td>
</tr>
<tr>
<td>4950</td>
<td>238.30</td>
<td>3.429</td>
<td>0.0526</td>
<td>1.553</td>
</tr>
<tr>
<td>5675</td>
<td>234.89</td>
<td>3.377</td>
<td>0.0519</td>
<td>1.780</td>
</tr>
<tr>
<td>7216</td>
<td>225.69</td>
<td>3.239</td>
<td>0.0498</td>
<td>2.194</td>
</tr>
<tr>
<td>7819</td>
<td>223.05</td>
<td>3.196</td>
<td>0.0491</td>
<td>2.452</td>
</tr>
<tr>
<td>8418</td>
<td>218.07</td>
<td>3.119</td>
<td>0.0479</td>
<td>2.640</td>
</tr>
<tr>
<td>9871</td>
<td>209.43</td>
<td>2.987</td>
<td>0.0459</td>
<td>3.096</td>
</tr>
</tbody>
</table>
### TABLE 4.10 cont.

<table>
<thead>
<tr>
<th>Time $t$ (s)</th>
<th>$t_a$ (s)</th>
<th>$V_N \times 10^{-4}$ (m³)</th>
<th>$V_N/n_3e^c$ (m³ mol⁻¹)</th>
<th>$U_0t/n_3$ (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3857</td>
<td>696.14</td>
<td>1.044</td>
<td>0.164</td>
<td>1.209</td>
</tr>
<tr>
<td>4950</td>
<td>670.30</td>
<td>1.004</td>
<td>0.157</td>
<td>1.552</td>
</tr>
<tr>
<td>4675</td>
<td>659.69</td>
<td>9.883</td>
<td>0.154</td>
<td>1.780</td>
</tr>
<tr>
<td>6375</td>
<td>644.49</td>
<td>9.650</td>
<td>0.151</td>
<td>2.005</td>
</tr>
<tr>
<td>7016</td>
<td>632.11</td>
<td>9.461</td>
<td>0.148</td>
<td>2.194</td>
</tr>
<tr>
<td>7819</td>
<td>619.05</td>
<td>9.261</td>
<td>0.145</td>
<td>2.452</td>
</tr>
<tr>
<td>8418</td>
<td>609.27</td>
<td>9.111</td>
<td>0.143</td>
<td>2.640</td>
</tr>
<tr>
<td>9192</td>
<td>597.40</td>
<td>8.929</td>
<td>0.139</td>
<td>2.883</td>
</tr>
<tr>
<td>9871</td>
<td>581.43</td>
<td>8.684</td>
<td>0.136</td>
<td>3.096</td>
</tr>
</tbody>
</table>

Solute: Benzene

<table>
<thead>
<tr>
<th>Time $t$ (s)</th>
<th>$t_a$ (s)</th>
<th>$V_N \times 10^{-4}$ (m³)</th>
<th>$V_N/n_3e^c$ (m³ mol⁻¹)</th>
<th>$U_0t/n_3$ (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3857</td>
<td>526.34</td>
<td>7.902</td>
<td>0.1228</td>
<td>1.209</td>
</tr>
<tr>
<td>4950</td>
<td>502.90</td>
<td>7.841</td>
<td>0.1172</td>
<td>1.553</td>
</tr>
<tr>
<td>4675</td>
<td>491.09</td>
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<td>0.1143</td>
<td>1.779</td>
</tr>
<tr>
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<td>473.11</td>
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<tr>
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<td>6.913</td>
<td>0.1081</td>
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</tr>
<tr>
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<td>459.87</td>
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<td>0.107</td>
<td>2.640</td>
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<tr>
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<td>0.10394</td>
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<td>437.43</td>
<td>6.479</td>
<td>0.1015</td>
<td>3.096</td>
</tr>
</tbody>
</table>
4. RESULTS

Table 4.10 cont.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3857</td>
<td>397.34</td>
<td>5.865</td>
<td>0.09153</td>
<td>1.209</td>
</tr>
<tr>
<td>4950</td>
<td>382.31</td>
<td>5.635</td>
<td>0.08794</td>
<td>1.553</td>
</tr>
<tr>
<td>5675</td>
<td>374.69</td>
<td>5.518</td>
<td>0.08612</td>
<td>1.780</td>
</tr>
<tr>
<td>6394</td>
<td>366.09</td>
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<td>0.08406</td>
<td>2.005</td>
</tr>
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<td>360.09</td>
<td>5.303</td>
<td>0.08275</td>
<td>2.193</td>
</tr>
<tr>
<td>7819</td>
<td>354.15</td>
<td>5.204</td>
<td>0.08121</td>
<td>2.452</td>
</tr>
<tr>
<td>8418</td>
<td>350.37</td>
<td>5.146</td>
<td>0.08031</td>
<td>2.64</td>
</tr>
<tr>
<td>9192</td>
<td>340.00</td>
<td>4.987</td>
<td>0.0778</td>
<td>2.883</td>
</tr>
<tr>
<td>9871</td>
<td>333.63</td>
<td>4.889</td>
<td>0.0763</td>
<td>3.096</td>
</tr>
</tbody>
</table>
Experiment 9. 3 % cis-decalin on column 9 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

\[ n_3/\text{mol} = 6.882 \times 10^{-3} \quad J_3 = 0.7605 \]

\[ P_f/\text{Pa} = 158997.07 \quad U_0/\text{m}^3 \text{ s}^{-1} = 1.8935 \times 10^6 \]

\[ P_o/\text{Pa} = 100271.75 \quad t_c/\text{s} = 15.68 \]

**TABLE 4.11.** Results obtained from column 9 (a 3% cis-decalin column) with solutes n-pentane, cyclopentane, n-hexane, cyclohexane and benzene run as a mixture.

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4. RESULTS

TABLE 4.11 cont.

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4. RESULTS

Table 4.11.cont

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Solute: Cyclohexane

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4. RESULTS

Table 4.11
cont.

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Experiment 10. 5% trans-decalin on column 10 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

\[ n_3/\text{mol} \quad 2.6151 \times 10^{-4} \]
\[ P_o/\text{Pa} \quad 139846.37 \]
\[ P_o/\text{Pa} \quad 102718.22 \]

TABLE 12. Results obtained from column 10 (a 5% trans-decalin column) with solutes n-pentane, cyclopentane, n-hexane, and cyclohexane run as a mixture.

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Solute: Cyclopentane

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<th>( V_N/n_3 e^C ) m³ mol⁻¹</th>
<th>( U_o t/n_3 ) m³ mol⁻¹</th>
</tr>
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<tbody>
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### TABLE 4.12 cont.

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<th>( V_N/n_3 ) ( \text{m}^3 \text{ mol}^{-1} )</th>
<th>( U_0t/n_3 ) ( \text{m}^3 \text{ mol}^{-1} )</th>
</tr>
</thead>
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<td>0.0465</td>
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<tr>
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<td>153.63</td>
<td>1.150</td>
<td>0.0429</td>
</tr>
<tr>
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<td>0.0425</td>
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<td>0.0338</td>
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<tr>
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<td>8.853</td>
<td>0.0330</td>
</tr>
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<td>124.22</td>
<td>8.859</td>
<td>0.0331</td>
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<td>7.653</td>
<td>0.0286</td>
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**Solute: Hexane**

<table>
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<th>Time ( t_\text{R} ) ( \text{s} )</th>
<th>( V_N \times 10^{-4} ) ( \text{m}^3 )</th>
<th>( V_N/n_3 ) ( \text{m}^3 \text{ mol}^{-1} )</th>
<th>( U_0t/n_3 ) ( \text{m}^3 \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>0.0891</td>
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<tr>
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**Solute: Cyclohexane**

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<th>( V_N \times 10^{-4} ) ( \text{m}^3 )</th>
<th>( V_N/n_3 ) ( \text{m}^3 \text{ mol}^{-1} )</th>
<th>( U_0t/n_3 ) ( \text{m}^3 \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
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<td>0.1609</td>
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<tr>
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<tr>
<td>4724</td>
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### TABLE 4.13
cont.

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<th>Time ($s$)</th>
<th>$t_R$ ($s$)</th>
<th>$V_N \times 10^4$ ($m^3$ mol$^{-1}$)</th>
<th>$V_{N/n_3} e^C$ ($m^3$ mol$^{-1}$)</th>
<th>$U_{ot/n_3}$ ($m^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>3.747</td>
<td>0.1425</td>
<td>2.944</td>
</tr>
<tr>
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<td>3.502</td>
<td>0.1332</td>
<td>3.929</td>
</tr>
<tr>
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<td>2.452</td>
<td>0.1313</td>
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</tr>
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</tr>
<tr>
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<td>0.1016</td>
<td>6.139</td>
</tr>
<tr>
<td>16300</td>
<td>299.77</td>
<td>2.464</td>
<td>0.0937</td>
<td>6.671</td>
</tr>
</tbody>
</table>
Experiment 11. 3% trans-decalin on column 11 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

\[
\begin{align*}
n_3/\text{mol} & \quad 2.2325 \times 10^{-3} \\
P_i/\text{Pa} & \quad 148056.23 \\
P_o/\text{Pa} & \quad 101658.3 \\
J^2 & \quad 0.805 \\
U_o/\text{m}^3 \text{s}^{-1} & \quad 2.3727 \times 10^{-6} \\
t_o/\text{s} & \quad 10.33
\end{align*}
\]

TABLE 4.13. Results obtained from column 10(a 3 % trans-decalin column) with solutes n-hexane, n-pentane, cyclopentane, and benzene.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>tR (s)</th>
<th>V_{N} \times 10^{-4} (m^3)</th>
<th>V_{N}/n_3 e_0 (m^3 \text{ mol}^{-1})</th>
<th>U_o t/n_3 (m^3 \text{ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>124.76</td>
<td>2.185</td>
<td>0.0970</td>
<td>0.2977</td>
</tr>
<tr>
<td>750</td>
<td>118.9</td>
<td>2.073</td>
<td>0.0926</td>
<td>0.797</td>
</tr>
<tr>
<td>1356</td>
<td>111.95</td>
<td>1.941</td>
<td>0.0862</td>
<td>1.442</td>
</tr>
<tr>
<td>1960</td>
<td>106.94</td>
<td>1.845</td>
<td>0.0819</td>
<td>2.084</td>
</tr>
<tr>
<td>2576</td>
<td>100.59</td>
<td>1.724</td>
<td>0.0765</td>
<td>2.739</td>
</tr>
<tr>
<td>3134</td>
<td>95.26</td>
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<td>0.072</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>78.48</td>
<td>1.302</td>
<td>0.0578</td>
<td>5.247</td>
</tr>
<tr>
<td>5540</td>
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</table>

Solute: Hexane (single)

<table>
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<tr>
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<th>tR (s)</th>
<th>V_{N} \times 10^{-4} (m^3)</th>
<th>V_{N}/n_3 e_0 (m^3 \text{ mol}^{-1})</th>
<th>U_o t/n_3 (m^3 \text{ mol}^{-1})</th>
</tr>
</thead>
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<td>0.0872</td>
<td>1.255</td>
</tr>
<tr>
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<td>1.878</td>
</tr>
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</table>
### TABLE 4.13 cont.

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<th>$V_N \times 10^4$ $m^3$</th>
<th>$V_N/n_3e^C$ $m^3$ mol$^{-1}$</th>
<th>$U_0/n_3$ $m^3$ mol$^{-1}$</th>
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</thead>
<tbody>
<tr>
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<td>0.797</td>
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<td>0.049</td>
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<tr>
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<td>67.59</td>
<td>1.093</td>
<td>0.047</td>
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</tr>
<tr>
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</tr>
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<tr>
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</table>

Solute: Benzene

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<th>$V_N/n_3e^C$ $m^3$ mol$^{-1}$</th>
<th>$U_0/n_3$ $m^3$ mol$^{-1}$</th>
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</thead>
<tbody>
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<td>0.797</td>
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### TABLE 4.13 cont.

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<th>( V_N/n_3e^c ) (( m^3 ) mol(^{-1} ))</th>
<th>( U_0t/n_3 ) (( m^3 ) mol(^{-1} ))</th>
</tr>
</thead>
<tbody>
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<td>0.3123</td>
<td>0.797</td>
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</tr>
<tr>
<td>1960</td>
<td>336.35</td>
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<td>0.279</td>
<td>2.084</td>
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</table>

solute: Heptane
4. RESULTS

Experiment 12. 5% cis-decalin on column 12 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

\[ n_\text{g/mol} = 2.31017 \times 10^{-3} \]
\[ P_i/\text{Pa} = 152761.72 \]
\[ P_o/\text{Pa} = 101431.75 \]
\[ J_3 = 0.837 \]
\[ U_o/\text{m}^3 \text{s}^{-1} = 1.2387 \times 10^{-6} \]
\[ t_o/\text{s} = 18.73 \]

TABLE 4.14. Results obtained from column 12 (a 5% cis-decalin column) with solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene, and heptane run as a mixture.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>(t_R) (s)</th>
<th>(V_N \times 10^4) (m(^3))</th>
<th>(V_N/n_3) (m(^3) mol(^{-1}))</th>
<th>(U_o t/n_3) (m(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
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<td>0.0257</td>
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<td>903</td>
<td>71.22</td>
<td>5.924</td>
<td>0.0249</td>
<td>0.524</td>
</tr>
<tr>
<td>1657</td>
<td>69.85</td>
<td>5.794</td>
<td>0.0244</td>
<td>0.9611</td>
</tr>
<tr>
<td>2382</td>
<td>68.10</td>
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<td>0.0236</td>
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</tr>
<tr>
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<td>4.260</td>
<td>0.01794</td>
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</tr>
<tr>
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<td>49.15</td>
<td>3.464</td>
<td>0.0146</td>
<td>7.997</td>
</tr>
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<td>$V_N/n_3c$</td>
<td>$U_0t/n_3$</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>---------------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>m$^3$</td>
<td>m$^3$ mol$^{-1}$</td>
<td>m$^3$ mol$^{-1}$</td>
</tr>
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</tr>
<tr>
<td>903</td>
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<td>0.0566</td>
<td>0.5238</td>
</tr>
<tr>
<td>1657</td>
<td>133.36</td>
<td>1.264</td>
<td>0.0565</td>
<td>0.9611</td>
</tr>
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Solute: Cyclopentane

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Solute: Hexane
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TABLE 4.14 cont.

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<th>V&lt;sub&gt;N&lt;/sub&gt;/n&lt;sub&gt;3&lt;/sub&gt;e&lt;sup&gt;c&lt;/sup&gt;</th>
<th>U&lt;sub&gt;0t/n&lt;/sub&gt;&lt;sub&gt;3&lt;/sub&gt;</th>
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<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</td>
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</table>
Experiment 13. 10 % trans-decalin on column 13 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

\[ \frac{n_3}{\text{mol}} = 1.2542 \times 10^{-6} \]
\[ P_f/Pa = 155360.56 \]
\[ P_0/Pa = 101364.99 \]

\[ \frac{V_3}{\text{s}} = 0.778 \]
\[ U_0/m^3 \text{ s}^{-1} = 1.2542 \times 10^{-6} \]
\[ t_c/s = 16.55 \]

**TABLE 4.15.** Results obtained from column 13 (a 10% trans-decalin column) with varying injection volumes of solutes n-pentane and n-hexane.

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<th>Time (s)</th>
<th>( t_R ) (s)</th>
<th>( V_n \times 10^{-4} ) m³</th>
<th>( V_n/n_3e_C ) m³ mol⁻¹</th>
<th>( U_0t/n_3 ) m³ mol⁻¹</th>
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<th>( V_n \times 10^{-4} ) m³</th>
<th>( V_n/n_3e_C ) m³ mol⁻¹</th>
<th>( U_0t/n_3 ) m³ mol⁻¹</th>
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### TABLE 4.15 cont.

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<td>m$^3$ mol$^{-1}$</td>
<td>m$^3$ mol$^{-1}$</td>
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<td>10743</td>
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Experiment 14. 5% trans column on column 14 (silanized chromasorb) Shandon U.K.3 T.C.D. detector at 298.15 K.

\[ n_s / \text{mol} = 2.2171 \times 10^3 \]
\[ P_s / \text{Pa} = 156813.35 \]
\[ P_0 / \text{Pa} = 103214.42 \]

\[ J_3 = 0.821 \]
\[ \bar{U}_0 / \text{m}^3 \text{ s}^{-1} = 2.6964 \times 10^{-6} \]
\[ \bar{t}_e / \text{s} = 18.27 \]

TABLE 4.16. Results obtained from column 14 (a 5% trans-decalin column) containing silanized chromasorb as its packing and solutes n-heptane and cyclohexane run separately.

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<th>( t_R ) (s)</th>
<th>( V_N \times 10^4 ) (m³)</th>
<th>( V_N / n_e ) (m³ mol⁻¹)</th>
<th>( U_0 / n_3 ) (m³ mol⁻¹)</th>
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</table>
Experiment 15. 3% cis-decalin on column 15 (silanized chromasorb) Shandon U.K.3 T.C.D. detector at 298.15 K.

\[ n_3/\text{mol} = 2.5121 \times 10^{-3} \]
\[ P_r/\text{Pa} = 150082.11 \]
\[ P_o/\text{Pa} = 100823.52 \]
\[ J_f = 0.860 \]
\[ U_o/\text{m}^3\text{s}^{-1} = 2.9239 \times 10^{-6} \]
\[ t_c/s = 15.01 \]

| TABLE 4.17. Results obtained from column 15 (a 3% cis-decalin column) containing silanized chromasorb as its packing and solutes n-heptane and cyclohexane run separately. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Time \( t \) s | \( t_R \) s | \( V_N \times 10^4 \) \( m^3\text{mol}^{-1} \) | \( V_N/n_3 e^c \) \( m^3\text{mol}^{-1} \) | \( U_o t/n_3 \) \( m^3\text{mol}^{-1} \) |
| solute: n-heptane | solute: cyclohexane |
| 765 | 319.71 | 7.662 | 0.305 | 0.89 |
| 1090 | 311.44 | 7.461 | 0.297 | 1.32 |
| 1501 | 294.72 | 7.034 | 0.280 | 1.62 |
| 2156 | 276.12 | 6.581 | 0.262 | 2.51 |
| 2672 | 264.68 | 6.280 | 0.253 | 3.11 |
| 4287 | 234.94 | 5.526 | 0.222 | 4.99 |
| 1288 | 175.83 | 4.044 | 0.161 | 1.59 |
| 1984 | 165.85 | 3.793 | 0.151 | 2.31 |
| 2758 | 150.86 | 3.416 | 0.136 | 3.21 |
| 3883 | 137.85 | 3.089 | 0.123 | 4.52 |
| 4639 | 128.87 | 2.836 | 0.114 | 5.46 |
Experiment 16. A 5% trans-decalin column run at 283.15 K (Shandon U.K.3 T.C.D. detector)

\[
\begin{align*}
n_x/mol & \quad 1.0910 \times 10^{-3} \\
P_x/Pa & \quad 137543.76 \\
P_y/Pa & \quad 100678.38 \\
J_2 & \quad 0.838 \\
U_0/m^3 \text{s}^{-1} & \quad 1.8196 \times 10^6 \\
t_0/s & \quad 15.68
\end{align*}
\]

TABLE 4.18. Results obtained from column 16 (a 5% trans-decalin column run at 283.15 K) with solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and heptane run as a mixture.

<table>
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<th>Time (s)</th>
<th>(t_R) (s)</th>
<th>(V_x \times 10^5) (m³)</th>
<th>(V_x/n_x e^c) (m³ mol⁻¹)</th>
<th>(U_0/t/n_3) (m³ mol⁻¹)</th>
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</tr>
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<td>0.03376</td>
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<td>2.8575</td>
<td>0.0263</td>
<td>12.83</td>
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## 4. RESULTS

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<th>$t_R$ (s)</th>
<th>$V_N \times 10^{-4}$ (m$^3$)</th>
<th>$V_N/n_3 e$ (m$^3$ mol$^{-1}$)</th>
<th>$U_0 t/n_3$ (m$^3$ mol$^{-1}$)</th>
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**Solute: cyclopentane**

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<th>$V_N/n_3 e$ (m$^3$ mol$^{-1}$)</th>
<th>$U_0 t/n_3$ (m$^3$ mol$^{-1}$)</th>
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**Solute: hexane**
### 4. RESULTS

**TABLE 4.18 cont.**

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<th>( t_R )</th>
<th>( V_{N} \times 10^{-4} )</th>
<th>( V_{N}/n_3 e^c )</th>
<th>( U_0/n_3 )</th>
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solute: benzene

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<th>( V_{N}/n_3 e^c )</th>
<th>( U_0/n_3 )</th>
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solute: cyclohexane

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<th>( V_{N}/n_3 e^c )</th>
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### TABLE 4.18 cont.

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solute: n-heptane

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Experiment 17. A 10% trans-decalin column at 283.15 K (Shandon U.K.3 T.C.D. detector)

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<th>U_0/m^3 s^{-1}</th>
<th>P_o/Pa</th>
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TABLE 4.19. Results obtained from column 17 with solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and heptane run as a mixture.

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<th>V_N/n_p e^c</th>
<th>U_0 t/n_p</th>
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<td>m^3</td>
<td>m^3 mol^{-1}</td>
<td>m^3 mol^{-1}</td>
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### TABLE 4.19 cont.

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<th>$V_{N/n_3} c$ (m$^3$ mol$^{-1}$)</th>
<th>$U_{ot/n_3}$ (m$^3$ mol$^{-1}$)</th>
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<tr>
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<td>218.33</td>
<td>4.863</td>
<td>0.222</td>
<td>0.85</td>
</tr>
<tr>
<td>1390</td>
<td>212.64</td>
<td>4.728</td>
<td>0.218</td>
<td>1.758</td>
</tr>
<tr>
<td>3335</td>
<td>205.07</td>
<td>4.548</td>
<td>0.2103</td>
<td>4.22</td>
</tr>
<tr>
<td>7835</td>
<td>165.30</td>
<td>3.606</td>
<td>0.1667</td>
<td>9.914</td>
</tr>
<tr>
<td>8753</td>
<td>132.72</td>
<td>2.835</td>
<td>0.1311</td>
<td>11.07</td>
</tr>
<tr>
<td>11417</td>
<td>123.77</td>
<td>2.623</td>
<td>0.1213</td>
<td>14.4</td>
</tr>
<tr>
<td><strong>solute: cyclohexane</strong></td>
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<tr>
<td>727</td>
<td>308.01</td>
<td>6.987</td>
<td>0.323</td>
<td>0.85</td>
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<tr>
<td>1390</td>
<td>297.02</td>
<td>6.727</td>
<td>0.311</td>
<td>1.758</td>
</tr>
<tr>
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<td>275.62</td>
<td>6.220</td>
<td>0.288</td>
<td>4.22</td>
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<tr>
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<td>218.08</td>
<td>4.857</td>
<td>0.225</td>
<td>9.914</td>
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<tr>
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<td>4.799</td>
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<td>11417</td>
<td>185.56</td>
<td>4.086</td>
<td>0.189</td>
<td>14.41</td>
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<tr>
<td>12581</td>
<td>181.28</td>
<td>3.985</td>
<td>0.184</td>
<td>15.92</td>
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### TABLE 4.19 cont.

<table>
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<tr>
<th>Time (s)</th>
<th>$t_r$ (s)</th>
<th>$V_N \times 10^3$ (m³)</th>
<th>$V_N/n_3e^c$ (m³ mol⁻¹)</th>
<th>$U_0t/n_3$ (m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>727</td>
<td>648.62</td>
<td>1.5057</td>
<td>0.696</td>
<td>0.311</td>
</tr>
<tr>
<td>1390</td>
<td>597.63</td>
<td>1.3849</td>
<td>0.6406</td>
<td>0.621</td>
</tr>
<tr>
<td>3335</td>
<td>564.65</td>
<td>1.3069</td>
<td>0.6045</td>
<td>1.49</td>
</tr>
<tr>
<td>7835</td>
<td>443.78</td>
<td>1.020</td>
<td>0.047</td>
<td>3.50</td>
</tr>
<tr>
<td>8753</td>
<td>427.27</td>
<td>1.0123</td>
<td>0.0468</td>
<td>3.91</td>
</tr>
<tr>
<td>11417</td>
<td>391.69</td>
<td>0.8970</td>
<td>0.04148</td>
<td>5.13</td>
</tr>
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</table>
Experiment 18. A 5% cis-decalin column run at 283.15 K (Shandon U.K 3 T.C.D. Detector)

\[ n_0 / \text{mol} = 5.8121 \times 10^{-6} \]

\[ J_3 = 0.771 \]

\[ P_1 / \text{Pa} = 145380.26 \]

\[ U_0 / \text{m}^3 \text{s}^{-1} = 1.9212 \times 10^{-6} \]

\[ P_0 / \text{Pa} = 100245.87 \]

\[ t_0 / \text{s} = 16.07 \]

TABLE 4.20. Results obtained from column 18 at 283.15 K for solutes \( n \)-pentane, cyclopentane and \( n \)-hexane run as a mixture.

<table>
<thead>
<tr>
<th>( t )</th>
<th>( t_\tau , \text{s} )</th>
<th>( V_N \times 10^{-4} , \text{m}^3 )</th>
<th>( V_N / n_3 e^C , \text{m}^3 \text{mol}^{-1} )</th>
<th>( U_0 t / n_3 , \text{m}^3 \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>solute: Pentane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1455</td>
<td>183.91</td>
<td>2.487</td>
<td>0.0428</td>
<td>0.481</td>
</tr>
<tr>
<td>5203</td>
<td>180.87</td>
<td>2.441</td>
<td>0.0422</td>
<td>1.72</td>
</tr>
<tr>
<td>7623</td>
<td>177.69</td>
<td>2.394</td>
<td>0.0412</td>
<td>2.52</td>
</tr>
<tr>
<td>11525</td>
<td>159.73</td>
<td>2.366</td>
<td>0.0407</td>
<td>3.81</td>
</tr>
<tr>
<td>13068</td>
<td>158.09</td>
<td>2.342</td>
<td>0.0402</td>
<td>4.32</td>
</tr>
<tr>
<td>solute: Cyclopentane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1455</td>
<td>248.30</td>
<td>3.440</td>
<td>0.0592</td>
<td>0.35</td>
</tr>
<tr>
<td>3479</td>
<td>238.11</td>
<td>3.289</td>
<td>0.0566</td>
<td>1.15</td>
</tr>
<tr>
<td>7623</td>
<td>220.89</td>
<td>3.033</td>
<td>0.0522</td>
<td>2.52</td>
</tr>
<tr>
<td>11525</td>
<td>208.7</td>
<td>2.854</td>
<td>0.0491</td>
<td>3.81</td>
</tr>
<tr>
<td>13068</td>
<td>201.27</td>
<td>2.743</td>
<td>0.0472</td>
<td>4.32</td>
</tr>
</tbody>
</table>
### TABLE 4.20 cont.

<table>
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<tr>
<th>t</th>
<th>tᵣ</th>
<th>$V_N \times 10^4$</th>
<th>$V_N/n_{3e}$</th>
<th>$U_{0t}/n_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
<td>m³</td>
<td>m³ mol⁻¹</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>1455</td>
<td>698.81</td>
<td>1.0113</td>
<td>0.174</td>
<td>0.35</td>
</tr>
<tr>
<td>5203</td>
<td>629.22</td>
<td>9.183</td>
<td>0.158</td>
<td>1.72</td>
</tr>
<tr>
<td>7623</td>
<td>616.41</td>
<td>8.893</td>
<td>0.153</td>
<td>2.52</td>
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<tr>
<td>11525</td>
<td>553.59</td>
<td>7.962</td>
<td>0.137</td>
<td>3.81</td>
</tr>
<tr>
<td>13068</td>
<td>534.01</td>
<td>7.672</td>
<td>0.132</td>
<td>4.32</td>
</tr>
</tbody>
</table>

solute: Hexane
Experiment 19. Column 19 (8%) cis decalin run at 283.15 K (Shandon U.K.3 T.C.D. Detector)

nₙ/mol 3.9112x10⁻³

P/Pa 165290.02

Pₒ/Pa 101631.64

TABLE 4.21. Results obtained from column 19 at 283.15 K with solute benzene, cyclohexane and n-heptane run as a mixture.

<table>
<thead>
<tr>
<th>t</th>
<th>tᵣ</th>
<th>Vₙ x 10⁴</th>
<th>Vₚ/nₑ</th>
<th>Uₒ/nₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
<td>m³</td>
<td>m³ mol⁻¹</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>solute</td>
<td>Benzene</td>
<td>solute</td>
<td>cyclohexane</td>
<td></td>
</tr>
<tr>
<td>712</td>
<td>556.05</td>
<td>1.075</td>
<td>0.275</td>
<td>0.51</td>
</tr>
<tr>
<td>2066</td>
<td>536.44</td>
<td>1.036</td>
<td>0.265</td>
<td>1.48</td>
</tr>
<tr>
<td>3491</td>
<td>529.63</td>
<td>1.005</td>
<td>0.257</td>
<td>2.52</td>
</tr>
<tr>
<td>3910</td>
<td>508.77</td>
<td>9.8141</td>
<td>0.251</td>
<td>2.84</td>
</tr>
<tr>
<td>5878</td>
<td>490.99</td>
<td>9.4622</td>
<td>0.242</td>
<td>4.21</td>
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<tr>
<td>7135</td>
<td>473.22</td>
<td>9.1103</td>
<td>0.233</td>
<td>5.11</td>
</tr>
</tbody>
</table>

solute : Cyclohexane

| 712  | 670.72 | 1.302 | 0.333 | 0.51 |
| 2066 | 634.35 | 1.231 | 0.316 | 1.48 |
| 3910 | 609.59 | 1.181 | 0.302 | 2.52 |
| 3491 | 599.49 | 1.161 | 0.276 | 2.84 |
| 5878 | 558.26 | 1.071 | 0.262 | 4.21 |
| 7135 | 528.26 | 1.024 | 0.297 | 5.11 |
### TABLE 4.21 cont.

<table>
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<tr>
<th>t</th>
<th>t&lt;sub&gt;R&lt;/sub&gt;</th>
<th>V&lt;sub&gt;N&lt;/sub&gt;x10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>V&lt;sub&gt;N&lt;/sub&gt;/n&lt;sub&gt;e&lt;/sub&gt;c</th>
<th>U&lt;sub&gt;0&lt;/sub&gt;t/n&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>s</td>
<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>solute</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1213.75</td>
<td>2.377</td>
<td>0.607</td>
<td>0.51</td>
</tr>
<tr>
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<td>0.578</td>
<td>1.48</td>
</tr>
<tr>
<td>3491</td>
<td>1097.06</td>
<td>2.146</td>
<td>0.549</td>
<td>2.52</td>
</tr>
<tr>
<td>3910</td>
<td>1067.79</td>
<td>2.092</td>
<td>0.535</td>
<td>2.84</td>
</tr>
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<td>962.97</td>
<td>1.880</td>
<td>0.481</td>
<td>4.21</td>
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<td>7135</td>
<td>911.67</td>
<td>1.779</td>
<td>0.455</td>
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TABLE 4.22. Summary of results obtained giving the values of the parameters $a$ and $b$ from equation 2.140, $\gamma_{13}^\infty$ (the activity coefficient at infinite dilution), and $P_3'$ the solute partial pressure.

<table>
<thead>
<tr>
<th>Column number</th>
<th>$a$</th>
<th>$b$</th>
<th>$\gamma_{13}^\infty$</th>
<th>$P_3'$</th>
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<tbody>
<tr>
<td></td>
<td>m$^3$ mol$^{-1}$</td>
<td>m$^3$ mol$^{-1}$</td>
<td></td>
<td>Pa</td>
</tr>
<tr>
<td>n-Pentane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.0282$\pm$0.0003</td>
<td>0.0024$\pm$0.0003</td>
<td>1.29$\pm$0.06</td>
<td>213.6$\pm$20.0</td>
</tr>
<tr>
<td>9</td>
<td>0.0265$\pm$0.0004</td>
<td>0.0014$\pm$3.8$\times$10$^{-5}$</td>
<td>1.41$\pm$0.08</td>
<td>135.2$\pm$6.7</td>
</tr>
<tr>
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<td>0.0271$\pm$0.0003</td>
<td>0.0019$\pm$5.9$\times$10$^{-5}$</td>
<td>1.34$\pm$0.05</td>
<td>179.2$\pm$4.1</td>
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<tr>
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<td>1.42$\pm$0.06</td>
<td>126.9$\pm$1.7</td>
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<tr>
<td>13</td>
<td>0.0288$\pm$0.0002</td>
<td>0.0022$\pm$4.2$\times$10$^{-5}$</td>
<td>1.32$\pm$0.04</td>
<td>194.6$\pm$4.9</td>
</tr>
<tr>
<td>Cyclopentane</td>
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<tr>
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<tr>
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<td>0.99$\pm$0.02</td>
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<tr>
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<td>173.5$\pm$3.3</td>
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<tr>
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<td>0.0031$\pm$5.8$\times$10$^{-5}$</td>
<td>1.01$\pm$0.02</td>
<td>134.4$\pm$1.2</td>
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</tr>
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</tr>
<tr>
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<td>0.00399$\pm$0.0010</td>
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<tr>
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<tr>
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<td>1.27$\pm$0.06</td>
<td>192.53$\pm$6.1</td>
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<tr>
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<tr>
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</table>
### 4. RESULTS

#### TABLE 4.22

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</tr>
<tr>
<td></td>
<td>0.0935±0.0004</td>
<td>0.0047±0.55X10⁻⁵</td>
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<tr>
<td></td>
<td>0.0984±0.0009</td>
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**Cyclohexane**

<table>
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<tr>
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<tr>
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<td>0.013±0.0002</td>
<td>1.06±0.05</td>
<td>236.09±11.29</td>
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<tr>
<td></td>
<td>0.1791±0.0004</td>
<td>0.0139±0.0003</td>
<td>1.03±0.02</td>
<td>184.02±3.42</td>
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<tr>
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<td>0.1804±0.0017</td>
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<td>1.04±0.02</td>
<td>201.34±12.31</td>
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</tr>
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<td>0.0106±0.0002</td>
<td>1.11±0.06</td>
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<tr>
<td></td>
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<td>1.06±0.02</td>
<td>190.21±2.18</td>
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</tr>
<tr>
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<td>0.1763±0.0052</td>
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<td>1.08±0.02</td>
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</tbody>
</table>

**Benzene**

<table>
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<tr>
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<th></th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.134±0.0009</td>
<td>0.0106±0.0005</td>
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<td>181.07±2.3</td>
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<tr>
<td></td>
<td>0.140±0.0014</td>
<td>0.0068±0.0002</td>
<td>1.39±0.09</td>
<td>125.48±7.7</td>
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<tr>
<td></td>
<td>0.027±0.00027</td>
<td>0.0019±5.9X10⁻⁵</td>
<td>1.42±0.06</td>
<td>173.17±3.8</td>
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<tr>
<td></td>
<td>0.128±0.0012</td>
<td>0.0094±0.0003</td>
<td>1.46±0.09</td>
<td>198.83±12.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.138±0.0012</td>
<td>0.0069±0.0002</td>
<td>1.42±0.09</td>
<td>120.48±6.8</td>
<td></td>
</tr>
</tbody>
</table>

**n-heptane**

<table>
<thead>
<tr>
<th></th>
<th>12</th>
<th>14</th>
<th></th>
<th>12</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.306±0.004</td>
<td>0.0156±0.0041</td>
<td>1.35±0.02</td>
<td>121.80±2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.145±0.005</td>
<td>0.0086±0.0019</td>
<td>1.31±0.02</td>
<td>127.42±2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.336±0.004</td>
<td>0.0257±0.0007</td>
<td>1.21±0.04</td>
<td>190.23±3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.332±0.003</td>
<td>0.0795±0.0002</td>
<td>1.22±0.04</td>
<td>194.29±5.3</td>
<td></td>
</tr>
</tbody>
</table>
4. RESULTS

TABLE 4.23. Data used in the calculation of $V_N$, where $P_i^*$ is the vapour pressure of the pure solute, $V_i^*$ is the molar volume of the solute, $B_{12}$ is the mixed virial coefficient and $B_{11}$ is the second virial coefficient of the solute at 298.15 K.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$P_i^*$ (38)</th>
<th>$V_i^*$ (38)</th>
<th>$B_{12}$</th>
<th>$-B_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>68325.66</td>
<td>117.38x10^{-6}</td>
<td>2.429x10^{-6}</td>
<td>992.81x10^{-6}</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>42324.21</td>
<td>93.71x10^{-6}</td>
<td>18.048x10^{-6}</td>
<td>1066.23x10^{-6}</td>
</tr>
<tr>
<td>n-hexane</td>
<td>19778.28</td>
<td>131.59x10^{-6}</td>
<td>29.0x10^{-6}</td>
<td>1519.31x10^{-6}</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>13009.88</td>
<td>108.74x10^{-6}</td>
<td>21.576x10^{-6}</td>
<td>1577.10x10^{-6}</td>
</tr>
<tr>
<td>benzene</td>
<td>12689.62</td>
<td>89.40x10^{-6}</td>
<td>17.658x10^{-6}</td>
<td>1570.35x10^{-6}</td>
</tr>
<tr>
<td>n-heptane</td>
<td>6095.26</td>
<td>147.46x10^{-6}</td>
<td>31.532x10^{-6}</td>
<td>2197.63x10^{-6}</td>
</tr>
</tbody>
</table>

TABLE 4.24. Data used in the calculation of $V_N$, where $P_i^*$ is the vapour pressure of the pure solute, $V_i^*$ is the molar volume of the solute, $B_{12}$ is the mixed virial coefficient and $B_{11}$ is the second virial of the solute at 283.15 K.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$P_i^*$ (38)</th>
<th>$B_{12}$x10^{-6}</th>
<th>$-B_{11}$x10^{-6}</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>37827.56</td>
<td>2.3828</td>
<td>1118.99</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>22597.87</td>
<td>17.4516</td>
<td>1728.29</td>
</tr>
<tr>
<td>n-hexane</td>
<td>10091.17</td>
<td>28.9528</td>
<td>1730.89</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>6320.68</td>
<td>20.9011</td>
<td>1806.41</td>
</tr>
<tr>
<td>benzene</td>
<td>6070.16</td>
<td>17.0044</td>
<td>1583.78</td>
</tr>
<tr>
<td>n-heptane</td>
<td>2743.77</td>
<td>33.1766</td>
<td>2523.74</td>
</tr>
</tbody>
</table>
TABLE 4.25. Summary of results obtained for n-hexane (0.1µ, 0.5µ and 1.0µ) and n-pentane (0.5µl and 1.0µl) in trans-decalin at 298.15 K.

<table>
<thead>
<tr>
<th>solute</th>
<th>solute volume</th>
<th>γ₁₃</th>
<th>P₃'</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>0.1</td>
<td>1.28</td>
<td>204.1</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.5</td>
<td>1.28</td>
<td>199.5</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.0</td>
<td>1.27</td>
<td>197.9</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.1</td>
<td>1.32</td>
<td>201.0</td>
</tr>
<tr>
<td>n-pentane</td>
<td>1.0</td>
<td>1.31</td>
<td>197.8</td>
</tr>
</tbody>
</table>

TABLE 4.26. The critical constants and ionization energies, I, used in the calculation of mixed second virial coefficient, B₁₂ at 298.15 and 283.15 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>V_c⁽³⁸⁾</th>
<th>T_c⁽³⁸⁾</th>
<th>I⁽³⁸⁾</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m³ mol⁻¹</td>
<td>K</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>Pentane</td>
<td>304.0</td>
<td>469.7</td>
<td>0.994</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>260.2</td>
<td>511.6</td>
<td>1.014</td>
</tr>
<tr>
<td>Hexane</td>
<td>370.0</td>
<td>507.3</td>
<td>0.982</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>308.3</td>
<td>553.4</td>
<td>0.943</td>
</tr>
<tr>
<td>Benzene</td>
<td>259.4</td>
<td>562.1</td>
<td>0.924</td>
</tr>
<tr>
<td>Heptane</td>
<td>432.6</td>
<td>540.1</td>
<td>0.953</td>
</tr>
<tr>
<td>Helium</td>
<td>5.2</td>
<td>57.8</td>
<td>5.248</td>
</tr>
</tbody>
</table>
TABLE 4.27. Results obtained from figures 1 to 6 for solutes in cis-decalin at 298.15K where a is the intercept and b the slope.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>$a$ ( \text{m}^3 \text{mol}^{-1} )</th>
<th>$b$ ( \text{m}^3 \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pentane</td>
<td>0.0257 ± 0.0003</td>
<td>0.00139 ± 2.88x10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>5$H$</em>{10}$</td>
<td>0.0579 ± 0.0004</td>
<td>0.00312 ± 3.5x10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>Hexane</td>
<td>0.0944 ± 0.0019</td>
<td>0.00451 ± 0.00015</td>
</tr>
<tr>
<td>4</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>0.1783 ± 0.0032</td>
<td>0.00980 ± 0.00029</td>
</tr>
<tr>
<td>5</td>
<td>Benzene</td>
<td>1.3772 ± 0.0019</td>
<td>0.00663 ± 0.00015</td>
</tr>
<tr>
<td>6</td>
<td>Heptane</td>
<td>0.3066 ± 0.0041</td>
<td>0.01560 ± 0.00408</td>
</tr>
</tbody>
</table>

TABLE 4.28. Calculated values for $\gamma_{13}^\infty$ (activity coefficient at infinite dilution) and $P_3'$ (partial pressure of solvent at 298.15 K) for solutes in cis-decalin using equation 2.139.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>$\gamma_{13}^\infty$</th>
<th>$P_3'$ ( \text{Pa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pentane</td>
<td>1.41 ± 0.07</td>
<td>134.0 ± 6.3</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>5$H$</em>{10}$</td>
<td>1.01 ± 0.07</td>
<td>133.4 ± 18.4</td>
</tr>
<tr>
<td>3</td>
<td>Hexane</td>
<td>1.31 ± 0.03</td>
<td>118.4 ± 3.0</td>
</tr>
<tr>
<td>4</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>1.07 ± 0.10</td>
<td>136.3 ± 13.1</td>
</tr>
<tr>
<td>5</td>
<td>Benzene</td>
<td>1.42 ± 0.01</td>
<td>119.3 ± 2.5</td>
</tr>
<tr>
<td>6</td>
<td>Heptane</td>
<td>1.35 ± 0.02</td>
<td>121.8 ± 2.6</td>
</tr>
</tbody>
</table>

: Cyclopentane  \(^{\dagger}\) : Cyclohexane
TABLE 4.29. Results obtained from figures 7 to 13 for solutes in trans-decalin at 298.15 K where \( a \) is the intercept and \( b \) the slope.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>( a ) ( \text{m}^3 \text{mol}^{-1} )</th>
<th>( b ) ( \text{m}^3 \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Pentane</td>
<td>0.02739 ± 0.00029</td>
<td>0.0021 ± 3.37 \times 10^{-5}</td>
</tr>
<tr>
<td>8</td>
<td>( \text{C}<em>5\text{H}</em>{10}^* )</td>
<td>0.05962 ± 0.00079</td>
<td>0.0045 ± 8.19 \times 10^{-5}</td>
</tr>
<tr>
<td>9</td>
<td>Hexane</td>
<td>0.09823 ± 0.00019</td>
<td>0.0074 ± 0.0002</td>
</tr>
<tr>
<td>10</td>
<td>( \text{C}<em>6\text{H}</em>{12}^s )</td>
<td>0.17994 ± 0.00255</td>
<td>0.0128 ± 0.0003</td>
</tr>
<tr>
<td>11</td>
<td>Benzene</td>
<td>0.13467 ± 0.00319</td>
<td>0.0105 ± 0.0005</td>
</tr>
<tr>
<td>12</td>
<td>Heptane</td>
<td>0.33235 ± 0.00343</td>
<td>0.0261 ± 0.0007</td>
</tr>
<tr>
<td>13</td>
<td>Pentane</td>
<td>0.02752 ± 0.00024</td>
<td>0.0022 ± 4.23 \times 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>0.09840 ± 0.00092</td>
<td>0.0795 ± 0.0002</td>
</tr>
</tbody>
</table>

\*: Cyclopentane \^: Cyclohexane

TABLE 4.30. Calculated values for \( \gamma_{13}^\infty \) (activity coefficient at infinite dilution) and \( P_3' \) (partial pressure of solvent at 298.15 K) for solutes in trans decalin using equation 2.139.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>( \gamma_{13}^\infty )</th>
<th>( P_3' ) ( \text{Pa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Pentane</td>
<td>1.32 ± 0.05</td>
<td>189.1 ± 2.7</td>
</tr>
<tr>
<td>8</td>
<td>( \text{C}<em>5\text{H}</em>{10}^* )</td>
<td>0.98 ± 0.02</td>
<td>189.1 ± 2.3</td>
</tr>
<tr>
<td>9</td>
<td>Hexane</td>
<td>1.28 ± 0.02</td>
<td>186.7 ± 2.3</td>
</tr>
<tr>
<td>10</td>
<td>( \text{C}<em>6\text{H}</em>{12}^s )</td>
<td>1.06 ± 0.08</td>
<td>175.6 ± 13.2</td>
</tr>
<tr>
<td>11</td>
<td>Benzene</td>
<td>1.45 ± 0.02</td>
<td>193.1 ± 9.3</td>
</tr>
<tr>
<td>12</td>
<td>Heptane</td>
<td>1.22 ± 0.04</td>
<td>194.3 ± 5.1</td>
</tr>
<tr>
<td>13</td>
<td>Pentane</td>
<td>1.32 ± 0.04</td>
<td>194.6 ± 4.8</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>1.28 ± 0.01</td>
<td>200.3 ± 4.2</td>
</tr>
</tbody>
</table>

\*: Cyclopentane \^: Cyclohexane
TABLE 4.31 Results obtained from figures 14 to 18 for solutes in trans-decalin at 283.15K where \(a\) is the intercept and \(b\) the slope.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>(a) (\text{m}^3\text{ mol}^{-1})</th>
<th>(-b) (\text{m}^3\text{ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Pentane</td>
<td>0.0046 ± 0.0003</td>
<td>0.00151 ± 0.00031</td>
</tr>
<tr>
<td>17</td>
<td>C(<em>5)H(</em>{10})</td>
<td>0.1004 ± 0.0002</td>
<td>0.00324 ± 2.98x10(^{-5})</td>
</tr>
<tr>
<td>18</td>
<td>Hexane</td>
<td>0.0782 ± 0.0007</td>
<td>0.00592 ± 0.00023</td>
</tr>
<tr>
<td>19</td>
<td>C(<em>6)H(</em>{12})</td>
<td>0.0328 ± 0.0038</td>
<td>0.00103 ± 0.00032</td>
</tr>
<tr>
<td>20</td>
<td>Benzene</td>
<td>0.0236 ± 0.0015</td>
<td>0.00781 ± 0.00023</td>
</tr>
<tr>
<td>21</td>
<td>Heptane</td>
<td>0.2355 ± 0.0041</td>
<td>0.01097 ± 0.00268</td>
</tr>
</tbody>
</table>

TABLE 4.32. Calculated values for \(\gamma_{13}^{\infty}\) (activity coefficient at infinite dilution) and \(P_3^{	ext{s}}\) (partial pressure of solvent at 283.15 K) for solutes in trans-decalin using equation 1.139.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>(\gamma_{13}^{\infty})</th>
<th>(P_3^{	ext{s}}) Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Pentane</td>
<td>1.33 ± 0.01</td>
<td>75.9 ± 15.2</td>
</tr>
<tr>
<td>17</td>
<td>C(<em>5)H(</em>{10})</td>
<td>0.97 ± 0.07</td>
<td>73.9 ± 5.2</td>
</tr>
<tr>
<td>18</td>
<td>Hexane</td>
<td>1.27 ± 0.03</td>
<td>75.1 ± 8.8</td>
</tr>
<tr>
<td>19</td>
<td>C(<em>6)H(</em>{12})</td>
<td>1.14 ± 0.10</td>
<td>78.1 ± 6.5</td>
</tr>
<tr>
<td>20</td>
<td>Benzene</td>
<td>1.63 ± 0.01</td>
<td>73.5 ± 2.2</td>
</tr>
<tr>
<td>21</td>
<td>Heptane</td>
<td>1.22 ± 0.02</td>
<td>79.8 ± 6.8</td>
</tr>
</tbody>
</table>
4. RESULTS

* : Cyclopentane  $ : Cyclohexane

TABLE 4.33 Calculated values for $\gamma_{13}^{\infty}$ (activity coefficient at infinite dilution) and $p_{13}'$ (partial pressure of solvent at 283.15 K) for solutes in cis decalin using equation 2.139.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Solute</th>
<th>$p_{13}'$</th>
<th>$\gamma_{13}^{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Pentane</td>
<td>32.6±6.7</td>
<td>1.44 ± 0.031</td>
</tr>
<tr>
<td>14</td>
<td>C$<em>2$H$</em>{10}$ *</td>
<td>116.4±116.4</td>
<td>1.014 ± 0.036</td>
</tr>
<tr>
<td>14</td>
<td>Hexane</td>
<td>131.7±19.1</td>
<td>1.292 ± 0.017</td>
</tr>
<tr>
<td>15</td>
<td>C$<em>6$H$</em>{12}$ $^\S$</td>
<td>121.9±9.0</td>
<td>1.096 ± 0.025</td>
</tr>
<tr>
<td>15</td>
<td>Benzene</td>
<td>75.8±15.2</td>
<td>1.387 ± 0.031</td>
</tr>
<tr>
<td>15</td>
<td>Heptane</td>
<td>126.6±7.2</td>
<td>1.363 ± 0.0476</td>
</tr>
</tbody>
</table>

* : Cyclopentane
$^\S$ : Cyclohexane
4.1 Error Analysis

4.1.1. Determination of the Error in $a$ and $b$.

The equation for the determination of $\gamma_{13}'$ is

$$\frac{V_N}{n_3 e^C} = \frac{RT}{\gamma_{13}' P_1} - \frac{U_o t}{n_3} \left[ \frac{P_3^I}{\gamma_{13}' P_1} \right]$$

(4.6)

where

$$C = \left[ \frac{B_{11} + V_1^*}{RT} \right] P_1^* + \left[ \frac{2B_{12} - V_1^*}{RT} \right] P_o J_2^3$$

(4.7)

The functional relationship between $y$ and $x$ can be approximated by a straight line

$$y = a - bx$$

(4.8)

where

$$y = \frac{V_N}{e^C n_3}$$

(4.9)
4. RESULTS
4.1. Error Analysis

To find the uncertainty in the estimation of coefficients $a$ and $b$ the following equations are used

$$
\sigma_a = \frac{\sigma}{\Delta^2} \left( \sum x_i \right)^2 \left[ N \sum x_i^2 - (\sum x_i)^2 \right] = \frac{\sigma^2}{\Delta} \sum x_i^2
$$

(4.11)

$$
\sigma_b = \frac{N \sigma^2}{\Delta^2} \left[ N \sum x_i^2 - (\sum x_i)^2 \right] = N \frac{\sigma^2}{\Delta}
$$

(4.12)

where

$$
\Delta = N \sum x_i^2 - (\sum x_i)^2
$$

(4.13)

and $\sigma$, the apparent standard deviation is given by

$$
\sigma^2 = \frac{1}{N-2} \sum (y_i - a - bx_i)^2
$$

(4.14)
4.1.2. Determination of the error in $\gamma_{13}$

From equation 4.6 $\gamma_{13}$ is obtained from the intercept of the graph $V_N/n_3 e^c$ against $U_d/n_3$.

Therefore

$$a = \frac{RT}{\gamma_{13} P_1} \quad (4.15)$$

The standard deviation of any function $x = f(u,v,\ldots)$ is given by

$$\sigma_x^2 = \sigma_u^2 \left( \frac{\partial x}{\partial u} \right)^2 + \sigma_v^2 \left( \frac{\partial x}{\partial v} \right)^2 + \ldots \quad (4.16)$$

Therefore

$$\sigma_a^2 = \sigma_{\gamma_{13}}^2 \left( \frac{\partial a}{\partial \gamma_{13}} \right)^2 \quad (4.17)$$

But

$$\frac{\partial a}{\partial \gamma_{13}} = \frac{RT}{\gamma_{13}^2 P_1} \quad (4.18)$$
Substituting eq. 4.18 into 4.17

\[
\sigma_{\gamma_{13}}^2 = \frac{\sigma_a \gamma_{13}^2 P_1^*}{RT} \tag{4.19}
\]

4.1.3. Determination of the error in \( P'_3 \)

From equation 4.6 \( P'_3 \) is obtained from the slope

\[
b = \frac{P'_3}{\gamma_{13}^* P_1^*} \tag{4.20}
\]

In this case the dependant variable is a function of more than one variable

\[
\rightarrow b = [f \left( P'_3 \ , \ \gamma_{13}^* \right)] \tag{4.21}
\]

\[
\therefore \sigma_b^2 = \left( \frac{\partial b}{\partial P'_3} \right)^2 \sigma_{P'_3}^2 + \left( \frac{\partial b}{\partial \gamma_{13}^*} \right) \sigma_{\gamma_{13}^*}^2 \tag{4.22}
\]
4.1. Error Analysis

4.1.4. Determination of the Error in the Partial Molar Enthalpy

The partial molar enthalpy of mixing at infinite dilution is given by

\[
\frac{H_1^{E\infty}}{RT^2} = \left[ \frac{\partial \ln \gamma_{13}^{\infty}}{\partial T} \right]_p
\]  

(4.24)

Solving for \(H_1^{E\infty}\)

\[
\frac{R}{1 - \frac{1}{T_1}} \left[ \ln \gamma_{13}(T_1) - \ln \gamma_{13}(T_2) \right] = H_1^{E\infty}
\]  

(4.25)

Let

\[
a = \frac{R}{1 - \frac{1}{T_1} - \frac{1}{T_2}}
\]  

(4.26)
4. RESULTS

4.1. Error Analysis

Using equation 4.16, equation 4.25 becomes

\[ \sigma_{H_1^{*}} = a^2 \sigma_u^2 + 2 \sigma_u \sigma_v + \sigma_v^2 \] (4.31)

In order to determine the error in \( H_1^{*} \), the error in \( \ln \gamma_1 \) has to be determined.
4. RESULTS

4.1. Error Analysis

\[ \sigma_{\text{max}} = \frac{\sigma_x}{x} \quad (4.32) \]

4.1.5. Sample Calculation

The following is a detailed calculation for the determination of \( \gamma_{13}^\infty \), \( P_i \), \( H_i^E \infty \) (together with the errors for each value) for n-pentane in trans-decalin at 298.15 K and 283.15 K.

STEP 1. The determination of \( \gamma_{13}^\infty \)

\( T_1 = 298.15 \quad T_2 = 283.15 \)

From graphs 7 and 14 the intercepts \( a \) are obtained.

\( a_{T_1} = 0.02739 \quad a_{T_2} = 0.0465 \)

\( \sigma a \) is obtained by equation 4.11. Thus

\( a_{T_1} = 0.02739 \pm 0.0003 \quad a_{T_2} = 0.0465 \pm 0.0003 \)

from equation 4.15
4. RESULTS
4.1. Error Analysis

\[ y_{13(T1)} = \frac{8.134 \times 298.15}{0.02739 \times 68325.66} = 1.32 \]

\[ y_{13(T2)} = \frac{8.314 \times 283.15}{0.0465 \times 37827.56} = 1.34 \]

STEP 2. Determination of \( \sigma y_{13} \)

\( \sigma y_{13} \) is determined by equation 4.19

At 298.15 K

\[ \sigma y_{13(T1)} = \frac{0.0003 \times 1.32^2 \times 68325.15}{8.314 \times 298.15} = 0.05 \]

At 283.15

\[ \sigma y_{13(T2)} = \frac{0.0003 \times 1.33^2 \times 37827.56}{8.314 \times 283.15} = 0.01 \]

STEP 3. The determination of \( P_3' \)

\( P_3' \) is obtained using the slope of graphs 7 and 14.

\[ b_{(T1)} = 0.0021 \pm 3.37 \times 10^{-5} \]

\[ b_{(T2)} = 0.0015 \pm 0.0003 \]
4. RESULTS

4.1. Error Analysis

The errors are obtained from equation 4.12.

To calculate $P'_3$, the ratio of the slope to the intercept is used (equation 5.2).

Therefore

$$\frac{0.0021}{0.02739} \text{ (8.314} \times 298.15) = P'_{1(T_1)} = 189.1 \text{Pa}$$

$$\frac{0.0015}{0.0465} \text{ (8.314} \times 283.15) = P'_{1(T_2)} = 75.9 \text{Pa}$$

STEP 4. The Determination of $\sigma P'_3$

$\sigma P'_3$ is determined from equation 4.23

At 298.15

$$\sigma_{P'_3} = 1.32 \times 68325.66 \sqrt{(3.37 \times 10^{-9})^2 - \left(\frac{189.1}{1.32^2 \times 68325.66}\right) 0.05^2} = 2.68$$

and at 283.15
4. RESULTS

4.1. Error Analysis

\[ \sigma_{P_{(T)}} = 1.33 \times 37827.56 \sqrt{0.0003^2 - \frac{75.9}{1.33^2 \times 37827.56}} \times 0.01^2 = 15.19 \]

STEP 5. The determination of \( H_1^{E_\infty} \)

The calculated values for \( \gamma_1^{\infty} \) at 298.15 K and 283.15 K are used to determine \( H_1^{E_\infty} \) using equation 4.25

\[ \frac{8.314}{298.15} - \frac{1}{283.15} \left[ \ln(1.32) - \ln(1.33) \right] = H_1^{E_\infty} = 990 \text{ J mol}^{-1} \]

STEP 6. The determination of \( \sigma H_1^{E_\infty} \)

\( \sigma H_1^{E_\infty} \) is determined using equation 4.31.

\[ \sigma_{H_1^{E_\infty}} = \sqrt{ \left( \frac{8.314}{298.15} - \frac{1}{283.15} \right)^2 \left[ 0.01^2 - \frac{0.01^2}{1.32^2} \right] - \frac{0.01^2}{1.33^2} } = 1500 \text{ J mol}^{-1} \]
FIGURE 1. n-Pentane in cis-decalin at 298.15 K
**FIGURE 2.** Cyclopentane in cis-decalin at 298.15 K
FIGURE 3. n-Hexane in cis-decalin at 298.15 K
FIGURE 4. Cyclohexane in cis-decalin at 298.15 K
FIGURE 5. Benzene in cis-decalin at 298.15 K
FIGURE 6. n-Heptane in cis-decalin at 298.15 K
FIGURE 7. n-Pentane in trans-decalin at 298.15 K
FIGURE 8. Cyclopentane in trans-decalin at 298.15 K
Figure 9. n-Hexane in trans-decalin at 298.15 K
FIGURE 10. Cyclohexane in trans-decalin at 298.15 K
FIGURE 11. Benzene in trans-decalin at 298.15 K
FIGURE 12. n-Heptane in trans-decalin at 298.15 K
FIGURE 13. n-Pentane and n-Hexane in trans-decalin at 298.15 K
FIGURE 14. n-Pentane, cyclopentane and n-hexane in cis-decalin at 283.15 K
Figure 15. Cyclohexane, Benzene and n-Heptane in cis-decalin at 283.15 K
Figure 16. n-Pentane in trans-decalin at 283.15 K
Figure 17. Cyclopentane in trans-decalin at 283.15 K
Figure 18. n-Hexane in trans-decalin at 283.15 K
Figure 19. Cyclohexane in trans-decalin at 283.15 K
Figure 20. Benzene in trans-decalin at 283.15 K
Figure 21. n-Heptane in trans-decalin at 283.15 K
5. DISCUSSION

The primary aim of this thesis was to develop a method to determine the activity coefficient at infinite dilution of solutes in volatile solvents at 298.15 K. The work was extended to include data at 283.15 K in order to test the possibility of determining the partial molar enthalpy at infinite dilution.

5.1. Experimental Error in $\gamma_{13}^\infty$

Table 5.1 shows the values obtained for $\gamma_{13}^\infty$ for the solutes investigated in cis- and trans-decalin at 283.15 K and 298.15 K. The experimental error for $\gamma_{13}^\infty$ was determined using equation 4.19.

TABLE 5.1. Calculated values of activity coefficients at infinite dilution ($\gamma_{13}^\infty$) for solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and heptane at 283.15 K and 298.15 K in cis- and trans-decalin.

<table>
<thead>
<tr>
<th>Solute</th>
<th>trans-decalin</th>
<th>cis-decalin</th>
<th>trans-decalin</th>
<th>cis-decalin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_{13}^\infty(298.15K)$</td>
<td>$\gamma_{13}^\infty(298.15K)$</td>
<td>$\gamma_{13}^\infty(283.15K)$</td>
<td>$\gamma_{13}^\infty(283.15K)$</td>
</tr>
<tr>
<td>n-pentane</td>
<td>1.32±0.05</td>
<td>1.41±0.07</td>
<td>1.33±0.01</td>
<td>1.44±0.03</td>
</tr>
<tr>
<td>C5H10</td>
<td>0.98±0.02</td>
<td>1.01±0.07</td>
<td>0.97±0.07</td>
<td>1.01±0.03</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.28±0.02</td>
<td>1.31±0.03</td>
<td>1.27±0.03</td>
<td>1.29±0.01</td>
</tr>
<tr>
<td>C6H12</td>
<td>1.06±0.08</td>
<td>1.07±0.10</td>
<td>1.14±0.10</td>
<td>1.09±0.02</td>
</tr>
<tr>
<td>benzene</td>
<td>1.45±0.02</td>
<td>1.42±0.01</td>
<td>1.63±0.01</td>
<td>1.39±0.03</td>
</tr>
<tr>
<td>n-heptane</td>
<td>1.22±0.04</td>
<td>1.35±0.02</td>
<td>1.22±0.02</td>
<td>1.36±0.04</td>
</tr>
</tbody>
</table>
5. DISCUSSION

The experimental errors range from 0.01 to 0.1 with most of the $\sigma(\gamma_{13}^{\infty})$ values at about 0.04. The error obtained at 283.15 K is similar to that obtained at 298.15 K.

Cruickshank\textsuperscript{(39)} obtained an error for $\gamma_{13}^{\infty}$ of 0.03 for various hydrocarbons in n-octadecane at 315.15 K. Everett\textsuperscript{(40)} obtained an error for $\gamma_{13}^{\infty}$ of 0.02 for various hydrocarbons using squalene as the stationary phase.

Although the errors obtained by these workers are lower than those obtained in this work it must be noted that the stationary phases used in both cases by Cruickshank and Everett were involatile. This was not the case with cis- and trans-decalin used in this work.

5.1.1. Precision of $\gamma_{13}^{\infty}$

Precision is a measure of the internal consistency of results obtained and describes the reproducibility of repeated determinations.

Using the values of $\gamma_{13}^{\infty}$ (for each solute) calculated for each column, given in table 4.22, the precision of $\gamma_{13}^{\infty}$ is calculated from the following equation

$$s^2 = \frac{1}{N - 1} \sum (x_i - \bar{x})^2$$ (5.1)

The precision for $\gamma_{13}^{\infty}$ at 298.15 K (table 5.2) for both cis-and trans-decalin ranges from 0.5 to 2 %, whereas at 283.15 K the precision ranges from 1.0 to 0.05 %. Some investigators have managed to reduce the standard deviation to the 0.02 - 0.05 % region. However this high precision was obtained from a single column\textsuperscript{(41)} unlike in this work where $\gamma_{13}^{\infty}$ is calculated from a number of columns differing in the amount of solvent on the column and in the flow-rate.
5. DISCUSSION

TABLE 5.2. Calculated values for the precision (as a percentage) of $\gamma_{13}$ for cis- and trans-decalin at 298.15 K and 283.15 K.

<table>
<thead>
<tr>
<th>Solute</th>
<th>T/ 298.15 K</th>
<th>T/ 283.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>trans-decalin</td>
<td>cis-decalin</td>
</tr>
<tr>
<td>n-pentane</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>benzene</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

5.2. Activity coefficient data at 298.15 K.

Due to the volatility of the stationary phase very little work has been done by other workers by the G.L.C. method for determining activity coefficients for the systems studied in this thesis. However Letcher and Baxter\(^{41}\) have attempted the determination of $\gamma_{13}$ of various solutes in decalin by G.L.C. using a method outlined in chapter 2 with n-hexane as the reference solute. Letcher's results were calculated from data which was more empirical and little was known about the rate at which solvent loss occurred.
Letcher\textsuperscript{(42)} has also successfully predicted $\gamma_{13}^\infty$ using an application of the Prigogine-Flory-Patterson theory. The $\gamma_{13}^\infty$ results obtained in this work compare favourably with Letcher's results. The only other literature values of measured $\gamma_{13}^\infty$ reported here have been conducted by Vernier et al.\textsuperscript{(43)} However loss of solvent from the column was not taken into consideration by Vernier. It is difficult to assess Vernier's results because we do not have a detailed description of his method. His results are however well within our experimental error. His results together with Letcher's results and the results obtained in this thesis are given in table 5.3.

**TABLE 5.3.** Comparison of results for the activity coefficient at infinite dilution for trans-decalin at 298.15 K with literature values. The standard deviation $\sigma$, is given for the work presented in this thesis. (see Error Analysis, Chapter 4)

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\gamma_{13}^\infty$ This work</th>
<th>$\gamma_{13}^\infty$\textsuperscript{a}</th>
<th>$\gamma_{13}^\infty$\textsuperscript{b}</th>
<th>$\gamma_{13}^\infty$\textsuperscript{c}</th>
<th>$\gamma_{13}^\infty$\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>1.22 $\sigma = 0.04$</td>
<td>1.27</td>
<td>1.26</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.28 $\sigma = 0.02$</td>
<td>1.32</td>
<td>1.31</td>
<td>1.32</td>
<td>1.26</td>
</tr>
<tr>
<td>benzene</td>
<td>1.45 $\sigma = 0.02$</td>
<td>1.40</td>
<td>2.17</td>
<td>2.09</td>
<td>1.47</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.06 $\sigma = 0.08$</td>
<td>1.10</td>
<td>1.09</td>
<td>0.96</td>
<td>1.06</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental values of Letcher by G.L.C.\textsuperscript{(41)} \textsuperscript{b} and \textsuperscript{c} Predicted values by Letcher using Prigogine-Flory-Patterson theory.\textsuperscript{(42)} \textsuperscript{d} Experimental values of Vernier by G.L.C.\textsuperscript{(43)}
5. DISCUSSION

5.2.1. Comparison of $\gamma_{13}^*$ for cis- and trans-decalin

From table 5.1 (comparing $\gamma_{13}^*$ for cis- and trans-decalin at 298.15 K) it is clear that cis-decalin has a higher $\gamma_{13}^*$ value than trans for every solute, the largest difference in $\gamma_{13}^*$ being for the solute n-heptane and the smallest for cyclopentane. At 283.15 K all the solutes show the same behaviour as at 298.15 K, except for the two six sided cyclic molecules (cyclohexane and benzene) where the effect is reversed and the $\gamma_{13}^*$ value for cis-decalin is lower than for trans-decalin.

5.2.2. Infinite Dilution Conditions

The volume of the solute required to satisfy infinite dilution conditions is investigated by injecting varying volumes of n-hexane (1.0 $\mu$l, 0.5$\mu$l and 0.1$\mu$l) and n-pentane (1.0$\mu$l and 0.1$\mu$l) on to the same column. $\gamma_{13}^*$ is calculated for each volume. These values are given in Table 5.4.

Table 5.4. $\gamma_{13}^*$ of n-hexane and n-pentane for different injection volumes.

<table>
<thead>
<tr>
<th></th>
<th>1.0$\mu$l n-hexane</th>
<th>0.5$\mu$l n-hexane</th>
<th>0.1$\mu$l n-hexane</th>
<th>1.0$\mu$l n-pentane</th>
<th>0.1$\mu$l n-pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{13}^*$</td>
<td>1.27</td>
<td>1.28</td>
<td>1.28</td>
<td>1.31</td>
<td>1.32</td>
</tr>
</tbody>
</table>

From table 5.4 it is clear that a volume between 1.0$\mu$l and 0.1$\mu$l of solute is required to satisfy infinite dilution conditions. The minimum detectable volume was 0.1 $\mu$l.
5.3. The Significance and Calculation of $P'_3$

Table 5.5. shows the values obtained for $P'_3$ (partial pressure of the solute in cis- and trans-decalin) at 298.15 K and 283.15 K, obtained from equation 4.6. From the equation the intercept $a = \frac{RT}{Y_1^o} P'_1$ and the slope $b = \frac{P'_j}{Y_1^o} P'_1$. dividing $b$ by $a$

$$\frac{b}{a} = \frac{P'_3}{RT} \quad (5.2)$$

from which $P'_3$ may be calculated. $\sigma$ ($P'_3$) is determined using eq. 4.31.

**TABLE 5.5.** Experimental and Literature values of the average $P'_3$ at temperatures 298.15 K and 283.15 K for cis- and trans-decalin.

<table>
<thead>
<tr>
<th></th>
<th>T/ 298.15 K</th>
<th>T/ 283.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>trans-decalin</td>
<td>cis-decalin</td>
</tr>
<tr>
<td></td>
<td>Pa</td>
<td>Pa</td>
</tr>
<tr>
<td>Experimental</td>
<td>189.0±8.1</td>
<td>127.3±6.4</td>
</tr>
<tr>
<td>values</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Literature</td>
<td>164.4</td>
<td>104.3</td>
</tr>
<tr>
<td>values$^{(44)}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Assuming equilibrium conditions are satisfied in the column, this method should be capable of predicting the vapour pressure of the solvent. Data for the vapour pressure...
of trans-decalin and cis-decalin have been reported by Camin and Rossini\(^{(44)}\), and fitted to an Antoine equation over the temperature range 372.95 K to 469.55 K for cis-decalin and 365.45 K to 461.05 K for trans-decalin. An extrapolation to 298.15 K using this equation gives values for the saturated vapour pressure of 104.3 Pa for cis-decalin and 164.4 Pa for trans-decalin at 298.15 K, and 33.7 Pa and 55.7 Pa for cis- and trans-decalin respectively at 283.15 K. In view of the length of the extrapolation involved it is quite probable that \(P_s\) obtained in this work at 298.15 K, \((189.0 \pm 8.1\text{ Pa} and 127.3 \pm 6.4\text{ Pa for trans- and cis-decalin respectively}\) is a good estimate for the saturated vapour pressure, but further work is required in order to establish whether the solvent is actually in equilibrium along the column.

The \(P_s\) results determined by G.L.C. at 283.15 K are very different from the extrapolated data using the Antoine equation. This could be due to the unreliability of the extrapolation and it is also possible that equilibrium is not as good at 283.15 K as it is at 298.15 K.

\(P_s\) is dependent on the slope, and is therefore very sensitive to experimental error. The precision, calculated from equation 5.1, depends on how far the range of the controlled variable (time) can be extended, to reduce the effect of data point scatter, before the uncertainty in the slope due to curvature becomes commensurate with scatter.\(^{(41)}\)

It is possible that the large scatter in \(P_s\) is largely due to the problem associated with the drawing of the correct slope for the line \(U_{\Delta}t/n_3\) versus \(V_{\Delta}/n_3e^C\). This effect can be explained with reference to figure 5.1, where + refers to the data points of any column allowed to operate for a short time and □ refers to the data points of a column allowed to operate for a longer time. It is clear that the slope is affected by points further along the x axis. Thus two different values for \(P_s\) could be obtained. This explanation can be directly associated with some of the work presented in this thesis where there are columns containing different amounts of decalin (eg. a 3% and
Figure 5.1. Diagramatic representation of the difficulty associated with obtaining the correct slope.
15 % column), where + could refer to the 3 % column and □ to the 15 % column since under normal circumstances the 15% column will be in operation for a longer time than the 3 % column and therefore contain more data points further along the x axis.

The error in $P'_3$ then depends on the difficulty associated in obtaining the same slope from different columns.

5.4. Determination of $H_1^{E\infty}$

5.4.1 Theory

5.4.1.1 $H_1^{E\infty}$ from $\gamma_{13}^{\infty}$ Values

The activity coefficient at infinite dilution $\gamma_{13}^{\infty}$, based on the pure component standard state is related to the partial molar excess free energy by

$$\ln \gamma_{13}^{\infty} = \frac{G_1^{E\infty}}{RT} \quad (5.3)$$

Applying the Gibbs-Helmholtz equation directly to equation 5.3
5. DISCUSSION

5.4.1.2. \( H_1^{E_{\infty}} \) from \( H^E \) data using the Redlich Kister equation.

Finite concentration enthalpies of mixing are usually expressed in the form:

\[
H^E = x_1(1-x_1)[A+B(1-2x_1)+C(1-2x_1)^2] \quad (5.7)
\]

Equation 5.7 is known as the Redlich Kister equation.
The partial molar enthalpy of mixing at mole fraction

\[ x_1 = \frac{n_1}{(n_1 + n_2)} \]  

is given by:

\[ H_1^E = (\frac{\partial H^E}{\partial n_1})_{n_2} = (1-x_1) \frac{dH^E}{dx_1} + H^E \]  

At infinite dilution \((x_1 = 0)\) this becomes:

\[ H_1^{E\infty} = \frac{dH^E}{dx_1} = A + B + C \]  

Errors for \(H_1^{E\infty}\) are in the order of 300-400 J mol\(^{-1}\) for an error of 5 J mol\(^{-1}\) in \(H^E\).

5.4.1.3. The Tangent to Intercept Method (Rhizobium method)\(^{(45)}\) of determining \(H_1^{E\infty}\)

The molar excess enthalpy of a solution is given by
Then

\[ H^E_m = \frac{H^E}{n_a + n_B} \quad (5.11) \]

Now the derivative with respect to mole number of \( A, n_a \), is transformed into a derivative with respect to mole fraction \( B, X_B \),

\[ H^E_{1n} = \left( \frac{\partial H^E}{\partial n_a} \right)_{n_B} = H^E_m (n_a + n_B) \left( \frac{\partial H^E_m}{\partial n_a} \right)_{n_B} \quad (5.12) \]

\[ \frac{\partial H^E}{\partial n_A}_{n_B} = \frac{dH^E_m}{dX_B} \left( \frac{\partial X_B}{\partial n_a} \right)_{n_B} \quad (5.13) \]

since

\[ X_B = \frac{n_B}{n_a + n_B} \quad (5.14) \]

and

\[ \left( \frac{\partial X_B}{\partial n_A} \right)_{n_B} = -\frac{n_B}{(n_a + n_B)^2} \quad (5.15) \]
Thus eq. 5.12 becomes

\[ H_1^E = H_m^E - \frac{n_B}{n_A + n_B} \cdot \frac{dH_m^E}{dX_B} \]  

(5.16)

\[ H_1^E = H_m^E - X_B \frac{dH_m^E}{dX_B} \]  

(5.17)

The application of this equation is illustrated in figure 5.2, where \( H^E \) is plotted against mole fraction. From the figure the distance \( S_1A_1 \) is equal to the slope at \( X_{B1} \) multiplied by \( X_B(dH^E_m/dX_B) \) (see equation 5.17). It follows that \( O_1S_1 = O_1A_1 - S_1A_1 \) equals \( H_1^E \) (partial molar excess enthalpy) since \( O_1A_1 \) equals the molar excess enthalpy \( (H_m^E) \).

Therefore drawing a tangent to the curve, the intercepts at \( x = 0 \) and \( x = 1 \) yields the values for the partial molar enthalpies of both components at the specified mixture composition. To determine the partial molar excess enthalpy at infinite dilution a tangent has to be drawn at \( x = 0 \) and extrapolated to the \( x = 1 \) axis. This intercept on the \( x = 1 \) axis is \( H_1^{E\infty} \). For the best results, values of \( H^E \) as close to \( x_1 = 0 \) as possible should be used, otherwise the tangent method will produce large errors in determining \( H_1^{E\infty} \), in the region of 300-400 J. This is true in this work as the value of \( H^E \) (from the literature)\(^{(46)}\) were taken from the whole concentration range and not particularily close to \( x = 0 \). No data was available in the literature in the concentration range \( 0.1 > x_1 > 0.05 \) mole fraction. \( H_1^{E\infty} \) values were calculated from \( \gamma_1 \) \( (T_1 = 298.15 \, \text{K and } T_2 = 283.15 \, \text{K}) \) and are given in table 5.6. together with errors calculated using equation 4.32. These values are compared with extrapolated enthalpy data from the literature using equation 5.7.
Figure 5.2. Graphical construction to obtain partial molar entalpies at infinite dilution showing the error incurred in the extrapolation
TABLE 5.6. Partial molar excess enthalpy at infinite dilution for cis- and trans-decalin with various solutes at 298.15 K.

<table>
<thead>
<tr>
<th>Solute</th>
<th>trans-decalin</th>
<th>cis-decalin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_1^{E\infty}$</td>
<td>$H_1^{E\infty}$ $^\S$</td>
</tr>
<tr>
<td></td>
<td>J mol$^{-1}$</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>350±1700</td>
<td></td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>-500±700</td>
<td>-1100±400</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>-700±660</td>
<td>-110±300</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>870±2000</td>
<td>100±300</td>
</tr>
<tr>
<td>Benzene</td>
<td>-5470±1400</td>
<td>2700±500</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0±40</td>
<td>-70±300</td>
</tr>
</tbody>
</table>

$^\S$ the enthalpy values in these columns have been determined from finite concentration data.$^{(46)}$

The errors in determining $H_1^{E\infty}$ from G.L.C. are very large, ranging between 450 J mol$^{-1}$ and 2000 J mol$^{-1}$. The error in determining $H_1^{E\infty}$ from finite concentration $H^E$ measurements is also large in the range 300-500 J mol$^{-1}$. From the table it can be seen that only the values obtained for $H_1^{E\infty}$ (using the temperature dependence of $\gamma_{13}$) for n-heptane (in solvents cis- and trans-decalin) and n-hexane (in solvents trans-decalin), compare favourably with the values from literature. It is apparent that due to the large errors in determining $\gamma_{13}$ from G.L.C. the accurate calculation of $H_1^{E\infty}$ is impossible. When an excess partial molar enthalpy of mixing is determined from retention measurements at two different temperatures, $T_1$ and $T_2$, there is an optimum temperature difference which should be employed to maximise precision.$^{(47)}$ If the
difference is too small the error in measuring retention is large in relation to the
difference in retention. Young\(^{(47)}\) states that the larger the difference in temperature
the smaller the error in \(H_1^{E_\infty}\).

Letcher and Marsicano\(^{(27)}\) attempted to extract entropy from the temperature
dependence of \(\log_{10} \gamma_{13}^\infty\) at 308.15 K and 328.15 K using short chain (C\(_5\) and C\(_6\))
saturated and unsaturated hydrocarbons in longer chain (C\(_{16}\) and C\(_{18}\)) saturated and
unsaturated liquid hydrocarbons. However this too proved unsuccessful since the
difference in \(\log_{10} \gamma_{13}^\infty\) at 308.15 and 328.15 K was of the order of the experimental scatter.

The activity coefficients of most systems which have been studied accurately by
G.L.C., exhibit small or medium temperature dependence i.e. \(\gamma_{13}^\infty\) does not change by
more than 0.002 per K.\(^{(47)}\) Since the experimental precision of \(\gamma_{13}^\infty\) is usually of the
order of 0.03, estimation of \(H_1^{E_\infty}\) requires measurements of \(\gamma_{13}^\infty\) over a 30-40 K
temperature range. Alternatively more precise values of \(\gamma_{13}^\infty\) must be determined.

Martire\(^{(48)}\) suggested that due to the above difficulties it was probably not possible
to obtain meaningful \(H_1^{E_\infty}\) results from chromatographic data. Moreover \(H_1^{E_\infty}\) of
systems for which \(\gamma_{13}^\infty\) have a low temperature dependence are greatly affected by gas
phase imperfections. A substantial part of \(H_1^{E_\infty}\) obtained in cases for which \(H_1^{E_\infty}\) is
small may actually be due to the correction for gas phase imperfections.\(^{(47)}\)

Young\(^{(47)}\) states that the gas chromatographic method (or indeed any method that
measures free energies as a function of temperature, and hence \(H_1^{E_\infty}\)), will never
provide as accurate or as convenient an alternative as the calorimetric techniques.
5.6. Conclusion

From the comparison of $\gamma_{13}^*$ with the literature data obtained it can be concluded that the method developed in this work for determining activity coefficients of solutes in volatile solvents is a reliable one.

However the attempt at determining $H_1^{E*}$ proved not to be conclusive. Due to the small range of temperatures involved the experimental errors were usually larger than the property being determined, $H_1^{E*}$.

The method does 'however' appear to be a good one for measuring vapour pressures of moderately volatile solvents.

5.7. Future Work

There are many moderately volatile solvents which can be used as stationary phases (bicyclohexyl, tetralin, decane, etc.) which will be studied to test the new technique. The technique could prove to be valuable in determining the vapour pressure of liquids in the range 10 to 1000 Pa i.e., between $10^{-4}$ atms. and $10^{-2}$ atms.
APPENDIX I

Computer Program (GAMMA) for the calculation of $V_N$ and $\gamma^{13}$

10 PRINT "Calculation of activity coefficient at infinite dilution using G.L.C. data"
20 INPUT "INPUT THE RETENTION TIME OF THE UNRETAINED GAS"; $t_g$
30 INPUT "INPUT THE FLOW RATE"; $U_o$
40 $V_D = t_g * U_o$
50 PRINT "THE DEAD SPACE IS"; $V_D$; PRINT
60 INPUT "INPUT THE RETENTION TIME OF THE SOLUTE"; $t_r$
70 $V_r = t_r * U_o$
80 PRINT "THE RETENTION VOLUME IS"; $V_r$
90 INPUT "THE OUTLET PRESSURE"; $P_i$
100 INPUT "THE INLET PRESSURE"; $P_o$
110 $A = (P_i/P_o)^2 -1$
120 $B = (P_i/P_o)^3 -1$
130 $J_2 = 3/2 * (A/B)$
140 PRINT "THE NET RETENTION VOLUME IS"; $V_N$
180 $R = 8.314$
190 INPUT "INPUT THE MOLES OF SOLVENT"; $n_3$
200 INPUT "INPUT THE TEMPERATURE"; $T$
210 INPUT "INPUT THE VAPOUR PRESSURE OF THE SOLUTE"; $P^*$
220 GAMMA = $(N*R*T)/(V_N P^*)$
230 PRINT "THE UNCORRECTED ACTIVITY COEFFICIENT IS"; GAMMA
240 INPUT "INPUT THE FIRST VIRIAL COEFFICIENT"; $B_{11}$
250 INPUT "INPUT THE MOLAR VOLUME OF THE SOLUTE"; $V^*$
260 $C = ((B_{11} - V^*)/RT)*P^*$
270 INPUT "INPUT THE MIXED VIRIAL COEFFICIENT"; $B_{12}$
280 $D = \{(2*B_{12} - V^*)/RT\} *P_o * J$
290 $G = GAMMA - C + D$
310 PRINT "THE CORRECTED ACTIVITY COEFFICIENT IS"; $G$
In the theoretical plate model, the column is regarded as divided up into large number of theoretical plates small enough so that the concentration of sample in both mobile and stationary phases can be regarded as uniform. Each plate consists of 2 volumes, i.e. the volume of free gas ($\Delta V_G$) and of liquid ($\Delta V_L$); the sum of the volumes being the total plate volume $\Delta x$, thus

\[ \Delta x = \Delta V_G + \Delta V_L \]  \hspace{1cm} (1)

The solute sample in the first theoretical plate is distributed between the stationary and mobile phase according to a partition coefficient, such that at equilibrium a fraction $z$ of solute exists in the gas phase and a fraction $y$ in the liquid phase. \(^{(17)}\)

The addition of $\Delta V_G$ of mobile phase carrier gas to the first plate causes an equal movement of carrier through every plate in the column, the $z$ ml of solute in the gas phase in plate 1 being swept to plate 2. When the movement of carrier gas ceases, re-
equilibrium occurs in plate 1 and 2. In plate 1 a volume $yz$ ml of solute enters the gas phase while $y^2$ ml of solute remains in the liquid phase. In plate 2 a volume $zy$ ml enters the liquid phase while $z^2$ remains in the gas phase.

The distribution of solute between the 2 plates after equilibrium is established is

\[ y^2 + yz \text{ (plate1)} + z^2 + zy \text{ (plate2)} = y^2 + 2yz + z^2 = (y + z)^2 \]  \tag{2}  

At this point a further volume of carrier gas is added ($\Delta V_g$) to the column and the process is repeated with solute being transported into plate 3.
the distribution of solute being

\[ y^3 + zy^2 + 2zy + z^2y + z^3 \]  \hspace{1cm} (3)

but

\[ zy = zy^2 + z^2y \]  \hspace{1cm} (4)

\[ eq.3 = y^3 + 3zy^2 + 3yz^2 + z^3 = (y+z)^3 \]  \hspace{1cm} (5)

Likewise after the addition of 4 volumes of carrier gas the solute distribution is
TABLE 1.

<table>
<thead>
<tr>
<th>Number of volumes of carrier gas</th>
<th>Number of plates</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(y + z)</td>
</tr>
<tr>
<td>1</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>2</td>
<td>y^2</td>
<td>2yz</td>
</tr>
<tr>
<td>3</td>
<td>y^3</td>
<td>3y^2z</td>
</tr>
<tr>
<td>4</td>
<td>y^4</td>
<td>4y^3z</td>
</tr>
</tbody>
</table>

Clearly in each plate, the quantity of solute corresponds to a term in a binomial expansion. This implies that if r volumes of carrier gas is added to the column and we designate the number of any plate by N, the quantity of solute in any plate is given by

\[
Q_{N+1} = \frac{r! (y)^{r-N} (z)^N}{N! (r-N)!}
\]  

(7)
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The determination of activity coefficients at
infinite dilution using g.l.c. with moderately
volatile solvents

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A novel method for determining activity coefficients at infinite dilution by g.l.c. is presented for
solutions involving a moderately volatile solvent. The loss of solvent in the column is related to
its partial pressure. In this work the activity coefficients for hexane in cis- and trans-
decahydronaphthalene (decalin) have been investigated at the temperature 298.15 K. The
method can be used for any solvent of low volatility such as decane, tetrahydronaphthalene,
cyclohexylbenzene, or bicyclohexyl.

1. Introduction
The usual method for determining activity coefficients at infinite dilutions developed
by Everett(1) and Cruickshank et al.(2) is restricted to volatile solutes (e.g. pentane,
hexane, and heptane) and involatile solvents (e.g. dotricontane, squalane, and:
dinonylphthalate). In the present work this method has been extended to
accommodate a solvent of low volatility.

2. Experimental
The g.l.c. apparatus has been described previously.(3) The columns used were
stainless-steel tubes (4.2 mm bore; length 1 m to 1.5 m). The support was celite
(Manville 80/100 mesh). A catharometer detector was used with helium as the carrier
gas, the flow rate of which was maintained constant for each set of runs on a column.
This rate was measured using a calibrated bubble meter and corrected for water
vapour. The column temperature was controlled to within 0.01 K.
Solvents: cis-decalin and trans-decalin, of purity 99 moles per cent, and supplied by
Aldrich, were used without further purification at a column loading of (3 to 15) mass
per cent. The solute used was hexane and was also supplied by Aldrich. It was
unnecessary to purify the solute further because of the nature of the experiment.
3. Theory: treatment of a volatile solute

Everett and Cruickshank developed the equation:

\[ \ln \gamma_f = \ln(n_3 RT/V_N p_f^*) - (B_{11} - V_f^*)p_f^*/RT + (2B_{12} - V_f^*)J_2 p_o/RT, \]  

(1)

for obtaining activity coefficients \( \gamma_f \), at infinite dilution of solutes in an involatile solvent from g.l.c. results. Here \( V_N \) denotes the net retention volume of the solvent, \( p_o \) the outlet pressure, \( J_2 p_o \) the mean column pressure, \( n_3 \) the amount of liquid solvent on the column, \( T \) the column temperature, \( p_f^* \) the saturated vapour pressure of the solute at temperature \( T \), \( B_{11} \) the second virial coefficient of pure solute, \( V_f^* \) the molar volume of the solute as liquid, \( V_f^\infty \) the partial molar volume of the solute at infinite dilution in the solvent, and \( B_{12} \) the mixed second virial coefficient of the solute and carrier gas.

The net solute retention volume \( V_N \) is given by

\[ V_N = J_3^2 U_o (t_R - t_G), \]  

(2)

where

\[ J_3^2 = (3/2)\left(\frac{p_o}{p_u}\right)^2 - 1)\left(\frac{p_o}{p_u}\right)^3 - 1), \]  

(3)

and

\[ J_3^2 = (J_3^2)^{-1}. \]  

(4)

where \( U_o \) is the volumetric flow rate of the carrier gas at the column outlet expressed at column temperature and corrected for vapour pressure and \( t_G \) and \( t_R \) the retention times for an unretained gas (nitrogen) and the solute respectively.

During its passage through the column, the carrier gas becomes charged with solvent vapour. The total amount of solvent \( n_3 \) lost from the column may be expressed in terms of the total volume of gas which has passed through the column, the partial pressure \( p_3 \) of the solvent in the gas at the column outlet, and the time \( t \) elapsed from the start of the carrier gas passing through the column. We assume that the observed retention times are negligible compared with the total flow time through the column. The gas flow rate \( U_o \) measured at the outlet is maintained constant during the whole experiment. The expression for \( n_3 \) is

\[ n_3 = p_3 U_o t/RT. \]  

(5)

In this work we found the partial pressure of the solvent in the carrier gas to be < 0.01 of the total. It is probably further reduced in the flowmeter. Therefore no correction was applied to the flow rate for the presence of the solvent and ideal-gas behaviour was assumed.

Equation (1) becomes

\[ \ln \gamma_f = \ln((n_3 RT - p_f^*/V_N p_f^*) + C, \]  

(6)

where

\[ C = -(B_{11} - V_f^*)p_f^*/RT + (2B_{12} - V_f^*)J_2 p_o/RT. \]  

(7)
Results were collected for five columns loaded with trans-decalin and two with cis-decalin using hexane as solute and helium as the carrier gas. Detailed results obtained for hexane (15.02 mass per cent) are given in table 1. The retention time $t_C$ was determined using nitrogen.

Table 2 summarizes all the results obtained showing those from table 1 as the first entry and lists the values obtained for $\gamma_{13}^*$ and $\rho_3^*$. The mixed virial coefficient $B_{12}$ for hexane was calculated (equation (9)) from McGlashan and Potter’s equation (4) and Hudson and McCoubrey’s combining rules (5, 6) following Letcher et al. (7):

$$B_{12}/V_{c,12} = 0.43 - 0.886(T_{e,12}/T) - 0.694(T_{e,12}/T)^2 - 0.0375(n_{12} - 1)(T_{e,12}/T)^{4.3}. \quad (9)$$

Hence

$$V_N \cdot \exp(-C)/n_3 = RT/\gamma_{13}^* \rho_3^* - (\rho_3^*/\gamma_{13}^* \rho_3^*)(U_\alpha/n_3) = a - b(U_\alpha/n_3). \quad (8)$$

The values of $\gamma_{13}^*$ and $\rho_3^*$ are obtained graphically from this linear relation.

### 4. Results

Results were collected for five columns loaded with trans-decalin and two with cis-decalin using hexane as solute and helium as the carrier gas. Detailed results obtained for hexane (15.02 mass per cent) are given in table 1. The retention time $t_C$ was determined using nitrogen.

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#### TABLE 1.
Experimental results for the determination of $\gamma_{13}^*$ for hexane in trans-decalin (15.02 moles per cent) at $T = 298.15$ K. The symbols are as defined for equations (1) and (2). For this experiment $U_\alpha = 8.87 \cdot 10^{-7}$ m$^3$ mol$^{-1}$ s$^{-1}$, $n_3 = 3.393 \cdot 10^{-3}$ mol, $J_3 = 0.914$, and $t_C = 20.3$ s.

<table>
<thead>
<tr>
<th>$t$ s</th>
<th>$t_s$ s</th>
<th>$10^4 \cdot V_N$ m$^3$</th>
<th>$V_N/n_3$ m$^3$ mol$^{-1}$</th>
<th>$U_\alpha/n_3$ m$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>428.8</td>
<td>3.312</td>
<td>0.0975</td>
<td>0.314</td>
</tr>
<tr>
<td>2400</td>
<td>419.2</td>
<td>3.348</td>
<td>0.09532</td>
<td>0.627</td>
</tr>
<tr>
<td>4800</td>
<td>413.9</td>
<td>2.191</td>
<td>0.0904</td>
<td>1.255</td>
</tr>
<tr>
<td>5700</td>
<td>413.3</td>
<td>3.183</td>
<td>0.09378</td>
<td>1.490</td>
</tr>
<tr>
<td>6600</td>
<td>401.8</td>
<td>3.089</td>
<td>0.09102</td>
<td>1.725</td>
</tr>
<tr>
<td>7200</td>
<td>401.1</td>
<td>3.088</td>
<td>0.09098</td>
<td>1.882</td>
</tr>
<tr>
<td>9000</td>
<td>399.7</td>
<td>3.076</td>
<td>0.09064</td>
<td>2.253</td>
</tr>
<tr>
<td>9600</td>
<td>396.1</td>
<td>3.047</td>
<td>0.08979</td>
<td>2.510</td>
</tr>
</tbody>
</table>

#### TABLE 2.
Summary of operating conditions for hexane in cis-decalin and trans-decalin at $T = 298.15$ K for six different columns. The first row relates to table 1.

<table>
<thead>
<tr>
<th>solvent: decalin isomer</th>
<th>$n_3$ mmol</th>
<th>$10^2 \cdot n_1$</th>
<th>$10^2 \cdot n_1/n_3$</th>
<th>$10^{-1} \cdot U_\alpha$ m$^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans</td>
<td>3.393</td>
<td>15.02</td>
<td>0.94</td>
<td>8.872</td>
</tr>
<tr>
<td>trans</td>
<td>2.124</td>
<td>10.01</td>
<td>0.94</td>
<td>9.542</td>
</tr>
<tr>
<td>trans</td>
<td>2.239</td>
<td>7.99</td>
<td>0.94</td>
<td>8.373</td>
</tr>
<tr>
<td>cis</td>
<td>3.693</td>
<td>10.00</td>
<td>0.94</td>
<td>9.543</td>
</tr>
<tr>
<td>cis</td>
<td>1.786</td>
<td>3.03</td>
<td>0.94</td>
<td>5.715</td>
</tr>
<tr>
<td>cis</td>
<td>1.790</td>
<td>9.97</td>
<td>0.94</td>
<td>9.828</td>
</tr>
</tbody>
</table>
where

\[ T_{c,12} = 128(T_{c,11} T_{c,22})^{1/2}(I_{c,11} I_{c,22})^{1/2} V_{c,11} V_{c,22}/I_{c,12}, \]

\[ V_{c,12} = (V_{c,11}^{1/2} + V_{c,22}^{1/2})^2/8, \]

\[ I_{c,12} = (I_{11} + I_{12})(V_{c,11}^{1/2} + V_{c,22}^{1/2})^6, \]

and

\[ n_{12} = (n_1 + n_2)/2. \]

The critical quantities and ionization energies used in the calculation of \( B_{12} \) are given in table 3 using \( n_1 = 6 \) (hexane) and \( n_2 = 1 \) (helium). The value for \( B_{12} \) was found to be \( 29 \text{ cm}^3 \cdot \text{mol}^{-1} \). The value of \( B_{11} \) for hexane used in the calculation was \( -1984 \text{ cm}^3 \cdot \text{mol}^{-1} \).

### 5. Discussion

From table 2 it can be seen that results have been collected from experiments in which the flow rates changed by approximately 50 per cent and the column loadings five-fold. These measurements fit a single linear relation (equation 8) shown in figures 1 and 2 to within experimental accuracy.

The points from figure 1 (trans-decalin) have been fitted to equation (8) giving

\[ a = (0.975 \pm 0.0012) \text{ m}^3 \cdot \text{mol}^{-1}, \quad b = -(0.00336 \pm 0.00017) \text{ m}^3 \cdot \text{mol}^{-1}, \quad \gamma_{13}^{\infty} = (1.28 \pm 0.01), \quad \text{and } p_{3} = (85.4 \pm 4.4) \text{ Pa}. \]

Similarly from figure 2 (cis-decalin) \( a = (0.0977 \pm 0.0024) \text{ m}^3 \cdot \text{mol}^{-1}, \quad b = -(0.00262 \pm 0.00032) \text{ m}^3 \cdot \text{mol}^{-1}, \quad \gamma_{13}^{\infty} = (1.28 \pm 0.03), \quad \text{and } p_{3} = (67.2 \pm 8.2) \text{ Pa}. \]

The values obtained for \( \gamma_{13}^{\infty} \) for both cis-decalin and trans-decalin are within 0.02 of the value predicted by Letcher and Baxter using the Prigogine-Flory-Patterson theory. Vernier et al. obtained a value for \( \gamma_{13}^{\infty} \) of 1.260 for hexane in decalin at \( T = 298.15 \text{ K} \). However vapour-phase imperfections and solvent loss were not taken into consideration by them.

Assuming that equilibrium conditions are satisfied in the column, the method should be capable of predicting the vapour pressure of the solvent. The saturated vapour pressure of trans-decalin and cis-decalin have been reported and fitted to an Antoine equation over the temperature range 363.45 K to 467.55 K. An extrapolation to 298.15 K using this equation gives a value of 104.4 Pa for cis-decalin and 164.35 Pa for trans-decalin. This places an upper bound on the acceptable values for \( p_{3} \). In view of the length of the extrapolation involved it is quite probable that \( p_{3} \) obtained in this work is a good estimate for the saturated vapour pressure at

<table>
<thead>
<tr>
<th>Compound</th>
<th>( V_{c,cm} )</th>
<th>( T_{c} )</th>
<th>( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>370.0</td>
<td>507.3</td>
<td>0.9822</td>
</tr>
<tr>
<td>Helium</td>
<td>5.20</td>
<td>57.76</td>
<td>5.2487</td>
</tr>
</tbody>
</table>
FIGURE 1. A plot of $V_0/n_0$ against $U_0/n_0$ for trans-decalin at $T = 298.15$ K. Column loadings: ●, 10.00 moles per cent; ▲, 10.01 moles per cent; ○, 7.99 moles per cent; ●, 15.02 moles per cent.

FIGURE 2. A plot of $V_0/n_0$ against $U_0/n_0$ for cis-decalin at $T = 298.15$ K. Column loadings: ○, 9.97 moles per cent; ●, 3.03 moles per cent.

$T = 298.15$ K, but further work is required to establish whether the solvent is actually in equilibrium along the column.

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