THE THERMODYNAMICS OF BINARY LIQUID MIXTURES OF COMPOUNDS CONTAINING MULTIPLE BONDS

THESIS

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ABSTRACT

Excess thermodynamic properties have been determined for several binary liquid mixtures with the aim of testing various thermodynamic theories and postulates. Excess molar enthalpies, H_m^E, have been determined using an LKB flow microcalorimeter and excess molar volumes, V_m^E, have been determined using an Anton Paar vibrating tube densitometer. The activity coefficients at infinite dilution, γ_{13}^{∞}, have been determined using an atmospheric pressure gas-liquid chromatograph.

The excess molar enthalpies and the excess molar volumes have been measured at 298.15 K for systems involving the bicyclic compounds decahydronaphthalene (decalin), 1,2,3,4-tetrahydronaphthalene (tetralin), bicyclohexyl, or cyclohexylbenzene mixed with 1-hexene, 1-hexyne, 1-heptene, 1-heptyne, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, or benzene. These excess properties have also been measured for systems where the bicyclic compound has been replaced with benzene, cyclohexane or *n*-hexane. The results show definite trends related to the size, shape, and the degree of unsaturation of the component molecules.

The Flory theory has been used to predict excess molar enthalpies and excess molar volumes for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne or a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The one parameter equations offer reasonably good correlations between the predicted and the experimental results.

More insight into the origins of the contributions to the excess thermodynamic properties for these systems has been gained by considering the approximate equations of Patterson and co-workers, which separate the interactional and the free volume

contributions to the excess molar enthalpy and the excess molar volume. The one parameter equations have adequately rationalized a good deal of the observed behaviour for H_m^E and V_m^E.

The theory of Liebermann and co-workers, which does not employ any adjustable parameters, has not been as successful at predicting the excess thermodynamic properties for the above systems.

The activity coefficients at infinite dilution have been measured at 278.15 K, 288.15 K and 298.15 K for *n*-hexane, 1-hexene, 1-hexyne, *n*-heptane, 1-heptene, 1-heptyne, cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and benzene, in decalin, tetralin, bicyclohexyl, and cyclohexylbenzene. Solvent losses from the column have been accounted for by an extrapolation procedure. The activity coefficient results together with the H_m^E and V_m^E values have been used to calculate the partial molar excess thermodynamic properties of mixing at infinite dilution. The partial molar excess properties at infinite dilution for decalin mixtures are similar to those for bicyclohexyl mixtures. There is also a similarity between the properties of the tetralin mixtures and the cyclohexylbenzene mixtures. The cycloalkadienes, benzene and the 1-alkynes exhibit a strong dissociation effect on being mixed with the saturated solvents, decalin and bicyclohexyl, but associate strongly with tetralin and with cyclohexylbenzene.

The Flory theory has been used to predict activity coefficients at infinite dilution from the experimentally determined H_m^E results for {(*n*-hexane or 1-hexene or 1-hexyne or *n*aheptane or 1-heptene or 1-heptyne) + (a bicyclic compound)}. The theory is much better at predicting values for mixtures where both components are either saturated molecules or are unsaturated molecules than for {saturated + unsaturated} mixtures.

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CHAPTER 1

INTRODUCTION

The behaviour of liquids can be understood by studying the properties of their mixtures. The thermodynamic study of liquid mixtures is commonly dealt with in terms of the excess properties of mixing,(1) these thermodynamic properties being of both practical and theoretical interest. Excess molar enthalpies and excess molar volumes are useful to chemical engineers at an industrial level in the design of chemical plants such as reactors. Activity coefficients at infinite dilution give a measure of the deviation of a component in a mixture from ideality and can offer information which may assist the chemist and the engineer alike. To the chemist, these coefficients aid in the choice of stationary phase in chromatographic applications and in an understanding of the interactions between species through various theories of liquid mixtures. To the chemical engineer, an understanding of the non-ideal behaviour of non-electrolyte mixtures is necessary to predict vapour-liquid equilibrium data used in the design of separation processes.

One of the other primary services which the field of thermodynamics offers is the capacity to transform certain macroscopic data of a system into related data for that system through certain mathematical relationships. Praunitz's *Molecular Thermodynamics of Fluid Phase Equilibria*(2) is an example of this kind of work, concerning itself with methods for calculating the phase equilibrium behaviour of fluid mixtures from thermodynamic data and theories. Sufficient experimental data is essential in applications of this nature.

From a theoretical point of view, experimental data is fundamental in the testing of the various thermodynamic theories and may serve as a guide in the formulation of new postulates. Of prime importance to the work presented in this thesis are the theories concerned with liquid mixtures of two component systems. At present no satisfactory theory exists which can adequately predict thermodynamic data for binary liquid mixtures. The importance of such a theory would be two-fold, namely: *(i)* for the interpolation of limited experimental results available for systems already studied to systems not previously studied, and *(ii)* as an aid to understanding the nature of liquids and liquid mixtures.

It is well known that molecular shape is an important and sensitive parameter in determining excess thermodynamic quantities.(1) The *corresponding states* theory is useful in lending physical insight into the origin of excess functions for mixtures of molecules differing in size. Mixtures of normal alkanes have received considerable attention in this regard due to their simplicity, and to the fact that they serve as a model for polymeric systems. The theory does not however deal with a new effect which arises for molecules differing in shape. A large amount of work has been carried out in this regard by Patterson and co-workers,(3-6) who attribute this effect to the short-range orientational order present in a system comprising molecules of highly anisotropic shape, *e.g.* *n*-alkanes. The mixing of molecules of different molecular shape, and consequently different degrees of orientational order, will result in a net decrease of order and a corresponding increase in the excess enthalpy for the mixture.(3) Extensive measurements have been carried out for systems where the order destroying molecule is cyclohexane.(6)

This material in this thesis is primarily concerned with determining excess molar enthalpies, H_m^E, excess molar volumes, V_m^E, and activity coefficients at infinite dilution, γ_{13}^{∞}, for binary liquid mixtures, with the aim of testing various thermodynamic theories. A study has been made of excess properties for systems concerning molecules not only differing vastly in size and in shape, but also with mixtures where at least one of the components contains multiple bonds. Excess molar enthalpies and excess molar volumes have been determined for the binary systems involving a bicyclic compound mixed with a chain molecule or with a cyclic compound. The bicyclic compounds used were the two saturated molecules, decahydronaphthalene (decalin) and bicyclohexyl, and the two unsaturated molecules, 1,2,3,4-tetrahydronaphthalene (tetralin) and cyclohexylbenzene. These compounds were mixed with a C_6 or a C_7 carbon chain 1-alkene or 1-alkyne, and the effect of the degree of unsaturation of the components on the excess properties was observed. The excess thermodynamic properties have also been measured for mixtures where the second component C_6 cyclo-compound contained 1, 2, or 3 double bonds. Valuable information has been obtained which could be related to intermolecular interactions and to the size, shape and degree of unsaturation of the components. The various trends and observations have been compared with work previously carried out concerning systems involving these bicyclic compounds mixed with *n*-alkanes and with cycloalkanes.(7-19) The choice of compounds was extended to include related systems where the bicyclic compound has been replaced by benzene, cyclohexane, or *n*-hexane. The results have been compared with previously determined results for related systems.(20-51)

Activity coefficients at infinite dilution have been determined at 278.15 K, 288.15 K and 298.15 K for the solutes an *n*-alkane, a 1-alkene, a 1-alkyne, cyclohexane, cyclohexene, a cycloalkadiene, and benzene in the four bicyclic compound solvents. The solutes *n*-hexane and cyclohexane were injected before and after each of the other solutes to monitor solvent losses from the columns. The losses were accounted for by an extrapolation procedure.

The study of the above mixtures has not only yielded a considerable amount of valuable experimental data which had not been previously reported, but has also afforded an excellent opportunity to test the Flory theory.(52-59) This theory saw its inception in the need to explain the major discrepancies that exist between the experimental results and the results predicted by the lattice theory, which fails to account for the changes in volume and in local disorder with mixture composition. The one parameter Flory theory was initially derived with the aim of explaining the thermodynamic properties of normal paraffin hydrocarbon mixtures(52,53) and was subsequently extended to cover non-polar molecules differing in size and shape.(55) In this thesis the experimental H_m^E and V_m^E results measured here and the results for related systems have been fitted to the equations derived by Flory and co-workers. The adjustable interaction parameters, X_{12}, which characterize the energetic weaknesses of unlike contacts, have been determined for each system from experimental H_m^E and V_m^E data, and have also been calculated from the Berthelot formula. In this work, the Flory theory has also been used to determine activity coefficients at infinite dilution, γ_{13}^∞, for the systems studied here.

The Flory theory considers excess thermodynamic properties of binary mixtures to be the sum of three contributions:(52,53) *(i)* a combinatorial term, *(ii)* an interactional term arising from the differences in the chemical nature of the two components, and *(iii)* a free volume contribution. More insight into the nature of these contributions is afforded by the approximate equations of Patterson and co-workers,(60,61) which lead to the separation of these contributions. The approximate form of their excess molar enthalpy equation(60) is divided into a free volume and an interactional contribution. The excess molar volume can be expressed as an interactional term, which is proportional to the X_{12} parameter, a free volume contribution, which originates from a difference in the degrees of thermal expansion between the two components, and a P^* contribution, which arises from the differences in the internal pressure and the reduced volumes of the components.(61) The H_m^E and V_m^E results predicted by these equations of the Prigogine-Flory-Patterson (PFP) theory have been compared with those predictions afforded by the Flory theory. The study of the above mixtures also affords an excellent opportunity to investigate the generality of the concept of molecular orientations proposed by Patterson and co-workers.(3-6)

A modification of the Flory theory by Lieberman(62,63) has also been tested. This modification employs no adjustable parameters and the excess molar enthalpy and excess molar volume are determined purely from macroscopic properties of the pure components. A comparison has been made between the predictive abilities of this theory, the Flory theory and the Prigogine-Flory-Patterson theory.

CHAPTER 2

EXCESS MOLAR ENTHALPIES AND EXCESS MOLAR VOLUMES OF BINARY LIQUID MIXTURES

2.1 INTRODUCTION

Rowlinson and Swinton(1) define an ideal solution as a hypothetical mixture whose properties are introduced into the thermodynamic description of real mixtures as convenient standards of normal behaviour. The concept of an idealized mixture is valuable in developing a theory of real solutions,(64,65) since the real behaviour can be related to the ideal behaviour through the introduction of concepts such as activities and fugacities.

Deviations from the ideal behaviour of mixtures are generally intepreted in terms of the various types of intermolecular forces operating between the molecules of the mixture. Wilhelm *et al.*(66) distinguish between two types of interactions: *(i)* strongly attractive "chemical" interactions, and *(ii)* weakly attractive non-specific "physical" attractions.

The quantitative behaviour of real solutions is conveniently expressed in terms of their thermodynamic excess functions.(1) Experimental results expressed in this form are used by physical chemists interested in reactions and interactions occurring in solution, and by chemical engineers employed in the operation or design of chemical reactions and separation devices such as distillation columns.(1)

It is customary to define the molar quantity of mixing for a binary liquid mixture, $\Delta_{mix}X_m$, by the following simple relationship which relates the value of the function per mole of the mixture to the sum of these functions per mole of unmixed components at the same temperature and pressure:(65)

$$\Delta_{mix}X_m = X - x_A X_A^* - x_B X_B^* \qquad 2.1$$

where x_A and x_B are the mole fractions of the components A and B respectively:

$$x_A = (1 - x_B) = n_A/(n_A + n_B) \qquad 2.2$$

and where n_i are the number of moles of component i. The general thermodynamic property, X, where $X = f(p, T, x_A, x_B)$ is the molar thermodynamic quantity at any pressure, p, and temperature, T, and is expressed for a binary mixture as:

$$X = x_A X_A - x_B X_B \qquad 2.3$$

$X_A^* = X_m(T, p)$ and $X_B^* = X_m(T, p)$ are the molar quantities of the pure components A and B at the same temperature and pressure. For an ideal mixture, the molar functions of mixing are given by:(65)

$$\Delta_{mix}G_m{}^{id} = RT[x_A \ln(x_A) + x_B \ln(x_B)] \qquad 2.4$$
$$\Delta_{mix}S_m{}^{id} = -R[x_A \ln(x_A) + x_B \ln(x_B)] \qquad 2.5$$
$$\Delta_{mix}H_m{}^{id} = H - x_A H_A^* - x_B H_B^* = 0 \qquad 2.6$$

and

$$\Delta_{mix}V_m{}^{id} = V - x_A V_A^* - x_B V_B^* = 0 \qquad 2.7$$

For an ideal mixture, the molar Gibbs function of mixing is negative and the molar entropy of mixing is positive.(65)

The departure of a system from ideal behaviour can be quantitatively expressed through the excess thermodynamic quantity, X_m^E, defined as the difference between the value of the function of mixing for the real mixture and the corresponding function for the ideal mixture at the same composition:(65)

$$X_m^E = \Delta_{mix}X_m - \Delta_{mix}X_m{}^{id} \qquad 2.8$$
$$= (X_A - X_A^*)x_A + (X_B - X_B^*)x_B \qquad 2.9$$

The excess mixing functions are then given by:

$$G_m^E = \Delta_{mix}G_m - RT[x_A \ln(x_A) + x_B \ln(x_B)] \qquad 2.10$$
$$S_m^E = \Delta_{mix}S_m + R[x_A \ln(x_A) + x_B \ln(x_B)] \qquad 2.11$$
$$H_m^E = \Delta_{mix}H_m \qquad 2.12$$

and

$$V_m^E = \Delta_{mix}V_m \qquad 2.13$$

2.2 Excess molar enthalpies

2.2.1 Introduction

In principle the excess molar enthalpy, H_m^E, can be calculated from the temperature coefficient of the excess molar Gibbs free energy:(67)

$$H_m^E = G_m^E - T(\delta G_m^E/\delta T)_p \qquad 2.14$$

where the Gibbs free energy of mixing, G_m^E, can be derived from the measurement of the total vapour pressure and the composition of the liquid and vapour in equilibrium. In addition to the procedure being rather difficult and time consuming, Williamson(67) has stated that for G_m^E at two temperatures 30 K apart and in the region of 300 K, the resulting error in the calculated H_m^E may be as much as fifteen fold greater than the error in G_m^E. The application of equation 2.14 is thus an unsatisfactory method for determining H_m^E. More precise results can be obtained more quickly and easily in many cases through direct measurements of H_m^E by calorimetric methods.

Two major problems can arise with the measurement of excess molar enthalpies. The first concerns the difficulty of ensuring complete mixing of the pure liquid components, this being particularly important when considering components with densities differing substantially. In the design of any calorimeter mixing vessel the air spaces in contact with the mixed liquids must be reduced to a minimum. This reduces possible errors due to condensation or evaporation of the liquids into the spaces. According to McGlashan,(68) vapour spaces of 0.1 cm^3 could contribute errors of up to 20% of the heat of mixing in some cases. Modern calorimeters avoid this common fault inherent in the earlier models by eliminating the vapour space. The formation of air bubbles within the mixing vessel can be avoided by degassing the liquids before use.

In addition to the above, various other basic requirements must be met for the accurate determination of excess molar enthalpies. The composition of the mixture must be accurately known and the liquids must have attained temperature equilibration prior to mixing. Heat leaks, if present, must also be accounted for if meaningful results are to be obtained. Since the excess molar enthalpy is related to $(\delta v/\delta p)$, volume changes on mixing must be taken into account.(68)

2.2.2 Measurement of excess molar enthalpies by calorimetric methods

The various methods developed prior to 1961 for measuring excess molar enthalpies have been extensively reviewed by McGlashan.(68) More recent articles by McGlashan,(69) Marsh(70-72) and Becker(73) review the basic concepts and the performances of some of the calorimetric methods currently employed in the determination of precise H_m^E measurements. Hansen and Eatough(74) have compared different calorimetric methods with regard to the minimum detectable heat effects and have concluded that the adiabatic flow method has the best potential detection limit. They stressed that factors such as the sample size and the expected magnitude of the enthalpy change should be considered when selecting the detection method.

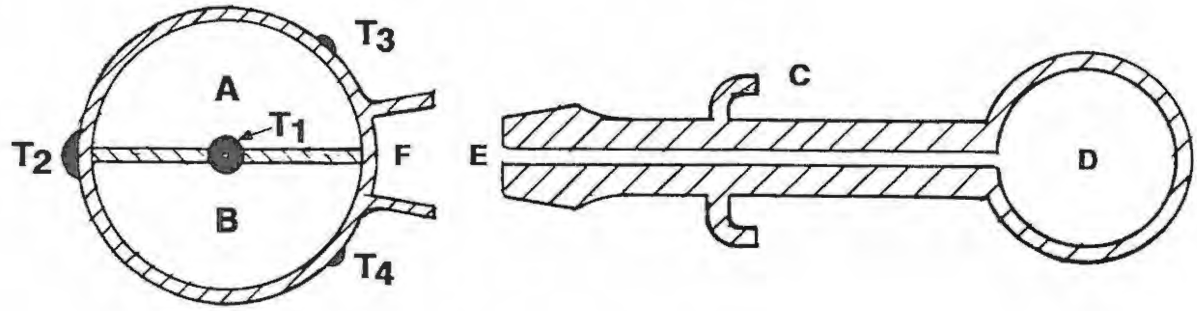
Calorimeters for the determination of excess molar enthalpies of liquid mixtures can be divided into three classes: *(i)* adiabatic calorimeters, *(ii)* isothermal calorimeters, and *(iii)* flow calorimeters.(75) The mixing of the liquids within the mixing vessel may take place all at once, by a continuous titration of the components, or by a continuous flow of both reactants through a mixing vessel.

(i) Adiabatic calorimeters

In adiabatic calorimeters, mixing occurs in a vessel which is thermally isolated from its surroundings. Endothermic mixing (positive H_m^E) is characterized by a lowering of the temperature of the calorimeter. The calorimeter is operated in a near isothermal manner by adding electrical energy to maintain a constant temperature during mixing. This reduces any errors due to heat losses and the excess enthalpy is then related to the electrical energy.(76) Exothermic (negative H_m^E) reactions are accompanied by a rise in temperature of the surroundings and necessitate the determination of the amount of energy required to reproduce an equivalent rise in temperature.

Letcher and Bayles(24) have discussed a simple adiabatic calorimeter. The apparatus consists of U-shaped glass mixing vessel mounted in a sealed brass cylinder which can be evacuated. The entire apparatus can be immersed in a water bath. The two unmixed liquids are separated by mercury and mixing is achieved through inversion of the apparatus followed by gentle rocking. In the original design of this instrument, the temperature change was determined from a graphical extrapolation of the resistance values obtained from a calibrated thermistor mounted in the calorimeter. Letcher and Bayles(24) have estimated an accuracy in their experimental excess molar enthalpies of ±5% or ±20 $J.mol^{-1}$, whichever is larger.

A significant advance in the determination of excess enthalpies by calorimetry can be associated with the development of a calorimeter by Larkin and McGlashan.(77) This apparatus is represented diagrammatically in Figure 2.1. According to a review by McGlashan *et al.*(78) this calorimeter largely meets the requirements necessary for any precise calorimetric determination, *viz.* the absence of a vapour space and the allowance for volume changes upon mixing. The calorimeter consists of a glass mixing vessel with



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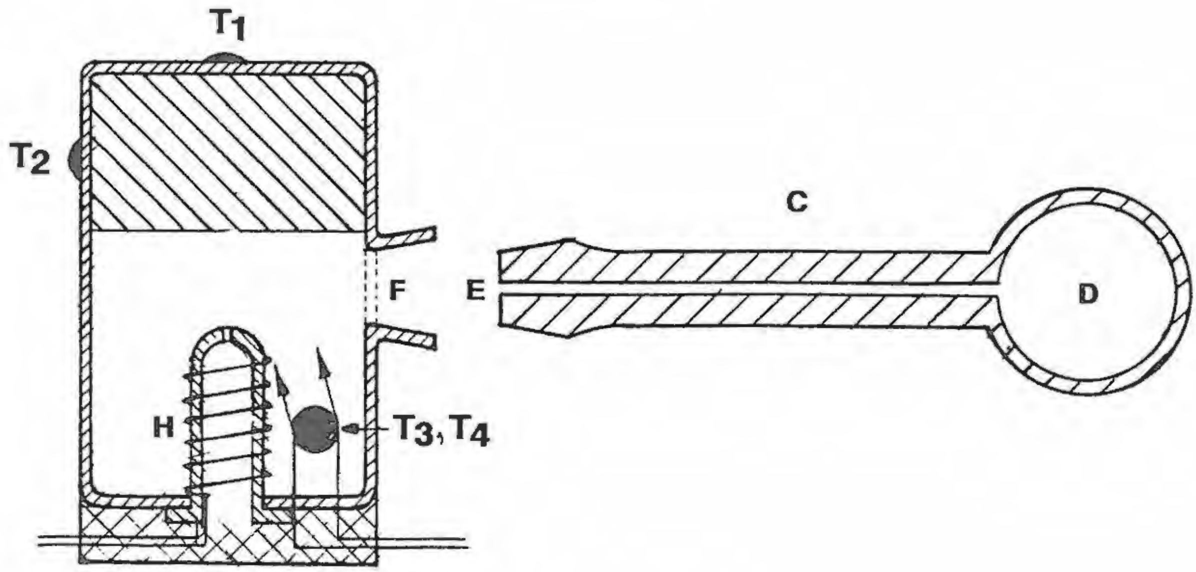

SIDE VIEW

Figure 2.1 An adiabatic calorimeter by Larkin and McGlashan two compartments, A and B, in its upper half, and a side arm connected by capillary, C, to an expansion bulb, D, *via* a greased joint, EF. A heating element, H, and four thermistors (T_1 to T_4) distributed over the surface of the mixing vessel form part of a Wheatstone bridge assembly. The vessel is filled with mercury and is immersed in a bowl of mercury. The mercury is displaced from the upper compartment by introducing weighed components of the mixture through the opening F by means of a hypodermic syringe. This is a cumbersome procedure however and is prone to error.

The loaded vessel with the capillary tube, C, half filled with mercury and attatched at the ground joint, F, is placed in an evacuated enclosure within a thermostat until temperature equilibration is achieved. The liquids are mixed in the absence of a vapour space by rotation of the apparatus through 180°, the direction of rotation being such that the liquid never comes into contact with the greased joint. The temperature change on mixing is measured by the four thermistors.

The precision of the apparatus has been quoted at 0.7 $J.mol^{-1}$ or 0.5% of the maximum value of H^E_m.(70*a*) The method is particularly useful when only small sample quantities are available, as the mixing chamber can be constructed as small as 1 cm^3. One of the major disadvantages of the technique is that it is very slow, with each measurement requiring a separate loading.

More recent modifications to the above calorimeter have been made.(78-81) These include a reduction in heat leaks and in the thermistor heat dissipation, and an amplification of the output bridge signal to a chart recorder.(78) A modification of the filling port by Howell and Stubley(79) eliminates the need for immersing the calorimeter in a mercury trough when loading the reagents. The apparatus of Hill and Swinton(81) only weighs 90g and hence the reagents can be weighed directly into the vessel placed on an analytical balance.

Spiteri(82) has constructed a calorimeter similar in design to that of Howell and Stubley.(79) After a comparison of Spiteri's H^E_m results for the system {cyclohexane + *n*-hexane} with those recommended by the IUPAC commission,(70) Spiteri quotes an error of 1.5% in the measured excess molar enthalpies. Watts *et al.*(83) employed the calorimeter of McGlashan to measure the H^E_m for the system {benzene + carbon tetrachloride} and observed the chemisorption of the carbon tetrachloride on the mercury. This was one example which served to indicate the limitations sometimes imposed through the use of mercury in excess enthalpy calorimeters.

(ii) Isothermal calorimeters

Malcolm and co-workers(84,85) describe an isothermal apparatus based on a Bunsen calorimeter.(67) A Bunsen calorimeter is shown in Figure 2.2. In a calorimeter of this type, the mixing process takes place in a mixing vessel which is housed in an inner chamber, A. The outer chamber, B, is competely filled with a liquid, part of which is frozen into a "mantle". Any energy absorbed or released during the mixing process causes melting or freezing of the liquid mantle surrounding the mixing vessel, while any volume change which may accompany mixing is measured by the movement of the mercury in the capillary tube, C. One advantage of a calorimeter of this type is that it can be used for measuring heat effects for slow processes. The major disadvantage of this technique is that measurements can only be made at the melting point of the calorimetric fluid.

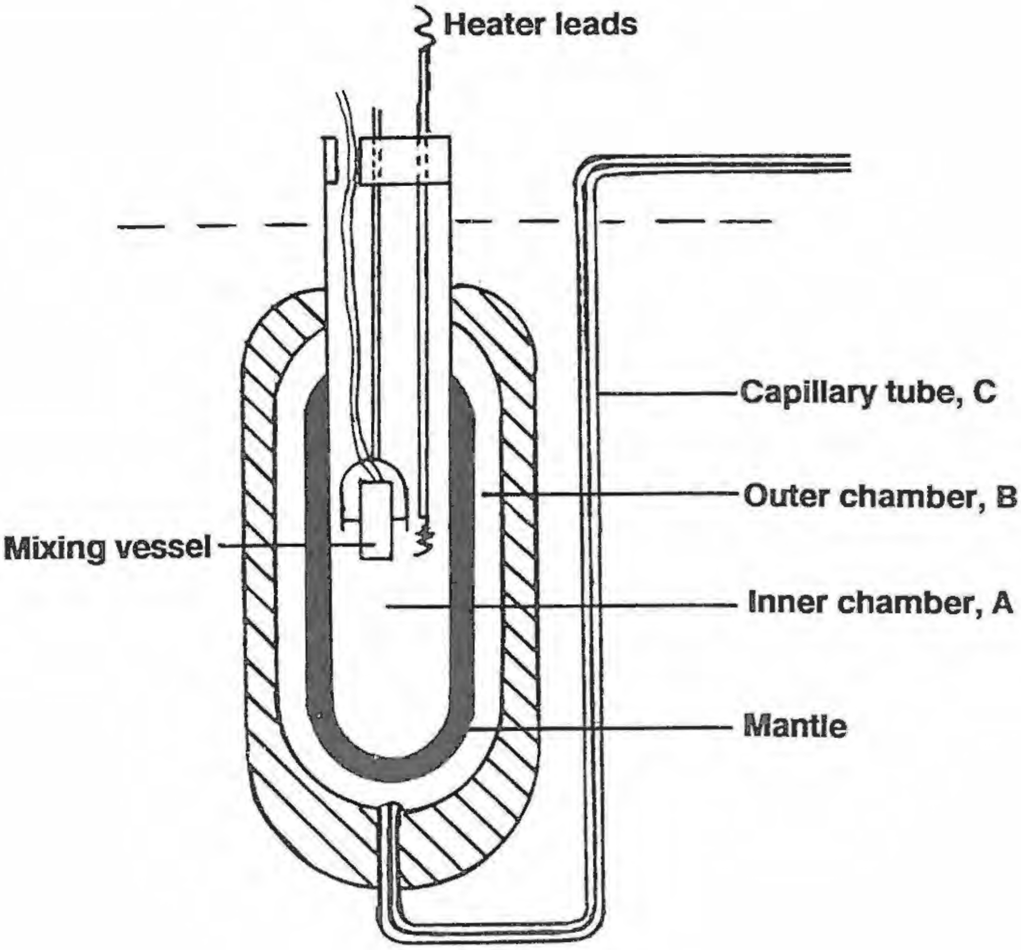

Figure 2.2 A Bunsen calorimeter

An alternative to this is an isothermal dilution calorimeter.(70*a*) For an endothermic system, the experimental procedure entails the injection of one component into another with the simultaneous addition of sufficient electrical energy to maintain isothermal conditions. The excess enthalpy is again related to the composition of the mixture and the amount of energy required to maintain isothermal conditions. The apparatus is normally designed so that the entire composition range can be covered in two experimental runs.

The majority of the stepwise dilution calorimeters which are suitable for endothermic measurements(86-92) are based on the original design of Mrazek and van Ness.(93) These workers quote a temperature sensitivity of 0.001 K and estimate an uncertainity of 2% in the heat of mixing data determined by their apparatus. They emphasize the importance of avoiding any vapour space above the liquid, and eliminate this by using a moving piston to enclose the liquid. Savini *et al.*(86) noted that the calorimeter of Mrazek and van Ness(93) did not permit the determination of the large excess molar enthalpies for mixtures of a small volume of alcohol in a large amount of hydrocarbon. Although they modified the design, the instrument still suffered from the drawback that complete mixing of the two liquids was sometimes not achieved for mixtures comprising components of very different densities. The heating contribution resulting from the mechanical stirrer(86) was eliminated by the addition of a cooling module in a later refinement by Winterhalter and van Ness.(87) These workers also employed a moving piston to enclose the liquid and reported an accuracy of 1% in measured excess molar enthalpies.

In a further refinement by Murakami and Benson(88) the cooling module was located below the mixing vessel and the mixing reservoir was immersed in a water bath. This arrangement eliminated the need for corrections resulting from changes in the mercury volume. The thermistors were installed in thin walled glass wells in contact with the mixing liquid. This change in design resulted from an observation that the thermistor resistance was pressure sensitive. The authors quote an overall accuracy of better than 1% in the excess molar enthalpy results.

Dilution calorimeters usually require about 50cm^3 of each component for analyses covering the entire composition range.(70*a*) The isothermal displacement calorimeter of Stokes *et al.*(89) is a modification of the calorimeter of Savini *et al.*(86) and uses smaller reagent sample sizes ($\pm$20 cm^3). A stirrer modification solved the problem of phase separation prevously observed for calorimeters of this type. The difficulty associated with sealing the mechanical piston without generating heat through frictional effects was overcome by the introduction of a mercury piston; the added liquid is accommodated through the displacement of mercury. Stokes *et al.*(89) report that the results at 298.15 K for {cyclohexane + *n*-hexane} had a standard deviation of 0.09 $J.mol^{-1}$ and an absolute deviation of 0.07 $J.mol^{-1}$ compared to the IUPAC reference curve(70*a*) for the same system.

A further modification by Stokes and co-workers(89,90) in the form of a directly driven stirrer initially introduced an undesirable dead volume of 0.03 cm^3 around the stirrer shaft. This dead volume was later reduced to 0.008 cm^3. Mixtures at various compositions are prepared by injecting known quantities of the pure components into the calorimeter from thermostatted calibrated syringes, rather than by the method of Savini and co-workers(86) where mercury is weighed into feed bottles to restore the volume. One advantage of the apparatus of Stokes and co-workers is that individual results at one temperature can be obtained much quicker by this apparatus than by a batch calorimeter, since the volume of sample added can be obtained directly from the calibrated syringes. Isothermal conditions are maintained either by direct electrical heating, for positive excess enthalpies, or through the use of a Peltier cooling device, for negative excess enthalpies.

There are several disadvantages to the use of mercury pistons. These include possible side reactions with the components and problems encountered with mercury spillages. The recent modification by Stokes(94) incorporates a capillary exit in the mixing vessel. The mixture is thus allowed to escape from the mixing vessel as the second component is added. Stokes quotes an error in the excess molar enthalpies measured by this instrument to be in the order of 1.0 $J.mol^{-1}$.

Gibbs and van Ness(95) have described an apparatus suitable for the measurement of exothermic enthalpies of mixing. The instrument contains a thermoelectric cooling module used to remove energy at a constant rate and is similar in basic design to the apparatus of Murakami and Benson.(88)

(iii) Flow calorimetry

The most recent advances in calorimetric techniques have been in the field of flow calorimetry. By this method, liquids are injected at a steady known rate into a mixing vessel, where complete mixing is achieved in the absence of a vapour space. The excess enthalpy is related to the power output of the heating element and the molar flow rates of the two components.(70a) The flow technique eliminates the time-consuming cell filling and weighing procedures and in many cases reduces the time required for thermal equilibration prior to measurement. The system can be made either adiabatic or isothermal.(96) The adiabatic condition is achieved when the flow cell and the temperature-sensitive elements are thermally insulated from their surroundings. In the isothermal mode the heat of mixing in the reaction vessel is transferred to a heat sink.(96)

McGlashan and Stoeckli(97) have constructed a single cell flow calorimeter. The apparatus is represented diagrammatically in Figure 2.3 and was constructed of Teflon.

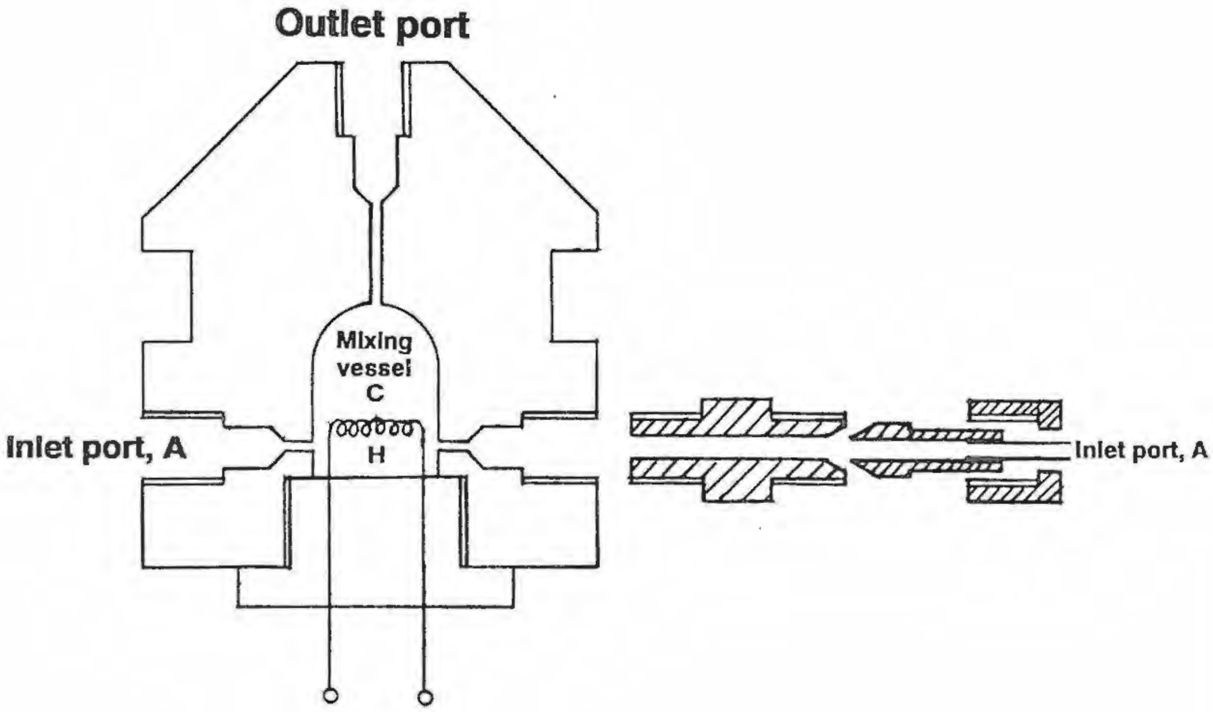

Figure 2.3 A flow calorimeter of McGlashan and Stoeckli

This minimized any heat transfer from the mixing zone to the environment. The liquids are introduced at opposite sides of the mixing zone through the inlet ports, A, and mixing takes place in the mixing chamber, C. In the case of endothermic mixing, four thermistors sense the temperature drop; the temperature can be restored to the pure component temperature by passing an electrical current through the heater, H. McGlashan and Stoeckli(97) concluded that the excess molar enthalpy could be measured with an accuracy of about 1%. However, one drawback to the apparatus was that 200 cm^3 of component liquid was required to cover the entire composition range. In addition, heat losses *via* the heating wire and the thermistor leads were not considered. A similar calorimeter designed by Sturtevant and Lyons(98) required smaller sample sizes. The reproducibility of the results was however only of the order of 2%. The ease and simplicity of the operation, coupled with the absence of any equilibration time, tended to compensate for the lack of precision obtained by these instruments, thus urging further development in this field.

Stoesser and Gill(99) have reported a twin flow microcalorimeter with the aim of overcoming the problems of vapour space, mechanical stirring effects and wall effects which occurred in some of the previous batch type instruments. However, their instrument did not use any mechanical inserts within the mixing cell, casting some doubt as to whether complete mixing of the liquid components was achieved. The authors reported an accuracy of 1% in excess molar enthalpies determined by this method.

Monk and Wadso(100) have designed a twin heat conduction calorimeter. The apparatus consists of a metal block heat sink containing a centrally located heat exchanger unit surrounded by calorimetric units in a twin arrangement. The calorimetric units comprise two flow reaction cells surrounded by surface thermopiles in contact with primary heat sinks. The heat sinks are thermally isolated and are immersed in a water bath. Heat evolved or absorbed during the mixing process is thus conducted to or from a heat sink arrangement *via* the semi-conductor thermopile. Peristaltic pumps are used to inject the liquids. These workers(100) observed a decrease in mixing efficiency when air bubbles became trapped within the mixing vessel. Thermal breaks within the flow lines were achieved by using PVC connections; these were ignored by previous workers such as Stoesser and Gill.(99)

Hsu and Clever(101) have observed that the use of peristaltic pumps with silicone tubing in the LKB microcalorimeter, a commercial version of the instrument of Monk and Wadso, presented limitations in the accuracy of the flows delivered. These authors(101) reported a maximum deviation from the IUPAC smoothing curve(70*a*) of about 22 J.mol^{-1} for excess molar enthalpies measured for the system {cyclohexane + *n*-hexane}. A heating effect due to frictional flow effects was not compensated for.

Tanaka *et al.*(102) have improved the performance of the LKB flow microcalorimeter through a number of changes to the auxiliary equipment design and to the operating procedures. The temperature control of the air bath containing the calorimeter unit was improved in addition to the digitization of the thermopile circuit and calibration circuit. Improved liquid flows were obtained with a pair of piston displacement pumps. The results for the {cyclohexane + *n*-hexane} test system were in excellent agreement with the smoothed function proposed by the IUPAC Commission.(70*a*) These workers estimated a precision of better than 0.5% for systems where the excess molar enthalpies at equimolar concentrations were of the order of 100 J.mol^{-1}.

In an attempt to reduce the primary error source present in many flow type calorimeters, namely the sensitivity of the apparatus to flow parameters such as the fluid velocity and the heat capacity of the fluids, Randzio and co-workers(103) have modified a commercial UNIPAK 600 microcalorimeter. The modifications included active heat exchanges in a negative feedback loop. This insures that the temperatures of the pure influents are always equal to the thermostat temperature, irrespective of the flow parameters. Raal and Webley(104) are of the opinion that these modifications are unnecessary if passive heat exchanges are designed in accordance with the guidelines that they have set out.

Picker *et al.*(105) used thermocouples instead of thermopiles in their isothermal differential flow calorimeter, since the large heat capacity of the thermopiles lengthened the temperature equilibration time. Mixing was achieved through turbulence as a result of a reduction in the flow line diameter in the mixing cell to 0.2 mm. These workers estimated an accuracy of 1% in their H_m^E data which was confirmed by Grolier *et al.*,(106) who obtained an average deviation of less than 1.6 J.mol^{-1} from the IUPAC smoothing equation(70*a*) for the {cyclohexane + *n*-hexane} system.

Picker and co-workers(107) have also investigated heat losses and boundary effects on calorimeter performance. They are of the opinion that the dilution of the second component by the first may occur through a process of molecular diffusion as a result of a thin film of liquid remaining on the walls of the mixing vessel. Errors of greater than 30% in heating effects in some cases were attributed to this effect.

Heat losses through heater lead wires have been minimized in a flow calorimeter design by Coomber and Wormald.(108) Lost energy is readsorbed by the pure liquids flowing over the lead wires. The frictional heating effect through the stirrer shaft seriously limited the accuracy of this calorimeter however. The authors(108) estimated an accuracy of 2% for endothermic enthalpies of mixing.

In an attempt to reduce the energy dissipation resulting from frictional effects for some of the more viscous organic compounds, Raal and Webley(104) have recently developed a differential microflow calorimeter design. They addressed the following basic requirements: *(i)* complete temperature equilibration of the mixture components before mixing, *(ii)* separation of the frictional energy from the excess enthalpy, *(iii)* the elimination of heat leaks, and *(iv)* complete mixing of the components. The H_m^E results measured for {cyclohexane + *n*-hexane} never differed from the results recommended by the IUPAC commission by more than 0.53 $J.mol^{-1}$.

Instruments capable of measuring heats of mixing at elevated temperatures and pressures have been developed.(109-111) These will however not be considered here.

Isothermal twin differential flow calorimeters are capable of yielding good results with an accuracy which is on a par with those obtained using batch type instruments. Dual piston pumps which can deliver accurate pulseless flows, and precise electronic measuring devices and control devices aid in the measurement of excess molar enthalpies by flow calorimetric methods. In addition, dead volumes are more easily avoided in flow calorimetry and vapour spaces are very often eliminated, while greater automation and the elimination of possible contamination by mercury contribute to the overall attractiveness of this experimental technique.

2.3 Excess Molar Volumes

2.3.1 Introduction

Volume changes on mixing liquids can arise as a result of a combination of factors. The most important of these are the difference in size and shape of the component molecules, the different intermolecular interactions which may exist between like and unlike molecules, and the possible formation of new chemical species on mixing. The relative ease with which excess volumes can be determined has resulted in this value becoming widely accepted as a favourable tool for the testing of various theories of liquid mixtures.

2.3.2 Measurement of excess molar volumes

The experimental aspects concerning the measurement of excess molar volumes have been discussed briefly in review articles by Stokes and Marsh,(112) Letcher(113) and Swinton.(114) The subject has been discussed in more detail in reviews by Battino,(115) Marsh(70*a*) and more recently by Handa and Benson(116) and Marsh.(71,72)

Excess molar volumes, V_m^E, can be determined either: *(i)* directly by observing the resultant volume change on mixing of liquid components, or *(ii)* indirectly by measuring the densities of the mixture at different compositions.(116)

(i) Direct measurement of V_m^E

Handa and Benson(116) regard direct measuring methods as being more readily capable of yielding results of higher precision than indirect methods. Direct measurements may be made either by *(a)* batch or single composition dilatometers, or by *(b)* continuous dilution dilatometers.(115,116) In both of these experimental methods the excess volume corresponds to the displacement of mercury in contact with the mixture.

(a) Single composition dilatometers

Keyes and Hildebrand(117) are often attributed with the first design of an apparatus for the direct measurement of excess volumes. Their single composition dilatometer is shown in Figure 2.4 and consists in essence of a U-shaped tube. The two components are contained within the arms of the apparatus and are separated by mercury. Graduated capillaries at the ends of the arms facilitate the measurement of the volumes before and after mixing. Complete mixing of the liquids is accomplished by simply rocking the apparatus, while temperature equilibration of the mixture is usually achieved by immersing the entire instrument in a liquid bath. The cantered design is such that the capillaries are always kept above the fluid level of the thermostat. The precision of the instrument is largely dependent on the volume of the liquid reservoirs and on the capillary bore.(115) The apparatus of Keyes and Hildebrand(117) was capable of a precision of ± 0.003 $cm^3.mol^{-1}$ in the measured V_m^E.

Most of the modifications to the existing design of Keyes and Hildebrand have been reviewed by Battino.(116) One of these modifications by Duncan *et al.*(118) is shown in Figure 2.5. The apparatus requires less than 1.0 cm^3 of sample and has the added advantage that interchangeable capillaries can be used to accommodate different

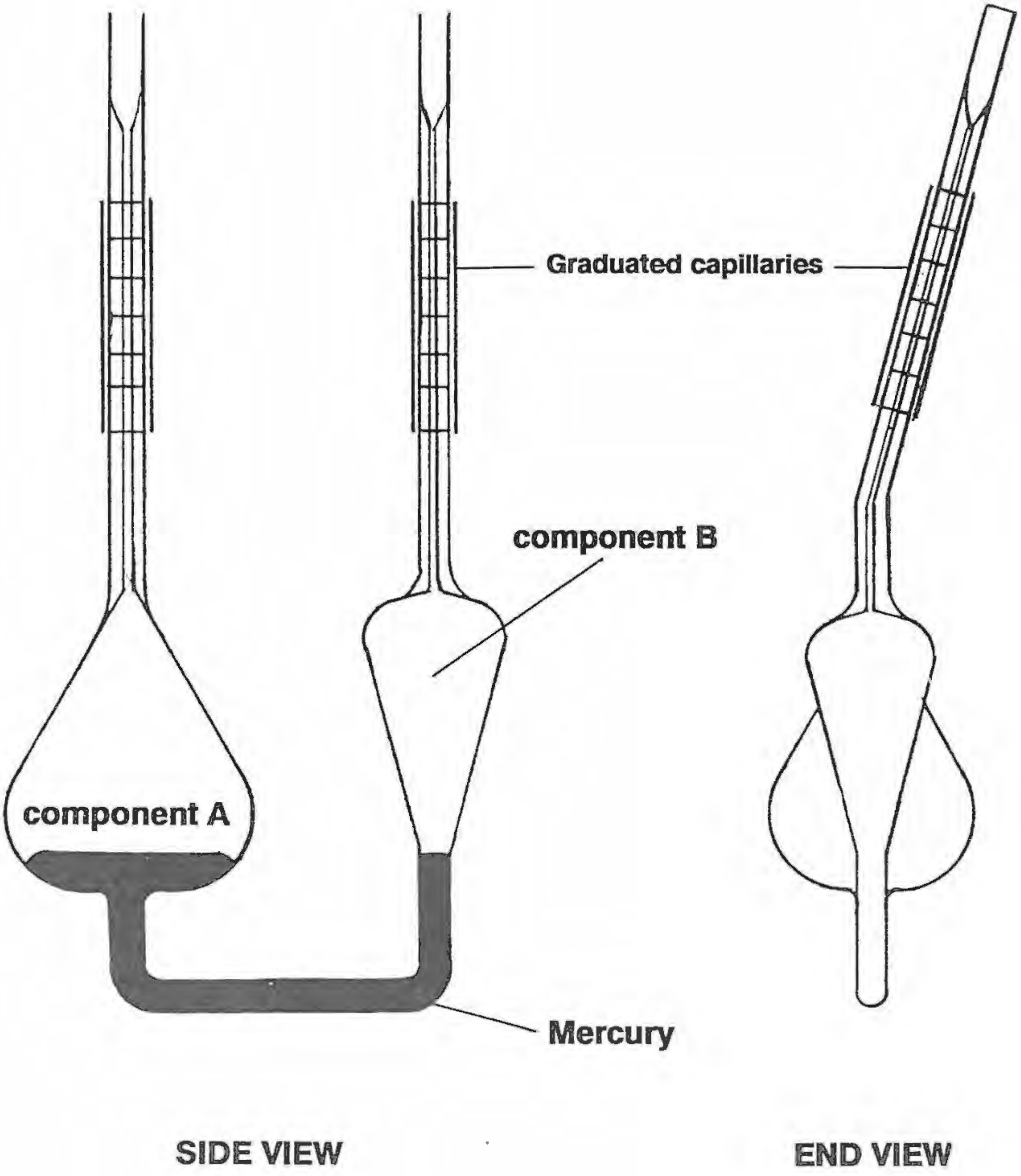

Figure 2.4 A single composition dilatometer of Keyes and Hildebrand

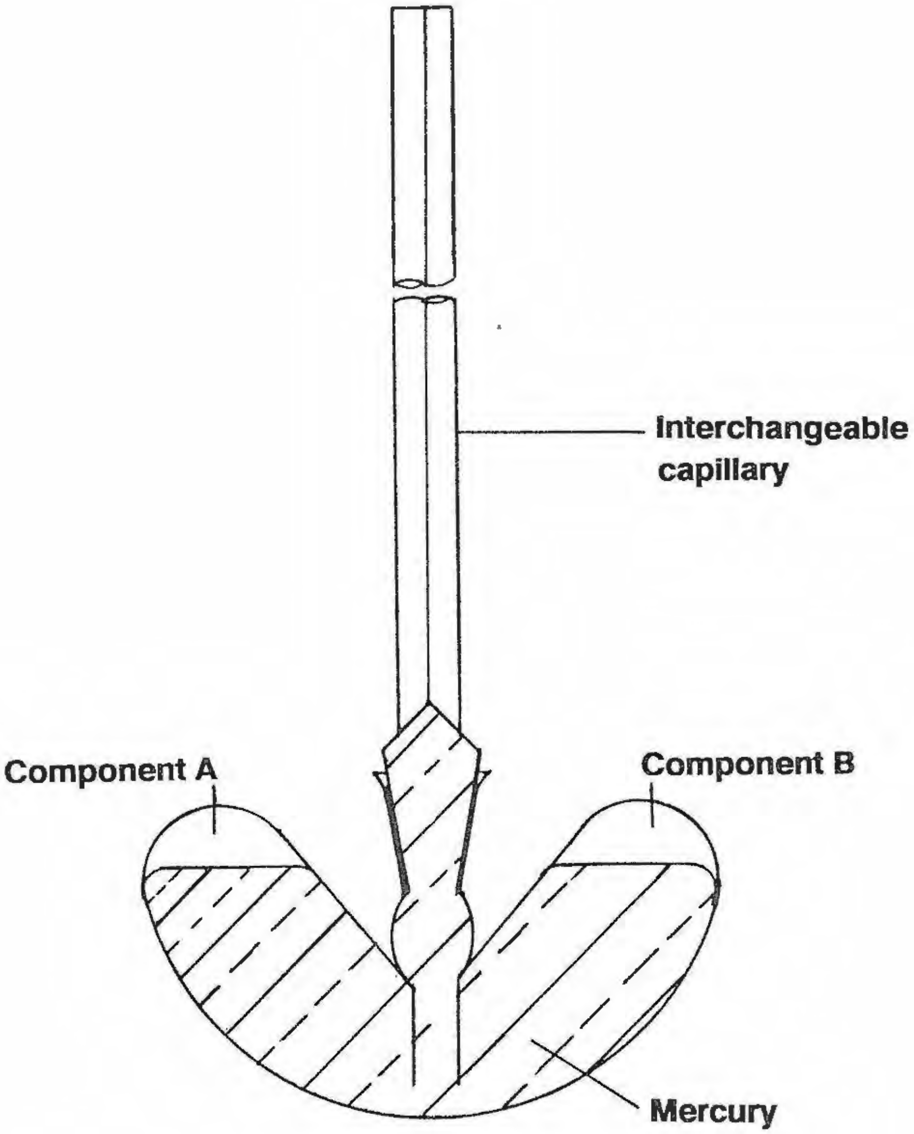

Figure 2.5 A dilatometer of Duncan, Sheridan and Swinton

magnitudes of the excess volume. Battino(115) quotes a precision of ±0.002 $cm^3.mol^{-1}$ or ±0.5% of the maximum excess molar volume measured using this apparatus.

The disadvantage with single composition dilatometers is that each measurement involves a separate loading of the apparatus. A variation of the basic design by Holleman(119) permits four different compositions to be measured per loading. An accuracy of 1-2% has been quoted for mixtures involving *n*-alkanes for V_m^E measured over the temperature range 313 - 389 K. The sample is usually introduced with a syringe in instruments of this type. The possible losses due to evaporation of volatile components during sample introduction is sometimes a limiting factor. Modifications by Brennan *et al.*(120) and by Ahmed *et al.*(121) to an apparatus of Powell and Swinton(122) include a smaller dilatometer vessel. This enables the apparatus to be accommodated directly on a balance pan so that the successive weights can be determined directly, thus reducing possible losses through evaporation.

Stookey *et al.*(123) have considered the corrections and errors associated with the dilution dilatometric technique. They stress that the possible compressibility corrections for those dilatometers in which the mercury displacement has a vertical component may lead to errors of 0.5 - 1.0% in the the measured excess volume. Error contributions to the measured V_m^E from other factors include 0.5% for V_m^E of the order of 0.5 $cm^3.mol^{-1}$ from bath temperature fluctuations of 0.001 K, and 0.1% from cathetometer measurements. Grease from the capillary - dilatometer joint can also constitute an additional source of error.

(b) Continuous dilution dilatometers

Handa and Benson(116) have pointed out that the term "continuous dilution dilatometer" is a slight misnomer, because dilatometers of this type require at least two runs to make the necessary measurements over the entire composition range. Since the original design of a dilution dilatometer by Geffcken *et al.*(124) in 1937, which had a mixing chamber capacity of 250 cm^3 and could reproducibly detect volume changes of 0.0002 cm^3, dilution dilatometers have undergone several modifications.(125-127)

The principle of operation of the early model by Geffcken *et al.*(124) is represented diagrammatically in Figure 2.6. The mixing vessel, C, is initially loaded with pure component, A, and with mercury. With the stopcock, S, in an open position, the mercury forces the second component, B, into the mixing vessel via the capillary, E. Some provision is made for stirring the mixture and the entire apparatus is thermostated. Successive increments of B are added and the volume change is measured directly by observing the change in the mercury level in the capillary column, D. Measurements are made over the entire composition range by making similar experimental runs with the roles of the components reversed. The different design modifications invariably employ different methods for determining the amount of A initially present and the amount of B added. Some designs incorporate interchangeable capillaries at D and have smaller mixing vessels.(115) One modification to the apparatus of Geffcken *et al.* by Stokes *et al.*(128) comprises a burette, containing one liquid component, which is attached to an upper

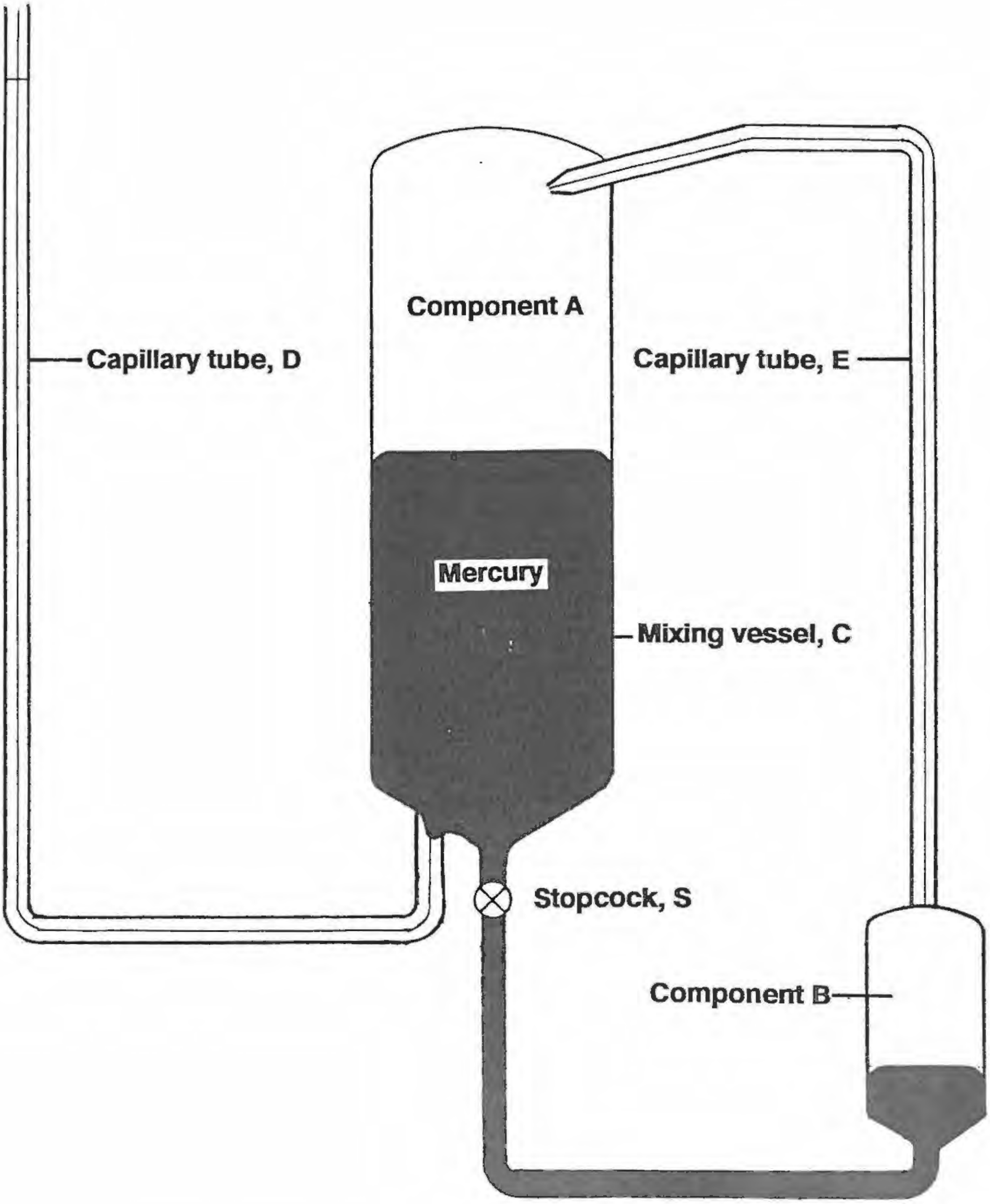

Figure 2.6 Principle of operation of the continuous dilution dilatometer of Geffcken, Kruis and Solana

bulb, containing the second component over mercury, by a fine stainless steel tube. Known amounts of component are forced from the burette into the bulb by a flow of mercury in the opposite direction *via* a greased tap. Marsh(70*a*) has quoted a precision of 0.001 $cm^3.mol^{-1}$ for excess molar volumes measured with this apparatus, provided that temperature control to better than 0.0004 K is achieved. The apparatus has the advantage of being simpler to fill and easier to operate than previous instruments of this type.

The volume change through the incorporation of grease into the mercury in any apparatus employing greased taps remains a possible scource of error.(116) The effect of the grease on V_m^E results has been investigated by Bottomley and Scott(129) and Tanaka *et al.*(130) These workers have suggested that a volume change of 0.00005 cm^3 can be incurred per turn of a stopcock for a greased tap. As a result of their studies, Bottomley and Scott(129) have constructed a dilution dilatometer without any stopcocks. Although the apparatus is easy to operate, it suffers from the drawback that it is difficult to calibrate. In addition, the apparatus must be filled under vacuum, making the operating procedure tedious.

The recent introduction of a grease-free tilting dilution dilatometer by Kumaran and McGlasham(131) is easier to operate and calibrate, can be filled under atmospheric conditions, and can be used for V_m^E determinations of almost any magnitude. The agreement between the results for the {benzene + cyclohexane} system determined using this instrument, and results reported by Stokes *et al.*(128) who used a dilution dilatometer, are very good. The largest deviation corresponds to 0.0019 $cm^3.mol^{-1}$ at $x_{Benzene} = 0.8$.

A drawback of most of the continuous dilution dilatometers is that they do not permit excess molar volume measurements at a constant pressure.(116) The height change, ΔH, of the mercury in the capillary causes a change in the mixing cell pressure which correspomds to $\rho g \Delta h$, where ρ is the density of the mercury and g is the gravitational constant. The elasticity of glass and the compressibility of the liquid may also change the apparent volume of the contents in the mixing cell by up to 1.5%,(115) with obvious effects on the excess volume.

An apparatus design by Janssens and Ruel(132) does not employ mercury. This is advantageous when organic compounds which can react with mercury are being considered.

(ii) Indirect measurement of V_m^E

Measurements of excess molar volumes by indirect methods were, until recently, carried out with pycnometers or density bottles. Many variations of the pycnometer have been discussed by Bauer and Lewin(133) while Kohler and Rott(134) have reported designs for mixing bottles. Although pycnometry remains a simple and inexpensive method for obtaining excess molar volumes by density measurements, determinations are nevertheless time consuming. Reproducible filling of instruments of this type is a difficult task.

A pycnometer based on the design of Wood and Brussie,(135) which was used for 5th place density measurements, is given in Figure 2.7. The bulb has an 11 cm^3 capacity and

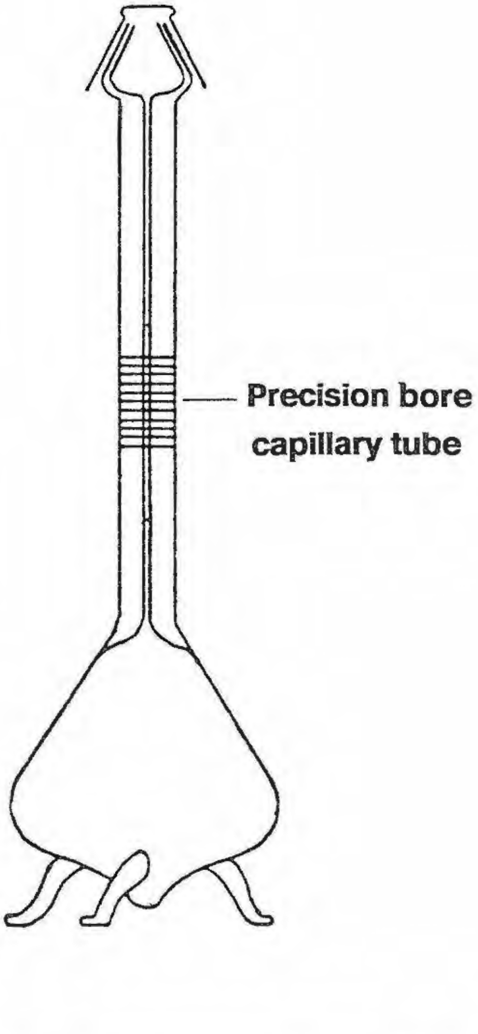

Figure 2.7 A single-arm pycnometer of Wood and Brusie

is filled with a hypodermic syringe. Reproducible filling of the apparatus is generally difficult, with the formation of bubbles being a frequent source of erro Unreproducible "wetting" of the capillary by the meniscus can lead to an error in the measurement of the liquid level, while pycnometric calibrations as a function of temperature are often difficult.(116) Pycnometric measurements are subject to a number of corrections, the more important ones being buoyancy corrections and vapour space corrections.(116) It is also important to measure the mixture composition precisely when performing measurements with this apparatus.

Digital readout densimeters are becoming increasingly popular. In this method the resonance frequency of an electronically excited mechanical oscillator, and hence the period of oscillation of the sample contained within the oscillator, is related to the density of the sample. The original design of Kratky and co-workers(136,137) employed a V-shaped hollow glass sample tube. This design facilitated the filling and mixing procedures and was easily adapted for measurements with flowing liquids. The sample cell of Picker *et al.*(138) was made of stainless steel and was similar in shape. The effects of sample evaporation have been considered in detail by Goates *et al.*(139)

Handa and Benson(116) have pointed out that excess molar volumes from density determinations are prone to errors in the composition of the mixtures. In order to obtain a precision of 0.001 $cm^3.mol^{-1}$, they state that the composition and the density should be precise to five and six significant figures respectively. Battino(115) is of the impression that thermostat temperatures should be controlled to ±0.01 K if densities are to be determined accurately to 0.00001 $g.cm^{-3}$.

Magnetic float densimeters operate on the principle of balancing the opposing effects of gravity, buoyancy and the magnetic field on a float containing a permanent magnet. This is achieved by passing a current through a solenoid placed below the sample cell; the density is thus related to the current at which the float first lifts off the bottom of the cell.(116) Benjamin(140) and Franks and Smith(141) have each described a magnetic float densitometer. These instruments have been quoted as having sensitivities of ±0.001% and ±0.0001% respectively.(115) Battino(115) has mentioned other designs. Errors resulting from possible surface tension effects can however introduce uncertainties in the results measured by this method.

Other methods for measuring V_m^E have been reviewed by Handa and Benson.(116) These include the apparatus of Chappelow *et al.*(142) which operates on the Archimedes principle and relates the density of the sample to the loss in weight of a sinker as it is immersed in a liquid. Handa and Benson(116) have reported that the primary source of error in an apparatus of this type is associated with the effect of surface tension on the wire attached to the sinker.

Dissolved gases in organic liquids are often a source of bubble formation. Handa and Benson(116) have reported that the densities of organic liquids can differ from those of degassed liquids by as much as 0.0003 $g.cm^{-3}$. This fact is of particular relevance to measurements employing density determinations.

2.4 Review of the excess molar enthalpies and excess molar volumes for related systems

The work reported in this thesis is primarily concerned with the experimental determination at 298.15 K of excess molar enthalpies and excess molar volumes for binary liquid mixtures of a bicyclic compound, benzene, cyclohexane or *n*-hexane with an *n*-alkane, a 1-alkene, a 1-alkyne, a cycloalkane, cyclohexene, a cycloalkadiene, or benzene. Since some of these systems have been studied before, it is pertinent to review the literature with reference to mixtures concerning these compounds and related systems.

A few data compilations and reviews concerning H_m^E and V_m^E data exist in the literature. Battino(115) has compiled experimental excess molar volumes at equimolar concentrations for binary liquid mixtures determined prior to 1969. A more recent review by Handa *et al.*(116) comprises a compilation of experimental excess molar volume data determined prior to 1979; the coefficients of the smoothed results are reported. *Specialist Periodical Reports*, edited by McGlashan,(70) contains extensive references to thermodynamic properties, including V_m^E and H_m^E, and encompasses the period 1960 to 1975. Wisniak and Tamir(143) have recently published a supplement to their 1978 bibliography(144) concerning H_m^E, V_m^E, and G_m^E data, covering the literature up until 1981. Excess molar enthalpy results determined prior to 1981 for binary and multicomponent mixtures have been tabulated directly in the *Handbook of Heats of Mixing* by Christensen *et al.*,(145) with the inclusion of Redlich Kister smoothing coefficients when they were recorded in the original publications. An example of serial and ongoing publications of data evaluations is the *International Data Series*, which publishes experimental H_m^E and V_m^E results.

2.4.1 Mixtures involving a bicyclic compound

(i) Decalin mixtures

Excess molar enthalpies reported at several temperatures from 298.15 K to 348.15 K by Croucher and Patterson(146) for the system {(*cis*-decalin or *trans*-decalin) + *n*-hexadecane} were observed to decrease as the temperature increased. *Trans*-decalin gave much smaller H_m^E values for mixtures with *n*-hexadecane than *cis*-decalin mixtures did. Furthermore, negative H_m^E values were observed at high temperatures in the case of *trans*-decalin. Croucher and Patterson(146) attribute the decrease in H_m^E displayed by the *trans*-decalin over the *cis*-decalin to an endothermic destruction of orientational ordering of segments of the *n*-hexadecane by the decalin isomer and an exothermic rotational ordering of the segments by the *trans*-decalin. de St. Romain and Patterson(147) have reported H_m^E for some mixtures involving *cis*- and *trans*-decalin with some normal and branched alkanes. These include *n*-hexane, *n*-heptane and *n*-hexadecane. The excess molar enthalpy values at equimolar concentrations were roughly three to four times smaller for mixtures involving decalin in the plate-like *ee* configuration of *trans*-decalin than for the more globular *ea* configuration of *cis*-decalin. The H_m^E were negative for {*trans*-decalin + (*n*-hexane or *n*-heptane)}, becoming positive for {*trans*-decalin + *n*-hexadecane}. The magnitude of the difference between the *cis*- and *trans*-decalin mixtures was influenced by the shape and flexibility of the *n*-alkane component, being small for compact isomers and large for the more flexible *n*-alkanes chains. These results once again afford evidence for the negative contribution to H_m^E for mixtures comprising flexible alkanes with a plate-like molecule. Since Croucher and Patterson(146) do not quote absolute experimental values but rather give graphs of the relative trends displayed by the experimental results, a quantitative comparison cannot be made with the results of de St. Romain and Patterson.(147)

Fujihara *et al.*(148) have also reported H_m^E at 298.15 K for {*trans*-decalin + n-heptane}. The excess molar enthalpy result at equimolar concentrations, $H_m^E(x=0.5)$, is -22.96 $J.mol^{-1}$ and is more positive than the corresponding value of -25.3 $J.mol^{-1}$ reported by de. St. Romain and Patterson.(147) The $H_m^E(x=0.5)$ for {*cis*-decalin + *n*-heptane}: 131.7 $J.mol^{-1}$ reported recently by Fujihara and co-workers(149) compares favourably with the value of 131.6 $J.mol^{-1}$ reported by de St. Romain and Patterson(147) for the same mixture.

Letcher *et al.*(9) have reported H_m^E for {decalin + (*n*-hexane or *n*-heptane or *n*-octane or *n*-dodecane or *n*-hexadecane)} at 283.15 K and 298.15 K. The decalin comprised a mixture of 53.3 mole% *cis*-isomer and 46.7 mole% *trans*-isomer. All the H_m^E results were positive. The $H_m^E(x=0.5)$ for the mixtures {decalin + *n*-heptane}: 68.6 J.mol^{-1} and for {decalin + *n*-hexadecane}: 198.6 J.mol^{-1} were 8 J.mol^{-1} and 13 J.mol^{-1} smaller respectively than those results reported by Lundberg(150) who used a 64 mole% *cis*-decalin and 36 mole% *trans*-decalin mixture.

Excess molar enthalpies have been reported for {*trans*-decalin + cyclopentane} by two different groups.(151,152) The $H_m^E(x=0.5)$ of -271.0 J.mol^{-1} reported by de St. Romain *et al.*(152) compares favourably with the value of -270.6 J.mol^{-1} reported by Benson and co-workers.(151) The value for {*cis*-decalin + cyclopentane}: -129.0 J.mol^{-1} is more positive.(152) Letcher and co-workers have reported H_m^E for {(*cis*-decalin or *trans*-decalin or decalin) + (cyclohexane(9) or cycloheptane(9) or cyclooctane(9) or cyclodecane(19))} at two different temperatures in some cases. Once again the decalin comprised a mixture of 53.3 mole% *cis*-isomer and 46.7 mole% *trans*-isomer. For the system {*trans*-decalin + cyclohexane}, the standard deviation for the H_m^E results reported by Letcher *et al.*(9) are within 3 J.mol^{-1} of those values reported by Sturtevant and Lyons,(98) Benson and co-workers,(153) Lundberg,(150) and de St. Romain *et al.*(152) The $H_m^E(x=0.5)$ by Letcher *et al.*(9) for {*cis*-decalin + cyclohexane}: 28.6 J.mol^{-1}, {*cis*-decalin + cycloheptane}: 12.5 J.mol^{-1}, and {*cis*-decalin + cyclooctane}: 23.1 J.mole^{-1} compare well with the respective values, 28.0 J.mol^{-1}, 11.0 J.mol^{-1}, and 20.0 J.mole^{-1} reported by de St. Romain *et al.*,(152) and with the values 28.0 and 29.2 J.mol^{-1} for {*trans*-decalin + cyclohexane} by Benson *et al.*(153) and by Sturtevant and Lyons(98) respectively. The H_m^E for the cyclopentane systems are very much more negative than for the other cycloalkane mixtures, pointing to a packing effect.(19)

Gómez-Ibáñez and Wang(154) have measured excess molar volumes at 298.15 K for the mixtures {*trans*-decalin + (*n*-heptane or *n*-nonane or *n*-dodecane or *n*-hexadecane)} while more recently Fujihara *et al.*(155) have reported V_m^E at 298.15 K for {*trans*-decalin + *n*-heptane}. The excess molar volume at equimolar concentrations, $V_m^E(x=0.5)$, reported by Fujihara *et al.* for {*trans*-decalin + *n*-heptane}: -0.630 cm^3.mol^{-1},(155) is similar to the value reported by Gómez-Ibáñez and Wang: -0.644 cm^3.mole^{-1} (154) for this system. Fujihara *et al.*(156) have also investigated excess molar volumes for {*cis*-decalin + *n*-heptane}. The difference between V_m^E values for these mixtures involving *cis*- and *trans*-decalin is very small. Excess molar volumes reported by Chylinski and Strykjek(157) for {*cis*-decalin + (*n*-octane or *n*-undecane or *n*-hexadecane)} are negative for *n*-alkanes of chain length $n=8$ and $n=11$, but increase with increasing chain length of the *n*-alkane, becoming positive for the *n*-hexadecane mixtures. The differences between the *cis*-isomer results(157) and the *trans*-isomer results of Gómez-Ibáñez and Wang(154) becomes larger for a large *n*. The *cis*-decalin results are larger and more positive than the values for the corresponding mixtures involving *trans*-decalin.

Letcher and Lucas(7) have reported V_m^E results at 283.15 K and at 298.15 K for {decalin + (*n*-pentane or *n*-hexane or *n*-heptane or *n*-octane or *n*-dodecane or *n*-hexadecane)}. In this work they used a mixture of *cis*- and *trans*-decalin in the same proportions as before. Their V_m^E results followed similar trends to those observed for mixtures involving *cis*-decalin and for mixtures involving *trans*-decalin, and lay between these results. The $V_m^E(x=0.5)$ result for {decalin + *n*-heptane}: -0.636 $cm^3.mole^{-1}$ (7) is similar to that for {*trans*-decalin + *n*-heptane}: -0.644 $cm^3.mol^{-1}$ reported by Gómez-Ibáñez and Wang(154) and {*cis*-decalin + *n*-heptane}: -0.630 $cm^3.mol^{-1}$ reported by Fujihara *et al.*(151) The $V_m^E(x=0.5)$ for {decalin + *n*-octane}: -0.457 $cm^3.mol^{-1}$ (7) is similar to the value for {*cis*-decalin + *n*-octane}: -0.434 cm^3. mol^{-1}.(157) The $V_m^E(x=0.5)$ reported by Letcher and Lucas(7) for the *n*-hexadecane system is 0.137 $cm^3.mol^{-1}$ and lies between the value of 0.034 $cm^3.mol^{-1}$ reported for the same compound mixed with *trans*-decalin(154) and 0.182 $cm^3.mol^{-1}$ for the *cis*-decalin mixture.(157)

Benson and co-workers(151) have reported V_m^E for *cis*-decalin or *trans*-decalin mixed with cyclopentane. The $V_m^E(x=0.5)$ for {*cis*-decalin + cyclopentane} is -0.589 $cm^3.mol^{-1}$ while that for {*trans*-decalin + cyclopentane} is -0.693 $cm^3.mol^{-1}$. The corresponding $V_m^E(x=0.5)$ by Letcher and Lucas(8) for {decalin + cyclopentane} is -0.630 $cm^3.mol^{-1}$. These values are significantly smaller than V_m^E values for decalin with a cycloalkane of higher carbon numbers.

The $V_m^E(x=0.5)$ reported by Gómez-Ibáñez and Wang(154) for {*trans*-decalin + cyclohexane}: -0.059 $cm^3.mol^{-1}$ is larger than the value of -0.075 $cm^3.mol^{-1}$ reported for the same system by Benson *et al.*(153) The corresponding $V_m^E(x=0.5)$ for {*cis*-decalin + cyclohexane}: (-0.182 $cm^3.mol^{-1}$ (157) and -0.172 $cm^3.mol^{-1}$ (158)) are more negative. The $V_m^E(x=0.5)$ reported by Letcher and Lucas(8) for {decalin + cyclohexane} lies between these values and is -0.132 $cm^3.mol^{-1}$. Letcher and Lucas(8) and Letcher(19) have also reported V_m^E for mixtures involving cycloheptane,(8) cyclooctane,(8) or cyclodecane(19) with decalin. The large negative excess molar volumes for mixtures involving cyclopentane can be attributed to the packing of the smaller cyclopentane molecules between the more "loosely" packed decalin molecules. This effect also helps to explain why these excess molar volumes are significantly smaller than the results for other cyloalkanes with higher carbon numbers.(19)

Lundberg(150) has reported H_m^E for {decalin + benzene} at 298.15 K, where the decalin mixture comprised 64 mole% *cis*-isomer and 36 mole% *trans*-isomer. More recently, Fujihara and co-workers have reported H_m^E and V_m^E for {(*cis*-decalin(149,156) or *trans*-decalin(148,155)) + benzene} and Chylinski and Stykjek(157) have measured V_m^E for {*cis*-decalin + benzene}. The large exothermic H_m^E results for the *cis*-decalin system reported by Lundberg are about 30 J.mol^{-1} larger than the values for the *cis*-decalin system reported by Fujihara *et al.*(149) The H_m^E results for the decalin system, where decalin comprises *cis*- and *trans*-isomers, are slightly larger than the results for the *cis*-decalin and for the *trans*-decalin systems. The V_m^E results for the *trans*-decalin system are slightly larger than the results for the *cis*-decalin mixture. Fujihara's(156) V_m^E results are larger than Chylinski's(157) results by about 1%.

The literature contains a few other references to work involving decalin systems. H_m^E and V_m^E results for mixtures of {*cis*-decalin + *trans*-decalin} have been reported,(98,157,159) the H_m^E results being small and negative.

(ii) Bicyclohexyl mixtures

Letcher and Scoones(13) have measured H_m^E for {bicyclohexyl + (*n*-hexane or *n*-octane or *n*-dodecane or *n*-hexadecane)} and for {bicyclohexyl + (cyclopentane or cyclohexane or cycloheptane or cyclooctane)} at 288.2 K and 298.2 K, while Letcher(19) has reported H_m^E data for {benzene + cyclodecane}. Lal and Swinton(160) have measured H_m^E for {bicyclohexyl + cyclohexane}. The values obtained by the two different groups of workers over the entire composition range for the cyclohexane system are within 2 J.mol^{-1} of each other. The four H_m^E results reported by Jessup and Stanley(161) for {bicyclohexyl + *n*-dodecane} are as much as 9 J.mol^{-1} larger than the corresponding values by Letcher and Scoones.(13)

Letcher has reported excess molar volumes for {bicyclohexyl + (*n*-pentane or *n*-hexane or cyclopentane)}(12) at 283.15 K and 298.15 K and for {bicyclohexyl + (*n*-heptane or *n*-octane or *n*-nonane or *n*-decane or *n*-dodecane)}(11) at two temperatures between 283.15 K and 313.15 K. Excess molar volumes for {bicyclohexyl + (cyclohexane(10) or cycloheptane(10) or cyclooctane(10) or cyclodecane(19))} were reported at 298.15 K. A direct comparison between the results by Letcher(10) for {bicyclohexyl + cyclohexane} with those of Mclure and Swinton(162) is difficult since the latter workers published their results in graphical form. The interpolated results appear to be within 0.010 cm^3.mol^{-1} of the results of Letcher.(10) Excess molar volume results for mixtures involving a cycloalkane or an *n*-alkane generally increase with an increase in the carbon number of the cycloalkane or the *n*-alkane.

Except for the cyclopentane mixture the H_m^E and V_m^E results for the mixtures involving a cycloalkane or an *n*-alkane are all positive. The negative H_m^E and V_m^E for the systems involving cyclopentane can once again be attributed to the accommodation of the small flatter cyclopentane molecule in interstices between the larger bicyclohexyl molecules.

(iii) Tetralin mixtures

Letcher and Scoones(16) have determined H_m^E results for {tetralin + (*n*-hexane or *n*-heptane or *n*-dodecane or *n*-hexadecane)} and for {tetralin + (cyclopentane or cyclohexane or cycloheptane or cyclooctane)} at two temperatures, while Letcher(19) has determined H_m^E at 298.15K for {tetralin + cyclodecane}. Some of these systems have been studied by other workers as well.(150,163,164) A standard deviation of 8.1 $J.mol^{-1}$ is observed on comparison of the results at 298.15 K of Letcher and Scoones(16) for {tetralin + *n*-heptane} with those values interpolated from the smoothing equations of Grolier.(163) The $H_m^E(x=0.5)$ at 298.15 K for {tetralin + *n*-heptane}: 488.4 $J.mol^{-1}$ reported by Letcher and Scoones(16) compares favourably with the value of 490.0 $J.mole^{-1}$ reported by Lundberg.(150)

The $H_m^E(x=0.5)$ for {tetralin + *n*-dodecane}: 570.3 $J.mol^{-1}$ of Letcher and Scoones(16) is larger than the corresponding value of 555.0 $J.mol^{-1}$ reported by Delmas and Purves.(164) A standard deviation of 6.9 $J.mol^{-1}$ is observed on comparison of the results of Letcher and Scoones(16) with the results interpolated from the equations of Grolier(163) for the system {tetralin + *n*-hexadecane}. The $H_m^E(x=0.5)$ for {tetralin + *n*-hexadecane} reported by Lundberg: 649.0 $J.mol^{-1}$,(150) by Delmas and Purves: 663.0 $J.mol^{-1}$ (164) and by Letcher and Scoones: 657.0 $J.mol^{-1}$ (16) are all similar. Delmas and Purves(164) have reported a value for $H_m^E(x=0.5)$ of 462.0 $J.mole^{-1}$ for the mixture {tetralin + *n*-octane}, which would appear to be incorrect if the basic trend of an increasing H_m^E with increasing *n*-alkane carbon chain length is observed.

Letcher and Scoones(16) obtained a standard deviation of 6.5 $J.mol^{-1}$ between their excess molar enthalpy results for {tetralin + cyclohexane} and the results quoted by Grolier.(163) Good agreement between the results of Letcher and Scoones: $H_m^E(x=0.5)$ = 488.8 $J.mol^{-1}$ (16) and Lundberg: $H_m^E(x=0.5)$ = 482.9 $J.mol^{-1}$ (150) is observed for this system. The large exothermic enthalpies for systems involving a cycloalkane or an *n*-alkane can be attributed to the endothermic dissociation of aromatic-aromatic interactions. Lundberg$^{(150)}$ has reported H_m^E for {tetralin + benzene}.

Letcher and Scoones have reported V_m^E for {tetralin + (*n*-pentane or *n*-hexane or *n*-heptane or *n*-octane or *n*-dodecane or *n*-hexadecane)}$^{(14)}$ and for {tetralin + (cyclopentane or cyclohexane or cycloheptane or cyclooctane)}$^{(15)}$ at 283.15 K and at 298.15 K, while Letcher$^{(19)}$ has reported data for the system {tetralin + cyclodecane}. The V_m^E results for mixtures involving *n*-pentane: $V_m^E(x=0.5)$ = -1.475 $cm^3.mol^{-1}$ increase with an increase in the chain length of the *n*-alkane, becoming positive for *n*-hexadecane mixtures: $V_m^E(x=0.5)$ = 0.146 $cm^3.mol^{-1}$.$^{(14)}$ The V_m^E results for {tetralin + cyclopentane}: $V_m^E(x=0.5)$ = -0.505 $cm^3.mol^{-1}$ are much lower than for all the other mixtures containing a cycloalkane.$^{(15)}$ This can once again be attributed to the more favourable packing configuration of cyclopentane. The V_m^E for all the other mixtures with a cycloalkane are positive and increase with an increase in the cycloalkane carbon number,$^{(15)}$ indicating the importance of molecular shape contribution to the excess molar volume. The results for *n*-pentane mixtures are also smaller than the results for the mixtures comprising longer chain *n*-alkanes. The same observations apply here.

Chylinski and Stykjek$^{(165)}$ have measured excess molar volumes for {tetralin + (*cis*-decalin or *trans*-decalin)}. The V_m^E results for systems involving *cis*-decalin are positive while negative V_m^E values are observed for {tetralin + *trans*-decalin}. This is probably due to the flat shape of the *trans*-decalin and the tetralin molecules, which facilitates packing of the molecules. Delmas and Purves$^{(164)}$ have measured H_m^E for tetralin mixed with branched alkanes, while Meares,$^{(166)}$ and Jackson and Morcom$^{(167)}$ have reported V_m^E results for tetralin mixed with ethylbenzene$^{(166)}$ and with hexalfluorobenzene$^{(167)}$ respectively. Excess molar volumes for {tetralin + tertiarybutylchloride} have been reported by Smith and Witten.$^{(168)}$

(iv) Cyclohexylbenzene mixtures

Letcher and co-workers have reported H_m^E and V_m^E for {cyclohexylbenzene + (*n*-pentane or *n*-hexane or *n*-heptane or *n*-octane or *n*-dodecane or *n*-hexadecane)}$^{(17)}$ and for {cyclohexylbenzene + (cyclopentane$^{(18)}$ or cyclohexane$^{(18)}$ or cycloheptane$^{(18)}$ or cyclooctane$^{(18)}$ or cyclodecane$^{(19)}$)} at 298.15 K. There is a remarkable resemblance between H_m^E values for mixtures involving cyclohexylbenzene with a cycloalkane or an *n*-alkane and the H_m^E curves for mixtures with tetralin. Once again the negative excess molar volume results for the cyclopentane mixture are much smaller than the V_m^E results for any of the other cycloalkane mixtures. The excess molar volumes, which are negative for *n*-pentane, are observed to increase with an increase in the *n*-alkane chain length, becoming positive for $n = 12$.

The H_m^E results for mixtures involving a bicyclic compound with an *n*-alkane or a cycloalkane bear a striking resemblance to the curves for similar mixtures involving benzene mixed with a cycloalkane or an *n*-alkane.(20-24,26,32,33) Similar observations can be made for the V_m^E results for the bicyclic mixtures and the results for related systems involving benzene.(24,33,40,41,48-50) The exothermic H_m^E results for the unsaturated bicyclic compounds with an *n*-alkane lie between those for benzene systems and for the systems involving a saturated bicyclic compound. Letcher(14) has assumed that the excess molar enthalpy is probably due to two types of contributions: *(i)* in the case of benzene or the unsaturated bicycic compound a $\pi ... \pi$ association between aromatic groups of the pure component which affords a contribution to the H_m^E, and *(ii)* weaker $CH_2 ... CH_2$ and $CH_2 ... \pi$ interactions between mixed species. The $\pi ... \pi$ interactions in pure benzene are reduced on mixing with an *n*-alkane because this molecule does not contain polarizable groups which may interact with the benzene molecule. The $\pi ... \pi$ interactions in the aromatic bicyclic compounds are probably weaker than those in benzene. This can be attributed to the presence of a non-aromatic moeity in the bicyclic compound which tends to dilute the aromatic moeity and would explain why the results for the aromatic bicyclic compounds lie between those for the benzene systems and the saturated bicyclic systems. A similar trend is displayed for mixtures of a bicyclic compound with a cycloalkane, where the H_m^E results are smaller than H_m^E results for mixtures involving benzene with a cycloalkane. The same observations as above apply here. Although in each case the H_m^E results for a bicyclic compound mixed with cyclopentane are much more negative than for cycloalkanes of higher carbon number, the results do not vary much with an increase in carbon number from 6 to 10.(14)

The V_m^E for a bicyclic compound with an *n*-alkane are all very much smaller and more negative than the corresponding values for related mixtures involving benzene with an *n*-alkane. Letcher *et al.*(17) have attributed this to the better packing of the rigid *n*-alkane molecules between the bicyclic molecules. The aromatic nature of the unsaturated bicyclic molecules was observed to have little affect on the overall V_m^E results.

The V_m^E results for a bicyclic compound mixed with a cycloalkane also appear to depend on the accommodation of differently shaped molecules in the mixture.(19) The anomalous values for cyclopentane and, to a smaller extent *n*-pentane, have already been associated with a packing effect.

2.4.2 Mixtures involving benzene

The excess molar enthalpies at various temperatures for {benzene + (*n*-pentane(20,33,81) or *n*-hexane(21,24,169,170) or *n*-heptane(24,150,171,172) or *n*-octane(20,33,169) or *n*-dodecane(20,33,169) or *n*-hexadecane(20,33,150,173,174))} are well represented in the literature. The H_m^E results are large and positive for {benzene + *n*-pentane} and increase with an increase in the *n*-alkane chain length. The $H_m^E(x=0.5)$ at 298.15 K for {benzene + *n*-hexane} reported by Romani and Paz-Andrade: 897.2 $J.mol^{-1}$ (21) compares favourably with a value of 900.0 $J.mol^{-1}$ reported recently by Hwang *et al.*(170) For the *n*-heptane system, a fair amount of agreement is observed for $H_m^E(x=0.5)$ in the results reported by Letcher and Bayles: 919.0 $J.mol^{-1}$,(24) Lundberg: 927.3 $J.mol^{-1}$(150) and Messow *et al.*: 894.5 $J.mol^{-1}$ (172) while the value of 999.0 $J.mol^{-1}$ reported by Munsch(171) appears to be in error. The H_m^E results for {benzene + (*n*-pentane or *n*-octane or *n*-dodecane or *n*-hexadecane) reported by Letcher and Perkins(33) are within the combined experimental error of these results and the values reported by Díaz Peña and Menduiña.(20) The $H_m^E(x=0.5)$ for {benzene + *n*-hexadecane} by Díaz Peña and Menduiña: 1255.8 $J.mol^{-1}$ (20) is larger than the value quoted by Lundberg: 1208.8 $J.mol^{-1}$ (150) and by Snow *et al.*: 1218.2 $J.mol^{-1}$.(174)

References to H_m^E measurements for {benzene + (cyclopentane(32,175) or cyclohexane(26,81,120,170,176,177) or cycloheptane(33,175) or cyclooctane(33,175))} appear in the literature. The results for these mixtures are all endothermic and increase with an increase in the number of carbons in the cycloalkane ring. Most of the $H_m^E(x=0.5)$ values for the system {benzene + cyclohexane} reported in the literature(26,81,102,177) agree to within 3 $J.mol^{-1}$ of each other. The $H_m^E(x=0.5)$ for {benzene + cycloheptane} reported by Letcher and Perkins(33) is of the order of 50 $J.mol^{-1}$ lower than the value reported by Watson *et al.*(175) The H_m^E results for {benzene + cyclooctane} of Letcher and Perkins(33) are all lower than the corresponding values by Watson *et al.*(175) and the discrepancies between equimolar values reported by the two groups is greater than 20 $J.mol^{-1}$.

Karbalai-Ghassemi *et al.*(22) and Letcher and Sack(26) have reported H_m^E for {benzene + (1-hexene(22,26) or 1-heptene(22))} while Wilhelm *et al.*(23) have measured H_m^E for {benzene + 1-hexyne}. The $H_m^E(x=0.5)$ for {benzene + 1-hexene}: 589.9 $J.mol^{-1}$ (22) is larger than the value of 539.3 $J.mol^{-1}$ reported by Letcher and Sack.(26) The $H_m^E(x=0.5)$ at

298.15 K reported by Letcher and Sack(26) for the system {benzene + cyclohexene}: 388.6 J.mol^{-1} is much larger than the result reported by Günzel and Bittrich: 316.6 J.mol^{-1} (29) for this system.

The excess molar volumes for the mixtures {benzene + (*n*-pentane(33,48,178,179) or *n*-hexane(40,179-182) or *n*-heptane(24,41,46,48) or *n*-octane(41,48,181,182) or *n*-dodecane(33,41,48,181-183) or *n*-hexadecane(33,41,48,181,182))} are well documented in the literature. The V_m^E results for benzene with an *n*-alkane are all positive and increase with an increase in the *n*-alkane chain length. The V_m^E results at 293.15 K by Letcher(48) for {benzene + *n*-pentane} are all within 0.004 cm^3.mol^{-1} of the smoothed curve generated by Mahl.(179) The $V_m^E(x=0.5)$ for this system at 298.15 K is 0.117 cm^3.mol^{-1}.(33) Excess molar volumes for {benzene + *n*-hexane} of Letcher *et al.*(40) and Rubio *et al.*(182) are lower than those reported by Nigam *et al.*(180) The $V_m^E(x=0.5)$ values by Letcher *et al.* (40) and Rubio *et al.* (182) are 0.397 cm^3.mol^{-1} and 0.395 cm^3.mol^{-1} respectively, while Nigam *et al.* (180) reported a value of 0.414 cm^3.mol^{-1}. The V_m^E results for {benzene + *n*-heptane} of Letcher and Bayles(24) are within the combined experimental error of those values reported by Harris and Dunlop(41) and those interpolated from the results reported by Letcher(48) at 308.15 K. The excess molar volumes at 323.15 K reported by Díaz Peña and Nũnez Delgado(181) for {benzene + (*n*-octane or *n*-dodecane)} agree within experimental error with the extrapolated values of Letcher.(48) However, a $V_m^E(x=0.5)$ of 0.919 cm^3.mol^{-1} at 298.15 K for the system {benzene + *n*-dodecane} reported by Letcher and Perkins(33) is lower than the corresponding value of 0.940 cm^3.mol^{-1} reported by Rubio *et al.*(182) The $V_m^E(x=0.5)$ values at 298.15 K reported by Letcher and Perkins(33) and by Rubio *et al.*(182) for the system {benzene + *n*-hexadecane} are 1.024 cm^3.mol^{-1} and 1.116 cm^3.mol^{-1} respectively.

A number of studies have been reported in the literature concerning the excess molar volumes for the systems {benzene + (cyclopentane(48,123,128,183,184) or cyclohexane(40,50,123,128,183,185) or cycloheptane(48,50,184) or cyclooctane(48,50,183,184) or cyclodecane(48))}. The excess molar volumes for these systems are all positive. The V_m^E results for {benzene + cyclopentane} are significantly smaller than the values for the cyclohexane system, and an increase in the number of carbons in the cycloalkane chain for cycloheptane and cyclooctane results in a small decrease in the excess molar volume.

The V_m^E results at 298.15 K for {benzene + cyclopentane} reported by Benson and Singh(184) are smaller than those reported by Stookey *et al.*(123) and, more recently, by Poveda Vilches *et al.*,(50) by Takenaka *et al.*(183) and by Letcher.(48) There is good agreement between the experimental results reported by the last four groups, with the $V_m^E(x=0.5)$ being 0.344 $cm^3.mol^{-1}$,(123) 0.343 $cm^3.mol^{-1}$,(50) 0.349 $cm^3.mol^{-1}$ (183) and 0.344 $cm^3.mol^{-1}$ (48) respectively. The $V_m^E(x=0.5)$ results for the system {benzene + cyclohexane} by Poveda Vilches *et al.*: 0.651 $cm^3.mol^{-1}$,(50) Letcher *et al.*: 0.653 $cm^3.mol^{-1}$ (40) and Stookey *et al.*: 0.643 $cm^3.mol^{-1}$ (123) are all in good agreement. Results by Benson and Singh: 0.635 $cm^3.mol^{-1}$ (184) and by Stokes *et al.*: 0.636 $cm^3.mol^{-1}$ (128) are slightly lower.

The V_m^E results of Benson and Singh(184) for the cycloheptane system are about 0.040 $cm^3.mol^{-1}$ larger than those reported by Poveda Vilches.(50) Fairly significant discrepancies exist between the V_m^E values reported by different workers for the system {benzene + cyclooctane}, with $V_m^E(x=0.5)$ values of 0.587 $cm^3.mol^{-1}$,(50) 0.570 $cm^3.mol^{-1}$ (184) and 0.608 $cm^3.mol^{-1}$ (183) being reported.

Letcher has reported V_m^E for {benzene + (1-hexene or cyclohexene)}(40) and for {benzene + (1,3-cyclohexadiene or 1,4-cyclohexadiene)}.(49) Harris and Dunlop(41) have reported V_m^E results for (benzene + cyclohexene} in a graphical form. Although this makes a direct comparison with the results of Letcher(40) rather difficult, the extrapolated value for $V_m^E(x=0.5)$ (about 0.245 $cm^3.mol^{-1}$) compares favourably with the value of 0.247 $cm^3.mol^{-1}$ reported by Letcher.(40) A comparison of V_m^E results for {benzene + (cyclohexane or *n*-hexane)} with {benzene + (cyclohexene or 1-hexene)} shows a decrease in V_m^E on introduction of a double bond into the unsaturated compound. Letcher(40) has attributed this to a combination of: *(i)* $\pi...\pi$ interactions between the benzene and the double bonds of the cyclohexene or 1-hexene, and *(ii)* the more rigid unsaturated compounds fitting into the benzene lattice more easily. The magnitude of the excess molar volumes for the systems {benzene + (cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene)} also increases with increasing association of the benzene molecule.

2.4.3 Mixtures involving cyclohexane

Numerous references appear in the literature concerning H_m^E results for {cyclohexane + (*n*-pentane(25) or *n*-hexane(25-28,102,177,186) or *n*-heptane(27,150) or *n*-octane(25,27,28) or *n*-dodecane(25,27,187) or *n*-hexadecane(4,27,28,150,174))} and {cyclohexane + (cyclopentane(32,34) or cycloheptane(35,152) or cyclooctane(36,86))}. The H_m^E results for mixtures involving cyclohexane are all positive and increase with an increase in the number of carbons in the *n*-alkane chain or in the cycloalkane.

The $H_m^E(x=0.5)$ values reported for {cyclohexane + n-hexane} by Lam *et al.*: 216.8 J.mol^{-1},(25) Tanaka *et al.*: 215.7 J.mol^{-1},(102) Aronosa *et al.*: 216.5 J.mol^{-1},(28) Yanes *et al.*: 216.1 J.mol^{-1},(177) Heintz and Lichtenthaler: 219.6 J.mol^{-1},(27) Costas and Patterson: 220.5 J.mol^{-1} (186) and Letcher and Sack: 219.6 J.mol^{-1} (26) all compare favourably with each other.

The $H_m^E(x=0.5)$ results of Heintz and Lichtenthaler: 245.7 J.mol^{-1} (27) and of Lundberg: 240.0 J.mol^{-1} (150) for the system {cyclohexane + n-heptane} are in good agreement with each other. This is also true of the $H_m^E(x=0.5)$ results for the system {cyclohexane + n-octane} reported by Arenosa *et al.*: 257.4 J.mol^{-1},(28) Heintz and Lichtenthaler: 261.6 J.mol^{-1} (27) and Lam *et al.*: 257.5 J.mol^{-1},(25) and for the system {cyclohexane + n-dodecane} where the $H_m^E(x=0.5)$ results are all within 4 J.mol^{-1} of each other. Equimolar excess molar enthalpies by Arenosa *et al.*: 501.5 J.mol^{-1},(28) by Heintz and Lichtenthaler: 502.1 J.mol^{-1} (27) and by Lundberg: 497.8 J.mol^{-1} (150) for the system {(cyclohexane + n-hexadecane} are slightly larger than the value of 493.5 J.mol^{-1} reported by Tancréde *et al.*(4) The $H_m^E(x=0.5)$ reported by Snow *et al.*(174) is 509.0 J.mol^{-1}.

The excess molar enthalpies for mixtures of a cyclohexane with a cycloalkane are positive but small. The $H_m^E(x=0.5)$ for the system {cyclohexane + cyclopentane}: 21.1 J.mol^{-1},(34) decreases to a value of 5.9 J.mol^{-1} for {cyclohexane + cycloheptane}(35) and to 0.8 J.mol^{-1} for {cyclohexane + cyclooctane}.(36) de St. Romain *et al.*(152) quote a value of 1.0 J.mol^{-1} for the cyclooctane system.

Large discrepancies between the reported excess molar enthalpies for {cyclohexane + cyclohexene} are observed. The $H_m^E(x=0.5)$ value of 115.5 J.mol^{-1} reported by Letcher and Sack(26) is larger than the results reported by both Woycicki: 92.0 J.mol^{-1} (188) and by Günzell and Bittrich: 54.5 J.mol^{-1}.(29) Wóycicki(188) has also measured excess molar enthalpies for {cyclohexane + (1,3-cyclohexadiene or 1,4-cyclohexadiene)}. Excess molar enthalpies for mixtures involving 1-hexene have been reported by Letcher and Sack(26) and mixtures involving 1-hexyne have been reported by Wilhelm *et al.*(23)

Excess molar volumes for the following systems {cyclohexane + (n-pentane(42,179,189) or n-hexane(40,43,46,189-193) or n-heptane(44,189,191,193) or n-octane(44,189-191) or n-dodecane(44,189-191) or n-hexadecane(44,189,190))} have been reported in the literature. Once again an increase in the chain length of the n-alkane is accompanied by an increase in the excess molar volume. Investigations have also indicated a decrease in V_m^E for an increase in the temperature.(44)

Letcher and Heyward$^{(42)}$ have reported a $V^E(x=0.5)$ value of -0.146 $cm^3.mol^{-1}$ for the pentane mixture, while more recently Awwad and Salman$^{(189)}$ quoted a value of -0.154 $cm^3.mol^{-1}$. Some discrepancies exist between the reported V_m^E values for mixtures involving *n*-hexane. Good agreement exists between V_m^E results reported by Bagley *et al.*$^{(46)}$ and by Gómez-Ibáñez and Lui$^{(43)}$ for the *n*-hexane system; the $V_m^E(x=0.5)$ values by both of these workers is 0.150 $cm^3.mol^{-1}$. The excess molar volumes reported by Awwad and Salman$^{(189)}$ are similar to these results. The $V_m^E(x=0.5)$ results reported by Saito and Tanaka: 0.128 $cm^3.mol^{-1}$,$^{(193)}$ by Ott *et al.*: 0.127 $cm^3.mol^{-1}$,$^{(192)}$ Goates *et al.*: 0.126 $cm^3.mol^{-1}$ $^{(191)}$ and by Sanches-Pajares and Nũnez Delgado: 0.119 $cm^3.mol^{-1}$ $^{(190)}$ are lower.

The $V_m^E(x=0.5)$ values reported by various workers for the *n*-heptane system vary from 0.295 $cm^3.mol^{-1}$ $^{(191,193)}$ and 0.310 $cm^3.mol^{-1}$ $^{(44)}$ to 0.325 $cm^3.mol^{-1}$.$^{(189)}$ The $V_m^E(x=0.5)$ results for the *n*-octane system all lie between 0.374 $cm^3.mol^{-1}$ $^{(190)}$ and 0.412 $cm^3.mol^{-1}$.$^{(44)}$ Good agreement exists between the V_m^E reported by Letcher and Spiteri$^{(44)}$ and by Awwad and Salman$^{(189)}$ for this system, with the largest difference between reported results by these two groups of workers being of the order of 0.004 $cm^3.mol^{-1}$.

The disagreement between reported results for the *n*-dodecane system is large. Goates *et al.*$^{(191)}$ have reported a $V_m^E(x=0.5)$ value of 0.495 $cm^3.mol^{-1}$ while more recent values reported by Awwad *et al.*: 0.568 $cm^3.mol^{-1}$ $^{(189)}$ and by Letcher and Spiteri: 0.535 $cm^3.mol^{-1}$ $^{(44)}$ are larger. For the *n*-hexadecane system, Awwad and Salman,$^{(189)}$ Letcher and Spiteri,$^{(44)}$ and Sanchez-Pajares and Nũnez Delgado$^{(190)}$ have reported $V_m^E(x=0.5)$ values of 0.644 $cm^3.mol^{-1}$, 0.632 $cm^3.mol^{-1}$, and 0.623 $cm^3.mol^{-1}$ respectively.

Ewing and Marsh have reported excess molar volumes for {cyclohexane + (cyclopentane$^{(36)}$ or cycloheptane$^{(35)}$ or cyclooctane$^{(36)}$)} at 298.15 K. The results are small and positive for the cyclopentane system and decrease with an increase in the size of the cycloalkane chain, becoming negative for the cycloheptane and the cyclooctane system. Letcher has reported V_m^E data for {cyclohexane + (1-hexene or cyclohexene)}$^{(40)}$ and for {cyclohexane + (1,3-cyclohexadiene or 1,4-cyclohexadiene)}.$^{(49)}$

2.4.4 Mixtures involving *n*-hexane

The $H_m^E(x=0.5)$ results for {*n*-hexane + (*n*-pentane$^{(29)}$ or *n*-heptane$^{(193-195)}$ or *n*-octane$^{(25)}$ or *n*-dodecane$^{(25,177,196,197)}$ or *n*-hexadecane$^{(4,25,198-200)}$)} are all positive. The $H_m^E(x=0.5)$ is small for the system involving *n*-pentane: 4.9 J.mol^{-1} (29) and increases with an increase in the *n*-alkane chain length. The corresponding value for the mixture with *n*-hexadecane is 113.3 J.mol^{-1}.(4)

The $H_m^E(x=0.5)$ by Lam *et al.*(25) for the system {*n*-hexane + *n*-dodecane} is 36.9 J.mol^{-1}. This is slightly smaller than the values reported for the same system by Ott *et al.*(196) and Haham *et al.*(197) The excess molar enthalpies at equimolar concentrations by these workers are 39.4 J.mol^{-1} and 39.1 J.mol^{-1} respectively. Good agreement is observed between the H_m^E results for {*n*-hexane + *n*-hexadecane}.

Excess molar enthalpies for the systems {*n*-hexane + (cyclopentane(37,186) or cyclohexane(26-28,112,177,186,188) or cycloheptane(38) or cyclooctane(39))} are larger than those for mixtures involving *n*-hexane with an *n*-alkane. The $H_m^E(x=0.5)$ for {*n*-hexane + cyclopentane} is 55.9 J.mol^{-1} (186) and increases dramatically up to 219.6 J.mol^{-1} (26) for {*n*-hexane + cyclohexane}. The results for {*n*-hexane + cycloheptane}: 209.4 J.mol^{-1} (38) and {*n*-hexane + cyclooctane}: 204.0 J.mol^{-1} (39) exhibit a small decrease in $H_m^E(x=0.5)$ for an increase in the number of carbons in the cycloalkane.

Letcher and Sack(26) and Wóycicki(201) have reported excess molar enthalpies for {*n*-hexane + 1-hexene} at 298.15 K. The $H_m^E(x=0.5)$ value of 53.0 J.mol^{-1} reported by Letcher and Sack(26) is smaller than the corresponding value of 61.3 J.mol^{-1} reported by Wóycicki.(201) Wóycicki and Rhensius(31) have also reported H_m^E values for {*n*-hexane + (1-hexyne or 1-heptyne)}. These values are large and positive and exhibit a small decrease for an increase in the carbon-chain length of the 1-alkyne. Large discrepancies exist between the measured H_m^E results at 298.15 K by Letcher and Sack(26) and by Günzel and Bittrich(29) for the system (*n*-hexane + cyclohexene}. The values at equimolar concentrations reported by these workers are 245.1 J.mol^{-1} and 164.3 J.mol^{-1} respectively.

Excess molar volumes for the mixtures {*n*-hexane + (*n*-pentane(45) or *n*-heptane(202,203) or *n*-octane(46,102,202) or *n*-dodecane(47,196) or *n*-hexadecane(47,204))} are all negative. The general trend shows a decrease in the excess molar volume for systems involving *n*-alkane chains with $n=8$, 12, and 16, indicating a better packing of the smaller *n*-hexane molecule between the larger *n*-alkane molecules.

The V_m^E results for {*n*-hexane + *n*-heptane} by Goates *et al.*(202) compares favourably with those values reported by Kumaran and Benson.(203) $V_m^E(x=0.5)$ values for these workers are -0.085 $cm^3.mol^{-1}$ and -0.086 $cm^3.mol^{-1}$ respectively. Good agreement is observed between the $V_m^E(x=0.5)$ values reported by Bagley *et al.*: -0.080 $cm^3.mol^{-1}$ (46) and Goates *et al.*: -0.085 $cm^3.mol^{-1}$ (202) for {*n*-hexane + *n*-octane}. The results reported by Gómez-Ibáñez and Liu(47) and those of Haham *et al.*(129) for the *n*-dodecane system are difficult to compare, because Gómez-Ibáñez and Liu (47) have represented their results in a graphical form. Haham *et al.*(197) report a $V_m^E(x=0.5)$ of -0.357 $cm^3.mol^{-1}$ for this system. The V_m^E by Gómez-Ibáñez and Liu(47) for the *n*-hexadecane system are much smaller than those values reported by Blinowska and Brostow.(204)

Letcher and Heyward(42) have reported V_m^E data for {*n*-hexane + cyclopentane} at two different temperatures. The $V_m^E(x=0.5)$ at 298.15 K for this system is -0.068 $cm^3.mol^{-1}$. The $V_m^E(x=0.5)$ values for {*n*-hexane + cyclohexane} reported by Letcher(40) and by Gómez-Ibáñez and Liu(43) are 0.143 $cm^3.mol^{-1}$ and 0.149 $cm^3.mol^{-1}$ respectively. Martin and Symons(51) have reported V_m^E results for {*n*-hexane + (cycloheptane or cyclooctane)}. The $V_m^E(x=0.5)$ for the cycloheptane system: -0.468 $cm^3.mol^{-1}$ is smaller than the value reported by Spiteri and Letcher: -0.494 $cm^3.mol^{-1}$.(39)

Letcher has reported excess molar volumes for {*n*-hexane + (1-hexene or cyclohexene)}(40) and for {*n*-hexane + (1,3-cyclohexadiene or 1,4-cyclohexadiene)}.(49)

2.5 Apparatus and experimental procedure

2.5.1 Excess molar enthalpies

A commercial LKB 2107-101 flow microcalorimeter was employed in this investigation for the determination of excess molar enthalpies for binary liquid mixtures.

(i) Instrument description and principle of operation

The mixing vessel arrangement for the LKB microcalorimeter is shown diagrammatically in Figure 2.8. The mixing vessel, A, has two separate inlets and comprises a bifilar spiral wound 24 carat gold tube of 1 mm i.d. and with a volume of 0.5 cm^3. The design is such that adequate mixing is achieved with no vapour space. The mixing vessel is in thermal contact with a pair of matched thermocouples in the thermopiles, B, and an aluminium heat-sink assembly, C, with heat sink compound covering all the surfaces of these items. An exothermic reaction results in an heat flow to the heat-sink assembly, while the opposite effect is observed for endothermic reactions. In each case the

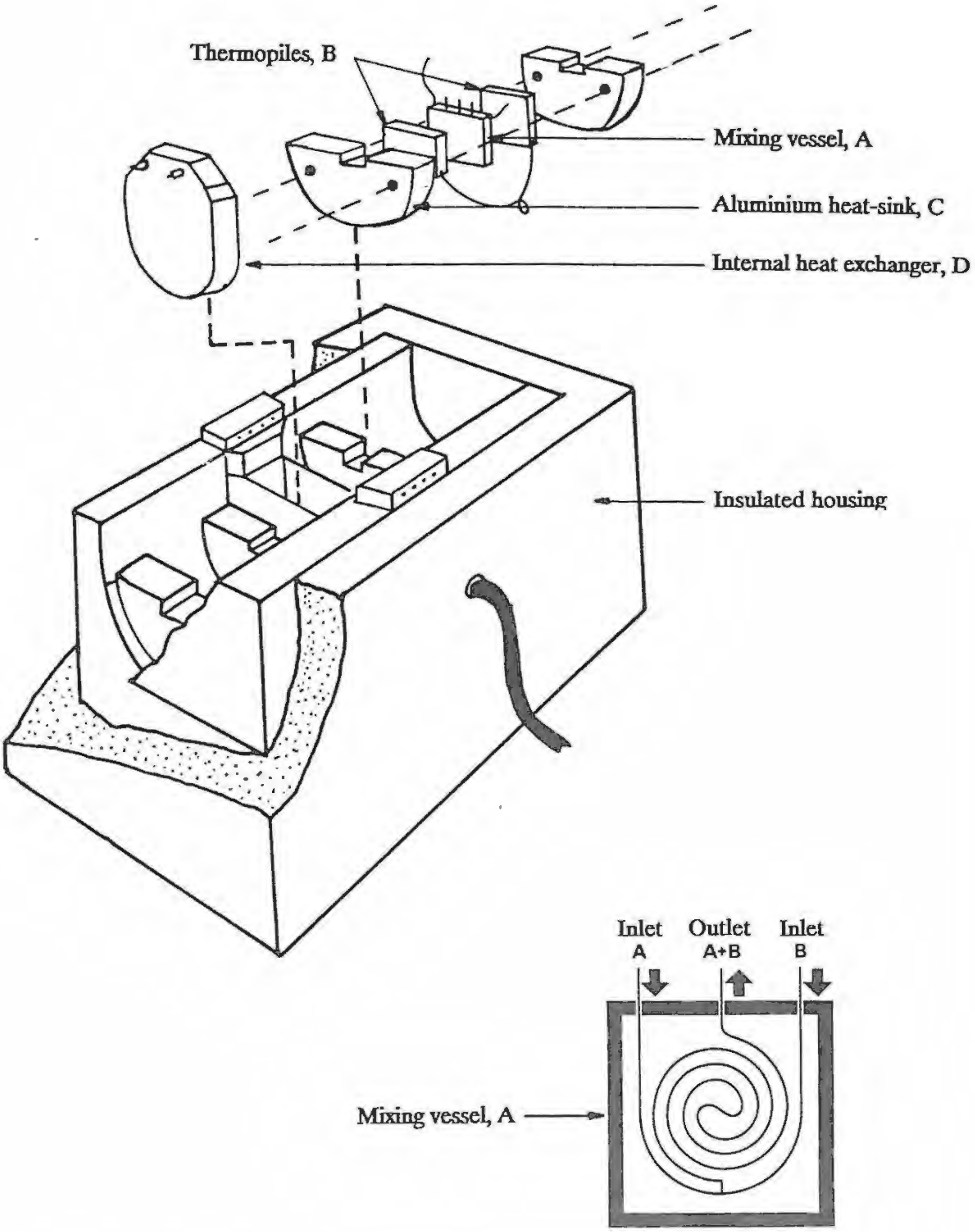

Figure 2.8 A diagrammatic representation of the LKB flow microcalorimeter mixing cell arrangement

resultant temperature difference is detected by the thermopile positioned between the vessel and the heat-sink. The output from the thermopiles is amplified and fed to a digital readout system and a Perkin-Elmer 561 chart-recorder.

The aluminium block heat-sink assembly is contained within an insulated housing. A heater and a temperature sensor are mounted within the main heat-sink. The entire arrangement is contained within an LKB thermostat which comprises a thermostatically controlled air bath. To maintain the temperatures required for this investigation an antifreeze - water mixture, cooled to 278 K by a Grants refrigeration coil, at 278 K was pumped through the thermostat at a rate of 500 $cm^3.min^{-1}$.

The LKB arrangement was used in conjunction with an LKB control unit. This incorporates a power supply capable of providing an adjustable current to the calibration heaters contained within the insulated mixing vessel assembly, and a facility for heating and monitoring the temperature of the calorimeter heat-sink assembly. This heating facility helps to reduce the equilibration time of the apparatus during "start-up" or when raising the operating temperature and was always switched off when measurements with the instrument were made.

Since liquids entering the microcalorimeter are required to be within 0.05 K of the experimental temperature, they were first routed through an external heat exchanger fitted into a recess in the bottom of the air bath of the thermostat unit and then through the internal heat exchanges, D, situated inside the insulated housing containing the mixing vessel assembly. Samples were introduced using two LKB 2102 Varioperpex II peristaltic pumps, capable of stable flow rates ranging from 0.03 - 2.0 $cm^3.min^{-1}$. Viton tubing, 1.5 mm *i.d.*, and Teflon tubing, 1.2 mm *i.d.*, were used in the pumps and flow lines respectively. Both types of tubing were unaffected by the liquids used in this work. The temperature inside the calorimeter was monitored by a Hewlett Packard 2804A quartz thermometer and was found to be constant to within 0.01 K.

(ii) Excess molar enthalpy measurements

An initial equilibration time of at least two days was required before start-up. Power to the equipment was left on continuously for the duration of the experimental determinations to ensure that the units concerned with temperature control would remain at thermal equilibrium. The flow lines were filled with water overnight and absolute alcohol was pumped through each flow line at a rate of 5 $cm^3.min^{-1}$ for 15 minutes before the introduction of new liquids. The two inlets were then flushed and primed separately with the two degassed components.

The calibration procedure discussed in the LKB instruction manual involves pumping a mixture similar to the one under investigation through the reaction vessel at a speed similar to that for the actual experimental determinations, thus producing a new base-line deflection on the chart recorder. The main experiment is thus conducted with respect to this new baseline. This procedure takes into account the heating effects due to friction resulting from the pumping of the liquids. The process is however time consuming and leads to a considerable wastage of chemicals. For this reason a method similar to the one described by Spiteri(82) was employed.

A typical recorder output as a function of time, for a steady state H_m^E experimental measurement is shown in Figure 2.9. Section A represents the steady state baseline obtained without any liquid flowing through the mixing vessel. This was always recorded before commencing a set of experimental measurements. Since accurate time elapse values were required for the determination of sample flow rates, the commencement of pumping at the desired flow rates was accompanied by the simultaneous activation of an electronic stopwatch. Pumping of the samples was continued until a new steady state was reached, depicted by the baseline deflection, B, in Figure 2.9. Thereafter a calibration current to the calibration heater was applied in order to nullify this deflection in the case of an endothermic reaction, restoring the original baseline. In the case of an exothermic reaction, enough current was applied to reproduce this baseline deflection, B. In practice, noise and non-uniform flow rates resulting from the peristaltic pumps operating at low speeds produced regular baseline deflections on the recorder. The current was thus always adjusted to a point where the spread about the mean value on the deflected baseline was reproduced about the zero-flow baseline.

Once the original baseline had been established the pumps were switched off. The molar flow rates, f_1 and f_2, were determined by weighing the two component reservoirs before and after each calorimetric run. Expressing these mass quantities in terms of the number of moles of each component used and dividing by the overall time elapse for the experimental run gave the molar flow rates. A Sauter AR 100 electronic balance, accurate to 0.1 mg, was used for all the mass determinations. The component reservoirs consisted of 25 cm^3 Quickfit conical flasks fitted with modified B14 stoppers. These stoppers had two 1.8 mm *i.d.* inlets, one connected by Teflon tubing to the pump, and the other open

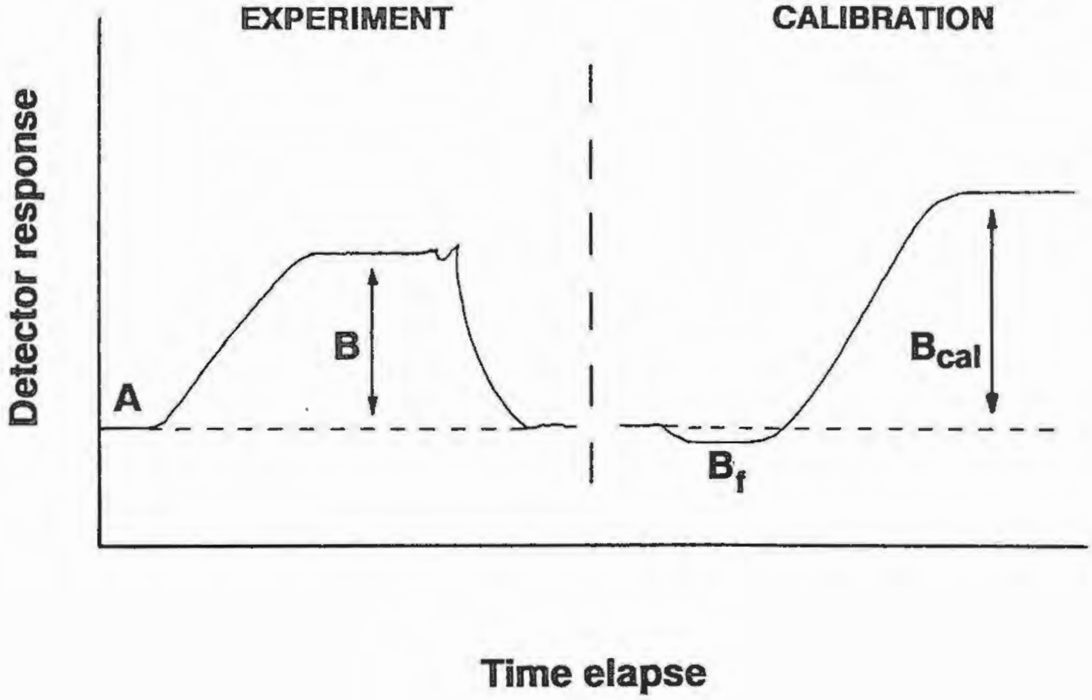

Figure 2.9 A chart recording for a flow calorimeter experiment

the atmosphere, thereby reducing solvent losses through evaporation. The masses of effluent collected after each run were compared to the amounts of pure component consumed, thus serving as a constant check against leaks in the system. The pumping rate was then adjusted and a new experimental run was started

(iii) Friction effects and flow rate determinations:

The values of the baseline deflections, B, and the corresponding currents, I, required to nullify these deflections were plotted for each system. In each case the resulting graph together with the mixture from each run were employed to adjust the experimental readings for frictional effects. These calibrations were carried out collectively at the end of a series of experimental runs for a system. Each calibration involved purging the mixing vessel with the effluent from a particular run. With the same pumping parameters as were employed for that particular run, any heating effect due to friction exhibited a deflection, B_f, in Figure 2.9. The experimental detector voltage shift was thus corrected to:

$$B_o = B - B_f \qquad 2.15$$

The indicated calibration current, I_{cal}, corresponding to B_o, was then interpolated from the experimentally determined graph and was passed through the calorimeter heater, thereby producing a baseline deflection corresponding to B_{cal} in Figure 2.9. The excess enthalpy was thus calculated from:

$$H_m^E = [\{B_o(I_{cal})^2R\}/B_{cal}]/(f_1 + f_2) \qquad 2.16$$

where R is the resistance of the calorimeter heater. It was, however, observed that $B \cong B_{cal}$ for flow rates less than 0.70 $cm^3.min^{-1}$. Since the majority of the experimental runs were carried out at flow rates less than this, the above calibration procedure became unnecessary in many cases and H_m^E was then determined by:

$$H_m^E = (I^2R)/(f_1 + f_2) \qquad 2.17$$

Three of the reactions in this investigation were exothermic. For these reactions, the steady state deflection, B, was noted and a current, I, was applied to double this deflection. Heating due to frictional effects would once again produce a deflection, B_f, and hence equation 2.15 becomes:

$$B_o = B + B_f \qquad 2.18$$

(iv) Test systems

McGlashan and Stoekli(97) have summarized excess molar enthalpy results for {cyclohexane + *n*-hexane} measured in five different laboratories,(83,88,97,98,205) with the objective of establishing a reference system for calorimetry. The IUPAC Commission on Thermodynamics has subsequently recommended this system as a standard test system(70*a*) and has suggested that excess molar enthalpies should be calculated according to the

McGlashan and Stoekli equation:(97)

$$H^E_m/(\mathrm{J.mol^{-1}}) = x_1(1 - x_1)\{866.1 - 249.4(1 - 2x_1) + 97.0(1 - 2x_1)^2 - 31.8(1 - 2x_1)^3] \qquad 2.19$$

where x_1 is the mole fraction of cyclohexane. McGlashan and Stoekli(97) obtained their results using an isothermal calorimeter and quoted a standard deviation of 1.1 $\mathrm{J.mol^{-1}}$.

The H^E_m results for the {cyclohexane + *n*-hexane} system determined in this investigation have been fitted to the Redlich and Kister polynomial equation:

$$H^E_m/(\mathrm{J.mol^{-1}}) = x_1(1 - x_1)[871.3 - 219.8(1 - 2x_1) + 77.0(1 - 2x_1)^2 - 89.9(1 - 2x_1)^3] \qquad 2.20$$

The standard deviation between experimental and smoothed results is 1.4 $\mathrm{J.mol^{-1}}$. The results are slightly higher than those values interpolated from equation 2.20, the standard deviation between these results and those interpolated from the IUPAC equation is 1.6 $\mathrm{J.mol^{-1}}$. The experimental results are however better than those results reported by Harsted and Thomsen(206) who also employed an LKB flow microcalorimeter.

2.5.2 Excess molar volumes

In this work, excess molar volumes were determined by indirect methods using a commercially available Anton Paar DMA 601 vibrating tube densitometer.

(i) Instrument description and principle of operation

The laboratory arrangement of the excess volume apparatus is shown diagrammatically in Figure 2.10. The measuring cell is contained within its own separate housing and consists of a hollow U-shaped borosilicate glass tube fused into a dual wall glass cylinder which serves as a water jacket. The volume of the cell is 0.7 $\mathrm{cm^3}$. The space between the U-tube and the cell is filled with a gas of high thermal conductivity, thus facilitating rapid equilibrium between the sample and the thermostat liquid flowing through the water jacket.

The determination of densities by this method is based on the measurement of the period of oscillation of the undamped vibrating sample tube of volume, v, which in this

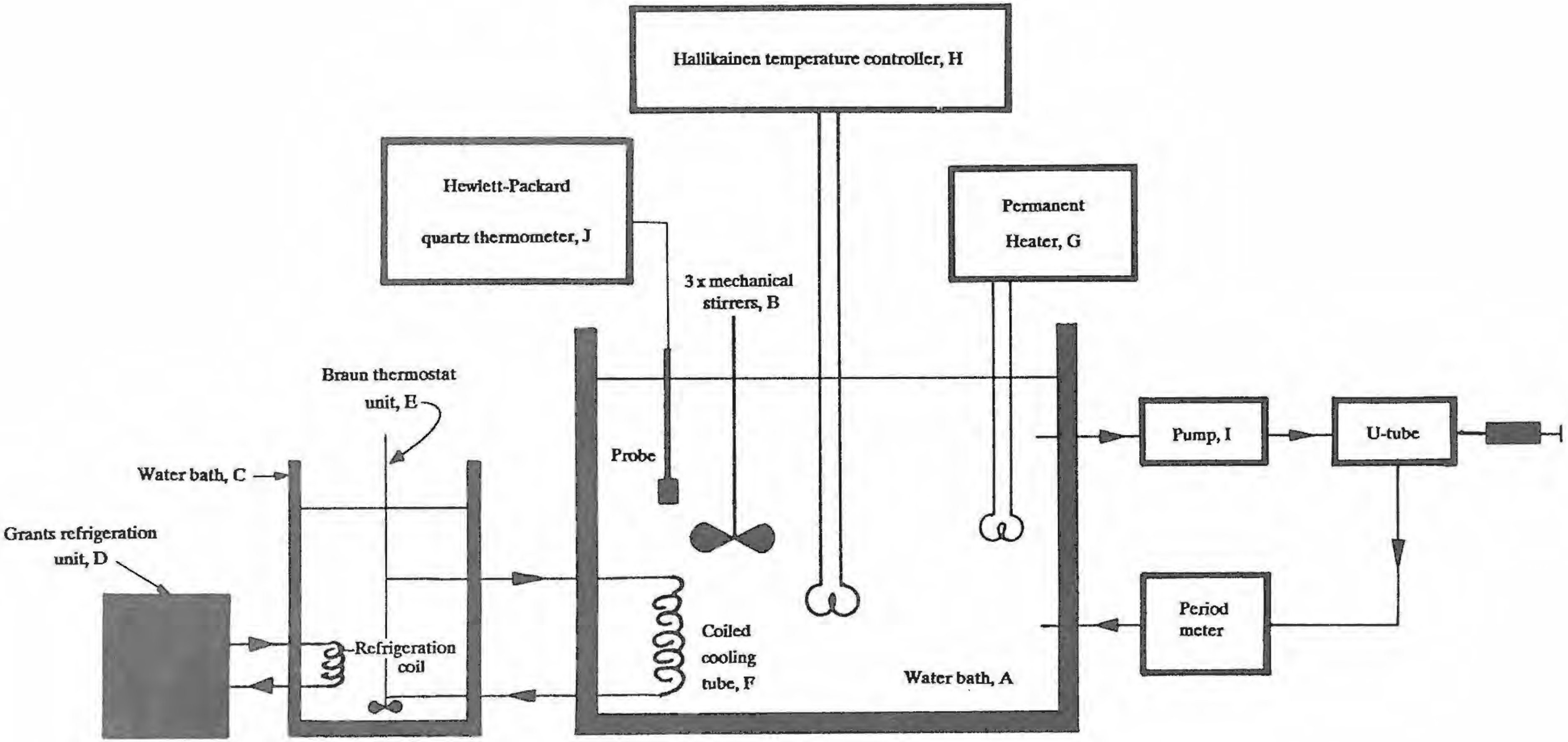

Figure 2.10 Laboratory arrangement of the Anton Paar DMA 601 vibrating tube densitometer

case is filled with sample liquid. In this way, the natural frequency of vibration of the cell is influenced by the mass and hence the density of the sample. For the purposes of a mathematical derivation, the system is analogous to a hollow body of mass, M, which is suspended by a spring with a constant of elasticity, C. The volume of the hollow body is assumed to be filled with a sample of density, ρ. The natural vibrational frequency of such a system is then given by:

$$\nu = [(1/2\pi)[C/M + \rho v]^{(1/2)} \qquad 2.21$$

In this instrument two remote cells generate square wave signals in synchronism with the zero amplitude positions of the oscillating sample tube. These signals are separated by an optical isolator and are filtered from any resulting noise. The signal from any one of these sources, depending on the operators choice, is then fed into a period meter. Time based pulses every 10^{-5} seconds permit the determination of the time lapse of a preselected number of oscillator periods and hence allow the determination of the period of vibration, T. The resulting period is related to the density of the sample through:(139)

$$\rho = a(T)^2 + b \qquad 2.22$$

where a and b are instrument constants and are determined by calibration measurements with pure substances of accurately known density.

(ii) Temperature control and measurement

The accuracy of the density measurements depends to a large extent on the constant control of the temperature. A temperature stability of 0.01 K yields an uncertainty in the density of the order of 10^{-5}g.cm^{-3}.(115) For this reason, temperature was controlled to ±2 mK in this work. Water was employed as the thermostat liquid.

A diagrammatic representation of the temperature control system is included in Figure 2.10. The primary cooling system consisted of a rectangular copper bath, A, of dimensions 1000 x 500 x 500 mm. The bath had a glass front and was built around a steel cradle, thus making it easier to clamp or suspend stirrers and probes within the bath. The bath was insulated with 50 mm thick sheets of expanded polystyrene. A layer of polystyrene chips covered the water surface, reducing temperature fluctuations through evaporation. The apparatus was housed on a 40 mm thick vibration free wooden laboratory bench in a constant temperature room. An ambient temperature of 296 K constant to ±0.5 K was maintained.

A uniform temperature throughout the bath was achieved through the use of three variable speed mechanical stirrers, B. An auxillary cooling system, C, comprising a 50 L water bath cooled by a Grants refrigeration coil, D, was incorporated to assist with the temperature control of the main water bath. Water from this auxiliary bath was pumped via a Braun immersion thermostat unit, E, at a rate of 2.8 $L.min.^{-1}$ through a coiled 4 metre copper tube, F, (12 mm i.d.) placed inside the primary cooling bath. Since the auxiliary bath was maintained at a temperature of approximately 1 K below the operating temperature, this arrangement served to cool the main water bath.

The thermostat system within the main water bath comprised of a permanent rheostated immersion heater, G, delivering up to 4W, and a 100W light bulb connected to a Hallikainen temperature controller, H. Water from the primary water bath was pumped through the water jacket by a centrifugal pump, I, at a rate of 1.8 $L.min.^{-1}$. Air blown through holes drilled in the sides of the pump casing aided in cooling. All rubber tubing to and from the densitometer was insulated to reduce heat losses. A Hewlett-Packard 2801 A quartz thermometer, J, calibrated as discussed in Appendix E, was employed to monitor the temperature within the main bath.

(iii) Instrument loading and V_m^E *measurements*

A warm-up time for the apparatus, including temperature equilibration, of at least 30 minutes was necessary before commencing experimental determinations. Before each run, the cell was flushed thoroughly with absolute alcohol and then acetone. For mixtures containing tetralin, chloroform was used instead of alcohol. After flushing, compressed air was blown through the cell. A constant period value for the empty cell indicated that the cell had been thoroughly dried.

Mixtures of approximately 2.5 cm^3 and covering the entire composition range were prepared just prior to use in specially designed 5 cm^3 flat bottom flasks with quickfit stoppers. Mixture compositions were determined by mass using a Sauter balance which was capable of measurements to within 0.1 mg. Thorough mixing of the two components was achieved by swirling the stoppered flasks. The injection syringe was equipped with a machined teflon nozzle, ensuring a leak-proof fit at the sample cell - syringe junction. The sample injection process was carried out slowly, enabling the liquid to properly wet the walls of the sample cell. A concave sample meniscus was maintained throughout the sample injection procedure, thus reducing the possibility of trapping air bubbles on the wall of the sample tube. The sample cell was always filled to beyond its nodal points and the syringe was left in place during the period determination cycle. The other opening of the cell was sealed with a teflon plug to reduce possible losses through evaporation.

With the cell illumination light off, the photoelectric portion of the excitation system was automatically activated. Each measuring cycle was allowed to continue until a constant period value was obtained. Period values for water and benzene standards and for the two pure components were determined between each mixture injection. These values were not only required in the calculations, but also permitted a running check on both the samples and the densitometer operation. A reproducibility of ±10 units in the 6th decimal place of the period value was easily achieved for any of the standards over the duration of a set of 20 to 25 measurements, which took between two and three hours. Any deviation was probably due to slight temperature changes in the bath and to the pumps. The pure liquids were degassed by boiling, with preliminary density and purity checks ensuring that azeotropes were not formed during the degassing procedure.

(iv) Excess molar volume calculations

The measurement of the period values, T_1 and T_2, for the two standards, water (1) and benzene (2), permitted the determination of the instrument constant, K:

$$\rho_1 - \rho_2 = K[(T_1)^2 - (T_2)^2] \qquad 2.23$$

The benzene standard had a purity of better than 99.3%. The densities of the two standards were obtained from the literature.(207*a*,207*b*)

According to the LKB operating manual, the instrument constants are usually determined at the beginning of an experimental run. However in this work, instrument constants were determined before the density determination for each mixture. This recalibration had the advantage of accounting for any temperature fluctuations.

The density of the mixture, $\rho_{mixture}$, at a composition, x_i, and the excess molar volume at that composition are given by the simple relations:

$$\rho_{mixture} = \rho_1 + K[(T_{mixture})^2 - (T_1)^2] \qquad 2.24$$

and $$V_m^E = [(x_A m_A + x_B m_B)/\rho_{mixture}] - [(x_A m_A)/\rho_A] - [(x_B m_B)/\rho_B] \qquad 2.25$$

where m_A and m_B are the molar masses of components A and B of the mixture. A computer programme using the above equations was written to determine the excess volume quantities. Details of the programme are given in Appendix F.

(v) Test systems

Following the suggestion of Powell and Swinton,(122) the system {cyclohexane + benzene} at 298.15 K was adopted as a test system for checking the performance of the technique used in this work. Handa and Benson(116) have reported results from selected sets of data obtained by various experimental methods for this system, and have fitted these results over the entire composition range to the Redlich-Kister smoothing equation:

$$V_m^E/(\text{cm.mol}^{-1}) = x_1(1-x_1)[2.60725 - 0.09271(1-2x_1) + 0.04476(1-2x_1)^2] \qquad 2.26$$

where x_1 is the mole fraction of cyclohexane. They also carried out a least squares analysis of the different results, thus facilitating a comparative investigation of the methods employed in these determinations. The two sets of measurements in closest agreement with one another were those obtained by Stokes *et al.*(128) and by Kumuran and McGlashan,(131) using dilution dilatometers. The results agree to better than 0.1% over most of the composition range, with standard deviations of 0.0008 $\text{cm}^3.\text{mol}^{-1}$ and 0.0007 $\text{cm}^3.\text{mol}^{-1}$ respectively.

Cibulka and Holub(208) have undertaken a similar detailed survey of the data on the excess molar volumes for the {cyclohexane + benzene} system. They have included some unpublished data in their work. In an attempt to obtain a "mean" V_m^E curve, they have published the following smoothing equation for V_m^E values at 298.15 K:

$$\begin{aligned} V_m^E/(\text{cm}^3.\text{mol}^{-1}) = x_1(1-x_1)[&2.60357 + 0.07521(1-2x_1) \\ &+ 0.06252(1-2x_1)^2 + 0.03249(1-2x_1)^3] \end{aligned} \qquad 2.27$$

where x_1 is the mole fraction of cyclohexane. The above equation yields practically identical values of excess volume to those yielded by the equation of Handa and Benson.(116) A more detailed critical evaluation has been carried out by Smith *et al.*(209) who formulated an equation based on smoothed values at x=0.25, 0.50 and 0.75 mole fractions. They have recommended the results of Kumaran and McGlashan(131) as most closely representing the true behaviour of the system at 298.15 K.

The excess molar volumes for the system {cyclohexane + benzene} determined here have been fitted to the Redlich-Kister smoothing equation:

$$\begin{aligned} V_m^E/(\text{cm}^3.\text{mol}^{-1}) = x_1(1-x_1)[&2.5909 + 0.0326(1-2x_1) \\ &+ 0.0536(1-2x_1)^2 + 0.0104(1-2x_1)^3] \end{aligned} \qquad 2.28$$

where x_1 is the mole fraction of cyclohexane. The standard deviation for these results is 0.0009 $cm^3.mol^{-1}$. The experimental results for this system are slightly lower than the results interpolated from the equation of Cibulka and Holub.(208) The standard deviation between their interpolated results and the experimental results determined here is 0.004 $cm^3.mol^{-1}$. The experimental results show good agreement with other literature values.(40,50,128,183,185)

2.5.3 Materials

The suppliers of the hydrocarbons used in this study are given in Table 2.1, which includes a summary of the g.l.c. analyses of all the compounds. The analyses were carried out with a Perkin Elmer GC-900 gas-liquid chromatograph using a 10% carbowax 20M column on a Chromosorb Q support. This instrument was later replaced by a Hewlett-Packard 5890A gas chromatograph and 3393A integrator using a 25 m carbowax 20M capillary column. Purification procedures were carried out when necessary.(210)

Decalin was supplied by Merck and was found by g.l.c. analysis to comprise a mixture of 55 mole% *cis*-isomer and 45 mole% *trans*-isomer with a purity of 98.9 moles%. Tetralin (BDH) and bicyclohexyl (EGA) were used without further purification. Cyclohexylbenzene (Fluka AG) was purified by low-pressure fractional distillation to a purity of 98.3 mole%.

The 1-hexene was obtained from Fluka AG (98 mole%) and the 1-heptene from Aldrich (97 mole%). Purification of these two chemicals involved refluxing over sodium wire followed by fractional distillation over a well lagged 75 mm column packed with porcelain saddles, collecting only the middle fraction. The 1-heptyne (Aldrich) was quoted as having a purity of better than 99 mole%. However, g.l.c. analysis indicated a purity of 97.7 mole%. The material was therefore distilled from $NaBH_4$ to remove any peroxides, left to stand with sodium for 24 hours and then fractionally distilled under reduced pressure. The resulting purity was 99.2 mole%.

The 1-hexyne and cyclohexene were supplied by Aldrich. Their purities were in excess of 99 mole% and consequently they were used without further purification. Cyclohexene was stabilized with 2,6-di-*tert*-butyl-4-methylphenol (0.01%).

Analar grade benzene was supplied by BDH. The purity was found to be better than 99.3 mole% and hence further purification was unnecessary. The chemical was stored over sodium.

The *n*-hexane and cyclohexane were supplied by Aldrich (Gold label). The cyclohexane, with a purity of better than 99 mole%, was used without further purification while *n*-hexane was fractionally distilled over sodium. The resulting purity was in excess of 99 mole%. The *n*-pentane (Riedel de Haën: 99.3 mole%) and *n*-octane (BDH: 99.7 mole%) were used without further purification.

The 1,3-cyclohexadiene and the 1,4-cyclohexadiene were both stabilized with 2,6-di-*tert*-butyl-4-methylphenol (0.2%) and were purified by distillation over $NaBH_4$. The distilled samples were stored in brown bottles to limit exposure to sunlight and were used within 3 hours of distillation. The measured densities at 298.15 K for 1,3-cyclohexadiene and 1,4-cyclohexadiene were 0.8402 $g.cm^{-3}$ and 0.8510 $g.cm^{-3}$ respectively. The density of 0.8353 $g.cm^{-3}$ for 1,3-cyclohexadiene reported by Wóycicki(188) was very different. The sample was distilled by spinning band distillation and the resultant measured density confirmed the value of 0.8402 $g.cm^{-3}$ for our sample. Analysis by g.l.c showed that impurities in the two cycloalkadienes were no greater than 0.8 mole%.

The *n*-heptane was supplied by Merck and had a purity of only 96.9 mole%. It was purified by washing with small portions of conc. H_2SO_4 until the acid layer remained colourless. The *n*-heptane was then washed with aqueous 10% Na_2CO_3, water, and subsequently dried with $CaCO_3$ and fractionally distilled over sodium. The resultant purity was better than 98.5 mole%.

The high prices of some of these materials (bicyclohexyl, cyclohexylbenzene, 1,3-cyclohexylbenzene, 1-hexyne, 1-heptene and 1-heptyne) necessitated that mixtures involving these chemicals be separated for reuse. The components of the mixture were separated by distillation and the separated chemicals were purified by the above methods. In addition, bicyclohexyl was washed repeatedly with aqueous $KMnO_4$, then with conc. H_2SO_4, followed with water. The purified product was dried with $CaCl_2$ and with sodium, and finally fractionally distilled. The 1-hexyne was purified as for 1-heptyne. In each of the above cases, the purities of the materials was always better than 98.7 mole%. The results for H_m^E and V_m^E determined with these "recycled" chemicals were comparable to results previously obtained with the new chemicals.

Table 2.1 Sources and purities of organic chemicals

Compound	Commercial make	Purities (mole%)
n-pentane	Riedel de Haën	99.3
n-hexane	Aldrich-Gold label	99.4
1-hexene	Fluka AG	98.9
1-hexyne	Aldrich	99.3
n-heptane	Merck	98.7
1-heptene	Aldrich	98.4
1-heptyne	Aldrich	99.2
n-octane	BDH	99.7
cyclohexane	Aldrich-Gold label	99.3
cyclohexene	Aldrich	99.3
1,3-cyclohexadiene	Fluka AG	99.5
1,4-cyclohexadiene	Fluka AG	99.3
benzene	BDH analar grade	99.3
decalin	Merck	98.9
bicyclohexyl	EGA Chemie	99.1
tetralin	BDH	98.7
cyclohexylbenzene	Fluka AG	98.3

CHAPTER 3

ACTIVITY COEFFICIENTS AT INFINITE DILUTION FROM GAS-LIQUID CHROMATOGRAPHY

3.1 The activity coefficient at infinite dilution

Solution properties are usually described in terms of their deviations from ideality.(1) Ideal solutions obey Raoult's Law and can be defined in terms of the chemical potentials, μ_i, of the components, i, as follows:

$$\mu_i(\text{ideal}) = \mu_i^* + RT\ln(p_i/p_i^*) \qquad 3.1$$

where μ_i^* is the chemical potential of the pure component, i. By Raoult's Law, the partial pressure of component i, p_i, and the vapour pressure of the pure component, p_i^*, are linearly related over the entire composition range:(211)

$$p_i = x_i p_i^* \qquad 3.2$$

where x_i is the mole fraction of component i. Behaviour of this kind is depicted diagrammatically in Figure 3.1, which shows typical vapour pressure curves for a liquid mixture comprising two components, 1 and 2. The broken lines AC and JK represent the partial pressures of components 1 and 2, respectively. In this case the negative deviations from Raoult's Law observed for real solutions are depicted by the solid curves AC and JK. These components are however observed to obey Raoults law in the pure region.

The curves AC and JK have finite slopes in the infinite dilution region. The vapour pressures obey Henry's Law in this region:(211)

$$p_i \longrightarrow K_i x_i \quad \text{as} \quad x_i \longrightarrow 0 \qquad 3.3$$

where K_i is the Henry's Law constant and is independent of the composition. In the dilute region:

$$(\delta p_i/\delta x_i) \longrightarrow K_i \quad \text{as} \quad x_i \longrightarrow 0 \qquad 3.4$$

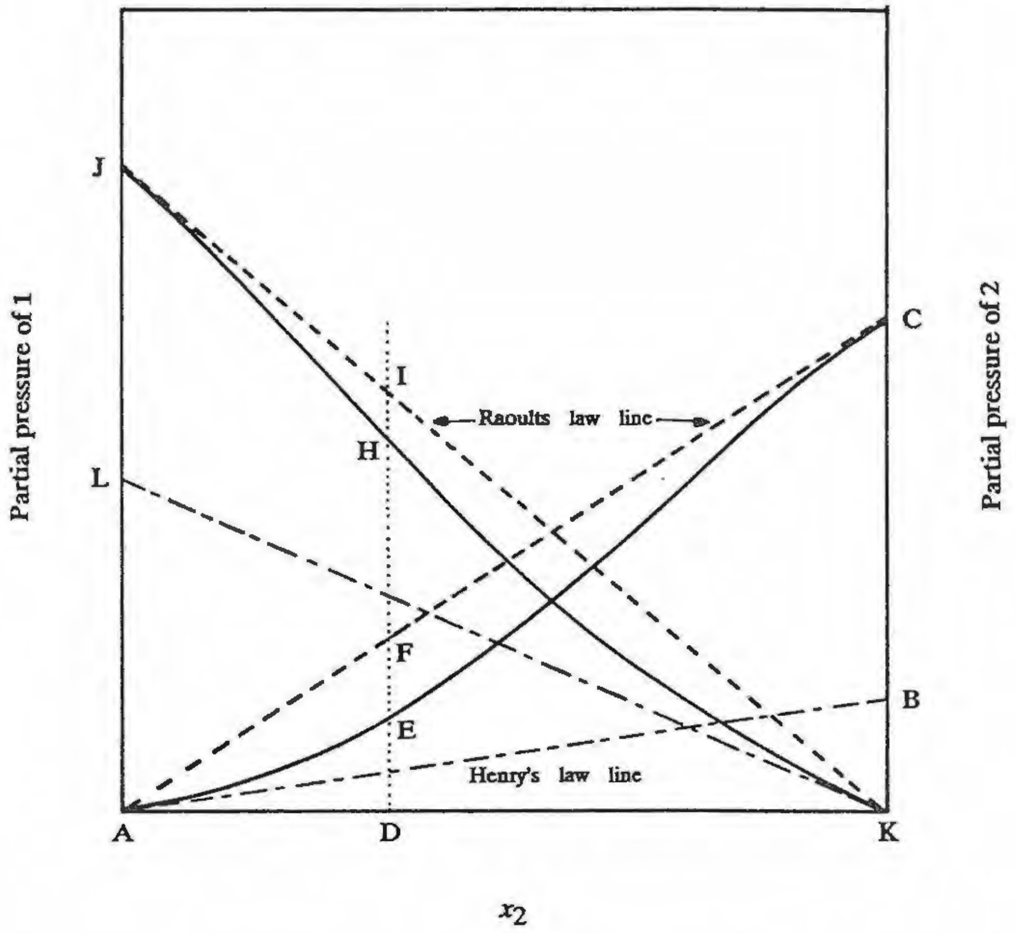

Figure 3.1 Partial pressures for a binary liquid mixture

The slopes in the infinite dilution region are shown in Figure 3.1 as broken lines AB and LK. The constants K_1 and K_2 correspond to the distances AL and KB respectively.(211) For the case where component 2 is at infinite dilution, $\mu_1{}^*$ is simply the chemical potential of pure 1 at the same temperature and pressure as the solution, while $\mu_2{}^*$ corresponds to the chemical potential of pure component 2 in a physically unattainable state corresponding to an extrapolation from the real solution line along the line AB up to $x_2 = 1$.

In a real solution, the activity coefficient, γ_i, is introduced into equation 3.1 so that equation 3.5 is correct, regardless of the deviation from ideality:(211)

$$\mu_i(\text{real}) = \mu_i{}^* + RT\ln \gamma_i x_i \qquad 3.5$$

In the above definition, $\mu_i{}^*$ is a function of the temperature and pressure while γ_i may be a function of the mole fractions of the solution components as well.

Since the value of μ_i^* in equation 3.5 is an unknown, it is necessary to define two conditions under which γ_i equals unity.(211) The first condition **(Convention I)** usually applies to solutions in which all the components in their pure state are liquids at the same temperature and pressure as the solution. For each component:

$$\gamma_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1 \qquad 3.6$$

Under these limiting conditions, the term ln $\gamma_i x_i$ in equation 3.5 becomes equal to zero and hence μ_i^* corresponds to the Gibbs free energy per mole of pure component at the same temperature and pressure as the solution. The activity coefficients at any concentration can be interpreted as the ratio of the actual partial pressure to the partial pressure for a solution obeying Raoult's Law. The significance can be more clearly seen from Figure 3.1. The partial pressure of component 2 at a mole fraction D for an ideal solution would be $p_2{}^*x_2$, which is represented by the distance DF. The actual partial pressure is represented by the distance DE and therefore:

$$\gamma_2 = DE/DF \qquad 3.7$$

and

$$\gamma_1 = DH/DI \qquad 3.8$$

The extent of the deviation of γ_i from unity is thus a measure of the deviation from Raoult's Law.

The second condition **(Convention II)** applies to solutions of gases, solids, and in some case liquids dissolved in liquids.(211) For the solvent, designated by a subscript i:

$$\mu_i = \mu_i{}^* + RT\ln \gamma_i x_i \qquad 3.9$$

and

$$\gamma_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1 \qquad 3.10$$

which is identical to **Convention I**. For the solute, designated by a subscript o, the same equation applies:

$$\mu_o = \mu_o{}^* + RT\ln \gamma_o x_o \qquad 3.11$$

but according to this convention:

$$\gamma_0 \longrightarrow 1 \quad \text{as} \quad x_0 \longrightarrow 0 \tag{3.12}$$

and the activity coefficient of the solute approaches unity at infinite dilution. The extent by which the activity coefficient differs from unity is a measure of the deviation from Henry's Law. This interpretation is made clearer by considering Figure 3.2 which depicts a typical plot of vapour pressure curves for a binary system where the mole fraction of component 2 cannot be varied up to unity.(211) At a concentration, E, the

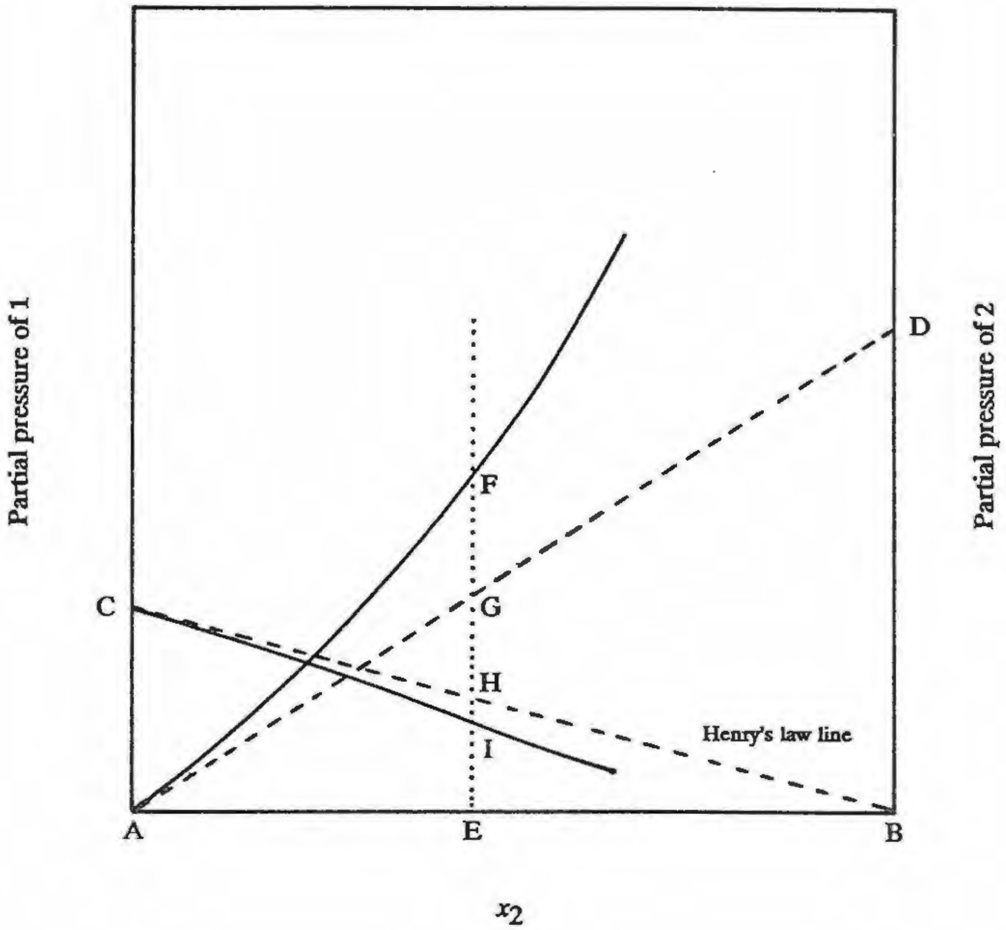

Figure 3.2 Activity coefficients according to Convention II

component 2 obeys Henry's law and hence its partial pressure is K_2x_2 and is represented by the distance EG. The actual partial pressure is represented by the line EF and hence:

$$\gamma_2 = EF/EG \qquad 3.13$$

The activity coefficient is thus equal to the ratio of the actual partial pressure to the "ideal" partial pressure given by Henry's law. The quantity therefore corresponds to the chemical potential of a pure solute in a hypothetical liquid state corresponding to an extrapolation to infinite dilution along the Henry's Law plot.(211)

Activity coefficients at infinite dilution, γ_{13}^{∞}, are of practical as well as theoretical importance. From a theoretician's point of view, these values at infinite dilution characterize the maximum non-ideality in a solution where a solute molecule is surrounded by the solvent, thus offering fundamental thermodynamic information on solute-solvent interactions in the absence of solute-solute effects. These thermodynamic properties can provide useful information in view of the application of perturbation theories for describing the behaviour of mixtures from macroscopic properties of their pure components.(212) The activity coefficients, γ_{13}^{∞},[1] are not only useful for verifying the reliability of proposed models, but also offer information both in the description of binary mixtures and multi-component systems, and in the prediction of vapour-liquid equilibria (VLE) data for these sytems.(213) For example, Schreiber and Eckert(214) used activity coefficients at infinite dilution with the Wilson equation to predict VLE data, while workers such as Duran and Kaliaguine(215) and Tai *et al.*(216) have used the same equation to represent simultaneously VLE and H_m^E data. Similar studies with this and other equations such as the NRTL or UNIQUAC equations have been reported in the literature.(217-219) From an industrialist's point of view, a knowledge of the activity coefficient at infinite dilution is useful in the selection of solvents for extraction and distillation processes.(212)

Despite the obvious uses of γ_{13}^{∞} values, the tedium involved in obtaining VLE data by classical methods and the high level of uncertainty associated with γ_{13}^{∞} values obtained

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[1] In this work, 1 refers to the solute, 2 refers to the carrier gas, and 3 refers to the liquid stationary phase solvent.

by extrapolations from such data has traditionally limited the extensive use of these values.(213) The development of new techniques and the modifications to existing ones over the last two decades now offers rapid and accurate methods for the study of mixture properties in the dilute region.

The experimental methods for determining γ_{13}^{∞} values can be broadly classified into two categories:(213) *(i)* methods based on the classical measurement of differential vapour-liquid equalibria, which include differential ebulliometry and differential static techniques,(211) and *(ii)* methods based on the flow of an inert third component, such as in gas-liquid chromatography.

3.2 Activity coefficients by classical methods

The ebulliometric technique involves the accurate measurement of boiling points, and can be traced back to work in 1925 by Swietoslawski.(220) Since then, ebulliometers have been used to measure molar masses, mutual solubilities, sample purities and activity coefficients at infinite dilution.(220,221)

Eckert and co-workers(213,220) give a detailed discussion of a differential ebulliometer and discuss an expression by Gautreaux and Coates(222) which relates γ_{13}^{∞} to the pure component properties and to the limiting slope of the measured temperature versus liquid phase mole fraction plots at constant pressure (boiling point elevation curves). For infinite dilution work, the slope is obtained by fitting various analytical expressions to this T-x data in the dilute region. The original expression for obtaining γ_{13}^{∞} values has been improved through the inclusion of expressions for vapour phase non-idealities and the resulting expression has been given in the literature.(218,221) An alternative expression relates γ_{13}^{∞} through an assumed solution of the Gibbs-Duhem equation to changes in pressure and temperature when small amounts of solute are added to a solvent in the dilute region.(220) Activity coefficients at infinite dilution determined by this method for binary systems comprising comparatively ideal solutions have compared well with literature values determined by g.l.c. techniques(221) and with values interpolated from the literature.(221) For non-ideal solutions however, where γ_{13}^{∞} lies outside the range 0.7 to 2.0, differences of up to 30% between g.l.c. values and literature values were attributed to the difficulty attached to the extrapolation of finite concentration data to infinite dilution.(221)

Scott(223) has recently reported an ebulliometric technique for the rapid and accurate measurement of boiling point diagrams for binary mixtures in both the finite and infinite dilution region. The apparatus, which is considered to constitute an improvement on the design of Eckert and co-workers,(213,220) permits the use of larger sample sizes of higher volatility, and allows the determination of data over a wider concentration range. A high speed stirrer reduces temperature cycling effects in the mixing vessel. Although Scott maintains that the method will yield γ_{13}^{∞} results with an accuracy unparalleled by any method described in the literature, as much as five hours are required to obtain the data necessary for the determination of one limiting activity coefficient. Accurate γ_{13}^{∞} values can be obtained directly in a much shorter time by g.l.c. methods. Other examples involving the determination of γ_{13}^{∞} values from T-*x* data can be found in the literature.(224-226)

Milanova and Cave(229) have mentioned the different types of equilibrium stills that can be used for activity coefficient determinations. These include distillation, dew- and bubble-point, circulation, static, and flow types. Results obtained from classical isothermal distillation stills are often prone to serious errors(227) while with circulation stills, uncertainties can arise as to whether the measured temperature and compositions are indeed related to equilibrium conditions.(229) In equilibrium stills, the boiling liquid and effluent vapour are equilibrated at a constant temperature and pressure. The technique involves the analysis of the composition of the vapour and the liquid phase. In each case it is assumed that the equilibrium is not affected by the sample withdrawal. The method allows the data to be tested for thermodynamic consistency. The method is however tedious and uncertainties are easily introduced through problems connected with superheating, vapour liquid entrainment, partial condensation within the apparatus, and sampling techniques.(230) In many cases the temperature versus concentration data obtained from a still is related to mixture concentrations far removed from infinite dilution and hence extrapolation techniques to infinite dilution may introduce unreliable results.(229,231)

Milanova and Cave(229) have reported an equilibrium still apparatus design which allows the repetitive measurement of very low vapour component concentrations. The design incorporates a chromatographic sampling loop of accurately known volume which constitutes an integral part of the vapour space above the mixture. In this way it is felt that the sampling procedure does not affect the equilibrium conditions within the apparatus. The reliability of the apparatus and the experimental procedure was confirmed by vapour concentration measurements for both components of the system {benzene + *n*-hexane} over the entire composition range. Activity coefficients at infinite dilution for these and other binary systems of polar and non-polar compounds were determined, taking into account vapour phase non-idealities. These results compared favourably with other literature results.(229)

Afrashtehfar and Cave(232) have extended this study to 24 binary non-electrolyte solutions comprising {polar + non-polar} and {polar + polar} mixtures. A similar apparatus was employed by Sagert and Lau(233) for the determination of γ_{13}^{∞} values for alcohol solutes in water, *n*-octane, or carbon tetrachloride solvents.

3.3 Activity coefficient determination by g.l.c.

3.3.1 Introduction

The term chromatograph is employed to describe a group of techniques which involve the separation of one or more solute components between a mobile phase and a stationary phase. Chromatographic methods are classified according to the nature of these two phases. For a solid stationary phase, the distribution process is one of adsorption while for a liquid stationary phase, the process involves partitioning.(234) Since the mobile phase may be either a liquid or a gas, further subdivisions may be made. These are shown in Figure 3.3.

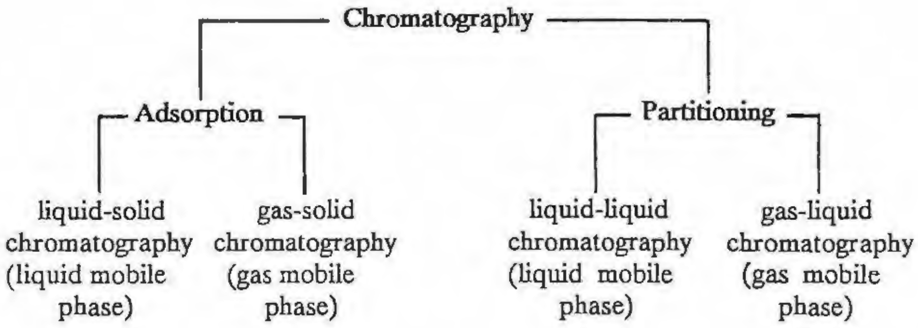

Figure 3.3 General subdivisions of chromatography

The "discovery" of the chromatographic technique is generally attributed to Tswett,(235) who recognised in 1904 while working on the separation of plant pigments that the process comprises of a series of sequential sorption - desorption interactions.(236) This early work aroused little interest until the 1930's when the value of the technique was recognised, particularly for the analysis of natural products.(234,236)

Wilson(237) was the first person to describe the chromatographic process mathematically. He treated the elution process as a passage of the concentration profile through the chromatographic column and recognised that the band width was dependent upon the column void space, diffusion and the finite rates of sorption and desorption.(236) In 1941, Martin and Synge(238) introduced liquid-liquid chromatography (l.l.c.) They proposed that the chromatographic process should be modelled on the distillation theory where the columns are divided into N theoretical "plates" of equal length and the "height equivalent to a theoretical plate", H, is the column length divided by N. They developed a plate theory which could be used to determine liquid-liquid partition coefficients, K. The partition coefficient is a dimensionless quantity and is related to the concentration of the solute in the stationary and the mobile phase.(239) The original theory was often criticized on the grounds that it postulated a discontinuous chromatographic process.(236) The theory of Martin and Synge did, however, provided a basis for the relations between the partition coefficient for a solute material and the retention volumes for the partitioning processes involving inert solvents.(239) The theory recognized that in addition to the dependence of N and H on diffusion, these parameters depend on factors such as flow rate, particle size, column pressure drop, solid support packing uniformity and the solute sorption isotherm.

James and Martin(240) introduced gas-liquid chromatography (g.l.c.) in 1952. Martin(241), in 1956, speculated that this technique could provide a useful tool for the study of the thermodynamic interactions of volatile solutes with non-volatile solvents. This was verified by Pierotti *et al.*(242) who determined partition coefficients and activity coefficients at infinite dilution for several alcohols and alkanes in hydrocarbon solvents. The results were in good agreement with values obtained for these systems by classical methods and prompted further investigation into the development and use of this method of elution chromatography. Work by investigators such as James and co-workers,(243,244) Ray,(245) and Bradford and co-workers(246) helped to establish the validity and usefulness of the technique by the 1960's.

In gas-liquid chromatography the sample is introduced into a moving carrier gas stream and is carried down a column packed with a liquid solvent stationary phase coated onto a sufficiently inert solid support. Since in general their solubilities differ, a distribution process occurs between the different components of the sample. The components thus emerge from the column at different times in distinct peaks or zones, separated by pure carrier gas. Detection of these peaks occurs by some suitable means.(234,239) This technique is known as the elution technique.(236) Other techniques such as the frontal analysis technique will not be considered here but are discussed in detail by Laub and Pecsok(236) and by Conder and Young.(239)

The chromatographic technique has a wide range of uses which have been subdivided by Young(247) into three different groups: *(i)* the quantitative and qualitative analyses of the constituents of mixtures, *(ii)* the preparative isolation of compounds from mixtures, and *(iii)* the determination of certain physicochemical properties. Over the last three decades, the subject of physiochemical measurements using chromatographic techniques has received considerable attention and numerous reviews and publications have appeared in the literature.(236,239,246-249) The work reported in this Chapter is concerned with the measurement of γ_{13}^{∞} values for a range or long chain and cyclic hydrocarbon solutes in bicyclic compound solvents, by the elution method of g.l.c.

3.3.2 The theory of non-ideal linear chromatography

In the plate model of chromatography by Martin and Synge(238) the chromatographic column is divided into a number, N, of "zones" or "theoretical plates" such that the concentration of the sample in both the mobile and stationary phases are regarded as being uniform within the zone. The length of any one of these zones is termed the "Height Equivalent to the Theoretical Plate" (HETP). The distribution of the solute between the mobile phase and the stationary phase on any theoretical plate is numerically described in terms of the partition coefficient, K, which is a fundamental value for each solute and depends on the stationary phase and the temperature. By definition:(236)

$$K = \frac{\text{(solute concentration in the stationary phase)}}{\text{(solute concentration in the mobile phase)}} \qquad 3.14$$

The model predicts that a solute traversing the column will be distributed over the N theoretical plates in a binomial manner. For a sufficiently large number of theoretical plates, sample distribution becomes Gaussian in nature. In developing the theory for the chromatographic process, Martin and Synge(238) and later James and Martin(240) adopted certain additional simplifying assumptions: *(i)* the partition coefficient is constant along the column and is independent of concentration, *(ii)* equilibration of the solute between the phases is rapid relative to the rate of travel of the mobile phase, *(iii)* column diffusion along the column length is negligible, and *(iv)* the flow of the mobile phase is discontinuous. The last assumption regards the process as consisting of a stepwise addition of volumes of mobile phase, each equal to the free volume per plate. Although the first assumption may be regarded as a good approximation, the second and third assumptions are contradictory since the rapid attainment of equilibrium will, by necessity, require rapid diffusion. The last assumption has been superceded by the more satisfactory consideration of a continuous addition of solute to the column.(250) The theory is thus an equilibrium theory and the process is sometimes refered to as linear ideal chromatography.(250) The above, and other theoretical models, have been discussed in more detail by Conder and Young(239) and by Purnell.(250)

Linear ideal chromotography is, however, unattainable in practice and the closest approximation to this form of chromatography is linear non-ideal chromatography.(250) In this case the partition isotherm may be linear, but equilibration between the phases is not necessarily immediate. In addition, various diffusional processes contributing to the spreading are taken into account. Since this type of system is the most likely one applicable to gas-liquid chromatography and is most amenable to theoretical treatment, it has received considerable attention in the literature. The rate theory of van Deemter *et al.*(251) takes into account the fact that a solute in a gas phase must spread longitudinally, while diffusion into the solvent is sufficiently slow so that equilibrium will not quite be achieved. Furthermore, it is assumed that the spreading of the solute will be due to the eddy diffusion of the gas. The longitudinal diffusion, non-equilibrium due to the resistance to mass transfer between the phases, and the band spreading, tend to spread a peak virtually symmetrically, provided that the concentration gradients are the same on each side of the peak. The resulting expression relates the HETP and band broadening to the carrier gas flow rate. A more detailed dissussion of this and other rate theories has been given by Purnell(250) and Littlewood.(252)

The general equation relating the adjusted retention volume of the solute, $V_R{}^{\prime}$, to the gas hold-up volume, V_m, and the solute volume, V_3, is:(239,249)

$$V_R{}^{\prime} = V_R - V_m = KV_3 \qquad 3.15$$

where V_R is the retention volume of the solute. It is obvious from equation 3.15 that the retention volume does not depend on the number of theoretical plates but on the column geometry through V_m and V_3.

Equation 3.15 assumes the existence of idealized chromatographic conditions. The assumptions that the pressure remains constant along the length of the column and that the carrier gases are ideal(236) are unreasonable since a resistance to gas flow resulting from a progression through the narrow interstices between the column packing is observed. This results in a pressure gradient along the length of the column(236,239) necessitating the introduction of a pressure gradient factor, J.

The pressure gradient existing within the column results in a continuous expansion of gas as it moves along the column. The need to introduce a gas compressibility correction was first recognized by Martin and James(240) in 1952. From their original derivation, with the introduction of Boyle's Law and the assumption of a carrier gas flowing at a pressure, p, and velocity, u, through a packed column of cross section, A, then the volume throughput must be constant everywhere within the column, and hence:

$$p\mathrm{uA} = p_o\mathrm{u_oA} = \bar{p}\bar{\mathrm{u}}\mathrm{A} \qquad 3.16$$

The subscript o refers to values measured at the column outlet and the bar indicates average values. Therefore at any point, the velocity is given by:(250)

$$\mathrm{u} = (p_o\mathrm{u_o})/p \qquad 3.17$$

The velocity can also be related through Darcy's equation to the pressure gradient, δp, within a length, δl, along the column:(250)

$$\mathrm{u} = -(\mathrm{K}\delta \mathrm{p})/(\varepsilon\eta\delta l) \qquad 3.18$$

where η, ε and K are the gas viscosity, gas porosity and specific permeability coefficient respectively. Mathematical manipulation of the above equation yields:

$$p\delta l = -(\mathrm{Kp}^2\delta \mathrm{p})/(\varepsilon\eta\mathrm{u_o}p_o) \qquad 3.19$$

Since the average value of a continuous function is given by the mathematical relationship:(253)

$$F(x) = [\int F(x)dx]/\int dx \tag{3.20}$$

the integration of equation 3.19 over the column pressure gradient bounded by the inlet pressure, p_i, and the outlet pressure, p_o, will yield:

$$\bar{p} = [\int p^2 dp]/[\int p dp] \tag{3.21}$$

which yields:

$$\bar{p} = (2/3)p_o[(p_i/p_o)^3_2 - 1]/[(p_i/p_o)^2_3 - 1] \tag{3.22}$$

Gas volumes measured at the column outlet can thus be corrected to the average column pressure by multiplying by the fraction, p_o/p, which is given the symbol, J, and in terms of the notation of Everett,(254) can be generalized as:

$$J_n^m = (n/m)[(p_i/p_o)^m - 1]/[(p_i/p_o)^n - 1] \tag{3.23}$$

The corrected retention volume, $V_R{}^o$, the corrected retention volume of a non-retained species (mobile phase holdup), V_G, and the net retention volume, V_N, are given by the equations 3.24 to 3.26 respectively:

$$V_R{}^o = J_3^2 U_o t_R \tag{3.24}$$

$$V_G = J_3^2 U_o t_G \tag{3.25}$$

$$V_N = J_3^2 V_R^1 \tag{3.26}$$

where U_o is the mobile gas phase flow rate measured at the column outlet. Hence the net retention volume, V_N, can be given by:(70*b*)

$$V_N = V_R{}^o - V_G = KV_3/J_2^3 \tag{3.27}$$

$$= U_o(t_R - t_G)J_3^2 \tag{3.28}$$

where t_R and t_G are the retention times for the solute and the unretained gas respectively.

Porter *et al.*(255) have related V_N to the activity coefficient at infinite dilution through:

$$V_N = (n_3RT)/(\gamma_{13}^{\infty}p_1^*) \qquad 3.29$$

where n_3 is the number of moles of solvent on the column and p_1^* is the saturated vapour pressure of the solute at a column temperature T.

In 1961, Everett and Stoddart(256) demonstrated the need to account for the solute-carrier gas interactions (1-2) as well as solute - solute interactions (1-1). As a result of their work and of later work by Desty *et al.*,(257) the retention volume is given by:

$$\ln V_N = \ln V_N^o + \beta p_o J_2^3 \qquad 3.30$$

where V_N^o is the extrapolated retention volume at zero mean column pressure and is related to the partition coefficient, K, by:

$$\ln V_N^o = \ln [(n_3RT)/(\gamma_{13}^{\infty}p_1^*)] - [(B_{11} - V_1^*)p_1^*]/RT \qquad 3.31$$

In equation 3.31, V_1^* and B_{11} are the molar volume of the solute and the second virial coefficient of the pure solute respectively. The coefficient β in equation 3.30 is related to the mixed second virial coefficient, B_{12}, by:

$$\beta = (2B_{12} - V_1^{\infty})/RT \qquad 3.32$$

where V_1 is the partial molar volume of the solute at infinite dilution in the stationary phase. Since the experimental conditions are at infinite dilution, V_1^{∞} is approximated to V_1.(256) Everett(254) has, however, indicated that for normal paraffins, as much as a 4-fold difference can exist between V_1 and V_1^{∞} and has hence advocated that the distinction between the two terms should be retained.

Everett and Stoddart(256) and Desty *et al.*(257) proposed the use of g.l.c. to determine B_{12} values. Desty and co-workers(257) have derived a relationship which includes fugacities as well as solute - carrier gas mixed virial effects and can be expressed in the simplified form:

$$\ln \kappa = A + p(2B_{12} - V_1^o)/RT \qquad 3.33$$

where $\kappa = KV_3/V_G$, V_1^o is the solute molar volume and A is a constant. The mean column pressure, $\bar{p}$, is given by $p_oJ_2^3$ and hence B_{12} values can be obtained from a simple plot of ln κ versus $\bar{p}$.

The relation derived at a later stage by Everett(254) differed in the method of calculating $\bar{p}$ $(=p_oJ_3^4)$. Neither of the above workers considered carrier gas solubility in the stationary phase, which can be significant at low column pressures.

Cruickshank *et al.*(258) reformulated the differential equation used to describe the elution rate in g.l.c. columns in terms of the local pressure and the carrier gas outlet flow rate, and suggested that:

$$\ln V_N = \ln V_N^o + \beta p_oJ_3^4 \qquad 3.34$$

Provided that the ratio of the inlet to the outlet pressure is less than 1.3:1, the difference between equation 3.34 and equation 3.30 is, for practical purposes, negligible.(239) Cruickshank *et al.*(258) extended the above to account for carrier gases which are appreciably non-ideal. The effects of carrier gas solubility in the stationary liquid and the corrections for this effect have been discussed by Cruickshank *et al.*(259) Laub and Pecsok(236) discuss some of the aspects concerning chromatographically determined B_{12} results. They are of the opinion that the reproducibility of these results depends on the accuracy with which ln V_N and $p_oJ_3^4$ are determined, which can generally be expected to be 1-5%. The g.l.c. technique is seen to be comparable to non-chromatographic methods.

Cruickshank and co-workers(259) have also discussed how non-equilibrium conditions shift the chromatographic peak while Hicks(260) has extended the g.l.c. theory to account for the resistance to mass transfer. From this work he showed that for a situation where the diffusion of the solute in the liquid phase is the rate-determining step for equilibration, then the peak average retention volume can be used to calculate γ_{13}^{∞}. This will be discussed in more detail in Section 3.4.9.

Other theoretical treatements have been well discussed in the literature(236,239,249) and will thus not be discussed here.

3.3.3 A comparison of γ_{13}^{∞} values determined by g.l.c. and non-g.l.c.

Numerous investigations have been initiated to substantiate the validity of γ_{13}^{∞} values determined by g.l.c. One of the fundamental questions is whether the properties of a liquid spread on an inert solid support, as is the case in gas-liquid chromatography, differ from those in the bulk solution. Ashworth and Everett(261) have investigated the effects of spreading a liquid on a solid support, paying particular attention to whether the properties of the bulk solution differ significantly from those of the liquid coated solid support. They measured the vapour pressure of solutes as a function of composition for both a bulk solution and a solvent spread on celite. Even when the accuracy of the measurements corresponded to 0.001 in log γ_{13}^{∞}, they were unable to detect any systematic difference between the two series of measurements. Studies by Cruickshank *et al.*(258) indicated that the relative lowering of the vapour pressure of a solvent spread on celite did not diminish the log γ_{13}^{∞} by more than 0.002 for a wide range of solutes.

Several comparisons have been made between activity coefficients measured at infinite dilution by g.l.c. and those measured by non-g.l.c methods such as values extrapolated from VLE data by the methods mentioned previously. The wide use of the non-volatile compound squalane as a stationary phase by early workers has resulted in the acceptance of this liquid as a test stationary phase.(239) Cruickshank *et al.*(258) have determined γ_{13}^{∞} values for hydrocarbon solutes in squalane, dinonylphthalate and *n*-hexadecane stationary phases. They have compared their results to values reported by Ashworth and Everett(261) who used a McBain balance(262) in their determination. The agreement is good, with the largest discrepancy amounting to 3% in the case of benzene and 2,2-dimethylbutane solutes. Conder and Young(239) are however of the opinion that a considerable error may have been introduced in the extrapolation procedure employed by Ashworth and Everet.(261) They also feel that the early results of studies at infinite dilution by g.l.c. are possibly not at infinite dilution at all, since in some cases large sample sizes were employed.

Numerous other workers have made comparisons between γ_{13}^{∞} results by g.l.c. and non-g.l.c.(263-267) Excellent agreement was observed between the γ_{13}^{∞} values by Ashworth(267) for the systems {*n*-hexane + squalane} and {*n*-heptane + dinonylphthalate} determined using a vacuum microbalance, and the g.l.c. values of Conder and Purnell.(239) The γ_{13}^{∞} results by g.l.c. reported by Adlard *et al.*(268) for benzene and cyclohexane in dinonylphthalate were corrected for gas-phase imperfections and agreed well with data by Ashworth and Everett.(261)

Conder and Young(239) have made a detailed comparison between some of the more recent γ_{13}^{∞} results obtained by classical and chromatographic methods, and which have been reported for a range of mixtures by various workers. They conclude that g.l.c. and classical data are generally in excellent agreement, with the discrepancies most often within the scatter of g.l.c. results obtained by different workers.

3.3.4 Liquid surface phenomena

A potential source of sytematic error in g.l.c. involves solute adsorption at the gas-liquid interface. The initial suggestion by Martin(269) that this phenomenon could affect solute retention times initially met with scepticism but was later substantiated through classical measurements by various workers.(263,270,271) The equation which relates the net retention volume to the number of moles of stationary phase on the column can be expanded to account for gas-liquid interfacial adsorption contributions to the retention time:(269)

$$V_N = K_L V_3 + K_S A_L \qquad 3.35$$

where K_L is the bulk liquid partition coefficient, K_S is the liquid surface adsorption coefficient which, unlike the dimensionless K_L, has dimensions of length, and A_L is the gas-liquid interface area. The bulk partition coefficient is found by plotting V_N/V_3 versus $1/V_3$ and extrapolating to the ordinate.(239) The absence of surface adsorption effects is indicated by a straight line. The form of equation 3.35 has been justified empirically by Martire *et al.*(271) who showed that chromatographic values of K_L and K_S derived from this equation were in good agreement with independent static measurements using a McBain static vapour pressure apparatus. Equation 3.35 is only valid for infinite dilution and applies only to retention data obtained from symmetrical peaks.

The importance of surface effects have been stressed by Martire,(272) who investigated solute adsorption at the gas-liquid interface in g.l.c. by varying the solvent loading. Martire measured activity coefficients for alcohol solutes in glycerol and concluded that two distinct classes of absorption occur at the gas-liquid interface. The first class occurs for large activity coefficients. In this case large surface adsorption effects are associated with a solute which is less polar than the solvent, and a solute which is relatively insoluble in the bulk liquid. Martin(269) studied non-polar hydrocarbon solutes on three stationary phases: the non-polar *n*-hexadecane, the moderately polar 1-chloronaphthalene and the strongly polar β,β'-thiodipropionitrile(TDPN). The strength of adsorption relative to solution was observed to increase with the polarity of the stationary phase. He concluded that for non-polar hydrocarbon solutes, liquid surface adsorption occurred for polar but not for non-polar stationary phases.(239) This generalized conclusion was reproduced and extended by Pecsok and co-workers,(264,271) who measured activity coefficients for 22 hydrocarbons and oxy-compounds in TDPN. Following this work, the Bristol group(259) performed measurements on the system {benzene + glycerol}. They argued that if there is a significant adsorption of the solute at the gas-liquid interface then the zero pressure retention volume, $V_N{}^o$, is a function of the mass ratio of the solid support to the solvent and an extrapolation to zero mass ratio should give $V_N{}^o$ corresponding to the bulk phase solvent gas partition coefficient of the solute. Retention values over a range of different column loadings are thus required.

The second class of adsorption is characterized by a relatively low solute activity coefficient, the solute and solvent being of comparable high polarity. Martire(272) demonstrated this for TDPN with solutes of similar polarity. In contrast, systems involving an alcohol with the strongly polar solvent β,β'-oxydipropionitile (ODPN) and with glycerol exhibited a trend of decreasing adsorption with increasing activity coefficient. Martire(272) suggested that alcohols constituted a separate class in which solute molecules are adsorbed through strong dipole-dipole interactions or through hydrogen bonding between the solute and the liquid surface, with a low activity coefficient.(239) Meen *et al.*(273) have supported these observations.

Contrary to the expectations of Martin(269) and Matire,(272) Pecsok and Gump(263) employed static methods and demonstrated strong surface adsorption effects for polar solutes such as alcohols and amines on the non-polar stationary phase squalane. Adsorption of this type has been discussed in more detail by Conder and Young.(239)

More recent work relating to the determinaton of γ_{13}^{∞} values and which take adsorption effects into account have been carried out by Thomas *et al.*(274) They have measured γ_{13}^{∞}

by g.l.c. for 35 solutes in 34 different solvents. The compounds covered a wide range of polarity, polarisability and degree of association. Martire *et al.*(275) have stated that the thin liquid coating on the column leads to a high surface area to volume ratio and hence, in the case of highly polar solvents, the non-polar solute molecules are "squeezed" out of the bulk phase into the surface layer, leading to a surface excess. Thomas *et al.*(274) are however of the impression that since the depth of this interfacial layer is small in comparison to the bulk solution, the overall concentrations would not be signficantly affected for the liquid loadings used in their study, typically of the order of 15% for a Chromasorb W solid support. Their experimental results compared favourably with literature values determined by ebulliometric methods or by extrapolations from VLE data.

Nitta *et al.*(276) have measured γ_{13}^{∞} for 20 polar and non-polar solutes in squalane. The polar solutes, which included alcohols, acetonitrile, ketones, acetates and ethers, exhibited gas-liquid interfacial adsorption effects for small sample sizes. The effects of adsorption on the solid support were minimized by increasing the stationary phase loadings.

Arnold *et al.*(279) have reported γ_{13}^{∞} values for 16 solutes of varying polarity in *n*-octane solvent. All the retention times for peaks outside the skew range 0.8 to 1.2, where the skew range is equal to the ratio of the slope of the trailing edge of the chromatogram to the slope of the leading edge of the peak profile, were corrected for the peak maximum retention time by an extrapolation to zero sample size. Solute adsorption effects at the gas-liquid interface and adsorption at the surface of the packing were minimized by using an inactive solid support, high liquid loadings (20-30%) and extrapolating the sample to zero sample size. Solvent losses were minimized by employing column presaturator methods and by operating at elevated pressures and low flow rates to minimize the pressure drop.

3.3.5 Sample size effects

The essential requirement for the injection of elution peaks in infinite dilution studies is that the sample size should be very small. Conder and Young,(239) and Purnell(250) describe a procedure for determining the maximum permissible sample size from information concerning the number of theoretical plates, the column length and the width at half-height of the peak at the column outlet. They calculate that, depending on the particular system under study, the amount of solute in the stationary phase should be restricted to 1 μmol at the column outlet. On the assumption that at least 90% of the sample in a column is located in the stationary phase, they quote a maximum sample size of the order of 1 μmol for a typical g.l.c. column. This corresponds to 0.1 μl or 0.1 mg of liquid for a solute of molecular weight 100 and density equal to 1 g.cm^{-3}.

Nitta *et al.*(276) have investigated the effect of sample size on γ_{13}^{∞} for 20 solutes in squalane solvent. Sample sizes as large as 4.0 μmol were injected in some cases. The retention volumes were observed to decrease for decreasing sample size. This was attributed to the concentration effects on the distribution coefficients of the bulk liquid. The values of the limiting retention volumes extrapolated to zero sample size were observed to be slightly dependent on the liquid loadings. A sample-size extrapolation procedure was applied to determine the retention volume at infinite dilution.

The average size of the samples injected in this investigation were of the order of 0.1μL. For density of 1 g.cm^{-3}, this corresponds to 0.1 mg of sample, or roughly 0.01 μmol for a 100 molecular weight sample, which was similar to that value suggested above.(239,250) The sample sizes were well within the limits set out above in all cases. Samples of this size represented quantitites which could easily be detected by the methods employed.

3.3.6 Problems encountered with solvent volatility

The problem of stationary phase volatility and the subsequent stationary phase losses from the column can restrict the general application of the g.l.c. technique. Different carrier gas saturation techniques have been reported in an attempt to deal with the volatile solvent losses from the column.(239,278-280) Kwantes and Rijnders(278) introduced the technique of presaturating the carrier gas with vapour of the volatile stationary phase before it enters the column. The simplest saturator design comprises a wash-bottle with the carrier gas dispersed as a fine stream of bubbles through the liquid by means of a fritted disc or a tube. Schaffer(279) has employed this method in the determination of the activity coefficients for a range of oxygenated organic compounds in water. Where comparisons were possible, he found reasonable agreement with values determined by static methods. Conder and Young,(239) however, argue that in such a design the gas does not necessarily become completely saturated with solute and hence there may be some doubt as to the exact concentration. Pecsar and Martin(280) have suggested the use of a precolumn saturated with liquid stationary phase. The advantage of this method is that better saturation is possible with the longer distances travelled by the carrier gas through the precolumn.

In an attempt to ensure complete saturation, some techniques employ evaporation followed by partial condensation. In one such arrangement, the carrier gas passes through a refluxing still.(239) The one drawback of this method is that flow rate fluctuations are difficult to overcome. Conder and Young(239) have discussed some other presaturation techniques.

When dealing with volatile solvents, it is still necessary to take into account the pressure drop which occurs along the length of the column. Even though the carrier gas is saturated with vapour on entry, it still may remove stationary phase as it expands during the passage down the column. A reduction in the pressure drop helps to reduce the amount of stationary phase lost from the column. In this respect, a packing of coarse particles reduces the pressure drop considerably.(239)

An important problem which arises with the interpretation of g.l.c. data when dealing with volatile solvents is the uncertainty in the amount of solvent on the column. Some workers(239) assume that the rate of solvent loss from the column is constant. The amount of solvent lost then simply corresponds to the difference in the column weight before and after use. Workers such as Langer *et al.*(281) and Kwantes and Rijnders(278) monitor the solvent loss by measuring the retention time for a reference solute, whose value is already known for that system, at intervals throughout the experiment, with the first measurement taken at the start of a run. This allows a plot of the retention time versus the time elapse of operation, which can be extrapolated back to the original time at startup. Correction factors to the measured retentions of all the solutes can then be made. This method has obvious drawbacks if no work has been done previously with the system under investigation.

Numerous examples concerning work related to the use of volatile solvents appear in the literature.(236,239,249,274,282) Thomas *et al.*(274) have observed good agreement between γ_{13}^{∞} values measured by g.l.c. methods and literature results determined by ebulliometric methods for a variety of solutes in the relatively volatile benzene and water solvents.

These workers presaturated the carrier gas with solvent and employed a reference solute with known activity coefficient to monitor the amount of solvent on the column.

Belfer and Locke(283) have reported an experimental technique for dealing with volatile solvents. In non-steady-state gas chromatography, the volatile solvent is injected onto the column where it condenses uniformally on the solid support and equilibrates with the carrier gas. The decrease in retention time with time elapse for repetitively injected solutes is then related to the rate of solvent loss from the column. The activity coefficient at infinite dilution is thus given by:(283)

$$\gamma_{13}^{\infty} = (p_1{}^{o}/p_2{}^{o})(\delta\theta/\delta t_N) = \pi/\phi \qquad 3.36$$

where π is ratio of solvent vapour pressure to solute vapour pressure, $(\delta t_N/\delta\theta)$ is the rate of change of retention time with time elapse, and ϕ is the retention time differential parameter. An interesting aspect of this technique is that the weight of solvent on the column is not required for calculations of γ_{13}^{∞}. In addition, the packing of new columns is eliminated, thus reducing any possible errors introduced by effects such as packing non-unimformity which could effect reproducibility. Solvents more volatile than solutes would be the limiting factor in this technique.

Belfer and Locke(283) have demonstrated the capabilities of the technique by measuring γ_{13}^{∞} values for a variety of solutes including *n*-alkanes, alkenes, cyclohexane and cyclohexene in acetonitrile, and some oxygen containing compounds in *n*-octane. The results were not corrected for vapour phase non-idealities since these workers were of the opinion that the uncertainties in the retention time difference measurements rendered this correction insignificant. They attributed the principle source of error in this method to the measurement of the retention times and estimated the overall accuracy of their results to be of the order of 10%. They expressed the hope that this error would be reduced at a later stage by automization and computerization of the equipment.

Other consequences of solvent volatility and subsequent solvent losses from the column, which include baseline noise and reduction in detector response, have been discussed by Conder and Young.(239)

3.3.7 Solid support effects on γ_{13}^{∞}

Several studies concerning solid supports appear in the literature.(239,250,252,284) Supports should ideally be chemically inert, have a reasonable particle size and should be sufficiently robust. Diatomaceous earths such as celite generally possess these properties and are almost universally employed as solid supports in work of this nature.(252) In addition, it is essential that the support has negligible adsorptive properties concerning the adsorption of solute by the solid support. This is usually checked by measuring the retention time of the solute on a column packed with uncoated support. In the case of celite with a non-polar solute, the retention volume is usually negligible compared to that observed on coated columns containing the same amount of celite.(247) Substantial adsorption of the solute by the coated support is often indicated by a decrease in retention time and peak tailing of the chromatogram.(239) Conder and Young(239) discuss various checks for adsorption at the solid support.

Support effects can be large when polar solutes or solutes which exhibit hydrogen-bonding effects are used. A silanized support or a polytetrafluoroethylene support is desirable in such cases, particularly if the solvent is non-polar. Although these supports tend to reduce surface activity, they are not easily wetted by normal chromatographic solvents, resulting in the distribution of the solvent in the form of capillaries or droplets in the interstices within the solid support, with much of the column remaining uncoated. Uneven distribution can lower the efficiency of the column. Comparative studies of surface-active and non-surface-active suports have shown that surface effects for polar solutes have been present in columns coated with 20% or more liquid phase.(249)

Conder and Young(239) have discussed several of the more pertinent studies concerning stationary phases.

3.3.8 Literature data on γ_{13}^{∞} by g.l.c.

To date few data collections concerning activity coeffients at infinite dilution are available in the literature. Dolezal and Holub(285) have prepared a data collection containing 8000 γ_{13}^{∞} values taken from references published up until 1980. These results were all determined by the retention time method of g.l.c. A comprehensive collection of activity coefficents at infinite dilution covering the data up to 1986 has been published by Tiegs *et al.*(212) Some shorter reviews also appear in the literature.(70*b*,247,249)

Hydrocarbon binary systems have been studied extensively by g.l.c. The large interest in *n*-alkane systems is attributable to the fact that a large number of possible combinations of systems, which differ only slightly from each other, can be investigated. In addition, a considerable amount of information is available concerning the pure component physical properties which are required in the determination of γ_{13}^{∞} values. The Bristol group(258,286-290) have reported accurate γ_{13}^{∞} values for a wide range of mixtures involving *n*-alkanes. Values for C_4-C_8 hydrocarbon solutes in long chain *n*-alkane solvents have been corrected for carrier gas and solute imperfections. Similar work has been carried out by other workers.(291-296)

Matire and co-workers(292) have studied a series of alkane solutes in *n*-alkane solvents of chain length $n = 17$, 24, 30 and 36, at temperatures ranging from 293 K to 353 K, while Parcher and co-workers(293,294,296) have more recently reported an extensive study of γ_{13}^{∞} for 36 binary *n*-alkane systems at temperatures of between 353 K and 393 K. Parcher and co-workers(293) found that the γ_{13}^{∞} values for C_4 to C_8 alkane solutes in C_{25} to C_{36} normal alkane solvents were effectively independent of the temperature in the temperature range 353-373 K. This was in agreement with calorimetric measurements where, according to Conder and Young,(239) the partial excess enthalpy of mixing at infinite dilution is small.

Gainey and Young(297) have investigated the dependence of γ_{13}^{∞} for the solute benzene on the chain length of an *n*-alkane solvent. Experimental impracticalities, such as solvent losses from the column, necessitated the measurement of these values at different temperatures for some of the mixtures; for the sake of comparison, all these results were extrapolated to a common temperature. The γ_{13}^{∞} values decreased with increasing chain length of the *n*-alkane.

Donohue *et al.*(298) have employed g.l.c. to study the effect of molecular size and aromaticity on the intermolecular interactions for mixtures of *n*-alkanes, benzene and toluene in high molecular mass solvents. Activity coefficients at infinite dilution for *n*-alkanes ($n = 5$ to $n = 7$) in squalane compare favourably with similar results by Evered and Pollard,(299) Bighi *et al.*(300) and Porter *et al.*(255)

Few references exist in the literature concerning work pertaining to the determination of activity coefficients at infinite dilution for long chain hydrocarbon solutes in shorter chain hydrocarbon solvents. Hutchings and van Hook(301) have reported γ_{13}^{∞} values for the *n*-alkane solutes, *n*-hexane, *n*-heptane and *n*-octane in each of two solvents, the first having a chain length equal to one carbon less than that of the solute and the second a chain length equal to one carbon more than that of the solute. Results for the longer chain solutes in the shorter chain solvents exhibited a strong dependence on solute carbon number with larger deviations from ideality than for systems of shorter chain solutes in longer chain solvents.

Besides work on simple *n*-alkane systems, work has been undertaken on a number of other relatively simple systems. Recently, Quaddora and Janini(302) have reported γ_{13}^{∞} values for oxygenated hydrocarbons and aromatic solutes in squalane stationary phase at four different temperatures ranging from 303 K to 313 K. The results for the aromatic solutes and cyclohexane exhibit negative deviations from Raoult's Law, indicating a better solvation for these solutes in squalane than for the oxygenated hydrocarbon solutes in squalane.

Letcher and Jerman have determined γ_{13}^{∞} for cycloalkanes (C_5 to C_7) in long chain *n*-alkanes ($n = 16$ to $n = 32$).(303,304) Chromatographic columns were tested for homogeneous packing, while solvent losses were monitored by periodic elution of an *n*-hexane standard solute. Letcher(305) has employed the same technique to monitor octamethylcyclotetrasiloxane solvent losses for systems involving hydrocarbon solutes with this solvent. In order to test for non-equilibrium and possible adsorption effects, the retention volume for each solute was determined at various carrier gas flow rates and column loadings. Letcher(305) found that retention times were independent of column loadings, carrier gas flow rates, or sample volume, in the range 0.200 - 0.02 mm^3.

Activity coefficients at infinite dilution have been reported by Letcher and Marsicano(306) for some unsaturated C_5 and C_6 unbranched hydrocarbons in *n*-octadecane, 1-octadecene, *n*-hexadecane and 1-hexadecane at two different temperatures. Activity coefficients for these systems did not form simple trends because the various double bonds influenced intermolecular interactions in different ways. The segment theory was relatively unsuccessful at fitting the results for both saturated and unsaturated stationary phases.

Meyer and co-workers(307) have attempted to estimate induction energies, *i.e.* dipole - induced dipole energies, between solutes and stationary phases. For the systems studied, which included acetone and *n*-hexane in Apiezon M, and 18 solutes of varying polarity and unsaturation in *n*-tetracosane and in *di-n*-nonylketone, the dipole - dipole and dipole - induced dipole contributions were equivalent to the solute - solvent interaction energies and were of the order of 4 $kJ.mol^{-1}$. The importance of eliminating the influence of solid support on the retention volume became apparent through this work.(307) Several of the above solutes were also subjected to investigation by Martire *et al.*(292) who used *n*-tetracosane as solvent. The agreement is generally satisfactory.

Several workers(272,308-312) have studied alcohol - hydrocarbon systems. Much of the work by these authors involved the study of aliphatic or aromatic alcohol-hydrocarbon mixtures. Studies by Kuchal *et al.*(308) inolved nine hydrocarbon solutes, including *n*-alkanes, cycloalkanes, and benzene, in alcohol solvents, and indicated a decrease in γ_{13}^{∞} with a decrease in the solvent polarity. Mixtures involving benzene as solute exhibited the smallest deviation from ideality here due to the proton donor - proton acceptor arrangement of the hydroxyl group and benzene, resulting in OH...π interactions. Solvent losses necessitated the use of column presaturators. Cadogan *et al.*(31) have reported γ_{13}^{∞} for alcohols (C_3 to C_5) in squalane at several different solvent loadings. They have accounted for the surface effects by plotting V_N/V_3 against $1/V_3$ and extrapolating to infinite liquid phase.

Hammers and de Ligny have reported retention volume measurements over a wide range of temperatures for alkanes, benzene, and carbon tetrachloride, in Apiezon M and polyisobutylene stationary phases,(314,315) and a series of alkanes in polydimethylsiloxane stationary phase.(316)

Gas-liquid chromatography has also been employed to determine γ_{13}^{∞} values for systems where the solvent is a polymer. Martire *et al.*(313) have considered hydrogen bonding effects on the activity coefficient and have used a conventional g.l.c. apparatus to study eight low molecular weight alcohols in the solvents *n*-heptadecane, *di-n*-octyl ether, and *di-n*-octyl ketone, at various temperatures. They chose the non-polar solvent as a "reference" solvent since it was similar in molecular polarizability, size and shape to the electron-donor solvents. The calculated equilibrium constants, standard enthalpies and standard entropies of hydrogen-bond formation were within the range normally observed for OH...O bonds.

Conder and Young(239) have described the relationships which relate γ_{13}^{∞} to the net retention volume at zero pressure, $V_N{}^o$, and the specific retention volume at zero pressure, Vg^o. The problem of accurate molecular weight determination for the polymer, which is required in these calculations, has been overcome by Guillet and co-workers,(312-315) who rederived the expressions for the activity coefficient in terms of the weight fraction. Guillet and co-workers(320) have demonstrated that for *n*-alkanes, weight-fraction based solute activity coefficients approach a finite limit as the molecular weight of the solvent increases while the mole fraction based data approach infinity. As a result of a study by Prausnitz and co-workers(321) concerning alkanes, benzene, toluene and chloroform on polyisobutylene, polyvinyl acetate and polydimethyl siloxane, these workers have suggested that polymer - solvent interactions for bulk polymers may differ from those interactions for a thin polymer film absorbed on a support. This suggestion is at variance with other findings which have observed reasonable agreement between static bulk results and chromatographic results.(322)

Laub and Pecsok(236) and Conder and Young(239) have discussed the subject of polymer studies in more detail.

3.3.9 Partial molar quantities from γ_{13}^{∞} data

Partial molar quantities can be determined from activity coefficient data. The thermodynamic relationship between the partial molar enthalpy at infinite dilution, $H_1^{E\infty}$, and the temperature dependence of γ_{13}^{∞} is:(239)

$$[\delta \ln \gamma_{13}^{\infty} / \delta T] = -H_1^{E\infty}/RT \qquad 3.37$$

It follows that a plot of $\ln\gamma_{13}^{\infty}$ against 1/T will yield the partial molar enthalpy of mixing at infinite dilution. In general however, the activity coefficients for most of the systems reported in the literature have exhibited variations of no more than about 0.002 for $\ln \gamma_{13}^{\infty}$ per Kelvin.(239) Since the experimental precision in measured $\ln\gamma_{13}^{\infty}$ values is seldom better than 0.003, the estimation of partial molar quantities by this method requires very accurate γ_{13}^{∞} results.

Some workers have claimed uncertainties of between 1% and 5% in their calculated partial molar quantitites.(239) However, considering that the differentiation of data is required, Locke(249) feels that an uncertainty of roughly 10 times this error would seem more credible. Gainey and Young(297) have quoted an uncertainty of 1% in their γ_{13}^{∞} results and a corresponding uncertainty of 10% in the derived partial molar enthalpy. These workers determined the partial molar enthalpies of mixing for benzene in aliphatic hydrocarbons with a precision of 7-10%. Letcher and Jerman(304) have determined partial molar thermodynamic excess functions at infinite dilution from γ_{13}^{∞} values reported by various workers for hydrocarbon solutes and solvents. They have discussed the results in terms of intermolecular forces.

There is a continuing effort by Meyer and co-workers(323-326) to improve the precision with which the thermodynamic properties of solution can be measured by g.l.c. They have observed that the differences between chromatographically and calorimetrically determined values are in many cases greater than the discrepancies often noted between results from different laboratories.

Conder and Young(239) conclude that except in exceptional cases, g.l.c. techniques do not provide as accurate or convenient an alternative to measurements by, for example, calorimetric methods. The technique is however useful when only small amounts of sample are available, or for samples of unsuitable purity.

3.3.10 Finite concentration data from g.l.c.

Gas chromatrography (g.c.) also constitutes a rapid technique for measuring activity cofficients at finite concentrations. The various g.c. techniques are generally quicker than the static methods, and in addition they often do not suffer from poor accuracy in the regions of the lower concentration range.(239) Other conventional methods are very often time consuming.

Finite concentration measurements are concerned with the measurement of equilibrium properties at finite concentrations of the solute where these concentrations are high enough to reveal non-linearity in the distribution isotherm. In contrast to the infinite dilution mode of operation, the solute injection profile in finite concentration work is adjusted to resemble any one of a number of shapes of varying concentration and duration.(239) The full theory of finite concentration g.c. has been presented elsewhere.(239) Two of the experimental methods, namely Elution by Characteristic Point and the Method of the Limiting Transition Point, have the same experimental requirements as infinite dilution studies. All the other techniques require a stream of solute vapour diluted with other sorbed or non-sorbed components to be passed continuously onto the column. In this case, the "boundary" between regions of different concentration migrates down the column and the retention time is dependent on how much solute is abstracted from the gas phase by the column. The actual shape of the boundary is modified because of the non-linearity of the distribution isotherm, local temperature variations accompanying sorption and desorption, and non-equilibrium spreading mechanisms.(236,237) In addition to the above, the treatment is further complicated by possible stationary phase swelling, interfacial adsorption on the liquid surface and the solid support, various apparatus effects, and the non-ideality of the gas phase.(237)

Laub and Pecsok(236) and Conder and Young(239) give good discussions of eight different methods for determining isotherms. They also discuss the apparatus required and the correlation between some results determined by chromatographic and non-chromatographic methods.

3.2.11 The retention time technique

Conder and Young(239) have divided chromatographic operating modes into three different categories depending on the method of introduction of the sample. The method mentioned earlier, which involves the introduction of a discrete solute sample onto the column, is often referred to as the elution technique. This technique constitutes one of the most popular chromatographic techniques available for determining γ_{13}^{∞} values directly. In an alternative mode of operation, referred to as frontal analysis chromatography, the solute concentration in a column fed with a continuous stream of a mixture comprising a carrier gas and the solute vapour is changed instantaneously, thus introducing a step-shaped concentration profile into the column. The components of the sample are sorbed by the stationary phase until an equilibrium condition for each component is established.(250) As with the elution technique, the passage of the boundary depends on the distribution coefficient of the solute; the volume of gas phase required to move the boundary down the column is refered to as the retention volume, V_N.(239) The third technique is termed displacement development chromatography. Once again a sample is injected, but in this case the mobile phase contains a component which is more strongly sorbed by the stationary phase. A competition for the stationary phase between this component and the sample results in the progressive displacement of the solutes along the column at different rates.(250) Considerably more support has been received for the elution technique than for the other two methods. This can probably be attributed to the fact that workers such as Purnell(250) are of the view that the sorptive method associated with the other two techniques can introduce possible error into the theory behind the methods.

Ferreira *et al.*(282) discuss three different methods using g.l.c techniques for the direct determination of activity coefficients at infinite dilution. The first method is the retention time method,(70*b*) where the activity coefficient is related to the retention time of a solute injected onto the column packed with solvent coated stationary phase. This technique is especially advantageous for volatile solute - involatile solvent systems and it is possible to obtain, at the same time, the limiting thermodynamic properties of several solutes for the same solvent. The second method, or static method, is based on the evaluation of the vapour-phase composition in equilibrium with a liquid mixture of known composition at a fixed temperature in a static isothermal still. The inert gas-stripping technique of Renon and co-workers(230) involves the periodic sampling of an inert gas which has been bubbled through a mixture, "stripping" the volatile component into the vapour phase. The variation of the concentration of the solute in the gas phase is measured by g.l.c. and affords a measure of γ_{13}^{∞}. Good dispersion of the gaseous phase, combined with the advantage of being able to study multicomponent systems makes this an attractive method for determining γ_{13}^{∞} results.(327) This method is however limited to the use of solutes which are volatile and to solvents which are relatively involatile. Renon and co-workers(327) have used their method to determine γ_{13}^{∞} values for hydrocarbons in *n*-hexadecane solvent. The results for *n*-alkane solutes and for branched alkane solutes are similar to those extrapolated from finite concentration data determined using a vapour sorption technique.(327) Accurate results were difficult to obtain for *n*-alkane solutes where the chain length, *n*, is greater than nine. Further work has been carried out by Cori and Delogu,(327) who report γ_{13}^{∞} results for {ethanol + *n*-alkane} systems. Their apparatus was capable of measurements at pressures of 3-4 atmospheres, thus permitting experimentation at temperatures above the normal boiling point of the solvent.

The retention time technique by the elution method of g.l.c. for the determination of γ_{13}^{∞} values is by far the most popular of the elution methods of g.l.c. and has been discussed by various workers.(70*b*,236,239,247,249) The factors affecting the retention time of the solute are numerous and include: *(i)* the choice and amount of solvent stationary phase, *(ii)* the carrier gas and flow rate, *(iii)* the temperature, *(iv)* the pressure, *(v)* the solute sample size, and *(vi)* the nature of the sample.(329) Gas-liquid chromatography offers several advantages for the study of physiocohemical phenomena over classical techniques. In general the relative simplicity associated with the experimental technique and the apparatus, and the advantage associated with the requirement that the small sample sizes required need only be of moderate purity, makes this technique most attractive for measuring γ_{13}^{∞} directly(239) The g.l.c. method is also more rapid than classical methods, but is however generally limited to systems involving volatile solutes and relatively involatile solvents.

The elution technique of g.l.c. has been used in this work for the determination of γ_{13}^{∞} values at 278.15 K, 288.15 K, and 298.15 K for an *n*-alkane, a 1-alkene, a 1-alkyne, a cycloalkane, cyclohexene, a cycloalkadiene, or benzene in a bicyclic compound solvent.

3.4 Apparatus and experimental details

The initial aim of this investigation was to construct a medium pressure gas-liquid chromatograph which would enable the measurement of both activity coefficients at infinite dilution as well as the determination of mixed second virial coefficients. Preliminary investigations, however, demonstrated significant solvent losses from the chromatographic column. At a temperature of 298 K and a flow rate of ± 75 ml.min.$^{-1}$, losses of up to 10% were observed for the solvent decalin after a period of 3-4 hours of operation. The relatively long times required for obtaining results by this experimental method would have necessitated the use of column presaturators in an attempt to reduce these solvent losses. With the result, an atmospheric pressure gas-liquid chromatograph was constructed for this work. Although B_{12} values could not be measured, this apparatus had the advantage that the measurements for a whole series of experimental runs with 11 solutes for each solvent could easily be accomplished in a relatively short time.

The different methods for monitoring solvent losses from the column and the adjustment of the mass of solvent on the column have already been discussed in Section 3.3.6. No reliable γ_{13}^{∞} values for any solute in any of the solvents used in this work were available in the literature and hence the method which involves monitoring the retention time of a sample of known activity coefficient and relating the change in γ_{13}^{∞} to the solvent losses to monitor solvent masses on the column, had to be modified. In this work, cyclohexane and *n*-hexane were employed to monitor the column loadings throughout each run. These two solutes were injected at least 5 times at the start of a run, and then before and after each solute or solute mixture. Plots of the retention time for these monitors versus time elapse, t, from the commencement of an experimental run were made. The graphs were extrapolated to the original time of start-up of gas flow, enabling the determination of the column loading as a function of time. A typical graph for such a run is shown in Figure 3.4. This particular example is for the solute *n*-hexane in a decalin solvent, at a column temperature of 278.15 K. The initial mass of the stationary phase on the column was determined assuming the initial extrapolated retention time to be correct.

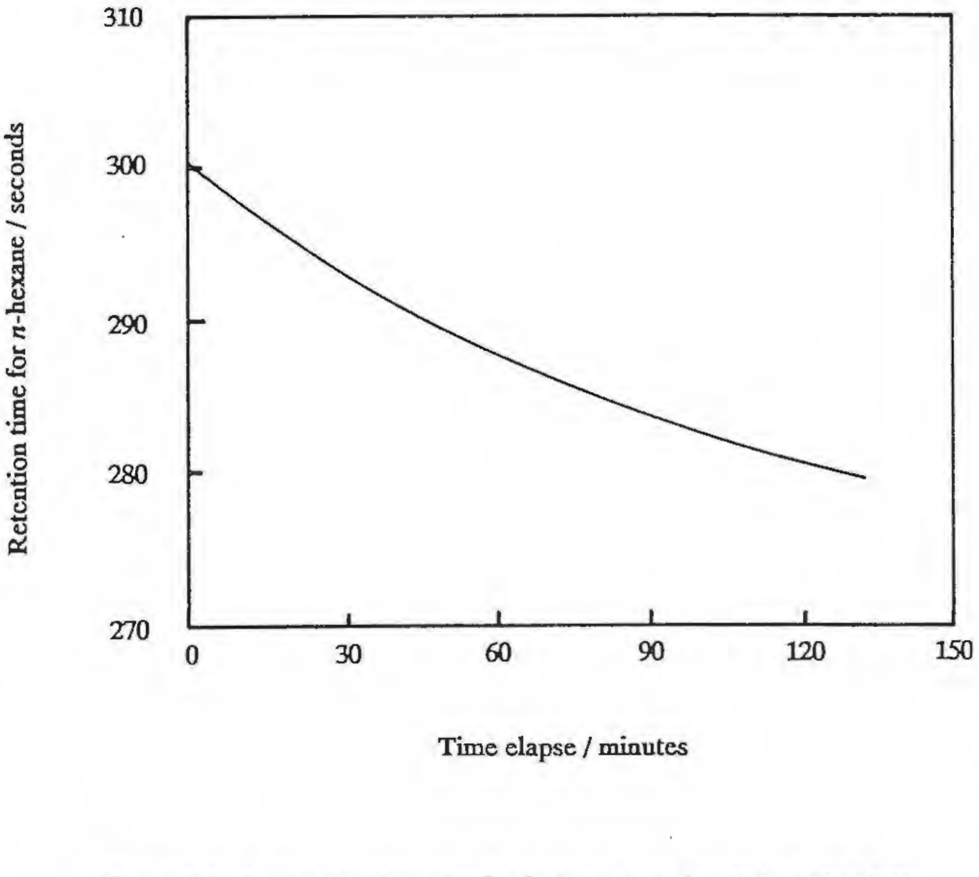

Figure 3.4 A retention time plot for {*n*-hexane + decalin} at 278.15 K

A diagrammatic representation of the g.l.c. apparatus is shown in Figure 3.5. The apparatus comprises a flowmeter, a sample introduction system, a packed column, a detector, a wide bore mercury monometer for pressure measurement, and a water bath for column temperature control. Conder and Young(239) have discussed apparatus contributions to the theoretical plate height and to band spreading. Areas such as the detector, injector, connecting tubing and fittings are particularly prone to enhancing band spreading effects. The apparatus used in this work was designed so as to reduce the unwanted dead spaces. Detector and recorder time constants were considered negligible in relation to the retention times observed.

A detailed discussion of the apparatus and the experimental prodecure is given below.

3.4.1 Columns

Stainless steel columns, as opposed to glass or copper columns, of 5mm bore were used. The columns of this material had the advantage over the more inert glass type in that they could be packed while straight and could then be deformed into coils, thus making it easy to accommodate the entire column in the water bath. The stainless steel columns are more inert than copper, while the heat transfer properties of metal columns are considered to be superior to glass columns.(284) The column lengths were dictated by the retention times of the solutes, and ranged from 1.0 to 1.8 metres.

3.4.2 Preparation of phase

Phase preparation techniques have been discussed by several workers.(239,247,252,287) According to Young(247) the most successful method is the method outlined by Purnell,(330) which is sometimes referred to as the "wet" or slurry method. A slurry comprising the solid support and stationary phase column solvent, with sufficient suitable inert volatile solvent to dissolve the column solvent and totally cover the solid support, is made up in a suitable container. Mixing is achieved by swirling the container and its contents. Mechanical stirrers are not employed for fear of resulting in the breakdown of the solid support. The inert volatile solvent can be removed through evaporation by gently warming in an oven or by boiling under vacuum. In this method however, due care must be taken not to lose any liquid stationary phase through bumping when evaporating. A problem sometimes encountered with this method during the evaporation process

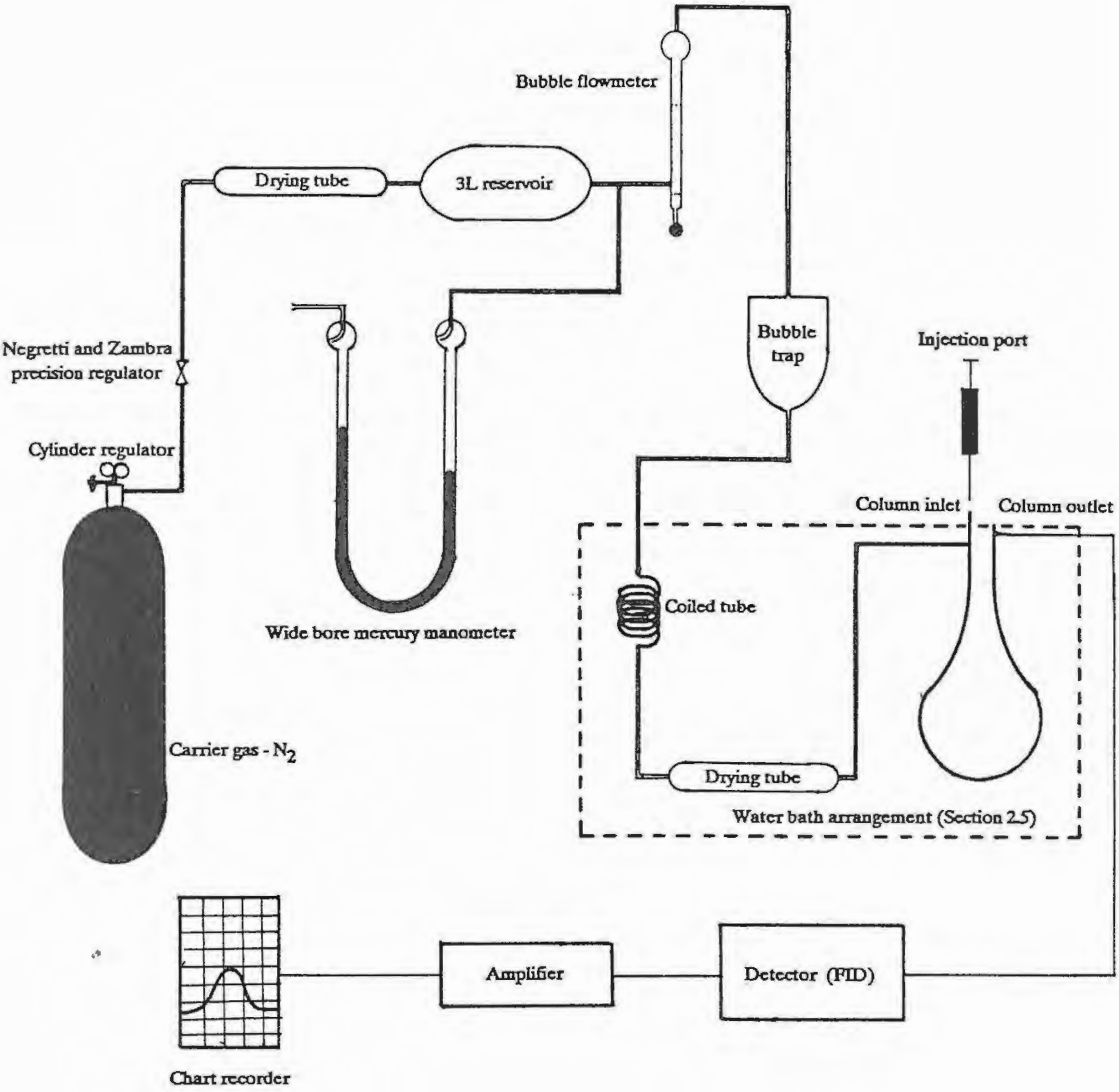

Figure 3.5 A diagrammatic representation of the g.l.c. apparatus

concerns liquid stationary phase which has condensed on the walls of the container. After evaporation of the inert solvent, some of the liquid stationary phase may remain on the wall. Conder and Young(239) overcome this problem by removing the inert solvent through a gas entrainment process.

An alternative method(249) known as the "dry" method involves mechanically shaking the liquid stationary phase and solid support in a suitable stoppered flask. In this way the solid support is coated with stationary phase. This method is much quicker, but may result in a reduction in size of the solid support particles (celite in this work). Naturally this method can only be used when the column stationary phase solvent is a liquid at the temperature at which the column is packed.

All the column solvents were liquids at the temperatures under consideration in this investigation. Preliminary investigations indicated that both coating methods yielding similar results for γ_{13}^{∞} for several hydrocarbon solutes in the four bicyclic compound solvents. Because the "dry" method was by far the easier of the two methods, this method was more popular in this work. Gentle shaking of the flask and its contents for 30 minutes was sufficient to achieve complete coating of the stationary phase. It was felt that shaking for longer would damage the solid support. As a check against liquid stationary phase losses during the coating process, the mass of the container and its contents were compared before and after shaking. Column loadings of ±12% were employed; above this value the retention times tended to become too long.

3.4.3 Solid support

Although non-polar solutes were employed in this investigation the importance of ensuring a relatively inactive solid support still remained. Celite supplied by BDH with a particle size of 80 - 100 mesh was used in this work. The retention times of the solutes measured on a column packed with uncoated solid support were negligible when compared to those retention times observed for columns packed with a similar amount of coated stationary phase, thus ensuring negligible adsorption effect.

3.4.4 Column packing

Cleaning of the unpacked solumns constituted an important part of the column preparation process. The straight empty columns were first flushed with hot water for 10 minutes. This was followed by ramrodding suitable solvent impregnated cotton wool plugs through the length of the column and finally by flushing with acetone. Drying was achieved by passing compressed air and then nitrogen through the column.

The numerous column packing procedures have been reviewed in the literature.(239,250) In this work, the stationary phase was added via a clean tared glass funnel attached to the open end of a column by a short length of teflon tubing. The opposite end of the column was stoppered with a glass wool plug. Continuous tapping of the column along its length, and on the laboratory floor, throughout the filling process, ensured uniform packing. Prolonged excessive tapping of the column, which could lead to disintegration of the solid support,(330) was avoided. The funnel was covered with a sheet of aluminium foil during the tapping process, thus minimizing the possibility of losses of the column packing through spillages. After packing this end of the column was also plugged with glass wool. Care was taken to ensure that excessive pressure was not applied when inserting the glass wool plug, as crushed packing could lead to a blockage of the gas flow. The columns were packed so that the glass wool plugs were situated as close to the ends of the columns as possible, thus minimizing the dead space. The packed columns were coiled with due care taken to prevent "kinking". The coiled columns could thus be accommodated in the water bath.

The mass of stationary phase and celite on the column corresponded to the difference in container masses before and after filling. Any packing which may have adhered to the funnel or to the connecting tube was accounted for in this calculation. The mass of solvent on the column was calculated from the mass and the percent of stationary phase on the support. All mass reading were carried out on a 5 figure Mettler H20 analytical balance, accurate to 0.01mg. Column loadings of up to ±12% were used in this work; above this value the retention times tended to become too long.

The effect of different column loadings on the measured activity coefficients at infinite dilution was investigated for the systems under consideration. No significant difference in the measured γ_{13}^{∞} values were observed for column loadings between 7 and 18%.

As already noted, non-uniform packing affects the retention times of the solutes through the resulting pressure variations along the column. This phenomenon is generally indicated by a difference in retention times between forwards and reversed column determinations. In this work, any large discrepances between forward and reversed column measurements led to the rejection of the column.(250)

3.4.5 Temperature control and measurement

Purnell(330) has indicated that in the extreme case, a 1 K variation of the column temperature may alter the retention time by ±5%. Conder and Young(239) have suggested that the temperature fluctuations should be controlled to ±0.05 K while Letcher(70*b*) has advised that temperature control to within 0.01 K is required for the accurate determination of γ_{13}^{∞} values. The column can be thermostatted within these limits through use of either a liquid bath or a stirred air bath.(236,239) Vapour jackets are usually unsuitable since they give inadequate constancy of temperature for the thermostatting of large areas.(239) The simple constructional and operational advantages of a liquid bath over an air thermostat dictated the use of this method.

Column temperature control was achieved by immersing the coiled column in a thermostatically controlled water bath of dimensions 500 x 500 x 500 mm, similar to the arrangement discussed in Section 2.5.2.*(ii)*. Sufficient stirring of the water bath was achieved through two mechanical stirrers. Temperature control of the bath to within ±0.004K was easily maintained.

3.4.6 Carrier gas

Carrier gases should ideally not interact with the solute in the gas phase, nor should they be sorbed into or onto the stationary phase. For the permanent gases such as nitrogen, helium, argon, and hydrogen, gas-phase interactions are small and necessitate the inclusion of gas-phase imperfection corrections in γ_{13}^{∞} determinations.(239) Most carrier gas adsorption on the stationary phase are negligible at pressures of less than a few atmospheres and hence the carrier gas solubility need only be considered when higher pressure variations are made.(239)

The choice of the carrier gas is also governed by the method of detection employed. For example hydrogen and helium both have higher thermal conductivites and lower densities than nitrogen and hence both result in better detector response when a katharometer is used.(239) Gases such as argon or carbon dioxide often possess thermal conductivities which fall in the middle of the range occupied by the more commonly occuring organic substances.(234) In addition, external factors such as cost, availablity and safety need to be observed when the choice of carrier gas is made.

In this work the cost of the carrier gas and the safety hazard associated with hydrogen dictated the use of medically pure nitrogen as carrier gas. The carrier gas was sufficiently inert and did not contribute to background noise. A two meter coiled stainless steel tube of 5 mm bore was immersed in the water bath before the column inlet. This ensured the temperature equilibration of the carrier gas on entering the g.l.c. column. A drying tube packed with molecular sieve and silica gel indicator, which was placed within the carrier gas line after the pressure regulator, ensured that any possible water vapour within the carrier gas was removed. A second similar drying tube placed between the 2 meter coiled equilibration column and the g.l.c. column served to remove any water vapour from the carrier gas which may have condensed at the temperatures of the water bath.

The apparatus was continually checked for leaks by spraying a soapy solution on all the joints.

3.4.7 Flow rate measurement

The simple soap-film flowmeter is considered to be the best instrument for the measurement of gas flow rates in the region 1-1000 ml.min^{-1}. Simplicity of use and ease of manufacture, coupled with a precision of better than 0.5%, make this instrument attractive for use in gas flow rate measurements. Other methods of flow rate measurement are discussed in the literature.(70*b*,239,284)

A simple soap film flowmeter was used in this work. The instrument consisted of a 50.0 cm^3 graduated and calibrated burette and a deformable rubber soap solution reservoir in the place of the burette tap. A soap bubble trap consisting of a large glass bulb was attached to the other end of the burette. This arrangement served to break the bubbles before they entered the carrier gas line. The time taken for the soap bubble to travel the graduated portion of the tube was measured using a precision stop watch. It was possible to achieve a consistent flow time over four or more measurements of within 0.05 seconds, or a reproducibility of better than 0.2%. Care was taken to ensure that the glass column was completely wet before any measurements were made, since the dry glass walls of the instrument led to unreproducible flow rate measurements.

The flowmeter was calibrated using water. The mass of the water contained between the end graduations was measured and the corresponding volume was determined from the density of water. The calibration was carried out five times with a reproducibility of better than 0.1%. The flowmeter was calibrated at 296K. The insignificantly small temperature fluctuations in the laboratory did not necessitate the calibration at other temperatures or the thermostatting of the flowmeter. A 3 L glass reservoir placed before the flowmeter further ensured temperature equilibration of the carrier gas entering the flowmeter.

The flowmeter was fitted upstream of the injector and the column. This was done because a flame ionization detector was used in this work. Two reservoirs were included downstream of the flowmeter but before the column and injector arrangement. The first was a felt trap to retain any soap bubbles and the second contained silica gel to remove water vapour from the carrier gas which may have been introduced from the soap bubbles.

Since the equations given in the previous Section 3.3.2 require carrier gas flow rates measured at the column outlet, the flow rates measured at the column inlet, U_i, needed to be adjusted to outlet flow rates, U_o. These were calculated from an approximate equation of state of carrier gas:(70*b*,239,258)

$$U_o = U_i[\{p_i RT + p_i p_o B_{22}(T)\}/\{p_o RT + p_i p_o B_{22}(T_f)\}] \qquad 3.38$$

where T_f is the temperature of the flowmeter and B_{22} is the second virial coefficient of the carrier gas.

A correction factor for incomplete carrier saturation by the water vapour at the temperature of the flowmeter was also necessary:

$$U_i = (50.0/t)[(p_i - p_w)/p_i](T/T_f) \qquad 3.39$$

where p_w is the vapour pressure of water at the temperature T_f, T is the temperature of the column, and *t* is the time taken for the soap bubble to traverse the graduated portion of the flowmeter. The average flow rates employed in this work were of the order of 60-100 $cm^3.min^{-1}$.

3.4.8 Pressure control and measurement

The different methods of measuring pressure differences have been dealt with in the literature.(70*b*,236,239) In this investigation the column inlet pressure was recorded by difference using a wide bore (20 mm *i.d.*) mercury manometer placed in the carrier gas flow line before the column inlet. One end of the manometer was open to the atmosphere. The atmospheric pressure was determined with a standard laboratory barometer. A brass precision cathetometer capable of reading to 0.002 mm was employed in the measurement of the mercury height differences in opposing limbs of the manometer. Care was taken to ensure that the manometer and cathetometer were set up vertically. Mercury meniscus height corrections due to gravitational and temperature effects were small, and were not considered.

A variety of pressure control systems have been described in the literature.(236,239,289) The flow of carrier gas was controlled by a Harris high pressure reducing valve attached to the cylinder and a Negretti and Zambra precision air regulating valve placed within the flow line. Ambient temperature fluctuations were too small to warrant the thermostatting of the latter valve. In a detailed discussion of a similar valve by Goedert and Guichon,(331) the outlet pressure was found to be seriously affected by the reference pressure. In the investigation reported in this thesis a high reference pressure was always maintained to prevent pressure surging and consequently hysteresis effects of the diaphgram of the Negretti and Zambra pressure regulator. The result was a pressure control in the flow line to better than 0.1 mmHg over a period of a few hours. The gas flow line was made of 6 mm stainless steel tubing.

3.4.9 Sample size, sample injection and retention time measurement

The main requirements of a sample introduction system are that it should have a small dead volume and should not interrupt the flow rate. The manner in which the sample is introduced onto the column is important, since it influences the shapes of the eluted peaks. It is desirable to introduce the sample as a defined plug(284) which reduces the width of the peak entering the column and thus limits the possibility of band spreading.

Various methods of sample introduction have been discussed in the literature.(236,239,284) In g.l.c. equipment of the type employed in this investigation, sample introduction with a microsyringe through a self-sealing septum has become the standard procedure and was employed here. Liquid samples were injected directly and rapidly onto the column using a 1.0 μL microsyringe with 0.1 μL graduations. The silicone rubber septa could easily withstand the relatively low pressures on the column. They had a lifespan of approximately 50 piercings.

Conder and Young(239) have suggested that the sample size for infinite dilution studies should be of the order of 0.1μL. Sample volumes of up to 0.7μl were however found to have little effect on the γ_{13}^{∞} values measured in this work. Sample sizes of the order of 0.1μL were used in this study and relatively symmetrical peaks were obtained for all the solutes investigated here.

Because several solutes were studied on each column, it was decided to investigate the effect of injecting several solutes simultaneously, rather than singly. The solutes chosen for combination as a mixture differed sufficiently in retention time to allow for complete resolution of each peak. In this work it was found that the retention volumes for a maximum of five solutes injected as a mixture did not vary from those injected as pure components.

The retention volume required in the determination of γ_{13}^{∞} is derived from measurements on the chromatogram and so depends on the correct interpretation of the concentration profile of the eluted solute. There is little doubt as to what the retention time for a symmetrical peak is. However, the retention time for unsymmetrical peaks has long been a source of contention. Conder and Young(239) consider three factors controlling peak shape: *(i)* non-linearity and other concentration dependent partitioning effects, *(ii)* non-ideality, and *(iii)* extra column effects such as dead volumes. Hicks(260) and Conder and Young(239) have considered these effects in detail. The actual peak shape may be characterized in several ways, the most common being the skew ratio, η. It has been suggested that η should lie between 0.8 and 1.2 for accurate determinations of physicochemical quantities.(236,239)

An example of a chromatogram exhibiting a slightly skewed profile is given in Figure 3.6. Peak properties corresponding to this profile are summarized in Table 3.1. Early workers(332,333) advocated the use of the peak initial time, t_i, in their calculations of activity coefficients, since it was this value which gave the best agreement with results determined by static methods and g.l.c. The value, t_i, corresponds to the point of intersection of the tangent drawn through the point of inflection for the leading edge of the peak profile, with the baseline. Retention times somewhere near the peak of the profile are a much more obvious choice and for a symmetrical peak the point t_m may be used. For slightly unsymmetrical peaks, the peak tangent time, t_t, which corresponds to the point of intersection of the two tangents through the points of inflection of the leading and trailing edges of the profile has been suggested as a measure of the solute retention time.(260)

Hicks(260,290) regards the difusion of solute in the liquid phase to be the rate determining step for equilibration and has shown that the peak average retention time, t_{if}, can be used in the determination of thermodynamic properties. He has supported this by showing that the flow rate dependence of retention times for mixtures of benzene with glycerol disappears if t_{if} rather than t_t is used.

Although the peak profiles obtained in this work were all within the skew rates of 0.8 to 1.2 advocated by Conder and Young,(239) peak average retention times, t_{if}, rather than peak maxima, t_m, were used. These peak average values correspond to the arithmetic mean of t_i and t_f and, although perhaps not as good as the values obtained by the first moments approach where the retention time depends on the location of the mass centre of the peak, they have the advantage that they can be obtained without the use of any elaborate equipment.

Various methods for the timing of peak profiles have been advocated, the simplest of which relies on a constant recorder speed.(239) Retention times can thus be determined from the simple relationship:

$$t_R = D_L C_S \qquad 3.40$$

where D_L corresponds to the distance as measured from the point of injection to the peak profile and C_s is the chart speed in units of distance.second^{-1}.

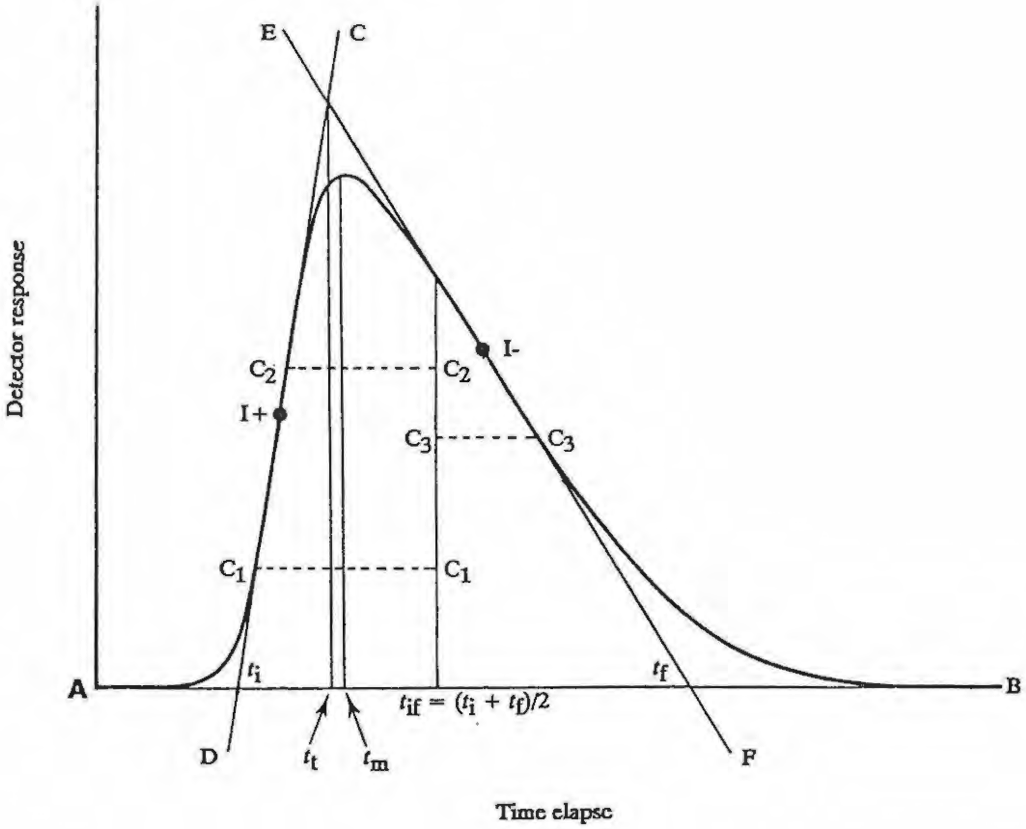

Figure 3.6 A slightly asymmetrical peak profile

Table 3.1 Peak properties corresponding to Figure 3.6

Symbol	Term	Definition
t_i	peak initial time	intersection of tangent, CD, through point of inflection, I+, with the baseline AB.
t_f	peak final time	intersection of tangent, EF, through point of inflection, I-, with the baseline AB.
t_m	peak maximum	net time of peak maximum
t_t	peak tangent	net time of the intersection of the tangents CD and EF
t_{if}	peak average	arithmetic mean of t_i and t_f

Because of paper stretching and mains frequency fluctuations, which could alter the drive rate of the chart recorder motor, it was felt that measurement of retention times by the above method would be unsuitable. In this work a calibrated stopwatch capable of readings accurate to 0.01 seconds was used to measure the time elapse between sample injection and arbitrary points, C_i, on the peak profile (see Figure 3.6). Distances C_iC_i' on the profile were accurately measured using a steel ruler and the retention times corresponding to the points Ci on the profile could be adjusted to the actual value corresponding to the peak average retention times, t_{if}, in Figure 3.6. The average of these values was taken as the unadjusted retention time, t_R, for the particular solute.

3.4.10 Sample detection

Numerous review articles and texts in the literature deal with gas chromatographic detectors.(70*b*,234,239,250,252,334,335) Design considerations such as dead volume and high sensitivity have been adequately considered in the literature and need little comment here. Preliminary investigations were carried out with both a flame ionization detector (FID) and a Katharometer mode of detection. The stationary phase solvent which had bled off the column tended to coat the electrodes of the FID and the filaments of the katharometer after a few days usage, thus reducing the sensitivites of both these detectors and also resulting in unstable baselines. Since the FID was easier to clean than the Katharometer, this mode of detection was rather employed. Both detectors gave similar results however.

The FID was manufactured by GO-MAC and is represented diagrammatically in Figure 3.7. The principle of operation is based on the ionization of the components of the eluent. This is achieved by mixing the eluent emerging from the column with hydrogen and then burning the resultant mixture in air at a platinum jet. A potential difference between the jet and a cylindrical electrode positioned directly above the jet ensures that the ions produced are collected on the cylindrical electrode. The advantages of this detector are its robustness, high sensitivity and lack of response to permanent gases. Water cannot be detected. In addition the FID is unaffected by small temperature changes.

The sensitivity of the FID was observed to be a function of the size of the flame. The best signal to noise ratios were achieved when the oxygen and hydrogen flow rates were just above the minimum required to maintain combustion of the flame. These flow rates

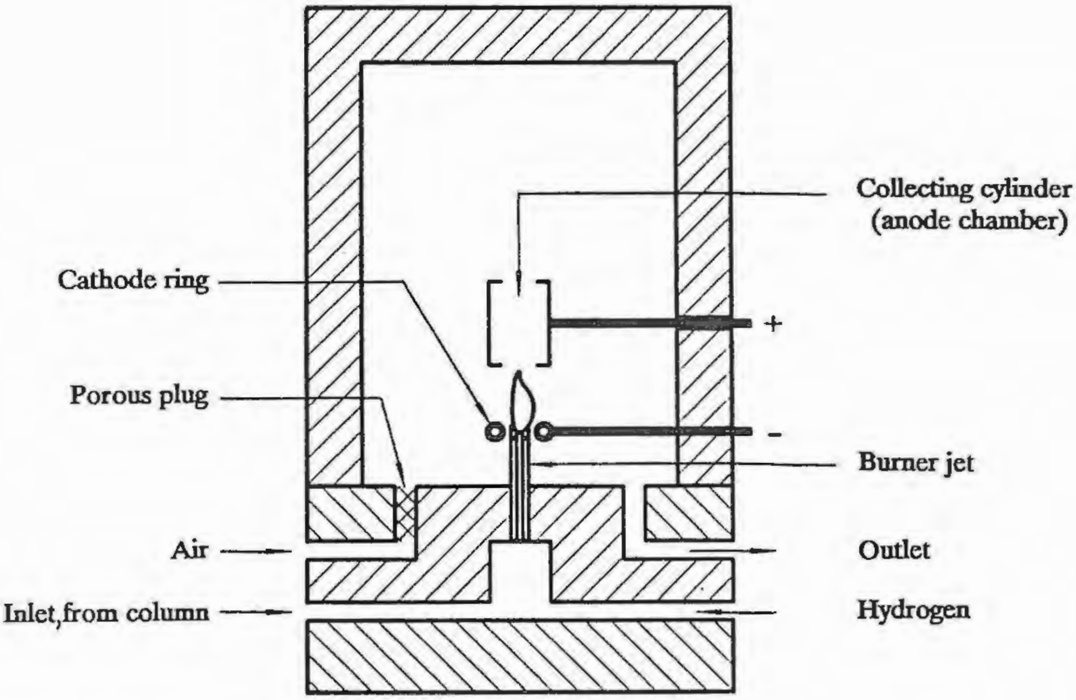

Figure 3.7 A diagrammatic representation of an FID

corresponded to 30 $cm^3.min.^{-1}$ and 50 $cm^{-3}.min.^{-1}$ for hydrogen and air respectively. A small glow-plug facilitated flame ignition, after which approximately 3 minutes warm-up time was required before readings were made. Periodic cleaning of the jet and electrode of the FID with emery paper ensured high sensitivity to eluted samples. Output signals from the FID were amplified before being sent to the Perkin-Elmer 561 chart recorder.

3.4.11 Dead volume determination

Laub and Pecsok(236) have mentioned several methods for determining the dead space. Dead volumes, V_G, were calculated in this investigation from the retention times, t_g, of methane gas on the packed column:

$$V_G = (U_o t_g)/J_2^3 \qquad 3.41$$

The methane gas samples of roughly 20 μL were injected onto the column using a 100μl gas-tight syringe. The value, V_G, was found to be independent of the flow rates used.

3.4.12 General experimental procedure

In order to verify the experimental technique, activity coefficients at infinite dilution were determined for benzene, *n*-hexane and cyclohexane solutes in *n*-hexadecane. These values all agreed to within ±0.005 of the literature values.(297,303,336)

Activity coefficient at infinite dilution were determined at 278.15 K, 288.15 K and 298.15 K for the solutes *n*-hexane, 1-hexene, 1-hexyne, *n*-heptane, 1-heptene, 1-heptyne, cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene and benzene in the solvents decalin, bicyclohexyl, tetralin and cyclohexylbenzene. At least three retention times for each solute were determined for each experimental run at a particular column loading and flow rate. Determinations for at least three different column loadings ranging from 8 - 12% were carried out at different flow rates for each of the four solvents at each temperature. Averages for a solute in a particular solvent at a given temperature were determined. The results were determined using equations 3.30 and 3.31, where β was given by equation 3.32 and the retention values were determined from equation 3.28. The necessary corrections for the outlet flow rate and water vapour saturation of the carrier gas were carried out using equations 3.38 and 3.39. A computer programme was written to calculate the results and is included in Appendix F.

Only results for the decalin solvent have been reported previously. These were for the solutes cyclohexane: γ_{13}^{∞} = 1.06, benzene: γ_{13}^{∞} = 1.47, 2-methyl-2-butene: γ_{13}^{∞} = 1.21, and 2-methyl-1,3-butadiene: γ_{13}^{∞} = -1.34, by Vernier *et al.*(337) using g.l.c techniques. Values determined for *n*-hexane by Vernier *et al.*(337) by g.l.c. and by Leroi *et al.*(338) using a dilutor technique are both equal to 1.26. These results were reported at 298.15 K without gas phase corrections.

3.4.13 Ancillary data requirements

Vapour pressures for 1-hexyne and 1-heptyne were determined experimentally by a method discussed in Appendix D. The values of p_1 for all the hydrocarbons used in this work were calculated from the coefficients of the Antoine equation and are given in Table 3.2. The values for V_1^o and V_3 were calculated from the densities given in Table 3.3.

In some cases second virial coefficients were unobtainable from the literature and were thus predicted. These values can be predicted by two methods:(236) *(i)* from a knowledge of the intermolecular potential, and *(ii)* through the principle of corresponding states. The McGlashan and Potter(340) equation of state is an example of the second theoretical approach and has been shown to apply to a wide range of hydrocarbons and permanent gases. This equation was employed to determine B_{11} and B_{12} for all the compounds studied. B_{12} is given by:

$$\begin{aligned} B/V^c = {} & 0.430 - 0.886(T^c/T) - 0.694(T^c/T)^2 \\ & - 0.0375(n - 1)(T^c/T)^{4/5} \end{aligned} \qquad 3.42$$

where V^c and T^c are the critical volumes and the critical temperatures of the pure substances. For permanent gases, $n = 1$, and can be estimated for other compounds.(340) The critical constants V^c and T^c for the pure components together with values for n are listed in Table 3.4. The calculated and the literature values for B_{11} at 298.15 K are listed in Table 3.5. The calculated results are all within 10% of the literature values.

Hudson and McCoubrey(344) have shown that a combining rule for T_{11}^c and T_{22}^c to give T_{12}^c requires a correction for the differences in ionization potential and collision parameters of the unlike molecules. Their proposed equation relates the mixed critical temperature, T_{12}^c, to the ionization potentials, I, of the pure components through:

$$T_{12}^c = \frac{\{2^7(T_{11}^cT_{22}^c)^{1/2}(I_1I_2)^{1/2}V_{11}^cV_{22}^c\}}{(I_1 + I_2)[(V_{11}^c)^{1/3} + (V_{22}^c)^{1/3}]^6} \qquad 3.43$$

Equation 3.43 was employed in this work as an alternative to the Berthelot form:(341)

$$T_{12}^c = (T_{11}^cT_{22}^c)^{1/2} \qquad 3.44$$

Equation 3.43 was observed to produce results for B_{12} which were in better agreement with available literature values. This is in agreement with work by Cruickshank *et al.*(341) who noted that use of equation 3.44 is generally only valid for components which are similar in size.

The mixed critical volumes were calculated using the Lorentz combining rule:(341)

$$V_{12}{}^{c} = (1/8)[(V_{11}{}^{c})^{1/3} + (V_{22}{}^{c})^{1/3}]^{6} \qquad 3.45$$

Values of n for the mixture correspond to the arithmetic mean of those values for the pure components:(341)

$$n_{12} = (n_{11} + n_{22})^{1/2} \qquad 3.46$$

The values of the ionization potential, I, for the solutes and for the nitrogen carrier gas are also included in Table 3.4. The mixed second virial coefficients at 298.15 K for all the solutes are given in Table 3.6. Once again the calculated and literature values are within 10% of each other.

Literature values for B_{11} and B_{12} were used when available in preference to calculated values. The experimentally determined γ_{13}^{∞} values at 278.15 K, 288.15 K and 298.15 K are listed in Table 5.1.

3.5 Estimated accuracy of activity coefficients

A comparison between γ_{13}^{∞} values determined by g.l.c. and by non-g.l.c. has been made in a previous section and in the literature. General views on the accuracy of activity coefficients at infinite dilution by g.l.c. vary. Laub and Pecsok(236) regard the volume of liquid stationary phase as constituting the largest possible source of random error in the determination of γ_{13}^{∞}. Other sources such as the retention time measurements are considered trivial by comparison. Conder and Young(239) agree with this. The above was verified in this work. For the system {benzene + decalin} at 278.15 K a variation of 1% in the number of moles of solvent on the column, corresponding to about 2.7×10^{-5} moles of decalin, produced a 1% change in the calculated γ_{13}^{∞}. For the same system at 288 K and for an 8% column loading, a variation in the retention time or dead time of one second, which corresponded to a 0.5% variation in the retention time, resulted in a change in γ_{13}^{∞} of 0.008 or 0.5%. A 0.2 second change in the flow rate affected γ_{13}^{∞} by $\pm$0.005. Column temperature variations of 0.1 K affected γ_{13}^{∞} by 0.007.

The measured γ_{13}^{∞} were also found to be very dependent on the solute vapour pressure. Varying the vapour pressure of the solutes by about 1% resulted in a variation in the measured γ_{13}^{∞} of between 0.005 and 0.015.

The γ_{13}^{∞} were less sensitive to variations in some of the other parameters. A variation corresponding to a 1 mmHg change in the outlet pressure only resulted in a change in γ_{13}^{∞} of less than 0.0003. The activity coefficients were even less sensitive to changes in the solute virial coefficient, where a change in B_{11} of 5-10% generally resulted in variations in the γ_{13}^{∞} value of less than 1%. Neglect of carrier solubilities lead to appreciable errors in g_{13}.

Recent studies(236,239) indicate that 0.5-3.0% are realistic figures for the accuracy of γ_{13}^{∞} results measured by g.l.c. The uncertainty in γ_{13}^{∞} values determined in this work is estimated to lie between $\pm$0.006 and $\pm$0.009, which corresponds to an error of $\pm$1% in the smallest value measured.

Table 3.2 Coefficients for the equation:

$$\log_{10} p^{a} = A - B/(C + T^{b} - 273.15)$$

Hydrocarbon	A	B	C	Reference
n-hexane	6.8760	1171.17	224.41	207*c*
1-hexene	6.8657	1148.62	225.85	207*d*
1-hexyne	6.6789	1042.62	225.85	This work
n-heptane	6.8968	1264.90	216.54	207*e*
1-heptene	6.9007	1257.34	219.30	207*f*
1-heptyne	7.3013	1382.48	217.94	This work
cyclohexane	6.8453	1206.47	223.46	339
cyclohexene	6.9088	1228.64	222.51	This work
1,3-cyclohexadiene	7.0673	1323.28	235.60	300
1,4-cyclohexadiene	6.9171	1273.92	225.36	This work
benzene	6.9057	1211.03	220.79	207*g*

[a]Units: mmHg. [b]Units: K.

Table 3.3 Coefficients for the density equation:

$$\rho^{a} = D + E(T^{b} - 273.15) + F(T^{b} - 273.15)^{2} + G(T^{b} - 273.15)^{3}$$

Hydrocarbon	ρ	$-10^{3}E$	$-10^{5}F$	$10^{7}G$	Reference
n-hexane	0.6771	0.885	-0.031	-0.046	207*h*
1-hexene	0.6920	0.935	-0.042	-0.056	207*i*
1-hexyne	0.7419	1.564	1.107	0.338	This work
n-heptane	0.7006	0.874	0.566	-1.092	207*j*
1-heptene	0.7146	0.876	-0.021	0.019	207*i*
1-heptyne	0.7694	1.461	0.548	1.185	This work
cyclohexane	0.7970	0.907	-0.058	–	207*k*
cyclohexene	0.8317	1.225	1.461	-2.453	This work
1.3-cyclohexadiene	0.8862	2.990	4.741	–	This work
1,4-cyclohexadiene	0.8669	0.013	-3.421	3.800	This work
benzene	0.8999	1.040	-0.042	-0.004	207*l*
decalin	0.9019	0.799	0.105	–	This work
bicyclohexyl	0.9043	0.675	-0.083	–	This work
tetralin	0.9804	5.948	-0.243	–	This work
cyclohexylbenzene	0.9507	0.265	-0.903	–	This work

[a]Units: $g.cm^{-3}$. [b]Units: K

Table 3.4 Critical constants and ionization potentials for nitrogen and for the hydrocarbons used in this work

Substance	T^c K	Reference	V $\mathrm{cm^3.mol^{-1}}$	Reference	I eV	Reference	n^a estimated
nitrogen	126.2	341	84.6	341	15.51	341	1
n-hexane	507.3	207*n*	370.0	207*n*	10.48	342	6
1-hexene	504.0	207*m*	354.0	207*m*	9.59	343	6
1-hexyne	534.0	estimated	337.0	estimated	10.30	estimated	4.5
n-heptane	540.2	341	426.0	341	10.35	341	7
1-heptene	537.3	207*m*	413.0	207*m*	9.46	estimated	7
1-heptyne	567.3	estimated	395.0	estimated	10.16	estimated	4.5
cyclohexane	553.5	207*l*	309.7	207*l*	291.7	estimated	4.5
cyclohexene	559.3	207	291.7	estimated	8.72	344	4.5
1.3-cyclohexadiene	565.3	estimated	278.0	estimated	8.03	estimated	4.5
1.4-cyclohexadiene	565.3	estimated	278.0	estimated	8.03	estimated	4.5
benzene	562.2	341	260.4	341	9.24	341	4.5

[a] Reference 340

Table 3.5 Second virial coefficients, B_{11}, at 298.15 K. The literature (experimental) values can be compared with the calculated values from the McGlashan-Potter equation

Substance	$-B_{11}{}^{a}$ (literature)	Reference	$-B_{11}{}^{a}$ (calculated)
nitrogen	5	345	-
n-hexane	1962	345	1901
1-hexene	1752	346	1785
1-hexyne	-	-	1750
n-heptane	2719	345	2862
1-heptene	2412	356	2728
1-heptyne	-	-	2426
cyclohexane	1733	345	1775
cyclohexene	-	-	1721
1,3-cyclohexadiene	-	-	1690
1,4-cyclohexadiene	-	-	1690
benzene	1479	343	1560

[a] Units: $cm^3.mol^{-1}$

Table 3.6 Mixed second virial coefficients, B_{12}, for (nitrogen + a hydrocarbon) at 298.15 K. The literature (experimental) values can be compared to the calculated values obtained from the McGlashan-Potter equation and the Hudson-McCoubrey combining rules

Hydrocarbon	$-B_{12}{}^{a}$ (literature)	Reference	$-B_{12}{}^{a}$ (calculated)
n-hexane	110	258	108
1-hexene	117	289	105
1-hexyne	-	-	112
n-heptane	128	346	118
1-heptene	124	346	112
1-heptyne	-	-	119
cyclohexane	117	346	117
cyclohexene	-	-	112
1,3-cyclohexadiene	-	-	104
1,4-cyclohexadiene	-	-	104
benzene	113	346	113

[a] Units: $cm^3.mol^{-1}$

CHAPTER 4

THEORIES OF NON-ELECTROLYTE SOLUTIONS

4.1 Introduction - background to the Flory theory

The development of a general theory of solutions suitable for the prediction and interpretation of the thermodynamic properties of non-electrolyte mixtures from the properties of the individual pure components has been the subject of much research.(52) In addition to the requirement that such a theory be universal in its application, considerations concerning the availability of experimental data and the simplicity of the theoretical equations are factors contributing to the overall success of any theory.

Theories of liquid mixtures have been discussed in the literature.(1,52,115,347-349) van Laar(349) in 1906 was the first worker to treat the changes in the entropy or in the enthalpy when two liquids are mixed. He based his work on the van der Waals equation of state and assumed no volume changes on mixing. The treatment of liquid solutions has historically been dominated by theories only applicable to mixtures of molecules equivalent in size and in shape.(347) The effects of molecular size differences on the equilibrium properties of a solution were first considered by Huckel(350) in 1936, while the effect of differences in sizes of molecules from a thermodynamic view were discussed by Guggenheim(351) in 1937. Theoreticians have since come to appreciate the need to depart from the classical concept which considers a molecule as being spherical and have extended theories to account for molecular features present in "real" liquids.(347)

Early workers considered two approaches in their development of liquid theories and attributed an intermediate status to liquids.(352) According to the van der Waals approach a liquid was considered to be a condensed gas.(350) This is reasonable since unlike a solid, liquids and gases cannot support sheer stresses but yield and flow in response to them.(350) Van der Waals modified the volume and pressure terms in the ideal gas equation to account for the intermolecular forces in liquids.

Further experimental evidence indicated that the liquid state had features in common with crystals, such as a large number of nearest neighbours and a local order.(347,350) The direct consequence of this was the developement of a lattice type model. The complete development of the lattice model can be attributed to Guggenheim.(348) The model is based on the notion that the motions of the molecules reduce to oscillations about their equilibrium positions and that the changes in any thermodynamic property on mixing may be expressed in terms of a lattice partition function.(347) Although the former assumption is true for solids, it is decidedly contentious when imposed upon liquids.(2) Further assumptions include: *(i)* the lattice is treated as rigid; that is that changes in intermolecular distance due to composition changes are ignored, and *(ii)* the thermal expansion of the lattice is ignored. These assumptions are seen to impose obvious constraints upon the system. Variations in the composition afford important contributions to the excess functions, while the latter constraint is only valid at low temperatures.(347)

Several workers based their theories on the original "simplified" lattice model. The quantitative predictions of the model were however in contrast to the experimental observations. Even for the simplest systems studied with molecules similar in size, the model incorrectly predicted the contribution of the excess entropy to the excess free energy to be of the same order of magnitude as the enthalpy of mixing.(347) Although the model was seen to be insufficient to afford a complete understanding of the thermodynamic functions of solutions, it did receive noteworthy success in the evaluation of a combinatorial factor for polymer solutions through work by Flory(353) and by Huggins.(347,354)

The term "regular solutions" was introduced by Hildebrand and co-workers(349,355) to describe a mixture with an excess entropy, S_V^E; equal to zero for no volume change on mixing. They differentiated between this value, S_V^E; and S_p^E, the experimentally determined excess entropy at a constant pressure, which would not be zero for a regular solution. For a regular solution, the excess Gibbs energy at a constant pressure, G_p^E, approximates the excess internal energy at a constant volume, U_V^E.

Hildebrand *et al.*(349,355) based their work on this and on earlier work by Scatchard(356) and derived on semi-empirical grounds an expression for U_V^E. They were able to eliminate the need to know the form of the distribution function, a mathematical representation of the distribution of the molecules about any given central atom, and arrived at relations for the changes in the properties of mixing in terms of the pure component properties. In their solubility parameter treatment it is assumed that the changes in internal energy on mixing can be attributed entirely to the energy of interaction of the molecules. This energy of interaction is assumed to be spherically symmetrical. This excludes mixtures which exhibit hydrogen bonding, charge transfer, or polar effects, which are orientation dependent. The contributions of the motions of the molecules to the liquid state behaviour is eliminated in the theory, since it is assumed that these do not change in going from a pure liquid to the liquid mixture. In addition it is assumed that the mutual energy between molecules is dependent on intermolecular distance but is independent of the temperature and the nature of the surroundings.(349) The theory also incorporates Scatchard's(356) concept of the cohesive energy density. This corresponds to a measure of the energy required to remove a molecule from a bulk liquid and through it the solubility parameter, δ, is defined. In the absence of a volume change on mixing at constant pressure, V_p^E, the internal energy at a constant volume, U_V^E simply corresponds to the constant pressure enthalpy of mixing, H_p^E.(67)

The solubility parameter was initially valid only for regular solutions, but has been extended to include solutions exhibiting polar effects and to solutions exhibiting hydrogen bonding effects.(358,359) Multicomponent solubility parameters comprising linear contributions from non-polar interactions, from polar interactions, and from hydrogen bonding or similar specific association interactions, have also been introduced. These have been discussed in detail by Barton.(358,359)

McMillan and Mayer(360) and Kirkwood and Buff(361) have expressed the thermodynamic properties of a multicomponent system in terms of intergrals of the radial distribution functions of the different types of molecular pairs present in the mixture. This work was however only applicable to very dilute solutions, because of the lack of reliable methods available for the calculation of distribution functions in the condensed media, and also to polymer solutions, where the molecular structure of the solvent can be neglected due to disymmetry between solvent and solute molecules.

The first real progress in the field of "concentrated solution" theories can be attributed to work by Lennard-Jones and Devonshire(362) who in 1937 applied the cell model (or free volume theory) to the interpretation of the thermodynamic properties of a liquid in terms of the intermolecular forces. The cell model had been used previously by workers such as Eyring and Hirschfelder.(363,364) It has as its basis the more or less rigid structure of a liquid, attributable to the realization that intermolecular distances smaller than the molecular diameter are prohibited by strong repulsive forces between the molecules, while distances much larger than the mean intermolecular distance are stastically unlikely.(347) The result is the regular spacing of neighbouring molecules with a separation, r, related to the intermolecular energy, ε^*, at an equilibrium distance of separation, r^*. In its simplest form it is assumed that each molecule is confined to its own "cell". The walls of each cell correspond to the nearest neighbours, which remain fixed in position. Lennard-Jones and Devonshire considered a close cubic-packed cell and assumed that the central molecule interacts with equal probability with its nearest neighbours.(347) The main advantage of the cell model is that each cell may be regarded as an independent thermodynamic system. The free energy of a system is related to the product of the free energy of one cell with the number of cells present in the system.

Prigogine and co-workers(347,365,366) extended the cell model approach for pure liquids to incorporate liquid mixtures. They assumed a random mixing of the components and demonstrated that for mixtures comprising molecules similar in size, the departure from random mixing which occurs in real solutions only afforded a small contribution to the excess thermodynamic functions. The Lennard-Jones potential was substituted by a square well potential, permitting excess free energies and excess volumes for mixtures to have opposite signs.

Hildebrand and Scott(357) have emphasized the shortcomings of the cell model. The crystal-like structure attributed to the liquid creates an unnatural situation of fixed nearest neighbours for any molecule, thus suppressing the freedom of movement of a molecule. The intermolecular energy for molecules moving in a cage of nearest neighbours is unrepresentative of the energy for a molecule surrounded by other randomly distributed molecules in a liquid. Furthermore, Flory(59) has stated that the nature of the model renders it unsuitable for application to mixtures of molecules differing vastly in size and in shape. Prigogine and co-workers(347) found that although the sign of the excess functions predicted by the cell model for a number of non-polar mixtures was correct, the quantitative agreement between the predicted cell theory results and experimental excess functions was poor.

While some early workers exploited the cell model as a basis for formulating the properties of liquid mixtures, other workers applied corresponding states methods to selected classes of liquid mixtures.(1,347) Pitzer is generally attributed with the formulation of the corresponding states approach in terms of molecular interactions.(367) The basic assumptions for any corresponding states theory are: *(i)* only central forces contribute to the intermolecular energy, and *(ii)* this has the same form for all pair interactions. The energy of a molecular pair at its equilibrium distance, ε, and the collision diameter, σ, characterize this theory. For theories of this type, a Lennard-Jones (6, 12) potential is usually used in conjunction with Lorentz-Bethelot combing rules for 1-2 type interactions in a binary liquid mixture.

The behaviour of mixtures comprising simple spherical molecules have been well described by theories based on the principle of corresponding states.(368-370) Longuet-Higgins and co-workers(371-373) have employed the corresponding states approach in conjunction with a perturbation method. Their theory is sometimes refered to as the theory of conformal solutions. They were able to show that by complying within the limits of first order perturbations, the properties of mixtures can be directly deduced from assumptions concerning intermolecular forces and thermodynamic properties of the pure components. These are conveniently expressed as functions of reduced variables. The main aspects of interest to the theory are that it is independent of any particular model and that it can be applied to both gaseous, liquid or solid solutions.(347) Although the theory did not give a correct interpretation of experimental data, it did indicate the possibilities afforded by the theorem of corresponding states to the field of multicomponent systems.(347)

Scott(374) has proposed three models for averaging the intermolecular energy parameters for liquids. The models are based on the empirical approach of Longuet-Higgins and are known as the "single-liquid", "two-liquid", and "three-liquid" models. The first two correspond to the average potential model of Prigogine with the collision diameter and the intermolecular distance determined by the "average" environment of a molecule. In the "single-liquid" model, the energy of a binary liquid mixture is assumed to be the sum of 1-1, 1-2, and 2-2 interactions. The mixture is assumed to behave as a single liquid. The "two-liquid" model corresponds to the refined average potential model of Prigogine(347,366) and employs the concept of introducing two "cell" types, one for each component. The mixture thus comprises the appropriate amounts of each type of liquid. The excess free energy of the "two-liquid" mixture is the sum of the free energy associated with the transfer of an amount x_1 of the 1-molecules from the pure liquid 1 to type 1 cells in the mixture, with the excess free energy associated with a similar process involving the type 2 liquid. The "three-liquid" model regards the mixture as comprising three independent liquids; pure 1, pure 2, and a hypothetical liquid with intermolecular parameters σ_{12} and ε_{12}. The effect of differences in sizes of the molecules is almost completely supressed in this formulation, since the absence of coupling between pairs allows freedom for the two species to fit together in the solution. The three-liquid model generally predicted negative V_m^E for mixtures of molecules similar in size. Battino(115) has reviewed work concerning the application of the three models and other work concerning the application of corresponding states approaches.

The theorem of corresponding states had a major influence on solution thermodynamics in the 1960's. The average potential model of Prigogine and co-workers(375) combines the basic ideas of both the cell model and the theory of conformed solutions. The latter introduces composition dependent averages for the interaction potentials, the averaging process being applied to each molecular species in the mixture. The mixture is considered to behave as a pure component. A knowledge of the average molecular parameters of the mixture permits the application of the theorem of corresponding states.

The macroscopic quantities of a system at a predescribed temperature, volume, and composition, can be obtained by averaging over all the accessible quantum states for the system, attaching a statistical weight, $-\beta E_r$, to each quantum state. The quantity E_r is the energy of the quantum state. If the energy characterized by E_r has g_r states, then the statistical weight corresponding to E_r is $g_r \exp(-\beta_r)$. The macroscopic equilibrium value, $\bar{p}$, of any property, p, is given by:

$$\bar{p} = \frac{\sum_r p_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \tag{4.1}$$

The quantity in the denominator is called the partition function, and is denoted Z.(347) Prigogine has shown that the partition function is closely related to the Helmoltz free energy, F:

$$F = -kT \ln Z \tag{4.2}$$

If the partition function is known, it is possible to deduce the thermodynamic properties of the system. In the cell model the mean energy of interaction with neighbouring molecules, $\omega(r)$, depends only on the distance r of the molecules from the cell centre. Prigogine has represented the cell function as ψ, where:

$$\psi = 4\pi \int_{\text{cell}} \exp \{-\beta[\omega(r) - \omega(0)]\} r^2 dr \tag{4.3}$$

where $\omega(0)$ is the value of $\omega(r)$ at the cell centre.

Prigogine and co-workers(347) were the first to introduce the concept of a structural contribution to the partition function and suggested that the excess functions are governed not only by combinatorial and energetic factors, but that the differences in the number of external degrees of freedom between the components of the mixture also contributed to the solution non-ideality. Prigogine and co-workers(347,376) generalized the cell model to incorporate chain molecules and their mixtures. Their extension to linear chain molecules or to complex molecules with two or more functional groups is based on the idea that a molecule may be subdivided into r segments. Each segment is considered as a point on a lattice (for the lattice model) or as a cell centre (for the cell model). This eliminates the obvious problems encountered when considering large chain molecules comprising individual groups which exhibit freedom of motion, as point centres.

In the extension to r-meric liquids, the principle of corresponding states relies on the assumption that the intermolecular potentials of the mixture components are equivalent in form when expressed as a function of the distance between molecular centres or as a function of the distance between segment centres. In addition it is assumed that interactions are due to dispersion forces only and that the potential energy of two point centres can be represented by the Lennard-Jones interaction potential. The properties of a liquid can thus be given in terms of the distance of molecular separation and the intermolecular potential. These two parameters are embodied in the characteristic temperature, T^*, and the characteristic pressure, P^*. Prigogine and co-workers introduced a third parameter, the number of degrees of freedom of molecular motion, where these degrees of freedom are independent of the valence forces but depend on the molecular environment.(347) Flory *et al.*(52) however consider the equations of state thus derived to be of little predictive value and criticize the average potential model for over-estimating the effects of size differences between component molecules.

Simha and Hadden(377-379) have extended the cell model to incorporate branched chain molecules, while Hermsen and Prausnitz(380) have modified the Prigogine treatment for branched molecules, taking into accounting the effect of lattice imperfections on the configurational energy. Modifications of the Prigogine cell theory to incorporate polar liquids have been made by Winnik.(381)

Flory and co-workers(52) rejected the cell model in the development of their theory and based their partition function on the one introduced for simple fluids by Eyring and Hirschfelder.(364,382) The Flory theory(52-59) relates the properties of a mixture to the characteristic properties of the pure components through the adjustable interaction parameter, X_{12}. This parameter reflects the replacement of 1-1 and 2-2 contacts with 1-2 contacts. A hard sphere repulsion potential is adopted for segments of the molecular chain and the intermolecular energy, which is of van der Waals type, is dependent on the volume. The derived partition function is independent of the form or symmetry of the forces of attraction acting between molecular pairs of the liquid and is free of the principle of corresponding states. The Flory theory has been used in this work, and will be discussed in detail Section 4.2.

More insight into the origins of the contributions to the excess thermodynamic properties can be gained by considering the equations of Patterson and co-workers.(60,61,186) Their approximate equations for H_m^E, V_m^E, and TS_m^E, separate these contributions. The H_m^E and TS_m^E comprise an interactional contribution, which is proportional to the Flory X_{12} parameter, and a free volume contribution, which originates from the volume change on mixing. Although the free volume effect is recognized by the quasi-lattice theories, a more convenient treatement is afforded by the molecular theories of Prigogine(347) and Flory(52-59) and more recently of Patterson.(60,61,186) In the approximate equation for V_m^E by Van and Patterson,(61) the free volume contribution is further divided into two terms. The $\tilde{V}$ curvature contribution is equivalent to the free volume term, while the P^* contribution arises from differences in the internal pressures and reduced volumes of the two components. The P^* contribution often dominates V_m^E, particularly when one component is of higher internal pressure, P^*, and lower reduced volume, $\tilde{V}$, than the other.(186) The approximate theory of Patterson and co-workers has also been used in this work and the predicted results are discussed in the light of these contributions. The necessary equations are given in Section 4.3.

Patterson and co-workers(6,60) have recently distinguished two additional contributions to the mixing functions which are concerned with molecular ordering effects. The first involves a thermodynamic effect associated with the presence of short-range ordering in one of the components, usually a long chain *n*-alkane, and affects the thermodynamic properties which depend on nearest neighbour interactions. This orientational ordering effect is associated with a partial alignment of neighbouring segments, or of possibly the entire molecule. The order is replaced by weaker correlations on mixing with a molecule which is incapable of entering into any correlation with the longer chain. This results in a net disruption of the order, and hence affords a positive contribution to H_m^E and TS_m^E. Since the order effects in H_m^E and TS_m^E are often similar in magnitude, the resulting contribution to G_m^E is invariably small. This destruction of order can be coupled with a possible creation of order, which leads to a negative contribution to H_m^E and to TS_m^E. The effect is associated with a restriction of the rotation of the molecular segments of one of the components by a second component whose molecules are either sterically crowded or are large and anisotropic. This second effect is termed a condensation effect and generally decreases with an increase in the temperature.

Several other workers have modified the theories of Prigogine and of Flory. One such extension by Pollin and Fried(383-385) employs the Flory concept(52) which relates the molar cohesive energy, E, to the molar volume, V, through two constants a and m. While Flory and co-workers(52,53) assume the value of m to be unity, Pollin and Fried regard m as a variable. They(383) have applied their theory to a range of systems including *n*-alkanes, cycloalkanes, toluene and xylene. The best fit value of m for six aliphatic hydrocarbon mixtures was found to vary between 1.22 and 1.30. An average value of $m = 1.29$ however afforded a satisfactory agreement between experimental and predicted H_m^E values. Their work indicated that for any of the systems studied, m is independent of the concentration and of the hard core volume ratio. The value of m is also independent of the temperature for a narrow temperature range. An alternative approach which involved the estimation of m from the enthalpies of vaporization of the ideal gas state yielded poorer results. Pollin and Fried have extended the range of mixtures investigated and have successfully applied the theory to 50 binary mixtures of non-polar and weakly polar constituents, and ten binary mixtures comprising normal alcohols.(386)

The perturbation hard chain theory (PHCT) was introduced by Prausnitz and co-workers(387) in the 1970's and can be used to predict the properties of fluid mixtures comprising molecules of different sizes, shapes, and intermolecular forces. These include polymer solutions. The theory takes into account the molecular motions which result from rotational and vibrational as well as translational degrees of freedom, and correctly reduces to the ideal-gas equation at low densities. Various workers have discussed modifications to the theory. Donohue and Vimalchand(388) have reviewed some of these modifications and the application of the theory to liquid mixtures.

A lattice theory by Barker(389) which accounted for the sizes of the molecules has recently been modified by Kehiaian.(390) As with many of the models which employ the concept of a rigid lattice without vacancies, the dependence of the volume on temperature and on pressure cannot however be reproduced. Hole models(391-393) acknowledge the presence of empty sites on the lattice and, in addition to considering volume effects, they are valid for both the liquid and the gaseous phases of a system. Smirnova and Victorov(394) have discussed the different versions of the hole theories which include the introduction of vacancies into the cell model. They have also proposed a model which accounts for the molecular shape, size, and orientational effects in liquid mixtures.

Liebermann's(62,63,395) theory for the prediction of excess thermodynamic properties of binary liquid mixtures is essentially a refinement of the original van der Waals concept of liquids where molecules are regarded as hard spheres. The Liebermann approach is particularly attractive in that the equations are free from empirical parameters and need not be fitted to solution properties. Basic predictions can be made with densities, isobaric expansivities, and isothermal compressibilities of the pure components. The theory is thus free from any adjustable parameters. The Liebermann approach has been examined in this work. The basic equations for V_m^E and H_m^E have been tested and are given in Section 4.4.

A detailed review of all the different theories is outside the scope of the present work. However, it is pertinent to mention those theories and models based on group contribution approaches.(396) Group contribution models are based on the notion that different classes of organic molecules can be considered as comprising combinations of distinct functional groups. These models employ empirical interaction parameters for specific atoms or functional groups. Each of the molecules of a mixture is divided into its component functional groups and each pair of groups is assigned a value of the group interactional parameter. These are computed from experimental vapour-liquid equilibrium data for a large number of carefully selected "key" binary mixtures.(1) The advantage of the group contribution method is that while a mixture may contain numerous different molecular species, it may nevertheless contain only a few structurally distinct chemical groups. The interactional parameter approach forms the basis of the various predictive treatements of which the Universal Quasi-Chemical Theory (UNIQUAC),(396,397) the UNIFAC (UNIQUAC Functional Group Activity Coefficients) theory,(396,398,399) DISQUAC(400) and ASOG(396) theories constitute a few of the more successful theories. To date the UNIFAC model has proved to be the most popular of the group contribution models. The model allows the prediction of activity coefficients at infinite dilution for both binary as well as for multicomponent mixtures, but exhibits shortcomings when attempting to characterize systems comprising molecules differing vastly in size and shape. The modification of the model by Nitta(401) presents a good theoretical basis for the prediction of the experimental behaviour of the mixture by means of H_m^E, but the quantitative predictions of H_m^E using the model are somewhat irregular.(402) Many of these group contribution theories neglect excess properties related to the excess volume.

Many of the above theories discuss the solution non-ideality in terms of physical intermolecular forces. Strong orientational effects such as electron donor - acceptor effects arise with liquid mixtures containing polar molecules, thus invalidating the assumption of random mixing. These effects can be expected to influence the excess thermodynamic functions to a greater extent than simple van der Waals interactions. The different theoretical approaches developed so far assume that the dipolar interactions are secondary to the central forces and that these dipolar interactions can be treated as small perturbations. Molecules exhibiting hydrogen bonding effects show large association and solvation tendencies.(400) These hydrogen bonding interactions affect the thermodynamic properties to a greater extent than either specific or physical interactions. No satisfactory theory exists which can deal with strong orientational effects.

4.2 The Flory theory

The failure of the regular solution theories to adequately predict excess thermodynamic properties of liquid mixtures has already been noted. Flory and co-workers(52) felt that this was due to the exclusion of those properties of the pure components which characterize them as liquids. Although the cell theory utilizes the intermolecular potential and is thus considered to be derived from a fundamental molecular entity, the excessive degree of order ascribed to the molecular arrangement results in the models failure to reflect changes in the liquid structure, an account of which is necessary to the understanding of solution properties. In addition the description of the liquid in terms of discrete cells makes it unsuitable for the application to mixtures differing in size and in shape.(59) The need for a better way of interpreting and correlating the properties of liquids and their mixtures initiated an investigation by Flory and his co-workers into the development of a suitable theory for the thermodynamic representation of liquid mixtures.(52)

Flory, Orwoll and Vrij(52,53) originally developed the theory for normal paraffin hydrocarbon mixtures. The theory started with a simple expression for the partition function of a liquid which was easily adapted to mixtures. The characteristic parameters, V^*, T^* and p^* can be evaluated from equation of state data for the pure components.(53) In conjunction with the adjustable interaction parameter, X_{12}, which characterizes the interactions between molecules, they found that their theory succeeded remarkably well in correlating equation of state data for *n*-paraffin hydrocarbons in the range $n=6$ to $n=40$. They postulated that their theory could probably be applicable up to $n=\infty$. Eichinger and Flory(403) have noted that their approach, although similar to corresponding states treatments, has the advantage of employing analytical expressions instead of graphical curve fitting methods. The initial theory(52,53) was less successful at representing any given member of a series of *n*-alkanes over a wide range of temperatures and pressures. The inadequacy of the Flory theory to describe the variation of pure fluid properties with temperature has been noted by Flory and Abe(56) who conclude that the pure fluid parameters should be adjusted to fit the experimental properties at each temperature.

The treatment was extended by Flory and Abe(54) to encompass liquid mixtures comprising small non-polar homologous molecules. Flory(55) later extended this to encompass mixtures of molecules differing in size. Abe and Flory(56) applied this treatment to twenty three binary liquid mixtures classed into four different groups: *(i)* mixtures of approximately spherical molecules, *(ii)* *n*-alkanes with cycloalkanes, *(iii)* benzene with biphenyl, and *(iv)* hydrocarbons with fluorocarbons. Except for the last group, the excess volumes determined using pair interactions calculated from excess enthalpy data were found to be in good agreement with experimental values. Predicted excess entropies were however lower than experimental values. Abe and Flory(404) extended the theory to liquid-liquid equilibria and evaluated interaction parameters from observed critical solution temperatures for mixtures of hydrocarbons and fluorocarbons. They found that H_m^E and V_m^E were well represented by the theory. Orwoll and Flory(57,58) subsequently applied their theory over a range of temperatures to mixtures of *n*-alkanes in the range $n=6$ to $n=36$ and to $n=\infty$, where the last example corresponded to linear polymethylene. Discrepancies between predicted and experimental V_m^E were small and were attributed to limitations inherent in the formal scheme of interpretation rather than in the particular values chosen for the parameters. The enthalpies of mixing were observed to depend strongly on the interaction parameter.

Eichinger and Flory(403) have applied the theory to rubber and benzene mixtures. The predicted V_m^E at 298 K compared well with the small positive experimental excess volumes. Similar work on the system {polyisobutene + benzene}$^{(403)}$ showed the theory to be successful in predicting the main features exhibited by the system. The predicted positive excess volume was of the correct sign, but overestimated the magnitude of the excess thermodynamic property. This was attributed in part to the overestimation of the surface to volume ratio s_1/s_2. The small X_{12} value for the system {polyisobutylene + cyclohexane}$^{(403)}$ indicated a small difference for the interactions between neighbouring pairs. Good agreement between predicted and experimental V_m^E was achieved for this system as well as for the system {polyisobutylene + *n*-pentane}.$^{(403)}$

The original notation employed by Flory and co-workers has been adopted in the following summary of the Flory equations concerning excess volumes, excess enthalpies, and excess Gibbs functions.

4.2.1 Normal paraffinic hydrocarbons

Flory and co-workers$^{(52)}$ based their equation of state on a partition function introduced for simple liquids by Eyring and Hirschfelder.$^{(364,382)}$ The intermolecular energy is assumed to be dependent on volume only, and a hard sphere repulsive potential is adopted for segments of the chain molecule.

In developing their partition function Flory *et al.*$^{(52)}$ considered a linear chain molecule, H-$(CH_2)_n$-H, with sufficient flexibility to enable it to assume a variety of configurations and with terminal groups exerting intermolecular forces differing from those of the mid-chain units. They employed Prigogine's$^{(347)}$ concept of *r*-meric molecules and considered the chain to be subdivided into *r* segments. Within the constraints of the lattice model it would have been necessary to define a segment in such a manner that its length would equal the diameter of the molecular chain. Flory$^{(52)}$ ignored this constraint however when formulating his partition function for *n*-paraffinic hydrocarbons. Since the definition of the segment was adaptable to circumstance, it followed that the original formulation could easily be extended to molecules differing in size and in shape. The only constraint imposed upon the segment choice was that $r \neq n$, although it was specified that *r* should be linear in *n* for the homologous members of a series.

The successive segments of any given molecule are considered to occupy a series of successive sites on a 3-dimensional lattice. The number of segments is taken to be proportional to the "hard core" molecular volume, V^*, or the "net volume". This "hard core" volume is linear in n for a homologous series. The "hard core" molecular volume and the net volume of a segment, v^*, are related through:$^{(52)}$

$$V^* = rv^* \tag{4.4}$$

By the Prigogine$^{(347)}$ formulation each r-mer chain molecule is surrounded by q first neighbours. The parameter q determines the number of contacts of an r-mer and is a function of the coordination number, z:

$$qz = rz - 2r + 2 \tag{4.5}$$

Flory and co-workers$^{(52)}$ refrained from specifying the number of intermolecular contacts in terms of the liquid coordination number by rejecting the above formula, since the desired arbitrariness in r would be lost. In their treatment the average number of contact sites per segment, qz/r, is given the symbol s. A measure of the molecular surface can thus be given by:

$$rs = rs_m + rs_e \tag{4.6}$$

where s_m is the number of contact sites per internal segment of the r-mer chain and s_e is the number of contact sites per chain end.

Patterson and co-workers$^{(6)}$ attribute the overall success of the Flory theory in part to the inclusion of the Prigogine$^{(347)}$ concept of external degrees of freedom, where each r-mer is considered to have $3c$ degrees of freedom. Each r-mer is considered to be "tied" to a lattice point by a spherically harmonic field arising from intermolecular forces and hence the $3c$ degrees of freedom can be separated into two categories: *(i)* internal degrees of freedom dependent on the intermolecular forces only, and *(ii)* external degrees of freedom dependent on intermolecular forces. It is assumed that the intramolecular potentials associated with the intermolecular modes can be disregarded and hence the intramolecular modes can be treated as translational (external) motions.$^{(52)}$ On the addition of the three degrees of freedom of the molecular centre of gravity, the total number of intermolecular degrees of freedom per molecule is $3rc$ and is given by:

$$3rc = 3(rc_m + c_e) \tag{4.7}$$

where c is assumed to be independent of temperature and volume over the range of application of the equation and the subscripts e and m are as defined above. The $3c$ degrees of freedom depend only on molecular environment and chemical structure.(347)

Tonks(405) has shown that by considering a one dimensional system of N particles with length, l, constrained to move between two fixed boundaries of separation, L, then the total configurational space available to the system is:

$$\Omega = (L - Nl^{*})/N! \qquad 4.8$$

where l^{*} is the space available per particle and is equal to L/N. By Rice:(406)

$$N! \cong N^{-N}/e^{N} \qquad 4.9$$

and hence substitution of equation 4.9 into equation 4.8 yields:

$$\Omega \cong [(l - l^{*})e]^{N} \qquad 4.10$$

Flory(55) gives the configurational integral for such a system as:

$$Z = \int \ldots \int \exp[-E(x)/kT]\, dx \qquad 4.11$$

where x represents the set of configurational coordinates x_1, x_2 ... x_n in a one dimensional space and k is the Boltzmans constant. Equation 4.11 may be expressed as:

$$Z = \Omega \exp[-E_o/kT] \qquad 4.12$$

where E_o is the mean intermolecular energy.(55) For a three-dimensional system:(55,405,406)

$$Z = \{ge^{3}[(v)^{1/3} - (v^{*})^{1/3}]^{3}\}^{N}\exp(-E_o/kT) \qquad 4.13$$

In the original Flory notation, the geometric factor was denoted by the symbol γ. To avoid confusion with the activity coefficient of Chapter 4, this has been replaced by the symbol g in equation 4.13. The geometric factor connects $[(gv^{*})^{1/3} = l^{*}]$ and $[(gv)^{1/3} = l]$; v is the volume per segment and is given as $[v = V/rN]$, where V is the volume of the system and N is the number of r-meric molecules. Flory *et al.*(52) take the "free length" associated with each intermolecular degree of freedom to be of the form $\{(g)^{1/3}[(\nu)^{1/3} - (\nu^*)^{1/3}]\}$. The form of the above result is equivalent to that given by the cell model.(347) The communal entropy factor, e^{3N}, is not included in the cell model treatment.

Flory(55) has followed Prigogine and co-workers(347,376,404) in assuming a partition function of the form:

$$Z = Z_{comb}\{g[(\nu)^{1/3} - (\nu^*)^{1/3}]^3\}^{rNc}\exp(-E_o/kT) \qquad 4.14$$

where Z_{comb} is a combinatorial factor independent of the volume and the temperature. It is sufficient to note that in terms of the lattice model, Z_{comb} characterizes the number of ways of interspacing the rN elements amongst one another with disregard for the precise location of each relative to its nearest neighbour. The communal entropy factor, e^{3N}, is considered to have been absorbed into Z_{comb}.

Prigogine and co-workers(376,404) adhered to the cell model as a guide to the formulation of the mean intermolecular energy E_o. The energy of interaction between a molecular pair is a function of the distance between the molecules, and the restriction of imposing the same intermolecular distance for all the first neighbours introduces an error in the intermolecular energy and in the dependence of E_o on the volume.(52) For this reason, Flory rejected the cell model as a basis for expressing the intermolecular energy in favour of an approach suggested by Hildebrand and Scott(355,357) which considers the connection between the energy and the radial distribution function. Hildebrand and Scott(367) have shown that the mean intermolecular energy per contact point, ε, can be expressed as:

$$\varepsilon = -\eta/\nu \qquad 4.15$$

where η is a constant for any given chain homologue and characterizes the mean interaction between a segment pair. Allowances are made for the fact that end segment interactions differ from those interactions within the chain. Flory has expressed E_o as:(52)

$$E_o = -rNs\eta/2\nu \qquad 4.16$$

It is implied that the intermolecular energy is related to the number of contact sites or the area of contact. This equation is similar in form to the equation of Hildebrand and Scott:(355,367)

$$E_o = \text{constant}/V^m \qquad 4.17$$

where for non-polar liquids, m is treated as a variable in the range 1.0 to 1.5. In an attempt to reduce the number of variables to a minimum, Flory and co-workers(55) have followed the van der Waals approach by assuming that all liquids can be characterized by a value of $m=1$. The work in this regard by Pollin and Fried(384-386) has already been mentioned.

The above can be extended to encompass different forces of attraction for terminal and mid-chain segments, and the intermolecular energy may be written as:(52)

$$E_o = (-1/v)[N_m\eta_m + N_{em}\eta_{em} + N_e\eta_e] \qquad 4.18$$

where the subscripts, m, e, and em, characterize the interactions between neighbouring mid-chain segments, neighbouring terminal sites, and between neighbouring terminal and mid-chain segments respectively. The parameter N denotes the number of neighbouring pairs in each category. Flory *et al.*(52) have taken the number of terminal sites involved in atypical interactions to be s_e, and give the following equation for E_o:(52)

$$E_o = (-rN/2vs)[s_m{}^2\eta_m + 2(s_m s_e/r)\eta_{em} + (s_e{}^2/r^2)\eta_e] \qquad 4.19$$

By comparison with equation 4.16, η is defined as:(52)

$$\eta = (s_m{}^2/s^2)\eta_m + 2(s_m s_e/s^2 r)\eta_{em} + (s_e{}^2/s^2 r^2)\eta_e \qquad 4.20$$

Flory *et al.*(52) have applied the Bethelot relationship(1) to η_{em}:

$$\eta_{em} \cong (\eta_e\eta_m)^{1/2} \qquad 4.21$$

which leads to:(52)

$$\eta \cong (s_m/s)^2\eta_m[1 + (s_e\eta_m/s_m\eta_m)^{1/2}/r]^2 \qquad 4.22$$

Introducing the reduced variables, denoted in each case by a tilde:(52)

$$\tilde{v} = v/v^{*} \qquad 4.23$$

and

$$\tilde{T} = T/T^{*} = 2v^{*}ckT/s\eta \qquad 4.24$$

and substituting equation 4.16 into equation 4.14 yields:(52)

$$Z = Z_{comb}(gv^{*})^{rNc}[(\tilde{v})^{1/3} - 1]^{3rNc}\exp(rNc/\tilde{v}T) \qquad 4.25$$

Flory *et al.*(52) obtain an equation of state from equation 4.25. Expressed in its reduced form:

$$\tilde{p}\tilde{v}/\tilde{T} = \{(\tilde{v})^{1/3}/[(\tilde{v})^{1/3} - 1]\} - 1/(\tilde{v}\tilde{T}) \qquad 4.26$$

where the reduced pressure, $\tilde{p}$, is given by:(52)

$$\tilde{p} = p/p^{*} = 2p(v^{*})^{2}/s\eta \qquad 4.27$$

or

$$\tilde{p} = pv^{*}/ckT^{*} \qquad 4.28$$

Equation 4.25 is identical in form to the reduced equation of state of Eyring and Hischfelder.(364,382) The definition of T^{*} by equation 4.24 differs from theirs through the incorporation of the parameter *c*.

The reduced equation of state can alternatively be expressed as:(52)

$$\tilde{p}/\rho^{2} = T/\tilde{\rho}[1 - (\tilde{\rho})^{1/3}] - 1 \qquad 4.29$$

where the reduced density, $\tilde{\rho}$, is equal to $1/\tilde{v}$. The reduced equation of state at zero pressure is:(52)

$$\tilde{T} = [(\tilde{v})^{1/3} - 1]/(\tilde{v})^{4/3} \qquad 4.30$$

In the definition of a segment, rv^{*} has been assumed to be linear in *n*, and hence it follows that v^{*} is the same for an entire homologous series. Flory has however observed that v^{*}, although consistent with *n* for a range of *n*-paraffinic hydrocarbons, portrays a small dependence on temperature. The parameter c and the product $s\eta$ depend asymptotically on n.(52)

The "characteristic" quantities v^* and T^* can be evaluated from the specific volume and the coefficient of thermal expansion, α. The coefficient of isothermal compressibility, κ, and the thermal pressure coefficient, γ, serve to define p^*. These macroscopic pure component properties can be expressed in terms of the reduced variables:(52)

$$\alpha = (1/v)(\delta v/\delta T)_p = (\tilde{T}/T\tilde{v})(\delta\tilde{v}/\delta\tilde{T})_{\tilde{p}} \qquad 4.31$$

$$\kappa = -(1/v)(\delta v/\delta p)_T = -(\tilde{p}/p\tilde{v})(\delta\tilde{v}/\delta\tilde{p})_{\tilde{T}} \qquad 4.32$$

and

$$\gamma = (\delta p/\delta T)_v = \alpha/\kappa = (\tilde{T}p/T\tilde{p})(\delta v/\delta\tilde{T})_{\tilde{v}} \qquad 4.33$$

A mathematical manipulation which involves solving equation 4.26 for T and for p, differentiating the resulting expressions, and finally eliminating T in each case yields at zero pressures:(52)

$$\alpha T = 3\{(\tilde{v})^{1/3} - 1]/[1 - 3[(\tilde{v})^{1/3} - 1]\} \qquad 4.34$$

$$\kappa = \{3[(\tilde{v})^{1/3} - 1]v^2\}/\{1 - 3[(\tilde{v})^{1/3} - 1]\}p^* \qquad 4.35$$

$$= \alpha T\tilde{v}^2/p^* \qquad 4.36$$

and

$$\gamma = p^*/T\tilde{v}^2 \qquad 4.37$$

The mathematical rearrangement of equation 4.34 yields:

$$[(\tilde{v})^{1/3} - 1] = \alpha T/3(1 + \alpha T) \qquad 4.38$$

The above equations afford a basis for the evaluation of the various parameters at zero pressure. On evaluating the terms v^*, T^*, and p^*, the primary parameters c and $s\eta$ are available from equations 4.24 and 4.27:(52)

$$s\eta = 2p^*(v^*)^2 = 2\gamma T v^2 \qquad 4.39$$

and

$$c = p^* v^*/kT^* = (\gamma v/k)(\alpha T)/(3 + 4\alpha T) \qquad 4.40$$

4.2.2 Adaption to mixtures of homologous chain molecules

Flory and co-workers(53) assumed a totally random arrangement of mid-chain and terminal segments about one another in a pure liquid. This assumption is not unreasonable and they applied it when extending the treatment of systems comprising one component to encompass binary mixtures of homologous chain molecules. The absence of structure is however insufficient to validate the assumption of random mixing of chain segments when considering mixtures comprising molecules differing in chain length. The distribution of segments in space can be expected to differ somewhat from a mixture comprising a random distribution of segments which have been severed from the chain. The different correlations between terminal and mid-chain segments were ignored by Flory and co-workers(53) when formulating the intermolecular energy and segment partition functions for species discussed above. Two assumptions were made in extending the above treatment for a single liquid to a liquid mixture: *(i)* the intermolecular energy was assumed to depend on the areas of contact between the molecules or segments, and *(ii)* core volumes of the components were assumed to be additive.(59) The latter premise was anticipated by expressing the energy as proportional to the number of contact sites.

In analogy to equations 4.16 and 4.39, Flory *et al.*(53) found that by starting with equation 4.16:

$$E_0 = -\bar{r}Ns\eta/2\nu \qquad 4.41$$

$$= -\bar{r}Np^*\nu^*/\tilde{\nu} \qquad 4.42$$

In this case $\bar{r}$ is the number average, and is defined by:(53)

$$\bar{r} = \Sigma\, r_iN_i/\Sigma N_i \qquad 4.43$$

$$= \Sigma\, r_iN_i/N \qquad 4.44$$

The subscript i represents the number of species of the mixture. If s and η are allowed to retain their previous definitions, then:(53)

$$s = s_m + s_e/\bar{r} \qquad 4.45$$

and

$$\eta = (s_m{}^2/s^2)/\eta_m + 2(s_m s_e/s^2\bar{r})\eta_{em} + (s_e{}^2/s^2\bar{r}^2)\eta_e \qquad 4.46$$

The specification of segment size is arbitrary and hence it is convenient to chose the segments so that $\nu_1{}^* = \nu_2{}^* = \nu^*$. This stipulation together with premises *(i)* and *(ii)* leads to the following expressions for the parameters $\bar{r}$, s and c for the mixture, expressed conveniently in terms of their pure component analogues:(53)

$$1/\bar{r} = \Sigma\, \phi_i/r_i \qquad 4.47$$

$$s = \Sigma\, \phi_i s_i \qquad 4.48$$

and $$c = \Sigma\, \phi_i c_i \qquad 4.49$$

The ϕ_i are redefined as segment fractions or core volume fractions for the species i:(53)

$$\phi_i = r_i N_i / \Sigma\, r_i N_i \qquad 4.50$$

rather than the more familiar volume fractions.

With the above revisions, the relationships derived for pure liquids can be adopted for mixtures of chain homologues by the substitution of the quantities defined in equations 4.47 to 4.49. The parameter r is simply replaced by $\bar{r}$.

The following is restricted to binary systems. Parameters without subscripts refer to quantities of the mixture, while subscripts 1 or 2 once again refer to the two pure components.

4.2.3 The excess volume

The "ideal" reduced volume per segment for no volume change on mixing, $\tilde{v}^o$, is given by:(53)

$$\tilde{v}^o = \phi\tilde{v}_1 + \phi_2\tilde{v}_2 \qquad 4.51$$

where $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volumes of the pure components at the same temperature and pressure as the mixture. The reduced excess volume per segment is then given by:(53)

$$\tilde{v}^E = \tilde{v} - \tilde{v}^o = \tilde{v} - \phi\tilde{v}_1 - \phi_2\tilde{v}_2 \qquad 4.52$$

where $\tilde{v}$ is the reduced volume of the mixture.

Flory *et al.*(52) have shown that $1/T^*$ increases linearly with $1/r$ for $r > 6$. Since from equation 4.47 it is evident that $1/\bar{r}$ is linear in ϕ_i, it follows that $\tilde{T}$ for a binary mixture should vary linearly with segment fraction composition at constant temperature. The above can be alternatively expressed as:(53)

$$\tilde{T} = \phi_1\tilde{T}_1 + \phi_2\tilde{T}_2 \qquad 4.53$$

and the reduced volume $\tilde{v}$ for the reduced temperature $\tilde{T}$ may be calculated from the equation of state for $p = 0$ given by equation 4.30.

The determination of the reduced excess volume by equation 4.52 is however complicated by the fact that equation 4.30 cannot be explicitly solved for $\tilde{v}$. This problem can however be overcome if $\tilde{T}$ is obtained by linear interpolation, employing $\tilde{v}_1$ and $\tilde{v}_2$ and the corresponding $\tilde{T}_1$ and $\tilde{T}_2$. Flory(53) gives the following approximation for the reduced excess volume per segment, $\tilde{v}^E$:

$$\begin{aligned}\tilde{v}^E &= (\delta\tilde{v}/\delta\tilde{T})(\tilde{T} - \tilde{T}^o)\\ &= 3(\tilde{v}^o)^{7/3}(\tilde{T} - \tilde{T}^o)[4 - 3(\tilde{v}^o)^{1/3}]^{-1} \qquad 4.54\end{aligned}$$

where the reduced temperature, $\tilde{T}^o$, corresponds to the reduced volume per segment, $\tilde{v}^o$, through equation 4.30. The excess molar volume is related to the reduced excess volume through:(56)

$$V^E_m = \tilde{v}^E(x_1V_1^* + x_2V_2^*) \qquad 4.55$$

4.2.4 The excess enthalpy

If the difference between the energy and the enthalpy of a condensed system at a low pressure can be ignored, then the excess enthalpy per mole of mixture can be written as:(55)

$$H^E_m = [E_o(\text{mixture}) - E_o(1) - E_o(2)]/N \qquad 4.56$$

The substitution of equations 4.41 and 4.42 into equation 4.56 yields for the excess enthalpy:(55)

$$H^E_m = rv^*[\phi_1p_1^*/\tilde{v}_1 + \phi_2p_2^*/\tilde{v}_2 - p^*/\tilde{v}] \qquad 4.57$$

where p^* is the characteristic pressure of the mixture, and will be dealt with later.

4.2.5 Mixtures of molecules differing in size and in shape

In extending the above to include binary mixtures of molecules which are not hydrogen bonded or highly polar and which comprise molecules differing in size and shape, then r_1 and r_2 are redefined to be in the ratio of their respective core volumes, V_1^* and V_2^*:(56)

$$r_1/r_2 = V_1^*/V_2^* \tag{4.58}$$

The ratio of the molecular surface areas of contact per segment for the respective components, s_1/s_2, is also required.(56) Since the segments have been chosen to have the same core volume, this corresponds to the ratio of surface per unit of core volume, which can be estimated from structural information or from the data of Bondi.(407) Abe and Flory(56) have assumed that for small molecules which are approximately spherical in shape:

$$s_1/s_2 = (r_2/r_1)^{1/3} = (V_2^*/V_1^*)^{1/3} \tag{4.59}$$

Flory(55) represents the number of contact pairs between respective species by A_{11}, A_{12}, and A_{22}, while η_{11}/ν, η_{22}/ν, and η_{12}/ν, represent the energies associated with each contact pair. E_o can then be given by:(55)

$$-E_o = (A_{11}\eta_{11} + A_{12}\eta_{12} + A_{22}\eta_{22})/\nu \tag{4.60}$$

According to Flory:(55)

$$2A_{11} + A_{12} = s_1 r_1 N_1 \tag{4.61}$$

and

$$2A_{22} + A_{12} = s_2 r_2 N_2 \tag{4.62}$$

and hence:

$$-E_o = (s_1 r_1 N_1 \eta_{11} - A_{12}\Delta\eta + s_2 r_2 N_2 \eta_{22})/2\nu \tag{4.63}$$

The term $\Delta\eta$ is given by:

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \tag{4.64}$$

Furthermore if the site fraction, θ_i, is defined as:(55)

$$\theta_2 = (1 - \theta_1) = s_2 r_2 N_2/\tilde{r} s N \tag{4.65}$$

and random mixing is assumed, then:(55)

$$A_{12} = s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \tag{4.66}$$

where according to equations 4.44 and 4.48:

$$\tilde{r} = (r_1 N_1 + r_2 N_2)/N \tag{4.67}$$

and $$s = (s_1 r_1 N_1 + s_2 r_2 N_2)/\tilde{r} N \tag{4.68}$$

where $$N = N_1 + N_2 \tag{4.69}$$

The following equations for E_o can be obtained by substituting equations 4.65 and 4.66 into equation 4.63:

$$-E_o/\tilde{r} N = (s/2v)(\theta_1 \eta_{11} + \theta_2 \eta_{22} - \theta_1 \theta_2 \Delta\eta) \tag{4.70}$$

or:

$$-E_o/\tilde{r} N = (s/2v)(\theta_1^2 \eta_{11} + \theta_2^2 \eta_{22} + 2\theta_1 \theta_2 \eta_{12}) \tag{4.71}$$

The segment fraction has been redefined as:(55)

$$\phi_2 = (1 - \phi_1) = r_2 N_2/\tilde{r} N \tag{4.72}$$

and hence:(55)

$$1/\tilde{r} = \phi_1/r_1 + \phi_2/r_2 \tag{4.73}$$

and $$s = s_1 \phi_1 + s_2 \phi_2 \tag{4.74}$$

The characteristic pressures, p_i^*, for the pure components, i, are:(55)

$$p_i^* = s_i \eta_{ii}/2(v^*)^2 \tag{4.75}$$

Flory and co-workers(54,55) have defined the interaction parameter X_{12} by:

$$X_{12} = s_1(\eta_{11} + \eta_{22} - 2\eta_{12})/2(v^*)^2 \qquad 4.76$$

and give the following equation for the energy, E_0:

$$-E_0/\bar{r}N = p^* v^*/v = ckT^*/\tilde{v} \qquad 4.77$$

where

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12} \qquad 4.78$$

and

$$c = (c_1 r_1 N_1 + c_2 r_2 N_2)/\bar{r}N \qquad 4.79$$

$$= \phi_1 c_1 + \phi_2 c_2 \qquad 4.80$$

On the basis of equations 4.77, 4.78, and 4.79, the characteristic temperature, T^*, for the mixture is given by:(54,55)

$$1/T^* = (\phi_1 p_1^*/T_1^* + \phi_2 p_2^*/T_2^*)/(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) \qquad 4.81$$

which can be rewritten in accordance with equation 4.24. Equations 4.56 and 4.57 can be rewritten as:(55)

$$H_m^E = \bar{r}Nv^*[\phi_1 p_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \phi_2 p_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (\phi_1 \theta_2 X_{12})/\tilde{v}] \qquad 4.82$$

$$= N_1 p_1^* V_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + N_2 p_2^* V_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (N_1 V_1^* \theta_2 X_{12})/\tilde{v} \qquad 4.83$$

In each of the above equations the last term is designated the "contact interaction term". For a binary liquid mixture this represents the contributions from contact interactions related to a difference between 1-2 pairs and the mean of 1-1 pairs and 2-2 contact pairs. The first two terms in each of the above equations 4.82 and 4.83 represent the contributions by the reduced volumes of the solutions and are referred to as the "equation of state" terms.(55) The "equation of state" terms may in turn be subdivided into a term proportional to the excess reduced volume, and a second term which depends on the difference between $\tilde{v}_1$ and $\tilde{v}_2$ and is independent of the excess reduced volume.(53,55) The latter term is zero for $\tilde{v}_1 = \tilde{v}_2$. The equation of state terms do not dissapear for $\tilde{v}^E = 0$.

4.2.6 The excess Gibbs function and the excess entropy

The various theories for predicting activity coefficients invariably agree upon the convention that ln γ comprises the sum of two or more contributions. The early work was based on the combination of two contributions: *(i)* a combinatorial or athermal term, and *(ii)* an energetic or thermal term.(408) Ashworth and Everett(261) employed an expression comprising two terms to represent their data for several alkane systems. The combinatorial term was calculated from Guggenheim's(348) treatment of athermal solutions and involved letting the number of nearest neighbours, z, approach infinity. Young(409) and Ashworth and Everett(261) analysed data using several values for z and concluded that the experimental results could be reproduced for values of $z=6$, 9, 12, or ∞ . Everett and Munn(410) treated the ratio of the solvent to solute molecules, r, as an adjustable parameter for different values of z and concluded that the data fit was independent of z. Parcher and Yun(408) state that the Flory-Huggins equation is generally considered to be as good for evaluating the combinatorial contribution to ln γ as some of the more complicated equations which appear in the literature.

In accordance with equation 4.14 for the configurational partition function and equation 4.83 for H_m^E, the Gibbs free energy of mixing comprises a combinatorial term, ΔG_{comb}, a contact interaction term, and equation of state terms.(55) For mixtures comprising molecules similar in size ΔG_{comb} can be given by the ideal law of mixing and the remaining terms can be identified with the excess free energy G_m^E:(55)

$$\Delta G_{comb} = -T\Delta S_{comb} = -kT(\ln Z_{comb}) \qquad 4.84$$

Because of the limitations of such a treatment, Flory and co-workers(55) have defined a "residual" free energy, G^R, such that G^R represents the sum of the contact interaction terms and the equation of state terms:

$$\Delta G_M = G^R + \Delta G_{comb} \qquad 4.85$$

where ΔG_M is the Gibbs free energy of mixing. The residual free energy, G^R, arises from the equation of state part of the partition function, $\Omega \exp^{(-E_o/kT)}$. For component molecules differing in size and shape, ΔS_{comb} may be expressed by the polymer solution theory:(53,353)

$$\Delta G_{comb} = -T\Delta S_{comb} = RT(N_1 \ln \phi_1 + N_2 \ln \phi_2) \qquad 4.86$$

According to equation 4.25 the residual free energy for a binary liquid mixture is given by:(55)

$$G^R = 3\tilde{r}N\nu^*\{(\phi_1 p_1{}^*\tilde{T}_1)\ln[(\tilde{v}_1)^{1/3} - 1/(\tilde{v})^{1/3} - 1] \\ + (\phi_2 p_2{}^*\tilde{T}_2)\ln[(\tilde{v}_2)^{1/3} - 1/(\tilde{v})^{1/3} - 1] + H^E \qquad 4.87$$

Equation 4.87 is of the form:

$$G^E_m = H^E_m - TS^E_m \qquad 4.88$$

The terms within the braces in equation 4.87 represent the residual entropy, S^R. For molecules similar in size the excess entropy, S^E_m, is related to S^R by:

$$S^E = S^R + \Delta S_{comb} \qquad 4.89$$

For molecules differing in size equation 4.89 becomes:(411)

$$S^E_m = S^R + \Delta S_{comb} - \Delta S_{ideal} \qquad 4.90$$

The term ΔS_{ideal} is given by:(55)

$$\Delta S_{ideal} = -R[x_1 \ln x_1 + x_2 \ln x_2] \qquad 4.91$$

In many cases ΔS_{ideal} offers a good representation of ΔS_{comb} and therefore: (55)

$$S^E_m = S^R \qquad 4.92$$

The chemical potential of component 1 is given by:(55)

$$(\mu_1 - \mu_1{}^o)^E/RT = (\delta G^E_m/\delta N_1)_{N_2, T, \tilde{v}} \qquad 4.93$$

The chemical potential of component 1 is usually represented by the sum of a combinatorial contribution, given by the Flory-Huggins approximation, and a non-combinatorial or residual contribution, characterized by the parameter X (not to be confused with the Flory X_{12} parameter):(53,55,403,411)

$$
\begin{aligned}
(\mu_1 - \mu_1^{o})^E &= (\mu_1 - \mu_1^{o})_{comb} + (\mu_1 - \mu_1^{o})_{non\text{-}comb} && 4.94\\
&= RT[\ln \phi_1 + (1 - 1/r)\phi_2 + X\phi_2^2] && 4.95
\end{aligned}
$$

where r is the ratio of the molar volumes of the solvent and the solute. Traditionally, ϕ_i was considered as the volume fraction. More recently however, ϕ_i has been identified with the segment fraction.(55,411) The parameter X represents the differences between neighbour interactions for unlike as opposed to like species.(403) By differentiating equation 4.87 the residual chemical potential is given by:(55)

$$
\begin{aligned}
(\mu_1 - \mu_1^{o})^R &= p_1^* V_1^* \{3\tilde{T}_1 \ln[(\tilde{v})^{1/3} - 1/(\tilde{v})^{1/3} - 1]\\
&\quad + (\tilde{v}_1)^{-1} - (\tilde{v})^{-1}\} + (V_1^* X_{12}/v)\theta_2^2\\
&= H_1^R - TS_1^R && 4.96
\end{aligned}
$$

where H_1^R and S_1^R are the partial molar residual enthalpy for component 1 and the partial molar residual entropy for component 1 respectively and are given as:(55)

$$
\begin{aligned}
H_1^R &= p_1^* V_1^* \{[(\tilde{v}_1)^{-1} - (\tilde{v})^{-1}] + (\alpha T/\tilde{v})(\tilde{T}_1 - \tilde{T})/\tilde{T}\}\\
&\quad + (V_1^* X_{12}/\tilde{v})(1 + \alpha T)\theta_2^2 && 4.97
\end{aligned}
$$

and

$$
\begin{aligned}
S_1^R &= -p_1^* V_1^* \{(3\tilde{T}_1/T)\ln[(\tilde{v}_1)^{1/3} - 1/(\tilde{v})^{1/3} - 1)]\\
&\quad - (\alpha/\tilde{v})(\tilde{T}_1 - \tilde{T})/\tilde{T}\} + \alpha(V_1 * X_{12}/\tilde{v})\theta_2^2 && 4.98
\end{aligned}
$$

Flory(403) has identified X as the reduced residual chemical potential, defined as:

$$
X = (\mu_1 - \mu_1^{o})^R/RT\phi_2^2 \qquad 4.99
$$

In the light of the above the mathematical manipulation of equations 4.95 and 4.96 yields:

$$
\begin{aligned}
(\mu_1 - \mu_1^{o})^E &= RT[\ln \phi_1 + (1 - 1/r)\phi_2] + p_1^* V_1^* \{3\tilde{T}_1 \ln[(\tilde{v}_1)^{1/3} - 1/(\tilde{v})^{1/3} - 1]\\
&\quad + (\tilde{v}_1)^{-1} - (\tilde{v})^{-1}\} + (V_1^* X_{12}/\tilde{v}) && 4.100\\
&= RT\ln \gamma_1 && 4.101
\end{aligned}
$$

At infinite dilution equation 4.100 and 4.101 become:

$$\begin{aligned}(\mu_1 - \mu_1^{0})^{\infty} &= RT[\ln(1/r) + (1 - 1/r)] + p_1^{*}V_1^{*}\{3\tilde{T}_1\ln[(\tilde{v}_1)^{1/3} - 1/(\tilde{v})^{1/3} - 1] \\ &\quad + (\tilde{v}_1)^{-1} - (\tilde{v}_2)^{-1}\} + (V_1^{*}X_{12}/\tilde{v}) && 4.102 \\ &= RT\ln\gamma_1^{\infty} && 4.103\end{aligned}$$

The terms within the braces multiplied by $p_1^{*}V_1^{*}$ in the above equation 4.102 constitute the equation of state contributions to the residual portion of the activity coefficient at infinite dilution, while the last term is the contact interaction contribution.(59)

Flory and co-workers(58) have argued that the X_{12} parameter has been treated as an enthalpy parameter and thus represents these interactions between neighbouring molecules in their entirety. Interactions between neighbouring molecules can be expected to affect the entropy as well where such an entropy contribution depends on the mixture composition but is independent of the volume. On the basis of their arguments they reformulated the free energy of mixing equation and introduced a term for the interactional entropy which takes the form $[-\theta_2 N_1 V_1^{*} T\ Q_{12}]$, where:(58)

$$Q_{12} = \Gamma s(1/r_1 - 1/r_2)^2/[(1 + s_e/s_m r_1)(1 + s_e/s_m r_2)^2] \qquad 4.104$$

and where Γ_s is a parameter for the entropy expressed in $J.cm^{-3}.^{o}C^{-1}$.

The parameter Q_{12} represents the entropy of interaction between unlike segments and its introduction replaces $X_{12}/\tilde{v}$ by $(X_{12}/\tilde{v} - TQ_{12})$. This parameter has not however met with much success, with many workers claiming that it was an artifact of the Flory theory which was forced to account for large end effects.(412)

4.3 The Prigogine-Flory-Patterson theory

It has already been noted that the theory of Prigogine(347) and of Flory,(52-56) referred to as the Prigogine-Flory theory in what follows, considers excess thermodynamic properties of binary liquid mixtures to be the sum of three contributions: *(i)* a combinatorial contribution, *(ii)* an interactional contribution arising from the differences in chemical nature of the two components, and *(iii)* a free volume contribution. More insight into the nature of these contributions is afforded by considering the approximate equations of Patterson and co-workers.(60,61,186) Their approximate equations separate these contributions. The approximate excess molar enthalpy equation is divided into an interactional contribution and a free volume contribution. The interactional contribution is represented by the X_{12} parameter, while the free volume contribution arises from the volume changes of mixing liquids of different degrees of thermal expansion or free volume. The excess molar volume can be expressed as an interactional term which is proportional to the Flory X_{12} parameter, a free volume contribution which originates from a difference in the degrees of thermal expansion of the two components, and a P^* contribution which arises from the differences in the internal pressures and reduced volumes of the components. For convenience the theory will be referred to as the Prigogine-Flory-Patterson theory (PFP) in this work. Where possible, the same notation will be followed as was used in the discussion concerning the Flory theory.

Flory and co-workers(57,58) observed the dependence of the characteristic parameters T_i^*, V_i^* and p_i^*, on the temperature for *n*-alkanes, attributing this to an imperfection in the corresponding states principle. They accounted for the decrease in p_i^* with *n*-alkane chain length in terms of the force fields surrounding methyl end groups which are weaker than those associated with methylene groups situated within the molecule.(57) For mixtures of chain molecules comprising identical segments the theory predicts negative H_m^E, the positive H_m^E values being associated with end-effects.(413,414) Patterson and co-workers(25) have however indicated that the magnitude of the force field associated with a difference between methyl and methylene groups would be expected to be unreasonably large if it were to constitute a major contribution to the excess functions for *n*-alkane mixtures. Evidence from several different treatments of the thermodynamic properties of pure *n*-alkanes and mixtures comprising *n*-alkanes has indicated little difference in the interactional energy between methyl and methylene molecular groups.(413,414) The corresponding states analysis is independent of theoretical models and for *n*-alkane molecules shows the variation of p^* to be due to a slight inaccuracy in the Flory model. Patterson and co-workers(25) introduce the quantity p^*/s, where s has been defined before as the molecular surface/volume ratio. They have considered p^* values for a range of normal and branched alkanes of increasing carbon number n. The p^* term has been found to be considerably smaller for a branched alkane isomer than for an *n*-alkane of the same chain length, but with a subsequently lower molecular surface/volume ratio. For each value of n however, p^*/s is almost identical, indicating almost identical force fields around the methyl and methylene groups.

By the Prigogine corresponding states theory, the molar configurational quantities of pure chain-molecule liquids are related to the reduced quantities through reduction parameters.(413,415) The configurational properties of the mixture are obtained from the reduced functions of the pure components. In the absence of end effects the reduction parameters are simply the mole fraction averages of the parameters for the pure components.(413) The reduced temperature for the mixture can be given by:(413)

$$\mathrm{T} = X_1\mathrm{T}_1 + X_2\mathrm{T}_2 \qquad 4.105$$

where X_i is the molecular "surface fraction" and is a concentration variable given by:(413)

$$X_i = (x_i q_i)/(x_1 q_1 + x_2 q_2) \qquad 4.106$$

The quantity q is obtained from r in the Prigogine treatment by:

$$q/r = (z-2)/z + 2/rz \qquad 4.107$$

In the Flory treatment the quantity q is replaced by rs. In the lattice model, $X \rightarrow \phi$ as the coordination number increases. These two terms are however not equal unless the reduction parameters for the two components are equal:(413)

$$\mathrm{U}_1^*/\mathrm{V}_1^* \equiv p_1^* = \mathrm{U}_2^*/\mathrm{V}_2^* \equiv p_2^* \qquad 4.108$$

The segment fraction ϕ_i is given by:(413)

$$\phi_i = x_2\mathrm{V}_2^*/(x_1\mathrm{V}_1^* + x_2\mathrm{V}_2^*) = x_2 r_2 v_2^*/(x_1 r_1 v_1^* + x_2 r_2 v_2^*) \qquad 4.109$$

The two component molecules are divided into segments of equal but arbitary size in the Flory theory so that $v_1^* = v_2^*$.(415) Prigogine and co-workers(347) consider the molecular chain to comprise molecules of length equal to the cross-sectional diameter of the chain. The Prigogine theory of solutions involves a parameter, ρ, which characterizes the differences in the diameters of spherical molecules or of chain molecules. Since Flory and co-workers divide the molecules into equal-sized segments, the diameter difference effect is zero. Patterson *et al.*(413) have observed that the approximation given by equation 4.108 does not hold for *n*-alkanes where p^* varies with the varying chain length of the *n*-alkane. The effect was to raise the reduced temperature, $\tilde{T}$, predicted by the Flory$^{(53)}$ approximate equation 4.53 above the $\tilde{T}$ determined by equation 4.105. This increased the predicted configurational energy of the solution and resulted in better predictions of H^E_m by Flory.$^{(53)}$ Patterson and Delmas$^{(415)}$ give the following corresponding states expression for the reduced temperature, $\tilde{T}$, for the solution:

$$\tilde{T} = (\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2)/(1 - \psi_1 X_2 \upsilon^2) \qquad 4.110$$

where υ^2 is the interactional parameter and is equivalent to X_{12}/p_1^* in the Flory terminology. For a value of $\upsilon^2=0$ the reduced temperature for the solution corresponds to a mole fraction average of $\tilde{T}$ for the components. Expression 4.110 is thus similar to the Flory expression 4.81 with $X_2=0$, with $\upsilon^2=X_{12}/p_1^*$, and with ψ_i transformed to ϕ_i through equation 4.111:$^{(415)}$

$$\psi_2 = (x_2U_2^*)/(x_1U_1^* + x_2U_2^*) = (p_2\phi_2)/(p_1^*\phi_1 + p_2^*\phi_2) = (1 - \psi_1) \qquad 4.111$$

where:

$$U_i^* = p_i^*V_i^* \qquad 4.112$$

Flory$^{(55)}$ assumes the volume parameter, V^*, for the solution to be linear in mole fraction of the components:

$$V^* = x_1V_1^* + x_2V_2^* \qquad 4.113$$

A large positive volume "interaction" term in ρ^2 (ρ characterizes the diameter difference of molecules) is added in the Prigogine average potential model approximation for V^* which, according to Patterson and Delmas,$^{(415)}$ is probably incorrect. In a similar manner the van der Waals combining rule for spherical molecules cannot be applied to systems of chain molecules because the volume "interaction" term is unrealistically large. For this reason, Patterson and co-workers$^{(415)}$ have adopted equation 4.113 in their approach.

4.3.1 Mixing functions

According to the corresponding states theory$^{(415)}$ a mixing function, denoted A^E_m, can be written as:

$$A_m^E = U^*\tilde{A}(\tilde{T}) - [x_1U_1^*\tilde{A}(\tilde{T}_1) + x_2U_2^*\tilde{A}(\tilde{T}_2)] \qquad 4.114$$

If the equation for U^* is substituted into equation 4.114, where according to Prigogine$^{(347)}$ U_i^* are the molar energy reduction parameters for the solute components and are given by equation 4.112, and U^* is related to the properties of the pure components through:

$$U^* = x_1U_1^* + x_2U_2^* - x_1U_1^*X_2\upsilon^2 \qquad 4.115$$

then:

$$A_m^E/(x_1U_1^* + x_2U_2^*) = -\psi_1X_2\upsilon^2\tilde{A}(\tilde{T}) + [\tilde{A}(\tilde{T}) - \psi_1\tilde{A}(\tilde{T}_1) - \psi_2\tilde{A}(\tilde{T}_2)] \qquad 4.116$$

The first term on the right hand side of equation 4.116 for the excess molar enthalpy can be recognised as the Flory interaction term, while the second term within square brackets corresponds to the equation of state terms. Equation 4.116 for the excess molar volume becomes:$^{(415)}$

$$V_m^E/(x_1V_1^* + x_2V_2^*) = \tilde{v}(\tilde{T}) - \phi_1\tilde{v}(\tilde{T}_1) - \phi_2\tilde{v}(\tilde{T}_2) \qquad 4.117$$

The interaction parameter, υ^2, enters the equation of state terms through the solution parameters ν and T. Patterson and co-workers$^{(415)}$ recognized the advantages of associating the mixing function by a different pair of contributions. For $\upsilon^2=0$ for a system the one contribution would be associated with a difference in free volumes of the components while the term corresponding to the remainder of the mixing function due to υ^2 is the interaction term. The mixing functions, H_m^E, V_m^E, and S_m^E, have been separated into these contributions through an approximation which, according to Patterson and Delmas,$^{(415)}$ correspond to an error of less than 1% in the calculated mixing functions for high polymer solutions. By defining a reduced temperature, $\tilde{T}_A$, such that:

$$\tilde{A}(\tilde{T}_A) - \psi_1\tilde{A}(\tilde{T}_1) - \psi_2\tilde{A}(\tilde{T}_2) = 0 \qquad 4.118$$

and developing the quantity $\tilde{A}(\tilde{T})$ in equation 4.116 around $\tilde{T}_A$ while ignoring terms of order $(\psi_1 X_2 \upsilon^2)^2$ and $(\psi_1 T_1 + \psi_2 T_2 - T_A)^2$, then an equation involving υ^2 explicitly in the first term only is obtained:(415)

$$\begin{aligned} A_m^E/(x_1 U_1^* + x_2 U_2^*) = {} & [-\tilde{A}(\tilde{T}_A) + \tilde{T}_A(\delta\tilde{A}/\delta\tilde{T}_A)]\psi_1 X_2 \upsilon^2 \\ & + (\delta\tilde{A}/\tilde{T}_A)[\psi_1 T_1 + \psi_2 \tilde{T}_2 - \tilde{T}_A\} \end{aligned} \tag{4.119}$$

The X_2 term in the above equation 4.119 has been incorrectly written as X_1 in equation 16 of the original reference 415 by Patterson and Delmas. For V_m^E:(415)

$$V_m^E/(x_1 V_1^* + x_2 V_2^*) = [\tilde{T}_v(\delta\tilde{T}/\delta\tilde{T}_v)]\psi_1 X_2 \upsilon^2 + (\delta\tilde{v}/\delta\tilde{T}_v)[\psi_1 \tilde{T}_1 + \psi_2 \tilde{T}_2 - \tilde{T}_v] \tag{4.120}$$

Patterson and Delmas(415) have expanded T_1 and T_2 around T_A, in powers of $A_1 - A_2$ in the second free volume term in equations 4.119 and 4.120. They have neglected third and higher powers and obtain the following approximation to the equation 4.119:

$$\begin{aligned} A_m^E/(x_1 U_1^* + x_2 U_2^*) = {} & [-\tilde{A}(\tilde{T}_A) + \tilde{T}_A(\delta\tilde{A}/\delta\tilde{T}_A)]\psi_1 X_2 \upsilon^2 \\ & - (1/2)[(\tilde{A}_1 - \tilde{A}_2)/(\delta\tilde{A}/\delta\tilde{T}_A)]^2(\delta^2\tilde{A}/\delta\tilde{T}_A{}^2)\psi_1\psi_2 \end{aligned} \tag{4.121}$$

They quote the above approximation to be better than 4% in the worst case.

In the approximation for V_m^E corresponding to equation 4.121, the free volume term separates into two terms, giving the following expression:(415)

$$\begin{aligned} V_m^E/(x_1 V_1^* + x_2 V_2^*) = {} & \tilde{T}_v(\delta\tilde{v}/\delta\tilde{T}_v)\psi_1 X_2 \upsilon^2 + (\tilde{v}_1 - \tilde{v}_2)(\psi_1 - \phi) \\ & - (1/2)[(\tilde{v}_1 - \tilde{v}_2)/(\delta\tilde{v}/\delta\tilde{T}_v)]^2(\delta^2\tilde{v}/\delta\tilde{T}_v{}^2)[\psi_1\psi_2 + (\psi_1 - \phi_1)^2] \end{aligned} \tag{4.122}$$

For computational purposes Patterson and Delmas(415) have eliminated the ϕ through:

$$\psi_1 - \phi_1 = (p_1^* - p_2^*)\psi_1\psi_2/(p_2^*\psi_1 + p_1^*\psi_2) \tag{4.123}$$

and

$$\psi_1\psi_2 + (\psi_1 - \phi) = \{[(p_2^*)^2\psi_1 + (p_1^*)^2\psi_2]\psi_1\psi_2\}/(p_1^*\psi_2 + p_2^*\psi_1)^2 \tag{4.124}$$

4.3.2 The configurational properties

Empirical data may be used to give the various configurational properties. As an alternative, various pure liquid models may be employed to predict these values theoretically. Prigogine and co-workers(347) used the cell partition function and a Lennard-Jones (m, n) dependence of the intermolecular potential on distance for the volume dependence of the configurational energy:(415)

$$U = [-n(\tilde{v})^{-m/3} + m(\tilde{v})^{-n/3}]/(n - m) \qquad 4.125$$

Patterson an co-workers(413,415) have applied the free volume cell partition function of Hirschfelder and Eyring(413) and give the following expression for the reduced equation state:

$$\tilde{p}\tilde{v}/\tilde{T} = 1/[1 - b(\tilde{v})^{-1/3}] + mn[(\tilde{v})^{-n/3} - (\tilde{v})^{-m/3}]/3(n - m)T \qquad 4.126$$

where b is the packing factor equal to $(m/n)^{1/(n-m)}$, and gives $\tilde{v}(T)$ at $p = 0$. The reduced entropy is given by:(415)

$$\tilde{S} = 3\ln[(\tilde{v})^{1/3} - b] \qquad 4.127$$

A different choice for the pair (m, n) will yield different mixing functions. For example a choice of $m = 3$ and $n = \infty$ in equation 4.125 yields:(415)

$$U = -1/\tilde{v} \qquad 4.128$$

The above equation 4.128 is equivalent to the mixing function employed by Flory and co-workers who used a van der Waals energy / volume relation given by equation 4.128. Flory(59) feels that the use of the $(3, \infty)$ intermolecular pair potential to achieve reasonable agreement with experiment is absurd. The view adopted by Flory avoids any specification of the pair potential. Patterson and co-workers(413-415) have compared excess properties calculated on the basis of different choices for (m, n) against the precise thermal expansion coefficient and isothermal compressibility coefficient data as determined by the methods of Orwoll and Flory(57) for *n*-alkanes. Although they found the predicted results to be almost independent of the choice of model, the $(3, \infty)$ choice corresponding to the model employed by Flory and co-workers produced better correlations on the whole. Patterson and Delmas(415) attribute this to the exaggerations by the average potential model of the size effect on the solution reduction parameters through the parameter ρ. Aicart *et al.*(417) have tested the Prigogine-Flory theory using van der Waals and Lennard-Jones energy potentials for systems comprising quasi-spherical molecules. They have predicted excess volumes at four different temperatures for systems involving cyclohexane, benzene and toluene, and for systems involving benzene mixed with an n-alkane.(418) Although the Lennard-Jones potential resulted in the prediction of results which were in agreement with experimental values for benzene mixed with an n-alkane, this choice did not constitute any improvement over the van der Waals potential for any of the other systems. Aicart and co-workers(418) are of the opinion that the nominal improvement for the first systems does not justify the the use of the more complicated equations afforded by the Lennard-Jones potential.

Patterson *et al.*(413) give the following equations of state involving the coefficient of thermal expansion and the coefficient of isothermal compressibility:

$$-3/(\alpha T) = -m + (n - m)/[(\tilde{v})^{(n-m/3)} - 1] + [b(\tilde{v})^{-1/3}]/[1 - b(\tilde{v})^{-1/3}] \qquad 4.129$$

$$(V^*/\kappa U^*) = 1/(\alpha T)\{(mn)/3(n - m)[(\tilde{v})^{-m/3} - (\tilde{v})^{(-n/3)}]/\tilde{v}\} \qquad 4.130$$

$$3\tilde{C}_p{}^{-1} = b(m + 1)(\tilde{v})^{-1/3} - m + \{[1 - b(\tilde{v})^{-1/3}](n - m)/[(\tilde{v})^{(n-m/3)} - 1]\} \qquad 4.131$$

and

$$\tilde{T} = [(mn)/3(n - m)](\tilde{v})^{-m/3}[1 - (\tilde{v})^{(n-m)/3}][1 - b(\tilde{v})^{-1/3}] \qquad 4.132$$

For $m = 3$ and $n = \infty$, equations 4.129, 4.130, and 4.132, reduce to the Flory equations 4.34, 4.35, and 4.30. The equation for $\tilde{C}_p$ reduces to:

$$\tilde{C}_p{}^{-1} = (4/3)(\tilde{v})^{-1/3} - 1 \qquad 4.133$$

This equation has been incorrectly written in reference 60.

On rearranging equation 4.122, Van and Patterson(61) give the following approximation to the excess volume V_m^E:

$$V_m^E/(x_1V_1{}^* + x_2V_2{}^*) = \tilde{T}(\delta\tilde{v}/\delta\tilde{T})(\psi_1\theta_2X_{12}/p_1{}^*) \qquad \text{(interactional)}$$

$$-(1/2)[(\tilde{v}_1 - \tilde{v}_2)/(\delta\tilde{v}/\delta T]^2(\delta^2\tilde{v}/\delta\tilde{T}^2)\psi_2\psi_2 \qquad (\tilde{V}\text{curvature})$$

$$+ [(\tilde{v}_1 - \tilde{v}_2)(p_1{}^* - p^{2*})/(p_2{}^*\psi_1 + p_1{}^*\psi_2)]\psi_1\psi_2 \qquad (P^*\text{effect}) \quad 4.134$$

where the quantities $\tilde{v}$ and $\tilde{T}$ without subscripts refer to solution properties and are evaluated at an average reduced volume given by:(61)

$$\tilde{v} = \psi\tilde{v}_1 + \psi_2\tilde{v}_2 \qquad 4.135$$

Equation 4.134 can be simplified by introducing expressions from the Flory model. Patterson and co-workers(419) used the following expression to represent the term $(\delta^2\tilde{v}/\delta\tilde{T}^2)$:

$$T^2(\delta^2\tilde{v}/\delta\tilde{T}^2) = [(\tilde{v})^{-1/3} - 1]^2\{[28/9 - 2(\tilde{v})^{1/3}]\tilde{v}\}/[(4/3) - (\tilde{v})^{1/3}]^3 \qquad 4.136$$

Equation 4.136 has been incorrectly written in reference 419. The resulting approximate expression for the excess volume is:(61)

$$V_m^E/(x_1V_1^* + x_2V_2^*) = \frac{[(\tilde{v})^{1/3} - 1](\tilde{v})^{2/3}\psi_1\theta_2X_{12}}{[4/3(\tilde{v})^{-1/3} - 1]p_1^*} \qquad \text{(interactional)}$$

$$-\frac{(\tilde{v}_1 - \tilde{v}_2)^2[14/9(\tilde{v})^{-1/3} - 1]\psi_1\psi_2}{[4/3(\tilde{v})^{-1/3} - 1]\tilde{v}} \qquad (\tilde{V}\text{ curvature})$$

$$+\frac{(\tilde{v}_1 - \tilde{v}_2)(p_1^* - p_2^*)\psi_1\psi_2}{(p_2^*\psi_1 + p_1^*\psi_2)} \qquad (P^*\text{ effect}) \quad 4.137$$

In equation 15 of reference 61 the $(\tilde{v})^{-1/3}$ term in the $\tilde{V}$ curvature contribution has been incorrectly written as $\tilde{v}^{1/3}$. This has however been corrected in reference 419.

Equation 4.122 can be rewritten for H_m^E at zero pressure (i.e. U_m^E):(61)

$$H_m^E/(x_1U_1^* + x_2U_2^*) = [-\tilde{U} + \tilde{T}\tilde{C}_p]\psi_1\theta_2X_{12}/p_1^* \qquad \text{(interactional)}$$

$$- (1/2)[(\tilde{v}_1 - \tilde{v}_2)/(\delta\tilde{U}/\delta\tilde{T})]^2(\delta^2\tilde{U}/\delta\tilde{T}^2)\psi_1\psi_2 \qquad (\tilde{V}\text{ curvature}) \quad 4.138$$

Once again the reduced quantities for the solution are written without any subscripts. Equation 4.138 can also be written in terms of the Flory theory to give an equation analagous to equation 4.137 for the excess volume. In a corresponding states form the interactional contribution to the excess enthalpy, H_m^E(int.), can be given according to:(60)

$$H^E_m(\text{int.})/(x_1U_1^* + x_2U_2^*) = [X_{12}\theta_2\psi_1/p_1^*][-\tilde{U}(\tilde{T}_u) + \tilde{T}_u\tilde{C}_p(\tilde{T}_u)] \qquad 4.139$$

while the free volume contribution, H^E(f.v.), is given by:(60)

$$H^E_m(\text{f.v.})/(x_1U_1^* + x_2U_2^*) = \tilde{C}_p(\tilde{T}_u)[\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2 - \tilde{T}_u] \qquad 4.140$$

The interactional contribution has been incorrectly written in the original publication.(60) The reduced properties for the pure components, i, namely the reduced configurational energy, $\tilde{U}_i$, the reduced heat capacity, $\tilde{C}_{p,i}$, the reduced entropy, $\tilde{S}_i$, and the reduced temperature, $\tilde{T}_i$, are related by a model to the reduced volume, $\tilde{v}_i$, and to the macroscopic quantities of the pure components, α_i. The Flory model has been used for this purpose:(60)

$$\tilde{U}_i = -1/\tilde{v}_i \qquad 4.141$$

$$\tilde{C}_{p,i}^{-1} = 4/3(\tilde{v})^{-1/3} - 1 \qquad 4.142$$

and

$$\tilde{S}_i = 3\ln[(\tilde{v})^{1/3} - 1] \qquad 4.143$$

where $(\tilde{v})^{1/3}$ and $\tilde{T}$ are given according to equations 4.38 and 4.30 respectively. The average configurational energy for the mixture, $\tilde{U}$, is related to the reduced configurational energy of the pure components through:(60)

$$\tilde{U}(\tilde{T}_u) = \psi_1\tilde{U}_1(\tilde{T}_1) + \psi_2\tilde{U}_2(\tilde{T}_2) \qquad 4.144$$

This can be rewritten as:

$$\tilde{v}_u^{-1} = \psi_1\tilde{v}_1^{-1} + \psi_2\tilde{v}_2^{-1} \qquad 4.145$$

where the contact energy fraction, ψ_i, has been defined by equation 4.411. This permits the calculation of the reduced heat capacity for the mixture, $\tilde{C}_p(\tilde{T}_u)$, through equation 4.142.

The parameters, $p_i^*$and $\tilde{v}_i$ are given through the relationships of the Flory model:

$$p_i^* = \gamma T\tilde{v}_i^2 \qquad 4.146$$

$$V_i^* = V_i/\tilde{v}_i \qquad 4.147$$

and U_i^* is given according to equation 4.112. The coefficients γ_i and V_i are the thermal pressure coefficient and the molar volume of component i respectively. For the excess entropy, S^E, S is substituted for V in equation 4.120.(415) This can be rewritten in the Flory notation in terms of an interactional contribution, S^E_m(int.) and a free volume S^E_m(f.v.), where:(60)

$$TS^E_m(\text{int.})/(x_1U_1^* + x_2U_2^*) = (X_{12}\theta_2\psi/p_1^*)[\tilde{T}_{TS}\tilde{C}_p(\tilde{T}_{TS})] \qquad 4.148$$

and $$TS^E_m(\text{f.v.})/(x_1U_1^* + x_2U_2^*) = [\tilde{S}(\tilde{T}_{TS}) + \tilde{C}_p(\tilde{T}_{TS})][\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2 - \tilde{T}_{TS}] \qquad 4.149$$

The reduced temperature for the mixture, $\tilde{T}_{TS}$, must satisfy the equation:(60)

$$\tilde{T}_{TS}\tilde{S}(\tilde{T}_{TS}) = \psi_1\tilde{T}_1\tilde{S}(\tilde{T}_1) + \psi_2\tilde{T}_2\tilde{S}(\tilde{T}_2) \qquad 4.150$$

where $\tilde{T}_{TS}$ and $\tilde{S}(\tilde{T}_{TS})$ is given by the product of the appropriate forms of equations 4.30 and 4.143:

$$\tilde{T}_{TS}\tilde{S}(\tilde{T}_{TS}) = 3\{[(\tilde{v}_{TS})^{1/3} - 1]/(\tilde{v}_{TS})^{4/3}\}\ln[(\tilde{v}_{TS})^{1/3} - 1] \qquad 4.151$$

The value of $\tilde{V}_{TS}$ which satisfies the above is determined by a method of successive approximations.

The general corresponding states approach of Prigogine and co-workers gives expressions for $(\mu_1 - \mu_1^o)^R$ which are similar in form to equation 4.96. From Chahal *et al.*:(411)

$$\begin{aligned}(\mu_1 - \mu_1^o)^R &= RTX\phi_2^2\\ &= V_1^*X_{12}\theta_2^2\{-\tilde{G}(\tilde{T}) + \tilde{T}(\delta\tilde{G}/\delta\tilde{T})_{\tilde{p}}\}\\ &\quad + p_1^*V_1^*\{\tilde{G}(\tilde{T}) - \tilde{G}(\tilde{T}_1) + (\tilde{T}_1 - \tilde{T})(\delta\tilde{G}/\delta\tilde{T})_{\tilde{p}}\}\end{aligned} \qquad 4.152$$

The expression for the partial molar excess enthalpy of component 1, H^E_1, and for the partial molar non-combinatorial excess entropy for component 1, TS^E_1, can be obtained from equation 4.152 by replacing $\tilde{G}$ by $\tilde{H} = \tilde{U}$ (at zero pressure) and by $\tilde{T}\tilde{S}$.(411) Substituting for:

$$(\delta\tilde{G}/\delta\tilde{T})_{\tilde{p}} = -\tilde{S} \qquad 4.153$$

and for $$(\delta\tilde{U}/\delta\tilde{T}) = \tilde{C}_p \qquad 4.154$$

into equation 4.152 yields:

$$(\mu_1 - \mu_1{}^o)^R = RTX\phi_2{}^2 = V_1{}^*X_{12}\theta_2{}^2\{-\tilde{U}(\tilde{T})\} + p_1{}^*V_1{}^*\{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_1) + \tilde{T}_1[\tilde{S}(\tilde{T}_1) - \tilde{S}(\tilde{T})]\} \qquad 4.155$$

and

$$H_1^E = U_1^E = V_1{}^*X_{12}\theta_2{}^2\{-\tilde{U}(\tilde{T}) + \tilde{T}\tilde{C}_p(\tilde{T})\} + p_1{}^*V_1{}^*\{\tilde{U}(\tilde{T}) - \tilde{U}(\tilde{T}_1) + (\tilde{T}_1 - \tilde{T})\tilde{C}_p(\tilde{T})\} \qquad 4.156$$

Equations 4.155 and 4.156 can be written for different models of the liquid state. The Flory model based on the assumption of a van der Waals energy for the liquid, given by equation 4.128, and a cell partition function for the entropy given by:

$$\tilde{C}_p = \alpha T/\tilde{v}\tilde{T} \qquad 4.157$$

and $\tilde{S}$ given according to equation 4.143, can be substituted into the equations 4.155 and 4.156 to yield equations equivalent to 4.96 and 4.97.

4.4 A Modified Theory by Liebermann

4.4.1 An approximate equation for V_m^E

Liebermann$^{(62,63)}$ has developed a method for calculating the excess volumes for binary non-associated liquid mixtures from the excess Gibbs function and excess enthalpy data. The theory employs a combination of the Scatchard-Hildebrand$^{(356,420)}$ concept which affords an estimate of the excess enthalpy at a constant volume for molecules of equal size, and the Flory-Huggins approach,$^{(62,353)}$ which accounts for difference in the molecular sizes of the component molecules. The resulting expression employs macroscopic quanties of the pure components and is free of any adjustable parameters. Liebermann$^{(395)}$ tested the method for 31 different hydrocarbon systems. Reasonable success was achieved with the incorrect sign predicted in only two of the cases. The following is a summary of the derivation of the Liebermann equations for the excess thermodynamic properties.

The excess Gibbs free energy, G_m^E, is considered to be represented by the sum of two independent contributions and is given by:$^{(421)}$

$$G_m^E = G^* + G^{FH} \qquad 4.158$$

G^* is a temperature dependent term and represents the interactional contributions, while the Flory-Huggins term, G^{FH}, arises from the differences in the sizes of the component molecules.

$$G^{FH} = RT[x_1\ln(\phi_1/x_1) + x_2\ln(\phi_2/x_2)] \qquad 4.159$$

$$= RTf(\phi) \qquad 4.161$$

Differentiating equation 4.159 with respect to the temperature and the pressure results in the following two relations:$^{(62)}$

$$(\delta G^E_m/\delta p)_{T,\,x} = V^E_m = V^* + \{\delta[RTf(\phi)]/\delta p\}_{T,\,x} \qquad 4.161$$

and

$$(\delta G^E_m/\delta T)_{p,\,x} = -S^E_p = -S_p{}^* + \{\delta[RTf(\phi)]/\delta T\}_{p,\,\mathrm{x}} \qquad 4.162$$

where S^E_p is the excess entropy at a constant pressure. Equation 4.161 yields on rearrangement:$^{(62)}$

$$(G^* - H^E)/T + Rf(\phi) = -S_p{}^* + \{\delta[RTf(\phi)]/\delta T\}_{p,\,x} \qquad 4.163$$

For simplicity it is assumed that $f(\phi)$ remains constant with temperature and hence equation 4.163 reduces to:

$$S_p{}^* = (H^E_m - G^*)/T \qquad 4.164$$

Scatchard$^{(356)}$ has shown that V^E_m at a negligible pressure is related to the excess entropies at a constant pressure, S^E_p, and the corresponding value at a constant volume, S^E_V. For small V^*:$^{(62)}$

$$V^* = (S_p{}^* - S_V{}^*)(\kappa_m/\alpha_m) \qquad 4.165$$

the properties, V^*, $S_p{}^*$, and $S_V{}^*$, in equation 4.165 are related to the corresponding quantities, V^E_m, S^E_p and S^E_V. The subscripts, m, in equation 4.165 refer to the mixture properties.

By differentiating the Flory-Huggins term with respect to pressure in equation 4.161 and substituting for V^* from equation 4.165, the following equation for V^E_m is yielded on rearrangement:(62)

$$V_m^E = (\kappa_m/\alpha_m)(S_p^* - S_v^*) + RT(\kappa_1 - \kappa_2)(\phi - x_1) \qquad 4.166$$

In order to estimate the S_v^* term it becomes necessary to employ the concepts of the Solubility Parameter Theory of Hildebrand and Scott.(349) On assuming a hypothetical mixture for which $V^* = 0$, then from equation 4.165:

$$S_v^* = S_p^* \qquad 4.167$$

and hence equations 4.158 and 4.162 imply that:(62)

$$S_p^* = -(\delta G^*/\delta T)_{p,\ x} \qquad 4.168$$

If the expression for G^* in terms of the Hildebrand solubility parameters,(349) δ_1 and δ_2, is substituted into equation 4.168, then:

$$S_p^* = S_v^* = \{-\delta[\phi_1\phi_2 V_m(\delta_1 - \delta_2)^2]/\delta T\}_{p,\ x} \qquad 4.169$$

where:(62)

$$G^* = \phi_1\phi_2 V_m(\delta_1 - \delta_2)^2 \qquad 4.170$$

and where:(62)

$$V_m = x_1V_1 + x_2V_2 \qquad 4.171$$

V_1 and V_2 are the hard core molar volumes for the two liquids, and have been defined through V_i/V_i^*. V_i is the molar volume of the system.

Liebermann(62) has made the further assumption that $\alpha_1 = \alpha_2 = \alpha_m$ and has derived the following equation:

$$\{\delta \ln[\phi_1\phi_2(x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2]/\delta T\}_{p,\ x} = -1.5\alpha_m \qquad 4.172$$

The substitution of equation 4.172 into 4.169 yields:

$$S_V^* = 1.5\alpha_m\phi_1\phi_2V_m(\delta_1 - \delta_2)^2 \qquad 4.173$$

It follows from equations 4.169 and 4.172 that $S_V^* = 1.5\alpha_mG^*$, and hence the equation for the excess volume becomes:(62)

$$V_m^E = \{(\kappa_m/\alpha_m)[(H_m^E - G^*)/T] - 1.5\kappa_mG^* + RT(\kappa_1 - \kappa_1)(\phi_1 - x_1) \qquad 4.174$$

where:(62)

$$\alpha_m = \alpha_1\phi_1 + \alpha_2\phi_2 \qquad 4.175$$

and

$$\kappa_m = \kappa_1\phi_1 + \kappa_2\phi_2 \qquad 4.176$$

The rearrangement of the above equation 4.174 offers a route for the prediction of G_m^E from experimental V_m^E and H_m^E data.(62)

4.4.2 A modified Flory theory by Liebermann

Liebermann(422) has shown that the molar configurational energy, E, for a system can be written in the familiar van der Waals form:

$$E = -a/V \qquad 4.177$$

where the van der Waals constant, *a*, is assumed to be independent of the volume at a constant composition. Equation 4.177 can be rewritten as:(63)

$$E = PV - cRT/[1 - (\tilde{v})^{-1/3}] \qquad 4.178$$

where the variables in the above expression have been defined previously in the section concerning the Flory theory. Once again the parameter, *c*, characterizes the number of intermolecular degrees of freedom and is given by:(63)

$$c = p^*V^*/RT^* \qquad 4.179$$

The *c* are additive in the mole fraction x_i. Substitution of the relevant Flory equations for, p^*, V^* and for T^*, together with equation 4.179 for c into the expression for the molar configurational energy, E, yields:(63)

$$a/V = p^*V^{*2}/V \qquad 4.180$$

At a zero pressure the molar excess enthalpy is given by the difference between the molar configurational energy of the mixture and the corresponding mole fraction averages of the energies of the unmixed components. For a binary mixture:(63)

$$H^E_m = (x_1p_1{}^*V_1{}^{*2}/V_1) + (x_2p_2V_2{}^{*2}/V_2) - (p^*V^{*2}/V) \qquad 4.181$$

here the unsubscripted quantities refer to the solution properties.

From a comparison of equations 4.178 and 4.180 at $p = 0$:

$$p^*V^{*2}/V = RTc/[1 - (\tilde{v})^{-1/3}] \qquad 4.182$$

The previously defined relationship:

$$p^* = T\gamma v^2 \qquad 4.183$$

can also be rewritten as:

$$p^*V^{*2} = T\gamma V^2 \qquad 4.184$$

Substituting this expression into the pure component part of equation 4.181 and replacing the second term by equation 4.182 yields the following expression for the excess molar enthalpy:

$$H^E_m/T = x_1\gamma V_1 + x_2\gamma_2V_2 - Rc/[1 - (\tilde{v})^{-1/3}] \qquad 4.185$$

Liebermann(63) has related the parameter c to the pure component properties. Equations 4.182 and 4.184 yield:

$$Rc = \gamma V[1 - (\tilde{v})^{-1/3}] \qquad 4.186$$

The substitution of the Flory expression for $\tilde{v}$ into the above yields the following equation 4.187 which applies to both the pure components and to the solution:

$$Rc/T = \alpha\gamma V/(3 + 4\alpha T) \qquad 4.187$$

From the additivity of *c* in the mole fractions, this reduces to the following expression for a binary mixture:

$$Rc/T = x_1\alpha_1\gamma_1V_1/(3 + 4\alpha_1T) + x_2\alpha_2\gamma_2V_2/(3 + 4\alpha T) \qquad 4.188$$

In order to relate the pure component data to the reduced volume of the mixture, Liebermann(63) has assumed that the segments are randomly distributed at zero excess volume. The excess molar entropy is then considered to be combinatorial in nature and is thus independent of the pressure. From the thermodynamic identity:(63)

$$(\delta S/\delta p)_{T,\,x} = -\alpha V \qquad 4.189$$

Liebermann(63) has concluded that at $V_m^E=0$, the excess of α_oV_o of the mixture over the contribution of the pure components α_aV_o will disappear since S_V^E is assumed to be independent of p:

$$\alpha_oV_o - \alpha_aV_o = 0 \qquad 4.190$$

where:

$$\alpha_a = x_1\alpha_1V_1/V_o + x_2\alpha_2V_2/V_o \qquad 4.191$$

and

$$V_o = x_1V_1 + x_2V_2 \qquad 4.192$$

The coefficients α_o and α_a are related through the relationship:(63)

$$\alpha_o = \alpha_a + (\delta\alpha/\delta V)_{T,\,x}\,V_m^E \qquad 4.193$$

and thus at $V_m^E=0$, $\alpha_o=\alpha_a$, while the difference $(\alpha_a - \alpha_o)$ for $V_m^E\neq 0$ is proportional to V_m^E. Upon making the assumption that:(63)

$$(\delta\alpha/\delta V)_{T,\,x} \cong (\alpha - \alpha_o)/V_m^E \qquad 4.194$$

then equation 4.193 becomes:(63)

$$\alpha = 2\alpha_o - \alpha_a \qquad 4.195$$

A value for the parameter α_o can be obtained from the pure component data, since the reduced volume from which α_o may be calculated is:

$$\tilde{V}_o = V_o/V^* \qquad 4.196$$

All the parameters required in the determination of H_m^E can thus be obtained from the pure component properties. The excess molar volume is simply determined from:

$$V_m^E = \tilde{v}V^* - V_o \qquad 4.197$$

The hard sphere model, which is essentially a refinement of the original van der Waals concept of a liquid, treats the molecules as hard spheres moving in a uniform background potential which is proportional to the reciprocal volume.(395) From the Flory concept the parameter, c, characterizing the number of intermolecular degrees of freedom should equal unity for rigid spheres. Liebermann(63) has examined the effect of replacing the N real molecules considered in the Flory partition function by Nc perfect spheres occupying the same total volume. From equation 4.182 Liebermann(63) has shown that equation 4.181 becomes:

$$H_m^E/RT = x_1c_1/[1 - (\tilde{v}_1)^{-1/3}] + x_2c_2/[1 - (\tilde{v}_2)^{-1/3}] - c/[1 - (\tilde{v})^{-1/3}] \qquad 4.198$$

On letting $c_1 = c_2 = c = 1$ in the above equation, as would be the case for hard spheres, and replacing the mole fractions by ζ_1 and by ζ_2, equation 4.198 becomes:(63)

$$H_m^E/RT = \{\zeta_1/[1 - (\tilde{v}_1)^{-1/3}]\} + \{\zeta_2/[1 - (\tilde{v}_2)^{-1/3}]\} - 1/[1 -(\tilde{v})^{-1/3}) \qquad 4.199$$

where since Nc spherical molecules of type 1 and of type 2 are being considered:(63)

$$\zeta_1 = 1 - \zeta_2 = N_1c_1/(N_1c_1 + N_2c_2) \qquad 4.200$$

Liebermann(63) observed that the above equation 4.199 gave better results for a series of n-alkane mixtures than did equation 4.185.

4.5 Published work concerning the Flory based theories

A large amount of work concerning the Flory theory and the Prigogine-Flory-Patterson theory, and the application of these theories to the prediction of excess thermodynamic properties of binary liquid mixtures, has been reported in the literature over the last 25 years. It is pertinent to consider some of the work which has a direct bearing on the work reported in this thesis.

Benson and co-workers(151,153) have interpreted excess enthalpies and excess volumes for mixtures of *cis*- and *trans*-decalin with cyclopentane and with cyclohexane. For the mixtures involving cyclopentane, two calculations were carried out for each system. The first calculation assumed $Q_{12}=0$ while the second employed a value of Q_{12} determined from a least squares fit of G_m^E for each system. The values of G_m^E and TS_m^E for $Q_{12}=0$ were of the correct magnitude. Better agreement between experimental and predicted values was however achieved when adjusted Q_{12} values were employed. These workers employed the spherical molecule approximation to determine values for the ratio s_1/s_2. In order to reproduce the sigmoid-shaped curves for the isomeric decalin, it was necessary to adjust the ratio s_1/s_2. This however necessitated the use of physically unreasonable s_1/s_2 values.

Battino and co-workers have investigated the thermodynamics of mixtures involving cyclohexane with isooctane(423) and with carbon tetrachloride.(424) They have predicted V_m^E, H_m^E, and TS_m^E, for these mixtures using the Flory theory together with the spherical molecule approximation. As a result of the very small volume changes on mixing for cyclohexane with isooctane, the predicted thermodynamic properties were almost identical to the constant pressure functions calculated using the Scatchard-Hildebrand solubility parameter theory.

Fujihara *et al.*(155) have analysed excess molar volumes and excess molar enthalpies for {*trans*-decalin + (benzene or toluene or isooctane or *n*-heptane)} using the Flory theory. They found that the contribution to H_m^E by the X_{12} term for mixtures of *trans*-decalin with a saturated hydrocarbon was much smaller in magnitude than the free volume contribution. For systems involving benzene and toluene however, the large positive contribution from the X_{12} term dominated the free volume contribution. This observation suggested that the intermolecular interaction between component molecules was large and repulsive, resulting in large positive H_m^E values. An extension of the above work to include *cis*-decalin mixtures has been reported recently.(149) The authors are presently obtaining additional information concerning the effect of sizes and shapes of the component molecules on the thermodynamic behaviour of these mixtures before attempting to explain quantitatively the isomer effect of the *cis*- and *trans*-decalin on the thermodynamic properties.

Molar excess volumes for mixtures involving *n*-alkanes,(425) *n*-alkanes mixed with branched alkanes,(27,197,203,425) and *n*-alkanes or branched alkanes mixed with cycloalkanes,(27) have been studied extensively from both an experimental as well as from a theoretical view point. These experimental results have been fitted to the Flory theory and to the Prigogine-Flory-Patterson theory with varying degrees of success.(425-427) Letcher and co-workers have applied the Flory theory to mixtures of benzene with a cycloalkane or an *n*-alkane,(33) and to mixtures of an *n*-alkane with a cycloalkane.(42,428) They have successfully predicted H_m^E and V_m^E for these systems using the spherical molecule approximation to determine the ratio s_1/s_2.

Awwad and co-workers have studied the packing and conformational contributions and the effect of the molecular shape on V_m^E for mixtures of an *n*-alkane with its corresponding alkane isomers.(429-433) They have used the Prigogine-Flory-Patterson theory and have in many cases interpreted the results in terms of the three contributions to V_m^E. Awwad and Salman(189) have investigated the effect of the orientational ordering in mixtures of *n*-alkanes with cyclohexane. They have related their predicted excess molar volumes, excess molar viscosities, and excess molar activation energies, to the results of Patterson *et al.*(186) who investigated V_m^E for some of these systems. The results have also been compared to the results for mixtures of cyclopentane with an *n*-alkane and with isooctane. Awwad and Salman(189) noted that the interactional contribution to V_m^E was large and positive and decreased through a mininum for an *n*-alkane of chain length $n = 9$. They attributed this phenomenon to the destruction on mixing of short range orientational ordering in the higher *n*-alkanes. The free volume contribution was observed to be large and negative for higher *n*-alkanes and smaller for lower *n*-alkanes, while the P^* effect was negative for lower *n*-alkanes but increased, becoming large and positive for higher *n*-alkanes.

Heintz and Lichtenthaler(27) have discussed the X_{12} parameter and its dependence on the chain length, the degree of branching, and on the temperature, for mixtures of *n*-alkanes and their branched isomers with cyclohexane. Further work carried out by one of these authors has involved mixtures of cyclohexane with saturated and with unsaturated hydrocarbons.(434) The excess molar enthalpy was observed to decrease for a double bond at the end of a 1-alkene chain with respect to the mixture comprising the corresponding saturated *n*-alkane chain. This effect was more noticeable for a double bond contained within the chain. The effect of the molecular size and shape on the excess enthalpy for hydrocarbon mixtures has been investigated by Lichtenthaler and co-workers for mixtures of *n*-alkanes,(435,436) of branched alkanes,(436) and of unsaturated hydrocarbons.(436) The results exhibited a contribution from the disruption of order of the *n*-alkane on mixing with a globular second component. From an investigation concerning mixtures of cyclohexane with *n*-octane or an isomer of octane,(436) the observed decrease in X_{12} with temperature indicated that the short-range order within the pure *n*-alkane was partially destroyed by thermal motion before mixing. The increase in X_{12} observed for an increase in the pressure was physically reasonable, since at high pressures the short range order is more distinct.

Aicart and co-workers have employed the van der Waals potential and a Lennard-Jones potential in the Prigogine-Flory theory to predict H_m^E, V_m^E, and the function $(\delta V_m^E/\delta p)_T$, for {benzene + an *n*-alkane},(418) {cyclohexane + (benzene or toluene)} and {benzene + toluene}.(417) It was generally felt that the more complicated expressions resulting from the Lennard-Jones potential did not constitute an improvement over the simple van der Waals potential equation.(417,437)

Patterson(3) has used the one fluid corresponding states theory together with two prescriptions of van der Waals type and a third used by Flory to predict excess thermodynamic properties of mixtures of spherical molecules. Patterson has assessed the physical significance of the prescriptions and has compared the results to values yielded by Monte Carlo calculations. The contributions to the excess quantities were discussed in terms of energetic weaknesses of 1-2 contacts relative to 1-1 and 2-2 contacts and in terms of the dissimilarity between the free volumes of the components. Two contributions to the free volume were distinguished. Further evidence indicated two additional effects. For mixtures comprising anisotropic molecules a third contribution can be attributed to short range orientational order or "correlations of molecular orientations (CMO)" in one or in both of the pure components. A net decrease in order resulting from the mixing of liquids of different degrees of ordering results in positive contributions to H_m^E and to S_m^E. Another contribution, which is accompanied by an order creation, is associated with a hindering of the rotation of a flat molecule such as cyclopentane, or with the hindering of the rotational motion of the segments of a flexible *n*-alkane chain, by a flat or sterically hindered second molecule. This effect results in a negative contribution to H_m^E. The contribution was first observed for systems involving alkanes of the same molecular shape but differing in the degrees of steric hinderance or torsional oscillations.(3)

Patterson(3) has investigated the CMO effect for straight chain alkanes and for branched alkanes and has observed that the molecular shape is an important parameter in determining the excess thermodynamic quantities. The addition of a methyl group to *n*-hexane reduces the orientational ordering in the mixture. As the methyl group is moved towards the centre of the chain the orientational ordering decreases further. Further work has been carried out in this regard by Patterson and co-workers, who have studied systems involving *n*-hexadecane mixed with octane isomers or with nonane isomers.(4,152) The larger negative H_m^E for similar mixtures involving *n*-octane with *n*-hexadecane could only be explained by the exothermic contribution associated with ordering effects on mixing. Patterson and co-workers have predicted excess thermodynamic properties for mixtures of *n*-hexane, *n*-heptane, and isomers of both of these, with *n*-hexadecane and with highly branched hexadecane isomers.(60,61,438) The negative H_m^E and G_m^E for isomeric hexane and isomeric heptane with isomeric hexadecane mixtures(60) were explained through negative free volume contributions to the H_m^E and to the TS^E. In the case of S_m^E these contributions were countered by positive combinatorial contributions for mixtures of molecules differing in size. No contribution was observed for methyl - methylene group interactions. H_m^E and S_m^E were positive while G_m^E were slightly negative for hexane and heptane isomers mixed with *n*-hexadecane. The results were interpreted in terms of molecular orientations and a negative contribution was ascribed to the rotational ordering of *n*-hexadecane segments on the sterically hindered second molecule.

Similar work involving *n*-hexane and an isomer of hexane mixed with a normal alkane or with a branched alkane(25) has indicated that the molecular orientation effect is highly sensitive to molecular shape, increasing with *n* for normal alkanes, remaining zero for branched alkanes, and being destroyed on mixing with spherically shaped molecules.

The steric hinderance or "condensational" contribution has been observed for molecules exhibiting a crowded central atom such as the highly branched alkanes, the SnR_4 compounds, some disubstituted cycloalkanes,(439) and for mixtures where one of the molecules has a flat shape such as in *trans*-decalin or in cyclopentane.(152) The result is an exothermic contribution to H_m^E. Negative H_m^E, V_m^E, and S_m^E values,(151-153) and positive

C_p^E (152) values for systems comprising *trans*-decalin mixed with cyclopentane were attributed to the hindering of the flat plate-like cyclopentane by the *trans*-decalin molecule. This effect was less enhanced for similar mixtures involving *cis*-decalin. Neither the *cis*-decalin nor the *trans*-decalin were observed to contain any appreciable orientational ordering in the pure components. This negative contribution to both H_m^E and S_m^E was also observed for mixtures involving sterically hindered nonanes with *n*-hexadecane, where the nonanes were said to condense on the relatively free rotating segments of the *n*-hexadecane molecule.(152) The steric hinderance contribution was less important at high temperatures.(439)

The H_m^E for {*trans*-decalin + *n*-hexadecane} is smaller than the corresponding value for {*cis*-decalin + *n*-hexadecane}. The subsequent decrease in H_m^E with an increasing temperature for the *trans*-decalin mixture has been attributed to an interference of the flat plate-like *trans*-decalin with the molecular motion of the *n*-hexadecane chain.(146) Investigations by de St. Romain and Patterson(147) concerning mixtures involving *cis*- and *trans*-decalin with an alkane and with an alkane isomer have indicated smaller H_m^E for mixtures involving the plate-like *ee* configuration than for the more globular *ea* configuration of decalin. The magnitude of the difference between H_m^E values for mixtures involving these two isomers was also been observed to have been influenced by the shape and flexibility of the alkane component of the mixture.

Couchon *et al.*(438) discuss the disorder and steric hinderance contributions to the predicted heats and free energies of mixing of an amine with 12 isomers of hexane, heptane and octane. They term the positive contribution to mixing which accompanies the destruction of order in an ordered liquid, H_m^E(dis.). Other investigations into enthalpies of mixing by various workers for systems involving *n*-hexadecane with 21 branched nonanes,(4) or mixtures involving tetraalkyl or trialkyl derivatives,(439) have also exhibited the steric hinderance or "condensation" contribution. Couchon *et al.*(438) attribute the contribution to a loss of mobility of either a sterically hindered compound, or of the second component, or possibly of both, in the solution.

Order destruction and order creation processes in solutions have further been investigated for a variety of systems. These include cyclohexane mixed with normal alkanes, with highly branched isomers,(419,440) with benzene,(418) with toluene,(441) and mixtures of xylene with an *n*-alkane.(441) Benzene has an order breaking ability which is comparable to that of cyclohexane, but toluene and *p*-xylene show a progressively lesser effect. The data for p-xylene is consistent with an ordering in solution between the plate-like p-xylene and the *n*-alkane molecules.

Delmas and Purves(442) have also investigated the thermodynamics of mixing spherical molecules with branched or linear alkanes in terms of order effects. They have considered systems comprising tetralin and decalin mixed with linear alkanes in the range C_6 to C_{16}, and mixed with highly branched alkanes. Although the decalin and tetralin molecules are cyclic in nature they did not appear to be good "order breakers" on mixing. The authors expected that the H^E_m values for tetralin with a second component, X, would lie between those H^E_m for mixtures of cyclohexane with X and benzene with X. This was substantiated for mixtures where X corresponded to a branched hexadecane, but did not hold for mixutures where X was *n*-hexadecane. This discrepancy was attributed to a condensation effect.

Patterson and Robard(443) have discussed the thermodynamics of polymer mixtures in terms of the polymer solution theory of Prigogine(347) and of Flory *et al.*(53) The interaction parameter was shown to be a function of temperature and of pressure. The positive free volume contribution was indicative of unfavourable mixing.

Hammers *et al.*(412) have examined the molar excess enthalpies for *n*-alkane systems within the scope of the polymer solution theory of Flory in the approximation by Delmas *et al.*(444) They used a semiempirical method of Patterson and Bardin(414) to obtain the characteristic properties for the *n*-alkane data rather than the partition function method of Flory. They obtained a physically realistic interpretation of the excess enthalpy over the entire composition range.

Independent of the work by Patterson and co-workers, Grolier and Wilhelm and co-workers(445-449) have observed effects in mixtures involving plate-like molecules with *n*-alkanes which indicate an ordering in the solution. Grolier and co-workers have suggested that the ordering is essentially intramolecular and is associated with a change in the *trans-gauche* population of the *n*-alkane.

Hicks and Young(290) have utilized Flory's 1964 treatment of chain molecular mixtures to predict ln γ^{∞}_{13} values for several *n*-alkane mixtures, obtaining only fair agreement with experimental results. Janini and Matire(450) have predicted γ_{13} for C_6-C_8 *n*-alkane solutes in long chain *n*-alkane solvents ranging from $n=16$ to $n=32$. The good agreement between predicted and experimental results can be attributed to the fact that experimental γ_{13}^{∞} values were used to obtain empirical expressions for $(c/r)_i$. These workers employed the corresponding states principle, introducing small differences in interactional energies between methyl end segments and methylene interior segments. Rodriguez and Patterson$^{(451)}$ have predicted ln γ_{13}^{∞} values for lower *n*-alkane solutes in higher *n*-alkane solvents. Patterson *et al.*$^{(452)}$ have investigated the importance of the contact interactional contribution by analysing data on branched *n*-alkane systems. They conclude that the non-combinatorial contribution to ln γ_{13}^{∞} is equation of state in character.

Chahal *et al.*$^{(411)}$ have used the Flory-Huggins approximation to the non-combinatotial contribution and have determined solvent chemical potentials and heats of dilution for systems containing polydimethyl siloxane with solvents comprising normal and branched alkanes and with aromatic hydrocarbons. The Flory theory and other models consistent with the Prigogine corresponding states approach gave poor predictions. This was attributed in part to an error in the Flory-Huggins approximation for a polymer of large chain diameter. They concluded that the procedure of fitting the theory to enthalpy data gave the best results.

De Ligny and co-workers$^{(453,454)}$ have calculated values for the Flory X_{12} parameter from retention volume values obtained from g.l.c. data for small *n*-alkanes and branched alkane solutes in large straight chain and branched chain solvents. The X_{12} terms decreased with an increase in temperature, increased with an increase in the chain length of the *n*-alkane solvent, and were dependent on the shape of the order-disturbing component. These results indicated the presence of short-range orientational ordering in the *n*-alkanes.

Awwad *et al.*$^{(455)}$ have separated internal and external contributions to volume effects in liquid alkane mixtures through ultrasonic attenuation and velocity measurements. The results indicate a geometrical packing component in the mixture interactional parameter, X_{12}.

Rubio and co-workers$^{(456)}$ have recently derived a thermodynamic model for multicomponent mixtures. The derivation of the model is equivalent to the Prigogine-Flory-Patterson model. Panayiotou and Vera$^{(457)}$ have modified the Prigogine-Flory-Patterson theory by introducing a variable number of external degrees of freedom in the mixture. These are estimated using a combining rule involving a binary parameter C_{12}. Shukla and Haile$^{(458)}$ have recently presented a method for determining excess properties of liquid mixtures based on Kirkwood's interpretation of the chemical potential in terms of a coupling parameter. In conjunction with a statistical mechanical perturbation theory, they have demonstrated their method by predicting excess Gibbs free energies for binary mixtures of repulsive soft spheres. The method was shown to be highly reliable. Treszczanowicz and Benson$^{(459)}$ have proposed a model of associated mixtures in which a chemical contribution term described by an athermal associated model is combined with a physical contribution term described by the Flory formalism. The theory employs five adjustable parameters. Three of these represent the enthalpy, entropy, and the volume, of the hydrogen bond formation, while two correlate the Flory interaction parameter with molecular characteristics of the component molecules. They have tested the theory for mixtures involving alcohol with alkane systems. The predicted V_m^E were in good agreement with experimental values.

4.6 This Work

Both the Flory theory as well as the Prigogine-Flory-Patterson theory have been employed in this work to predict excess thermodynamic properties for binary liquid mixtures comprising an *n*-alkane, a 1-alkene, a 1-alkyne, a cycloalkane, cyclohexene, a cycloalkadiene or benzene with a bicyclic compound, benzene, cyclohexane or *n*-hexane. The Liebermann theory has also been applied to the same systems. A detailed discussion of the application of the theories, and a comparison between the predicted and the experimental results, is made in Chapter 6.

CHAPTER 5

EXPERIMENTAL RESULTS AND OBSERVATION OF TRENDS

5.1 Introduction

Excess molar enthalpies and excess molar volumes have been determined at 298.15 K for {a bicyclic compound + (1-hexene or 1-hexyne or 1-heptene or 1-heptyne)} and {a bicyclic compound + (cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)}. H_m^E values have been measured for {(decalin or bicyclohexyl or tetralin) + *n*-pentane}, {bicyclohexyl + *n*-heptane} and {tetralin + *n*-octane} in order to complete the series {a bicyclic compound + an *n*-alkane} where the chain length of the *n*-alkane varies from $n=5$ to $n=16$. Excess molar enthalpies have also been determined at 298.15 K for the mixtures {benzene + 1-heptyne}, {(cyclohexane or *n*-hexane) + (1-heptene or 1-heptyne)} and {(benzene or cyclohexane or *n*-hexane) + (cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene)}. Excess molar volumes have been determined for {(benzene or cyclohexane or *n*-hexane) + (1-hexyne or 1-heptene or 1-heptyne)}. This completes H_m^E and V_m^E for the series {(benzene or cyclohexane or *n*-hexane) + (1-hexene or 1-hexyne or 1-heptene or 1-heptyne)} and for {(benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}.

The experimental excess molar enthalpy results are tabulated in Appendix A and are reported diagrammatically in Figures 5.1 to 5.7. The experimental excess molar volumes are given in Appendix B and are plotted in Figures 5.8 to 5.14. The experimental H_m^E and V_m^E results have been fitted to the Redlich-Kister smoothing equations:

$$\delta_H = H_m^E/(\text{J.mol}^{-1}) - x_1(1-x_1)\sum_r A_r(1-2x_1)^r \qquad 5.1$$

and

$$\delta_V = V_m^E/(\text{cm}^3.\text{mol}^{-1}) - x_1(1-x_1)\sum_r B_r(1-2x_1)^r \qquad 5.2$$

The smoothing coefficients, A_r, are tabulated in Appendix C in Tables C1 and C2, and the coefficients B_r are tabulated in Tables C3 and C4. The computer programme employed in the determination of the above coefficients, A_r and B_r, was written by Spiteri(82) and will not be included in this thesis.

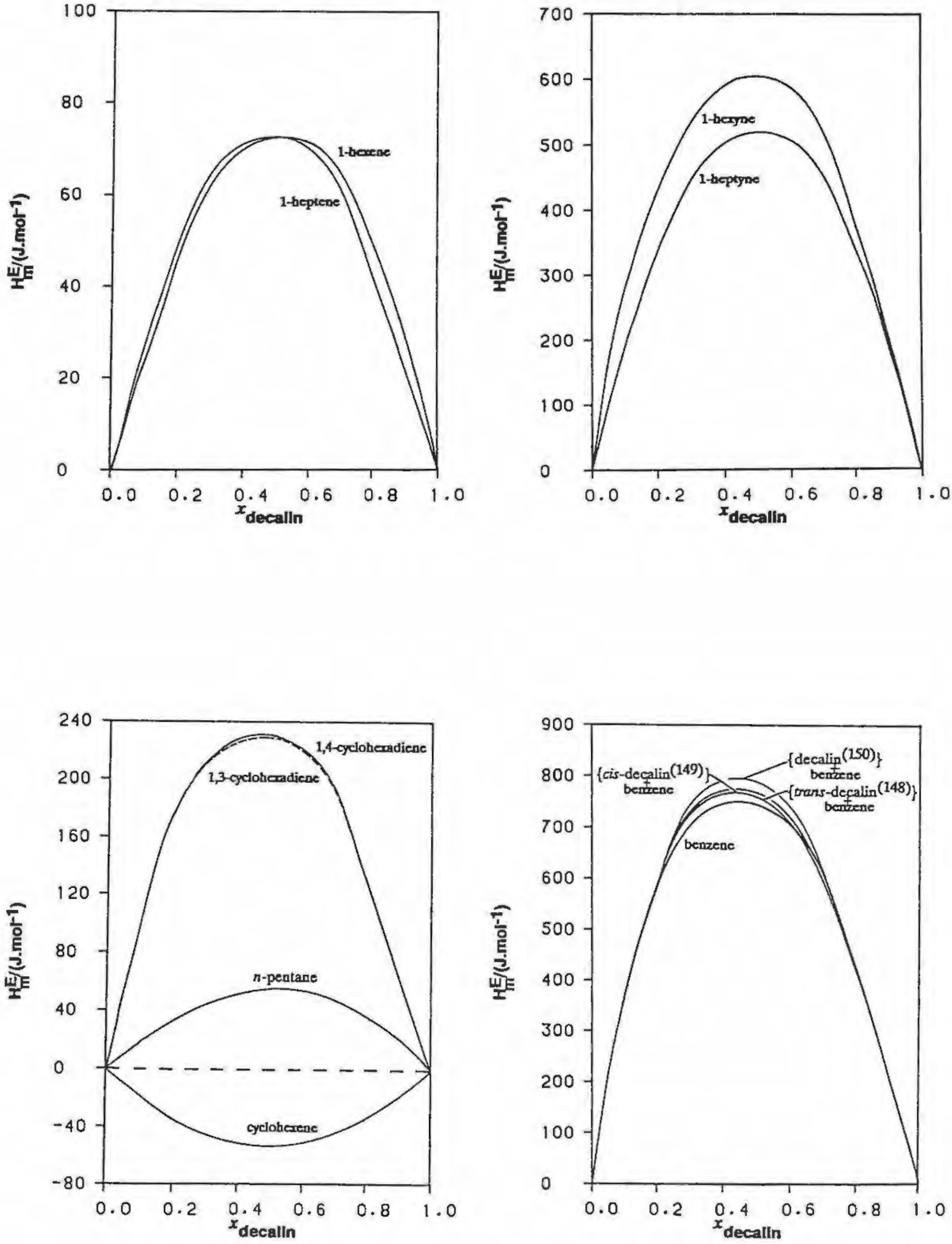

Figure 5.1 Experimental excess molar enthalpies for decalin systems at 298.15 K

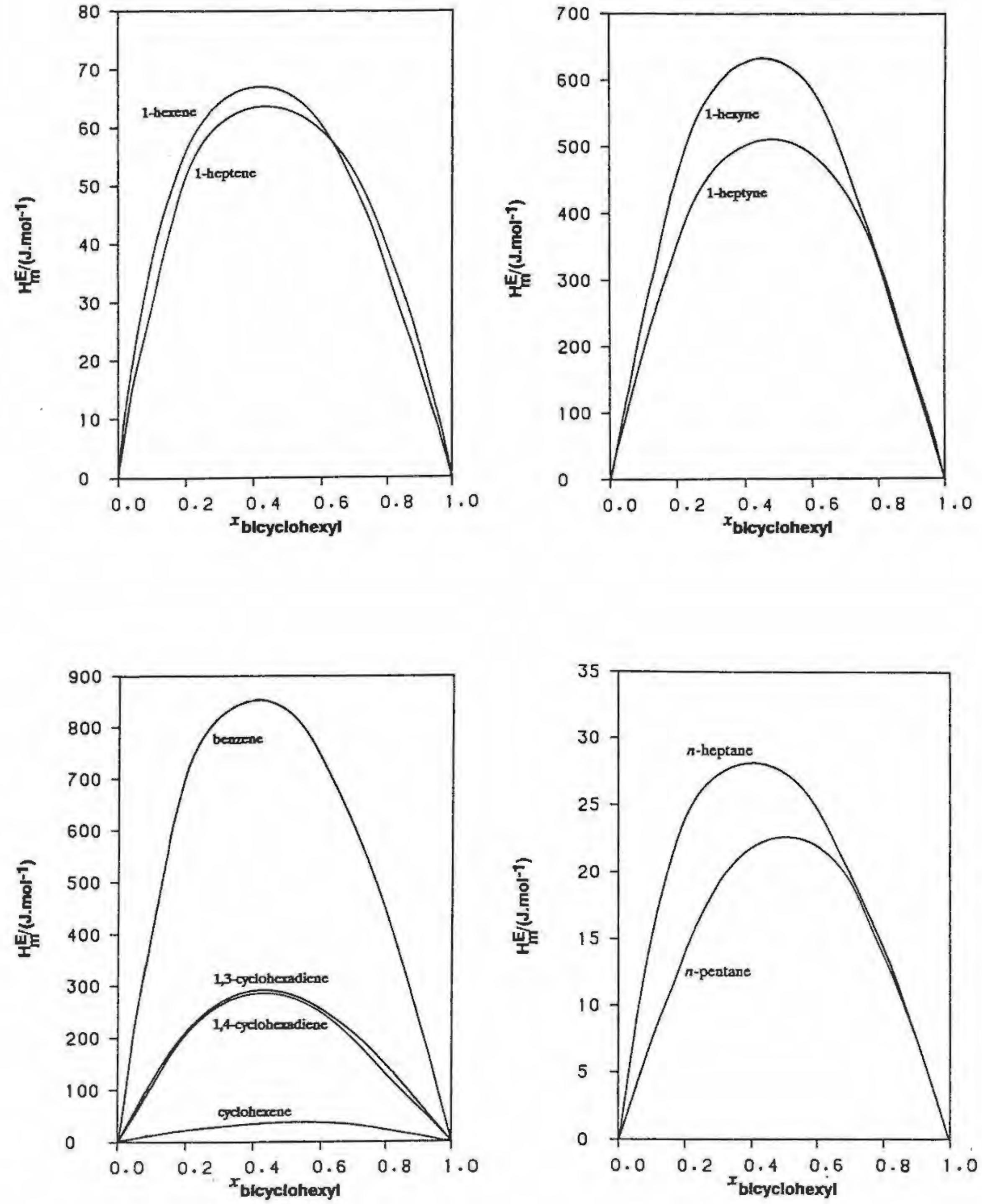

Figure 5.2 Experimental excess molar enthalpies for bicyclohexyl systems at 298.15 K

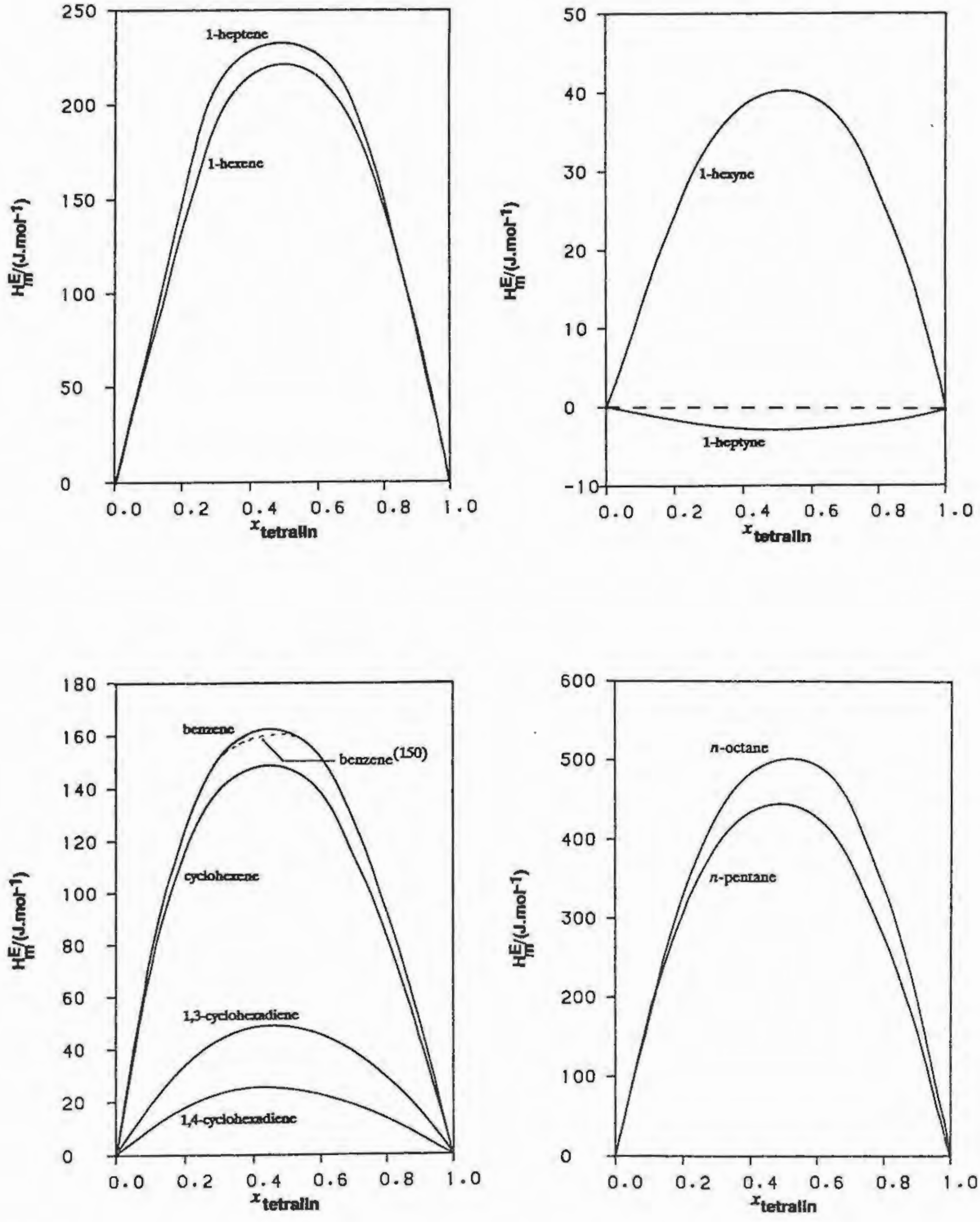

Figure 5.3 Experimental excess molar enthalpies for tetralin systems at 298.15 K

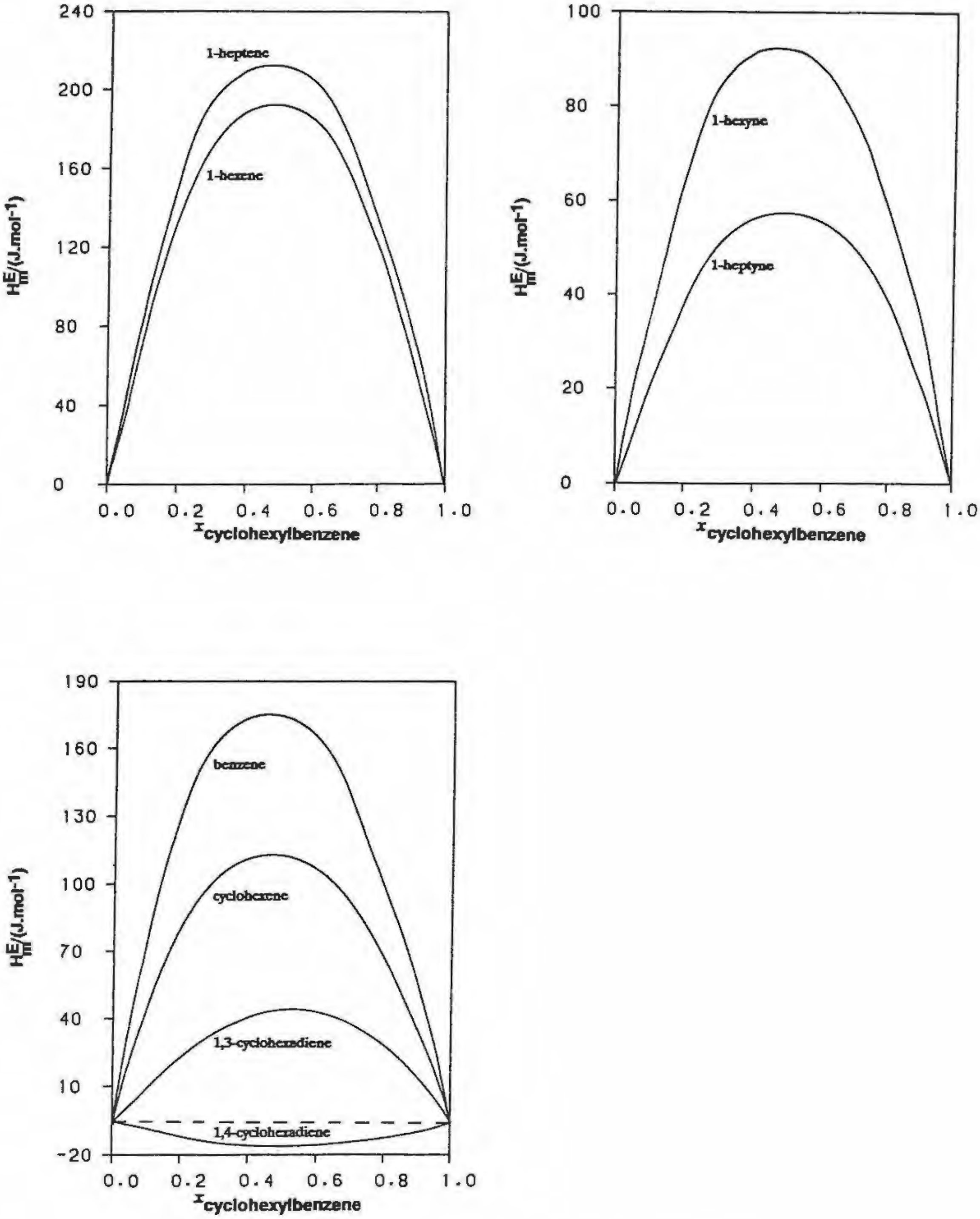

Figure 5.4 Experimental excess molar enthalpies for cyclohexylbenzene systems at 298.15 K

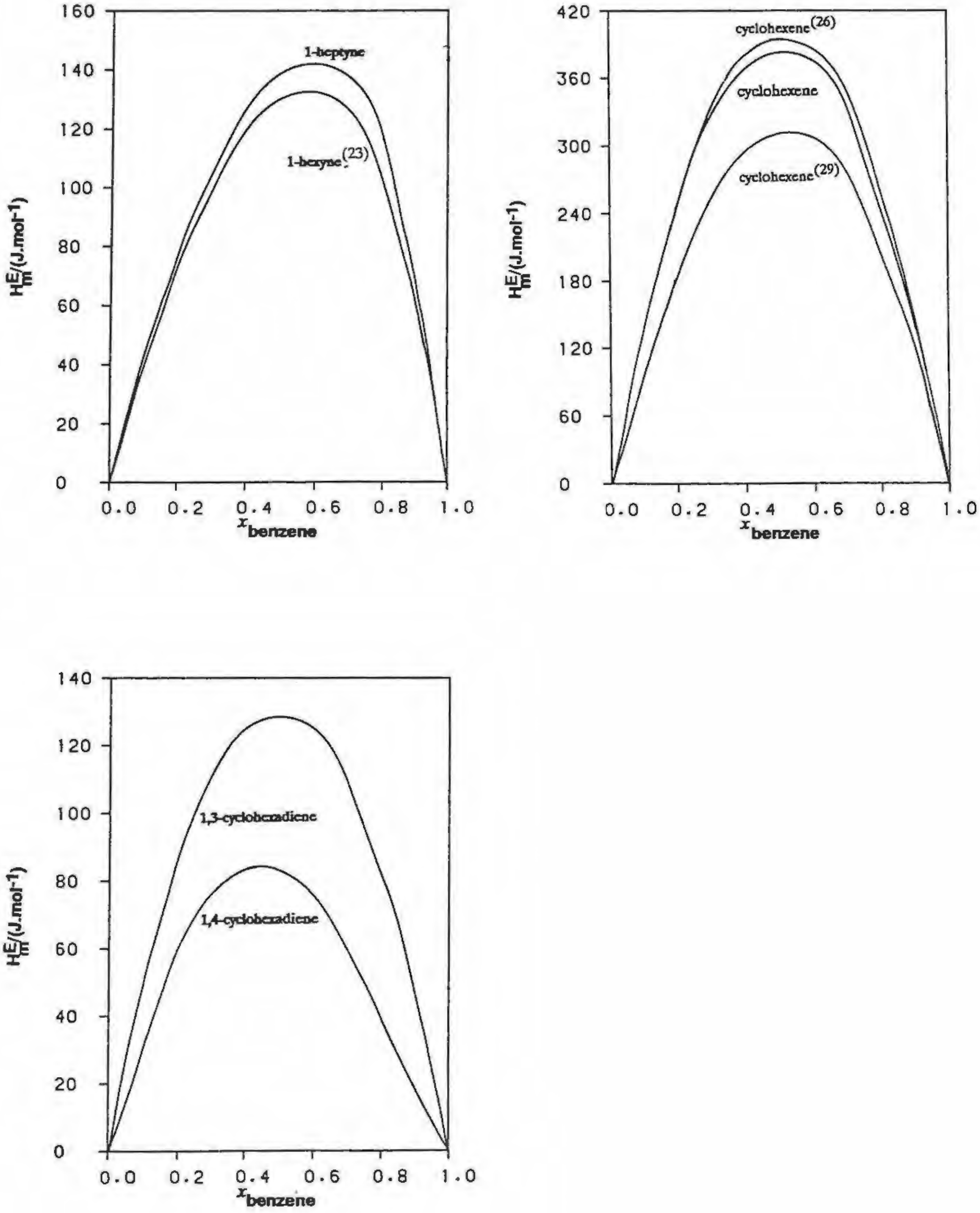

Figure 5.5 Experimental excess molar enthalpies for benzene systems at 298.15 K

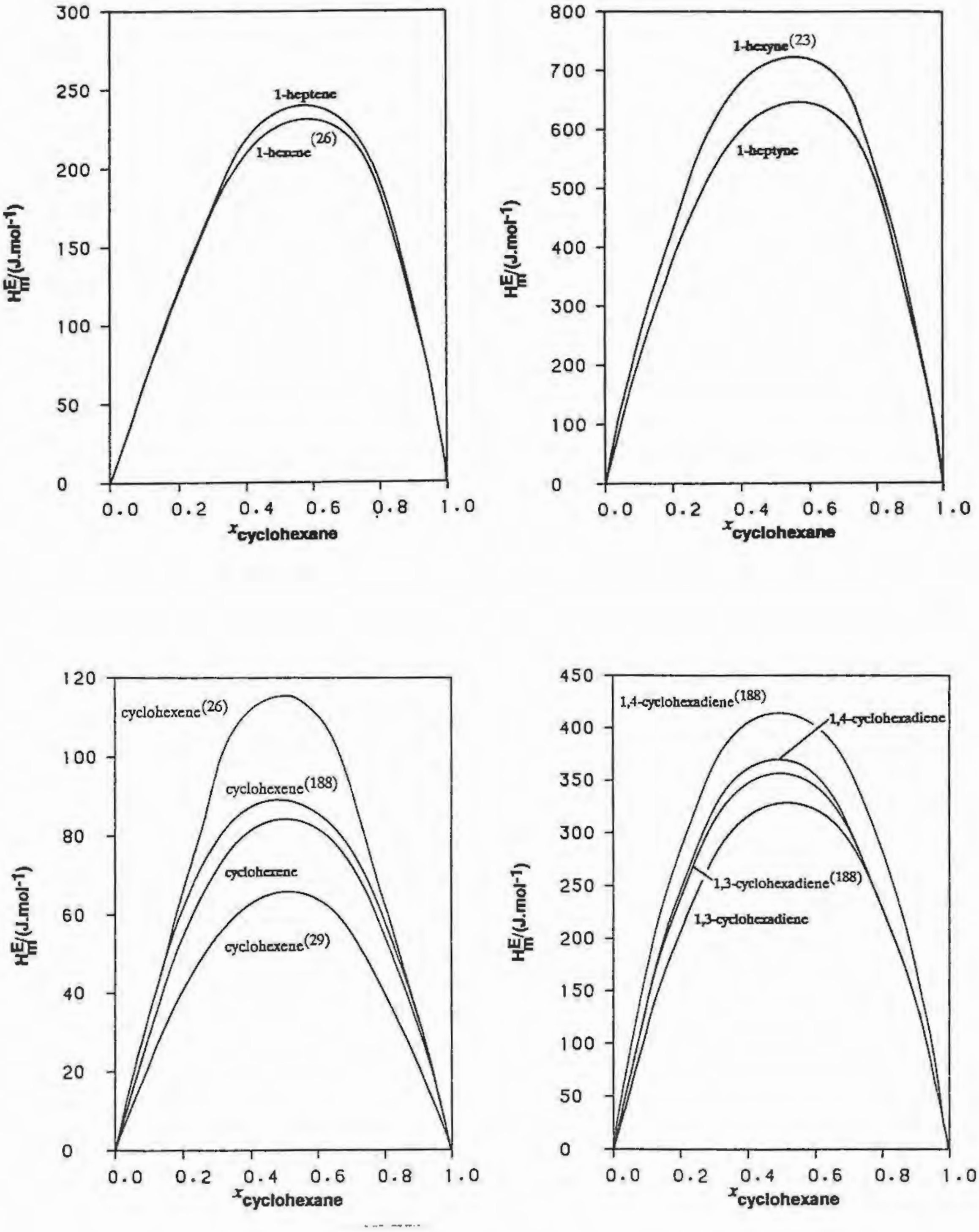

Figure 5.6 Experimental excess molar enthalpies for cyclohexane systems at 298.15 K

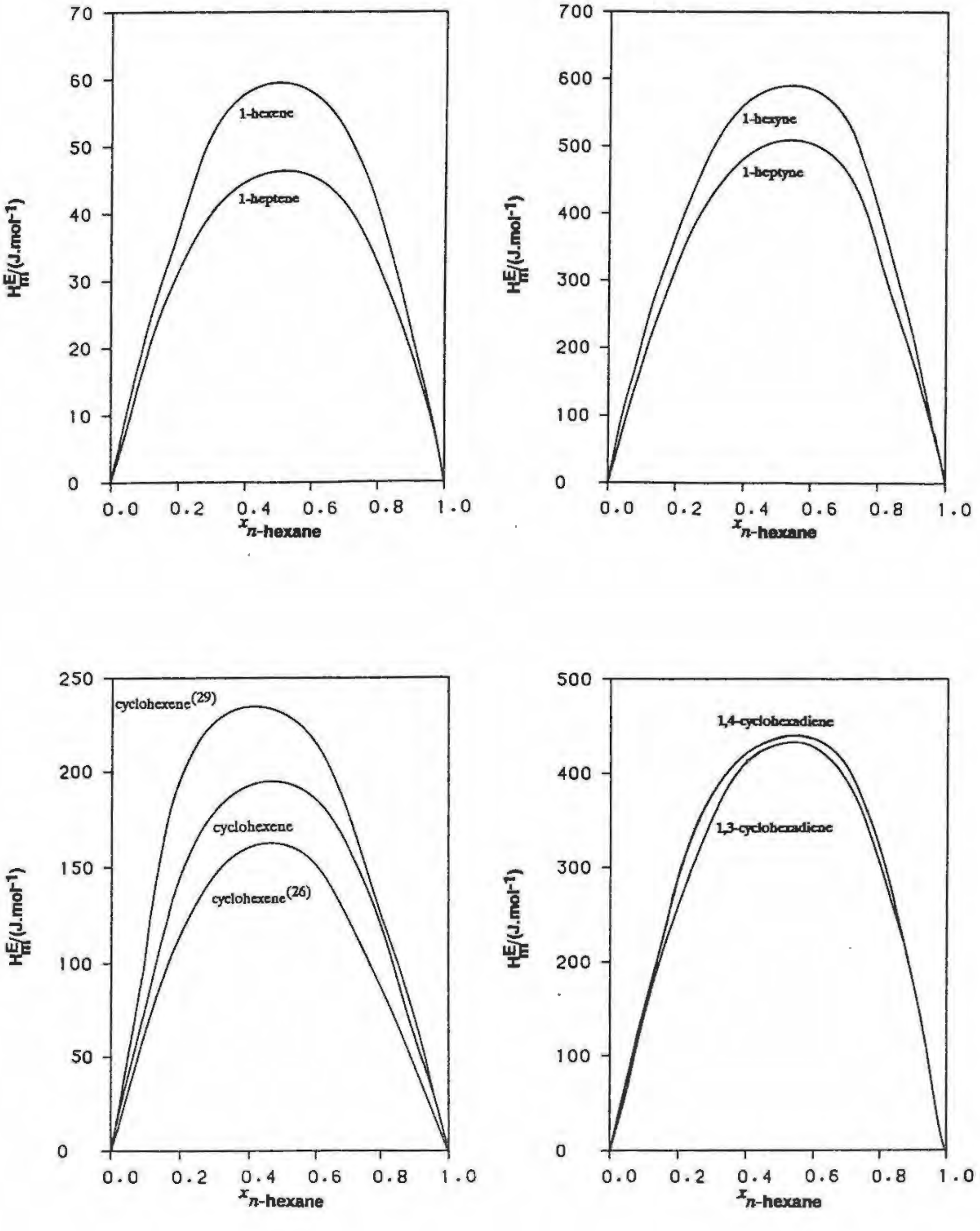

Figure 5.7 Experimental excess molar enthalpies for *n*-hexane systems at 298.15 K

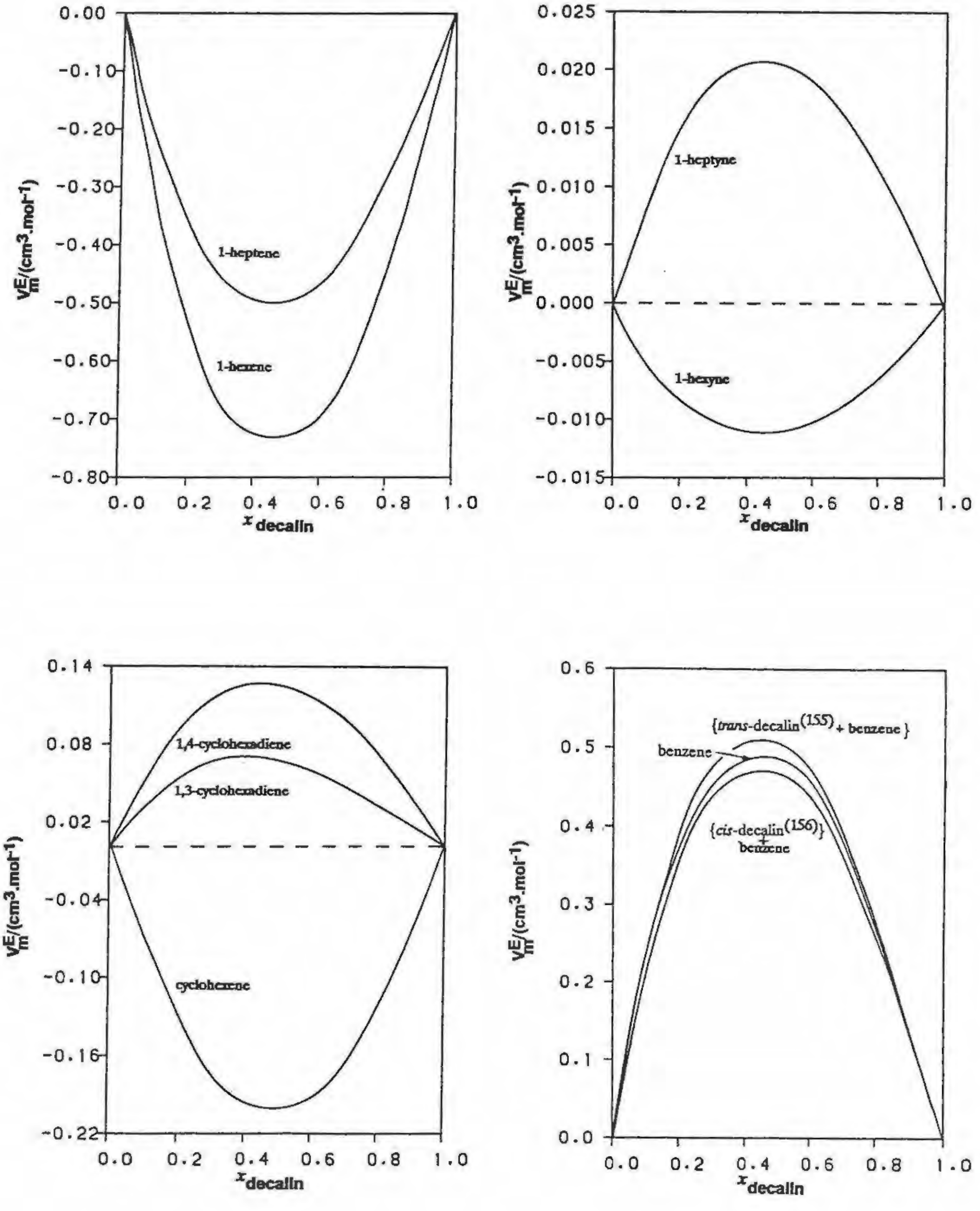

Figure 5.8 Experimental excess molar volumes for decalin systems at 298.15 K

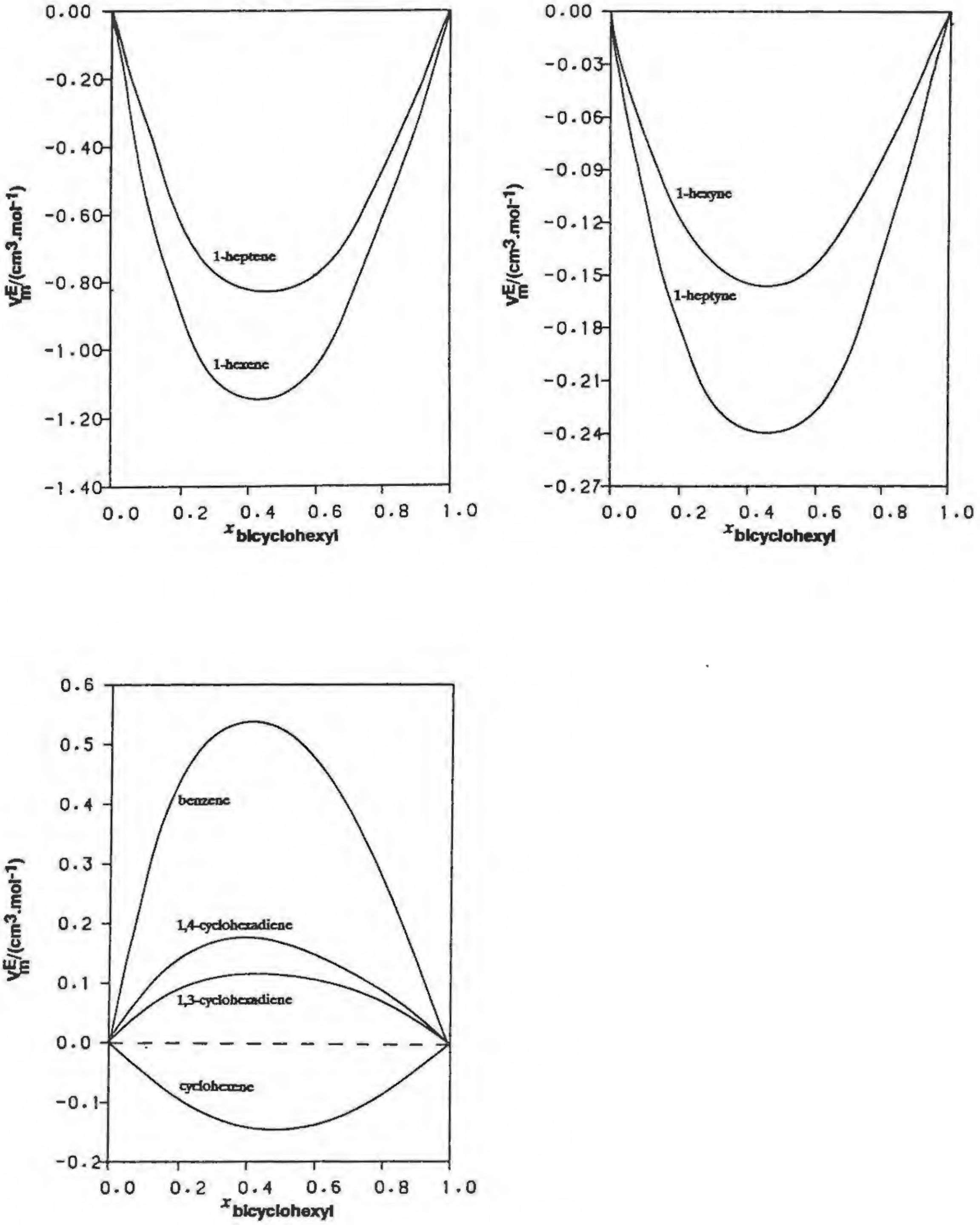

Figure 5.9 Experimental excess molar volumes for bicyclohexyl systems at 298.15 K

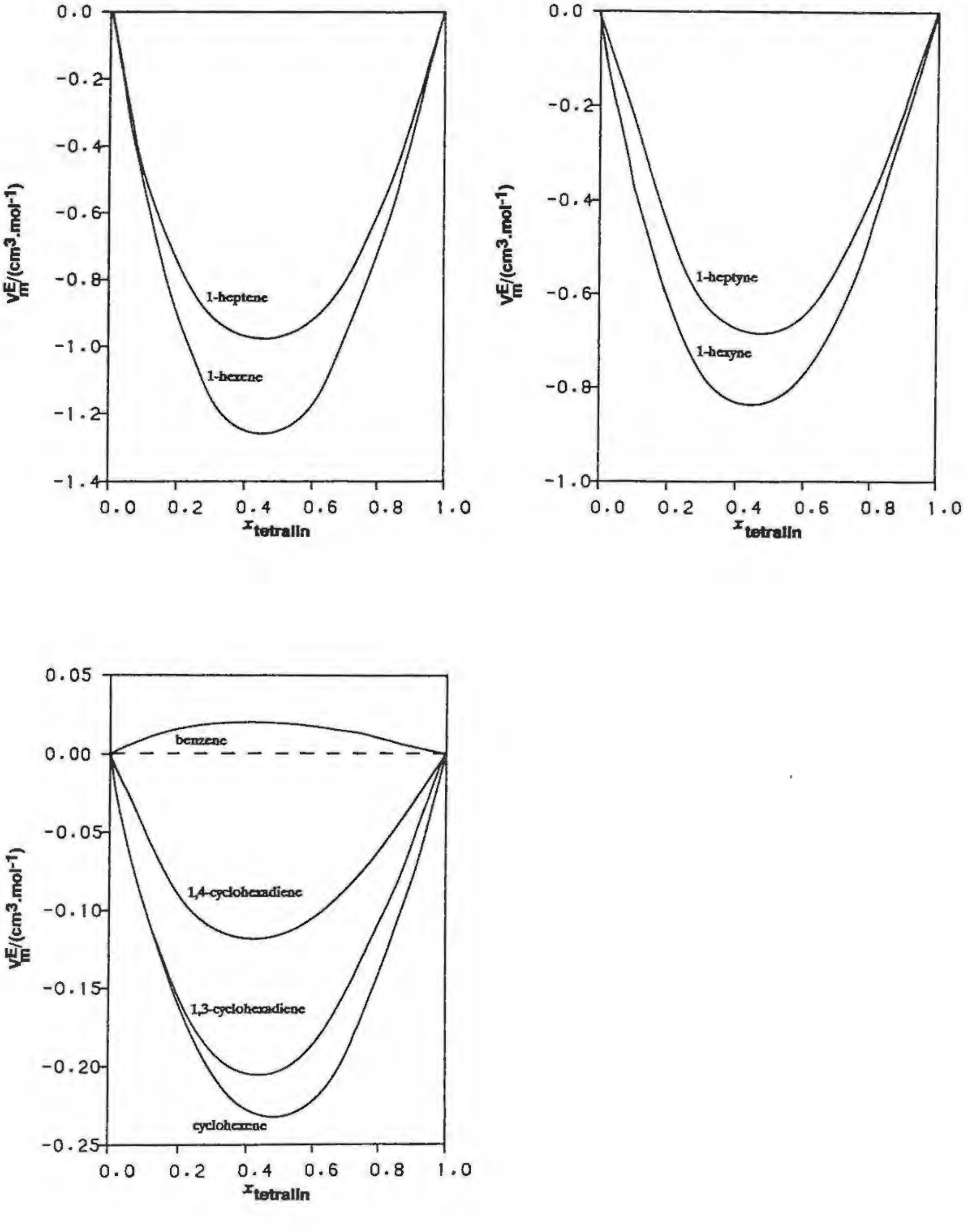

Figure 5.10 Experimental excess molar volumes for tetralin systems at 298.15 K

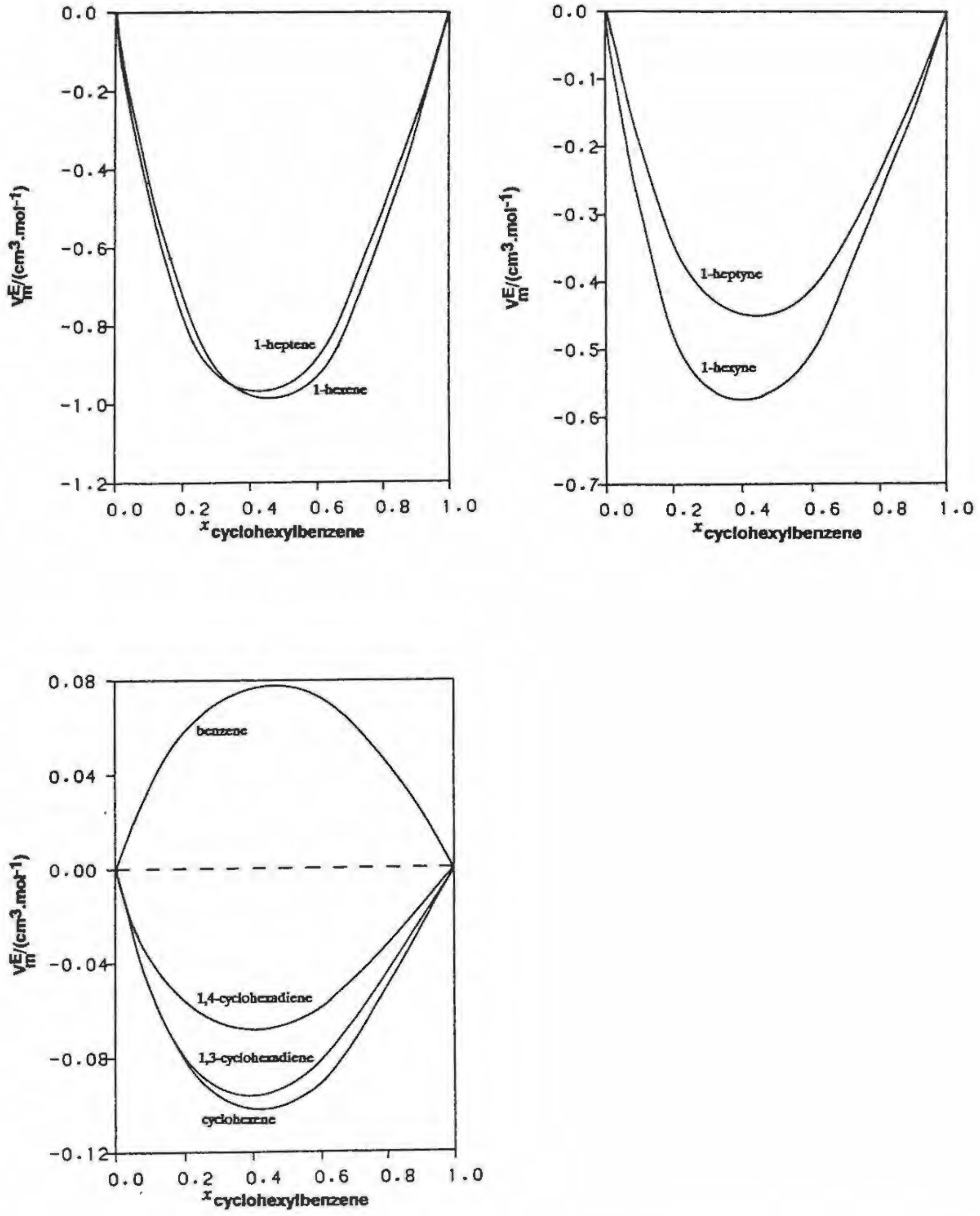

Figure 5.11 Experimental excess molar volumes for cyclohexylbenzene systems at 298.15 K

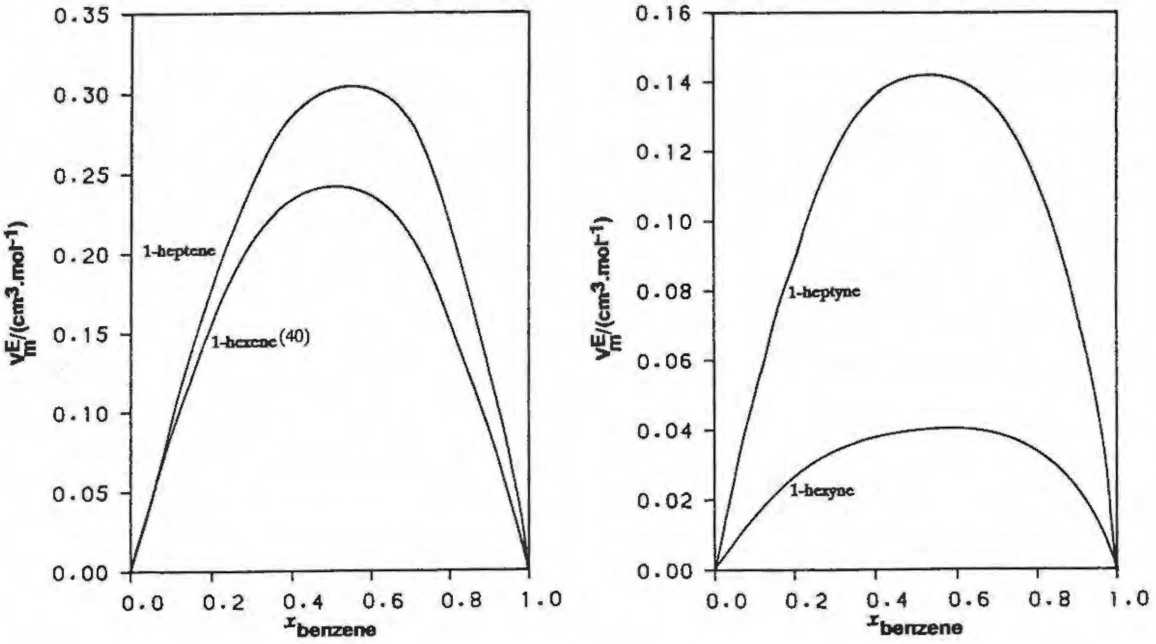

Figure 5.12 Experimental excess molar volumes for benzene systems at 298.15 K

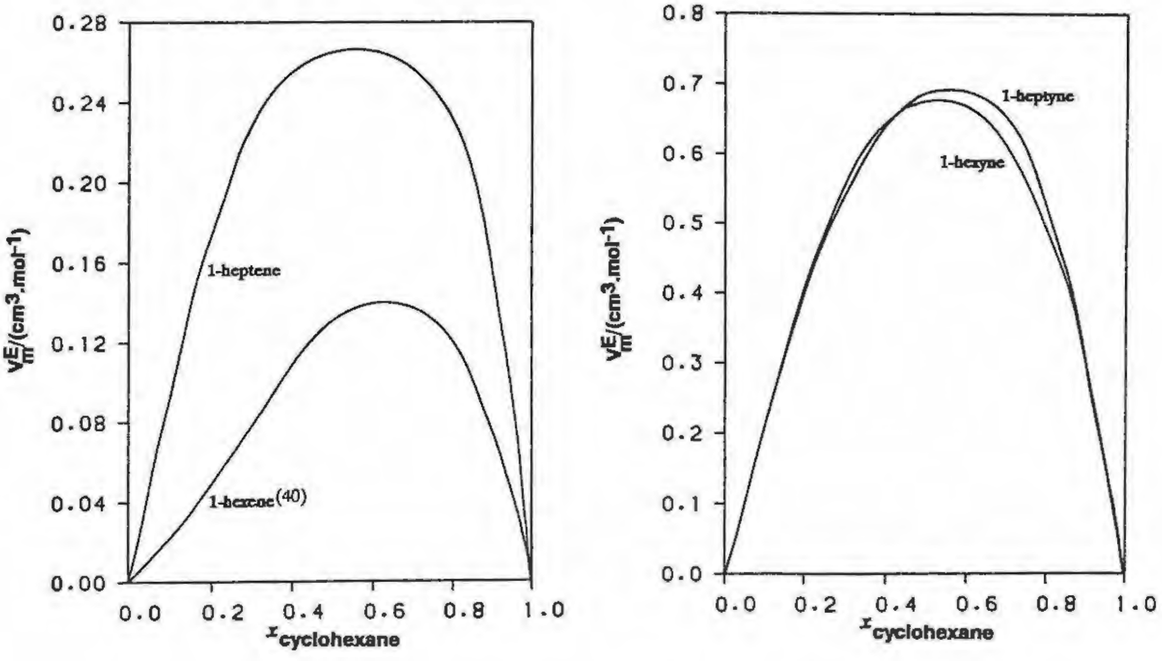

Figure 5.13 Experimental excess molar volumes for cyclohexane systems at 298.15 K

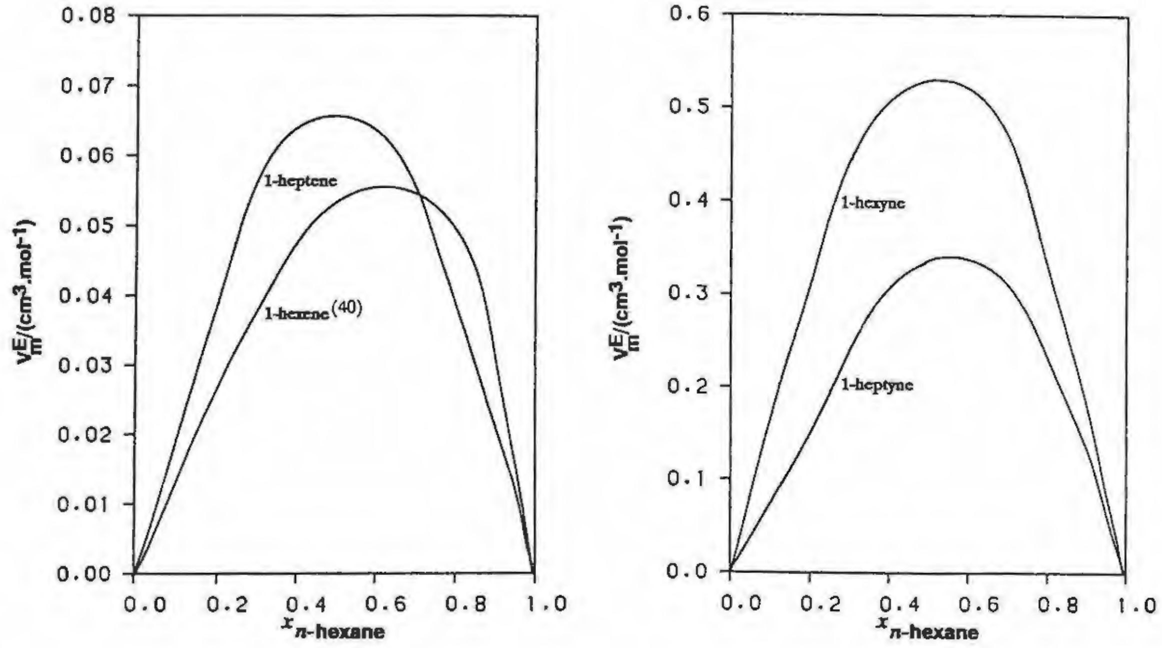

Figure 5.14 Experimental excess molar volumes for *n*-hexane systems at 298.15 K

The experimental γ_{13}^{∞} results are given in Table 5.1.

In this Chapter, the experimental results are compared where possible to any previously reported values for related mixtures and are interpreted in terms of observed trends related to the sizes and shapes of the component molecules.

5.2 Experimental excess molar enthalpies

5.2.1 Mixtures involving a bicyclic compound, benzene, cyclohexane or *n*-hexane with an *n*-alkane, a 1-alkene or a 1-alkyne

The excess molar enthalpies measured in this investigation for {(decalin or tetralin) + *n*-pentane}, {bicyclohexyl + *n*-heptane} and for {tetralin + *n*-octane} fit the patterns generated by previously reported results for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + an *n*-alkane}(9,13,16,17,20-31), namely an increase in the H_m^E for an increase in the chain length of the *n*-alkane. The excess molar enthalpy at equimolar concentrations, $H_m^E(x=0.5)$, for the system {bicyclohexyl + *n*-pentane}: 22.9 $J.mol^{-1}$ is however slightly larger than the $H_m^E(x=0.5)$ for the system {bicyclohexyl + *n*-hexane}: 21.6 $J.mol^{-1}$.(13) The large positive heats of mixing observed for mixtures involving an unsaturated compound such as tetralin, cyclohexylbenzene or benzene with an *n*-alkane indicates that the dominant contribution is the endothermic dissociation of strong $\pi...\pi$ interactions of the unsaturated compounds being replaced by weaker $CH_2...\pi$ and $CH_2...CH_2$ interactions in the mixture. The endothermic mixing effect is smaller in the case of mixtures involving a saturated bicyclic compound mixed with an *n*-alkane, and is probably due to stronger $CH_2...CH_2$ associations in the mixture.

The excess molar enthalpies for mixtures involving decalin with an *n*-alkane or a 1-alkene or a 1-alkyne follow a similar pattern to those exhibited by similar mixtures involving bicyclohexyl. This can be seen from Figure 5.15, where the $H_m^E(x=0.5)$ for {decalin + (*n*-hexane(9) or 1-hexene or 1-hexyne or *n*-heptane(9) or 1-heptene or 1-heptyne)} and for {(bicyclohexyl) + (*n*-hexane(13) or 1-hexene or 1-hexyne or *n*-heptane or 1-heptene or 1-heptyne)} have been plotted against the number of bonds, *b*, present in the C_6 (Figure 15*a*) or C_7 (Figure 15*b*) hydrocarbon. The $H_m^E(x=0.5)$ for {decalin + *n*-hexane}(9) and for {bicyclohexyl + *n*-hexane}(13) are 62.4 $J.mol^{-1}$ and 21.6 $J.mol^{-1}$ respectively. The introduction of a double bond, $b=1$, into *n*-hexane in the 1-carbon position produces a small positive effect on the $H_m^E(x=0.5)$ values for {decalin + 1-hexene}: 74.2 $J.mol^{-1}$ and for {bicyclohexyl + 1-hexene}: 72.9 $J.mol^{-1}$. The introduction of a triple

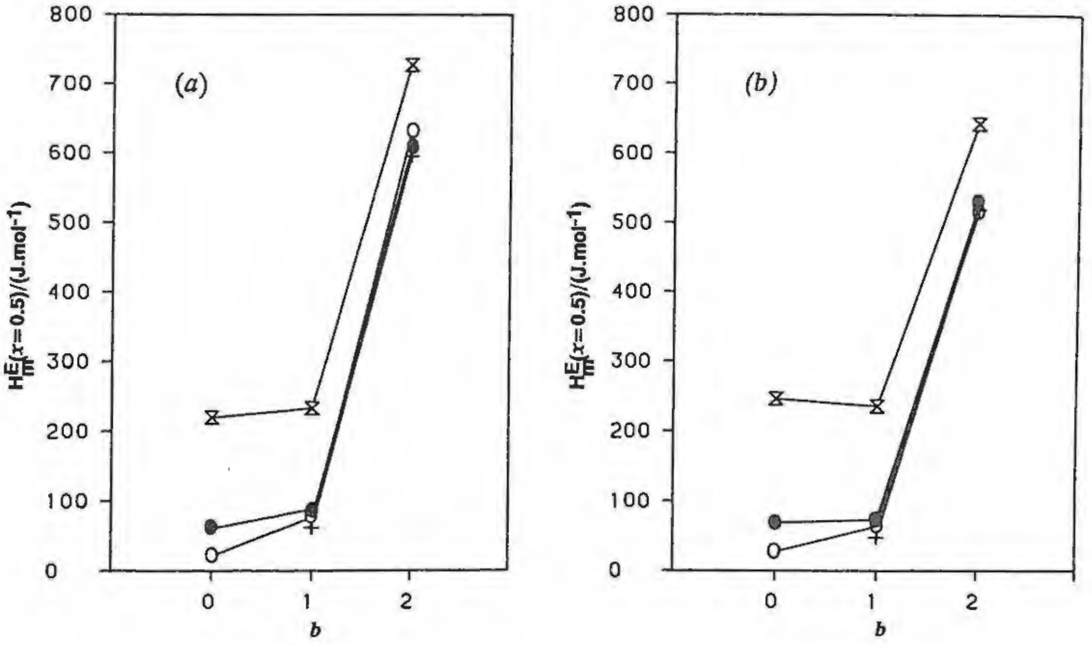

Figure 5.15 Excess molar enthalpies at equimolar concentrations for (*a*), {(decalin or bicyclohexyl or cyclohexane or *n*-hexane) + (*n*-hexane or 1-hexene or 1-hexyne)} and (*b*), {(decalin or bicyclohexyl or cyclohexane or *n*-hexane) + (*n*-heptane or 1-heptene or 1-heptyne)} at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the C_6 or C_7 compound: $b=0$, *n*-alkane; $b=1$, 1-alkene; $b=2$, 1-alkyne. ● , decalin; o , bicyclohexyl; ⧖ , cyclohexane; + , *n*-hexane.

bond, $b=2$, into *n*-hexane in the 1-carbon position however has a pronounced positive effect on the $H^E_m(x=0.5)$ values for {decalin + 1-hexyne}: 604.2 J.mol^{-1} and for {bicyclohexyl + 1-hexyne}: 630.5 J.mol^{-1}.

A similar pattern is displayed by the C_7 hydrocarbon mixtures. Once again a small positive rise in the $H^E_m(x=0.5)$ values are observed for {decalin + 1-heptene}: 72.9 J.mol^{-1} and for {bicyclohexyl + 1-heptene}: 62.8 J.mol^{-1} over the $H^E_m(x=0.5)$ values for {decalin + *n*-heptane}: 68.6 J.mol^{-1} (9) and for {bicyclohexyl + *n*-heptane}: 26.9 J.mol^{-1}. As with the 1-hexene systems, these results indicate a weak $\pi ... \pi$ self association in the 1-alkene molecules which is easily broken on mixing with the bicyclic compound. A large endothermic mixing effect is observed for {decalin + 1-heptyne}: $H^E_m(x=0.5)$ = 524.8 J.mol^{-1}

and for {bicyclohexyl + 1-heptyne}: $H_m^E(x=0.5)$ = 512.8 $J.mol^{-1}$. As with the mixtures involving 1-hexyne, this large endothermic effect can be attributed to the replacement of the strong $\pi...\pi$ interactions of the 1-alkyne molecules with weaker $\pi...CH_2$ interactions between the π electrons of the 1-alkyne molecules and the CH_2 groups of the saturated bicyclic compounds. The introduction of an extra carbon into the C_6 chain does not have a noticeable affect on the excess molar enthalpy results for the mixtures involving a 1-alkene or a 1-alkyne.

In a parallel manner the excess molar enthalpies for {cyclohexane + *n*-hexane(26) or 1-hexene(26) or 1-hexyne(23))} follow a similar pattern to the one displayed by the excess molar enthalpies for {cyclohexane + (*n*-heptane(27) or 1-heptene or 1-heptyne)}. The plot of $H_m^E(x=0.5)$ against the number of bonds, *b*, in the C_6 and the C_7 hydrocarbon chain for these systems is included in Figure 5.15. The $H_m^E(x=0.5)$ values for {cyclohexane + *n*-hexane}: 219.6 $J.mol^{-1}$ (26) and for {cyclohexane + *n*-heptane}: 245.7 $J.mol^{-1}$ (27) are similar to the $H_m^E(x=0.5)$ values for {cyclohexane + 1-hexene}: 232.6 $J.mol^{-1}$ (26) and for {cyclohexane + 1-heptene}: 234.9 $J.mol^{-1}$. The endothermic mixing effect for a 1-alkene mixed with cyclohexane is larger than the effect observed for similar mixtures involving a saturated bicyclic compound, indicating a weaker $CH_2...\pi$ association on mixing with the cyclohexane. The large positive rise in the excess molar enthalpy exhibited for the systems {cyclohexane + 1-hexyne}: $H_m^E(x=0.5)$ = 725.9 $J.mol^{-1}$ (23) and {cyclohexane + 1-heptyne}: $H_m^E(x=0.5)$ = 641.1 $J.mol^{-1}$ can once again be attributed to the strong $\pi...\pi$ self association that exists between the 1-alkyne molecules which in this case is disrupted on mixing with cyclohexane.

The trends exhibited by the $H_m^E(x=0.5)$ values for the above mixtures are also displayed by {*n*-hexane + 1-hexene}: 61.3 $J.mol^{-1}$ (30) and {*n*-hexane + 1-hexyne}: 593.8 $J.mol^{-1}$ (31) and in a parallel manner by the mixtures {*n*-hexane + 1-heptene}: 47.2 $J.mol^{-1}$ and {*n*-hexane + 1-heptyne}: 517.5 $J.mol^{-1}$. The $H_m^E(x=0.5)$ results for these systems have also been included in Figure 5.15. Once again a reduced $\pi...\pi$ association on mixing can account for the endothermic mixing effect. The introduction of an extra carbon into the C_6 hydrocarbon has a noticeable effect on the excess molar enthalpies for the mixtures {*n*-hexane + (1-heptene or 1-heptyne}. The H_m^E results for these mixtures are smaller than those for the corresponding systems involving 1-hexene or 1-hexyne. This can be attributed to packing effects.

The excess molar enthalpies for {tetralin + (*n*-hexane(16) or 1-hexene or 1-hexyne)} follow a similar pattern to the one displayed by the H_m^E results for {cyclohexylbenzene +

(n-hexane$^{(17)}$ or 1-hexene or 1-hexyne)}. This is also true for mixtures involving C_7 hydrocarbons. The trends are displayed in Figure 5.16, where the $H_m^E(x=0.5)$ values for these mixtures have been plotted against the number of double bonds, b, present in the C_6 or C_7 hydrocarbon. The $H_m^E(x=0.5)$ values for {tetralin + n-hexane} and for {cyclohexylbenzene + n-hexane} are 463.3 J.mol^{-1} $^{(16)}$ and 391.1 J.mol^{-1} $^{(17)}$ respectively. The introduction of a double bond into n-hexane in the 1-carbon position produces a large negative effect on the $H_m^E(x=0.5)$ values for {tetralin + 1-hexene}: 224.5 J.mol^{-1} and for {cyclohexylbenzene + 1-hexene}: 194.4 J.mol^{-1}. This trend is replicated for systems involving a C_7 hydrocarbon, with the negative effect evident on consideration of the $H_m^E(x=0.5)$ values for {tetralin + n-heptane}: 488.4 J.mol^{-1} $^{(16)}$ and {cyclohexylbenzene + n-heptane}: 414.1 J.mol^{-1},$^{(17)}$ and for {tetralin + 1-heptene}: 235.3 J.mol^{-1} and {cyclohexylbenzene + 1-heptene}: 212.9 J.mol^{-1}. The introduction of a triple bond into n-hexane and into n-heptane in the 1-carbon position results in an even larger negative

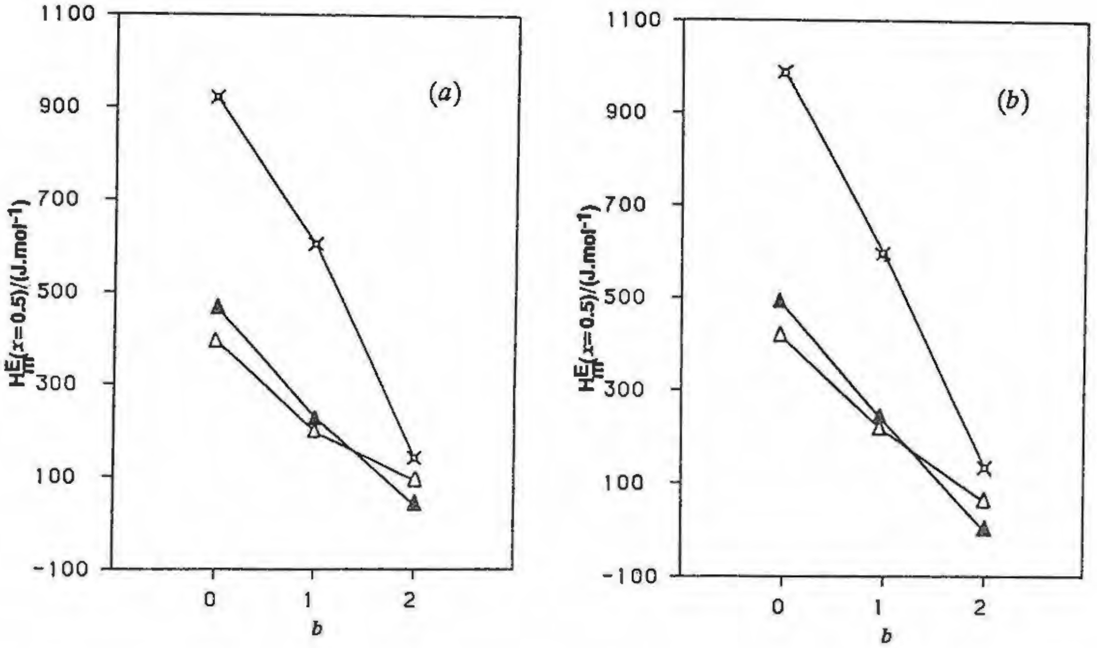

Figure 5.16 Excess molar enthalpies at equimolar concentrations for (a), {(tetralin or cyclohexylbenzene or benzene) + (n-hexane or 1-hexene or 1-hexyne)} and (b), {(tetralin or cyclohexylbenzene or benzene) + (n-heptane or 1-heptene or 1-heptyne)} at 298.15 K as a function of the number of double bonds, b, in the functional group of the C_6 or C_7 compound: $b=0$, n-alkane; $b=1$, 1-alkene; $b=2$, 1-alkyne. ▲, tetralin; Δ, cyclohexylbenzene; ✕,benzene.

contribution to the excess molar enthalpies for the mixtures {tetralin + 1-hexyne}: $H_m^E(x=0.5)$ = 40.3 J.mol^{-1}, {cyclohexylbenzene + 1-hexyne}: $H_m^E(x=0.5)$ = 92.5 J.mol^{-1}, and for {cyclohexylbenzene + 1-heptyne}: $H_m^E(x=0.5)$ = 57.9 J.mol^{-1}. The experimental excess molar enthalpy results indicate that the $\pi ... \pi$ interactions between the 1-alkene and the aromatic bicyclic compound are greater than the interactions between 1-alkene molecules or between the molecules of the aromatic bicyclic compound. The larger negative effect produced on the introduction of a triple bond into the C_6 or C_7 hydrocarbon molecule indicates an even stronger $\pi ... \pi$ association between the 1-alkyne molecules and the aromatic bicyclic molecules on mixing. Exothermic mixing is exhibited for the mixture {tetralin + 1-heptyne}. The $H_m^E(x=0.5)$ for this system is -2.9 J.mol^{-1}. This result indicates that the endothermic effect associated with the disruption of the $\pi ... \pi$ self association in the case of the pure components is smaller than the exothermic $\pi ... \pi$ association on mixing of these compounds.

The $H_m^E(x=0.5)$ values for {benzene + (*n*-hexane(21) or 1-hexene(22) or 1-hexyne(23))} and for {benzene + (*n*-heptane(24) or 1-heptene or 1-heptyne)} have also been included in Figure 5.16. A comparison of $H_m^E(x=0.5)$ for {benzene + *n*-hexane}: 897.2 J.mol^{-1} (21) with the $H_m^E(x=0.5)$ values for {benzene + 1-hexene}: 589.9 J.mol^{-1} (22) and for {benzene + 1-hexyne}:131.9 J.mol^{-1} (23) indicates that the presence of a double bond in 1-hexene or a triple bond in 1-hexyne once again has a significant effect on the excess molar enthalpies for these mixtures. This is probably due to a strong association between the π electrons of the benzene molecule and the π electrons of the double bond of the 1-alkene or the triple bond of the 1-alkyne. The $\pi ... \pi$ association in the case of mixtures involving 1-hexyne is much stronger. A similar trend is displayed for mixtures involving a C_7 hydrocarbon where the $H_m^E(x=0.5)$ values for {benzene + (*n*-heptane or 1-heptene or 1-heptyne)} are 919.0 J.mol^{-1},(24) 603.1 J.mol^{-1},(22) and 138.7 J.mol^{-1} respectively. The introduction of an extra carbon into the C_6 hydrocarbon chain only results in a small positive effect on the experimental excess molar enthalpies.

The excess molar enthalpies for mixtures involving an aromatic bicyclic compound exhibit similar trends to those displayed by mixtures involving benzene. The H_m^E results for the aromatic bicyclic mixtures are however smaller. This indicates a "dilution" effect of the aromatic moeity of the unsaturated bicyclic compound by the cyclohexane moeity.

5.2.2 Mixtures involving a bicyclic compound, benzene, cyclohexane or *n*-hexane with a cyclic C_6 hydrocarbon

The excess molar enthalpies for decalin and a *c*-C_6 compound follow a similar pattern to those observed for mixtures involving bicyclohexyl with a *c*-C_6 hydrocarbon. This can be seen from Figure 5.17 where $H_m^E(x=0.5)$ values for {decalin + (cyclohexane(9) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} and for {bicyclohexyl + (cyclohexane(13) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} are plotted against the number of double bonds, *b*, in the cyclic C_6 compound. The introduction of one double bond into cyclohexane has a small negative effect on the excess molar enthalpy results for these mixtures. The $H_m^E(x=0.5)$ values for {(decalin or bicyclohexyl) + cyclohexane} are 25.9 $J.mol^{-1}$ (9) and

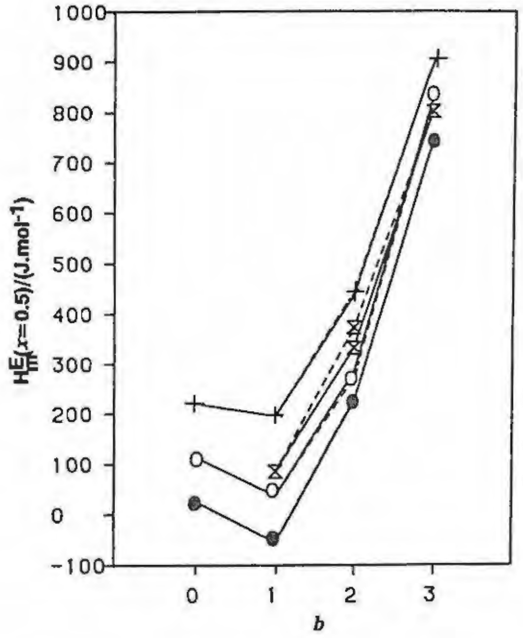

Figure 5.17 Excess molar enthalpies at equimolar concentrations for {(decalin or bicyclohexyl or cyclohexane or *n*-hexane) + (cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene) at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the *c*-C_6 compound. The $H^E(x=0.5)$ results for mixtures containing cyclohexane, ($b=0$); cyclohexene, ($b=1$); 1,4-cyclohexadiene, ($b=2$); and benzene ($b=3$) have been linked with broken lines to indicate the overall trend. ●, decalin; ○ , bicyclohexyl; ⧖ , cyclohexane; + , *n*-hexane.
——— , 1,3-cyclohexadiene; - - - - - , 1,4-cyclohexadiene.

113.6 $J.mol^{-1}$ (13) respectively, while the $H_m^E(x=0.5)$ for {bicyclohexyl + cyclohexene} is 37.2 $J.mol^{-1}$. The system {decalin + cyclohexene}: $H_m^E(x=0.5)$ = -55.4 $J.mol^{-1}$ exhibits exothermic mixing, indicating a stronger association between the molecules of the mixture. The excess molar enthalpies for these systems are similar to the H_m^E values for the related mixture {cyclohexane + cyclohexene}. The $H_m^E(x=0.5)$ for this mixture is included in Figure 5.17 and has a value of 85.2 $J.mol^{-1}$. The excess molar enthalpies reported by other workers(26,29,188) for {cyclohexane + cyclohexene} have also been included in Figure 5.6. The $H_m^E(x=0.5)$ vary between 54.5 $J.mol^{-1}$ (29) and 115.5 $J.mol^{-1}$,(26) and the H_m^E results measured in this investigation compare best with the results reported more recently by Woycicki.(188) The largest deviation over the entire composition range between these two sets of results is about 8 $J.mol.^{-1}$

The introduction of two double bonds into the cyclohexane molecule has a pronounced positive effect on the excess molar enthalpy for mixtures with a saturated bicyclic compound. Conjugation or unconjugation of the double bonds in 1,3-cyclohexadiene or 1,4-cyclohexadiene appears to have little effect on the excess molar enthalpies, the differences between the $H_m^E(x=0.5)$ values for {decalin + 1,3-cyclohexadiene}: 225.5 $J.mol^{-1}$ and {decalin + 1,4-cyclohexadiene}: 228.7 $J.mol^{-1}$, and the $H_m^E(x=0.5)$ values for {bicyclohexyl + 1,3-cyclohexadiene}: 283.8 $J.mol^{-1}$ and for {bicyclohexyl + 1,4-cyclohexadiene}: 272.0 $J.mol^{-1}$, being very small. The $H_m^E(x=0.5)$ values for {cyclohexane + 1,3-cyclohexadiene}: 331.5 $J.mol^{-1}$ and for {cyclohexane + 1,4-cyclohexadiene}: 372.1 $J.mol^{-1}$ have been included in Figure 5.17. These values are slightly larger than those for similar systems involving a saturated bicyclic compound. This points to an enhanced packing effect in the case of systems involving a bicyclic compound. The excess molar enthalpy results for {cyclohexane + (1,3-cyclohexadiene or 1,4-cyclohexadiene)} have also been reported by Wóycicki(188) and are higher than the results measured in this study. The $H_m^E(x=0.5)$ for the 1,3-cyclohexadiene mixture is 358.9 $J.mol^{-1}$ (as opposed to the value of 331.5 $J.mol^{-1}$ reported here), while the value for the 1,4-cyclohexadiene mixture is 423.3 $J.mol^{-1}$ (372.1 $J.mol^{-1}$ reported in this work). The introduction of a third double bond into cyclohexane has an even larger positive effect on the excess molar enthalpy. The $H_m^E(x=0.5)$ for {(decalin or bicyclohexyl or cyclohexane(26)) + benzene}, are 741.7 $J.mol^{-1}$, 827.5 $J.mol^{-1}$ and 801.7 $J.mol^{-1}$ respectively. This is consistent with the notion of a positive contribution from the $\pi...\pi$ dissociation of the pure benzene molecules in a predominantly CH_2 group environment. The H_m^E determined in this work for {decalin + benzene} are slightly smaller than the values reported in the literature for {(*cis*-decalin(149) or *trans*-decalin(148) or decalin(150)) + benzene} (Figure 5.1). The $H_m^E(x=0.5)$ for these systems are 741.8 $J.mol^{-1}$, 767.7 $J.mol^{-1}$,(148) 757.0 $J.mol^{-1}$ (147) and 776.8 $J.mol^{-1}$ (149) respectively. The decalin mixture employed by Lundberg(150) comprised 64 mol% *cis*-isomer and 36 mol% *trans*-isomer.

The $H_m^E(x=0.5)$ values for {*n*-hexane + (cyclohexane(13) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene(21))} have also been included in Figure 5.17 and follow similar patterns to the ones displayed above. The excess molar enthalpy curve from this investigation for the system {*n*-hexane + cyclohexene}: $H_m^E(x=0.5)$ = 195.2 $J.mol^{-1}$ lies between the curves reported by Letcher and Sack : $H_m^E(x=0.5)$ = 245.1 $J.mol^{-1}$ (26) and by Gunzel and Bittrich : $H_m^E(x=0.5)$ = 164.3 $J.mol^{-1}$ (29) and is similar in shape to the curve of Gunzel and Bittrich.(29) The $H_m^E(x=0.5)$ values for {*n*-hexane + cyclohexane}: 219.6 $J.mol^{-1}$ (13) and for {*n*-hexane + cyclohexene}: 195.2 $J.mol^{-1}$ are once again much smaller than the corresponding values for {*n*-hexane + 1,3-cyclohexadiene}: 435.3 $J.mol^{-1}$, {*n*-hexane + 1,4-cyclohexadiene}: 443.4 $J.mol^{-1}$ and {*n*-hexane + benzene}: 897.2 $J.mol^{-1}$.(21)

These large positive mixing effects observed for mixtures with 1,3-cyclohexadiene, 1,4-cyclohexadiene and benzene are the result of a dissociation of the $\pi...\pi$ interactions of the unsaturated cyclic C_6 compounds on mixing with the saturated bicyclic compounds or with cyclohexane or with *n*-hexane. The endothermic mixing effects for *n*-hexane mixed with cyclohexane or with cyclohexene are larger than the corresponding values for the mixtures involving a saturated bicyclic compound with cyclohexane or cyclohexene, indicating a weaker association on mixing. The association between a saturated bicyclic compound and cyclohexane is too weak to have a significant effect on the $H_m^E(x=0.5)$ values.

In a parallel manner the $H_m^E(x=0.5)$ values for {tetralin + (cyclohexane(16) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} follow a similar pattern to the $H_m^E(x=0.5)$ results for {cyclohexylbenzene + (cyclohexane(18) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)}. This can be seen from Figure 5.18 where $H_m^E(x=0.5)$ values for these mixtures are plotted against the number of double bonds, *b*, in the cyclic C_6 compound. The $H_m^E(x=0.5)$ values for the systems {benzene + (cyclohexane(26) or cyclohexene(26) or 1,3-cyclohexadiene or 1,4-cyclohexadiene)} have also been included in Figure 5.18. The $H_m^E(x=0.5)$ values for {tetralin + cyclohexane}: 482.9 $J.mol^{-1}$ (16) and for {cyclohexylbenzene + cyclohexane}: 402.8 $J.mol^{-1}$ (18) are

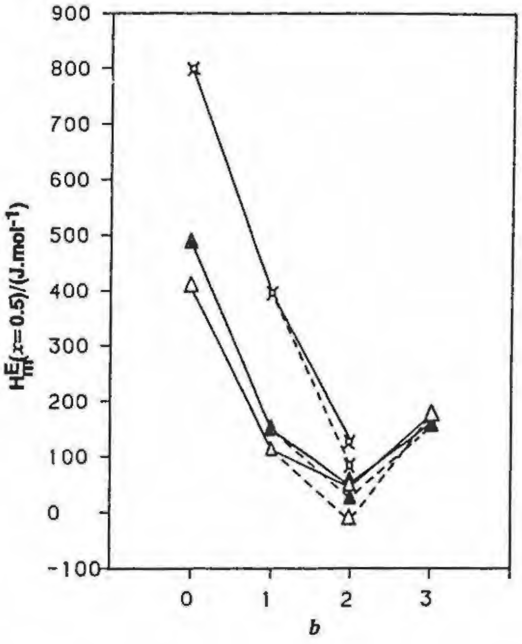

Figure 5.18 Excess molar enthalpies at equimolar concentrations for {(tetralin or cyclohexylbenzene or benzene) + (cyclohexane or cyclohexene or 1,3- or 1,4-cyclohexadiene or benzene) at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the *c*-C_6 compound. The $H^E(x=0.5)$ results for mixtures containing cyclohexane, ($b=0$); cyclohexene, ($b=1$); 1,4-cyclohexadiene, ($b=2$); and benzene ($b=3$) have been linked with broken lines to indicate the overall trend. ▲ , tetralin; ⌑ ,benzene, △ ,cyclohexylbenzene.
——— , 1,3-cyclohexadiene; - - - - - , 1,4-cyclohexadiene.

smaller than the $H_m^E(x=0.5)$ for the related mixture {benzene + cyclohexane}: 801.7 $J.mol^{-1}$.(26) This is probably due to an association on mixing of the cyclohexane with the saturated portion of the tetralin or of the cyclohexylbenzene, which is not possible in the case of benzene mixed with cyclohexane. Enhanced packing effects in the case of the larger unsaturated bicyclic molecules with the smaller cyclohexane molecule could also contribute to the smaller H_m^E for these mixtures. The introduction of a double bond into the cyclohexane molecule has a significant negative effect on the excess molar enthalpy results for the mixtures {tetralin + cyclohexene}: $H_m^E(x=0.5)$ = 148.8 $J.mol^{-1}$, {cyclohexylbenzene + cyclohexene}: $H_m^E(x=0.5)$ = 112.8 $J.mol^{-1}$ and {benzene + cyclohexene}: $H_m^E(x=0.5)$ = 395.6 $J.mol^{-1}$. Fair agreement is observed between the excess molar enthalpy values reported by Letcher and Sack(26) and the results measured here for the system {benzene + cyclohexene} (Figure 5.5). The results determined in this work are all within 7 J.mol of the curve reported by Letcher and Sack,(26) indicating that there is a possible error in the results reported by Gunzel and Bittrich.(29) The introduction of two double bonds into the cyclic C_6 compound has an increased negative effect on the excess molar enthalpy. Once again the positions of the double bonds within the cycloalkadiene molecules do not appear to have a significant effect on the experimental excess molar enthalpies for {(tetralin or cyclohexylbenzene) + (1,3-cyclohexadiene or 1,4-cyclohexadiene)}. The $H^E_m(x=0.5)$ values for {tetralin + (1,3-cyclohexadiene or 1,4-cyclohexadiene)} are 48.2 $J.mol^{-1}$ and 24.8 $J.mol^{-1}$ respectively, while the $H^E_m(x=0.5)$ results for {cyclohexylbenzene + (1,3-cyclohexadiene or 1,4-cyclohexadiene)} are 44.1 $J.mol^{-1}$ and -15.5 $J.mol^{-1}$ respectively. The exothermic mixing for {cyclohexylbenzene + 1,4-cyclohexadiene} is once again indicative of a strong association between the molecules of the mixture. The $H^E_m(x=0.5)$ for {benzene + 1,3-cyclohexadiene}: 129.8 $J.mol^{-1}$ is also fairly similar to the value for {benzene + 1,4-cyclohexadiene}: 83.4 $J.mol^{-1}$. The above results can once again be interpreted in terms of the association and dissociation of $\pi ... \pi$ interactions. The negative effect can be attributed to a disruption of the $\pi ... \pi$ association between π electrons of the unsaturated compounds which are replaced by a stronger association between the π electrons of the cycloalkene or of the cycloalkadiene and the π electrons of the unsaturated portion of the bicyclic compound or benzene.

The addition of a third double bond into the cyclohexane molecule has a small positive effect on the $H^E_m(x=0.5)$ values for {tetralin + benzene}: 160.1 $J.mol^{-1}$ and {cyclohexylbenzene + benzene}: 173.0 $J.mol^{-1}$. This indicates that the positive effects associated with the breakdown of the π interactions between the molecules of an aromatic bicyclic compound or between benzene molecules is greater than the negative effect resulting from the $\pi ... \pi$ association between unlike molecules on mixing. the H^E_m results discussed in this investigation for {tetralin + benzene} compare favourably with the results reported by Lundberg(150) (Figure 5.3).

5.3 Experimental excess molar volumes

5.3.1 Mixtures involving a bicyclic compound, benzene, cyclohexane or *n*-hexane with an *n*-alkane, a 1-alkene or a 1-alkyne

The experimental excess molar volumes at equimolar concentrations, $V^E_m(x=0.5)$, for {(decalin or bicyclohexyl or tetralin or cyclohexylbenzene) + (*n*-hexane or 1-hexene or

1-hexyne)} and for {(decalin or bicyclohexyl or tetralin or cyclohexylbenzene) + (*n*-heptane or 1-heptene or 1-heptyne)} have been plotted against the number of double bonds, *b*, in the C_6 or C_7 hydrocarbon and are given in Figures 5.19*a* (a C_6 hydrocarbon) and 5.19*b* (a C_7 hydrocarbon). The discernment of any trends displayed by the $V_m^E(x=0.5)$ values is a more difficult task than was possible for the excess molar enthalpies. With the exception of the system {decalin + 1-heptyne} which exhibits a small positive $V_m^E(x=0.5)$ of 0.020 $cm^3.mol^{-1}$, all the excess molar volumes for the other mixtures are negative. This would seem to indicate an organized packing effect between the dissimilar molecules on mixing. This result is to be expected if the large differences between the molar volumes of the different components for each mixture are considered. This is particularly true for all the tetralin mixtures. The $V_m^E(x=0.5)$ values for {tetralin + 1-hexene}: -1.268 $cm^3.mol^{-1}$, {tetralin + 1-hexyne}: -0.835 $cm^3.mol^{-1}$, {tetralin + 1-heptene}: -0.998 $cm^3.mol^{-1}$ and for {tetralin + 1-heptyne}: -0.693 $cm^3.mol^{-1}$ are more

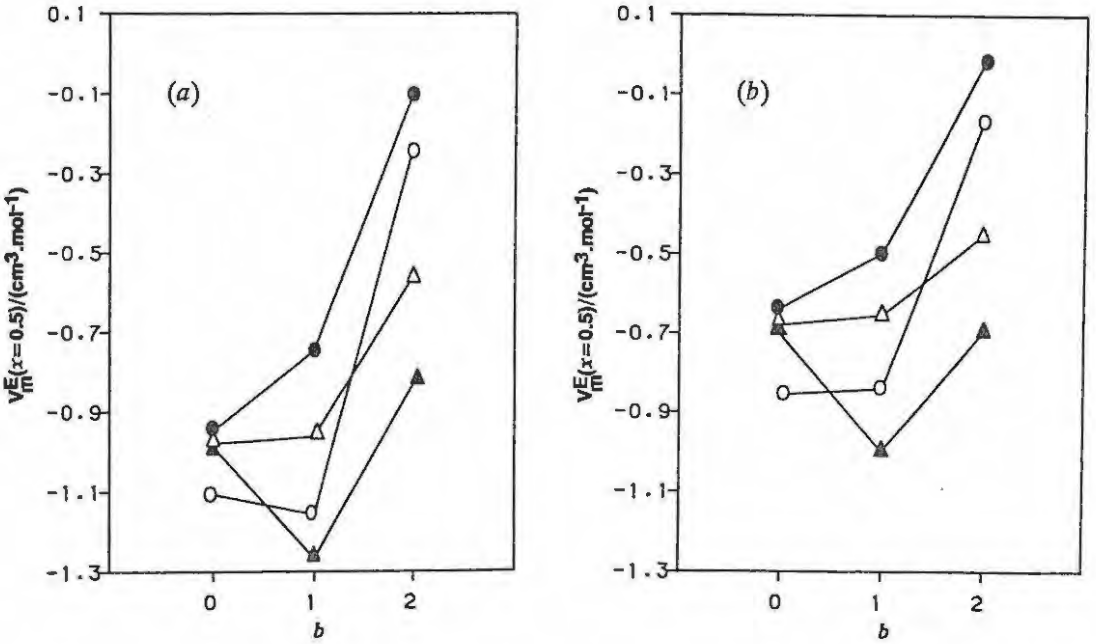

Figure 5.19 Excess molar volumes at equimolar concentrations for (*a*), {(decalin or bicyclohexyl or tetralin or cyclohexylbenzene) + (*n*-hexane or 1-hexene or 1-hexyne)} and (*b*), {(decalin or bicyclohexyl or tetralin or cyclohexylbenzene) + (*n*-heptane or 1-heptene or 1-heptyne)} at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the C_6 or C_7 compound: *b* = 0, *n*-alkane; *b* = 1, 1-alkene; *b* = 2, 1-alkyne. ● , decalin; ○ , bicyclohexyl; ▲ , tetralin; △ , cyclohexylbenzene.

negative than the $V_m^E(x=0.5)$ values for any of the other corresponding mixtures involving a bicyclic compound with a 1-alkene or with a 1-alkyne.

These organized packing effects are displayed to a lesser degree for mixtures involving an *n*-alkane or a 1-alkene. The mixtures involving an *n*-alkane and a bicyclic compound exhibit packing effects which are similar to those exhibited by the mixtures involving a bicyclic compound and a 1-alkene, with the $V_m^E(x=0.5)$ values for {a bicyclic compound + *n*-hexane} being similar in magnitude to the V_m^E results for the 1-hexene counterpart. The similarity in molar volumes for *n*-hexane and for 1-hexene can account for this. The $V_m^E(x=0.5)$ values for {a bicyclic compound + *n*-hexane} are generally more negative than the $V_m^E(x=0.5)$ values for {a bicyclic compound + *n*-heptane}. The more positive excess molar volumes for the mixtures involving *n*-heptane can be accounted for by a longer *n*-alkane chain and a subsequent reduction in the "packing efficiency" of the molecules of the mixture. This is manifested through a larger difference between the molar volumes for a bicyclic compound and *n*-hexane than the difference between the molar volumes for a bicyclic compound and *n*-heptane. The $V_m^E(x=0.5)$ values for {(decalin$^{(7)}$ or bicyclohexyl$^{(12)}$ or tetralin$^{(14)}$ or cyclohexylbenzene$^{(17)}$) + *n*-hexane} are -0.948 $cm^3.mol^{-1}$, -1.108 $cm^3.mol^{-1}$, -0.989 $cm^3.mol^{-1}$ and -0.981 $cm^3.mol^{-1}$ respectively, as opposed to the corresponding values of -0.636 $cm^3.mol^{-1}$, -0.856 $cm^3.mol^{-1}$, -0.660 $cm^3.mol^{-1}$ and -0.679 $cm^3.mol^{-1}$ for {(decalin$^{(7)}$ or bicyclohexyl$^{(11)}$ or tetralin$^{(14)}$ or cyclohexylbenzene$^{(17)}$ + *n*-heptane}.

The $V_m^E(x=0.5)$ values for {(decalin or bicyclohexyl or tetralin or cyclohexylbenzene) + 1-hexene} and for the mixtures {decalin or bicyclohexyl or tetralin or cyclohexylbenzene) + 1-heptene} fall within the ranges -0.747 $cm^3.mol^{-1}$ to -1.268 $cm^3.mol^{-1}$ and -0.499 $cm^3.mol^{-1}$ to -0.998 $cm^3.mol^{-1}$ respectively. The excess molar volumes for mixtures involving 1-hexene are generally more negative than the results for the 1-heptene counterparts, indicating a slightly less favourable packing in the case of the longer 1-heptene chain. This is also manifested by a smaller difference in the molar volumes for the bicyclic compounds and for 1-heptene.

The excess molar volumes for the mixtures involving a bicyclic compound with a 1-alkyne are in all cases less negative than the results for the mixtures involving a 1-alkene or an *n*-alkane. It would appear in this case that the negative packing effect is dominated by a positive effect resulting from the dissociation of strong $\pi...\pi$ interactions between the 1-alkyne molecules on mixing with the bicyclic compounds. This latter observation has already been made when considering the excess enthalpy results (Section 5.2.1) and would also explain why the $V_m^E(x=0.5)$ values for {decalin + 1-hexyne}: -0.011 $cm^3.mol^{-1}$ and for {bicyclohexyl + 1-hexyne}: -0.244 $cm^3.mol^{-1}$ are more positive than the $V_m^E(x=0.5)$ for {tetralin + 1-hexyne}: -0.835 $cm^3.mol^{-1}$ and for {cyclohexylbenzene + 1-hexyne}: -0.564 $cm^3.mol^{-1}$. The association between the unsaturated bicyclic compounds with 1-hexyne is stronger than the association between the saturated bicyclic compounds with 1-hexyne. The excess molar volumes for mixtures involving 1-heptyne display a similar trend. The $V_m^E(x=0.5)$ values for {(decalin or bicyclohexyl) + 1-heptyne} are 0.020 $cm^3.mol^{-1}$ and -0.159 $cm^3.mol^{-1}$ respectively, while $V_m^E(x=0.5)$ results for {(tetralin or cyclohexylbenzene) + 1-heptyne} are -0.693 $cm^3.mol^{-1}$ and -0.449 $cm^3.mol^{-1}$ respectively.

The excess molar volumes for {(cyclohexane or *n*-hexane) + (*n*-hexane or 1-hexene or 1-hexyne)} follow similar trends to those displayed by the systems involving a bicyclic compound but are large and positive, indicating a disorganized packing between the molecules of the mixture. Plots of $V_m^E(x=0.5)$ values for the mixtures against the number of double bonds, *b*, in the C_6 or C_7 hydrocarbon are given in Figure 5.20. The introduction of a double bond into *n*-hexane and into *n*-heptane in the 1-carbon position has a small negative effect on the excess volume. The $V^E(x=0.5)$ values for {cyclohexane + (*n*-hexane(43) or *n*-heptane(44))} are 0.149 $cm^3.mol^{-1}$ and 0.310 $cm^3.mol^{-1}$ respectively, as opposed to a $V_m^E(x=0.5)$ of 0.129 $cm^3.mol^{-1}$ for the mixture {cyclohexane + 1-hexene}(40) and a $V_m^E(x=0.5)$ of 0.266 $cm^3.mol^{-1}$ for {cyclohexane + 1-heptene}. The excess molar volumes for the C_7 hydrocarbons are understandably more positive than those for the C_6 compounds, indicating an enhanced packing effect in the case of the mixtures involving a C_6 hydrocarbon.

By contrast however the $V_m^E(x=0.5)$ values for {cyclohexane + 1-hexyne}: 0.677 $cm^3.mol^{-1}$ and for {cyclohexane + 1-heptyne}: 0.687 $cm^3.mol^{-1}$ exhibit a large positive excess mixing effect, which can be attributed to the breakdown of the strong $\pi ... \pi$ association between the π electrons of the 1-alkyne molecules that occurs on mixing with cyclohexane. Similar observations were made for the excess molar enthalpies for mixtures containing cyclohexane.

The excess molar volumes for {*n*-hexane + (1-hexene(40) or 1-hexyne)} and for {*n*-hexane) + (1-heptene or 1-heptyne)} display a similar pattern to that observed above for mixtures containing cyclohexane. A large positive effect is observed when comparing

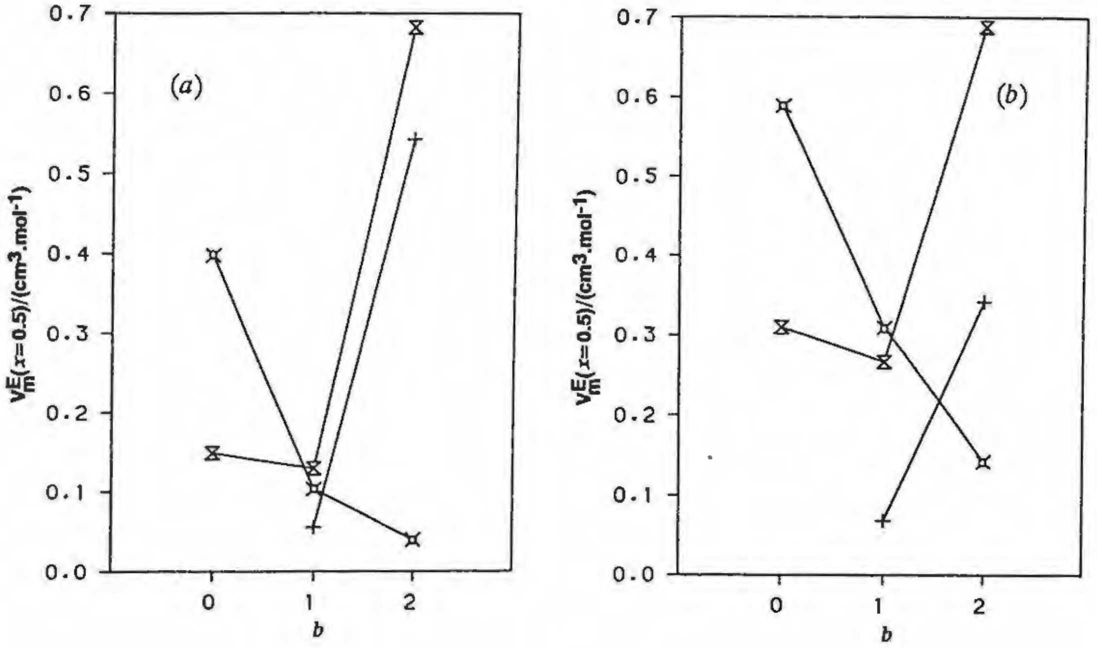

Figure 5.20 Excess molar volumes at equimolar concentrations for *(a)*, {(benzene or cyclohexane or *n*-hexane) + (*n*-hexane or 1-hexene or 1-hexyne)} and *(b)*, {(benzene or cyclohexane or *n*-hexane) + (*n*-heptane or 1-heptene or 1-heptyne)} at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the C_6 or C_7 compound: $b=0$, *n*-alkane; $b=1$, 1-alkene; $b=2$, 1-alkyne. ⋈, benzene; ⧗, cyclohexane; +, *n*-hexane.

the $V_{\rm m}^{\rm E}(x=0.5)$ values for {*n*-hexane + 1-hexyne}: 0.542 $\rm cm^3.mol^{-1}$ and for {*n*-hexane + 1-heptyne}: 0.342 $\rm cm^3.mol^{-1}$ to the $V^{\rm E}(x=0.5)$ values for {*n*-hexane + 1-hexene}: 0.055 $\rm cm^3.mol^{-1}$ and for {*n*-hexane + 1-heptene}: 0.068 $\rm cm^3.mol^{-1}$. The reasons for these trends are similar to those discussed above for the excess molar volumes for mixtures containing cyclohexane and have also been mentioned in the discussion concerning the excess molar enthalpies for systems involving *n*-hexane. The smaller excess molar volumes observed for {*n*-hexane + 1-heptyne}: $V_{\rm m}^{\rm E}(x=0.5) = 0.342\ \rm cm^3.mol^{-1}$ compared to a value of 0.542 $\rm cm^3.mol^{-1}$ for the 1-hexyne is indicative of an enhanced packing effect between the shorter *n*-hexane molecules and the longer 1-heptyne molecules.

The $V_{\rm m}^{\rm E}(x=0.5)$ values for {benzene + (*n*-hexane(40) or 1-hexene(40) or 1-hexyne)} and for {*n*-heptane(24) or 1-heptene or 1-heptyne)} are plotted against the number of double bonds, *b*, in the C_6 or C_7 hydrocarbon, and are included in Figure 5.20. The $V^E_m(x=0.5)$ values for {benzene + *n*-hexane}: 0.397 $cm^3.mol^{-1}$ (40) and for {benzene + *n*-heptane}: 0.589 $cm^3.mol^{-1}$ (24) once again exhibit a decrease on addition of a double bond into *n*-hexane. $V^E_m(x=0.5)$ values for {benzene + (1-hexene(40) or 1-heptene)} are 0.103 $cm^3.mol^{-1}$ (40) and 0.313 $cm^3.mol^{-1}$ respectively. In this case however the addition of a triple bond into *n*-hexane in the 1-carbon position produces a similar decrease in the excess molar volume. The $V^E_m(x=0.5)$ values for {benzene + (1-hexyne or 1-heptyne)} are 0.040 $cm^3.mol^{-1}$ and 0.142 $cm^3.mol^{-1}$ respectively. The trends displayed by the excess molar volumes for these mixtures are indicative of a strong association between the π electrons of the benzene molecule and those of the bonds of the 1-alkene or the triple bonds of the 1-alkyne. The interactions in the last case are the stronger of the two.

5.3.2 Mixtures involving a bicyclic compound, benzene, cyclohexane or *n*-hexane with a cyclic C_6 hydrocarbon

Plots of $V^E_m(x=0.5)$ values for {(decalin or bicyclohexyl) + (cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} and for {(tetralin or cyclohexylbenzene) + (cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} against the number of double bonds, *b*, in the cyclic C_6 compound are shown in Figure 5.21. Also included are plots of the $V^E_m(x=0.5)$ values for the mixtures {(cyclohexane or *n*-hexane) + (cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)}. The $V^E_m(x=0.5)$ values for mixtures containing decalin follow a similar pattern to that displayed by mixtures containing bicyclohexyl. These trends are similar to those exhibited by the mixtures containing the saturated *n*-hexane and cyclohexane compounds. The $V^E_m(x=0.5)$ values for {(decalin(8) or bicyclohexyl(16)) + cyclohexane} are -0.132 $cm^3.mol^{-1}$ and -0.039 $cm^3.mol^{-1}$ respectively, whereas the $V^E_m(x=0.5)$ for the system {*n*-hexane + cyclohexane}: 0.143 $cm^3.mol^{-1}$ (40) is positive. The negative effect in the case of the mixtures containing a large bicyclic compound can be attributed to the enhanced packing effect. The introduction of a double bond into the cyclohexane ring has a small negative effect on the $V^E_m(x=0.5)$ results. The $V^E_m(x=0.5)$ results for {decalin + cyclohexene} and for {bicyclohexyl + cyclohexene} are -0.208 $cm^3.mol^{-1}$ and -0.151 $cm^3.mol^{-1}$ respectively. The $V^E_m(x=0.5)$ values for {(*n*-hexane + cyclohexane}: -0.103 $cm^3.mol^{-1}$ (40) is similar, but the $V^E_m(x=0.5)$ value for {cyclohexane + cyclohexene}: 0.097 $cm^3.mol^{-1}$ (40) is small and positive. A large positive effect is however exhibited in all cases on the introduction of two double bonds into the C_6 cycloalkane ring. The $V^E_m(x=0.5)$ values for {decalin + 1,4-cyclohexadiene}: 0.124 $cm^3.mol^{-1}$

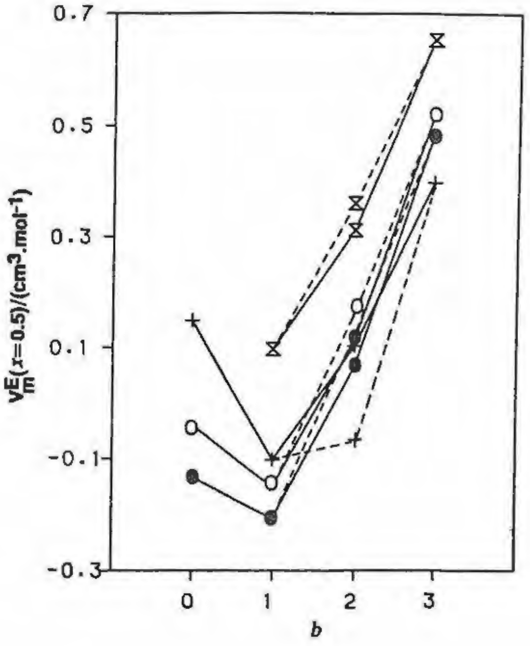

Figure 5.21 Excess molar volumes at equimolar concentrations for {(decalin or bicyclohexyl or cyclohexane or *n*-hexane) + (cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene) at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the *c*-C_6 or compound. The $V^E(x=0.5)$ results for mixtures containing cyclohexane, ($b=0$); cyclohexene, ($b=1$); 1,4-cyclohexadiene, ($b=2$); and benzene ($b=3$) have been linked with broken lines to indicate the overall trend. ● , decalin; ○ , bicyclohexyl; ⧖ , cyclohexane; + , *n*-hexane.
———— , 1,3-cyclohexadiene; - - - - - , 1,4-cyclohexadiene.

and for {bicyclohexyl + 1,4-cyclohexadiene}: 0.162 $cm^3.mol^{-1}$ are more positive than the $V_m^E(x=0.5)$ values for {decalin + 1,3-cyclohexadiene}: 0.065 $cm^3.mol^{-1}$ and for {bicyclohexyl + 1,3-cyclohexadiene}: 0.113 $cm^3.mol^{-1}$. These $V_m^E(x=0.5)$ results indicate a stronger $\pi ... \pi$ association between the unconjugated 1,4-cyclohexadiene molecules than between the 1,3-cyclohexadiene molecules. This is more obvious on considering the decalin mixtures, but was more difficult to observe from excess molar enthalpy results. The $V_m^E(x=0.5)$ results for the mixtures {*n*-hexane + 1,3-cyclohexadiene}: 0.102 $cm^3.mol^{-1}$ (49) is very similar to the values for the mixtures involving decalin or bicyclohexyl. The $V_m^E(x=0.5)$ for {*n*-hexane + 1,4-cyclohexadiene}: -0.067 $cm^3.mol^{-1}$ is small and negative and approximates ideal mixing. The $V_m^E(x=0.5)$ for {cyclohexane + 1,3-cyclohexadiene}: 0.311 $cm^3.mol^{-1}$ (49) is similar to the $V_m^E(x=0.5)$ for {cyclohexane + 1,4-cyclohexadiene}: 0.359 $cm^3.mol^{-1}$.(49) These values are large and positive.

The addition of a third double bond into the cyclohexane ring has an even larger positive effect on the excess molar volumes. The large $V_m^E(x=0.5)$ values for {decalin + benzene}: 0.484 $cm^3.mol^{-1}$ and for {bicyclohexyl + benzene}: 0.519 $cm^3.mol^{-1}$ are similar in magnitude to the results for {cyclohexane + benzene}: 0.653 $cm^3.mol^{-1}$ (40) and for {*n*-hexane + benzene}: 0.397 $cm^3.mol^{-1}$ (40) and even for the related mixtures {benzene + cycloheptane}: 0.628 $cm^3.mol^{-1}$ (50) and {benzene + cyclodecane}: 0.583 $cm^3.mol^{-1}$ (48) at 283 K. This can be attributed once again to the breakdown of the strong $\pi...\pi$ self association which exists between the benzene molecules in an environment of mainly CH_2 groups. The disparity in molar volumes between the components does not appear to be important. This effect was also observed for H_m^E for these mixtures. Only the literature results reported by Fujihara and co-workers for {*cis*-decalin(156) or *trans*-decalin(155)) + benzene} have been included in Figure 5.8. The results reported by Chylinski and Strykjek(157) are within 1% of these values. The H_m^E reported in this investigation for {decalin + benzene} lie between the literature values for *cis*-decalin and for *trans*-decalin.

In an analagous manner the $V_m^E(x=0.5)$ results for {tetralin + (cyclohexane(15) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} follow a similar pattern to the $V_m^E(x=0.5)$ results for {cyclohexylbenzene + (cyclohexane(18) or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} (Figure 5.22). The small positive $V_m^E(x=0.5)$ for {tetralin + cyclohexane}: 0.102 $cm^3.mol^{-1}$ (15) is similar to the value for the mixture {cyclohexylbenzene + cyclohexane}: 0.106 $cm^3.mol^{-1}$.(18) These values are much smaller than the excess molar volumes for {benzene + cyclohexane}: $V_m^E(x=0.5)$ = 0.650 $cm^3.mol^{-1}$ (40) (Figure 5.22) indicating a stronger $CH_2...CH_2$ association between the cyclohexane molecules and the cyclohexane moeity of the unsaturated bicyclic compounds. The introduction of a double bond into the cyclohexane ring produces a negative effect on the $V_m^E(x=0.5)$ results for {tetralin + cyclohexene}: -0.235 $cm^3.mol^{-1}$ and for {cyclohexylbenzene + cyclohexane}: -0.102 $cm^3.mol^{-1}$. This is similar to the trend displayed by the mixture {benzene + cyclohexene}: $V_m^E(x=0.5)$ = 0.245 $cm^3.mol^{-1}$ (40) and is indicative of an increased $\pi...\pi$ association between the π electrons of the cyclohexene molecule and the π electrons of benzene or of the aromatic portion of the bicyclic molecule. The introduction of two or three double bonds into the cyclohexane ring results in small positive rises in the $V_m^E(x=0.5)$ values for mixtures involving an unsaturated bicyclic compound. Once again the $V_m^E(x=0.5)$ results for the mixture {tetralin + 1,4-cyclohexadiene}: -0.119 $cm^3.mol^{-1}$ and for {cyclohexylbenzene + 1,4-cyclohexadiene}: -0.066 $cm^3.mol^{-1}$ are more positive than the $V_m^E(x=0.5)$ for {tetralin + 1,3-cyclohexadiene}: -0.205 $cm^3.mol^{-1}$ and for {cyclohexylbenzene + 1,3-cyclohexadiene}: -0.091 $cm^3.mol^{-1}$,

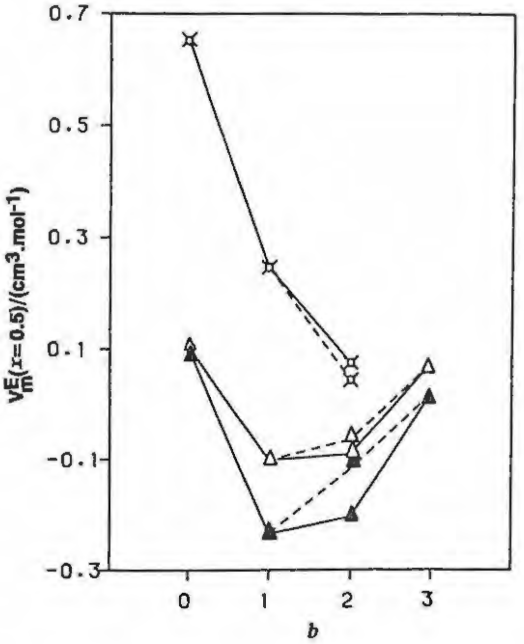

Figure 5.22 Excess molar volumes at equimolar concentrations for {(tetralin or cyclohexylbenzene or benzene) + (cyclohexane or cyclohexene or 1,3- or 1,4-cyclohexadiene or benzene) at 298.15 K as a function of the number of double bonds, *b*, in the functional group of the *c*-C_6 compound. The $V^E(x=0.5)$ results for mixtures containing cyclohexane, ($b=0$); cyclohexene, ($b=1$); 1,4-cyclohexadiene, ($b=2$); and benzene ($b=3$) have been linked with broken lines to indicate the overall trend. ▲ , tetralin; ¤ , benzene, Δ ,cyclohexylbenzene.
——— , 1,3-cyclohexadiene; - - - - - , 1,4-cyclohexadiene.

indicating stronger π...π associations between the 1,4-cyclohexadiene molecules. The $V^E_m(x=0.5)$ for {benzene + 1,3-cyclohexadiene}: 0.074 $cm^3.mol^{-1}$ (49) and for {benzene + 1,4-cyclohexadiene}: 0.042 $cm^3.mol^{-1}$ (49) are small and positive, approximating ideal mixing. These $V^E_m(x=0.5)$ for {benzene + a cycloalkadiene} exhibit a decrease on mixing, reflecting an increased association of the second component with benzene, related to the increasing number of double bonds. Small positive $V^E_m(x=0.5)$ values for {tetralin + benzene}: 0.017 $cm^3.mol^{-1}$ and for {cyclohexylbenzene + benzene}: 0.072 $cm^3.mol^{-1}$ are observed. These V^E_m are smaller than the excess molar volumes for mixtures involving decalin or bicyclohexyl with benzene. This can be attributed to the stronger association between the benzene molecules and the aromatic portion of the bicyclic compound. It would appear that the effect on V^E_m from the "dilution" of the aromatic moeity in the unsaturated bicyclic compounds is balanced by a packing effect which is probably negative and which results from the disparities in the molar volumes.

5.4 Activity coefficients at infinite dilution

The activity coefficients at infinite dilution, γ_{13}^{∞}, obtained from g.l.c. measurements at 278.15 K, 288.15 K and at 298.15 K , are given in Table 5.1. The uncertainty in the γ_{13}^{∞} values determined from experimental values of B_{11} and B_{12} is estimated to be ± 0.006. For the cases where B_{11} and B_{12} values were calculated from the Hudson and McCoubrey combining rule, the estimated uncertainty in γ_{13}^{∞} is ± 0.009. At infinite dilution an activity coeficient equal to unity reflects the equivalence of the 1-1 interactions and the 1-2 interactions. As expected the mixtures which exhibit γ_{13}^{∞} values tending towards unity comprise similar molecules with similar degrees of saturation or unsaturation. Examples of these are {cyclohexane + (decalin or bicyclohexyl)} and {benzene + (tetralin or cyclohexylbenzene)}. Mixtures comprising "unlike" molecules exhibit large deviations from unity. The γ_{13}^{∞} values in Table 5.1 are generally observed to decrease with an increase in the temperature.

For the purposes of discussion the results have been expressed in terms of partial molar excess properties. The partial molar excess property at infinite dilution in a mixture is the contribution by one mole of solute to the overall property of the mixture which contains an infinite amount of solvent. The γ_{13}^{∞} values at 298.15 K have been used to determine the partial molar excess Gibbs function at infinite dilution, $G_1^{E\infty}$:(239)

$$G_1^{E\infty} = RT\ln \gamma_{13}^{\infty} \qquad 5.3$$

The partial molar excess enthalpies of mixing at infinite dilution, $H_1^{E\infty}$, have also been determined at 298.15 K from finite concentration data which has been summarized in Tables C1 and C2 in the form:

$$H_m^E/(J.mol^{-1}) = x_1(1-x_1)\sum_r A_r(1-2x_1)^r \qquad 5.4$$

The partial molar enthalpy is given by:(465)

$$H_1^E = (\delta H_m^E/\delta n_1)_{n2} = (1-x_1)(\delta H_m^E/\delta x_1) + H_m^E \qquad 5.5$$

Table 5.1 Activity coefficients at infinite dilution at 278.15 K, 288.15 K and 298.15 K, for various hydrocarbon solutes in bicyclic compound solvents

Solute	γ_{13}^{∞} (278.15 K)	γ_{13}^{∞} (288.15 K)	γ_{13}^{∞} (298.15 K)	γ_{13}^{∞} (278.15 K)	γ_{13}^{∞} (288.15 K)	γ_{13}^{∞} (298.15 K)
		decalin			**bicyclohexyl**	
n-hexane	1.3338	1.3281	1.3229	1.2141	1.2080	1.2035
1-hexene	1.3348	1.3279	1.3221	1.1640	1.1555	1.1479
1-hexyne	1.9253	1.8476	1.7729	1.7101	1.6299	1.5575
n-heptane	1.2486	1.2786	1.2733	1.1368	1.1312	1.1261
1-heptene	1.2829	1.2772	1.2711	1.1826	1.1747	1.1677
1-heptyne	1.8559	1.7903	1.7359	1.6956	1.6319	1.5773
cyclohexane	1.0950	1.0969	1.0988	1.0312	1.0212	1.0128
cyclohexene	1.1671	1.0701	1.0729	0.9607	0.9572	0.9557
1,3-cyclohexadiene	1.0692	1.1450	1.1238	1.1157	1.0910	1.0668
1,4-cyclohexadiene	1.0909	1.0714	1.0537	1.0289	1.0074	0.9882
benzene	1.5803	1.4845	1.3957	1.4969	1.3954	1.2964
		tetralin			**cyclohexylbenzene**	
n-hexane	2.0238	1.9625	1.9029	1.7006	1.6501	1.6003
1-hexene	1.5259	1.5070	1.4881	1.3559	1.3374	1.3194
1-hexyne	1.2171	1.2140	1.2113	1.1937	1.1855	1.1775
n-heptane	2.0107	1.9387	1.8719	1.7101	1.6557	1.6060
1-heptene	1.5672	1.5437	1.5202	1.3947	1.3699	1.3465
1-heptyne	1.2519	1.2507	1.2499	1.2088	1.1998	1.1936
cyclohexane	1.4683	1.4205	1.3727	1.3207	1.2739	1.2311
cyclohexene	1.1428	1.1299	1.1171	1.0542	1.0449	1.0359
1,3-cyclohexadiene	0.9843	0.9799	0.9761	0.9509	0.9485	0.9465
1,4-cyclohexadiene	0.9171	0.9155	0.9140	0.8529	0.8539	0.8548
benzene	0.9865	0.9719	0.9585	0.9982	0.9831	0.9693

Table 5.2 Partial molar excess thermodynamic properties at 298.15 K

Mixtures	$G_1^{E\infty}$ / J.mol^{-1}	$H_1^{E\infty}$ / J.mol^{-1}	$S_1^{E\infty}$ / J.K.mol^{-1}	$V_1^{E\infty}$ / cm^3.mol^{-1}
decalin +				
n-hexane	694	252	-1.48	-3.99
1-hexene	692	214	-1.60	-4.41
1-hexyne	1419	2701	4.30	-0.05
n-heptane	599	290	-1.04	-2.68
1-heptene	595	358	-0.79	-2.51
1-heptyne	1367	1961	1.99	0.07
cyclohexane	234	-118	-1.18	-0.99
cyclohexene	174	-193	-1.23	-0.76
1,3-cyclohexadiene	290	1214	3.10	0.37
1,4-cyclohexadiene	130	1183	3.53	0.66
benzene	826	4101	10.98	0.66
bicyclohexyl +				
n-hexane	459	153	-1.03	-6.13
1-hexene	342	424	0.30	-6.57
1-hexyne	1098	2822	5.80	-1.49
n-heptane	294	204	-0.30	-5.27
1-heptene	384	388	0.01	-4.61
1-heptyne	1129	2282	3.87	-1.13
cyclohexane	32	542	1.71	-0.17
cyclohexene	-112	110	0.75	-0.33
1,3-cyclohexadiene	160	1508	4.52	0.74
1,4-cyclohexadiene	-29	1616	5.52	1.17
benzene	644	4829	14.04	3.27

Table 5.2 (continued)

Mixtures	$G_1^{E\infty}$ / $J.mol^{-1}$	$H_1^{E\infty}$ / $J.mol^{-1}$	$S_1^{E\infty}$ / $J.K.mol^{-1}$	$V_1^{E\infty}$ / $cm^3.mol^{-1}$
tetralin +				
n-hexane	1595	2126	1.78	-5.82
1-hexene	985	944	-0.14	-5.72
1-hexyne	475	194	-0.94	-4.91
n-heptane	1554	2057	1.69	-3.24
1-heptene	1038	1089	0.17	-4.95
1-heptyne	533	-14	-1.90	-2.47
cyclohexane	785	2455	5.60	0.78
cyclohexene	275	851	1.93	-1.14
1,3-cyclohexadiene	-60	251	1.04	-1.14
1,4-cyclohexadiene	-223	105	1.10	-0.56
benzene	-105	913	3.41	0.10
cyclohexylbenzene +				
n-hexane	1166	2004	2.81	-5.55
1-hexene	687	878	0.64	-5.48
1-hexyne	405	454	0.17	-3.28
n-heptane	1174	2055	2.95	-3.31
1-heptene	737	1071	1.17	-3.46
1-heptyne	376	304	-0.24	-2.41
cyclohexane	515	2343	6.13	0.92
cyclohexene	87	582	1.66	-0.63
1,3-cyclohexadiene	-136	144	0.94	-0.71
1,4-cyclohexadiene	-389	-77	1.05	-0.54
benzene	-77	1010	3.64	0.56

At infinite dilution equation 5.3 reduces to:

$$H_1^{E\infty} = (\delta H_m^E/\delta x_1)^\infty = \sum_r A_r \qquad 5.6$$

The estimated uncertainty in $H_1^{E\infty}$ is ±200 J.mol^{-1}. This is high because the experimental excess molar enthalpy results were never obtained at concentrations below 0.08 mole fraction. The partial molar excess volume at infinite dilution, $V_1^{E\infty}$, has been calculated in a similar manner from the experimental excess molar volume results at 298.15 K. The $G_1^{E\infty}$ and $H_1^{E\infty}$ results have been used to determine the partial molar excess entropy at infinite dilution, $S_1^{E\infty}$ at 298.15 K. All the above results for $G_1^{E\infty}$, $H_1^{E\infty}$, $S_1^{E\infty}$, and $V_1^{E\infty}$ are summarized in Table 5.2.

The results at 298.15 K will be discussed under subdivisions relating to the solvent. A high positive $G_1^{E\infty}$, $H_1^{E\infty}$ and $S_1^{E\infty}$ have been interpreted as an indication of the incompatibility of the solute in the solvent.

5.4.1 A cyclic C_6 hydrocarbon solute + decalin or bicyclohexyl

The $G_1^{E\infty}$ results for {(cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene) + decalin} form a pattern which is very similar to the pattern displayed by the $G_1^{E\infty}$ results for {(cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene) + bicyclohexyl}. This can be seen in Figure 5.23*a* from a plot of $G_1^{E\infty}$ values against the number of double bonds, *b*, in the cyclic C_6 compound. The $H_1^{E\infty}$, $S_1^{E\infty}$ and $V_1^{E\infty}$ results have been included in similar plots in Figures 5.23*b*, 5.23*c* and 5.23*d* respectively. Once again similar trends are displayed by mixtures involving each of the two solvents, indicating similar interactions between the solutes and the decalin or bicyclohexyl solvents. This is to be expected considering the similarity between the type of C-H bonding in decalin and in bicyclohexyl. Most of the partial molar enthalpies are endothermic. This is a direct result of the solute - solute and solvent - solvent interactions which are more energetic than the solvent - solute interactions. This is particularly true for benzene where the $\pi \ldots \pi$ interactions between the benzene molecules is the dominant contribution to the enthalpy. The same observations can be made for the $G_1^{E\infty}$ results which display similar patterns to the $V_1^{E\infty}$ results. The increase in the enthalpy of mixing with an increase in the number of double bonds in the solute is an indication of the decreasing strength of the solute-solvent interactions. The similarity between the $S_1^{E\infty}$ and $V_1^{E\infty}$ patterns is an indication

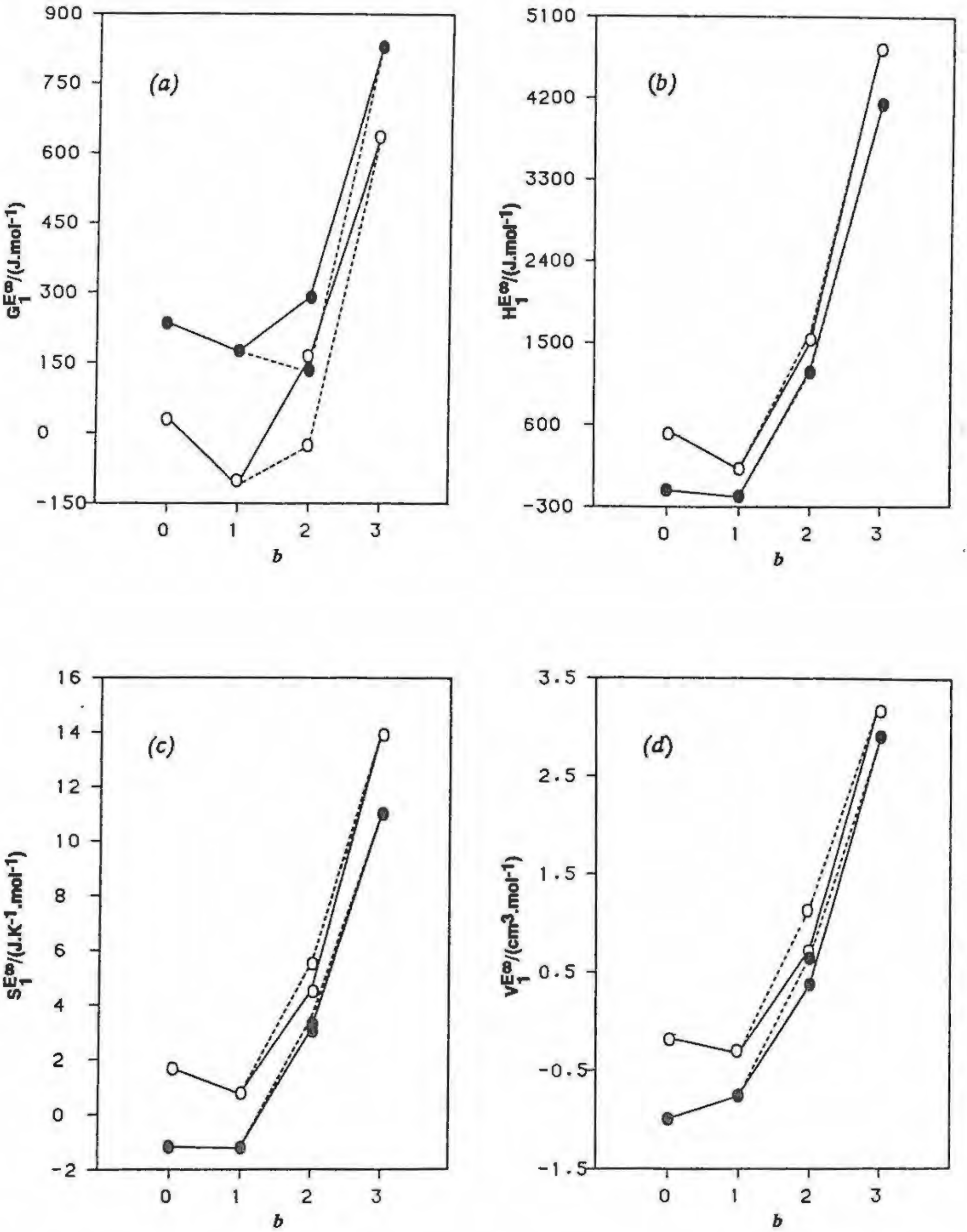

Figure 5.23 A plot of *(a)*, $G_1^{E\infty}$; *(b)*, $H_1^{E\infty}$; *(c)*, $S_1^{E\infty}$; and *(d)*, $V_1^{E\infty}$ against the number of double bonds, *b*, in the solute for {(cyclohexane or cyclohexene or 1,3- or 1,4-cyclohexadiene or benzene) + (decalin or bicyclohexyl)} 298.15 K: $b=0$, cyclohexane; $b=1$, cyclohexene; $b=2$, 1,3- or 1,4-cyclohexadiene; $b=3$, benzene. The solvents are: ● , decalin; ○ , bicyclohexyl.

——— , 1,3-cyclohexadiene; - - - - - - , 1,4-cyclohexadiene.

that the volume change on mixing contributes significantly to the entropy change on mixing.

The addition of a double bond into the cyclohexane molecule has little effect on any of the thermodynamic properties. However the addition of two double bonds into cyclohexane to form 1,3-cyclohexadiene or 1,4-cyclohexadiene has a significant positive effect on all the properties except the excess Gibbs function. The introduction of another double bond to form benzene has a large positive effect on all the excess properties. This positive effect can be attributed to the breakdown of the strong $\pi ... \pi$ self-association in benzene and in the cyclohexadiene molecules. This effect is unnoticed in the mixtures involving cyclohexene, indicating a relatively weak association between the π bonds of this compound. This observation has been made previously when considering $H_1^{E\infty}$ and $V_1^{E\infty}$ results for mixtures involving cyclohexene with a bicyclic compound, benzene, cyclohexane or *n*-hexane.

The results for 1,3-cyclohexadiene are in most cases not significantly different from the results for 1,4-cyclohexadiene.

5.4.2 An *n*-alkane, a 1-alkene or a 1-alkyne solute + decalin or bicyclohexyl

The $G_1^{E\infty}$, $H_1^{E\infty}$, $S_1^{E\infty}$ and $V_1^{E\infty}$ results for {(*n*-hexane or 1-hexene or 1-hexyne) + (decalin or bicyclohexyl)} and for {(*n*-heptane or 1-heptene or 1-heptyne) + (decalin or bicyclohexyl)} have been plotted against the number of double bonds, *b*, in the C_6 or C_7 hydrocarbon in Figures *5.24a*, *5.24b*, *5.24c* and *5.24d* respectively. Decalin behaves in a similar way to bicyclohexyl in mixtures with these solutes. There is once again a strong similarity between the pattern displayed by the $S_1^{E\infty}$ results and the $V_1^{E\infty}$ results, pointing to a significant volume change contribution to the entropy of mixing. This is particularly interesting if we consider that the shape of the C_6 and C_7 hydrocarbons are very different to the shape of decalin and of bicyclohexyl. The size effect resulting from the difference in the length of the C_6 and the C_7 hydrocarbon chain has a significant effect on the $V_1^{E\infty}$ results for the systems involving an *n*-alkane or a 1-alkene. The trend displayed by the entropy results once again confirms a decrease in the solute-solvent interactions with an increase in the number of double bonds in the solute.

The large positive values for all the thermodynamic properties for the mixtures involving a 1-alkyne with decalin or with bicyclohexyl is once again indicative of a breakdown of

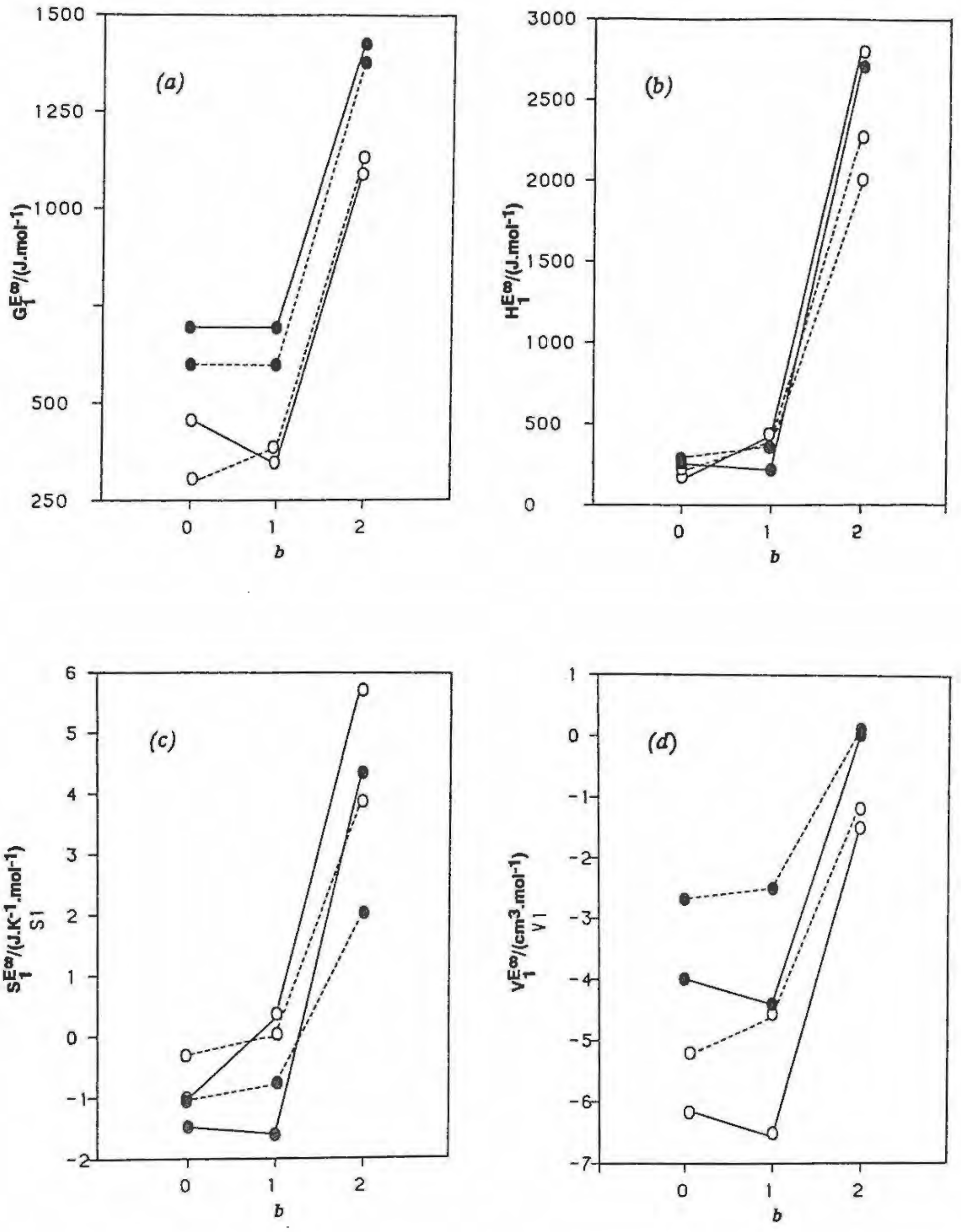

Figure 5.24 A plot of *(a)*, $G_1^{E\infty}$; *(b)*, $H_1^{E\infty}$; *(c)*, $S_1^{E\infty}$; and *(d)*, $V_1^{E\infty}$ against the number of double bonds, *b*, in the solute for {(*n*-hexane or 1-hexene or 1-hexyne or *n*-heptane or 1-heptene or 1-heptyne) + (decalin or bicyclohexyl)} at 298.15 K: *b* = 0, *n*-alkane; *b* = 1, 1-alkene; *b* = 2, 1-alkyne.The solvents are: ● , decalin; ○ , bicyclohexyl. ———— , C_6; ------ , C_7.

the strong $\pi ... \pi$ interactions between the 1-alkyne molecules. The 1-alkenes do not exhibit as positive an effect when mixed with decalin or with bicyclohexyl, indicating that self association between the 1-alkene molecules is relatively weak. This substantiates the observations made in Section 5.2.1.

5.4.3 A cyclic C_6 hydrocarbon solute + tetralin or cyclohexylbenzene

The $G_1^{E\infty}$, $H_1^{E\infty}$, $S_1^{E\infty}$ and $V_1^{E\infty}$ results for {(cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene) + (tetralin or cyclohexylbenzene)} have been plotted against the number of double bonds, *b*, in the cyclic C_6 compound, in Figures *5.25a*, *5.25b*, *5.25c* and *5.25d* respectively. The patterns generated by these results indicates that tetralin behaves in a similar way to cyclohexylbenzene in their interactions with the cyclic C_6 compounds. This is to be expected if it is considered that tetralin and cyclohexylbenzene both comprise only a six membered aromatic ring and a six membered saturated ring.

The $G_1^{E\infty}$ and $H_1^{E\infty}$ results are characterized by high positive values for the mixtures involving cyclohexane. This reflects the incompatibility of the cyclohexane with the aromatic solvents. The addition of one or two double bonds to the cyclic C_6 molecule results in a decrease in the $G_1^{E\infty}$ and $H^{E\infty}$ results. This is a result of the association between the π electrons of the aromatic moeity of the tetralin or the cyclohexylbenzene molecules, and of the cyclohexene or the cycloalkadiene molecules. The $G_1^{E\infty}$ and $H_1^{E\infty}$ for the mixtures involving benzene are generally more positive than the values for the cycloalkadiene mixtures. This is probably due to a stronger $\pi ... \pi$ interaction between the benzene molecules than between the molecules of the mixture. This is in keeping with the proposal put forward earlier that the aromatic moeity of the unsaturated bicyclic compound is diluted by the non-aromatic moeity.

The similarity between the $S_1^{E\infty}$ patterns and the $V_1^{E\infty}$ patterns for these mixtures indicates once again that the entropy change is strongly related to the volume change on mixing. The trends displayed by the entropy reflects what has been discussed above.

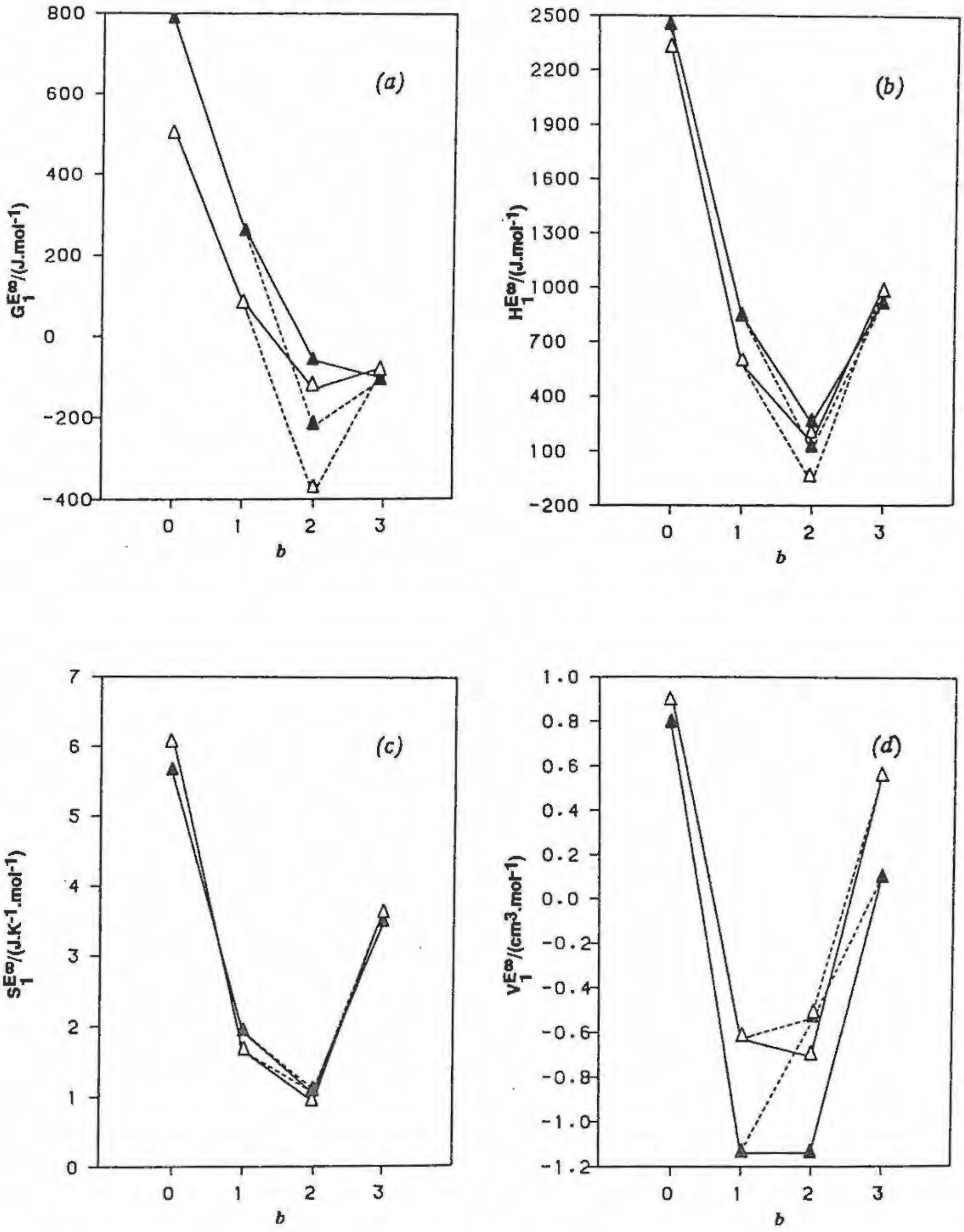

Figure 5.25 A plot of *(a)*, $G_1^{E\infty}$; *(b)*, $H_1^{E\infty}$; *(c)*, $S_1^{E\infty}$; and *(d)*, $V_1^{E\infty}$ against the number of double bonds, *b*, in the solute for {(cyclohexane or cyclohexene or 1,3- or 1,4-cyclohexadiene or benzene) + (tetralin or cyclohexylbenzene)} 298.15 K: $b=0$, cyclohexane; $b=1$, cyclohexene; $b=2$, 1,3- or 1,4-cyclohexadiene; $b=3$, benzene. The solvents are: ▲ , tetralin; △ , cyclohexylbenzene.

———— , 1,3-cyclohexadiene; - - - - - - - , 1,4-cyclohexadiene.

5.4.4 An *n*-alkane, a 1-alkene or a 1-alkyne solute + tetralin or cyclohexylbenzene

The $G_1^{E\,\infty}$, $H_1^{E\,\infty}$, $S_1^{E\,\infty}$ and $V_1^{E\,\infty}$ results for {(*n*-hexane or 1-hexene or 1-hexyne) + (tetralin or cyclohexylbenzene} and for {(*n*-heptane or 1-heptene or 1-heptyne) + (tetralin or cyclohexylbenzene)} have been plotted against the number of double bonds, *b*, in the C_6 or C_7 hydrocarbon in Figures *5.26a*, *5.26b*, *5.26c* and *5.26d* respectively. The trends displayed by the tetralin results are once again similar to those observed for the cyclohexylbenzene results. The $G_1^{E\,\infty}$, $H_1^{E\,\infty}$ and $S_1^{E\,\infty}$ results all show a decrease in value as the number of bonds in the terminal group of the C_6 or C_7 hydrocarbon increases from one to three. This decrease is most likely the result of a strong association between the π electrons of the aromatic portion of the bicyclic compound with the double or triple bonds of the solute. The differences between the shapes of the solute and solvent molecules are probably responsible for the complicated $V_1^{E\,\infty}$ results which do not fit the pattern of the other thermodynamic properties.

In conclusion it has been shown that the partial molar excess thermodynamic properties for the decalin mixtures are similar to those for the bicyclohexyl mixtures. There is also a similarity between the properties of the tetralin mixtures and the properties of the cyclohexylbenzene mixtures. The experimental results also indicate that the cyclohexadienes, benzene and the 1-alkynes exhibit a strong dissociation effect on mixing with the saturated solvents decalin and bicyclohexyl. Cyclohexene, the cyclohexadienes, benzene, the 1-alkenes and the 1-alkynes exhibit strong association with tetralin and with cyclohexylbenzene.

It would be interesting to observe the effect of the position of the double bond within the 1-alkene chain, or the effect of conjugated or unconjugated double bonds within the chain on the thermodynamic properties. The high cost of some of these compounds would however probably limit an investigation of this nature to measurements at infinite dilution.

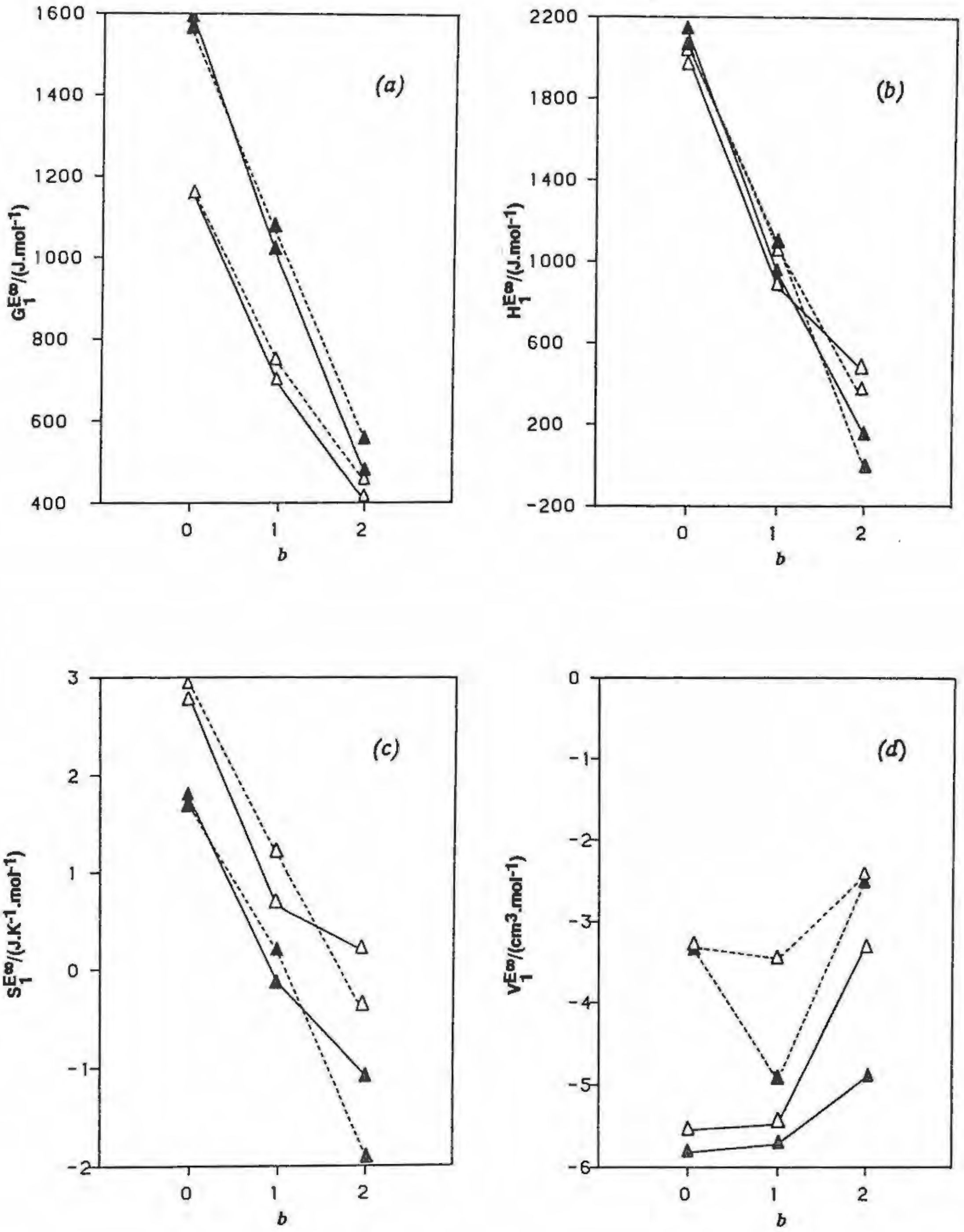

Figure 5.26 A plot of *(a)*, $G_1^{E\infty}$; *(b)*, $H_1^{E\infty}$; *(c)*, $S_1^{E\infty}$; and *(d)*, $V_1^{E\infty}$ against the number of double bonds, *b*, in the solute for {(*n*-hexane or 1-hexene or 1-hexyne or *n*-heptane or 1-heptene or 1-heptyne) + (tetralin or cyclohexylbenzene)} at 298.15 K: *b* = 0, *n*-alkane; *b* = 1, 1-alkene; *b* = 2, 1-alkyne.The solvents are: ▲, tetralin; △, cyclohexylbenzene. ———— , C_6; - - - - - - - , C_7.

CHAPTER 6

APPLICATION OF THE THEORIES OF NON-ELECTROLYTE SOLUTIONS

6.1 Introduction

The Flory theory(52-58) and the approximation of Patterson and co-workers(60,61) have already been discussed in detail in Chapter 4. These theories have been tested by fitting the various parameters to the experimental H_m^E and V_m^E results for the binary mixtures {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne or a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. In each case an interaction parameter, X_{12}, was derived either from an experimental excess thermodynamic property or from the equation of Berthelot, and was in turn used to predict another excess thermodynamic property. In this investigation the experimental excess molar enthalpies were used to predict excess molar volumes and similarly the excess molar volumes were employed in the prediction of excess molar enthalpies. Similar work has been carried out by other workers.(27,33,56,60,151,153,438,460,461) The two theories were compared in the light of these predictions. Excess molar enthalpies and excess molar volumes have also been predicted by the Liebermann theory.(62,63) This theory does not employ any adjustable parameters and the excess properties are calculated from macroscopic properties of the pure components. The Flory theory has also been used to predict the partial molar Gibbs functions and hence the activity coefficients at infinite dilution. The interaction parameters derived from excess molar enthalpy results were employed in these calculations.

Two computer programmes were used to calculate the necessary parameters. One of these programmes was written by Spiteri(82) and employs the equations of Flory to predict H_m^E and V_m^E data over the entire composition range at 0.1 mole fraction intervals. The equations of Liebermann and co-workers are also included and the calculations are performed at equimolar concentrations. The programme originally employed the spherical molecule approximation to determine the ratio of the number of sites per segment, s_1/s_2, but has been modified in this work to include the calculation of this ratio from surface areas determined using the methods of Bondi(407) and to perform calculations at 0.01 mole fraction intervals. Programmme comments have been added to the original code. The other computer programme was written in this work and employs the approximate equations of Patterson and co-workers to predict H_m^E and V_m^E data. The ratio of the number of surface sites per segment can once again be determined by the two different methods. Activity coefficients at infinite dilution are also determined using the Flory theory. A programme listing for this programme, together with the necessary operating instructions for both of these programmes is included in Appendix F.

6.2 Data requirements

The only data requirements for the the application of the theories used in this work are the densities, ρ, the thermal expansion coefficients, α, and the isothermal compressibilities, κ, for the two pure components, and the experimental H_m^E and V_m^E. The values for the pure component properties, together with literature references, are given in Table 6.1. Densities for 1,3-cyclohexadiene and 1,4-cyclohexadiene were measured in this work. The coefficients of thermal expansion, α, at 298.15 K for 1-heptene and 1-heptyne were calculated from density measurements determined at temperatures between 288.15 K and 308.15 K using the Paar DMA 601 vibrating tube densitometer.

The predictive success of the theory relies on the accuracy of the coefficients α and κ. The accuracy of the calculated excess molar volume depends on the errors in T^* and p^* for the pure components, where the former depends on the thermal expansion coefficients and the latter on the thermal pressure coefficients, γ. Flory$^{(56)}$ has determined that an error in α_2 is approximately proportional to $(p_1^* - p_2^*)/(p_1^* + p_2^*)$, and he states that in some cases an error of 2% in α_2 would alter V_m^E by ± 0.05 cm^3.mol^{-1}. The sensitivity of the predicted V_m^E to the thermal pressure coefficient is approximately proportional to $(\tilde{T}_1 - \tilde{T}_2)$, and an error in γ_2 would alter V_m^E by about 0.15 cm^3.mol^{-1} for $(\tilde{T}_1 - \tilde{T}_2)$ approximately equal to 0.015.

For the test system {cyclohexane + *n*-hexane} an increase in α_2 by 5% for *n*-hexane resulted in a 7% change in the $X_{12}(V_m^E)$ and an 8% change in the predicted $H_m^E(x=0.5)$ value compared to the predictions using α_2 obtained from Table 6.1. A reduction in α_2 by 5% resulted in a 6% change in $X_{12}(V_m^E)$ and a corresponding 16% change in the predicted $H_m^E(x=0.5)$. An increase or decrease of 5% in κ_2 resulted in 8% changes in the predicted $H_m^E(x=0.5)$, while the same increase or decrease in κ_2 resulted in 79% and 50% changes in the V_m^E predicted from H_m^E data. Varying the value of α_1 for cyclohexane by the same amount affected the predicted V_m^E by as much as 50%. The affect of varying both α and κ together for one component by up to 5% affected the predicted V_m^E by as much as 65%

Table 6.1 Physical properties at 298.15 K for isobaric expansivities, α, isothermal compressibilities, κ, densities, ρ, and intermolecular contact sites per segment, *s*, for the pure compounds used in this study

Hydrocarbon	$10^3\alpha / \text{K}^{-1}$	Reference	$10^{12}\kappa / \text{Pa}^{-1}$	Reference	$\rho / \text{g.cm}^{-3}$	Reference	s^a / A^{-1}
n-pentane	1.643	33	2120	33	0.6212	33	0.975
n-hexane	1.375	33	1669	33	0.6548	33	0.967
1-hexene	1.414	462	1689	462	0.6690	462	0.961
1-hexyne	1.371	462	1404	462	0.7293	462	1.041
n-heptane	1.245	33	1438	33	0.6795	33	0.996
1-heptene	1.273	This work	1450	This work	0.6926	207*p*	0.960
1-heptyne	1.245	This work	1200	This work	0.7380	207*p*	1.018
n-octane	1.150	33	1282	33	0.6985	33	0.964
n-dodecane	0.970	33	988	33	0.7452	33	0.963
n-hexadecane	0.898	33	857	33	0.7699	33	0.965
cyclopentane	1.351	462	1332	33	0.7374	207*q*	0.933
cyclohexane	1.215	36	1120	462	0.7739	207*r*	0.961
cyclohexene	1.177	462	1036	462	0.8059	462	0.931
1,3-cyclohexadiene	1.142	462	962	462	0.8402	This work	0.898
1,4-cyclohexadiene	1.141	462	944	462	0.8510	This work	0.908
cycloheptane	1.000	463	967	463	0.8060	207*r*	0.969
cyclooctane	0.979	464	801	464	0.8315	207*r*	0.995
decalin	0.857	9	724	9	0.8826	9	0.795
bicyclohexyl	0.819	462	674	462	0.8827	462	0.867
tetralin	0.824	462	607	462	0.9646	462	0.805
cyclohexylbenzene	0.818	462	627	462	0.9390	462	0.856
benzene	1.218	462	966	462	0.8737	207*b*	0.868

[a] Reference 407.

This served to illustrate the critical dependence of the predicted values on the coefficients α and κ. These effects were also observed for all the other systems investigated, the variations depending to a large extent on the system.

In the Prigogine-Flory-Patterson theory the free volume contributions to the predicted H_m^E and V_m^E are dependent on the differences in the coefficients α and κ of the pure components, and hence variations in these coefficients had a pronounced effect on the predictions in most cases. The Liebermann theory employs no adjustable parameters but calculates H_m^E and V_m^E from the properties of the pure components; the predictions are also dependent on the accuracy of these coefficients.

The coefficients of isothermal compressibility were not available in the literature for 1-heptene and for 1-heptyne. Values for these coefficients were thus extraplolated from the literature values for related compounds. By an alternative method, κ values were treated as variables and the value that produced the best standard deviation for the predicted H_m^E, $\sigma(H_m^E)$, using only excess molar enthalpy data, and the best standard deviation for V_m^E using only excess molar enthalpy data, $\sigma^*(V_m^E)$, was chosen. These standard deviations were observed to converge rapidly for a small change in κ. The minima of $\sigma(H_m^E)$ and $\sigma^*(V_m^E)$ always occured at much the same κ with the difference always less than 5%. The values of κ obtained were in good agreement with the values extrapolated from the literature, the difference between them never greater than 4%. Although it has been shown that the predicted values are sensitive to the uncertainties in κ data we feel that it is still useful to predict excess thermodynamic data for these systems from these extrapolated coefficients. The Flory fit is remarkably good for such a two parameter theory and it can be seen from Tables 6.4 and 6.7 that the predicted results are still better the an the predictions using the X_{12}(Berthelot) or the predictions using the theory of Liebermann (Tables 6.2 and 6.3).

6.3 Application of the Flory theory

6.3.1 Introduction

Battino and co-workers$^{(423,424,460)}$ have determined contact interaction parameters using the Berthelot geometric mean rule:

$$X_{12}(\text{Berthelot}) = p_1^*[1 - (s_1/s_2)^{1/2}(p_1^*/p_2^*)^{1/2}]^2 \qquad 6.1$$

They used the Flory theory to predict excess thermodynamic properties with qualitative success for the approximately ideal systems such as {2.2,4-trimethylpentane + cyclohexane}. Similar work has been carried out by Spiteri(82) who concluded that the Berthelot formula was inadequate for the prediction of thermodynamic properties for mixtures involving an *n*-alkane with a cycloalkane. This non-empirical route has been employed in this investigation.

The approach of Benson has also been followed in this work.(151,153) Adjustable interaction parameters for each system were calculated to fit the experimental excess molar enthalpy and experimental excess molar volume results. These $X_{12}(H_m^E)$ and $X_{12}(V_m^E)$ parameters were then used to check whether the Flory equations were capable of reproducing the experimental H_m^E and V_m^E curves over the entire composition range. Finally, the ability of the theory to predict excess molar volumes from excess molar enthalpy data, and conversely excess molar enthalpies from excess molar volume data, was examined.

6.3.2 Calculation of the Flory parameters

The thermal pressure coefficients, γ_i, for the pure components were calculated from the pure component properties through:

$$\gamma_i = \alpha_i/\kappa_i \qquad 6.2$$

The reduced volumes, $\tilde{v}_i$, and the hard core molar volumes, V_i^*, were determined from:

$$\tilde{v}_i = \{[1 + (4/3)\alpha_i T]/[1 + \alpha_i T]\}^3 \qquad 6.3$$

and
$$V_i^* = V_i/\tilde{v}_i \qquad 6.4$$

where V_i is the molar volume calculated from the density. The characteristic pressures, p_i^*, and the characteristic temperatures, T_i^*, were determined using equations 4.37 and 4.30 respectively, while the reduced temperatures were calculated from:

$$\tilde{T}_i = T/T_i^* \qquad 6.5$$

The ratio of the number of segments in the molecules is given by the ratios of the respective core volumes according to equation 4.58.

Two methods have been used in each case to determine the ratio of the number of surface contact sites per segment, s_1/s_2, for the respective components. One method has been used by numerous workers(9,59,61,82,153,419) and employs the spherical molecule approximation of Abe and Flory:(56)

$$s_1/s_2 = (V_2^*/V_1^*)^{1/3} \qquad 6.6$$

In an alternative method the number of intermolecular contact sites per segment for each pure component, s, have been determined from the surface area information of Bondi.(407) The values of s for the pure components in Table 6.1. This approach has been used before by other workers.(4,418,434) In an alternative approach by Benson *et al.*(153) the ratio was treated as an adjustable parameter. This method has been mentioned before and was not used here.

The segment fractions, ϕ_i, and the site fraction, θ_i, were calculated from:

$$\phi_2 = (1 - \phi_1) = (x_2)/(x_2 + x_1 r_1/r_2) \qquad 6.7$$

and

$$\theta_2 = (1 - \theta_1) = \phi_2/(\phi_1 s_1/s_2 + \phi_2) \qquad 6.8$$

where x_i is the mole fraction of component i. The "ideal" reduced volume of the mixture, $\tilde{v}^o$, is related to the reduced volumes of the pure components and was determined according to equation 4.51.

The value of the ideal reduced temperature, $\tilde{T}^o$, was determined from:

$$\tilde{T}^o = [(\tilde{v}^o)^{1/3} - 1]/(\tilde{v}^o)^{4/3} \qquad 6.9$$

The reduced temperature for the mixture was determined from:

$$\tilde{T} = (\phi_1 p_1^*\tilde{T}_1 + \phi_2 p_2^*\tilde{T}_2)/(\phi_1 p_1^* + \phi_2 p_2^* - \psi_1\theta_2 X_{12}) \qquad 6.10$$

The reduced excess volume, $\tilde{v}^E$, was determined from:

$$\tilde{v}^E = [(\tilde{v}^o)^{7/3}(\tilde{T} - \tilde{T}^o)]/[4/3 - (\tilde{v}^o)^{1/3}] \qquad 6.11$$

The excess molar volume for the mixture was then calculated from:

$$V_m^E = (x_1V_1^* + xV_2^*)\tilde{v}^E \qquad 6.12$$

The V_m^E were determined over the entire composition range at 0.01 mole fraction intervals. These predicted values were compared to the experimental V_m^E determined at the same mole fractions from the coefficients of the smoothing curve, and the standard deviation, $\sigma(V_m^E)$, over all the mole fractions was calculated according to the general expression:

$$\sigma^2 = \{\sum_{i=1}^{99}[X_m^E(\text{experimental}, x_i) - X_m^E(\text{predicted}, x_i)]^2\}/98 \qquad 6.13$$

where X_m^E is the excess thermodynamic property.

Excess molar enthalpies have been predicted according to:

$$H_m^E = x_1V_1^*p_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + x_2V_2^*p_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (x_1V_1^*\theta_2X_{12}/\tilde{v}) \qquad 6.14$$

where in this case:

$$\tilde{v} = \tilde{v}^o + \tilde{v}^E \qquad 6.15$$

Once again the predicted values were compared to the experimental H^E values, and the standard deviation, $\sigma(H^E)$, was determined for each system from equation 6.13.

6.3.3 Predictions using the Berthelot geometric mean rule

The Bethelot interaction parameter, X_{12}(Berthelot) was determined according to equation 6.1 and was employed in the prediction of excess molar enthalpies and excess molar volumes according to equations 6.14 and 6.12 respectively. The values for X_{12}(Berthelot) together with the experimental and predicted H_m^E and V_m^E results at equimolar mole fractions for the systems {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)} and {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)} are given in Tables 6.2 and 6.3. The standard deviations $\sigma(H_m^E$, Berthelot) and $\sigma(V_m^E$, Berthelot) are included in these Tables.

The predictions were carried out for s_1/s_2 ratios determined from equation 6.6 and for s_1/s_2 ratios determined according to the methods of Bondi. The combination of X_{12}(Berthelot) and s_1/s_2 values determined from Bondi surface areas was more successful in predicting the correct signs for the excess thermodynamic properties and hence only these predicted results are included in Tables 6.2 and 6.3.

In most cases the correct sign of the V_m^E curves were predicted, and the general trends displayed by the experimental V_m^E results (discussed previously in Chapter 5) were adequately reproduced in most cases. The correlation between the predicted and the experimental results varies however. Large differences are observed in many cases with the predicted excess volumes often being smaller in magnitude than the corresponding experimental results. The agreement is however surprisingly good for the systems {cyclohexylbenzene + (an *n*-alkane or a 1-alkene or a 1-alkyne)} and for a few other isolated cases. This achievement is surprising if we consider that X_{12}(Berthelot) values were determined from pure liquid properties only.

The ability of the X_{12}(Berthelot) parameter to predict H_m^E was also better than expected. The trends displayed by H_m^E were adequately reproduced for the systems where one of the components of the mixture was an unsaturated bicyclic compound or benzene. The X_{12}(Berthelot) was not as successful at reproducing trends for mixtures where one of the components was a saturated bicyclic compound or cyclohexane or *n*-hexane. The predicted results for a bicyclic compound with an *n*-alkane, a 1-alkene or a 1-alkyne are generally larger than the corresponding experimental results, while predicted results for benzene, cyclohexane or *n*-hexane with an *n*-alkane, a 1-alkene or a 1-alkyne are smaller than the experimental results in most cases. Predictions for a bicyclic compound, benzene, cyclohexane or *n*-hexane with a cyclic compound are smaller than the experimental results in most cases.

The X_{12}(Berthelot) parameter tended to predict symmetrical V_m^E and H_m^E curves for almost all of the systems. This was also previously observed by Spiteri,(82) who noted that the sinusoidal shapes for the excess thermodynamic properties for the systems involving {cyclohexane + an *n*-alkane} were not predicted.

The predictions using X_{12}(Berthelot) are better than expected if it is considered that no adjustable parameters are used. This method cannot however be recommended as a practical route for the prediction of the excess thermodynamic properties using the Flory theory.

Table 6.2 Excess molar volumes and excess molar enthalpies at equimolar concentrations calculated by the Flory theory and X_{12}(Berthelot), for the mixtures {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)}. The s_1/s_2 values have been determined from Table 6.1.

Mixture	X_{12}(Berthelot) ($J.cm^{-3}$)	V_m^E(experimental)[a] ($cm^3.mol^{-1}$)	V_m^E(predicted) ($cm^3.mol^{-1}$)	σ(V_m^E, Berthelot) ($cm^3.mol^{-1}$)	H_m^E(experimental)[b] ($J.mol^{-1}$)	H_m^E(predicted) ($J.mol^{-1}$)	σ(H_m^E, Berthelot) ($J.mol^{-1}$)
decalin +							
n-pentane	16.996	-1.4310	1.0803	0.2597	53.9	400.9	255.1
n-hexane	16.941	-0.9478	-0.5545	0.2795	62.4	492.2	316.9
1-hexene	14.491	-0.7468	-0.6175	0.0948	74.2	391.9	234.9
1-hexyne	10.262	-0.0111	-0.2348	0.1675	604.3	262.0	256.0
n-heptane	18.281	-0.6363	-0.2921	0.2504	68.6	596.7	388.7
1-heptene	13.813	-0.4985	-0.3502	0.1116	72.9	424.9	259.3
1-heptyne	7.464	0.0203	-0.0962	0.0872	524.8	210.7	228.6
n-octane	15.205	-0.4565	-0.1080	0.2555	81.6	531.5	331.6
n-dodecane	12.769	0.0726	0.1996	0.2004	125.1	534.3	305.5
n-hexadecane	10.236	0.1371	0.2574	0.0912	198.6	470.7	206.1
bicyclohexyl +							
n-pentane	11.810	-1.5915	-1.4933	0.0846	23.0	230.1	153.4
n-hexane	11.760	-1.1075	-0.9268	0.1375	21.6	320.7	221.0
1-hexene	9.661	-1.1582	-0.9685	0.1336	65.4	231.3	121.7
1-hexyne	6.142	-0.2435	-0.4761	0.1827	630.5	123.9	372.7
n-heptane	10.856	-0.8556	-0.6324	0.1867	26.9	342.2	231.9

Table 6.2 (continued)

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V_m^E(experimental)[a] (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	σ (V_m^E, Berthelot) (cm^3.mol^{-1})	H_m^E(experimental)[b] (J.mol^{-1})	H_m^E(predicted) (J.mol^{-1})	σ (H_m^E, Berthelot) (J.mol^{-1})
bicyclohexyl +							
1-heptene	9.086	-0.8406	-0.6744	0.1249	62.9	263.6	146.4
1-heptyne	3.944	-0.1590	-0.2963	0.1157	512.8	85.0	319.5
n-octane	10.262	-0.6921	-0.4228	0.1882	35.8	360.6	239.6
n-dodecane	8.206	-0.2247	-0.0409	0.1323	65.3	365.2	222.4
n-hexadecane	6.113	-0.1017	0.0732	0.1115	128.0	306.9	135.1
tetralin +							
n-pentane	30.061	-1.4745	-1.3431	0.1080	449.9	721.4	201.9
n-hexane	29.988	-0.9889	-0.7249	0.2057	463.3	840.2	275.0
1-hexene	26.692	-1.2682	-0.8140	0.3228	224.5	710.5	358.8
1-hexyne	20.788	-0.8345	-0.4210	0.3142	40.3	537.9	367.1
n-heptane	28.582	-0.6596	-0.4102	0.1901	488.4	874.1	213.5
1-heptene	25.764	-0.9977	-0.4927	0.3780	235.3	759.7	385.2
1-heptyne	16.687	-0.6932	-0.2510	0.3161	-2.9	472.5	351.1
n-octane	27.648	-0.4999	-0.1801	0.2368	508.4	904.2	292.9
n-dodecane	24.322	-0.0648	0,2455	0.2302	570.3	932.5	281.4
n-hexadecane	20.737	0.1586	0.3654	0.1606	657.0	866.7	171.6

Table 6.2 (continued)

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	σ (V_m^E, Berthelot) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted) (J.mol^{-1})	σ (H_m^E, Berthelot) (J.mol^{-1})
cyclohexylbenzene +							
n-pentane	19.268	-1.4459	-1.5626	0.0968	372.2	441.1	45.2
n-hexane	19.207	-0.9807	-0.9490	0.0308	391.1	549.4	109.9
1-hexene	16.510	-0.9635	-0.9131	0.0454	194.4	436.8	178.8
1-hexyne	11.815	-0.5635	-0.5477	0.0109	92.5	293.8	147.5
n-heptane	18.051	-0.6785	-0.6314	0.0361	415.1	578.7	113.0
1-heptene	15.759	-0.6536	-0.6944	0.0323	212.9	478.9	192.4
1-heptyne	8.691	-0.4493	-0.3636	0.0626	58.0	239.7	132.9
n-octane	17.281	-0.4734	-0.3966	0.0568	433.6	604.4	116.8
n-dodecane	14.602	0.0077	0.0358	0.0771	507.2	623.7	78.9
n-hexadecane	11.775	0.2366	0.1708	0.0490	619.6	559.9	49.1
benzene +							
n-pentane	29.500	0.1166	-0.0543	0.1244	856.6	612.1	186.3
n-hexane	29.377	0.3970	0.3738	0.0239	897.2	661.9	169.3
1-hexene	26.049	0.1030	0.2472	0.1083	589.9	572.6	20.3
1-hexyne	20.012	0.0396	0.2372	0.1429	132.0	435.4	225.2
n-heptane	27.990	0.5885	0.5541	0.0317	919.0	661.7	184.4
1-heptene	25.098	0.3092	0.4430	0.0947	603.1	583.3	16.8
1-heptyne	15.847	0.1422	0.2736	0.0935	138.8	365.2	167.7

Table 6.2 (continued)

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	σ(V_m^E, Berthelot) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted) (J.mol^{-1})	σ(H_m^E, Berthelot) (J.mol^{-1})
benzene +							
n-octane	23.613	0.7106	0.5959	0.1182	969.4	570.7	297.0
n-dodecane	23.621	0.9192	0.8144	0.0860	1100.9	620.8	360.9
n-hexadecane	19.960	1.0236	0.7422	0.2191	1255.8	540.7	554.7
cyclohexane +							
n-pentane	6.689	-0.1464	0.3714	0.1675	190.9	128.3	49.7
n-hexane	6.598	0.1485	-0.0909	0.1645	219.6	110.7	92.3
1-hexene	5.021	0.1292	-0.1172	0.1836	232.6	84.1	111.6
1-hexyne	2.488	0.6815	-0.0108	0.5171	725.9	54.4	504.2
n-heptane	5.939	0.3098	0.1122	0.1424	245.7	152.2	70.1
1-heptene	4.587	0.2664	0.0005	0.1750	235.0	114.7	92.9
1-heptyne	1.122	0.6886	0.0180	0.4997	641.1	27.7	462.9
n-octane	5.480	0.4120	0.1937	0.1559	257.5	145.9	88.0
n-dodecane	3.937	0.5353	0.2432	0.2204	358.1	103.7	195.7
n-hexadecane	2.469	0.6225	0.1408	0.3858	501.5	51.7	344.1
n-hexane +							
n-pentane	0.001	-0.1109	-0.0635	0.0308	4.9	-8.4	9.8
1-hexene	0.108	0.0555	0.0059	0.0376	61.3	2.6	43.4

Table 6.2 (continued)

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V_m^E(experimental)[a] (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	σ (V_m^E, Berthelot) (cm^3.mol^{-1})	H_m^E(experimental)[b] (J.mol^{-1})	H_m^E(predicted) (J.mol^{-1})	σ (H_m^E, Berthelot) (J.mol^{-1})
n-hexane +							
1-hexyne	0.988	0.5413	0.0240	0.3718	593.8	25.2	422.3
1-heptene	0.183	0.0678	-0.0248	0.0660	47.2	3.4	32.9
1-heptyne	2.292	0.3421	-0.0745	0.2951	517.5	59.7	340.6
n-octane	1.248	-0.0851	-0.0603	0.0183	2.2	26.8	18.2
n-dodecane	0.356	-0.3473	-0.4064	0.1100	36.9	-24.7	45.4
n-hexadecane	1.022	-0.5321	-0.6975	0.2270	113.6	-20.2	100.8

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[a] Literature references given in Table C3. [b] Literature references given in Table C1.

Table 6.3 Excess molar volumes and excess molar enthalpies at equimolar concentrations calculated by the Flory theory and X_{12}(Berthelot), for the mixtures {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The s_1/s_2 values have been determined from Table 6.1.

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	σ(V_m^E, Berthelot) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted) (J.mol^{-1})	σ(H_m^E, Berthelot) (J.mol^{-1})
decalin +							
cyclopentane	3.090	-0.6303	-0.2644	0.2678	-185.0	32.6	164.3
cyclohexane	3.134	-0.1323	-0.0837	0.0535	25.9	61.4	30.4
cyclohexene	0.432	-0.2076	-0.0461	0.1161	-55.4	-13.2	30.3
1,3-cyclohexadiene	0.082	0.0650	0.0145	0.0393	225.5	-17.7	182.3
1,4-cyclohexadiene	0.044	0.1238	0.0386	0.0642	228.7	-18.6	184.8
benzene	0.158	0.4839	0.1360	0.2626	741.7	-2.2	561.3
cycloheptane	9.183	-0.0383	0.0810	0.0901	8.8	287.8	206.6
cyclooctane	2.750	0.0175	0.0829	0.0499	18.0	89.1	52.3
bicyclohexyl +							
cyclopentane	0.935	-0.6602	-0.4147	0.1855	-142.4	-37.5	78.1
cyclohexane	0.960	-0.0388	-0.2088	0.1293	113.6	-12.8	93.6
cyclohexene	0.547	-0.1512	-0.1115	0.0278	37.2	-32.7	51.1
1,3-cyclohexadiene	0.325	0.1125	-0.0206	0.1031	283.8	-19.1	225.5
1,4-cyclohexadiene	0.421	0.1618	0.0111	0.1178	272.0	-16.5	218.4
benzene	3.971	0.5191	0.1499	0.2823	827.5	57.7	582.4

Table 6.3 (continued)

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V^E_m(experimental)^a (cm^3.mol^{-1})	V^E_m(predicted) (cm^3.mol^{-1})	σ (V^E_m, Berthelot) (cm^3.mol^{-1})	H^E_m(experimental)^b (J.mol^{-1})	H^E_m(predicted) (J.mol^{-1})	σ (H^E_m, Berthelot) (J.mol^{-1})
bicyclohexyl +							
cycloheptane	5.271	0.1689	-0.0696	0.1753	140.6	164.5	18.4
cyclooctane	0.745	0.2587	0.0264	0.1828	164.6	17.4	111.1
tetralin +							
cyclopentane	9.630	-0.5051	-0.4790	0.0239	246.4	182.8	52.5
cyclohexane	9.708	0.1020	-0.2446	0.2616	482.9	230.5	192.9
cyclohexene	5.745	-0.2349	-0.1941	0.0304	148.8	120.1	24.7
1,3-cyclohexadiene	3.053	-0.2051	-0.1409	0.0469	48.2	51.2	1.9
1,4-cyclohexadiene	2.391	-0.1186	-0.1233	0.0044	24.8	34.4	7.7
benzene	0.062	0.0167	-0.1103	0.0952	160.1	-35.8	147.1
cycloheptane	19.216	0.2022	0.0821	0.0964	426.8	564.0	100.9
cyclooctane	9.018	0.2626	0.0657	0.1496	404.9	278.3	96.7
cyclohexylbenzene +							
cyclopentane	3.7	-0.4997	-0.5279	0.0252	161.8	35.3	97.7
cyclohexane	3.8	0.1055	-0.2995	0.3094	402.9	69.6	254.1
cyclohexene	1.5	-0.1018	-0.2154	0.0866	112.8	6.2	80.2
1,3-cyclohexadiene	0.7	-0.0914	-0.1129	0.0290	44.1	-9.5	39.1
1,4-cyclohexadiene	0.1	-0.0657	-0.1080	0.0325	-15.5	-24.9	7.4

Table 6.3 (continued)

Mixture	X_{12}(Berthelot) ($J.cm^{-3}$)	V_m^E(experimental)^a ($cm^3.mol^{-1}$)	V_m^E(predicted) ($cm^3.mol^{-1}$)	σ (V_m^E, Berthelot) ($cm^3.mol^{-1}$)	H_m^E(experimental)^b ($J.mol^{-1}$)	H_m^E(predicted) ($J.mol^{-1}$)	σ (H_m^E, Berthelot) ($J.mol^{-1}$)
cyclohexylbenzene +							
benzene	1.0	0.0715	-0.0328	0.0828	173.1	-16.3	143.3
cycloheptane	10.6	0.3246	-0.0469	0.2870	428.2	329.0	82.9
cyclooctane	3.4	0.4566	0.0002	0.3557	440.1	106.2	257.7
benzene +							
cyclopentane	8.770	0.3443	0.0461	0.2208	597.6	170.1	324.9
cyclohexane	8.847	0.6525	0.1446	0.3747	801.7	185.6	454.1
cyclohexene	4.964	0.2448	0.0893	0.1147	396.1	99.7	213.0
1,3-cyclohexadiene	0.724	0.0736	0.0259	0.0365	129.8	12.6	86.7
1,4-cyclohexadiene	1.808	0.0423	0.0361	0.0055	83.4	33.7	34.5
cycloheptane	18.412	0.6284	0.4784	0.1117	802.5	398.2	303.9
cyclooctane	8.165	0.5872	0.1609	0.3232	807.7	177.5	474.4
cyclohexane +							
cyclopentane	0.001	0.0412	-0.0323	0.0549	21.1	-2.8	19.1
cyclohexene	0.617	0.0968	0.0036	0.0688	85.2	12.4	76.2
1,3-cyclohexadiene	2.665	0.3112	0.0165	0.2254	331.5	52.6	207.9
1,4-cyclohexadiene	2.941	0.3592	0.0151	0.2606	372.1	58.1	226.8
benzene	9.795	0.6525	0.1446	0.3747	801.7	185.6	454.1

Table 6.3 (continued)

Mixture	X_{12}(Berthelot) (J.cm^{-3})	V_m^E(experimental)[a] (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	σ (V_m^E, Berthelot) (cm^3.mol^{-1})	H_m^E(experimental)[b] (J.mol^{-1})	H_m^E(predicted) (J.mol^{-1})	σ (H_m^E, Berthelot) (J.mol^{-1})
cyclohexane +							
cycloheptane	1.919	-0.0305	0.0854	0.0856	5.9	36.6	22.8
cyclooctane	0.015	-0.1073	-0.1265	0.0304	0.8	-12.6	11.7
n-hexane +							
cyclopentane	6.761	-0.0678	0.1404	0.1575	60.2	148.0	64.1
cyclohexane	6.645	0.1485	-0.0275	0.1285	219.6	156.6	48.5
cyclohexene	11.317	-0.1024	-0.0129	0.0664	195.2	253.6	14.1
1,3-cyclohexadiene	17.753	0.1017	0.0187	0.0615	485.3	375.9	47.1
1,4-cyclohexadiene	18.457	-0.0673	0.0131	0.0656	443.4	391.1	40.6
benzene	32.663	0.3970	0.3725	0.2459	897.2	660.7	170.3
cycloheptane	1.433	-0.2046	-0.3604	0.1252	209.4	12.0	148.6
cyclooctane	7.344	-0.4938	-0.5936	0.0782	204.0	170.5	32.9

[a] Literature references given in Table C4. [b] Literature references given in Table C2.

6.3.4 Predicted H_m^E and V_m^E from adjustable interaction parameters

An adjustable interaction parameter from experimental excess molar volume data, $X_{12}(V_m^E$, Flory), was obtained for each system. The procedure involves obtaining $\tilde{v}^E$ for each system from equation 6.12 using experimental excess molar volumes. $\tilde{T}$ values were calculated using equation 6.11 and were used to determine an "experimental" or adjusted interaction parameter, $X_{12}(V_m^E$, Flory). The values for $X_{12}(V_m^E$, Flory) were observed to vary considerably with the mole fraction and hence the above calculations were carried out at 0.01 mole fraction intervals over the entire composition range for each mixture. The approach of Benson and co-workers(151,153) was followed and the $X_{12}(V_m^E$, Flory) which minimized the standard deviation over all the mole fractions was determined. This minimizing $X_{12}(V_m^E$, Flory) value was used to predict excess molar volumes over the entire composition range at 0.01 mole fraction intervals and the standard deviation $\sigma(V_m^E$, Flory) was determined.

The determination of the minimised $X_{12}(H_m^E$, Flory) for each system involved a similar procedure. In this case however, $X_{12}(H_m^E$, Flory) cannot be determined directly from the equation for H^E, since it appears in the equation for the reduced temperature as well. Spiteri(82) has shown that by simple algebraic manipulation of equations 6.10, 6.14 and 6.15 for T, H_m^E, and v, a value for $X_{12}(H_m^E$,Flory) can be obtained by solving the quadratic equation:

$$AX_{12}^2 - BX_{12} + C = 0 \qquad 6.16$$

where A, B and C are complex algebraic expressions and are related to the pure component properties and to the experimental excess molar enthalpies.(82) One of the above solutions to the quadratic equation yields a nonsensical negative value for $\tilde{T}$ and can be discarded. Once again the $X_{12}(H_m^E$, Flory) were determined at 0.01 mole fraction intervals and the value which minimized the standard deviation $\sigma(H_m^E$, Flory) was chosen. The minimized $X_{12}(H_m^E$, Flory) was then used to calculate the excess molar enthalpy over the entire composition range and the predicted values were compared to the experimental values through the standard deviation, $\sigma(H_m^E$, Flory).

The $X_{12}(V_m^E$, Flory) parameters were then used to predict the excess molar enthalpies and conversely the $X_{12}(H_m^E$, Flory) were used to predict the the excess molar volumes. In each case the predictions were carried out at 0.01 mole fraction intervals over the entire composition range, and were compared to the corresponding experimental curves through the standard deviations $\sigma^*(H^E_m$, Flory) and $\sigma^*(V^E_m$, Flory) in each case.

In order to check the computer programme, the V^E_m and H^E_m predicted by the above methods for the system {cyclopentane + (*cis*-decalin or *trans*-decalin)} have been compared to the values reported by Benson *et al.*(151) The results have been summarized in Table 6.4 and are observed to be within the expected precision considering that the results of Benson were averaged over ten data points while the X_{12} used in this investigation were averaged over 100 points.

Table 6.4 Summary of the results of the Flory fit to the test systems

System	$\frac{X_{12}(H^E_m)}{J.cm^{3}}$		$\frac{\sigma(H^E_m)}{J.mol^{-1}}$		$\frac{\sigma^*(V^E_m)}{cm^3.mol^{-1}}$	
cyclopentane + *cis*-decalin	-3.62 [a]	-3.44 [b]	11.7 [a]	12.1 [b]	0.08 [a]	0.09 [b]
cyclopentane + *trans*-decalin	-9.95 [a]	-9.79 [b]	20.6 [a]	21.4 [b]	0.19 [a]	0.21 [b]

[a]Reference 151. [b]This work.

The values for the experimental $H^E_m(x=0.5)$ together with the predicted excess molar enthalpies at equimolar concentrations (using experimental excess molar enthalpy data) and the $\sigma(H^E_m$, Flory) values are given in columns 3, 4 and 5 of Table 6.5 for the systems {(a bicyclic compound or benzene or cyclohexane on *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)} and in Table 6.6 for the systems {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The best fit $X_{12}(H^E_m$, Flory) values and the standard deviations $\sigma^*(H^E_m$, Flory) are also included in columns 2 and 6 of these Tables. These predictions were carried out using s_1/s_2 ratios determined from the spherical molecule approximation of Flory.

Table 6.5 Excess molar enthalpies predicted at equimolar concentrations by the Flory theory for {a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)}. The s_1/s_2 values have been determined by two different methods.[a,c]

Mixture	$X_{12}(H^E_m$, Flory)[a] (J.cm^{-3})	H^E_m(experimental)[b] (J.mol^{-1})	H^E_m(predicted)[a] (J.mol^{-1})	$\sigma(H^E_m$, Flory)[a] (J.mol^{-1})	$\sigma^*(H^E_m$, Flory)[a] (J.mol^{-1})	$\sigma(H^E_m$, Flory)[c] (J.mol^{-1})	$\sigma^*(H^E_m$, Flory)[c] (J.mol^{-1})
decalin +							
n-pentane	-5.049	53.9	-187.2	5.5	208.3	6.1	208.1
n-hexane	4.040	62.4	62.8	1.5	25.0	3.5	26.0
1-hexene	4.694	74.2	73.6	1.1	123.4	1.1	123.5
1-hexyne	22.884	604.3	605.8	18.0	37.3	6.7	33.2
n-heptane	3.404	68.6	69.8	1.2	3.3	2.1	72.0
1-heptene	3.716	72.9	73.6	2.9	114.9	5.1	116.0
1-heptyne	18.141	524.8	518.6	16.2	107.9	4.7	105.9
n-octane	3.239	81.6	82.9	3.1	11.7	1.0	11.2
n-dodecane	3.558	125.1	127.7	8.8	11.3	3.1	9.6
n-hexadecane	5.164	198.6	205.9	6.8	62.1	8.4	63.6
bicyclohexyl +							
n-pentane	4.994	23.0	26.0	10.9	77.2	9.0	77.5
n-hexane	2.924	21.6	23.4	8.3	49.5	7.7	49.5
1-hexene	4.527	65.4	68.5	9.4	45.1	8.0	45.4
1-hexyne	21.440	630.5	623.8	5.9	117.1	6.6	117.5
n-heptane	2.254	26.9	28.8	5.6	19.5	5.7	19.5

Table 6.5 (continued)

Mixture	$X_{12}(H^E_m,$ Flory$)^a$ (J.cm^{-3})	H^E_m(experimental)^b (J.mol^{-1})	H^E_m(predicted)^a (J.mol^{-1})	$\sigma(H^E_m,$ Flory$)^a$ (J.mol^{-1})	$\sigma^*(H^E_m,$ Flory$)^a$ (J.mol^{-1})	$\sigma(H^E_m,$ Flory$)^c$ (J.mol^{-1})	$\sigma^*(H^E_m,$ Flory$)^c$ (J.mol^{-1})
bicyclohexyl +							
1-heptene	3.480	62.9	66.2	5.7	20.3	5.4	20.3
1-heptyne	16.412	512.8	515.5	11.5	151.6	10.4	152.1
n-octane	1.908	35.8	36.1	5.4	21.6	5.8	21.4
n-dodecane	1.769	65.3	65.2	0.4	19.1	2.1	19.3
n-hexadecane	2.864	128.0	128.3	1.0	47.1	5.5	46.9
tetralin +							
n-pentane	21.557	449.9	448.2	7.1	76.8	14.2	78.8
n-hexane	19.100	463.3	468.2	7.3	8.9	17.3	14.3
1-hexene	11.000	224.5	224.1	2.3	65.8	7.3	66.6
1-hexyne	4.109	40.3	40.4	1.6	89.5	4.2	90.1
n-heptane	18.278	488.4	491.5	5.3	19.3	11.9	24.4
1-heptene	10.048	235.3	238.5	4.8	141.1	10.9	140.9
1-heptyne	1.612	-2.9	-3.0	1.9	132.7	3.2	132.8
n-octane	17.754	508.4	511.6	5.3	50.5	12.3	48.5
n-dodecane	17.051	570.3	571.2	6.3	86.4	21.2	85.1
n-hexadecane	18.352	657.1	665.0	21.2	102.2	18.8	98.8

Table 6.5 (continued)

Mixture	$X_{12}(H^E_m$, Flory$)^a$ (J.cm^{-3})	H^E_m(experimental)^b (J.mol^{-1})	H^E_m(predicted)^a (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma^*(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^c$ (J.mol^{-1})	$\sigma^*(H^E_m$, Flory$)^c$ (J.mol^{-1})
cyclohexylbenzene +							
n-pentane	16.921	372.2	382.0	9.8	160.8	8.1	160.3
n-hexane	14.732	391.1	401.4	8.7	77.9	8.8	77.9
1-hexene	8.847	194.4	196.1	3.6	236.6	3.0	236.5
1-hexyne	5.541	92.5	95.2	3.2	138.0	3.8	138.4
n-heptane	14.053	415.1	425.9	9.2	66.3	9.6	67.3
1-heptene	8.240	212.9	217.7	5.0	236.8	5.8	237.3
1-heptyne	3.464	58.0	59.7	2.1	37.6	2.9	37.7
n-octane	13.604	433.6	446.3	11.5	36.5	12.2	37.4
n-dodecane	13.413	507.2	522.7	14.0	51.2	14.9	54.2
n-hexadecane	14.829	619.6	631.0	12.4	33.4	17.1	39.5
benzene +							
n-pentane	44.658	856.6	863.0	44.8	76.8	22.1	68.0
n-hexane	43.605	897.2	894.9	10.4	152.8	19.3	150.3
1-hexene	29.761	589.9	599.8	11.1	131.4	11.0	129.2
1-hexyne	6.958	132.0	132.6	8.9	57.5	4.1	58.0
n-heptane	43.098	919.0	916.9	28.7	154.4	11.5	149.9
1-heptene	29.031	603.1	610.9	19.1	123.7	4.2	121.5
1-heptyne	6.938	138.8	142.6	10.4	51.4	5.0	51.4

Table 6.5 (continued)

Mixture	$X_{12}(H^E_m$, Flory)^a ($J.cm^{-3}$)	H^E_m(experimental)^b ($J.mol^{-1}$)	H^E_m(predicted)^a ($J.mol^{-1}$)	$\sigma(H^E_m$, Flory)^a ($J.mol^{-1}$)	$\sigma^*(H^E_m$, Flory)^a ($J.mol^{-1}$)	$\sigma(H^E_m$, Flory)^c ($J.mol^{-1}$)	$\sigma^*(H^E_m$, Flory)^c ($J.mol^{-1}$)
benzene +							
n-octane	44.724	969.4	976.9	25.1	200.3	12.5	199.7
n-dodecane	47.923	1100.9	1120.1	41.8	249.4	27.0	247.9
n-hexadecane	52.837	1255.8	1291.4	47.2	244.8	47.1	246.6
cyclohexane +							
n-pentane	9.625	190.9	193.7	12.8	101.7	12.3	103.0
n-hexane	9.482	219.6	219.6	14.7	78.1	12.8	78.3
1-hexene	10.388	232.6	232.6	20.7	72.7	22.0	81.5
1-hexyne	32.943	725.9	735.4	32.6	57.8	24.2	57.4
n-heptane	10.037	245.7	245.7	13.7	79.0	10.2	80.1
1-heptene	9.935	235.0	239.8	12.5	89.8	9.8	91.3
1-heptyne	27.736	641.1	653.2	32.5	117.7	22.3	117.2
n-octane	10.516	257.5	264.6	13.5	84.1	8.5	83.5
n-dodecane	13.817	358.1	365.8	16.8	82.9	3.3	81.5
n-hexadecane	18.371	501.5	508.3	15.6	181.0	13.2	178.4
n-hexane +							
n-pentane	0.522	4.9	4.9	0.1	33.2	0.1	33.3
1-hexene	2.350	61.3	61.4	0.8	13.0	0.6	13.0

Table 6.5 (continued)

Mixture	$X_{12}(H^E_m$, Flory$)^a$ (J.cm^{-3})	H^E_m(experimental)^b (J.mol^{-1})	H^E_m(predicted)^a (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma^*(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^c$ (J.mol^{-1})	$\sigma^*(H^E_m$, Flory$)^c$ (J.mol^{-1})
n-hexane +							
1-hexyne	23.673	593.8	596.9	20.4	86.2	18.6	86.0
1-heptene	1.817	47.2	47.9	0.9	26.3	0.9	26.2
1-heptyne	19.710	517.5	520.6	13.4	54.9	9.5	54.1
n-octane	0.386	2.2	2.2	0.2	1.1	0.4	1.1
n-dodecane	2.325	36.9	36.3	1.8	34.2	3.8	36.0
n-hexadecane	5.132	113.6	113.8	7.1	97.0	13.6	103.3

$^a s_1/s_2$ from equation 6.6. ^{b}Literature references given in Table C1. $^c s_1/s_2$ from Table 6.1.

Table 6.6 Excess molar enthalpies at equimolar concentrations predicted by the Flory theory for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The s_1/s_2 values have been determined by two different methods.[a,c]

Mixture	$X_{12}(H^E_m$, Flory)[a] ($J.cm^{-3}$)	H^E_m(experimental)[b] ($J.mol^{-1}$)	H^E_m(predicted)[a] ($J.mol^{-1}$)	$\sigma(H^E_m$, Flory)[a] ($J.mol^{-1}$)	$\sigma^*(H^E_m$, Flory)[a] ($J.mol^{-1}$)	$\sigma(H^E_m$, Flory)[c] ($J.mol^{-1}$)	$\sigma^*(H^E_m$, Flory)[c] ($J.mol^{-1}$)
decalin +							
cyclopentane	-5.049	-185.0	-187.2	15.5	208.3	16.1	208.1
cyclohexane	1.875	25.9	22.7	11.0	24.9	10.6	24.9
cyclohexene	-1.017	-55.4	-53.6	4.4	146.0	4.6	145.8
1,3-cyclohexadiene	9.039	225.5	227.6	4.2	120.8	2.2	120.8
1,4-cyclohexadiene	9.164	228.7	229.9	3.7	83.2	1.9	83.2
benzene	29.409	741.7	750.8	7.9	150.5	11.7	151.8
cycloheptane	0.442	8.8	7.7	3.7	69.1	3.5	69.9
cycloctane	7.356	18.0	18.3	1.6	30.9	1.0	30.5
bicyclohexyl +							
cyclopentane	-2.545	-142.4	-140.0	11.9	192.9	13.8	190.9
cyclohexane	4.799	113.6	112.9	2.3	105.3	1.2	104.4
cyclohexene	2.225	37.2	35.8	1.2	88.0	2.3	87.6
1,3-cyclohexadiene	10.134	283.8	282.4	8.7	57.9	4.6	58.4
1,4-cyclohexadiene	9.955	272.0	275.6	9.4	25.2	1.3	24.9
benzene	29.542	827.5	835.7	18.7	123.2	15.0	125.5

Table 6.6 (continued)

Mixture	$X_{12}(H^E_m$, Flory)[a] (J.cm^{-3})	H^E_m(experimental)[b] (J.mol^{-1})	H^E_m(predicted)[a] (J.mol^{-1})	$\sigma(H^E_m$, Flory)[a] (J.mol^{-1})	$\sigma^*(H^E_m$, Flory)[a] (J.mol^{-1})	$\sigma(H^E_m$, Flory)[c] (J.mol^{-1})	$\sigma^*(H^E_m$, Flory)[c] (J.mol^{-1})
bicyclohexyl +							
cycloheptane	4.441	140.6	140.6	6.0	297.7	5.1	297.1
cyclooctane	4.983	164.6	167.1	5.6	203.8	6.0	203.9
tetralin +							
cyclopentane	12.365	246.4	251.9	12.5	63.6	12.4	63.6
cyclohexane	19.916	482.9	490.4	9.8	219.7	15.0	221.7
cyclohexene	7.061	148.8	151.9	6.8	71.8	7.5	71.8
1,3-cyclohexadiene	2.933	48.2	49.0	1.1	78.8	1.0	78.9
1,4-cyclohexadiene	1.956	24.8	24.1	1.5	15.0	1.4	15.0
benzene	8.099	160.1	162.2	3.2	17.5	1.9	16.9
cycloheptane	15.827	426.8	431.5	16.2	250.7	24.4	252.9
cyclooctane	14.263	404.9	403.5	19.5	173.2	30.8	175.4
cyclohexylbenzene +							
cyclopentane	8.011	161.8	166.5	5.5	63.9	3.2	64.3
cyclohexane	14.919	402.9	411.5	8.8	235.1	6.8	234.3
cyclohexene	4.955	112.8	112.7	0.3	63.9	2.4	62.3
1,3-cyclohexadiene	2.448	44.1	43.0	1.8	9.9	3.0	9.7
1,4-cyclohexadiene	0.425	-15.5	-15.5	2.5	48.9	2.3	48.5

Table 6.6 (continued)

Mixture	$X_{12}(H^E_m$, Flory$)^a$ (J.cm^{-3})	H^E_m(experimental)^b (J.mol^{-1})	H^E_m(predicted)^a (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma^*(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^c$ (J.mol^{-1})	$\sigma^*(H^E_m$, Flory$)^c$ (J.mol^{-1})
cyclohexylbenzene +							
benzene	7.715	173.1	175.6	2.3	5.8	5.7	7.2
cycloheptane	14.066	428.2	439.7	15.0	389.2	15.0	389.3
cyclooctane	13.930	440.1	454.1	21.0	372.6	24.5	372.8
benzene +							
cyclopentane	32.586	597.6	609.8	17.4	62.7	24.3	63.5
cyclohexane	38.074	801.7	800.9	1.8	25.9	2.6	46.7
cyclohexene	20.337	396.1	394.5	2.3	58.8	8.6	59.0
1,3-cyclohexadiene	7.013	129.8	130.0	0.6	35.9	0.4	35.9
1,4-cyclohexadiene	4.277	83.4	78.6	9.2	27.3	8.5	27.3
cycloheptane	40.747	802.5	811.5	8.8	155.0	20.7	155.3
cyclooctane	40.053	807.7	819.3	9.8	16.1	30.5	14.0
cyclohexane +							
cyclopentane	1.197	21.1	22.6	3.4	43.6	3.7	43.6
cyclohexene	3.927	85.2	85.3	0.2	32.8	0.7	32.8
1,3-cyclohexadiene	15.756	331.5	334.4	3.2	81.8	3.7	82.2
1,4-cyclohexadiene	17.280	372.1	365.4	12.8	112.1	17.6	113.0
benzene	38.573	801.7	800.9	1.8	25.9	2.6	46.7

Table 6.6 (continued)

Mixture	$X_{12}(H^E_m$, Flory)[a] (J.cm^{-3})	H^E_m(experimental)[b] (J.mol^{-1})	H^E_m(predicted)[a] (J.mol^{-1})	$\sigma(H^E_m$, Flory)[a] (J.mol^{-1})	$\sigma^*(H^E_m$, Flory)[a] (J.mol^{-1})	$\sigma(H^E_m$, Flory)[c] (J.mol^{-1})	$\sigma^*(H^E_m$, Flory)[c] (J.mol^{-1})
cyclohexane +							
cycloheptane	0.644	5.9	5.9	1.6	86.5	1.7	86.5
cyclooctane	0.554	0.8	0.8	6.6	20.6	6.8	21.8
n-hexane +							
cyclopentane	2.625	60.2	62.3	3.7	83.4	4.7	83.5
cyclohexane	8.952	219.6	219.6	14.7	78.1	12.8	78.8
cyclohexene	8.470	195.2	200.7	7.1	29.7	4.9	29.2
1,3-cyclohexadiene	18.811	435.3	440.3	4.9	17.2	8.9	20.3
1,4-cyclohexadiene	19.199	443.4	447.6	9.4	106.1	2.4	104.6
benzene	38.621	897.2	894.9	10.4	152.8	19.3	150.3
cycloheptane	9.088	209.4	211.9	17.4	21.9	17.2	21.9
cyclooctane	8.876	204.0	206.4	17.7	59.5	19.5	59.7

[a] s_1/s_2 from equation 6.6. [b] Literature references given in Table C2. [c] s_1/s_2 from Table 6.1.

The Flory one-parameter equation provides a good fit of the H_m^E results for {a bicyclic compound + an *n*-alkane}, with the theory adequately reproducing the general shapes of the experimental curves. The value of $\sigma(H_m^E$, Flory) does not exceed 5% of $H_m^E(x=0.5)$ or 11 $J.mol^{-1}$ in the worst case for these systems. The predicted $H_m^E(x=0.5)$ for {(benzene or cyclohexane or *n*-hexane) + an *n*-alkane} are as good with $\sigma(H_m^E$, Flory) never exceeding 6% of $H_m^E(x=0.5)$ or 16 $J.mol^{-1}$ in the worst case. The theory also offers good fits for the systems {a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a 1-alkene or a 1-alkyne)} with the standard deviation $\sigma(H_m^E$, Flory) never exceeding 5% of the $H_m^E(x=0.5)$ or 21 $J.mol^{-1}$ in the worst case.

The standard deviations for the systems {a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} never exceed 18 $J.mol^{-1}$ or 5% of the experimental $H_m^E(x=0.5)$, whichever is larger. The Flory theory correctly predicted the negative excess molar enthalpies for {decalin + (cyclopentane or cyclohexene)}, {bicyclohexyl + cyclopentane}, {cyclohexylbenzene + 1,4-cyclohexadiene} and for {tetralin + 1-heptyne}, but was unable to reproduce the sinusoidal shape of the H_m^E curve for the system {cyclohexane + cyclooctane}.

The values for the experimental $V_m^E(x=0.5)$ together with the predicted excess molar volumes at equimolar concentrations (from experimental excess molar volume data) and the $\sigma(V_m^E$, Flory) values are given in columns 3, 4 and 5 of Tables 6.7 for the systems {(a bicyclic compound or benzene or cyclohexane on *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)} and in Table 6.8 for the systems {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The best fit $X_{12}(V_m^E$, Flory) and the standard deviations $\sigma^*(V_m^E$, Flory) are also included in these Tables in columns 2 and 6 respectively. The predictions have been carried out using s_1/s_2 ratios determined according to the spherical molecule approximation.

The $X_{12}(V_m^E$, Flory) values adequately reproduce the general shapes of the experimental curves for all these systems with the correct sign predicted in all but one case. The standard deviations for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + a cyclic compound} never exceed 0.040 $cm^3.mol^{-1}$. The $\sigma(V_m^E$, Flory) for the mixtures involving an *n*-alkane, a 1-alkene or a 1-alkyne are very similar and only exceed 0.040 $cm^3.mol^{-1}$ in four cases.

Table 6.7 Excess molar volumes predicted at equimolar concentrations by the Flory theory for {a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)}. The s_1/s_2 values have been determined by two different methods.[a,c]

Mixture	$X_{12}(V_m^E$, Flory)^a (J.cm^{-3})	V_m^E(experimental)^b (cm^3.mol^{-1})	V_m^E(predicted)^a (cm^3.mol^{-1})	(V_m^E, Flory)^a (cm^3.mol^{-1})	$\sigma^*(V_m^E$, Flory)^a (cm^3.mol^{-1})	$\sigma(V_m^E$, Flory)^c (cm^3.mol^{-1})	$\sigma^*(V_m^E$, Flory)^c (cm^3.mol^{-1})
decalin +							
n-pentane	4.367	-1.4310	1.4032	0.0553	0.0624	0.0563	0.0633
n-hexane	2.990	-0.9478	-0.9198	0.0283	0.0345	0.0293	0.0352
1-hexene	10.202	-0.7468	-0.7370	0.0252	0.1037	0.0276	0.1043
1-hexyne	21.242	-0.0111	-0.0173	0.0145	0.0306	0.0058	0.0026
n-heptane	3.486	-0.6363	-0.6281	0.0101	0.0103	0.0099	0.0565
1-heptene	8.603	-0.4985	-0.5001	0.0020	0.0889	0.0048	0.0895
1-heptyne	13.432	0.0203	0.0186	0.0097	0.0773	0.0032	0.0757
n-octane	2.761	-0.4565	-0.4532	0.0050	0.0101	0.0047	0.0096
n-dodecane	3.880	-0.0726	-0.0707	0.0062	0.0086	0.0027	0.0068
n-hexadecane	7.240	0.1371	0.1403	0.0077	0.0402	0.0063	0.0406
bicyclohexyl +							
n-pentane	8.167	-1.5915	-1.5697	0.0582	0.0867	0.0558	0.0849
n-hexane	4.881	-1.1075	-1.1198	0.0397	0.0556	0.0389	0.0552
1-hexene	2.788	-1.1582	-1.1304	0.0381	0.0512	0.0374	0.0508
1-hexyne	16.628	-0.2435	-0.2408	0.0069	0.0842	0.0066	0.0846
n-heptane	1.636	-0.8556	-0.8721	0.0359	0.0378	0.0359	0.0379

Table 6.7 (continued)

Mixture	$X_{12}(V_m^E, \text{Flory})^a$ (J.cm^{-3})	$V_m^E(\text{experimental})^b$ $(\text{cm}^3.\text{mol}^{-1})$	$V_m^E(\text{predicted})^a$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma(V_m^E, \text{Flory})^a$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma^*(V_m^E, \text{Flory})^a$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma(V_m^E, \text{Flory})^c$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma^*(V_m^E, \text{Flory})^c$ $(\text{cm}^3.\text{mol}^{-1})$
bicyclohexyl +							
1-heptene	2.768	-0.8406	-0.8329	0.0296	0.0325	0.0294	0.0323
1-heptyne	10.493	-0.1590	-0.1468	0.0251	0.1076	0.0247	0.1073
n-octane	1.209	-0.6921	-0.6675	0.0344	0.0373	0.0346	0.0375
n-dodecane	2.377	-0.2247	-0.2201	0.0042	0.0130	0.0044	0.0132
n-hexadecane	1.479	-0.1017	-0.0770	0.0053	0.0295	0.0039	0.0287
tetralin +							
n-pentane	25.306	-1.4745	-1.4761	0.0320	0.0701	0.0385	0.0756
n-hexane	19.215	-0.9889	-0.9971	0.0177	0.0178	0.0223	0.0227
1-hexene	7.842	-1.2682	-1.2318	0.0385	0.0626	0.0410	0.0638
1-hexyne	-0.393	-0.8345	-0.8336	0.0180	0.0641	0.0178	0.0640
n-heptane	19.069	-0.6596	-0.6675	0.0083	0.0149	0.0062	0.0165
1-heptene	3.501	-0.9977	-0.9960	0.0197	0.1028	0.0213	0.1024
1-heptyne	-4.706	-0.6932	-0.6726	0.0253	0.0893	0.0234	0.0892
n-octane	15.512	-0.4999	-0.5016	0.0051	0.0359	0.0077	0.0336
n-dodecane	13.588	-0.0648	-0.0648	0.0167	0.0583	0.0035	0.0520
n-hexadecane	14.650	0.1586	0.1592	0.0065	0.0608	0.0124	0.0592

Table 6.7 (continued)

Mixture	$X_{12}(V^E_m, \text{Flory})^a$ (J.cm^{-3})	$V^E_m(\text{experimental})^b$ (cm^3.mol^{-1})	$V^E_m(\text{predicted})^a$ (cm^3.mol^{-1})	$\sigma(V^E_m, \text{Flory})^a$ (cm^3.mol^{-1})	$\sigma^*(V^E_m, \text{Flory})^a$ (cm^3.mol^{-1})	$\sigma(V^E_m, \text{Flory})^c$ (cm^3.mol^{-1})	$\sigma^*(V^E_m, \text{Flory})^c$ (cm^3.mol^{-1})
cyclohexylbenzene +							
n-pentane	23.871	-1.4459	-1.4473	0.0353	0.1349	0.0326	0.1333
n-hexane	17.919	-0.9807	-0.9807	0.0178	0.0605	0.0182	0.0604
1-hexene	18.778	-0.9635	-0.9585	0.0144	0.1782	0.0134	0.1782
1-hexyne	11.547	-0.5635	-0.5570	0.0089	0.0946	0.0085	0.0948
n-heptane	16.653	-0.6785	-0.6762	0.0115	0.0487	0.0143	0.0500
1-heptene	17.745	-0.6536	-0.6536	0.0043	0.1700	0.0058	0.1701
1-heptyne	5.011	-0.4493	-0.4463	0.0032	0.0256	0.0036	0.0247
n-octane	14.921	-0.4734	-0.4756	0.0061	0.0248	0.0100	0.0269
n-dodecane	15.101	0.0077	0.0139	0.0141	0.0343	0.0057	0.0337
n-hexadecane	15.824	0.2366	0.2401	0.0161	0.0250	0.0005	0.0216
benzene +							
n-pentane	39.827	0.1166	0.1080	0.0392	0.0855	0.0184	0.0727
n-hexane	33.455	0.3970	0.3970	0.0367	0.1542	0.0161	0.1445
1-hexene	20.905	0.1030	0.1007	0.0320	0.1309	0.0206	0.1241
1-hexyne	10.864	0.0396	0.0441	0.0082	0.0494	0.0048	0.0494
n-heptane	33.288	0.5885	0.5970	0.0319	0.1438	0.0092	0.1360
1-heptene	21.097	0.3092	0.3174	0.0223	0.1137	0.0109	0.1093
1-heptyne	10.261	0.1422	0.1487	0.0109	0.0419	0.0065	0.0413

Table 6.7 (continued)

Mixture	$X_{12}(V^E_m, \text{Flory})^a$ (J.cm^{-3})	$V^E_m(\text{experimental})^b$ (cm^3.mol^{-1})	$V^E_m(\text{predicted})^a$ (cm^3.mol^{-1})	$\sigma(V^E_m, \text{Flory})^a$ (cm^3.mol^{-1})	$\sigma^*(V^E_m, \text{Flory})^a$ (cm^3.mol^{-1})	$\sigma(V^E_m, \text{Flory})^c$ (cm^3.mol^{-1})	$\sigma^*(V^E_m, \text{Flory})^c$ (cm^3.mol^{-1})
benzene +							
n-octane	32.812	0.7106	0.7235	0.0599	0.1798	0.0819	0.1889
n-dodecane	33.952	0.9192	0.9440	0.0351	0.1648	0.0072	0.1525
n-hexadecane	40.106	1.0236	1.0459	0.0278	0.1740	0.0247	0.1763
cyclohexane +							
n-pentane	15.565	-0.1464	-0.1547	0.0399	0.1170	0.0390	0.1171
n-hexane	13.946	0.1485	0.1421	0.0354	0.0868	0.0326	0.0866
1-hexene	14.577	0.1292	0.1266	0.0369	0.0797	0.0358	0.0794
1-hexyne	36.230	0.6815	0.6863	0.0565	0.0763	0.0478	0.0704
n-heptane	14.351	0.3098	0.3013	0.0292	0.0802	0.0245	0.0789
1-heptene	14.883	0.2664	0.2853	0.0347	0.0914	0.0315	0.0904
1-heptyne	34.371	0.6886	0.6946	0.0450	0.1100	0.0337	0.1061
n-octane	14.958	0.4120	0.4028	0.0320	0.0809	0.0261	0.0794
n-dodecane	17.784	0.5353	0.5382	0.0122	0.0668	0.0039	0.0649
n-hexadecane	26.503	0.6225	0.6431	0.0178	0.1348	0.0198	0.1337
n-hexane +							
n-pentane	-1.239	-0.1109	-0.1042	0.0059	0.0434	0.0060	0.0434
1-hexene	1.700	0.0550	0.0555	0.0092	0.0176	0.0093	0.0177

Table 6.7 (continued)

Mixture	$X_{12}(V_m^E, \text{Flory})^a$ (J.cm^{-3})	V_m^E(experimental)^b (cm^3.mol^{-1})	V_m^E(predicted)^a (cm^3.mol^{-1})	$\sigma(V_m^E, \text{Flory})^a$ (cm^3.mol^{-1})	$\sigma^*(V_m^E, \text{Flory})^a$ (cm^3.mol^{-1})	$\sigma(V_m^E, \text{Flory})^c$ (cm^3.mol^{-1})	$\sigma^*(V_m^E, \text{Flory})^c$ (cm^3.mol^{-1})
n-hexane +							
1-hexyne	19.136	0.5413	0.5285	0.0113	0.0945	0.0110	0.0943
1-heptene	3.118	0.0678	0.0645	0.0035	0.0294	0.0036	0.0294
1-heptyne	16.993	0.3421	0.3226	0.0203	0.0581	0.0187	0.0585
n-octane	0.430	-0.0851	-0.0849	0.0014	0.0017	0.0012	0.0016
n-dodecane	3.380	-0.3473	-0.3221	0.0905	0.0928	0.0878	0.0909
n-hexadecane	8.553	-0.5321	-0.4987	0.1687	0.1825	0.1599	0.1773

$^a s_1/s_2$ from equation 6.6. ^{b}Literature references given in Table C3. $^c s_1/s_2$ from Table 6.1.

Table 6.8 Excess molar volumes predicted at equimolar concentrations by the Flory theory for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The s_1/s_2 values have been determined by two different methods.[a,c]

Mixture	$X_{12}(V^E_m$, Flory)[a] $(J.cm^{-3})$	V^E_m(experimental)[b] $(cm^3.mol^{-1})$	V^E_m(predicted)[a] $(cm^3.mol^{-1})$	$\sigma(V^E_m$, Flory)[a] $(cm^3.mol^{-1})$	$\sigma^*(V^E_m$, Flory)[a] $(cm^3.mol^{-1})$	$\sigma(V^E_m$, Flory)[c] $(cm^3.mol^{-1})$	$\sigma^*(V^E_m$, Flory)[c] $(cm^3.mol^{-1})$
decalin +							
cyclopentane	-15.272	-0.6303	-0.6080	0.0420	0.1530	0.0433	0.1529
cyclohexane	0.696	-0.1323	-0.1323	0.0386	0.0426	0.0385	0.0424
cyclohexene	-7.998	-0.2076	-0.1987	0.0154	0.0966	0.0162	0.0967
1,3-cyclohexadiene	3.102	0.0656	0.0666	0.0038	0.0773	0.0034	0.0773
1,4-cyclohexadiene	5.054	0.1238	0.1241	0.0017	0.0529	0.0023	0.0529
benzene	21.796	0.4839	0.4849	0.0079	0.0979	0.0131	0.0993
cycloheptane	3.521	-0.0383	-0.0401	0.0134	0.0469	0.0124	0.0467
cyclooctane	-0.598	0.0175	0.0155	0.0063	0.0195	0.0065	0.0194
bicyclohexyl +							
cyclopentane	-10.994	-0.6602	-0.6480	0.0324	0.1341	0.0381	0.1344
cyclohexane	9.173	-0.0388	-0.0394	0.0027	0.0686	0.0053	0.0684
cyclohexene	-1.492	-0.1512	-0.1413	0.0157	0.0572	0.0163	0.0571
1,3-cyclohexadiene	7.641	0.1125	0.1146	0.0060	0.0354	0.0095	0.0370
1,4-cyclohexadiene	8.897	0.1618	0.1662	0.0049	0.0156	0.0014	0.0153
benzene	24.035	0.5191	0.5210	0.0030	0.0762	0.0183	0.0806

Table 6.8 (continued)

Mixture	$X_{12}(V_m^E, \text{Flory})^a$ (J.cm^{-3})	$V_m^E(\text{experimental})^b$ $(\text{cm}^3.\text{mol}^{-1})$	$V_m^E(\text{predicted})^a$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma(V_m^E, \text{Flory})^a$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma^*(V_m^E, \text{Flory})^a$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma(V_m^E, \text{Flory})^c$ $(\text{cm}^3.\text{mol}^{-1})$	$\sigma^*(V_m^E, \text{Flory})^c$ $(\text{cm}^3.\text{mol}^{-1})$
bicyclohexyl +							
cycloheptane	16.230	0.1689	0.1635	0.0069	0.1864	0.0090	0.1864
cyclooctane	12.762	0.2587	0.2721	0.0117	0.1189	0.0120	0.1189
tetralin +							
cyclopentane	8.998	-0.5051	-0.4890	0.0227	0.0473	0.0227	0.0473
cyclohexane	31.079	0.1020	0.1009	0.0043	0.1397	0.0017	0.1406
cyclohexene	3.338	-0.2349	-0.2324	0.0097	0.0441	0.0099	0.0440
1,3-cyclohexadiene	-1.273	-0.2051	-0.2029	0.0024	0.0459	0.0024	0.0459
1,4-cyclohexadiene	2.751	-0.1186	-0.1177	0.0013	0.0087	0.0013	0.0087
benzene	9.031	0.0167	0.0154	0.0016	0.0101	0.0032	0.0101
cycloheptane	28.046	0.2022	0.2068	0.0125	0.1529	0.0213	0.1549
cyclooctane	22.419	0.2626	0.2662	0.0167	0.0980	0.0266	0.1000
cyclohexylbenzene +							
cyclopentane	5.054	-0.4997	-0.4988	0.0128	0.0437	0.0112	0.0438
cyclohexane	25.318	0.1055	0.1057	0.0022	0.1495	0.0056	0.1491
cyclohexene	7.843	-0.1018	-0.1017	0.0019	0.0388	0.0038	0.0380
1,3-cyclohexadiene	2.898	-0.0914	-0.0915	0.0050	0.0076	0.0057	0.0080
1,4-cyclohexadiene	2.898	-0.0657	-0.0627	0.0045	0.0066	0.0041	0.0084

Table 6.8 (continued)

Mixture	$X_{12}(V^E_m$, Flory$)^a$ (J.cm^{-3})	V^E_m(experimental)^b (cm^3.mol^{-1})	V^E_m(predicted)^a (cm^3.mol^{-1})	$\sigma(V^E_m$, Flory$)^a$ (cm^3.mol^{-1})	$\sigma^*(V^E_m$, Flory$)^a$ (cm^3.mol^{-1})	$\sigma(V^E_m$, Flory$)^c$ (cm^3.mol^{-1})	$\sigma^*(V^E_m$, Flory$)^c$ (cm^3.mol^{-1})
cyclohexylbenzene +							
benzene	7.458	0.0716	0.0729	0.0040	0.0051	0.0069	0.0079
cycloheptane	30.506	0.3246	0.3347	0.0129	0.2375	0.0130	0.2374
cyclooctane	29.087	0.4566	0.4780	0.0319	0.2126	0.0364	0.2135
benzene +							
cyclopentane	28.237	0.3443	0.3448	0.0076	0.0512	0.0020	0.0492
cyclohexane	42.920	0.6525	0.6544	0.0016	0.0198	0.0156	0.0258
cyclohexene	16.188	0.2448	0.2450	0.0018	0.0442	0.0055	0.0443
1,3-cyclohexadiene	4.410	0.0736	0.0751	0.0041	0.0261	0.0040	0.0261
1,4-cyclohexadiene	2.424	0.0423	0.0434	0.0010	0.0181	0.0010	0.0183
cycloheptane	30.310	0.6284	0.6304	0.0070	0.1168	0.0205	0.1182
cyclooctane	40.371	0.5872	0.5947	0.0275	0.0277	0.0490	0.0490
cyclohexane +							
cyclopentane	3.975	0.0412	0.0419	0.0336	0.0385	0.0027	0.0385
cyclohexene	5.968	0.0968	0.0968	0.0025	0.0236	0.0032	0.0264
1,3-cyclohexadiene	20.954	0.3112	0.3223	0.0098	0.0645	0.0123	0.0650
1,4-cyclohexadiene	24.353	0.3592	0.3689	0.0082	0.0863	0.0099	0.0870
benzene	40.203	0.6525	0.6544	0.0016	0.0198	0.0156	0.0258

Table 6.8 (continued)

Mixture	$X_{12}(V^E_m$, Flory)[a] ($J.cm^{-3}$)	V^E_m(experimental)[b] ($cm^3.mol^{-1}$)	V^E_m(predicted)[a] ($cm^3.mol^{-1}$)	$\sigma(V^E_m$, Flory)[a] ($cm^3.mol^{-1}$)	$\sigma^*(V^E_m$, Flory)[a] ($cm^3.mol^{-1}$)	$\sigma(V^E_m$, Flory)[c] ($cm^3.mol^{-1}$)	$\sigma^*(V^E_m$, Flory)[c] ($cm^3.mol^{-1}$)
cyclohexane +							
cycloheptane	-4.416	-0.0305	-0.0301	0.0053	0.0678	0.0059	0.0678
cyclooctane	1.374	-0.1073	-0.1032	0.0283	0.0271	0.0244	0.0269
n-hexane +							
cyclopentane	-2.104	-0.0678	-0.0728	0.0058	0.0892	0.0051	0.0892
cyclohexane	13.120	0.1485	0.1421	0.0354	0.0868	0.0326	0.0866
cyclohexene	6.845	-0.1024	-0.1030	0.0074	0.0295	0.0049	0.0286
1,3-cyclohexadiene	19.740	0.1017	0.1017	0.0090	0.0180	0.0016	0.0175
1,4-cyclohexadiene	13.135	-0.0673	-0.0700	0.0124	0.1013	0.0059	0.0986
benzene	29.632	0.3970	0.3970	0.0367	0.1542	0.0162	0.1445
cycloheptane	7.952	-0.2046	-0.1998	0.0364	0.0417	0.0363	0.0416
cyclooctane	11.729	-0.4938	-0.4989	0.0297	0.0578	0.0317	0.0580

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[a] s_1/s_2 from equation 6.6. [b] Literature references given in Table C4. [c] s_1/s_2 from Table 6.1.

The ability of the flory theory to predict V_m^E from $X_{12}(H_m^E$, Flory) is best summarized through the standard deviations $\sigma^*(V_m^E$, Flory). The predictions of V_m^E from H^E data are surprisingly good for the systems {a bicyclic compound + an *n*-alkane}. With the exception of {(bicyclohexyl or tetralin or cyclohexylbenzene) + *n*-pentane} the standard deviation $\sigma^*(V_m^E$, Flory) is better than 0.07 $cm^3.mol^{-1}$. The correct sign for V_m^E was predicted in all but two cases, and the relative shapes of the experimental curves were adequately reproduced. The incorrect sign for V_m^E was predicted for {(cyclohexylbenzene or tetralin) + *n*-dodecane}. The standard deviations $\sigma^*(V_m^E$, Flory) for the systems {(*n*-hexane or cyclohexane) + an *n*-alkane} are in most cases better than 0.09 $cm^3.mol^{-1}$. The exceptions are the systems {cyclohexane + (*n*-pentane or *n*-hexadecane)} and {*n*-hexane + (*n*-dodecane or *n*-hexadecane)}. The correct sign is predicted in all cases. The predictions for the systems {(benzene + an *n*-alkane} are much worse with a standard deviation $\sigma^*(V_m^E$, Flory) larger than 0.17 $cm^3.mol^{-1}$ for systems involving *n*-octane or *n*-hexadecane. The correct signs are predicted in each case. The predictions for the systems {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a 1-alkene or a 1-alkyne)} are almost as good as those for {a bicyclic compound + an *n*-alkane} with $\sigma^*(V_m^E$, Flory) generally smaller than 0.11 $cm^3.mol^{-1}$. The exceptions were for the systems {(cyclohexylbenzene or benzene) + a 1-alkene} with $\sigma^*(V_m^E$, Flory) as large as 0.178 $cm^3.mol^{-1}$ in the case of cyclohexylbenzene mixed with 1-hexene. The incorrect sign is predicted for {decalin + 1-hexyne}. Predictions for {(a saturated bicyclic compound or cyclohexane or *n*-hexane) + a 1-alkene} are generally better than those for the corresponding mixtures involving a 1-alkyne, while predictions for the unsaturated bicyclic compounds or benzene mixed with the unsaturated 1-alkynes are generally better than the predictions for the 1-alkene mixtures.

The results are generally not as good for the mixtures comprising a cycloalkane, cyclohexene, a cycloalkadiene or benzene. The standard deviations are usually better than 0.15 $cm^3.mol^{-1}$. The exceptions are for the systems {cyclohexylbenzene + (cycloheptane or cyclooctane)} where $\sigma^*(V_m^E$, Flory) are as large as 0.21 $cm^3.mol^{-1}$. The incorrect sign for V_m^E are predicted in at least ten cases.

In general the predictive powers of the Flory theory has been shown to be similar to previous work carried out by Letcher and co-workers(38,39,42) for systems involving cycloalkanes and *n*-alkanes.

The prediction of excess molar volumes from experimental excess molar enthalpies does not yield results which are as good as those predictions of V_m^E from experimental H_m^E data. This is evident through the standard deviations $\sigma^*(H_m^E$, Flory) listed in column 6 of Tables 6.5 and 6.6. This is to be expected since the X_{12} parameter appears in the equation for

H^E_m, whereas it only affects V^E_m calculations via the reduced temperature for the mixture, $\tilde{T}$. The capability of the Flory theory can therefore only be judged on the results of fitting the V^E_m data.

The results of the Flory fit have also been determined for s_1/s_2 ratios determined from Bondi surface areas. The standard deviations, $\sigma(H^E_m$, Flory) and $\sigma^*(H^E_m$, Flory), for calculations using these values are included in columns 7 and 8 of Tables 6.5 and 6.6, while the standard deviations, $\sigma(V^E_m$, Flory) and $\sigma^*(V^E_m$, Flory), are given in columns 7 and 8 of Tables 6.7 and 6.8. The V^E_m and H^E_m predictions are not much different to those values predicted using the spherical molecule approximation of Flory. This would appear to indicate that the spherical molecule approximation is adequate for the predictions made in this work.

In spite of its relative simplicity the one parameter Flory theory is remarkable in its predictions of V^E_m from H^E_m data and in the fitting of the experimental H^E_m data to molecules which differ to an appreciable degree in size, shape and chemical nature.

6.4 Application of the Prigogine-Flory-Patterson theory

6.4.1 Calculation of parameters

The excess molar volumes were determined using the approximate equation:

$$V^E_m/(x_1V_1^* + x_2V_2^*) = \frac{[(\tilde{v}_1)^{1/3} - 1]\tilde{v}^{2/3}\phi_1\theta_2X_{12}}{[4/3(\tilde{v})^{-1/3} - 1]p_1^*} \qquad [V^E_m(\text{int.})]$$

$$- \frac{(\tilde{v}_1 - \tilde{v}_2)^2[14/9(\tilde{v})^{-1/3} - 1]\psi_1\psi_2}{[4/3(\tilde{v})^{-1/3} - 1]\tilde{v}} \qquad [\text{Vcurv.}]$$

$$+ \frac{(\tilde{v}_1 - \tilde{v}_2)(p_1^* - p_2^*)\phi_1\phi_2}{(p_2^*\psi_1 + p_1^*\psi_2)} \qquad [P^*] \qquad 6.16$$

and the excess molar enthalpies were determined using the approximate equation:

$$H^E_m/(x_1U_1^* + x_2U_2^*) = [-\tilde{U}(\tilde{T}_u) + \tilde{T}_u\tilde{C}_p(\tilde{T}_u)]X_{12}\psi_1\theta_2/p_1^* \qquad [H^E_m(\text{int.})]$$

$$+ \tilde{C}_p(\tilde{T}_u)[\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2 - \tilde{T}_u] \qquad [H^E_m(\text{f.v.})] \qquad 6.17$$

The contact-energy fraction, ψ_i, is given by:

$$\psi_2 = (1 - \psi_1) = (\phi_2 p_2^*)/(\phi_1 p_1^* + \phi_2 p_2^*) \qquad 6.18$$

In this approximation, ν has been equated to ν^o. The term T_u is the average reduced temperature for the solution appropriate to the reduced configurational energy, U, and is defined by:

$$\tilde{U}(\tilde{T}_u) = \psi_1 \tilde{U}(\tilde{T}_1) + \psi_2 \tilde{U}(\tilde{T}_2) \qquad 6.19$$

In the van der Waals model used by Flory and by Patterson:(60)

$$\tilde{U} = -(\tilde{v})^{-1} \qquad 6.20$$

and the configurational energy, U^*, is defined as:

$$U_i^* = p_i^* V_i^* \qquad 6.21$$

The reduced heat capacity, $\tilde{C}_p$, for the pure components and for the mixture is given by:

$$\tilde{C}_p = [4/3(\tilde{v})^{-1/3} - 1]^{-1} \qquad 6.22$$

Once again the ratio of the number of sites per segment were determined by the two methods discussed above in Section 6.3.

A procedure identical to that discussed in Section 6.3 was employed in the testing of the Prigogine-Flory-Patterson theory. This involved the determination of best-fit $X_{12}(H_m^E$, PFP) and $X_{12}(V_m^E$, PFP) values from experimental H_m^E and V_m^E data and the prediction of the respective excess thermodynamic properties from these best-fit values. Experimental and predicted values were compared and the standard deviations $\sigma(H_m^E$, PFP) and $\sigma(V_m^E$, PFP) were determined. The $X_{12}(H_m^E$, PFP) were then used to predict V_m^E data and the $X_{12}(V_m^E$, PFP) values were used in the prediction of H_m^E data. The predictive abilities of the theory was once again expressed through the standard deviations $\sigma^*(V_m^E$, PFP) and $\sigma^*(H_m^E$, PFP).

As a check on the computer programme the Patterson equations were fitted to the data reported by Costas and Patterson(186) for {(benzene or cyclohexane) + an *n*-alkane}. The results are given in Tables 6.9 and 6.10 and are within the experimental precision, considering that Patterson$^{(186)}$ used a $X_{12}(H_m^E)$ at $x = 0.5$ to fit all his data.

The V_m^E and H_m^E were also predicted over the entire composition range at 0.01 mole fraction intervals using the approximate equations of Patterson in conjunction with a value for X_{12}(Berthelot). The results are not much different to the predictions using the Flory theory together with this non-empirical interaction parameter, and hence will not be included again.

6.4.2 Predicted results

The experimental $H_m^E(x = 0.5)$ values, the $\sigma(H_m^E$, PFP) values and the predicted contributions to the excess molar enthalpy at equimolar concentrations (from excess molar enthalpy data) are given in columns 3, 5, 6 and 7 of Table 6.9 for the systems {(a bicyclic compound or benzene or cyclohexane on *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)}. The same format is adopted in Table 6.11 where the results are summarized for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The best fit $X_{12}(H_m^E$, PFP) are included in column 2 of these Tables. The excess molar enthalpies predicted from V_m^E data are similar to the values predicted by $X_{12}(V_m^E$, Flory), and the predicted excess molar volume results from experimental V_m^E data are similar to the results of the Flory fit. These results will not be include here. The ability of the theory to predict excess molar volumes from experimental excess molar enthalpy data has also been investigated. The experimental $V_m^E(x = 0.5)$, the values of $\sigma^*(V_m^E$, PFP) and the predicted contributions at equimolar concentrations to the excess molar volume are given in columns 2, 4, 5, 6 and 7 of Tables 6.10 and 6.12 for the above systems.

(i) A bicyclic compound, benzene, cyclohexane or n-hexane with an n-alkane

The $\sigma(H_m^E$, Flory) values have been included in column 4 of Tables 6.9 and 6.11. A comparison between the $\sigma(H_m^E$, Flory) values and the $\sigma(H_m^E$, PFP) values indicates that the Patterson equation is an excellent approximation for all the mixtures studied. For the system {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + an *n*-alkane} the standard deviation $\sigma(H_m^E$, PFP) never exceeds 17 $J.mol^{-1}$ or 6% of the experimental excess molar enthalpy at equimolar concentrations. The correct sign is predicted in each case.

The interactional contribution to the predicted excess molar enthalpy, H_m^E(int.), at equimolar concentrations, is positive for all of these systems and is the dominant contribution to the excess molar enthalpy in each case. The large H_m^E(int.) contributions to the predicted H_m^E for {benzene + an *n*-alkane}, which increase with an increase in the

Table 6.9 Calculated contributions to the H^E_m data at equimolar concentrations predicted by the Prigogine-Flory-Patterson theory (PFP) for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)}. The s_1/s_2 values have been determined by two different methods.[b,c]

Mixture	$X_{12}(H^E_m, \text{PFP})^a$ (J.mol^{-1})	$H^E_m(\text{experimental})^b$ (J.mol^{-1})	$\sigma(H^E_m, \text{Flory})^a$ (J.mol^{-1})	$\sigma(H^E_m, \text{PFP})^a$ (J.mol^{-1})	$H^E_m(\text{int.})^a$ (J.mol^{-1})	$H^E_m(\text{f.v.})^a$ (J.mol^{-1})	$\sigma(H^E_m, \text{PFP})^c$ (J.mol^{-1})	$H^E_m(\text{int.})^c$ (J.mol^{-1})
decalin +								
n-pentane	5.634	53.9	15.5	5.3	163.6	-106.7	6.9	163.8
n-hexane	3.950	62.4	1.5	1.6	121.3	-58.1	3.6	121.4
1-hexene	4.605	74.2	1.1	1.5	138.9	-64.9	0.9	139.2
1-hexyne	22.890	604.3	18.0	18.8	663.6	-57.8	25.9	660.0
n-heptane	3.364	68.6	1.2	1.5	107.3	-37.3	2.4	107.4
1-heptene	3.675	72.9	2.9	3.2	116.3	-42.5	5.6	116.4
1-heptyne	18.144	524.8	16.2	17.9	557.9	-39.3	17.9	559.2
n-octane	3.210	81.6	3.1	3.5	107.4	-24.4	1.2	107.3
n-dodecane	3.558	125.1	8.8	9.7	132.5	-4.8	3.4	131.4
n-hexadecane	5.164	198.6	6.8	7.5	206.6	-0.7	9.3	201.4
bicyclohexyl +								
n-pentane	4.699	23.0	10.9	10.5	152.8	-126.1	8.5	152.5
n-hexane	2.798	21.6	8.3	8.6	96.5	-72.8	8.0	96.9
1-hexene	4.408	65.4	9.4	9.3	149.2	-80.5	8.5	149.2
1-hexyne	21.441	630.5	5.9	6.4	696.4	-72.6	7.2	696.1

Table 6.9 (continued)

Mixture	$X_{12}(H^E_m, \text{PFP})^a$ ($J.mol^{-1}$)	$H^E_m(\text{experimental})^b$ ($J.mol^{-1}$)	$\sigma(H^E_m, \text{Flory})^a$ ($J.mol^{-1}$)	$\sigma(H^E_m, \text{PFP})^a$ ($J.mol^{-1}$)	$H^E_m(\text{int.})^a$ ($J.mol^{-1}$)	$H^E_m(\text{f.v.})^a$ ($J.mol^{-1}$)	$\sigma(H^E_m, \text{PFP})^c$ ($J.mol^{-1}$)	$H^E_m(\text{int.})^c$ ($J.mol^{-1}$)
bicyclohexyl +								
n-heptane	2.192	26.9	5.6	9.9	79.3	-50.3	6.1	79.4
1-heptene	3.420	62.9	5.7	6.2	121.9	-55.5	5.9	121.8
1-heptyne	16.414	512.8	11.5	12.6	567.6	-52.2	11.5	568.0
n-octane	1.880	35.8	5.4	6.1	71.0	-34.5	6.3	70.6
n-dodecane	1.766	65.3	0.4	0.4	75.0	-9.8	2.3	74.9
n-hexadecane	2.864	128.0	1.0	1.1	131.5	-3.2	6.1	129.7
tetralin +								
n-pentane	21.166	449.9	7.1	6.8	566.5	-117.4	14.5	567.0
n-hexane	18.976	463.3	7.3	8.3	535.8	-66.7	19.0	535.0
1-hexene	10.771	224.5	2.3	2.2	298.9	-73.9	7.5	299.2
1-hexyne	4.013	40.3	1.6	1.6	107.2	-66.5	4.3	107.2
n-heptane	18.232	488.4	5.3	6.1	537.5	-45.4	13.1	536.1
1-heptene	9.954	235.3	4.8	5.4	289.3	-50.3	11.9	288.6
1-heptyne	1.562	-2.9	1.9	1.9	44.2	-47.0	3.4	44.0
n-octane	15.024	508.4	5.3	5.8	542.4	-30.7	13.5	539.9
n-dodecane	17.042	570.3	6.3	7.0	578.9	-8.2	23.4	568.4
n-hexadecane	18.353	657.1	21.2	23.4	667.5	-2.5	20.7	647.7

Table 6.9 (continued)

Mixture	$X_{12}(H^E_m, PFP)^a$ ($J.mol^{-1}$)	$H^E_m(experimental)^b$ ($J.mol^{-1}$)	$\sigma(H^E_m, Flory)^a$ ($J.mol^{-1}$)	$\sigma(H^E_m, PFP)^a$ ($J.mol^{-1}$)	$H^E_m(int.)^a$ ($J.mol^{-1}$)	$H^E_m(f.v.)^a$ ($J.mol^{-1}$)	$\sigma(H^E_m, PFP)^c$ ($J.mol^{-1}$)	$H^E_m(int.)^c$ ($J.mol^{-1}$)
cyclohexylbenzene +								
n-pentane	16.609	372.2	9.8	11.0	508.8	-125.6	9.6	508.2
n-hexane	14.603	391.1	8.7	10.1	474.0	-72.5	10.1	474.7
1-hexene	8.681	194.4	3.6	3.6	276.6	-80.1	3.0	276.4
1-hexyne	5.476	92.5	3.2	3.5	167.6	-72.3	4.1	167.7
n-heptane	13.997	415.1	9.2	10.3	476.0	-50.0	10.8	476.8
1-heptene	8.163	212.9	5.0	5.7	273.4	-53.3	6.5	273.3
1-heptyne	3.440	58.0	2.1	2.3	111.9	-51.9	3.2	120.0
n-octane	13.583	433.6	11.5	12.7	480.7	-34.3	13.5	481.1
n-dodecane	13.415	507.2	14.0	15.4	532.4	-9.8	16.4	529.0
n-hexadecane	14.830	619.6	12.4	13.7	634.2	-3.2	18.9	623.9
benzene +								
n-pentane	44.738	856.6	44.8	49.5	885.7	-22.7	24.3	884.1
n-hexane	43.601	897.2	10.4	11.5	898.7	-3.8	21.3	891.4
1-hexene	29.770	589.9	11.1	12.2	605.3	-5.7	12.1	601.3
1-hexyne	6.959	132.0	8.9	9.8	136.9	-3.6	4.5	136.2
n-heptane	43.033	919.0	28.7	31.7	917.0	-0.1	12.5	906.7
1-heptene	29.014	603.1	19.1	21.1	611.4	-0.5	4.6	605.7
1-heptyne	6.937	138.8	10.4	11.5	142.7	-0.1	5.5	141.7

Table 6.9 (continued)

Mixture	$X_{12}(H^E_m, \text{PFP})^a$ (J.mol^{-1})	$H^E_m(\text{experimental})^b$ (J.mol^{-1})	$\sigma(H^E_m, \text{Flory})^a$ (J.mol^{-1})	$\sigma(H^E_m, \text{PFP})^a$ (J.mol^{-1})	$H^E_m(\text{int.})^a$ (J.mol^{-1})	$H^E_m(\text{f.v.})^a$ (J.mol^{-1})	$\sigma(H^E_m, \text{PFP})^c$ (J.mol^{-1})	$H^E_m(\text{int.})^c$ (J.mol^{-1})
benzene +								
n-octane	44.691	969.4	25.1	27.6	979.6	-0.9	13.9	964.6
n-dodecane	47.742	1100.9	41.8	45.6	1134.8	-14.9	29.9	1096.3
n-hexadecane	52.792	1255.8	47.2	51.3	1322.2	-27.9	52.5	1255.3
cyclohexane +								
n-pentane	9.609	190.9	12.8	14.2	217.2	-23.5	13.6	217.1
n-hexane	9.485	219.6	14.7	16.2	223.7	-4.1	14.1	223.7
1-hexene	10.393	232.6	20.7	22.9	238.5	-5.9	22.0	238.5
1-hexyne	32.905	725.9	32.6	36.0	739.2	-3.9	26.8	740.6
n-heptane	10.035	245.7	13.7	15.2	245.8	-0.2	11.2	245.8
1-heptene	9.934	235.0	12.5	13.8	240.4	-0.6	10.9	240.6
1-heptyne	27.703	641.1	32.5	35.9	653.3	-0.2	24.7	653.2
n-octane	10.506	257.5	14.9	13.5	265.4	-0.8	9.4	264.3
n-dodecane	13.843	358.1	16.8	18.5	382.1	-15.0	3.6	375.6
n-hexadecane	18.349	501.5	15.6	17.4	536.5	-28.3	23.6	513.1
n-hexane +								
n-pentane	0.522	4.9	0.1	0.0	13.3	-8.4	0.1	13.3
1-hexene	2.349	61.3	0.8	0.9	61.6	-0.2	0.7	61.6

Table 6.9 (continued)

Mixture	$X_{12}(H^E_m, PFP)^a$ ($J.mol^{-1}$)	H^E_m(experimental)^b ($J.mol^{-1}$)	$\sigma(H^E_m, Flory)^a$ ($J.mol^{-1}$)	$\sigma(H^E_m, PFP)^a$ ($J.mol^{-1}$)	$H^E_m(int.)^a$ ($J.mol^{-1}$)	$H^E_m(f.v.)^a$ ($J.mol^{-1}$)	$\sigma(H^E_m, PFP)^c$ ($J.mol^{-1}$)	$H^E_m(int.)^c$ ($J.mol^{-1}$)
n-hexane +								
1-hexyne	23.637	593.8	20.4	21.3	596.9	0.0	20.6	596.6
1-heptene	1.817	47.2	0.9	0.9	49.6	-1.7	1.0	49.6
1-heptyne	19.706	517.5	13.4	14.8	523.4	-2.8	10.5	524.1
n-octane	0.386	2.2	0.2	0.6	11.0	-8.8	0.4	11.0
n-dodecane	2.313	36.9	1.8	2.1	72.6	-36.3	4.3	71.7
n-hexadecane	5.106	113.6	7.1	8.1	170.3	-56.4	15.1	166.0

$^a s_1/s_2$ from equation 6.6. ^{b}Literature values from Table C1. $^c s_1/s_2$ from Table 6.1.

length of the *n*-alkane chain, is indicative of the large endothermic destruction of the orientational ordering of the molecular segments in the pure *n*-alkanes and the destruction of the $\pi...\pi$ association between the pure benzene molecules. These strong associations are replaced by relatively weak $CH_2..\pi$ interactions between the molecules of the mixture. Smaller H_m^E(int.) values for mixtures involving tetralin or cyclohexylbenzene point to an increased association between the *n*-alkane molecules and the saturated portion of the bicyclic molecule on mixing. The H_m^E(int.) for the mixtures involving an unsaturated bicyclic compound with an *n*-alkane are all similar, pointing to a similar molecular orientation between the bicyclic molecules and the longer *n*-alkane molecules. The relatively large increase in the H_m^E(int.) with an increase in the chain length of the *n*-alkane for the mixtures {cyclohexane + an *n*-alkane} could possibly result from the endothermic destruction of the short-range orientational ordering between the *n*-alkane molecules by the cyclohexane molecule, which is relatively incapable of entering into molecular orientation with the longer *n*-alkane chain. This results in a net disruption of order. The relatively small interactional contributions to the total H_m^E for the mixtures {*n*-hexane + an *n*-alkane} increase with an increase in the chain length of the *n*-alkane, indicating a decrease in the molecular interaction in the mixtures for a short *n*-hexane with a longer chain *n*-alkane. The predicted $H_m^E(x=0.5)$ for {decalin + *n*-hexadecane}: 205 $J.mol^{-1}$ lies between the values reported by Croucher and Patterson(148) for the mixture {*cis*-decalin + *n*-hexadecane}: 275 $J.mol^{-1}$ and for {*trans*-decalin + *n*-hexadecane}: 95 $J.mol^{-1}$.

The free volume contributions to the predicted excess molar enthalpies for these systems are all negative, indicating that the difference in the free volume between the mixed components leads to a net contraction on mixing. The magnitude of the free volume contribution depends on the differences in the free volumes of the mixture components and hence on the differences in $\tilde{v}$ or $\tilde{T}$. These are in turn dependent on the differences in the coefficients of thermal expansion, α, and the coefficients of isothermal compressibility, κ, for the pure components of the mixture. The free volume contribution to the excess molar enthalpy, H_m^E(f.v.), is significant for the components with large differences in these properties, and in the case of mixtures involving a bicyclic compound the free volume contribution decreases with an increase in the chain length of the molecule, becoming negligible for the longer *n*-alkanes. This is to be expected if cognizance is taken of the size difference effect on the free volume contribution. The free volume contribution is important for the mixtures involving a saturated bicyclic compound mixed with a relatively short chain *n*-alkane. Mixtures involving an unsaturated bicyclic compound with the shorter *n*-alkanes are less affected by H_m^E(f.v.) since these are much smaller than the large interactional contributions.

For mixtures involving {(benzene or cyclohexane) + an *n*-akane} the H_m^E(f.v.) terms are negligible and do not affect the predicted H_m^E significantly. Although the free volume terms are small for {*n*-hexane + an *n*-alkane}, the relatively small H_m^E(int.) term results in H_m^E(f.v.) having an appreciable effect on the predicted excess molar enthalpies.

With the exception of the systems {decalin or tetralin or cyclohexylbenzene) + *n*-dodecane}, the signs of the experimental excess molar volumes from $X_{12}(V_m^E$, PFP) data for the mixtures {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + an *n*-alkane} are correctly predicted in each case. The predictions of V_m^E using the Patterson approximation equations are similar to the predicted V_m^E from the Flory theory. This is evident from a comparison of the standard deviations $\sigma^*(V_m^E$, Flory) and $\sigma^*(V_m^E$, PFP) in Table 6.10. Once again the Patterson approach appears to be an excellent approximation. The difference between predicted results are never more than 3%. The standard deviations, $\sigma^*(V_m^E$, PFP), for the mixtures containing a bicyclic compound with an *n*-alkane are all less than 0.07 $cm^3.mol^{-1}$. The results are not as good for the mixtures {(benzene or cyclohexane or *n*-hexane) + an *n*-alkane} with the standard deviations $\sigma^*(V_m^E$, PFP) being as large as 0.18 $cm^3.mol^{-1}$ in some cases.

The excess molar volumes predicted using the $X_{12}(H_m^E$, PFP) for the systems {(benzene or cyclohexane) + an *n*-alkane} compare well with those results reported by Costas and Patterson.(186) The difference is never more than 5% of the experimental excess molar volume. This is acceptable since the pure liquid properties and the experimental H_m^E and V_m^E results employed in the predictions in this work were in many cases obtained from different literature sources and were hence often different to the values employed by Costas and Patterson. Costas and Patterson also derived their X_{12} values from equimolar values of H_m^E only.

An inspection of the three contributions to the predicted V_m^E aids in the explanation of the origins of the excess molar volumes. In all cases the interactional contributions to V_m^E are positive. This term is the dominant contributiont for mixtures involving an unsaturated compound with an *n*-alkane. This behaviour is consistent with a maximum destruction of the $\pi ... \pi$ association between the unsaturated compounds and the $CH_2...CH_2$ association between the pure *n*-alkane molecules being replaced by relatively weak $CH_2...\pi$ associations on mixing, and is also consistent with the destruction of orientational ordering between the *n*-alkane molecules on mixing with the benzene. The term is relatively small for mixtures comprising a saturated compound with an *n*-alkane. This is due to an increased $CH_2...CH_2$ association between the mixture components and is consistent with the notion of an enhanced possibility of molecular orientation in the

Table 6.10 Calculated contributions to the V_m^E data at equimolar concentrations predicted by the Prigogine-Flory-Patterson theory (PFP) for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkane or a 1-alkyne)}. The s_1/s_2 valnes have been determined by two different methods.[b,c]

Mixture	V_m^E(experimental)[a] / $(cm^3.mol^{-1})$	$\sigma^*(V_m^E$, Flory)[b] / $(cm^3.mol^{-1})$	$\sigma^*(V_m^E$, PFP)[b] / $(cm^3.mol^{-1})$	V_m^E(int.)[b] / $(cm^3.mol^{-1})$	$\tilde{V}$(curv.)[b] / $(cm^3.mol^{-1})$	P^* [b] / $(cm^3.mol^{-1})$	$\sigma^*(V_m^E$, PFP)[c] / $(cm^3.mol^{-1})$	V_m^E(int.)[c] / $(cm^3.mol^{-1})$
decalin +								
n-pentane	-1.4310	0.0624	0.0438	0.1400	-0.7981	-0.7186	0.0438	0.1402
n-hexane	-0.9478	0.0345	0.0328	0.0974	-0.4218	-0.5685	0.0320	0.0975
1-hexene	-0.7468	0.1037	0.0977	0.1111	-0.4684	-0.5118	0.0982	0.1113
1-hexyne	-0.0111	0.0306	0.0368	0.4857	-0.3914	-0.0835	0.0292	0.4874
n-heptane	-0.6363	0.0103	0.0135	0.0833	-0.2703	-0.4404	0.0532	0.0839
1-heptene	-0.4985	0.0889	0.0865	0.0894	-0.3005	-0.4052	0.0866	0.0895
1-heptyne	0.0203	0.0773	0.0773	0.3914	-0.2577	-0.0158	0.0750	0.3928
n-octane	-0.4565	0.0101	0.0128	0.0800	-0.1714	-0.3477	0.0177	0.0799
n-dodecane	0.0726	0.0086	0.0085	0.0903	-0.0331	-0.1354	0.0066	0.0895
n-hexadecane	0.1371	0.0402	0.0403	0.1320	-0.0050	-0.0401	0.0407	0.1286
bicyclohexyl +								
n-pentane	-1.5915	0.0867	0.0642	0.1210	-0.9378	-0.8590	0.0633	0.1209
n-hexane	-1.1075	0.0556	0.0415	0.0724	-0.5228	-0.6990	0.0409	0.0727
1-hexene	-1.1582	0.0512	0.0411	0.1115	-0.5752	-0.6317	0.0412	0.1115

Table 6.10 (continued)

Mixture	V_m^E(experimental)[a] ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, Flory)[b] ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)[b] ($cm^3.mol^{-1}$)	V_m^E(int.)[b] ($cm^3.mol^{-1}$)	$\tilde{V}$(curv.)[b] ($cm^3.mol^{-1}$)	P^* [b] ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)[c] ($cm^3.mol^{-1}$)	V_m^E(int.)[c] ($cm^3.mol^{-1}$)
bicxyclohexyl +								
1-hexyne	-0.2435	0.0842	0.0825	0.4792	-0.4899	-0.1350	0.0831	0.4789
n-heptane	-0.8556	0.0378	0.0329	0.0575	-0.3532	-0.5605	0.0329	0.0576
1-heptene	-0.8406	0.0325	0.0247	0.0881	-0.3880	-0.5163	0.0246	0.0880
1-heptyne	-0.1590	0.1076	0.1078	0.3772	-0.3407	-0.0524	0.1075	0.3774
n-octane	-0.6921	0.0373	0.0342	0.0500	-0.2387	-0.4589	0.0343	0.0497
n-dodecane	-0.2247	0.0130	0.0125	0.0490	-0.0660	-0.2190	0.0126	0.0489
n-hexadecane	-0.1017	0.0295	0.0297	0.0814	-0.0211	-0.0978	0.0288	0.0803
tetralin +								
n-pentane	-1.4745	0.0701	0.0339	0.4528	-0.8141	-1.1678	0.0331	0.4527
n-hexane	-0.9889	0.0178	0.0229	0.4012	-0.4507	-0.9286	0.0195	0.4006
1-hexene	-1.2682	0.0626	0.0698	0.2228	-0.4955	-0.8818	0.0697	0.2230
1-hexyne	-0.8345	0.0641	0.0654	0.0727	-0.4166	-0.4112	0.0648	0.0727
n-heptane	-0.6596	0.0149	0.0141	0.3868	-0.3017	-0.7537	0.0063	0.3858
1-heptene	-0.9977	0.1028	0.1115	0.2074	-0.3315	-0.7262	0.1103	0.2069
1-heptyne	-0.6932	0.0893	0.0897	0.0288	-0.2866	-0.2997	0.0896	0.0287
n-octane	-0.4999	0.0359	0.0438	0.3778	-0.2020	-0.6192	0.0403	0.3760
n-dodecane	-0.0648	0.0583	0.0592	0.3712	-0.0533	-0.3056	0.0530	0.3644
n-hexadecane	0.1586	0.0608	0.0599	0.4042	-0.0158	-0.1482	0.0583	0.3921

Table 6.10 (continued)

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	$\sigma^*(V_m^E$, Flory)^b (cm^3.mol^{-1})	$\sigma^*(V_m^E$, PFP)^b (cm^3.mol^{-1})	V_m^E(int.)^b (cm^3.mol^{-1})	$\tilde{V}$(curv.)^b (cm^3.mol^{-1})	$P^{*\,b}$ (cm^3.mol^{-1})	$\sigma^*(V_m^E$, PFP)^c (cm^3.mol^{-1})	V_m^E(int.)^c (cm^3.mol^{-1})
cyclohexylbenzene +								
n-pentane	-1.4459	0.1349	0.1096	0.3931	-0.8919	-1.1072	0.1090	0.3926
n-hexane	-0.9807	0.0605	0.0446	0.3461	-0.4989	-0.8923	0.0443	0.3466
1-hexene	-0.9635	0.1782	0.1677	0.2011	-0.5481	-0.8348	0.1676	0.2009
1-hexyne	-0.5635	0.0946	0.0968	0.1118	-0.4656	-0.3331	0.0968	0.1119
n-heptane	-0.6785	0.0487	0.0383	0.3359	-0.3378	-0.7267	0.0390	0.3364
1-heptene	-0.6536	0.1700	0.1628	0.1922	-0.3707	-0.6908	0.1631	0.1921
1-heptyne	-0.4493	0.0256	0.0253	0.0721	-0.3247	-0.2287	0.0253	0.0721
n-octane	-0.4734	0.0248	0.0181	0.3295	-0.2289	-0.6005	0.0195	0.3298
n-dodecane	0.0077	0.0343	0.0336	0.3391	-0.0640	-0.3025	0.0328	0.3369
n-hexadecane	0.2366	0.0250	0.0256	0.3828	-0.0208	-0.1495	0.0222	0.3770
benzene +								
n-pentane	0.1166	0.0855	0.0907	0.9154	-0.1596	-0.5410	0.0779	0.9138
n-hexane	0.3970	0.1542	0.1478	0.8488	-0.0267	-0.2325	0.1380	0.8418
1-hexene	0.1030	0.1309	0.1299	0.5711	-0.0393	-0.2604	0.1235	0.5674
1-hexyne	0.0396	0.0494	0.0491	0.1167	-0.0229	-0.1159	0.0491	0.1161
n-heptane	0.5885	0.1438	0.1338	0.8159	-0.0009	-0.0419	0.1259	0.8067
1-heptene	0.3092	0.1137	0.1099	0.5437	-0.0035	-0.0782	0.1054	0.5386
1-heptyne	0.1422	0.0419	0.0420	0.1141	-0.0008	-0.0199	0.0414	0.1133

Table 6.10 (continued)

Mixture	V_m^E(experimental)^a ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, Flory)^b ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)^b ($cm^3.mol^{-1}$)	V_m^E(int.)^b ($cm^3.mol^{-1}$)	$\tilde{V}$(curv.)^b ($cm^3.mol^{-1}$)	$P^{*\,b}$ ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)^c ($cm^3.mol^{-1}$)	V_m^E(int.)^c ($cm^3.mol^{-1}$)
benzene +								
n-octane	0.7106	0.1798	0.1683	0.8294	-0.0062	0.1109	0.1771	0.8167
n-dodecane	0.9192	0.1648	0.1736	0.8155	-0.1033	0.4349	0.1706	0.8135
n-hexadecane	1.0236	0.1740	0.1556	0.0912	-0.1924	0.5357	0.1560	0.8556
cyclohexane +								
n-pentane	-0.1464	0.1170	0.1151	0.2360	-0.1772	-0.3554	0.1151	0.2359
n-hexane	0.1485	0.0868	0.0866	0.2234	-0.0302	-0.1567	0.0864	0.2229
1-hexene	0.1292	0.0797	0.0795	0.2367	-0.0431	-0.1627	0.0792	0.2367
1-hexyne	0.6815	0.0763	0.0810	0.6703	-0.0262	-0.0373	0.0755	0.6715
n-heptane	0.3098	0.0802	0.0808	0.2311	-0.0012	-0.0302	0.0796	0.2311
1-heptene	0.2664	0.0914	0.0918	0.2260	-0.0043	-0.0511	0.0909	0.2262
1-heptyne	0.6886	0.1100	0.1146	0.5557	-0.0011	-0.0047	0.1109	0.5556
n-octane	0.4120	0.0809	0.0819	0.2375	-0.0061	0.0679	0.0805	0.2365
n-dodecane	0.5353	0.0668	0.0686	0.2994	-0.1083	0.2564	0.0677	0.2943
n-hexadecane	0.6225	0.1348	0.1442	0.3777	-0.2020	0.2793	0.1435	0.3666
n-hexane +								
n-pentane	-0.1109	0.0434	0.0432	0.0172	-0.0721	0.0083	0.0433	0.0172
1-hexene	0.0550	0.0176	0.0175	0.0730	-0.0017	0.0042	0.0176	0.0730

Table 6.10 (continued)

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	σ^*(V_m^E, Flory)^b (cm^3.mol^{-1})	σ^*(V_m^E, PFP)^b (cm^3.mol^{-1})	V_m^E(int.)^b (cm^3.mol^{-1})	$\tilde{V}$(curv.)^b (cm^3.mol^{-1})	$P^{*\,b}$ (cm^3.mol^{-1})	σ^*(V_m^E, PFP)^c (cm^3.mol^{-1})	V_m^E(int.)^c (cm^3.mol^{-1})
n-hexane +								
1-hexyne	0.5413	0.0945	0.0886	0.6503	0.0000	-0.0035	0.0884	0.6499
1-heptene	0.0678	0.0294	0.0294	0.0552	-0.0137	-0.0167	0.0294	0.0552
1-heptyne	0.3421	0.0581	0.0558	0.5306	-0.0213	-0.1163	0.0562	0.5313
n-octane	-0.0125	0.0548	0.0549	0.0116	-0.0722	-0.0259	0.0549	0.0115
n-dodecane	-0.3473	0.0928	0.0837	0.0938	-0.2902	-0.1332	0.0849	0.0647
n-hexadecane	-0.5321	0.1825	0.1738	0.1376	-0.4407	-0.3021	0.1689	0.1342

^{a}Literature references given in Table C3. $^b s_1/s_2$ from equation 6.6. $^c s_1/s_2$ from Table 6.1.

mixture. The V_m^E(int.) term for an unsaturated bicyclic compound mixed with an *n*-alkane lies between the values for the mixtures involving benzene and similar mixtures involving a saturated molecule. This is associated with the increase in the possibility of CH_2...CH_2 association between the CH_2 groups of the saturated portion of the bicyclic compound and the *n*-alkane molecule.

The $\tilde{V}$(curv.) contribution to the excess molar volume depends on the the difference in the reduced volumes of the components, $(\tilde{v}_1 - \tilde{v}_2)$. This in turn is related to the thermal expansion coefficients of the component molecules. This difference is significant for mixtures involving the large bicyclic compounds and the shorter *n*-alkanes, becoming insignificant for {a bicyclic compound + *n*-hexadecane}. The $\tilde{V}$(curv.) contribution is therefore large and negative for the mixtures {a bicyclic compound + *n*-pentane} but decreases in magnitude for an increase in the chain length of the *n*-alkane. The fairly similar coefficients of thermal expansion for the mixtures involving benzene or cyclohexane or *n*-hexane with an *n*-alkane results in the $\tilde{V}$(curv.) term offering a fairly insignificant contribution to the predicted V_m^E for these mixtures.

Both the magnitude as well as the sign of the P^* contribution are dependent on the relative magnitudes of the thermal expansion coefficients and the isothermal compressibilities of the components. The P^* contribution is important in the case of the mixtures {a bicyclic compound + an *n*-alkane}. For these systems the P^* contribution is always negative. The trend displayed is one of a decrease in the importance of the P^* contribution with an increase in the chain length of the *n*-alkane. This is due to a decrease in the magnitude of the differences between the coefficients α and κ for the pure components. With the exception of a few systems the contribution of the P^* term to the total excess molar volume is always larger than that of the $\tilde{V}$(curv.) contribution. The $\tilde{V}$(curv.) term coupled with the P^* effect constitute the dominant contribution to V_m^E for most of the mixtures {a bicyclic compound + an *n*-alkane}. Except for {(decalin or bicyclohexyl or tetralin) + *n*-hexadecane} and {tetralin + *n*-dodecane}, negative excess molar volumes are predicted.

The P^* contribution for {(benzene or cyclohexane) + *n*-pentane} are negative, becoming more positive with an increase in the *n*-alkane chain length. The total contribution to the V_m^E by the P^* term for these mixtures with an *n*-alkane is however not as important as in the mixtures involving a bicyclic compound. This term is overshadowed by the relatively large interactional contribution in the case of the benzene mixtures, resulting in positive predictions for the V_m^E. Positive predictions are also afforded for mixtures involving cyclohexane.

The P^* contribution is small and insignificant for the system {n-hexane + n-pentane} and increases in magnitude for an increase in the n-alkane chain length, becoming negative for {n-hexane + (n-octane or n-dodecane or n-hexadecane)}. This can be attributed to the increase in the value of the term $(p_1^* - p_2^*)$ with an increase in the chain length. The positive value for {n-hexane + n-pentane} arises since $p_2^* > p_1^*$ and $\tilde{v}_2 > \tilde{v}_1$.

(ii) A bicyclic compound, benzene, cyclohexane or n-hexane with a 1-alkene or a 1-alkene

The Patterson equations offer an excellent approximation to the Flory theory for the systems {(a bicyclic compound or benzene or cyclohexane or n-hexane) + (a 1-alkene or a 1-alkyne)}. The difference between the $\sigma(H_m^E$, Flory) values and the $\sigma(H_m^E$, PFP) values in Table 6.9 is never greater than 2%. The theory correctly predicts the correct sign for all the systems under consideration, adequately accounting for the shapes of all but one of the experimental excess enthalpy curves. The sinusoidal shape of the curve for {cyclohexane + cyclooctane} was not reproduced.

The interactional contribution to H_m^E is positive for mixtures involving a 1-alkene or a 1-alkyne, displaying similar trends to those displayed by $X_{12}(H_m^E$, PFP). The interactional term is the dominant contribution in all but one case and reflects the interactions between the different species. The one exception is for {tetralin + 1-heptyne} where the H_m^E(f.v.) contribution is larger in magnitude. H_m^E(int.) for {benzene + an n-alkane} are large and positive, but decrease on the addition of a double bond into the n-alkane molecule. This reflects the increased $\pi...\pi$ association between the molecules of the mixture. The introduction of a triple bond results in a large decrease in the H_m^E(int.) contribution and reflects a strong $\pi...\pi$ interaction between the π electrons of the benzene molecule and the π electrons of the triple bond in the 1-alkyne molecule. These effects are evident to a smaller extent in mixtures involving an unsaturated bicyclic compound, indicating that the aromatic nature of these compounds is masked by the cyclohexane moeity.

The H_m^E(int.) for mixtures involving a saturated component such as n-hexane, cyclohexane, decalin or bicyclohexyl mixed with a 1-alkyne is much more positive than the H_m^E(int.) for the similar mixtures involving an n-alkane or a 1-alkene. This reflects the endothermic dissociation of the $\pi...\pi$ and the interactions between the 1-alkyne molecules. The chances of association between the molecules of the mixture are reduced when one of them is a 1-alkyne. The slightly smaller H_m^E(int.) for {n-hexane + (a 1-alkene or a 1-alkyne)} serves to indicate an increased orientational ordering between these molecules on mixing. The interactional contribution for mixtures involving 1-hexene or 1-hexyne are in most cases slightly smaller than the contribution for mixtures involving 1-heptene or 1-heptyne. This could be due to an increased orientational ordering between the bicyclic compound or cyclohexane or *n*-hexane and the CH_2 groups of the longer C_7 chain. In the case of benzene mixtures or of mixtures involving an unsaturated bicyclic compound the contributions for the C_6 and the C_7 molecules are similar, indicating that the $\pi ... \pi$ association overshadows the other effect.

The magnitude of the free volume contributions are small for the mixtures involving species with similar thermal expansion coefficients and are large and negative for species with very different expansion coefficients. The H_m^E(f.v.) contribution is negligible for the mixtures {(benzene or cyclohexane or *n*-hexane) + (a 1-alkene or a 1-alkyne)}. The terms are larger in the mixtures containing a bicyclic compound, but still constitute a negligible contribution to the predicted excess molar enthalpy, because the large interactional contributions overshadow these effects. The thermal expansion coefficients for a 1-alkene or a 1-alkyne are smaller than those for the components a bicyclic compound or benzene or cyclohexane or *n*-hexane, and hence the free volume terms are negative for all the systems under consideration here.

The theory adequately predicts the molar excess volumes for systems involving a 1-alkene or a 1-alkyne, with the exception of {(decalin or benzene) + 1-hexyne} where the incorrect sign for the excess molar volumes are predicted. The standard deviation $\sigma^*(V_m^E$, PFP) is always less than 0.18 $cm^3.mol^{-1}$. A comparison of $\sigma^*(V_m^E$, Flory) with $\sigma^*(V_m^E$, PFP) shows once again that the approximate equations of Patterson are an excellent approximation to the Flory theory. The V_m^E(int.) terms reflect the same trends as exhibited by the H_m^E(int.) terms and are positive in all cases. The differences between the coefficients of thermal expansion and hence the reduced volumes for the pure components of the mixtures involving a bicyclic compound are large and hence the $\tilde{V}$(curv.) and P^* terms are large and negative for {a bicyclic compound + (a 1-alkene or a 1-alkyne)}, offering a significant contribution to the excess molar volumes. This is reflected through the prediction of large negative excess molar volumes. On the other hand the thermal expansion coefficients of benzene, cyclohexane and *n*-hexane are similar to the coefficients for the 1-alkenes and the 1-alkynes and hence the contribution by the $\tilde{V}$(curv.) and the P^* terms to the predicted H_m^E for the mixtures {(benzene or cyclohexane or *n*-hexane) + an *n*-alkane} are small and negative. The exception to this is the system {*n*-hexane + 1-hexene} where the P^* contribution is positive but small. The $\tilde{V}$(curv.) and P^* contributions are dominated by the V_m^E(int.) term, which would explain the positive predicted excess molar volumes.

(iii) A bicyclic compound, benzene, cyclohexane or n-hexane with a cyclic C_6 compound

The Patterson theory adequately predicts excess molar enthalpies for the systems {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. This is reflected by the standard deviations $\sigma^*(H_m^E$, PFP) given in column 5 of Table 6.11 which never exceed 13 $J.mol^{-1}$ or 9% of $H_m^E(x=0.5)$, whichever is the larger.

The H^E(int.) terms are dominant for all the mixtures and reflect similar trends to those exhibited by $X_{12}(H^E$, PFP). Except for {cyclohexane + a cycloalkane} the H_m^E(int.) increase with an increase in the number of carbons in the cycloalkane ring. Once again the H_m^E(int.) for mixtures involving benzene are large and positive and reflect the endothermic destruction of the $CH_2...CH_2$ interactions between the cycloalkane molecules and the $\pi...\pi$ interactions between the benzene molecules on mixing. There is a reduced tendancy for association between the molecules of the mixture when one of them is a benzene molecule, while a greater tendancy towards association between the molecules of the mixture exists when a cycloalkane is mixed with a saturated bicyclic compound, cyclohexane or *n*-hexane. This is reflected through small H_m^E(int.) contributions. The interactional contribution to H_m^E for decalin or bicyclohexyl mixed with cyclopentane are negative. This can be associated with a packing effect.

The lowering of the interactional term with the addition of a double bond into the cyclohexane molecule for the mixtures {benzene + cyclohexene} is indicative of an increased $\pi...\pi$ association between the π electrons of the benzene and the cyclohexene. The addition of two double bonds into the cyclohexane ring (a cycloalkadiene) produces an even larger decrease in H_m^E(int.) for mixtures with benzene, indicating a strong association between the electrons of the molecules of the mixture. For mixtures involving an unsaturated bicyclic molecule the effects are similar but smaller, since the aromatic nature of these components is masked by the cyclohexane moeity. The positive H_m^E(int.) and the resulting negative H_m^E for {(decalin or bicyclohexyl) + cyclopentane} is probably the result of the small size of the cyclopentane molecule allowing for a more intimate interaction with the large bicyclic molecule.(9)

Opposite trends are exhibited by the mixtures {(decalin or bicyclohexyl or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene}. The addition of a single double bond, as in cyclohexene, or two double bonds, as in a cycloalkadiene, or three double bonds, as in benzene, results in an increase in the H_m^E(int.) in each case. This is indicative of the reduced association between the molecules of the mixture with the increase in the aromatic nature of one of the components.

Table 6.11 Calculated contributions to the H_m^E data at equimolar concentrations predicted by the Prigogine-Flory-Patterson theory (PFP) for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The s_1/s_2 values have been determined by two different methods.[a,c]

Mixture	$X_{12}(H_m^E, \text{PFP})^a$ (J.mol^{-1})	$H_m^E(\text{experimental})^b$ (J.mol^{-1})	$\sigma(H_m^E, \text{Flory})^a$ (J.mol^{-1})	$\sigma(H_m^E, \text{PFP})^a$ (J.mol^{-1})	$H_m^E(\text{int.})^a$ (J.mol^{-1})	$H_m^E(\text{f.v.})^a$ (J.mol^{-1})	$\sigma(H_m^E, \text{PFP})^c$ (J.mol^{-1})	$H_m^E(\text{int.})^c$ (J.mol^{-1})
decalin +								
cyclopentane	-5.075	-185.0	15.5	17.0	-137.7	-49.4	17.7	-137.8
cyclohexane	1.873	25.9	11.0	12.1	53.9	-31.2	11.7	54.0
cyclohexene	-1.017	-55.4	4.4	4.9	-28.6	-25.0	5.1	-28.5
1,3-cyclohexadiene	9.034	225.5	4.2	4.6	247.4	-19.8	2.4	246.7
1,4-cyclohexadiene	9.157	228.7	3.7	4.1	249.7	-19.8	2.1	249.0
benzene	29.356	741.7	7.9	8.7	781.8	-30.8	13.2	777.1
cycloheptane	0.450	8.8	3.7	4.1	13.6	-5.6	3.9	13.6
cyclooctane	0.735	18.0	1.6	1.7	23.1	-4.8	1.1	23.2
bicyclohexyl +								
cyclopentane	-2.578	-142.4	11.9	12.9	-78.1	-61.9	15.1	-76.8
cyclohexane	4.797	113.6	2.3	2.5	154.6	-41.7	1.3	153.8
cyclohexene	2.225	37.2	1.2	1.3	70.0	-34.2	2.6	69.3
1,3-cyclohexadiene	10.132	283.8	8.7	9.6	310.2	-27.8	5.0	306.2
1,4-cyclohexadiene	9.950	272.0	9.4	10.4	303.4	-27.7	1.4	299.5
benzene	29.488	827.5	18.7	20.5	876.6	-41.0	15.0	860.6

Table 6.11 (continued)

Mixture	$X_{12}(H^E_m, PFP)^a$ (J.mol^{-1})	H^E_m(experimental)^b (J.mol^{-1})	$\sigma(H^E_m$, Flory$)^a$ (J.mol^{-1})	$\sigma(H^E_m$, PFP$)^a$ (J.mol^{-1})	H^E_m(int.)^a (J.mol^{-1})	H^E_m(f.v.)^a (J.mol^{-1})	$\sigma(H^E_m$, PFP$)^c$ (J.mol^{-1})	H^E_m(int.)^c (J.mol^{-1})
bicyclohexyl +								
cycloheptane	4.443	140.6	6.0	6.2	151.0	-9.9	5.6	150.5
cyclooctane	4.982	164.6	5.6	6.2	176.4	-9.3	6.6	176.6
tetralin +								
cyclopentane	12.319	246.4	12.5	13.8	308.9	-57.0	13.6	308.8
cyclohexane	19.917	482.9	9.8	10.8	528.0	-37.7	16.5	528.4
cyclohexene	7.053	148.8	6.8	7.5	182.8	-30.9	8.3	182.6
1,3-cyclohexadiene	2.927	48.2	1.1	1.3	74.0	-25.0	1.1	74.0
1,4-cyclohexadiene	1.952	24.8	1.5	1.6	49.2	-25.0	1.5	49.1
benzene	8.099	160.1	3.2	3.6	199.4	-37.2	2.0	198.8
cycloheptane	15.831	426.8	16.2	17.9	440.2	-8.7	27.0	439.0
cyclooctane	14.263	404.9	19.5	21.6	411.4	-7.9	34.1	410.6
cyclohexylbenzene +								
cyclopentane	7.991	161.8	5.5	6.0	228.6	-61.7	3.6	226.8
cyclohexane	14.919	402.9	8.8	9.6	453.0	-41.6	7.5	452.0
cyclohexene	4.952	112.8	0.3	0.4	146.8	-34.1	2.6	147.5
1,3-cyclohexadiene	2.446	44.1	1.8	2.0	70.7	-27.7	3.3	70.1
1,4-cyclohexadiene	0.423	-15.5	2.5	2.8	12.2	-27.7	2.5	12.2

Table 6.11 (continued)

Mixture	$X_{12}(H_m^E, PFP)^a$ (J.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	$\sigma(H_m^E$, Flory)^a (J.mol^{-1})	$\sigma(H_m^E$, PFP)^a (J.mol^{-1})	H_m^E(int.)^a (J.mol^{-1})	H_m^E(f.v.)^a (J.mol^{-1})	$\sigma(H_m^E$, PFP)^c (J.mol^{-1})	H_m^E(int.)^c (J.mol^{-1})
cyclohexylbenzene +								
benzene	7.715	173.1	2.3	2.6	216.5	-40.9	6.4	213.5
cycloheptane	14.070	428.2	15.0	16.4	449.7	-10.0	16.5	499.7
cyclooctane	13.939	440.1	21.0	23.1	463.3	-9.3	27.0	463.0
benzene +								
cyclopentane	32.579	597.6	17.4	19.2	612.7	-2.6	26.8	610.9
cyclohexane	37.983	801.7	1.8	2.0	801.2	0.0	22.6	797.4
cyclohexene	20.357	396.1	2.3	2.5	394.8	-0.3	9.5	395.7
1,3-cyclohexadiene	7.010	129.8	0.6	0.6	131.0	-1.0	0.4	131.0
1,4-cyclohexadiene	4.275	83.4	9.2	10.1	79.6	-1.0	9.4	80.1
cycloheptane	40.613	802.5	8.8	9.9	820.5	-9.0	23.1	813.0
cyclooctane	40.002	807.7	9.8	10.9	831.9	-12.3	33.8	820.0
cyclohexane +								
cyclopentane	1.197	21.1	3.4	3.8	25.4	-2.7	4.0	25.2
cyclohexene	3.926	85.2	0.2	0.2	85.5	-0.3	0.8	85.5
1,3-cyclohexadiene	15.794	331.5	3.2	3.5	335.3	-0.9	4.1	334.9
1,4-cyclohexadiene	17.273	372.1	12.8	14.1	366.4	-1.0	19.5	365.2
benzene	38.522	801.7	1.8	2.0	801.2	-0.0	22.6	797.4

Table 6.11 (continued)

Mixture	$X_{12}(H^E_m$, PFP)^a (J.mol^{-1})	H^E_m(experimental)^b (J.mol^{-1})	$\sigma(H^E_m$, Flory)^a (J.mol^{-1})	$\sigma(H^E_m$, PFP)^a (J.mol^{-1})	H^E_m(int.)^a (J.mol^{-1})	H^E_m(f.v.)^a (J.mol^{-1})	$\sigma(H^E_m$, PFP)^c (J.mol^{-1})	H^E_m(int.)^c (J.mol^{-1})
cyclohexane +								
cycloheptane	0.643	5.9	1.6	1.8	14.9	-9.0	1.8	14.9
cyclooctane	0.551	0.8	6.6	7.3	13.2	-12.3	7.5	13.2
n-hexane +								
cyclopentane	2.625	60.2	3.7	4.0	62.4	-0.1	5.2	62.3
cyclohexane	8.955	219.6	14.7	16.2	223.7	-4.1	14.1	223.7
cyclohexene	8.538	195.2	7.1	7.8	200.7	-6.2	5.3	206.9
1,3-cyclohexadiene	18.824	435.3	4.9	5.3	449.0	-8.7	9.8	447.1
1,4-cyclohexadiene	19.213	443.4	9.4	10.4	456.4	-8.8	2.6	454.3
benzene	38.618	897.2	10.4	11.5	898.7	-3.8	21.2	891.4
cycloheptane	9.085	209.4	17.4	19.2	236.6	-24.7	19.1	236.6
cyclooctane	8.872	204.0	17.7	19.6	238.7	-31.0	21.6	237.7

$^a s_1/s_2$ from equation 6.6. ^{b}Literature values from Table C2. $^c s_1/s_2$ from Table 6.1.

The free volume contributions are negative in all cases and are small in magnitude for those mixtures for which the thermal expansion coefficients of the pure components are similar.

The V^E predictions using the approximate equations of Patterson and the $X_{12}(H_m^E, \text{PFP})$ values have the correct sign in all but seven cases. With the exception of the mixtures {cyclohexylbenzene + (cycloheptane or cyclooctane)} and the mixture {bicyclohexyl + cycloheptane)}, the standard deviation $\sigma^*(V_m^E, \text{PFP})$ is always less than 0.160 $\text{cm}^3.\text{mol}^{-1}$.

The $V_m^E(\text{int.})$ terms reflect similar trends to those exhibited by the $H_m^E(\text{int.})$ terms. The interactional term is positive and is the dominant contribution to predicted values for the mixtures {benzene + (a cycloalkane or cyclohexene or a cycloalkadiene}, resulting in the prediction of positive excess molar volumes for these systems. The relative sign of the P^* contributions are positive or negative, depending on the sign of the difference $(\tilde{v}_1 - \tilde{v}_2)$ and $(p_1^* - p_2^*)$.

Once again the differences between the thermal expansion coefficients of the pure components are large for the mixtures involving a bicyclic compound. This is particularly true when the second component is cyclopentane or cyclohexane. The P^* term and the $\tilde{V}$(curv.) terms are the dominant contributions to the predicted excess molar volumes for these mixtures. The same is true for the mixtures {(cyclohexane or *n*-hexane) + (cycloheptane or cyclooctane)}.

The results for the Patterson model have also been calculated using the s_1/s_2 values determined from Bondi surface areas. The results of the calculations have been summarized through the standard deviations $\sigma^*(H_m^E, \text{PFP})$, $H_m^E(\text{int.})$, $\sigma^*(V_m^E, \text{PFP})$ and $V_m^E(\text{int.})$ in columns 8 and 9 of Tables 6.9 to 6.12. These predictions are similar to the values predicted for the ratio calculated using the spherical molecule approximation of Flory. It can be concluded that the spherical molecule approximation given by equation 6.6 has proved adequate for the prediction of the excess thermodynamic properties for the mixtures discussed in this investigation.

Table 6.12 Calculated contributions to V_m^E data at equimolar concentrations predicted by the Prigogine-Flory-Patterson theory (PFP) for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}. The s_1/s_2 values have been determined by two different methods.[b,c]

Mixture	V_m^E(experimental)[a] (cm^3.mol^{-1})	σ^*(V_m^E, Flory)[b] (cm^3.mol^{-1})	σ^*(V_m^E, PFP)[b] (cm^3.mol^{-1})	V_m^E(int.)[b] (cm^3.mol^{-1})	$\tilde{V}$(curv.)[b] (cm^3.mol^{-1})	P^* [b] (cm^3.mol^{-1})	σ^*(V_m^E, PFP)[c] (cm^3.mol^{-1})	V_m^E(int.)[c] (cm^3.mol^{-1})
decalin +								
cyclopentane	-0.6303	0.1530	0.1466	-0.0968	-0.3310	0.0003	0.1465	-0.0968
cyclohexane	-0.1323	0.0426	0.0461	0.0361	-0.2016	0.0529	0.0459	0.0362
cyclohexene	-0.2076	0.0966	0.0952	-0.0185	-0.1589	0.1026	0.0952	-0.0185
1,3-cyclohexadiene	0.0656	0.0773	0.0759	0.1555	-0.1239	0.1352	0.0760	0.1551
1,4-cyclohexadiene	0.1238	0.0529	0.0515	0.1557	-0.1228	0.1588	0.0517	0.1553
benzene	0.4839	0.0979	0.0905	0.4875	-0.1888	0.3034	0.0923	0.4846
cycloheptane	-0.0383	0.0469	0.0468	0.0088	-0.0372	-0.0715	0.0468	0.0088
cyclooctane	0.0175	0.0195	0.0195	0.0138	-0.0295	0.0562	0.0194	0.0138
bicyclohexyl +								
cyclopentane	-0.6602	0.1341	0.1250	-0.0516	-0.4144	-0.0393	0.1252	-0.0508
cyclohexane	-0.0388	0.0686	0.0714	0.0983	-0.2690	0.0353	0.0714	0.0978
cyclohexene	-0.1512	0.0572	0.0540	0.0431	-0.2169	0.0990	0.0539	0.0427
1,3-cyclohexadiene	0.1125	0.0354	0.0337	0.1856	-0.1736	0.1436	0.0358	0.1832
1,4-cyclohexadiene	0.1618	0.0156	0.0125	0.1802	-0.1723	0.1726	0.0135	0.1779
benzene	0.5191	0.0762	0.0668	0.5205	-0.2526	0.3624	0.0733	0.5111

Table 6.12 (continued)

Mixture	V_m^E(experimental)^a ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, Flory)^b ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)^b ($cm^3.mol^{-1}$)	V_m^E(int.)^b ($cm^3.mol^{-1}$)	$\tilde{V}$(curv.)^b ($cm^3.mol^{-1}$)	$P^{*\,b}$ ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)^c ($cm^3.mol^{-1}$)	V_m^E(int.)^c ($cm^3.mol^{-1}$)
bicyclohexyl +								
cycloheptane	0.1689	0.1864	0.1863	0.0927	-0.0646	-0.1122	0.1864	0.0924
cyclooctane	0.2587	0.1189	0.1192	0.1023	-0.0563	0.0670	0.1192	0.1013
tetralin +								
cyclopentane	-0.5051	0.0473	0.0448	0.1994	-0.3523	-0.2855	0.0448	0.1993
cyclohexane	0.1020	0.1397	0.1391	0.3260	-0.2260	-0.1847	0.1398	0.3263
cyclohexene	-0.2349	0.0441	0.0434	0.1086	-0.1814	-0.1039	0.0433	0.1085
1,3-cyclohexadiene	-0.2051	0.0459	0.0456	0.0425	-0.1445	-0.0420	0.0456	0.0425
1,4-cyclohexadiene	-0.1186	0.0087	0.0097	0.0280	-0.1432	-0.0158	0.0097	0.0280
benzene	0.0167	0.0101	0.0133	0.1135	-0.2101	0.0948	0.0138	0.1132
cycloheptane	0.2022	0.1529	0.1523	0.2607	-0.0532	-0.2040	0.1543	0.2600
cyclooctane	0.2626	0.0980	0.0984	0.2262	-0.0451	-0.0468	0.1103	0.2257
cyclohexylbenzene +								
cyclopentane	-0.4997	0.0437	0.0401	0.1459	-0.3932	-0.0209	0.0410	0.1447
cyclohexane	0.1055	0.1495	0.1505	0.2781	-0.2559	-0.1163	0.1502	0.2774
cyclohexene	-0.1018	0.0388	0.0405	0.0871	-0.2062	-0.0372	0.0399	0.0875
1,3-cyclohexadiene	-0.0914	0.0076	0.0107	0.0406	-0.1650	0.0219	0.0112	0.0403
1,4-cyclohexadiene	-0.0657	0.0066	0.0304	0.0069	-0.1637	0.0505	0.0303	0.0069

Table 6.12 (continued)

Mixture	V_m^E(experimental)^a ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, Flory)^b ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)^b ($cm^3.mol^{-1}$)	V_m^E(int.)^b ($cm^3.mol^{-1}$)	$\tilde{V}$(curv.)^b ($cm^3.mol^{-1}$)	$P^{*\,b}$ ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)^c ($cm^3.mol^{-1}$)	V_m^E(int.)^c ($cm^3.mol^{-1}$)
cyclohexylbenzene +								
benzene	0.0715	0.0051	0.0089	0.1236	-0.2394	0.1859	0.0127	0.1218
cycloheptane	0.3246	0.2375	0.2372	0.2661	-0.0621	-0.1851	0.2372	0.2661
cyclooctane	0.4566	0.2126	0.2134	0.2563	-0.0540	-0.0099	0.2143	0.2561
benzene +								
cyclopentane	0.3443	0.0512	0.0476	0.5039	-0.0162	-0.0798	0.0454	0.5024
cyclohexane	0.6525	0.0198	0.0272	0.6143	-0.0001	0.0017	0.0321	0.6113
cyclohexene	0.2448	0.0442	0.0424	0.2869	-0.0017	0.0170	0.0425	0.2861
1,3-cyclohexadiene	0.0736	0.0261	0.0259	0.0934	-0.0057	0.0219	0.0258	0.0934
1,4-cyclohexadiene	0.0423	0.0181	0.0180	0.0562	-0.0058	0.0174	0.0182	0.0565
cycloheptane	0.6284	0.1168	0.1069	0.5950	-0.0575	0.2360	0.1085	0.5896
cyclooctane	0.5872	0.0277	0.0295	0.5447	-0.0722	0.1073	0.0501	0.5369
cyclohexane +								
cyclopentane	0.0412	0.0385	0.0350	0.0270	-0.0184	-0.0140	0.0385	0.0222
cyclohexene	0.0968	0.0263	0.0264	0.0680	-0.0018	-0.0052	0.0680	0.0265
1,3-cyclohexadiene	0.3112	0.0645	0.0656	0.2586	-0.0058	-0.0190	0.0660	0.2583
1,4-cyclohexadiene	0.3592	0.0863	0.0876	0.2801	-0.0060	-0.0242	0.0883	0.2792
benzene	0.6525	0.0198	0.0272	0.6143	0.0000	0.0017	0.0320	0.6113

Table 6.12 (continued)

Mixture	V_m^E(experimental)[a] ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, Flory)[b] ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)[b] ($cm^3.mol^{-1}$)	V_m^E(int.)[b] ($cm^3.mol^{-1}$)	$\tilde{V}$(curv.)[b] ($cm^3.mol^{-1}$)	P^* [b] ($cm^3.mol^{-1}$)	$\sigma^*(V_m^E$, PFP)[c] ($cm^3.mol^{-1}$)	V_m^E(int.)[c] ($cm^3.mol^{-1}$)
cyclohexane +								
cycloheptane	-0.0305	0.0678	0.0613	0.0116	-0.0610	0.1107	0.0677	0.0116
cyclooctane	-0.1073	0.0271	0.0261	0.0093	-0.0769	-0.0502	0.0260	0.0093
n-hexane +								
cyclopentane	-0.0678	0.0892	0.0891	0.0670	-0.0006	-0.0186	0.0892	0.0669
cyclohexane	0.1427	0.0848	0.0866	0.2234	-0.0302	-0.1567	0.0864	0.2229
cyclohexene	-0.1024	0.0295	0.0305	0.2009	-0.0455	-0.2183	0.0296	0.2009
1,3-cyclohexadiene	0.1017	0.0180	0.0174	0.4261	-0.0620	-0.2822	0.0164	0.4243
1,4-cyclohexadiene	-0.0673	0.1013	0.1026	0.4298	-0.0623	-0.2988	0.0999	0.4278
benzene	0.3970	0.1542	0.1478	0.8488	-0.0267	-0.2325	0.1380	0.8419
cycloheptane	-0.2046	0.0417	0.0461	0.2246	-0.1897	-0.2043	0.0459	0.2246
cyclooctane	-0.4938	0.0578	0.0555	0.2023	-0.2185	-0.5400	0.0566	0.2014

[a] Literature references given in Table C4. [b] s_1/s_2 from equation 6.6. [c] s_1/s_2 from Table 6.1.

6.5 Application of the Liebermann theory to the prediction of H_m^E and V_m^E

Liebermann(63) has reported relative sucess in applying his modified Flory theory to mixtures involving various *n*-alkanes. The predictive ability of these equations is compared in this section to the predictions afforded by the previous two theories.

6.5.1 Calculation of parameters

The ideal characteristic hard core molar volume for the mixture, V^*, and the ideal molar volume, V_o, are related to the mole fraction average of the pure component data through:

$$V^* = x_1V_1^* + x_2V_2^* \qquad 6.23$$

and

$$V_o = x_1V_1 + x_2V_2 \qquad 6.24$$

where the hard core molar volumes for the two components are given by the Flory theory and where V_1 and V_2 are the molar volumes of the pure components. The excess molar volume was obtained from:

$$V^E = \tilde{v}V^* - V_o \qquad 6.25$$

where the reduced volume, $\tilde{v}$, is given by the Flory equation:

$$\tilde{v} = [(3 + 4\alpha T)/(3 + 3\alpha T)]^3 \qquad 6.26$$

and the "ideal" reduced volume, $\tilde{V}_o$, is given according to:

$$\tilde{V}_o = V_o/V^* \qquad 6.27$$

The thermal expansion coefficients for the mixtures were calculated from:

$$\alpha = 2\alpha_o - \alpha_a \qquad 6.28$$

where α_o is obtained from:

$$\alpha_o = \{3[(\tilde{V}_o)^{1/3} - 1]/[T(4 - 3(\tilde{V}_o)^{1/3}]\} \qquad 6.29$$

and α_a is given according to equation 4.191.

The number of external degrees of freedom, c_i, for the pure components i were calculated from equation 4.187 and the corresponding values for the mixture were calculated from the mole fraction average of the pure component values:

$$c = x_1 c_1 + x_2 c_2 \qquad 6.30$$

The excess enthalpies were determined from:

$$H_m^E = T\{x_1 \gamma_1 V_1 + x_2 \gamma_2 V_2 - [Rc\ /(1 - \tilde{v}^{-1/3})]\} \qquad 6.31$$

and in the case where molecules are considered as hard spheres:

$$H_m^E = RT\{[\zeta 1_1/(1 - \tilde{v}_1{}^{-1/3})] + [\zeta_2/(1 - \tilde{v}_2{}^{-1/3})] - [1/(1 - \tilde{v}^{-1/3})]\} \qquad 6.32$$

ζ_1 and ζ_2 are calculated according to equation 4.200.

6.5.2 Predicted results

The predicted excess molar volumes and excess molar enthalpies at equimolar concentrations for the systems {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)} and for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene of benzene)} have been given in Tables 6.13 and 6.14 respectively. The H_m^E have been calculated using both of equations 6.31 and 6.32. Neither the H_m^E nor the V_m^E are adequately predicted by this theory. The Liebermann theory has predicted negative V_m^E values in all cases while the incorrect sign for H_m^E data has been predicted in many cases. The predicted results are generally worse than those predicted by the Flory theory in conjunction with X_{12}(Bethelot). The theory was also incapable of adequately reproducing the observed trends displayed by the experimental H_m^E and V_m^E. No preference can be given to either of the excess molar enthalpy predictive equations.

Table 6.13 Excess molar volumes and excess molar enthalpies at equimolar concentrations from the equations of Liebermann for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)}

Mixture	V_m^E(experimental)[a] / (cm^3.mol^{-1})	V_m^E(predicted) / (cm^3.mol^{-1})	H_m^E(experimental)[b] / (J.mol^{-1})	H_m^E(predicted)[c] / (J.mol^{-1})	H_m^E(predicted)[d] / (J.mol^{-1})
decalin +					
n-pentane	-1.4310	-0.9769	53.9	512.1	412.0
n-hexane	-0.9478	-0.4951	62.4	563.6	438.8
1-hexene	-0.7468	-0.5516	74.2	417.1	368.6
1-hexyne	-0.0111	-0.4487	604.3	-35.2	-27.3
n-heptane	-0.6363	-0.3084	68.6	489.0	363.9
1-heptene	-0.4985	-0.3440	72.9	431.5	322.7
1-heptyne	0.0203	-0.2894	524.8	-66.8	-48.4
n-octane	-0.4565	-0.1917	81.6	419.0	299.2
n-dodecane	-0.0726	-0.0356	125.1	191.1	116.0
n-hexadecane	0.1371	-0.0053	198.6	61.7	32.0
bicyclohexyl +					
n-pentane	-1.5915	-0.1849	23.0	612.6	443.9
n-hexane	-1.1075	-0.6318	21.6	713.8	502.2
1-hexene	-1.1582	-1.6908	65.4	595.6	420.9
1-hexyne	-0.2435	-0.5691	630.5	-17.6	-12.3
n-heptane	-0.8556	-0.4131	26.9	643.9	434.8
1-heptene	-0.8406	-0.4549	62.9	567.3	384.8

Table 6.13 (continued)

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted)^c (J.mol^{-1})	H_m^E(predicted)^d (J.mol^{-1})
bicyclohexyl +					
1-heptyne	-0.1590	-0.3858	512.8	-52.7	-39.7
n-octane	-0.6921	-0.2731	35.8	572.6	372.5
n-dodecane	-0.2247	-0.0718	65.3	318.0	178.2
n-hexadecane	-0.1017	-0.0225	128.0	152.8	74.0
tetralin +					
n-pentane	-1.4745	-1.0121	449.9	152.8	921.4
n-hexane	-0.9889	-0.5327	463.3	1093.5	863.5
1-hexene	-1.2682	-0.5893	224.5	1008.9	800.7
1-hexyne	-0.8345	-0.4858	40.3	437.8	343.7
n-heptane	-0.6596	-0.3440	488.4	964.0	727.1
1-heptene	-0.9977	-0.3802	235.3	914.5	693.3
1-heptyne	-0.6932	-0.3243	-2.9	358.2	262.8
n-octane	-0.4999	-0.2241	508.4	840.8	608.3
n-dodecane	-0.0648	-0.0555	570.3	468.0	287.2
n-hexadecane	0.1586	-0.0160	657.0	242.5	127.0

Table 6.13 (continued)

Mixture	V_m^E(experimental)[a] (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)[b] (J.mol^{-1})	H_m^E(predicted)[c] (J.mol^{-1})	H_m^E(predicted)[d] (J.mol^{-1})
cyclohexylbenzene +					
n-pentane	-1.4459	-1.1399	372.2	984.5	726.0
n-hexane	-0.9807	-0.6071	391.1	1016.9	727.6
1-hexene	-0.9635	-0.6692	194.4	910.9	654.8
1-hexyne	-0.5635	-0.5490	92.5	287.2	204.4
n-heptane	-0.6785	-0.3968	415.1	910.2	624.7
1-heptene	-0.6536	-0.4369	212.9	844.7	582.5
1-heptyne	-0.4493	-0.3918	58.0	232.2	198.1
n-octane	-0.4734	-0.2619	433.6	804.1	531.4
n-dodecane	0.0077	-0.0688	507.2	460.4	261.5
n-hexadecane	0.2366	-0.0217	619.6	243.1	119.2
benzene +					
n-pentane	0.1166	-0.0015	856.6	225.3	187.5
n-hexane	0.3970	-0.0292	897.2	241.2	213.5
1-hexene	0.1030	-0.4341	599.9	269.9	238.7
1-hexyne	0.0396	-0.0257	132.0	129.7	114.1
n-heptane	0.5885	-0.0010	919.0	47.0	39.5
1-heptene	0.3092	-0.0038	603.1	87.2	73.8
1-heptyne	0.1422	-0.0009	138.8	24.7	20.1

Table 6.13 (continued)

Mixture	V_m^E(experimental)[a] (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)[b] (J.mol^{-1})	H_m^E(predicted)[c] (J.mol^{-1})	H_m^E(predicted)[d] (J.mol^{-1})
benzene +					
n-octane	0.7106	-0.0064	969.4	-132.0	-106.0
n-dodecane	0.9192	-0.1032	1100.9	-601.1	-402.9
n-hexadecane	1.0236	-0.1901	1255.8	-820.5	-463.1
cyclohexane +					
n-pentane	-0.1464	-0.2059	190.9	280.9	252.5
n-hexane	0.1485	-0.0339	219.6	150.0	130.0
1-hexene	0.1292	-0.0491	232.6	166.7	136.0
1-hexyne	0.6815	-0.0297	725.9	33.5	28.9
n-heptane	0.3098	-0.0013	245.7	31.8	26.2
1-heptene	0.2664	-0.0047	235.0	53.3	44.2
1-heptyne	0.6886	-0.0012	641.1	5.1	4.1
n-octane	0.4120	-0.0066	257.5	-77.2	-60.8
n-dodecane	0.5353	-0.1154	358.1	354.0	-233.4
n-hexadecane	0.6225	-0.2159	501.5	-449.2	-250.0
n-hexane +					
n-pentane	-0.1109	-0.0833	4.9	-23.9	-21.5
1-hexene	0.0555	-0.0019	61.3	-4.0	-3.5

Table 6.13 (continued)

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted)^c (J.mol^{-1})	H_m^E(predicted)^d (J.mol^{-1})
n-hexane +					
1-hexyne	0.5413	-0.0001	593.8	3.2	2.8
1-heptene	0.0678	-0.0156	47.2	11.6	9.7
1-heptyne	0.3421	-0.0244	517.5	109.0	87.2
n-octane	-0.0851	-0.0822	2.2	5.9	4.7
n-dodecane	-0.3472	-0.3513	36.9	43.2	41.6
n-hexadecane	-0.5321	-0.5293	113.6	187.6	104.5

[a] Literature references given in Table C3. [b] Literature references given in Table C1. [c] Predicted H_m^E from equation 6.31. [d] Predicted H_m^E from equation 6.32.

Table 6.14 Excess molar volumes and excess molar enthalpies at equimolar concentrations from the equations of Liebermann for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)}

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted)^c (J.mol^{-1})	H_m^E(predicted)^d (J.mol^{-1})
decalin +					
cyclopentane	-0.6303	-0.3781	-185.0	-133.2	-109.6
cyclohexane	-0.1323	-0.2253	25.9	-151.6	-117.9
cyclohexene	-0.2076	-0.1758	-55.4	-214.6	-169.9
1,3-cyclohexadiene	0.0656	-0.1355	225.5	-257.6	-207.9
1,4-cyclohexadiene	0.1238	-0.1337	228.7	-296.3	-238.5
benzene	0.4839	-0.2035	741.7	-550.0	-436.0
cycloheptane	-0.0383	-0.0416	8.8	98.4	78.9
cyclooctane	0.0175	-0.0323	18.0	-103.8	-74.0
bicyclohexyl +					
cyclopentane	-0.6602	-0.4786	-142.4	-139.1	-102.9
cyclohexane	-0.0388	-0.3024	113.6	-162.7	-114.3
cyclohexene	-0.1512	-0.2405	37.2	-244.4	-174.5
1,3-cyclohexadiene	0.1125	-0.1897	283.8	-303.8	-220.8
1,4-cyclohexadiene	0.1618	-0.1873	272.0	-352.5	-255.6
benzene	0.5191	-0.2704	827.5	-655.1	-468.5
cycloheptane	0.1689	-0.0733	140.6	158.6	114.6
cyclooctane	0.2587	-0.0614	164.6	-135.7	-88.1

Table 6.14 (continued)

Mixture	V_m^E(experimental)[a] ($cm^3.mol^{-1}$)	V_m^E(predicted) ($cm^3.mol^{-1}$)	H_m^E(experimental)[b] ($J.mol^{-1}$)	H_m^E(predicted)[c] ($J.mol^{-1}$)	H_m^E(predicted)[d] ($J.mol^{-1}$)
tetralin +					
cyclopentane	-0.5051	-0.4137	246.4	281.7	235.3
cyclohexane	0.1020	-0.2574	482.9	208.3	164.3
cyclohexene	-0.2349	-0.2053	148.8	100.3	80.5
1,3-cyclohexadiene	-0.2051	-0.1624	48.2	13.1	10.7
1,4-cyclohexadiene	-0.1186	-0.1604	24.8	-31.6	-25.8
benzene	0.0167	-0.2337	160.1	-255.5	-205.5
cycloheptane	0.2022	-0.0601	426.8	325.6	265.0
cyclooctane	0.2626	-0.0496	404.9	69.0	49.9
cyclohexylbenzene +					
cyclopentane	-0.4997	-0.4636	161.8	133.6	100.6
cyclohexane	0.1055	-0.2925	402.9	79.5	56.8
cyclohexene	-0.1018	-0.2332	112.8	-25.1	-19.0
1,3-cyclohexadiene	-0.0914	-0.1844	44.1	-106.9	-79.0
1,4-cyclohexadiene	-0.0657	-0.1820	-15.5	-155.9	-115.0
benzene	0.0716	-0.2628	173.1	-423.6	-308.2
cycloheptane	0.3246	-0.0711	428.2	288.2	212.0
cyclooctane	0.4566	-0.0595	440.1	-1.9	-1.2

Table 6.14 (continued)

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted)^c (J.mol^{-1})	H_m^E(predicted)^d (J.mol^{-1})
benzene +					
cyclopentane	0.3443	-0.0183	597.6	92.0	85.6
cyclohexane	0.6525	-0.0001	801.7	-2.2	-1.9
cyclohexene	0.2448	-0.0019	396.1	-23.5	-21.3
1,3-cyclohexadiene	0.0736	-0.0064	129.8	-32.7	-30.1
1,4-cyclohexadiene	0.0423	-0.0066	83.4	-26.6	-24.5
cycloheptane	0.6284	-0.0628	802.5	-341.8	-313.2
cyclooctane	0.5872	-0.0795	807.7	-188.9	-151.4
cyclohexane +					
cyclopentane	0.0412	-0.0209	21.1	10.2	9.4
cyclohexene	0.0968	-0.0018	85.2	6.0	5.3
1,3-cyclohexadiene	0.3112	-0.0065	331.5	22.9	20.6
1,4-cyclohexadiene	0.3592	-0.0067	372.1	29.8	26.8
benzene	0.6525	-0.0001	801.7	-2.2	-1.9
cycloheptane	-0.0305	-0.0680	5.9	-160.1	-143.4
cyclooctane	-0.1073	-0.0868	0.8	44.4	34.9

Table 6.14 (continued)

Mixture	V_m^E(experimental)^a (cm^3.mol^{-1})	V_m^E(predicted) (cm^3.mol^{-1})	H_m^E(experimental)^b (J.mol^{-1})	H_m^E(predicted)^c (J.mol^{-1})	H_m^E(predicted)^d (J.mol^{-1})
n-hexane +					
cyclopentane	-0.0678	-0.0007	60.2	17.2	15.9
cyclohexane	0.1485	-0.0340	219.6	150.0	129.9
cyclohexene	-0.1024	-0.0507	195.2	214.7	189.7
1,3-cyclohexadiene	0.1017	-0.0684	435.3	284.6	257.0
1,4-cyclohexadiene	-0.0673	-0.0686	433.4	304.8	274.4
benzene	0.3970	-0.0292	897.2	241.2	213.5
cycloheptane	-0.2046	-0.2141	209.4	166.6	149.5
cyclooctane	-0.4938	-0.2543	204.0	572.4	450.4

[a] Literature references given in Table C4. [b] Literature references given in Table C2. [c] Predicted H_m^E from equation 6.31. [d] Predicted H_m^E from equation 6.32.

6.6 The prediction of activity coefficients at infinite dilution

The Flory theory has been used in the prediction of activity coefficients at infinite dilution according to equations 4.102 and 4.103. The minimized $X_{12}(H_m^E$, Flory) has been used in these calculations and the ratio s_1/s_2 has been determined by the two different methods for each system. The experimental and predicted results for the systems {(*n*-hexane or 1-hexene or 1-hexyne or *n*-heptane or 1-heptene or 1-heptyne or cyclohexane or cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene) + a bicyclic compound} and {an *n*-alkane + (benzene or cyclohexane or *n*-hexane)} are given in Tables 6.15 and 6.16 respectively.

A comparison between the experimental and the predicted values indicates that the Flory theory is better at predicting γ_{13} values for mixtures comprising "like + like" molecules. This can be substantiated by comparing the predicted γ_{13}^{∞} results in Table 6.15 for the systems {(*n*-hexane or *n*-heptane) + (decalin or bicyclohexyl)} where the predicted values for these systems comprising "like" components (both saturated molecules) are all within 7% of the experimental results. Predictions for {(*n*-hexane or *n*-heptane) + (tetralin or cyclohexylbenzene)} are not as good. Here the predicted and experimental results differ by as much as 25%.

The theory adequately predicts values which decrease with an increase in the length of the *n*-alkane chain for the mixtures {(benzene or cyclohexane) + an *n*-alkane}. However the differences between the experimental and the predicted values increases with an increase in the *n*-alkane chain length. The predicted γ_{13}^{∞} values for the system {benzene + *n*-hexadecane} are almost double the experimental value.

The predicted and the experimental results are within 0.16 of each other for the "like + like" systems 1-hexene or 1-heptene mixed with the unsaturated bicyclic compounds, decalin or bicyclohexyl. This is also true for the unsaturated solvents, 1-hexyne and 1-heptyne, mixed with the unsaturated bicyclic solvents, tetralin or cyclohexylbenzene. The predicted γ_{13}^{∞} for the solutes 1-hexyne or 1-heptyne mixed with a saturated bicyclic compound solvent, and the γ_{13}^{∞} values for the 1-alkenes mixed with the unsaturated bicyclic solvents are not as good. The predictions for the mixtures {(cyclohexane or cyclohexene) + (decalin or bicyclohexyl)} and {(benzene or a cycloalkadiene) + (tetralin or cyclohexylbenzene)} are also good. These mixtures can also be thought of as comprising "like + like" molecules. Relatively poor predictions are made for the systems {(benzene + (decalin or bicyclohexyl)} and for {(cyclohexane + (tetralin or cyclohexylbenzene)}. This is to be expected considering the relatively large differences in the degree of saturation or

Table 6.15 Experimental and predicted activity coefficients at infinite dilution for a hydrocarbon solute in a bicyclic compound solvent. The s_1/s_2 values have been determined by two different methods.[b,c]

Solute	γ_{13}^{∞} [a]	γ_{13}^{∞} [b]	γ_{13}^{∞} [c]	γ_{13}^{∞} [a]	γ_{13}^{∞} [b]	γ_{13}^{∞} [c]
		decalin			**bicyclohexyl**	
n-hexane	1.323	1.309	1.320	1.204	1.250	1.248
1-hexene	1.322	1.339	1.348	1.148	1.321	1.315
1-hexyne	1.773	2.298	2.412	1.558	2.230	2.217
n-heptane	1.273	1.262	1.276	1.126	1.216	1.216
1-heptene	1.271	1.281	1.294	1.168	1.277	1.275
1-heptyne	1.736	2.112	2.234	1.577	2.039	2.048
cyclohexane	1.099	1.086	0.955	1.013	1.091	1.146
cyclohexene	1.073	0.955	0.955	0.956	1.005	1.001
1,3-cyclohexadiene	1.124	1.240	1.231	1.067	1.228	1.210
1,4-cyclohexadiene	1.054	1.236	1.227	0.988	1.212	1.181
benzene	1.396	2.172	2.087	1.296	2.172	1.979
		tetralin			**cyclohexylbenzene**	
n-hexane	1.903	2.281	2.394	1.600	1.990	1.993
1-hexene	1.488	1.717	1.756	1.319	1.583	1.579
1-hexyne	1.211	1.316	1.330	1.178	1.323	1.326
n-heptane	1.872	2.256	2.417	1.606	1.997	2.025
1-heptene	1.520	1.655	1.709	1.347	1.568	1.575
1-heptyne	1.250	1.205	1.212	1.194	1.263	1.267
cyclohexane	1.373	2.002	2.049	1.231	1.675	1.654
cyclohexene	1.117	1.290	1.293	1.036	1.145	1.136
1,3-cyclohexadiene	0.976	1.097	1.096	0.947	1.005	0.999
1,4-cyclohexadiene	0.914	1.063	1.063	0.855	0.940	0.939
benzene	0.959	1.270	1.259	0.969	1.171	1.147

[a] Experimental values. [b] Predicted values using s_1/s_2 from equation 6.6. [c] Predicted values using s_1/s_2 from Table 6.1.

Table 6.16 Experimental and predicted activity coefficients at infinite dilution for the solutes *n*-hexane, *n*-heptane, benzene or cyclohexane in an *n*-alkane solvent. The s_1/s_2 values have been determined by two different methods.[b,c]

Solute	γ_{13}^{∞} [a]	γ_{13}^{∞} [b]	γ_{13}^{∞} [c]	γ_{13}^{∞} [a]	γ_{13}^{∞} [b]	γ_{13}^{∞} [c]
		benzene			**cyclohexane**	
n-pentane	1.926	2.540	2.361			
n-hexane	1.673	2.377	2.172			
n-heptane	1.617	2.227	2.056			
n-octane	1.463	2.293	2.060	1.079	1.232	1.211
n-dodecane				0.904	1.214	1.169
n-hexadecane	1.086	2.156	1.767	0.792	1.228	1.143
		***n*-hexane**				
n-hexadecane	0.900	1.029	1.009			

[a] Experimental values from Reference 465. [b] Predicted values using s_1/s_2 from equation 6.6. [c] Predicted values using s_1/s_2 from Table 6.1.

unsaturation between the components.

The predicted γ_{13}^{∞} values using the the two different methods for determining s_1/s_2 values are similar.

6.7 Conclusions

The systems studied in this work have afforded valuable information relating the experimental excess thermodynamic properties to the size, shape and the degree of unsaturation of the component molecules. The one parameter Flory theory and the one parameter Prigogine-Flory-Patterson theory have adequately reproduced the excess thermodynamic properties in most cases, and have rationalized a good deal of the observed behaviour.

The investigation reported in this thesis has once again shown that the development of a theory which will afford a complete undestanding of the thermodynamic properties of liquid mixtures must take into consideration the geometric, packing, and energetic effects present in the liquid mixtures. The development of an equation of state for liquid mixtures which includes both the geometric and energetic factors, but which at the same time remains simple and easy to use, is eagerly awaited. Meanwhile the success of the Flory theory and the diversity of its application justifies its popularity.

APPENDIX A - EXPERIMENTAL EXCESS MOLAR ENTHALPIES

Table A1 Excess molar enthalpies at 298.15 K for {x(a bicyclic compound or benzene or cyclohexane or n-hexane) + $(1-x)$(an n-alkane or a 1-alkene or a 1-alkyne)} and deviations δ_H calculated from equation 5.1 and the coefficients of Table C1

x	$\frac{H^E_m}{\mathrm{J.mol^{-1}}}$	$\frac{\delta_H}{\mathrm{J.mol^{-1}}}$	x	$\frac{H^E_m}{\mathrm{J.mol^{-1}}}$	$\frac{\delta_H}{\mathrm{J.mol^{-1}}}$	x	$\frac{H^E_m}{\mathrm{J.mol^{-1}}}$	$\frac{\delta_H}{\mathrm{J.mol^{-1}}}$
				decalin + *n*-pentane				
0.1355	26.2	0.6	0.3315	47.9	0.1	0.6546	49.7	-0.3
0.1656	29.4	-0.7	0.4193	53.0	0.6	0.8053	36.4	-0.4
0.2986	45.0	-0.3	0.5848	53.3	0.4	0.8899	24.4	0.2
				decalin + 1-hexene				
0.3363	63.9	-0.1	0.5910	72.8	-0.2	0.7715	54.4	0.2
0.4183	71.7	-0.2	0.6276	70.0	-0.4	0.8410	41.9	0.1
0.4503	73.3	0.4	0.6787	65.9	-0.2	0.8519	39.5	-0.1
0.5896	72.5	0.2	0.7336	59.9	0.2			
				decalin + 1-hexyne				
0.3422	550.5	-0.5	0.5671	592.6	0.2	0.6435	552.2	-1.1
0.3962	584.5	2.4	0.5674	592.2	-0.2	0.7660	432.8	0.4
0.4266	591.6	-2.1	0.5778	590.8	2.6	0.8276	343.9	-0.1
0.5075	603.0	-1.0	0.6307	561.2	-0.7			
				decalin + 1-heptene				
0.2704	60.8	-0.1	0.5122	72.7	-0.1	0.7105	58.0	-0.1
0.3346	69.3	0.5	0.5552	71.6	0.2	0.8418	36.5	-0.1
0.4579	72.3	-0.7	0.6216	67.6	0.2	0.8721	30.4	0.1
				decalin + 1-heptyne				
0.3001	430.6	-2.1	0.5929	507.2	-0.8	0.7628	376.0	-1.9
0.3345	463.8	3.2	0.6020	506.0	1.6	0.7871	350.8	1.7
0.4319	512.6	-0.2	0.6721	463.8	0.5	0.8636	242.4	-0.2
0.5000	522.9	-1.9						

Table A1 (continued)

x	$\frac{H_m^E}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$	x	$\frac{H_m^E}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$	x	$\frac{H_m^E}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$
			bicyclohexyl + *n*-pentane					
0.3307	20.2	0.1	0.4901	22.9	0.0	0.7297	17.3	0.1
0.4091	21.9	-0.1	0.5973	21.9	0.1			
			bicyclohexyl + 1-hexene					
0.2399	58.7	0.1	0.4947	65.3	-0.3	0.7722	39.4	-0.2
0.2999	63.5	-0.2	0.5529	63.0	0.3	0.7925	36.8	0.2
0.3848	67.0	0.0	0.6484	54.7	-0.1	0.8537	26.8	0.0
0.4549	66.9	0.2						
			bicyclohexyl + 1-hexyne					
0.2276	485.5	0.3	0.4149	632.8	-0.3	0.6268	558.0	-0.1
0.2890	556.9	-1.5	0.4722	633.5	-2.2	0.7697	397.0	0.4
0.3619	616.5	2.8	0.5360	618.6	0.9	0.8268	312.5	-0.2
			bicyclohexyl + *n*-heptane					
0.1406	19.8	0.3	0.3355	28.2	0.0	0.7425	17.9	0.0
0.1860	23.1	0.0	0.4513	27.9	0.1	0.7553	17.3	0.1
0.2371	25.5	-0.3	0.5874	24.6	0.4	0.8296	13.0	-0.2
0.2539	26.1	-0.4						
			bicyclohexyl + 1-heptene					
0.2605	57.4	0.1	0.5012	62.5	-0.3	0.8118	37.2	-0.2
0.3303	61.6	-0.3	0.5786	60.0	0.6	0.8447	32.9	0.2
0.4104	64.0	0.1	0.6642	53.4	-0.3			
			bicyclohexyl + 1-heptyne					
0.2504	404.5	-1.1	0.4522	512.9	0.5	0.6468	461.1	0.6
0.2998	450.6	2.0	0.5035	511.4	-1.0	0.7882	337.4	0.7
0.3928	498.7	-0.5	0.5638	499.0	-0.6	0.8286	287.0	-0.5

Table A1 (continued)

x	$\frac{H_m^E}{\text{J.mol}^{-1}}$	$\frac{\delta_H}{\text{J.mol}^{-1}}$	x	$\frac{H_m^E}{\text{J.mol}^{-1}}$	$\frac{\delta_H}{\text{J.mol}^{-1}}$	x	$\frac{H_m^E}{\text{J.mol}^{-1}}$	$\frac{\delta_H}{\text{J.mol}^{-1}}$
tetralin + *n*-pentane								
0.0920	152.2	-1.0	0.3624	426.3	-1.5	0.6899	368.7	1.4
0.1510	240.4	1.6	0.4928	446.2	-2.7	0.7749	298.5	1.0
0.2095	312.3	1.8	0.5706	432.1	0.8	0.8427	226.4	-0.9
0.2343	335.9	-0.6						
tetralin + 1-hexene								
0.2995	189.5	0.1	0.4613	223.1	-0.3	0.7147	181.6	0.0
0.3645	208.2	-0.4	0.5719	219.8	0.2	0.8148	133.0	0.1
0.4163	219.1	0.6	0.6316	208.0	-0.3	0.8601	105.0	-0.1
tetralin + 1-hexyne								
0.2804	31.0	0.0	0.5406	40.5	0.2	0.7731	28.9	-0.4
0.3523	35.6	0.0	0.6152	38.4	-0.5	0.8278	24.0	0.3
0.3570	35.8	-0.1	0.6682	36.8	0.0	0.8767	17.8	-0.1
0.4417	39.4	0.2	0.6967	35.5	0.4			
tetralin + 1-heptene								
0.3265	212.0	-0.2	0.5999	224.9	-0.4	0.8299	135.2	0.1
0.3996	228.6	0.3	0.6617	210.3	-0.3	0.8952	90.7	-0.1
0.4893	235.6	0.2	0.7315	186.0	0.3			
tetralin + 1-heptyne								
0.3250	-2.7	0.0	0.5590	-2.9	0.0	0.7529	-2.2	0.0
0.3795	-2.8	0.0	0.6156	-2.8	0.0	0.8215	-1.8	0.0
0.4505	-2.9	0.0						

Table A1 (continued)

x	$\frac{H^E_m}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$	x	$\frac{H^E_m}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$	x	$\frac{H^E_m}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$
			tetralin + *n*-octane					
0.1954	305.6	-0.5	0.5719	503.4	0.9	0.7338	409.4	-1.4
0.2768	402.2	2.0	0.5774	502.6	1.6	0.7754	371.4	0.4
0.3529	462.2	-0.4	0.6549	467.8	0.0	0.8733	246.8	0.1
0.4136	491.3	-2.6						
			cyclohexylbenzene + 1-hexene					
0.2580	157.2	0.1	0.4550	194.1	-0.4	0.6679	167.8	0.0
0.3259	177.2	-0.1	0.5037	194.8	0.5	0.7796	127.5	-0.7
0.4090	191.3	-0.2	0.5811	186.9	0.4	0.8196	110.3	0.4
			cyclohexylbenzene + 1-hexyne					
0.2444	75.0	-0.1	0.4868	92.4	-0.3	0.7324	70.8	-0.1
0.3059	84.1	0.0	0.5001	92.3	-0.2	0.7752	63.9	0.4
0.3913	91.5	0.3	0.5548	90.1	-0.1	0.8407	49.3	-0.2
0.4786	93.2	0.3	0.6436	82.8	-0.1			
			cyclohexylbenzene + 1-heptene					
0.2854	185.6	0.2	0.5010	212.9	0.1	0.7933	140.0	-0.1
0.3376	198.4	-0.6	0.5477	208.9	-0.6	0.8222	125.8	0.2
0.4020	209.7	0.2	0.6089	200.3	-0.2	0.8709	97.7	0.1
0.4342	212.7	0.6	0.6906	180.3	0.2			
			cyclohexylbenzene + 1-heptyne					
0.2639	48.5	0.0	0.4695	57.7	-0.3	0.7560	43.2	-0.1
0.3385	54.0	0.0	0.5181	57.3	-0.5	0.8033	37.0	-0.4
0.4119	57.1	0.0	0.5931	56.5	0.8	0.8590	29.3	0.2
0.4819	57.3	0.1	0.6759	51.0	0.2			

Table A1. (continued)

x	$\frac{H_m^E}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$	x	$\frac{H_m^E}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$	x	$\frac{H_m^E}{J.mol^{-1}}$	$\frac{\delta_H}{J.mol^{-1}}$
benzene + 1-heptyne								
0.2339	85.3	-0.1	0.3490	111.9	-2.2	0.6005	144.5	-0.1
0.2823	99.5	1.1	0.4025	125.6	0.9	0.7301	133.8	0.2
0.3439	112.9	-0.1	0.5059	139.7	0.3	0.8247	107.4	-0.1
cyclohexane + 1-heptene								
0.3440	193.8	-0.4	0.5091	236.9	0.5	0.6817	229.3	0.9
0.4234	219.0	0.3	0.5649	239.9	-1.6	0.7462	210.5	1.9
0.4242	218.7	-0.2	0.5666	241.4	-0.1	0.8101	173.9	-0.7
0.4528	266.9	1.0						
cyclohexane + 1-heptyne								
0.2377	423.0	-0.6	0.4694	631.5	-0.6	0.6681	624.6	4.0
0.2941	494.4	0.4	0.5606	645.9	-3.4	0.8002	485.7	-0.7
0.4154	605.9	0.3						
***n*-hexane + 1-heptene**								
0.1982	31.2	0.1	0.5047	47.1	-0.1	0.6777	42.4	-0.1
0.3084	40.2	-0.1	0.5770	46.8	0.1	0.8115	30.1	0.1
0.3974	44.9	0.1	0.6391	44.7	0.1			
***n*-hexane + 1-heptyne**								
0.2567	381.1	0.8	0.5044	517.8	-0.1	0.7181	440.7	-0.4
0.3013	419.9	-1.6	0.6342	495.1	0.1	0.7714	389.8	0.2
0.3974	487.2	1.0						

Table A2 Excess molar enthalpies at 298.15 K for {*x*(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (1-*x*)(cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} and deviations δ_H from equation 5.1 and the coefficients of Table C2

x	H_m^E / J.mol^{-1}	δ_H / J.mol^{-1}	*x*	H_m^E / J.mol^{-1}	δ_H / J.mol^{-1}	*x*	H_m^E / J.mol^{-1}	δ_H / J.mol^{-1}
			decalin + cyclohexene					
0.2265	-35.3	0.3	0.5009	-55.2	0.2	0.7055	-46.5	0.1
0.2479	-38.4	-0.3	0.5386	-55.4	0.1	0.7847	-37.5	-0.3
0.3727	-50.3	-0.4	0.5974	-54.1	0.0	0.8183	-32.0	0.2
0.4752	-54.6	0.4	0.6409	-52.0	-0.2			
			decalin + 1,3-cyclohexadiene					
0.2207	180.8	0.2	0.5001	225.3	-0.2	0.7431	154.5	-0.6
0.3616	222.4	-1.1	0.5326	219.3	-1.8	0.7946	130.3	0.3
0.4662	230.7	2.5	0.6183	202.5	0.8			
			decalin + 1,4-cyclohexadiene					
0.2194	180.9	-0.2	0.4675	231.1	-0.4	0.7498	152.8	-0.1
0.2748	205.3	0.5	0.5318	224.8	0.7	0.8440	104.0	0.3
0.3619	226.4	-0.3	0.6187	203.5	-0.2	0.8765	84.1	-0.2
			decalin + benzene					
0.0891	309.8	0.2	0.3270	712.6	-0.3	0.6388	653.5	3.4
0.1462	457.5	1.6	0.3583	731.0	-0.6	0.6872	592.5	-3.8
0.1532	469.6	-1.8	0.4044	745.6	-2.1	0.8004	429.6	-2.3
0.2542	642.2	-0.2	0.5415	729.1	5.1	0.8963	248.0	0.9
			bicyclohexyl + cyclohexene					
0.3315	33.0	-0.1	0.5523	36.3	0.1	0.6901	29.5	-0.1
0.4215	36.7	0.1	0.5716	35.5	-0.1	0.7570	24.6	0.2
0.5029	37.2	0.1	0.5917	34.8	-0.1	0.8283	17.9	-0.1

Table A2. (continued)

x	H_m^E / J.mol^{-1}	δ_H / J.mol^{-1}	x	H_m^E / J.mol^{-1}	δ_H / J.mol^{-1}	x	H_m^E / J.mol^{-1}	δ_H / J.mol^{-1}
			bicyclohexyl + 1,3-cyclohexadiene					
0.3158	274.3	-2.7	0.4112	292.6	0.4	0.6363	238.0	0.7
0.3165	280.3	3.1	0.4186	291.2	-1.0	0.6416	235.2	0.4
0.3666	287.7	-0.7	0.4783	287.0	-0.6	0.8123	134.4	-1.0
0.3845	291.0	0.4	0.4822	287.5	0.4	0.8671	98.1	0.5
			bicyclohexyl + 1,4-cyclohexadiene					
0.2895	261.6	-1.6	0.4225	280.3	-1.1	0.6420	226.0	-0.1
0.3192	273.4	1.8	0.4839	274.8	-0.2	0.8105	136.5	0.7
0.3801	282.1	1.3	0.5719	252.3	-0.6	0.8791	90.2	-0.3
			bicyclohexyl + benzene					
0.1277	492.0	2.2	0.3847	855.5	1.0	0.6346	698.9	-0.1
0.1806	625.2	0.1	0.4649	850.3	5.2	0.7243	562.0	-2.6
0.1896	642.9	-1.7	0.5174	819.6	3.5	0.8216	399.7	0.8
0.2821	783.6	-7.7	0.5426	800.6	4.0	0.9042	229.9	0.8
0.3431	840.3	0.2						
			tetralin + cyclohexene					
0.2538	130.5	0.2	0.5085	148.3	0.2	0.6607	124.1	-0.6
0.3121	141.5	-0.4	0.5746	140.8	0.1	0.7737	93.9	0.2
0.4037	150.5	0.0	0.6189	133.6	0.2	0.8245	76.1	0.0
0.4630	150.8	0.2						
			tetralin + 1,3-cyclohexadiene					
0.2493	39.8	0.0	0.4191	48.0	-0.1	0.7297	36.5	0.2
0.3001	43.5	0.0	0.5016	48.4	0.2	0.8329	24.9	-0.3
0.3899	47.6	0.1	0.6547	42.0	0.1	0.8749	19.8	0.1

Table A2. (continued)

x	H^E_m / J.mol^{-1}	δ_H / J.mol^{-1}	x	H^E_m / J.mol^{-1}	δ_H / J.mol^{-1}	x	H^E_m / J.mol^{-1}	δ_H / J.mol^{-1}
tetralin + 1,4-cyclohexadiene								
0.2412	19.1	0.0	0.4966	24.8	0.0	0.7872	13.2	0.0
0.2293	21.8	0.0	0.5659	23.5	-0.1	0.8345	10.3	0.1
0.3899	24.5	0.1	0.6490	20.8	0.0	0.8865	6.7	-0.1
tetralin + benzene								
0.0613	49.9	0.9	0.3860	158.9	0.6	0.6640	135.4	-0.9
0.0959	70.3	-0.9	0.4704	163.0	2.0	0.7588	106.9	-1.6
0.1718	106.6	-2.5	0.5462	157.3	0.8	0.8681	65.0	0.5
0.2566	136.0	-0.9	0.5943	149.5	-0.7	0.9250	37.7	0.1
0.3167	151.9	2.3						
cyclohexylbenzene + cyclohexene								
0.2207	86.6	-0.1	0.4001	112.1	0.3	0.7078	89.9	0.7
0.2587	94.8	-0.1	0.4548	113.6	0.2	0.8011	68.7	0.0
0.3561	108.7	0.1	0.5255	111.0	-0.7	0.8394	56.2	-0.7
0.3563	109.0	0.4	0.6289	101.1	-0.1			
cyclohexylbenzene + 1,3-cyclohexadiene								
0.3417	39.4	0.2	0.5595	43.4	0.2	0.7751	29.2	-0.2
0.3989	42.0	-0.1	0.6006	42.2	0.3	0.8013	26.2	-0.5
0.4486	43.3	-0.3	0.6634	39.0	0.4	0.8478	21.7	0.3
0.5086	43.9	-0.2						
cyclohexylbenzene + 1,4-cyclohexadiene								
0.3390	-13.8	0.0	0.6125	-15.3	0.0	0.8160	-11.2	-0.1
0.4493	-15.2	0.0	0.6759	-14.7	0.1	0.8545	-9.6	0.0
0.5051	-15.6	-0.1	0.7484	-13.3	0.0			

Table A2. (continued)

x	$\frac{H^E_m}{\mathrm{J.mol^{-1}}}$	$\frac{\delta_H}{\mathrm{J.mol^{-1}}}$	x	$\frac{H^E_m}{\mathrm{J.mol^{-1}}}$	$\frac{\delta_H}{\mathrm{J.mol^{-1}}}$	x	$\frac{H^E_m}{\mathrm{J.mol^{-1}}}$	$\frac{\delta_H}{\mathrm{J.mol^{-1}}}$
cyclohexylbenzene + benzene								
0.0706	62.1	1.2	0.3098	164.5	0.5	0.6264	154.9	0.5
0.0987	80.7	0.3	0.4177	178.4	3.3	0.7241	126.8	-1.3
0.1443	103.9	-3.4	0.4794	175.8	1.5	0.7997	98.3	-2.3
0.2110	135.6	-1.4	0.5650	166.0	0.3	0.9095	51.1	0.8
benzene + cyclohexene								
0.2206	265.1	0.0	0.4778	393.6	-1.3	0.7347	313.1	1.2
0.3259	343.2	-0.5	0.5805	383.9	-3.3	0.8019	254.1	-1.1
0.4739	398.0	3.5	0.7057	333.3	1.4	0.8977	148.8	-0.1
benzene + 1,3-cyclohexadiene								
0.0927	42.4	-0.2	0.4434	127.2	-0.4	0.6735	116.3	0.2
0.1967	80.9	0.5	0.4863	129.0	-0.6	0.7969	86.0	-0.5
0.2916	105.6	-0.1	0.5577	128.8	0.1	0.8643	63.5	0.3
0.3715	120.5	0.5	0.6008	125.7	0.1			
benzene + 1,4-cyclohexadiene								
0.2030	33.3	-1.2	0.5598	85.0	-0.5	0.8063	55.3	-1.3
0.2983	57.0	2.2	0.6008	86.7	-0.2	0.8116	55.6	0.1
0.3811	69.9	0.0	0.6152	84.3	0.1	0.8661	42.4	0.9
0.4481	79.3	0.4	0.6829	78.2	-0.4			
cyclohexane + cyclohexene								
0.2160	58.4	0.1	0.4174	83.3	0.2	0.6946	72.0	-0.1
0.2738	67.9	-0.3	0.5297	85.1	0.2	0.7820	58.0	0.2
0.3542	78.2	-0.1	0.6516	76.9	-0.3	0.8489	43.4	0.0

Table A2. (continued)

x	H^E_m / J.mol^{-1}	δ_H / J.mol^{-1}	x	H^E_m / J.mol^{-1}	δ_H / J.mol^{-1}	x	H^E_m / J.mol^{-1}	δ_H / J.mol^{-1}
cyclohexane + 1,3-cyclohexadiene								
0.0925	121.1	-0.3	0.4261	327.7	0.2	0.7022	272.8	-0.5
0.1990	225.0	1.2	0.4715	330.9	-0.7	0.7876	217.8	-0.8
0.3186	295.8	-0.7	0.5536	327.8	2.0	0.8819	137.0	0.3
0.3722	315.1	-0.8	0.6032	314.2	0.0			
cyclohexane + 1,4-cyclohexadiene								
0.1102	126.9	-0.1	0.5089	375.0	2.6	0.7624	267.1	-2.9
0.2505	260.7	-0.4	0.5482	370.5	-0.2	0.8324	207.6	1.7
0.3114	305.1	0.0	0.6416	344.7	-0.8	0.8917	140.0	0.0
0.4542	366.1	-0.1						
***n*-hexane + cyclohexene**								
0.2226	156.8	0.7	0.4285	196.2	-0.3	0.6028	180.1	-2.1
0.2725	172.2	-0.9	0.4694	198.6	2.0	0.6409	176.3	2.1
0.3534	189.5	-0.7	0.5848	184.9	-0.5	0.7340	147.2	-0.3
***n*-hexane + 1,3-cyclohexadiene**								
0.1347	229.7	0.6	0.4496	435.6	-0.4	0.5678	421.7	0.1
0.2211	325.2	-1.4	0.4736	436.9	0.2	0.7188	340.1	-0.9
0.3334	405.1	0.1	0.5652	424.0	1.6	0.8024	266.9	0.2
***n*-hexane + 1,4-cyclohexadiene**								
0.1837	300.9	-0.4	0.4441	441.4	-0.9	0.6807	365.5	-1.2
0.2656	379.7	1.5	0.4955	443.3	-0.8	0.7921	270.1	-0.3
0.2915	395.8	-0.4	0.5712	427.7	2.9	0.9328	100.9	0.1
0.3612	429.8	-0.6						

APPENDIX B - EXPERIMENTAL EXCESS MOLAR VOLUMES

Table B1 Excess molar volumes at 298.15 K for {x(a bicyclic compound or benzene or cyclohexane or n-hexane) + (1-x)(a 1-alkene or a 1-alkyne)} and deviations δ_V calculated from equation 5.2 and the coefficients of Table C3

x	V^E_m / $cm^3.mol^{-1}$	$10^4\delta_V$ / $cm^3.mol^{-1}$	x	V^E_m / $cm^3.mol^{-1}$	$10^4\delta_V$ / $cm^3.mol^{-1}$	x	V^E_m / $cm^3.mol^{-1}$	$10^4\delta_V$ / $cm^3.mol^{-1}$
decalin + 1-hexene								
0.1624	-0.4733	25	0.4913	-0.7383	90	0.8051	-0.4171	-25
0.2770	-0.6467	-95	0.5989	-0.7101	-20	0.8440	-0.3290	28
0.3859	-0.7178	34	0.7243	-0.5666	-36			
decalin + 1-hexyne								
0.1500	-0.0065	0	0.4549	-0.0115	-2	0.6395	-0.0094	2
0.2996	-0.0102	1	0.5545	-0.0110	-4	0.7124	-0.0083	1
0.3499	-0.0111	-2	0.5890	-0.0103	-1	0.8673	-0.0051	0
0.4009	-0.0108	4						
decalin + 1-heptene								
0.1754	-0.3288	-8	0.5790	-0.4791	-37	0.7747	-0.3174	25
0.3307	-0.4661	23	0.6380	-0.4424	-8	0.8144	-0.2723	10
0.4159	-0.4940	41	0.7099	-0.3829	24	0.8699	-0.2022	-16
0.5045	-0.5031	-54						
decalin + 1-heptyne								
0.1755	0.0131	0	0.4564	0.0108	1	0.6401	0.0179	-2
0.2561	0.0175	0	0.5135	0.0206	4	0.7181	0.0169	1
0.3588	0.0201	-3	0.5746	0.0191	-2			
bicyclohexyl + 1-hexene								
0.1745	-0.8338	-72	0.4983	-1.1804	-210	0.7705	-0.6903	39
0.2459	-0.9972	143	0.6133	-1.0199	64	0.8604	-0.4466	-29
0.3271	-1.1243	24	0.7343	-0.7799	40			

Table B1. (continued)

x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$
			bicyclohexyl + 1-hexyne					
0.1394	-0.1450	-22	0.4651	-0.2449	-16	0.6259	-0.2219	11
0.1977	-0.1731	33	0.5089	-0.2476	-45	0.7159	-0.1828	30
0.2565	-0.1988	27	0.5465	-0.2363	36	0.7889	-0.1443	-19
0.3851	-0.2388	-36						
			bicyclohexyl + 1-heptene					
0.2700	-0.7364	-16	0.5352	-0.8292	-26	0.7604	-0.5671	-44
0.3917	-0.8308	44	0.6060	-0.7822	-64	0.8241	-0.4309	53
0.4426	-0.8456	14	0.6635	-0.7077	48	0.9203	-0.2108	-9
			bicyclohexyl + 1-heptyne					
0.1700	-0.1056	5	0.4423	-0.1557	41	0.6370	-0.1330	-22
0.3162	-0.1439	-26	0.4718	-0.1566	28	0.8001	-0.0421	4
0.3916	-0.1557	-23	0.5728	-0.1506	-8			
			tetralin + 1-hexene					
0.1270	-0.6270	27	0.4361	-1.2861	-39	0.7545	-0.8278	-101
0.2087	-0.9301	-64	0.5462	-1.2288	15	0.9103	-0.3228	14
0.3576	-1.2034	28	0.5989	-1.1487	121			
			tetralin + 1-hexyne					
0.1594	-0.5532	-10	0.4903	-0.8410	-37	0.6567	-0.7055	68
0.2745	-0.7427	43	0.5361	-0.8212	-20	0.7442	-0.5837	-25
0.3549	-0.8150	-20	0.5914	-0.7814	-5	0.8056	-0.4639	0
0.4024	-0.8361	6						

Table B1. (continued)

x	$\frac{V^E_m}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V^E_m}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V^E_m}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$
				tetralin + 1-heptene				
0.3482	-0.9513	-17	0.6547	-0.8689	-28	0.8329	-0.5022	54
0.4556	-0.9972	53	0.7371	-0.7279	-15	0.8815	-0.3774	-24
0.5432	-0.9809	-23						
				tetralin + 1-heptyne				
0.1745	-0.4007	5	0.5263	-0.6890	-34	0.6595	-0.5895	-30
0.3127	-0.6171	-33	0.5503	-0.6700	50	0.7769	-0.4292	7
0.4071	-0.6807	35						
				cyclohexylbenzene + 1-hexene				
0.1378	-0.5830	8	0.5352	-0.9479	-83	0.7058	-0.7183	-14
0.2372	-0.8302	-39	0.5761	-0.9062	-45	0.8039	-0.5099	94
0.3777	-0.9707	54	0.6333	-0.8328	-11	0.8467	-0.4243	-51
0.4884	-0.9608	87						
				cyclohexylbenzene + 1-hexyne				
0.1490	-0.2706	-27	0.4109	-0.5860	-49	0.6031	-0.4936	60
0.1998	-0.4432	32	0.4677	-0.5724	18	0.7438	-0.3539	-14
0.2372	-0.4876	38	0.5495	-0.5409	-27	0.8847	-0.1610	0
0.3392	-0.5688	-30						
				cyclohexylbenzene + 1-heptene				
0.3482	-0.9513	-17	0.6547	-0.8689	-28	0.8329	-0.5022	54
0.4556	-0.9972	53	0.7371	-0.7279	-15	0.8815	-0.3774	-24
0.5432	-0.9810	-23						

Table B1. (continued)

x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$
			cyclohexylbenzene + 1-heptyne					
0.1803	-0.3147	-20	0.4717	-0.4583	-48	0.6905	-0.3487	16
0.2410	-0.3705	26	0.5492	-0.4330	22	0.7528	-0.2927	13
0.2941	-0.4087	26	0.6121	-0.4068	-15	0.8534	-0.1842	-7
0.4006	-0.4527	-13						
			benzene + 1-hexyne					
0.1273	0.0196	-4	0.4426	0.0387	4	0.7628	0.0384	-4
0.2367	0.0299	6	0.5123	0.0400	-2	0.8289	0.0343	6
0.3700	0.0365	7	0.6190	0.0404	-14			
			benzene + 1-heptene					
0.3675	0.2692	-2	0.5903	0.3146	-10	0.7967	0.2309	1
0.3958	0.2802	1	0.6078	0.3135	-7	0.8928	0.1372	5
0.4610	0.2998	-7	0.7038	0.2884	-1	0.9286	0.0936	-3
0.5213	0.3149	24						
			benzene + 1-heptyne					
0.2863	0.1158	-39	0.5457	0.1428	31	0.8163	0.1111	-14
0.3712	0.1320	20	0.6044	0.1388	-12	0.8546	0.0966	-20
0.4612	0.1416	52	0.7723	0.1204	-36	0.9323	0.0583	18
			cyclohexane + 1-hexyne					
0.1547	0.3009	-6	0.5264	0.6817	-13	0.7501	0.5609	21
0.2695	0.5022	16	0.6458	0.6479	11	0.8062	0.4859	-1
0.3475	0.5982	13	0.6708	0.6293	-14	0.8806	0.3516	-4
0.4410	0.6623	-23						

Table B1. (continued)

x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$
cyclohexane + 1-heptene								
0.1728	0.1498	10	0.3640	0.2452	-5	0.6910	0.2655	22
0.2233	0.1812	-24	0.4589	0.2649	20	0.8126	0.2318	-14
0.2922	0.2219	16	0.5595	0.2655	-30	0.8678	0.1996	5
cyclohexane + 1-heptyne								
0.1547	0.3009	3	0.5001	0.6885	-1	0.7113	0.6323	-16
0.2776	0.4926	-15	0.5487	0.7016	26	0.8300	0.4704	7
0.3274	0.5579	9	0.6290	0.6866	-7	0.9182	0.2662	-1
0.4759	0.6783	-5						
***n*-hexane + 1-hexyne**								
0.2002	0.3131	-2	0.5048	0.5407	-10	0.7479	0.4016	9
0.2821	0.4103	6	0.5946	0.5278	10	0.7787	0.3605	-6
0.3970	0.5050	0	0.6606	0.4871	-7			
***n*-hexane + 1-heptene**								
0.1414	0.0246	-1	0.3815	0.0629	-2	0.6872	0.0561	9
0.2607	0.0477	1	0.4999	0.0675	-3	0.8455	0.0314	-1
0.2627	0.0484	5	0.6085	0.0624	-6			
***n*-hexane + 1-heptyne**								
0.1315	0.0903	-1	0.3836	0.2941	-10	0.6915	0.3080	1
0.2233	0.1712	-2	0.5080	0.3431	-5	0.8126	0.2148	-1
0.2989	0.2368	12	0.6123	0.3402	5			

Table B2 Excess molar volumes at 298.15 K for {x(a bicyclic compound) + (1-x)(cyclohexene or 1,3-cyclohexadiene or 1,4-cyclohexadiene or benzene)} and deviations δ_V calculated from equation 5.2 and the coefficients of Table C4

x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$
			decalin + cyclohexene					
0.2214	-0.1325	2	0.5873	-0.1961	26	0.7528	-0.1462	-4
0.3036	-0.1767	9	0.6995	-0.1757	-81	0.8088	-0.1156	25
0.5268	-0.2028	25						
			decalin + 1,3-cyclohexadiene					
0.1282	0.0408	1	0.4336	0.0695	6	0.6537	0.0493	-6
0.2228	0.0592	-4	0.4939	0.0658	3	0.7364	0.0414	9
0.3225	0.0690	1	0.5748	0.0575	-8	0.8228	0.0298	-2
0.3634	0.0703	2						
			decalin + 1,4-cyclohexadiene					
0.2459	0.1054	5	0.4175	0.1254	1	0.6133	0.1118	-3
0.3090	0.1152	-13	0.4899	0.1252	10	0.7366	0.0880	-1
0.3544	0.1219	2	0.5461	0.1200	-3	0.9041	0.0380	0
			decalin + benzene					
0.0489	0.1266	9	0.3711	0.4811	12	0.6287	0.4292	-12
0.1520	0.3073	-49	0.4428	0.4923	29	0.6816	0.3888	-32
0.2418	0.4107	1	0.4824	0.4910	42	0.8467	0.2169	15
0.2858	0.4427	1	0.5648	0.4605	-36	0.9075	0.1326	-3
0.4543	0.4771	22						
			bicyclohexyl + cyclohexene					
0.1394	-0.0627	10	0.3806	-0.1465	11	0.6798	-0.1227	-11
0.2109	-0.0999	-21	0.4537	-0.1512	14	0.7626	-0.1020	-20
0.3243	-0.1384	-14	0.5261	-0.1472	18	0.8271	-0.0791	13

Table B2 (continued)

x	$\frac{V_m^E}{\mathrm{cm^3.mol^{-1}}}$	$\frac{10^4\delta_V}{\mathrm{cm^3.mol^{-1}}}$	x	$\frac{V_m^E}{\mathrm{cm^3.mol^{-1}}}$	$\frac{10^4\delta_V}{\mathrm{cm^3.mol^{-1}}}$	x	$\frac{V_m^E}{\mathrm{cm^3.mol^{-1}}}$	$\frac{10^4\delta_V}{\mathrm{cm^3.mol^{-1}}}$
bicyclohexyl + 1,3-cyclohexadiene								
0.0720	0.0477	-1	0.3948	0.1115	-17	0.7003	0.0922	0
0.1891	0.0880	2	0.5388	0.1110	4	0.7917	0.0730	-1
0.3078	0.1088	9	0.6114	0.1047	3			
bicyclohexyl + 1,4-cyclohexadiene								
0.1160	0.0988	13	0.4943	0.1642	-1	0.7495	0.1048	7
0.1501	0.1151	-22	0.5745	0.1461	-24	0.8180	0.0842	23
0.2730	0.1615	6	0.6726	0.1257	0	0.8375	0.0730	-20
0.3878	0.1730	19						
bicyclohexyl + benzene								
0.0586	0.1695	-8	0.2359	0.4662	-46	0.5806	0.4785	26
0.0883	0.2424	8	0.3343	0.5295	-20	0.7215	0.3555	-7
0.1256	0.3176	-5	0.3959	0.5378	-34	0.7840	0.2921	-9
0.1694	0.3947	36	0.4806	0.5286	22	0.8794	0.1770	3
0.1947	0.4282	27	0.5384	0.5012	7			
tetralin + cyclohexene								
0.1869	-0.1542	3	0.4849	-0.2350	2	0.6601	-0.2062	0
0.2580	-0.1901	-8	0.5321	-0.2332	-2	0.7328	-0.1776	-3
0.3834	-0.2258	5	0.6004	-0.2223	2	0.8273	-0.1256	1
tetralin + 1,3-cyclohexadiene								
0.1555	-0.1304	7	0.4595	-0.2063	16	0.6600	-0.1674	13
0.2636	-0.1834	-30	0.5097	-0.2047	-6	0.7499	-0.1334	-13
0.3498	-0.1992	21	0.5789	-0.1930	-9	0.8884	-0.0601	2

Table B2 (continued)

x	V_m^E / $\mathrm{cm^3.mol^{-1}}$	$10^4\delta_V$ / $\mathrm{cm^3.mol^{-1}}$	x	V_m^E / $\mathrm{cm^3.mol^{-1}}$	$10^4\delta_V$ / $\mathrm{cm^3.mol^{-1}}$	x	V_m^E / $\mathrm{cm^3.mol^{-1}}$	$10^4\delta_V$ / $\mathrm{cm^3.mol^{-1}}$
tetralin + 1,4-cyclohexadiene								
0.1539	-0.0720	6	0.3945	-0.1201	5	0.6223	-0.1038	-3
0.2049	-0.0902	-6	0.4472	-0.1201	10	0.7352	-0.0809	-3
0.2445	-0.1011	-9	0.5145	-0.1177	-2	0.8500	-0.0504	1
0.3507	-0.1175	2						
tetralin + benzene								
0.0998	0.0023	3	0.3560	0.0176	9	0.7262	0.0103	-2
0.1431	0.0042	-7	0.4832	0.0172	5	0.7833	0.0072	-8
0.1388	0.0102	-1	0.5141	0.0162	-3	0.8375	0.0062	6
0.2316	0.0142	1						
cyclohexylbenzene + cyclohexene								
0.1298	-0.0616	-7	0.3830	-0.1087	-25	0.6440	-0.0860	-3
0.2141	-0.0816	19	0.4344	-0.1028	11	0.8871	0.2195	0
0.3151	-0.0970	-16	0.5401	-0.0960	19			
cyclohexylbenzene + 1,3-cyclohexadiene								
0.2194	-0.0833	-8	0.5111	-0.0923	-17	0.6997	-0.0644	-5
0.3158	-0.0895	30	0.5595	-0.0870	-8	0.7871	-0.0440	-2
0.4035	-0.0971	-22	0.6041	-0.0774	32	0.9029	-0.0156	0
cyclohexylbenzene + 1,4-cyclohexadiene								
0.1568	-0.0499	0	0.4297	-0.0660	0	0.7152	0.0462	-5
0.2131	-0.0569	3	0.5105	-0.0652	1	0.8620	0.0180	1
0.3007	-0.0638	-4	0.6190	-0.0578	5			

Table B2 (continued)

x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$	x	$\frac{V_m^E}{cm^3.mol^{-1}}$	$\frac{10^4\delta_V}{cm^3.mol^{-1}}$
			cyclohexylbenzene + benzene					
0.0416	0.0191	-12	0.3156	0.0680	-3	0.5610	0.0740	40
0.0586	0.0216	13	0.3249	0.0677	-10	0.7189	0.0561	-9
0.0911	0.0382	5	0.4627	0.0748	30	0.7816	0.0425	-30
0.1856	0.0562	-23	0.5584	0.0694	-7	0.9261	0.0173	6

APPENDIX C - SMOOTHING COEFFICIENTS A_r AND B_r

Table C1 Smoothing coefficients A_r from equation 5.1 for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1 alkyne)} at 298.15 K

Mixture	Reference	A_0	A_1	A_2	A_3
decalin +					
n-pentane	This work	215.8	-6.6	28.2	-19.1
n-hexane	9	249.4	-4.1	6.2	-
1-hexene	This work	296.9	-20.3	-22.3	-40.2
1-hexyne	This work	2417.2	45.6	127.6	110.6
n-heptane	9	274.5	-20.2	35.8	-
1-heptene	This work	291.6	24.3	16.4	25.7
1-heptyne	This work	2099.2	-54.9	-122.1	38.8
n-octane	9	326.4	-50.7	37.9	-
n-dodecane	9	500.4	-183.0	69.1	-
n-hexadecane	9	794.2	-215.9	232.3	-
bicyclohexyl +					
n-pentane	This work	91.9	2.9	-14.1	-
n-hexane	13	86.3	52.4	14.4	-
1-hexene	This work	261.4	80.9	45.7	36.1
1-hexyne	This work	2521.8	524.3	-82.0	-142.3
n-heptane	This work	107.6	40.8	37.0	-18.9
1-heptene	This work	251.0	58.4	79.6	-0.7
1-heptyne	This work	2051.0	169.8	143.7	-82.4
n-octane	13	143.0	63.0	5.2	-
n-dodecane	13	261.1	-10.4	-0.7	-
n-hexadecane	13	512.0	-58.7	19.4	-
tetralin +					
n-pentane	This work	1799.7	128.0	-54.8	-
n-hexane	16	1853.3	130.3	142.3	-
1-hexene	This work	898.1	6.9	-5.8	44.6

Table C1 (continued)

Mixture	Reference	A_0	A_1	A_2	A_3
tetralin +					
1-hexyne	This work	161.1	-16.5	-5.7	10.3
n-heptane	16	1953.4	-53.9	157.6	-
1-heptene	This work	941.2	31.9	97.3	18.6
1-heptyne	This work	-11.8	-0.4	-2.1	0.3
n-octane	This work	2033.5	-148.1	97.1	-
n-dodecane	16	2281.2	-452.6	63.2	-
n-hexadecane	16	2627.8	-954.8	307.3	-
cyclohexylbenzene +					
n-pentane	17	1488.8	196.3	263.0	-
n-hexane	17	1564.3	140.4	298.8	-
1-hexene	This work	777.6	74.6	30.3	-4.3
1-hexyne	This work	370.0	48.3	56.3	-20.2
n-heptane	17	1660.5	85.4	309.1	-
1-heptene	This work	851.4	73.5	138.1	7.5
1-heptyne	This work	231.8	13.0	44.7	14.0
n-octane	17	1734.2	26.5	376.8	-
n-dodecane	17	2028.7	-254.5	442.0	-
n-hexadecane	17	2478.2	-564.0	367.8	-
benzene +					
n-pentane[a]	20	3426.2	-834.4	181.5	-9.13
n-hexane	21	3588.7	-562.1	-21.5	-
1-hexene	22	2359.4	-348.7	284.0	-
1-hexyne	23	527.9	-162.0	27.5	-
n-heptane	24	3676.0	-1012.0	-	-
1-heptene	22	2412.5	-553.0	245.0	-208.0
1-heptyne	This work	555.1	-216.4	123.1	17.1
n-octane	20	3877.7	-1156.3	329.0	-12.2

Table C1 (continued)

Mixture	Reference	A_0	A_1	A_2	A_3
benzene +					
n-dodecane[b]	20	4403.6	-2050.2	688.8	-4.4
n-hexadecane	20	5023.2	-2396.7	1637.6	-1026.3
cyclohexane +					
n-pentane	25	763.5	-185.7	77.7	-
n-hexane	26	878.5	-256.4	-	-
1-hexene	26	930.3	-316.3	-	-
1-hexyne	23	2903.7	-446.4	295.0	-
n-heptane	27	982.6	-294.3	3.2	-
1-heptene	This work	939.9	-313.8	126.8	203.1
1-heptyne	This work	2564.2	-603.8	328.6	21.9
n-octane	25	1029.9	-327.9	192.5	-
n-dodecane	25	1432.4	-617.4	274.2	-
n-hexadecane	28	2005.9	-791.5	168.7	11.9
n-hexane +					
n-pentane	[c]	19.5	-	-	-
1-hexene	30	245.1	16.4	2.7	-
1-hexyne	31	2375.0	-184.0	103.0	51.0
1-heptene	This work	188.8	-13.7	21.2	36.6
1-heptyne	This work	2069.9	-215.1	98.1	39.9
n-octane	25	8.8	-5.3	-	-
n-dodecane	25	147.5	20.3	-16.5	-
n-hexadecane	4	454.2	-18.8	49.9	-

[a] A_4 = -125.4. [b] A_4 = 398.7. [c] Interpolated from reference 29.

Table C2 Smoothing coefficients A_r from equation 5.1 for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)} at 298.15 K

Mixture	Reference	A_0	A_1	A_2	A_3
decalin +					
cyclopentane	9	-739.9	30.0	-150.4	-
cyclohexane	9	103.5	-153.3	-68.3	-
cyclohexene	This work	-221.6	24.4	32.5	-28.4
1,3-cyclohexadiene	This work	902.0	217.1	75.5	20.1
1,4-cyclohexadiene	This work	914.8	229.3	53.7	-14.7
benzene	This work	2966.7	639.8	395.3	99.0
cycloheptane	9	35.0	-51.7	-21.6	-
cyclooctane	9	72.1	-18.0	7.5	-
bicyclohexyl +					
cyclopentane	13	-569.7	-35.5	-59.6	-
cyclohexane	13	454.2	104.7	-17.0	-
cyclohexene	This work	148.6	15.6	-37.7	-15.9
1,3-cyclohexadiene	This work	1135.2	403.1	-4.0	-26.2
1,4-cyclohexadiene	This work	1088.1	402.5	122.3	3.7
benzene	This work	3309.9	1213.6	404.0	-98.5
cycloheptane	13	562.4	170.8	7.9	-
cyclooctane	13	658.4	157.3	73.9	-
tetralin +					
cyclopentane	16	985.4	290.6	128.7	-
cyclohexane	16	1931.4	305.6	217.5	-
cyclohexene	This work	595.0	141.3	77.8	36.8
1,3-cyclohexadiene	This work	192.9	25.9	19.8	12.6
1,4-cyclohexadiene	This work	99.0	19.8	-21.3	7.9
benzene	This work	640.2	100.8	69.7	101.8
cycloheptane	16	1707.3	315.2	127.3	-
cyclooctane	16	1619.6	308.3	-25.0	-

Table C2 (continued)

Mixture	Reference	A_0	A_1	A_2	A_3
cyclohexylbenzene +					
cyclopentane	18	647.0	119.9	131.9	111.3
cyclohexane	18	1611.4	288.3	273.8	169.7
cyclohexene	This work	451.3	63.0	44.8	22.9
1,3-cyclohexadiene	This work	176.3	2.9	-25.0	-10.2
1,4-cyclohexadiene	This work	-62.0	7.6	-20.7	-1.6
benzene	This work	692.2	150.1	102.5	49.7
cycloheptane	18	1712.8	279.9	312.0	311.3
cyclooctane	18	1760.3	292.3	368.7	362.1
benzene +					
cyclopentane	32	2390.4	-151.6	349.8	-
cyclohexane	26	3206.9	-184.5	-	-
cyclohexene	This work	1584.5	-38.8	-37.8	-55.4
1,3-cyclohexadiene	This work	519.2	-21.7	7.4	-
1,4-cyclohexadiene	This work	333.6	-126.5	-127.6	-
cycloheptane	33	3210.1	-465.1	297.3	-
cyclooctane	33	3230.7	-543.3	401.8	-
cyclohexane +					
cyclopentane	34	84.5	-40.3	26.8	-
cyclohexene	This work	340.8	3.4	2.4	2.9
1,3-cyclohexadiene	This work	1325.9	80.5	81.8	-
1,4-cyclohexadiene	This work	1488.2	-102.6	-187.1	-
benzene	26	3206.9	184.5	-	-
cycloheptane	35	23.5	20.7	1.2	-2.6
cyclooctane	36	3.2	101.3	12.9	-9.2

Table C2 (continued)

Mixture	Reference	A_o	A_1	A_2	A_3
n-hexane +					
cyclopentane	37	240.6	17.0	70.5	-
cyclohexane	26	878.5	256.4	-	-
cyclohexene	This work	780.8	122.5	157.6	35.3
1,3-cyclohexadiene	This work	1741.1	191.8	156.9	-
1,4-cyclohexadiene	This work	1773.7	295.9	120.9	-
benzene	21	3588.7	562.1	-21.5	-
cycloheptane	38	837.6	254.3	78.7	-7.6
cyclooctane	39	816.1	226.1	94.8	43.6

Table C3 Smoothing coefficients B_r from equation 5.2 for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (an *n*-alkane or a 1-alkene or a 1-alkyne)} at 298.15 K

Mixture	Reference	B_0	B_1	B_2	B_3
decalin +					
n-pentane	7	-5.7238	-1.1650	-0.5337	-1.3860
n-hexane	7	-3.7910	-0.9955	0.3400	0.4600
1-hexene	This work	-2.9871	-0.1679	-0.0725	-1.1851
1-hexyne	This work	-0.0442	-0.0120	-0.0064	0.0135
n-heptane	7	-2.5450	-0.6766	0.1744	0.3634
1-heptene	This work	-1.9940	-0.3165	-0.0968	-0.1006
1-heptyne	This work	0.0811	0.0225	0.0312	-0.0674
n-octane	7	-1.8261	-0.1701	0.0805	-0.2459
n-dodecane	7	-0.2904	-0.0594	0.0438	0.1412
n-hexadecane	7	0.5482	-0.0138	0.0782	-0.3433
bicyclohexyl +					
n-pentane	12	-6.3658	-1.9556	-1.4222	-1.5782
n-hexane	12	-4.4301	-1.3143	-0.6024	0.2157
1-hexene	This work	-4.6327	-1.4049	-0.3041	-0.2249
1-hexyne	This work	-0.9739	-0.0581	-0.0072	-0.4542
n-heptane	11	-3.4222	-0.6018	-0.9509	-0.2944
1-heptene	This work	-3.3622	-0.5788	-0.2978	-0.3782
1-heptyne	This work	-0.6358	-0.0861	0.3977	-0.8090
n-octane	11	-2.7684	-0.3884	0.3687	0.4617
n-dodecane	11	-0.8989	-0.0337	0.1282	0.1137
n-hexadecane	11	-0.4069	-0.0499	0.0711	0.0321
tetralin +					
n-pentane	14	-5.8980	-1.6902	-0.8882	0.1616
n-hexane	14	-3.9556	-0.5220	-0.4632	-0.8812
1-hexene	This work	-5.0729	-1.1503	0.3562	0.1471

Table C3 (continued)

Mixture	Reference	B_0	B_1	B_2	B_3
tetralin +					
1-hexyne	This work	-3.3378	-0.6303	-0.3749	-0.5707
n-heptane	14	-2.6385	-0.4021	-0.2021	0.0021
1-heptene	This work	-3.9908	-0.5579	-0.1962	-0.2022
1-heptyne	This work	-2.7729	-0.4150	0.3900	0.3342
n-octane	14	-1.9996	-0.0379	-0.0217	-0.2712
n-dodecane	14	-0.2592	-0.0453	-0.0347	-
n-hexadecane	14	0.6345	-0.0887	-0.0492	0.1171
cyclohexylbenzene +					
n-pentane	17	-5.7835	-2.1224	-1.3195	-
n-hexane	17	-3.9226	-1.0915	-0.5397	-
1-hexene	This work	-3.8540	-1.1188	-0.3934	-0.1119
1-hexyne	This work	-2.2538	-0.8095	-0.0426	-0.1703
n-heptane	17	-2.7140	-0.4632	-0.1310	-
1-heptene	This work	-2.6143	-0.5154	-0.1539	-0.1721
1-heptyne	This work	-1.7972	-0.4017	-0.0349	-0.1807
n-octane	17	-1.8937	-0.1867	-0.1093	-
n-dodecane	17	0.0308	-0.0084	0.1702	-
n-hexadecane	17	0.9465	-0.1748	0.0385	-
benzene +					
n-pentane	33	0.4665	-0.0023	-0.0780	-
n-hexane	40	1.5878	-0.1980	-	-
1-hexene	40	0.4121	-0.2612	-	-
1-hexyne	This work	0.1582	-0.0292	0.1122	-0.0564
n-heptane	24	2.3541	-0.3269	0.1936	-0.1079
1-heptene	This work	1.2366	-0.3628	0.1568	0.3923
1-heptyne	This work	0.5689	-0.0255	0.1745	-0.3105
n-octane	41	2.8425	0.6129	0.3215	0.0556

Table C3 (continued)

Mixture	Reference	B_0	B_1	B_2	B_3
benzene +					
n-dodecane	33	3.6766	-1.4268	0.8984	-0.6273
n-hexadecane	33	4.0944	-1.9251	1.3578	-1.0891
cyclohexane +					
n-pentane	42	-0.5855	-0.4759	0.0101	-0.0330
n-hexane	43	0.5940	-0.5026	-0.0773	0.4097
1-hexene	40	0.5168	-0.3839	-	-
1-hexyne	This work	2.7260	-0.2512	0.0822	-0.8684
n-heptane	44	1.2390	-0.3760	-0.2200	-
1-heptene	This work	1.0654	-0.1210	0.5734	-0.6802
1-heptyne	This work	2.7543	-0.6866	0.1616	-0.1772
n-octane	44	1.6480	-0.5590	-0.3220	-
n-dodecane	44	2.1410	-0.8450	0.2340	-
n-hexadecane	44	2.4900	-1.296	1.0320	-
n-hexane +					
n-pentane	45	-0.4437	-0.0260	0.1733	-
1-hexene	40	0.2219	-0.1269	-	-
1-hexyne	This work	2.1653	-0.1953	-0.4204	0.2772
1-heptene	This work	0.2710	0.0123	-0.0953	-0.0735
1-heptyne	This work	1.3685	-0.3960	-0.5249	-0.0010
n-octane	46	-0.3403	0.0376	-0.0070	-
n-dodecane	47	-1.3890	-0.7692	-0.1063	-
n-hexadecane	47	-2.1284	-1.2404	-1.0320	-

Table C4 Smoothing coefficients B_r from equation 5.2 for {(a bicyclic compound or benzene or cyclohexane or *n*-hexane) + (a cycloalkane or cyclohexene or a cycloalkadiene or benzene)} at 298.15 K

Mixture	Reference	B_0	B_1	B_2	B_3
decalin +					
cyclopentane	8	-2.5213	-0.3898	-0.0455	-0.1743
cyclohexane	8	-0.5293	-0.7525	0.0971	0.1976
cyclohexene	This work	-0.8304	-0.0443	0.1006	0.0113
1,3-cyclohexadiene	This work	0.2600	0.1507	0.0487	-0.0845
1,4-cyclohexadiene	This work	0.4951	0.1112	0.0522	0.0032
benzene	This work	1.9357	0.3906	0.2145	0.3275
cycloheptane	8	-0.1533	-0.2019	-0.0019	-0.0511
cyclooctane	8	0.0700	-0.0151	-0.0454	-0.1862
bicyclohexyl +					
cyclopentane	12	-2.6409	-0.7465	-0.5151	-0.3916
cyclohexane	10	-0.1551	-0.0820	-0.0062	0.0751
cyclohexene	This work	-0.6046	-0.1324	0.0997	0.3107
1,3-cyclohexadiene	This work	0.4501	0.0781	0.1522	0.0643
1,4-cyclohexadiene	This work	0.6470	0.2898	0.1812	0.0548
benzene	This work	2.0765	0.8177	0.3683	0.0040
cycloheptane	10	0.6755	0.1421	-0.0650	-0.0233
cyclooctane	10	1.0349	0.1837	0.3909	0.2127
tetralin +					
cyclopentane	15	-2.0203	-0.5040	0.1005	0.3501
cyclohexane	15	0.4079	0.2766	0.0950	-
cyclohexene	This work	-0.9397	-0.0626	-0.0276	-0.1090
1,3-cyclohexadiene	This work	-0.8205	-0.2037	-0.0006	-0.1140
1,4-cyclohexadiene	This work	-0.4745	-0.1454	-0.0056	0.0607
benzene	This work	0.0667	0.0228	-0.0087	0.0199
cycloheptane	15	0.8086	0.3998	0.1439	0.1646
cyclooctane	15	1.0505	0.4098	0.0603	-

Table C4 (continued)

Mixture	Reference	B_o	B_1	B_2	B_3
cyclohexylbenzene +					
cyclopentane	18	-1.9989	-0.6595	-0.4399	-0.2041
cyclohexane	18	0.4218	0.2309	0.1378	0.1253
cyclohexene	This work	-0.4070	-0.1159	-0.0245	-0.0811
1,3-cyclohexadiene	This work	-0.3657	-0.1360	-0.0246	-0.1803
1,4-cyclohexadiene	This work	-0.2628	-0.0583	-0.0172	-0.2046
benzene	This work	0.2862	0.0243	0.0993	0.1519
cycloheptane	18	1.2984	0.5874	0.3342	0.1206
cyclooctane	18	1.8265	0.7016	0.5449	0.2443
benzene +					
cyclopentane	48	1.3771	0.0881	0.0273	–
cyclohexane	40	2.6101	0.0248	-	–
cyclohexene	40	0.9791	0.0180	-	-
1,3-cyclohexadiene	49	0.2942	-0.0619	0.0389	-
1,4-cyclohexadiene	49	0.1692	-0.0050	0.0320	-
cycloheptane	50	2.5136	-0.0934	0.0649	-0.1123
cyclooctane	50	2.3489	-0.2124	0.7239	0.1672
cyclohexane +					
cyclopentane	36	0.1646	0.0746	0.0145	-
cyclohexene	40	0.3872	-0.0424	- -	-
1,3-cyclohexadiene	49	1.2447	-0.0828	0.2918	-
1,4-cyclohexadiene	49	1.4367	-0.0578	0.2494	-
benzene	40	2.6101	-0.0248	–	-
cycloheptane	35	-0.1220	-0.0497	-	–
cyclooctane	36	-0.4290	-0.2824	0.0257	0.0061

Table C4 (continued)

Mixture	Reference	B_0	B_1	B_2	B_3
n-hexane +					
cyclopentane	42	-0.2710	-0.0597	-0.1419	–
cyclohexane	43	0.5940	0.5026	-0.0773	-0.4097
cyclohexene	40	-0.4097	0.0608	–	–
1,3-cyclohexadiene	49	0.4068	-0.1047	–	–
1,4-cyclohexadiene	49	-0.2692	0.0418	-0.0395	–
benzene	40	1.5878	0.1980	–	–
cycloheptane	51	-0.8184	0.4529	0.2779	0.1085
cyclooctane	39	-1.9750	0.8680	-0.0110	-0.3150

APPENDIX D - VAPOUR PRESSURE MEASUREMENTS OF PURE SUBSTANCES

D.1 Introduction

The vapour pressure of a substance is temperature dependent and is related to the pressure exerted by the saturated vapour in equilibrium with the substance. Vapour pressures may be determined by two general methods: *(i)* static methods, and *(ii)* dynamic methods.(466) The line of demarcation between these two techniques is however rather diffuse and very often an experimental procedure may constitute a combination of both methods.

The static method involves the direct measurement of the pressure exerted by a sample confined within an isolated system at a constant temperature. The equation $p = \Sigma x_i p_i^o$ relates the vapour pressure, p, to the mole fraction of the components, x_i, and to the vapour pressures of the pure components, p_i^o. The absolute purity of the components is therefore essential to this technique and the presence of lower or higher boiling point impurities tends to lower or raise the measured pressure. Ambrose(70c) has suggested that the presence of impurities will be manifested by different vapour pressures measured for different volumes of the same substance. This technique also requires completely degassed samples.

The dynamic or ebulliometric method entails the measurement of the boiling point of a sample at a fixed temperature. The advantage of this method is that temperature measurements can very often be carried out more accurately and with greater ease than can pressure measurements. The constant pressure within the apparatus is usually maintained by means of an inert gas. It is ssumed that this gas does not affect the behaviour of the substance. Helium is very often employed for this purpose, since its solubility in most liquids is often small.(466)

Ambrose(70c) has reviewed the various experimental techniques for measuring vapour pressures and has included a section concerned with experimental data fitting procedures and theoretical prediction methods. Boublik *et al.*(339) have published a concise compilation of vapour pressures, for a wide range of substances, measured prior to 1984, while the American Petroleum Institute(207) continually updates its vapour pressures of hydrocarbons and of related compounds.

Vapour pressures of all the solutes were required in the determination of the activity coefficients at infinite dilution, as discussed in Chapter 3. Vapour pressures for 1-hexyne and for 1-heptyne were not available in the literature and were determined over the temperature range 273 K to 313 K by a static technique. Vapour pressures for cyclohexene and for 1,4-cyclohexadiene were not reported in the literature(306) at temperatures below 303 K. Since all the calculations for the activity coefficients were carried out at temperatures below 303 K, the vapour pressures for these compounds were also measured.

D.2 Apparatus and experimental details

The apparatus employed in this investigation is represented diagrammatically in Figure D.1. Approximately 5 cm^3 of pure sample was maintained at a constant temperature, and the pressure exerted by the pure component vapour was measured using a large bore mercury manometer. The second arm of the manometer was connected to a reference vacuum.

D.2.1 The vacuum system

The vacuum system is represented diagrammatically in Figure D.1. Boro-silicate glass tubing was used throughout the vacuum system and the number of ground glass joints and taps within the system was reduced to a minimum. This minimized the possibility of leaks occuring in the system and also reduced the contact between the sample vapour and the vacuum grease. The glass tubing was flamed under vacuum between successive sample determinations to remove any adsorbed vapour. High pressure rubber hose was used to connect the vacuum pump to the vacuum system. The entire apparatus was erected around a metal frame attached to a brick wall and resting on a wooden laboratory bench.

The pressure was measured directly with a 20 mm *i.d.* mercury manometer constructed of glass. Care was taken to ensure that the manometer was clamped in a vertical position. The manometer was designed with bulbous traps above each of the limbs, serving to contain the mercury in the event of a pressure surge. Double distilled mercury was used. This was replaced between successive determinations. A check of the optical quality of the glass tubing, which entailed the measurement of the diameter of a steel ball at intervals along the length of the tube, ensured minimal distortion.

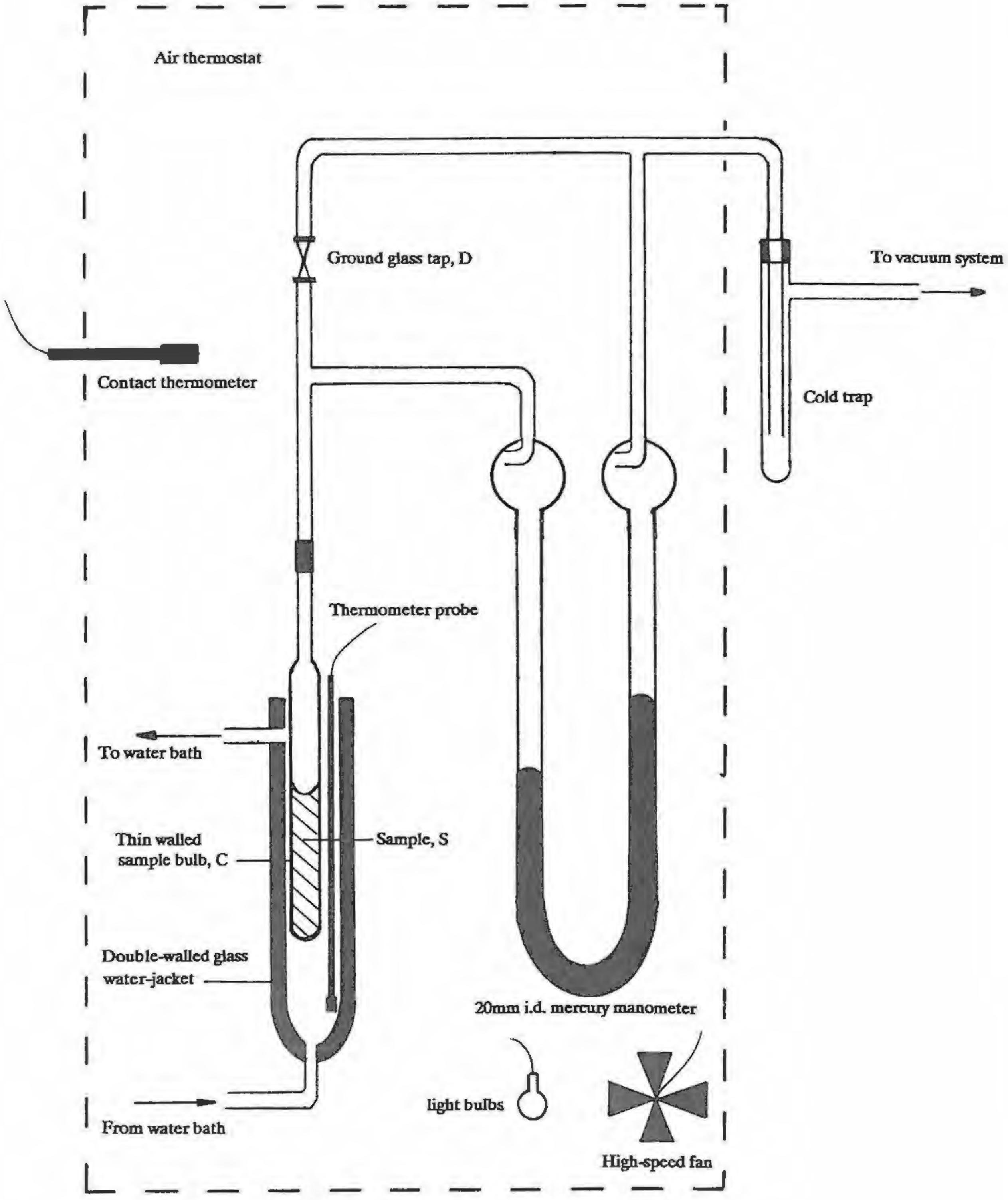

Figure D.1 A diagrammatic representation of the static vapour pressure apparatus

D.2.2 Temperature control and measurement

The sample in the thin glass walled sample bulb, C, was housed in the double walled glass water-jacket, H. A constant temperature was maintained by pumping water through the water-jacket from the water bath system similar to the arrangement described in Section 2.5.2.*(ii)*. The sample temperature corresponded to the temperature of the water within the water-jacket and was measured using a Hewlett-Packard quartz thermometer. The turbulence created by the pumped water was sufficient to ensure against temperature gradients in the water-jacket. The resulting steady state temperature could easily be maintained to within 0.005 K for at least an hour (this was the time taken to ensure thermal equilibrium of the sample).

To prevent condensation of the sample vapour within the cooler parts of the apparatus, those sectious surrounded by a dotted line in Figure D.1 were housed in a large air thermostat of dimensions 600 x 660 x 1200 mm. This was constructed of 30 mm thick sheets of expanded polystyrene. The removable front section was fitted with a transparent perspex observation window, thus facilitating the direct measurement of the mercury levels in the manometer.

The temperature within the thermostat was controlled by a Jumo DBP mercury contact thermometer and a mercury float relay. Heating was achieved through four 250 W standard light bulbs. A 20 cm diameter high speed fan, mounted on a polystyrene base so as to minimize vibration effects, ensured adequate circulation of the air in the thermostat. At 323 K, for example, the maximum temperature fluctuation between the top and the bottom section of the thermostat was only 0.2 K

D.2.3 Introduction and degassing of the sample

The sample cell was attached to the vacuum system via a ground glass joint, D. Wire clamps and Apiezon L grease ensured a leak proof seal at this joint. Degassing of the sample was carried out within the system. The process involved the repeated freezing, evacuation, and thawing of the sample. This sequence was repeated until the mercury levels in the opposite limbs of the manometer were identical for a frozen sample. A completely degassed sample was verified by taking values of the vapour pressure at a single temperature after each sequence. A constant value indicated complete degassing.

D.2.4 The reference vacuum

A schematic representation of the pumping system is given in Figure D.2. An oil diffusion pump was used to maintain the backing vacuum of better than 0.5 torr (measured with a Penning vacuum gauge) required by the Edwards diffusion pump. A reference vacuum of better than 10^{-5} torr (measured with a Penning high vacuum gauge) was maintained throughout the experimental determinations. Two cold traps were used to ensure that no sample vapour entered into the pumping system.

D.2.5 Vapour pressure corrections

A diagrammatic representation of mercury in a manometer under a pressure, *p*, exerted by the vapour of a hypothetical sample, S, is given in Figure D.3. The heights of the mercury levels were measured using a precision brass cathetometer capable of accurate readings to within 0.05 mm. A tripod base with independently adjustable legs ensured that the reference scale of this instrument could be maintained in a vertical position.

The height difference, h_T, corresponding to the difference in height between the two levels of the mercury, A and B, at a temperature, T, is a direct measure of the pressure exerted by the sample. This assumes that the reference arm of the manometer is connected to a good vacuum, C. This pressure relates to the temperature, T, of the sample and to the earths gravitational effect at the place of measurement. It is thus necessary to correct the height readings for temperature effects relating to a standard gravitational effect at sea level and at a standard temperature of 273.15 K. Furthermore, any capillary effects must also be taken into account.

(i) Temperature corrections

In addition to the mercury temperature correction, the brass cathetometer was at ambient temperature, T_a, and not at the calibrated temperature, T_c. Taking into account the thermal expansion of brass, the height difference corrected to 273.15 K is $h_o{}^o$ and is given according to:$^{(467)}$

$$h_o{}^o = h_T[1 + \alpha_B(T_a - T_c)]/[1 + K_m(T - 273.15)] \qquad \text{D.1}$$

where α_B is the coefficient of linear expansion of brass (= 1.84E-05 K^{-1}) and K_m is the coefficient of volumetric expansion of mercury (= 1.818E-04 K^{-1})

1. Vacuum system
2. High vacuum isolation valve
3. Diffusion pump
4. Roughing valve
5. Backing valve
6. Backing pressure guage
7. Throttle valve
8. Air admittance valve
9. Backing pump

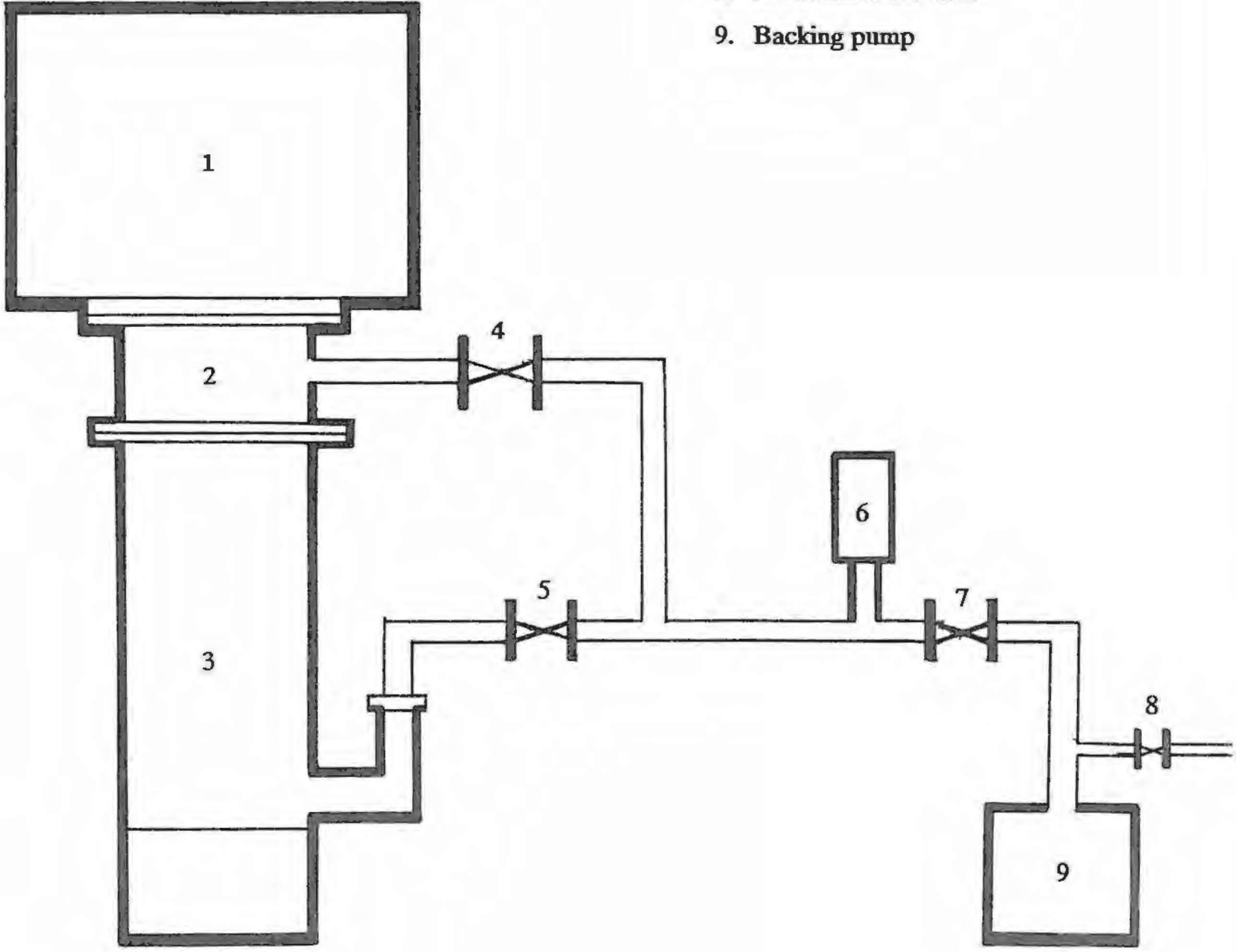

Figure D.2 A diagrammatic representation of the pumping system

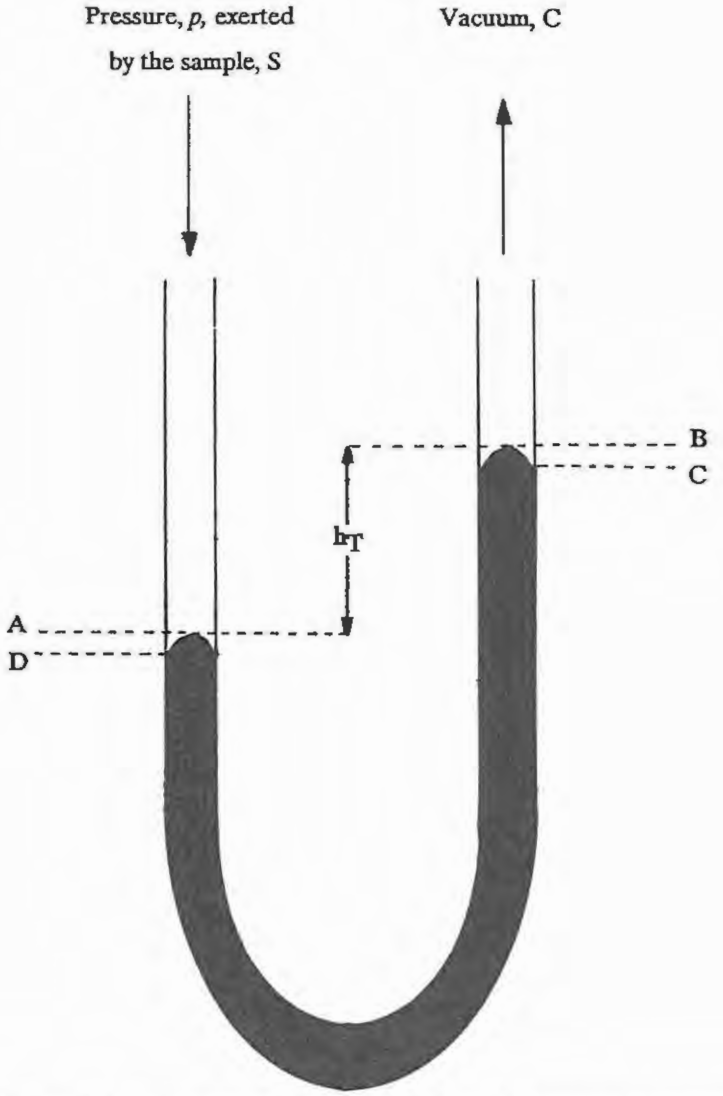

Figure D.3 A diagrammatic representation of a mercury manometer under a pressure *p*

(ii) Capillary corrections

The error introduced by the capillary depression of mercury is independent of the height of the mercury column and of the temperature of the mercury. The capillary depression is however a function of the contact angle of the mercury with the wall of the manometer. The nature of the wall and the presence of moisture and traces of impurities in the mercury may result in variations in this contact angle of between 30 and 90 degrees. The resulting shape of these menisci cannot be predicted by analytical means, nor can they be accurately controlled in a laboratory. The capillary effect can however be minimized by choosing a wide bore tube.(467)

Tables of the capillary depression of clean dry mercury, related to the meniscus height (AD and BC in Figure D.3) and to the diameter of the tube, have been constructed. One such Table by Hala *et al.*(467) was employed in this work.

(iii) Influence of gravity

The thermally corrected height of the mercury column in terms of the standard value of the acceleration due to gravity is given by:(467)

$$h_s = h_o{}^o(g/g_o) \qquad D.2$$

where the gravitational constant is given as 980.66 cm.s^{-1}. The gravitational acceleration, g, in the laboratory is given to a good approximation by:(467)

$$g = 978.039(1 + 0.005294\sin^2\phi - 0.000007\sin^2 2\phi) - 0.0003086H \qquad D.3$$

where ϕ an H are the lattitude and the height above sea-level respectively.

(iv) Error of parallax

Errors of parallax were avoided by ensuring that the cathetometer telescope and the mercury meniscus were always in a horizontal plane. To guard against distortions through insufficient illumination of the meniscus, a small pilot light was placed behind the manometer. Heating effects from this source were considered to be too small to take into account.

D.3 General experimental procedure

The vapour pressure for cyclohexane has been determined by various workers(339) and has been suggested as a standard test compound.(70c) In order to test the experimental technique the vapour pressures for cyclohexane were measured at approximately 5 K intervals in the range 273 K to 313 K. Corrected values were found to lie within 0.2% or 0.2 mm.Hg of the literature values and are given in Table D.1.

The vapour pressures for the substances 1-hexyne, 1-heptyne, cyclohexene and 1,4-cyclohexadiene were measured over the temperature range 273 K to 313 K. The corrected values are included in Table D.1. The results for cyclohexene and for 1,4-cyclohexadiene are within 0.3 mm.Hg of the extrapolated literature values.(306)

Table D.1 Vapour pressures for 1-hexyne, 1-heptyne, cyclohexane, cyclohexene and 1,4-cyclohexadiene at various temperatures

$\frac{p}{\text{mm.Hg}}$	$\frac{T}{K}$	$\frac{p}{\text{mm.Hg}}$	$\frac{T}{K}$	$\frac{p}{\text{mm.Hg}}$	$\frac{T}{K}$
1-hexyne					
59.14	281.36	91.23	289.76	141.93	299.16
69.33	284.34	94.87	290.55	167.59	302.85
74.37	285.67	107.55	293.15	190.39	305.81
83.26	287.91	127.70	296.81		
1-heptyne					
12.59	278.14	25.34	289.68	51.37	302.89
13.53	279.29	29.29	292.14	57.65	304.72
14.54	280.41	33.51	294.51	62.47	306.33
18.14	283.89	37.29	296.48	72.99	309.35
19.67	285.31	39.93	297.72	82.51	311.91
23.09	287.94	47.43	301.00		
cyclohexane					
33.65	276.37	58.28	287.16	101.26	299.10
41.22	280.30	70.32	291.13	128.41	304.36
47.99	283.38	82.02	294.39	160.22	308.69
cyclohexene					
30.97	277.32	55.13	288.53	98.14	300.50
38.43	281.37	67.42	292.37	115.31	304.05
46.27	285.14	84.41	297.27	132.19	309.32
1,4-cyclohexadiene					
23.22	277.26	47.92	291.03	81.42	302.30
30.49	282.23	59.17	295.31	95.31	305.82
39.21	287.26	72.51	299.62		

The estimated uncertainty in the vapour pressure results is of the order of 0.1-0.2 mmHg. This is attributed to the errors resulting from small vibrations caused by the action of the high speed fan and the uncertainty of 0.05 mm in the cathetometer readings.

D.4 Curve fitting of results

The introduction of the pressure correction factor Δz into the Clausius-Clapeyron equation yields the more precise equation:(467)

$$[\delta \ln p/\delta(1/T)] = -\Delta H_v/R\Delta z_v \qquad \text{D.4}$$

The term Δz corresponds to the difference between the compressibility factors of the vapour and the liquid and takes into account the correction for non-ideality of the vapour phase and the liquid phase. Most equations for the estimation of the vapour pressure stem from the integration of equation D.4. To this end it becomes necessary to make certain assumptions concerning the dependence of $\Delta H_v/\Delta z_v$ on the temperature. The simplest approach is to assume that this term is a constant. The integration of equation D.4 yields:(467)

$$\log_{10} p = A - B/T \qquad \text{D.5}$$

where $B = \Delta H_v/\Delta z_v$, and A is a constant of integration. Equation D.5 is however a rather crude approximation and is only suitable for conditions relating to small temperature ranges or for application to substances with low boiling points.(467)

A series of semi-empirical equations relating the pressure to the temperature have been reviewed in detail in the literature.(467-469) One of the oldest and yet the most widely used of these equations is the Antoine equation:

$$\log_{10} p = A - B/(C + T) \qquad \text{D.6}$$

where A, B and C are commonly refered to as the Antoine coefficients. This equation has the advantage of being precise and at the same time permits the representation, for most substances, of the dependence of the vapour pressure to the temperature, for a wide range of temperatures. Reid(468) does not advocate the use of this equation for pressures above 1500 - 2000 mmHg when the constants have been determined from experimental data at temperatures below the boiling point of the substance.

The regression from experimental data remains the best method for obtaining the Antoine coefficients. Methods for the graphical fitting of equations and the evaluation of constants from selected points have been given by Hala *et al.*,(467) Thomson,(470) and by Miller,(471) while Willingham *et al.*(472) discuss various least squares methods.

A Fortran computer programme, LSQRS, was written in this work for the determination of the Antoine coefficients. A listing of this programme is given in Appendix F. Also included are operating instructions for both this programme as well as for a similar programme written by Marsicano.(473) Antoine coefficients for all of the solutes used in this investigation were estimated using both of these pragrammes. The resulting coefficients agreed in all cases to within at least 2 decimal places of each other. The standard deviations between the experimental values and the predicted values determined by the programme LSQRS were generally smaller in magnitude than those values predicted by the programme of Marsicano. Coefficients predicted by LSQRS were employed in preference for determining the γ_{13}^{∞} results and are given in Table 3.2.

APPENDIX E - CALIBRATION OF THE HEWLETT-PACKARD 2804 A QUARTZ THERMOMETER

The Hewlett Packard quartz thermometer was used for all the accurate temperature measurements in this work, and was calibrated against a Tinsley platinum resistance thermometer, which had been previously calibrated by the CSIR-South Africa. The resistance of the platinum thermometer at any temperature, T, was measured with an FE Smith difference bridge. This is a modification of a Kelvin double bridge. This and other Wheatstone bridge type assemblies have been discussed by Hall and Barber.(474) The off-balance current was amplified using a PYE Galvanometer Photocell preamplifier, and was fed to a PYE Scalamp galvanometer. A 2V emf source was used to drive the circuit.

The heating effects could not be neglected for accurate readings. To a first approximation the heating effect at different temperatures is constant if the current in the thermometer bulb is kept constant. This is only true if the conditions of heat transfer between the bulb and its surroundings remain approximately the same. For this reason calibration was carried out in an environment closely resembling that in which later measurements would be made. The calibration of the quartz thermometer was carried out at 5 K intervals over the temperature range 273 K to 323 K in a thermostatted bath similar to the one described in Section 2.5.2 *(ii)*.

To eliminate any stray emf's it was necessary to take resistance readings of both the platinum resistance thermometer and of the standard resistance with the current flowing in both directions in turn; that is four readings, x_i, for each temperature. The resistance, R_T, of the thermometer at the temperature, T, is given to a good approximation by:

$$R_T = [(x_3 + x_4)/2] - [(x_1 + x_2)/2] \qquad \text{E.1}$$

where the first term in equation E.1 corresponds to the average of the resistance of the standard resistance, R, with the current flowing in both directions, and the second term is with respect to the platinum resistance thermometer at the temperature, T.

Resistance readings were converted to temperature values using the iterative relationship:

$$T^* = [(R_T - R_o)/\alpha R_o] + \delta[(T/100) - 1)](T/100) \qquad \text{E.2}$$

together with:

$$t_{68} = T^* + 0.045(T^*/100)[(T^*/100) - 1][(T^*/630.74) - 1] \qquad \text{E.3}$$

where α, δ and R_0 are the constants for the platinum resistance thermometer. In this case: $\alpha = 3.9214\text{E-}03$, $\delta = 1.4962$ and $R_0 = 24.9573\Omega$.

APPENDIX F - COMPUTER PROGRAMMES

The following is intended as a brief guide to the computer programmes used in this work. The *Fortran* programmes were written for a dual processor Control Data Cyber 820 mainframe computer at Rhodes University. The programmes written in *Applesoft Basic* can be run on any Apple 11 or Apple compatible computer.

APPENDIX F1. Computer programme to determine excess molar volumes from density measurements.

```
10   REM   **********************************************************
20   REM
30   REM  THE FOLLOWING PROGRAM IS WRITTEN IN APPLESOFT BASIC FOR ANY
          APPLE 11 COMPUTER .
40   REM  THIS PROGRAM CALCULATES EXCESS VOLUMES FOR BINARY LIQUID
          MIXTURES FROM DENSITY MEASUREMENTS . BY THE FOLLOWING SIMPLE
          RELATIONSHIP :
50   REM
60   REM
70   REM     VE = ((XA*MA + XB*MB) / P.UNKNOWN ) - (CA + CB)
80   REM
90   REM
100   REM      WHERE : P.UNKNOWN IS THE DENSITY OF THE MIXTURE
110   REM             C1 = ((XA*MA) / P.A)
120   REM             C2 = ((XB*MB) / P.B)
130   REM
140   REM
150   REM    ( AN ANTON PAAR VIBRATING TUBE DENSITOMETER WAS USED IN THIS
             STUDY ) .
160   REM
170   REM
180   REM                                  R C BAXTER
190   REM                                  RHODES UNIVERSITY
200   REM
210   REM   *********************************************************
220   HOME
230   PRINT " THE FOLLOWING PROGRAM CALCULATES EXCESS VOLUMES "
240   PRINT : PRINT : PRINT
250   PRINT " INPUT THE FOLLOWING CONSTANTS :
260   PRINT " ------------------------------ "
270   PRINT
280   REM   *********************************************************
290   REM  INPUT CONSTANTS.
300   REM   *********************************************************
310   PRINT " ( MA AND MB - MOLAR MASSES . T- PERIODS FOR WATER(W) , UNKNOW
      N(U) , STD.(S) AND COMPOUNDS A AND B . B- MASSES OF SAMPLE CONTAINER(
      B0) , CONTAINER+A(BA) AND CONTAINER+A+B(BB) ."
320   PRINT " DS AND DW ARE THE DENSITIES OF STD AND WATER RESPECTIVELY ) "

330   PRINT
340   PRINT " NOTE :- SEPARATE VALUES BY COMMAS "
350   PRINT : PRINT
360   PRINT " INPUT YOUR VALUES FOR : MA,MB,TW,TS,TA,TB,DW,DS "
370   INPUT MA,MB,TW,TS,TA,TB,DW,DS
380   PRINT : PRINT
390   PRINT " INPUT YOUR VALUES FOR : B0,BA,BB,TU "
400   INPUT B0,BA,BB,TU
410   PRINT : PRINT
420   INPUT " IS THE PRINTER SWITCHED ON ? > ";YN$
430   IF (YN$ = "YES") OR (YN$ = "Y") GOTO 450
440   IF (YN$ = "NO") OR (YN$ = "N") GOTO 470
450   PR# 1
460   PRINT  CHR$ (137)"B0N"
470   PRINT : PRINT
```

```
480  PRINT " THE CONSTANTS ARE : "
490  PRINT " ----------------- "
500  PRINT
510  PRINT MA,MB,TW,TS,TA,TB,DW,DS,B0,BA,BB,TU
520  PR# 0
530  REM   ***************************************************************
540  REM  PERFORM CALCULATIONS.
550  REM   ***************************************************************
560  REM   CALCULATE MOLE RACTIONS .
570  REM   ***************************************************************
580 XA = ((BA - B0) / MA) / ((BA - B0) / MA + (BB - BA) / MB)
590 XB = 1.0 - XA
600  REM   ***************************************************************
610  REM  CALCULATE EXCESS VOLUME .
620  REM   ***************************************************************
630 C = (DW - DS) / (TW ^ 2 - TS ^ 2)
640 DU = C * (TU ^ 2 - TW ^ 2) + DW
650 DA = C * (TA ^ 2 - TW ^ 2) + DW
660 DB = C * (TB ^ 2 - TW ^ 2) + DW
670 VE = (XA * MA + XB * MB) / DU - XA * MA / DA - XB * MB / DB
680  REM   ***************************************************************
690  REM  PRINT RESULTS
700  REM   ***************************************************************
710  PRINT : PRINT
720  PRINT " THE RESULTS WILL NOW BE PRINTED OUT "
730  PRINT : PRINT
740  INPUT " IS THE PRINTER SWITCHED ON ? > ":YN$
750  IF (YN$ = "YES") OR (YN$ = "Y") GOTO 770
760  IF (YN$ = "NO") OR (YN$ = "N") GOTO 790
770  PR# 1
780  PRINT  CHR$ (137),"80N"
790  PRINT : PRINT
800  PRINT " *************************************** "
810  PRINT
820  PRINT " THE RESULTS ARE :- "
830  PRINT " ---------------- "
840  PRINT : PRINT
850  PRINT " DENSITY OF MIXTURE = "DU
860  PRINT " ------------------- "
870  PRINT " MOLE FRACTION OF COMPONENT A = "XA
880  PRINT " ---------------------------- "
890  PRINT " EXCESS VOLUME = "VE
900  PRINT " ------------- "
910  PRINT
920  PRINT " *************************************** "
930  PRINT : PRINT
940  PR# 0
950  INPUT " DO YOU WANT TO USE THE PROGRAM AGAIN ? > ";YN$
960  IF (YN$ = "YES") OR (YN$ = "Y") GOTO 990
970  IF (YN$ = "NO") OR (YN$ = "N") GOTO 1020
980  PRINT : PRINT
990  INPUT " DO YOU WANT TO EMPLOY THE SAME CONSTANTS IN YOUR NEXT CALCULA
     TION? > ";YN$
1000  IF (YN$ = "YES") OR (YN$ = "Y") GOTO 380
1010  IF (YN$ = "NO") OR (YN$ = "N") GOTO 350
1020  PR# 6
1030  END
```

APPENDIX F2. Computer programme to determine the density of a pure liquid sample.

```
10  REM  ***************************************************************
20  REM
30  REM  THIS PROGRAM IS WRITTEN IN APPLESOFT BASIC FOR AN APPLE 11.
40  REM  FROM A MACHINE CONSTANT C FOR AN ANTON PAAR VIBRATING TUBE
50  REM  DENSITOMETER , TOGETHER WITH PERIOD AND DENSITY VALUES FOR 2
60  REM  STANDARDS (AT A GIVEN TEMPERATURE) , THE DENSITY OF A LIQUID
70  REM  SAMPLE CAN BE GIVEN BY :
80  REM
90  REM
100  REM     P.SAMPLE = C*(TU^2 - TW^2) + PW
110  REM
120  REM      WHERE : TU & TW ARE THE PERIODS OF VIBRATION VALUES OF THE

130  REM             SAMPLE , AND FOR WATER RESPECTIVELY
140  REM             PW = THE DENSITY OF WATER
150  REM
160  REM      NOTE : THE ABOVE CONSTANTS ARE AT TEMPERATURE T .
170  REM
180  REM
190  REM                      R C BAXTER
200  REM                      RHODES UNIVERSITY
210  REM
220  REM  **************************************************************
230  HOME
240  PRINT " THE FOLLOWING PROGRAM DETERMINES A DENSITY VALUE PU FOR "
250  PRINT " YOUR LIQUID SAMPLE , AT A TEMPERATURE T."
260  PRINT
270  PRINT " INPUT THE FOLLOWING CONSTANTS (VALID FOR AN ANTON PAAR "
280  PRINT " VIBRATING TUBE DENSITOMETER.) "
290  PRINT
300  REM  **************************************************************
310  REM  INPUT THE NECESSARY CONSTANTS . PS AND TS ARE THE DENSITY AND
320  REM  PERIOD VALUES FOR THE STANDARD AT TEMPERATURE T
330  REM  **************************************************************
340  PRINT : PRINT
350  PRINT " 1. PW AND PS ARE THE DENSITIES FOR WATER AND FOR THE STD. "
360  PRINT " 2. TW , TS AND TU ARE THE PERIOD OF VIBRATION VALUES FOR "
370  PRINT " WATER , STANDARD AND SAMPLE. "
380  PRINT " NOTE: THE ABOVE ARE ALL AT TEMPERATURE T (IN KELVIN). "
390  PRINT
400  PRINT " INPUT YOUR VALUES IN THE ABOVE ORDER . SEPARATE EACH BY "
410  PRINT " A COMMA . "
420  PRINT
430  INPUT PW,PS,TW,TS,TU,T
440  REM  **************************************************************
450  REM  CALCULATE THE CONSTANT C
460  REM  **************************************************************
470 C = ((PW - PS) / (TW ^ 2 - TS ^ 2))
480  REM  ***************************************************************
490  REM  DETERMINE THE DENSITY (PU)
500  REM  ***************************************************************

510 PU = C * (TU ^ 2 - TW ^ 2) + PW
520  REM  ***************************************************************
530  REM  PRINT OUT RESULT
540  REM  ***************************************************************
```

```
550   HOME
560   INPUT " PRINT OUT THE RESULT . IS THE PRINTER ON ? > ";YN$
570   IF (YN$ = "YES") OR (YN$ = "Y") GOTO 590
580   IF (YN$ = "NO") OR (YN$ = "N") GOTO 600
590   PR# 1
600   PRINT : PRINT : PRINT
610   PRINT " THE DENSITY OF YOUR SAMPLE AT TEMP=  "T"  K ; IS  "PU
620   PRINT " ---------------------------------------------------------"
630   PR# 0
640   PRINT : PRINT : PRINT
650   INPUT " DO YOU WISH TO USE THE PROGRAM AGAIN ? > ";YN$
660   IF (YN$ = "YES") OR (YN$ = "Y") GOTO 270
670   IF (YN$ = "NO") OR (YN$ = "N") GOTO 680
680   END
```

APPENDIX F3. Computer programme to determine activity coefficients at infinite dilution.

Notes on the use of the programme:

(1) A menu is initially displayed.

(2) The cursor can be moved using the *left* and *right* arrows. The *left* arrow moves the cursor up through the field and the *right* arrow moves the cursor down through the field.

(3) Press <return> to enter any value.

(4) When all the values have been entered, move the cursor to the *perform calculations* option and press <return>.

(5) The process can be repeated for further runs. Only the new data values need to be entered.

(6) <ctrl> <R> will replot the screen.

```
10  REM  ***************************************************************
20  REM
30  REM
40  REM  THIS PROGRAM IS WRITTEN IN APPLESOFT BASIC FOR ANY APPLE 11
         COMPUTER .
50  REM  ACTIVITY COEFFICIENTS AT INFINITE DILUTION ARE CALCULATED ,
         EMPLOYING VALUES DETERMINED BY GAS-LIQUID CHROMATOGRAPHY .
60  REM  COLUMN PRESSURE AND FLOWRATES WERE MEASURED AT THE COLUMN
         INLET . THESE VALUES ARE ADJUSTED TO THE OUTLET VALUES , BY
         TAKING INTO ACCOUNT CORRECTIONS FOR COMPRESSIBILITY OF THE
70  REM  MOBILE PHASE .
80  REM   THE PROGRAM IS ONLY VALID FOR EXPERIMENTS CARRIED OUT WITH
90  REM  NITROGEN AS CARRIER GAS . ( FOR OTHER CARRIER GASSES THE
100  REM  NECESSARY ALTERATIONS NEED TO BE MADE TO CONSTANTS Q0-Q3 ) .
110  REM
120  REM    MANY THANKS TO  S . LAWRIE FOR PROGRAMMING HELP RECEIVED IN
130  REM  REFINING THE CURSOR AND CHARACTER INPUT SECTIONS OF THIS
140  REM  PROGRAM .
150  REM
160  REM
170  REM
180  REM                                   R . C . BAXTER
190  REM                                   RHODES UNIVERSITY
200  REM
210  REM
220  REM  ****************************************************************

230  REM  VARIABLE DECLARATION .
240  REM
250  REM  ***************************************************************
260  REM
270 CH = 1: REM  CHOICE
280 PR = 1: REM  PRINTER SLOT
290 N3 = 0: REM  # MOLES
300 T = 0: REM   BATH TEMP
310 A = 0: REM    ANTOINE
320 B = 0: REM    COEFFICIENTS
330 C = 0: REM    FOR WATER
340 TG = 0: REM  DEAD TIME
350 IS = 0: REM  INJECTION SIZE
360 CL = 0: REM  COLUMN LOADING
370 TT = 0: REM  ROOM TEMP
380 TF = 0: REM  FLOW TIME
390 B1 = 0: REM  SOL.VIR.COEFF
400 B2 = 0: REM  MIX.VIR.COEFF
410 V1 = 0: REM  SOL.MOL.VOL
420 PI = 0: REM  INLET PRESSURE
430 PO = 0: REM  OUTLET PRESSURE
440 TR = 0: REM  RETENTION TIME
450 AS = 0: REM   ANTOINE
460 BS = 0: REM   COEFFICIENTS
470 CS = 0: REM   FOR SOLUTES
480  REM
490  REM  ***************************************************************
500  REM  END OF DECLARATIONS .
510  REM  ***************************************************************
520  REM
530  REM  DECLARE CONSTANTS USED THROUHOUT THE PROGRAM .
540  REM  ***************************************************************
550  REM
560 R = 8.314: REM  UNIVERSAL GAS CONSTANT
570 FA = 1.0E - 6
580  REM
590  REM  ***************************************************************
600  REM  Q0-Q3 ARE THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF B11 VERSUS
610  REM  TEMPERATURE FOR NITROGEN CARRIER GAS .
620  REM  NOTE :- THESE COEFFICIENTS MUST BE CHANGED IF ANOTHER CARRIER
           GAS IS USED .
630  REM  ***************************************************************
640  REM
```

```
650 Q0 =  - 10.0420894184
660 Q1 = .2518122528206
670 Q2 =  - .001326996342857
680 Q3 = .00000464
690  REM
700  REM  ************************************************************
710  REM  DEFINE THE POLYNOMIAL DISCUSSED ABOVE .
720  REM  ************************************************************
730  REM
740  DEF  FN CG(K) = Q0 + (Q1 * K) + (Q2 * K * K) + (Q3 * K * K * K)
750  REM
760  REM  ***********************************************************
770  REM
780  REM
790  REM                            MAIN PROGRAM
800  REM                            ------------
810  REM
820  REM
830  REM   **********************************************************
840  REM  LOOPING TO GET THE PARAMETER VALUES .
850  REM  **********************************************************
860  HOME
870  PRINT " INSTRUCTIONS ON HOW TO USE THIS PROGRAM := "
880  PRINT " ------------------------------------------ "
890  PRINT " 1. PRESS <RETURN> TO ENTER A VALUE . "
900  PRINT " 2. <LEFT ARROW> MOVES CURSOR UP THROUGH THE FIELD . "
910  PRINT " 3. <RIGHT ARROW> MOVES CURSOR DOWN THROUGH THE FIELD ."
920  PRINT : PRINT : PRINT
930  INPUT " INPUT HEADING PLEASE := ";H$
940  FOR J = 1 TO  LEN (H$)
950 L$ = L$ + "-"
960  NEXT J
970  REM
980  GOSUB 1710: REM  SKELETON
990  GOSUB 1440: REM  FIGURES
1000  REM
1010  REM  ***********************************************************
1020  REM  ORGANISE THE CURSOR .
1030  REM  **********************************************************
1040  REM
1050  VTAB 2 + CH: HTAB 1: INVERSE : PRINT " ": NORMAL
1060  WAIT  - 16384,128: GET A$
1070  IF A$ =  CHR$ (18) THEN  GOSUB 1710: GOSUB 1440: GOTO 1050
1080  IF A$ =  CHR$ (13) THEN 1150
1090  VTAB 2 + CH: HTAB 1: PRINT " ";
1100  IF A$ =  CHR$ (8) THEN CH = CH - 1: IF CH < 1 THEN CH = 21
1110  IF A$ =  CHR$ (21) THEN CH = CH + 1: IF CH > 21 THEN CH = 1
1120  GOTO 1050
1130  PRINT  SPC( LU);H$
1140  PRINT  SPC( LU);L$
1150  REM
1160  REM  **********************************************************
1170  REM  HANDLE THE ABOVE CHOICE .
1180  REM  **********************************************************
1190  REM
1200  IF CH = 21 THEN 2010
1210  VTAB CH + 2: HTAB 27: CALL  - 868: INPUT "";ZZ
1220  ON CH GOTO 1230,1240,1250,1260,1270,1280,1290,1300,1310,1320,1330,13
    40,1350,1360,1370,1380,1390,1400,1410,1420,1500
1230 N3 = ZZ: GOTO 1430
1240 T = ZZ: GOTO 1430
1250 A = ZZ: GOTO 1430
1260 B = ZZ: GOTO 1430
1270 C = ZZ: GOTO 1430
1280 TG = ZZ: GOTO 1430
1290 IS = ZZ: GOTO 1430
1300 CL = ZZ: GOTO 1430
1310 TT = ZZ: GOTO 1430
1320 TF = ZZ: GOTO 1430
1330 B1 = ZZ: GOTO 1430
1340 B2 = ZZ: GOTO 1430
1350 V1 = ZZ: GOTO 1430
```

```
1360 PI = ZZ: GOTO 1430
1370 PO = ZZ: GOTO 1430
1380 TR = ZZ: GOTO 1430
1390 AS = ZZ: GOTO 1430
1400 BS = ZZ: GOTO 1430
1410 CS = ZZ: GOTO 1430
1420 PR = ZZ: GOTO 1430
1430  GOTO 1050
1440  REM
1450  REM  *************************************************************
1460  REM  FILL IN THE FIGURES .
1470  REM  *************************************************************
1480  REM
1490  VTAB 3
1500  HTAB 27: PRINT N3
1510  HTAB 27: PRINT T
1520  HTAB 27: PRINT A
1530  HTAB 27: PRINT B
1540  HTAB 27: PRINT C
1550  HTAB 27: PRINT TG
1560  HTAB 27: PRINT IS
1570  HTAB 27: PRINT CL
1580  HTAB 27: PRINT TT
1590  HTAB 27: PRINT TF
1600  HTAB 27: PRINT B1
1610  HTAB 27: PRINT B2
1620  HTAB 27: PRINT V1
1630  HTAB 27: PRINT PI
1640  HTAB 27: PRINT PO
1650  HTAB 27: PRINT TR
1660  HTAB 27: PRINT AS
1670  HTAB 27: PRINT BS
1680  HTAB 27: PRINT CS
1690  HTAB 27: PRINT PR
1700  RETURN
1710  REM
1720  REM  *************************************************************

1730  REM  PRINTING OUT THE BASIC DISPLAY .
1740  REM  *************************************************************
1750  REM
1760  HOME : VTAB 1
1770  HTAB 8: PRINT "CARRIER GAS IS NITROGEN"
1780  PRINT
1790  PRINT " NO. MOLES. . . . . . . . .."
1800  PRINT " BATH TEMPERATURE (K) . .."
1810  PRINT " ANTOINE COEFFICIENTS  A.."
1820  PRINT "   FOR WATER AT        B.."
1830  PRINT "   BATH TEMPERATURE    C.."
1840  PRINT " DEAD TIME (SEC). . . . .."
1850  PRINT " INJECTION SIZE . . . . .."
1860  PRINT " COLUMN LOADING . . . . .."
1870  PRINT " ROOM TEMPERATURE (K) . .."
1880  PRINT " FLOW TIME (SEC). . . . .."
1890  PRINT " SOL.VIR.COEFF  (M3/MOL).."
1900  PRINT " MIXED VIR.CFF. (M3/MOL).."
1910  PRINT " SOLUTE MOL.VOL (M3/MOL).."
1920  PRINT " INLET PRESSURE (MMHG). .."
1930  PRINT " OUTLET PRESSURE (MMHG) .."
1940  PRINT " RETENTION TIME (SEC) . .."
1950  PRINT " ANTOINE COEFFICIENTS  A.."
1960  PRINT " FOR SOLUTE            B.."
1970  PRINT "                       C.."
1980  PRINT " PRINTER SLOT . . . . . .."
1990  INVERSE : HTAB 6: PRINT "PERFORM CALCULATIONS": NORMAL
2000  RETURN
2010  REM
2020  REM  *************************************************************
2030  REM  PERFORM CALCULATIONS
2040  REM  **************************************************************
```

```
2050  REM
2060 TD = T - 273.15:K = TD: REM  TEMP IN DEGREES C
2070 BC = ( FN CG(K)) * FA
2080 K = TT - 273.15
2090 CB = ( FN CG(K)) * FA
2100 I1 = (101325 / 760) * PI: REM  INLET PRESSURE IN PASCALS
2110 O1 = (101325 / 760) * PO: REM  OUTLET PRESSURE IN PASCALS
2120 PS = I1 / O1
2130  REM  PRESSURE CORRECTION TERM
2140 J32 = (2 / 3) * (((PS * PS * PS) - 1) / ((PS * PS) - 1))
2150  REM  DETERMINATION OF THE VAPOUR PRESSURE OF WATER
2160 W = (A - (B / (C + TD)))
2170 WA = 2.303 * W
2180 WB =  EXP (WA)
2190 PW = WB * (101325 / 760): REM  VAPOUR PRESSURE IN PASCALS
2200 UI = ((50 / TF) * ((I1 - PW) / I1) * (T / TT)): REM  INLET FLOWRATE
2210 UO = (UI) * (((I1 * R * T) + (I1 * O1 * BC)) / ((O1 * R * TT) + (I1 *
     O1 * CB))): REM  OUTLET FLOWRATE
2220 VN = (UO * (TR - TG) / J32) * 0.000001: REM  RETENTION VOLUME
2230 BB = (2 * B2 - V1) / (R * T)
2240  REM  DETERMINATION OF THE VAPOUR PRESSURE OF THE SOLUTE
2250 P = (AS - (BS / (CS + TD)))
2260 PA = P * 2.303
2270 PB =  EXP (PA)
2280 P1 = PB * (101325 / 760): REM  VAPOUR PRESSURE IN PASCALS
2290  REM  ACTIVITY COEFFICIENTS AT INFINITE DILUTION
2300 LNG =  LOG ((N3 * R * T) / (VN * P1)) - ((B1 - V1) / (R * T)) * P1 +
     (BB * O1 * J32)
2310 LG = LNG / 2.303
2320 ELNG =  EXP (LNG)
2330 X =  LOG ((N3 * R * T) / (VN * P1))
2340 Y = ((B1 - V1) / (R * T)) * P1
2350 Z = (BB * O1 * J32)
2360  REM
2370  REM  ************************************************************
2380  REM  OUTPUT TO PRINTER
2390  REM  ************************************************************
2400  REM
2410  PRINT
2420  PRINT  CHR$ (4);"PR#";PR
2430  PRINT  SPC( LU);H$
2440  PRINT  SPC( LU);L$
2450  PRINT : PRINT
2460  PRINT "SOLUTE AMOUNT (MOLES) = ";N3
2470  PRINT "ROOM TEMPERATURE (KELVIN) = ";TT
2480  PRINT "BATH TEMPERATURE (KELVIN) = ";T
2490  PRINT "FLOW TIME (SEC) = ";TF
2500  PRINT "SOLUTE VAPOUR PRESSURE (PA) = ";P1
2510  PRINT "SOLUTE VIRIAL COEF (M3.MOL-1) = ";B1
2520  PRINT "MIXED VIRIAL COEF (M3.MOL-1) = ";B2
2530  PRINT "SOLUTE MOLAR VOLUME (M3.MOL-1) = ";V1
2540  PRINT "INLET PRESSURE (PA) = ";I1
2550  PRINT "OUTLET PRESSURE (PA) = ";O1
2560  PRINT "INLET FLOWRATE = ";UI
2570  PRINT "OUTLET FLOWRATE = ";UO
2580  PRINT "RETENTION TIME (SEC) = ";TR
2590  PRINT "DEAD TIME (SEC) = ";TG
2600  PRINT "INJECTION SIZE = ";IS;"MICROLITRES"
2610  PRINT "COLUMN LOADING = ";CL;"%"
2620  PRINT "J32 = ";J32
2630  PRINT "VN = ";VN
2640  PRINT "BB = ";BB
2650  PRINT "LN GAMMA = ";LNG
2660  PRINT "LOG GAMMA = ";LG
2670  PRINT "GAMMA = ";ELNG
2680  PRINT "AS A CHECK :- LN(GAMMA) = X-Y+Z"
2690  PRINT "X = ";X
2700  PRINT "Y = ";Y
2710  PRINT "Z = ";Z
2720  PRINT "BC1 = ";BC
2730  PRINT "BC2 = ";CB
```

```
2740  PRINT "(A-(B/(C+TD))) = ";W
2750  PRINT "PW IN PASCALS = ";PW
2760  PRINT "PW IN MMHG = ";WB
2770  PRINT "AS-(BS/(CS+TD)) = ";P
2780  PRINT "PS IN MM.HG = ";P1
2790  PRINT  CHR$ (12)
2800  PRINT
2810  PRINT  CHR$ (4);"PR#0"
2820  REM
2830  REM  ************************************************************
2840  REM  END OF OUTPUT LOOP
2850  REM  ************************************************************
2860  REM
2870  INPUT " DO YOU WANT TO USE THIS PROGRAM AGAIN ? ";YN$
2880  IF (YN$ = "YES") OR (YN$ = "Y") GOTO 750
2890  IF (YN$ = "NO") OR (YN$ = "N") GOTO 2900
2900  END
```

APPENDIX F4. Computer programme to calculate second virial coefficients and mixed virial coefficients.

```
10   REM
20   REM  ***************************************************************
30   REM  THE FOLLOWING PROGRAMME IS WRITTEN IN BASIC FOR ANY APPLE 11
40   REM  COMPUTER. IT CAN BE USED TO DETERMINE THE SECOND VIRIAL
50   REM  COEFFICIENTS B11 FOR A PURE COMPONENT, AND THE MIXED VIRIAL
60   REM  COEFFICIENTS B12 FOR A BINARY MIXTURE.
70   REM  THESE VIRIAL COEFFICIENTS ARE TEMPERATURE DEPENDENT AND
80   REM  CHARACTERISE INTERACTIONS BETWEEN PAIRS OF MOLECULES. THE
90   REM  MCGLASHAN AND POTTER CORRESPONDING STATES EQUATION HAS BEEN
100  REM  SHOWN TO APPLY TO A WIDE RANGE OF HYDROCARBONS AND PERMANENT
110  REM  GASES (REF. 1) AND IS EMPLOYED IN THIS PROGRAMME :
120  REM
130  REM    B/VC = 0.430 - 0.886(TC/T) - 0.694(TC/T)^2
140  REM           - 0.0375(N-1)(TC/T)^4.5
150  REM
160  REM   WHERE: TC IS THE CRITICAL TEMPERATURE OF THE PURE SUBSTANCE;
170  REM          (IN THIS PROGRAMME TC IN K )
180  REM          VC IS THE CRITICAL VOLUME OF THE PURE SUBSTANCE;
190  REM          (VC IN CM3/MOL)
200  REM          N IS THE NUMBER OF CARBON EQUIVALENTS. N CAN BE
210  REM          ESTIMATED.
220  REM
230  REM  IN ORDER TO USE THE ABOVE EQN. FOR B12 DETERMINATIONS THE
240  REM  MIXED CRITICAL TEMP. T12C, THE MIXED CRITICAL VOLUME V12C,
250  REM  AND THE N FOR THE MIXTURE ARE REQUIRED.
260  REM  THE CRITICAL TEMPERATURE CAN BE CALCULATED BY TWO METHODS :
270  REM
280  REM      1) THE HUDSON AND MCCOUBREY COMBINING RULE (REF. 1) :-
290  REM
300  REM      T12C = (2^7)*((T11C*T22C)^0.5)*((I1*I2)^0.5)*(V11C*V22C)
310  REM             ----------------------------------------------
320  REM                  (I1 + I2)*(V11C^(1/3) + V22C^(1/3))^6
330  REM
340  REM
350  REM       2) BY THE GEOMETRIC MEAN RULE (REF. 1) :
360  REM
370  REM      T12C = (T11C*T22C)^0.5
380  REM
390  REM  IN THE ABOVE :
400  REM
410  REM     V12C = (1/8)((V11C^(1/3)) + (V22C^(1/3))^3
420  REM
430  REM      AND I IS THE IONIZATION POTENTIAL OF THE PURE COMPONENT.
440  REM      (I IN ELECTRON VOLTS)
450  REM
460  REM      N12 IS GIVEN BY (REF. 1) :
470  REM
480  REM     N12 = 0.5*(N1 + N2)
490  REM
500  REM
510  REM  REFERENCES :
520  REM   ----------
530  REM   1. CRUICKSHANK, A. J. B.; WINDSOR, A. L.; YOUNG, C. L.
540  REM      TRANS. FARADAY SOC. 1966, 62, 2341.
550  REM
```

```
560  REM
570  REM                       R. C. BAXTER
580  REM                       RHODES UNIVERSITY  1988
590  REM  **************************************************************
600  HOME
610  PRINT "THE FOLLOWING PROGRAMME CAN BE USED TO  DETERMINE :"
620  PRINT
630  PRINT "1) SECOND VIRAL COEFFICIENTS B11, AND"
640  PRINT "2) MIXED SECOND VIRAL COEFFICIENTS B12"
650  PRINT
660  PRINT "THESE CALCULATIONS CAN BE MADE AT ANY   TEMPERATURE"
670  PRINT
680  PRINT " THE PROGRAMME REQUIRES : "
690  PRINT "  1) CRITICAL TEMPERATURES (IN KELVIN);"
700  PRINT "  2) CRITICAL VOLUMES (IN CM3/MOL);"
710  PRINT "  3) IONIZATION POTENTIALS (IN ELECTRON      VOLTS); AND"
720  PRINT "  4) VALUES FOR N."
730  PRINT : PRINT
740  INPUT "INPUT WHICH CALCULATION YOU WISH TO PERFORM (1 OR 2) ";C
750  IF (C = 1) GOTO 820
760  IF (C = 2) GOTO 1260
770  HOME
780  REM  **************************************************************
790  REM  DETERMINE THE SECOND VIRIAL COEFFICIENT B11 FOR THE PURE
800  REM  SUBSTANCE 1.
810  REM  **************************************************************

820  HOME
830  PRINT " B11 DETERMINATION : "
840  PRINT " ------------------- "
850  PRINT : PRINT
860  INPUT "INPUT SUBSTANCE NAME             >  ";N$
870  PRINT : PRINT : PRINT
880  INPUT " INPUT THE CRITICAL TEMPERATURE TC >  ";TC
890  PRINT
900  INPUT " INPUT THE CRITICAL VOLUME VC      >  ";VC
910  PRINT
920  INPUT " INPUT A VALUE FOR THE CONSTANT N  >  ";N
930  PRINT
940  INPUT " INPUT THE TEMPERATURE IN KELVIN   >  ";T
950  REM  **************************************************************

960  REM  PERFORM THE CALCULATION
970  REM  **************************************************************

980 B1 = 0.43 - 0.886 * (TC / T) - 0.694 * (TC / T) ^ 2 - 0.0375 * (N - 1)
      * ((TC / T) ^ (4.5))
990 B11 = B1 * VC
1000  REM  **************************************************************
      *
1010  REM  PRINT OUT THE RESULT.
1020  REM  **************************************************************
      *
1030  HOME
1040  INPUT " IS THE PRINTER ON ?";Y$
1050  IF (Y$ = "YES") OR (Y$ = "Y") GOTO 1070
1060  IF (Y$ = "NO") OR (Y$ = "N") GOTO 1100
1070  PR# 1
1080  PRINT  CHR$ (137);"80N"
1090  PRINT : PRINT : PRINT
1100  PRINT " DETERMINATION OF B11 FOR :   "N$
1110  PRINT " --------------------------"
1120  PRINT
1130  PRINT " B11 =  "B11"  AT T =  "T"  (IN KELVIN)."
1140  PR# 0
1150  PRINT : PRINT : PRINT
1160  INPUT " DO YOU WISH TO RUN THE PROGRAMME AGAIN ? ";Y$
1170  IF (Y$ = "YES") OR (Y$ = "Y") GOTO 1200
1180  IF (Y$ = "NO") OR (Y$ = "N") GOTO 2260
1190  HOME
1200  INPUT "DO YOU WISH TO DETERMINE 1) B11, OR 2) B22 ?  ";NO
```

```
1210  IF (NO = 1) GOTO 820
1220  IF (NO = 2) GOTO 1260
1230  REM  ***************************************************************

1240  REM  DETERMINE B12 VALUES
1250  REM  ***************************************************************

1260  HOME
1270  PRINT "B12 DETERMINATION : "
1280  PRINT "-------------------- "
1290  PRINT
1300  PRINT " THE CRITICAL TEMP. IS DETERMINED "
1310  PRINT " BY TWO METHODS :"
1320  PRINT " A) USING THE HUDSON & MCCOUBREY RULE ;"
1330  PRINT " B) USING THE GEOMETRIC MEAN RULE."
1340  PRINT : PRINT
1350  INPUT "INPUT COMPONENT 1                 >  ";C1$
1360  PRINT
1370  INPUT "INPUT COMPONENT 2                 >  ";C2$
1380  PRINT
1390  INPUT "INPUT CRITICAL TEMPERATURE FOR 1  >  ";T1
1400  PRINT
1410  INPUT "INPUT CRITICAL TEMPERATURE FOR 2  >  ";T2
1420  PRINT
1430  INPUT "INPUT THE CRITICAL VOLUME FOR 1   >  ";V1
1440  PRINT
1450  INPUT "INPUT THE CRITICAL VOLUME FOR 2   >  ";V2
1460  PRINT
1470  INPUT "INPUT IONIZATION POTENTIAL FOR 1  >  ";I1
1480  PRINT
1490  INPUT "INPUT IONIZATION POTENTIAL FOR 2  >  ";I2
1500  PRINT
1510  INPUT "INPUT COEFFICIENT N1 FOR 1        >  ";N1
1520  PRINT
1530  INPUT "INPUT COEFFICIENT N2 FOR 2        >  ";N2
1540  PRINT
1550  INPUT "INPUT THE TEMPERATURE IN KELVIN  >   ";T
1560  REM  ***************************************************************
1570  REM  CALCULATE MIXED VIRIAL COEFFICIENTS
1580  REM
1590  REM  CALCULATE T12C BY THE HUDSON AND MCCOUBREY COMBINING RULE
1600  REM  ***************************************************************

1610 TA = (2 ^ 7)
1620 TB = (T1 * T2) ^ (0.5)
1630 TC = (I1 * I2) ^ (0.5)
1640 TT = TA * TB * TC * V1 * V2
1650 TD = (1 / 3)
1660 BT = ((V1 ^ TD + V2 ^ TD) ^ 6) * (I1 + I2)
1670 KT = TT / BT
1680  REM  ***************************************************************

1690  REM  CALCULATE T12C BY THE GEOMETRIC MEAN RULE
1700  REM  ***************************************************************
1710 GT = (T1 * T2) ^ (0.5)
1720  REM  ***************************************************************

1730  REM  CALCULATE THE MIXED CRITICAL VOLUME
1740  REM  ***************************************************************

1750 V = (1 / 8) * ((V1 ^ TD + V2 ^ TD) ^ 3)
1760  REM  ***************************************************************

1770  REM  CALCULATE N12
1780  REM  ***************************************************************

1790 N12 = (0.5) * (N1 + N2)
1800  REM  ***************************************************************
1810  REM  DETERMINE B12 USING THE TWO DIFFERENT T12 VALUES
1820  REM  FIRSTLY USING T12 FROM THE HUDSON AND MCCOUBREY RULE
1830  REM  ***************************************************************
```

```
1840 IN = (KT / T)
1850 BB = 0.43 - 0.886 * IN - 0.694 * (IN) ^ 2 - 0.0375 * (N12 - 1) * ((IN
     ) ^ 4.5)
1860 CB = V * BB
1870  REM  **************************************************************
1880  REM  SECONDLY USING T12 FROM THE GEOMETRIC MEAN RULE
1890  REM  **************************************************************
1900 IM = (GT / T)
1910 DB = 0.43 - 0.886 * (IM) - 0.694 * (IM) ^ 2 - 0.0375 * (N12 - 1) * ((
     IM) ^ 4.5)
1920 FB = DB * V
1930  REM  **************************************************************
1940  REM  PRINT OUT THE RESULTS
1950  REM  **************************************************************
1960  HOME
1970  INPUT "IS THE PRINTER ON ? ";Y$
1980  IF (Y$ = "YES") OR (Y$ = "Y") GOTO 2000
1990  IF (Y$ = "NO") OR (Y$ = "N") GOTO 2020
2000  PR# 1
2010  PRINT  CHR$ (137);"80N"
2020  PRINT
2030  PRINT "B12 FOR :  "C1$," AND  "C2$
2040  PRINT "--------- "
2050  PRINT
2060  PRINT "THE MIXED CRITICAL TEMPERATURE FOR THE MIXTURE IS : "
2070  PRINT
2080  PRINT "    1) BY THE HUDSON AND MCCOUBREY RULE > "KT
2090  PRINT "    2) BY THE GEOMETRIC MEAN RULE        > "GT
2100  PRINT
2110  PRINT "THE COEFFICIENT N12 FOR THE MIXTURE IS >  "N12
2120  PRINT
2130  PRINT "THE CRITICAL VOLUME FOR THE MIXTURE IS >  "V
2140  PRINT
2150  PRINT "B12 USING (1) IS :   "CB
2160  PRINT
2170  PRINT "B12 USING (2) IS :   "FB
2180  PR# 0
2190  PRINT : PRINT
2200  INPUT " DO YOU WISH TO USE THE PROGRAMME AGAIN ? ";Y$
2210  IF (Y$ = "YES") OR (Y$ = "Y") GOTO 2230
2220  IF (Y$ = "NO") OR (Y$ = "N") GOTO 2260
2230  INPUT " DO YOU WANT TO CALCULATE : 1) B11, OR 2) B12 ? ";N
2240  IF (N = 1) GOTO 820
2250  IF (N = 2) GOTO 1260
2260  HOME
2270  END
```

APPENDIX F5. A *Fortran* computer programme to determine Antoine coefficients.

Notes on the algorithms:

The *Fortran* programme LSQRS was written in this work and employs the *IMSL* mathematical subroutine *ZXMIN* to find the optimum coefficients by a method of successive approximations combined with a minimization of the sums of the squares of the residuals. The approximations stop only when the coefficients have reached a stable form (*i.e.* differing only in the 7th figure between successive approximations). The *IMSL* subroutine is based on the Harwell Library routine *VA10A* and uses a Quasi-Newton method to find the minimum of a function f(x) of N variables, where $x = (x_1; x_2; \ldots ; x_N)$. More information on the algorithm is available in the IMSL handbook.

The programme ANTO was written by Marsicano(473) and was used to check the results. The algorithm utilizes the partial derivatives of the Antoine function with respect to the three Antoine coefficients and once again finds the optimum values while minimizing the sums of the squares of the residuals. The programme was adapted in this work to accept input in the same form as that for LSQRS. A programme listing will not be included here. A "driver" procedure was written to facilitate the running of both the programmes.

Running the programmes:

Input data is contained within a local file called DATA with the following structure:

```
p(1)      T(1)
p(2)      T(2)
 .         .
 .         .
 .         .

p(N)      T(N)
-9999     -9999
 A
 B
 C
```

where p(1) ... P(N) are the vapour pressures in mmHg and T(1)...T(N) are the corresponding temperatures in °C. The data pair (-9999, -9999) serves as an end-of-data marker, and A, B and C are the initial estimates of the Antoine coefficients. The ability of the programme LSQRS to converge on the best fit coefficient is dependent to some extent on the initial guesses and it is sometimes necessary to experiment with different guesses before a satisfactory result is obtained. The standard deviations between the experimental values and the values predicted from the Antoine coefficients were smaller for the predictions using ***LSQRS***.

Programme LSQRS

```
      PROGRAM LSQRS (INPUT,OUTPUT,DATA,RES,TAPE5 = DATA,TAPE7 = RES)
      EXTERNAL RAT
C-------------------------------------------------------------------
C THIS PROGRAM WILL CALCULATE ANTOINE COEFFICIENTS FOR THE EQUATION
C
C          LOG (P) = A - B/(C+T)
C
C WHERE      P = PRESSURE (IN MM HG)
C            T = TEMPERATURE (IN DEGREES CENTIGRADE)
C            A,B,C ARE THE ANTOINE COEFFICIENTS TO BE FOUND
C
C THE INITIAL GUESS VALUES OF A,B AND C MUST BE INPUTTED
C
C
C A BETTER SET OF COEFFICIENTS IS OBTAINED USING THE IMSL PROCEDURE
C "ZXMIN" TOGETHER WITH A METHOD OF SUCCESSIVE APPROXIMATIONS
C
C DATA TO BE INPUTTED IN THE FORM:
C
C       P(1)   T(1)
C       P(2)   T(2)
C       ....   ....
C       ....   ....
C       P(N)   T(N)
C       -9999  -9999
C       A
C       B
C       C
C
C MANY THANKS TO MR STEVE LAWRIE FOR INVALUABLE
C HELP WITH THE FORTRAN PROGRAMMING
C
C                         R C BAXTER
C                         RHODES UNIVERSITY
C                         1986
C-------------------------------------------------------------------
C FIRST DECLARE ALL VARIABLES USED
C-------------------------------------------------------------------
     COMMON /DATA/ X(100),Y(100),NO,Z(100)
     DIMENSION C(3),H(6),G(3),W(9),CA(3)
C-------------------------------------------------------------------
C READ IN THE DATA NOW, USING X(I) FOR P AND Y(I) FOR CORRESPONDING T
C-------------------------------------------------------------------
     I = 1
10   READ (5,*) X(I),Y(I)
     IF ((X(I).EQ.-9999).AND.(Y(I).EQ.-9999)) GOTO 20
     Z(I)=ALOG10(X(I))
     I = I+1
     GOTO 10
20   CONTINUE
     NO = I-1
```

```
C------------------------------------------------------------------
C READ IN THE INITIAL ESTIMATES FOR A,B AND C INTO C(1),C(2) AND C(3)
C MAKE COPIES OF THESE IN CA(1),CA(2),CA(3)
C------------------------------------------------------------------
      READ (5,*) C(1),C(2),C(3)
      CA(1) = C(1)
      CA(2) = C(2)
      CA(3) = C(3)
C------------------------------------------------------------------
C NOW CALL THE FUNCTION ZXMIN TO FIND THE NEXT BEST SET OF VALUES
C
C THERE ARE 3 PARAMETERS WE WANT TO FIND OPTIMUM VALUES FOR
C
C WE REQUIRE 1 FIGURE ACCURACY
C
C ZXMIN MAY ONLY CALL RAT (OUR FUNCTION) 20000 TIMES
C
C WE CHOOSE OPTION 0 (HESSIAN MATRIX WILL BE INITIALISED TO IDENTITY)
C
C THE PARAMETERS ARE HELD IN ARRAY C
C
C H IS THE HESSIAN MATRIX WORKSPACE.  IT MUST BE OF SIZE
C N*(N+1)/2, WHERE N IS THE NUMBER OF PARAMETERS TO BE OPTIMISED
C
C G IS A MATRIX OF LENGTH N CONTAINING AN ESTIMATE OF THE GRADIENTS
C
C F IS A SCALAR CONTAINING THE VALUE OF THE FUNCTION AT THE FINAL
C PARAMETER ESTIMATES
C
C W IS A WORK-SPACE MATRIX OF LENGTH 3*N USED BY THE FUNCTION
C
C A IS AN ERROR PARAMETER
C------------------------------------------------------------------
      CALL ZXMIN (RAT,3,1,20000,0,C,H,G,F,W,A)
C------------------------------------------------------------------
C NOW PUT THE DATA INTO THE OUTPUT FILE.
C------------------------------------------------------------------
      WRITE (7,1003)
      WRITE (7,1010)
      WRITE (7,1011)
      WRITE (7,1012)
      WRITE (7,1013)
      WRITE (7,1003)
      WRITE (7,1000) C(1),CA(1)
      WRITE (7,1001) C(2),CA(2)
      WRITE (7,1002) C(3),CA(3)
      WRITE (7,1003)
      WRITE (7,1007)
      WRITE (7,1004)
      WRITE (7,1008)
      WRITE (7,1006)
      T = 0
      DO 30 I = 1,NO
      A = C(1)-(C(2)/(C(3) + Y(I)))
```

```
   A=10**A
   D=A-X(I)
   P=100*D/X(I)
   T=T+(D*D)
   WRITE (7,1005) Y(I),X(I),A,D,P
30  CONTINUE
   WRITE (7,1006)
   T=(T/(NO-1))**.5
   WRITE (7,1009) T
C
1000 FORMAT (1H ,'THE VALUE OF A IS ',F13.7,'   FROM ',F12.6)
1001 FORMAT (1H ,'THE VALUE OF B IS ',F13.7,'   FROM ',F12.6)
1002 FORMAT (1H ,'THE VALUE OF C IS ',F13.7,'   FROM ',F12.6)
1003 FORMAT (1H ,'--------------------------------------------------')
1004 FORMAT (1H ,'   T      P EXP.    P CALC.    DEV. P    PCNT')
1005 FORMAT (1H ,F7.3,4X,F8.3,4X,F8.3,5X,F6.3,4X,F5.3)
1006 FORMAT (1H ,'--------------------------------------------------')
1007 FORMAT (1H ,' ')
1008 FORMAT (1H ,'   C      (MM.HG)    (MM.HG)    (MM.HG)   ')
1009 FORMAT (1H ,'            STANDARD DEVIATION = ',F7.5)
1010 FORMAT (1H ,'     ANTOINE COEFFICIENTS AS CALCULATED USING    ')
1011 FORMAT (1H ,'   THE IMSL FUNCTION ZXMIN TO MINIMISE THE SUMS   ')
1012 FORMAT (1H ,'  OF THE SQUARES OF THE RESIDUALS BY VARYING THE  ')
1013 FORMAT (1H ,'           VALUES OF THE COEFFICIENTS     ')
C
   STOP
   END
```

```
C
C------------------------------------------------------------------
C
    SUBROUTINE RAT (N,X,F)
C
C------------------------------------------------------------------
C SUBROUTINE TO EVALUATE THE SUM OF THE SQUARES OF THE RESIDUALS
C FOR THE NEW PARAMETERS.
C
C GET THE OLD DATA POINTS IN ORDER TO USE THEM
C------------------------------------------------------------------
   COMMON /DATA/ A(100),B(100),NO,C(100)
C------------------------------------------------------------------
C DIMENSION THE NEW ARRAYS
C------------------------------------------------------------------
   DIMENSION X(3)
C------------------------------------------------------------------
C SET UP THE INITIAL VALUES OF THE WORK VARIABLES
C------------------------------------------------------------------
   I = 1
```

```
      F = 0
C------------------------------------------------------------------
C CALCULATE THE VALUE OF THE FUNCTION AT THE DATA POINT
C------------------------------------------------------------------
2000 Y = X(1)-(X(2)/(X(3)+B(I)))
C------------------------------------------------------------------
C FIND THE DIFFERENCE BETWEEN THIS AND THE EXPERIMENTAL VALUE
C------------------------------------------------------------------
      Z = Y-C(I)
C------------------------------------------------------------------
C ADD THE SQUARE OF THIS VALUE TO THE FINAL VALUE
C------------------------------------------------------------------
      F = F+(Z*Z)
C------------------------------------------------------------------
C MOVE ON TO THE NEXT POINT UNTIL FINISHED
C------------------------------------------------------------------
      I = I + 1
      IF (I.LE.NO) GOTO 2000
2010 CONTINUE
C
C------------------------------------------------------------------
C FINISHED, LETS GET OUT OF HERE.
C------------------------------------------------------------------
C
      RETURN
      END
```

```
PROGRAM-UNIT LENGTH          47B = 39
CM LABELLED COMMON LENGTH    455B = 301
CM STORAGE USED          63500B = 26432
COMPILE TIME           0.090 SECONDS
```

Driver subroutine

```
.PROC, ANTOINE
TRMDEF,PL=0.
NOTE,OUTPUT,NR.? YOUR DATA MUST BE IN A LOCAL FILE CALLED "DATA"
NOTE,OUTPUT,NR.?
NOTE,OUTPUT,NR.? GETTING IMSL LIBRARY ROUTINES...
ATTACH,IMSL5/UN=LIBRARY.
LIBRARY,IMSL5.
NOTE,OUTPUT,NR.? DONE!
NOTE,OUTPUT,NR.?
NOTE,OUTPUT,NR.? GETTING COMPILED FORTRAN PROGRAMS...
GET,LSQRSB.
GET,ANTOB.
NOTE,OUTPUT,NR.? DONE!
NOTE,OUTPUT,NR.?
REWIND,*.
NOTE,OUTPUT,NR.? RUNNING ZXMIN PROGRAM...
LSQRSB.
NOTE,OUTPUT,NR.? DONE!
REWIND,DATA.
NOTE,OUTPUT,NR.?
NOTE,OUTPUT,NR.? RUNNING DERIVATIVE PROGRAM...
ANTOB.
NOTE,OUTPUT,NR.? DONE! - THE FILE CONTAINING THE RESULTS IS
NOTE,OUTPUT,NR.? A LOCAL FILE CALL "RES"
NOTE,OUTPUT,NR.?
TRMDEF,PL=23.
REVERT,NOLIST.
```

APPENDIX F6. A *Fortran* computer programme to predict excess thermodynamic properties using the PFP theory.

```
      PROGRAM PFP (INPUT,OUTPUT,DATA,RESULT,TAPE5 = DATA,TAPE7 = RESULT)

C
C
C**********************************************************************
C
C
C THIS COMPUTER PROGRAMME IS USED TO PREDICT EXCESS THERMODYNAMIC
C PROPERTIES OF BINARY LIQUID MIXTURES. MOLAR EXCESS VOLUMES ARE
C PREDICTED (BY THE THEORY NOW COMMONLY KNOWN AS THE PRIGOGINE -
C FLORY - PATTERSON THEORY - PFP THEORY ), USING EQUATION 15 IN A
C PUBLICATION BY VAN & PATTERSON - J. SOL. CHEM. 1982, 11, 793.
C THIS EQUATION SEPARATES THE EXCESS MOLAR VOLUME TERM INTO AN
C INTERACTIONAL CONTRIBUTION, A FREE VOLUME CONTRIBUTION, AND A
C CONTRIBUTION RELATED TO THE REDUCED VOLUMES OF THE COMPONENTS.
C THE EQUATION FOR THE MOLAR EXCESS ENTHALPY SEPARATES THE
C INTERACTIONAL AND THE FREE VOLUME CONTRIBUTIONS. (SEE PUBLICATION
C BY BARBE AND PATTERSON - J. SOL. CHEM. 1980, 9(10), 753.
C
C VALUES OF THE INTERACTION PARAMETER CHI REQUIRED BY THE ABOVE HAVE
C BEEN OBTAINED BY THREE DIFFERENT METHODS: (1) FROM BERTHELOTS
C RELATION FOR CHI, (2) FROM EXPERIMENTAL ENTHALPIES OF MIXING DATA
C AND THE EQUATIONS OF THE FLORY THEORY, AND (3) FROM EXPERIMENTAL
C ENTHALPY DATA USING PFP EQUATIONS. VALUES FOR CHI(BERTHELOT) AND FOR
C CHI(PFP) ARE DETERMINED WITHIN THE PROGRAM, WHILE A VALUE FOR
C CHI(FLORY) MUST BE INPUTTED. PARAMETERS PERTAINING TO THE PURE
C COMPONENTS AND TO THE MIXTURES ARE GIVEN IN THE ABOVE PUBLICATIONS.
C
C ENTROPY VALUES ARE PREDICTED BY AN 'APPROXIMATE' EQUATION (SEE
C SECOND  REFERENCE) ; THIS EQUATION SPLITS THE ENTROPY INTO A FREE -
C VOLUME CONTRIBUTION AND AN INTERACTION CONTRIBUTION. THE
C COMBINATORIAL CONTRIBUTION TO THE ENTROPY IS RELATED TO THE SEGMENT
C FRACTION.  ENTROPY VALUES ARE ALSO DETERMINED USING AN EQUATION
C CONTAINING A RESIDUAL TERM OF FLORY, AND THE ABOVE COMBINATORIAL
C TERM. HENCE A VALUE FOR GE CAN BE DETERMINED WITHIN THE PROGRAM
C (GE = HE - TSE). EXCESS GIBBS FUNCTIONS ARE ALSO PREDICTED USING AN
C EQUATION BY LIEBERMANN.
C
C ACTIVITY COEFFICIENTS AT INFINITE DILUTION ARE PREDICTED
C USING AN EQUATION CONTAINING THE FORY - HUGGINS COMBINATORIAL
C TERM AND A RESIDUAL TERM (OF FLORY). (FLORY , J.AM. CHEM SOC. 1965,
C 87, 1833.)
C
C THE ABOVE CALCULATIONS CAN BE PERFORMED USING TWO DIFFERENT
C METHODS FOR DETERMINING THE MOLECULAR SURFACE TO VOLUME RATIOS,
C S1/S2: (1) FROM THE SPHERICAL MOLECULE APPROXIMATION OF FLORY (ABE AND FLORY,
C J. AM. CHEM. SOC. 1965, 87, 1838.), AND (2) FROM SURFACE AREA
C INFORMATION OF BONDI (BONDI, J. PHYS. CHEM. 1964, 68, 441.)
```

```
C
C    FOR CONVENIENCE THE FORMAT OF THE DATA INPUT AS WELL AS THE
C BASIC CODE IN THIS PROGRAMME ARE SIMILAR TO THAT OF A PROGRAMME BY
C W. L. SPITERI (DOCTORAL THESIS - 1982) .
C
C *****************************************************************
C DATA INPUT AS FOLLOWS:
C ------------------
C
C       LABEL (MAX OF 60 CHARACTERS) - E.G. DECALIN + HEXANE (RUN#1)
C TEMPERATURE (K)
C DENSITY OF LIQ.1  DENS.LIQ.2  (G/CC)
C MOL.WT. OF LIQ.1   M.W.LIQ.2
C THERMAL EXPANSION COEFFT. OF 1  THRM.EXP. COEFFT. OF 2  (PER DEGREE)
C ISOTHERMAL COMPRESSIBILITY OF 1  ISOTHRML.COMPRS. OF 2  (/PA)
C A0  A1  A2  A3  A4  (WHERE THESE ARE THE COEFFICIENTS
C    OF THE SMOOTHING CURVES OF THE EXPERIMENTAL
C    EXCESS VOLUME RESULTS (IN CC/MOL).)
C    NB. IF LESS THAN 5 SMOOTHING COEFFICIENTS ARE AVAILABLE THEN
C       DEFINE EACH ADITIONAL VALUE AS 0.0000 .
C    THE CURVE MUST BE OF THE FORM:
C    VE=X1*X2*(A0+(A1*(X2-X1))+(A2*((X2-X1)**2))+(A3*((X2-X1)**3))
C       +(A4.....ETC.))))
C B0  B1  B2  B3  B4  (WHERE THESE ARE THE COEFFICIENTS
C    OF THE SMOOTHING CURVES OF THE EXPERIMENTAL
C    EXCESS ENTHALPY RESULTS (IN J/MOL)).
C    ONCE AGAIN THE CURVE MUST BE IN THE SAME FORM AS ABOVE FOR VE .
C CHI(HE) = INTERACTION PARAMETER FROM HE DATA BY FLORY EQUATIONS
C        AND METHODS .(SEE DISSERTATION FOR REFERENCES)
C S1  S2   (WHERE THESE ARE THE MOLECULAR SURFACE/VOLUME RATIOS -
C         UNITS OF 1/ANGSTROM) (0.0 AND 0.0 IF NO VALUES ARE
C         AVAILABLE . THE PROGRAMME WILL THEN USE FLORYS
C         APPROXIMATION FOR SPHERICAL MOLECULES)
C
C
C
C
C
C *****************************************************************
C
C                    R . C . BAXTER
C                    1987.
C
C ----------------------------------------------------------
C THESE VARIABLES ARE ALL USED IN THE MAIN PROGRAM
C ----------------------------------------------------------
   DIMENSION A(99),B(99),C(99),W(99),E(99),F(99),G(99),H(99),Y(99)
   DIMENSION PSI1(99),PSI2(99),THETA1(99),THETA2(99),PHI1(99)
   DIMENSION PHI2(99),VEXP(99),VDO(99),PVDO(99),X1(99),X2(99)
   DIMENSION VPFP(99),VEPFP(99),Z(99),CHIVEX(99),VECHI(99),VCPFP(99)
   DIMENSION HEXP(99),VEM(99),VD(99),VDEX(99),FPHI1(99),FPHI2(99)
   DIMENSION ALM(99),BETM(99),GS(99),GFH(99),GE(99),FVDO(99),DL1(99)
   DIMENSION DL2(99),GEL(99),TENT(99),GFL(99),FPSI1(99),FPSI2(99)
   DIMENSION U(99),TD(99),CP(99),HA(99),HB(99),HC(99),CHIHEX(99)
```

```
      DIMENSION HF(99),FTDO(99),FTD(99),VDEXP(99),FVD(99),FVDE(99)
      DIMENSION DLE1(99),DLE2(99),TENTE(99),CHIEXP(99),GEFL(99)
      DIMENSION TSFR(99),TSFRE(99),TSCM(99),TSE1(99),TSE2(99),FVDXP(99)
      DIMENSION FDEXP(99),FVDEX(99),TSFEX(99),DLEX1(99),DLEX2(99)
      DIMENSION GEXFL(99)
      REAL A,B,C,W,E,F,G,H,Y,CHIVEX,VECHI,VCPFP,S1,S2
      REAL T,BET1,BET2,ALPH1,ALPH2,V1,V2,TS1,TS2
      REAL P1,P2,VD1,VD2,VPFP,VEPFP,DIFF,Z
      REAL RHO1,RHO2,MW1,MW2,X1,X2
      REAL VS1,VS2,GAM1,GAM2,TD1,TD2,RATR,RATS,PSI1,PSI2
      REAL THETA1,THETA2,PVDO,VDO,CHI,VEXP
      REAL PHI1,PHI2,A0,A1,A2,A3,A4,SD,CHIHE
      REAL HEXP,VEM,VD,VDEX,FPHI1,FPHI2,ALM,BETM,GS,GFH
      REAL GE,FVDO,DL1,DL2,GEL,TENT,GFL,FPSI1,FPSI2
      REAL U,TD,CP,HA,HB,HC,HF,CHIHEX,US1,US2
      REAL FTDO,FTD,VDEXP,FVD,FVDE,DLE1,DLE2,TENTE,GEFL
      REAL TSFR,TSFRE,TSCM,TSE1,TSE2,FVDEX,FDEXP,DLEX1,DLEX2,TSFEX
      REAL GEXFL,FVDXP,CARRY,SVR1,SVR2
      CHARACTER*1 LABEL(60)
C -----------------------------------------------------------------
C                  START OF PROGRAM
C                  ----------------
C
C READ IN LABEL
C -----------------------------------------------------------------
      READ (5,12) (LABEL(I),I=1,60)
C -----------------------------------------------------------------
C WRITE IT TO OUTPUT FILE, AND UNDERLINE WITH STARS
C -----------------------------------------------------------------
12    FORMAT (60A1)
      WRITE (7,10)(LABEL(I),I=1,60)
10    FORMAT(/T28,60A1)
      WRITE (7,9)
9     FORMAT(/T2,100('*'))
C -----------------------------------------------------------------
C READ IN DATA FROM INPUT FILE
C
C T = TEMPERATURE IN KELVIN
C -----------------------------------------------------------------
      READ (5,*)T
C -----------------------------------------------------------------
C                                      -3
C RHO1,2 = DENSITY OF 1,2 IN G.CM
C
C MW1,2 = MOLAR MASS OF 1,2 IN G
C                                                          -1
C ALPH1,2 = THERMAL EXPANSION COEFFICIENT OF 1,2 IN K
C                                                      -1
C BET1,2 = COMPRESSIBILTY COEFFICIENT OF 1,2 IN  PA
C -----------------------------------------------------------------
      READ (5,*) RHO1,RHO2,MW1,MW2,ALPH1,ALPH2,BET1,BET2
C -----------------------------------------------------------------
C A0...A4 = SMOOTHING COEFFICIENTS FROM VOLUME EQUATION
C -----------------------------------------------------------------
```

```
    READ (5,*)A0,A1,A2,A3,A4
C ---------------------------------------------------------------------
C B0...B4 = SMOOTHING COEFFICIENTS FROM HEAT EQUATION
C ---------------------------------------------------------------------
    READ (5,*)B0,B1,B2,B3,B4
C ---------------------------------------------------------------------
C READ IN CHI(HE)
C ---------------------------------------------------------------------
    READ(5,*)CHIHE
C ---------------------------------------------------------------------
C READ IN THE VALUES FOR S1 AND S2
C ---------------------------------------------------------------------
    READ(5,*)SVR1,SVR2
C ---------------------------------------------------------------------
C READ IN ALL THE DATA                                        -1
C CONVERT THE COMPRESSIBILITY COEFFICIENT FROM PA   TO ( J/CM )   .
C ---------------------------------------------------------------------
    BET1 = BET1 * 1E06
    BET2 = BET2 * 1E06
C ---------------------------------------------------------------------
C NOW WRITE DATA TO THE OUTPUT FILE
C ---------------------------------------------------------------------
    WRITE(7,20)
20   FORMAT(/T5,'INPUT DATA :',/,'+',T5,'------------')
    WRITE(7,50)T
    WRITE(7,60)RHO1,RHO2
    WRITE(7,70)MW1,MW2
    WRITE(7,80)ALPH1,ALPH2
    WRITE(7,90)BET1,BET2
    WRITE(7,40)A0,A1,A2,A3,A4
    WRITE(7,45)B0,B1,B2,B3,B4
    WRITE (7,30) CHIHE
    WRITE(7,31)SVR1,SVR2
    WRITE(7,100)
C ---------------------------------------------------------------------
C FORMAT STATEMENTS FOR ABOVE
C ---------------------------------------------------------------------
100  FORMAT (/T2,100('*'))
30   FORMAT (/T8,'CHIHE  =',G14.7,5X,'THE INTERACTION PARAMETER OBTAINED FROM
   &EXP HEATS BY FLORY (IN J/CC)')
40   FORMAT (/T5,'A0=',F9.5,3X,'A1=',F9.5,3X,'A2=',F9.5,3X,'A3=',F9.5,3
   &X,'A4=',F9.5,'------ CC/MOL.---(VE).')
45   FORMAT (/T5,'B0=',F12.5,3X,'B1=',F12.5,3X,'B2=',F12.5,3X,'B3=',
   &F12.5,3X,'B4=',F12.5,'------- J/MOL.---(HE).')
50   FORMAT (/T8,'TEMPERATURE=',F7.3,'K')
60   FORMAT (/T8,'DENSITY OF LIQ.1=',F9.7,'G/CC',3X,'DENSITY OF LIQ.2='
   &,F9.7,'G/CC')
70   FORMAT (/T8,'MW1=',F7.3,5X,'MW2=',F7.3)
80   FORMAT (/T8,'THERM.EXP.COEFFT.1=',G13.6,'/K',3X,'THERM.EXP.COEFFT.
   &2=',G13.6,'/K')
90   FORMAT (/T8,'COMPRESS.1= ',G13.6,3X,'COMPRESS.2= ',G13.6,2X,'-----
   &------/(J/CC) ')
31   FORMAT(/T8,'S1 = ',F8.4,10X,'S2 = ',F8.4,10X,'------ 1/ANGSTROMS')

```

```
C ----------------------------------------------------------------------
C NOW FOR THE HARD WORK . CALCULATE THE CONSTANTS (REDUCED VALUES ETC.)
C                                 3
C V1,2 = MOLAR VOLUMES IN CM
C ----------------------------------------------------------------------
      V1=MW1/RHO1
      V2=MW2/RHO2
C ----------------------------------------------------------------------
C VD1,2 = REDUCED VOLUMES
C ----------------------------------------------------------------------
      VD1=((1+((4./3.)*ALPH1*T))/(1+(ALPH1*T)))**3
      VD2=((1+((4./3.)*ALPH2*T))/(1+(ALPH2*T)))**3
C ----------------------------------------------------------------------
C VS1,2 = HARD CORE MOLAR VOLUMES
C ----------------------------------------------------------------------
      VS1=V1/VD1
      VS2=V2/VD2
C ----------------------------------------------------------------------
C GAM1,2 = THERMAL PRESSURE COEFFICIENTS
C
      GAM1=ALPH1/BET1
      GAM2=ALPH2/BET2
C ----------------------------------------------------------------------
C P1,P2 = CHARACTERSITICS PRESSURES
C ----------------------------------------------------------------------
      P1=GAM1*T*(VD1**2)
      P2=GAM2*T*(VD2**2)
C ----------------------------------------------------------------------
C TD1,2 = REDUCED TEMPERATURES
C ----------------------------------------------------------------------
      TD1=((VD1**(1./3.))-1)/(VD1**(4./3.))
      TD2=((VD2**(1./3.))-1)/(VD2**(4./3.))
C ----------------------------------------------------------------------
C TS1,2 = CHARACTERISTIC TEMPERATURES
C ----------------------------------------------------------------------
      TS1=T/TD1
      TS2=T/TD2
C ----------------------------------------------------------------------
C RATR = RATIO OF MOLECULAR SEGMENTS IN DIFFERENT MOLECULES
C ----------------------------------------------------------------------
      RATR=VS1/VS2
C ----------------------------------------------------------------------
C THE RATIO S1/S2 IS DETERMINED . IN THE ABSENCE OF S1 AND S2 VALUES
C THE MOLECULAR SURFACE SIZES/SEGMENT RATIO FOR DIFFERENT MOLECULES IS
C APPROXIMATED BY FLORYS EQUATION FOR SPHERICAL MOLECULES
C ----------------------------------------------------------------------
      IF ((SVR1).EQ.(0.0)) GOTO 111
      RATS = (SVR1/SVR2)
      WRITE(7,227)SVR1,SVR2,RATS
227   FORMAT(/T2,'SVR1= ',F8.6,2X,'SVR2 = ',F8.6,2X,'RATS = ',F8.6)
      GOTO 131
111   RATS=(VS2/VS1)**(1./3.)
C ----------------------------------------------------------------------
C WRITE THESE VALUES TO THE OUTPUT FILE
C ----------------------------------------------------------------------
```

```
131 WRITE(7,185)
    WRITE(7,110) V1,V2
    WRITE(7,120) VD1,VD2
    WRITE(7,130) VS1,VS2
    WRITE(7,160) GAM1,GAM2
    WRITE(7,170) P1,P2
    WRITE(7,180) TD1,TD2
    WRITE(7,190) TS1,TS2
    WRITE(7,186)
185 FORMAT(/T5,'OUTPUT DATA FOR PURE COMPONENTS :',/ ' + ',T5,33('-'))
186 FORMAT(/T2,100('*'))
190 FORMAT(/T2,'THE CHARACTERISTIC TEMPERATURES ARE...T*1 = ',F9.2,'K',
   &3X,'AND T*2 = ',F9.2,'K')
    WRITE(7,200)
200 FORMAT(/T2,'IN THE FLORY NOTATION THE RATIOS R1/R2 AND S1/S2 ARE :
   &....')
    WRITE(7,210)RATR
    WRITE(7,220)RATS
110 FORMAT(/T2,'MOLAR VOLUME 1 = ',F7.3,T35,'MOLAR VOLUME 2 = ',F7.3,' -
   &------CC/MOL')
120 FORMAT(/T2,'RED.VOL.1(VD1) = ',F9.6,T35,'RED.VOL.2(VD2) = ',F9.6)
130 FORMAT(/T2,'V*1 = ',F7.3,T35,'V*2 = ',F7.3,' ---CC/MOL, ---WHERE V* IS
   & THE HARD CORE MOLAR VOLUME')
160 FORMAT(/T2,'GAMMA 1 = ',G12.5,T35,'GAMMA 2 = ',G12.5,' ---J/CC.K--I.
   &E. THE THERMAL PRESSURE COEFFTS.')
170 FORMAT(/T2,'CHARACTERISTIC PRESSURE 1 = ',G13.6,T50,'CHARACT,PRESSU
   &RE 2 = ',G13.6,' --- J/CC')
180 FORMAT(/T2,'TD1 = ',F11.9,T35,'TD2 = ',F11.9,3X,'....I.E. THE REDUCE
   &D TEMPERATURES.')
210 FORMAT(/T2,'R1/R2 = ',F5.3,3X,'...THE RATIO OF THE RESPECTIVE NO.
   &OF SEGMENTS IN THE RESP. MOLECULES.')
220 FORMAT(/T2,'S1/S2 = ',F5.3,3X,'...THE RATIO OF SURFACE SITES PER S
   &EGMENT FOR RESPECTIVE MOLECS.')
C ---------------------------------------------------------------------
C CHIB = CONTACT INTERACTION PARAMETER. CALCULATED HERE BY THE
C     BERTHELOT METHOD
C ---------------------------------------------------------------------
    CHIB = P1*((1-(RATS**(1./2.))*((P2/P1)**(1./2.)))**2)
C ---------------------------------------------------------------------
C WRITE TO OUTPUT FILE
C ---------------------------------------------------------------------
    WRITE (7,230)CHIB
230 FORMAT(/T2,'THE CHI VALUE OBTAINED USING THE BERTHELOT EQN. IS ',G
   &12.5,'UNITS OF J/CC *****************.')
    WRITE (7,240)
240 FORMAT(/T2,'IN WHAT FOLLOWS X1 REFERS TO THE MOLE FRACTION OF LIQ.
   &1')
    WRITE(7,250)
250 FORMAT(T2,'-----------------------------------------------------')
    WRITE(7,260)
260 FORMAT(/T5,'(PHI IS THE SEGMENT FRACTION, AND THETA IS THE SURFACE
   &FRACTION.) *********')
C ---------------------------------------------------------------------
C LOOP X FROM .01 TO .99 , TO CALCULATE THE FOLLOWING COMPOSITION
```

```
C VARIABLES : THE CONTACT ENERGY FRACTION , THE SEGMENT FRACTION AND
C THE SURFACE FRACTION . THE VARIABLES ARE DETERMINED OVER THE WHOLE
C COMPOSITION RANGE .
C -------------------------------------------------------------------
    I=0
    DO 66 I=1,99
C -------------------------------------------------------------------
C GIVE X1 VALUES BETWEEN 0 AND 1.0 IN STEPS OF 0.01 .
C -------------------------------------------------------------------
    X1(I)=I*0.01
C -------------------------------------------------------------------
C PHI1,2 = SEGMENT FRACTION OR HARD - CORE VOLUME FRACTION ( VAN &
C PATTERSON ) .
C -------------------------------------------------------------------
    PHI1(I) = ((X1(I)*VS1)/(X1(I)*VS1 + (1-X1(I))*VS2))
    PHI2(I) = 1-PHI1(I)
C -------------------------------------------------------------------
C PSI1,2 = CONTACT ENERGY FRACTION ( VAN & PATTERSON) .
C -------------------------------------------------------------------
    PSI1(I)= ((X1(I)*P1*VS1)/((X1(I)*P1*VS1)+((1-X1(I))*P2*VS2)))
    PSI2(I)=1-PSI1(I)
C -------------------------------------------------------------------
C THETA 1,2 = SITE FRACTIONS
C -------------------------------------------------------------------
    THETA2(I)=((PHI2(I))/(PHI1(I)*RATS + PHI2(I)))
    THETA1(I)=1-THETA2(I)
C -------------------------------------------------------------------
C PRINT ONLY EVERY .1TH VALUE
C -------------------------------------------------------------------
    X=FLOAT(I)
    IF ((X/10.).EQ.(INT(X/10.))) GOTO 1000
    GOTO 66
1000 WRITE(7,270)X1(I),PHI1(I),THETA1(I),PSI1(I)
270  FORMAT(T2,'X1= ',F3.1,4X,'PHI1= ',F10.8,4X,'THETA1= ',F10.8,4X,'PS
   &I= ',F10.8)
66   CONTINUE
C -------------------------------------------------------------------
C END OF LOOP
C
C DETERMINATION OF THE EXPERIMENTAL EXCESS VOLUMES AND EXPERIMENTAL
C EXCESS ENTHALPIES .
C -------------------------------------------------------------------
    DO 59 I=1,99

    VEXP(I)=X1(I)*(1.-X1(I))*(A0+(A1*(1.-2.*X1(I)))
   &      +(A2*((1.-2.*X1(I))**2.))+(A3*((1.-2.*X1(I))**3))
   &      +(A4*((1.-2.*X1(I))**4)))

    HEXP(I)=X1(I)*(1.-X1(I))*(B0+(B1*(1.-2.*X1(I)))
   &      +(B2*((1.-2.*X1(I))**2.))+(B3*((1.-2.*X1(I))**3))
   &      +(B4*((1.-2.*X1(I))**4.)))

59   CONTINUE
```

```
C ----------------------------------------------------------------------
C END OF LOOP
C
C HEADER FOR NEXT SECTION
C ----------------------------------------------------------------------
    WRITE(7,798)
798  FORMAT(/T5,'EXCESS THERMODYNAMIC PROPERTIES ARE NOW DETERMINED '
   &/ ' + ',50('-'))
C ----------------------------------------------------------------------
C THE EXCESS VOLUME IS PREDICTED USING THE CHI(BERTHELOT) DETERMIND
C ABOVE . THE NECESSARY CODE IS CONTAINED WITHIN A SUBROUTINE , VOLUME ,
C CONTAINED AT THE END OF THIS PROGRAM
C ----------------------------------------------------------------------
    WRITE (7,300)
300  FORMAT(/T2,'USING THE BERTHELOT CHI VALUE OBTAINED ABOVE THE
   &VE (BY PFP EQN) IS CALCULATED . (VE IN CC/MOL)')
    WRITE (7,310)
310  FORMAT(T2,'THIS VE(BERTHELOT) IS THEN COMPARED TO THE EXPERIMENTAL
   &EXCESS VOLUME (VEXP)')
C ----------------------------------------------------------------------
C CALL THE SUBROUTINE , PASSING THE NECESSARY PARAMETERS
C ----------------------------------------------------------------------

    CALL VOLUME (CHIB,THETA2,PSI1,PSI2,P1,VD1,VD2,VEXP,VS1,VS2,
   &         X1,P2)

C ----------------------------------------------------------------------
C USING THE CHI OBTAINED FROM HE DATA (EMPLOYING FLORY RELATIONSHIPS) ,
C VE ARE AGAIN PREDICTED  .
C ----------------------------------------------------------------------
    WRITE (7,380) CHIHE
380  FORMAT(/T2,'THE FOLLOWING CHI(HE) IS THE ADJUSTED INTERACTION
   &PARAMETER (IN J/CUBIC METRES) FROM HE(EXP.).',2X,G14.8,'*******')
C ----------------------------------------------------------------------
C CALCULATE VPFP WITH THE CHI(HE)
C
C CALL THE SUBROUTINE
C ----------------------------------------------------------------------
    WRITE(7,381)
381  FORMAT(/T5,'USING THE FLORY CHI VALUE OBTAINED PREVIOUSLY , THE
   &VE (BY PFP EQN) IS PREDICTED (VE IN CC/MOL) ')
    WRITE(7,382)
382  FORMAT(/T2,'(THIS VE IS THEN COMPARED TO THE EXPERIMENTAL EXCESS
   &VOLUMES)')

    CALL VOLUME (CHIHE,THETA2,PSI1,PSI2,P1,VD1,VD2,VEXP,VS1,VS2,
   &         X1,P2)

C ----------------------------------------------------------------------
C CHIEX = EXPERIMENTAL CHI VALUE.  CALCULATED BY REARRANGING THE VE
C EQUATION ABOVE .
C ----------------------------------------------------------------------
    WRITE(7,423)
423  FORMAT(/T2,'DETERMINE THE MINIMISING CHI VALUE FROM VE DATA')
    WRITE(7,424)
```

```
424 FORMAT(T2,'---------------------------------------------------')

   D=0.00000
   DO 71 I=1,99
C ------------------------------------------------------------------
C VDO = "IDEAL" REDUCE VOLUME OF MIXTURE
C ------------------------------------------------------------------
   VDO(I)=(PHI1(I)*VD1)+(PHI2(I)*VD2)

   A(I)=((((VDO(I))**(1./3.))-1)*((VDO(I))**(2./3.)))
   B(I)=(((4./3.)*((VDO(I))**(-1./3.)))-1)
   W(I)=(((14./9.)*((VDO(I))**(-1./3.)))-1)
   E(I)=(VD1-VD2)
   F(I)=((PSI1(I)*PSI2(I))*((E(I)**2)*W(I))/(B(I)*VDO(I)))
   G(I)=(P2*PSI1(I) + P1*PSI2(I))
   H(I)=((E(I)*(P1-P2)*PSI1(I)*PSI2(I))/(G(I)))

   Y(I)=(X1(I)*VS1 + (1-X1(I))*VS2)
   Z(I)=(VEXP(I)/Y(I)) + F(I) - H(I)

C ------------------------------------------------------------------
C CHIVEX IS THE CHI VALUE FROM EXPERIMENTAL DATA .
C ------------------------------------------------------------------
   CHIVEX(I)=((Z(I)*B(I)*P1)/(A(I)*PSI1(I)*THETA2(I)))
C ------------------------------------------------------------------
C PRINT EVERY .1TH VALUE
C ------------------------------------------------------------------

   X=FLOAT(I)
   IF ((X/10.).EQ.(INT(X/10.))) GOTO 3000
   GOTO 71
3000 WRITE(7,450)X1(I),Z(I),CHIVEX(I)
450 FORMAT(/T2,'X1 = ',F3.1,2X,'Z(I) = ',F10.8,2X,'CHIEX = ',F14.5)
71  CONTINUE

C ------------------------------------------------------------------
C END OF LOOP
C ------------------------------------------------------------------
C WE NOW LOOP THROUGH ALL THE VALUES OF CHI DETERMINED ABOVE, AND USE
C THE ONE WHICH GIVING THE LOWEST STD.DEV .
C
C DMIN IS USED IN THE DETERMINATION OF THE BEST CHI VALUE .
C ------------------------------------------------------------------
   DMIN=1.0E10
C ------------------------------------------------------------------
C LOOP THROUGH ALL THE VALUES OF CHI
C ------------------------------------------------------------------
   DO 72 M=1,99
C ------------------------------------------------------------------
C FOR EACH VALUE, USE EVERY POINT WE KNOW
C ------------------------------------------------------------------
   DO 73 I=1,99

   VECHI(I)=((A(I)*PSI1(I)*THETA2(I)*CHIVEX(M))/(B(I)*P1))
```

```
C -----------------------------------------------------------------
C VCPFP = THEORETICAL EXCESS VOLUME USING EXPERIMENTAL CHI-(CHIEX) ,
C INPUTTED IN THE ABOVE PFP EQUATION
C -----------------------------------------------------------------

   VCPFP(I) = ((VECHI(I)-F(I) + H(I))*Y(I))

73  CONTINUE
C -----------------------------------------------------------------
C CALCULATED ALL THE POINTS.  NOW FIND SUM OF SQUARES OF RESIDUALS
C
C D IS USED FOR THIS
C -----------------------------------------------------------------

   D = 0.0000000
   DO 74 J = 1,99
   D = D + ((VEXP(J)-VCPFP(J))*(VEXP(J)-VCPFP(J)))

74  CONTINUE

C -----------------------------------------------------------------
C CALCULATED SUM OF SQUARES OF RESIDUALS. NOW SEE IF BETTER THAN
C PREVIOUS BEST
C -----------------------------------------------------------------

   IF (D.GE.DMIN) GO TO 4000
   CHIMIN = CHIVEX(M)
   DMIN = D
4000 CONTINUE

C -----------------------------------------------------------------
C NOW MOVE ON TO THE NEXT VALUE OF CHI
C -----------------------------------------------------------------
72  CONTINUE
C -----------------------------------------------------------------
C CALCULATE STANDARD DEVIATION FOR THE BEST VALUE OF CHI FOUND
C -----------------------------------------------------------------
   SD = (DMIN/98)**0.5
C -----------------------------------------------------------------
C OUTPUT BEST VALUE
C -----------------------------------------------------------------

   WRITE (7,460)CHIMIN
460  FORMAT(/T2,'THE MINIMIZING CHI VALUE, FROM VE(EXP.) , IS ',F14.5,'
  & J/CC ********************')

C -----------------------------------------------------------------
C NOW RECALCULATE THE THEORETICAL EXCESS VOLUMES FOR BEST CHI
C -----------------------------------------------------------------

   WRITE(7,470)
470  FORMAT(/T2,'DETERMINE THE VE(PFP) USING THIS MINIMISED CHI VALUE ,
  &FROM VE DATA')
   WRITE(7,471)
```

```
471  FORMAT(T2,67('-'))

C ---------------------------------------------------------------------
C CALL THE VOLUME SUBROUTINE
C ---------------------------------------------------------------------

   CALL VOLUME (CHIMIN,THETA2,PSI1,PSI2,P1,VD1,VD2,VEXP,VS1,VS2,
  &         X1,P2)

C ---------------------------------------------------------------------
C PREDICT THE EXCESS ENTHALPY USING THE MINIMISED CHI(VE) . THE
C NECESSARY CODE IS CONTAINED WITHIN A SUBROUTINE , HEATS , AT THE END
C OF THIS PROGRAM .
C ---------------------------------------------------------------------

   WRITE(7,1541)
1541  FORMAT(/T2,'PREDICT EXCESS ENTHALPIES USING THE CHI(VE) - TSE AND
   & HENCE GE VALUES ARE ALSO INCLUDED (HE IN J/MOL)')
   WRITE(7,1542)
1542  FORMAT(T2,'(COMPARE THE PREDICTED AND EXPERIMENTAL HEATS VALUES)')
   WRITE(7,1543)
1543  FORMAT(T2,51('-'))

C ---------------------------------------------------------------------
C CALL THE HEATS SUBROUTINE
C ---------------------------------------------------------------------
   V1=V1
   V2=V2
   WRITE(7,6543)V1,V2
6543  FORMAT(/T2,'V1= ',F16.8,2X,'V2= ',F16.8)
   CALL HEATS (CHIMIN,THETA2,PSI1,PSI2,P1,P2,VD1,VD2,TD1,TD2,VS1,
  &         VS2,HEXP,X1,PHI1,PHI2,V1,V2,T)

C ---------------------------------------------------------------------
C PREDICT EXCESS ENTHALPIES USING CHI(BERTHELOT)
C ---------------------------------------------------------------------

   WRITE(7,541)
541  FORMAT(/T2,'PREDICT EXCESS ENTHALPIES USING THE CHI(BERT) - TSE AN
  &D GE VALUES ARE ALSO INCLUDED HERE (HE IN J/MOL)')
   WRITE(7,542)
542  FORMAT(T2,'(COMPARE THE PREDICTED AND EXPERIMENTAL HEATS VALUES)')
   WRITE(7,543)
543  FORMAT(/T2,'---------------------------------------------------')

C ---------------------------------------------------------------------
C CALL THE HEATS SUBROUTINE
C ---------------------------------------------------------------------

   CALL HEATS (CHIB,THETA2,PSI1,PSI2,P1,P2,VD1,VD2,TD1,TD2,VS1,
  &         VS2,HEXP,X1,PHI1,PHI2,V1,V2,T)
```

```
C ---------------------------------------------------------------------
C PREDICT THE EXCESS ENTHALPIES USING CHI(FLORY)
C ---------------------------------------------------------------------

      WRITE(7,544)
  544 FORMAT(/T2,'DETERMINE THE EXCESS ENTHALPY FROM CHI(FLORY) - ONCE
     &AGAIN TSE AND GE VALUES ARE INCLUDED')
      WRITE(7,545)
  545 FORMAT(T2,'(COMPARE THE PREDICTED AND EXPERIMENTAL HEATS VALUES)')
      WRITE(7,546)
  546 FORMAT(T2,67('-'))

C ---------------------------------------------------------------------
C CALL HEATS SUBROUTINE
C ---------------------------------------------------------------------

      CALL HEATS (CHIHE,THETA2,PSI1,PSI2,P1,P2,VD1,VD2,TD1,TD2,VS1,
     &        VS2,HEXP,X1,PHI1,PHI2,V1,V2,T)

      CARRY = CHIHE
C ---------------------------------------------------------------------
C DETERMINE THE BEST FIT CHI FROM THE EXPERIMENTAL EXCESS ENTHALPY DATA
C USING THE APPROXIMATE HEATS EQUATION OF BARBE AND PATTERSON
C ---------------------------------------------------------------------

      WRITE(7,600)
  600 FORMAT(/T2,'DETERMINE THE MINIMISED CHI VALUE FROM HE DATA')
      WRITE(7,610)
  610 FORMAT(T2,'----------------------------------------------')

      D = 0.00000
      DMIN = 0.0000

      DO 65 I = 1,99

C ---------------------------------------------------------------------
C DETERMINE THE VARIABLES REQUIRED IN THIS CALCULATION . FOR DEFINITIONS
C SEE HEATS SUBROUTINE (LOCATED AT END OF PROGRAM)
C ---------------------------------------------------------------------

      U(I) = (PSI1(I)/VD1 + PSI2(I)/VD2)
      PVDO(I) = (1./U(I))
      CP(I) = (1.0)/((4./3.)*((PVDO(I)**(-1./3.)))-1)
      TD(I) = (((PVDO(I)**(1./3.))-1)/(PVDO(I)**(4./3.)))
      US1 = (P1*VS1)
      US2 = (P2*VS2)
      HA(I) = ((X1(I)*US1) + ((1-X1(I))*US2))
      HB(I) = CP(I)*((PSI1(I)*TD1) + (PSI2(I)*TD2) - TD(I))
      HC(I) = (U(I) + (TD(I)*CP(I)))

C ---------------------------------------------------------------------
C CHIHEX IS THE CHI VALUE FROM EXPERIMENTAL HEATS .
C ---------------------------------------------------------------------

```

```
   CHIHEX(I) = ((((HEXP(I)/HA(I))-HB(I))*P1)/(THETA2(I)*PSI1(I)
  &        *HC(I)))

C -----------------------------------------------------------------
C PRINT OUT EVERY 0.1 VALUE
C -----------------------------------------------------------------
   X = FLOAT(I)
   IF((X/10.).EQ.(INT(X/10.))) GOTO 7500
   GOTO 65
7500 WRITE(7,620)X1(I),HA(I),HB(I),HC(I)
620  FORMAT(/T2,'X1 = ',F3.1,2X,'HA = ',F16.8,2X,'HB = ',F16.8,2X,'HC = ',
  &F16.8)
   WRITE(7,630)X1(I),HEXP(I),CHIHEX(I)
630  FORMAT(/T2,'X1 = ',F3.1,2X,'HEXP = ',F16.8,2X,'CHIHEX = ',F16.4)
65   CONTINUE

C -----------------------------------------------------------------
C END OF LOOP
C LOOP THROUGH ALL THESE CHI VALUES DETERMINED ABOVE . FIND THAT ONE
C WHICH GIVES THE LOWEST STD DEVIATION
C -----------------------------------------------------------------

   DMIN = 1.0E10
   DO 44 M = 1,99
   DO 46 I = 1,99

   HF(I) = (((((CHIHEX(M)*THETA2(I)*PSI1(I))*HC(I))/(P1)) + (HB(I)))*
  &   HA(I))

C -----------------------------------------------------------------
C HF(I) = THEORETICAL EXCESS ENTHALPY USING EXPERIMENTAL CHIHEX
C -----------------------------------------------------------------

46   CONTINUE

   D = 0.0000

   DO 47 J = 1,99

   D = D + ((HEXP(J) - HF(J))*(HEXP(J) - HF(J)))

47   CONTINUE
C -----------------------------------------------------------------
C CALCULATED SUM OF SQUARES OF RESIDUALS . NOW SEE IF BETTER THAN
C PREVIOUS BEST
C -----------------------------------------------------------------

   IF (D.GE.DMIN) GOTO 3500

   CHIHIN = CHIHEX(M)
   DMIN = D
3500 CONTINUE

```

```
C ----------------------------------------------------------------------
C NOW MOVE ON TO THE NEXT VALUE OF CHI
C ----------------------------------------------------------------------

44   CONTINUE

C ----------------------------------------------------------------------
C CALCULATE THE STD DEVIATION FOR THE BEST VALUE OF CHI FOUND
C ----------------------------------------------------------------------

      SD = (DMIN/98)**0.5

C ----------------------------------------------------------------------
C OUTPUT BEST VALUE
C ----------------------------------------------------------------------

      WRITE(7,635)CHIHIN
635   FORMAT(/T2,'THE MINIMISED CHI VALUE FROM EXPERIMENTAL EXCESS
     &ENTHALPIES IS = ',F18.4)
      WRITE(7,636)
636   FORMAT(/T2,'--------------------------------------------------')

C ----------------------------------------------------------------------
C PREDICT EXCESS ENTHALPIES AND EXCESS VOLUMES , USING THE ABOVE
C MINIMISED CHI VALUE
C ----------------------------------------------------------------------

      WRITE(7,650)
650   FORMAT(/T2,'PREDICT EXCESS VOLUMES USING THE ABOVE MINIMISED CHI
     &VALUE (VE IN CC/MOL)')
      WRITE(7,1991)
1991  FORMAT(T2,'(COMPARE EXPERIMENTAL AND PREDICTED VE VALUES)')
      WRITE(7,651)
651   FORMAT(T2,67('-'))

C ----------------------------------------------------------------------
C CALL THE VOLUME SUBROUTINE
C ----------------------------------------------------------------------

      CHI = CHIHIN
      CALL VOLUME (CHI,THETA2,PSI1,PSI2,P1,VD1,VD2,VEXP,VS1,VS2,
     &          X1,P2)
C ----------------------------------------------------------------------
C CALL THE HEATS SUBROUTINE
C ----------------------------------------------------------------------
      WRITE(7,652)
652   FORMAT(/T2,'PREDICT EXCESS ENTHALPY VALUES USING THE ABOVE
     &MINIMISED CHI VALUE - TSE AND GE VALUES INCLUDED (HE IN J/MOL)')
      WRITE(7,1992)
1992  FORMAT(/T2,'(COMPARE EXPERIMENTAL AND PREDICTED HE VALUES)')
      WRITE(7,1993)
1993  FORMAT(T2,67('-'))
C ----------------------------------------------------------------------
C CALL THE HEATS SUBROUTINE
C ----------------------------------------------------------------------
```

```

        CALL HEATS (CHIHIN,THETA2,PSI1,PSI2,P1,P2,VD1,VD2,TD1,TD2,
     &         VS1,VS2,HEXP,X1,PHI1,PHI2,V1,V2,T)

C ----------------------------------------------------------------------
C EXCESS ENTROPIES ,TSE , AND EXCESS GIBBS FUNCTIONS ARE PREDICTED IN
C THE FOLLOWING SECTION . THE EXCESS ENTROPY IS FIRST RELATED TO A
C COMBINATION OF A RESIDUAL TERM (DETERMINED FROM FLORY EQUATIONS) ,
C AND A COMBINATORIAL TERM . EXCESS GIBBS FUNCTIONS CAN HENCE BE
C PREDICTED . BY AN ALTERNATE APPROACH,GE ARE PREDICTED USING EQUATIONS
C OF LIEBERMANN . EXPERIMENTAL HEATS AND VOLUMES ARE USED IN THESE
C CALCULATIONS . VALUES ARE DETERMINED THROUGHOUT THE WHOLE MOLE
C FRACTION RANGE BUT ARE PRINTED OUT AT 0.1 MOLE FRACTION INTERVALS .
C ----------------------------------------------------------------------

      WRITE(7,800)
800   FORMAT(/T2,'EXCESS ENTROPIES ,TSE , AND EXCESS GIBBS FUNCTIONS ARE
     &PREDICTED IN THIS SECTION .')
      WRITE(7,801)
801   FORMAT(T2,'TSE IS RELATED TO A COMBINATION OF A RESIDUAL TERM AND
     &A COMBINATORIAL TERM . GE CAN HENCE BE PREDICTED .')
      WRITE(7,805)
805   FORMAT(T2,'GE VALUES ARE ALSO PREDICTED USING LIEBERMANNS EQU.')
      WRITE(7,820)
820   FORMAT(T2,100('-'))

C ----------------------------------------------------------------------
C LOOP AND CALCULATE VALUES OF GE FROM .1 TO .9 BY .01
C ----------------------------------------------------------------------
      DO 6000 I = 1,99
      VEM(I) = VEXP(I)*1.0E-06
C ----------------------------------------------------------------------
C CALCULATE THE REDUCED VOLUME FOR THE MIXTURE USING THE FLORY'S
C SEGMENT FRACTION EQN - (FPSI 1,2)
C ----------------------------------------------------------------------
      FPSI2(I) = (1-X1(I))/((1-X1(I)) + (X1(I)*RATR))
      FPSI1(I) = 1-FPSI2(I)

C ----------------------------------------------------------------------
C IN THE FOLLOWING DETERMINATION OF THE REDUCED VOLUME FOR THE MIXTURE,
C THE "IDEAL" REDUCED VOLUME AND THE REDUCED EXCESS VOLUME ARE REQUIRED
C IN THE CALCULATION . THE REDUCED EXCESS VOLUME IS DETERMINED BY TWO
C METHODS : (1) USING THE EXP. EXCESS VOLUME ,AND (2) A PREDICTED VALUE
C FROM AN EQUATION BY FLORY
C ----------------------------------------------------------------------
C DETERMINE THE "IDEAL" REDUCED VOLUME  (FVDO)
C ----------------------------------------------------------------------

      FVDO(I) = (FPSI1(I)*VD1) + (FPSI2(I)*VD2)

C ----------------------------------------------------------------------
C THE IDEAL REDUCED TEMPERATURE (FTDO) AND THE REDUCED TEMPERATURE (FTD)
C FOR THE MIXTURE ARE REQUIRED
C ----------------------------------------------------------------------
```

```
      FTDO(I)=(((FVDO(I)**(1./3.))-1)/(FVDO(I)**(4./3.)))
      FTD(I)=(((FPSI1(I)*P1*TD1)+(FPSI2(I)*P2*TD2))/((FPSI1(I)*P1)+
     &    (FPSI2(I)*P2)+(FPSI1(I)*THETA2(I)*CARRY)))
C -------------------------------------------------------------------
C VDEXP IS THE "EXPERIMENTAL" REDUCED EXCESS VOLUME AND VDEX THE REDUCED
C EXCESS VOLUME
C -------------------------------------------------------------------
      FVDE(I)=((FVDO(I)**(7./3.))/((4./3.)-(FVDO(I)**(1./3.))))*(FTD(I)
     &    -FTDO(I))
      FVDEX(I)=(VEXP(I))/(X1(I)*VS1 + (1-X1(I))*VS2)

C -------------------------------------------------------------------
C THE REDUCED VOLUME FOR THE MIXTURE (FVDE) COMPRISES THAT REDUCED
C EXCESS VOLUME CONTAINING THE EXP. EXCESS VOLUME
C -------------------------------------------------------------------
      FVD(I)=FVDO(I)+FVDE(I)
      FVDXP(I)=FVDO(I)+FVDEX(I)
C -------------------------------------------------------------------
C DETERMINE THE RESIDUAL ENTROPY BY AN EUUATION OF FLORY - J. AM. CHEM.
C SOC. 1965, 87, 1833 .
C ONCE AGAIN,FOR SIMPLICITY,THE EQN FOR THE RESIDUAL ENTROPY IS SPLIT UP
C -------------------------------------------------------------------

      DLE1(I)=(ALOG(((VD1**(1./3.))-1)/((FVD(I)**(1./3.))-1)))
      DLE2(I)=(ALOG(((VD2**(1./3.))-1)/((FVD(I)**(1./3.))-1)))
      DLEX1(I)=(ALOG(((VD1**(1./3.))-1)/((FVDXP(I)**(1./3.))-1)))
      DLEX2(I)=(ALOG(((VD2**(1./3.))-1)/((FVDXP(I)**(1./3.))-1)))

C -------------------------------------------------------------------
C TSFRE IS THE RESIDUAL ENTROPY USING THE REDUCED VOLUME FOR THE MIXTURE
C -------------------------------------------------------------------
      TSFRE(I)=(-1.0*3.0*((((X1(I)*P1*VS1*TD1))*DLE1(I))
     &+((((1-X1(I))*P2*VS2*TD2))*DLE2(I))))
      TSFEX(I)=(-1.0*3.0*((((X1(I)*P1*VS1*TD1))*DLEX1(I))
     &+((((1-X1(I))*P2*VS2*TD2))*DLEX2(I))))

C -------------------------------------------------------------------
C DETERMINE THE COMBINATORIAL ENTROPY .
C -------------------------------------------------------------------
      TSCM(I) = (-1.0*T*8.314)*((X1(I)*(ALOG(PHI1(I)/X1(I))))+
     &     ((1-X1(I))*(ALOG(PHI2(I)/(1-X1(I))))))
C -------------------------------------------------------------------
C DETERMINE TSE ( = TSE(RESID.) + TSE(COMB.) + TSE(ID.) )
C -------------------------------------------------------------------
      TSE1(I) = TSFRE(I)+TSCM(I)
      TSE2(I) = TSFEX(I)+TSCM(I)
C -------------------------------------------------------------------
C DETERMINE THE EXCESS GIBBS FUNCTION .
C -------------------------------------------------------------------
      GEFL(I)=((-1.0)*TSE1(I))+HEXP(I)
      GEXFL(I)=((-1.0)*TSE2(I))+HEXP(I)
C -------------------------------------------------------------------
C CALULATE PHI1,PHI2 TERMS
C -------------------------------------------------------------------
```

```
   FPHI1(I)=X1(I)/(X1(I)+(1-X1(I))*(V2/V1))
   FPHI2(I)=1-FPHI1(I)
C -----------------------------------------------------------------
C ALM,BETM
C -----------------------------------------------------------------
   ALM(I)=ALPH1*FPHI1(I)+ALPH2*FPHI2(I)
   BETM(I)=BET1*FPHI1(I)+BET2*FPHI2(I)
C -----------------------------------------------------------------
C R IS UNIVERSAL GAS CONSTANT
C -----------------------------------------------------------------
   R=8.3143
C -----------------------------------------------------------------
C *
C G EQUATION
C -----------------------------------------------------------------
   GS(I)=((R*T*(BET1-BET2)*(FPHI1(I)-X1(I)))-VEXP(I)+((BETM(I)*
  &HEXP(I)) /(ALM(I)*T)))/((BETM(I)*1.5)+(BETM(I)/(ALM(I)*T)))
   GFH(I)=(X1(I)*(ALOG(FPHI1(I)/X1(I))))+((1-X1(I))*(ALOG(FPHI2(I)/
  &(1-X1(I)))))
C -----------------------------------------------------------------
C GE(LIEBERMANN)
C -----------------------------------------------------------------
   GEL(I)=GS(I)+(R*T*GFH(I))
C -----------------------------------------------------------------
C PRINT OUT GE VALUES AT 0.1 INTERVALS
C -----------------------------------------------------------------
   X=FLOAT(I)
   IF ((X/10.).EQ.(INT(X/10.))) GOTO 6500
   GOTO 6000
6500 WRITE(7,830)X1(I),FPSI1(I),FPHI1(I),VEXP(I),HEXP(I)
830  FORMAT(/T2,'X1 = ',F3.1,2X,'PSI1 = ',F10.8,2X,'PHI1 = ',F10.8,2X,
  &'VEXP = ',F12.8,2X,'HEXP = ',F14.6)
   WRITE(7,840)X1(I),TSFRE(I),TSCM(I),TSFEX(I)
840  FORMAT(T2,'X1 = ',F3.1,2X,'RESID. TSE = ',F18.8,2X,'COMB TSE=',
  &F10.6,2X,'TSFRE= ',F18.6)
   WRITE(7,841) X1(I),GEFL(I),GEL(I),TSE1(I),TSE2(I)
841  FORMAT(T2,'X1= ',F3.1,2X,'GE= ',F14.6,2X,'GE(LIEB)= ',F14.6,2X,
  &'TSE1= ',F18.8,2X,'TSE2= ',F18.8)
   WRITE(7,888)VDEX(I),FVDO(I),FVDEX(I),FVD(I)
888  FORMAT(T2,'VDEX=',F14.7,2X,'FVDO= ',F16.8,2X,'FVDEX= ',F16.8,2X,'
  &FVD= ',F16.8)
   WRITE(7,889)ALM(I),BETM(I),GS(I),GFH(I)
889  FORMAT(T2,'ALM=',F14.7,2X,'BETM=',F16.14,2X,'GS=',F14.7,2X,
  &'GFH=',F14.7)
   WRITE(7,909)VD1,VD2
909  FORMAT(T2,'VD1=',F14.7,2X,'VD2=',F14.7)
   WRITE(7,910)GFH(I),FPHI1(I),GS(I)
910  FORMAT(T2,'GFH= ',F16.8,2X,'FPHI1= ',F16.8,2X,'GS= ',F16.8)
   WRITE(7,1)VEM(I),FPSI1(I)
1    FORMAT(T2,'VEM= ',F16.8,2X,'FPSI1= ',F16.8)
   WRITE(7,911)V1,V2
911  FORMAT(/T2,'V1= ',F10.6,2X,'V2= ',F10.6)
   WRITE(7,1213)FTDO(I),FTD(I),FVDE(I)
1213 FORMAT(T2,'FTDO= ',F16.8,2X,'FTD= ',F16.8,2X,'FVDE= ',F16.8)
```

```
      WRITE(7,8005)FVDO(I),FTDO(I),FVDE(I),FVDEX(I)
 8005 FORMAT(/T2,'FVDO = ',F14.6,2X,'FTDO = ',F14.6,2X,'FVDE = ',F14.6,2X
     &,'FVDEX = ',F14.6)
      WRITE(7,8001)FVD(I),FVDXP(I),DLE1(I),DLE2(I)
 8001 FORMAT(/T2,'FVD = ',F14.6,2X,'FVDXP = ',F14.6,2X,'DLE1 = ',F14.6,2X,
     &'DLE2 =',F14.6)
      WRITE(7,8002)DLEX1(I),DLEX2(I)
 8002 FORMAT(/T2,'DLEX1 = ',F14.6,2X,'DLEX2 = ',F14.6)
      WRITE(7,8003)FPSI1(I),P1,P2,TD1
 8003 FORMAT(/T2,'FPSI1 = ',F14.6,2X,'P1 = ',F14.6,2X,'P2 =',F14.6,2X,'TD1
     &= ',F14.6)
      WRITE(7,8004)TD2,THETA2(I),CARRY
 8004 FORMAT(/T2,'TD2 = ',F14.6,2X,'THETA2 = ',F14.6,2X,'CARRY = ',F14.6)

 6000 CONTINUE
C --------------------------------------------------------------------
C END OF LOOP
C --------------------------------------------------------------------

C --------------------------------------------------------------------
C CALL THE SUBROUTINE GAMMA TO CALCULATE ACTIVITY COEFFICIENTS AT
C INFINITE DILUTION . PASS CHI(BERT) , CHI(FLORY) AND CHI(PATTERSON) -
C ONE IN EACH OF THE THREE CALLS
C --------------------------------------------------------------------


      WRITE(7,1520)
 1520 FORMAT(/T2,'(1). ACTIVITY COEFF. AT INF. DIL. USING CHI(BERT)')
      WRITE(7,1530)
 1530 FORMAT(T2,'------------------------------------------------')

C --------------------------------------------------------------------
C CALL THE SUBROUTINE , PASSING CHI(BERT)
C --------------------------------------------------------------------
      CHI = CHIB
      CALL GAMMA (CHI,VS1,VS2,VD1,VD2,P1,T,TD1,V1,V2)

      WRITE(7,1540)
 1540 FORMAT(/T2,'(2). ACTIVITY COEFF. AT INF. DIL. USING CHI(FLORY)')
      WRITE(7,1550)
 1550 FORMAT(T2,'------------------------------------------------')

C --------------------------------------------------------------------
C CALL THE SUBROUTINE , PASSING CHI(FLORY)
C --------------------------------------------------------------------
      WRITE(7,1345)CARRY
 1345 FORMAT(/T2,'CHIHE = ',F17.8)
      CHI = CARRY
      CALL GAMMA (CHI,VS1,VS2,VD1,VD2,P1,T,TD1,V1,V2)

      WRITE(7,1560)
 1560 FORMAT(/T2,'(3). ACTIVITY COEFF. AT INF. DIL. USING CHI(PFP.)')
      WRITE(7,1570)
 1570 FORMAT(T2,'------------------------------------------------')
```

```

C ------------------------------------------------------------------
C CALL THE SUBROUTINE , PASSING CHI(PATTERSON)
C ------------------------------------------------------------------

   CHI = CHIHIN
   CALL GAMMA (CHI,VS1,VS2,VD1,VD2,P1,T,TD1,V1,V2)




   END
```

```

C ******************************************************************
C
C SUBROUTINES TO DETERMINE HEATS , VOLUMES , AND ACTIVITY COEFFICIENTS
C AT INFINITE DILUTION .
C
C ******************************************************************

   SUBROUTINE VOLUME (CHI,THETA2,PSI1,PSI2,P1,VD1,VD2,VEXP,VS1,
  &          VS2,X1,P2)

C ------------------------------------------------------------------
C THE VOLUMES OF MIXING ARE DETERMINED IN THIS SUBROUTINE USING THE
C APPROXIMATION BY PATTERSON , WHICH SEPARATES THE INTERACTIONAL ,
C V-CURVATURE AND P-STAR EFFECTS (EQUATION 15 - TRA VAN AND PATTERSON.
C J. SOL. CHEM. 1982, 11(11), 793 .
C ------------------------------------------------------------------

   DIMENSION THETA2(99),PSI1(99),PSI2(99),VDO(99),VEXP(99),A(99)
   DIMENSION B(99),C(99),W(99),E(99),F(99),G(99),H(99),Y(99),VPFP(99)
   DIMENSION X1(99),VEINT(99),VCURV(99),VPSTR(99),PHI1(99),PHI2(99)
   REAL THETA2,PSI1,PSI2,VDO,VEXP,A,B,C,W,E,F,G,H,Y,VPFP
   REAL VS1,VS2,X1,VEINT,VCURV,VPSTR,PHI1,PHI2
   WRITE(7,888)CHI
888 FORMAT(/T5,'THE CHI VALUE PASSED ACROSS FOR THIS CALCULATION IS = '
   &,F18.6,'------- J/CC')
C ------------------------------------------------------------------
C D IS USED TO CALCULATE STD.DEV
C ------------------------------------------------------------------
   D = 0.00000
C ------------------------------------------------------------------
C START OF LOOP - LOOP 99 TIMES OVER THE WHOLE MOLE FRACTION
C ------------------------------------------------------------------
   DO 68 I = 1,99
```

```
C -----------------------------------------------------------------
C THE EQN. HAS BEEN SPLIT INTO SECTIONS TO FACILITATE THE CALCULATIONS
C
C VDO = "IDEAL" REDUCE VOLUME OF MIXTURE
C -----------------------------------------------------------------
   PHI1(I) = (X1(I)*VS1)/(X1(I)*VS1+(1-X1(I))*VS2)
   PHI2(I) = 1.0-PHI1(I)
   VDO(I)=(PHI1(I)*VD1)+(PHI2(I)*VD2)
   A(I)=((((VDO(I))**(1./3.))-1)*((VDO(I))**(2./3.)))
   B(I)=(((4./3.)*((VDO(I))**(-1./3.)))-1)
   C(I)=(((A(I))*PSI1(I)*THETA2(I)*CHI)/(B(I)*P1))
   W(I)=(((14./9.)*((VDO(I))**(-1./3.)))-1)
   E(I)=(VD1-VD2)
   F(I)=((PSI1(I)*PSI2(I))*((E(I)**2)*W(I))/(B(I)*VDO(I)))
   G(I)=(P2*PSI1(I) + P1*PSI2(I))
   H(I)=((E(I)*(P1-P2)*PSI1(I)*PSI2(I))/(G(I)))
   Y(I)= (X1(I)*VS1 + (1-X1(I))*VS2)

C -----------------------------------------------------------------
C DETERMINE THE THREE CONTRIBUTIONS TO THE EXCESS VOLUME .
C -----------------------------------------------------------------

   VEINT(I)=Y(I)*(C(I))
   VCURV(I)=Y(I)*(F(I))
   VPSTR(I)=Y(I)*(H(I))

C -----------------------------------------------------------------
C CALCULATE VE (=VPFP)
C -----------------------------------------------------------------

   VPFP(I)=((C(I)-F(I)+H(I))*Y(I))

C -----------------------------------------------------------------
C COMPARE THE VEXP AND VE
C -----------------------------------------------------------------
   DIFF=VEXP(I)- VPFP(I)
C -----------------------------------------------------------------
C ADD ON TO SUM FOR STD.DEV
C -----------------------------------------------------------------
   D=D+(DIFF*DIFF)
C -----------------------------------------------------------------
C OUTPUT ONLY ON .1 INTERVALS
C -----------------------------------------------------------------
   X=FLOAT(I)
   IF ((X/10.).EQ.(INT(X/10.))) GOTO 1001
   GOTO 68
1001 WRITE (7,320)X1(I),A(I),B(I),C(I),W(I)
320 FORMAT (/T2,'X1= ',F3.1,2X,' A= ',F10.8,2X,'B= ',F10.8,2X,'C= ',F1
  &0.8,2X,'W = ',F14.8)
   WRITE (7,330) X1(I),E(I),F(I),G(I),H(I)
330 FORMAT(T2,'X1= ',F3.1,2X,'E= ',F10.8,2X,'F= ',F10.8,2X,'G= ',F14.4
  &,F14.4,2X,'H = ',F10.8)
   WRITE(7,340)X1(I),Y(I),VPFP(I),VEXP(I)
340 FORMAT(T2,'X1= ',F3.1,2X,'Y= ',F6.2,2X,'VPFP= ',F12.8,2X,'VEXP= ',
```

```
     &F12.8,2X)
      WRITE(7,350)X1(I),DIFF
 350  FORMAT(T2,'X1 = ',F3.1,2X,'(VEXP - VPFP) = ',F10.8)
      WRITE(7,351)X1(I),VEINT(I),VCURV(I),VPSTR(I)
 351  FORMAT(T2,'X1 = ',F3.1,2X,'VE(INT) = ',F18.8,2X,'VE(CURV.) = ',F18.8
     &,2X,'VE(PSTAR) = ',F18.8)
      WRITE(7,1212)VDO(I)
 1212 FORMAT(T5,'THE REDUCED VOLUME , FOR THE MIXTURE , USED IN THIS CAL
     &CULATION IS = ',F10.8)
 68   CONTINUE
C ---------------------------------------------------------------------
C END OF LOOP
C ---------------------------------------------------------------------
C PRINT STANDARD DEVIATION
C ---------------------------------------------------------------------

      SD = (D/98)**0.5
      WRITE(7,771)SD
 771  FORMAT(/T2,'THE STD. DEVIATION IS = ',F12.6 )
      WRITE(7,772)
 772  FORMAT(T2,34('-'))

      RETURN

      END
```

```
C ********************************************************************


      SUBROUTINE HEATS (CHI,THETA2,PSI1,PSI2,P1,P2,VD1,VD2,TD1,TD2,
     &            VS1,VS2,HEXP,X1,PHI1,PHI2,V1,V2,T)



C ********************************************************************
C THE ENTHALPIES OF MIXING AND THE ENTROPIES OF MIXING ARE PREDICTED IN
C THIS SUBROUTINE , USING AN APPROXIMATE FORM OF THE PRIGOGINE-FLORY
C THEORY WHICH SEPARATES THE FREE VOLUME AND INTERACTIONAL CONTRIBUTIONS
C (BARBE AND PATTERSON - J. SOL. CHEM. 1980, 9(10), 753 .) . VARIABLES
C LOCAL TO THIS SUBROUTINE ARE DEFINED IN THE ABOVE PUBLICATION .
C ---------------------------------------------------------------------
C DIMENSION ALL ARRAYS .
C ---------------------------------------------------------------------

      DIMENSION THETA2(99),PSI1(99),PSI2(99),PVDO(99),U(99),TD(99)
      DIMENSION CP(99),PA(99),PB(99),PC(99),PD(99),PE(99),PF(99),PHE(99)
      DIMENSION HEXP(99),TSE(99),GEP(99),S(99),PHEX(99),X1(99)
      DIMENSION TS(99),PG(99),PH(99),ANS1(99),ANS3(99),ANS4(99),AINT(99)
      DIMENSION ANS5(99),VEN(99),CPNT(99),TDNT(99),PHI1(99),PHI2(99)
```

```
      DIMENSION AGES(99),VENT(99),TSINT(99),TSFV(99),TSCM1(99),START(99)
      DIMENSION HINT(99),HFV(99),TSCM2(99),DPHI1(99),DPHI2(99)
      REAL THETA2,PSI1,PSI2,PVDO,U,TD,CP,PA,PB,PC,PD,PE,PFS1
      REAL PHE,CHI,P1,P2,VD1,VD2,TD1,TD2,VS1,VS2,US1,US2
      REAL DIFF,D,HEXP,TSE,GEP,PHEX,X1,TS,PF,PG,PH,S1,S2
      REAL ANS1,ANS3,ANS4,ANS5,VEN,CPNT,TDNT,PHI1,PHI2,TSCM1,TSCM2
      REAL AGES,VENT,TSINT,TSFV,TSCM,START,AINT,HINT,HFV,DPHI1,DPHI2
      REAL V1,V2,T
C -----------------------------------------------------------------
C FIRST DETERMINE THE VARIABLES REQUIRED IN THIS SUBROUTINE .
C -----------------------------------------------------------------
     US1=(P1*VS1)
     US2=(P2*VS2)
     WRITE(7,600)US1,US2
600  FORMAT(/T2,'PARAMETER USTAR1 = ',F18.4,10X,'PARAMETER USTAR2 = ',
    &F18.4,2X,'------- J/MOL')
     WRITE(7,1011)CHI
1011 FORMAT(/T5,'THE CHI VALUE PASSED ACROSS FOR THESE CALCULATIONS IS
    &= ',F14.6,2X,'J/CC')
     D=0.0000000
     I=0.00000
     DO 61 J=1,9
     I = (J * 10)
C -----------------------------------------------------------------
C FIRST DETERMINE THE HEATS .
C PVD0 , TD , AND CP ARE THE REDUCED VOLUME , THE IDEAL REDUCED TEMP.
C AND THE HEAT CAPACITY FOR THE MIXTURE .
C -----------------------------------------------------------------
     S1=(3*(ALOG((VD1**(1./3.))-1)))
     S2=(3*(ALOG((VD2**(1./3.))-1)))
     U(I)=((PSI1(I)/VD1) + (PSI2(I)/VD2))
     PVDO(I)=(1./U(I))
     TD(I)=(((PVDO(I)**(1./3.))-1)/(PVDO(I)**(4./3.)))
     CP(I)=((1.0)/(((4./3.)*((PVDO(I)**(-1./3.)))-1)))
     PA(I)=((CHI*THETA2(I)*PSI1(I))/(P1))
     PB(I)=(U(I) + (CP(I)*TD(I)))
     PC(I)=((PSI1(I)*TD1) + (PSI2(I)*TD2) - TD(I))
     PD(I)=((X1(I)*US1) + ((1-X1(I))*US2))
     PHEX(I)=(((PA(I)*PB(I)) + (PC(I)*CP(I)))*(PD(I)))
C -----------------------------------------------------------------
C DETERMINE THE TWO CONTRIBUTIONS TO THE EXCESS ENTHALPY .
C -----------------------------------------------------------------

     HINT(I)=PD(I)*(PA(I)*PB(I))
     HFV(I)=PD(I)*(CP(I)*PC(I))

C -----------------------------------------------------------------
C DETERMINE THE ENTROPIES
C
C THE FIRST TASK IS TO SOLVE FOR THE IDEAL REDUCED VOLUME FOR THE MIXT.
C THIS IS DONE BY AN  .TERATIVE METHOD .
C
C SOLVE FOR (T*CP)
C -----------------------------------------------------------------
```

```
   ANS1(I) = ((PSI1(I)*TD1*S1) + (PSI2(I)*TD2*S2))
   WRITE(7,4444)ANS1(I),PSI1(I),PSI2(I)
4444 FORMAT(/T2,'ANS1 = ',F16.8,2X,'PSI1 = ',F16.8,2X,'PSI2 = ',F16.8)
   WRITE(7,8888)TD1,TD2,S1,S2
8888 FORMAT(/T2,'TD1 = ',F16.8,2X,'TD2 = ',F16.8,2X,'S1 = ',F16.8,2X,'S2 = ',
   &F16.8)
C -------------------------------------------------------------------
C START THE ITERATIVE PROCESS . AGES IS THE INITIAL GUESS FOR V    .
C -------------------------------------------------------------------
   TOL = 0.0000001
   AGES(I) = 1.25
   WRITE(7,2221)AGES(I)
2221 FORMAT(/T2,'AGES = ',F16.8)
   GRAD = 0.125
   ITT = 0
2222 ANS3(I) = (((3*((AGES(I)**(1./3.))-1))/((AGES(I))**(4./3.)))
  **(ALOG((AGES(I)**(1./3.))-1)))
   IF (ABS(ANS3(I)-ANS1(I)).LT.TOL) GOTO 2224
   IF (ITT.GT.35) GOTO 2224
   IF (ANS3(I).LT.ANS1(I)) GOTO 2226
   AGES(I) = AGES(I) + GRAD
   GOTO 2223
2226 AGES(I) = AGES(I)-GRAD
2223 GRAD = GRAD/2.0
   ITT = ITT + 1
   GOTO 2222
C -------------------------------------------------------------------
C DETERMINE THE ENTROPY .
C -------------------------------------------------------------------
2224 S(I) = (3*(ALOG((AGES(I)**(1./3.))-1)))
   CPNT(I) = ((1.0)/(((4./3.)*((AGES(I)**(-1./3.)))-1)))
   TDNT(I) = (((AGES(I)**(1./3.))-1)/(AGES(I)**(4./3.)))
   PF(I) = (S(I) + CPNT(I))
   PG(I) = ((PSI1(I)*TD1) + (PSI2(I)*TD2)-TDNT(I))
   PH(I) = (TDNT(I)*CPNT(I))
C -------------------------------------------------------------------
C INTERACTION TERM .
C -------------------------------------------------------------------
   TSINT(I) = PA(I)*PH(I)*PD(I)
C -------------------------------------------------------------------
C FREE VOLUME TERM .
C -------------------------------------------------------------------
   TSFV(I) = PF(I)*PG(I)*PD(I)
C -------------------------------------------------------------------
C DETERMINE THE COMBINATORIAL PART OF THE ENTROPY .
C -------------------------------------------------------------------
   DPHI1(I) = (X1(I))/(X1(I) + (1-X1(I))*(V2/V1))
   DPHI2(I) = 1.0 - DPHI1(I)
   WRITE(7,8721)DPHI1(I),DPHI2(I)
8721 FORMAT(/T2,'DPHI1 = ',F16.8,2X,'DPHI2 = ',F16.8)
   TSCM1(I) = (-1.0*T*8.314)*((X1(I)*(ALOG (PHI1(I)/X1(I))))
  &      + (1-X1(I))*(ALOG(PHI2(I)/(1-X1(I)))))
   TSCM2(I) = (-1.0*T*8.314)*((X1(I)*(ALOG(DPHI1(I)/X1(I))))
  &      + (1-X1(I))*(ALOG(DPHI2(I)/(1-X1(I)))))
```

```
C -------------------------------------------------------------------
C CALCULATE THE EXCESS GIBBS FUNCTIONS (GE=HE-TSE)
C -------------------------------------------------------------------
   GEP(I)=PHEX(I) - TSE(I)
C -------------------------------------------------------------------
C COMPARE PREDICTED AND EXPERIMENTAL ENTHALPIES
C -------------------------------------------------------------------
   DIFF=HEXP(I) - PHEX(I)
C -------------------------------------------------------------------
C ADD ON TO SUM FOR STADARD DEVIATION
C -------------------------------------------------------------------

   D=D + (DIFF*DIFF)

C -------------------------------------------------------------------
C OUTPUT ONLY AT 0.1 INTERVALS
C -------------------------------------------------------------------

   X=FLOAT(I)
   IF ((X/10.).EQ.(INT(X/10.))) GOTO 8000
   GOTO 61

8000 WRITE (7,610)X1(I),U(I),CP(I),TD(I),AGES(I)
610  FORMAT(/T2,'X1= ',F3.1,2X,'U= ',F14.8,2X,'CP= ',F14.8,2X,'TD= ',
    &F14.8,2X,'REDUCED VOLUME= ',F14.8)
     WRITE(7,620)X1(I),PA(I),PB(I),PC(I),PD(I)
620  FORMAT(T2,'X1= ',F3.1,2X,'PA= ',F14.8,2X,'PB= ',F14.8,2X,'PC= ',
    &F14.8,2X,'PD= ',F14.8)
     WRITE(7,625)X1(I),S(I),CPNT(I),TDNT(I)
625  FORMAT(T2,'X1= ',F3.1,2X,'S= ',F14.8,2X,'CPNT= ',F14.8,2X,'TDNT= '
    &,F14.8)
     WRITE(7,626)X1(I),PF(I),PG(I),PH(I)
626  FORMAT(T2,'X1= ',F3.1,2X,'PF= ',F14.8,2X,'PG= ',F14.8,2X,'PH= ',F1
    &4.8)
     WRITE(7,630)X1(I),PHEX(I),HEXP(I)
630  FORMAT(T2,'X1= ',F3.1,2X,'PHEX= ',F14.8,2X,'HEXP= ',F14.8,2X)
     WRITE(7,640)X1(I),TSCM1(I),TSCM2(I),GEP(I)
640  FORMAT(T2,'X1= ',F3.1,2X,'TSCM1 ',F14.8,2X,'TSCM2= ',F14.8,2X,'
    &GEP= ',F14.8)
     WRITE(7,641)X1(I),HINT(I),HFV(I)
641  FORMAT(T2,'X1= ',F3.1,2X,'HE(INT)= ',F14.8,2X,'HE(FV)=',F14.8)
     WRITE(7,642)TSINT(I),TSFV(I),AGES(I)
642  FORMAT(T2,'TSE(INT)= ',F16.8,2X,'TSE(FV)= ',F16.8,2X,'AGES=',F18.6
    &)
     WRITE(7,643)V1,V2,ANS3(I)
643  FORMAT(/T2,'V1= ',F10.6,2X,'V2= ',F10.6,2X,'ANS3= ',F10.6)
61   CONTINUE

C -------------------------------------------------------------------
C END OF LOOP
C -------------------------------------------------------------------
C PRINT STANDARD DEVIATION
C -------------------------------------------------------------------

```

```
      SD=(D/8)**0.5
      WRITE(7,650)SD
650   FORMAT(/T2,'THE STD. DEVIATION IS = ',F12.6 )
      WRITE(7,660)
660   FORMAT(T5,34('-'))

      RETURN

      END
```

```
C ****************************************************************************


      SUBROUTINE GAMMA (CHI,VS1,VS2,VD1,VD2,P1,T,TD1,V1,V2)


C ****************************************************************************
C THIS SUBROUTINE CONTAINS THE CODE NECESSARY TO PREDICT ACTIVITY
C COEFFICIENTS AT INFINITE DILUTION :
C
C       LN GAMMA(INFINITE) = LN GAMMA(COMBINATORIAL) + CHI(RESIDUAL)
C
C WHERE :  LN GAMMA(COMB.) = FLORY - HUGGINS COMB. TERM
C                        = LN (1/R) + (1-1/R)
C
C AND  :  CHI(RESID.) = RTLN GAMMA(RESID.)
C                   = PS1*VS1*(3*T*LN(((VD1**0.3)-1)/((VD2**0.3)-1))
C                     + (CHI*VS1/VD2)
C
C ---------------------------------------------------------------------
      REAL RAT,CHI,VD1,VD2,P1,T,TD1,TD2,V1,V2,GAMB,GAMC,GAMD,GAMG
      REAL GAMF,LNGC,LNGR,R,VS1,VS2,GAM1,GAM2
      WRITE(7,1003)T,P1,VS1,VS2
1003 FORMAT(/T2,'T=',F10.4,2X,'P1=',F18.4,2X,'VS1=',F18.10,2X,'VS2= ',
     &F18.6)
C ---------------------------------------------------------------------
C R = RATIO OF THE MOLAR VOLUMES OF THE TWO COMPONENTS
C R IN UNITS J/K
C R1 IN UNITS PA.CUBIC CM
C ---------------------------------------------------------------------
      RAT1 = 0.000
      RAT = V2/V1
      RAT1 = VS2/VS1
      WRITE(7,1001)V1,V2,RAT,RAT1
1001 FORMAT(/T2,'V1=',F16.8,2X,'V2=',F16.8,2X,'RAT= ',F12.6,2X,'RAT1= '
     &,F12.6)
      R = 8.314
      WRITE(7,1235)CHI
1235 FORMAT(/T2,'CHI= ',F16.8)
```

```
          GAMB = ((VS1*CHI)/(R*T*VD2))
          GAMC = (3*TD1*(ALOG(((VD1**(1./3.))-1)/((VD2**(1./3.))-1))))
          GAMD = ((1/VD1) - (1/VD2) + GAMC)
          GAMG = ((P1*VS1*GAMD)/(R*T))
          LNGC = (ALOG(1/RAT)) + (1-(1/RAT))
          LNGC1 = (ALOG(1/RAT1))+(1-(1/RAT1))
          LNGR = (GAMB + GAMG)
          GAM1 = (LNGC + LNGR)
          GAM2 = (LNGC1+LNGR)
    C ----------------------------------------------------------------
    C WRITE OUT RESULTS TO THE OUTPUT FILE
    C ----------------------------------------------------------------

          WRITE (7,1000)GAMB,GAMC,GAMD
    1000 FORMAT(/T2,'GAMB =',F18.10,2X,'GAMC =',F18.10,2X,'GAMD =',F18.10,
         &2X,'GAME =',F18.10)
          WRITE(7,1020)GAMG
    1020 FORMAT(T2,'GAMG =',F18.10)
          WRITE(7,1010)LNGC,LNGR,GAM1,GAM2
    1010 FORMAT(T2,'LNGC =',F18.10,2X,'LNGR =',F18.10,2X,'LN GAMMA INF. =',
         &F18.10,2X,'LN GAMMA INF. = ',F18.6)

          RETURN

          END
```

```
PROGRAM-UNIT LENGTH        271B = 185
CM STORAGE USED          63500B = 26432
COMPILE TIME           0.254 SECONDS
```

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LIST OF PUBLICATIONS

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