THE THERMODYNAMICS OF BINARY LIQUID MIXTURES

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by

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Abstract

A systematic study of the excess thermodynamic properties of two-ring compounds (bicyclohexyl, tetralin and decalin) in cycloalkanes and n-alkanes was conducted. The excess enthalpies were determined at 288,15 K and 298,15 K by using a flow microcalorimetric technique.

The excess volumes of tetralin and cycloalkanes, and tetralin and n-alkanes at 283,15 K and 298,15 K were determined by using a vibrating tube densitometer. The results showed trends relating to the size and shape of the n-alkane and cycloalkane molecules.

The theory developed by Flory was applied to the decalin + cycloalkane and + n-alkane systems and this gave qualitative predictions of the excess enthalpies from the excess volumes and vice versa.

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1. INTRODUCTION

Of the three states of matter we know the least about the liquid state. In view of our paucity of knowledge regarding pure liquids it is easier to study and understand liquid mixtures, because we can deal primarily with the differences in chemical properties of the mixing species and can ignore a large component of the liquid properties. A real system, like any physical chemistry system such as a liquid mixture can be studied according to Figure 1(1).

When the real system is a liquid mixture, the physical quantities that can be studied are the thermodynamic properties of enthalpy (H), volume (V), Gibbs function (G) and Helmholtz function (A).

Referring to Figure 1, the model is chosen to represent the physical reality of the mixing molecules and is a compromise between the imagined real mixture and the mathematics involved in expressing the mixing process. In expressing the model in terms of mathematical equations and bulk physical properties it is necessary to define certain parameters which refer to the interactions of the molecules. These parameters can be calculated by fitting the equations to the experimentally determined bulk properties for a few systems. This knowledge, together with the mathematical equations can be tested by predicting bulk properties of other liquid mixtures. When the predicted models fail to compare well with experimentally determined quantities then the original model must be altered or the mathematical techniques improved.

If we mix two liquids A and B we can argue as follows:

$$A \text{ (liquid)} + B \text{ (liquid)} \rightarrow (A + B) \text{ (liquid mixture)}$$

$$N_A \text{ moles} + N_B \text{ moles} \rightarrow (N_A + N_B) \text{ moles}$$

In considering a thermodynamic property X, the effect on mixing is ΔX and is the difference in X before and after mixing.

$$\begin{aligned}
\Delta X = {} & (N_A + N_B) \text{ (Calculated X for mixture)} \\
& + (N_A + N_B) \text{ (Ignorance of liquid state, mixture)} \\
& - N_A \text{ (Calculated X for pure A)} \\
& - N_A \text{ (Ignorance of liquid state, A)} \\
& - N_B \text{ (Calculated X for pure B)} \\
& - N_B \text{ (Ignorance of liquid state, B)}
\end{aligned}$$

In the above equation we expect the terms in "Ignorance of liquid state" to almost cancel out. Hence we expect our model to yield reasonable changes in properties of mixing.

Successful predictive theories have evolved to the stage when the parameters have little meaning in relation to the original model. Equations contain fitting parameters which may number more than one or two, depending on the complexity of the model.

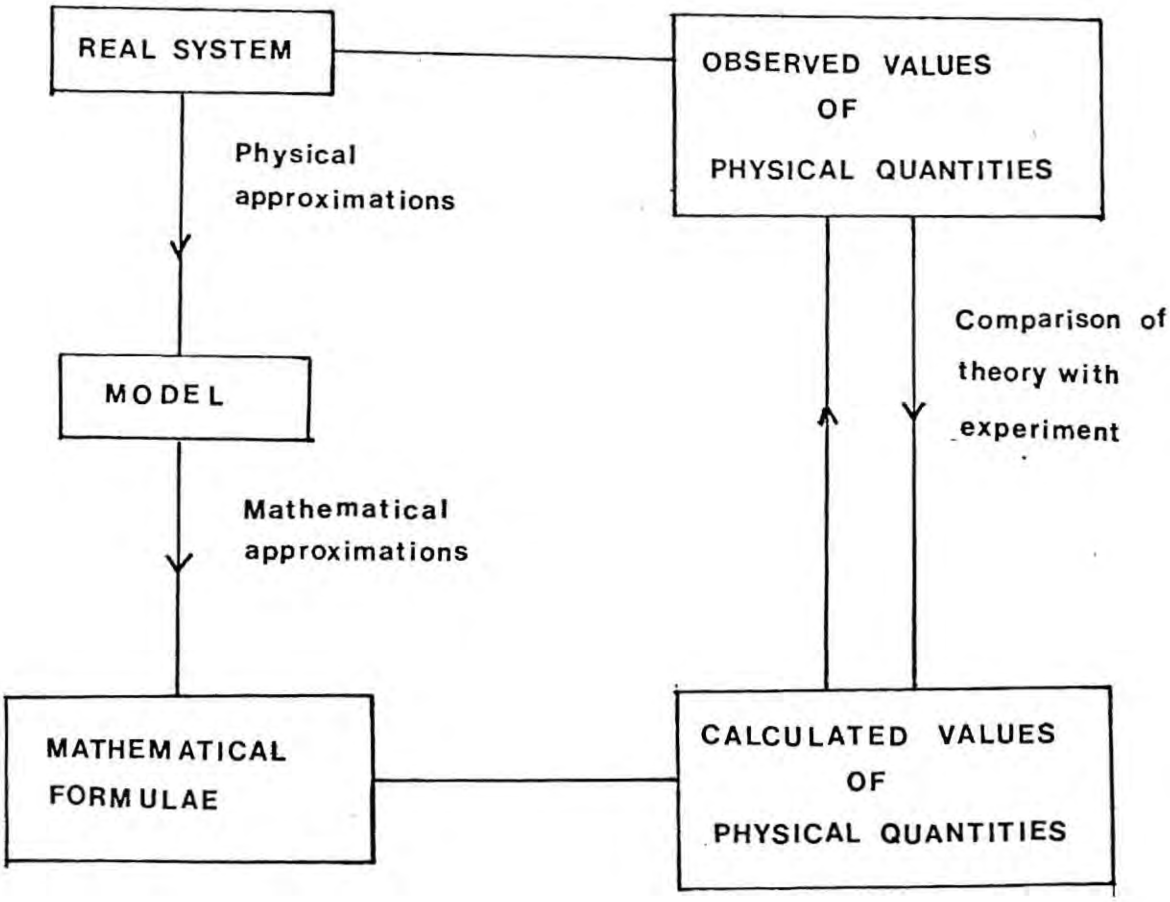

FIG 1 FORMULATION OF A PHYSICAL THEORY[1]

Excess thermodynamic functions of liquid mixtures are useful in that they provide data to test theories of liquid mixtures. The main properties measured are the excess molar properties of volume, enthalpy and Gibbs free energy.

By excess molar property we mean the property in excess of the ideal for the mixture, i.e.

X^E_M = [X (real mixture) - X (ideal mixture)]/Number of moles

By developing a successful theory of liquid mixtures we can predict an excess thermodynamic function such as for example H^E_M, by establishing the aforementioned theoretical parameters with an alternative experimental set of results of an excess thermodynamic function, such as V^E_M. The fundamental idea therefore is to be able to predict excess thermodynamic properties without having to do the work.

In this work we are primarily concerned with the theories of solutions of non-electrolytes, and in particular of mixtures of normal alkanes and cycloalkanes with two-ring hydrocarbon molecules. Experimental results in this field can be considered as an extension of the recent studies done on cycloalkanes and alkanes by Spiteri(2); Gomez-Ibanez and Liu(3); Heintz(4); Vesely and Pick(5); and Patterson, Lam, Picker and Tancrede(6). Apart from Sturtevant and Lyons(7); Jones, Weeks and Benson(8); and Benson, Murakami, Lam and Singh(9); no one has conducted a study of 2-ring hydrocarbons with alkanes and cycloalkanes. In this work bicyclohexyl, decahydronapthalene and tetrahydronapthalene are mixed with n-alkanes and cycloalkanes.

The excess enthalpies of mixing were measured by a flow calorimetric technique using an LKB 2107 flow microcalorimeter.

The excess volumes of mixing were determined by an indirect method using a Paar mechanical oscillator densimeter. An attempt was made to experimentally determine the isothermal compressibility of tetralin and bicyclohexyl by a piezometric technique but was abandoned due to lack of time.

The Flory theory was used to analyse the experimental excess volumes and excess enthalpies with moderate success.

2. EXCESS MOLAR ENTHALPIES OF BINARY LIQUID MIXTURES

2.1 Background

In an ideal solution there is no enthalpy change on mixing. In real solutions, however, interactions between liquids often result in a change of enthalpy. A means of investigating these interactions between component molecules in the liquid state is achieved by studying the excess molar enthalpies of binary mixtures. The excess enthalpy can be represented by

$$H^E = H\ (\text{real mixture}) - H\ (\text{ideal mixture}) \quad (2.1)$$

H (ideal mixture) is considered to be zero. The excess molar enthalpy $H^E{}_M$ can then be represented by

$$H^E{}_M = H\ (\text{real mixture})/(N_A + N_B) \quad \text{J.Mol}^{-1} \quad (2.2)$$

N_A, N_B are the number of moles of A and B respectively.

It is possible to calculate the excess molar enthalpy from the temperature coefficient of the excess molar Gibbs free energy by the expression

$$H^E_M = G^E_M - T(\partial G^E_M/\partial T)_p \quad (2.3)$$

The Gibbs free energy of mixing $G^E{}_M$ can be derived from measurements of the total vapour pressure and the compositions of the liquid and the vapour in equilibrium. The latter determination is difficult. Williamson (10) has analysed the errors inherent in the application of equation (2.3).

If G^E_M is determined at two temperatures 30 K apart in the region of 300 K and G^E_M is assumed independent of temperature then an error of $\pm \sigma$ in G^E_M will lead to an error of $\pm 15\sigma$ in H^E_M. Application of equation (2.3) for the determination of H^E_M is therefore unsatisfactory and we must look at alternative methods.

2.2 Adiabatic Calorimeter

To obtain precise values of H^E_M it is necessary to measure H^E_M directly by calorimetric means. There are various types of these. An adiabatic calorimeter is an apparatus which is thermally isolated from its surroundings. Known quantities of two liquids which are initially separated can be thermally equilibrated and then rapidly mixed. A temperature sensing device measures the change in temperature at mixing. An electrical heating device measures the amount of energy transmitted to the liquid mixture necessary for calibration purposes. This amount of energy is comparable to the heat of mixing.

If H^E is positive there will be an endothermic change in the enthalpy of mixing and a consequent drop in temperature. Electrical heating is supplied to nullify the drop in temperature. If there is an exothermic physical change (i.e. if H^E is negative) then there is a rise in temperature on mixing and the amount of energy required to produce the same temperature rise must be determined.

A simple apparatus in which $H^E{}_M$ determinations can be made is shown in Figure 2. A measured quantity of liquid A is placed in the calorimeter which is constructed from a Dewar flask i.e. the vessel is vacuum jacketed and hence isolated. It is insulated from the environment by a cork. A measured quantity of component B is placed in the sample tube which has a silicon gel (silicon grease) plug at the bottom, to keep component B from mixing with component A. After both components have reached thermal equilibrium in the calorimeter, pressure is applied to the top of the sample tube to remove the plug and mixing takes place. The change in temperature is noted after the temperature has become constant. The heat capacity of the apparatus is determined by passing a measured current through the heater at a constant voltage for a measured time. The molar enthalpy of mixing is then given by the expression

$$H^E_M = \frac{-\Delta T_1}{\Delta T_2} \int_0^T EIdt/n_1 + n_2) \qquad (2.4)$$

where T_1 = temperature change on mixing (^oK)
T_2 = temperature rise on calibration (determination of heat capacity of sample container) (^oK)

E = potential difference across heating element (V)

I = measured current (A)

t = time (seconds)

n_1, n_2 = Number of moles of components 1 and 2 respectively.

If the heater has a known resistance R ohms then the rate of heating P ($J.sec^{-1}$) can be given by the expression

$$P = I^2R \qquad (2.5)$$

The chief fault with this simple type of calorimeter is the presence of a vapour space. A temperature change results in evaporation or condensation. As $H^E{}_M$ is small compared to the molar heat of evaporation, the presence of even a small amount of vapour would produce meaningless results. For instance, $H^E{}_M$ for equimolar hydrocarbon liquid mixtures usually varies from approximately 10 to 1 000 $J.Mole^{-1}$. The enthalpy of vaporisation is usually 3 orders of magnitude larger. When the heat of mixing is small the evaporation or condensation of 10^{-3} moles of material can produce a heat effect as large as the enthalpy of mixing.

Any good design of calorimeter must take this into account, and much effort has been expended in designing mixing vessels in which vapour spaces are eliminated.

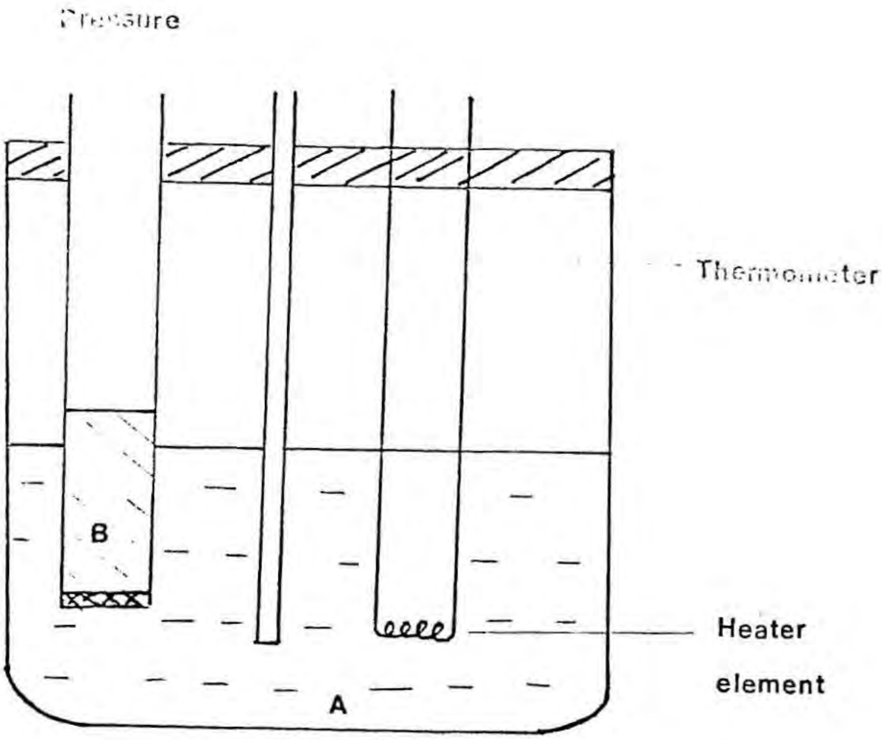

FIG 2 A SIMPLE CALORIMETER

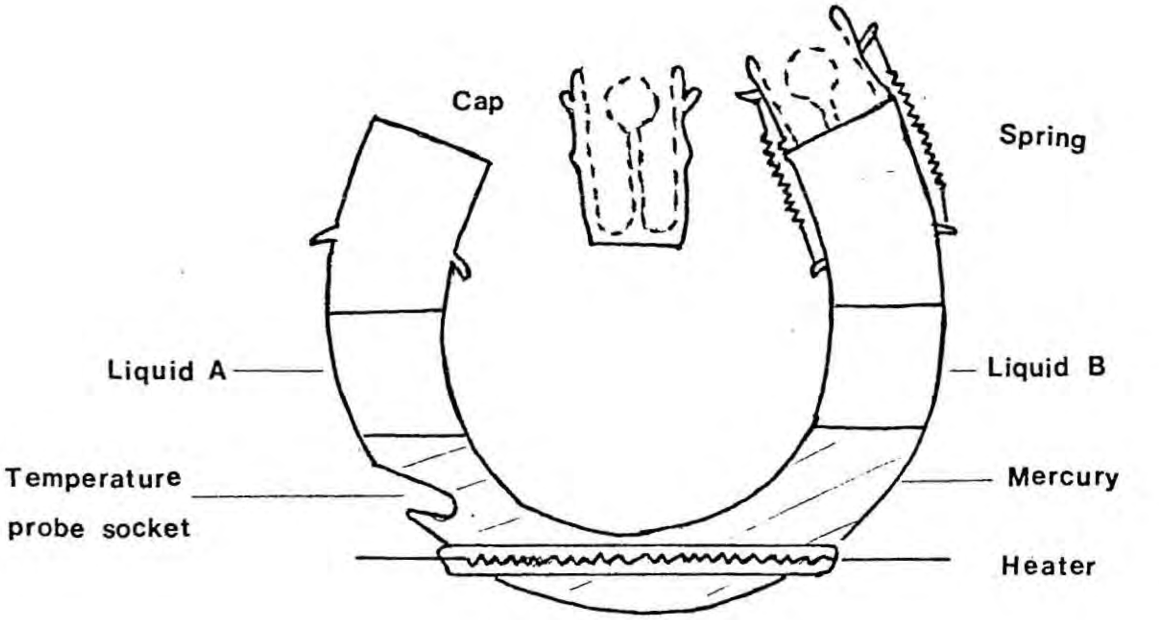

FIG 3 AN ADIABATIC CALORIMETER USING MERCURY TO SEPARATE THE LIQUIDS

It goes without saying that there must be no heat leaks in the calorimeter if a meaningful result is to be achieved.

A simultaneous consideration is that the volume change which occurs on mixing must be allowed for as this will cause a pressure change and H^E is related to $\partial V/\partial P$.

An adiabatic calorimeter which goes towards meeting the above requirements is illustrated in Figure 3 (87). This apparatus uses mercury, which half fills the U-tube, to separate the liquids, which are placed above the mercury levels. The caps enclose the liquids and ensure that the only vapour space is in their bulbs. After thermal equilibrium has been reached the cell is rotated and the liquids mix.

A batch calorimeter which has been widely used is described by Larkin and McGlashan (11) An illustration of this method is shown in Figure 4. Their apparatus consisted of a glass vessel in which the two liquids are initially separately confined over mercury in two compartments in the upper half of the vessel. An expansion bulb connected to a capillary containing mercury is connected to a ground-glass joint socket attachment of the glass vessel.

The vessel is originally filled completely with mercury.

Mercury is displaced from the upper compartments by introducing known quantities of the liquid components by means of a hypodermic syringe with a bent needle. (See Fig. 5) The capillary is half-filled with mercury and attached to the mixing vessel.

After temperature equilibration the liquids are mixed in the absence of a vapour space by rotating the vessel a number of times through 180° so that the two liquids are displaced into the single lower chamber. The temperature change is measured by thermistors distributed over the surface of the vessel. The calorimeter is calibrated by a heater and a correction factor for the energy dissipated by stirring is determined. This apparatus fulfils the condition of an absence of vapour space by means of the mercury in the vessel, and the volume change on mixing is taken up by the movement of the mercury in the capillary. The precision of this apparatus is 0,7 $J.mol^{-1}$ or 0,5 % of the maximum value of $H^E{}_M$. Sample volumes are of the order of 1 ml and samples must be purified.

Brown and Fock (12) describe a U-tube adiabatic calorimeter which used mercury to separate the liquids and two expansion capillaries to prevent mixing of the vapour phases. After thermal equilibrium has been reached the cell is rotated and the liquids mix. (See Figure 3)

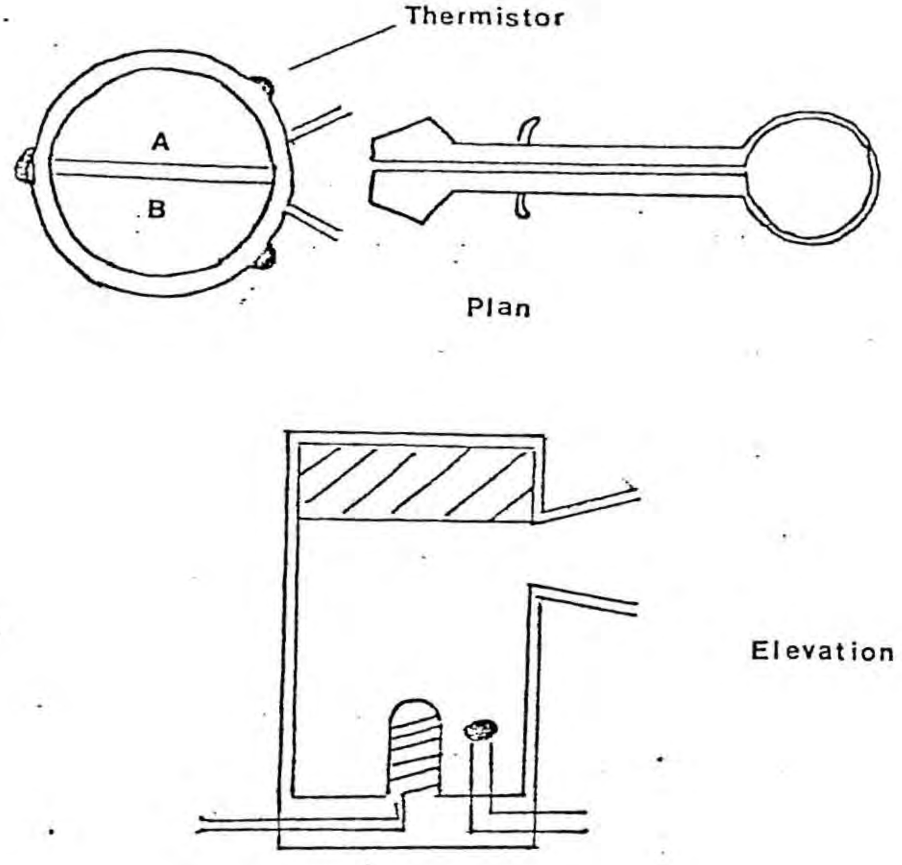

FIG 4 LARKIN-TYPE CALORIMETER

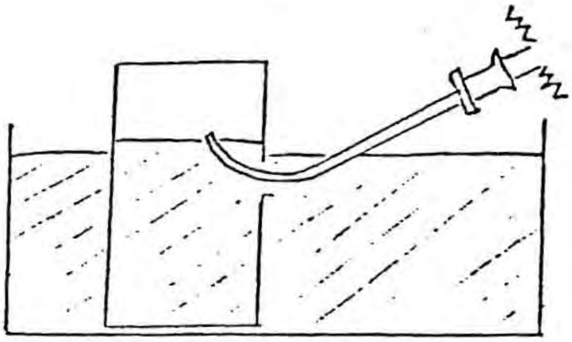

FIG 5 METHOD OF LOADING LARKIN-TYPE CALORIMETER

2.3 Isothermal Calorimeters

Malcolm and Rowlinson describe an isothermal apparatus based on the Bunsen calorimeter. In the Bunsen calorimeter the mixing vessel is surrounded by a vessel completely filled with a liquid, part of which is frozen to give a mantle around the walls of the mixing vessel. H^E_M causes melting or freezing of the mantle and the volume change which accompanies this process can be measured by the movement of mercury in a capillary tube. The calorimeter is calibrated by means of an electrical heater situated in the mixing vessel. The sensitivity of this method is limited by the ratio of the volume change on melting to the latent heat of fusion of the calorimetric fluid. The most important advantage of the Bunsen calorimeter is that it is suited to the measurement of H^E_M for slow processes, such as when one component is viscous and mixing is not instantaneous. The disadvantage of the system is that it is limited to the determination of H^E_M at the temperature of the melting point of the calorimetric fluid.

Davies and Pritchard (13) used diphenyl ether as the calorimetric fluid, a major advantage of this liquid being that its melting temperature (26,9 °C) is close to the standard reference temperature of 25 °C . The calibration constant of the calorimeter was reproducible to within a standard deviation of 0,009 % and using the system HCl/water the instrument gave an accuracy of 0,1%

(17 kcal/mol) A disadvantage of this method is that it takes 1 day to get 1 measurement.

2.4 Isothermal Dilution Calorimeter

An isothermal method which is an alternative to the Bunsen calorimeter is the isothermal dilution calorimeter which was developed by van Ness and co-workers (14) and subsequently improved by Stokes, Marsh and Tomlins (15). This apparatus has the advantage that the entire mole fraction range can be covered in two experimental runs. For an endothermic system one component is injected into the second component with the simultaneous addition of electrical energy in order that isothermal conditions are observed. The addition is stopped at any desired composition and the molar excess enthalpy determined from component masses and the electrical energy added to maintain isothermal conditions. For exothermic systems a thermoelectric cooling device is connected to the calorimeter by a defined heat-leak path which removes energy from the calorimeter at a constant rate. The calorimeter is maintained isothermal by the continuous addition of electrical energy.

This instrument is suited to the determination of partial molar enthalpies of one component at high dilution in the other to a precision of better than 1 % by using small increments in the initial stages of the experiment. Isothermal dilution calorimeters require approximately 50 cm^3 of each component for the two runs necessary to cover the entire mole fraction range. 20 to 30 points can be measured, the precision of H^E_M being 0,2 J.mol^{-1} or 0,1 % of the maximum value of H^E, whichever is the greater in magnitude. These calorimeters thus have the advantage of high precision and the fact that a large number of results can be obtained fairly rapidly.

2.5 Flow Calorimeters

In a flow calorimeter the two liquids are introduced into a mixing vessel at a steady, determinable rate. For an endothermic system the power P in the heater needed to exactly restore the temperature of the mixed liquids to that of the unmixed liquids is measured. The molar excess enthalpy of mixing and the mole fraction x of liquid B are then given by the formulae

$$H^E_M = P/(f_A + f_B) \qquad (2.7)$$

$$x_B = f_B/(f_A + f_B) \qquad (2.8)$$

where $P = I^2R$ (J.S^{-1})

(I = current (A) through heating resistance R(

$_A$ = flow rate of component A (moles.s^{-1})

$_B$ = flow rate of component B (moles.s^{-1})

x_B = mole fraction of component B

The flow rates can be determined by weighing the component reservoirs before and after the calorimetric run, converting the mass into the number of moles and hence finding the molar flow rate, knowing the duration in seconds of the calorimetric run.

Flow calorimetry has several advantages over a batch calorimetric method.

(a) Operational procedure at a calorimetric experiment is simplified. The flow method is automatic and doesn't require any equilibration time.

(b) Mixing of reactants is achieved without the presence of a gaseous phase, when small condensation-evaporation effects may affect the result.

(c) Surface adsorption effects which may cause systematic errors can be neglected if a steady liquid flow is allowed to continue until possible wall reactions have occured.

(d) The flow method is rapid (approximately 30 minutes per reading) and is thus suited for an extensive series of measurements.

The major problem with flow calorimeters is in producing a constant flow rate. McGlashan and Stoeckli(16) used a vapour-pressure-driven flow system and obtained a 0,25 % reproducibility in the flow rates. They made a series of measurements on n-hexane and cyclohexane at 298,15 K, fitted their results to a Redlich-Kister smoothing polynomial, and obtained a precision of 1 % in H^E_M. However, 200 cm^3 of sample was needed to cover the composition range.

Sturtevant and Lyons$^{(17)}$ used two 2,5 cm^3 syringes which contained the two liquids to be mixed. The syringes have plungers which were driven independently by motors equipped with readily changeable gear reductions. A reproducibility in flow of 2 % was claimed. A Beckman Model 190 Microcalorimeter which is a conduction type calorimeter was used. This had a rather long response time (5-8 minutes to reach a steady state) but it was possible to determine a mixing curve in one day, using 10-20 cm^3 of each component.

McGlashan and Stoeckli$^{(16)}$ used a flow microcalorimeter to measure the enthalpy of mixing of n-hexane and cyclohexane, a pair of liquids recommended for testing new microcalorimeters. They achieved a precision of 0,6%. They found the temperature coefficient $\partial H^E_M/\partial T$ near 298 K to have a value of $-1{,}3 JK^{-1}$ mole^{-1} at values of the mole fraction near to which H^E_M had its maximum. This low value ensures that it is sufficient for temperature control to be $\pm$ 0,1K to obtain results within experimental errors arising from other factors.

Monk and Wadso$^{(18)}$ designed a flow microcalorimeter based on a twin heat conduction principle. The heat evolved or absorbed in a flow mixing cell is conducted to or from a surrounding heat sink, through a semiconductor thermopile which transduces the heat flow into a voltage reading.

Picker et al(19) describe a scanning differential flow microcalorimeter. The instrument reaches a steady state within 1 minute and by continuously varying the flow rates of the two liquids it is possible to obtain the complete H^E_M composition curve in 20 minutes. The main feature of the apparatus is the differential use of counter flow heat exchangers. Thermal energy from the mixing cell is transferred to the heat exchanger liquid. The temperature variations of this liquid are measured relative to those of a twin reference system. At a constant flow rate of the exchanger liquid the temperature difference is directly proportional to the energy flux from the mixing cell and is independent of the heat capacity of the mixture for isothermal conditions. The proportionality constant is determined by electrical calibration. Zener diode junctions are used as heaters. The low response time of the temperature detection system (approx. 10 seconds) makes composition scanning feasible.

By using this scanning technique with the Picker flow microcalorimeter a precision of 1 % was obtained investigating the hexane/cyclohexane system(20). The main advantage of this apparatus is that a mixing curve can be obtained in about 20 minutes and with the use of about 6 cm^3 of each of the liquids.

3. EXCESS MOLAR VOLUMES OF BINARY LIQUID MIXTURES

3.1 Introduction

There are two principal methods for determining the excess volumes of binary liquid mixtures.

(a) A direct method by mixing the liquid components and observing the volume change in a dilatometer.

(b) An indirect method by measuring the density of the liquid mixture and hence determining the excess volume.

The average coefficient of thermal expansion of organic solvents necessitates temperature control of within 0,01 °C for a thermostat in order to determine the density of the mixture to within 0,00001 gcm^{-3} (21) This could result in a low precision of 10 % in V^E.

The majority of liquid mixtures have volume changes less than 0,1 % of the total volume of their components. To attain an accuracy of 1 % in the excess volume the density measurement must be accurate to within 0,0001 % and this requires temperature control to 0,001 °C .

In composing mixtures care must be taken that the evaporation into vapour spaces must be corrected for. The mole fractions of components in compositions are determined by weighing each component. Buoyancy corrections must be taken into account during the weighing procedure(22)

The purity of the components is not very critical in the determination of V^E. McLure and Swinton(23) found no change in V^E for mixtures with cyclohexane of 99,7 vs 99,99 mol % purity, using the direct method. When V^E is determined indirectly by density measurement the same applies with the proviso that the density of the individual components is determined to the same precision as the density of the mixture. It is essential in both methods to assure adequate mixing of the components.

Powell and Swinton (24) suggest that the system benzene-cyclohexane is used as a test system for measurements of V^E.

3.2 Direct Measurement of V^E

A mixing vessel is used in which the two components can initially be separately placed and subsequently thoroughly mixed when desired. The volume change can be measured by following the displacement of mercury along a graduated capillary by using a travelling microscope. It is imperative in order to obtain meaningful results that the liquid components are degassed. The presence of a small bubble, say 10^{-3} cm^3, may cause a 100 % error in the measurement of the volume of mixing.

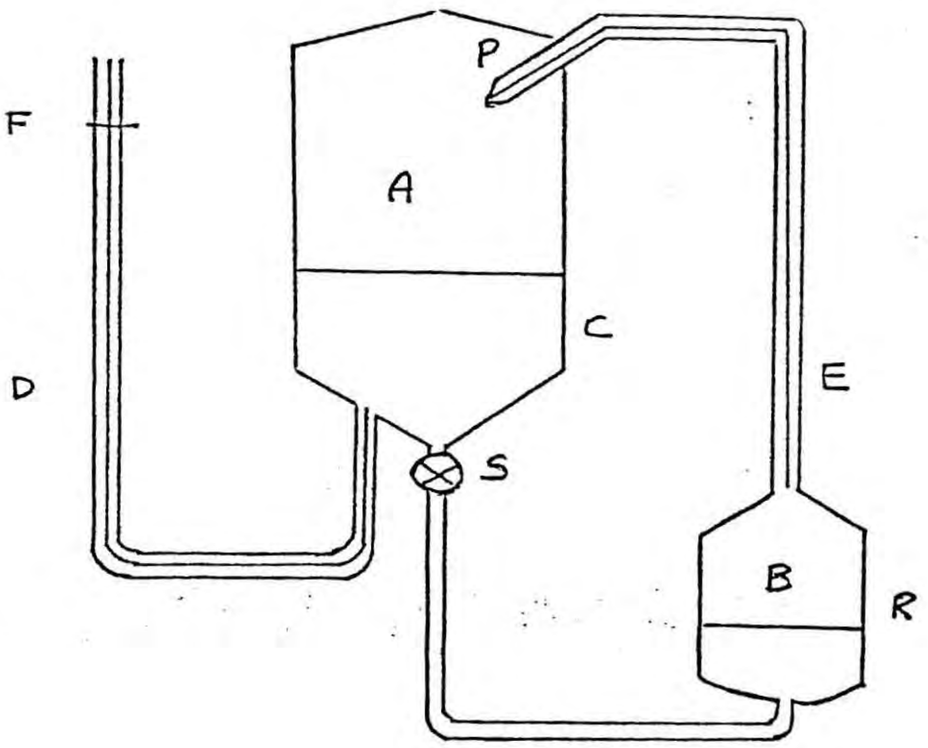

FIG 6 DILUTION DILATOMETER (GEFFCKEN ET AL)[26]

A general method used to ensure the absence of air bubbles is to distil weighed amounts of two components under vacuum into the mixing apparatus. Liquids exposed to air always contain dissolved air and on mixing in a closed vessel this air is often displaced.

There are two basic classes of apparatus for the direct measurement of V^E. The one class allows one measurement of V^E at one composition per loading of the apparatus at a single temperature. The other class allows for the determination of V^E for a number of compositions per loading.

The double-arm pycnometer of Keyes and Hildebrand(25) was the prototype for many subsequent developments. The apparatus is a U-tube with mercury at the bottom to separate the two components and with graduated capillaries on the ends of the tubes to record volumes before and after mixing, which is accomplished by rocking. The precision of this apparatus depends on the volumes of the components used and on the size of the capillaries used. Swinton (24) and colleagues used a version of the above apparatus and claimed an accuracy of 0,5 % or 0,001 $cm^3.mol^{-1}$.

Dilution dilatometers for measuring V^E have the advantage that the composition range can be covered in two runs. Geffcken, Kruis and Solana(26) designed an apparatus of this type, (Figure 6), which has subsequently been used and modified by other researchers.

The mixing chamber C is initially filled with pure component A over mercury. Stopcock S allows access via a tube to the reservoir R where pure component B is present over mercury. D is a calibrated capillary where the height of mercury can be read. Provision is made in chamber C for mixing and the entire apparatus is thermostatted. When stopcock S is opened the weight of the mercury in C pushes component B through the connecting tube E into C. The change in the level of the mercury in the capillary D is noted. Successive increments of B are added to directly determine V^E as a function of composition at one temperature.

Pflug and Benson(27) have described an accurate dilatometer based on the above principle in which the volume of added component is determined from the mass of mercury displaced in a piston-type arrangement.

The mixing process is carried out in cell A which can be connected by two three-way stopcocks B and C to a tube D. Cell A can also be connected by these stopcocks to a mercury reservoir F and a solvent reservoir E. One cell opening is to a calibrated capillary tube G which has an extension leading to the bottom of the cell. The other opening H is used for filling the cell and has an efficient seal. The cell is fitted with an externally driven magnetic stirrer. The contents of the cell are separated from the solvent to be added by a cup I which

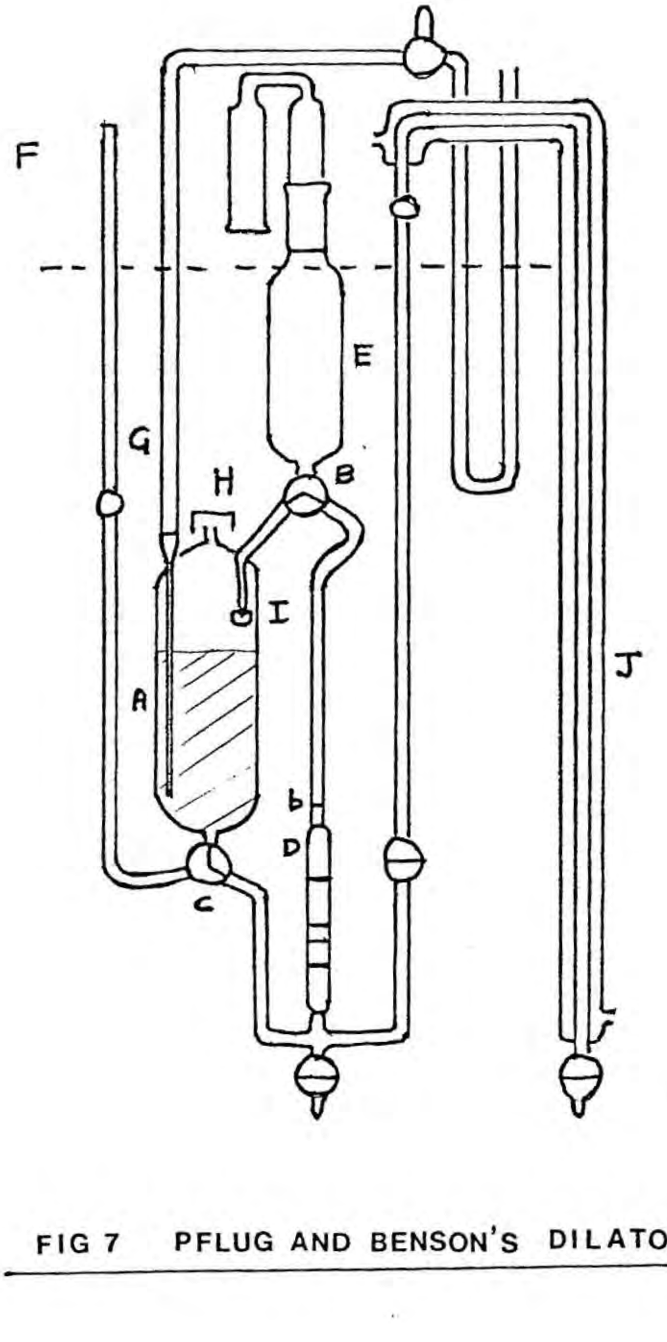

FIG 7 PFLUG AND BENSON'S DILATOMETER[27]

contains mercury to cover the end of the inlet tube.

Before mixing, the desired quantity of component (B) is dropped from the reservoir E into D, displacing mercury which is drawn off through J and subsequently weighed. Stopcocks C and B are then turned joining tube D and cell A in a loop. Mercury from the cell then forces component (B) from tube D into the cell. The amount of component (B) added is calculated from the weight of the mercury removed via tube J.

The volume change accompanying the mixing is obtained from differences in cathetometer measurements of the level of the mercury in tube G. The procedure of drawing mercury from D and displacing component B into the cell was repeated with increasing increments until the liquid volume in the cell was more than doubled. The measurements yielded the volumes of mixing for a series of solutions predominantly rich in (A). To cover the whole mole fraction range, another run was carried out with the positions of the two components interchanged.

The overall error of the volume measurements using this apparatus varied from ± 0,5% in cases where the volume change per addition was of the order of 0,02 cm^3 to where the change was only 0,0002 cm^3 . Stokes, Levien and Marsh(28) have also used a version of the Geffcken et al apparatus. This contained a burette B containing one component joined to a bulb A containing the other component by a fine stainless-steel capillary tubing sealed into bulb A.

On opening tap T1 (see figure 8) mercury flows from the bulb A to the burette, simultaneously forcing the liquid in the burette through the stainless-steel tubing S and a coupling. The volume change is observed on the calibrated tubing C. The composition is determined from the change in mercury height in the burette, which is constructed from precision-bore tubing. The tap T2 allows mercury to be added to, or removed from, the system when the volume change on mixing is too large to be accommodated in the capillary C. This apparatus has the advantage that it is not necessary to weigh the one component liquid into A as the volume of liquid in A is defined by the mercury heights M1 and M3 provided the volume of mercury is adjusted to F2, F3 and F4 before loading with the liquids.

Compressibility corrections due to a change in the pressure head on the liquids as the mercury levels change must be considered in all direct measurements of V^E.

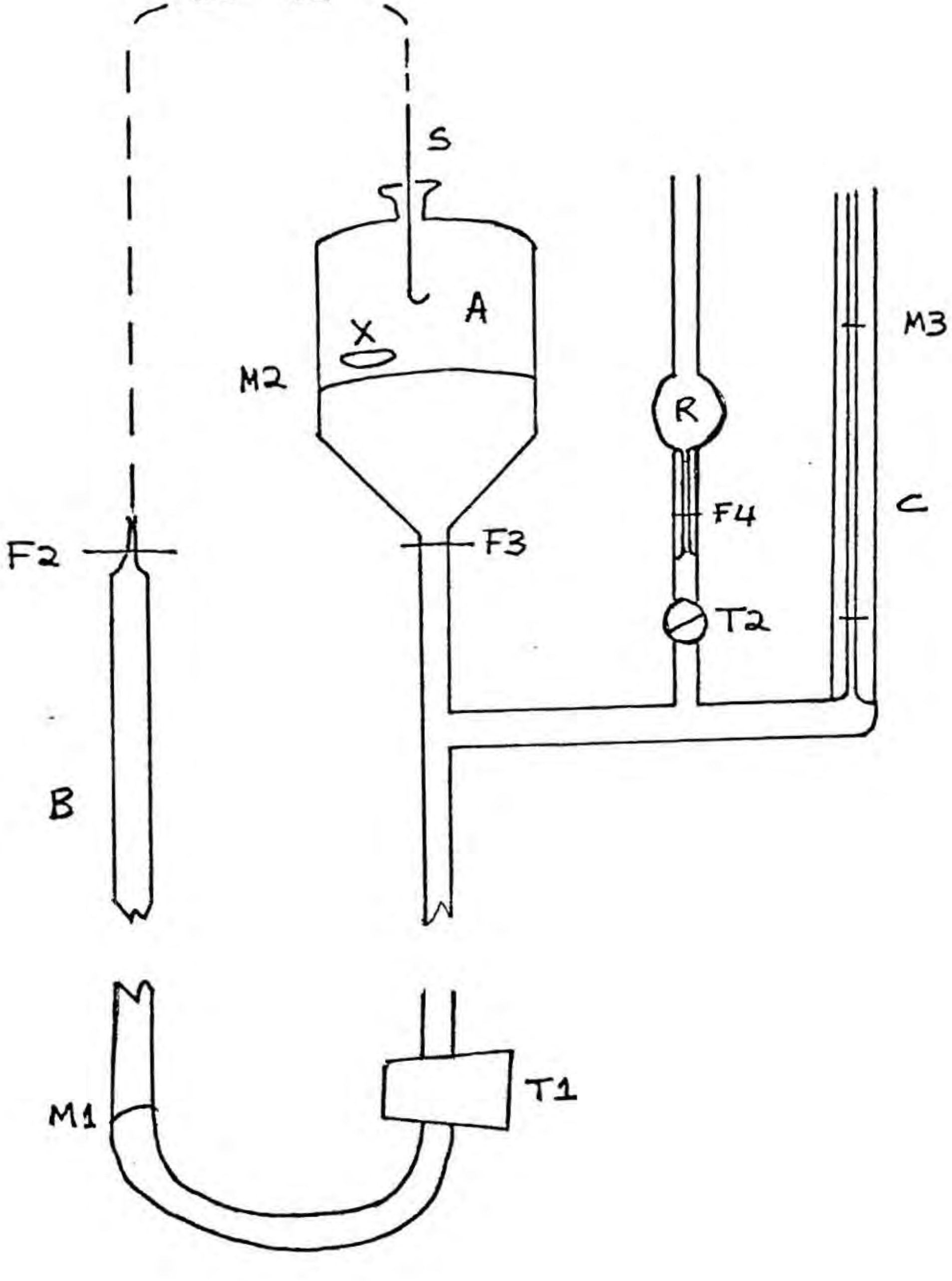

FIG 8 DILUTION DILATOMETER

(Stoke's et al) [28]

With a dilution dilatometer $V^E_M(x)$ can be determined over the whole range of mole fraction x of one of the components in two dilution runs which overlap through some range of values of x. Such overlapping provides a sensitive check on the quality of the measurements. Bottomley and Scott$^{(29)}$ asserted that small errors revealed by failure of the two dilution runs to overlap were due to the injection of grease with the diluent liquid through the greased tap T1 of Stokes dilatometer. Bottomley and Scott redesigned the dilatometer by excluding all taps. Dilution was effected by tilting the dilatometer. They claimed a precision of 0,00015 cm^3mol^{-1}. A disadvantage of Bottomley and Scott's dilatometer is that the liquid mixture and the pure diluent liquid are separated only through a diffusion boundary in a capillary, with consequent uncontrollable errors due to diffusion.

Kuruman and McGlashan$^{(30)}$ redesigned Bottomley and Scott's dilatometer so as to allow easier calibration, loading and operation and to remove the capillary defect. It has two advantages:

(i) No liquid passes through any tap and no tap is opened or closed during a series of measurements.

(ii) There is no possibility of error from diffusion of one liquid into the other as the liquids are always separated by mercury.

McGlashan and Kurunan's dilatometer was used to make a series of measurements of the molar excess volume of the standard system viz. benzene and cyclohexane, at 298,15 K . The results compared well with those of previous measurements and had a standard deviation of 0,0007 $cm^3.mol^{-1}$.

3.3 Indirect Measurements of V^E
(i.e. Density Measurements on Liquid Mixtures)

(a) Pycnometers

A pycnometer (Figure 9) is a glass container whose volume is precisely known. It is used to determine the densities of liquid mixtures as well as of pure liquids. The pycnometer is first weighed empty. It is then filled with distilled water and placed in a thermostatted water bath so that only the ends of the capillaries are not immersed. After thermal equilibrium the level of the water is brought to marks A and B exactly by removing or adding water. The pycnometer is then weighed, and then subsequently dried. The process is then repeated using the liquid mixture.

In order to accurately determine the density of the mixture, buoyancy corrections are made from(62)

$$\rho = \rho_{H_2O}M/M_{H_2O} - 0{,}0012\ (M-M_{H_2O})\ /M_{H_2O}$$

Where ρ_{H_2O} and M_{H_2O} are the density and mass of the

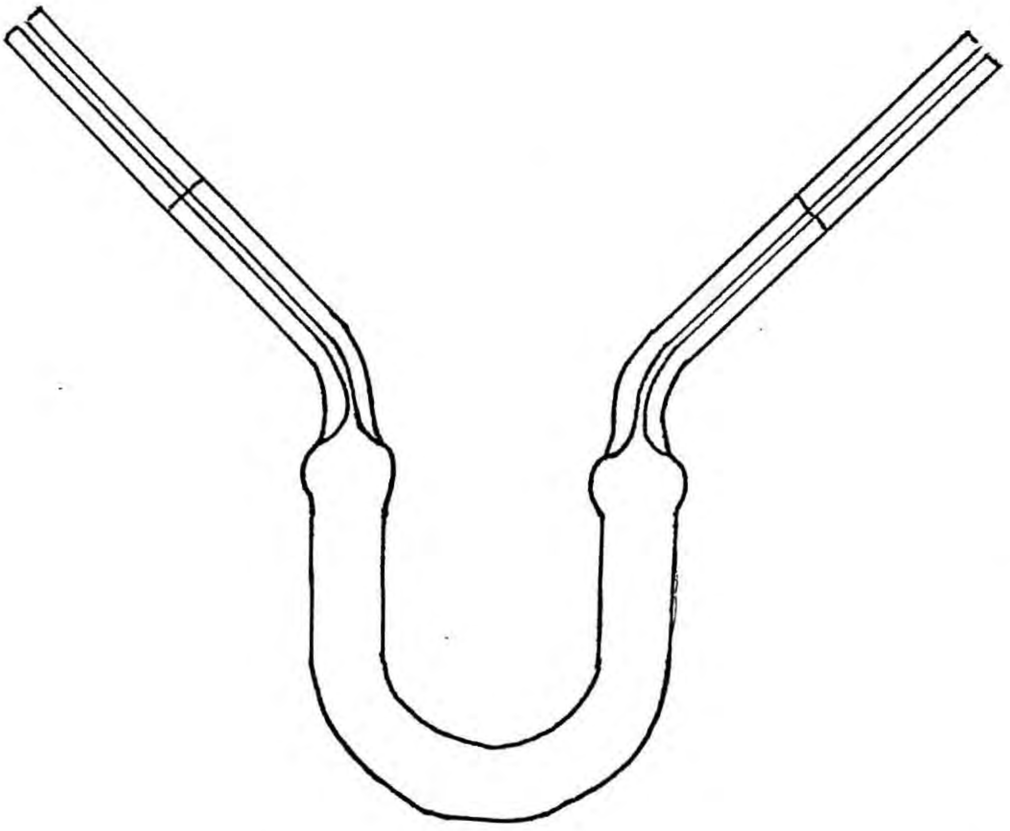

FIG 9 A PYKNOMETER

water in the pycnometer respectively, and M is the mass of the liquid in the same pycnometer 0,0012 is the density of the air at ordinary conditions.

From measured densities of the mixtures and the pure liquids the molar volumes V_M, V_1 and V_2 are determined. The molar excess volume V^E is then found from

$$V^E = V_M - (x_1V_1 + x_2V_2)$$

where x_1 and x_2 are the mole fractions of component 1 and component 2 respectively.

Woods and Brusie(31) describe a single arm pycnometer which was used for fifth-place density measurements.

(b) Magnetic Float Method

The magnetic float method has been used for sixth-place density measurements on liquid mixtures. Benjamin(32) describes apparatus having a sensitivity of ± 0,0001% . A glass float containing a soft iron core is just buoyant in the liquid studied and floats against a glass stop. The float is immersed at all times.

The float is attracted by the field of a solenoid and the current which just fails to cause the float to move away from the glass stop is determined by extrapolation of the measured float velocity as a function of current i . It can then be shown that

$$i_0^2 \propto \rho$$

where ρ is the liquid density.

(c) Vibrating-Tube Densimeter

This method for obtaining densities is based on the principle that the density of a fluid contained in a small U-shaped tube is related to the natural vibrational frequency of the tube. The density ρ of the liquid is linearly related to the period of vibration T, by the equation (33)

$$\rho = a + bT^2$$

where a and b are constants. A precision of 1 x 10^{-6} gcm^{-3} is possible. This method has the advantage that it is rapid and is not subject to the possibility of cumulative systematic errors of the type that can occur in a dilution dilatometer.

The U-shaped sample tube is completely filled with the liquid sample by a hypodermic syringe. The sample tube is electromagnetically excited and the density is indirectly determined by the measurement of the period of oscillation of the sample tube. Accuracy is not affected by liquid viscosity, volatility or surface tension of the sample liquid. A digital period value for external calculation of the density is read. Temperature control to 0,001 K must be maintained. The densimeter is water-jacketed and insulated. Constant temperature is maintained by circulating water from the constant-temperature bath through the meter.

Principle of the Density Measurement

The natural frequency of the U-tube is influenced by the mass of the sample, and therefore also its density. The system is analogous to a hollow body with mass M, which is suspended on a spring with a spring constant c . Its volume V is assumed to be filled by a sample of density . The natural frequency of such a system is given by

$$f = 1/2\Pi \{C/(M + \rho V)\}^{\frac{1}{2}}$$
$$T = 1/f$$
$$T^2 = 4\Pi^2 \{(M + \rho V)/C\}$$

Hence $T^2 = A\rho + B$

where $A = 4\Pi^2 V/C$

$B = 4\Pi^2 M/C$

The following therefore applies for the density difference of two samples

$$\rho_1 - \rho_2 = 1/A\ (T_1^2 - T_2^2)$$

Constants A and B contain the spring constants of the oscillator as well as the empty oscillator's mass and that volume of the sample which participates in the oscillation. These constants are, therefore, instrument constants for each individual oscillator and can be determined by two calibration measurements with samples of known density.

Goates, Ott and Moellmer(34) measured excess volumes by means of a vibrating-tube densimeter for cyclohexane + benzene at 298.15 K. This system $\{V^E(x=0,5) = 0,650 \pm 0,001\ CM^3.mol^{-1}\}$ is used for checking dilatometers. Goates et al obtained $V^E(x=0,5) = 0,655\ cm^3.mol^{-1}$. Kiyohara and Benson(35), also using this method and system, obtained a result $V^E(x=0,5) = 0,653\ cm^3.mol^{-1}$.

4. THE ISOTHERMAL COMPRESSIBILITY

The isothermal compressibility, κ_T, is defined by

$$\kappa_T = -(\partial \ln V/\partial \rho)_T \qquad (4.1)$$

κ_T can be related to C_p, the heat capacity at constant pressure; C_V, the heat capacity at constant volume, and the isobaric expansitivity, $\alpha = (\partial \ln V/\partial T)p$ by the equation

$$\kappa_T = T\alpha^2 V/(Cp-Cv) \qquad (4.2)$$

κ_T can also be related to the isentropic compressibility, $\kappa_s = (\partial \ln v/\partial P)_s$ by the equation

$$\kappa_T = \kappa_s + T\alpha^2 V/Cp \qquad (4.3)$$

Hence, knowing κ_s, α, and C_p it is possible to calculate κ_T.

Measurement of K_S

$$TdS = Q + (W + pdV) \qquad (4.4)$$

is an equation for a change of state of a phase of fixed composition.

It follows from the above equation that any change of state that takes place adiabatically ($Q = 0$) and reversibly ($W = -pdV$), is also isentropic ($S=o$). An expansion or contraction can be carried out adiabatically by thermally insulating the apparatus and then rapidly changing the pressure and re-measuring the volume and pressure. If the thermal insulation is good enough then we can carry out an expansion or compression both adiabatically and reversibly by changing the pressure slowly.

An alternative method for the determination of depends on the measurements of the speed of sound u in the phase. The isentropic compressibility κ_s of a fluid is related to the speed of sound u by the formula

$$\kappa_s = 1/u^2\rho \qquad (4.5)$$

Low and Moelwyn-Hughes(36) determined the isentropic compressibilities of acetone and methyl iodide at temperatures from -20° to +35 °C from measurements of ultrasonic velocities in them. Velocities were measured by means of an ultrasonic interferometer immersed in an alcohol thermostat. An electric field of 4 MHz frequency produced by a crystal oscillator excited a transducer crystal which generated a sound wave in a cell containing the experimental liquid. The distance travelled by the sound wave between the transducer and a reflector could be adjusted by means of a micrometer attached to the reflector. A change in the height of the vibrating column altered the damping resistance of the liquid and gave rise to maxima and minima in the current absorbed from the oscillator and recorded on an ammeter. The distance travelled by the reflector between 2 minima was one-half of the wavelength of sound in the liquid. About 50 wavelengths were passed through and a mean value of the wavelength was obtained. The resultant velocities were accurate to 0,1 %, and the adiabatic compressibilities were calculated from equation (4.5) to an accuracy of 0,2 % . The isothermal compressibility κ_T was calculated using equation (4.3).

Measuring κ_T directly

The most reliable method is to observe the changes of volume when the pressure is increased in steps of about 100 bar to 1 000 bar or more(37). The value of κ_T at a certain pressure is obtained by an extrapolation of the mean values over these large pressure changes. With such measurements there is little difficulty in measuring the changes of volume, nor is there much trouble in performing the compression isothermally. The temperature rise accompanying an increase in pressure is soon dissipated if the liquid is enclosed in a metal vessel in the thermostat. The final (isothermal) change of volume is thus soon observable. However, extrapolation needs considerable care if it is to give values of κ_T at low pressures.

A second method is to directly measure κ_T at near atmospheric pressure by observing the small change of volume following a pressure change of about 1 bar.

However, it is now difficult to conduct the experiment isothermally, for the initial (adiabatic) rise of temperature is only about 10^{-2}K and such an increase will not be dissipated smoothly unless the thermostat is maintained constant to 10^{-3} to 10^{-4}K . However, the main problem is the measurement of the very small volume change. An average value of β is 10^{-4} atm and the compressibilities of most liquids do not exceed this. Assuming that the piezometer volume is 1 dm^3 we can approximate that the change in volume for a change in pressure of 1 bar is 0,01 cm^3 .

Because of the small volume change expected it is necessary to use a dilatometer. By making the bulb of the dilatometer sufficiently large and the bore of the measuring capillary sufficiently small the necessary accuracy may be achieved.

It must be borne in mind that the volume change is a result of change in external pressure. Allowance must be made for the pressure effects on the volume of the dilatometer itself. The volume change corresponding to the observed movement of the meniscus in the dilatometer capillary when the applied pressure is changed will include the volume change of the dilatometer bulb and the capillary. In most cases the volume increase of the dilatometer bulb will be a significant fraction of the volume decrease of the liquid when the applied (internal) pressure is increased.

This effect is obviated by completely enclosing the dilatometer in a pressure jacket so that the internal and external pressures are always equal in order to eliminate the gross volume changes accompanying changes in applied pressure.

The apparatus used by Tyrer (1913) is shown in Figure 10. β was measured by applying a known external pressure at points P, allowing the system to reach thermal equilibrium with the thermostat and then releasing the pressure. The volume change δV of the liquid was measured by following the movement of the mercury slug which sealed the liquid in the calibrated capillary C. Knowing ΔP , V and ΔV, β could be calculated.

The disadvantages of Tyrer's apparatus were the following

(a) The outer pressure jacket was filled with air. As $(\partial T/\partial P)$ is large for air heat goes in and the system takes a long time to equilibrate.

(b) The horizontal calibrated capillary C was not in the thermostat nor the pressure jacket. The sample in the capillary will be near to room temperature and the measuring capillary is under pressure from the inside but is uncompensated from the outside.

(c) Glass taps were used which is undesirable as they are subject to leakage under internal pressure and also because the tap grease can cause contamination of the liquid sample.

Coleman improved on this design by including the measuring capillary inside the pressure jacket and placing the whole piezometer unit in the thermostat. The piezometer was made entirely of Pyrex glass (See Fig. 11)

The specimen vessel A (volumes 150 ml) has joined to it a measuring capillary B (precision bore). The actual bore was determined before assembly. The specimen vessel was filled by first evacuating it and then allowing the sample liquid to enter through the capillary by atmospheric pressure. When the vessel A and the capillary B were full of sample liquid a small amount of mercury was introduced into the well C at the entrance to the capillary B . By slightly heating the whole piezometer and then cooling to just above the experimental temperature a slug of mercury about 2 cm long was drawn into the outer part of the capillary B . After removal of the excess sample liquid and mercury from C, the mass of the specimen was determined by weighing the whole piezometer. The mass of the mercury slug was calculated from its length and the known diameter of the capillary bore. On completion of a series of experiments the specimen vessel was emptied by cutting off the tip D of the emptying extension.

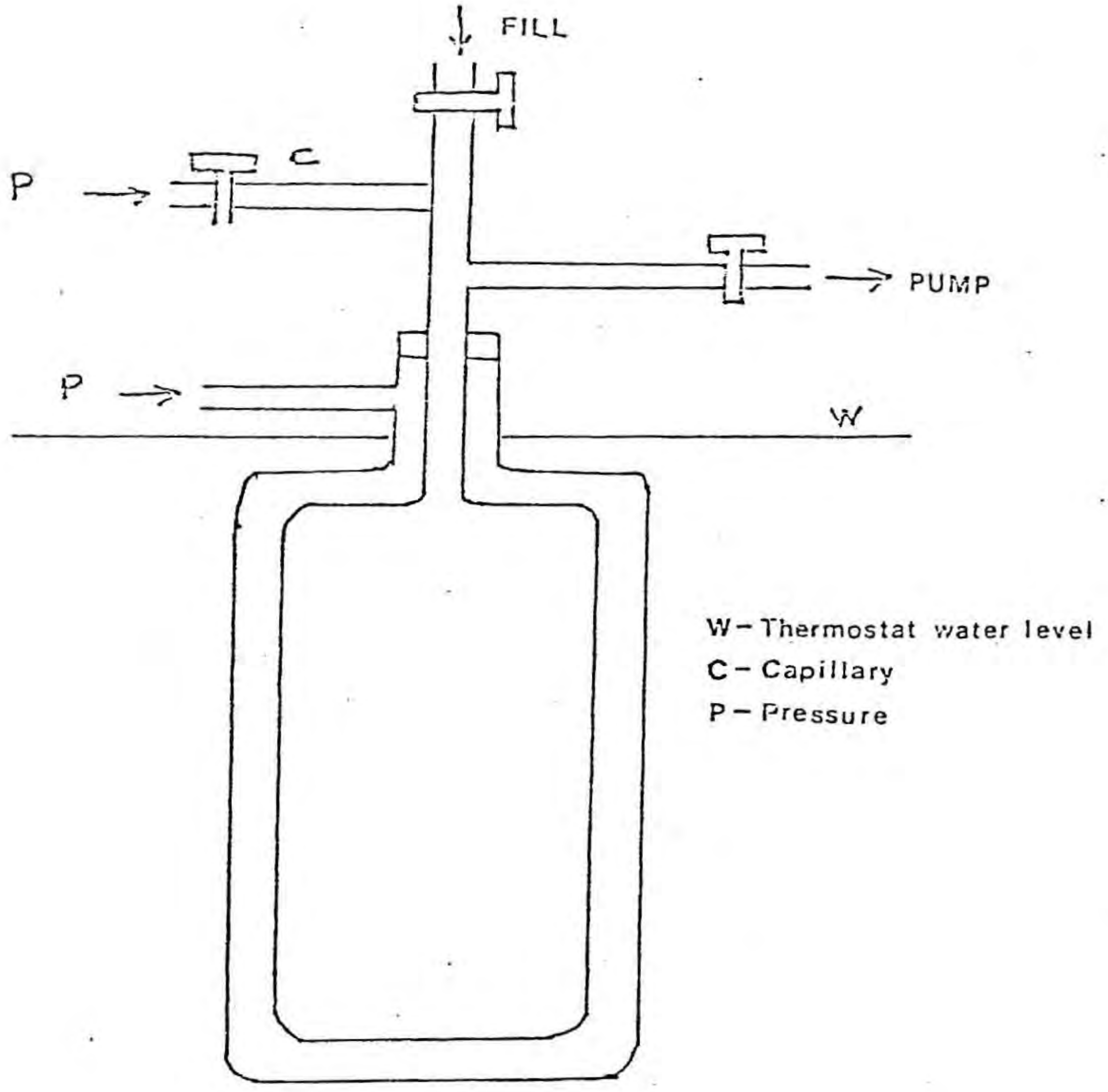

FIG 10 TYRER'S COMPRESSIBILITY APPARATUS

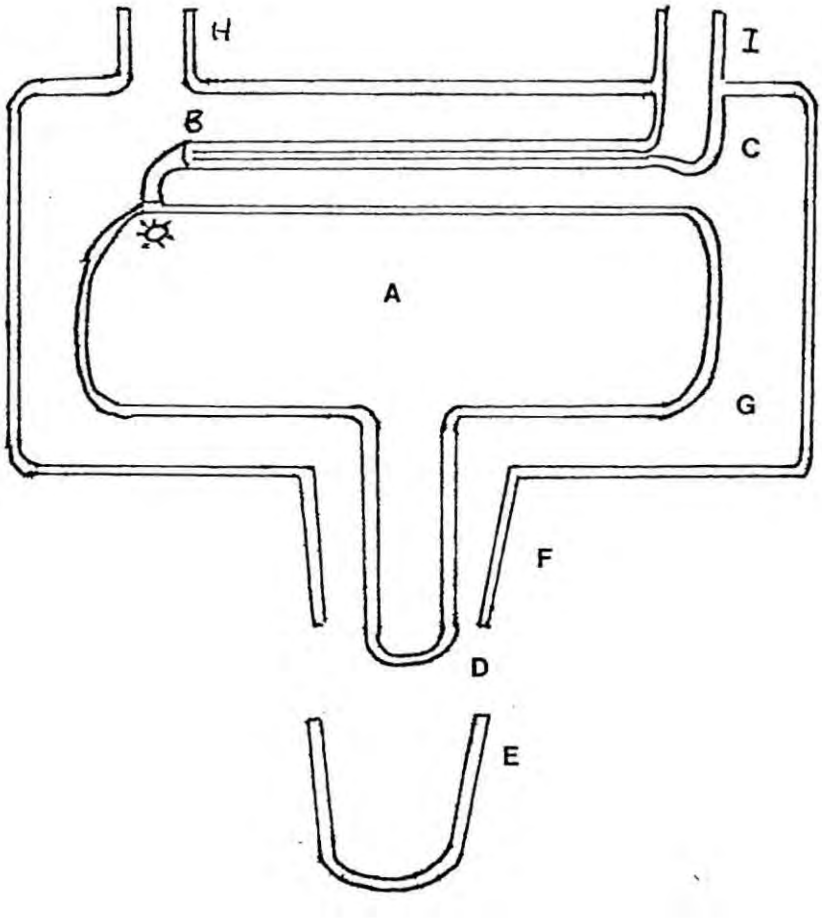

FIG 11 COLEMAN'S PIEZOMETER

After the specimen vessel has been filled and weighed the cap E was fitted over the cone F . The pressure jacket G was then filled through the inlet H .

The piezometer was then placed in the thermostat and the inlets H and I were connected to the pressure system. When thermal equilibrium was established the position of the inner end of the mercury slug was observed with a travelling microscope. Pressure was then applied slowly and equally to the inlets H and I and the movement of the mercury slug was observed. After thermal equilibrium was again established final observations of the position of the mercury slug in B were made and the pressure was then vented to atmosphere. The mercury slug moved rapidly outwards and soon attained a steady position if the value of $(\partial T/\partial P)_s$ of the ballast liquid in the jacket G had been chosen to be slightly greater than that of the specimen liquid. This difference offsets the heating of the sample resulting from the fact that the adiabatic cooling on decompression of the glass is much smaller than that of the liquids in the piezometer.

By using a series of increasing applied pressures a series of results can be obtained from which κ_T could be calculated in terms of the slopes of plots of displacement of the mercury slug against applied pressure. A series of 10 to 20 measurements at applied pressures ranging from about 100 torr to 1 500 torr was recommended.

The most likely source of error in the isothermal measurement was loss of sample liquid by creeping past the mercury slug during the application of the pressure. This loss could be minimised by the use of a relatively long mercury slug. The whole of the space C could alternatively have been filled with mercury, in which case a known mass of mercury was introduced.

Diaz-Pena and McGlashan(38) described an apparatus suitable for measurements of κ_T of liquids at pressures up to 30 atm. and at temperatures up to 60 °C . They constructed a piezometer made of Pyrex glass with a vertical precision bore capillary tube and a specimen liquid chamber connected through a U-bend. The expansion of the liquid was monitored by a mercury thread in the capillary.

The piezometer was placed in a pressure chamber, which was a cylinder of Perspex closed at its ends by brass plates. The charged piezometer was placed in the pressure chamber which was then filled with water, immersed in the constant temperature bath, and connected to the pressure line. Temperature regulation of the bath was important since for liquids a change in temperature of 0,1 °C causes about the same change in volume as change in pressure of 1 atmosphere. When the piezometer had reached temperature equilibrium measurements were made of the height (referred to a reference mark R) of the mercury column at 5 atm. intervals between 1 atm. and 31 atm., alternate measurements being made on the way up to 31 atm. and on the way back to 1 atm. After each change of pressure a measurement was delayed until the heat of compression or expansion had been dissipated so that the measurements were isothermal. Pressure was applied through needle valves from a nitrogen cylinder.

Ewing, Marsh and Stokes(39) have described a dilution piezometer for the measurement of the isothermal compressibilities of mixtures which follows the principle of the apparatus described above. Their apparatus is capable of a precision of 0,2 % .

5. THEORY OF BINARY LIQUID MIXTURES

Many of the observable, bulk properties of physico-chemical systems depend on the interaction between molecules i.e. on molecular properties. In the last two decades many theories have been constructed in an attempt to explain the behaviour of liquid mixtures. The aim of these theories has been to evolve a mathematical model of the bulk state whose behaviour can be analyzed by mathematical approximations in order to relate bulk properties in terms of molecular properties and hence to predict excess properties. The test of the validity of the theory comes when the observed properties of the real system are compared to the calculated properties generated by the theory.

In constructing a theory for liquids we must bear in mind the detailed form of the potential energy of intermolecular interaction, which will be different for different kinds, shapes and sizes of molecules. A useful approach to the problem is to construct a theory which will account for the bulk properties of a liquid mixture in terms of the bulk properties of the components and reasonable assumptions about the liquid state and about the relations between the various intermolecular interactions, rather than directly in terms of the molecular properties of the components.

One approach to the theory of the liquid state attempts to calculate the distribution function of the liquid in terms of the intermolecular forces for various conditions of average density and temperature. Hildebrand(40, 41) developed a theory of mixing based on the distribution function approach to the structure of the liquid state. He made approximations about the relations between the distribution functions of pure liquids and those of mixtures, as well as the relation of the potential energy of a collection of molecules to measurable macroscopic properties. By so doing he was able to dispense with the need to know the form of the distribution function and was able to formulate a relation for the changes in properties on mixing entirely in terms of the component properties.

In Hildebrand's solubility parameter theory it was assumed that the changes in the energy on mixing can be attributed entirely to the energy of interaction of the molecules. The basic equation of this treatment is

$$\Delta E_m = (n_A V_A^o + n_B V_B^o)\phi_A \phi_B (\delta_A - \delta_B)^2$$

where $$\delta_i^2 = \Delta_v U_i / V_i^o$$

$\Delta_v U_i$ being the energy of vaporisation of component i . Although the theory predicts relations for the thermodynamic properties of the right form it does not give the correct absolute values. The theory has been more successful in accounting for the behaviour of solutions of solids in liquids.

A somewhat different approach to the calculation of the properties of liquid mixtures is contained in the lattice theories, which are based on the short-range interactions between molecules in the liquid state. It is assumed that the molecules are arranged in a crystalline lattice and that the only interactions of importance in determining the changes in the properties after mixing has occured are those between molecules which are immediate neighbours. The simple lattice model makes use of the following assumptions:

(a) The molecules of both pure components and of the mixture are regarded as being arranged on a regular lattice with a well-defined co-ordination number.

(b) The molecules are sufficiently similar in size to fit on the same lattice.

(c) The changes in thermodynamic properties on mixing are determined only by the potential energy of interaction of nearest neighbour molecules regarded as fixed on their lattice sites.

The model in its simplest form is applicable only to mixtures of compounds with approximately the same molar volumes. Since the bulk properties are independent of time there must exist a time-independent way of relating the molecular behaviour to the bulk behaviour. This method is given by statistical thermodynamical equations, according to which the bulk behaviour may be calculated by taking a correctly weighted average of the properties over all the conceivable microscopic states of the system. Each microscopic state is described by a specification of a distribution of the molecules on the lattice distinguishable from all other distributions.

This method is summarized in the equation

$$A = -kT\ln\sum_i g_i \exp(-E_i/kT)$$

where g_i is the number of distinguishable ways of $\sum_i g_i \exp(-E_i/kT)$ arranging the molecules on the lattice so that the total potential energy is E_i. The summation is taken over all possible values of E_i. The quantity

is called a partition function.

The value of the lattice theory lies in the fact that because of the well defined model upon which it is based it is easily extended to more complex situations where the distribution function of the solubility parameter theory becomes too difficult to manipulate. Examples of this advantage are the extensions of the lattice model to polymer solutions, and to solutions in which the interactions between the molecules are dependent to a large degree on orientation.

Prigogine's(42) cell theory of mixtures extended the lattice theory by allowing for effects such as molecular motion by regarding the individual molecules as not being fixed on a lattice site but rather as being confined to a small region of space by its neighbours. Within this volume, or "cell", the molecule moves in a potential field arising from its neighbours.

Pitzer(43) is responsible for the formulation of the corresponding states approach in terms of molecular interactions. The basic assumption of the corresponding states theory is that the intermolecular potential energy is due to central forces only, and has the same form for all pair interactions. The theory is characterized by parameters, $-\varepsilon$, the energy of a molecular pair at its equilibrium distance and σ , the collision diameter.

FLORY'S EQUATION OF STATE

Flory and co-workers have developed an approach which relates the excess properties of the liquid mixture to measurable macroscopic properties of the pure liquid components. The pure components are characterized by the following equation of state parameters:

(i) the specific volume v

(ii) the thermal expansion coefficient $\alpha = v^{-1}\,(\partial v/\partial T)p$

(iii) the isothermal compressibility $\kappa = -v^{-1}\,(\partial v/\partial p)_T$

The properties of the liquid mixture are related to those of the pure components by a partition function that has general application to mixtures, including those comprising component molecules which are disparate in size and shape.

Flory, Orwoll and Vrij(44, 45) originally developed the theory for normal paraffin hydrocarbons. Flory and Abe(46) extended the theory to mixtures of small molecules. Flory(47) subsequently developed the equations for liquid mixtures and Abe and Flory(48) applied the excess volumes, enthalpies and entropies of a number of binary liquid mixtures to the theory and interpreted them according to the relationships which had been developed. Orwoll and Flory(49) used the theory for equation of state parameters for normal alkanes and then interpreted the excess thermodynamic properties of mixtures of normal paraffin hydrocarbons according to the statistical mechanical theory which had been developed.

Flory and co-workers(44) formulated a partition function for chain molecule liquids by using a model consisting of a linear sequence of segments with hard sphere type repulsive potentials and soft attractions of unspecified character. The intermolecular energy is assumed to depend only on the volume and is represented as varying inversely with it and a hard sphere repulsive potential is adopted for segments of the chain. The number of external degrees of freedom per segment are expressed as 3c (where $c<1$), where c is a parameter in order to take account of intermolecular constraints on the segments.

THE PARTITION FUNCTION

A linear chain molecule can be pictured, $H-(CH_2)_n-H$, consisting of a succession of n repeating units. The terminal groups may exert intermolecular forces differing from those of the mid-chain repeating units. The chain molecule is assumed to be flexible in order to assume a variety of spatial configurations. We can sub-divide the chain into x segments, where in general "x does not equal n", although it must be specified that x shall be linear with n for homologous members of the series. x will be proportional to the "hard core" molecular volume V (or net volume). A further assumption is that for homologs of the series

$$V^* = xv^*$$

where v^* is the net volume of a segment.

If s represents the mean number of external contact sites per segment of the molecule, then we can take

$$xs = xs_m + s_e \qquad (5.1)$$

where s_m = number of contacts per internal segment

s_e = number of contacts per chain end

xs may thus be regarded as a measure of molecular surface.

Assume that the normal oscillatory modes of the isolated chain molecule can be separated into intramolecular and intermolecular categories. It is further assumed that the intramolecular potentials associated with the intermolecular modes can be disregarded and, hence, that they may be treated as translational motions. When we include the three degrees of freedom of the molecular centre of gravity we can evaluate the total number of intermolecular degrees of freedom to be:

$$3xc = 3(xc_m + c_e) \qquad (5.2)$$

per molecule. The number of degrees of freedom is thus linear in x, and hence in n as well. c is assumed to be independent of temperature and volume over the range of application of the equations to be set down.

Consider a 1-D system comprising N particles each of length l^* distributed within a space of length L . It is assumed that overlaps of particles are excluded. According to Tonks$^{(50)}$ the totality of configuration space available to the system is

$$\Omega = (L-Nl^*)^N/N!$$
$$\simeq \{ (l-l^*)e\}^N$$

where $l = L/N$ is the space available per particle.

The configuration integral for such a system can be written

$$Z = \int \text{---} \int \exp \{-E(x)/kT\}dx$$

where x denotes the set of configuration co-ordinates

$x_1, x_2, \ldots\ldots, x_n$ and $dx = dx_1, dx_2 \ldots\ldots dx_n$.

Assuming hard sphere repulsion between segments, we take the "free length" associated with each intermolecular degree of freedom to be of the form

$$f^{\frac{1}{3}}(v^{\frac{1}{3}}-v^{*\frac{1}{3}})$$

where $v = V/xN$ is the volume per segment, V being the volume of the system and N the number of molecules; v^* is the net volume per segment, and f is a geometric constant. This expression is given by treatment of a hard sphere liquid in one-dimension according to the method of Tonks. On the basis of these concepts and extending the argument to three dimensions one obtains

$$Z = \{fe^3(v^{\frac{1}{3}}-v^{*\frac{1}{3}})^3\}^N \exp(-E_o/kT)$$

This form of the result, derived from the concept of a hard sphere liquid in one dimension with hard-sphere repulsion between segments, is equivalent to that given by the cell model of Prigogine(42, 51, 52).

In order to arrive at an equation not limited to spherical molecules, and which can be adapted to the treatment of mixtures of molecules differing in size, we can define a segment as an isometric portion of the molecule which is chosen arbitrarily. Let there be r such segments in the molecule. Following Prigogine's treatment of "r-mer" chain molecules, we let 3c represent the number of external degrees of freedom per segment, and we assume the partition function to take the form

$$Z = Z_{\mathrm{COMB.}} \{f(v^{\frac{1}{3}} - v^{*\frac{1}{3}})^{3}\}^{rNc} \exp(-E_{o}/kT) \qquad (5.3)$$

where $Z_{\mathrm{COMB.}}$ is a combinational factor which takes account of the number of ways of interspersing the rN elements among one another.

Prigogine and co-workers adhered to the cell model in order to formulate the mean intermolecular energy E_o. It was empirically found however that the cell model leads to energy values which depend too steeply on volume. Hildebrand and Scott(53) advocate the approach which considers the radial distribution function. The energy is well represented by an expression of the form suggested by Frank(54)

$$E_o = \mathrm{CONSTANT}/V^{M}$$

where m may be treated as a constant, usually in the range of 1.0 to 1.5 for nonpolar liquids. If we take M to be unity then the mean intermolecular energy per contact pair can be expressed as

$$\bar{\varepsilon} = -\eta/v \qquad (5.4)$$

where η characterizes the mean interaction between a segment pair in the liquid.

It follows that $E_o = -xNs\eta/2V$ (5.5)

If we assume that terminal segments show different attractive forces to neighbours than do the mid-chain segments which outnumber the former, then the intermolecular energy can be written

$$E_o = -(1/v)(N_m\eta_m+N_{em}\eta_{em}+N_e\eta_e) \qquad (5.6)$$

where η_m, η_{em}, and η_m characterize interactions between sites on two neighbouring mid-chain segments, between a mid-chain and a terminal segment site, and between two terminal sites respectively. N denotes the number of neighbour pairs in the respective categories and these are assumed to equal those for random mixing of sites. For simplicity, we take the number of terminal sites having atypical interactions to be just s_e, the excess number of sites for the two end groups, defined by equation 5.1.

Using this approach

$$E_o = -(xN/evs)\{s_m^2\eta_m + 2(s_m s_e/x)\eta_{em} + (s_e^2/x^2)\eta_e$$

which by comparison with equation 5.5 defines η as

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

Using the approximate geometric mean rule for non-polar molecules i.e. the Berthelot relationship(55)

$$\eta_{em} \simeq (\eta_e \eta_m)^{\frac{1}{2}}$$

which is appropriate for dispersion interactions

$$\eta \simeq (s_m/s)^2 \eta_m \{1 + (s_e \eta^{\frac{1}{2}}/s_m \eta_m^{\frac{1}{2}})x\}^2$$

Substituting equation 5.5 in equation 5.3 and introducing reduced variables as

$$\tilde{v} = v/v^*$$
$$\tilde{T} = T/T^* = 2v^* ckT/s_\eta$$

gives

$$Z = Z_{COMB.} (fv^*)^{xNc} (\tilde{v}^{\frac{1}{3}} - 1)^{3xNc} \exp(xNc/\tilde{v}\tilde{T}) \qquad (5.7)$$

THE EQUATION OF STATE

The reduced equation of state obtained from the above reduced partition function is identical with Hirschfelder and Eyring's theory(56, 57).

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{\frac{1}{3}}/(\tilde{v}^{\frac{1}{3}}-1) - 1/\tilde{v}\tilde{T} \qquad (5.8a)$$

The reduced pressure p is defined by

$$\tilde{p} = p/p^* = 2pv^{*2}/s_\eta \qquad (5.9a)$$

or

$$\tilde{p} = pv^*/ckT^* \qquad (5.9b)$$

The reduced equation of state may be alternatively expressed as

$$\tilde{p}/\tilde{\rho}^2 = \tilde{T}/\tilde{\rho}(1-\tilde{\rho}^{\frac{1}{3}})-1 \qquad (5.8b)$$

where $\tilde{\rho} = 1/\tilde{v}$ is the reduced density.

The parameters v^*, c and s_η characterise the chain molecule according to equations 7 and 8. The first of the parameters is taken to be identical for all homologs of the series and follows from the manner of defining a segment and the assumed linearity of xv^* with n .

The coefficient of thermal expansion α the coefficient of isothermal compressibility κ, and the thermal pressure coefficient γ may be expressed in terms of the reduced variables as

$$\alpha = v^{-1}(\partial v/\partial T)_p = (\tilde{T}/T\tilde{v})(\partial\tilde{v}/\partial\tilde{T})_{\tilde{p}} \qquad (5.10)$$

$$\kappa = -v^{-1}(\partial v/\partial p)_T = -(\tilde{p}/p\tilde{v})(\partial\tilde{v}/\partial\tilde{p})_{\tilde{T}} \qquad (5.11)$$

$$\gamma = (\partial\tilde{p}/\partial\tilde{T})_v = \alpha/\kappa = (\tilde{T}p/T\tilde{p})(\partial\tilde{p}/\partial\tilde{T})_{\tilde{v}} \qquad (5.12)$$

Equation 5.8 is first solved for $\tilde{T}$ and then for $\tilde{p}$. The resulting expressions are differentiated, and by eliminating $\tilde{T}$ in each case the following equations are obtained.

$$(\alpha T)^{-1} = \frac{1}{3}(v^{\frac{1}{3}}-1)-1 + 2\tilde{p}\tilde{v}^2/(\tilde{p}\tilde{v}^2 + 1) \qquad (5.13)$$

$$(\kappa p)^{-1} = \{\frac{1}{3}\ (\tilde{v}^{\frac{1}{3}}-1)\ -1\}(1 + 1/\tilde{p}\tilde{v}^2) + 2 \qquad (5.14)$$

$$\gamma T/P = 1 + 1/\tilde{p}\tilde{v}^2 \qquad (5.15)$$

At zero pressure

$$(\tilde{v}^{\frac{1}{3}}-1)/\tilde{v}^{\frac{4}{3}} = \tilde{T} \qquad (5.16)$$

$$\alpha T = 3(\tilde{v}^{\frac{1}{3}}-1)/\{1-3(\tilde{v}^{\frac{1}{3}}-1)\} \qquad (5.17)$$

$$\kappa = 3(\tilde{v}^{\frac{1}{3}}-1)\tilde{v}^2/\{1-3(\tilde{v}^{\frac{1}{3}}-1)\}p^* \qquad (5.18a)$$

$$= \alpha T\tilde{v}^2/p^* \qquad (5.18b)$$

$$\gamma = p^*/T\tilde{v}^2 \qquad (5.19)$$

Solving equation 5.17 for $(\tilde{v}^{\frac{1}{3}}-1)$ we have

$$\tilde{v}^{\frac{1}{3}}-1 = \alpha T/3(1 + \alpha T) \qquad (5.17b)$$

which permits $\tilde{v}$ to be computed from the coefficient of expansion of the liquid at p = 0 . The net volume follows from $\tilde{v} = v/v^*$. Substitution of $\tilde{v}$ in equation 5.16 yields $\tilde{T}$ and hence T*. The value of p* is then calculated using equation 5.18b. After having evaluated v*, T*, and p*, the parameters c and s_η are found from

$$\tilde{T} = 2v^{*}ckT/s_{\eta} \quad (5.20)$$

and

$$\tilde{p} = pv^{*}/ckT^{*} \quad (5.20)$$

Thus

$$s_{\eta} = 2p^{*}v^{*2} = 2\gamma Tv^{2} \quad (5.22)$$

$$c = p^{*}v^{*}/kT^{*} = (\gamma v/k)(\alpha T)/(3+4\alpha T) \quad (5.23)$$

The partition function and equation of state are now reformulated for mixtures of homologous chain molecules.

THE THERMODYNAMIC PROPERTIES OF MIXTURES OF HOMOLOGOUS CHAIN MOLECULES

The theory thus far presented for pure liquids can be adapted to mixtures of homologous chain molecules by extending the treatment of systems of one component . The partition function and equation of state are reformulated for mixtures of homologs and the thermodynamic properties of these mixtures are interpreted according to the relationships derived.

It is assumed that the distribution of segments of the two kinds about one another in the liquid mixture is random. Referring to the expression for the intermolecular energy equation 5.6, it is found, in analogy to equation 5.5 and equation 5.22

$$E_{o} = -\bar{x}Ns_{\eta}/2v = -\bar{x}Np^{*}v^{*}/\tilde{v} \quad (5.24)$$

where $\bar{x}$ is the number average defined by all species i present in the mixture being included in the summations.

It follows that

$$s = s_m + s_e / \bar{x} \qquad (5.25)$$

$$\eta = (s_m^2/s^2)\eta_m + 2(s_m s_e/s^2\bar{x})\eta_{em} + (s_e^2/s^2\bar{x}^2)\eta_e \qquad (5.26)$$

The various parameters are expressed in terms of their analogs for the pure components as

$$1/\bar{x} = \Sigma\phi_i/x_i \qquad (5.27)$$

$$S = \Sigma\phi_i s_i \qquad (5.28)$$

where ϕ_i is the segment fraction for species i

$$\phi_i = {}_i N_i/\Sigma x_i N_i \qquad (5.29)$$

The parameter c applicable to the mixture is given by

$$C = \Sigma\phi_i C_i \qquad (5.30)$$

THE EXCESS VOLUME

Let $\tilde{v}^o$ represent the reduced volume per segment if no volume change occured on mixing. For a binary mixture

$$\tilde{v}^o = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2 \tag{5.31}$$

where $\tilde{v}_1$, and $\tilde{v}_2$ are the reduced volumes of the pure components at the same temperature and pressure.

The reduced excess volume per segment is

$$\begin{aligned} \tilde{v}^E &= \tilde{v} - \tilde{v}^o \\ &= \tilde{v} - \phi_1\tilde{v}_1 - \phi_2\tilde{v}_2 \end{aligned} \tag{5.32}$$

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

$\tilde{T}$ for a binary mixture varies linearly with the segment fraction composition at constant temperature

$$\tilde{T} = \phi_1\tilde{T}_1 + \phi_2\tilde{T}_2 \tag{5.33}$$

The reduced volume $\tilde{v}$ for the reduced temperature $\tilde{T}$ may then be calculated from the equation of state for p = o

$$\tilde{T} = (\tilde{v}^{\frac{1}{3}}-1)/\tilde{v}^{\frac{4}{3}} \tag{5.34}$$

$\tilde{v}^E$ can be calculated by evaluating the difference between $\tilde{v}^o$ and the reduced volume for the mixture $\tilde{v}$ which can be determined by linear interpolation from the reduced volumes $\tilde{v}_1$, and $\tilde{v}_2$ of the components.

This method of calculation is made difficult by the fact that equation 5.34 is not explicitly solvable for $\tilde{v}$. This problem can be circumvented as follows. Given $\tilde{v}_1$, and $\tilde{v}_2$ and the $\tilde{T}_1$ and $\tilde{T}_2$ corresponding to them according to equation 5.34, $\tilde{T}$ can be obtained by linear interpolation. The reduced temperature $\tilde{T}^o$ corresponding to $\tilde{v}_o$ given by equation 5.31 is calculated. Then, with negligible error

$$\tilde{v}^E = (\partial\tilde{v}/\partial\tilde{T})(\tilde{T} - \tilde{T}^o)$$
$$= 3(\tilde{v}^o)^{7/3}\cdot\{4 - 3(\tilde{v}^o)^{\frac{1}{3}}\}^{-1}(\tilde{T} - \tilde{T}^o) \qquad (5.35)$$

The excess molar volume is related to the excess reduced volumes by the characteristic volumes for the pure components, and their mole fractions in the mixture according to the following formula

$$mV = \tilde{v}^E(x_1V_1^* + x_2V_2^*) \qquad (5.36)$$

THE EXCESS ENTHALPY

If we ignore the small difference between enthalpy and energy for condensed systems we may write the following expression for the molar excess enthalpy

$$H^E = \{E_o(\text{mixture}) - E_o(1) - E_o(2)\}/N \qquad (5.37)$$

which, considering equation 23, can be written

$$H^E = \bar{x}v^*(\phi_1p_1^*/\tilde{v}_1 + \phi_2p_2^*/\tilde{v}_2 - p_1^*/\tilde{v}) \qquad (5.38)$$

where p^* is the characteristic pressure of the mixture. Since $\tilde{v}^E$ is very small, the reciprocal of $\tilde{v}$ may be approximated with negligible error by

$$1/\tilde{v} = 1/\tilde{v}^o - \tilde{v}^E/(\tilde{v}^o)^2 \tag{5.39}$$

BINARY MIXTURES OF MOLECULES DIFFERING IN SIZE AND SHAPE

In the following analysis the components are indexed by subscripts 1 and 2. This treatment is generally applicable to liquid solutions, irrespective of the size and shape of the molecular species, provided that they are not hydrogen bonded or highly polar. The molecular segment is to be defined in correspondence for the two species such that r_1 and r_2 shall be in the ratio of the respective molar core volumes v_1^* and v_2^*. Similarly, s_1 and s_2 shall be in the ratio of the molecular surface areas of contact per segment.

$$r_1/r_2 = V_1^*/V_2^* \tag{5.40}$$

$$r_1 s_1/r_2 s_2 = (V_1^*/V_2^*)^{\frac{2}{3}} \tag{5.41}$$

$$s_1/s_2 = (r_1/r_2)^{-\frac{1}{3}} = (v_1^*/v_2^*)^{-\frac{1}{3}} \tag{5.42}$$

Let A_{11}, A_{12} and A_{22} represent the numbers of contact pairs between the respective species. Let η_{ii}/v be the energies associated with each species. Then

$$-E_o = (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})/v \tag{5.43}$$

Since

$$2A_{11} + A_{12} = s_1 r_1 N_1 \tag{5.44}$$

$$2A_{22} + A_{12} - s_2 r_2 N_2 \qquad (5.45)$$

it follows that

$$-E_o = (s_1 r_1 N_1 \eta_{11} + s_2 r_2 N_2 \eta_{22} - A_{12} \Delta\eta)/2v \qquad (5.46a)$$

where $$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \qquad (5.46b)$$

Random mixing of the two species will be assumed. We make a further approximation by taking the expectation that a species of kind i neighbours any given site to be equal to its site fraction Θi, defined for a binary mixture by

$$\Theta_2 = 1-\Theta_1 = s_2 r_2 N_2 \; s\bar{r}N \qquad (5.47)$$

On this basis

$$A_{12} = s_1 r_1 N_1 \Theta_2 = s_2 r_2 N_2 \Theta_1 \qquad (5.48)$$

where $$\bar{r} = (r_1 N_1 + r_2 N_2)/N \qquad (5.49)$$

$$s = (s_1 r_1 N_1 + s_2 r_2 N_2)/\bar{r}\,N \qquad (5.50)$$

$$N = N_1 + N_2 \qquad (5.51)$$

By substitution of equation 46 and 47 in equation 45 we get

$$-E_o/\bar{r}N = (s/2v)(\Theta_1\eta_{11} + \Theta_2\eta_{22} - \Theta_1\Theta_2\Delta\eta) \qquad (5.52a)$$

or

$$-E_o/\bar{r}N = (s/2v)(\Theta_2^2\eta_{11} + \Theta_2^2\eta_{22} + 2\Theta_1\Theta_2\eta_{12}) \qquad (5.52b)$$

Defining the segment fractions ϕ_1 and ϕ_2 by

$$\phi_2 = 1 = \phi_1 = r_2N_2/\bar{r}N \qquad (5.53)$$

we have

$$1/\bar{r} = \phi_1/r_1 + \phi_2/r_2 \qquad (5.54)$$

$$s = \phi_1s_1 + \phi_2s_2 \qquad (5.55)$$

$$\Theta_2 = (s_2/s)\phi_2 \qquad (5.56)$$

The characteristic pressures for the pure components are

$$P_1^* = s_1\eta_{11}/2v^{*2}$$

$$P_2^* = s_2\eta_{22}/2v^{*2} \qquad (5.57)$$

By analogy, we define

$$X_{12} = s_1\Delta\eta/2v^{*2} \qquad (5.58)$$

Then

$$-E_o/\bar{r}N = p^*v^*/\tilde{v} = ckT^*/\tilde{v} \qquad (5.59)$$

where
$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \Theta_2 X_{12} \qquad (5.60)$$

$$c = (c_1 r_1 N_1 + c_2 r_2 N_2)/\bar{r}N \qquad (5.61a)$$

$$= \phi_1 c_1 + \phi_2 c_2 \qquad (5.61b)$$

From equations 5.59, 5.60 and 5.61, the characteristic temperature T* for the mixture is given by

$$1/T^* = (\phi_1 P_1^*/T_1^* + \phi_2 P_2^*/T_2^*)(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \Theta_2 X_{12})^{-1} \qquad (5.62a)$$

Since $\tilde{T} = T/T^*$ we can rewrite this as

$$\tilde{T} = (\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2)\ (\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \Theta_2 X_{12})^{-1} \qquad (5.62b)$$

X_{12} influences the excess volume through $\tilde{T}$ and through equation 34.

Adoption of the Berthelot relationship(1, 16)

$$\eta_{12} = (\eta_{11}\eta_{22})^{\frac{1}{2}} \qquad (5.63)$$

for homopolar species whose interactions are dominated by the intermolecular dispersion energy leads to

$$\Delta\eta = (\eta_{11}^{\frac{1}{2}} - \eta_{22}^{\frac{1}{2}})^2 \qquad (5.64)$$

$$X_{12} = P_1^*\{1-(s_1/s_2)^{\frac{1}{2}}(P_2^*/P_1^*)^{\frac{1}{2}}\}^2 \qquad (5.65)$$

$$P^* = \{(\phi_1 \Theta_1 P_1^*)^{\frac{1}{2}} + (\phi_2 \Theta_2 P_2^*)^{\frac{1}{2}}\}^2 \qquad (5.66)$$

The intermolecular energy is given in terms of P^* by equation 58. It may be expressed alternatively by

$$-E_o/\bar{r}N = (s/2v)(\theta_1\eta_{11}^{\frac{1}{2}} + \theta_2\eta_{22}^{\frac{1}{2}})^2 \qquad (5.67)$$

Ignoring the difference between the energy and enthalpy of a condensed system at low pressure, we have for the molar excess enthalpy

$$\begin{aligned} H_M^E &= E_o(\text{mixture}) - E_o(1) = E_o(2) \\ &= \bar{r}Nv^*\{\phi_1 P_1^*/\tilde{v}_1 + \phi_2 P_2^*/\tilde{v}_2 - P^*/\tilde{v}\} \qquad (5.68) \end{aligned}$$

Equations given above allow this result to be expressed in the alternative forms

$$\begin{aligned} H_M^E &= \bar{r}Nv^*\{\phi_1 P_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \phi_2 P_2^*(1/\tilde{v}_2 - 1/\tilde{v}) \\ &\quad + (\phi_1\theta_2/\tilde{v})\chi_{12} \qquad (5.69a) \\ &= N_1 P_1^* v_1^*(1/\tilde{v}_1 - 1/v) + N_2 P_2^* v_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + \\ &\quad (N_1 v_1^*\theta_2/\tilde{v})\chi_{12} \qquad (5.69b) \end{aligned}$$

The final term in each of the above equations for the excess enthalpy of mixing represents the contributions from contact interactions attributable to a difference between 1,2 pairs and the mean of 1,1 and 2,2 contact pairs. It can generally be described as "the contact interaction term". The first two terms in the above equation, called the "equation of state" terms, represent the contribution of the reduced (i.e. excess) volume of the solution compared to those of the pure components.

THE CONTACT INTERACTION PARAMETER X_{12}

The use of equation 64 to calculate X_{12} has been found to be unsatisfactory owing to the inadequacies of the Berthelot geometric mean rule on which it is based. The quantity X_{12} is therefore treated as an empirical parameter and its value is usually adjusted to give the best fit between theoretical and experimental values of the molar excess enthalpy. X_{12} can subsequently be used to predict some other thermodynamic property such as the molar excess volume. The experimental excess volumes could theoretically also be used to determine X_{12}. However it is preferable to use the experimental excess enthalpies since the contact interaction parameter appears intrinsically in equations 5.69^a and 5.69^b to calculate the excess enthalpy whereas it only affects V^E via the reduced temperature, and consequently the excess volume is comparatively insensitive to the contact interaction parameter.

6. THEORETICAL DISCUSSION

1. Application of the Flory Theory of mixtures

The Flory theory (44,45,47,48) has been applied to excess volume and enthalpy data by many workers(4,6,8,21) and has been found to be moderately successful. The following approach follows that of Flory(44,45) and Benson(9).

The molar volume V of a pure liquid can be written as:

$$V = rv$$

where v is the volume of a mole of segments and r is the number of segments. Each segment is considered to have S intermolecular contact sites. The characteristic volume is given by:

$$V^* = rv^*$$

and the reduced volume defined by:

$$\tilde{v} = v/v^* = V/V^*$$

and can be calculated from

$$\tilde{v} = \{(1 + (4/3)\ \alpha T)/(1 + \alpha T)\}^3$$

where α is the coefficient of thermal expansion at temperature T.

At zero pressure, the reduced volume and reduced temperature ($\tilde{T}$) are related by the equation of state

$$\tilde{T} = (\tilde{v}^{\frac{1}{3}} - 1)/\tilde{v}^{\frac{4}{3}}$$

This is the central equation of Flory's theory. The characteristic temperature T* and pressure p* are obtained from the relations

$$T^* = T/\tilde{T}$$

$$P^* = (\alpha/\beta)T\tilde{v}^2$$

The reduced temperature for a mixture of type 1 molecules and type 2 molecules is given by

$$\tilde{T} = (\phi_1 P_1^* T_1 + \phi_2 P_2^* \tilde{T}_2)/(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \Theta_2 \chi_{12})$$

where X_{12} is the interaction parameter. The segment fraction ϕ_1 is defined by

$$\phi_1 = 1 - \phi_2 = x_1/(x_1 + x_2 r_2/r_1)$$

and the site fraction Θ_2 by:

$$\Theta_2 = \phi_2/(\phi_2 + \phi_1 s_1/s_2)$$

where S_1 and S_2 are the intermolecular contact sites for molecules of type 1 and type 2 respectively. The excess molar volume and excess molar enthalpy are given by

$$V_M^E = (x_1V_1^* + x_2V_2^*)(\tilde{v} - \tilde{v}^o) \qquad (6.1)$$

where $$\tilde{v}^o = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2$$

and $$H_M^E = (x_1V_1^*\theta_2X_{12}/\tilde{v})$$

$$+ x_1V_1^*\phi_2\{(\tilde{v}_1 - \tilde{v}_2)/\tilde{v}^o\}P_2^*/\tilde{v}_2 - P_1^*/\tilde{v}_1)$$

$$+ \{V_M^E/(\tilde{v}^o)^2\}(\phi_1p_1^* + \phi_2p_2^*) \qquad (6.2)$$

It is assumed that

$$s_1/s_2 = (v_2^*/v_1^*)^{\frac{1}{3}}$$

The following calculations, based on the approach of Flory were carried out for each system. $\chi_{12}(V_M^E)$ was first determined from V_M^E data using equation (6.1). Because it was found to be concentration dependent $\chi_{12}(V_M^E)$ was determined at all compositions between 0 and 1,0 at 0.01 mole fraction intervals and the value of $\chi_{12}(V_M^E)$ which minimised the standard deviation $\sigma(V_M^E)$, was chosen.

The standard deviation of $\sigma(V_M^E)$ was determined from:

$$\sigma(\chi_M^E)^2 = \sum_{i=1}^{98}\{\chi_M^E(\text{expt.})\ (x_i) = \chi_M^E\ (\text{calc.})\ (x_i)\}^2/97 \qquad (6.3)$$

where χ_M^E refers to excess molar volume. The values of H_M^E calculated were then determined from $\chi_{12}(V_M^E)$ using equation (6.2) and hence $\sigma^*(H_M^E)$ was determined from equation (6.3) where χ_M^E refers to excess molar enthalpy H_M^E.

For the sake of comparison the best value of $\chi_{12}(H_M^E)$ from H_M^E data, can be determined and $\sigma(H_M^E)$ calculated. V_M^E data can then be predicted.

7. EXPERIMENTAL

The H_M^E measurements were determined using a commercial LKB2107 flow microcalorimeter. The V_M^E measurements were measured by the vibrating tube densitometer (Paar DMA601) method.

The purities of the hydrocarbons used are given in Table 1, together with the suppliers of the hydrocarbons. The purities were determined by g.l.c. In most cases the supplied hydrocarbon had an estimated purity greater than 99,2 mole per cent. n-Octane, cycloheptane, cis-decalin and trans-decalin were distilled under low pressure and dried before using. The n-hexadecane was purified by fractional crystallisation followed by distillation. It was found that the volatile hydrocarbons used in this work caused bubble formation on mixing. As a result the n-hexane, cyclopentane and cyclohexane were degassed before use.

Degassing of Liquids

Liquids are usually saturated with air and when two liquids are mixed air is displaced from the solution. This is most commonly achieved(59) by repeated freezing, evacuating and thawing of the liquids. An eightfold repetition of the cycle is usually found to be sufficient. The liquids were degassed in test tubes (30-60 cm^3) fitted with rotaflo seals and subsequently frozen by immersing the test tubes into liquid nitrogen.

Once degassing was complete, the pressures inside and outside the collection tube were equalized by allowing mercury to run into the test tube under vacuum. The rotaflow seals were improved by filling the tubes immediately above the seals with mercury. The degassed liquids in contact with mercury were stored in these sealed test tubes. The degassing apparatus is shown in Fig. 12.

DETERMINATION OF THE EXCESS ENTHALPY OF MIXING

The flow calorimeter used in this study is the commercial LKB 2107-020 model. The prototype of this model is described by Monk and Wadso(18). In this method peristaltic pumps are used which give a reproducibility of flow rate better than 0,5 %. H^E_M is determined to a precision of 2 % or better with n-hexane and cyclohexane at 298K.

The arrangement of the apparatus is shown in Fig. 13. A metal block heat sink B enclosed by foam A is situated in a thermostatted air bath. The heat sink contains a centrally located heat exchange unit C. On either side of this are calorimetric units D in a twin arrangement. The calorimetric units consist of flow reaction cells surrounded by surface thermopiles which are in contact with primary heat sinks E. The calorimetric liquids are pumped through the heat exchange unit to one of the reaction cells and from there to a receiver outside the calorimeter.

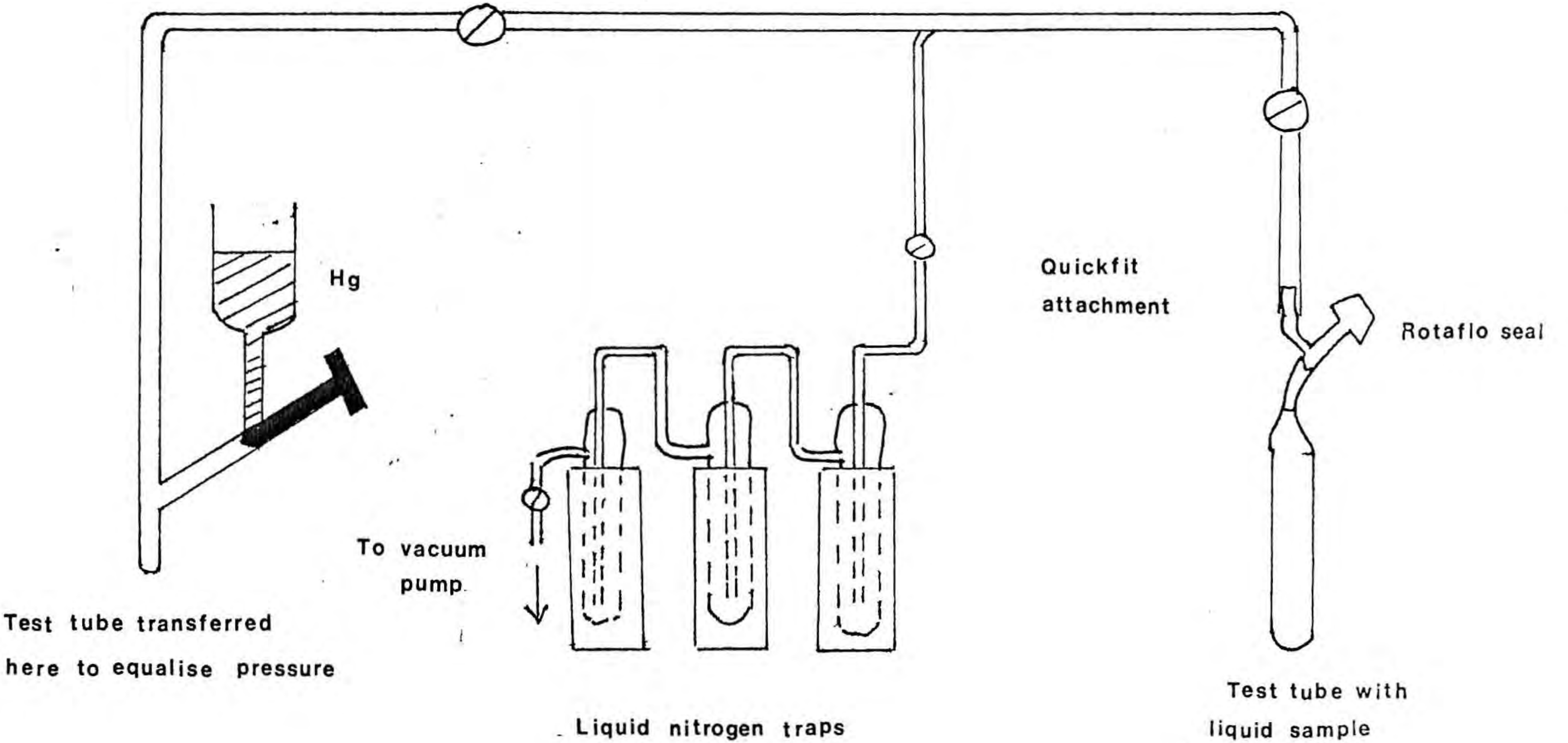

FIG 12 THE DEGASSING APPARATUS

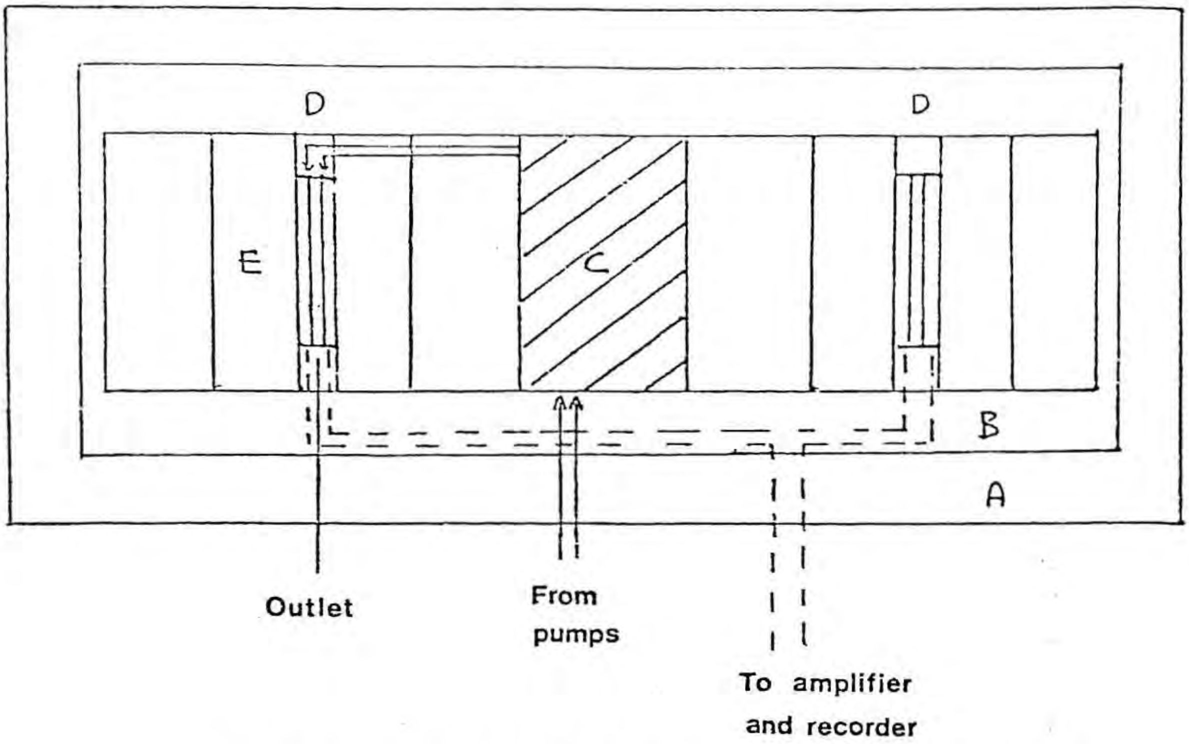

FIG 13 TOP VIEW OF FLOW MICROCALORIMETER

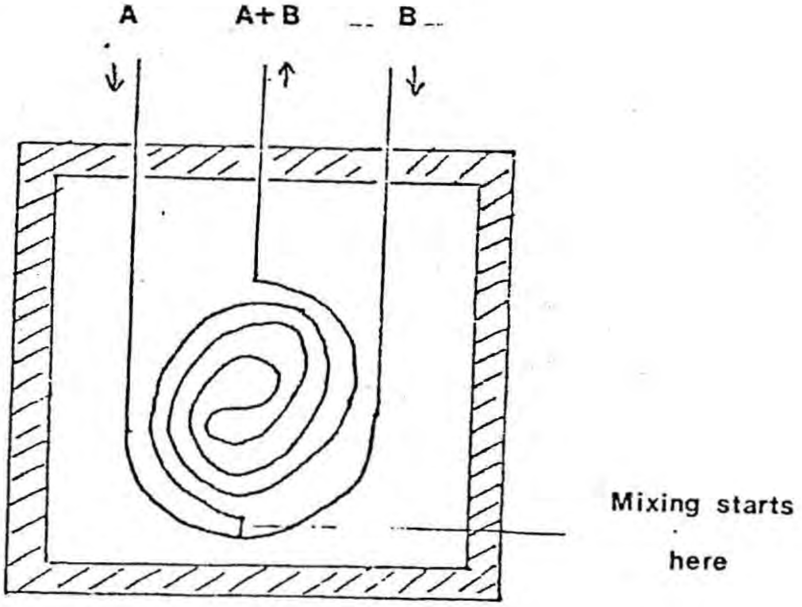

FIG 14 MIXING VESSEL OF FLOW MICROCALORIMETER

The heat flow across the thermopiles is transduced to a voltage signal. This is a differential signal from the two thermopiles in order to cancel common external thermal disturbances. Liquid flows through only one cell during the calorimetric run.

The flow microcalorimeter operates on a heat-leakage principle, and can be used for exothermic or endothermic mixing. The heat evolved or absorbed in a mixing process within the flow cell is conducted to or from a heat sink through the pair of thermopiles which sandwiches the cell.

The two liquids are brought together in the mixing zone of the flow cell (see Fig. 14). Mixing of reactants can be achieved without the presence of a gaseous phase (bubbles) - an important factor as condensation-evaporation effects can affect the result. A constant flow rate will give rise to a constant heat effect. Steady state conditions are attained after approximately 10 minutes when the heat generated in the cell per unit time is equal to the heat transmitted out from the cell.

Steady state conditions must exist in the cell before readings can be taken.

A major part (approximately 97 %) of the total heat generated in the cell (W) is transmitted from the cell by heat conduction to the heat sink through the surrounding thermopiles (W_t) A minor portion (approximately 3 %) will leave the cell by radiation by the liquid flow, and by conduction along the cables and tubing.

When a particular calorimeter is used under specified experimental conditions (flow rate, physical properties of the liquids that are to be mixed) then the ratio W_t/W will be constant

$$W = \alpha W_t \qquad (7.1)$$

Heat flows through a thermopile when there is a temperature gradient.

$$W_t = a.\Delta T \qquad (7.2)$$

(Newton's Law of Cooling).

a - heat leakage constant

ΔT - temperature difference

The voltage E generated by the thermopile arises from the temperature gradient across it and is directly proportional to Δ T

$$E = b.\Delta T \qquad (7.3)$$

b - proportionally constant

E - thermopile voltage

By equations (7.2) and (7.3) we can derive the expression

$$W_t = \beta . E \qquad (7.4)$$

β - constant

Combination of equations (7.1) and (7.4) lead to the expression

$$W = \varepsilon . E \qquad (7.5)$$

During an experiment a small fraction of the heat effect generated in the cell is due to frictional effects of the liquid flow. This contribution to the thermopile signal may be determined at a blank experiment. This blank reading is taken as a reference point for the thermopile voltage during the actual experiment.

Monk and Wadso(18) investigated the zero effects by (a) varying the flow rate and (b) varying the viscosity of the calorimetric liquid. At a flow rate of 0,4 ml/min. the zero heat effect was 8×10^{-6} J.sec^{-1}. In the determination of the mixing curve for n-hexane/cyclohexane the heat effect was 21×10^{-3} J.sec^{-1}

therefore constitutes a 0,4 % error which need not be taken into consideration as the overall precision is 3 % . The zero heat effect due to a 20 % sugar solution was 4×16^{-6} J.sec^{-1} and variations in the zero heat effect with the viscosity of the calorimetric hydrocarbon liquids were safe to ignore.

The constant ε in equation (7.5) is determined by electrical calibration. Heat evolution at a calibration procedure and at a process under investigation must be comparable as the calibration constant ε varies from run to run in a binary system. Each separate binary mixture should be calibrated.

The procedure for determining enthalpies of mixing was as follows:

All thermostatting units viz. the control unit, the thermostat and the pre-thermostat were set at the required temperatures and initiated. The equipment was allowed to equilibrate overnight before use. The power was left on continuously to allow the units concerned with temperature control to maintain temperature equilibrium. The temperature of the pre-thermostat was set at 10 °C lower than the air bath of the calorimeter thermostat in order to allow for optimum control. A temperature sensor is mounted in the main heat sink of the micro-calorimeter between the two detector units. This provides a signal to enable the temperature of the heat-sink to be monitored on a meter on the front panel of the Control Unit.

The two liquids are sucked into the system by the peristaltic pump until they reach the mixing cell. When steady state conditions are reached the deflection on the recorder will become constant. The pump tubes are made of Viton and the interconnecting tubes are Silicone. The reservoirs containing the components were weighed to two decimal places.

A calorimetric run was initiated by starting the pumps and an electronic stopwatch simultaneously to record the time.

If the mixing was endothermic the cell heater was activated and the heating current adjusted until the recorder deflection returned to baseline. The rate of heating supplied to the mixing cell was determined by the formula

$$P = I^2 R$$

where R = 50,18 Ω (Table of Individual Apparatus Data)

I = current in A

If the mixing was exothermic then the steady-state recorder deflection was noted and a heating current was applied to double the deflection.

The mixtures were individually calibrated by applying the heating currents used during the experiment at the same flow rate used and recording the deflection E_c. The calorimeter was fitted with a calibrated ammeter so that the current through the heater could be accurately determined. The temperature of the mixing cell was monitored using a calibrated thermocouple placed against the cell. The calibration constant ε was determined by the formula

$$\varepsilon = W_c/E_c$$

where $W_c = I^2Rt$ (Joules)

and $E_c =$ recorder deflection (arbitrary units)

The excess molar enthalpy of mixing is then given by

$$H^E_M = \frac{I^2Rt}{E_c} \cdot E \quad /\text{Total number of moles}$$

For low flow rates ($<0,3$ ml/min^{-1}) it was found that $E = E_c$ for the same heating current. In this case the calibration procedure was therefore unnecessary and H^E_M was determined by the formula

$$H^E_M = I^2Rt \quad (\text{Total number of moles})$$

and it was unnecessary to record the recorder deflection.

The number of moles of each component were calculated from the mass differences between the starting and stopping of a run, and the respective molecular masses. The techniques and calibrations were periodically checked by determining H^E_M for the well documented system of n-hexane and cyclohexane at various temperatures. The results were always within $3 J.mol^{-1}$ of the results reported by Ewing and Marsh(60)

Determination of the Excess Volume of Mixing

The vibrating tube densitometer method has been described by Siddigi et al(61). The temperature was controlled to within 2mK and the densitometer was calibrated using tetralin, water and cyclohexane. The densities of the standards were independently measured using precision pycnometry. The mixtures were made up in 5 cm^3 bottles fitted with ground-glass stoppers. The less volatile liquid was always added first to reduce vapour-space errors.

Control and Measurement of Temperature

The precision of the above method depended primarily on constant temperature conditions. The U-tube was immersed in water from thermostatted copper water bath with a glass window on one side. The surface of the water was covered with floating polystyrene balls. Two mechanical stirrers ensured uniform temperature throughout the bath. The thermostat included a permanent rheostatted heater, an intermittent light bulb (25 W) connected to the temperature controller and a refrigerator coil.

The temperature was monitored by means of a Hewlett Packard 2801 A quartz thermometer.

TABLE 7.1 Hydrocarbon suppliers and estimated purities

Liquid	Purity mol per cent	Supplier
cyclopentane	99,3	Aldrich
cyclohexane	99,5	Riedel de Hahn
cycloheptane	99,5	Merck-Schuchardt
cyclo-octane	99,2	Pfaltz and Brauer
n-hexane	99,2	British Drug House
n-octane	99,6	Merck-Schuchardt
n-dodecane	99,2	British Drug House
n-hexadecane	99,1	Merck-Schuchardt
bicyclohexyl	99,2	Aldrich
tetrahydronapthalene	99,3	British Drug House
decahydronapthalene[a]	99,85	Riedel de Hahn
cis-decahydronapthalene	99,6	Aldrich
trans-decahydronapthalene	99,8	Aldrich

[a] A mixture of 53,3 mole per cent cis isomer and 46,7 mole per cent trans isomer

8. RESULTS AND DISCUSSION OF TRENDS

8.1 Introduction

The excess molar enthalpies obtained by flow microcalorimetry, and the excess molar volumes obtained by vibrating tube densitometer, are given in the Appendix. The excess molar quantities were fitted to Redlich-Kister polynomials by a computer program. The Redlich-Kister polynomial has the form

$$X^E(\text{Theory}) = x_1(1-x_1)\{\sum_{r=o}^{n} A_r(1-2x_1)^r\} \qquad (8.1)$$

where x_1 denotes the mole franction of the first component in the binary mixture and A_r are the smoothing equation coefficients. The "closeness" of the theoretical results to the actual results is given by the deviation δX^E given by

$$\delta X^E = X_M^E(\text{exptl.}) - X_M^E\ (\text{Theory}) \qquad (8.2)$$

Units of $H^E{}_M$ are $J.mol^{-1}$ and the units of $V^E{}_M$ are $cm^3.mol^{-1}$. Actual results and the deviation δX^E from the theoretical equation (8.2) are given in tables in the appendix.

8.2 Excess Molar Enthalpy of Mixing

8.2.1 Bicyclohexyl and cycloalkane systems

Lal and Swinton(69) have previously reported the excess molar enthalpies of mixing for bicyclohexyl and cycloalkanes. Our results are within 3 $J.mol^{-1}$ of their results over the whole composition range. The excess molar enthalpies of mixing for the cyclopentane system does not fit into the pattern established by the other cycloalkanes (see Table 8.1). Although the trend is for the excess enthalpy to increase with increasing size of cycloalkane, the excess enthalpy for the cyclopentane system is very much lower than that for the other cycloalkane systems. This behaviour is also seen in the excess volume results reported by Letcher(70) and is probably due to the cyclopentane molecule being flat and smaller than the other cycloalkanes, and allowing for more intimate interaction with the larger bicyclohexyl molecule.

The value of $(\partial H^E/\partial T)$ at $x = 0,5$ increases in magnitude with increasing size of the cycloalkane. See Table (8.2)

8.2.2 Tetralin and cycloalkane systems

Grolier(72) and Lundberg(73) have reported results for the cyclohexane system. Our results at 298,2k compare well with their work. When compared with results interpolated from the equations given by Grolier(72) we obtain a standard deviation of 6,5 $J.mol^{-1}$.

The excess enthalpy results reported here are all positive and show a strong similarity to results for benzene and a cycloalkane as reported by Benson's group(74) and by Diaz Pena and his group(75). It is suggested that the dominant effect in the mixing process is the endothermic disassociation of aromatic-aromatic interactions. The pattern for the excess molar enthalpies is different to that reported for bicyclohexyl and decalin see Table (8.1). As in the case of the bicyclohexyl systems and the benzene systems(74, 75) the values of $(\partial H_M^E/\partial T)$ at $x = 0,5$ increases in magnitude with increasing carbon number (see Table 8.2)

8.2.3 Decalin and cycloalkanes systems

The molar excess enthalpies for cis-decalin in cyclohexane and trans-decalin in cyclohexane have been reported by Sturtevant(76), Benson(77) and Lundberg(78). The standard deviation between our results and the smoothing curve of Benson's(77) is less than 1,5 $J.mol^{-1}$ in both cases and within 3 $J.mol^{-1}$ of the results of Sturtevant(76). We feel that this is a result of impurities and a difference in measuring techniques.

The molar excess enthalpy for decalin with cyclopentane is very much more negative than the molar excess enthalpy for decalin in cyclohexane, cycloheptane or in cyclooctane. The same effect was seen in bicyclohexyl in cycloalkanes and in tetralin in cycloalkanes, for the same reasons as earlier suggested.

It is interesting to note that the values obtained for

$(\partial H_M^E/\partial T)_{x=0,5}$ for decalin in cycloalkanes are much less than were obtained for bicyclohexyl in cycloalkanes and tetralin in cycloalkanes. The result for cycloheptane is surprising in that it does not conform to the general trend.

8.2.4 Bicyclohexyl and n-alkane systems

The only system for which H^E_M has been published is the n-dodecane system by Jessup and Stanley(79). Some of our results are as much as 9 J.mol^{-1} lower than points on the curve obtained by these authors from four data points. As in the case of the cycloalkanes the $H^E_M(x=0,5)$ for the n-alkane systems increases with increasing carbon number. See Table 8.1. The magnitude of $(\partial H_M^E/\partial T)$ at $x = 0,5$ also increases with carbon number. (See Table 8.2)

8.2.5 Tetralin and n-alkane systems

Grolier(72) and Lundberg(73) have investigated the n-heptane and n-hexadecane systems. Our results at 298,2k compares well with their work and upon comparing our results to those interpolated from the equations given by Grolier(72) we obtained standard deviations of 8,1 J.mol^{-1} and 6,1 J.mol^{-1} respectively.

The H^E_M results reported here are all positive and show a strong similarity to H^E_M results for benzene and an n-alkane as reported by Benson's group(74) and Diaz Pena and his group(75). As in the case of the cycloalkanes this suggests that the dominant effect in the mixing process is the endothermic disassociation of aromatic-aromatic interactions.

H^E_M increases with increasing n-alkane carbon number as in the case of the bicyclohexyl system, although the magnitude of the H^E_M is very much lower for the bicyclohexyl systems.

As in the case of the bicyclohexyl systems and the benzene systems the values of $(\partial H^E/\partial T)_{x=0,5}$ increase in magnitude with increasing carbon number (See Table 8,2)

8.2.3 Decalin and n-alkane systems

The H^E_M for decalin in n-heptane and in n-hexadecane has been reported by Lundberg(73). Lundberg used a different cis- and trans-decalin mixture (64 mole per cent cis and 36 mole per cent trans) so our results are not directly comparable. Our results are 12 J.mole^{-1} and 8 J.mole^{-1} lower than Lundberg's for decalin in hexadecane and heptane at 25 °C and at equimolar composition, respectively. We did not investigate the isomer effect on mixing with alkanes due to our shortage in stock of cis- and trans-decalin.

The H^E_M results for decalin with n-alkanes show similar trends to that obtained for bicyclohexyl or tetralin in n-alkanes. In all cases H^E_M increases with increasing n-alkane carbon number. Furthermore, the value of

$(\partial H^E/\partial T)_{x=0,5}$ also increases in magnitude with n-alkane carbon number.

TABLE 8.1 H^E_M $(x = 0,5)$ at 25 °C

	Bicyclohexyl	Decalin	Tetralin
c-C5	-142,4	-185,0	246,4
c-C6	113,6	25,9	482,9
c-C7	140,6	8,8	426,8
c-C8	164,6	18,0	404,9
n-C6	21,6	62,4	463,3
n-C7	-	68,6	488,4
n-C8	35,8	81,6	-
n-C12	65,3	125,1	570,3
n-C16	128,0	198,6	657,0

TABLE 8.2 $(\partial H^E_M/\partial T)_{x=0,5}$ between 15 °C and 25 °C

	Bicyclohexyl	Decalin	Tetralin
c-C5	-0,9	-0,02	-0,8
c-C6	-1,0	-0,09	-1,6
c-C7	-1,4	+0,09	-2,4
c-C8	-1,5	-0,10	-3,3
n-C6	-0,9	-0,4	-1,0
n-C7	-	-0,9	-1,7
n-C8	-0,9	-1,0	-
n-C12	-1,9	-2,3	-2,8
n-C16[a]	-4,1	-3,0	-3,1

[a] Between 25 °C and 35 °C

8.3 Excess Molar Volume of Mixing

8.3.1 Tetralin and n-alkanes

No V^E_M measurements have ever been reported for mixtures of tetralin with n-alkanes. Letcher(80, 81) has investigated bicyclohexyl + n-alkane systems, and Letcher and Lucas(82, 83) have investigated decalin + n-alkane and + cycloalkane systems. The results presented in this work show strong similarities to the V^E_M results for bicyclohexyl in n-alkanes as well as for decalin in n-alkanes. In both sets the $V^E_M(x=0,5)$ increases with increasing with n-alkane chain length. Furthermore, the temperature coefficients $(\partial V^E_M/\partial T)_{x=0,5}$ show similar trends.

8.3.2 Tetralin and cycloalkanes

These results again show strong similarities to the V^E_M results of bicyclohexyl in cycloalkanes, and decalin in cycloalkanes. In all cases V^E_M for the cyclopentane containing mixtures are very much lower, probably due to the more favourable packing configuration of the flatter cyclopentane molecule. The effect on V^E_M of increasing the cycloalkane carbon number is similar to the bicyclohexyl and decalin systems. The pattern is very different for other mixtures such as an n-alkane in a cycloalkane(83, 84).

This points to the importance of molecular shape in determining excess volumes of liquid mixtures. The $(\partial V_M^E/\partial T)$ values also show a strong similarity to the (bicyclohexyl + cycloalkane)(81) and to the (decalin + cycloalkane) systems(83).

TABLE 8.3 $V_M^E(x=0,5)$ at 25 °C

	Tetralin	Decalin	Bicyclohexyl
c-C5	-0,5051	-0,6303	-0,6602
c-C6	0,1020	-0,1323	-0,0388
c-C7	0,2022	-0,0383	0,1689
c-C8	0,2626	0,0175	0,2587
n-C5	-1,4745	-1,4310	-1,5915
n-C6	-0,9889	-0,9478	-1,1075
n-C7	-0,6596	-0,6363	-0,8556
n-C8	-0,4999	-0,4565	-0,6921
n-C10	-	-	-0,4182
n-C12	-0,0648	-0,0726	-0,2247
n-C16	-	0,1371	-0,0789

TABLE 8.4 $(\partial V_M^E/\partial T)_{x=0,5}$ between 15 °C and 25 °C

	Tetralin	Bicyclohexyl	Decalin
c-C5	-0,0047	-0,0052	-0,0035
c-C6	-0,0029	-0,0031	-0,0012
c-C7	-0,0017	-0,0018	-0,0004
c-C8	-0,0015	-0,0015	-0,0003
n-C5	-0,0129	-0,0097	-0,0150
n-C6	-0,0093	-0,0089	-0,0117
n-C7	-0,0044	-0,0050	-0,0086
n-C8	-0,0049	-0,0047	-0,0061
n-C12	-0,0013	-0,0012	-0,0047

8.4 Results of the application of the Flory theory to the decalin + cyclo-alkane en + n-alkane systems

The approach taken in chapter 6 was used to apply the Flory theory to the decalin + cycloalkane and + n-alkane systems. The H^E_M results measured in this work and V^E_M results reported by Letcher and Lucas$^{(82, 83)}$ of those systems were fitted to the Flory theory of liquid mixtures. The values of densities, ρ (units gcm^{-1}), coefficients of thermal expansion, α (units deg^{-1}), and isothermal compressibility, β (units Pa^{-1}), used in the calculations are given in Table 8.5. The experimental values of excess molar volume and enthalpy were calculated from the smoothing Redlich-Kister polynomials of Letcher and Lucas$^{(82, 83)}$ and those presented in this work.

The values of $X_{12}(V^E_M)$, σ (V^E_M) and σ^* (H^E_M) are given in columns 1, 2 and 3 of Table 8.6. For sake of comparison the best value of $X_{12}(H^E_M)$ has been determined from H^E_M data. Hence σ (H^E_M) has been determined, V^E_M(calculated) predicted and σ^* (V^E_M) has been calculated. The values of $X_{12}(H^E_M)$, σ (H^E_M) and σ^* (V^E_M) are given in columns 4, 5 and 6 of Table 8.6

It can be seen from Table 8.6 that the Flory theory fits the excess thermodynamic data reasonably well and provides a satisfactory estimate of V^E_M from H^E_M data and vica versa

TABLE 8.5 Physical Properties of Pure liquids at 25 $^{\circ}C$ used in the Flory Equations

Hydrocarbon	ρ^a	lit.	$10^3 \times \alpha^b$	lit.	$10^{12} \times \beta^c$	lit.
cis-dacalin	0.89286	(9)	0.851	(9)	691.8	(9)
trans-dacalin	0.86590	(9)	0.865	(9)	760.5	(9)
decalin^d	0.88263	This work	0.857		724.1	
cyclopentane	0.74041	(58)	1.325	(63)	133.1	(66)
cyclohexane	0.77387	(58)	1.217	(9)	112.0	(68)
cycloheptane	0.80731	(58)	1.00	(67)	967.2	(67)
cyclooctane	0.83151	(58)	0.979	(66)	803	(66)
hexane	0.65481	(64)	1.375	(65)	1669	(65)
heptane	0.67951	(64)	1.245	(65)	1438	(65)
octane	0.69849	(64)	1.150	(65)	1282	(65)
dodecane	0.74516	(64)	0.970	(65)	988	(65)
hexadecane	0.76996	(64)	0.898	(65)	857	(65)

[a] Units cm^{-3}

[b] Units deg^{-1}

[c] Units Pa^{-1}

[d] a mixture of 53.3 mole per cent cis and 46.7 mole per cent trans

TABLE 3.6 A summary of calculations using the Flory theory for decalin-hydrocarbon mixtures

	$X_{12}(V^E_M)$	$\sigma(V^E_M)$	$\sigma^*(H^E_M)$	$X_{12}(H^E_M)$	$\sigma(H^E_M)$	$\sigma^*(H^E_M)$
	$J.cm^{-3}$	$cm^3.mol^{-1}$	$J.mol^{-1}$	$J.cm^{-3}$	$J.mol^{-1}$	$cm^3.mol^{-1}$
c-C5	-15.17	0.042	20.50	-5.10	15.6	0.151
c-C6	-0.885	0.038	64.4	2.16	10.9	0.059
c-C7	3.53	0.013	69.4	0.441	3.7	0.047
c-C8	-0.469	0.006	27.8	0.734	1.5	0.018
n-C6	3.00	0.028	24.6	4.04	1.5	0.034
n-C7	3.51	0.010	3.8	3.40	1.2	0.010
n-C8	2.76	0.005	11.6	3.24	3.1	0.010
n-C12	3.84	0.006	10.4	3.56	8.8	0.008
n-C16	7.22	0.008	61.6	5.16	6.8	0.040

CONCLUSION AND PROPOSALS FOR FURTHER STUDY

The theory developed by P J Flory and his co-workers has been shown to be successful in predicting liquid mixture poperties for a non-associated liquid mixture viz decalin + cycloalkane and + n-alkane. To further the investigation into the excess thermodynamic properties of two-ring compounds (bicyclohexyl, tetralin and decalin) it would be interesting to test the Flory theory for the bicyclohexyl + n-alkane and + cycloalkane system and for the tetralin + n-alkane and + cycloalkane system. The V^E_M data for the tetralin system has been determined in this work, and the V^E_M data for the bicyclohexyl system has been reported by Letcher(80, 81, 86)

The outstanding quantity needed for application of the Flory theory to these systems is the isothermal compressibility for both tetralin and bicyclohexyl. Work to collect this data is done by M Diaz Pena.

APPENDIX

TABLE A 1 Molar Excess Enthalpies for mixing cis or trans decalin with several cycloalkanes at 25 °C. The deviations calculated from equation (8.1) and coefficients of Table A 2 are also included.

x^a	H^E_M	δH^E_M	x^a	H^E_M	δH^E_M	x^a	H^E_M	δH^E_M
				cis-decalin + cyclohexane				
0.0935	-3.5	0.3	0.3968	17.2	-1.0	0.6742	40.6	2.1
0.1812	-1.0	0.2	0.4219	19.3	-1.5	0.7540	37.9	0.5
0.2665	4.5	-0.5	0.5250	31.3	0.5	0.8978	22.1	-0.5
				trans-decalin + cyclohexane				
0.1223	-6.2	-0.1	0.4009	13.9	0.3	0.6815	23.3	-0.8
0.2864	3.4	-0.1	0.4871	20.5	0.6	0.7509	20.8	-0.7
0.3750	11.4	-0.1	0.5502	23.5	0.5	0.9117	9.2	0.2
				cis-decalin + cycloheptane				
0.1362	0.5	0.3	0.4557	10.5	-0.6	0.7131	14.5	0.5
0.2181	2.1	-0.3	0.5264	13.3	0.2	0.8368	10.0	-0.3
0.3616	7.2	-0.6	0.5614	14.7	0.9			
				trans-decalin + cycloheptane				
0.0762	-5.2	-0.2	0.3765	-7.4	0.2	0.7045	-4.3	-0.3
0.1824	-7.8	0.2	0.4891	-6.6	-0.4	0.8550	-2.5	0.2
0.2391	-7.9	0.6	0.6223	-5.0	0.3			
				cis-decalin + cyclooctane				
0.1079	8.7	0.1	0.4805	22.7	-0.3	0.7356	18.7	0.3
0.2310	15.8	-0.1	0.5636	23.1	0.2	0.8629	11.0	-0.2
0.3664	20.7	-0.4	0.6704	21.2	0.4			
				trans-decalin + cyclooctane				
0.0725	-1.5	-0.1	0.4789	6.0	0.3	0.7220	4.0	-0.5
0.2248	0.9	0.4	0.5638	5.9	-0.1	0.8151	2.4	-0.2
0.3502	3.8	0.4	0.6715	4.9	-0.4	0.9034	1.2	0.3

[a] Mole fraction decalin

TABLE A 2 Smoothing coefficients A_r in equation (1) for x decalin + (1-x) cycloalkane at 25 °C

mixture	A_0	A_1	A_2
cic-decalin + cyclohexane	114.3	-180.7	-18.0
trans-decalin + cyclohexane	82.5	-112.7	-94.6
cis-decalin + cycloheptane	49.8	-51.9	-20.0
trans-decalin + cycloheptane	-24.1	-26.3	-33.5
cis-decalin + cyclooctane	-92.4	-4.2	-0.3
trans-decalin + cyclooctane	23.3	-16.1	-40.1

TABLE A 3 Molar Excess Enthalpies for mixing Decalin with cycloalkanes and witn n-alkanes. The deviations, calculated from equation (8.1) and the coefficients from Table A 4 are included.

x^a	H^E_M	δH^E_M	x^a	H^E_M	δH^E_M	x^a	H^E_M	δH^E_M
cyclopentane at 15 °C								
0.1156	-79.7	-2.1	0.4721	-183.4	0.5	0.7436	-145.8	-0.4
0.1875	-110.5	3.7	0.4962	-184.3	0.4	0.7950	-126.7	-1.0
0.2542	-140.7	0.3	0.5460	-182.9	0.8	0.8862	-79.9	-0.3
0.3376	-166.0	-0.7	0.6952	-162.0	-1.8	0.9400	-44.6	0.6
cyclopentane at 25 °C								
0.0836	-63.4	-0.6	0.4715	-186.7	-2.6	0.7815	-136.4	0.9
0.2514	-138.9	4.5	0.5514	-185.3	-1.1	0.9022	-76.3	-0.3
0.3765	-176.2	-2.1	0.6911	-163.8	1.2			
cyclohexane at 15 °C								
0.0605	-4.5	0.0	0.2998	5.7	-1.3	0.6206	35.2	1.6
0.0837	-4.8	0.3	0.3979	15.9	-1.3	0.6663	35.2	0.9
0.1198	-5.1	0.1	0.4722	24.0	-0.4	0.7815	30.4	-0.1
0.2056	-1.4	-0.2	0.5717	32.8	1.1	0.8523	23.4	-0.6
cyclohexane at 25 °C								
0.0547	-4.7	-0.2	0.2638	2.2	-0.9	0.6415	34.3	1.7
0.0936	-5.0	0.6	0.3704	11.7	-2.1	0.6830	34.1	1.5
0.1522	-4.1	0.6	0.4326	17.9	-2.1	0.7918	28.2	2.1
0.1930	-2.4	0.2	0.5936	32.5	1.1	0.9005	15.7	-0.7
cycloheptane at 15 °C								
0.0914	-3.2	0.2	0.4005	4.5	-0.1	0.7234	10.8	0.3
0.2047	-3.0	-0.2	0.4653	7.2	0.4	0.8210	9.3	0.9
0.2684	-1.1	-0.2	0.5652	9.7	0.1	0.8661	6.8	0.0
0.3412	1.1	-0.8	0.6305	10.2	-0.3	0.9312	3.5	-0.3
cycloheptane at 25 °C								
0.0754	-1.5	0.2	0.3220	2.8	-0.2	0.6674	10.5	-0.6
0.1264	-1.8	-0.1	0.4531	8.1	0.6	0.7956	9.4	-0.3
0.1676	-1.5	-0.3	0.5716	10.9	0.6	0.8923	6.0	0.2
0.2261	-0.3	-0.3						

[a] Mole fraction decalin

TABLE A 3 (cont.)

x	H^E_M	δH^E_M	x	H^E_M	δH^E_M	x	H^E_M	δH^E_M
				cyclooctane at 15 °C				
0.1163	6.4	0.1	0.4753	19.4	0.7	0.7913	14.5	-0.1
0.2144	10.5	-0.3	0.5451	19.5	0.2	0.8431	12.5	0.5
0.2851	13.5	-0.2	0.6224	18.5	-0.5	0.9334	5.8	-0.1
0.4153	18.0	0.4	0.6697	17.7	-0.6			
				cyclooctane at 25 °C				
0.0715	4.2	0.1	0.3723	15.6	-0.2	0.7161	16.2	-0.3
0.1552	8.0	-0.3	0.4437	18.1	0.7	0.7920	14.0	-0.1
0.2916	13.8	0.2	0.5875	18.1	-0.2	0.8819	9.5	-0.1
				n-hexane at 15 °C				
0.1096	26.2	0.3	0.4069	64.6	0.1	0.6928	55.7	-0.2
0.2014	42.4	-0.4	0.4854	66.8	0.1	0.7623	47.8	0.5
0.3040	56.2	-0.3	0.5395	66.6	0.4	0.8403	34.3	-0.3
0.3562	61.0	-0.3	0.5776	65.1	0.3			
				n-hexane at 25 °C				
0.0954	21.2	-0.3	0.4405	61.3	-0.1	0.6774	54.6	-0.3
0.1736	36.1	0.3	0.4936	62.0	-0.3	0.7505	47.4	0.1
0.2519	47.8	0.8	0.5720	60.8	-0.4	0.9026	22.7	0.1
0.3762	58.6	0.2						
				n-heptane at 15 °C				
0.0810	22.8	0.5	0.4486	76.8	0.1	0.7046	67.9	0.2
0.1554	39.2	-0.3	0.5173	78.3	0.1	0.7848	55.1	-0.1
0.2365	53.5	-1.1	0.5958	76.8	0.5	0.8912	32.0	-0.3
0.3476	68.6	-0.8	0.6507	73.3	0.7			

[a] Mole fraction decalin

TABLE A 3 (cont)

x^a	H^E_M	δH^E_M	x^a	H^E_M	δH^E_M	x^a	H^E_M	δH^E_M
n-heptane at 25 °C								
0.0615	17.1	0.7	0.3967	65.1	0.1	0.7174	58.8	0.0
0.1115	26.8	-0.9	0.4705	69.2	1.0	0.8413	40.5	-0.2
0.2056	44.0	-0.9	0.5559	69.0	0.5	0.8946	29.4	-0.1
0.3250	59.2	-0.4	0.6235	66.4	0.2	0.9439	17.0	0.0
n-Octane at 15 °C								
0.0963	28.7	-0.6	0.3751	84.5	1.7	0.7382	78.3	-0.5
0.1546	44.5	0.3	0.4607	90.1	0.0	0.8054	65.2	-0.9
0.2866	71.3	0.7	0.5183	91.8	-0.5	0.8869	45.2	0.9
0.3179	76.0	0.5	0.6510	87.3	-1.5			
octane at 25 °C								
0.0936	26.8	0.4	0.4647	80.7	0.3	0.7836	62.0	-0.2
0.1742	44.3	-0.2	0.5513	83.1	0.9	0.8151	56.6	0.3
0.2351	54.8	-0.9	0.6809	76.8	0.8	0.9051	33.4	-0.3
0.3865	73.8	-1.3	0.7114	73.0	0.1			
dodecane at 15 °C								
0.1706	48.1	-2.4	0.4241	139.7	2.2	0.7380	136.2	-2.4
0.1762	71.0	0.2	0.4832	146.7	0.1	0.8382	105.7	-1.0
0.2282	90.6	2.3	0.5574	152.0	-1.0	0.8913	79.8	0.7
0.3321	122.1	4.5	0.6630	145.9	-4.7	0.9466	43.7	0.4
dodecane at 25 °C								
0.0836	29.4	-0.9	0.3884	112.0	2.0	0.7650	108.4	-2.4
0.2073	69.8	1.2	0.4517	122.9	3.1	0.8621	77.8	-1.7
0.2967	93.3	2.0	0.5118	127.2	1.0	0.9550	32.0	0.8
0.3360	102.8	-3.0	0.6427	126.0	-2.2			
hexadecane at 25 °C								
0.1632	102.1	-0.8	0.4515	193.0	0.9	0.7743	171.6	-1.1
0.2516	141.4	1.2	0.5117	199.3	-0.4	0.8542	130.6	-1.8
0.4046	183.7	2.6	0.6315	201.7	-0.1	0.9226	82.5	0.9
hexadecane at 35 °C								
0.0865	43.7	0.8	0.4743	165.3	-0.3	0.8008	125.0	1.7
0.2153	95.8	-2.5	0.5638	170.4	-0.1	0.8736	87.0	-1.0
0.3762	148.6	0.1	0.7115	154.1	1.7	0.9225	57.9	-0.2

[a] Mole fraction decalin

TABLE A 4 Smoothing coefficients A_r in equation (8.1) for x decalin + (1-x)cycloalkane and + (1-x)n-alkane at temperaures 15, 25 and 35 °C . The decalin is a mixture of 53.3 mole per cent cis-isomer and 46.7 mole per cent trans-isomer.

hydrocarbon	°C	A_0	A_1	A_2	$\partial H_M^E/\partial T$ / $J\ mol^{-1}K^{-1}$
cyclopentane	15	-739.07	19.4	-58.8	-0.02
cyclopentane	25	-739.9	30.0	-150.4	
cyclohexane	15	107.3	-160.4	-59.0	-0.09
cyclohexane	25	103.5	-153.3	-68.3	
cycloheptane	15	31.6	-61.8	-34.0	0.09
cycloheptane	25	35.0	-51.7	-21.6	
cyclooctane	15	75.9	-20.5	1.3	-0.10
cyclooctane	25	72.1	-18.0	7.5	
n-hexane	15	266.7	5.8	-9.9	-0.43
n-hexane	25	249.4	-4.1	6.2	
n-heptane	15	312.2	-21.6	7.7	-0.94
n-heptane	25	274.5	-20.2	35.8	
n-octane	15	367.6	-67.2	36.1	-1.03
n-octane	25	326.4	-50.7	37.9	
n-dodecane	15	594.1	-218.7	83.4	-2.34
n-dodecane	25	500.4	-183.0	69.1	
n-hexadecane	25	794.2	-215.9	232.3	-3.03
n-hexadecane	35	672.8	-162.2	5.5	

TABLE A 5 H^E_M for x $C_{10}H_{12}$ (tetralin) + (1 - x) C_yH_{2y} (cycloalkane) and + (1 - x)c C_yH_{2y+2} (n-alkane) and the deviations calculated from equation (8.1) and the coefficients of table (A6)

x	H^E_M	δH^E_M	x	H^E_M	δH^E_M	x	H^E_M	δH^E_M
n-hexane at 288.2 K								
0.0661	139.1	2.6	0.3903	455.4	-5.7	0.6688	420.6	6.5
0.1911	313.8	-7.8	0.4926	476.6	2.9	0.7782	326.4	1.1
0.3378	437.4	-2.8	0.5698	465.3	5.3	0.9030	166.9	-2.1
n-hexane at 298.2 K								
0.0754	146.1	2.0	0.4277	457.6	-1.3	0.6934	389.9	2.0
0.1345	235.0	-0.6	0.4936	464.7	1.0	0.7474	346.3	2.0
0.2234	336.3	-5.2	0.5462	460.3	3.6	0.8925	174.6	-1.8
0.3551	431.9	-3.8	0.6166	435.1	2.1			
n-heptane at 288.2 K								
0.0637	130.3	2.4	0.4007	484.4	3.6	0.7244	430.8	-2.7
0.1504	260.7	-4.5	0.4932	504.8	0.0	0.8631	276.0	0.0
0.1937	314.2	-5.9	0.5168	504.8	-1.7			
0.3662	469.6	5.0	0.6083	498.6	3.8			
n-heptane at 298.2 K								
0.1257	220.1	0.1	0.5016	490.4	3.7	0.8055	321.3	6.6
0.2351	353.7	-0.6	0.6094	464.2	-1.8	0.8836	208.2	-1.5
0.3743	456.1	-0.3	0.7212	392.4	-6.1			
n-dodecane at 288.2 K								
0.1599	265.1	-3.1	0.4216	555.8	-4.3	0.7298	533.5	2.4
0.2354	377.9	3.5	0.5139	598.9	-3.3	0.8137	428.3	2.5
0.3402	502.2	8.3	0.6206	594.3	-5.5	0.9515	138.4	-0.3
n-dodecane at 298.2 K								
0.1941	317.2	-0.0	0.4758	562.1	-1.4	0.6846	531.7	1.2
0.2526	393.3	1.9	0.4806	562.7	-2.3	0.7266	502.6	6.1
0.3426	482.5	-0.6	0.5424	574.7	1.1	0.8172	390.2	2.7
0.4360	547.1	0.1	0.6265	556.2	-5.3	0.9306	174.2	-1.3

TABLE A 5 (cont.)

x	H^E_M	δH^E_M	x	H^E_M	δH^E_M	x	H^E_M	δH^E_M
n-hexadecane at 298.2 K								
0.1094	202.1	-3.6	0.5460	671.6	-1.4	0.8401	458.9	0.6
0.2020	359.8	6.6	0.6220	679.1	3.3	0.9497	179.3	1.0
0.3681	564.2	4.2	0.6792	648.2	-5.7			
0.4532	634.5	4.1	0.7302	607.2	-8.2			
n-hexadecane at 308.2 K								
0.0775	156.4	-2.4	0.4967	689.0	2.6	0.7727	601.8	-5.4
0.1936	366.7	7.6	0.5862	708.7	-5.5	0.8641	444.7	3.4
0.3825	598.6	-0.4	0.6230	712.9	0.0			
cyclopentane at 288.2 K								
0.1536	164.2	-0.9	0.4448	258.6	1.8	0.7936	145.7	-0.7
0.2732	232.4	1.4	0.5630	240.1	0.3	0.9056	75.7	0.6
0.3514	251.3	-0.2	0.6911	194.2	-2.6			
cyclopentane at 298.2 K								
0.0630	81.4	2.4	0.4258	252.8	0.6	0.7549	161.8	0.6
0.1425	148.8	-5.0	0.4298	253.5	1.3	0.8657	97.0	-0.8
0.1754	176.4	-1.2	0.5403	241.6	2.4	0.9238	58.3	-0.2
0.2805	227.2	-2.4	0.6326	215.4	2.1			
cyclohexane at 288.2 K								
0.0932	210.5	-0.9	0.4736	503.0	0.0	0.7762	315.7	-5.0
0.2176	394.1	7.6	0.5019	498.8	0.3	0.8821	193.3	2.8
0.3802	501.9	4.9	0.7035	387.2	-2.9			
cyclohexane at 298.2 K								
0.0421	95.3	-1.2	0.4326	486.9	1.7	0.7063	376.7	-5.4
0.1286	253.3	-2.0	0.5129	482.5	1.9	0.8215	264.5	-3.0
0.1951	353.7	8.4	0.5469	470.4	-1.5	0.9056	160.1	3.9
0.3372	464.4	5.3	0.6710	400.9	-8.0			
cycloheptane at 288.2 K								
0.1288	227.9	-1.2	0.4608	451.9	-2.4	0.7188	336.8	3.3
0.2335	356.3	2.4	0.4827	450.0	-2.9	0.8419	207.2	-0.4
0.3572	439.8	4.1	0.5921	417.3	-2.7			
cycloheptane at 298.2 K								
0.1475	246.2	-4.4	0.3447	417.3	6.8	0.5447	410.4	-6.3
0.2000	313.1	2.3	0.4020	428.5	2.0	0.7994	246.9	-3.9
0.2140	326.5	1.9	0.4686	426.5	-1.0	0.8852	1.58.9	2.4

TABLE A 5 (cont.)

x	H^E_M	δH^E_M	x	H^E_M	δH^E_M	x	H^E_M	δH^E_M
cyclooctane at 288.2 K								
0.1353	226.5	1.2	0.4214	436.7	-1.4	0.7432	300.8	0.2
0.2324	337.8	0.7	0.5050	436.0	-0.7	0.8551	181.2	-1.9
0.3345	404.6	-5.6	0.6605	375.2	7.5			
cyclooctane at 298.2 K								
0.0492	88.2	0.3	0.4275	405.6	-1.6	0.8404	191.1	3.6
0.1730	261.4	2.3	0.5401	387.3	-8.8	0.9024	114.7	-4.7
0.2820	352.6	-1.5	0.6793	337.2	9.1			
0.3538	383.5	-6.9	0.7152	310.1	8.1			

TABLE A 6 Coefficients of equation (1) for x $C_{10}H_{12}$ (tetralin) + (1 + x) c - C_yH_{2y} (cycloalkane) and + (1 - x) C_yH_{2y+2} (n-alkane) at temperature T

	$\frac{T}{K}$	A_0	A_1	A_2	$-(\partial H_M^E/\partial T)$
C_5H_{10}	288.2	1007.1	278.2	146.2	0.8
C_5H_{10}	298.2	985.4	290.6	128.7	
C_6H_{12}	288.2	1995.2	411.9	258.8	1.6
C_6H_{12}	298.2	1931.4	305.6	217.5	
C_7H_{14}	288.2	1802.3	399.3	-21.2	2.4
C_7H_{14}	298.2	1707.3	315.2	127.3	
C_8H_{16}	288.2	1750.4	312.9	-100.0	3.3
C_8H_{16}	298.2	1619.6	308.3	-25.0	
C_6H_{14}	288.2	1892.7	152.1	246.7	1.0
C_6H_{14}	298.2	1853.3	130.3	142.3	
C_7H_{16}	288.2	2022.1	-173.0	357.0	1.7
C_7H_{16}	298.2	1953.4	-53.9	157.6	
$C_{12}H_{26}$	288.2	2393.6	-624.2	59.9	2.8
$C_{12}H_{26}$	298.2	2281.2	-452.6	63.2	
$C_{16}H_{34}$	298.2	2627.8	-954.8	307.3	3.1
$C_{16}H_{34}$	308.2	2752.4	-1030.8	477.8	

TABLE A 7 Molar Excess Enthalpies H^E_M for x bicyclohexyl + (1-x) cycloalkane and + (1-x) n-alkane, with the deviations calculated from equation (8.1) and the coefficients of Table 8 A

x	H^E_M $J.mol^{-1}$	δH^E_M $J.mol^{-1}$	x	H^E_M $J.mol^{-1}$	δH^E_M $J.mol^{-1}$	x	H^E_M $J.mol^{-1}$	δH^E_M $J.mol^{-1}$
C_6H_{14} at 288.2 K								
0.1017	17.2	-0.7	0.4146	33.0	-0.1	0.6722	21.8	-0.2
0.1543	25.4	1.3	0.4876	30.8	0.0	0.8317	12.2	0.1
0.3477	33.0	-0.2	0.5478	28.1	-0.4			
C_6H_{14} at 298.2 K								
0.0735	10.0	0.3	0.3975	23.9	0.5	0.6337	17.5	0.4
0.1953	17.9	-1.5	0.4811	22.2	0.1	0.8550	6.9	0.0
0.3007	23.2	0.1	0.5426	20.3	0.0	0.8739	6.0	-0.1
C_8H_{18} at 288.2 K								
0.0836	16.4	-0.3	0.4637	46.2	0.5	0.7764	22.5	-0.4
0.2526	39.2	0.2	0.5514	41.8	-0.5	0.8531	15.6	0.9
0.3405	46.0	1.5	0.6938	29.4	-2.2			
C_8H_{18} at 298.2 K								
0.1117	19.6	-0.6	0.4469	37.2	1.7	0.8635	11.5	-0.2
0.2278	31.8	0.3	0.4625	36.2	0.5	0.9226	7.2	0.5
0.3491	38.5	1.5	0.5630	33.1	-0.1			
$C_{12}H_{26}$ at 288.2 K								
0.2394	52.8	-1.5	0.5433	84.1	-0.8	0.9003	34.4	0.2
0.3410	72.9	2.2	0.6478	79.8	-1.2			
0.4181	80.6	1.3	0.7502	68.3	0.3			
$C_{12}H_{26}$ at 298.2 K								
0.0915	20.8	-0.1	0.4562	65.7	1.1	0.7104	53.2	-1.3
0.1614	33.9	-0.4	0.5655	65.3	0.0	0.7995	41.3	-1.5
0.3137	56.8	1.4	0.6273	61.0	-0.6	0.9136	22.0	0.7
$C_{16}H_{34}$ at 298.2 K								
0.0579	25.9	0.0	0.5285	128.0	-0.4	0.8369	77.7	1.2
0.1959	75.2	-0.9	0.6077	122.6	-2.6	0.9478	28.5	-0.2
0.3651	119.5	4.1	0.6814	113.5	-2.8			
0.4975	127.8	-0.1	0.7615	101.5	1.9			

TABLE A 7 (cont.)

x	H^E_M J.mol^{-1}	δH^E_M J.mol^{-1}	x	H^E_M J.mol^{-1}	δH^E_M J.mol^{-1}	x	H^E_M J.mol^{-1}	δH^E_M J.mol^{-1}
$C_{16}H_{34}$ at 308.2 K								
0.1016	24.0	0.4	0.4474	84.2	-0.2	0.7532	68.4	0.8
0.1911	43.1	-1.0	0.5206	87.4	-0.2	0.8265	51.0	-0.7
0.3042	66.4	-0.1	0.6117	86.3	0.9			
C_5H_{10} at 288.2 K								
0.1115	-60.3	1.1	0.3362	-122.9	0.4	0.7982	-90.8	-1.4
0.1821	-89.5	-1.0	0.4446	-131.6	0.8	0.8583	-68.7	0.4
0.2228	-102.7	-2.0	0.6090	-124.9	1.5			
C_5H_{10} at 298.2 K								
0.0795	-44.2	2.7	0.3407	-129.2	2.7	0.7014	-118.5	-0.1
0.1391	-78.8	-3.7	0.3826	-135.3	2.0	0.8003	-92.5	-1.4
0.1475	-80.6	-2.0	0.4852	-142.6	0.0	0.9481	-28.7	0.1
0.2525	-115.6	-2.0	0.5812	-135.8	1.8			
C_6H_{12} at 288.2 K								
0.0715	41.2	0.6	0.3915	124.7	-0.3	0.6133	110.9	0.8
0.1154	60.3	-0.8	0.4462	126.0	0.0	0.7415	82.3	0.1
0.2683	108.2	-1.3	0.5831	116.2	1.3	0.8736	42.9	-0.3
C_6H_{12} at 298.2 K								
0.0973	46.3	-2.9	0.4108	114.9	0.5	0.8054	60.5	0.3
0.1546	67.8	0.0	0.5005	113.2	-0.3	0.8763	39.5	-0.1
0.2734	99.1	0.1	0.5736	107.0	-0.2			
0.3361	108.2	-0.3	0.6992	86.2	0.0			
C_7H_{14} at 288.2 K								
0.0754	58.3	0.2	0.3876	158.4	-0.1	0.7611	91.3	-2.6
0.1776	112.6	-0.5	0.5009	154.7	0.5	0.8197	74.4	0.8
0.2741	143.5	-0.5	0.6540	127.8	2.2			
C_7H_{14} at 298.2 K								
0.0682	45.9	0.4	0.4007	145.1	1.8	0.6636	114.3	1.0
0.1697	95.5	-0.1	0.4549	144.3	1.0	0.7581	88.1	0.7
0.2938	127.8	-3.7	0.5331	136.5	-0.6	0.9003	38.2	-0.4

TABLE A 7 (cont.)

x	H^E_M $J.mol^{-1}$	δH^E_M $J.mol^{-1}$	x	H^E_M $J.mol^{-1}$	δH^E_M $J.mol^{-1}$	x	H^E_M $J.mol^{-1}$	δH^E_M $J.mol^{-1}$
C_8H_{16} at 288.2 K								
0.0799	64.2	0.4	0.4165	177.8	-2.8	0.8054	98.4	-2.3
0.1923	126.1	-1.5	0.5364	178.2	2.2	0.8735	70.2	0.5
0.2941	164.0	1.1	0.6876	146.0	2.3			
C_8H_{16} at 298.2 K								
0.0436	36.4	0.3	0.5282	162.9	0.9	0.8815	62.2	1.4
0.1791	115.0	-1.1	0.5556	159.0	0.5	0.9258	38.4	-1.3
0.3070	154.7	-0.6	0.6285	147.5	2.0			
0.4122	163.3	-3.4	0.7316	119.2	1.1			

TABLE A 8 Smoothing coefficients Ar for x bicyclohexyl + (1-x) cycloalkane and + (1-x) n-alkane at temperature T

hydrocarbon	$\frac{T}{K}$	A_0	A_1	A_2
C_6H_{14}	288.2	121.9	72.2	26.9
C_6H_{14}	298.2	86.3	52.4	14.4
C_8H_{18}	288.2	178.6	68.9	-26.3
C_8H_{18}	298.2	143.0	63.0	5.3
$C_{12}H_{26}$	288.2	336.9	-66.1	-15.1
$C_{12}H_{26}$	298.2	261.1	-10.4	-0.7
$C_{16}H_{34}$	298.2	512.0	-58.7	19.4
$C_{16}H_{34}$	308.2	348.7	-61.8	-65.9
C_5H_{10}	288.2	-531.9	-27.6	-110.6
C_5H_{10}	298.2	-569.7	-35.5	-59.6
C_6H_{12}	288.2	495.3	136.4	-28.4
C_6H_{12}	298.2	454.2	104.7	-17.0
C_7H_{14}	288.2	617.2	215.8	44.3
C_7H_{14}	298.2	562.4	170.8	7.9
C_8H_{16}	288.2	717.9	145.7	37.7
C_8H_{16}	298.2	658.4	157.3	73.9

TABLE A 9 Molar Excess Volumes of x Tetralin + (1-x) n-alkane and + (1-x) cycloalkane

x	V^E_M	$10^4\,\delta V^E_M$	x	V^E_M	$10^4\,\delta V^E_M$
n-Pentane at 10 °C					
0.0915	-0.5411	9	0.5709	-1.2169	-77
0.1208	-0.6823	-16	0.5914	-1.1769	39
0.2393	-1.0869	-2	0.7036	-0.9794	-70
0.3104	-1.2228	11	0.7982	-0,7233	72
0.4657	-1.2964	22	0.8283	-0.6408	2
0.4936	-1.2820	25	0.9115	-0.3616	-11
n-Pentane at 25 °C					
0.0582	-0.4370	0	0.5426	-1.4308	-11
0.2010	-1.1562	-12	0.5917	-1.3576	-1
0.3005	-1.4082	8	0.6985	-1.1370	-45
0.3492	-1.4726	9	0.7969	-0.8471	12
0.3920	-1.5009	13	0.8611	-0.6193	28
0.4633	-1.4982	3	0.9516	-0.2408	-6
n-Hexane at 10 °C					
0.0807	-0.2999	-9	0.6486	-0.7369	-25
0.1092	-0.3870	0	0.6721	-0.7065	-16
0.2776	-0.7390	26	0.6845	-0.6891	0
0.3067	-0.7756	13	0.7410	-0.6032	-17
0.3820	-0.8339	28	0.8685	-0.3461	1
0.5391	-0.8314	-9	0.9167	-0.2281	9

TABLE A 9 (cont.)

x	V^E_M	$10^4\delta V^E_M$	x	V^E_M	$10^4\delta V^E_M$
			n-hexane at 25 °C		
0.0368	−0.1960	3	0.4910	−0.9905	5
0.1132	−0.5077	−13	0.5883	−0.9387	−6
0.2017	−0.7440	−3	0.6906	−0.8075	−9
0.2776	−0.8732	6	0.8022	−0.5732	4
0.2951	−0.8954	7	0.9116	−0.2698	0
0.3919	−0.9762	7			
			n-heptane at 10 °C		
0.0735	−0.1827	−12	0.6486	−0.5260	2
0.1429	−0.3155	40	0.7191	−0.4607	3
0.2168	−0.4344	−7	0.7628	−0.4095	8
0.3159	−0.5398	−27	0.8500	−0.2866	−4
0.3540	−0.5630	−2	0.9122	−0.1788	0
0.5537	−0.5808	0			
			n-heptane at 25 °C		
0.0536	−0.1603	−1	0.5117	−0.6572	−3
0.1870	−0.4509	5	0.6337	−0.5909	0
0.2613	−0.5540	12	0.7233	−0.4995	7
0.3997	−0.6553	−9	0.8266	−0.3524	6
0.4985	−0.6613	−14	0.9415	−0.1347	−2

TABLE A 9 (cont.)

x	V^E_M	$10^4\ \delta V^E_M$	x	V^E_M	$10^4 \delta\ V^E_M$
			n-octane at 25 °C		
0.0756	−0.1553	−6	0.6138	−0.4702	12
0.1223	−0.2298	18	0.7513	−0.3650	−3
0.2449	−0.3830	−19	0.7714	−0.3436	−11
0.3363	−0.4817	−6	0.8357	−0.2671	−9
0.5703	−0.4869	17	0.8860	−0.1896	8
			n-octane at 10 °C		
0.0784	−0.1346	−24	0.5113	−0.4307	−37
0.1284	−0.1963	39	0.6095	−0.4071	−20
0.1463	−0.2204	16	0.7512	−0.3104	−1
0.3054	−0.3680	−32	0.8084	−0.2483	4
0.4567	−0.4211	30	0.9409	−0.0835	−6
			n-dodecane at 10 °C		
0.1135	−0.0213	3	0.6232	−0.0382	2
0.2683	−0.0417	−13	0.7105	−0.0308	−1
0.4409	−0.0458	7	0.7866	−0.0219	8
0.4937	−0.0451	4	0.9158	−0.0086	2
0.5514	−0.0440	−8			

TABLE A 9 (cont.)

x	V^E_M	$10^4\,\delta V^E_M$	x	V^E_M	$10^4\,\delta V^E_M$
n-dodecane at 25 °C					
0.0839	−0.0249	−2	0.4915	−0.0673	−24
0.1562	−0.0397	7	0.5548	−0.0611	16
0.2217	−0.0508	1	0.6835	−0.0532	3
0.3513	−0.0627	1	0.7702	−0.0424	9
0.4102	−0.0660	−10	0.8860	−0.0249	−4
cyclopentane at 10 °C					
0.0422	−0.0809	−2	0.4717	−0.4371	−1
0.1471	−0.2394	40	0.4970	−0.4356	−7
0.1546	−0.2555	−23	0.5724	−0.4135	26
0.2120	−0.3178	3	0.6151	−0.3989	−14
0.2927	−0.3873	−28	0.7364	−0.3158	7
0.3085	−0.3936	5	0.8891	−0.1581	−6
0.3381	−0.4097	0	0.9263	−0.1085	2
0.4124	−0.4335	−4			
cyclopentane at 25 °C					
0.0514	−0.1038	4	0.6191	−0.4451	27
0.1654	−0.3068	−20	0.6732	−0.4062	4
0.2158	−0.3757	−16	0.6863	−0.3935	19
0.3196	−0.4704	20	0.7754	−0.3124	−40
0.4093	−0.5062	30	0.8748	−0.1898	0
0.5499	−0.4909	−34	0.9307	−0.1115	4

TABLE A 9 (cont)

x	V^E_M	$10^4\,\delta V^E_M$	x	V^E_M	$10^4\,\delta V^E_M$
			cyclohexane at 10 °C		
0.0293	0.0298	5	0.5432	0.1365	6
0.1253	0.0983	-30	0.6135	0.1164	-34
0.2232	0.1405	-26	0.6586	0.1049	-4
0.3651	0.1657	51	0.6944	0.0924	-23
0.4147	0.1592	15	0.7682	0.0713	-8
0.4939	0.1501	38	0.8849	0.0367	8
			cyclohexane at 25 °C		
0.0755	0.0498	1	0.5738	0.0899	-3
0.1019	0.0619	-11	0.6374	0.0771	-12
0.1587	0.0866	10	0.7592	0.0544	13
0.2426	0.1071	13	0.8263	0.0404	19
0.3473	0.1149	12	0.9017	0.0209	-9
0.4628	0.1033	-33			
			cycloheptane at 10 °C		
0.0973	0.1234	-3	0.6231	0.1880	-31
0.1920	0.1960	11	0.6318	0.1867	-12
0.2541	0.2206	-8	0.6856	0.1655	-9
0.3118	0.2364	11	0.7050	0.1615	35
0.5093	0.2254	4	0.7770	0.1261	21
0.6211	0.1904	-14	0.9073	0.0531	-5

TABLE A 9 (cont)

x	V^E_M	$10^4\ \delta V^E_M$	x	V^E_M	$10^4 \delta\ V^E_M$
cycloheptane at 25 °C					
0.1671	0.1652	0	0.6755	0.1482	−6
0.3214	0.2124	−7	0.7340	0.1250	7
0.4273	0.2156	26	0.7949	0.0962	1
0.5063	0.2005	−3	0.8503	0.0699	8
0.5936	0.1757	−22	0.9173	0.0360	−3
cyclooctane at 10 °C					
0.0885	0.1218	−1	0.5107	0.2744	−18
0.2055	0.2263	−3	0.5559	0.2652	16
0.2537	0.2604	22	0.6368	0.2320	2
0.4316	0.2865	−14	0.8003	0.1403	5
0.4515	0.2856	−7	0.9354	0.0466	−1
cyclooctane at 15 °C					
0.0702	0.0945	−1	0.6429	0.2166	11
0.1574	0.1814	10	0.6713	0.2072	48
0.3902	0.2701	−19	0.7699	0.1487	−13
0.4545	0.2665	−33	0.8561	0.0945	−27
0.5613	0.2483	17	0.9354	0.0454	7

TABLE A 10 Smoothing coefficients A_r for x tetralin + (1-x) n-alkane and + (1-x) cycloalkane

hydrocarbon	^oC	A_0	A_1	A_2	A_3
n-pentane	10	-5.1211	-1.3906	-0.5598	0.2029
n-pentane	25	-5.8980	-1.6902	-0.8882	0.1616
n-hexane	10	-3.3894	-0.6155	-0.1765	-
n-hexane	25	-3.9556	-0.5220	-0.4632	-0.8812
n-heptane	10	-2.3771	-0.2591	-0.0960	0.0053
n-heptane	25	-2.6385	-0.4021	-0.2021	0.0021
n-octane	10	-1.7089	-0.0093	0.0507	-0.2477
n-octane	25	-1.9996	-0.0379	-0.0217	-0.2712
n-dodecane	10	-0.1814	-0.0649	0.0274	-
n-dodecane	25	-0.2592	-0.0453	-0.0347	
cyclopentane	10	-1.7378	-0.2716	-0.0667	0.0625
cyclopentane	25	-2.0203	-0.5040	0.1005	0.3501
cyclohexane	10	0.5802	0.3881	0.1070	-0.0147
cyclohexane	25	0.4079	0.2766	0.0950	
cycloheptane	10	0.9077	0.4204	0.1807	0.0877
cycloheptane	25	0.8086	0.3998	0.1439	0.1646
cyclooctane	10	1.1145	0.4254	0.0548	0.0189
cyclooctane	25	1.0505	0.4098	0.0603	0

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