THERMODYNAMIC PROPERTIES OF SOME BINARY LIQUID MIXTURES CONTAINING AN AROMATIC FLUOROCARBON

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Ъy

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STATEMENT

The work presented in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester between October 1976 and August 1979 unless otherwise accredited.

This work has not been presented and is not concurrently being presented for any other degree.

C. G. Osborney

June 1980

CHRISTOPHER G. OSBORNE

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Pablo Picasso

SUMMARY

The excess enthalpies, volumes and Gibbs free energies of mixing have been measured for a series of cyclic ethers with hexafluorobenzene. These results indicate the presence of a specific interaction in these systems. Use of a stronger fluorocarbon acceptor, pentafluorobenzonitrile, was found to enhance this interaction.

The freezing curve of the system tetrahydropyran + hexaflucrobenzene has been determined showing only a simple eutectic, indicating that the complex exists only in solution.

Nuclear magnetic resonance studies of some of these systems gave an insight into the possible orientation of the complex.

An improved static vapour pressures apparatus is described, using a liquid burette system for mixture preparation and incorporating a pressure transducer system.

The freezing curves and enthalpies of mixing of some aromatic hydrocarbon systems with pentafluorobenzonitrile have been measured. The results indicate relatively strong interactions between the components of these mixtures.

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To My Mother

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CHAPTER ONE

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INTRODUCTION

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1.1 MOLECULAR COMPLEXES

This work has as its common denominator the investigation of molecular complexes, formed by various interactions of the moieties, of some binary liquid mixtures. Although individual interpretations may vary, a typical definition of a molecular complex, proposed by Foster (1) and which applies to this work, is "a substance formed by the interaction of two or more component molecules, which may have an independent crystal structure and which will reversibly dissociate into its components, at least partially, in the vapour phase and on dissolution." A minimal stabilisation of the ground state of the complex by covalent bonding is implicit in this definition.

The length of time that two (or more) species must interact in close proximity for the association to be termed a complex is somewhat arbitrary but must be in excess of any random molecular collisional contacts. Swinton (18) poignantly describes the strength and permanence of a typical molecular complex as probably being, in most cases, no more than just a slightly 'sticky' interaction. Frequently mixtures that are thought to form complexes in the liquid phase also give rise to solid compounds upon freezing (2-4, 57-60). Often these melt congruently and have a 1:1 stoichiometry.

All molecules interact with other molecules, regardless of any specific complexing interaction, as was realised by van der Waals. The existence of powerful cohesive intermolecular forces in all liquids is well recognised and this molecular

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attraction was first satisfactorily explained by London. He advanced the postulate that all molecules possess an instantaneous dipole moment which time averages to zero if the molecule has no net moment. This is a direct consequence of the Heisenberg uncertainty principle which states that the energy of a molecule is non-zero even in its lowest state, the zero point energy. This was envisaged as a vibration between the nuclei and electrons leading to a fluctuating temporary dipole. As a consequence of these transient oscillating moments further dipoles were induced in neighbouring molecules, in phase with themselves, and hence producing a net attractive force between the molecules.

Since the molecules of a liquid have a finite volume with a measurable collision diameter it is evident that intermolecular repulsive forces are present also. The collision diameter represents the distance r between molecular centres when the repulsive forces begin to overcome the attractive forces. This repulsion is caused by the interactions of the electron clouds between neighbouring molecules and is a power of six times more distance dependent than the attractive terms, producing a net resultant attractive force in the liquid state. The total pair potential energy can be represented by the Lennard-Jones equation

$$U(\mathbf{r}) = -2\mathscr{E}\left[\frac{\mathbf{r}^*}{\mathbf{r}}\right]^6 + \mathscr{E}\left[\frac{\mathbf{r}^*}{\mathbf{r}}\right]^{12}$$

where \mathcal{E} is the depth of the potential energy well and r^* is the distance apart of the molecular centres at

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this point.

The van der Waals forces described above in no way exclude stronger, specific interactions, for example electron donor acceptor interactions more popularly known as 'charge transfer complexes'. This work will attempt to investigate the strength, orientation and equilibrium constants, of any complexes formed with reference to a suitable test system for which specific interactions are not thought to occur, between a series of electron donors and an aromatic fluorocarbon acceptor.

1.2 CHARGE TRANSFER COMPLEXES

Hexafluorobenzene and pentafluorocyanobenzene have been widely used as electron acceptor components in charge-transfer complexes with a variety of aromatic and non-aromatic amine electron donors (5-8, 61-65). Striking optical absorptions, not present in either pure component instantly appeared on mixing. Mulliken (9) has formulated a rigorous interpretation of the mechanism of this interaction showing that the new spectral absorption (s) is produced by a transition from a no bond ground state to an ionic, charge transfer excited state. He proposed that the ground state of this complex was a resonance interaction between a non-bonded ground state and a dipolar excited state represented by an approximate wave function of the form

$$\Psi_{N}$$
 (D,A) = $a\Psi_{0}$ (D,A) + $b\Psi_{1}$ (D⁺A) (1.2.1)

The acceptor (A) and the donor (D) can be neutral molecules

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or ions but must be in their totally symmetric ground states. Ψ_{0} represents the wave function for a no-bond structure in which classical intermolecular forces are responsible for the binding. Ψ_{1} , the dative bond wave function, corresponds to a state where an electron has been transferred from the donor to the acceptor. The ground state is essentially 'no-bond' in character and the main contribution to Ψ_{N} is provided by Ψ_{0} , thus for weak complexes b<a.

An excited state wave function, $\Psi_{\rm f}$, is associated with this complex and is represented by

$$\Psi_{\mathbf{E}} = \mathbf{a}^* \Psi_{\mathbf{i}} \left(\mathbf{D}^{\dagger} \mathbf{A} \right) - \mathbf{b}^* \Psi_{\mathbf{0}} (\mathbf{D}, \mathbf{A}) \qquad (1.2.2)$$

and for weak complexes b << a.

The characteristic new U.V/Visible absorption observed is produced by an electronic transition from the ground to the excited state of the complex.

The electronic transition is assumed to occur from the highest occupied molecular orbital of the donor to the lowest unoccupied acceptor orbital. The geometry of the complex must be such that favourable orbital overlap between the moieties can occur. The observation of a charge-transfer transition is not conclusive evidence as to the existence of a groundstate molecular complex. Equally, the lack of an optical absorption, as in the case of the benzene / hexafluorobenzene complex, does not rule out the existence of a specific interaction.

Despite the vociferous claims of many authors in the past, it has now been extensively demonstrated that forces, similar to van der Waals forces, are mainly responsible for the stabilisation of many molecular complexes. The discovery of a charge transfer band does not even necessarily demonstrate the existence of a molecular complex since 'contact chargetransfer' interactions, showing the usual characteristic absorption, have been produced from random intermolecular collisions.

If the molecules possess a permanent dipole moment then coulombic attractions viz dipole-dipole, dipole induced dipole or quadrupolar interactions can lead to a stabilisation of the ground state of a complex. Hanna and Lippert (10) have calculated quadrupole-quadrupole energies for the complexes of benzene and p-xylene, each with various halogens and tetracyanoethylene, and found these interactions to be large and significant in comparison with the binding energies of the complexes. A trend was also observed between the quadrupole contribution and the strength of the interaction. For these benzene-halogen complexes they found that the axial configuration adopted corresponds to a maximisation of the quadrupole-quadrupole interaction. Swinton (11) has calculated the quadrupolar interactions for the benzene -hexafluorobenzene complex and predicts the geometries of the pure components and the equimolar mixture, in their solid states. purely on this basis and his calculations are in excellent

-6-

agreement with X-ray structural data. The same author (17) has also measured the dipole moment of hexafluorobenzene in a series of aromatic hydrocarbon solutions, where complexing was thought to occur, and reports a non-zero result but of small magnitude. This he interpreted as a mutual polarisation of the two aromatic nuclei and was thought too small a value if chargetransfer interactions were involved.

The orientation and stability of the complex is influenced by a suitable combination of the above described forces together with an important contribution from the repulsive interactions between the molecules due to steric hindrance effects. These repulsive forces play a cardinal role in determining the geometry of the complex.

Hanna and Lippert advance four tenets for consideration for the description of a molecular complex ;

- 1) Complexes assume the geometry where charge-transfer interaction is the greatest.
- 2) Complexes assume the geometry where electrostatic interactions are the greatest.
- 3) Complexes assume the geometry that minimises repulsion.
- 4) Some combination of factors 1-3 determines the geometry.

1.3 FLUOROCARBON SOLUTIONS

Many of the solutions in which one of the components is an aliphatic or alicyclic fluorocarbon were discovered to deviate markedly from ideality and the predictions of solubility parameter theory (12). Large positive values for the thermodynamic excess functions were found to be characteristic of these systems, in some cases leading to partial miscibility. Scott (13) has suggested that the unlike interactions in these mixtures are much weaker than expected and the molecular interactions do not obey the geometric mean rule.

In complete contrast to this behaviour aromatic fluorocarbonhydrocarbon mixtures have in recent years precipitated an abundance of thermodynamic evidence unequivocally demonstrating the formation of molecular complexes. Compelling evidence for the existence of a stronger fluorocarbon-hydrocarbon interaction was initially provided by Patrick and Prosser (2) on their discovery of a solid molecular addition compound between hexafluorobenzene and benzene. Duncan and Swinton (3) have determined the phase diagrams for each of the systems hexafluorobenzene + benzene, + toluene, + p-xylene, + mesitylene and in every case an equimolar congruently melting compound was found.

Fenby and Scott (14) have measured the enthalpies of mixing of many of these systems finding both positive and negative deviations from ideality. They interpret their results as essentially embracing contributions from two different kinds of interactions :

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a) a non-specific "physical" interaction which is large, positive and not necessarily symmetrical in mole fraction.

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 b) a specific "chemical" interaction due to complex
formation contributing a negative deviation from ideality.

This latter interaction they consider may be entirely due to electrostatic forces ie. quadrupole-dipole type interactions with little or no stabilisation due to charge transfer.

An abundance of spectroscopic evidence strongly suggesting complex formation has been provided by Beaumont and Davis (6) for a whole range of amine donors with hexafluorobenzene. This was interpreted by Armitage and Morcom (16) in terms of a $\pi - \pi$ interaction since triethylamine, capable of acting only as an n-donor, resulted in only a very weak complex presumably due to the limited overlap possible between the localised lone pair and the diffuse π -acceptor orbital of the fluorocarbon.

1.4 THERMODYNAMIC MEASUREMENTS

The strengths of the like and unlike interactions present in the binary liquid mixture can be inferred from the sign and magnitude of the principal excess functions. Weak unlike interactions are indicated by large positive excess enthalpies, free energies, entropies and volumes of mixing together with a negative excess heat capacity. The excess Gibbs free energy for a system of this type is shown graphically in figure (1.4.1) together with the mixture benzene-hexafluorobenzene, discussed earlier, displaying a strong unlike interaction and much other evidence for complex formation.

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Since the large positive "physical" contribution to the excess function is always present in fluorocarbon-hydrocarbon mixtures then any measured excess function must always be considered relative to the value for a similar system for which no complexing is thought to occur.

1.5 THE PRESENT WORK

Most of the work presented in this thesis is a development of preliminary measurements made on the system hexafluorobenzene + 1,4 dioxan in these laboratories (15). A weak specific interaction was found to occur and it was thought that an extensive investigation of a series of cyclic ethers with hexafluorobenzene and in part pentafluorocyanobenzene was justified. The latter electron acceptor was used to assess the effect of increasing the inductive effect from the ring.

The series of compounds chosen allows the effect of variations in both ring size and the number of oxygen atoms within each ether to be studied. The relationship between the cyclic ethers used in this work is shown graphically in figure (1.5.1).

Murray and Martin (19,20) have measured the excess volumes and Gibbs free energies of mixing of a series of aliphatic ethers with hexafluorobenzene and state that their results are ambiguous but consistent with weak complex formation. The extent of specific interaction in these aliphatic n-electron donors could not be ascertained since the dominant feature remained the size of the weak unlike interactions.

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FIG (1.5.1)

Relationship Between Some Cyclic Ethers



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CHAPTER TWO

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MATERIALS

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2.1 INTRODUCTION

The most common impurities encountered in the samples used throughout this work were dissolved gases and traces of moisture. Air dissolved in the samples is a two fold problem since it may, during the measurement of some property of mixing, fall out of solution due to a reduced solubility in the binary mixture. The appearance of air bubbles during the course of a volume change on mixing measurement leads to large errors, since correction is impossible. The determination of the vapour pressure of a sample containing any trace of dissolved air is meaningless and leads to a value which is too high.

Many of the cyclic ethers are subject to decomposition in the presence of oxygen (21) and inhibitors are added in trace amounts to the commercially supplied products to prevent the formation of peroxides. The distillation and purification procedures employed in this work remove these inhibitors and a process was developed to distil, degas and store the materials sealed from contact with the atmosphere.

The distillation apparatus employed a 1.5 m, fluted, electrically heated column, of the type described by Ray (22), which proved highly efficient for the removal of impurities from the starting material. A slow stream of dry nitrogen was constantly fed through the system to ensure the absence of moisture or oxygen from the apparatus. Only the middle fraction was collected in each case in a vessel of the type shown in figure (2.1.1). When the bulb was full to just below the stem the sample was frozen, still

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FIG (2.1.1)

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A SAMPLE STORAGE AMPOULE

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under an atmosphere of nitrogen, and quickly removed to the degassing line. A freeze-thaw method was adopted for this purpose, periodically evacuating the space above the sample to remove any gases driven from solution. Mercury, from a reservoir located in the vacuum line, was then used to completely cover the stem of the ampoule, thus sealing the liquid.in a perfectly degassed state, from the atmosphere. The only problem encountered with this design of vessel was the necessity to store at a reasonably constant temperature, to prevent sample loss due to expansion. Liquid was removed as necessary from the ampoules using a hypodermic syringe fitted with a long needle, the mercury level never falling below the top of the glass stem during this process.

The cyclic ethers commercially supplied gave a black scum on contact with mercury, before purification, due to the presence of peroxides. This would have impeded cathetometry measurements which are dependent on a clean mercury-sample interface. However, after purification the mercury surface remained clean. The peroxides were removed either by refluxing with sodium metal, or lithium aluminium hydride, both of which also remove any moisture present.

The presence of water in the samples is undesirable since only small quantities on a volume basis represent a considerable amount in terms of the total number of moles present. The ratio of the relative molecular masses of hexafluorobenzene to water is greater than ten to one. All samples used were therefore

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thoroughly dried using a suitable dehydrating agent. Phosphorus pentoxide was added to all samples with which there was no possibility of a reaction. Molecular seive, type 4A, freshly activated by heating to 373 K for a long period under vacuum was used to remove moisture from more reactive species.

Several techniques were used for the analysis of the samples as criteria of purity. All of the purified materials were analysed by gas-liquid chromatography using a Pye Unicam 104/P.E. F11 chromatograph, using either a 10 % APL or E 30 column at several temperatures. In addition the cooling curves of some of the samples were examined analytically using the method described by Guggenheim and Prue (23). This method assumes that the degree of curvature of the portion of the curve during the actual process of freezing is proportional to the concentration of the impurities present. The purity can thus be calculated quantitatively. The vapour pressure of many samples was measured and compared with values stated in the literature.

2.2 PURIFICATION OF MATERIALS

1) Mercury

The mercury used for calorimetry, excess volume measurements and storage of materials was first washed with running water and then dried with filter paper. It was then filtered through a pierced filter paper and passed through a continuous recycling nitric acid column (1.5 m) under a reduced pressure for twenty

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four hours. It was then washed and dried as before. A mercury still (Gallenkamp) was used to distil the mercury twice, under reduced pressure.

Higher purity mercury, enabling the use of published density data, was necessary for use in the manometer for vapour pressure determinations. This had been previously purified (24) by shaking the above mercury with a 5 % nitric acid solution containing mercurous nitrate until the acid no longer became discoloured. This was followed by shaking with de-ionised water and then shaking with 10 % potassium hydroxide solution until the aqueous layer remained colourless. After further washings with de-ionised water and drying, it was distilled under reduced pressure in a current of air. This was followed by two vacuum distillations.

2) <u>Hexafluorobenzene</u>

Hexafluorobenzene, supplied by Bristol Organics Ltd. of stated purity 99+%, was dried over phosphorus pentoxide and used without further purification. The purity of the sample was determined by an analysis of its freezing curve and found to be 99.8 % pure. G.L.C. of the sample gave a single sharp peak. The vapour pressure of the sample was determined at 303.15 K to be 14336 N m⁻², and at 323.15 K to be 34041 N m⁻², in comparison with the values obtained by Gaw and Swinton (64) of 14322 N m⁻² and 34076 N m⁻² respectively and the values obtained by Counsell et al (65) of 14304 N m⁻² and 34080 N m⁻² at the same temperatures. The freezing point of the pure substance was found to be 278.19 K

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compared with a literature value of 278.23 K obtained by Counsell et al (65).

3) Pentafluorocyanobenzene

Pentafluorocyanobenzene, supplied by Bristol Organics Ltd. of stated purity 99+%, was distilled from freshly activated molecular seive (type 4A) and activated charcoal, which was found to remove a slight trace of coloured impurity, under slightly reduced pressure. Decomposition of the sample occurred if the temperature of the column was set too high. G.L.C. of the sample, using an E 30 column at 363 K and 387 K, gave only a single sharp peak. The value obtained for the freezing point of the sample of 275.91 K is in close agreement with the result of Hall and Morcom (55) of 275.75 K.

4) <u>Tetrahydrofuran</u>

Fluka puriss grade tetrahydrofuran of stated purity 99.5+ % and stabilised with 0.025 % 2,6-Di-tert-butyl-p-cresol was purified by refluxing over lithium aluminium hydride for one hour followed by distillation in an atmosphere of dry nitrogen. The middle fraction that was collected had a boiling point of 338 K. G.L.C. analysis gave only a single sharp peak. The vapour pressure of the pure sample, at 303.15 K, was determined as 26982 N m⁻²in comparison with the extrapolated value obtained from the results of Scott (67) of 26933 N m⁻².

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5) TETRAHYDROPYRAN

Tetrahydropyran, supplied by Fluka, of stated purity 99+ %, was purified according to the method described by Pickett et al (25). After drying over calcium sulphate the sample was refluxed over and distilled from sodium in an atmosphere of dry nitrogen. The middle fraction was collected having a boiling point of 361 K. G.L.C. analysis showed one sharp peak, and at high resolution a small peak, corresponding to an impurity of lower volatility, appeared. The purity was estimated to be 99.7 mole %.

6) TRIMETHYLENE OXIDE

Trimethylene oxide, supplied by Aldrich Chemical Company Inc. (T7 620-1) of stated purity 97 % was dried over freshly activated molecular seive (Type 4A). A trace of scum formed on the mercury surface in the storage ampoule indicative of the presence of peroxides. Because of the high cost and ready decomposition of the compound it was decided to use it without further purification. G.L.C. revealed a broadening of the shoulder of the peak at higher volatility. The purity of the sample was estimated to be no better than 98 %.

7) HEXAMETHYLENE OXIDE

Fluka (purum) hexamethylene oxide of stated purity 97+ % was refluxed with sodium then distilled. The middle fraction which

-20-

was collected boiled at 393 K. G.L.C. at high resolution revealed only a single sharp peak. During the course of the determination of the vapour pressure of the sample a small portion was distilled from the cell. After the re-establishment of equilibrium the recorded vapour pressure, 3426.3 Nm^{-2} at 303.15 K, was identical to the previous measurement, thus confirming the high degree of purity of the sample.

8) 2-METHYL TETRAHYDROFURAN

Aldrich Chemical Co. Ltd. 2-methyltetrahydrofuran (15581-0) of stated purity 97+ %, was refluxed for two hours over sodium, and distilled. A boiling point of 351-352 K was recorded for the middle fraction which was collected. G.L.C. gave a single sharp peak.

9) 3-METHYL TETRAHYDROFURAN

The sample was supplied by Aldrich Chemical Co. Ltd. (M8235-3) of stated purity 99 %. This was then dried over freshly activated molecular seive (Type 4A) and used without further purification. G.L.C. showed a slightly broad peak at high resolution and the purity was estimated to be 99+ %.

10) 2,5-DIMETHYL TETRAHYDROFURAN

The sample, supplied by Aldrich Chemical Co. Ltd. (D18,720-8), was a mixture of the cis and trans isomer. The purity was stated to be 97+ %. After refluxing the sample for two hours over sodium the middle fraction of the distillation, boiling point 364 K, was collected. G.L.C. showed only a single sharp peak.

11) CYCLOHEXANE

Analar cyclohexane (B.D.H.) of stated purity 99.8 % was dried over phosphorus pentoxide and used without further purification. G.L.C. gave only a single sharp peak. The vapour pressure of the sample was measured and found to be 24565 N m⁻² comparison with the value reported by Chao et al (26) of 24564 N m⁻², both measurements being made at 313.15 K.

12) BENZENE

B.D.H. 'special for chromatography' grade benzene of stated purity 99.8 %, was dried over phosphorus pentoxide and used without further purification. G.L.C. gave only a single sharp peak. Vapour pressure measurement yielded a value of 24304 Nm^{-2} relation to the value obtained by Chao et al (26) of 24298 Nm^{-2} , both measurements being made at 313.15 K.

13) MESITYLENE

Aldrich 'gold label' mesitylene of stated purity 99+% was dried over molecular seive and used without further purification. G.L.C. showed only a single sharp peak.

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14) CYCLOPENTANE

Cyclopentane, supplied by Fluka, with a stated purity of 99+% was dried over phosphorus pentoxide and used without further purification. G.L.C. gave only a single sharp peak.

15) PARA-XYLENE

Aldrich Chemical Co.Ltd. p-xylene (13,444-9) of stated purity 99+% was dried over phosphorus pentoxide and used without further purification. Analysis by U.V. spectroscopy (Pye Unicam sp 200g) gave no spurious peaks.

16) TOLUENE

Aldrich 'spectrophotometric grade' toluene of stated purity 99+% was dried over phosphorus pentoxide and used without further purification. G.L.C. gave only a single sharp peak and analysis of the freezing curve gave a purity of 99.8%. Analysis by U.V. spectroscopy gave no spurious peaks.

17) FURAN

Furan supplied by Aldrich, of stated purity 99+%, was dried over molecular seive and used without further purification. G.L.C. gave only a single sharp peak and analysis by I.R. spectroscopy using a Perkin Elmer 580 spectrophotometer, showed no spurious peaks and no absorption at the characteristic frequency of water.

18) P-DIOXAN

'Gold label' para-dioxan, supplied by Aldrich of stated purity 99+ % was dried over lithium aluminium hydride. The estimated purity by an analysis of the freezing curve was determined to be 99.5 %. G.L.C. gave only a single sharp peak.

CHAPTER THREE

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EXCESS VOLUMES OF MIXING
3.1_INTRODUCTION

The molar excess volume of mixing results, V_m^E , presented in this thesis have been measured using two separate techniques, both giving the volume change directly. One method using a batch dilatometer (17) has already been described in great detail (27,28) by various workers and will be only briefly described here. A dilution dilatometer constructed to the original design of Armitage (29) has also been used. This allowed precise measurements of the volume change to be made over most of the range of mole fraction, x, in one dilution run. Two runs starting at opposite ends of the mole fraction range and overlapping through a range of mole fraction gave a sensitive check on the results.

It was easier to load and use than previous designs (30) and had several other advantages. Neither of the two liquids had to pass through any taps, which eliminated the problems of dissolved grease encountered by Scott (36), and the liquids were always separated by mercury through a capillary.

3.2 THE DILUTION DILATOMETER

The apparatus was relatively easy to construct, consisted entirely of Pyrex glass and is shown in figure (3.2.1). The mixing chamber A was made large enough to accept all of the contents of the liquid burette (B) and shaped so that the diluent from (B) would not stick to the walls below the mercury surface before mixing had taken place. The tapered bottom also reduced the

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THE DILUTION DILATOMETER

mass of mercury required to fill the apparatus. The capillary tube C1 of nominal diameter 0.3 mm, through which the liquid in (B) flowed to the mixing chamber, was ground at the top to a point so that the liquid did not remain trapped there. The liquid burette (B) made from precision bore Veridia tubing was measured at construction by an internal micrometer and found to be 1.000 cm (\pm 0.005) diameter. It is capable of holding 15 cm³ of liquid of which 12 cm³ can be usefully added. Tap (T) of hollow glass, filled with mercury to ensure the tap remained perfectly in place when in the thermostat, could be either in the position shown in the diagram, allowing liquid to flow from (B) to (A), or rotated 180° to manipulate the level in the capillary (C) when required.

Rapid uniformity of the mixture was attained using a magnetic stirrer and a metal-in-glass stirrer bead in (A). Only positive volume changes have been measured in this work but the apparatus can equally well be used for negative volume changes provided the mercury thread in (C) is set high enough initially.

3.3 LOADING PROCEDURE

Before each filling the dilatometer was soaked in nitric acid, then washed with de-ionised water followed by acetone. The apparatus, permanently fixed to a metal frame for support, was loaded under vacuum, the connection being made to the B 10 Quickfit ground glass joint S2 with flexible pressure tubing. During this procedure the dilatometer was in an almost horizontal position with both Joints S3 and S2 had lightly greased B 10 stoppers inserted and tap (T) was also lightly greased. Apiezon L (Edwards) high vacuum grease was used for the measurements at 303.15 K and Apiezon T for the measurements at higher temperatures.

When the apparatus was completely evacuated, mercury, from a reservoir located above as part of the vacuum line, was run in, tube (D) being filled first by suitable manipulation of tap (T), followed by the rest of the dilatometer. Tap (T) was then rotated to a position 90° to that shown in the diagram and the vacuum was released. A lightly greased stopper was then placed in joint S2. The apparatus was then repositioned so that the burette (B) made an angle of approximately 70° to the horizontal, S3 and S2 remained pointing upwards. The stopper from S3 was then removed and one of the components was injected into (A)from a syringe fitted with a suitably bent needle. The weight was accurately recorded by difference weighings using a balance capable of measuring to 0.0001 g. A minimum of 3 cm³ was injected. The stirrer bead was then inserted and the stopper replaced and secured by an elastic band. The stopper from S2 was then removed and the second component injected into (B) until the burette was full, the weight of component injected was not recorded. Premature mixing could be seen not to take place through the capillary C1, and the mercury thread remained in place throughout. A calibrated capillary (C), lightly greased, was then placed into socket S2 and held securely by elastic bands. The complete dilatometer was then placed into the thermostat and adjusted so that (B) and (C) were vertical by observation through a cathetometer telescope. The apparatus was then allowed to reach

equilibrium. During this period tiny droplets of mercury moved from (A) to (B) through the capillary C1 and thus no premature mixing occurred.

The stopper in S1 was then taken out and mercury removed with a hypodermic syringe from D until the level was approximately the same as in the burette. Tap (T) was then opened so that (D)was connected to the rest of the apparatus and the height of the mercury thread in the capillary fell to the level of the burette also. Tap (T) was then rotated through 90° and the apparatus was ready for use.

3.4 OPERATION OF THE DILATOMETER

The heights of the mercury meniscii in the burette and capillary \bigcirc were measured relative to reference marks on each. Tap T was then opened (to the position shown in the diagram) and the component from the burette flowed into \bigcirc through capillary C1 as mercury moved down under gravity through tube \bigcirc , until the tap was closed. After re-establishment of equilibrium, which took only a short period, the heights of the meniscii relative to the reference marks were again measured. This process was repeated until the burette was emptied. During the course of a run the height of the meniscus in the capillary was periodically lowered to its starting position as necessary, by the use of tap \bigcirc .

3.5 PRESSURE CORRECTIONS

During the course of a series of dilutions the thread of mercury in the capillary \bigcirc will either fall or rise dependent on the properties of the liquids in the dilatometer. For positive volume changes the meniscus will rise causing an increased pressure to be applied to the contents of the dilatometer. This will not only compress the components and the mercury but also expand the volume of the apparatus. For the apparatus described of total volume 70 cm³ (excluding tube \bigcirc) used only for adjusting the capillary meniscus height) and for a capillary of 0.5 mm internal diameter, for hexafluorobenzene + cyclic ether, pressure corrections were typically of the order of 5 %. The apparatus used for determining these corrections is shown in figure (3.5.1) and is similar to that described by Kumuran and McGlashan (31).

The U-tube was filled with mercury to a height of approximately 30 cm. A rubber pipette filler (Griffin) was attached to the limb carrying the P.T.F.E. tap T1 at (A) Rubber pressure tubing connected the apparatus at (B) to the top of the capillary of the dilatometer. By opening tap T1 and squeezing the pipette filler the dilatometer was subjected to pressures equal to or greater than those caused by height changes of the capillary meniscus during a run. After closing tap T1 the reduction in the height of the mercury thread in the capillary, caused by the applied pressure, was measured. The difference in the heights of the mercury levels in the U-tube gave a direct measure of the applied pressure. Several compressions were made before and after each run.

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PRESSURE CORRECTION APPARATUS

FIG¹(3.5.1)

3.6 CALIBRATION OF CAPILLARY TUBES

The capillaries used with this apparatus were made from Veridia precision bore tubing. These were calibrated by measuring the length of a thread of mercury in the capillary using a travelling microscope at a given temperature. The thread of mercury was then weighed and its density at the temperature used was ascertained (32). The results are shown in table (3.6.1).

TABLE (3.6.1)

CALIBRATION OF CAPILLARY TUBES

Capil	lary 1	Capillary 2
Nominal Diameter/ cm 0	•05	0.05
Mass of Mercury Used/ g	0.1717	0.2460
Average Length of Thread/ cm	6.266	8.914
True Diameter/ cm	0.05075	0.05092
Density of mercury at 292.05	K 13.5490	g/ cm ³

3.7 THE THERMOSTAT

This consisted of an insulated tank of approximate volume 0.3 m^3 having a glass window on one side. Precise temperature control was achieved using a combination of two heaters, an intermittent and a permanent, both made from Pyrotenax cable wound on a frame mounted in the tank. The intermittent heater was controlled by a mercury toluene regulator connected to an electronic relay. Stirring was effected using a pump from

Messrs D.A.Gunn (Engineering) Ltd.

The stability of this thermostat was found to be better than 0.001 K over long time periods. The temperature of the tank was measured using a platinum resistance thermometer (Tinsley) and Precision Comparison Bridge (Model VLF 51 A Rosemount Engineering Company limited).

3.8 CALCULATION OF RESULTS

The number of moles of pure liquid in the mixing chamber (A)at the beginning of a run is calculated from the mass injected $W_A \cdot U_A$

$$\Pi_{A} = \frac{W_{A}}{M_{A}}$$
(3.8.1)

Where M is the relative molecular mass of the component.

Liquid from the burette (B) is then added to form the resultant mixture. The weight of component (B) added is calculated from the measured burette heights. For a change in height, relative to the reference mark, from B1 to B2 the number of moles added is

$$n_{B} = \frac{\pi d^{2} (B2 - B1) D}{4 M_{B}}$$
(3.8.2)

where D is the density of the component in the burette at the temperature of the thermostat, d is the internal diameter of the burette and M the relative molecular mass of the componentin the burette.

As the run progresses and the burette heights measured are

B1, B2,...., Bi and the total number of moles added at any time is given by

$$n_{Bi} = \frac{\pi d^2 (Bi - B1) D}{4 M_B}$$
 (3.8.3)

The error in the burette heights is non-cumulative since these measurements are made relative to a reference mark located on the burette. The mole fraction after any dilution is thus given by

$$\mathbf{x}_{i} = \frac{\Pi_{A}}{\Pi_{A} + \Pi_{Bi}} \qquad (3.8.4)$$

The excess volume of mixing, V^E , is calculated from the measured meniscus heights in the capillary, having made the appropriate pressure corrections. If a pressure H cm of mercury applied to the apparatus during a pressure correction caused a decrease in the height of the meniscus in \bigcirc of δ h cm then the correction to be added to each measured capillary meniscus height is

$$\frac{\delta h hc}{H}$$
(3.8.5)

Where h_C is the measured change in capillary height for any dilution. If the measured capillary meniscus heights relative to the reference mark are h1, h2,hi the total volume change at any time is given by

$$v_{(hi)} = \frac{(hi-h1)(1+\frac{\delta h}{H})\pi dc}{4}$$
 (3.8.6)

where d_{C} is the diameter of the capillary \bigcirc . Then the total excess molar volume is given by

$$V_{ij}^{E} = \frac{\pi (hi - h1)(1 + \frac{\delta h}{H}) M_{B}(d)^{2}}{\left[(B_{i} - B1) d_{11}^{2} D + \frac{n_{A}}{4} \right]}$$
(3.8.7)

3.9 THE PARTIAL MOLAR EXCESS VOLUME

The partial molar, volume of a component i in a binary liquid mixture can be defined as

$$v_i^{\mathsf{E}} = v_i - v_i^{\circ} \tag{3.9.1}$$

where V_i is the partial molar volume of component i in the mixture and V_i^o is the molar volume of pure component i at the same temperature and pressure.

The design of this dilution dilatometer is such that aliquots of pure component are continually added to the mixture and the partial molar excess volume of the component from the burette in the mixture, V_B^E , is given by

$$\mathbf{v}_{\mathbf{B}}^{E} = \left(\frac{\delta V}{\delta \Pi_{\mathbf{B}}}\right)_{\mathbf{T}_{\mathbf{A}}\mathbf{P}}$$
(3.9.2)

For each new addition there exists a composition x^* such that

$$\mathbf{v}_{\mathbf{B}}^{\mathcal{E}}(\mathbf{x}^{*}) = \frac{\Delta V}{\Delta \Pi_{\mathbf{B}}}$$
(3.9.3)

The composition \mathbf{x}^* lies between the compositions of the mixture before and after the addition.

Armitage (33) has recently suggested that the composition x^* is more appropriately given by the geometric mean rather than the arithmetic mean used by Marsh (30). Geometric mean compositions

$$x^* = \sqrt{x_j x_{j+1}}$$
 (3.9.4)

were used throughout this work for the calculation of partial molar excess volumes, where x; is the composition of the mixture after adding j aliquots from the burette.

3.10 DENSITY MEASUREMENTS

In order to calculate the number of moles of component added from the burette it is necessary to know the density of the liquid accurately. As these values are not generally available at the temperature required they were measured using a simple density bottle. This was constructed from a capillary of approximately 20 cm in length and a nominal internal diameter of 0.5 mm joined to a glass bulb. The apparatus was calibrated by filling to a fixed reference mark with de-ionised water at a known temperature in a thermostat. The results are shown in table (3.10.1).

The density of any liquid to be measured is found by simply filling the bottle to the mark in a thermostat, using a hypodermic syringe with a suitably long needle, and then weighing.

TABLE (3.10.1)

CALIBRATION VALUES OF DENSITY BOTTLE

Mass of density bottle

water to reference mark/ g	25.4320
Mass of density bottle empty/ g	19.1387
Density of water (303.15 K) (7) / g cm^{-3}	0.99567
Calculated volume of density bottle/ cm ³	6.31866

3.11 ACCURACY OF THE DILATOMETER

The amount of component (B) transferred when the burette height changes by ΔB is

$$n_{B} = \frac{\pi d^{2} \rho_{B} \Delta B}{4M_{B}} \qquad (3.11.1)$$

where ρ_B is the density of (B) and M_B its relative molecular mass.

Thus the error in n_B arising from cathetometry, δn_B is

$$\delta n_{\rm B} = \frac{\pi d^2 \rho_8 \delta [\Delta B]}{4 M_8} \qquad (3.11.2)$$

where $\delta[\Delta B]$ is the error due to cathetometry. If $\delta[\Delta B]$ is for example 0.004 cm then

$$\delta n_{B} = \frac{\pi d^{2} \rho_{B} 10^{3}}{M_{B}}$$
 moles (3.11.3)

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Now the mole fraction of component A is

$$\mathbf{x}_{A} = \frac{\mathbf{n}_{A}}{\mathbf{n}_{A} + \mathbf{n}_{B}}$$
 (3.11.4)

$$n_{B} = \frac{(1 - x) n_{A}}{x_{A}}$$
 (3.11.5)

Since the error in n_B is δn_B then this will cause an associated error in mole fraction, x_A , of δx_A . thus

$$n_{B} + \delta n_{B} = \left[\frac{1 - (x_{A} - \delta x_{A})}{(x_{A} - \delta x_{A})} \right] n_{A}$$
 (3.11.6)

Substituting for n_B from equation (3.11.5) above

$$\delta n_{B} = \begin{bmatrix} \frac{1 - x_{A} + \delta x_{A}}{x_{A} - \delta x_{A}} & - & \frac{(1 - x_{A})}{x_{A}} \end{bmatrix} n_{A} \quad (3.11.7)$$

Factorising, and assuming that $~\delta x_A^2~\approx~0$

$$\delta n_{g} = \frac{n_{A} \delta x_{A}}{x_{A}}$$
(3.11.8)

Thus using equation (3.11.3) and noting that d for this particular apparatus is 1.00 cm leads to

$$\delta \mathbf{x}_{A} = \frac{\pi \, {}^{10^{-3}} \, \mathbf{x}_{A} \, \rho_{B}}{\mathbf{w}_{B} \, \mathbf{n}_{A}} \tag{3.11.9}$$

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Using typical values for ρ_{g} , x_{A} , M_{B} , n_{A} of 0.9 g cm⁻³, 0.5, 100, 0.05 then the estimated error in mole fraction, δx_{A} , is of the order of 0.0002. This error is in direct proportion to the mole fraction x_{A} .

The error in the measured volume change due to cathetometry is very small. If the error in meniscus height in the capillary for a typical volume change is 0.004 cm, then the corresponding error in volume change is

$$\mathbf{S}[\Delta \mathbf{V}] = \frac{\pi 0.05^2 \quad 0.004}{4}$$

$$\mathbf{6}[\Delta \mathbf{V}] \approx 0.0000075 \,\mathrm{cm}^3$$

The corresponding error in V^E , at the beginning of a run when this error has its greatest effect, is thus

$$6 v^{\mathcal{E}} \approx 0.00015 \text{ cm}^3 \text{ mol}^{-1}$$

3.12 TEST MEASUREMENTS

The final test of a new piece of apparatus is its ability to reproduce for a system, the results for which have been well established by previous workers. The system chosen, after the suggestion of Swinton (34) was benzene + cyclohexane. Two runs, commencing at opposite ends of the mole fraction range, were completed and the results shown in tables (3.14.1) and (3.14.2). It can be seen that the two runs overlap showing consistency of operation of the dilution dilatometer. The results are shown graphically in figure (3.14.2).

Since the majority of results made by other workers are quoted at 298.15 K and since $(\delta V^{E}/\delta T)_{p}$ for this system is small then all of the results are corrected to 298.15 K using the equation of Powell and Swinton (34).

$$\left(\frac{\delta v^{E}}{\delta r}\right)_{p} = x_{1} x_{2} \left[-0.0045 + 0.00224(x_{1} - x_{2}) + 0.0213(x_{1} - x_{2})^{2}\right]$$

These results and those obtained with the dilution dilatometer are presented graphically in figure (3.14.1).

3.13 THE BATCH DILATOMETER

This apparatus was a development made by previous workers in this laboratory of a dilatometer previously described by Swinton (17). It is shown in figure (3.13.1) and was constructed entirely from Pyrex glass. A B 10 socket attached to the base of the U-tube made loading easy. It was initially evacuated then filled with mercury under vacuum, and the degassed components injected into either side of the U-shaped vessel. The capillaries used, along with the thermostat and pressure correction apparatus, were the same as for the dilution dilatometer. Mixing was accomplished by rotating the frame on which the dilatometer was mounted, without allowing the liquids to come into contact with FIG (3.13.1)

THE BATCH DILATOMETER

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the greased B 10 joint.

Pressure corrections were made on each point measured using the same technique as described earlier. These, although less than 1 % of V^{E} were thought necessary in order to keep errors to a minimum. Not all earlier workers have bothered to make such corrections.

The excess volume change on mixing is given by

$$v^{\mathcal{E}} = \frac{\pi d^2 \Delta h}{4(n_{\rm A} + n_{\rm B})}$$

where d is the diameter of the capillary, Δh the change in meniscus height, and $(n_{B} + n_{B})$ the total number of moles of components used.

The disadvantages of this type of apparatus compared with the dilution dilatometer include the time taken for a series of measurements to be made. Using the dilution method, although taking longer to set up initially, a complete range of mole fraction can be concluded in a much shorter period than with the batch method, the dilatometer having to be cleaned and reloaded after every point. One advantage of the single point method however, is that any mistakes are confined to just that point and are easily spotted, whereas using the dilution method a series of points could be in error.

The batch method was principally used in this work to check

the accuracy of the measurements made with the dilution dilatometer thus giving a sensitive check on the results, and also for studying systems of relatively expensive components where filling the burette in the dilution apparatus was considered wasteful.

3.14 PRESENTATION OF RESULTS

The excess volume of mixing results, obtained using the methods described are shown in tables (3.14.1-3.14.18). In all cases the mole fraction, X (P), of the fluorocarbon is given. The curves were fitted to a Guggenheim function of the form

$$\mathbf{v}_{(X_1)}^{\mathbf{E}} = \sum_{J=1}^{q} \mathbf{x}_1 \quad \mathbf{x}_2 \quad \mathbf{c}_j \quad \left(\mathbf{x}_2 - \mathbf{x}_1\right)^{J-1}$$

and the parameters C_j required to give the best fit, shown by a minimum in the standard deviation, are presented together with the root mean square (R.M.S.) and standard deviations of the measured points from the computed curves in table (3.14.20). The smoothed curves, with experimental points superimposed, are shown in figures (3.14.2-3.14.10). The temperature dependence of the excess volume of mixing ($\delta v^E/\delta T$)_p is also given, where appropriate in table (3.14.21).

Partial molar excess volumes, V_i^{ϵ} , calculated from the dilution dilatometer measurements are given in the tables as is the amount of pure component, (A), initially placed in the

mixing chamber. Density measurements, necessary to calculate the amount of diluent added, were made on the relevant components and the results shown in table (3.14.19).

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TABLE (3.14.1)

EXCESS VOLUME OF MIXING RESULTS

Benzene (1) + Cyclohexane (2)

At 303.15 K

X (1)		X (1)	$v_2^{\mathcal{E}} / \operatorname{cm}^{3} \operatorname{mol}^{-1}$
0.9251	0.179	0.9618	2.388
0.8354	0.352	0.8791	1.962
0.8021	0.408	0.8186	1.764
0.7539	0.475	0.7777	1.522
0.6971	0.544	0.7249	1.387
0.6626	0.577	0.6796	1.211
0.6303	0.604	0.6462	1.146
0.6021	0.620	0.6160	0.956
0.5760	0.637	0.5889	0.998
0.5396	0.647	0.5575	0.809
0.5091	0.655	0.5242	0.786
0.4764	0.655	0.4925	0.652
0.4513	0.652	0.4637	0.596
0.4182	0.642	0.4344	0.520

Mass of benzene used = 3.6648 g

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TABLE (3.14.2)

EXCESS VOLUME OF MIXING RESULTS

Benzene (1) + Cyclohexane (2)

At 303.15 K

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I (1)	$\nabla^{\mathcal{E}}/\mathrm{cm}$ mol ¹	I (1)	$V_1^{\mathcal{E}}/\mathrm{cm}^3\mathrm{mol}^1$
0.0527	0.132	0.0267	2.503
0.1371	0.317	0.0959	2.204
0.1975	0.429	0.1679	1.922
0.2492	0.503	0.2238	1.583
0.3189	0.583	0.2849	1.361
0.3810	0.628	0.3507	1.077
0.4486	0.656	0.4158	0.883
0.4883	0.658	0.4688	0.692
0.5405	0.655	0.5151	0.629
0.5908	0.636	0.5664	0.476
0.6352	0.610	0.6136	0.403
0.6688	0.583	0.6524	0.307
0.6953	0.557	0.6823	0.269

Mass of cyclohexane used = 3.3381 g

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TABLE (3.14.3)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Cyclopentane (2)

At 303.15 K

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X (F)	v ^E /cm ³ moī ¹	X (F)	$v_2^{\ell}/cm^3 mol^{-1}$
0.8958	0.614	0.9465	5.896
0 . 798 7	0.890	0.8458	3.155
0.6941	1.440	0.7446	5.095
0.6501	1.548	0.6717	3.140
0.5846	1.683	0.6165	2.886
0•5490	1.736	0.5665	2.559
0.5169	1.779	0.5327	2.477
0.4832	1.796	0.4998	2.040
0.4547	1.801	0.4688	1.868
0.4340	1.792	0.4443	1.615
0.4073	1.784	0.4205	1.658
0.3634	1.737	0.3847	1.347
0.3293	1.681	0.3459	1.145
0.2635	1.516	0.2946	0.854
0.2199	1.366	0.2407	0.608
0.1834	1.213	0.2008	0.446

Mass of hexafluorobenzene used = 3.6884 g

BATCH MEASUREMENTS

0.4682	1.805
0.4675	1.815
0.2844	1.575

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TABLE (3.14.4)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Trimethylene Oxide (2)

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At 313.15 K

BATCH MEASUREMENTS

I (F)	V ^E /cm ³ mol ¹	I (F)	V ^E /cm mol
0.4680	1.391	0.3890	1.307
0.5431	1.320	0.4755	1.372
0.3728	1.300	0.4623	1.390

At 303.15 K

BATCH MEASUREMENTS

0.2317	1.036	0.7737	0.878	
0.5877	1.260	0.1794	0.871	
0.3181	1.224	0.4135	1.332	
0.4643	1.344	0.5095	1.323	
0.4735	1.349			

TABLE (3.14.5)

EXCESS VOLUME OF MIXING RESULTS

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Hexafluorobenzene + Tetrahydrofuran (2)

At 323.15 K

X (F)	V ^E /cm ³ mol ¹	X (F)	$V_2^E / cm^3 mol$
0.9424	0.223	0.9708	3.868
0.8400	0.566	0.8897	3.383
0.7820	0.770	0.8105	3.516
0.7310	0.912	0.7561	2.949
0.6847	1.035	0.7074	2.845
0.6447	1.113	0.6644	2.388
0.6045	1.171	0.6243	2.037
0.5456	1.251	0.5743	1.993
0.4849	1.279	0.5144	1.503
0.4421	1.285	0.4630	1.350
0.4148	1.277	0.4282	1.149
0.3794	1.262	0.3967	1.098
0.3478	1.228	0.3633	0.854
0.3173	1.187	0.3322	0.768
0.2799	1.120	0.2980	0.613
0.2523	1.059	0.2657	0.508
0.2324	1.012	0.2421	0.458
0.1952	0.906	0.2130	0.351
0.1712	0.826	0.1828	0.257
0.1466	0.738	0.1584	0.208

Mass of hexafluorobenzene used = 3.2565 g

TABLE (3.14.6)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Tetrahydrofuran (2)

At 283.15 K

BATCH MEASUREMENTS

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X (P)	$\mathbf{v}^E / \mathbf{c}^3 \mathbf{mol}'$	I(F)	$v^{E}/cm mol$
0.5679	1.182	0.4413	1.238
0.1727	0.795	0.5159	1.230
0.5975	1.146	0.4236	1.245
0.3522	1.179	0.2490	1.005
0.4561	1.243	0.1736	0.760
0.4054	1.241	0.5343	1.207
0.6621	1.056	0.5306	1.221
0.6493	1.082	0.4195	1.238

At 323.15 K

BATCH MEASUREMENTS

	0.4196	1.299	0.4766	1.290
• `	0.4102	1.294	0.5683	1.233
	0.4460	1.310	0.3267	1.194

TABLE (3.14.7)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Tetrahydrofuran (2)

At 303.15 K

BATCH MEASUREMENTS

I (F)	V ^E /cm ³ mol ¹	X (F)	$v^{E} / cm^{3} mol^{l}$
0.5688	1.187	0.8187	0.665
0.8820	0.483	0.1166	0.587
0.3831	1.234	0.6469	1.089
0.2073	0.899	0.5218	1.250
0.4708	1.262	0.2496	1.003
0.3255	1.201	0.3677	1.211
0.4635	1.262	0.0553	0.302
0.7298	0.862	0.0795	0.424

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TABLE (3.14.8)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Tetrahydropyran (2)

At 303.15 K

X (F)	V ^E /cm ³ mol ¹	X (F)	
0.0501	0.283	0.0254	5.647
0.1068	0.530	0.0789	4.429
0.1535	0.690	0.1305	3.589
0.2075	0.824	0.1809	2.782
0.2451	0.918	0.2265	2.818
0.2867	0.986	0.2662	2.153
0.3183	1.042	0.3027	2.252
0.3488	1.073	0.3337	1.722
0.3722	1.065	0.3606	0.857
0.4087	1.078	0.3907	1.295
0.4396	1.096	0.4244	1.409
0.4711	- 1.093	0.4556	1.046
0.5048	1.087	0.4882	0.997
0.5686	1.039	0.5378	0.714
0.6061	1.004	0.5878	0.636
0.6391	0.962	0.6230	0.501
0.6820	0.902	0.6613	0.463
0.7038	0.860	0.6931	0.292
0.7401	0.788	0.7226	0.268
0.7659	0.730	0.7534	0.205
0.7887	0.675	0.7776	0.166

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Mass of tetrahydropyran used = 1.5677 g

TABLE (3.14.9)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Tetrahydropyran (2)

At 323.15 K

I (F)	V ^E /cm ³ mol ¹	X (P)	V ^F /cm ³ mol
0.9370	0.223	0.9680	3.538
0.8261	0.582	0.8798	3.260
0.7848	0.667	0.8052	2.270
0.7290	0.836	0.7564	3.046
0.6880	0.898	0.7082	1.947
0.6436	0.993	0.6654	2.370
0.6011	1.045	0.6220	1.773
0.5547	1.096	0.5774	1.704
0.5041	1.117	0.5288	1.326
0.4714	1.137	0.4875	1.428
0.4386	1.124	0.4547	0.956
0.3995	1.116	0.4186	1.030
0.3471	1.068	0.3724	0.751
0.3131	1.029	0.3297	0.671
0.2854	0,982	0.2989	0.501
0.2581	0.933	0.2714	0.466
0.2255	0.864	0.2413	0.384
0.2037	0.810	0.2143	0.313
0.1726	0.721	0.1875	0.222

Mass of hexafluorobenzene used = 3.1671 g

TABLE (3.14.10)

-EXCESS VOLUME OF MIXING RESULTS

-Hexafluorobenzene + Tetrahydropyran (2)

At 323.15 K BATCH MEASUREMENTS

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I (F)	y ^E /cm ³ mol	I (F)	y ^E /cm ³ mol ¹
0.4256	1.112	0.5938	1.047

At 303.15 K

BATCH MEASUREMENTS

	0.3936	1.079	0.4001	1.081
•	0.3313	1.050		

TABLE (3.14.11)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Hexamethylene Oxide (2)

At 323.15 K

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X (F)	V ^E /cm ³ mol ¹	I(F)	$V_2^{E}/cm^3 mol^{1}$
0.9445	0.249	0.9719	4.488
0.8940	0.473	0.9189	4.424
0.8108	0.778	0.8514	3.757
0 . 763 7	0.926	0.7869	3.332
0.7088	1.065	0.7358	2.853
0.6291	1.204	0.6678	2.306
0.5730	1.261	0.6004	1.838
0.5278	1.287	0.5499	1.591
0.4819	1.293	0.5043	1.353
0.4519	1.282	0.4667	1.118
0.4013	1.249	0.4259	0.984
0.3768	1.222	0.3889	0.814
0.3357	1.161	0.3557	0.663
0.3042	1.101	0.3196	0.524
0.2623	1.012	0.2825	0.457
0.2362	0.944	0.2489	0.331
0.2060	0.861	0.2206	0.294

Mass of hexafluorobenzene used = 3.3271 g

TABLE (3.14.12)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Hexamethylene Oxide (2)

At 303.15 K

BATCH MEASUREMENTS

X (F)	V ^E /cm ³ mol ¹	X (F)	$v^{E}/cm^{3}mol$
0.7107	1.030	0.2518	0.962
0 . 095 7	0.444	0.2866	1.065
0.5699	1.235	0.4061	1.227
0.9169	0.363	0.4627	1.253
0.1938	0.785	0.5458	1.263
0.1596	0.690		

At 323.15 K

BATCH MEASUREMENTS

0.5445	1.288	0.4984	1.310
0.4820	1.306	0.4531	1.292

At 303.15 K

 $I(F) \quad v_2^E / cm \mod^{-1}$

0.9238	0.290	0.9611	3.810
0.8008	0.714	0.8601	3.471

Mass of hexafluorobenzene used = 3.2106 g

TABLE (3.14.13)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + 2-Methyl Tetrahydrofuran (2)

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At 303.15 K

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X (P)	v ^E /cm ³ mol	X (F)	$v_2^E / cm^3 mol$
0.9332	0.186	0.9660	2.777
0.8534	0.430	0.8924	3.047
0.7755	0.620	0.8135	2.505
0.7062	0.773	0.7400	2.336
0.6536	0.851	0.6794	1.822
0.6099	0.912	0.6314	1.758
0.5684	0.954	0.5888	1.539
0.5307	0.988	0.5492	1.465
0.5060	0.999	0.5182	1.221
0.4717	1.009	0.4885	. 1.151
0.4382	1.007	0.4546	0.982
0.4016	0.996	0.4195	0.871
0.3783	0.983	0.3897	0.765
0.3600	0.971	0.3690	0.746
0.3329	0.944	0.3462	0.611
0.3106	0.918	0.3216	0.551
0.2922	0.891	0.3013	0.460
0.2604	0.842	0.2759	0.444
0.2392	0.802	0.2496	0.351
0.2192	0.760	0.2290	0.298
0.2053	0.727	0.2121	0.249

Mass of hexafluorobenzene used = 4.8465 g

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BACESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + 2-Methyl Tetrahydrofuran (2)

At 303.15 K BA

BATCH MEASUREMENTS

I (P)	V ^E /cm ³ mol ¹	X (F)	v ^E /cm ³ mol
0.4943	1.008	0.6300	0.896
0.4936	1.008	0.4505	1.012
0.1564	0.595		

TABLE (3.14.15)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + 3-Methyl Tetrahydrofuran (2)

At 303.15 K

BATCH MBASUREMENTS

I (F)	V ^E /cm ³ mol	X (F)	V ^E /cm ³ mol ¹
0.1761	0.786	0.5592	1.290
0.9430	0.277	0.8055	0.777
0.2391	0.978	0.7184	1.010
0.4047	1.275	0.6324	1.258
0.5026	1.307	0.3894	1.255

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EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + 2,5-Dimethyl Tetrahydrofuran (2)

At 303.15 K

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•	X (F)	V ^E /cm ³ mol ⁱ	X (P)	$V_2^{\mathcal{E}}$ /cm ³ mol
	0.9688	0.086	0.9843	2.752
	0.9135	0.256	0.9407	3.065
	0.8536	0.428	0.8830	2.873
	0.7924	0.561	0.8224	2.290
	0.7542	0.649	0.7730	2.379
	0.7120	0.724	0.7328	1.991
	0.6746	0.783	0.6930	1.847
	0.6464	0.812	0.6603	1.477
•	0.6061	0.845	0.6259	1.342
	0.5642	0.877	0.5848	1.307
	0.5148	0.897	0.5389	1.111
	0.4805	0.900	0.4974	0.940
	0.4576	_ 0.899	0.4689	0.866
	0.4270	0.891	0.4421	0.791
. `	0.4026	0.876	0.4146	0.622
	0.3743	0.855	0.3882	0.581
	0.3484	0.827	0.3611	0.455
	0.3264	0.805	0.3372	0.467
	0.3019	0.781	0.3181	0.344
	0.2891	0.753	0.2993	0.357

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Mass of hexafluorobenzene used = 5.0882 g

TABLE (3.14.17)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + 2,5-Dimethyl Tetrahydrofuran (2)

At 303.15 K

BATCH MEASUREMENTS

X (F)	V [€] /cm ³ moĺ	I (F)	
0.5906	0.855	0.5248	0.885
0.4343	0.877	0.2647	0.682
0.1868	0.538		
TABLE (3.14.18)

EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Furan (2)

At 303.15 K

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I (F)	V ^E /cm ³ mol ¹	X (F)	$V_2^E / cm^3 mol^1$
0.8625	0.192	0.9287	1.397
0.7716	0.327	0.8158	1.469
0.6961	0.422	0.7329	1.304
0.6388	0.490	0.6668	1.242
0.5671	0.563	0.6019	1.146
0.4725	0.634	0.5176	0.988
0.4498	- 0.657	0.4610	1.112
0.4182	0.665	0.4337	0.771
0.3896	0.678	0.4037	0.855
0.3590	0.677	0.3740	0.665
0.3356	0.680	0.3471	0.718
0.3146	0.671	0.3249	0.538
0.2970	0.663	0.3056	0.534
0.2816	0.657	0.2892	0.549
0.2690	0.650	0.2752	0.490
0.2550	0.638	0.2619	0.424
0.2390	0.623	0.2469	0.390

Mass of hexafluorobenzene used 6.4506 g

At 303.15 K

BATCH MEASUREMENTS

0.3115	0.6686
0.4282	0.6711

TABLE (3.14.19)

DENSITIES OF THE COMPONENTS USED IN THE DILATOMETER

	T/K	$\rho/g \text{ cm}^{-3}$	
Furan	303.15	0.92465	(35)
Benzene	303.15	0.86825	(35)
Cyclohexane	303.15	0.7693	(35)
2,5-Dimethyl THF	303.15	0.8196	
2-Methyl THF	303.15	0.8447	
Hexamethylene Oxide	303.15	0.8943	
	323.15	0.8754	
Cyclopentane	303.15	0.73552	(25)
Tetrahydropyran	323.15	0.8544	
Tetrahydrofuran	323.15	0.8547	
Hexafluorobenzene	303.15	1.59547	(65)

TABLE (3.14.21)

TEMPERATURE DEPENDENCE OF THE VOLUME OF MIXING

System	$(\partial v/\partial T)_{p} / cm^{3-1-1} (at x_{p} = 0.5)$
C ₆ F ₆ + TMO	0.003
C ₆ F ₆ + THF	0.001
C ₆ F ₆ + THP	0.001
с ₆ ғ ₆ + нмо	0.001

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TABLE (3.14.20)

PARAMETERS FOR THE GUGGENHEIM FUNCTION

RMS/cm³ mol⁻¹ d/cm³ mol⁻¹ 0.003 0.038 0.005 0.012 0.008 0.026 0.008 0.008 0.011 0.003 0.006 0.023 0.005 0.008 0.003 0.003 0.035 0.003 600°0 **0.**006 0.022 0.008 600°0 0.003 0,006 0.007 0.005 0.003 0.021 0,008 **v**(4)/cm³ mol⁻¹ -0.276 0.307 0.387 0.432 0.243 $v(3)/cm^3 mol^{-1}$ 0.276 -5.154 0.261 0.686 -0.156 000 0 0.018 0.575 -0.081 **v**(2)/cm³ mol⁻¹ 0.098 0.828 1.452 1.000 1.045 0.019 1.463 0.791 0.781 0.129 0.781 0.159 0.264 0.767 1.446 $v(1)/cm^3 mol^{-1}$ 2.632 7.139 5.110 5.484 4.940 5.337 4.997 4-344 5.078 5.178 5.252 4**.**007 3.602 +•504 2.486 303.15 303.15 313.15 303.15 283.15 303.15 323.15 303.15 303.15 323.15 303.15 303.15 303.15 323.15 303.15 ЧŽ $c_{6F_{6}} + c$ -pentane $c_{6F_6} + 2,5$ -DMTHF $c_{6H_6} + c$ -hexane c₆f₆ + 3-mthf c₆F₆ + 2-MTHF $c_6 F_6 + HMO$ $c_{6F_{6}} + HMO$ $c_6F_6 + Furan$ $c_{6F_{6}} + IMO$ c₆F₆ + THF c₆F₆ + THP c₆F₆ + THF c₆F₆ + THF $c_{6F_6} + TMO$ SYSTEM $c_6F_6 + THP$

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EXCESS VOLUME OF MIXING RESULTS

KEY TO THE FIGURES

The results presented in this work at various temperatures are depicted by the following symbols

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С.

Δ.	for measurements at 283.15 K
0	for measurements at 303.15 K
D	for measurements at 313.15 K
V	for measurements at 323,15 K



Deviations, δ , of the excess molar volume of mixing for the system benzene (1) + cyclohexane (2), at 298.15 K, from the equation of Kumuran and McGlashan (31).

	this work
B	Stokes, Levien and Marsh (30)
	Stokes, Levien and Marsh (30) piston dilatometer
D	Beath, O'Neill and Williamson (67)
E	Powell and Swinton (34)
P	Wood and Austin (68)

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EXCESS VOLUME OF MIXING RESULTS



`Benzene(1) + Cyclohexane(2)



FIG (3·14·3)







FIG (3·14·5)

Hexafluorobenzene + Tetrahydrofuran



FIG (3.14.6)

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EXCESS VOLUME OF MIXING RESULTS

Hexafluorobenzene + Hexamethylene Oxide



FIG (3·14·7)



FIG (3·14·8)



Hexafluorobenzene + 2,5-Dimethyltetrahydrofuran

FIG (3.14.9)



FIG (3.14.10)

EXCESS VOLUME OF MIXING RESULTS



Hexafluorobenzene + Furan

CHAPTER FOUR

BICESS ENTHALPIES OF MIXING

4.1 INTRODUCTION

The apparatus for measuring the excess enthalpies of mixing, $H^{\mathcal{E}}$, presented in this work, is a development by Armitage (27) of the original design of Larkin and McGlashan (37) with the A.C. modification of Faulkner and Stubley (38).

The previous calorimeter in use in this laboratory employed a D.C. bridge network and initial measurements were made on the systems water + 1,4-dioxan, as a comparison with the results of previous workers (42-44), using this apparatus, and hexafluorobenzene + tetrahydrofuran. Twin calorimeters were used for all of the mixtures studied so that effects of stirring were minimised, and off scale deflections for exothermic heats of mixing were avoided.

A diagram of this system and a full description of the operation of the calorimeters has already been given (39,27-29) and will not be duplicated here.

To improve the accuracy of this system several important modifications were accomplished, the principal of these being the introduction of an A.C. bridge.

4.2 THE A.C. BRIDGE NETWORK

This was comparable to that described by Faulkner and Stubley (38) with only minor differences. A block diagram of the circuit is shown in figure (4.2.1). The thermistor bridge, with

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matched sets of three ITT M52 W thermistors on each calorimeter, wired in parallel, was operated at the much higher frequency of 1500 Hz A.C. for greater sensitivity. Because of this a variable capacitor had to be introduced across the bridge to correct the capacitive unbalance, since the approximation to a simple resistive bridge can no longer be made. To make balancing a simple process an oscilloscope (Roband Type RO 50) was introduced into the system to monitor the incoming signal from the bridge.

This signal was minimised by use of a resistance box forming one arm of the bridge, and the variable capacitor. The bridge was then considered balanced. A small out of balance signal was then introduced by use of the resistance box and this signal was maximised using the phase shifter incorporated into the phase sensitive detector. The bridge signal was then returned to its minimum value and was ready for use. Any slight imbalance caused by capacitive drift no longer has any effect on the system.

4.3 ANCILLARY EQUIPMENT

Other improvements to the original design include a digital electronic timer (Advance Instruments timer counter T.C. 9B) activated by the switch controlling the flow of current to the calorimeters, and a digital panel meter (XL 2000) that measures the potential drop across a one ohm standard resistor, thus giving a direct readout of the applied current to the calorimeters. The output from the bridge after amplification was plotted

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graphically using a potentiometric recorder (Servoscribe RE 516.20 Venture) to ensure that the cooling curves were accurately reproduced. The thermostat was almost identical to that used for measuring the excess volumes of mixing, described earlier. The electrical energy to the calorimeters was provided by a constant voltage supply (Weir 403).

4.4 OPBRATION OF THE CALORIMETER

The calorimeter was loaded in a manner very similar to that used with the batch dilatometer, the capillary however being replaced by an expansion bulb. The procedure has been described several times elsewhere (37,27,28), and a diagram of the calorimeter is shown in figure (4.4.1). The calorimeter was then placed in a polystyrene jacket (40) and sealed in a brass watertight vessel placed in the thermostat. The calorimeters were left overnight to attain thermal equilibrium.

4.5 ENDOTHERMIC MEASUREMENTS

The mode of operation has been described in sufficient detail by various workers (37,24,27-29) for it not to warrant a further repetition here.

A typical endothermic trace is shown in figure (4.5.1). The thermodynamic energy change for this calorimeter can be written in the form :-

FIG (4.4.1)

A CALORIMETER VESSEL





FIG (4.5.1)

A SCHEMATIC ENDOTHERMIC RECORDER TRACE



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$$\Delta \mathbf{U}_{exp} = \mathbf{W}_{e1} + \mathbf{n} \mathbf{W}_{g} - \int_{\mathbf{T}}^{\mathbf{T}_{f}} \mathbf{C}_{i} d\mathbf{T} - \int_{\mathbf{V}}^{\mathbf{V}_{f}} \mathbf{d} \mathbf{V} + q \quad (4.5.1)$$

 $= \Delta u_{mix} + \Delta u_{comp}$

where;

- V

Wel is the electrical energy supplied to the mixing calorimeter to compensate for the energy change on mixing.

nW is the energy supplied to the calorimeter by stirring n times.

$$\int_{T}^{T} G_{i} dT \text{ is the energy required to raise the temperatur}$$

of the calorimeter and its contents from T to T_{r} .

$$\int_{V}^{V} ext dV \text{ is the work done by the calorimeter in expanding}$$

from volume V to V_f against an external pressure of P_{ext} . This term has been shown to be less than 10⁻⁵ J by Armitage (27) and so can be discounted.

-q is the energy lost to the surroundings.

 ΔU_{mix} is the change in energy on mixing the two components in the calorimeter.

 $\triangle U_{\text{comp}}$ is the thermodynamic energy change on compressing the calorimeter and its contents. This has been shown to be negligible by McGlashan (41) provided the expansion bulb is large enough.

Heat losses to the surroundings are compensated for on the

recorder pen trace by extrapolation of the cooling curves. Thus equation (4.5.1) can be written as

$$\Delta U_{exp} = W_{el} + nW_{g} - \int_{T}^{T} dT \qquad (4.5.2)$$

If the heat capacity of the calorimeter is assumed constant over the small temperature change $(T_{p} - T)$ then

$$\Delta U_{exp} = W_{e1} + nW_{g} - C_{i} (T_{f} - T)$$
 (4.5.3)

Electrical energy is supplied to the calorimeter to compensate for the energy change on mixing and a deflection on the chart paper will be observed if this compensation is not exact. Let the deflection due to unbalance in calorimeter (2) be M_2 . Since mixing is always arranged to take place in calorimeter (2)then

$$\Delta U_{exp} = \Delta U_{mix} = I_1^2 R_2 t_1 + n W_8 - C_2 (T_f - T) \quad (4.5.4)$$

Since the temperature change of the thermistors is proportional to the deflection on the chart paper:-

$$\Delta U_{\text{mix}} = I_1^2 R_2 t_1 + n W_{s2} - C_2 M_2 X_2 \qquad (4.5.5)$$

again stirred n times. Let the deflection of the bridge due to this be S_2 . Thus :-

$$nW_{S2} = C_2 S_2 X_2$$
 (4.5.6)

Electrical energy was then again put into calorimeter 2 causing a further deflection of the bridge, the calorimeter being stirred a further n times during this process. Thus :-

$$I_2^2 R_2 t_2 = -n W_{S2} + C_2 B_2 X_2$$
 (4.5.7)

where E_{2} is the unbalance in the bridge.

Since calorimeter (1), acting simply as the other arm of the bridge, is also being stirred during the processes of mixing, stirring and calibration then the following deflections of the bridge are caused by calorimeter (1) :-For mixing in calorimeter (2)

 $nW_{S1} - C_1 X_1 H_1 = 0 \qquad (4.5.8)$ For stirring the calorimeters

 $nW_{S1} - C_1 X_1 S_1 = 0 \qquad (4.5.9)$

For calibration of calorimeter (2)

$$nW_{S1} - C_1E_1X_1 = 0 (4.5.10)$$

Combining equations (4.5.5-4.5.7) to eliminate the heat capacity and constant of proportionality for calorimeter (2) leads to :-

$$\Delta U_{\text{mix}} = I_1^2 R_2 t_1 + I_2^2 R_2 t_2 \frac{(S_2 - M_2)}{(B_2 - S_2)}$$
(4.5.11)

The measured chart recorder deflections for these three processes, Φ_1 , Φ_2 , Φ_3 , are simply the combinations of the deflections due to calorimeters (1) and (2) and thus :-

$$\Phi_1 = \mathbf{M}_2 - \mathbf{M}_1$$

$$\Phi_2 = \mathbf{S}_2 - \mathbf{S}_1$$

$$\Phi_3 = \mathbf{B}_2 - \mathbf{B}_1$$

Combining these with equations (4.5.8-4.5.10) then substituting into equation (4.5.11) leads to :-

$$\Delta U_{\text{mix}} = I_1^2 R_2 t_1 - I_2^2 R_2 t_2 \underbrace{(\Phi_1 - \Phi_2)}_{(\Phi_3 - \Phi_2)}$$
(4.5.12)

The molar thermodynamic excess energy of mixing, U^{E} , can be obtained from the energy of mixing change ΔU_{mix} , by :-

$$\mathbf{U}^{\mathsf{E}} = \frac{\Delta \mathbf{U}_{\mathsf{mix}}}{(\mathsf{n}_1 + \mathsf{n}_2)}$$

Since the thermodynamic function H is defined by :

$$H = U + PV$$

Thus :-

$$\mathbf{H}^{\mathsf{E}} = \mathbf{U}^{\mathsf{E}} + \mathbf{P}\mathbf{V}^{\mathsf{E}}$$

Since V^E is typically of the order of 1 cm³mol⁻¹ then PV^E will be of the order of 0.1 J mol⁻¹ and so can be discounted for all but the smallest measurements of ΔU_{mix} . Thus :-

$$H^{E} = \left\{ I_{1}^{2}R_{2}t_{1} - I_{2}^{2}R_{2}t_{2} \frac{(\Phi_{1} - \Phi_{2})}{(\Phi_{3} - \Phi_{2})} \right\}$$
(4.5.13)

4.6 EXOTHERMIC MEASUREMENTS

Mixing was again carried out in calorimeter (2), four processes were involved for the necessary determination of the energy of mixing.

a) Energy was supplied to calorimeter (1) to compensate for the heat generated in calorimeter (2) due to mixing. The measured chart recorder deflection was Φ_1 .

b) The calorimeters were stirred n times, the measured deflection was Φ_2 .

c) Energy was supplied to both calorimeters and the recorder deflection Φ_3 noted.

d) Electrical energy was supplied to calorimeter (1) as a calibration, the noted deflection was Φ_4 . The necessary equations relating to these changes are as follows For calorimeter (2) :-

$$\Delta U_{\text{mix}} = -nW_{32} + C_2 \chi_2 W_2 \qquad (4.6.1)$$

$$nW_{S2} = C_2 S_2 X_2 \qquad (4.6.2)$$

$$I_2^2 R_2 t_2 = C_2 X_2 B_2 - n W_{S2}$$
 (4.6.3)

$$nW_{S2} = C_2 S_2 X_2$$
 (4.6.4)

where the symbols are as before excepting B_i is the deflection due to calorimeter i. For calorimeter (1) :-

$$I_{1}^{2}R_{1}t_{1} = -nW_{31} + C_{1}X_{1}M_{1}$$
 (4.6.5).

$$\mathbf{n}\mathbf{W}_{s1} = \mathbf{C}_1 \mathbf{S}_1 \chi_1$$
 (4.6.6)

$$I_2^2 R_1 t_2 = -n W_{S1} + C_1 X_1 B_1$$
 (4.6.7)

$$I_{3}^{2}R_{1}t_{3} = -nW_{S1} + C_{1}X_{1}E_{1}$$
 (4.6.8)

Combining these sets of equations as before and noting that :-

Leads to :-

$$\Delta \mathbf{U}_{mix} = \frac{\mathbf{I}_{2}^{2}\mathbf{R}_{2}\mathbf{t}_{2}}{\left\{\mathbf{I}_{1}^{2}\mathbf{t}_{1}(\mathbf{\Phi}_{4}-\mathbf{\Phi}_{2}) - \mathbf{I}_{3}^{2}\mathbf{t}_{3}(\mathbf{\Phi}_{1}-\mathbf{\Phi}_{2})\right\}}{\left\{\mathbf{I}_{2}^{2}\mathbf{t}_{2}(\mathbf{\Phi}_{4}-\mathbf{\Phi}_{2}) - (\mathbf{\Phi}_{3}-\mathbf{\Phi}_{2})\mathbf{I}_{3}^{2}\mathbf{t}_{3}\right\}}$$
(4.6.9)

The excess enthalpy, H^E, is calculated as before.

4.7 PRESENTATION OF RESULTS

The excess enthalpies measured during the period of this work are shown in the following tables. An extensive series of cyclic ether mixtures with either hexafluorobenzene or pentafluorocyanobenzene as the second component has been investigated. The composition dependence was studied in detail at 303.15 K and measurements at other temperatures were also undertaken to allow a determination of the excess heat capacity, $C_p^B /J K^{-1}mol^{-1}$, at X=0.5 to be ascertained. As a comparison in figure (4.7.1) are plotted the excess enthalpy curves for a series of aliphatic ethers with hexafluorobenzene measured by Murray and Martin (45). These curves show that any complexing interaction is smaller for the aliphatic ethers. A fuller discussion of the results and interpretation of the interactions is given in chapter 8.

The system hexafluorobenzene + cyclopentane was also investigated to observe the effect due simply to a change in the size of the ring and also to give an estimate of the non-complexing interactions. Hexafluorobenzene + cyclohexane has already been determined by other workers (17,69) and both curves are shown plotted in figure (4.7.8).

To complement and complete the work of a predecessor in this laboratory (24) the systems pentafluorocyanobenzene + benzene, + mesitylene were measured at 323.15 K and a more limited investigation was made at 343.15 K in order to facilitate the calculation of C_p^E at X=0.5. Shown plotted are the results for the measurements of pentafluorocyanobenzene with a whole series of aromatic hydrocarbons in figure (4.7.10). A more detailed discussion of the results has been given (46).

The measurements at 303.15 K and 323.15 K have been fitted to the usual expression:-

$$H^{\mathbb{E}}/J \text{ mol}^{-1} = I(1-I) \sum_{i=1}^{n} h_{i} (1-2I)^{i-1}$$

where X is the mole fraction of the fluorinated species. The parameter h_i that produce the necessary minimum in the standard deviation $\sigma'(H^E)$ concordant with a satisfactory fit are also given.

TABLE (4.7.1)

EXCESS BNTHALPY OF MIXING RESULTS

Hexafluorobenzene + Tetrahydrofuran

At 323.15 K

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X (F)	H ^E /J mol ⁻¹	I (F)	H ^E /J mol ⁻¹
0.3395	-89.8	0.3558	-98.1
0.7047	-133.7	0.6597	-139.5
0.5504	-139.7	0.6194	-141.9
0.6338	-144.8	0.5978	-141.4
0.8287	- 99 .9	0.5459	-140.6
0.8273	-100.1	0.0933	12.17
0.0515	12.95	0.1060	12.48
0.0975	9.8	0.2623	-43.4
0.4158	-115.2	0.5282	-139.9
0.2534	-40.3	0.3442	-89.1

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At 303.15 K

0.4838	-125.5	0.8661	-78.7
0.0352	6.91	0.1865	-22.7
0.0608	9.17	0.1037	1.83

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EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Tetrahydropyran

At 303.15 K

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X (F)	H ^E /J mol ⁻¹	X (P)	H ^E /J mol ⁻¹
0.7495	-261	Q.8266	-202
0.3264	-267	0.2116	-179
0.0946	-75	Q.4848	-311
0.6394	-313	0.4460	-317
0.5373	-327		
		•	

At 323.15 K

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0.2337	-179	0.5245	-302
0.7203	-254	0.2946	-213
0.4469	-282	0.7736	-215
0.1636	-124	0.0908	-60
0.0930	-60	0.0501	-32

TABLE (4.7.3)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Hexamethylene Oxide

At 323.15 K

X (F)	H ^E /J mol ⁻¹	X (F)	H ^E /J mol ⁻¹
0.3669	65	Q. 3486	67
0.4086	63	Q. 3258	63
0.5968	51		

At 303.15 K

0.2670	42	9.7737	22
0.1242	34	0.4627	38
0.2551	39	0.1890	39
0.4354	37	0.5471	37
0.5614	34	9.4605	38

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Trimethylene Oxide

At 303.15 K

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X (F)	H ^E /J mol ⁻¹	X (F)	H ^E /J mol ⁻¹
0.2548	128.2	Q.1247	106.1
0.1614	123.3	0.2061	128.8
0.2136	132.8	0.4559	89.1
0.9169	10.86	0.6467	46.7
0.7220	31.4	0.7579	17.9

Pentafluorocÿanobenzene + Trimethylene Oxide

At 303.15 K

0.2887

-66.5

TABLE (4.7.5)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + 2-Methyltetrahydrofuran

At 303.15 K

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X (F)	H ^E /J mol ⁻¹	X (F)	$H^E / J mol^{-1}$
0.2047	-252	0,4665	-422
0.6212	-389	0,8085	-242
0.3976	-410	0,3257	-379
0.7726	-277	0,8957	- 91
0.8705	-165	0,3364	-371
0.6934	-353	0,0775	-115
0.6758	-364	0,1918	-239
0.1406	-203	0,5135	-410
0.2674	-302		

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EXCESS ENTHALPIES OF MIXING RESULTS

Hexafluorobenzene + 3-Nethyltetrahydrofuran

At 303.15 K

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X (F)	H ^E /J mol ⁻¹	I (P)	H ^E /J mol ⁻¹
0.9548	3.4	0.6827	-88
0.7340	-64	0.5638	-110
0.5088	-113	0.9463	2.0
0.8795	-17	0.7444	-60
0.0577	-4	0.0929	-8
0.1854	-42	0,2441	-59
0.3079	-82	0.4759	-111
0.4135	-103	0.4042	-115

TABLE (4.7.7)

EXCESS ENTHALPIES OF MIXING RESULTS

Hexafluorobenzene + 2,5-Dimethyltetrahydrofuran

At 303.15 K

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X (F)	H ^E /J mol ⁻¹	X (F)	H ^E /J mol ⁻¹
0.5767	-276	0.2931	-275
0.3538	-310	0.2188	-240
0.1762	-210	0.5492	-273
0.5170	-294	0.7 013	-202
0.8421	-108	0.5623	-279
0.4605	-326	Q.4986	-288
TABLE (4.7.8)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Furan

At 303.15 K

I (F)	H ^E /J mol ⁻¹	X (F)	$H^{E}/J mol^{-1}$
0.8035	-139.6	0.1829	65.6
0.5081	-123.7	0.3267	-10.97

At 298.45 K

0.7457	-169.9	0.7218	-174.4
0.7151	-170.1	0.5968	-160.5
0.5580	-151.1	Q.3812	-50.2
0.2178	50.2	0. 201 7	61.2
0.1222	69.5		

TABLE (4.7.9)

EXCESS ENTHALPY OF MIXING RESULTS

Pentafluorocyanobenzene + Furan

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At 303.15 K

0.5570	-202.4	0.6872	-210.3
0.7902	-170.4	0.5401	-199.1
0.2995	-47.6	Q. 0880	61.1
0.1195	58.5	Q.1501	47.2
0.2421	-1.45		

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Cyclopentane

At 303.15 K

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I (F)	H ^E /J mol ⁻¹	I (F)	H ^E /J mol ⁻¹
0.1048	480	0.5174	1121
0.4756	1135	0.5244	1136
0.8284	595	0.1688	674
0.6634	1016	0.4951	1142
0.3583	1059	0.4255	1132
0.4367	1141		

TABLE (4.7.11)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Benzene

At 313.15 K

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X (F)	H ^E /J mol ⁻¹	I (F)	H ^E /J mol ⁻¹
0.0891	-20.2	0,9257	-170.0
0.7119	-455.8	0,1450	-61.8
0.6088	-486.9	0,5298	-471.3
0.5610	-487.5	0,6677	-478.2

TABLE (4.7.12)

EXCESS ENTHALPY OF MIXING RESULTS

Pentafluorocyanobenzene + Benzene

At 323.15 K

0.6565	-479	0.4531	-448
0.5453	-511	0.4894	-498
0.7048	-392	0,5435	-541
0.3877	-429	0,2826	-302

EXCESS ENTHALPY OF MIXING RESULTS

Pentafluorocyanobenzene + Mesitylene

At 323.15 K

X (F)	$H^E / J mol^{-1}$	X (F)	$H^E / J mol^{-1}$
0.5100	- 225 7	0.4497	-2283
0.8410	-945	0.9046	-576
0.6071	-2034	0.6684	- 1854
0.4889	-2237	0.3335	-2082
0.2168	-1502	0.1421	-1112
0.0722	-564	- :: -	

At 343.15 K

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0.4049	-2073	0.4805	-2100
0.4963	-2096	0.5726	-1983
0.5021	-2112		

TABLE (4.7.14)

 TEMPERATURE DEPENDENCE OF H^E

 System
 $C_p^E / J K^{-1} mol^{-1} (at x_F 0.5)$
 $C_6F_6 + THF$ -0.3

 $C_6F_6 + THP$ 1.3

 $C_6F_6 + HMO.$ 1.2

 $C_6F_5CN + benzene$ 1.0

 $C_6F_5CN + 1,3,5$ trimethyl
 8.5

benzene

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PARAMETERS FOR THE GUGGENHEIM FUNCTION

ơ ∕J mol[−]l 2.32 3.2 2.9 15.1 **9.**4 3.8 5.8 4.5 1.2 3.8 13.7 12 5 RMS/J mol-1 1.73 0.97 2.8 13.7 2.3 **3.**8 11.9 8.1 3.2 3.4 4.3 h(4)/J mol⁻¹ 300.4 329 179 -455 254 h(3)/J mol⁻¹ 822.7 1084 2151 372 578 169 535 163 419 317 5 425 h(2)/J mol⁻¹ 892.5 1082 1357 343 **4**0% -486 260 198 568 667 -18 4 85 h(1)/J mol⁻¹ -734.5 4560 -1196 -1193 -1294 -1701 -492 -1964 -9022 51 -459 147 313 298.45 303.15 323.15 303.15 323.15 303.15 303.15 303.15 303.15 303.15 303.15 323.15 323.15 ž $c_{6F_6} + 2,5$ -dimth $c_{6F_5}c_N + 1,3,5TMB$ $c_{6F_{6}} + c_{-pentane}$ $c_{6F_5CN} + Furan$ c₆F₆ + 3-MTHF c₆F₆ + 2mthf c₆r₆ + Furan $c_6 F_5 c_N + c_6 H_6$ с₆ғ₆ + нмо $c_6 F_6 + TMO$ c₆f₆ + thd SYSTEM c₆F₆ + THP c₆F₆ + THF

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EXCESS ENTHALPY OF MIXING RESULTS

KEY TO THE FIGURES

The results presented in this work at various temperatures are depicted by the following symbols

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Δ.	for measurements at 298.45 K
	for measurements at 303.15 K
	for measurements at 313.15 K
O ●	for measurements at 323.15 K
Δ.	for measurements at 313 15 K

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FIG (4.7.1)

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THE RESULTS OF MURRAY AND MARTIN AT 29815 K (45)



FIG (4.7.2)

EXCESS ENTHALPY OF MIXING RESULTS



Hexafluorobenzene + Tetrahydrofuran

FIG (4.7.3)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Tetrahydropyran



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FIG (4.7.4)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Hexamethylene Oxide



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FIG (4.7.5)

EXCESS ENTHALPY OF MIXING RESULTS



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FIG (4.7.7)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Furan (A) Pentafluorocyanobenzene + Furan (B)



FIG (4.7.6)

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EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + 2-Methyltetrahydrofuran (A)

+ 3-Methyltetrahydrofuran (B)

+2,5-Dimethyltetrahydrofuran (







FIG (4.7.9)

EXCESS ENTHALPY OF MIXING RESULTS

Hexafluorobenzene + Benzene



FIG (4.7.10)

EXCESS ENTHALPY OF MIXING RESULTS

Pentafluorocyanobenzene + Benzene

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- + 1,3,5-Trimethylbenzene o
- + Methylbenzene A (24)
- + 1,4-Dimethylbenzene B (24)



CHAPTER FIVE

THE EXCESS GIBBS FREE ENERGY OF MIXING

5.1 INTRODUCTION

If it is possible to determine experimentally the saturation vapour pressure of a binary liquid mixture, in equilibrium with its vapour at a known temperature, and provided that other necessary data are available or can be directly measured, for example the second virial coefficients of the components, then the excess Gibbs free energy of mixing can be calculated.

The apparatus previously employed in this laboratory for this purpose required that each component be individually prepared and sealed in a glass ampoule and placed in the cell which involved many weighings, bouyancy corrections, glass blowing and a cumbersome sample breaking apparatus (24). This method had proved both slow and tedious and since it involved many unnecessary operations a new apparatus was constructed. This employed a dilution method of mixture preparation that required only two cathetometer readings for each new mixture. Using this system measurements spanning composition range were made using only two experimental rung.

Sample preparation was performed on a separate vacuum line specially constructed for this purpose and the liquids stored if necessary in the vessels described in section (5.2).

The excess Gibbs function, G^E , was calculated from the measured total vapour pressures of the mixtures, where only the overall composition was known, using the method described by Barker (47). An iterative procedure enabled the liquid and vapour

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compositions to be calculated.

The pressure in the cell was measured using the original mercury manometer. However, a completely new apparatus has recently been constructed by the author, which uses a 'Baratron' capacitance pressure transducer to give direct pressure readings, and this apparatus is described in section (5.9).

5.2 THE SAMPLE PREPARATION LINE

Air dissolved in the liquids used for the measurement of vapour pressure using this static method has a sensitive effect on the results obtained. Most of the errors of previous workers were caused either by the incomplete degassing of their samples or a failure to remove all traces of moisture from them, causing the measured vapour pressure to be higher than the true value. Extra care was therefore taken throughout this work to eliminate these sources of error. The vacuum line constructed for this purpose is shown in figure (5.2.1).

All of the taps used throughout the vacuum line and on the sample storage vessels were the greaseless P.T.F.E. variety (J.Young, Acton) and were made absolutely vacuum tight by the injection of mercury between the tap and the barrel, having partially removed the barrels for this purpose. P.T.F.E. sleeves (Fisons) were placed on all of the B 14 Quickfit joints removing the necessity for grease.

The sample, initially purified as described previously, was

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placed in a vessel of the type shown in figure (5.2.2) together with a small quantity of phosphorus pentoxide. Other drying agents have been compared in a previous study (24) and have been found to lead to a higher vapour pressure when used for pure substances. Phosphorus pentoxide was used throughout this work for all substances with which it did not react, otherwise freshly activated molecular seive was used. The vessel was then attached to the vacuum line at (A) and similar empty containers at (B) and (C). A sample storage vessel of the type shown in figure (5.2.3) was positioned at (D). The caps of these four receptacles were then filled with mercury above the level of the teflon sleeves thus providing a perfect seal.

Degassing was accomplished by repeated freezings of the pure component with liquid nitrogen and then evacuating the space above the solid. Bubble formation as the solid was allowed to thaw indicated that degassing was incomplete and this process was continued long after no further bubble formation was observed. At least ten freeze-thaw cycles were executed. Vacuum sublimations between vessels (A) and (B), achieved by cooling the relevant container with liquid nitrogen, were then effected to ensure the complete removal of all traces of any dissolved gases.

The pure component was then sublimed through (C) and into (D) to ensure that no drying agent would be carried onto the main vacuum line. Taps T1 and T2 were then closed and the vessel removed from the line. On performing this operation mercury flowed from the cap and surrounded the barrel of tap T1 thus

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A SAMPLE VESSEL



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FIG (5.2.3)

A SAMPLE STORAGE VESSEL

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giving an absolute seal. A vacuum remaining between taps T1 and T2 precludes the possibility of any air reaching th sample. The component may be stored almost indefinitely in this state, totally degassed.

5.3 THE LIQUID BURETTES

Each burette was constructed from a length of Veridia bore precision tubing of length greater than 30 cm and nominal internal diameter, 1.0 cm. These dimensions allowed suitable amounts of either component to be added. The internal crosssectional area of the tubing was measured during construction and found to be 0.7854 cm². Further tubing of normal pyrex glass was added to the base of each burette to form two U-tubes. These were connected at the rear via a three-way tap, and another tap immediately adjacent to this allowed the rear of either burette to be evacuated if desired.

The apparatus is shown in figure (5.3.1). Chao (26) describes a similar apparatus where mixtures are prepared volumetrically using piston injectors to transfer known volumes of samples into a cell. Murray and Martin (48) also describe a system for mixture preparation volumetrically using liquid burettes, their system however requires one of the components to be accurately weighed into the cell.

The whole burette system was housed in an air thermostat, with only the ends of the taps protruding from the thermostat box. This ensured that all of the liquid was at the temperature

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FIG (5.3.1)

THE LIQUID BURETTES



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of the thermostat, which was maintained to better than ±1 K at 298 K. Basically, the thermostat consisted of a perspex box with a hinged removable lid and sliding plate glass front, allowing easy access to the burettes, and through which a cathetometer telescope (Precision Tool and Instrument Co.Ltd.) was focused on the mercury meniscus inside the Veridia tubing. A single heater comprised of three resistors wired in parallel was situated at the centre of the base of the box. Immediately to the rear of this a fan blade driven by an externally mounted motor provided the necessary air circulation. A contact thermometer and relay in conjunction with this heater provided adequate temperature control. A calibrated mercury-in-glass thermometer mounted in an adjacent position to the burettes in the thermostat displayed the temperature of the air enclosed in the box.

The liquids in the burettes were completely enclosed by a greaseless tap at the top of the veridia tubing and a mercury piston below. Opening the tap caused the liquid to move into the evacuated space above, and the mercury level to rise. Two cathetometer readings of the distance travelled by the mercury piston in relation to a fixed reference mark, together with a knowledge of the diameter of the burette and the density of the liquid at the temperature of the thermostat, is sufficient to determine the mass of pure component transferred from the burette.

Two marks, one on the knurled ring of the barrel and one on the tap itself, allowed its return to its exact original

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position, ensuring that the pressure exerted on the liquid in the burette remained constant.

Re-filling a burette required the mercury level to be initially lowered. This was achieved by evacuating both sides of the mercury piston. Having extracted the ground glass stopper from the rear of the burette system, additional mercury could be removed with a hypodermic syringe. Care was taken during this process to ensure that both sides of the mercury piston were always subjected to the same pressure. All trace of the previous sample was eliminated by continued evacuation until the pressure guage (Pirani Type PGH 3) mounted into the line gave a satisfactory reading. The new sample, positioned onto the main vacuum line at (E), shown in figure (5.4.1), was then sublimed onto one of the cold fingers situated directly above one of the burettes. Tap T3 was then closed and the frozen sample allowed to thaw and drain into the burette. During this process the vapour pressure of the sample was exerted on one side of the mercury piston and suitable manipulation of tap T4, allowing air pressure onto the reverse side of the piston and closing tap T6, was necessary. Familiarisation with the apparatus made this a facile process. The liquids may be stored, perfectly degassed, in this condition indefinitely.

During the course of a series of dilutions from one burette, a small differential pressure was applied to the liquid due to the movement of the mercury piston around the U-tube. This, although insignificant, was corrected for during a run by periodic

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additions of more mercury to the rear of the burette, equalising the levels.

The accuracy of a burette system of this type has already been discussed in section (3.11) in relation to the dilution dilatometer, earlier described, and found to give a non-accumulative error in mole fraction of no greater than ± 0.0002 for each successive addition.

5.4 THE VAPOUR PRESSURE APPARATUS

The original vapour pressure line in use in this laboratory employed a design somewhat similar to that described by Marsh (49). The present apparatus, shown in figure (5.4.1), has retained the original manometer but replacing the cell, removing the degassing line, modifying other sections of the line and installing a liquid burette system has greatly enhanced the ease of operation of the system.

The pumping system was comprised of a three stage mercury diffusion pump with a single stage rotary oil pump (Type GRS 2 Genevac) used as a back up. A liquid nitrogen cold trap was situated between the main line and the diffusion pump to prevent contamination from fouling the pumps. The pressure in the line was measured using Pirani and Penning guages (Types PGH 3 and PNG 1, General Engineering Co.). The measured pressure in the line was typically better than 10^{-2} Nm⁻².

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5.5 THE THERMOSTAT

This consisted of a stainless steel tank of approximate volume 0.4 m³ copiously lagged with expanded polystyrene sheet and surrounded by a wooden exterior. A plate glass window the full length of the manometer was incorporated into one side of the tank allowing a cathetometer telescope to be focused on the interior. A wooden panel covering half of the roof of the tank was used to support two heaters both constructed from pyrotenax heating cable, wound onto a nylon frame, and spread throughout the tank. Two Gunn stirrers, sampling water from differing depths of the tank, were set into this panel and their output jets deployed to give the maximum possible turbulent effect. A platinum resistance thermometer (H.Tinsley and Co. Type 51875 A) was situated in the tank close to the cell and used in conjunction with a precision comparison bridge (Rosemount Engineering Co. Model VLF 51A) and standard resistor. During the course of the measurements to determine vapour pressure results at 303.15 K the temperature stabilisation was found to be better than 0.002 K for long time periods.

Situated beneath this tank a similarly insulated galvanised steel tank, capable of receiving approximately half of the volume of the thermostat, was located. This allowed the water to be drained through a control valve in order to expose the cell prior to making a further addition of pure component. A centrifugal pump (Stuart Turner Ltd. Type 10) enabled the water to be returned to the tank above when required.

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5.6 THE CELL

The manometer and cell are shown in figure (5.6.1). A metalin-glass stirrer bead was located in the cell during construction and operated from below by an electrically driven magnet sealed in a waterproof case. The motor, mounted above the thermostat, was controlled to allow intermittent stirring at varying rates and time intervals.

Transference of a sample to a mixture already in the cell initially required the tank to be drained to a suitable level below the base of the cell. Having removed the water present, the cold finger was filled with liquid nitrogen enabling the sample to be frozen down. The main vacuum pumps were then isolated from the line by closing tap T7, and the long barreled tap T5, isolating the cell, was then opened. Either of the two samples in the burettes could then be sublimed into the cell. A Pirani guage (PGH 3) situated between the cell and the burettes ensured that the pressure in the line before and after an addition was constant, verifying that all of the sample had been transferred. A tap at the base of the Pirani head was closed during the actual distillation thus preventing a possible decomposition of the sample on the hot wires of the guage head. The sample was then sealed in the cell by closing the long barreled tap T5. This was situated so that upon refilling the tank the knurled top still projected above the water level but ensured that all of the vapour space of the cell was well immersed.

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[•] FIG (5.6.1)

THE MANOMETER AND CELL



5.7 DETERMINATION OF THE VAPOUR VOLUME OF THE CELL

Since only the total composition of the mixture in the cell was measured experimentally then in order to calculate the activity coefficients, necessary for a determination of the excess Gibbs function, the vapour composition must be calculated. To accomplish this the volume of the vapour space must be determined experimentally for each mixture. This was carried out by introducing a sample of dry nitrogen into the cell and performing isothermal compressions, using the mercury in the manometer as a piston. The volume of the cell and side-arm, to its position of conjunction with the main Veridia bore glass stem of the manometer, was calculated and found to be 123.76 cm³. The vapour space volume for any subsequent mixture is then simply the sum of this volume and the volume moved by the mercury piston, down the stem from this position less the sample volume.

5.8 THE MERCURY MANOMETER

The manometer was constructed from 20 mm Veridia bore tubing. The mercury reservoir is shown in figure (5.6.1) at the base of the manometer in the thermostat. In this position mercury could be readily raised, by applying a pressure of dry nitrogen, or lowered, by evacuating the nitrogen supply line. Mixtures exerting high vapour pressures required the mercury level to be elevated high up the limbs of the manometer before the frozen sample in the cell had thawed. This prevented a loss of vapour caused by the level of the mercury in the lower limb

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being forced below the level of the side-arm. Once set however, adjustment rarely had to be made during the course of a series of dilutions.

Illumination for the manometer consisted of several 8 W fluorescent tubes housed in a waterproof glass container mounted in the thermostat. These in conjunction with a white plastic reflector, mounted to the rear of the manometer, ensured that even illumination was achieved.

Some problems were encountered when measuring the vapour pressure of pure components, and in some instances mixtures of composition widely displaced from the centre of the mole fraction range. Distillation onto the surface of the mercury in the manometer, which affected the shape of the meniscus, and the ability to focus on it clearly, led ultimately to the development of the present apparatus described below.

5.9 THE IMPROVED VAPOUR PRESSURES APPARATUS

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In order to overcome the problems that are outlined above the mercury manometer was replaced by an externally mounted pressure transducer system. A schematic illustration of this system is shown in figure (5.9.1). Degassing of samples and mixture preparation in the cell, using a similar burette arrangement to that described, has remained unchanged.

The connection to the cell previously made by the mercury manometer however was replaced by a glass-to-metal seal and

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linked with the capacitance head (MKS Baratron Type 315 BH) via a Cajon joint with an aluminium washer. These were found to produce a more reliable vacuum than stainless steel. The head, controlled by its own thermostat (MKS Type 170M-39), was mounted directly above the tank. Insulated heating tape covered all parts of the connecting tube above the waterline, ensuring that distillation of the sample from the cell did not occur. Any part of the system not immersed in the thermostat with which the sample could have possibly come into contact was maintained at a temperature well above that of the thermostat.

The reference side of the head was connected via another cajon joint to the main vacuum line. An electronics unit (MKS Type 170 M-6B) linked directly to a digital panel meter (0-10 V Type XL 2000) provided a direct readout of the pressure in the cell over the range -800 to +1000 \pm 0.001 mm of mercury. The Baratron manometer was initially calibrated against a normal mercury manometer at one atmosphere, and also at zero pressure by evacuating the cell. The head is of the bakeable type and may be heated to 500 K for cleaning purposes before a new sample is introduced into the cell.

5.10 CALCULATION OF THE EXCESS GIBBS FUNCTION

For a two component mixture to be in equilibrium with its vapour at constant temperature and pressure the following condition must be observed:

$$\mu_{i[T,P,\underline{x}]}^{\text{liq}} = \mu_{i[T,P,\underline{y}]}^{\text{Vap}}$$
(5.10.1)
where μ_{i}^{liq} is the chemical potential of component i in the liquid phase.

 μ_i^{Vap} is the chemical potential of component i in the vapour phase.

The chemical potential of a component in the liquid phase may also be expressed in terms of the rational activity coefficient & using the equation

$$\mu_{i}^{\text{liq}} = \mu_{i}^{\text{oliq}} + \operatorname{RT} \ln x_{i} \mathscr{V}_{i}[T, P, \underline{x}] \quad (5.10.2)$$

where $\forall_{i} = a_i / x_i$

and $\forall_i \rightarrow 1$ as $x_i \rightarrow 1$

The chemical potential of a component in the vapour phase may be expressed in terms of the fugacity, f, which measures the departure of a real system from perfect gas behaviour and is a function of temperature, pressure and system composition.

$$\mu_{\mathbf{i}[\mathbf{T},\mathbf{P},\underline{y}]}^{\mathrm{Vap}} = \mu_{\mathbf{i}[\mathbf{T}]}^{\bullet} + \mathrm{RT} \ln \frac{f_{\mathbf{i}}[\mathbf{T},\mathbf{P},\underline{y}]}{p^{\bullet}}$$
(5.10.3)

Combining equations (5.10.2) and (5.10.3) leads to

$$\mu_{\mathbf{i}}^{\circ \mathbf{liq}} + \mathbf{RT} \ln \mathbf{x}_{\mathbf{i}} \overset{\diamond}{\mathbf{i}}_{\mathbf{i}} [\mathbf{T}, \mathbf{P}, \underline{\mathbf{x}}] = \mu_{\mathbf{i}}^{\bullet} [\mathbf{T}] + \mathbf{RT} \ln \frac{\mathbf{f}_{\mathbf{i}}}{\mathbf{p}^{\bullet}} [\mathbf{T}, \mathbf{P}, \underline{\mathbf{y}}] \quad (5.10.4)$$

For a pure liquid, at the same temperature, exerting a vapour pressure, P_i^0 , in equilibrium with its vapour;

$$\mu_{i[T,P_{i}^{o}]}^{oliq} = \mu_{i[T]}^{o} + RT \ln \frac{f_{i}^{o}[T,P_{i}^{o}]}{p^{o}} \qquad (5.10.5)$$

and subtraction from equation (5.10.4) leads to

$$\mu_{i[T,P]}^{\circ} - \mu_{i[T,P_{i}]}^{\circ} + RT \ln x_{i} \delta_{i[T,P,\underline{x}]} = RT \ln \left[\frac{f_{i[T,P,\underline{y}]}}{f_{i[T,P_{i}]}^{\circ}} \right] (5.10.6)$$

Since $\left(\frac{\partial \mu_{i}^{o}}{\partial p}\right)_{T} = V_{i}^{o}$ and assuming that V_{i}^{o} remains constant

over the pressure range P_{i}^{O} to P then

$$\int_{\mathbf{P}=\mathbf{P}_{\mathbf{i}}}^{\mathbf{P}=\mathbf{P}} = \mathbf{V}_{\mathbf{i}}^{\circ} \int_{\mathbf{d}}^{\mathbf{P}} d\mathbf{P} \quad \text{At constant temperature(5.10.8)}$$
$$\mathbf{P}=\mathbf{P}_{\mathbf{i}}^{\circ} \qquad \mathbf{P}_{\mathbf{i}}^{\circ}$$

$$\therefore \quad \mu_{i[T,P]}^{\circ} - \mu_{i[T,P_{i}^{\circ}]}^{\circ} = V_{i}^{\circ} (P - P_{i}^{\circ}) \quad (5.10.9)$$

Combining equations (5.10.6) and (5.10.9)

$$RT \ln \delta_{i[T,P,\underline{x}]} = RT \ln \left[\frac{f_{i[T,P,\underline{y}]}}{x_{i}f_{i[T,P_{i}]}} \right] - V_{i}^{\circ} (P - P_{\underline{i}}^{\circ}) \quad (5.10.10)$$

Correcting the values of δ_{i} to a common reference pressure, P^{Φ} , using

$$\operatorname{RT}\left(\frac{\partial \ln \partial_{i}}{\partial P}\right)_{T} = V_{i}^{E} \qquad (5.10.11)$$

where V_i^E is the partial molar excess volume of component i.

Integration of this equation between the limits P and P^{\bullet} results in

$$RT \int_{P=P}^{P=P} \frac{P}{P} = P \qquad P \qquad (5.10.12)$$

and thus :

$$\operatorname{RT} \ln \overset{\circ}{\operatorname{i}}_{[\mathrm{T}, \mathrm{P}, \underline{x}]} = \operatorname{RT} \ln \overset{\circ}{\operatorname{i}}_{[\mathrm{T}, \mathrm{P}, \underline{x}]} + \overset{\varepsilon}{\operatorname{V}}_{\underline{i}}^{\mathrm{E}} (\mathrm{P}^{-} \mathrm{P}) \quad (5.10.13)$$

and substitution of equation (5.10.10) leads to

$$\ln \delta_{i}[\mathbf{T}, \mathbf{P}, \mathbf{X}] = \ln \left[\frac{f_{i}[\mathbf{T}, \mathbf{P}, \mathbf{y}]}{\mathbf{x}_{i} f_{i}^{o}[\mathbf{T}, \mathbf{P}_{i}^{o}]} - \frac{\mathbf{v}_{i}^{o}(\mathbf{P} - \mathbf{P}_{i}^{o})}{\mathbf{R}\mathbf{T}} + \frac{\mathbf{v}_{i}^{E}(\mathbf{P} - \mathbf{P})}{\mathbf{R}\mathbf{T}} \right]$$
(5.10.14)

Recalling equation (5.10.3) and noting that for a perfect gas

$$\mu_{i[T,P,\underline{y}]}^{PG} = \mu_{i[T]}^{\Phi} + RT \ln \frac{P_{i}}{P^{\Phi}}$$
(5.10.15)

where P_i is the partial pressure of component i in the mixture and $P_i = y_i P$, leads to

$$\operatorname{RT} \ln \frac{\operatorname{I}_{i}[\mathrm{T}, \mathrm{P}, \underline{y}]}{\operatorname{P}_{i}} = \mu_{i}[\mathrm{T}, \mathrm{P}, \underline{y}] - \mu_{i}^{\mathrm{PG}}[\mathrm{T}, \mathrm{P}, \underline{y}] \qquad (5.10.16)$$

Differentiation with respect to pressure at constant temperature

results in

.

$$\operatorname{RT}\left(\frac{\partial \ln}{\partial p} \frac{f_{i}}{P_{i}}\right)_{T} = V_{i} - V_{i}^{PG} \qquad (5.10.17)$$

The equation of state for the wapour phase can be used to show that

$$\mathbf{v}_{\mathbf{i}}^{\mathbf{PG}} = \frac{\mathbf{RT}}{\mathbf{P}}$$

And thus

$$\operatorname{RT}\left(\frac{\partial \ln}{\partial p} \frac{f_{i}}{P_{i}}\right)_{T} = V_{i} - \frac{\operatorname{RT}}{P} \qquad (5.10.18)$$

Noting that

$$\lim_{\mathbf{P}\to 0} \mathbf{f}_{\mathbf{i}} \longrightarrow \mathbf{P}_{\mathbf{i}}$$

And integrating between the limits P=0 and P=P leads to

$$RT \int_{P=0}^{P=P} \frac{f_{i}}{P_{i}} = \int_{P}^{P} (v_{i} - \frac{RT}{P}) dP \qquad (5.10.19)$$

$$P=0 \qquad 0$$

And thus

2

$$\operatorname{RT} \ln \frac{f_{i}}{P_{i}} = \int_{0}^{P} (v_{i} - \frac{\operatorname{RT}}{P}) dP$$

or more conveniently

$$\operatorname{RT} \ln \frac{f_{1}}{P^{\bullet}}[T, P, \underline{y}] = \operatorname{RT} \ln \frac{y_{1}P}{P^{\bullet}} + \int_{O}^{O} (v_{1}[T, P, \underline{y}] - \frac{\operatorname{RT}}{P}) dP \quad (5.10.20)$$

At moderate pressures the Virial equation can be truncated to the form

$$PV = \sum_{j=1}^{2} n_{j} (RT + PB_{[T,\underline{y}]})$$
 (5.10.21)

where B is known as the second virial coefficient and is a function of temperature and composition.

From statistical mechanics

$${}^{B}[\mathbf{T},\mathbf{y}] = \sum_{k=1}^{2} \sum_{l=1}^{2} {}^{y}_{k} {}^{y}_{l} {}^{B}_{k,l}[\mathbf{T}]$$
(5.10.22)

where $B_{k,l} = B_{l,k}$ and characterises the k,l pair interaction. Differentiation of equation (5.10.21) with respect to n_i leads to

$$\mathbf{v}_{\mathbf{i}} = \left(\frac{\partial \mathbf{v}}{\partial \mathbf{n}_{\mathbf{i}}}\right)_{[\mathbf{T},\mathbf{P},\mathbf{n}_{\mathbf{j}}]} = \frac{\mathbf{R}\mathbf{T}}{\mathbf{P}} + \sum_{\mathbf{k}=1}^{2} \mathbf{y}_{\mathbf{k}} \left(2\mathbf{B}_{\mathbf{k},\mathbf{i}} - \sum_{\mathbf{l}=1}^{2} \mathbf{y}_{\mathbf{l}}\mathbf{B}_{\mathbf{k},\mathbf{l}}\right) (5.10.23)$$

and by substitution into equation (5,10.20) an expression for the fugacity of component i results

$$\ln \frac{\mathbf{f}_{i}[\mathbf{T},\mathbf{y}]}{\mathbf{p}^{\bullet}} = \ln \frac{\mathbf{P}_{i}}{\mathbf{p}^{\bullet}} + \sum_{k=1}^{2} \mathbf{y}_{k} \left(2\mathbf{B}_{k,i} - \sum_{l=1}^{2} \mathbf{y}_{l} \mathbf{B}_{k,l} \right) \frac{\mathbf{P}}{\mathbf{R}^{\bullet}} \quad (5.10.24)$$

and for a pure substance i , the corresponding fugacity term is given by

$$\ln \frac{f_{i}^{\circ}[T,P_{i}^{\circ}]}{p^{\circ}} = \ln \frac{P_{i}^{\circ}}{p^{\circ}} + B_{ii} P_{i}^{\circ}/RT \qquad (5.10.25)$$

Combination of these equations leads to an expression for the rational activity coefficient of a component, i, for a binary liquid mixture.

RT
$$\ln \delta_{i}[T, P, \underline{x}] = RT \ln \frac{P_{i}}{x_{i}P_{i}^{\circ}} + (B_{ii} - V_{i}^{\circ})(P - P_{i}^{\circ})$$

+ $(1 - y_{i})^{2}(2B_{12} - B_{11} - B_{22}) + V_{i}^{E}(P^{\circ} - P)$ (5.10.26)

Rearranging these equations for ϑ_1 and ϑ_2 leads to

$$P = (1 - x) \delta_{1} P_{1}^{\circ} (exp \left[\left((B_{11} - V_{1}^{\circ}) (P - P_{1}^{\circ}) + (2B_{12} - B_{11} - B_{22}) y^{2} P + V_{1}^{E} (P^{\bullet} - P) \right) / RT \right]$$

$$+ x \delta_{2} P_{2}^{\circ} (exp \left[\left((B_{22} - V_{2}^{\circ}) (P - P_{2}^{\circ}) + (2B_{12} - B_{11} - B_{22}) (1 - y)^{2} P + V_{2}^{E} (P^{\bullet} - P) \right) / RT \right]$$

$$+ y E_{2}^{E} (P^{\bullet} - P) / RT \right]$$

$$(5.10.27)$$

If a function is chosen to represent G^E, which is of the form

$$\frac{G^{E}}{RT} = x(1-x) \sum_{j=1}^{P} G_{j} (1-2x)^{j-1}$$
 (5.10.28)

Then expressing this in terms of \aleph_i results in

$$\vartheta_{1} = \exp \left[x^{2} \sum_{j=1}^{P} G_{j} (1-2x)^{j-2} (2j(1-x)-1) \right]$$

$$\vartheta_{2} = \exp \left[(1-x)^{2} \sum_{j=1}^{P} G_{j} (1-2x)^{j-2} (1-2jx) \right]$$
(5.10.29)

These equations can then be used to develop a non-linear least squares fit for the vapour pressure.

An initial approximation for the parameters was made by assuming that the mixture was quadratic and that the vapour phase was ideal. Thus

$$G_1 = 4 \ln \left(\frac{2 P_{12}}{P_1^{\circ} + P_2^{\circ}} \right)$$
 (5.10.30)

The equation

$$\mathbf{y} = \mathbf{x} \, \delta_2 \mathbf{P}_2^{\circ} / \mathbf{P} \, \exp\left[\left((\mathbf{B}_{22}^{\circ} - \mathbf{V}_2^{\circ}) (\mathbf{P} - \mathbf{P}_2^{\circ}) + (2\mathbf{B}_{12}^{\circ} - \mathbf{B}_{11}^{\circ} - \mathbf{B}_{22}^{\circ}) (1 - \mathbf{y})^2 \mathbf{P} + \mathbf{V}_2^{\mathbf{E}} (\mathbf{P} - \mathbf{P}) \right) / \mathbf{RT} \right]$$
(5.10.31)

is then solved iteratively to give the vapour composition, y. Equation (5.10.27) can then be solved to give a calculated vapour pressure, $P_{(calc)}$.

A set of pressure residuals, $P_{(exp)} - P_{(calc)}$, is then obtained using the vapour composition to correct for vapour phase non-ideality. The least squares procedure is then used to obtain corrections for the previous estimates of the parameters δG_p . The corrected parameters are then used to re-calculate new corrections until the corrections become trivially small.

Since the liquid phase composition is not exactly known the Barker method (47) assumes that it is equivalent to the total composition of the mixture. The true liquid phase composition is then calculated by use of a further iterative cycle to correct for the material in the vapour phase. The total amount of substance present in the vapour phase is given by

$$(n_1^{Vap} + n_2^{Vap}) = \frac{PV}{RT + B_{mixt}P}$$
 (5.10.32)

and the corrected liquid phase composition is thus

$$\mathbf{x} = \left(\mathbf{n_2^{tot}} + \mathbf{n_2^{Vap}} \right) / \left[\mathbf{n_1^{tot}} + \mathbf{n_2^{tot}} - \left(\frac{\mathbf{PV}}{\mathbf{RT} - \mathbf{B_{mixt}^{P}}} \right) \right] (5.10.33)$$

where V is the volume of the vapour space

$$B_{mixt} = (1-y)^2 B_{11} + 2y(1-y) B_{12} + y^2 B_{22}$$

This procedure is then repeated until the corrections are once again trivially small.

Upon convergence of all the iterative cycles the final values of the parameters G_p are obtained and thus the Gibbs free energy of mixing has been found.

5.11 TEMPERATURE CORRECTIONS

Since the vapour pressures tank could not be returned to exactly the same temperature after every new addition temperature corrections had to be implemented. These were typically of the order of 10^{-2} K with a corresponding pressure correction of no greater than 10^{-1} mm Hg. The Clapyron equation can be written in the form

 $\frac{dP}{dT} = \frac{\Delta H_{v}}{T \Delta V} = \frac{\Delta H_{v}}{T(V^{Vap} - V^{liq})}$ (5.11.1)

and for a small change in temperature, $\triangle T$ the corresponding change in vapour pressure, $\triangle P$, is given by

$$\Delta P = \frac{\Delta H_{v}P}{T^{2}R} \Delta T \qquad (5.11.2)$$

 ΔH is the molar enthalpy of vaporisation of the mixture which can be calculated from the known values for the two pure liquids.

$$\Delta H_{V} = H^{vap} - H^{mixt} = (1-x)H_{1}^{o} + xH_{2}^{o} - (1-x)H_{1} - xH_{2} \quad (5.11.3)$$
wapour

and the molar enthalpy of mixing, H^E , is given by

$$H^{E} = (1-x)H_{1} + xH_{2} - (1-x)H_{1}^{o} - xH_{2}^{o}$$
 (5.11.4)

and thus the molar enthalpy of vaparisation of the mixture is simply

$$\Delta H_{\mathbf{v}} = (1-\mathbf{x}) \Delta H_{\mathbf{v}(1)}^{\circ} + \mathbf{x} \Delta H_{\mathbf{v}(2)}^{\circ} - H^{\mathbf{B}} \quad (5.11.5)$$

Corrections were made, where necessary, to each individual point using the measured enthalpy of mixing curve for the relevant value of H^E.

The Barker method was then employed as described.

5.12 TEST SYSTEMS

To satisfactorily test new equipment intended for the precise measurement of the saturation vapour pressure of a binary liquid mixture it is not sufficient merely to record the result for a pure component. The major innovation described in this work requiring extensive verification was the use of a liquid burette system using a continuous dilution technique for the preparation of mixtures in a cell. It was therefore decided to try to reproduce the results obtained by previous workers for the systems cyclohexane + benzene (at 313.15 K), + hexafluoro-- benzene (at 323.15 K), for which excellent data exist in the literature.

The results obtained are presented in tables (5.12.1) and (5.12.2). A graphical representation of the observed vapour pressure as a function of liquid composition is given in figures (5.12.1) and (5.12.2). The consistency of operation of the equipment is demonstrated by the near perfect overlap obtained for two separate dilution runs commencing at either end of the mole fraction range. Figures (5.12.3) and (5.12.4) show a plot of the composition of the liquid as a function of the composition of the vapour, both calculated using the Barker analysis. Good agreement was again obtained with other

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TABLE (5.12.1) EXCESS GIBBS FUNCTION RESULTS

Cyclohexane (1) + Benzene (2)

At 313.15 K

X (2)	Y (2)	Pexp/Nm ⁻²	P _{calc} /Nm ⁻²	G ^E / Jmol ⁻¹
0.9540	0.9315	24914.7	24912.2	50.8
0.8472	0.7967	26097.4	26064.4	154.5
0.7492	0.7004	26754 .4	26785.9	227.3
0.6533	0.6187	27213.9	27215.9	274.6
0.6179	0.5915	27301.3	27313.5	285.7
0.5043	0.5071	27425.8	27431.3	297.4
0.3319	0.3723	27082.7	27066.0	248.8
0.3114	0.3540	27035.1	26977.7	238.2
0.2310	0.2798	26476.2	26531.5	188.6

Parameters

G(1)	G(2)	G(3)
0.45647/	-0.05203	-0.07136

Standard deviation

ơ/ №m⁻²

38.5

TABLE (5.12.2)

EXCESS GIBBS FUNCTION RESULTS

Hexafluorobenzene + Cyclohexane

At 323.15 K

× _F	Y _F	P _{exp} /Nm ⁻²	P_{calc}/Nm^{-2}	G ^E / Jmol ⁻¹
0.0544	0.1464	40382.7	40340	186.3
0.1242	0.2443	43218.6	43 278	37 7•3
0.2203	0.3219	45304.3	4528 3 =	5 65•8
0.2817	0.3593	46001.9	45979	648.3
0.2956	0.3669	46150 .7	46098	663.3
0.3157	0.3780	46239 .6	46245	682.8
0.3424	0.3927	46356.4	46404	704.7
0.4281	0.4383	46543.5	4 666 <i>6</i>	747.2
0.4827	0.4661	46729 .9	4 6 6 51	753 •7
0.5284	0.4915	46527.5	46524	7 47•7
0.5321	0.4932	· 46550 .2	46510	7 46 • 7
0.5966	0.5297	46177.4	46145	71.9.5
0.6308	0.5503	45856.3	45863	696.8
0.6342	0.5524	45817.6	45831	694.2
0.6684	0.5737	45451.7	45476	6.64.8

G(1)	G(2)	G(3)
1.1205	0.0785	0.1974
Standard deviation	546 Nm ⁻²	

FIG (5.12.1)

VAPOUR PRESSURE v LIQUID COMPOSITION

AT 313.15 K

Cyclohexane(1) + Benzene(2)



FIG (5.12.2)

VAPOUR PRESSURE v LIQUID COMPOSITION

AT 323.15 K

Cyclohexane (1) + Hexafluorobenzene



FIG (5.12.3)

VAPOUR COMPOSITION v LIQUID COMPOSITION

AT 313.15 K

Cyclohexane (1) + Benzene (2)





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VAPOUR COMPOSITION v LIQUID COMPOSITION

AT 323.15 K

Cyclohexane + Hexafluorobenzene



— Gaw and Swinton (63)



workers.

The G^E function obtained for benzene + cyclohexane is shown graphically in figure (5.12.5) and a comparison of the results with available literature data (3), (10), and (12) is excellent. The second test system on comparison with the results of Gaw and Swinton shows a slight discrepancy at the centre of the mole fraction range of approximately 0.2 %. It is shown in figure (5.12.6). Since the vapour pressure they obtained for the pure component cyclohexane is also slightly higher this may possibly indicate the presence of trace amounts of moisture or air in their sample.

5.13 PRESENTATION OF RESULTS

Tables (5.13.1 - 5.13.5) list the results obtained for the five hexafluorobenzene + cyclic ether systems studied. All of the results given, including the two test systems, were measured using the mercury manometer described earlier. For each mixture the calculated liquid and vapour phase compositions are presented in terms of the mole fraction of hexafluorobenzene x_F , y_F , respectively. The excess Gibbs function, G^E , the experimental, (P_{exp}) and calculated, (P_{calc}) vapour pressures of the mixtures, and also the parameters G_p required to generate the function

$$\frac{G^{E}}{RT} = x_{F} (1-x_{F}) \sum_{j=1}^{P} G_{j} (1-2x_{F})^{j-1}$$
(5.13.1)

EXCESS GIBBS FUNCTION RESULTS

AT 313.15 K

Cyclohexane (1) + Benzene (2)



FIG (5.12.6)

EXCESS GIBBS FUNCTION RESULTS

AT 323.15 K



to fit the data are also listed. The standard deviation of the experimental vapour pressures from this curve are given, as are the molar volumes for the two pure components and also the value of the excess volume of mixing function at $x_F = 0.5$, necessary for a determination of the free energy of mixing.

Although the second virial coefficient of hexafluorobenzene is well established (65) there are few if any measured values of the second virial coefficients of cyclic ethers in the literature. A value of $-0.0011 \text{ m}^3 \text{ mol}^{-1}$ was calculated for tetrahydrofuran from critical temperature and pressure data. Deshpande et al (70) arrive at a value of $-0.0015 \text{ m}^3 \text{ mol}^{-1}$ for the virial coefficient of 1,4 dioxan calculated from the Berthelot equation. What data there are suggest that B_{11} lies between $-0.0005 \text{ and } -0.0015 \text{ m}^3 \text{ mol}^{-1}$ and we have adopted a value of $-0.001 \text{ m}^3 \text{ mol}^{-1}$ in the absence of other information. In order to test this assumption trial values of -0.0005 and $-0.0015 \text{ m}^3 \text{ mol}^{-1}$ were also used. The maximum deviation of the Gibbs free energy caused by using these three values for the virial coefficient was less than $\pm 5 \%$ for trimethylene oxide,

 ± 1 % for tetrahydropyran and less than ± 1 % for hexamethylene oxide. In all cases the higher value of G^E was generated by the higher estimate for the second virial coefficient of the cyclic ether concerned. The enthalpy of vaporisation of the pure liquids was calculated, using the Clapeyron equation, from the measured vapour pressure at several temperatures, and is also given.

For all of the systems presented it was assumed that the

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cross second virial coefficient, B₁₂, where unknown, is the arithmetic mean of the values for the pure component

$$B_{12} = \frac{B_{11} + B_{22}}{2}$$

A graphical display of the five curves is shown in figure (5.13.1).

TABLE (5.13.1)

EXCESS GIBBS FUNCTION RESULTS

Hexafluorobenzene + Trimethylene Oxide

At 303.15 K

-

x _r	۲ _۴	P _{exp} /Nm ⁻²	P _{calc} /Nm ⁻²	G ^E / Jmol ⁻¹
0.8405	0.5729	21003.0	21025.8	32.6
0.7875	0.4869	23339.0	23289.4	44.4
0.6630	0.3332	28505.0	28578.2	71.9
0.6005	0.2794	31250.0	31217.9	85.3
0.5307	0.2253	34093.0	34133.0	99 .7
0.5242	0.2235	34470.0	34399.9	101.0
0.4320	0.1675	38159.0	38128.9	117.5
0.4307	0.1657	38160.0	38181.0	117.7
0.3380	0.1213	41654.0	41701.3	128.6
0.2231	0.0789	45658.0	45644.4	126.0
0.1260	0.0469	48640.0	48615.2	98.2
0.0579	0.0229	50579.0	50590.7	56.2
Paramete	7 8			
	. G(1)	G(2)	G(3)	G(4)
	0.16765	0,14957	0.09792	· 0.04641

.

Standard Deviation

o'/nm⁻² 50.5

TABLE (5.13.2)

EXCESS GIBBS FUNCTION RESULTS

Hexafluorobenzene + Tetrahydrofuran

At 303.15 K

X _F	Y.p	Perp/Nm ⁻²	P _{calc/Nm} -2	$G^E / Jmol^{-1}$
0.0004	0 0005	0(777 0		00.4
0.0284	0.0205	20111.8	20762.9	20.1
0.0662	0.0445	26441.0	26451.5	42.5
0.1175	0.0773	26012.7	25997.1	65.7
0.1656	0.1057	25542.9	25540.3	80.9
0.2413	0.1506	24753.2	24761.6	94.2
0.3486	0.2195	23531.6	23529.7	96.1
0.4352	0.2811	22399 .9	22426.0	87.9
0.4733	0.3128	21935.7	21914.8	82.5
0.5608	0.3893	20688.6	20686.4	67 .7
0.6647	0.4971	19175.0	19170.9	48.6
0.7737	0.6318	17557.9	17564.3	29.7
0.9056	0.8218	15736.3	15734.1	11.4

7

-	Parameters		
		G(1)	

G(1)	G(2)	G(3)
0.12421	0.13001	0.04746

Standard deviation

ơ/nm^{−2} 14.3

TABLE (5.13.3)

EXCESS GIBBS FUNCTION RESULTS

Hexafluorobenzene + Tetrahydropyran

At 303.15 K

x _F	Y _F	Pexp/Nm ⁻²	P _{calc} /Nm ⁻²	G ^E Jmol ⁻¹
0.9257	0.9344	14203.	14203.3	0.3
0.8274	0.8446	14024.	14029.9	3.8
0.7208	0.7433	13856.	13856.2	10.3
0.6273	0.6527	13725.	13710.8	17.0
0.5534	0.5818	13595.	13596.3	22.2
0.5064	0.5361	13521.	13522.5	25.2
0.5022	0.5320	13515.	13515.9	25.4
0.4733	0.5048	13438.	13469.2	27.0
0.4167	0.4462	13436.	13376.7	29.5
0.3904	0.4224	13319.	13331.0	30.4
0.3276	0.3604	13187.	13218.7	31.3
0.2532	0.2839	13071.	13074.0	30.1
0.1916	0.2193	12947.	12942.2	26.9
0.1183	0.1393	12795.	12767.0	19.9
0.0741	0.0894	12629.	12649.4	13.8

Parameters

G(1)	G(2)

0.04058 0.04568

Standard deviation

o /Nm⁻² 23.4

TABLE (5.13.4)

EXCESS GIBBS FUNCTION RESULTS

Hexafluorobenzene + Hexamethylene Oxide

At 303.15 K

× _F	Y _F	P _{exp} /N m ⁻²	P _{calc} /N m ⁻²	G ^E /J mol ⁻¹
0.0561	0.2782	4480	4490	69.5
0.1013	0.4022	5242	5215	115.7
0.1676	0.5237	6158	6139	169.9
0.2395	0.6184	6977	7024	212.9
0.2993	0.6763	7637	7702	238.0
0.3548	0.7092	8361	8303	253.7
0.3984	0.7472 -	8722	8760	261.5
0.4046	0.7404	8915	8825	262.3
0.4548	0.7772	9353	9339	266.2
0.5085	0.8090	9861	9 87 7	265.4
0.5684	0.8393	10433	10462	258.7
0.6167	0.8593	10915	10924	248.9
0.6866	0.8896	11547	11575	227.6
0.7524	0.9097	12204	12171	199.3
0.8511	0.9469	13041	13039	139.5
0.9285	(0.9725	13730	13710	75 .5
Parameter	8			
	G(1)	G(2)	G(3)
	0.42195	0.03706	0.082	97

Standard deviation

d∕Nm⁻² 42.9

TABLE (5.13.5)

EXCESS GIBBS FUNCTION RESULTS

Hexafluorobenzene + 1,4-Dioxan

At 303.15 K

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×F	۲ _Р	P _{exp} /Nm ⁻²	P_{calc}/Nm^{-2}	G ^E /Jmol ⁻¹
0.0545	0.1836	7372	7349.4	87.2
0.2164	0.4266	9073	9092.6	227.9
0.2703	0.4775	9487	9497.0	245.3
0.3105	0.5131	9767	.97 7 8.8	251.2
0.3109	0.5121	9797.5	9781.9	251.3
0.3453	0.5428	10001	10014.2	252.3
0.4003	0.5873	10380	10378.2	247 .7
0.4050	0.5912	10411	10409.4	247.0
0.4561	0.6314	10762	10744.4	236.7
0.4915	0.6592	10999	10976.7	227.2
0.5169	0.6801	11148	11143.7	219.4
0.5822	0.7305	11580	11577.1	196.5
0.6491	0.7809	1201 7	12025.5	170.1
0.6985	0.8171	12331	12357.7	149.3
0.8082	0.8878	13096	13094.1	100.3
0.9258	0.9570	13879	13863.8	42.2
Parameter	8			
	G(1)	G(2)	G(3)	
0	•35652	0.23986	0.12655	
Standard	deviation	ע /Nm ^{−2}	16.2	

TABLE (5.13.6)

PROPERTIES OF THE COMPONENTS

Component	T/K	B/m ³ mol ⁻¹	Mola	ar Volume/m ³	$v^{E}/cm^{3} mol^{-1}$	Vap P/N m	2
TMO	303.15	estimated		65E-6	1.0 (+GF)	52281	
THF	303.15	-0.0011		80.18E-6	1.22 (+CF)	26982	
THP	303.15	estimated		98.61E-6	1.1 (+CF)	12429	
нмо	303.15	estimated		112E-6	1.3 (+CF)	3426	
1,4-dioxan	303.15	-0.001458		86.1E-6	0.82 (+ CFJ)	6309	
C6 F6	303.15	-0.00196		116E-6		14340	
С6Н6	313.15	-0.001276	(95)	110.78E-6		24304	
c-hexane	313.15	-0.001456	(95)	91.06E-6		24565	
c-hexane	323.15	-0.001380	(63)	112E-6		36117	
C6 F6	323.15	-0.00163	(63)	120E-6		34041	

Component	T/K	$\Delta H_v / J mol^{-1}$
TMO	303.15	30185.7
THP	303.15	33344.9
HMO	303.15	36601

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 $C_{6}F_{6} + C_{6}H_{12}$

Cyclohexane + Benzene $B_{12} = -0.001329 \text{ m}^3 \text{ mol}^{-1}$ (96) $B_{12} = -0.0011 \text{ m}^3 \text{ mol}^{-1}$ (63)

FIG (5.13.1)

EXCESS GIBBS FUNCTION RESULTS





CHAPTER SIX

SOLID LIQUID PHASE DIAGRAMS

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6.1 INTRODUCTION

Since the initial discovery by Fatrick and Prosser in 1960 (2) of an equimolar, congruently melting 1-1 molecular complex formed between hexafluorobenzene and benzene in the solid state, the phase diagrams of many such related systems have been investigated in some considerable detail. Hexafluorobenzene has been shown to form solid compounds with all simple aromatic hydrocarbons and several nitrogen containing compounds. The existing literature in this area has been reviewed by Swinton (18) and Fenby (50) and the tendency for the formation of congruently melting 1-1 complexes was clearly demonstrated.

Mixtures of hexafluorobenzene with N,N-dimethylaniline and several other similar amine donors were shown by Morcom et al (51) to exhibit, in every case, a single, well defined maximum at the mid-point of the mole fraction range indicative of 1-1 complex formation. These mixtures were studied in the liquid phase by U.V. spectroscopy (7) and the results interpreted in terms of a charge transfer interaction.

Systems of n-electron donors, for example tetrahydrofuran and triethylamine, with hexafluorobenzene have been investigated by Ott et al (52-54) who found no addition compound and only a simple eutectic. A comprehensive investigation of the system hexafluorobenzene + tetrahydropyran is reported here to complement other thermodynamic measurements made on the cyclic ether systems during the course of this work. Swinton et al (4) have investigated the phase diagrams for pentafluorobenzene with each of a series of six methyl substituted benzenes and several gave rise to incongruently melting compounds. Hall and Norcom (55) found two maxima in the solid-liquid phase diagram for pentafluorobenzonitrile + benzene. These measurements were seen as unusual in the light of previous work involving hexafluorobenzene with a variety of donors, where, if maxima were found to occur they did so singly at a mole fraction of 0.5. To extend this area of work further the systems pentafluorobenzonitrile + toluene, + p-xylene have been investigated and in both cases one maximum at mole fraction 0.5 and an incongruently melting compound were found.

6.2 THE FREEZING POINT CELL

The freezing temperatures of the mixtures studied were measured using a cell similar to that described by Duncan and Swinton (3). A diagram of the cell is shown in figure (6.2.1). The sample was stirred, with a reciprocating motion, by a helical nichrome wire stirrer driven by an externally mounted motor using a flexible coupling. Samples were introduced into the cell through the septum cap, using a hypodermic syringe fitted with a long needle. A four junction copper-to-constantan thermocouple was constructed from 30 s.w.g. thermocouple wire in a manner ensuring that each of the individual junctions would be exposed to different areas of the sample. The junctions were then encased in 'Araldite'.

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The thermocouple was calibrated by measuring the EMF generated when placed in a series of constant temperature baths, the temperatures of which were determined concurrently using a platinum resistance thermometer. The reference junction was submerged in a crushed ice/water mixture. The calibration values are shown in table (6.2.1). A graph of the deviation of the observed EMF from the value obtained for a standard thermocouple was plotted against the observed EMF and is shown in figure (6.2.2). Experimentally determined EMF's were then corrected to a standard value using this curve, enabling the temperature to be read directly from the standard thermocouple tables (56).

TABLE (6.2.1)

VALUES FOR THE CALIBRATION OF THE THERMOCOUPLE

E _{obs} /mV	E _{stand} /mV	$\Delta^{\underline{E}(\underline{B}_{obs}-\underline{E}_{stand})}$	T/K	Bath
-21.779	-21.868	0.089	77.651	Liquid Nitrogen
-12.749	-12.848	0.099	177.971	Melting Toluene
-3.733	-3.802	0.069	247.661	Melting CCl ₄
0.007	-0.001	0.007	273.146	Melting Ice
3.349	3.375	-0.025	294.557	Water
4.796	4.843	-0.047	303.556	Water

6.3 OPERATION OF THE APPARATUS

Before use the cell was thoroughly cleaned with chromic acid,

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FIG(6.2.2)

THERMOCOUPLE CALIBRATION CURVE



washed with de-ionised water followed by washing with acetone, and finally dried in an air oven. The thermocouple and stirrer were then inserted into the relevant Quickfit sockets and the whole cell flushed through with dry nitrogen immediately prior to use. Mixtures were made up in the cell, the weights of samples used being determined by difference weighings of the syringes. The minimum total volume of sample used was approximately 5 cm³, sufficient to ensure that every thermocouple junction was adequately submerged. Stirring was then commenced.

The cell was supported in a polystyrene bung and then lowered into a silvered Dewar vessel. Another Dewar vessel, filled with liquid nitrogen, was placed around the first vessel to act as a coolant. This arrangement gave the required slow, linear rate of cooling over the range of temperatures concerned. The Emf generated by the thermocouple was converted into a papertape output by a digital voltmeter (Solartron Type LM 1604), a data transfer unit (Solartron Type 3230) and a Facit papertape punch (Solartron). Readings were taken automatically every ten seconds until the stirrer ceased to function. A typical cooling run would last for a period of approximately two hours. The freezing curves were then plotted from the generated tapes by computer. A typical cooling curve, having three discontinuities, is shown in figure (6.3.1).

Because of the tendency of pentafluorobenzonitrile mixtures to exhibit marked supercooling at compositions containing very little of the second component, warming runs to attempt to

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overcome this problem, were also undertaken. The inherent difficulties of stirring encountered using this method gave results which are not of the highest precision, but compare favourably with the corresponding freezing runs. A stirred sample in the cell was initially frozen with liquid nitrogen and then the cell surrounded with a single Dewar vessel to give a slow, steady rise in temperature. Stirring was commenced as soon as possible. A temperature against time graph for the sample was then plotted as before.

6.4 PRESENTATION OF RESULTS

For the three systems studied the freezing temperatures, obtained from cooling and warming runs, and temperatures of any arrest points are given, together with the compositions of the samples, in tables (6.4.1-6.4.3). Results obtained from warming runs are indicated with an asterisk (*). The three solid-liquid phase diagrams obtained, are shown in figures (6.4.1-6.4.3). The unusual arrest points indicated for the system pentafluorocyanobenzene + p-Xylene, at high mole fractions of the fluorocarbon, are not without some uncertainty due to the afore mentioned problems of supercooling encountered in this region. The ideal curve for the system hexafluorobenzene + tetrahydropyran has been calculated and is shown in the appropriate diagram.

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TABLE (6.4.1)

EXPERIMENTAL FREEZING TEMPERATURES

Hexafluorobenzene + Tetrahydropyran

x _F	Freezing Temperature T/K	Eutectic Point T/K
1.0000	278.19	
0.9236	274.04	
0.8632	270.19	
0.7683	263.80	
0.6726	256.45	
0.5976	250.16	
0.5055	241.72	191.13
0.5011	242.39	
0.4137	233.27	
0.3633		191.55
0.3560	225.19	190.21
0.28 98	214.51	187.80
0.0707	207.28	
0.0000	225.72	

IDEAL FREEZING CURVE

x _F	Tfreezing/ K	x _p	T _{freezing} / K
1.0000	278.19	0,9000	272.5
0.8000	266.3	0.7000	259.7
0.6000	252.5	0.5000	244.4
0.4000	235.2	0.3000	224.3
0.2000	210.6	0.1000	190.6

EXPERIMENTAL FREEZING TEMPERATURES

Pentafluorocyanobenzene + Toluene

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	X _F	T _f /K	™ _K ∕K	3 rd Arrest Point/K
*	1.0000	275.91		
#	0.9762	275.07		
	0.9422	272.70		
	0.9220	271.91		
	0.8985	271.46	265.11	
	0.8553	268.66	265.11	
	0.8114		264.93	
	0.7993	266.45		
	0.7975	265.80	265.00	
	0.7899	265.80		
	0.7670	266.38		-
	0.7654	266.52	264.87	
	0.7480	266.72	264.87	
	0.7306	267.52	264.87	267.12
	0.7118	269.45		267.44
	0.7117	270.05	264.37	267.45
	0.6863	272.78		267.72
	0.6836	272.56		
	0.6531	275.32		
	0.6496			266.99
	0.6415	276.72		266.93
	0.6149	277.94		
	0.5586	281.11		

TABLE (6.4.2) - continued

x _F	T _f /K	T _E /K	3 rd Arrest Point/k
0.4905	281.82		
0.4327	281.11		
0.3198	274.62		
0.2853	270.91		
0.2364	264.18		
0.1047	235.31		
0.0886	232.18		
0.0486		178.40	890 1997 - 1997
0.0486		178,83	• • • • •
0.0207		179,26	
* 0.0207	181.85		
0.0207		178,83	
* 0.0115	186.12		
* 0.0115	180.95		
0.0115		178.66	
* 0.0000	180.95		
0.0000	180.99		

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TABLE (6.4.3)

EXPERIMENTAL FREEZING TEMPERATURES

Pentafluorocyanobenzene + p-Xylene

	x _F	T _f /K	т _е /к 3 ¹	rd	Arrest Point/K
	0.9785	275.71	261.69		
	0.9469	274.07	263.04		
	0.9067	271.75	263.04		
	0.8579	269.10	263.38		
	0.8507		264.41		261.29
¢.	0.8507	268.70			261.29
	0.8436	268.29	263.98		
	0.8170	268.09	264.08		
	0.8106		264.00		
	0.8049	266.69			262.08
	0.8035		263.91		-
	0.7832		263.91		
	0.7793	268.09	263.73		
	0.7727	266.35	264.00		
	0.7721	264.54			
	0.7611	261.62			261.01
	0.7598	267.37	264.16		
	0.7491	263.91			
	0.7424	264.28			
	0.7410	268.93	261.15		
	0.7369		261.37		
	0.7810	265.46			264.13
	0.7187	270.43	264.08		

TABLE (6.4.3) - continued

x _p	T _f /K	т _в /к	3 rd Arrest Point/K
0.7139	271.10	261.20	
0.7113	270.59		261.16
0.6728	275.05	261.37	
0.6670	274.84		261.16
0.6624	275.72	, ,	
0.6299	277.70		
0.5859	280.07		
0.5087	282.09		
0.5066	282.11		271.51
0.4715	281.96		271.81
0.465 6	282.05	271.71	<i></i>
0.4417	281.16	271.81	269.77
0.4389	281.21	269.24	272.03
0.4348	281.22	271.97	
0.4186	280.48	271.81	270.35
0.4164	280.34	269.77	271.97
0.3905	279.10	270.87	271.97
0.3630	277.52	271.81	270.87
0.3605	277.22	270.93	271.83
0.3303	274.67	271.04	271.81
0.3251	273.22	271.64	
0.3952	279.36	271.82	270.72
0.2894	271.59	271.12	
0.2852	271.64	271.10	
0.2557	273.64	270. 87	

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TABLE (6.4.3) - continued

x _F	T _f /K	T _E /K	3 rd Arrest Point/K
0.4602	281.79		
0.2248	275.95	271.12	
0.2010	276.91	270.72	
0.1789	278.39	271.12	
0.1226	280.42	270.54	
0.0986	282.11	271.10	
0.0907	281.82		
* 0.0597	283.33		
0.0597	283.33		,
* 0.0332	284.69		
0.0332	284.57		·
* 0.0166	285.39		
0.0166	285.02		- .
* 0.0000	286.38		
0.0000	285.92		
0.7446	265.08	261.08	
0.7481	268.56	264.35	
0.7536	268.09	263.95	
0.7573	268.16	264.41	
0 .7 618	267.76	261.01	
0.7702	266.42	263.73	
* 1.0000	275.91		

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FIG (6.4.1)

SOLID LIQUID PHASE DIAGRAM

Hexafluorobenzene + Tetrahydropyran



FIG (6.4,2)

SOLID LIQUID PHASE DIAGRAM





FIG (6. .3)

SOLID LIQUID PHASE DIAGRAM





6.5 CALCULATION OF THE FREEZING CURVE FROM THERMODYNAMIC DATA

At this stage in the work it is possible to check the thermodynamic consistency of the results obtained by the various techniques described in previous chapters. The data necessary for a calculation of the freezing curve of the system tetrahydropyran + hexafluorobenzene have been measured during the course of this work. A comparison of a set of calculated freezing points with the experimental values, reported here, can then be used as a sensitive check on the three techniques involved.

For equilibrium to exist between the solid and liquid phases

where T is the freezing temperature of the liquid and thus

$$\mathbf{P}_{\mathbf{F}}^{\mathsf{oliq}} + \operatorname{RT} \ln \mathbf{x}_{\mathbf{F}} \delta_{\mathbf{F}}[\mathbf{T}, \mathbf{P}, \mathbf{x}_{\mathbf{F}}] = \mathbf{P}_{\mathbf{F}}^{\mathsf{o}} \operatorname{solid}_{[\mathbf{T}, \mathbf{P}, \mathbf{P}]}$$

$$(6.5.2)$$

Rearranging leads to

$$\ln \mathbf{x}_{\mathbf{F}} \mathcal{S}_{\mathbf{F}[\mathbf{T},\mathbf{P}^{\bullet},\mathbf{x}_{\mathbf{F}}]} = - \underbrace{\mathcal{V}_{\mathbf{F}}^{\mathsf{oliq}}}_{\mathbf{F}[\mathbf{T},\mathbf{P}^{\bullet}]} - \underbrace{\mathcal{V}_{\mathbf{F}}^{\mathsf{osolid}}}_{\mathbf{RT}}$$

$$= \frac{-\Delta_{\beta}^{1} G_{m} [T, P^{\bullet}]}{RT} \qquad (6.5.3)$$

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Differentiation and integration of this equation leads to

$$\int_{0}^{\ln x_{p}} \int_{\mathbf{r}^{p}}^{\ln x_{p}} \int_{\mathbf{r}^{p}, \mathbf{r}, \mathbf{r}, \mathbf{r}}^{\mathbf{T}} = \int_{\mathbf{r}^{0}}^{\mathbf{T}} \frac{\Delta_{\mathbf{s}}^{1} H_{\mathbf{m}}[\mathbf{T}, \mathbf{r}^{p}]}{\mathbf{r}^{0} \mathbf{RT}^{2}} d\mathbf{T} \qquad (6.5.4)$$

and thus

$$\ln \mathbf{x}_{\mathbf{p}} \delta_{\mathbf{F}[\mathbf{T},\mathbf{p}^{\bullet},\mathbf{x}_{\mathbf{p}}]} = \frac{\Delta_{\mathbf{s}}^{1} H_{\mathbf{m}}[\mathbf{T},\mathbf{p}^{\bullet}]}{R} \left[\frac{1-1}{\mathbf{T}^{\circ}} \frac{1}{\mathbf{T}}\right] \quad (6.5.5)$$

Rearranging leads to

$$\mathbf{\bar{r}} = \frac{\mathbf{T}^{\circ} \triangle_{s}^{1} \mathbf{H}_{m}[\mathbf{T}, \mathbf{P}^{\bullet}]}{\triangle_{s}^{1} \mathbf{H}_{m}[\mathbf{T}, \mathbf{P}^{\bullet}]^{-R} \mathbf{T}^{\circ} \ln \mathbf{x}_{F} \delta_{F}[\mathbf{T}, \mathbf{P}^{\bullet}, \mathbf{x}_{F}]}$$
(6.5.6)

The ideal curve has been calculated from this equation by substituting a value for the activity coefficient, δ_F , of unity and solving for T for values between $x_F = 1$ and 0.1. These results are presented in table (6.4.1) and shown graphically in figure (6.4.1).

Noting that

$$\ln \vartheta_{\mathbf{p}} = \frac{\mathbf{g}^{\mathbf{E}}[\mathbf{T}, \mathbf{p}^{\mathbf{\Phi}}, \mathbf{x}_{\mathbf{p}}]}{\mathbf{R}\mathbf{T}} + (1 - \mathbf{x}_{\mathbf{p}}) \left(\frac{\partial}{\partial \mathbf{x}_{\mathbf{p}}} - \frac{\mathbf{g}^{\mathbf{E}}[\mathbf{T}, \mathbf{p}^{\mathbf{\Phi}}, \mathbf{x}_{\mathbf{p}}]}{\mathbf{R}\mathbf{T}} \right)_{\mathbf{T}} (6.5.7)$$

and assuming that the Gibbs free energy of mixing can be represented

by the equation

$$\frac{g^{E}}{RT} = x_{F} (1-x_{F}) \sum_{J=1}^{P} G_{J[T]} (1-2x_{F})^{J-1}$$
(6.5.8)

then

$$\ln \delta_{\mathbf{F}[\mathbf{T},\mathbf{P},\mathbf{x}_{\mathbf{F}}]} = (1-\mathbf{x}_{\mathbf{F}})^{2} \sum_{J=1}^{P} G_{J[\mathbf{T}]} (1-2\mathbf{x}_{\mathbf{F}})^{J-2} (1-2J\mathbf{x}_{\mathbf{F}}) \quad (6.5.9)$$

Integrating the Gibbs-Helmholtz equation

$$\frac{d}{dT}\left(\frac{G^{E}}{RT}\right) = \frac{-H^{E}}{RT^{2}} \qquad (6.5.10)$$

leads to

$$\frac{\mathbf{g}^{\mathbf{E}}}{\mathbf{R}\mathbf{T}}[\mathbf{T},\mathbf{P},\mathbf{x}_{\mathbf{p}}] = \frac{\mathbf{g}^{\mathbf{E}}[\mathbf{T}^{*},\mathbf{P},\mathbf{x}_{\mathbf{p}}]}{\mathbf{R}\mathbf{T}^{*}} + \frac{\mathbf{H}^{\mathbf{E}}}{\mathbf{R}}\left[\frac{1}{\mathbf{T}} - \frac{1}{\mathbf{T}}\right] \quad (6.5.11)$$

and use of equation (6.5.8) gives

$$\frac{G^{E}}{RT}[T, P^{\bullet}, x_{P}] = x_{P} (1-x_{P}) \sum_{J=1}^{P} \left(G_{J}^{*} + \frac{H}{R} \frac{J}{L} \left[\frac{1}{T} - \frac{1}{T^{*}} \right] (1-2x_{P})^{J-1} (6.5.12)$$

where the asterisk, *, indicates values measured at the experimental temperature, in this case 303.15 K. Similarly

$$\ln \delta_{\mathbf{F}[\mathbf{T}, \mathbf{P}^{\bullet}, \mathbf{x}_{\mathbf{F}}]} = (1 - \mathbf{x}_{\mathbf{F}})^{2} \sum_{J=1}^{P} \left(\mathbf{G}_{J}^{*} + \frac{\mathbf{H}_{J}}{\mathbf{R}}^{*} \left[\frac{1 - 1}{\mathbf{T}} \right] \right) (1 - 2\mathbf{x}_{\mathbf{F}})^{J-2} (1 - 2J\mathbf{x}_{\mathbf{F}})$$
(6.5.13)

From equation (6.5.5)

$$\frac{1}{T} = \frac{1}{T^{\circ}} - \frac{R \ln x_{F}}{\Delta_{g}^{1} H_{m}} - \frac{R \ln \delta_{F}}{\Delta_{g}^{1} H_{m}}$$
(6.5.14)

and thus

$$\frac{1}{T} = \frac{1}{T^{\circ}} - \frac{R \ln x_{F}}{\Delta_{s}^{1} H_{m}} - \frac{R(1-x_{F})^{2}}{\Delta_{s}^{1} H_{m}} \sum_{J=1}^{P} G_{J}^{*} (1-2x_{F})^{J-2} (1-2Jx_{F})$$

$$(6.5.15)$$

$$- \left[\frac{1}{T} - \frac{1}{T^{*}}\right] \frac{(1-x_{F})^{2}}{\Delta_{s}^{1} H_{m}} \sum_{J=1}^{P} H_{J}^{*} (1-2x_{F})^{J-2} (1-2Jx_{F})$$

Rearranging gives

$$\frac{1}{T} \left[1 + \frac{(1-x_{\rm F})^2}{\Delta_{\rm s}^1 H_{\rm m}} \sum_{\rm J=1}^{\rm F} H_{\rm J}^* (1-2x_{\rm F})^{\rm J-2} (1-2Jx_{\rm F}) \right] = \frac{1}{T^{\circ}} \frac{R \ln x_{\rm F}}{\Delta_{\rm s}^1 H_{\rm m}} + \frac{(1-x_{\rm F})^2}{\Delta_{\rm s}^1 H_{\rm m}} \sum_{\rm J=1}^{\rm F} \left(\frac{H_{\rm J}^*}{T^*} - R G_{\rm J}^* \right) (1-2x_{\rm F})^{\rm J-2} (1-2Jx_{\rm F})$$

$$(6.5.16)$$

And thus the freezing point for any composition $x_{\mathbf{F}}$ is given by

$$\mathbf{T} = \frac{\Delta_{s}^{1} H_{m}}{R} + (1-\mathbf{x}_{p})^{2} \sum_{J=1}^{P} \frac{H_{J}}{R}^{*} (1-2\mathbf{x}_{p})^{J-2} (1-2J\mathbf{x}_{p})$$

$$\frac{\Delta_{s}^{1} H_{m}}{RT^{0}} - \ln \mathbf{x}_{p} - (1-\mathbf{x}_{p})^{2} \sum_{J=1}^{P} \left(G_{J}^{*} - \frac{H_{J}^{*}}{RT^{*}} \right) (1-2\mathbf{x}_{p})^{J-2} (1-2J\mathbf{x}_{p})$$
(6.5.17)

Values of the parameters, H_J^* and G_J^* , used in this analysis are reported in chapters 4 and 5 respectively, the value for the latent heat of fusion of hexafluorobenzene, 11590 J mol⁻¹, was obtained by Counsell et al (65). The results obtained are presented in table (6.5.1) and can be seen to be in good agreement with the experimental freezing curve. They are represented by the dotted line in figure (6.4.1)

• TABLE (6.5.1)

CALCULATED FREEZING CURVE

Hexafluorobenzene + Tetrahydropyran

x _F	t / K	x _F	т /К
0.99	277.63	0.94	274.76
0.89	271.75	0.84	268.61
0.79	265.33	0.74	261.90
0.69	258.31	0.64	254.54
0.59	250.56	0.54	246.34
0.49	241.84	0.44	237.01
0.39	231.78	0.34	226.10
0.29	219.85	0.24	212.88
0.19	204.96		

A key assumption of this analysis required that only pure hexafluorobenzene was precipitated upon cooling. The validity of this approach can be estimated by calculating the mole fraction of the solid phase supposing that solid phase solutions were formed. If the composition of the solid phase is denoted by z_{p} and the equilibrium between the solid phase mixture and the liquid phase, composition denoted by x_{p} , is considered then at equilibrium

$$\mu_{i}^{sol} = \mu_{i}^{liq}$$

$$T^{sol} = T^{liq} \quad (6.5.18)$$

$$P^{sol} = P^{liq}$$

Since the properties of both phases must satisfy the Gibbs-Duhem equation, then for the solid phase

$$\frac{(1-z_{\mathbf{p}})}{RT} \stackrel{d\mu_1^{\mathrm{sol}}}{\to} + \frac{z_{\mathbf{p}}}{RT} \frac{d\mu_2^{\mathrm{sol}}}{RT} = \frac{-H_m^{\mathrm{sol}}}{RT^2} dT + \frac{V_m^{\mathrm{sol}}}{RT} dp \quad (6.5.19)$$

and for the liquid phase

$$(1-\mathbf{x}_{\mathbf{F}}) \frac{d \mu_{1}^{\text{liq}}}{RT} + \frac{\mathbf{x}_{\mathbf{F}} d \mu_{2}^{\text{liq}}}{RT} = \frac{-H_{\text{m}}^{\text{liq}}}{RT^{2}} + \frac{V_{\text{m}}^{\text{liq}}}{RT} dp (6.5.20)$$

and since the two phases are at equilibrium

$$(1-z_{\mathbf{F}}) d\left[\frac{\mu_{1}^{1}}{RT}\right] + z_{\mathbf{F}} d\left[\frac{\mu_{2}^{1}}{RT}\right] = \frac{-H_{m}^{\text{sol}}}{RT^{2}} dT + \frac{V_{m}^{\text{sol}}}{RT} dp \quad (6.5.21)$$

Also considering the liquid phase

$$\frac{\mu_{i}^{\text{liq}}}{RT} = \frac{\mu_{i}^{\text{oliq}}}{RT} + \ln x_{i} \delta_{i} \qquad (6.5.22)$$

and thus at constant pressure

$$d\left[\frac{\mu_{i}^{\text{liq}}}{\text{RT}}\right] = \frac{-H_{i}^{\text{oliq}}}{\text{RT}^{2}} d\mathbf{T} + \frac{1}{\mathbf{x}_{i}} d\mathbf{x}_{i} + \left(\frac{\partial \ln \vartheta_{i}}{\partial \mathbf{x}_{i}}\right) \mathbf{T} d\mathbf{x}_{i} - \frac{H_{i}^{\text{E,liq}}}{\text{RT}^{2}}$$

$$(6.5.23)$$

combining equations (6.5.21) and (6.5.23) leads to

$$(1-z_{\mathbf{F}})\left(\begin{array}{c} -H_{1}^{o\,liq}d\mathbf{T} & -\frac{1}{(1-x_{\mathbf{F}})} dx_{\mathbf{F}} + \left(\frac{\partial\ln\vartheta_{1}}{\partial x_{\mathbf{F}}}\right) dx_{\mathbf{F}} & -\frac{H_{1}^{E}d\mathbf{T}}{R\mathbf{T}^{2}} \end{array}\right) \\ + z_{\mathbf{F}}\left(\begin{array}{c} -H_{2}^{o\,liq} d\mathbf{T} + \frac{1}{x_{\mathbf{F}}} dx_{\mathbf{F}} + \left(\frac{\partial\ln\vartheta_{2}}{\partial x_{\mathbf{F}}}\right) dx_{\mathbf{F}} - \frac{H_{2}^{E}d\mathbf{T}}{R\mathbf{T}^{2}} \end{array}\right) \\ = \frac{-H_{m}^{sol}}{R\mathbf{T}^{2}} d\mathbf{T} \qquad (6.5.24)$$

Re-arranging this equation and noting that the latent heat of of fusion $\Delta_{\text{sol}}^{\text{liq}} H_{i} = H_{i}^{0,\text{liq}} - H_{i}^{0,\text{sol}}$

$$\frac{\mathrm{d}\mathbf{x}_{\mathbf{F}}}{\mathbf{x}_{\mathbf{F}}(1-\mathbf{x}_{\mathbf{F}})} \left\{ \begin{bmatrix} (1-\mathbf{z}_{\mathbf{F}}) \left(\frac{\partial \ln \aleph_{1}}{\partial \mathbf{x}_{\mathbf{F}}} \right)_{\mathbf{T}} + \mathbf{z}_{\mathbf{F}} \left(\frac{\partial \ln \aleph_{2}}{\partial \mathbf{x}_{\mathbf{F}}} \right)_{\mathbf{T}} \end{bmatrix} \right\}$$

$$= \left\{ (1-\mathbf{z}_{\mathbf{F}}) \bigtriangleup_{\text{sol}}^{\text{liq}} \mathbf{H}_{1}^{\mathbf{o}} + \mathbf{z}_{\mathbf{F}} \bigtriangleup_{\text{sol}}^{\text{liq}} \mathbf{H}_{2}^{\mathbf{o}} + (1-\mathbf{z}_{\mathbf{F}}) (\mathbf{H}_{1}^{\mathbf{E},\text{liq}} - \mathbf{H}_{1}^{\mathbf{E},\text{sol}}) \right\}$$

$$+ \mathbf{z}_{\mathbf{F}} (\mathbf{H}_{2}^{\mathbf{E},\text{liq}} - \mathbf{H}_{2}^{\mathbf{E},\text{sol}}) \mathbf{d}_{\mathbf{T}} \right\} \left\{ \mathbf{R}^{\mathbf{T}^{2}} \quad (6.5.25)$$

The activity coefficients of the components can be expressed in the form

$$\ln \delta_{1} = \left[\frac{G^{E}}{RT}\right] - \kappa_{F} \left(\frac{\partial}{\partial \kappa_{F}} \left[\frac{G^{E}}{RT}\right]\right) \qquad (6.5.26)$$

and differentiation leads to

$$\left(\frac{\partial \ln \delta_{1}}{\partial \mathbf{x}_{F}}\right)_{\mathbf{T},\mathbf{P}} = \left(\frac{\partial}{\partial \mathbf{x}_{F}}\left[\frac{\mathbf{G}^{E}}{\mathbf{R}\mathbf{T}}\right]\right)_{\mathbf{T},\mathbf{P}} - \left(\frac{\partial}{\partial \mathbf{x}_{F}}\left[\frac{\mathbf{G}^{E}}{\mathbf{R}\mathbf{T}}\right]\right)_{\mathbf{T},\mathbf{P}} - \mathbf{x}_{F} - \left(\frac{\partial^{2}}{\partial \mathbf{x}_{F}}\left[\frac{\mathbf{G}^{E}}{\mathbf{R}\mathbf{T}}\right]\right)_{\mathbf{T},\mathbf{P}}$$
(6.5.27)

Similarly

$$\ln \aleph_2 = \left[\frac{\mathbf{g}^{\mathbf{E}}}{\mathbf{RT}}\right] + (1-\mathbf{x}_{\mathbf{F}}) \left(\frac{\partial}{\partial \mathbf{x}_{\mathbf{F}}} - \left[\frac{\mathbf{g}^{\mathbf{E}}}{\mathbf{RT}}\right]\right)_{\mathbf{T},\mathbf{P}}$$
(6.5.28)

and thus

$$\begin{pmatrix} \frac{\partial}{\partial \mathbf{x}_{\mathbf{F}}} & \ln \vartheta_{2} \end{pmatrix}_{\mathbf{T},\mathbf{P}} = \left(\frac{\partial}{\partial \mathbf{x}_{\mathbf{F}}} \begin{bmatrix} \mathbf{G}^{\mathbf{E}} \\ \mathbf{RT} \end{bmatrix} \right)_{\mathbf{T},\mathbf{P}} \begin{pmatrix} \frac{\partial}{\partial \mathbf{x}_{\mathbf{F}}} \begin{bmatrix} \mathbf{G}^{\mathbf{E}} \\ \mathbf{RT} \end{bmatrix}_{\mathbf{T},\mathbf{P}} \end{pmatrix} + (1-\mathbf{x}_{\mathbf{F}}) \left(\frac{\partial}{\partial \mathbf{x}_{\mathbf{F}}}^{2} \begin{bmatrix} \mathbf{G}^{\mathbf{E}} \\ \mathbf{RT} \end{bmatrix} \right)_{\mathbf{T},\mathbf{P}}$$
(6.5.29)

Substitution of equations (6.5.27) and (6.5.29) into equation (6.5.25) leads to

$$\frac{(\mathbf{z}_{\mathbf{F}} - \mathbf{x}_{\mathbf{F}}) \, d\mathbf{x}_{\mathbf{F}}}{\mathbf{x}_{\mathbf{F}} (1 - \mathbf{x}_{\mathbf{F}})} \left\{ \begin{array}{c} 1 + \mathbf{x}_{\mathbf{F}} (1 - \mathbf{x}_{\mathbf{F}}) \left(\frac{\partial^2}{\partial \mathbf{x}_{\mathbf{F}}^2} \left[\frac{\mathbf{G}^E}{\mathbf{R}^T} \right] \right)_{\mathbf{T}, \mathbf{F}} \right\}$$
(6.5.30)
$$= \left\{ (1 - \mathbf{z}_{\mathbf{F}}) \Delta \lim_{sol} \mathbf{H}_1^o + \mathbf{z}_{\mathbf{F}} \Delta \lim_{sol} \mathbf{H}_2^o + (1 - \mathbf{z}_{\mathbf{F}}) (\mathbf{H}_1^{\mathbf{E}, \operatorname{liq}} - \mathbf{H}_1^{\mathbf{E}, \operatorname{sol}}) \right\}$$
$$+ \mathbf{z}_{\mathbf{F}} (\mathbf{H}_2^{\mathbf{E}, \operatorname{liq}} - \mathbf{H}_2^{\mathbf{E}, \operatorname{sol}}) \, \mathrm{d}\mathbf{T} \right\} / \mathbf{R}^T^2$$

And thus the gradient of the freezing curve $\frac{dT}{dx_F}$ can be

expressed in the form

$$\frac{dT}{dx_{F}} = \frac{RT^{2}(z_{F}-x_{F})\left\{1+x_{F}(1-x_{F})\left(\frac{\partial}{\partial x^{2}}\left[\frac{G^{E}}{RT}\right]\right)_{T,P}\right\}}{x_{F}(1-x_{F})\left\{(1-z_{F})\Delta_{sol}^{1iq}H_{1}^{o}+z_{F}\Delta_{sol}^{1iq}H_{2}^{o}+(1-z_{F})(H_{1}^{E,1iq}-H_{1}^{E,sol})\right\}}{+z_{F}(H_{2}^{E,1iq}-H_{2}^{E,sol})\right\}}$$
(6.5.31)

This equation can be approximated to the form

$$\frac{dT}{dx_{F}} = \frac{RT^{2} (z_{F} - x_{F})}{x_{F} (1 - x_{F}) \left\{ (1 - z_{F}) \bigtriangleup_{sol}^{1iq} H_{1}^{o} + z_{F} \bigtriangleup_{sol}^{1iq} H_{2}^{o} \right\}}$$
(6.5.32)

and thus the solid phase composition can be obtained by iterative solution of the equation

$$z_{\mathbf{F}} = x_{\mathbf{F}} \left\{ 1 + (1-x_{\mathbf{F}}) \frac{\left\{ (1-z_{\mathbf{F}}) \bigtriangleup_{sol}^{1iq} H_{1}^{o} + z_{\mathbf{F}} \bigtriangleup_{sol}^{1iq} H_{2}^{o} \right\} dT}{RT^{2}} \right\}$$
(6.5.33)

A value for the latent heat of fusion of tetrahydropyran

could not be found in the literature and an estimated value of 9000 J mol⁻¹, based on similar molecules, was used. Equation (6.5.33) was then solved iteratively for z_p as a function of the liquid composition x_p and the results presented in table (6.5.2). It can be seen that z_p is larger than unity for all values of x_p and regular, which is a fallacious result. Thus the original assumption that only pure hexafluorobenzene is precipitated on cooling is justifiable.

TABLE (6.5.2)

CALCULATED SOLID PHASE COMPOSITIONS Hexafluorobenzene + Tetrahydropyran

× _F	T /K	^z f
0.9	272.2	1.003
0.8	266.0	1.023
0.7	258.1	1.046
0.6	250.4	1.036
0.5	241.9	1.096
0.4	230.8	1.232
0.3	216.7	1.383
0.2	198.8	1.439

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CHAPTER SEVEN

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SPECTROSCOPIC TECHNIQUES

7.1 INTRODUCTION

Nuclear magnetic resonance spectroscopy is extremely sensitive to small changes in the electronic environment of a magnetic nucleus and is therefore perfectly suited as a tool for the investigation of weak molecular complexes. Studies employing this technique have been conducted in addition to thermodynamic investigations as an aid to probe the structure and composition of the complexes formed by a series of cyclic ether electron donors with hexafluorobenzene.

Various workers in the past have obtained precise thermodynamic data for the formation of a wide variety of donor-acceptor type complexes in an inert solvent, as for example cyclohexane (71-80). Huggins et al (81) found that the chemical shift of a donor chloroform proton, used as the nmr probe, was largely dependent upon both the chloroform concentration and also upon the nature of the solvent, used as acceptor. This dependence was attributed to intermolecular associations between the solvent molecules and chloroform through hydrogen bonding.

Many problems have been encountered in both the measurement and interpretation of the complexing interaction. Homer et al (73) found that by varying the supposedly inert solvents they could obtain widely differing values for the calculated equilibrium constant, in some cases obtaining apparent negative results. Carper et al (75) found that a complex was formed between the tri-nitro-benzene used as a proton acceptor and carbon tetrachloride used as an inert solvent and report an equilibrium constant of 0.091 /mol at 313 K for this process.

The cases cited above demonstrate the possible errors that may arise due to effects relating to the solvent environment. To try to overcome these difficulties and eliminate such effects it was decided to study the complexing in binary liquid mixtures of the two pure components. However the assumption usually made that dimerisation or non-1:1 complex formation was absent may no longer be valid due to the high relative concentration of the components.

7.2 EXPERIMENTAL

All samples were run on a Jeol 100 MHz high resolution spectrometer (Type JNM PS 100) at 299 ± 1 K unless otherwise specified. Mixtures were prepared immediately prior to spectroscopic analysis, by difference weighings from hypodermic syringes, and sealed into 5 mm Pyrex tubes to prevent evaporation. Tetramethylsilane, TMS, was used as an internal standard for proton resonance and the spectra calibrated using the 500 Hz sideband of TMS. Hexafluorobenzene was used as an external reference for the ¹⁹P fluorine nmr studies, a sideband technique again being used to calibrate the spectra. A total sweep width of 540 Hz was encompassed for both sets of measurements.

7.3 PRESENTATION OF RESULTS

Almost all workers in the past have measured the chemical shift of a proton directly involved in hydrogen bonding or complex formation. However the donor acceptor interaction postulated in this work involves the ether oxygen atom and the fluorocarbon acceptor and does not directly involve hydrogen bonding, although this may play a part in the stabilisation of the complex. The protoms used as the nmr probe are situated at a distance from the interaction site and the resulting chemical shifts are consequently small in comparison to those of other workers.

The ¹H nmr spectra of tetrahydropyran and tetrahydrofuran at high resolution consist of two multiplets each with a band width of approximately 25 Hz and a sharp central absorption. The four protons adjacent to the oxygen atom, H^{α} , give rise to the resonance at lower field which was observed to be a function of the concentration of the cyclic ether donor. Although remote from the interaction centre the resonant position of the remaining protons, H^{β} , was also observed to be a function of the concentration of the ether donor. This shift in contrast to the former, was observed to be to lower field.

The chemical shift of both peaks for the system tetrahydrofuran + hexafluorobenzene was measured relative to the absorption of pure cyclic ether, at three temperatures, over the whole range of mole fraction. These value are reported as \triangle obs H^{α} and \triangle obs H^{β} in table (7.3.1) and shown in figures (7.3.1) and (7.3.2). In this work the usual convention of representing shifts to lower field as negative values is observed throughout. Proton nmr investigations of the system tetrahydropyran + hexafluorobenzene were conducted in a similar manner and the results presented in table (7.3.2) and figure (7.3.3).

To ensure that the observed results are not simply due to dilution effects cyclohexane, assumed for the purposes of this experiment to be a non-interacting solvent, was added to several of the mixtures studied with no measureable deflection of the original absorptions.

Hexafluorobenzene displays a single sharp peak in the fluorine nmr produced by the six equivalent fluorine atoms attached to the aromatic ring. The chemical shift of this absorption as a function of composition is presented in table (7.3.4). Addition of cyclohexane as before resulted in comparatively large displacements of the fluorine resonance. This dilution shift of hexafluorobenzene as a function of composition is presented in table (7.3.5). From these two sets of data the corrected chemical shift of the fluorocarbon resonance due simply to complexing interactions was calculated over the entire range of mole fraction and presented in table (7.3.6) and figure (7.3.5).

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PROTON NMR CHEMICAL SHIFT VALUES

Tetrahydrofuran + Hexafluorobenzene

At 283.15 K

×ŗ	\triangle obs H ^{α} /Hz	\triangle obs H ^{β} /Hz
0.1533	2.6	- 2.4
0.2910	4.7	- 1.8
0.4434	7.1	- 2.8
0.6730	9.3	- 3.5
0.8721	11.8	

At 303.15 K

0.1533	4.5	- 0.4
0.4434	7.1	- 3.2
0.6730	10.0	- 4.7
0.8721	12.8	

At 323.15 K

0.1533	2.0	- 1.4
0.2910	4.3	- 1.8
0.4434	7.9	- 2.0
0.6730	8.5	- 3.4
0.8721	11.6	- 4.9

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TABLE (7.3.2)

PROTON NMR CHEMICAL SHIFT VALUES

Tetrahydropyran + Hexafluorobenzene

At 299 K

×F	\triangle obs H ^{α} /Hz		
0.0683	0.5		
0.1850	5.5		
0.2255	6.0		
0.2877	6.2		
0.4084	6.3		
0.5501	10.7		
0.7514	10.9		
0.8787	13.0		
0.9468	14.3		

TABLE (7.3.3)

FLUORINE NMR CHEMICAL SHIFT VALUES

Tetrahydropyran + Hexafluorobenzene

At 299 K

×F	\triangle obs /Hz	× _F	\triangle obs /Hz
0.0683	- 219.5	0.1850	- 191.5
0.2255	-180.5	0.2877	- 167.2
0.4084	- 145.0	0.5501	- 101.0
0.6410	- 91.3	0.7514	- 73.0
0.8787	- 50.5	0.9468	- 35.2

TABLE (7.3.4)

DILUTION SHIFT OF HEXAFLUOROBENZENE

Cyclohexane + Hexafluorobenzene

At 299 K

* _F	∆obs /Hz	× _F	\triangle obs /Hz
0.0828	- 332.5	0.1958	-272.0
0.4221	- 178,9	0.5262	- 147. 0 ·
0.6437	- 109.3	0 .7 85 8	- 63.7

TABLE (7.3.5)

FLUORINE NMR CORRECTED CHEMICAL SHIFT VALUES

Tetrahydropyran + Hexafluorobenzene

At 299 K

x _F	🛆 calc /Hz	x _P	\triangle calc /Hz
0.000	140	0.1000	110
0.2000	85	0.3000	65
0.4000	48	0.5000	32 .5
0.6000	18	0.7000	6
0.8000	- 5	0.9000	- 16.5
1.0000	0	•	

FIG (7·3·1)

PROTON NMR CHEMICAL SHIFTS

Hexafluorobenzene + Tetrahydrofuran

ΔH^{α}



FIG (73·2)

PROTON NMR CHEMICAL SHIFTS



FIG (7·3·3)

PROTON NMR CHEMICAL SHIFTS

Hexafluorobenzene + Tetrahydropyran

 ΔH^{α}

· 🛆 obs/Hz



FIG (7·3·4)



FIG (7·3·5)

CALCULATED FLUORINE NMR CHEMICAL SHIFTS



7.4 INTERPRETATION OF RESULTS

The proton nmr results presented in the previous section indicate that the dominant contribution to the observed chemical shifts arises from magnetic anisotropy effects. If the spectra were to be predicted solely on the basis of a complexing interaction due to electron donation then it would have been expected that the H^{α} protons would experience a small shift to lower field with no observable change of the resonance position of the H^{β} protons.

FIG (7.4.1)



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In figure (7.4.1) is a schematic representation of a possible structure of the envisaged complex with the magnetic field generated by the aromatic ring superimposed. Since the contribution from the magnetic anisotropy to the H^{∞} protons would be an increase of the shielding on the respective nuclei then the observed high field shift is a direct consequence of ring current effects which in this case are the dominant force. Very similar results have been observed by Schneider (77) when using aromatic solvents. The smaller low field shift of the $H^{ar{b}}$ protons of tetrahydrofuran perfectly fits this interpretation, their greater distance from the aromatic ring being responsible for the low value of the deshielding effect. Tetrahydropyran shows only a broadening of the peak generated by the H^{β} protons on dilution with hexafluorobenzene since two of these protons are at a much greater distance from the aromatic ring and less affected by the ring current.

A variation of chemical shift with temperature is good evidence for the existence of a complexing interaction. The results obtained for the tetrahydrofuran system shown in figures (7.3.1) and (7.3.2) are ambiguous and the scatter involved is larger than any temperature coefficient. This although suggesting that complexing is weak is not totally unexpected since the temperature coefficients of other thermodynamic properties of the same system reported in this work are also small.

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After correcting for the large dilution shift in the 19 F nmr spectra of hexafluorobenzene mixtures, possibly caused by self association of the aromatic species, the net result, with tetrahydropyran, is a positive shift. This, although small in comparison with the dilution shift, is nevertheless large in comparison with the proton nmr results and in the direction predicted if behaviour as an electron acceptor in the proposed complex is as supposed. On dilution with the cyclic ethers the single sharp peak of the hexafluorobenzene resonance remains as a singlet indicating that the equivalence of the six fluorine atoms is unchanged and that the ether oxygen atom has interacted perpendicularly to the plane of the ring.

7.5 ULTRA VIOLET SPECTROSCOPY

Many workers in the past (6) have reported the existence of charge transfer interactions based on evidence obtained from U.V. spectroscopy. Characteristic absorption bands are usually associated with this type of interaction.

A preliminary investigation, using an Hitachi model 340 U.V. recording spectrophotometer, failed to reveal any new absorptions. However a weak absorption band may have been masked by the intense fluorocarbon absorption.

CHAPTER EIGHT

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DISCUSSION OF RESULTS

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8.1 THE EXCESS VOLUME OF MIXING

It was stated early in this work that large positive values for the thermodynamic excess functions are usually characteristic of weak unlike interactions. Large negative deviations are synonymous with strong complexing interactions. However it is often difficult to estimate the strength of the intermolecular forces from the sign and magnitude of the excess volume of mixing. The partial molar volumes of the components for example are an important contributory factor to the experimentally determined volume change. Large positive deviations from ideality are often observed if the molecular packing geometry in the mixture is very different to that in the pure components.

Shown in figure (8.1.1) is a plot of the excess volume of mixing, at equimolar composition, as a function of the ring size of the cyclic ether with the three components hexafluorobenzene, cyclohexane and benzene. A cursory examination would indicate that the fluorocarbon interacts the least strongly with the cyclic ethers, but a substantial increment of this total volume change arises from a non-specific "physical" interaction of the type discussed in chapter one, between a fluorocarbon and a saturated hydrocarbon.

To estimate this contribution, Gaw and Swinton (64) have used, as a non-complexing reference, the system cyclohexane +

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hexafluorobenzene. In this work, this system has been used for comparison with hexafluorobenzene + tetrahydropyran, and cyclopentane + hexafluorobenzene used as reference for the system tetrahydrofuran + hexafluorobenzene. Both reference systems are shown in figure (3.14.3).

The specific "chemical" interaction can now be estimated by simple subtraction of the excess volume change on mixing of the appropriate reference system from the experimentally determined results for the cyclic ethers. Comparison of the values obtained at equimolar composition for the five and six membered ring species, of the order of $1.25 \text{ cm}^3 \text{ mol}^{-1}$ and $1.1 \text{ cm}^3 \text{ mol}^{-1}$ respectively, with those values for the corresponding cyclic ether with benzene apparently indicates that the interaction weakens on changing to the aromatic fluorocarbon. However it is known that pure hexafluorobenzene, in the liquid state, is to some extent structured (97), and this effect is reflected in the large dilution shifts in the ¹⁹F nmr. How this structure is purturbed on dilution with various species has a considerable influence on the excess volume change.

The most conclusive evidence of a specific interaction from these measurements is demonstrated by the series formed by successive substitution of tetrahydrofuran. The size of the volume change decreases in the order 3-methyl THF > THF > 2-methyl THF > 2,5-dimethyl THF. It is well established that addition of a methyl group to an electron donor can enhance its effectiveness by increasing the electron density at the donating centre and

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lowering the ionisation potential and also increasing the size of the dipole moment. However the 3-position of the ring is too distant from the nucleophile to exert any positive influence in this respect and so, as observed, 3MTHF and THF give almost identical results. The slightly increased volume change using the substituted ether may possibly be due to an increased steric hindrance. Addition of a methyl group at the 2-position, close to the nucleophile, would be expected to exert a strong positive influence on the interaction and this is reflected in the reduced volume change on mixing. The di-substituted ether gives rise to the smallest observed change of this series, complementary to a complexing interaction.

Furan, although a cyclic ether, is fundamentally dissimilar to the saturated ethers so far discussed since it possesses a degree of aromatic character. The lone pair electrons, delocalised around the ring, are less readily available for interaction as an n-donor and it is probable that π - π interaction produces the smallest observed volume change in this work.

The temperature derivative $(\partial v^E / \partial T)_p$ is shown in table (3.14.21) and is seen to be predominantly small, but positive. Since the contribution to v^E due to complex formation might be expected to decrease with increasing temperature, this result can be interpreted as tentative evidence for a specific interaction. Several systems have however been reported in the literature with a negative value for $(\partial v^E / \partial T)_p$ but with much other evidence for complex formation.

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FIG (8.1.2)

RESULTS OF MURRAY AND MARTIN (19) at 298-15 K



Murray and Martin (19,20,48) have studied the interaction between aliphatic ethers and hexafluorobenzene, their results for the excess volume of mixing are reproduced graphically in figure (8.1.2). In accord with the cyclic ethers these are ambiguous and similarly would not, in the absence of supporting evidence, indicate complexing.

8.2 THE EXCESS ENTHALPY OF MIXING

While the excess volume results discussed in the previous section show trends that can be interpreted in terms of a complexing interaction, they all exhibit positive deviations from ideality and as such are somewhat inconclusive. Shown in figure (8.2.1) is a plot of the excess enthalpies of equimolar mixtures with hexafluorobenzene of the cyclic ether as a function of the size of the ring. Also displayed for comparison are the values obtained by other workers using benzene and cyclohexane. The strength of the interaction is clearly demonstrated by these results. Again the same approach of removing the large positive "physical" term from the interaction, by comparison with a suitable reference system, enables an estimate to be made of the strength of the complex. A close analogue of tetrahydropyran is for comparison purposes cyclohexane and the enthalpy of mixing diagram of hexafluorobenzene + cyclohexane is shown in figure (4.7.8). The specific "chemical" interaction obtained by simple subtraction of this value for the equimolar mixture from the experimental result for hexafluorobenzene + tetrahydropyran gives a value of the order of -1700 J mol^{-1} .



EXCESS ENTHALPY OF MIXING AT $X_F = 0.5$



An interesting feature of both figures (8.2.1) and (8.1.1) is the reversal, on increase of ring size, of the trend in the magnitude of the excess property replacing benzene by hexafluorobenzene. The slopes of both plots for the systems containing cyclohexane and hexafluorobenzene are of the same sign and opposite to that of mixtures containing benzene. However comparison of the benzene/ether series with the corresponding results of Mclure et al (83) for the benzene/cyclic hydrocarbon systems, as in the case of the fluorocarbon mixtures, to give the specific "chemical" interaction yields a value that is little affected by changing the ring size of the ether but now has a slope in the same sense as both the hexafluorobenzene and cyclohexane systems.

The relative electron donor strengths of some of the cyclic ethers has been measured by Clemett (98) and Searles and Tamres (82) using chemical shift techniques and the order of increasing electron donor strength was found to be open chained ethers, THP, 1,4-dioxan < THF < TMO. The sets of results of both authors however all relate to hydrogen bond formation either in aqueous mixtures in the case of Clemett, or in deuterated methanol, CH_3OD , in the latter case. This may possibly be an explanation of the opposite trend to the above being observed in this work. Little resistance in the form of steric hindrance is likely to be offered to hydrogen bonding with either water or CH_3OD , which is less true for a donor-acceptor type complex between hexafluorobenzene and a cyclic ether.

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The dipole moments of the ethers, where known (32,25) follow a trend similar to that observed by chemical shift techniques. If electron donation is a contributory factor towards the stabilisation energy of the complex it might be useful to postulate from which hybridised oxygen orbital this may occur. Trimethylene oxide is a very strained ring system with bond angles of almost 90° which would require mostly p-orbital character. The remaining orbitals occupied by the lone pair electrons thus have a much greater proportion of s-character than the sp³ orbitals occupied by the lone pairs of tetrahydropyran. This results in their being less directional but much closer to the oxygen atom of the ether and consequently less available for donation. Tetrahydrofuran lies between these extremes.

Although no evidence of a charge transfer absorption has been found this does not entirely exclude the possibility that electron donation contributes a small proportion to the total energy of the complex. If this is justified the treatment outlined above may explain the increase of interaction as the ring size of the ether increases. The ionisation potentials of several of the compounds studied are shown in table (8.2.1) (32) and these values seem to parallel the trends indicated by the experimentally determined thermodynamic excess properties of mixtures with hexafluorobenzene. However the anilines, which are known to give a charge transfer absorption with hexafluorobenzene in the ultra violet (16), have much lower ionisation potentials than any of the ethers, whose values are not significantly lower than those of the cyclic hydrocarbons used as reference.

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TABLE (8.2.1)

IONISATION POTENTIALS

	• •
Component	I.P. / el
cyclohexane	9.8
cyclopentane	10.53
di-methyl ether	9.98
di-ethyl ether	9.6
trimethylene oxide	9.667
tetrahydrofuran	9.42
tetrahydropyran	9.25
1,4-dioxan	9.13
furan	8.89
N methyl aniline	7.32
NN diethyl aniline	6.99

In view of this evidence it now appears probable that dipole-induced dipole forces are mainly responsible for the interaction of the cyclic ethers with both benzene and hexafluorobenzene. Swinton et al (17) have measured the induced dipole moment of hexafluorobenzene in a series of aromatic hydrocarbons and give values in the range 0.3 - 0.4 D at 298 K. These values would have been expected to be much higher if donor-acceptor type interactions were mainly resonsible for the interaction.

Substitution of a nitrile group into hexafluorobenzene would be expected to enhance the interaction since it is both a powerful electrophile and produces a permanent dipole moment on the fluorocarbon. This was indeed observed and the excess enthalpy results, shown earlier, between pentafluorobenzonitrile and furan and the single measurement with trimethylene oxide are all more negative relative to the respective mixtures containing hexafluorobenzene, confirming this supposition.

As was found with the excess volume results the strength of the interaction between tetrahydrofuran and hexafluorobenzene is little changed on substitution of a methyl group into the 3-position of the ether ring. The excess enthalpy curve being marginally less negative over most of the range of mole fraction. The size of the enthalpy change was found to become more negative in the order 3-MTHF > THF > 2,5-DiMTHF > 2-MTHF. In the liquid phase 2,5-dimethyl tetrahydrofuran is a mixture of the cis and trans isomers. A possible explanation of the weaker interaction of the di-substituted ether is the interference caused by one of the methyl groups of the trans isomer, which is relatively close to the interaction site.

The excess heat capacity, C_p^E , obtained by simple interpolation of the enthalpy curves, is small but almost exclusively positive. An increase of temperature would be expected to weaken any complexing interaction leading to a more positive enthalpy change and a positive excess heat capacity. Thus this result may be interpreted as further supporting evidence of complex formation.

Murray and Martin (45) found that the enthalpies of mixing of a series of aliphatic ethers with hexafluorobenzene were all positive, these curves have been shown in figure (4.7.1). Only the positive excess heat capacity in this case gives any direct evidence of a specific interaction.

8.3 THE GIBBS FREE ENERGY OF MIXING

All of the systems studied gave small but positive values for the excess Gibbs function, the trend closely paralleling those for the heats and volumes reported earlier. If the assumption of the usual non-specific fluorocarbon-hydrocarbon interaction being large and positive is valid then these results yield strong ewidence of complex formation in the hexafluorobenzene/ cyclic ether series. Gaw (84) has reported a value for G^E at 303.15 K for the equimolar mixture cyclohexane/hexafluorobenzene of 801.4 J mol⁻¹. Tetrahydropyran is the closest ether analogue of cyclohexane and since it gave the strongest interaction of the non-substituted series was used for comparison purposes. if the difference in G^E on replacing cyclohexane by tetrahydropyran is assumed to be entirely due to complex formation then it is possible to calculate a value of the association constant for this process.

The difference in G^E between the two systems when mixed with hexafluorobenzene was found to be 776 J mol⁻¹. Using a "non-ideal" associated solution treatment, developed by Saroleo-Mathot (85), an equilibrium constant of 2.0, on a mole fraction scale, was calculated for the interaction. The treatment however required the further assumption that the system behaved as an "ideal" ternary mixture. This perhaps is a drawback of the model since it is probable that a degree of hexafluorobenzene selfcomplexing is present in solution. The treatment is not well suited to such comparatively weakly interacting systems in view of the assumptions involved, but it at least enables an estimate to be made of the strength of the interaction. The detailed calculations of this treatment have already been described by predecessors in this laboratory (24).

To complement the work of Andrews the free energy of mixing curve of the system hexafluorobenzene + 1,4-dioxan was determined at 303.15 K and is shown in figure (5.13.1). The value obtained for the equimolar mixture, 220 J mol⁻¹, is similar to the value obtained by Quitzsch (87) for the benzene + 1,4-dioxan system, 190 J mol⁻¹, at the same temperature. The excess enthalpy curves of Andrews (15) for the systems hexafluorobenzene + 1,4-dioxan and benzene + 1,4-dioxan are reproduced in figure (8.3.2). The former system can be seen to give a highly skewed result in the same sense as the free energy function. This is much less pronounced in the case of benzene and may be related to a combination of the disruption of the hexafluorobenzene selfcomplex and the ability of 1,4-dioxan to form 1:1 or 2:1 complexes with an acceptor molecule. 1,4-Dioxan does not possess a permanent dipole moment which may account for its weaker interaction than was observed for some of the other cyclic ethers investigated, localised dipoles associated with the ether oxygen may make a significant contribution to the interaction.

Since both the excess enthalpy and free energies of mixing

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FIG (8·3·1)

EXCESS ENTROPY CURVES



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of the cyclic ether/fluorocarbon systems have been determined during the course of this work, then use of the Gibbs-Helmholtz equation enables the excess entropy term to be calculated. These results are presented graphically in figure (8.3.1). The values are all predominantly negative which is further supporting evidence for the existence of complexing in solution.

The excess Gibbs free energies of some aliphatic ethers with hexafluorobenzene have been measured by Murray and Martin (20) and reproduced graphically in figure (8.3.3). As with the excess enthalpies and volumes of these systems the results are positive, not directly indicating complexing in solution. However the excess entropy is uniformly negative for the diethyl ether system which may indicate the presence of a weak interaction. They conclude that the role of the ether oxygen in these systems is largely masked by the usual unlike interactions between hexafluorobenzene and saturated hydrocarbons.

8.4 FREEZING POINT STUDIES

For a complex formed in the liquid phase to persist on freezing it must be strong enough to overcome the constraints of geometrical packing considerations. Swinton et al (11) found that pure hexafluorobenzene, in the solid phase, had the preferred orientation in which neighbouring molecules were oriented in a perpendicular manner but on complexing with benzene the solid structure consisted of alternate layers arranged in a face-toface orientation.

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RESULTS OF MURRAY AND MARTIN AT 298-15 K (20)



Goates et al (52) have completed a study of the hexafluorobenzene/tetrahydrofuran system and report only a simple eutectic at 163.50 K and $x_{\rm p}$ = 0.049 mole fraction. The freezing curve of mixtures of hexafluorobenzene with tetrahydropyran, giving the strongest interaction of the non-substituted cyclic ethers in the liquid phase, has been determined during the course of this work and again only a simple eutectic found. Negative deviations from ideality were however observed. The conclusion is therefore evident that the complex formed in the liquid phase is too weak to influence the structure of the solid phase to any degree. The same authors have also determined the freezing curve of the system hexafluorobenzene + 1,4-dioxan and report the formation of an incongruently melting solid addition compound. Since they did not find a compound formed in the case of the chemically similar 1,2-dimethoxyethane they suggest that packing geometry, not bonding, is more important in these systems.

As an extension of the work of Hall (55) who found a double maxima for the system pentafluorobenzonitrile + benzene, mixtures of this fluorocarbon with p-xylene and toluene have been studied in this work. As can be seen form figures (6.4.2) and (6.4.3) incongruently melting compounds were found using both of the latter compounds. The results obtained by Swinton et al (3) using hexafluorobenzene have been shown for comparison. It seems possible that the double maxima observed by Hall may simply be due to the formation of an incongruently melting compound near the peak of the interaction. The results of Hall are reproduced in figure (8.4.1). Weak electrostatic interactions

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of the aromatic hydrocarbons with the nitrile group may be responsible for these secondary compounds.

8.5 CONCLUSION

The studies undertaken during the course of this work suggest that a specific interaction occurs between hexafluorobenzene and the cyclic ethers which is stronger than that between benzene and the cyclic ethers. The evidence presented in previous chapters seems to indicate that a donor-acceptor type interaction is responsible for at least some of the observed properties of mixing. However the dominant contribution is more likely to be dipole-induced dipole type electrostatic forces.

Toczylkin and Young (93) have calculated the interaction parameters, using gas liquid critical temperatures, for mixtures of aliphatic and cyclic ethers with aromatic hydrocarbons and fluorocarbons. They conclude that the electron donors, 1,4-dioxan and tetrahydrofuran, give rise to an enhanced interaction with benzene in comparison with cyclohexane. They also suggest that the observed enhanced specific interaction with hexafluorobenzene is composed of three separate interactions;

- 1) association of the cyclic ether
- 2) the characteristic, non-specific, fluorocarbon-hydrocarbon interaction
- 3) a "specific "chemical" interaction between the lone pairs of the cyclic ether and the N electrons of hexafluorobenzene.

These conclusions are seen to be in accord with the results obtained in this work.

Kreglewski et al (94) have calculated the hypothetical thermodynamic excess functions of the system hexafluorobenzene + 1,4-dioxan using a hard sphere equation of state, neglecting any specific donor-acceptor interactions. The values they obtained for G^E and H^E were respectively 390 J mol⁻¹ and 840 J mol⁻¹ for the equimolar mixture at 298 K. The experimental values obtained by Andrews (15) and in this work for this system are much lower, again indicating the presence of a specific "chemical" interaction.

The strength of the complex as indicated by the determination of the equilibrium constant is weaker than amine/hexafluorobenzene mixtures which gave a value of K = 2.3 at 323 K (86) using the same treatment.

Only a lower limit can be given for the lifetime of the complex and this must be of the order of the nmr relaxation time, or longer, to produce the spectra reported earlier.

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SUMMARY

The excess enthalpies, volumes and Gibbs free energies of mixing have been measured for a series of cyclic ethers with hexafluorobenzene. These results indicate the presence of a specific interaction in these systems. Use of a stronger fluorocarbon acceptor, pentafluorobenzonitrile, was found to enhance this interaction.

The freezing curve of the system tetrahydropyran + hexafluorobenzene has been determined showing only a simple eutectic, indicating that the complex exists only in solution.

Nuclear magnetic resonance studies of some of these systems gave an insight into the possible orientation of the complex.

An improved static vapour pressures apparatus is described, using a liquid burette system for mixture preparation and incorporating a pressure transducer system.

The freezing curves and enthalpies of mixing of some aromatic hydrocarbon systems with pentafluorobenzonitrile have been measured. The results indicate relatively strong interactions between the components of these mixtures.