THERMODYNAMIC PROPERTIES OF SOME BINARY MIXTURES CONTAINING HEXAFLUOROBENZENE

A Thesis presented for the Degree of Doctor of Philosophy in the Faculty of Science of Leicester University by

David A. Armitage

Department of Chemistry,
The University,
Leicester,
LE1 7RH.
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STATEMENT

All the work presented in this thesis has been carried out by the Author in the laboratories of the Department of Chemistry, University of Leicester between October 1st, 1966 and August 31st, 1969, unless otherwise accredited.

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

Signed

David A. Armitage

September, 1969

DAVID A. ARMITAGE
ACKNOWLEDGEMENTS

I should like to express my sincere gratitude to my mother and father for the interest they have shown and the encouragement they have given me not only during this work but throughout my life.

I am also very appreciative of the interest and understanding which Dr. K.W. Morcom, who supervised this research, has shown. His continuous availability and willingness to consider any proposal was especially helpful.

I should like to acknowledge the assistance given to me by the technical staff of the department; in particular to Mr. C. Masters and his staff for guidance when designing equipment, to Mr. D. Hopkins for assistance with glass-blowing and to Mr. M.J. Kyle and his staff for general maintenance.

I should also like to thank my colleagues, notably Miss S. Dhabanananda, Messrs. B.L. Muju, D. McWilliams, T.G. Beaumont, R.W. Smith, A.W. Andrews and D. Waddington for their friendship, for the interesting discussions and for the information which they have given me.

Thanks are also due to Mr. A.W. Andrews, B.Sc., for typing this thesis.

I must also acknowledge the receipt of a Science Research Council Studentship for the past three years, without which this work would have been impossible.

(iii)
FOR MY FIANCEE

VALERIE
SUMMARY

A detailed investigation into the thermodynamic properties of binary mixtures containing hexafluorobenzene is described.

The excess enthalpies of mixing of hexafluorobenzene with eight amines and two hydrocarbons are presented and the excess heat capacity determined in the case of the amines.

Measurements were made using a twin version of the "Larkin-McGlashan" Calorimeter. The extension to a twin calorimeter together with the advantages which ensue are fully discussed.

An apparatus is described for the precise measurement of vapour pressure. The results obtained in the case of pure hexafluorobenzene are compared with other precise measurements and satisfactory agreement is found.

Computer programs have been developed to calculate the excess Gibbs Function of Mixing $G^E$ from experimental vapour pressure measurements. The computer programs were tested using reliable literature data and the results were judged to be satisfactory.

An apparatus to measure the volume change on mixing is described and the technique was checked by studying the benzene-cyclohexane system. The excess volume of mixing is reported for hexafluorobenzene + N,N-dimethylaniline.
Preliminary investigations are reported into the use of N.M.R. and solid liquid phase diagrams in interpreting the behaviour of specifically interacting media. The results of all the thermodynamic data are discussed in terms of complex formation and the possibility of considerable stabilisation by charge transfer forces is considered.

The work on aqueous solutions described in Appendix I centres around the properties of acetonitrile water mixtures. The excess volume of mixing for this system is presented at two temperatures as also are the partial molar volumes. The results are discussed in terms of solute - solvent and solvent - solvent interactions. Also presented is an analysis of the maximum density properties of aqueous solutions. Particular emphasis is placed upon alcohol water mixtures and visual correlations are explained thermodynamically.

In this department some studies of the behaviour of cadmium chloride in formamide were carried out by Dr. B.L. Muju. The work done by the present author in interpreting these data is summarised in Appendix II.
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c) Using the Function

\[
\chi^E \approx \sum_{i=1}^{n} x_i x_i A_i (x_i - x_i)^{i+1} / (1 - k(x_i - x_i)) \]

299

d) Using the Function

\[
\chi^E \approx \sum_{i=1}^{n} A_i \phi_i (x_i) \]

Where the \( \phi_i \) are suitably chosen

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CHAPTER ONE

INTRODUCTION
HEXAFLUOROBENZENE, the fully fluorinated analogue of benzene, was first prepared in 1947 (1), by treating hexachlorobenzene with bromine trifluoride. The resulting fluorochlorobromocyclohexane was then partially dehalogenated to form hexafluorobenzene in small yield. Subsequently, preparations can be divided into three basic groups notably those due to pyrolysis of short chain aliphatic halogen compounds (2 - 11), those due to partial dehalogenation of haloalyclics (1, 12 - 19) and those due to nucleophillic substitution in hexahalobenzenes (20 - 22). The most important synthesis commercially is that from hexachlorobenzene and potassium fluoride which gives hexafluorobenzene in 20 - 22% yield when the reactants are heated in an autoclave at 460 - 470°C for 20 hours. The other principal products are fluorochlorobenzenes of all degrees of fluorination.

The physical properties first reported for the compound differ markedly from those now accepted and indicate the low purity of initial samples. Samples of high purity have now been studied (2, 23, 24) and a table of some of the principal physical properties is given in Table (1.1.1).

The chemical properties of hexafluorobenzene are typically those of an aromatic compound having strongly electron withdrawing groups from the aromatic nucleus. The properties can be summarised into those arising from nucleophillic substitution at one or more ring positions (4, 26 - 30) and those due to the formation of weak intermolecular complexes with aromatic hydrocarbons, amines, ethers etc. (31 - 37).
### TABLE (1.1.1)

THE PRINCIPAL PROPERTIES OF PURE HEXAFLUOROBENZENE

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy of Combustion, $-\Delta U^0$/J·kg$^{-1}$</td>
<td>$1.31558 \times 10^9$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiling Point, $T_b$/K</td>
<td></td>
<td>353.45</td>
<td>353.41</td>
<td></td>
</tr>
<tr>
<td>Triple Point, $T_3$/K</td>
<td></td>
<td></td>
<td>278.249</td>
<td></td>
</tr>
<tr>
<td>Freezing Point, $T_f$/K</td>
<td></td>
<td></td>
<td></td>
<td>278.23</td>
</tr>
<tr>
<td>Critical Temperature, $T_c$/K</td>
<td></td>
<td>518.15</td>
<td>516.72</td>
<td></td>
</tr>
<tr>
<td>Critical Pressure, $P_c$/Pa·m$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td>$4.35 \times 10^6$</td>
</tr>
<tr>
<td>Density:</td>
<td></td>
<td></td>
<td></td>
<td>$\rho$/kg·m$^{-3}$</td>
</tr>
<tr>
<td>$T$/K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293.15</td>
<td></td>
<td></td>
<td></td>
<td>1618.16</td>
</tr>
<tr>
<td>298.15</td>
<td></td>
<td></td>
<td></td>
<td>1606.82</td>
</tr>
<tr>
<td>303.15</td>
<td></td>
<td></td>
<td></td>
<td>1595.47</td>
</tr>
<tr>
<td>Coefficient of Cubical Expansion, $\gamma$/degC$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td>$1.412 \times 10^{-3}$</td>
</tr>
<tr>
<td>T/K</td>
<td>ΔH_v/J·mol⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>3.575 x 10⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>315.96</td>
<td>3.168 x 10⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333.41</td>
<td>3.434 x 10⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>353.41</td>
<td>3.268 x 10⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>353.45</td>
<td>1.159 x 10⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T/K</th>
<th>B_p/m³·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>315.96</td>
<td>-2.104 x 10⁻³</td>
</tr>
<tr>
<td>333.41</td>
<td>-1.792 x 10⁻³</td>
</tr>
<tr>
<td>353.41</td>
<td>-1.498 x 10⁻³</td>
</tr>
</tbody>
</table>

For vapour pressures see Table (8.1.2)
Although the compound has only been available commercially for a short time it has found several uses in industry and has been investigated by the medical profession as a possible anaesthetic (38, 39). It has found use in the field of radiochemistry, (40 - 43) in counters, as the chemical is extremely stable to bombardment and irradiation. At the present time much work is being done to study the compound in the field of rocket and combustion technology. Initial work suggests that it may slow down the rate of burning of hydrocarbon fuels and therefore find a use as a petrol or diesel fuel additive (44, 45).

1.2 CHARGE TRANSFER COMPLEXES

Molecular complexes have been known for a long time and recently certain classes of these weak complexes have become known as "Charge Transfer Complexes". (46). They are characterised by spectroscopic absorption bands, which do not occur in either component of the complex. The new bands may be found almost anywhere in the electromagnetic spectrum and even magnetic resonance techniques may be needed to explore them fully. Frequently, however, the new absorption occurs in the visible or near ultraviolet region and it is here that the original work was done as occasionally colour changes were observed on mixing the components of the complex (47).

The stability of these complexes has been attributed to the transfer of charge from one species (the donor) to the other (the acceptor) and for 1:1 complexes can be represented by
This has been theoretically interpreted in terms of two wave functions

\[
\psi_1 = a \psi[A,D] + b \psi[A^- D^+], a \gg b \quad (1,2,2)
\]

and

\[
\psi_2 = a^* \psi[A^- D^+] + b^* \psi[A,D], a^* \gg b^* \quad (1,2,3)
\]

where \(\psi[A^- D^+]\) is the wave function of the ionic state, \(\psi[A,D]\) is the wave equation for a Van der Waals complex and \(a, b, a^*, b^*\) are constants.

The various arguments which have been presented as to which is the lower energy form have not been resolved but the absorption band is explained by transition between these states.

Benisi and Hildebrand (46) continued this argument and produced their famous equation

\[
\frac{1}{OD} = \frac{1}{K} \cdot \frac{1}{b \varepsilon} \cdot \frac{1}{a} + \frac{1}{b \varepsilon} \quad (1,2,4)
\]

relating optical density, \(OD\), to concentration, \(a\), which is often used to calculate the equilibrium constant, \(K\), of formation of a charge transfer complex.

However not all complexes of the donor/acceptor type have been interpreted in terms of charge transfer, as often complexing is so weak that no spectroscopic evidence is forthcoming. Thermodynamic evidence may indicate presence of complexes, for example, carbon tetrachloride and pyridines (48), where the excess heat capacity is positive, indicating complex formation. Many other
systems have been studied using thermodynamic/techniques when spectroscopic evidence for complex formation has not been available (for example hexafluorobenzene + benzene) and the results interpreted in terms of complex formation. Other systems have been studied both spectroscopically and thermodynamically to investigate complexing due to hydrogen bonding (for example acetone + chloroform (49) and 1 hydro perfluoro-n-heptane + acetone (50)) and the thermodynamic evidence has been found to be consistent with the other data available.

§1.3 ELECTRON DONORS

In Section 2 donor/acceptor complexes were briefly discussed in relation to their spectroscopic and thermodynamic properties and in Section 1 it was suggested that one of the chemical properties of hexafluorobenzene was as an electron acceptor.

Amines have been commonly used in the study of charge transfer interactions, since their properties can be widely varied by conjugation of lone electron pairs with aromatic rings. Other compounds which are commonly used as donors in charge transfer complexes are other Lewis bases, for example, ethers, thioethers, phosphines and aromatic hydrocarbons, especially those of higher molecular weight such as anthracene, pyrene and phenanthrene.

The characteristic strength of an electron donor is measured
by its ionisation potential (the energy required to remove an electron from the molecule). The ionisation potentials of the amines are normally lower than that of the comparable hydrocarbon and would be expected to form much more stable charge transfer complexes.

6.1.4 LIQUID MIXTURES

The thermodynamic properties of binary liquid mixtures are being investigated by many people in order to gain further insight into such properties as the structure of solvent mixtures (particularly aqueous solutions, eg (51)), the theories of solutions (52) and specific and non-specific interactions between molecules in the liquid phase (33).

Many donor/acceptor systems are suitable for study in this way and the necessary apparatus for investigating the thermodynamics of binary liquid mixtures has been developed over the last few years. Measurements of the excess enthalpy of mixing $H^E$, the excess Gibbs Function of mixing $G^E$, the excess volume of mixing $V^E$, and solid-liquid and liquid-liquid phase diagrams can all be obtained quickly and to a high degree of accuracy. With the aid of a suitable model, maybe only an equilibrium as in (1,2,1), the thermodynamic data may be used to reinforce the conclusions reached from other techniques which more closely examine the properties of the individual molecules.
When perfluorinated hydrocarbons became available it was discovered that many solutions involving them deviated markedly from predictions of theories such as Solubility Parameter Theory (53), whilst other solutions (54) agree quite well with the predictions of this theory (for example perfluoro-n-heptane + carbon tetrachloride).

As early as 1948 Scott was investigating this anomalous behaviour (55). More detailed study revealed that in general when a fluoro-carbon is mixed with a hydrocarbon the deviations from ideal behaviour will be large and positive and may even be so large that partial miscibility will occur (52 - 55).

However when Patrick and Prosser reported the formation of a 1:1 complex in the solid phase for hexafluorobenzene + benzene (31) interest was renewed and other similar interactions were soon reported (34, 37). The complex formation in this system contrasts markedly with the behaviour described above and with that of hexafluorobenzene with cyclohexane (56, 57). This conclusive evidence for complex formation in the solid phase has stimulated a number of workers to make precise thermodynamic measurements on this and related systems.

Duncan and Swinton (32) pointed out the strong nature of this interaction with hexafluorobenzene and aromatic hydrocarbons and studied the solid-liquid phase diagrams of six binary systems; hexafluorobenzene + benzene, toluene, p-xylene, mesitylene, cyclohexane and n-hexane. Stable 1:1 complexes were observed in the solid phase for the first four systems mentioned above and several complexes with incongruent melting points were observed with the...
fifth system, whilst in the case of n-hexane a simple eutectic was formed. It is difficult to infer from the behaviour of the solid phase, where packing is of prime importance, that complexing occurs in the liquid phase but the evidence for a strong interaction in the solid with aromatic hydrocarbons is consistent with a specific interaction.

Duncan, Sheridan and Swinton (38) studied the excess volume of mixing $V^E$ as a function of composition at 40°C for a number of hydrocarbons, namely cyclohexane, cyclohexene, 1,3 cyclohexadiene, benzene, toluene, p-xylene, mesitylene and cumene with hexafluorobenzene. From the results presented they concluded that complexing in the liquid phase increased as the electron donating power of the hydrocarbon increases.

Gaw and Swinton (36) studied the vapour pressures of mixtures of hexafluorobenzene with cyclohexane over a range of temperatures and compositions. The deviations from ideal behaviour were large and positive as would be expected from the earlier work on fluorocarbon solutions described above. The excess Gibbs Function derived from the vapour pressures was used to test the thermodynamic consistency of the data and reproduced exactly the calorimetric $H^E$ of Morcom et al. (37). Gaw and Swinton continued their vapour pressure studies with the hydrocarbon "donors" benzene, toluene and p-xylene (39). With benzene a double azeotrope occurs and the excess Gibbs Function $G^E$ shows a sign inversion (60). It is however principally negative with a minimum value of $\sim 100$ J.mol$^{-1}$. For the other two systems $G^E$ is negative throughout the composition range. They have interpreted their data in terms of an equilibrium and show values of the equilibrium constant.
and the enthalpy of formation of 1 mole of complex in the liquid phase.

Fenby and Scott have concentrated upon mixtures of fluoro-benzenes of the type $C_6H_{m}F_{6-m} + C_6H_nF_{6-n}$ (33,61) and in an earlier paper commented upon the surprising differences in excess enthalpy observed when benzene is mixed with hexafluorobenzene, pentafluorobenzene and 1,2,4,5 tetrafluorobenzene. They then extended their work considerably, though principally within the bounds of the general programme above and discussed their results in terms of three effects; physical non-specific contribution due to mixing a fluorocarbon with a hydrocarbon when no interaction occurs, a specific interaction due to charge transfer, and a specific interaction between matching pairs of H and F atoms on adjacent rings. They found that their data was not inconsistent with charge transfer but considered the specific interaction between matching pairs of H and F atoms on adjacent rings to be important. They also stated that the entire chemical contribution to $H^E$ may arise from electrostatic (quadrupole and dipole) interactions in which case there may be no stabilisation due to charge transfer.

With solutions of hydrocarbons and hexafluorobenzene the issue of charge transfer stabilisation remains open as there is no spectroscopic evidence to confirm the thermodynamic and structural evidence for this type of complex. However the report of a weak intermolecular complex between aniline and hexafluorobenzene (37) stimulated the work subsequently described with hexafluorobenzene and tertiary amines which proceeded in two directions, spectroscopically and thermodynamically.
Beaumont and Davis (35) observed charge transfer bands in the ultraviolet region for several amine electron donors but were unable to obtain such bands with hydrocarbons of similar electronegativity. From the charge transfer bands they obtained an equilibrium constant and a value for the enthalpy of formation of 1 mole of complex. These values will be compared with the thermochemical study in a later chapter of this thesis.

§1.6 A PRELIMINARY INVESTIGATION

A preliminary investigation of the likely properties of some binary liquid mixtures involving hexafluorobenzene was made by mixing approximately equimolar quantities of hexafluorobenzene with the following compounds at room temperature. The sign of $H^E$ is shown together with the approximate melting point of the solid complex, when one was formed.

<table>
<thead>
<tr>
<th>Component</th>
<th>Complex Form</th>
<th>Sign</th>
<th>M.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>aniline</td>
<td>solid complex</td>
<td>negative</td>
<td>$\sim 44^\circ C$</td>
</tr>
<tr>
<td>N,N-dimethylaniline</td>
<td>solid complex</td>
<td>negative</td>
<td>$\sim 42^\circ C$</td>
</tr>
<tr>
<td>pyridine</td>
<td>no solid complex</td>
<td>positive</td>
<td>-</td>
</tr>
<tr>
<td>triethylamine</td>
<td>no solid complex</td>
<td>positive</td>
<td>-</td>
</tr>
<tr>
<td>2,6 dimethylpyridine</td>
<td>no solid complex</td>
<td>negative</td>
<td>-</td>
</tr>
<tr>
<td>2,4,6 trimethylpyridine</td>
<td>no solid complex</td>
<td>negative</td>
<td>-</td>
</tr>
<tr>
<td>o-toluidine</td>
<td>solid complex</td>
<td>negative</td>
<td>$\sim 67^\circ C$</td>
</tr>
<tr>
<td>m-toluidine</td>
<td>no solid complex</td>
<td>negative</td>
<td>-</td>
</tr>
<tr>
<td>Compound</td>
<td>Complex Form</td>
<td>Result</td>
<td>Temperature</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----------------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>o-xylene</td>
<td>solid complex</td>
<td>negative</td>
<td>~38°C</td>
</tr>
<tr>
<td>m-xylene</td>
<td>no solid complex</td>
<td>negative</td>
<td>-</td>
</tr>
<tr>
<td>o-N,N-dimethyldimethylaniline</td>
<td>no solid complex</td>
<td>negative</td>
<td>-</td>
</tr>
<tr>
<td>m-N,N-dimethyldimethylaniline</td>
<td>solid complex</td>
<td>negative</td>
<td>~32°C</td>
</tr>
<tr>
<td>p-N,N-dimethyldimethylaniline</td>
<td>solid complex</td>
<td>negative</td>
<td>~41°C</td>
</tr>
</tbody>
</table>

From these results it was decided that initially the study should be centred around tertiary amines and comparison made between triethylamine, a group of pyridines and a group of N,N disubstituted anilines, the latter could also be studied spectroscopically for comparison at a later stage.
CHAPTER TWO

MATERIALS

In this chapter the purification of all the materials used in this investigation will be fully described, together with the apparatus used for both the purification and the determination of sample purity.
Several attempts were made at preparing a sample of high purity hexafluorobenzene, none of which proved entirely satisfactory. Commercially available hexafluorobenzene supplied by The Imperial Smelting Corporation was shaken with oleum for several hours, changing the acid frequently until the acid layer no longer became discoloured. The hexafluorobenzene was then washed with deionised water four times, shaking frequently each time, followed by drying with fresh phosphorus pentoxide. After filtration to remove the drying agent the filtrate was distilled using a metre long, high efficiency fractionating column of the type described by Ray (62) with a high reflux ratio of at least 50:1. The following fractions were collected from a 180 ml sample.

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>BOILING RANGE</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>76 - 79.5°C</td>
<td>20 (cm$^3$)</td>
</tr>
<tr>
<td>2</td>
<td>79.5 - 79.7°C</td>
<td>50 (cm$^3$)</td>
</tr>
<tr>
<td>3</td>
<td>79.7 - 79.7°C</td>
<td>50 (cm$^3$)</td>
</tr>
<tr>
<td>4</td>
<td>79.7 - 79.7°C</td>
<td>40 (cm$^3$)</td>
</tr>
</tbody>
</table>

These fractions were each examined by gas chromatography using a Perkin Elmer F11 instrument fitted with a DE 201 carbowax 1500 column. Each sample showed multiple peaks and appeared of low purity, not noticeably different from the starting material. The treatment with oleum had had little effect upon the material and distillation did not appear to be effective in separating the mixture.
A sample (Fraction 3 above) was re-distilled using a spinning band fractionating column and a middle fraction showed this procedure to be equally as ineffective as the fractionating column of the type described by Ray.

Swinton et al. (32) purified hexafluorobenzene by fractionally freezing the material obtained after the washing and distilling procedure described above. In order to obtain material of very high purity (99.95%) many cycles were necessary although tests carried out on Fraction 4 (above) showed that after five freezing cycles the impurities were much reduced.

Preparative gas chromatography is capable of yielding samples of high purity and a sample was prepared from the crude starting material using an Aerograph Autoprep Model A700 with a carbowax column. This produced a sample of high purity but the collection was inefficient with a volatile compound like hexafluorobenzene.

The Imperial Smelting Corporation made available to us their anaesthetic grade, which has a stated purity of 99.95% and was shown in subsequent measurements on its vapour pressure to have a purity certainly better than 99.9%. This material was used without further purification for all the measurements with hexafluorobenzene to be described.


\[ \text{2.2 EFFECT OF DISSOLVED GASES AND THE USE OF MERCURY SEALED}
\]

\[ \text{STORAGE AMPOULES.} \]

a) Chemical Effect of Dissolved Gas.

When air dissolves in some amines such as N,N-dimethylaniline a charge transfer complex is formed between the amine and oxygen (63). The formation is reversible and the yellow coloration due to complex formation is easily removed by bubbling nitrogen through the solution. It is also removed by degassing the liquid thoroughly, either by pumping hard on the frozen material or by vacuum distillation.

However this charge transfer complex with oxygen provides a path for decomposition of the amine. When the complex is exposed to sunlight, oxidation of the amine occurs and a characteristic blue coloration is formed. It would appear that the formation of the charge transfer complex is not so easily reversed when the amine is m-N,N-dimethyltoluidine as the yellow coloration could not be removed with this compound. It has however been stated that the heat of formation of these complexes is small and that their presence would not interfere with experimentally determined enthalpies of mixing (63). However it is desirable to avoid any possibility of this occurring by using effectively degassed liquids.

b) Physical Effect of Dissolved Gas.

Dissolved gases can also cause trouble by coming out of solution during the measurement of some property. This may be due either to reduced solubility in the mixture compared with the pure components or to reduced solubility at high temperatures.
This is particularly important in excess volume measurements as no correction can be applied but it is also significant in calorimetric measurements as evaporation of liquid into the vapour space created would occur as an additional process to that of mixing (64).

c) Mercury Sealed Ampoules.

These were designed in order that liquid samples could be safely stored for long periods of time in the absence of dissolved air. They were also designed so that liquid could be easily removed with a hypodermic syringe and suitable needle. The ampoules together with the filling device are shown in Fig (2.2.1).

The ampoules are filled by placing a cold trap around the bottom bulb of the ampoule which is connected to the variable take off head of the fractionating column. Frequently a vapour lock forms during the filling process, which can be removed by warming the ampoule to expand the affending vapour. When the desired quantity of liquid has been introduced, it is degassed by repeated freezing and thawing, then sealed by filling with mercury, whilst the material is frozen down, from a reservoir having a P.T.F.E. tap, placed immediately above the ampoule. When withdrawing liquid it is only necessary to ensure that the capillary tube stump remains covered with mercury to keep the liquids in an adequately degassed condition.
THE MERCURY SEALED AMPULES
AND FILLING APPARATUS

Fig (2-2.1)
9.2.3 Amines

a) N,N-dimethylaniline

"Analar" N,N-dimethylaniline was refluxed for seven hours with acetic anhydride under reduced pressure to remove any primary or secondary amines as involatile acyl derivatives.

\[ \text{N-H} + \text{Ac O} \rightarrow \text{N-Ac} + \text{Ac OH} \]

The mixture was then distilled under a reduced pressure of approximately 3000 N.m\(^{-2}\) using a fractionating column of the type described by Ray with a reflux ratio of about 50:1. The distillate was condensed in a solid carbon dioxide/acetone trap and initially consisted of acetic acid and acetic anhydride. The distillation continued using a slow nitrogen bleed and the N,N-dimethylaniline collected as a white solid in the trap.

This product was then redistilled through the column using a high reflux ratio in an atmosphere of nitrogen, under reduced pressure. The middle third was collected and redistilled as above, the small centre fraction was collected and stored in an ampoule. The sample was degassed by freezing and thawing and the ampoule sealed with mercury.

Gas chromatography showed no trace of impurity.

b) o-, m-, p-N,N-dimethyltoluidines

The best quality reagent grade materials were purified using the same method as described above for N,N-dimethylaniline. The o- and p-N,N-dimethyltoluidines were colourless whilst the
m-N,N-dimethyltoluidine was pale yellow and this coloration was not reduced during degassing. The compounds all showed traces of impurities which were identified as the other isomers but in each case this was less than 0.5%.

c) Aniline

"Analar" grade aniline was purified by drying with anhydrous potassium carbonate and fractionating the filtrate using the high efficiency column. A middle fraction b.p. 184°C was collected and redistilled in an atmosphere of nitrogen. A middle fraction from the second distillation was degassed and ampouled as described in Section 2.2. It was not used subsequently and its purity was not determined.

g) Pyridine

"Analar" pyridine was purified via the chlorozincate complex using a method similar to that described in Vogel (65). The starting material was dried with solid potassium hydroxide and filtered. Four hundred ml. of the filtrate was added to a solution of 340 g. anhydrous zinc chloride and 210 ml. concentrated hydrochloric acid in 1 litre of absolute ethanol. The precipitate formed was allowed to cool and then filtered and the residue washed sparingly with absolute ethanol. After the compound had been recrystallised from absolute ethanol the pyridine was liberated by adding an excess of aqueous potassium hydroxide. The resulting mixture was steam distilled, using deionised water in the steam generator, until the distillate was no longer alkaline to litmus. The distillate was then treated with excess potassium hydroxide pellets and the organic layer was separated. This layer was thoroughly dried with
m-N,N-dimethyltoluidine was pale yellow and this coloration was not reduced during degassing. The compounds all showed traces of impurities which were identified as the other isomers but in each case this was less than 0.5%.

c) Aniline

"Analar" grade aniline was purified by drying with anhydrous potassium carbonate and fractionating the filtrate using the high efficiency column. A middle fraction b.p. 184°C was collected and redistilled in an atmosphere of nitrogen. A middle fraction from the second distillation was degassed and ampouled as described in Section 2.2. It was not used subsequently and its purity was not determined.

d) Pyridine

"Analar" pyridine was purified via the chlorozincate complex using a method similar to that described in Vogel (65). The starting material was dried with solid potassium hydroxide and filtered. Four hundred ml. of the filtrate was added to a solution of 340 g. anhydrous zinc chloride and 210 ml. concentrated hydrochloric acid in 1 litre of absolute ethanol. The precipitate formed was allowed to cool and then filtered and the residue washed sparingly with absolute ethanol. After the compound had been recrystallised from absolute ethanol the pyridine was liberated by adding an excess of aqueous potassium hydroxide. The resulting mixture was steam distilled, using deionised water in the steam generator, until the distillate was no longer alkaline to litmus. The distillate was then treated with excess potassium hydroxide pellets and the organic layer was separated. This layer was thoroughly dried with
anhydrous potassium carbonate and the pyridine fractionated using the usual column and reflux ratio. A middle fraction was redistilled in a similar manner after drying with potassium hydroxide pellets and a middle fraction was collected, degassed and sealed in an ampoule. Gas chromatography failed to reveal any trace of impurity.

e) 2,6-dimethylpyridine and 2,4,6-trimethylpyridine

These compounds were purified by fractionation from potassium hydroxide pellets. A middle fraction was collected, refluxed for several hours over fresh potassium hydroxide pellets and then refractionated using the usual apparatus and collecting a middle fraction, which was degassed and sealed in an ampoule. In each case traces of impurity were present but they were judged to be below 0.5% in each case.

f) Triethylamine

This material was also purified by distillation from potassium hydroxide in a similar manner to the purification of the substituted pyridines. No trace of impurity was observed in the gas chromatograph.

2.4 HYDROCARBONS

The hydrocarbons used in this work were not given any purification. "Analar" grade benzene was used and reagent grade cyclohexane. The cumene (isopropylbenzene) was supposedly 99% pure.
whilst the isopropylocyclohexane was only 95 % pure and blackened mercury considerably when shaken with it.

$2.5 \text{ MERCURY}$

Two purification procedures were employed since the mercury for the precision manometer and cut-offs used in the vapour pressure measurements had to be of higher purity than that normally used in the laboratory.

The mercury used for ampoules, calorimetry and excess volume measurements was purified by filtering stock mercury and shaking the filtrate firstly with a solution of mercurous nitrate in 5% nitric acid, secondly with deionised water and thirdly with potassium hydroxide solution. After a number of shakings with deionised water the mercury was twice distilled in vacuum.

As stated above the mercury used for the vapour pressure measurements had to be of high purity for two reasons

(1) In order that published data for the density could be used when determining the pressures.

(2) To prevent any tendency to foul the surfaces of the menisci with oxidised impurities and to prevent any "tailing" on the surface of the manometers.

Mercury, purified as described above, was vigorously shaken with a 5% nitric acid solution containing mercurous nitrate until
the acid no longer became discolored, and vigorous washing with deionised water followed until the aqueous layer remained colourless. The mercury was then shaken with 10% potassium hydroxide solution until there was no discoloration of the aqueous layer. The product was washed three times with deionised water which remained colourless. The mercury was then dried in a current of air at high temperature followed by distillation under reduced pressure in a current of air. The product was then redistilled in a current of air under reduced pressure and finally given two vacuum distillations. Mercury purified in this way gave a stable foam lasting 15 - 20 seconds (66) when shaken with deionised water and showed no tendency to mark the surface of the storage bottle or manometer in use.
CHAPTER THREE

ENTHALPY AND ENERGY OF MIXING

(Design of Apparatus)
Larkin and McGlashan have published details of a calorimeter designed to measure accurately the energy change on mixing two liquids (67). The outstanding contribution of this work lies in the fact that their calorimeter combines the desirable features of easy loading with complete absence of vapour spaces.

Their calorimeter is shown in Fig (3.1.1) and consists of a glass vessel containing a partition and a pocket, which contains an electric heater. In use the vessel is filled with mercury and the liquids injected, with a hypodermic syringe, above the surface of the mercury but separated with a glass partition. Mixing is brought about by inverting the calorimeter in a direction such that liquids do not contact the ground glass joint, nor do they enter the capillary tube.

For such a calorimeter we can write the thermodynamic energy change

$$ \Delta U_{exp} = W_{el} + nW_s - \int_T^{T_f} C_f dT + q_V - \int_V P_{ext} dV $$  \hspace{1cm} (3.1.1)$$

where

- $W_{el}$ = electrical energy introduced

- $nW_s$ = work of stirring the calorimeter $n$ times

- $\int_T^{T_f} C_f dT$ = energy change required to raise the temperature of the calorimeter and the mercury and the liquids from $T$ to $T_f$.

- $q_V$ = energy lost to the surroundings
\[ \int_{V}^{V_f} P_{ext} \, dV \] 
work done by the calorimeter in expanding from \( V \) to \( V_f \) against the external pressure \( P_{ext} \).

Now
\[ \Delta U_{exp} = \Delta U_{mix} + \Delta U_{comp} \]  (3.1.2)

where \( \Delta U_{mix} \) is the thermodynamic energy change on mixing \( n_1 \) moles of component 0 with \( n_2 \) moles of component 2 at a pressure \( P \) and a temperature \( T \), and \( \Delta U_{comp} \) is the thermodynamic energy change on compressing the calorimeter and its contents from a pressure \( P \) to a pressure \( P_f \) within the calorimeter.

Now
\[ \Delta U_{comp} = \int_{P}^{P_f} \sum \left( \frac{\partial U}{\partial P} \right)_{T} \, dP \]
\[ = -\int_{P}^{P_f} \sum \left( P \left( \frac{\partial V}{\partial P} \right)_{T} + T \left( \frac{\partial V}{\partial T} \right)_{P} \right) \, dP \]  (3.1.3)

where the summation extends over the calorimeter and its contents.

If the pressure change is not too large (\(< 10 \, N/m^2\)) then we can assume \( \left( \frac{\partial V}{\partial P} \right)_{T} \) and \( \left( \frac{\partial V}{\partial T} \right)_{P} \) are constants, thus
\[ \Delta U_{mix} = \Delta U_{exp} + (P_f - P) \sum \left[ P \left( \frac{\partial V}{\partial P} \right)_{T} + T \left( \frac{\partial V}{\partial T} \right)_{P} \right] \]

Now if we assume \( PV = \) constant for the air in the bulb and writing the initial and final volumes of the air space as \( V_b \) and \( V_{af} \), we find
\[ P_{V_b} = P_f V_{af} \]  (3.1.4)

and
\[ \Delta V_{mix} = V_{af} - V_b = (n_1 + n_2) \, V^E \]  (3.1.5)

where \( V^E \) is the excess volume of mixing, and by combining equations
(4) and (5) above we find

\[ P_f - P = -P \frac{(n_1 + n_2)}{V_{af}} V^E \]  

(3.1.6)

Then

\[ \Delta U_{mx} = \Delta U_{exp} - \frac{P (n_1 + n_2)}{V_{af}} V^E \sum \left( \frac{dV}{dP} + T \frac{dV}{dT} \right) \]  

(3.1.7)

Larkin (64) has evaluated the second term on the R.H.S. of equation (7) and found, using reasonable values for the excess volume of mixing, the isothermal compressibility and the coefficient of thermal expansion of the mercury and the liquids but neglecting the glass that this term is negligible when \( V_{af} \) is adequate.

In Larkin's work the calorimeter was surrounded by a vacuum and as this implies \( P_{ext} = 0 \) equation (1) reduces to

\[ \Delta U_{exp} = w_{el} + n w_s - \int_T^{T_f} \rho_c dT + q \]  

(3.1.8)

They were able to work out suitable calibration procedures to correct for the heat losses and the work of stirring and also to eliminate the precise measurement of the heat capacity. The calorimeter was tested with many systems and was found to work well, being simple and convenient to use with systems having endothermic energies of mixing but not so convenient for exothermic energies of mixing. The method of calculating \( \Delta U_{exp} \) has not been described here as it is essentially equivalent to that described in the next section.
3.2 THE CALORIMETER USED BY MORCOM AND TRAVERS

This calorimeter closely resembles that described above and was primarily designed for measuring endothermic energies of mixing. The principal design difference (48, 68) was the use of an expanded polystyrene jacket which supported the calorimeter and also provided the necessary thermal insulation rather than the vacuum used in the original version. This further simplified the design of the apparatus and, as will be shown, does not seriously affect the accuracy of the results.

If we recall equation (3.1.1)

\[ \Delta U_{\text{exp}} = w_{s1} + n w_s - \int^T_T C_f \, dT + q - \int^V_V \rho_{\text{ext}} \, dV \]

the use of the polystyrene without a vacuum means that \( \rho_{\text{ext}} \neq 0 \) and that \( \int^V_V \rho_{\text{ext}} \, dV \) should be evaluated. However the volume change of the calorimeter on mixing is extremely small, thus

\[ \int^V_V \rho_{\text{ext}} \, dV = \rho_{\text{ext}} \, [V_f - V] \]

taking

\[ \rho_{\text{ext}} = 10^5 \, \text{N} \cdot \text{m}^{-2} \]

then if

\[ \int^V_V \rho_{\text{ext}} \, dV > 10^{-5} \, \text{J} \]

then

\[ V_f - V > 10^{-10} \, \text{m}^3 \]
Now the volume of the calorimeter \( v \approx 20 \text{ (cm)}^3 \) and taking the coefficient of cubical expansion of glass to be \( 3 \times 10^{-5} \text{ K}^{-1} \), then for a temperature change of \( 0.1 \text{ K} \),

\[
V_f - V = 3 \times 10^{-5} \times 10^{-1} \times 2 \times 10^{-5} = 6 \times 10^{-11} \text{ m}^3,
\]

thus even with a temperature rise of \( 0.1 \text{ K} \) the assumption is valid and since temperature rises are more often in the order of \( 10^{-2} \text{ K} \) we are justified in writing

\[
\Delta U_{\text{exp}} = w_{el} + n w_s - \int_{T}^{T_f} C_f dT + q \quad (3.2.1).
\]

The use of such a calorimeter will now be described, firstly to measure endothermic energies of mixing. The assumption that for a small temperature change, the heat capacity of the calorimeter + the mercury + the liquids + air space after mixing, \( C_f \), is constant will be made, and also that for a small change in temperature Newton's law of cooling is obeyed. Then equation (1) can be written

\[
\Delta U_{\text{exp}} = w_{el} + n w_s - C_f [T_f - T] - k \int_{T}^{T_f} [T^* - T] dt \quad (3.2.2)
\]

since Newton's Law states

\[
- \frac{dq}{dt} = k [T^* - T]
\]

where \( T^* \) is the surface temperature of the calorimeter. In order to determine \( \Delta U_{\text{exp}} \), three processes are carried out and from these it is possible to correct for or calculate the unknowns in equation (2).
a) The Mixing Process

A quantity of electrical energy $i_m^2 R t_m$ is introduced and the calorimeter is stirred n times to promote mixing and achieve a uniform temperature for both the contents of and on the surface of the calorimeter. For this process we can write

$$\Delta U_{\text{exp}} = i_m^2 R t_m + n w_s - C_f [T_f - T] - k \int_t^{t_f} [T^* - T] \, dt \quad (3.2.3)$$

The energy introduced electrically is intended to compensate for the energy change on mixing. Since the rate at which energy is introduced electrically is not equal to the rate at which energy changes on mixing we obtain a temperature vs. time plot of the form as shown in Fig (3.2.1a).

The quantity of energy $C_f [T_f - T]$ is represented by the area under the $T^*$ vs. time $(t)$ curve

i.e. $k \int_t^{t_f} [T^* - T] \, dt = \text{Area (ABC)} - \text{Area (CDE)} + \text{Area (EFGHK)}$

The required value $(T_f - T)$ is that temperature change which would occur if there were no energy losses. A line PQR can be drawn such that

$$\text{Area (QRF)} = \text{Area (ABC)} - \text{Area (CDE)} + \text{Area (EQP)} + \text{Area (FGH)}$$

Then PQR corresponds to the temperature change corrected for energy losses $(T_f - T)$.

b) The Stirring Process

The calorimeter is stirred n times and no energy is introduced
Fig (3.2.1a)

Fig (3.2.1b)
electrically, nor is it introduced by mixing. Thus

$$w_{el} = \Delta U_{exp} = 0,$$

for the stirring process, and equation (2) reduces to

$$n w_s = C_f [T_f' - T'] + k \int_t^{t_f} [T^* - T'] \, dt \quad (3.2.4)$$

The energy introduced on stirring is small and the temperature vs. time plot will be as shown in Fig. (3.2.1b).

The quantity of energy $C_f [T_f' - T]$ is represented by the area of $ABCDK$, i.e.

$$k \int_t^{t_f} [T^* - T'] \, dt$$

A line $PQR$ can be drawn such that

$$\text{Area (AQP)} + \text{Area (BCD)} = \text{Area (QRB)}$$

then $PQR$ represents the temperature rise which would be achieved without any energy losses, $(T_f' - T')$.

c) The Calibration Process

A quantity of electrical energy $\dot{\imath}_c R t_c$ is introduced into the calorimeter, which is simultaneously stirred $n$ times. As $\Delta U_{exp} = 0$ equation (2) reduces to

$$\dot{\imath}_c R t_c = -n w_s + C_f [T_f'' - T''] + k \int_t^{t_f} [T^* - T''] \, dt \quad (3.2.5)$$

The corrected temperature rise (if there were no energy losses) is calculated in exactly the same manner to that described for stirring, the only difference being that in this case

$$(T_f'' - T'') > (T_f' - T')$$
d) Calculation of $\Delta U_{\text{exp}}$

From the equations above we can easily calculate the quantity $\Delta U_{\text{exp}}$. From (3.2.4) we have

$$nw_s = C_f \left[ T_f' - T' \right]$$  \hspace{1cm} (3.2.6)

then using equation (6) in (5)

$$C_f = \frac{i_c^2 R t_c}{\left\{ \left[ T_f'' - T'' \right] - [T_f' - T'] \right\}}$$  \hspace{1cm} (3.2.7)

and substituting equations (6) and (7) into (3) gives

$$\Delta U_{\text{exp}} = i_m^2 R t_m - \frac{i_c^2 R t_c}{\left\{ \left[ T_f'' - T'' \right] - [T_f' - T'] \right\}} \left\{ \left[ T_f - T \right] - [T_f' - T'] \right\}$$  \hspace{1cm} (3.2.8)

It has been shown that the change in internal energy on mixing $\Delta U_{\text{mix}} = \Delta U_{\text{exp}}$ (Section 3.1 above) and if we know all the parameters in equation (8) we can calculate $\Delta U_{\text{mix}}$. The measurement of current, resistance and time are all standard techniques and will be described later. However equation (8) assumes that we know the temperature changes involved in each process. As this is not true we must consider the nature of the thermometer.

The Thermometer.

The thermometer used by Morcom and Travers was similar to that used by Larkin and McGlashan. A number of thermistors (semiconductor material having a large negative temperature coefficient of resistance) were attached to the surface of the calorimeter using Araldite (Messrs. Ciba (A.R.L.) Ltd., Duxford,
Cambridge). The thermistors were wired in parallel and formed one arm of a D.C. Wheatstone Bridge. If we assume that for a small temperature change, $\Delta T$, the change in resistance, $\Delta R$, is given by

$$\Delta R = R \alpha \Delta T$$

where $\alpha = R^{-1} \frac{\partial R}{\partial T}$ is the temperature coefficient of resistance, then, as will be proved later, the galvanometer current, $i_g$, due to a change in resistance $\Delta R$, is proportional to $R \alpha \Delta T$. Then provided the galvanometer provides linear deflection,

$$\Delta = \beta \Delta T,$$

where $\Delta$ is the galvanometer deflection and $\beta$ is constant, we can define a value of

$$\Delta = \beta [T_f - T]$$

and

$$\Delta' = \beta [T'_f - T']$$

and

$$\Delta'' = \beta [T''_f - T'']$$

(3.2.9).

(3.2.10).

(3.2.11).

The assumptions are valid for small temperature changes and, provided compensation is reasonably accurate, no serious error will be introduced.

Substituting equations (9), (10) and (11) into (8) gives

$$\Delta U_{exp} = \dot{i}_m^2 R t_m - \dot{i}_c^2 R t_c \frac{[\Delta - \Delta']}{[\Delta'' - \Delta']}$$

(3.2.12)

an equation for $\Delta U_{exp}$, in which the unknowns are all readily calculated.
Exothermic Energies of Mixing

Larkin (64) discussed the possibility of using Peltier devices in a calorimeter of the type he described and some success has been achieved (69). However when the thermodynamic energies of mixing are large, Peltier effect cooling proved to be inadequate and other methods must be studied. The Larkin-McGlashan Calorimeter can be used successfully without compensating and many measurements have been made in this way on the Morcom-Travers calorimeter now being described (48, 49). The theory for use with exothermic energies of mixing is identical to that described for endothermic energies except that no compensation can be made and therefore $i_M^2 R t_M = 0$. Then

$$- \Delta U_{\text{exp}} = \frac{\mu_c^2 R t_c \left[ \Delta - \Delta' \right]}{\left[ \Delta'' - \Delta' \right]}$$

(3.2.13)

63.3 THE NEED FOR A TWIN CALORIMETER

The calorimeters which have been described so far in this chapter are ideally suited for the measurement of endothermic energies of mixing. In the previous section it was explained that exothermic energies of mixing can be studied. However the errors in this procedure are quite large and the calorimeter is not so easy to operate.

The principal sources of error in exothermic energy measurements, carried out using a single calorimeter, arise from the galvanometer
being run on relatively low sensitivities and uncertainties due to extrapolation of the cooling curves, even using semi-log graph paper. However, with the null technique used for endothermic measurements the galvanometer can be run at higher sensitivity, provided that compensation is carefully carried out, and extrapolation of the cooling curves proves to be easy as the overall temperature change is small.

It was therefore decided to rebuild the calorimeter of Morcom and Travers using two similar calorimeter vessels, thermally insulated from one another, and also from the thermostat bath, using expanded polystyrene. A procedure has been worked out to enable the thermodynamic energy of mixing to be calculated from a series of electrical measurements, time measurements and from the temperature time plot obtained from the recording galvanometer.

The calorimeter vessels are of the same design as those described by Larkin and McGlashan, Fig (3.1.1), each being equipped with an electrical heater and carrying a thermometer on the surface.

The procedure for evaluating exothermic thermodynamic energy changes on mixing will now be discussed in relation to four processes studied with the calorimeters. Initially we shall assume that there are no heat losses, so that equation (3.2.2) reduces to

$$
\Delta U_{exp} = w_{e1} + nw_s - C_f [T_f - T]
$$

(3.3.1)

a) The Mixing Process

If we label the two calorimeters 0 and 2 and calorimeter 0
contains \( \eta_1 \) moles of \( A \) and \( \eta_2 \) moles of \( B \) to be mixed, then if the heat capacity of calorimeter 0 + contents (after mixing) is \( C_1 \), the work done in stirring calorimeter 0 \( n \) times is \( nW_{s1} \), and the change in thermodynamic energy for mixing and compression is \( \Delta U_{\text{exp}} \) (negative for exothermic energies of mixing) then from (3.3.1)

\[
- \Delta U_{\text{exp}} = -nW_{s1} + C_1 [T_{1f} - T_1] \tag{3.3.2}
\]

Calorimeter 1 contains a small amount of a pure liquid above the surface of the mercury in order that the heat is rapidly transferred to the surface. During mixing a quantity of electrical energy is introduced \( \left( i^2 R t_m \right) \) and the work of stirring \( n \) times is denoted by \( nW_{s2} \). Then if the heat capacity of calorimeter 1 + contents is \( C_2 \), we can write

\[
i^2 R t_m = -nW_{s2} + C_2 [T_{2f} - T_2] \tag{3.3.3}
\]

b) The Stirring Process

Neither electrical energy nor mixing energy is introduced so

\[
nW_{s1} = C_1 [T_{1f}' - T_1'] \tag{3.3.4}
\]

and

\[
nW_{s2} = C_2 [T_{2f}' - T_2'] \tag{3.3.5}
\]

c) The First Calibration

The heaters of the two calorimeters are connected in series and a current \( i_a \) is passed through them for a time \( t_a \) whilst the
calorimeters are stirred n times, then

\[ i_a^2 R_1 t_a = -n w_{s1} + C_1 [T_{1f}'' - T_1''] \]  \hspace{1cm} (3.3.6)

and

\[ i_a^2 R_2 t_a = -n w_{s2} + C_2 [T_{2f}'' - T_2''] \]  \hspace{1cm} (3.3.7)

d) The Second Calibration

The calorimeters are stirred n times and a quantity of electrical energy \((i^2_b R_2 t_b)\) is introduced into calorimeter \(2\), then

\[ n w_{s1} = C_1 [T_{1f}''' - T_1'''] \]  \hspace{1cm} (3.3.8)

and

\[ i_b^2 R_2 t_b = -n w_{s2} + C_2 [T_{2f}''' - T_2'''] \]  \hspace{1cm} (3.3.9)

By analogy with the previous Section (3.2) we can write for each calorimeter and process,

\[ T_{i+1} - T_i = \Delta_i \beta_i \], \hspace{1cm} i = 1, 2; \hspace{1cm} n = 0, \ldots, 3.

where \(\beta_1\) and \(\beta_2\) are constants and in general \(\beta_1 \neq \beta_2\) since the thermistors are not perfectly matched. The thermistors are arranged so that the observed deflections

\[ \Delta = \Delta_1 - \Delta_2 \], \hspace{1cm} \Delta'' = \Delta_1'' - \Delta_2'' \]

\[ \Delta' = \Delta_1' - \Delta_2' \], \hspace{1cm} \Delta''' = \Delta_1''' - \Delta_2''' \]

From equations (4) and (8)

\[ \Delta_1''' = \Delta_1' \]
thus

\[ \Delta'' - \Delta' = -(\Delta_{x''} - \Delta_{x'}) \]  

(3.3.10)

but substituting equation (5) into (9) using (10) and writing

\[ A_x = C_x / \beta_x \]

\[ A_x = -i_b^2 R_x t_a / (\Delta'' - \Delta') \]  

(3.3.11)

Now substituting equation (4) into (6) and (5) into (7), using the relation above and also

\[ A_1 = C_1 / \beta_1 \]

\[ \frac{i_a^2 R_1 t_a}{A_1} = \Delta_{r''} - \Delta' \]  

(3.3.12)

\[ \frac{i_a^2 R_2 t_a}{A_2} = \Delta_{r''} - \Delta' \]  

(3.3.13)

subtracting equation (13) from (12) and substituting for \( A_2 \)

\[ \frac{i_a^2 R_1 t_a - i_b^2 R_2 t_b}{A_2 (\Delta'' - \Delta')} = \frac{i_a^2 t_a (\Delta'' - \Delta')}{i_b^2 t_b (\Delta'' - \Delta')} \]  

(3.3.14)

Substituting equation (4) into (2) and (5) into (3) we can write

\[ \Delta_1 - \Delta_1' = -\Delta U_{\text{exp}} \]  

(3.3.15)

\[ \Delta_2 - \Delta_2' = \frac{i_m^2 R_2 t_m}{A_2} \]  

(3.3.16)

Subtracting equation (16) from (15) and substituting for \( A_1 \) and \( A_2 \) with (14) and (11) we can write
\[-\Delta U_{\text{exp}} = \frac{i_a^2 R_i t_a \{ i_b^2 t_b (\Delta - \Delta') - i_m^2 t_m (\Delta'' - \Delta') \}}{\{ i_b^2 t_b (\Delta'' - \Delta') - i_a^2 t_a (\Delta'' - \Delta') \}} \quad (3.3.17)\]

The currents, times and resistance in this formula can be readily obtained as will be described later but the assumptions made must be reconsidered. Initially we assumed that there were no energy losses and this will now be examined.

Consider the two diagrams Fig (3.3.1a) and Fig (3.3.1b), the former representing a section of the temperature time plot observed and the latter representing the temperature change in one of the calorimeters. In Fig (3.3.1b) a line PQR can be drawn such that

\[ \text{Area} (QRB) = \text{Area} (APQ) + \text{Area} (BCD) \]

as was described in Section (3.2), then the length PQR represents the temperature rise corrected for energy losses. From the nature of the thermometer the temperature rise is related to a hypothetical deflection, e.g.

\[ \Delta_1 = \beta_1 [T_{1f} - T_1] \]

and similarly, for any process in calorimeter 2

\[ \Delta_2 = \beta_2 [T_{2f} - T_2] \]

But \( \Delta_1 \) and \( \Delta_2 \) are functions of time and unless

\[ \Delta_1(t) = \beta_1 [T_{1f} - T_1] \]

at the same time, \( t \), as

\[ \Delta_2(t) = \beta_2 [T_{2f} - T_2] \]
**Fig (3.3.1a)**

**Fig (3.3.1b)**
then
\[ \Delta_1(t) - \Delta_2(t) \neq \Delta \]

where \( \Delta \) is the deflection which would be observed if there were no energy losses.

We must therefore arrange the conditions so that the theoretical temperature rises occur at the same time, as we do not sense the temperatures independently. The thermistors form two arms of a Wheatstone Bridge and, as we shall show later in this chapter, the galvanometer deflection is proportional to

\[ \beta_1 [T_1^* - T_1] - \beta_2 [T_2^* - T_2] \]

where \( \beta_1 \) and \( \beta_2 \) are related to the temperature coefficients of resistance for the thermistors on calorimeters 1 and 2. As we only observe a function of the temperature difference between the two calorimeters we must ensure that we can calculate the difference in the temperatures corrected for energy losses. Consider in turn the processes being studied, leaving the mixing process until last since it is more complicated.

i) Stirring

The effect of stirring is to do a certain amount of work on each calorimeter and to observe the temperature change associated with this work. The temperature vs. time plots for the individual calorimeters will be as in Fig (3.3.1b) and the corrected deflection due to stirring in 1 and 2 will occur at similar times, close to halfway through the stirring procedure. In Fig (3.3.1a) if we
(41)

take
\[ \Delta' = \Delta'_1 - \Delta'_2 , \]
as the deflection corrected by extrapolation to the time when \( n/2 \)
stirs have been completed then \( \Delta' \) will represent
\[ B_1 [T'_1 - T'_1] - B_2 [T'_2 - T'_2] \]

ii) First Calibration

Here the temperature rise will be large compared with that
due to stirring but a similar argument will be used as energy is
being introduced into both calorimeters at similar rates provided
the heaters are matched, i.e. \( R_1 = R_2 \).

The corrected temperature rises \( P, Q, R \) will occur at
similar times, approximately halfway through the heating period.
Then \( \Delta'' \) is taken to be the deflection at halfway through the
heating period obtained by extrapolation.

iii) Second Calibration

For the second calibration we can again say the temperature
rise due to stirring will be small compared with that due to the
introduction of electrical energy. Thus as a good approximation the
observed trace is a plot of \( T'''' - T'''' \) and extrapolation can be carried
out making
\[ \text{Area}(QRB) = \text{Area}(APQ) + \text{Area}(BCD) \]
in Fig (3.3.1b), then \( \Delta''' \) is taken to be the deflection calculated
assuming stirring is small. In practice as the time \( t_b \) is small
compared with the time taken for $n$ stirs, the procedure adopted is

1) stir $n/2$ times
2) introduce $k R_b t_b$ units of energy
3) stir $n/2$ times.

Thus if $t_b$ is small the deflection due to stirring will occur at a similar time to that due to heating, reducing any errors still further.

iv) Mixing

During the mixing process the temperatures of both calorimeters will rise markedly but in this case the heating time $t_M$ will be much larger than the time taken to mix. As the temperature changes due to stirring are small and the time taken to stir is quite long, stirring will be ignored as regards calculating this deflection. As argued above, the corrected temperature rise in each calorimeter falls approximately after half the time taken to carry out the process in that calorimeter. Thus if $t_M$ is large compared with the time for mixing, if mixing is carried out after $t_M/2$ then the deflections $\Delta_1$ and $\Delta_2$ due to temperature rises $[T_{1f} - T_1]$ and $[T_{2f} - T_2]$ will fall at the same time. Our only failure is to correct for the stirring which is relatively long and is used to bring about mixing and to distribute the energy to the calorimeter surface. If $\Delta'$, that due to stirring, is small and the calorimeters are well insulated, then the error this extrapolation procedure introduces will be negligible.

The assumption which was made earlier in this section has therefore been satisfied and procedures have been formulated making
\[ \Delta = \beta_1 (T_1 - T_1') - \beta_2 (T_2 - T_2'), \quad \Delta' = \beta_1 (T_1' - T_1) - \beta_2 (T_2' - T_2) \]
\[ \Delta'' = \beta_1 (T_1'' - T_1'') - \beta_2 (T_2'' - T_2''), \quad \Delta''' = \beta_1 (T_1''' - T_1'') - \beta_2 (T_2''' - T_2'') \]

thus permitting the energy change on mixing \( \Delta U_{\text{mix}} \) to be calculated.

3.4 THE DESIGN AND PREPARATION OF THE CALORIMETER VESSELS

The basic requirement of the glass vessels to be used in this work was described in Section (3.1). The vessels used in the twin calorimeter described above were made specially (Messrs. Jencons (Scientific) Ltd., Hemel Hempstead, Hertfordshire) in order that the minimum quantity of mercury would be used, since the quantity of mercury largely determines the heat capacity. The vessels used by Larkin and McGlashan (64, 67) and also by Morcom and Travers (48, 68) allowed rotation through \( \pi \) radians to ensure complete mixing. However it is not necessary to rotate through this angle and, if this is reduced a considerable reduction in mercury volume can be achieved without the liquids coming into contact with the ground glass joint. The glass vessels used were of two types, varying only in the maximum quantity of liquid sample taken. The two designs are shown in Fig (3.4.1) and Fig (3.4.2). The smaller type is normally used when studying the energy change on mixing of approximately equal volumes of liquid whilst the larger vessels are useful in studying
a) Calorimeter Heater

A teflon plug was machined as shown in Fig (3.4.2). The upper part of the plug was reduced in diameter by twice the diameter of the cotton covered eureka wire from which the heater was to be wound, such that the heater would be a push fit into the heater pocket. The plug had a fine hole drilled through its centre and also a groove and hole machined through the base.

The eureka wire (cotton covered constantan of 38 S.W.G.) was soldered to a small length of copper wire which was pushed through the hole in the base of the plug and laid along the groove. The heater wire was then tightly wound around the reduced diameter section of the plug, ensuring that no kinks occurred in the wire and that the maximum quantity was wound. When the end of the plug was nearly reached a copper wire was soldered to the heater wire and the copper lead taken down the centre hole in the plug. With care it was possible to keep the wire tight and also to ensure that all the heater wire would be in contact with the glass of the heater pocket. The heater was then screwed into the pocket ensuring that the windings remained in place.

b) Placing the Thermistors

The thermometer used in these measurements consisted of three thermistors (Standard Telephones and Cables, Type M52, with a resistance at room temperature \( \approx 450 \Omega \)), wired in parallel and spread around the surface of the calorimeter in such a position that they were normally adjacent to the mercury rather than the liquids.
This was done so that no temperature inaccuracies would occur due to localised non-equilibrium "hot-spots" immediately after mixing when the liquids are at a different temperature to the mercury in the calorimeter.

The thermistors were placed around the centre of the calorimeter body and were secured in the following manner. The calorimeter was held using a micro-clamp by the ground glass socket and placed in a suitable orientation. The thermistors, with their copper discs towards the glass were placed on a small drop of Araldite already on the glass and pushed down to squeeze out the excess adhesive. A small drop of Araldite was then placed over the thermistor so that the thermistor was completely covered with adhesive. The same procedure was employed with the other two thermistors and the assembly was then left to harden for 24 hours.

Before the thermistors were wired together two copper leads were laid along the surface of the glass and secured at each end of the calorimeter with rubber bands. The very fine leads from the thermistors were soldered to the copper leads to connect up the thermistors in parallel and care was taken to ensure a dry joint did not result. The fine leads and the copper leads were then coated with Araldite and a further 24 hours was allowed for the adhesive to harden.

The rubber bands were then removed and the copper leads trimmed to a suitable length. The heater and thermistor copper leads were then covered with sleeving and a four pin non-reversible plug soldered to these. The plug was then bent to a suitable
position and a thick coat of Araldite applied to all the exposed wires and also to the leads to the plug to minimise any flexing.

3.5 THE THERMISTOR NETWORK

The thermistors are used to form two arms of a Wheatstone network, the off-balance current of which is measured using a recording galvanometer (Kipp and Zonen Micrograph Type B,D.2.). Larkin has pointed out (64) that it is desirable to make the power dissipated in the thermistors a minimum consistent with high sensitivity of the galvanometer. He concluded that for his single calorimeter,

1) $R_2$ should be large
2) $R_3$ should be small
3) $R_1 = R_4 = R_g$
4) The galvanometer with the lowest possible value of $R_g / \sigma^2$ should be used,

where $R_1$, $R_2$, $R_3$, $R_4$ and $R_g$ are as shown in Fig (3.5.1) and $\sigma$ is the galvanometer sensitivity and the thermistors are represented by $R_i$. This argument is necessary when only one calorimeter is used since pronounced drifting of the galvanometer will occur when the power dissipated in the thermistors is large.

However with the twin calorimeter this tendency is greatly reduced as the effects of the two calorimeters are arranged in opposition to each other.
The Basic Bridge Circuit

Fig (3.5.1)
Consider the circuit shown in Fig (3.5.1), and apply Kirchoff's Second Law then

\[ i \cdot R_v + i_t (R_1 + R_2) - i_g R_2 = E \quad (3.5.1) \]

\[ i \cdot R_3 - i_t (R_1 + R_3) - i_g R_9 = 0 \quad (3.5.2) \]

\[ i \cdot R_4 - i_t (R_2 + R_4) + i_g (R_2 + R_4 + R_9) = 0 \quad (3.5.3) \]

i.e. a set of simultaneous linear equations in \( i, i_t, \) and \( i_g \).

Solving this set of equations for \( i_g \) we find writing

\[ F(R) = \frac{R_v [R_g (R_1 + R_2 + R_3 + R_4) + (R_1 + R_3) (R_2 + R_4)]}{\} + R_9 (R_1 + R_2) (R_3 + R_4) + R_9 R^2 (R_1 + R_2) \quad (3.5.4) \]

then

\[ i_g = \frac{E (R_1 R_4 - R_2 R_3)}{F(R)} \quad (3.5.5) \]

For thermistors we can write

\[ R(T) = R(S) [1 + \alpha \Delta T] \quad (3.5.6) \]

where \( \Delta T = T - S \), \( T \) the final temperature and \( S \) the initial temperature and \( \alpha = R^{-1} \frac{\partial R}{\partial T} \) is the temperature coefficient of resistance. If \( R_1 \) and \( R_2 \) represent the thermistors of a twin calorimeter then

\[ i_g = \frac{E [R_4 R_1 (1 + \alpha_1 \Delta T_1) - R_3 R_2 (1 + \alpha_2 \Delta T_2)]}{F(R)} \]
When $\Delta T_1 = \Delta T_2 = 0$, $R_3$ and $R_4$ are chosen such that

$$R_1 \cdot R_4 = R_1 \cdot R_3$$

i.e., the network is balanced. At any time later then

$$i_3 = E R_3 R_4 [\alpha_1 \Delta T_1 - \alpha_2 \Delta T_2] / F(R).$$

Assuming that any change in $F(R)$ is small, the deflection of the galvanometer is proportional to $\alpha_1 \Delta T_1 - \alpha_2 \Delta T_2$.

Consider now the power dissipated by the thermistors. If they are well matched then $\alpha_1 = \alpha_2$ and as $i_3$ is small ($i_3 \ll i_1$) then $\Delta T_1 \approx \Delta T_2$. If the heat capacities of the two calorimeters, $C_1$ and $C_2$, are similar the rate of increase of temperature in $C_1 = i_1^2 R_1 / C_1$ is approximately equal to the rate of increase of temperature in $C_2 = (i_1 - i_3)^2 R_1 / C_2$ and, furthermore, as the surfaces of the calorimeters are similar the heat losses will be similar, thus approximately $\Delta T_1 \approx \Delta T_2$, and then $i_3 \approx 0$.

Experimentally this is seen to be true, as even with high bridge currents there is only a very slight drift on the recorder, and for very small energies of mixing high bridge currents can be used to increase sensitivity.

For the twin calorimeter we can establish a condition for maximum galvanometer current, $i_3$, and if the thermistor resistances are well matched we are justified from equation (6) in writing

$$R_1 = R [1 + \alpha_1 \Delta T_1]$$

(3.5.7)

$$R_2 = R [1 + \alpha_2 \Delta T_2]$$

(3.5.8)

and when $\Delta T_1 = \Delta T_2 = 0$, if the bridge is balanced we can write...
\[ R_3 = R_4 = mR \]

where \( m \) is a constant. Then from equation (4)

\[
\frac{F(R)}{R} = m^2 (2R^2 + RR_v) + 2m(R_v R_g + R_v R + 2R_g R + R^2) + (2R_v R_g + R_v R)
\]

and from equation (5)

\[ i_g = E R^2 (\Delta T_1 - \Delta T_2) \frac{m}{F(R)} \]

We require \( m \) such that \( \frac{di_g}{dm} = 0 \) and \( \frac{d^2 i_g}{dm^2} \) is negative, in order that \( i_g \) will be a maximum

\[
\frac{di_g}{dm} = E R (\alpha_1 \Delta T_1 - \alpha_2 \Delta T_2) \left[ \frac{(2R_v R_g + R_v R) - m^2 (2R^2 + RR_v)}{m^2 (2R^2 + RR_v) + 2m (R_v R_g + R_v R + 2R_g R + R^2) + (2R_v R_g + R_v R)} \right] \]

\[
= 0 \quad \text{when} \quad m = \pm \sqrt[3]{\frac{R_v (2R_g + R)}{R (2R + R_v)}}
\]

and

\[
\frac{d^2 i_g}{dm^2} = E R (\alpha_1 \Delta T_1 - \alpha_2 \Delta T_2) \left( 2m^3 (2R^2 + RR_v) \right)
\]

\[-4m (2R^2 + RR_v)(2R_v R_g + R_v R) - 2 (2R_v R_g + R_v R)(R_v R_g + R_v R + 2R_g R + R^2)|
\]

\[
\left[ m^2 (2R^2 + RR_v) + 2m (R_v R_g + R_v R + 2R_g R + R^2) + (2R_v R_g + R_v R) \right]^3
\]

then when \( m = \sqrt[3]{\frac{R_v (2R_g + R)}{R (2R + R_v)}} \)
\[-\frac{d^2 \text{f}}{dm^2}\] takes the sign of \((\alpha_1 \Delta T_1 - \alpha_2 \Delta T_2)\) and since we are not concerned with the direction of the deflection here the sensitivity of the galvanometer will be a maximum when

\[
m = \sqrt{\frac{R_y (2R_g + R)}{R(2R + R_y)}}
\]

A bridge of this type was constructed using a large panel to accommodate the various resistance boxes and recorder. The resistance \(R_y\) was a four-decade resistance box wired in series with a ten ohm standard resistance which was housed in a vacuum flask to minimize temperature variations. Four other decades were used, \(R_3\) (labelled bridge sensitivity control) and \(R_3\) were four-decade resistance boxes. \(R_4\) (labelled bridge balance control) was a six-decade resistance box ranging from 0.01 to 9999.99 ohms whilst the fourth resistance box was controlled by a double pole switch and was used to stabilize the 6 volt high capacity accumulator, which supplied the current to the bridge, after the battery had been recharged. The use of the bridge together with a discussion of the sensitivity obtained will be in the next chapter. The wiring diagram covering the bridge and heater circuits is shown in Fig (3.6.1).

\[3.6 \text{ THE HEATER CIRCUIT AND MEASUREMENT OF HEATING TIME}\]

The heater circuit is shown diagramatically in Fig (3.6.2) as it relates to one calorimeter and the full circuit is shown in Fig (3.6.1).
The timer is a Time Interval Meter, consisting of an electrically operated stop watch, supplied by Messrs. Camera Cuss, and is used to measure the duration of time which current is passing through the calorimeter heater. The instrument is wired so that when the switch $S$ is closed the stop watch is started and continues to run until switch $S$ is opened. The heating time is then read from the stop watch.

The heater currents are measured by determining with a potentiometer (Type 4025, Messrs. H. Tinsley and Co. Ltd., London, S.E.25.) the voltage drop across a one ohm standard resistance (Type 1659, Messrs. H. Tinsley and Co. Ltd., London, S.E.25.). The potentiometer reading for balance $V_S$ thus represents the current flowing in the heater circuit if the resistance is exactly one ohm.

The resistance of the heater and leads is determined also using the potentiometer by passing a current $I_R$ through the heater. Then, if the heater resistance is $R_H$, and the voltage drop across the standard one ohm resistance is $V_S$ and that measured across the heater $V_H$, applying Ohm's Law

$$R_H = \frac{V_H}{V_S} R_S = \frac{V_H}{V_S}$$  \hspace{1cm} (3.6.1)

The heater resistance must be corrected for the length of wire used to connect from the terminal plug in the thermostat tank to the point in the heater circuit where the potentiometer leads from switch $P$ are connected. The true heater resistance is then determined

$$R_{H\text{ (true)}} = R_{H\text{ (measured)}} - R_{\text{leads}}$$
Whenever a new set of leads are made up then $R(\text{leads})$ must be redetermined.

The circuit actually used, Fig (3.6.1), allows heat to be introduced to either heater or through both heaters when necessary. In order to keep the number of switches to a minimum the connection from switch $P$ to the heater circuit is made at $S_{12}$ and thus $R(\text{leads})$ contains terms due to the resistance of the switches and terminal blocks. However, measurements of the heater resistances were always constant and no serious error was incurred by this procedure.

Two resistance boxes are used in the heater circuit, namely the heater current control and the dummy heater resistance. The former, a four-decade resistance box controls the current supplied to the heaters and the latter, of similar type, is set equal to the resistance of the calorimeter heater, and the leads and switches, thus allowing a known current to be set up with the heater current control. It is then used to allow the battery to stabilise before heating commences, and also when the six volt accumulator, which supplies the heating current, had been recharged.

§3.7 THE ANCILLARY EQUIPMENT

In this section the waterproof jacket, the calorimeter stirring mechanism and the thermostat tank will be described.
The thermostat consists of a large galvanized tank holding approximately 0.2 m³ of deionised water. It is lagged using expanded polystyrene sheeting on five faces and then covered with wood. The tank is fitted with a wooden lid covered with "Formica", to the lower side of which is attached a frame which supports the regulator, intermittent and permanent heaters and the stirrer. The regulator consists of a length of copper tubing to which is attached a glass to metal seal. The glass tubing is then connected to a capillary head which is used to control a high speed relay. The regulator is filled with toluene and mercury in the usual way. The intermittent heater consists of a length a pyrotenax wire of resistance ten ohms wound around the frame and fed by current drawn from a reduction transformer, the output of which is controlled by the relay operated from the regulator. The permanent heater consists of a five hundred watt electric fire element placed in a glass tube bent round to form a U. The current to the permanent heater is supplied from a variable transformer which is set to a low voltage (maximum 80 volts) in order that the glass does not crack with the heat of the wire. The water is stirred with a Gunn stirrer (Continuous Rating Pump Stirrer, Messrs. D.A. Gunn (Engineering) Ltd., Gloucester), which draws out water from the bottom of the tank and pumps it on to the calorimeter jacket. The thermostat temperature was measured using N.P.L. calibrated mercury in glass thermometers.

The calorimeter jacket is a brass cylinder fitted with an end plate, which is held on with 8 x 2BA bolts, trapping an O ring between the joint whilst from the centre of the vessel a short stub of copper tubing is used to bring the leads out of the calorimeter, through a length of stout rubber tubing which is pushed over the
stub and secured with a "Jubilee Clip". The assembly, which holds the calorimeters and their polystyrene jacket, was made as large as possible, in order to accommodate the maximum amount of polystyrene lagging.

The assembled brass jacket is supported in the thermostat by a stand equipped with gears and a handle which enabled the vessel to be rotated through a maximum of \( \pi \) radians. There is a variable stop on the handle which allows the angle of rotation to be reduced when \( \pi \) radians rotation would mean liquids contacting the ground glass joint.
CHAPTER FOUR

ENTHALPY OF MIXING

(OPERATION OF APPARATUS)
4.1 LOADING THE CALORIMETER

The calorimeter vessel is filled with mercury under vacuum in order to ensure that no air space exists in the calorimeter to contaminate the liquids or to cause uncertainties due to evaporation. The apparatus used is that described in Section (2.2) and illustrated in Fig (2.2.1). The calorimeter is thoroughly washed out with "Analar" acetone and with the aid of a suitable adaptor pumped out using the assembly described above. When all the acetone has evaporated the mercury is run in slowly from the reservoir taking care that no air bubbles are trapped. When full, the vacuum is released and the calorimeter removed from the filling apparatus. It is then clamped above a mercury tray and tilted back so that the ground glass joint is nearly horizontal with the glass partition uppermost.

The liquids to be mixed are weighed in hypodermic syringes and injected from them into the appropriate compartment using a bent needle (length 2 inches, gauge 26). It is convenient to load the component of lower volume first as this permits greater accuracy in determining a particular composition. The first component is removed from the storage container with a syringe and the syringe checked to ensure that

1) All air has been removed from the syringe and the liquid level is at the top of the needle,
2) No mercury has been introduced from the ampoule,
3) That no liquid is leaking between the needle and the syringe joint.
The syringe is weighed rapidly when the excess liquid, above that desired for the particular run, has been removed and the contents of the syringe injected smoothly into the appropriate compartment of the calorimeter. The syringe is again weighed immediately after injection and the weight of sample calculated. Before the second component is injected the approximate volume is calculated in order that the compositions are suitably chosen. Thus if $\text{©}_1$ represents the component injected and $\text{©}_2$ the component to be injected, then

\[
V_2 = \frac{W_1}{M_1} \times \frac{M_2}{\rho_2} \times \frac{x_2}{x_1},
\]

where $W_1 = \text{weight of ©}_1$ injected,
$M_1 = \text{molecular weight of ©}_1$,
$M_2 = \text{molecular weight of ©}_2$,
$\rho_2 = \text{density of ©}_2$,
$x_1 = (1 - x_1) = \text{mole fraction of ©}_1$ required
and $V_2 = \text{volume of component ©}_2$ to be injected.

The second component is then introduced in a similar manner.

The calorimeter is then installed in the waterproof jacket, placed in the thermostat and allowed to reach equilibrium, the thermistors being switched on in order to stabilise the battery.
The twin calorimeter can be used to measure endothermic energies of mixing in exactly the same way as Larkin described (64) except that the bridge arm resistances are equivalent. Despite the lower sensitivity at the same bridge current the use of two calorimeters reduces the stirring correction and there is a smaller tendency for the recording galvanometer to drift.

When thermal equilibrium has been achieved the galvanometer series resistance is reduced to a suitable value and the recorder is started. A suitable compensating current is determined from the expected energy change on mixing and the heater resistance of the calorimeter to be used, (say calorimeter 0). This value is set on the potentiometer and with the heater switch, SHT, connected to the dummy heater resistance (and the switch SP connected to the one ohm standard resistance), the heater current control is adjusted for zero deflection of the potentiometer galvanometer. After about ten minutes when the recorder has drawn a suitable base line the heater switch, SHT, is thrown, which starts the timer, and passes a current through the calorimeter heater. Leaving SP unchanged the potentiometer is readjusted to determine the precise value of the heater current, and after half the expected heater time has elapsed, the brass jacket is inverted several times, promoting mixing and stirring and causing a recorder deflection in the opposite direction to that of heating. The precise heating time is used to allow adjustment of the compensation energy during a measurement, and after accurate compensation is achieved switch SHT is returned to the dummy position and the calorimeter is stirred.
several times more to promote an even temperature. The heater current and time are noted and the recorder allowed to plot the curve to be used for extrapolation.

About twenty minutes later the calorimeter is stirred for the same number of times (n) as the total above and the deflection recorded. When steady conditions have existed for about ten minutes the calorimeter is stirred n/2 times and the heater switched on (S_H), leaving all the other switches set as above, for a short time during which the current is determined using the potentiometer. The heater is then switched off (S_H) and the calorimeter stirred a further n/2 times to promote a uniform temperature. When the recorder has plotted the cooling curve for about ten minutes the recorder is switched off and the calibration current and time are noted. The heater resistance is then determined by placing switch S_P into contact with the heater and passing a current through the heater by closing switch S_H. It is necessary to ensure that the heater current control is set to at least two hundred ohms in order that the potential difference across the heater can be measured with the potentiometer. When this is completed switch S_P is transferred and the current flowing through the heater is again measured. The energy change on mixing can then be calculated using the procedure described in the previous chapter. A typical recorder trace is shown in Fig (4.2.1a) and the corresponding run sheet is shown in Fig (4.2.1b).
$\Delta_{1} = 0.22 \text{ cm}$

$\Delta_{2} = 0.13 \text{ cm}$

$\Delta_{3} = 9.65 \text{ cm}$

\[ \Delta_{4} = 0.12 \text{ cm} \]

\[ \Delta_{5} = 0.13 \text{ cm} \]

\[ \Delta_{6} = 9.65 \text{ cm} \]

\[ \Delta_{7} = 0.12 \text{ cm} \]
\[ n(1) = 0.0017719 \]
\[ n(2) = 0.001879 \]

Total No. of Holes = 0.0024598

\[ x(1) = 0.5987 \]

Expected Value of Heat = 1,871 J.

Suitable current = 0.02953 A

1st. Heater current = 0.02953 A

1st. Heater time = 60.87 sec.

1st. Heater resistance = 0.4379/0.02953 = 35.34 ohms.

Correction for leads = 0.62 ohms.

True Resistance = 34.92 ohms.

Stirred (1) = 20

Deviation (1) = 0.22 \text{ corr. 0.09}

Stirred (2) = 20

Deviation (2) = 0.13

2nd. Heater current = 0.02949 A

2nd. Heater time = 12.31 sec.

2nd. Heater resistance = ohms.

Correction for leads = ohms.

True Resistance = ohms.

Stirred (3) = 20

Deviation (3) = 9.65 \text{ corr. 9.52}

3rd. Heater current =

3rd. Heater time =

3rd. Heater resistance =

Correction for leads =

True resistance =

Stirred (4) =

Deviation (4) =

\[ \Delta \Delta U_{\text{amp}} = 1.8536 - 0.0035 \]

\[ H^E = 625 \text{ J. mol}^{-1} \]

\[ x_{\text{e}_6} = 0.5987 \]

\[ F_{\text{e}} (4.2.1 b) \]
4.3 PROCEDURE WITH EXOTHERMIC ENERGIES OF MIXING

A null technique is again used, mixing being carried out in calorimeter 1 while compensating energy is introduced into calorimeter 2. The detailed procedure is as follows.

The recorder is started and whilst it is drawing the initial base line the calculated value of the heater current is set up in the same way as with endothermic measurements. After about ten minutes, with switch $S_{18}$ in the one heater position and $S_{12}$ set for calorimeter 2, the switch $S_{HT}$ is thrown, switching on the heater and timer. The heater current is measured with the potentiometer, switch $S_P$ across the one ohm resistance, and when half the expected heater time has elapsed the calorimeter is stirred several times to promote mixing where upon the recorder deflects in the opposite direction to that achieved on heating. The heater time is varied to provide accurate compensation and when this is achieved the heater and timer are switched off by returning switch $S_{HT}$ to the dummy heater position. The heater current and time are noted and the calorimeter stirred several (total n) times to provide uniform temperatures in each calorimeter. The recorder is allowed to follow the cooling of the two calorimeters until after about twenty minutes the calorimeters are again stirred n times, the recorder following the temperature changes.

When a further ten minutes have elapsed the switch $S_{18}$ is moved so that the same current passes through both heaters when switch $S_{HT}$ is again closed. The current is measured using the
potentiometer, leaving switch $S_p$ in the same position. After a suitable time the circuit is broken and the timer stopped by moving switch $S_{HT}$ back to the dummy heater position. The calorimeters are then stirred $n$ times again to promote a uniform temperature and the current and time are noted.

When about fifteen minutes have elapsed switch $S_{16}$ is returned to the single calorimeter position and switch $S_{12}$ set for energy into calorimeter 2. The switch $S_{HT}$ is thrown, after the calorimeters have been stirred $n/2$ times, and the current flowing is measured using the potentiometer with switch $S_p$ in the same position. The circuit is then broken by returning switch $S_{HT}$ to the dummy heater position and the calorimeters again stirred $n/2$ times. After approximately ten minutes the resistance is determined of calorimeter 0 heater, as described for endothermic energies of mixing, and the energy change on mixing calculated from the equation given in Chapter 3. The details of a typical measurement are shown in Fig (4.3.3a) and Fig (4.3.3b).

4.4 CALCULATION OF THE EXCESS ENTHALPY OF MIXING, $H^E$

Care has been taken to stress the fact that the calorimeter is of the constant volume type and that the thermodynamic energy of mixing has been measured. The molar excess thermodynamic energy of mixing, $U^E$, is readily calculated from the thermodynamic energy change on mixing, $\Delta U_{exp}$. 
\[ \Delta U_{\text{exp}} = -1.9891 \]

\[ H^E = -919.8 \]

\[ x_{2F} = 0.5020 \]
since in §3.1 we showed

\[ \Delta U_{\text{mix}} = \Delta U_{\exp} \]

provided that \( P_f \neq P \).

The thermodynamic function \( H \) is defined by

\[ H = U + PV \]  \hspace{1cm} (4.4.2)

and then for mixing:

\[ \Delta H_{\text{mix}} = \Delta U_{\text{mix}} + P \Delta V_{\text{mix}} \]

or

\[ H^E = U^E + PV^E \]  \hspace{1cm} (4.4.3)

The term involving the excess volume, \( V^E \), is readily calculated and since \( P \approx 10^5 \text{ N.m}^{-2} \) and \( |V^E| \approx 10^{-6} \text{ m}^3 \text{.mol}^{-1} \)

\[ |P V^E| \approx 10^{-1} \text{ J. mol}^{-1} \]

It is therefore justifiable to write

\[ H^E = \Delta U_{\exp} / (n_1 + n_2) \]  \hspace{1cm} (4.4.4)

provided that \( \Delta U_{\exp} \) is not so small as to be comparable with \( P \Delta V_{\text{mix}} \).

If \( U^E \) is very small then recalling equation (3.1.7)

\[ \Delta U_{\text{mix}} = \Delta U_{\exp} - \frac{P(n_1 + n_2)V^E}{V_{\text{of}}} \sum \left( \frac{P}{T} \frac{\partial V}{\partial P} + T \frac{\partial V}{\partial T} \right) \]
\[ \Delta H_{\text{mix}} = \Delta U_{\text{exp}} + P (n_1 + n_2) V \left[ 1 - \frac{\sum (P \left( \frac{\partial V}{\partial P} \right)_T + T \left( \frac{\partial V}{\partial T} \right)_P)}{V_{af}} \right] \quad (4.4.5) \]

or

\[ H^E = \frac{\Delta U_{\text{exp}}}{(n_1 + n_2)} + PV \left[ 1 - \frac{\sum (P \left( \frac{\partial V}{\partial P} \right)_T + T \left( \frac{\partial V}{\partial T} \right)_P)}{V_{af}} \right] \quad (4.4.6) \]

thus whatever corrections are necessary can be made provided the parameters can be measured.
CHAPTER FIVE

EXCESS ENTHALPY OF MIXING RESULTS
§5.1 THE PRESENTATION OF EXCESS ENTHALPY DATA

a) Tabulation of the Experimental Data

The excess enthalpy measurements consist of a set of discrete points, one calculated for each experimental run. These values are tabulated here in Tables (5.1.1) - (5.1.10) for each system studied and for each temperature at which the measurements were carried out.

b) Representation as a Curve

If we assume that the excess enthalpy of mixing as a function of composition can be represented by a smooth curve, then it is necessary to consider how the best curve can be drawn. If there were no errors in the experimental data then the points would all lie on a smooth curve. In practice, this is not so and the data must be fitted to a suitable function of composition.

c) Derived Quantities

In addition to the excess enthalpy it is possible to calculate other quantities from the experimental data. Two such quantities are the partial molar excess enthalpy and the excess heat capacity. These quantities may be useful in interpreting the experimental data. The excess heat capacity $C_p^E$ is defined by

$$C_p^E = \left( \frac{\partial H^E}{\partial T} \right)_p \quad (5.1.1)$$

and may be determined when $H^E$ has been measured as a function of
TABLE (5.1.1)

THE EXCESS ENTHALPY OF MIXING, $H^E$, FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + N,N-DIMETHYL-m-TOLUIDINE (2),

a) At 323.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.644 x 10^{-4}</td>
<td>4.745 x 10^{-4}</td>
<td>0.0898</td>
<td>-2.611</td>
<td>-677</td>
</tr>
<tr>
<td>0.969 x 10^{-4}</td>
<td>2.742 x 10^{-4}</td>
<td>0.2043</td>
<td>-3.875</td>
<td>-1520</td>
</tr>
<tr>
<td>1.453 x 10^{-4}</td>
<td>2.407 x 10^{-4}</td>
<td>0.3049</td>
<td>-5.409</td>
<td>-2111</td>
</tr>
<tr>
<td>1.792 x 10^{-4}</td>
<td>2.045 x 10^{-4}</td>
<td>0.3890</td>
<td>-6.138</td>
<td>-2479</td>
</tr>
<tr>
<td>2.687 x 10^{-4}</td>
<td>1.947 x 10^{-4}</td>
<td>0.5007</td>
<td>-8.110</td>
<td>-2811</td>
</tr>
<tr>
<td>1.848 x 10^{-4}</td>
<td>1.007 x 10^{-4}</td>
<td>0.5715</td>
<td>-4.958</td>
<td>-2852</td>
</tr>
<tr>
<td>3.116 x 10^{-4}</td>
<td>0.847 x 10^{-4}</td>
<td>0.7278</td>
<td>-5.501</td>
<td>-2390</td>
</tr>
<tr>
<td>4.647 x 10^{-4}</td>
<td>0.563 x 10^{-4}</td>
<td>0.8571</td>
<td>-4.207</td>
<td>-1444</td>
</tr>
</tbody>
</table>

b) At 343.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.452 x 10^{-4}</td>
<td>1.826 x 10^{-4}</td>
<td>0.4071</td>
<td>-6.916</td>
<td>-2357</td>
</tr>
<tr>
<td>1.764 x 10^{-4}</td>
<td>1.867 x 10^{-4}</td>
<td>0.4939</td>
<td>-5.491</td>
<td>-2592</td>
</tr>
<tr>
<td>2.883 x 10^{-4}</td>
<td>1.499 x 10^{-4}</td>
<td>0.5829</td>
<td>-6.885</td>
<td>-2589</td>
</tr>
<tr>
<td>3.344 x 10^{-4}</td>
<td>1.344 x 10^{-4}</td>
<td>0.6439</td>
<td>-7.021</td>
<td>-2515</td>
</tr>
</tbody>
</table>
**TABLE (5.1.2)**

THE EXCESS ENTHALPY OF MIXING, $\Delta H^E$, FOR THE SYSTEM:

**HEXAFLUOROBENZENE (1) + N,N-DIMETHYL-p-TOLUIDINE (2),**

a) At 323.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$\Delta H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.828 \times 10^{-4}$</td>
<td>$3.358 \times 10^{-4}$</td>
<td>0.1520</td>
<td>-3.176</td>
<td>-1079</td>
</tr>
<tr>
<td>$1.595 \times 10^{-4}$</td>
<td>$2.679 \times 10^{-4}$</td>
<td>0.3020</td>
<td>-5.492</td>
<td>-1934</td>
</tr>
<tr>
<td>$2.052 \times 10^{-4}$</td>
<td>$2.220 \times 10^{-4}$</td>
<td>0.4018</td>
<td>-6.519</td>
<td>-2375</td>
</tr>
<tr>
<td>$2.871 \times 10^{-4}$</td>
<td>$2.061 \times 10^{-4}$</td>
<td>0.5030</td>
<td>-8.026</td>
<td>-2616</td>
</tr>
<tr>
<td>$2.511 \times 10^{-4}$</td>
<td>$1.181 \times 10^{-4}$</td>
<td>0.6071</td>
<td>-5.798</td>
<td>-2607</td>
</tr>
<tr>
<td>$3.306 \times 10^{-4}$</td>
<td>$1.084 \times 10^{-4}$</td>
<td>0.6891</td>
<td>-5.959</td>
<td>-2311</td>
</tr>
<tr>
<td>$4.260 \times 10^{-4}$</td>
<td>$0.572 \times 10^{-4}$</td>
<td>0.8440</td>
<td>-3.698</td>
<td>-1363</td>
</tr>
</tbody>
</table>

b) At 343.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$\Delta H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.030 \times 10^{-4}$</td>
<td>$2.220 \times 10^{-4}$</td>
<td>0.3992</td>
<td>-6.077</td>
<td>-2224</td>
</tr>
<tr>
<td>$2.537 \times 10^{-4}$</td>
<td>$1.818 \times 10^{-4}$</td>
<td>0.5035</td>
<td>-6.843</td>
<td>-2527</td>
</tr>
<tr>
<td>$2.809 \times 10^{-4}$</td>
<td>$1.528 \times 10^{-4}$</td>
<td>0.5719</td>
<td>-6.683</td>
<td>-2531</td>
</tr>
<tr>
<td>$3.305 \times 10^{-4}$</td>
<td>$1.354 \times 10^{-4}$</td>
<td>0.6395</td>
<td>-6.659</td>
<td>-2397</td>
</tr>
</tbody>
</table>
# Table 5.1.3

**The Excess Enthalpy of Mixing, $H^E$, for the System:**

*Hexafluorobenzene (1) + N,N-Dimethylaniline (2),*

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.987 \times 10^{-4}$</td>
<td>$5.778 \times 10^{-4}$</td>
<td>0.1000</td>
<td>-2.770</td>
<td>-467</td>
</tr>
<tr>
<td>$1.511 \times 10^{-4}$</td>
<td>$4.000 \times 10^{-4}$</td>
<td>0.1979</td>
<td>-3.737</td>
<td>-911</td>
</tr>
<tr>
<td>$1.989 \times 10^{-4}$</td>
<td>$3.170 \times 10^{-4}$</td>
<td>0.2901</td>
<td>-4.643</td>
<td>-1260</td>
</tr>
<tr>
<td>$3.035 \times 10^{-4}$</td>
<td>$3.024 \times 10^{-4}$</td>
<td>0.3953</td>
<td>-6.478</td>
<td>-1570</td>
</tr>
<tr>
<td>$3.409 \times 10^{-4}$</td>
<td>$2.431 \times 10^{-4}$</td>
<td>0.4773</td>
<td>-6.651</td>
<td>-1733</td>
</tr>
<tr>
<td>$3.396 \times 10^{-4}$</td>
<td>$1.487 \times 10^{-4}$</td>
<td>0.5980</td>
<td>-5.444</td>
<td>-1784</td>
</tr>
<tr>
<td>$4.170 \times 10^{-4}$</td>
<td>$1.255 \times 10^{-4}$</td>
<td>0.6840</td>
<td>-5.362</td>
<td>-1636</td>
</tr>
<tr>
<td>$6.630 \times 10^{-4}$</td>
<td>$0.760 \times 10^{-4}$</td>
<td>0.8504</td>
<td>-3.938</td>
<td>-940</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.829 \times 10^{-4}$</td>
<td>$1.787 \times 10^{-4}$</td>
<td>0.4000</td>
<td>-3.757</td>
<td>-1524</td>
</tr>
<tr>
<td>$2.424 \times 10^{-4}$</td>
<td>$1.616 \times 10^{-4}$</td>
<td>0.4942</td>
<td>-4.381</td>
<td>-1666</td>
</tr>
<tr>
<td>$2.766 \times 10^{-4}$</td>
<td>$1.344 \times 10^{-4}$</td>
<td>0.5727</td>
<td>-4.437</td>
<td>-1709</td>
</tr>
<tr>
<td>$3.372 \times 10^{-4}$</td>
<td>$1.178 \times 10^{-4}$</td>
<td>0.6509</td>
<td>-4.514</td>
<td>-1621</td>
</tr>
</tbody>
</table>
TABLE (5.1.4)

THE EXCESS ENTHALPY OF MIXING, $H^E$, FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + 2,4,6-TRIMETHYLPYRIDINE (COLLIDINE) (2),

a) At 298.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.050 x 10$^{-4}$</td>
<td>2.021 x 10$^{-4}$</td>
<td>0.3978</td>
<td>-3.341</td>
<td>-1206</td>
</tr>
<tr>
<td>2.510 x 10$^{-4}$</td>
<td>1.646 x 10$^{-4}$</td>
<td>0.4983</td>
<td>-3.717</td>
<td>-1372</td>
</tr>
<tr>
<td>3.140 x 10$^{-4}$</td>
<td>1.347 x 10$^{-4}$</td>
<td>0.6029</td>
<td>-3.888</td>
<td>-1389</td>
</tr>
</tbody>
</table>

b) At 323.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.898 x 10$^{-4}$</td>
<td>3.282 x 10$^{-4}$</td>
<td>0.1512</td>
<td>-1.528</td>
<td>-478</td>
</tr>
<tr>
<td>1.392 x 10$^{-4}$</td>
<td>2.117 x 10$^{-4}$</td>
<td>0.2998</td>
<td>-2.212</td>
<td>-886</td>
</tr>
<tr>
<td>1.965 x 10$^{-4}$</td>
<td>1.921 x 10$^{-4}$</td>
<td>0.3998</td>
<td>-2.907</td>
<td>-1100</td>
</tr>
<tr>
<td>2.626 x 10$^{-4}$</td>
<td>1.712 x 10$^{-4}$</td>
<td>0.4997</td>
<td>-3.541</td>
<td>-1253</td>
</tr>
<tr>
<td>2.835 x 10$^{-4}$</td>
<td>1.260 x 10$^{-4}$</td>
<td>0.5944</td>
<td>-3.248</td>
<td>-1267</td>
</tr>
<tr>
<td>3.333 x 10$^{-4}$</td>
<td>0.959 x 10$^{-4}$</td>
<td>0.6936</td>
<td>-3.137</td>
<td>-1214</td>
</tr>
<tr>
<td>5.321 x 10$^{-4}$</td>
<td>0.643 x 10$^{-4}$</td>
<td>0.8435</td>
<td>-2.497</td>
<td>-736</td>
</tr>
</tbody>
</table>

c) At 343.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.946 x 10$^{-4}$</td>
<td>1.953 x 10$^{-4}$</td>
<td>0.3935</td>
<td>-2.640</td>
<td>-933</td>
</tr>
<tr>
<td>2.565 x 10$^{-4}$</td>
<td>1.691 x 10$^{-4}$</td>
<td>0.4969</td>
<td>-3.164</td>
<td>-1140</td>
</tr>
<tr>
<td>3.348 x 10$^{-4}$</td>
<td>1.216 x 10$^{-4}$</td>
<td>0.6420</td>
<td>-3.283</td>
<td>-1171</td>
</tr>
</tbody>
</table>
### Table (5.1.5)

**The Excess Enthalpy of Mixing, $H^E$, for the System, Hexafluorobenzene (1) + N,N-Dimethyl-o-toluidine (2),**

**a) At 298.15 K**

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.679 \times 10^{-4}$</td>
<td>$1.774 \times 10^{-4}$</td>
<td>0.4075</td>
<td>-2.167</td>
<td>-978</td>
</tr>
<tr>
<td>$2.460 \times 10^{-4}$</td>
<td>$1.744 \times 10^{-4}$</td>
<td>0.5062</td>
<td>-2.787</td>
<td>-1067</td>
</tr>
<tr>
<td>$3.155 \times 10^{-4}$</td>
<td>$1.455 \times 10^{-4}$</td>
<td>0.6118</td>
<td>-2.936</td>
<td>-1059</td>
</tr>
</tbody>
</table>

**b) At 323.15 K**

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.034 \times 10^{-4}$</td>
<td>$4.052 \times 10^{-4}$</td>
<td>0.1564</td>
<td>-1.349</td>
<td>-379</td>
</tr>
<tr>
<td>$1.333 \times 10^{-4}$</td>
<td>$2.254 \times 10^{-4}$</td>
<td>0.3006</td>
<td>-1.640</td>
<td>-688</td>
</tr>
<tr>
<td>$1.802 \times 10^{-4}$</td>
<td>$1.987 \times 10^{-4}$</td>
<td>0.3972</td>
<td>-2.003</td>
<td>-821</td>
</tr>
<tr>
<td>$2.587 \times 10^{-4}$</td>
<td>$1.908 \times 10^{-4}$</td>
<td>0.4963</td>
<td>-2.650</td>
<td>-930</td>
</tr>
<tr>
<td>$2.511 \times 10^{-4}$</td>
<td>$1.776 \times 10^{-4}$</td>
<td>0.5068</td>
<td>-2.446</td>
<td>-918</td>
</tr>
<tr>
<td>$3.338 \times 10^{-4}$</td>
<td>$1.530 \times 10^{-4}$</td>
<td>0.6132</td>
<td>-2.646</td>
<td>-904</td>
</tr>
<tr>
<td>$3.997 \times 10^{-4}$</td>
<td>$1.240 \times 10^{-4}$</td>
<td>0.7008</td>
<td>-2.569</td>
<td>-838</td>
</tr>
<tr>
<td>$4.883 \times 10^{-4}$</td>
<td>$0.719 \times 10^{-4}$</td>
<td>0.8315</td>
<td>-1.804</td>
<td>-571</td>
</tr>
</tbody>
</table>

**c) At 343.15 K**

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.990 \times 10^{-4}$</td>
<td>$2.122 \times 10^{-4}$</td>
<td>0.4052</td>
<td>-1.904</td>
<td>-721</td>
</tr>
<tr>
<td>$2.691 \times 10^{-4}$</td>
<td>$1.904 \times 10^{-4}$</td>
<td>0.5067</td>
<td>-2.219</td>
<td>-777</td>
</tr>
<tr>
<td>$3.260 \times 10^{-4}$</td>
<td>$1.330 \times 10^{-4}$</td>
<td>0.6404</td>
<td>-2.199</td>
<td>-803</td>
</tr>
</tbody>
</table>
**TABLE (5.1.6)**

**THE EXCESS ENTHALPY OF MIXING, \( H^E \), FOR THE SYSTEM:**

**HEXAFLUOROBENZENE (1) + 2,6-DIMETHYL PYRIDINE (LUTIDINE) (2),**

a) At 298.15 K

<table>
<thead>
<tr>
<th>( w_1/\text{kg} )</th>
<th>( w_2/\text{kg} )</th>
<th>( x_1 )</th>
<th>( \Delta U_{\text{exp}}/J )</th>
<th>( H^E/\text{J.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.095 \times 10^{-4} )</td>
<td>( 1.805 \times 10^{-4} )</td>
<td>0.4006</td>
<td>-2.291</td>
<td>-750</td>
</tr>
<tr>
<td>( 2.020 \times 10^{-4} )</td>
<td>( 1.154 \times 10^{-4} )</td>
<td>0.5020</td>
<td>-1.989</td>
<td>-919</td>
</tr>
<tr>
<td>( 3.346 \times 10^{-4} )</td>
<td>( 1.276 \times 10^{-4} )</td>
<td>0.6016</td>
<td>-2.817</td>
<td>-942</td>
</tr>
</tbody>
</table>

b) At 323.15 K

<table>
<thead>
<tr>
<th>( w_1/\text{kg} )</th>
<th>( w_2/\text{kg} )</th>
<th>( x_1 )</th>
<th>( \Delta U_{\text{exp}}/J )</th>
<th>( H^E/\text{J.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0.709 \times 10^{-4} )</td>
<td>( 3.465 \times 10^{-4} )</td>
<td>0.1054</td>
<td>-0.791</td>
<td>-218</td>
</tr>
<tr>
<td>( 1.215 \times 10^{-4} )</td>
<td>( 2.760 \times 10^{-4} )</td>
<td>0.2022</td>
<td>-1.312</td>
<td>-406</td>
</tr>
<tr>
<td>( 1.941 \times 10^{-4} )</td>
<td>( 2.518 \times 10^{-4} )</td>
<td>0.3074</td>
<td>-2.034</td>
<td>-599</td>
</tr>
<tr>
<td>( 2.504 \times 10^{-4} )</td>
<td>( 2.062 \times 10^{-4} )</td>
<td>0.4115</td>
<td>-2.205</td>
<td>-713</td>
</tr>
<tr>
<td>( 2.489 \times 10^{-4} )</td>
<td>( 1.442 \times 10^{-4} )</td>
<td>0.4985</td>
<td>-2.178</td>
<td>-811</td>
</tr>
<tr>
<td>( 2.508 \times 10^{-4} )</td>
<td>( 1.340 \times 10^{-4} )</td>
<td>0.5187</td>
<td>-2.149</td>
<td>-826</td>
</tr>
<tr>
<td>( 3.227 \times 10^{-4} )</td>
<td>( 1.152 \times 10^{-4} )</td>
<td>0.6173</td>
<td>-2.212</td>
<td>-787</td>
</tr>
<tr>
<td>( 3.312 \times 10^{-4} )</td>
<td>( 0.606 \times 10^{-4} )</td>
<td>0.7588</td>
<td>-1.599</td>
<td>-681</td>
</tr>
<tr>
<td>( 4.869 \times 10^{-4} )</td>
<td>( 0.341 \times 10^{-4} )</td>
<td>0.8916</td>
<td>-1.161</td>
<td>-395</td>
</tr>
</tbody>
</table>

c) At 343.15 K

<table>
<thead>
<tr>
<th>( w_1/\text{kg} )</th>
<th>( w_2/\text{kg} )</th>
<th>( x_1 )</th>
<th>( \Delta U_{\text{exp}}/J )</th>
<th>( H^E/\text{J.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.739 \times 10^{-4} )</td>
<td>( 1.830 \times 10^{-4} )</td>
<td>0.3537</td>
<td>-1.456</td>
<td>-550</td>
</tr>
<tr>
<td>( 2.821 \times 10^{-4} )</td>
<td>( 1.600 \times 10^{-4} )</td>
<td>0.5038</td>
<td>-2.134</td>
<td>-702</td>
</tr>
<tr>
<td>( 3.212 \times 10^{-4} )</td>
<td>( 1.040 \times 10^{-4} )</td>
<td>0.6401</td>
<td>-1.921</td>
<td>-712</td>
</tr>
</tbody>
</table>
TABLE (5.1.7)

THE EXCESS ENTHALPY OF MIXING, $H^E$, FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + iso-PROPYLBENZENE (CUMENE) (2),

At 323.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.723 \times 10^{-4}$</td>
<td>$13.530 \times 10^{-4}$</td>
<td>0.1509</td>
<td>$-2.409$</td>
<td>$-182$</td>
</tr>
<tr>
<td>$4.933 \times 10^{-4}$</td>
<td>$7.202 \times 10^{-4}$</td>
<td>0.3067</td>
<td>$-2.797$</td>
<td>$-324$</td>
</tr>
<tr>
<td>$6.428 \times 10^{-4}$</td>
<td>$6.047 \times 10^{-4}$</td>
<td>0.4071</td>
<td>$-3.404$</td>
<td>$-401$</td>
</tr>
<tr>
<td>$3.680 \times 10^{-4}$</td>
<td>$2.424 \times 10^{-4}$</td>
<td>0.4951</td>
<td>$-1.803$</td>
<td>$-451$</td>
</tr>
<tr>
<td>$9.603 \times 10^{-4}$</td>
<td>$4.084 \times 10^{-4}$</td>
<td>0.6030</td>
<td>$-3.857$</td>
<td>$-451$</td>
</tr>
<tr>
<td>$12.672 \times 10^{-4}$</td>
<td>$3.490 \times 10^{-4}$</td>
<td>0.7011</td>
<td>$-4.003$</td>
<td>$-412$</td>
</tr>
<tr>
<td>$16.750 \times 10^{-4}$</td>
<td>$1.935 \times 10^{-4}$</td>
<td>0.8483</td>
<td>$-2.799$</td>
<td>$-264$</td>
</tr>
</tbody>
</table>
TABLE (5.1.8)

THE EXCESS ENTHALPY OF MIXING, $\Delta H^E$, FOR THE SYSTEM:

HEXAFLUOROBENZENE (1) + PYRIDINE (2),

a) At 298.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$\Delta H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.420 \times 10^{-4}$</td>
<td>$3.351 \times 10^{-4}$</td>
<td>0.1526</td>
<td>1.508</td>
<td>+299</td>
</tr>
<tr>
<td>$2.211 \times 10^{-4}$</td>
<td>$2.167 \times 10^{-4}$</td>
<td>0.3025</td>
<td>1.470</td>
<td>+374</td>
</tr>
<tr>
<td>$2.536 \times 10^{-4}$</td>
<td>$1.723 \times 10^{-4}$</td>
<td>0.3849</td>
<td>1.353</td>
<td>+382</td>
</tr>
<tr>
<td>$2.804 \times 10^{-4}$</td>
<td>$1.224 \times 10^{-4}$</td>
<td>0.4934</td>
<td>1.015</td>
<td>+332</td>
</tr>
<tr>
<td>$3.309 \times 10^{-4}$</td>
<td>$1.037 \times 10^{-4}$</td>
<td>0.5756</td>
<td>0.848</td>
<td>+274</td>
</tr>
<tr>
<td>$3.938 \times 10^{-4}$</td>
<td>$0.773 \times 10^{-4}$</td>
<td>0.6841</td>
<td>0.579</td>
<td>+187</td>
</tr>
<tr>
<td>$5.391 \times 10^{-4}$</td>
<td>$0.423 \times 10^{-4}$</td>
<td>0.8442</td>
<td>0.246</td>
<td>+71.7</td>
</tr>
</tbody>
</table>

b) At 323.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$\Delta H^E$/J·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.651 \times 10^{-4}$</td>
<td>$2.421 \times 10^{-4}$</td>
<td>0.1025</td>
<td>0.747</td>
<td>+219</td>
</tr>
<tr>
<td>$1.115 \times 10^{-4}$</td>
<td>$1.825 \times 10^{-4}$</td>
<td>0.2062</td>
<td>1.001</td>
<td>+344</td>
</tr>
<tr>
<td>$1.540 \times 10^{-4}$</td>
<td>$1.639 \times 10^{-4}$</td>
<td>0.2854</td>
<td>1.074</td>
<td>+370</td>
</tr>
<tr>
<td>$2.427 \times 10^{-4}$</td>
<td>$1.556 \times 10^{-4}$</td>
<td>0.3987</td>
<td>1.165</td>
<td>+356</td>
</tr>
<tr>
<td>$2.285 \times 10^{-4}$</td>
<td>$0.911 \times 10^{-4}$</td>
<td>0.5160</td>
<td>0.736</td>
<td>+309</td>
</tr>
<tr>
<td>$2.448 \times 10^{-4}$</td>
<td>$0.704 \times 10^{-4}$</td>
<td>0.5965</td>
<td>0.538</td>
<td>+243</td>
</tr>
<tr>
<td>$3.803 \times 10^{-4}$</td>
<td>$0.723 \times 10^{-4}$</td>
<td>0.6910</td>
<td>0.556</td>
<td>+187</td>
</tr>
<tr>
<td>$4.682 \times 10^{-4}$</td>
<td>$0.474 \times 10^{-4}$</td>
<td>0.8077</td>
<td>0.282</td>
<td>+90.6</td>
</tr>
<tr>
<td>$5.562 \times 10^{-4}$</td>
<td>$0.303 \times 10^{-4}$</td>
<td>0.8864</td>
<td>0.153</td>
<td>+45.5</td>
</tr>
</tbody>
</table>
TABLE (5.1.8) (Continued)

c) At 343.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_i$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.409 \times 10^{-4}$</td>
<td>$3.306 \times 10^{-4}$</td>
<td>0.1534</td>
<td>+1.448</td>
<td>+293</td>
</tr>
<tr>
<td>$2.430 \times 10^{-4}$</td>
<td>$2.136 \times 10^{-4}$</td>
<td>0.3260</td>
<td>+1.541</td>
<td>+384</td>
</tr>
<tr>
<td>$2.550 \times 10^{-4}$</td>
<td>$2.238 \times 10^{-4}$</td>
<td>0.3263</td>
<td>+1.559</td>
<td>+371</td>
</tr>
<tr>
<td>$2.946 \times 10^{-4}$</td>
<td>$1.280 \times 10^{-4}$</td>
<td>0.4945</td>
<td>+0.995</td>
<td>+310</td>
</tr>
</tbody>
</table>
### TABLE (5.1.9)

THE EXCESS ENTHALPY OF MIXING, $H^E$, FOR THE SYSTEM:

**HEXAFLUOROBENZENE (1) + TRIETHYLAMINE (2)**

#### a) At 298.15 K

<table>
<thead>
<tr>
<th>$w_1/\text{kg}$</th>
<th>$w_2/\text{kg}$</th>
<th>$x_1$</th>
<th>$\Delta U_{\text{exp}}/J$</th>
<th>$H^E/\text{J.mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.054 \times 10^{-4}$</td>
<td>$1.640 \times 10^{-4}$</td>
<td>0.4052</td>
<td>+1.717</td>
<td>+630</td>
</tr>
<tr>
<td>$2.581 \times 10^{-4}$</td>
<td>$1.344 \times 10^{-4}$</td>
<td>0.5108</td>
<td>+1.768</td>
<td>+651</td>
</tr>
<tr>
<td>$3.297 \times 10^{-4}$</td>
<td>$1.202 \times 10^{-4}$</td>
<td>0.5987</td>
<td>+1.850</td>
<td>+625</td>
</tr>
</tbody>
</table>

#### b) At 323.15 K

<table>
<thead>
<tr>
<th>$w_1/\text{kg}$</th>
<th>$w_2/\text{kg}$</th>
<th>$x_1$</th>
<th>$\Delta U_{\text{exp}}/J$</th>
<th>$H^E/\text{J.mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.674 \times 10^{-4}$</td>
<td>$2.591 \times 10^{-4}$</td>
<td>0.1239</td>
<td>+0.817</td>
<td>+279</td>
</tr>
<tr>
<td>$1.018 \times 10^{-4}$</td>
<td>$2.180 \times 10^{-4}$</td>
<td>0.2025</td>
<td>+1.087</td>
<td>+402</td>
</tr>
<tr>
<td>$1.506 \times 10^{-4}$</td>
<td>$1.741 \times 10^{-4}$</td>
<td>0.3199</td>
<td>+1.457</td>
<td>+575</td>
</tr>
<tr>
<td>$1.880 \times 10^{-4}$</td>
<td>$1.468 \times 10^{-4}$</td>
<td>0.4105</td>
<td>+1.566</td>
<td>+634</td>
</tr>
<tr>
<td>$2.583 \times 10^{-4}$</td>
<td>$1.413 \times 10^{-4}$</td>
<td>0.4985</td>
<td>+1.906</td>
<td>+682</td>
</tr>
<tr>
<td>$3.027 \times 10^{-4}$</td>
<td>$1.296 \times 10^{-4}$</td>
<td>0.5595</td>
<td>+1.964</td>
<td>+675</td>
</tr>
<tr>
<td>$3.042 \times 10^{-4}$</td>
<td>$0.723 \times 10^{-4}$</td>
<td>0.6960</td>
<td>+1.324</td>
<td>+563</td>
</tr>
<tr>
<td>$4.599 \times 10^{-4}$</td>
<td>$0.423 \times 10^{-4}$</td>
<td>0.8553</td>
<td>+0.925</td>
<td>+320</td>
</tr>
</tbody>
</table>
TABLE (5.1.10)

THE EXCESS ENTHALPY OF MIXING, $H^E$, FOR THE SYSTEM:

HEXAFLUOROBENZENE (1) + iso-PROPYLCYCLOHEXANE (2),

At 323.15 K

<table>
<thead>
<tr>
<th>$w_1$/kg</th>
<th>$w_2$/kg</th>
<th>$x_1$</th>
<th>$\Delta U_{exp}$/J</th>
<th>$H^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.054 \times 10^{-4}$</td>
<td>$3.149 \times 10^{-4}$</td>
<td>0.1851</td>
<td>+2.322</td>
<td>+759</td>
</tr>
<tr>
<td>$1.827 \times 10^{-4}$</td>
<td>$2.864 \times 10^{-4}$</td>
<td>0.3021</td>
<td>+3.488</td>
<td>+1073</td>
</tr>
<tr>
<td>$2.726 \times 10^{-4}$</td>
<td>$2.752 \times 10^{-4}$</td>
<td>0.4019</td>
<td>+4.562</td>
<td>+1251</td>
</tr>
<tr>
<td>$3.326 \times 10^{-4}$</td>
<td>$2.189 \times 10^{-4}$</td>
<td>0.5076</td>
<td>+4.502</td>
<td>+1278</td>
</tr>
<tr>
<td>$3.404 \times 10^{-4}$</td>
<td>$1.563 \times 10^{-4}$</td>
<td>0.5964</td>
<td>+3.861</td>
<td>+1259</td>
</tr>
<tr>
<td>$4.112 \times 10^{-4}$</td>
<td>$1.255 \times 10^{-4}$</td>
<td>0.6897</td>
<td>+3.589</td>
<td>+1120</td>
</tr>
<tr>
<td>$6.441 \times 10^{-4}$</td>
<td>$0.876 \times 10^{-4}$</td>
<td>0.8330</td>
<td>+3.163</td>
<td>+761</td>
</tr>
</tbody>
</table>
TABLE (5.1.11)
THE EXCESS HEAT CAPACITIES, $C_P^E$, AT 323.15 K FOR EQUIMOLAR MIXTURES

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>$C_P^E$/J.mol$^{-1}$.degC$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexafluorobenzene + N,N-dimethyl-m-toluidine</td>
<td>+11.0</td>
</tr>
<tr>
<td>Hexafluorobenzene + N,N-dimethyl-p-toluidine</td>
<td>+5.0</td>
</tr>
<tr>
<td>Hexafluorobenzene + N,N-dimethylaniline</td>
<td>+4.0</td>
</tr>
<tr>
<td>Hexafluorobenzene + 2,4,6-trimethylpyridine</td>
<td>+4.3</td>
</tr>
<tr>
<td>Hexafluorobenzene + N,N-dimethyl-o-toluidine</td>
<td>+5.6</td>
</tr>
<tr>
<td>Hexafluorobenzene + 2,6-dimethylpyridine</td>
<td>+4.9</td>
</tr>
<tr>
<td>Hexafluorobenzene + pyridine</td>
<td>0</td>
</tr>
<tr>
<td>Hexafluorobenzene + triethylamine</td>
<td>+1.2</td>
</tr>
</tbody>
</table>
temperature. It is an important quantity when the experimental data is to be interpreted in terms of complex formation and thus the computed values are shown here in Table (5.1.11).

The partial molar excess enthalpy is defined as

$$\left( \frac{\partial H^E}{\partial n_1} \right)_{n_2, T, P}$$

and can be calculated from a knowledge of the composition dependence of $H^E$. When $n_1 \neq 0$ the value of $\left( \frac{\partial H^E}{\partial n_1} \right)_{T, P, n_2}$ represents the heat of solution of $\theta$ in $\phi$ at infinite dilution and although this quantity is not discussed here it is desirable to evaluate procedures to calculate it for use in other work (see Appendix 1).

§5.2 CURVE FITTING

a) General Method

We stated above that the composition dependence of $H^E$ is usually represented by a smooth curve. Then we can write

$$H^E(x_1, x_2) = F(x_1, x_2)$$  \hspace{1cm} (5.2.1)

where $x_1$ and $x_2$ are the mole fractions of species A and B such that

$$S = \sum_{i=1}^{N} (H^E_{x_i} - F(x_{1i}, x_{2i}))^2$$
is a minimum where \( H^E_{i} \), \( x_{ii} \) and \( x_{ji} \) are the experimentally observed quantities. The nature of the function, \( S \), will now be discussed. As a criterion of the fit, we will use as the best fit that which causes \( \left[ S / (N - n) \right]^{1/2} \) to be a minimum where \( n \) is the number of coefficients in \( F(x_{i}, x_{j}) \) and \( N \) is the number of experimental points.

b) The Function used by Guggenheim (70), Scatchard (71), Redlich (72) and Barker (73). Guggenheim first suggested, and other workers have since commonly used the function

\[
F(x_{i}, x_{j}) = \sum_{j=0}^{n} x_{i} x_{j} F_{j} (x_{1} - x_{2})^{j}
\]

which satisfies many requirements, namely \( F(x_{i}, x_{j}) = 0 \) when \( x_{1} = 0 \) and when \( x_{2} = 0 \). Increasing the number of terms (i.e. \( n \)) will allow more skewed or flattened curves to be represented.

Using equation (5.2.2) in (5.2.1)

\[
S = \sum_{i=1}^{N} \left( H^E_{i} - \sum_{j=0}^{n} x_{i} x_{j} F_{j} (x_{i} - x_{j})^{j} \right)^{2}
\]

\[
\frac{dS}{dF_{j}} = -2 \sum_{i=1}^{N} \left( H^E_{i} - \sum_{j=0}^{n} x_{i} x_{j} F_{j} (x_{i} - x_{j})^{j} \right) (x_{i} - x_{j})^{j} x_{i} x_{j}
\]

for all \( j = 0, 1, \ldots, n \).
When $S$ is a minimum $\frac{dS}{dF_k} = 0$ for all $k = 0, 1, \ldots, n$.

Thus

$$\sum_{j=0}^{\infty} \sum_{i=1}^{N} x_{1i} x_{2i} (x_{1i} - x_{2i})^{j+1} F_j = \sum_{i=1}^{N} x_{1i} x_{2i} H_i (x_{1i} - x_{2i})^j$$

for all $k = 0, 1, \ldots, n$, i.e. a set of $(n + 1)$ simultaneous equations in the $(n + 1)$ unknowns $F_0, F_1, \ldots, F_n$. Solution of these equations yields the constants $F_j$. Normally when $(n + 1) < N$ the function $F(x, x')$ will not collate $H_i$ at all $i = 1, \ldots, N$ and we therefore fit our data to the best curve.

In practice fitting by this method has been done in two ways. If we define

$$H_i \left( (x_{1i}, x_{2i}) \right) = Y_i$$

and

$$\left( x_{1i} - x_{2i} \right) = Z_i$$

then we can fit $Y_i$ to a simple polynomial in $Z$. Computationally this is easier than solving the equations shown in (5.2.4), since a standard library least squares procedure can be used.

However this procedure does not fit the given $H^E$ data so well as does that represented by equations (5.2.4). Computer programs are presented in Appendix 3 for curve fitting excess function data by these procedures and in Fig (5.2.1) the resulting smooth curves are plotted at 323.15 K as a function of composition.
THE EXCESS ENTHALPY OF MIXING, $H^e$
AT 323.15 K FOR HEXAFLUOROBENZENE
WITH
ISO PROPYL CYCLOHEXANE

1.000

0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9

MOLE FRACTION (C$_6$F$_3$)

1.000

TRIETHYLAMINE

PYRIDINE

CUMENE

2,6-LUTIDINE

N,N-DIMETHYL-α-TOLUIDINE

2,4-L COLIDINE

N,N-DIMETHYLANILINE

N,N-DIMETHYL-p-TOLUIDINE

N,N-DIMETHYL-m-TOLUIDINE

FIG (5.2.1)
c) The Function used by Myers and Scott (74), (Skewed Curve Fitting)

Myers and Scott pointed out that the function proposed by Guggenheim converges only slowly and is inefficient when the excess function curve is asymmetric in mole fraction. They suggested the use of the function

\[ F(x_1, x_2) = \frac{x_1 x_2}{1 - k(x_1 - x_2)} \sum_{j=0}^{n} F_j (x_1 - x_2)^j \]  

(5.2.7)

which again satisfies the requirements that \( F = 0 \) when \( x_1 = 0 \) or \( x_2 = 0 \). The skewing parameter \( k \), where \(-1 < k < 1\), is used to allow for large deviations from symmetrical distribution of the \( H^E \) curve about \( x_1 = x_2 = 0 \). When this function is used the criterion of the best fit is again that

\[ S = \sum_{i=1}^{N} \left( \frac{H^E_{i} - \frac{x_{1i} x_{2i}}{1 - k(x_{1i} - x_{2i})} \sum_{j=0}^{n} F_j (x_{1i} - x_{2i})^j}{1 - k(x_{1i} - x_{2i})} \right)^2 \]  

(5.2.8)

should be a minimum. This occurs when \( \frac{dS}{dF_j} = 0 \),

\[ \frac{dS}{dF_j} = -2 \sum_{i=1}^{N} \left( \frac{H^E_{i} - \frac{x_{1i} x_{2i}}{1 - k(x_{1i} - x_{2i})} \sum_{j=0}^{n} F_j (x_{1i} - x_{2i})^j}{1 - k(x_{1i} - x_{2i})} \right) \left( \frac{x_{1i} x_{2i} (x_{1i} - x_{2i})^j}{1 - k(x_{1i} - x_{2i})} \right) \]  

(5.2.9)

for all \( j = 0, 1, \ldots, n \), and also when \( \frac{dS}{dk} = 0 \), i.e. when

\[ 2 \sum_{i=1}^{N} \left( \frac{H^E_{i} - \frac{x_{1i} x_{2i}}{1 - k(x_{1i} - x_{2i})} \sum_{j=0}^{n} F_j (x_{1i} - x_{2i})^j}{1 - k(x_{1i} - x_{2i})} \right) \left( \frac{x_{1i} x_{2i} \sum_{j=0}^{n} F_j (x_{1i} - x_{2i})^j}{(1 - k(x_{1i} - x_{2i}))^2} \right) \]  

(5.2.10)

The set of equations represented in equations (9) and (10) are nonlinear and the simultaneous equations do not necessarily provide a unique solution for the \((n + 2)\) coefficients \((F_0, F_1, \ldots, F_n, k)\).
Myers and Scott suggested that \( k \) should be determined empirically for each system and once found the same value should be used for all properties and for all temperatures. They calculated \( k \) in order that the maximum in the first term of the series, i.e., when \( j = 0 \), should occur at the same composition as the experimentally observed maximum. If \( x_{2_{\text{max}}} \) is the mole fraction where \( |H^E| \) is a maximum then

\[
\frac{k}{2} = \frac{2(1 - 2x_{2_{\text{max}}})}{(1 + (1 - 2x_{2_{\text{max}}})^2)}.
\]

We have standardised our technique in two ways. If the best possible fit is required then \( k \) is fitted for, as also are the parameters, but if the skewing factor \( k \) is to be used for comparison purposes then one value is determined by fitting with \( j = 0 \), and this value used subsequently for all other operations on that system. When curve fitting for \( k \) is carried out a method of successive approximations is used. If a better fit is given by

\[
F^*(x_1, x_2) = \frac{x_1 x_2}{1 - k(x_1 - x_2)} \sum_{j=0}^{n} f_j^* (x_1 - x_2)^j
\]

\[
= \frac{F(x_1, x_2)}{F(x_1, x_2) + \delta F(x_1, x_2)} (5.2.11).
\]

Now

\[
\delta F = \sum_{j=0}^{n} \frac{\partial F(x_1, x_2)}{\partial F_j} \delta F_j + \frac{\partial F(x_1, x_2)}{\partial k} \delta k (5.2.12),
\]

then since

\[
S = \sum_{i=1}^{N} \left( H^E_{i} - F(x_{i_1}, x_{i_2}) \right)^2
\]
if \( F^*(x_i, x_t) \) is a better representation we can choose values of \( \delta F_j, \delta k \) such that

\[
S = \sum_{i=1}^{N} \left( H_i - F(x_i, x_t) - \delta F(x_i, x_t) \right)^2.
\]

is a minimum. And if we write \( R_i = H_i - F(x_i, x_t) \), then

\[
S = \sum_{i=1}^{N} \left( R_i - \sum_{j=0}^{n} \frac{\partial F}{\partial F_j} \delta F_j - \frac{\partial F}{\partial k} \delta k \right)^2
\]

is a minimum when \( \frac{\partial S}{\partial F_j} = \frac{\partial S}{\partial k} = 0 \) for all \( j = 0, 1, \ldots, n \), i.e. when

\[
-2 \sum_{i=1}^{N} \left( R_i - \sum_{j=0}^{n} \frac{\partial F}{\partial F_j} \delta F_j - \frac{\partial F}{\partial k} \delta k \right) \left( \frac{\partial F}{\partial F_j} \delta F_j + \frac{\partial F}{\partial k} \delta k \right) = 0 \quad (5.2.13)
\]

for all \( j = 0, 1, \ldots, n \), and also

\[
-2 \sum_{i=1}^{N} \left( R_i - \sum_{j=0}^{n} \frac{\partial F}{\partial F_j} \delta F_j - \frac{\partial F}{\partial k} \delta k \right) \left( \frac{\partial F}{\partial F_j} \delta F_j + \frac{\partial F}{\partial k} \delta k \right) = 0 \quad (5.2.14)
\]

We can therefore solve the set of \((n + 2)\) linear simultaneous equations:

\[
\sum_{i=1}^{N} \sum_{j=0}^{n} \left( \frac{\partial F}{\partial F_j} \right) \delta F_j + \sum_{i=1}^{N} \left( \frac{\partial F}{\partial k} \right) \delta k = \sum_{i=1}^{N} R_i \frac{\partial F}{\partial F_i} \quad (5.2.15)
\]

for all \( j = 0, 1, \ldots, n \) and

\[
\sum_{i=1}^{N} \sum_{j=0}^{n} \left( \frac{\partial F}{\partial F_j} \right) \delta F_j + \sum_{i=1}^{N} \left( \frac{\partial F}{\partial k} \right) \delta k = \sum_{i=1}^{N} R_i \frac{\partial F}{\partial k} \quad (5.2.16)
\]

uniquely to give the \( \delta F_j \) and \( \delta k \). The new values of \( F_j^* = F_j + \delta F_j \) and \( k^* = k + \delta k \) are then calculated and the process repeated until a minimum is found.
If \( k \) is set equal to zero and the value is not changed by fitting, this procedure produces identical results to those obtained using the Guggenheim function.

The program for performing these "skewed" curve fits is given in Appendix 3. However if \( k \) is regarded as a parameter along with the other parameters \( F_j \) then this procedure normally gives only a slightly better fit than the Guggenheim function with the same total number of parameters.

d) Curve Fitting using Orthogonal Polynomials

This technique has not yet achieved widespread use for representing thermodynamic functions but owing to its speed in use it will probably do so in the near future.

Consider the function

\[
F(x_1, x_2) = \sum_{j=1}^{n} F_j \phi_j(x_i)
\]  

(5.2.17)

where \( \phi_j \) is a polynomial in \( x_i \), then

\[
S = \sum_{i=1}^{N} \left( H_i^E - \sum_{j=1}^{n} F_j \phi_j(x_i) \right)^2
\]

(5.2.18)

This will be a minimum when \( \frac{\partial S}{\partial F_j} = 0 \) for all \( j = 1, 2, \ldots, n \), i.e.

\[
\sum_{i=1}^{N} \left( H_i^E - \sum_{j=1}^{n} F_j \phi_j(x_{i,j}) \right) \phi_j(x_{i,j}) = 0
\]

(5.2.19)

for all \( j = 1, 2, \ldots, n \).
Now orthogonal polynomials are defined by the relationships

$$\sum_{k=1}^{N} \phi_r \phi_s = 0 \quad \text{when} \quad r \neq s \quad \ldots \quad (5.2.20)$$

and

$$\sum_{k=1}^{N} \phi_r \phi_s \neq 0 \quad \text{when} \quad r = s$$

Then

$$F_r = \sum_{x=1}^{N} \frac{H^E \phi_r(x_i)}{\sum_{x=1}^{N} (\phi_r(x_i))^2} \quad (5.2.21).$$

Thus the coefficients $F_1, F_2, \ldots, F_n$ are uniquely determined by solving $n$ simple equations.

If the $N$ values cover the range $0 \leq x_i \leq 1$ then the orthogonality condition, $\sum_{x=1}^{N} \phi_r \phi_s = 0$ when $r \neq s$ for all $r, s$, can be written (using the mean value theorem)

$$\int_0^1 \phi_r(x_i) \cdot \phi_s(x_i) \, dx_i = 0 \quad \text{when} \quad r \neq s$$

Consider the function

$$\phi_r(x_i) = x_i (1 - x_i) \sum_{a=1}^{r} a x_i^{a-1}$$

and similarly

$$\phi_s(x_i) = x_i (1 - x_i) \sum_{b=1}^{s} b x_i^{b-1}$$

which satisfies the obvious conditions $\phi_r = \phi_s = 0$ when $x_i = 0$ and when $x_i = 1$. 

Then
\[
\int_0^1 x_i^2 (1-x_i)^2 \sum_{i=1}^r a_i x_i^{i-1} \sum_{j=1}^s b_j x_i^{j-1} = 0
\]
which may be written
\[
\int_0^1 \sum_{j=1}^s b_j \sum_{i=1}^r a_i \left( x_i^{i+j} - 2 x_i^{i+j+1} + x_i^{i+j+2} \right) = 0
\]
on integration this yields
\[
\sum_{j=1}^s b_j \sum_{i=1}^r a_i \frac{2}{(i+j+1)(i+j+2)(i+j+3)} = 0
\]
(5.2.22)
for all \( r = 1, 2, \ldots, S - 1 \). Thus the set of \( S - 1 \) equations in the \( S \) unknowns \( b_1, b_2, \ldots, b_S \) enables us to determine a solution involving one arbitrary parameter.

Choosing the parameter such that \( b_1 = 1 \) enables \( b_2, \ldots, b_S \) to be uniquely determined. A program has been written to determine the set of orthogonal polynomials and to determine the coefficients as above and it is shown in Appendix 3. However with only a limited amount of data the integral is not an adequate representation of the orthogonality condition and all the parameters must be determined in a similar way to that described for the Guggenheim function above. At the present time it is not clear to what extent orthogonal polynomials will be used in the future (75).
5.3 PRESENTATION OF CURVE FITTING RESULTS

The parameters calculated for each system by each curve fitting method described above are shown in Tables (5.3.1) - (5.3.10). These results are presented along with the Root Mean-Square deviations and the Standard deviations.
TABLE (5.3.1)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + N,N-DIMETHYL-m-TOLUIDINE (2),

a) Method 1, using \( \frac{H^E}{x_1, x_2} \sum_{j=1}^{n} H_j (x_1 - x_2)^{j-1} \)

<table>
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<tr>
<th>( H_j )</th>
<th>( J \cdot mol^{-1} )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \text{RMS} )</th>
<th>( \text{STD} )</th>
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b) Method 2, using \( \frac{H^E}{x_1, x_2} \sum_{j=1}^{n} H_j (x_1 - x_2)^{j-1} \)

<table>
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<tr>
<th>( H_j )</th>
<th>( J \cdot mol^{-1} )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \text{RMS} )</th>
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TABLE (5.3.1) (Continued)

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<tr>
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<td>where the $\phi_i$ are suitably chosen orthogonal polynomials</td>
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TABLE (5.3.2)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM: HEXAFLUOROBENZENE (1) + N,N-DIMETHYL-p-TOLUIDINE (2),

a) Method 1, using $H^E/x_1 x_2 = \sum_{i=1}^{n} H_i (x_i - x_1)^{i-1}$

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<th>$H_4$</th>
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b) Method 2, using $H^E = \sum_{i=1}^{n} x_1 x_2 H_i (x_i - x_1)^{i-1}$

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TABLE (5.3.2) (Continued)

c) Method 3, Skewed Curve Fitting, using
\[ H^E = \sum_{i=1}^{n} \lambda_i \alpha_i H_i (\alpha_i - \alpha_j)^{i-1} / (1 - k(\alpha_i - \alpha_j)) \]

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d) Method 4, Orthogonal Polynomials, using
\[ H^E = \sum_{i=1}^{n} H_i \phi_i \]
where the $\phi_i$ are suitably chosen orthogonal polynomials

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TABLE (5.3.3)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + N,N-DIMETHYLANILINE (2),

a) Method 1, using \( H^E / x_1, x_2 = \sum_{i=1}^{n} H_i (x_i - x) \)

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b) Method 2, using \( H^E = \sum_{i=1}^{n} x_i, x_1 H_i (x_i - x) \)

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TABLE (3.3.3) (Continued)

c) Method 3, Skewed Curve Fitting, using

\[ H_i^E = \sum_{x_i}^n x_i, x_i = H_i \left( x_i - x_i \right)^{\phi - 1} / \left( 1 - k(x_i - x_i) \right) \]

<p>| ( H_1 ) | ( H_2 ) | ( H_3 ) | ( H_4 ) | ( H_5 ) | ( H_6 ) | ( H_7 ) | RMS | STD |</p>
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d) Method 4, Orthogonal Polynomials, using

\[ H_i^E = \sum_{\phi = 1}^n H_i \phi_i \]

where the \( \phi_i \) are suitably chosen orthogonal polynomials

<p>| ( H_1 ) | ( H_2 ) | ( H_3 ) | ( H_4 ) | ( H_5 ) | ( H_6 ) | ( H_7 ) | RMS | STD |</p>
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TABLE (5.3.4)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + 2,4,6-TRIMETHYL PYRIDINE (2),

a) Method 1, using $H^E / \chi, \chi_2 \approx \sum_{i=1}^{n} H_i (\chi_i - \chi_2)^{i-1}$

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b) Method 2, using $H^E = \sum_{i=1}^{n} \chi_i \chi_2 H_i (\chi_i - \chi_2)^{i-1}$

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TABLE (3.5.4) (Continued)

c) Method 3, Skewed Curve Fitting, using
\[ H_i \triangleq \sum_{i=1}^{n} x_i \cdot x_i \cdot H_\alpha \cdot (x_i - x_i)^{i-1} / (1 - k(x_i - x_i)) \]

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d) Method 4, Orthogonal Polynomials, using
\[ H_i \triangleq \sum_{i=1}^{n} \phi_i \]
where the \( \phi_i \) are suitably chosen orthogonal polynomials

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TABLE (5.3.5)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + N,N-DIMETHYL-o-TOLUIDINE (2),

a) Method 1, using \( \frac{H^E}{x_1, x_2} = \sum_{i=1}^{n} H_i (x_i - x_i)_{i-1} \)

<table>
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<tr>
<th>( H_1 )</th>
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<th>( H_3 )</th>
<th>( H_4 )</th>
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b) Method 2, using \( H^E = \sum_{i=1}^{n} x_1, x_2, H_i (x_i - x_i)_{i-1} \)

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<th>( H_3 )</th>
<th>( H_4 )</th>
<th>( H_5 )</th>
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TABLE (5.3.5) (Continued)

c) Method 3, Skewed Curve Fitting, using

\[
H^E = \sum_{i=1}^{n} x_i x_i H_i (x_i - x_i)^{i-1} / (1 - k (x_i - x_i))
\]

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<th>(H_4) J.mol(^{-1})</th>
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<th>(H_6) J.mol(^{-1})</th>
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d) Method 4, Orthogonal Polynomials, using

\[
H^E = \sum_{i=1}^{n} H_i \phi_i
\]

where the \(\phi_i\) are suitably chosen orthogonal polynomials

<table>
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<tr>
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TABLE (5.3.6)
CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFUOROBENZENE (1) + 2,6-DIMETHYL PYRIDINE (2),
a) Method 1, using

\[ H^E / x_1, x_2 = \sum_{i=1}^{n} H_i (x_i - x_2)^{i-1} \]

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<tr>
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<th>( H_4 )</th>
<th>( H_5 )</th>
<th>( H_6 )</th>
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b) Method 2, using

\[ H^E = \sum_{i=1}^{n} x_i, x_i | H_i (x_i - x_2)^{i-1} \]

<table>
<thead>
<tr>
<th>( H_1 )</th>
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<th>( H_3 )</th>
<th>( H_4 )</th>
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<th>( H_6 )</th>
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</table>
c) Method 3, Skewed Curve Fitting, using

\[
H^E = \sum_{i=1}^{n} x_i \sum_{i=1}^{n} h_i (x_i - x_t) + \frac{i}{1 - k(x_i - x_t)}
\]

<table>
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<th>$H_3$ (J.mol$^{-1}$)</th>
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d) Method 4, Orthogonal Polynomials, using

\[
H^E = \sum_{i=1}^{n} h_i \phi_i
\]

where the $\phi_i$ are suitably chosen orthogonal polynomials

<table>
<thead>
<tr>
<th>$H_1$ (J.mol$^{-1}$)</th>
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TABLE (5.3.7)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:

HEXAFLUOROBENZENE (1) + iso-PROPYLBENZENE (CUMENE) (2),

\[ H^E / \chi_i \chi_j = \sum_{i \neq j} H_{ij} (\chi_i - \chi_j)^{\alpha - 1} \]

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</table>

b) Method 2, using

\[ H^E = \sum_{i \neq j} \chi_i \chi_j H_{ij} (\chi_i - \chi_j)^{\alpha - 1} \]

<table>
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</table>
TABLE (5.3.7) (Continued)

c) Method 3, Skewed Curve Fitting, using

\[ H^E = \sum_{i=1}^{n} x_i x_j H \left( x_i - x_j \right)^{\lambda-1} \left/ \left( 1 - k \left( x_i - x_j \right) \right) \right. \]

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<th>( H_4 )</th>
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d) Method 4, Orthogonal Polynomials, using

\[ H^E = \sum_{i=1}^{n} \phi_{\lambda} \]

where the \( \phi_{\lambda} \) are suitably chosen orthogonal polynomials

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TABLE (5.3.8)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + PYRIDINE (2),

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<th>Method 2, using $H^E = \sum_{i=1}^{n} H_i x_1 x_2 (x_i - x_an$</th>
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TABLE (5.3.8) (Continued)

c) Method 3, Skewed Curve Fitting, using

\[ H^E = \sum_{i=1}^{n} x_i x_i H_i \left( x_i - x_i \right) (i - k (x_i - x_i)) \]

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d) Method 4, Orthogonal Polynomials, using \( H^E = \sum_{i=1}^{n} H_i \phi_i \)

where the \( \phi_i \) are suitably chosen orthogonal polynomials

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TABLE (5.3.9)
CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + TRIETHYLAMINE (2),

\[ H^E / x_1 x_2 = \sum_{i=1}^{n} H_{i} (x_1 - x_2) ^{-1} \]

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b) Method 2, using

\[ H^E = \sum_{i=1}^{n} x_1 x_2 H_{i} (x_1 - x_2) ^{-1} \]

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TABLE (5.3.9) (Continued)

c) Method 3, Skewed Curve Fitting, using
\[ H^E = \sum_{i=1}^{n} x_i \alpha_i H_i \left( x_i - x_i \right)^{n-1} / (1 - k(x_i - x_i)) \]

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d) Method 4, Orthogonal Polynomials, using
\[ H^E = \sum_{i=1}^{n} H_i \phi_i \]
where the \( \phi_i \) are suitably chosen orthogonal polynomials

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TABLE (5.3.10)

CURVE FITTING THE EXCESS ENTHALPY DATA FOR THE SYSTEM:

HEXAFLUOROBENZENE (1) + ISO-PROPILCYCLOHEXANE (2),

a) Method 1, using \( H^E / x_1, x_2 = \sum_{i=1}^{n} H_i (x_i - x_t)^{i-1} \)

| \( H_1 \) | \( H_2 \) | \( H_3 \) | \( H_4 \) | \( H_5 \) | \( H_6 \) | RMS | STD |
| J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) |
| 5161 | 281 | 194 | 111 | 15 |
| 5166 | 72 | 151 | 634 | 8 | 13 |
| 5173 | 74 | -9 | 617 | 356 | 8 | 16 |
| 5174 | -27 | -20 | 1763 | 440 | -2172 | 8 | 21 |

b) Method 2, using \( H^E = \sum_{i=1}^{n} x_i x_t H_i (x_i - x_t)^{i-1} \)

| \( H_1 \) | \( H_2 \) | \( H_3 \) | \( H_4 \) | \( H_5 \) | \( H_6 \) | RMS | STD |
| J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) | J.mol\(^{-1}\) |
| 5183 | 242 | 12 | 23 |
| 5163 | 243 | 174 | 11 | 15 |
| 5167 | 65 | 141 | 660 | 8 | 13 |
| 5170 | 66 | 80 | 653 | 145 | 8 | 16 |
| 5171 | -27 | 65 | 1753 | 239 | -2133 | 8 | 21 |
(107)

**TABLE (5.3.10) (Continued)**

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**c) Method 3, Skewed Curve Fitting, using**

\[
\frac{1}{k} = \sum_{x_i} x_i x_i' H_i \left( x_i - x_i' \right)^{-1} \left( 1 + k \left( x_i - x_i' \right) \right)
\]

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</table>

**d) Method 4, Orthogonal Polynomials, using**

\[
\frac{1}{k} = \sum_{x_i} H_i \phi_i
\]

where the \(\phi_i\) are suitably chosen orthogonal polynomials.
CHAPTER SIX

THE DESIGN AND OPERATION OF AN
APPARATUS TO MEASURE VAPOUR PRESSURE
6.1 STATIC METHODS FOR VAPOUR PRESSURE MEASUREMENT

It is in recent years that static measurements of vapour pressure have been refined to compete successfully with equilibrium still dynamic methods. Much of the pioneering work in this field was due to Baxandale (76), Everett and Penney (77) and Williamson and McGlashan (78, 79). They constructed an apparatus (Fig 6.1.1) in which a liquid sample was sealed in equilibrium with vapour by a mercury cut-off. They stated that the most favourable apparatus would have a cut-off assembly capable of directly measuring a pressure of $10^{-5}$ N·m$^{-2}$ but considered the difficulties in building a really accurate thermostat of large size to be greater than using two mercury manometers connected in series.

Other workers have improved the ease of operation of a static apparatus. Gaw and Swinton (56, 59) have used a similar apparatus (Fig 6.1.2) but have replaced the buffer line and second manometer, with a second cell containing a reference liquid, in equilibrium with its vapour, the vapour pressure of which is known accurately. With suitable choice of reference material the method can be applied to any system and involves measuring only two mercury heights. Furthermore, the entire manometer apparatus is housed in the thermostat and the thermostat dimensions are not excessively large.

Marsh (80) has followed the suggestion of Williamson (79) and has built an apparatus where a large U-tube manometer is housed in a suitably sized thermostat. Whilst larger temperature
Differential manometer. A, the manometer limbs; B, side vessels; C, mercury cut-offs; D, stirrers; E, stirrer magnets; F, to mercury reservoir.

Vacuum line. A, differential manometer; C1, C2, J1, J2, mercury cut-offs; G1, G2, ampoule-loading devices; H, main vacuum line; I1, I2, twin sample reservoirs; K, greased stopcocks for filling ampoules; Z, to vacuum pumps.

Ampoule-loading device. L, ampoule; M, mercury-sealed B19 stopper; N, metal breaker; O, to differential manometer via mercury cut-off C; P, twin bulbs for final outgassing.

Fig (6.1.2)
fluctuations (±0.05 K) were recorded with this thermostat. Marsh considered that the errors which this incurred were less significant than those incurred by either a gas buffer line or by using a pure liquid to generate a reference pressure, and that sample preparation and operation of the apparatus were considerably simplified.

§6.2 THE BASIC REQUIREMENTS OF THE APPARATUS

A basic apparatus similar to that described by Williamson had been built by Morcom but no successful measurements had been made. However, as much of the apparatus had been constructed, including a manometer and a suitable thermostat bath it was decided to retain the Williamson method using a buffer line to link the two manometers. The existing apparatus together with the author's modifications will now be described, initially dealing only with the principle of operation, before the actual designs of the various sections are presented.

Static methods of vapour pressure measurement involve the measurement of the pressure generated at the surface of the liquid which is in equilibrium with its vapour. The liquid is housed in a cell which is connected to a U-tube manometer. This manometer is governed in size by the size of the thermostat used but should be as large as possible. The thermostat has a plate glass window through which the manometer can be viewed. In addition to this
manometer which is of necessity small with our apparatus a large (1 m) U-tube manometer is provided. One side of this manometer can be evacuated whilst the other side is connected to the opposite side of the thermostat manometer to the cut-off. This connecting tube will be called the buffer line and can be filled with dry nitrogen to the required pressure.

The liquid sample was introduced into the cell by distillation through the cut-off, after the mercury had been removed. In order to do this it was necessary to be able to pump the cut-off assembly down to a hard vacuum and also an apparatus had to be designed in order that the mercury in the cut-off could be either raised or lowered. A number of ground glass sockets and a vessel provided with a tap were incorporated in the vacuum line in order that all the materials to be used could be degassed and ampouled. Fig (6.2.1) shows the completed apparatus diagrammatically and the individual sections will now be fully described.

§ 6.3 THE CUT-OFF AND THERMOSTAT

The thermostat tank which housed the cut-off assembly was very similar to that designed by Williamson (78, 79) but was rigidly mounted on a "Dexion" frame. Placed below the thermostat tank was a water tank of the same size as the thermostat into which the water could be drained off, through a stopcock. The lower tank was lagged with expanded polystyrene sheeting and was fitted
with a centrifugal pump which was used to raise the water from the lower tank into the upper thermostat tank. Stirring of the water in the thermostat tank was achieved with a Gunn Stirrer (Continuous Rating Pump Stirrer, Messrs. D.A. Gunn (Engineering) Ltd., Gloucester) and the tank housed a (400 W 80 V) pyrotenax permanent heater controlled with a "Variac" transformer and a (250 W 50 V) pyrotenax intermittent heater fed from a "Variac" transformer and controlled with a cyclohexane - mercury regulator of the same design as that used by Williamson (79). The thermostat temperature was measured using a platinum resistance thermometer (Type 5187 H, Messrs. H. Tinsley and Co. Ltd., London, S.E.25.) and a Muller Bridge (Type 4772, Messrs. H. Tinsley and Co. Ltd., London, S.E.25.) with the Kipp - Zonen recorder (Micrograph type BD2) as galvanometer. At 30°C the temperature was steady to within ±0.001 K for long periods of time and at 60°C the temperature was steady to within ±0.005 K for long periods of time.

Two types of cut-off were made, both of which were designed to house two samples within the thermostat at any one time. The first type (Fig. 6.3.1) was not used for any measurements as it was extremely difficult to handle and was extremely fragile. The arms which supported the cells both broke off before any measurements had been made using it and so it was decided to rebuild the assembly.

This design (Fig 6.3.2) incurred some loss of versatility since the manometer design adopted (81) could not be used to measure small pressures. The cut-off on the left of Fig (6.3.2) is used for measurements of relatively high pressure as will be described later whilst that on the right is used when the vapour
CUT-OFF ASSEMBLY

MODIFIED DESIGN

TANK TOP

WATER LEVEL

TANK WINDOW

TANK BASE

Fig (b.3.2)
pressures to be measured are extremely small. In this case a buffer line to the other manometer has to be used.

The heights of the mercury levels were measured through the plate glass window of the thermostat tank using a cathetometer (Precision Tool and Instrument Co. Ltd). The instrument could be read to 0.01 mm and it was found possible to set the cathetometer on a given meniscus with an accuracy of better than ±0.01 mm. The menisci were illuminated from behind with a 9" fluorescent tube (8 W 250 V) housed in a long glass tube placed in the tank. The light was diffused by also inserting into the glass tube a translucent roll of paper. The low power of the fluorescent tube did not cause the paper to burn and this illumination together with light shields around the manometers ensured even illumination of the menisci. The manometers were constructed from Veridia precision bore tubing of 20.00 mm diameter and the taps used for the cut-off were of a greaseless design (Type Uni-Form (10mm), supplied by Messrs. Jencons (Scientific) Ltd., Hemel Hempstead, Hertfordshire). The mercury reservoir was placed below the two manometers, in order that the mercury could be removed from the cut-off, and was filled with the minimum possible quantity of pure mercury. The top of the reservoir was connected to that section of the apparatus which allowed a pressure of dry nitrogen to be applied, in order that the mercury could be raised when required.

Every time the cut-off was removed from the tank it was thoroughly cleaned with fresh hot chromic acid and washed with deionised water. The mercury which had been removed was filtered
at this time but it was not found necessary to repurify it.

§ 6.4 THE BUFFER LINE, VACUUM LINE AND THE MAIN MANOMETER

The buffer line and the vacuum line are joined to the cut-off assembly and then pass on to taps $T_5$ and $T_6$ in Fig (6.2.1). Tap $T_6$ connects the cut-off assembly directly to the high vacuum system, which consisted of a three stage mercury diffusion pump backed by a single stage rotary oil pump. The pumps were both protected by a cold trap, as shown in Fig (6.2.1). With the aid of $T_6$, the cut-off and the ampoule breaking apparatus (yet to be described) could be evacuated without disturbing any other sections of the apparatus.

Tap $T_5$ connected the buffer line to the main manometer by way of tap $T_{12}$ which allowed the buffer gas pressure to be adjusted. The main manometer was a larger version of the precision manometers (81) used for the twin cut-off assembly and was 1 m long in order that the apparatus could measure pressures over $10^5$ N.m$^{-2}$. The manometer was constructed from Veridia precision bore tubing of 20.00 mm diameter and was housed in a wooden case having a plate glass window on one side and a ground glass window on the other. Behind the ground glass window was a 4 ft. fluorescent tube which gave even illumination for the mercury menisci. Light shields were provided in order that sharp images of the menisci could be obtained. A given mercury meniscus height could always be read to
within ±0.01 mm, using a second P.T.I. cathetometer.

The low pressure side of the main manometer was connected by way of tap \( T_{14} \) to the main vacuum line which ran by way of taps \( T_1 \) and \( T_7 \) to the trap and pumps. The pressure was measured with a Pirani gauge and a Penning gauge but before the apparatus was completed the Penning gauge became faulty and was removed. The pressure in the system even with all sections of the line evacuated was certainly below \( 10^{-2} \text{ N m}^{-2} \) which was quite satisfactory for this apparatus.

\[ \text{6.5 THE SAMPLE PREPARATION LINE} \]

With static methods it is essential that the samples are thoroughly degassed before measurements are made on them and a section of line Fig (6.5.1) was provided for the degassing operation. It consisted of five B10 ground glass sockets to which ampoules or cells could be attached, and a storage container with a tap, \( T_{10} \). The apparatus was connected to the main vacuum line by tap, \( T_q \), with which it could be isolated from the remainder of the apparatus when not required.
THE SAMPLE PREPARATION LINE

Fig (6.5.1)
6.6 THE AMPOULE BREAKING APPARATUS

The apparatus was designed so that the composition of the sample in the cell could be changed by lowering the mercury in the cut-off and quantitatively distilling a known amount of one component into the cell. The ampoule breaking equipment is shown in Fig (6.6.1) and is designed so that compositions may be changed without any glass blowing.

The apparatus consists of a vertical glass tube at the top of which is a pocket in which a breaker can be held. The breaker itself consists of a heavy piece of soft iron sealed in a glass envelope. Running horizontally below this vertical tube is the tube which houses the ampoule which is to be broken. The open end of this tube is connected to the buffer line as close to the cell as possible whereas the other end can be sealed using the mercury sealed stopper (56). This section consists of a B19 ground glass socket and stopper which can be surrounded by mercury which effectively seals the joint without the use of any grease. In use an ampoule of the type to be described later in this chapter is inserted through the B19 socket and is positioned with its break seal under the vertical tube by using further pieces of soft iron sealed in glass, controlled externally with magnets. The ampoule can be opened when desired simply by moving the breaker from its pocket with a magnet and allowing it to fall onto the fragile break seal of the ampoule.

It is important that the distilling vapour should not come
into contact with grease used to lubricate taps as quantitative distillation may not then occur. Every effort was made to eliminate greased taps entirely by the use of Teflon greaseless taps (Messrs. Jencons (Scientific) Ltd., Hemel Hempstead, Hertfordshire). These taps were, however, highly unreliable and could not be guaranteed to hold a good vacuum. Taps $T_5$ and $T_6$ were to have been greaseless taps of this type but had to be replaced by greased taps owing to leakage. However the vapour did not pass through these greased taps and Williamson (79) showed that under suitable conditions the loss of vapour following this distillation procedure was negligible. After distillation when the cut-off mercury had been raised the pressure in the line was always below $10^{-1} \text{ N.m}^{-2}$, and did not show any tendency to rise when the grease was left to equilibrate with the space of the vacuum line.

6.7 THE NITROGEN SUPPLY

"White Spot" nitrogen from the laboratory supply was dried by passing it through a tube containing active silica gel and then to the nitrogen supply line of the apparatus. Taps $T_8$ and $T_{15}$ were arranged so that the nitrogen could be distributed to any desired part of the apparatus. Between taps $T_{14}$, $T_{15}$ and $T_{13}$ was a simple U-tube manometer capable of recording $1.5 \times 10^5 \text{ N.m}^{-2}$ total pressure change. This was connected via tap $T_{13}$ to another manometer of the same size and a $2.5 \times 10^{-4} \text{ m}^3$ glass bulb, and then by the two way tap $T_{142}$ to either the buffer line or the cut-off mercury supply.
The use of two manometers and the large expansion bulb permitted fine control of the pressure in either section of the apparatus, which was particularly necessary when adjustments were made to the nitrogen pressure in the buffer line.

§ 6.8 PREPARATION AND DESIGN OF CELLS

The principal feature affecting the design of cells was the volatility of the materials whose vapour pressure was to be studied. If one component of the mixture was relatively involatile it was necessary to use a cell having a break seal as this component could not be quantitatively distilled through the apparatus. The design of cell adopted is shown in Fig (6.8.1) and includes a break seal in order that the apparatus may be used with involatile materials. The cell is attached to the cut-off by means of the breaker attachment shown in Fig (6.8.2).

The procedure used to fill a cell with N,N-dimethylaniline will now be described. A cell was thoroughly cleaned using freshly prepared hot chromic acid, washed fully with deionised water and dried in an air oven. The outside of the cell was wiped with a dry cloth and the inside examined for any solid material. If the cell was judged satisfactory then a stirrer, made from a small nail sealed in glass was inserted and the opening drawn down to a constriction. The cell was then completely filled with water using a hypodermic syringe and a long needle taking care that no air
THE CELL

Fig (b.8.1)
THE BREAKER ATTACHMENT

Fig (6.8.2)
remained trapped in the break seal and that the water level at balance room temperature was halfway up the constriction. The cell was placed upon a weighed aluminium pan on the most accurate suitable balance and weighed twice, leaving an hour between weighings. The water was then emptied and the cell dried over night in an air oven. The cell was then placed on the sample preparation section of the vacuum line using only a very small amount of grease at the lower edge of the B10 cone and B10 stoppers in the other sockets. With tap \( \text{T}_0 \) closed the cell was pumped down to hard vacuum and then air was let back to fill the cell. The grease was washed away with 40 - 60 petroleum ether and the cell placed on the aluminium plate and weighed twice on a suitable balance, the case of which contained a dish of active silica gel. Half an hour was always allowed for moisture to be removed from the surface of the cell, and half an hour was allowed between weighings. The B10 ground glass cone was then re-washed in 40 - 60 petroleum ether and the cell was again reweighed twice. The weights always agreed to within \( \pm 0.0001 \) g of the mean. The desired quantity of \( N,N\text{-dimethylam}i\text{line} \) was then placed in the cell from a hypodermic syringe and the cell attached to the sample preparation line of the apparatus. The liquid was frozen down in liquid nitrogen and after about ten minutes the tap opened and the frozen material pumped hard down. The material was then allowed to thaw and the process repeated a further four times. When this had been done the degassing operation was continued by repeated vacuum distillation from one bulb to the other using a liquid nitrogen trap to cause the distillation; and an industrial hot air blower, to heat gently the liquid in the other bulb. The metal-in-glass stirrer was moved around with a magnet so that it was not cracked by the cold trap
and after each distillation had been completed the cell was pumped down to hard vacuum. After three such distillations the pressure did not rise above $10^{-2} \text{N.m}^{-2}$ but the process was continued until twelve distillations had been carried out, when the cell was detached from the B10 cone by sealing off at the constriction with the liquid frozen down in liquid nitrogen and the tap open to the pumps. Whilst the cell was being weighed in exactly the same way as was previously described the B10 cone was washed firstly in toluene and then in 40 - 60 petroleum ether. The joint was weighed twice and then rewashed before a second series of weighings was made.

After each weighing the temperature of the balance room was noted in addition to the weight recorded as this was needed for the calculation of the weight of sample taken. It is important to make buoyancy corrections to every weight recorded in order that the true weight can be accurately calculated. If

$$W_i = \text{weight of aluminium pan (observed)}$$

$$W_2 = \text{weight of aluminium pan + complete cell (observed)}$$

$$W_3 = \text{weight of aluminium pan + filled cell (observed)}$$

$$W_4 = \text{weight of ground glass joint (observed)}$$

$$W_5 = \text{weight of aluminium pan + complete cell}$$

$$+ \text{water (observed)}$$

and $W_{it}$ represents the true mass of component(s) $i$ and $\rho_i$ denotes the density of air for each of the weighings and $\rho_{\text{AL}}$, $\rho_{\text{G}}$ and $\rho_{\text{W}}$ are the densities of aluminium, glass and the balance weights respectively, then

$$W_{it} = W_i \left[ 1 - \frac{\rho_i}{\rho_{\text{W}}} \right] \left[ 1 - \frac{\rho_i}{\rho_{\text{AL}}} \right]$$

(6.8.1)
\[ w_{4t} = w_4 \left[ 1 - \frac{\sigma_2}{\rho_w} \right] \left[ 1 - \frac{\sigma_3}{\rho_g} \right]^{-1} \]  

(6.8.2)

and \( w_{2t} \) (the true weight of the cell alone)

\[ w_2 \left[ 1 - \frac{\sigma_2}{\rho_w} \right] \left[ 1 - \frac{\sigma_3}{\rho_g} \right]^{-1} = w_{1t} \left[ 1 - \frac{\sigma_3}{\rho_{nl}} \right] \left[ 1 - \frac{\sigma_3}{\rho_g} \right]^{-1} \]  

(6.8.3)

and if \( V \) is the internal volume of the cell, to the constriction, and if \( \rho_{w0} \) is the density of water at the temperature of weighing (5) then

\[ V = \frac{w_5 \left[ 1 - \frac{\sigma_2}{\rho_w} \right] - w_{1t} \left[ 1 - \frac{\sigma_3}{\rho_{nl}} \right] - w_{2t} \left[ 1 - \frac{\sigma_3}{\rho_g} \right]}{\left[ \rho_{w0} - \sigma_s \right]} \]  

(6.8.4)

and also

\[ w_{3t} = w_3 \left[ 1 - \frac{\sigma_3}{\rho_w} \right] - w_{1t} \left[ 1 - \frac{\sigma_3}{\rho_{nl}} \right] + \left[ V + \frac{(w_{2t} - w_{4t})}{\rho_g} \right] \]  

(6.8.5)

Then weight of sample

\[ w_5 = w_{3t} + w_{4t} - w_{2t} \]  

(6.8.6)

The cell is now ready to be attached to the cut-off assembly on the appropriate manometer. This is accomplished by joining the extension above the break seal to the cell breaker housing in such a way that there is no constriction of the breaker tube. The other arm is attached to the cut-off and care is taken to ensure that the water-proof stirrer motor can be inserted under the cell when it is in position in the tank. The cut-off assembly is then
placed in the thermostat and the gas buffer line and mercury supply lines connected to the corresponding tubes on the vacuum line.

6.9 PREPARATION OF AMPOULES OF VOLATILE COMPONENT

The procedure used here was similar to that employed with cells, except that a number of ampoules were filled from the same sample of material. The ampoules themselves were prepared from 9 mm external diameter tubing as shown in Fig (6.9.1). The tubing was twice pulled down to form an extremely thin capillary which would break easily in the ampoule breaking apparatus. The ampoule was then cleaned by filling with freshly prepared hot chromic acid and immersing it completely in this mixture. After several hours it was removed and washed thoroughly with deionised water. The ampoules were then dried in an air oven overnight, the outside wiped with a soft cloth and the inner surface examined for any solid material. Those which were satisfactory were pumped out on the sample preparation line using grease only very sparingly on the lower edge of the B10 cone. Air was then let back to the ampoules and they were marked on the outside with a sharp glass knife to identify each ampoule and also as a guide when they were being filled. The ampoules were then drawn down to a narrow constriction and placed in a balance case containing a tray of active silica gel. They were then weighed empty, using a micro balance of 0.002 mg sensitivity, and after weighing they were again
THE PREPARATION OF AN AMPOULE

(a)  (b)  (c)  (d)

Fig (6.9.1)
dried in the air oven at 110°C for several hours. They were allowed to cool in a silica gel vacuum desiccator and reweighed. Agreement between the four weighings was always better than ± 0.00001 g.

During the time taken for these weighings a sample of pure hexafluorobenzene had been degassed by repeated vacuum distillation from the storage reservoir below tap $T_{10}$ (Fig 6.5.1) to a suitable vessel connected to the line at one of the B10 sockets. Liquid nitrogen was used to cool the collecting vessel and a beaker of cold water surrounded that containing the hexafluorobenzene. The section of apparatus was pumped down to hard vacuum after each distillation and, in all, twelve distillations were carried out. The final one returned the material to the storage container and after this distillation the tap, $T_{10}$, was closed and the hexafluorobenzene was allowed to warm up. The weighed ampoules were then attached to the sample preparation line and pumped down. When a satisfactory vacuum had been achieved the ampoules were filled in turn by slowly raising a beaker containing ice + water around them with tap $T_q$ closed and tap $T_{10}$ open. The hexafluorobenzene slowly distilled into the ampoule and when the ampoule contained the required amount of hexafluorobenzene the tap, $T_{10}$, was closed and the ice bath replaced by a solid carbon dioxide + acetone cold trap. The ampoule was then sealed at the constriction with the apparatus open to the pumps using tap $T_q$. The procedure was repeated for all the other ampoules required for a given series of measurements and the ampoules were again weighed.
The ground glass joints which had been detached from the ampoules were washed initially in toluene and then in 40 - 60 petroleum ether. They were then dried by placing them in the air oven at 110°C whilst the ampoules were dried in a desiccator containing active silica gel after they had been wiped with a soft cloth.

Both the filled ampoules and the detached joints were weighed in the same way as the ampoules before filling, four weighings being carried out for each ampoule and joint. The external volume of the filled ampoules was determined to an accuracy of ± 0.05 cm$^3$ by immersing the filled ampoule in a burette and noting the change in reading on immersion.

If

$W_i = \text{the weight recorded for the ampoule before filling}$

$W_f = \text{the weight recorded for the ampoule after filling}$

$W_j = \text{the weight recorded for the detached cone}$

then if $\sigma_1$, $\sigma_2$ and $\sigma_3$ are the densities of dry air at the temperatures at which $W_i$, $W_f$ and $W_j$ were recorded and $\rho_w$ and $\rho_g$ are the densities of the balance weights and pyrex glass respectively then if the external volume of the ampoule is $V$,

$$w_{it} = W_i \left[1 - \frac{\sigma_1}{\rho_w}\right] \left[1 - \frac{\sigma_1}{\rho_g}\right]^{-1} \quad (6.9.1)$$

$$w_{jt} = W_j \left[1 - \frac{\sigma_2}{\rho_w}\right] + V \sigma_2 \quad (6.9.2)$$
and the true weight of sample taken $W_S$ is given by

$$W_S = W_{4t} + W_{3t} - W_{1t} \quad (6.9.4)$$

§6.10 OPERATION OF THE APPARATUS

a) Determination of the Vapour Volume

When static vapour pressure measurements with total composition data are used to determine activity coefficients and excess Gibbs function changes on mixing it is necessary to know the composition of the liquid. When only the total composition (liquid + vapour) is determined a further piece of information is required, namely the volume of the vapour space.

The total volume of the cell up to the break seal has been determined (see preparation of cell) and now the volume of the vapour space from the break seal to a mark on the cut-off manometer must be determined. A suitable mark was chosen to be the lower surface of the glass seal running across the centre of the manometer, and the volume from here to the break seal was determined by the isothermal compression of nitrogen.
With the cut-off drained of mercury the cut-off, cell and buffer line are pumped down to a pressure of about $10^{-2}$ N·m$^{-2}$. The pump is then shut off from the apparatus and dry nitrogen at approximately $1.5 \times 10^4$ N·m$^{-2}$ is used to fill the buffer line, cut-off and the cell up to the break seal, by expanding one atmosphere aliquots of dry nitrogen, from the section of line enclosed by taps $T_{13}$, $T_{14}$ and $T_{15}$ with tap $T_3$ into the buffer line. Tap $T_4$ is then opened and tap $T_{14}$ is moved to the mercury supply position. After checking that taps $T_1$ and $T_2$ are closed, tap $T_{15}$ is opened and the pressure in this section allowed to rise to the atmospheric level. The mercury level can then be raised in the cut-off by opening either tap $T_1$ or tap $T_2$, thus trapping a sample of nitrogen.

The volume of nitrogen trapped by the mercury in the cut-off is now studied by varying the buffer line pressure as described above. The vacuum side of the main U-tube manometer is continuously evacuated by way of taps $T_7$ and $T_8$ during the measurement. Only two pressure measurements are necessary to determine this volume sufficiently accurately. Let the diameter of the tubing be $a$ m and the cathetometer readings, $h_k$, for the mercury levels and the mark be as shown in Fig (6.10.1). Then, if at low pressures for dry nitrogen we can write $PV = \text{constant at constant temperature}$, and if $V$ is the volume from the mark to the break seal and $\rho_M$ and $\rho_T$ are the densities of mercury at the temperature of the manometer and the thermostat respectively, then we may write,

$$
\left[ (h_4 - h_3) \rho_M g + (h_2 - h_1) \rho_T g \right] \left[ V + \frac{\pi a^2}{4} (h_0 - h_1) \right] (6.10.1)
$$
A Diagramatic Representation of the Apparatus,

$h_2 \text{ m}$

Showing Cathetometer Readings $h_4$

$h_3 \text{ m}$

$h_6 \text{ m}$

$h_0 \text{ m}$

$h_1 \text{ m}$

Fig (6.10.1)
\[
\begin{align*}
&= \left[ (h_4' - h_3') \rho_m g + (h_2' - h_1') \rho_T g \right] \left[ V + \frac{\pi a^2}{4} (h_0' - h_1') \right] \\
&\text{and since} \\
P &= (h_4 - h_3) \rho_m g + (h_2 - h_1) \rho_T g \\
(6.10.3) \\
\rho' &= (h_4' - h_3') \rho_m g + (h_2' - h_1') \rho_T g \\
(6.10.4) \\
V &= \frac{\pi a^2}{4} \left[ \frac{P'(h_0' - h_1') - P(h_0 - h_1)}{P - P'} \right] \\
(6.10.5),
\end{align*}
\]

where \( g \) is the acceleration due to gravity and was calculated to be 9.81288 m/sec\(^2\) (G.W.C. Kaye and T.H. Laby, Tables of Physical and Chemical Constants). It is however desirable to note that this calculation assumes that the tubing is smooth and continuous between the mercury meniscus and the mark and also that when the low pressure cut-off is used the heights \( h_1 \) and \( h_1' \) will be greater than the heights \( h_2 \) and \( h_2' \).

b) Measurement of Vapour Pressure

1) Small Pressures (Less than 5000 N.m\(^{-2}\)).

Small vapour pressures were measured on the specially designed cut-off, namely that enclosed between taps \( T_1 \) and \( T_4 \). It will be assumed that a cell has been attached to the cut-off and that the break seal is as yet intact. Also it will be assumed that an ampoule must be broken and the contents distilled into this cell before the measurements commence.
Initially the apparatus is completely evacuated. All the vacuum taps are used here but it is important particularly to note that tap $T_{12}$ is in the mercury reservoir position so that the mercury reservoir is evacuated by way of taps $T_3$, $T_4$ and $T_7$, and that the buffer line is evacuated by means of tap $T_6$, taps $T_4$, $T_5$ and $T_2$ also being open. The taps $T_1$ and $T_3$ are closed as also are taps $T_{16}$ and $T_{19}$. When a satisfactory vacuum is achieved the contents of the cell are frozen with liquid nitrogen, the water having been removed from the thermostat, before the operation commenced. Taps $T_4$ and $T_5$ were then closed after ensuring that tap $T_2$ was fully covered with mercury (if necessary the level was raised slightly by applying a small nitrogen pressure). With tap $T_6$ still open the break seal was opened by dropping the breaker and the pressure gauge observed to ensure that there was no leak in the cell.

With the contents of the cell still frozen at liquid nitrogen temperature the taps $T_6$ and $T_7$ were closed and preparations were made to distil from an ampoule which had been inserted into the apparatus before the operations commenced. The ampoule was accurately positioned under the breaker tube using the iron-in-glass movers. The cold trap surrounding the cell was topped up and then the ampoule was opened by dropping the ampoule breaker onto the fragile break seal. Twenty minutes were allowed for complete distillation, after which tap $T_6$ was opened to ensure that no leakage had occurred and that distillation was complete.

Tap $T_{14}$ was closed and using tap $T_{15}$ a pressure of $10^5 \text{ N.m}^{-2}$ was applied to the mercury in the reservoir. With tap $T_6$ still open tap $T_2$ was opened slowly and the mercury allowed to fill the
cut-off to the glass partition. The water was now pumped back into
the thermostat tank and the heaters set, rapidly to achieve the
approximate thermostat temperature. Whilst this was taking place
the tap $T_2$ was turned to the completely closed position and the
section of line between taps $T_{12}$, $T_4$ and $T_5$ was evacuated by
opening taps $T_7$ and $T_4$ after $T_6$ and $T_5$ had been closed.

As soon as the solid material in the cell had melted, the
liquid was stirred vigorously using the submersible stirrer, which
had been placed under the cell before the water was replaced in the
thermostat, together with the metal-in-glass stirrer, which had
been moved onto the frozen liquid from the other compartment
of the cell with a magnet. The taps $T_4$ and $T_{14}$ were now closed and
taps $T_5$ and $T_5$ opened. Tap $T_{12}$ was moved to the buffer line opening
and nitrogen let in to the apparatus until the pressure registered
on the main manometer was between 15000 and 25000 N m$^{-2}$ at the
temperature of the manometer. Tap $T_{12}$ was then closed completely
and tap $T_4$ slowly opened which caused the mercury levels in the
cut-off to move. The apparatus was then adjusted finally, by
carefully adjusting the buffer pressure to place the mercury levels
in suitable positions to be measured with the cathetometers. The
thermostat was then set to a suitable temperature and the
apparatus left overnight to achieve equilibrium.

The cathetometers were leveled and the apparatus checked
over before measurements were made. Each experimental determination
of the vapour pressure was the mean of twelve pressure
measurements and six thermostat temperature measurements. Initially
the temperature of the thermostat was measured using the platinum
resistance thermometer. The heights of the four mercury menisci and the height of the fixed mark were determined four times at any given thermostat setting and the temperature of the thermostat was then remeasured. It was important that the cathetometer should be used in exactly the same way for every measurement or spurious results could be obtained. The method adopted here was always to level the telescope finally by turning the levelling screw clockwise as viewed from the operating position and to set the telescope by always moving the fine adjustment screw anticlockwise. Only with this cathetometry procedure could reproducible results be achieved. The thermostat was then twice reset for a small temperature change and the same measurement procedure employed at each temperature, leaving at least two hours between the measurements.

By suitable choice of temperatures it was possible to determine quite accurately the vapour pressure at a given temperature from a graph of vapour pressure against temperature which can be assumed linear over the small temperature range studied for each measurement. The vapour pressures were measured at other temperatures in exactly the same manner and with small pressures it was rarely necessary to adjust the buffer line pressure.

2) Small Pressures (5000 \( \leq V_P/N \cdot m^2 \leq 25000 \))

It is in this range that the apparatus is most accurate and most easily operated, as it is not necessary to use nitrogen in the buffer line; all measurements being made on the cut-off. The procedure for opening a cell and for distilling in from an ampoule is analogous to that described above, except that \( T_1 \) replaces \( T_2 \) and \( T_3 \) replaces \( T_4 \). When the cut-off mercury has been raised using the
same procedure as described above tap $T_5$ remains closed and tap $T_6$ is only closed to pump away the excess gas not used in filling the cut-off with mercury. Tap $T_7$ is closed and tap $T_8$ is opened and the apparatus is operated with the cut-off manometer serving as the only pressure measuring device.

The measurements are carried out in exactly the same way as described above but since the buffer line is not used it is only necessary to measure the heights of the menisci in the tank and the fixed mark of the manometer.

3) Large Pressures ($VP > 25000 \text{ N.m}^{-2}$)

Here the method used is similar to those described above and may be regarded as a combination of them. The opening and distillation procedures are analogous to those described in subsection 2) above. When distillation is complete, as the sample warms up the vapour pressure is greater than the pressure which can be accommodated on the cut-off manometer and thus a buffer line must be used as in subsection 1). In this case the value of the buffer line pressure is adjusted to be about $6000 \text{ N.m}^{-2}$ lower than the vapour pressure of the sample in the cell.

In this way it is possible to measure large vapour pressures by measuring the heights of the four mercury menisci and of course the reference mark.

4) Calculation of Vapour Pressure.

Consider the apparatus shown diagrammatically in Fig (6.10.2) which represents the cell, cut-off manometer, buffer line and the main manometer.
A Diagrammatic Representation of the Apparatus.

Fig (6.10.2)
The pressure at the liquid surface \( P \) is given by

\[
P = p_1 g l_1 + p_2 g l_2 + p_3 g l_3 + p_4 g l_4 + p_5 g l_5\) \quad (6.10.6)
\]

where \( p_1 \) is the density of the equilibrium vapour at thermostat temperature,

\( p_2 \) is the density of the mercury at thermostat temperature,

\( p_3 \) is the density of nitrogen at thermostat temperature,

\( p_4 \) is the density of nitrogen at laboratory temperature,

\( p_5 \) is the density of mercury at manometer temperature,

and \( g \) is the acceleration due to gravity, taken to be 9.81288 m sec\(^{-2}\).

It was pointed out above that when the cut-off is filled with mercury, the mercury levels with zero pressure on either side are adjusted to coincide with the glass partition in the manometer. This is also the case with the main manometer. If \( l_1' \) represents the height from the liquid surface to the cut-off glass seal, \( l_3' \) the height from this seal to the thermostat water level and \( l_4' \) represents the height from the water level to the seal across the main manometer then provided that the liquid level in the cell does not change appreciably, the heights \( l_1' \), \( l_3' \) and \( l_4' \) are constants of the apparatus for each set of measurements and

\[
l_1 = l_1' - l_2 / 2 \quad (6.10.7)
\]

\[
l_3 = l_3' - l_2 / 2 \quad (6.10.7)
\]

\[
l_4 = l_4' - l_5 / 2 \quad (6.10.7)
\]
Assuming that for nitrogen \( PV_m = RT \), and if \( M \) is the molecular weight of nitrogen then

\[
\rho_{N_2} = \frac{M}{V_m} = \frac{MP}{RT}
\]  

(6.10.8)

The pressure in the buffer line \( P(\text{above}) \) is \( P_5 \), then

\[
P_4 = J_4 p_4 g = \left[ J_4 - \frac{J_5}{2} \right] \frac{M}{RT} \rho_5 g^2
\]  

(6.10.9)

where \( T_R \) is the room temperature. Similarly

\[
P_3 = J_3 p_3 g = \left[ J_3' - \frac{J_2}{2} \right] \frac{M}{RT} \rho_5 g^2
\]  

(6.10.10)

where \( T_T \) is the temperature of the thermostat.

If we also assume that for the vapour we can write

\[
\rho_{\text{VAP}} = \frac{M_{\text{VAP}}}{V_m} = \frac{M_{\text{VAP}} P}{RT}
\]

then similarly

\[
P_1 = J_1 \rho_1 g = \left[ J_1' - \frac{J_2}{2} \right] \frac{M_{\text{VAP}}}{RT} (J_2 \rho_2 + J_5 \rho_5) g^2
\]  

(6.10.11)

It is valid to write

\[
P = (J_2 \rho_2 + J_5 \rho_5) g
\]

since the pressures \( P_1, P_3 \), and \( P_4 \) are small compared with \( P \).

Before the calculation of the vapour pressure is described it is necessary to consider the corrections to the cathetometer.
readings. The instrument scale is ruled at $20^\circ C$ and therefore only at this temperature is the reading of the instrument the true height. It can be shown that

$$ h_{true} = h_{read} (1 + \alpha (t - 20)) $$

(6.10.12)

where $h_{true}$ and $h_{read}$ are the true height and the height read from the cathetometer and $t$ is the temperature of the room in degrees centigrade. Using the previous notation

$$ h_{true} = h_{read} (1 + \alpha (T_A - 293.15)) $$

(6.10.13)

where $\alpha = 1.9 \times 10^{-5}$ deg$^{-1}$ is the coefficient of linear expansion of brass.

The vapour pressures for the hexafluorobenzene, N,N-dimethyl-aniline and for mixtures of these compounds were calculated by computer to ensure accuracy and avoid the tedium. The program is shown in Appendix 3. Using the predetermined constants described above and correcting all the cathetometer readings for expansion, the vapour pressure was calculated for each experiment.

A specimen run sheet is shown in Fig (6.10.3a) and the corresponding computer output is shown in Fig (6.10.3b).
## VAPOR PRESSURE MEASUREMENT

**Date:** 24th March 1964  
**Time:** 10:00  
**System:** $C_6F_6 + D.M.A$  
**Temperature:** $60.006^\circ C$

<table>
<thead>
<tr>
<th>Ref</th>
<th>Height of Upper Meniscus</th>
<th>Height of Lower Meniscus</th>
<th>Vapour Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.380</td>
<td>22.377 cm</td>
<td>39.050 cm</td>
<td>cm</td>
</tr>
<tr>
<td>14.382</td>
<td>22.374 cm</td>
<td>39.044 cm</td>
<td>cm</td>
</tr>
<tr>
<td>14.380</td>
<td>23.376 cm</td>
<td>39.044 cm</td>
<td>cm</td>
</tr>
<tr>
<td>14.378</td>
<td>22.380 cm</td>
<td>39.043 cm</td>
<td>cm</td>
</tr>
</tbody>
</table>

**Temperature:** $60.005^\circ C$

**Room** | $25.9^\circ C$

**Manometer** | $30.7^\circ C$
VAPOUR PRESSURE = 10403.9 Pa = 10409.2 Pa = 10410.5 Pa = 10407.9 Pa

VAPOR PRESSURE OF VAPOUR
BUFFER LINE PRESSURE (THEMOSAT) = 7209.6 Pa = 7209.9 Pa = 7208.6 Pa = 7208.5 Pa

BUFFER LINE PRESSURE (ROOM TEMP) = 0.20373 m = 0.20376 m = 0.20374 m = 0.20378 m

Hg Vapor Pressure = 0.186 kG/mole

PRESSURE (MANOMETER) = 16626.9 Pa = 16631.9 Pa = 16622.9 Pa = 16625.9 Pa

CORRECTED HEIGHT = 0.12599 m = 0.12604 m = 0.12596 m = 0.12593 m

OBSERVED HEIGHT = 0.12591 m = 0.12594 m = 0.12596 m = 0.12593 m

MERCURY DENSITY = 13549.7 KG/M3

CUT-OFF

THEMOSAT TEMP = 60.06ºC

ROOM TEMP = 25.9ºC

MERCURY TEMP = 30.70ºC

GTF6 + D.M.A (0.2) AT 60.06ºC

G = 9.81269 MSEC²
CHAPTER SEVEN

THE DETERMINATION OF THE EXCESS GIBBS FUNCTION FOR MIXING, $G^E$, FROM VAPOUR PRESSURE MEASUREMENTS
THE THERMODYNAMICS OF LIQUID - VAPOUR EQUILIBRIUM

Consider the definition of the chemical potential of a component \( i \) defined by

\[
\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j}
\] (7.1.1)

thus \( \mu_i \) is the partial molar Gibbs function and is an intensive property of a system (i.e. it is independent of how much system is considered). It can be shown that for any system

\[
\mu_i = \mu_i^0 + R T \ln a_i \] (7.1.2)

where \( a_i \) is the activity of the component \( i \). For a liquid we can write \( a_i = x_i f_i \) where \( x_i \) is the mole fraction of species \( i \) and \( f_i \) is the rational activity coefficient of component \( i \) then

\[
\mu_i = \mu_i^0 + R T \ln x_i f_i \] (7.1.3)

Now the Gibbs function, \( G \), for a multicomponent system is given by

\[
G = n_1 \mu_1 + n_2 \mu_2 + \ldots \] (7.1.4)

at constant temperature and pressure. Then for a process of mixing \( n_1 \) moles of \( \text{(1)} \) with \( n_2 \) of \( \text{(2)} \) at some temperature \( T \) and pressure \( P \) we can write

\[
\Delta G = n_1 \mu_1 + n_2 \mu_2 - n_1 \mu_1^0 - n_2 \mu_2^0 \] (7.1.5)
If we define the excess Gibbs function for mixing $G^E$ by

$$G^E = \Delta_m G - \Delta_m G^\text{(ideal)}$$

then clearly

$$G^E = RT \left\{ x_i \ln f_i + x_2 \ln f_2 \right\}$$

$$= 0 \text{ for an ideal solution.}$$
Before the calculation of the rational activity coefficient from vapour pressure measurements is described, an equation for one activity coefficient in terms of \( G^E \) will be deduced and the Virial Equation of State must be discussed. Differentiating equation (10) with respect to \( x_i \), and noting that \( x_i + x_j = 1 \), we obtain

\[
\frac{\partial G^E}{\partial x_i} = RT \left[ \ln f_i - \ln f_2 + x_i \frac{\partial \ln f_i}{\partial x_i} + x_j \frac{\partial \ln f_2}{\partial x_i} \right] \quad (7.1.11)
\]

At constant temperature and pressure we write

\[
x_i \frac{d\mu_i}{dx_i} + x_j \frac{d\mu_j}{dx_j} = 0 \quad (7.1.12)
\]

where equation (12) is one of the more common forms of the Gibbs - Duhem equation, and thus we can write

\[
x_i \frac{d}{dx_i} \ln f_i + x_j \frac{d}{dx_j} \ln f_j = 0 \quad (7.1.13)
\]

Using equation (13) in equation (11) then

\[
\frac{\partial G^E}{\partial x_i} = RT \left[ \ln f_i - \ln f_2 \right] \quad (7.1.14)
\]

and rearranging equation (10) and (15) and combining them

\[
\ln f_2 = \frac{G^E}{RT} - x_i \frac{\partial}{\partial x_i} \left[ \frac{G^E}{RT} \right] \quad (7.1.15)
\]

and similarly
The pressure, volume temperature behaviour of a gas can be represented by a power series, the two normally used being

\[ PV = RT + BP + CP^2 + \ldots \ldots \ldots \ldots \ldots \ldots (7.1.17) \]

and

\[ PV = RT \left[ 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \ldots \ldots \right] \ldots (7.1.18) \]

At sufficiently low pressures it is usual to truncate the series shown in equation (18) using only one coefficient; thus

\[ PV = RT \left[ 1 + \frac{B'}{V} \right] \ldots (7.1.19) \]

where \( B' \neq B \) but includes terms due to \( C, D, \ldots \) etc.

For a mixture of two gases, \( \text{\textcircled{1}} \) and \( \text{\textcircled{2}} \), using a result of statistical mechanics (82) we find

\[ \frac{PV}{RT} = (n_1 + n_2) + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{V} \ldots (7.1.20) \]

Rewriting equation (20) as a quadratic in \( V \) and solving the resulting equation gives

\[ 2 \frac{PV}{RT} = (n_1 + n_2) + \sqrt{(n_1 + n_2)^2 + \frac{4P (n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22})}{RT}} \ldots (7.1.21) \]
The partial molar volume, \( V_i \), of component \( i \) of the mixture is defined by

\[
V_i = \left( \frac{\partial V}{\partial n_i} \right)_{n_j, T, P} \quad j \neq i
\]  

(7.1.22)

and therefore

\[
\frac{\partial P}{\partial T} \cdot V_i = 1 + \frac{(n_1 + n_2)}{n} \left( 1 + \frac{4P}{RT} \left( n_1 B_{11} + n_2 B_{12} \right) \right)
\]

(7.1.23)

\[
= 1 + \left[ 1 + \frac{4P}{RT} \left( y_1 B_{11} + y_2 B_{12} \right) \right] \left[ 1 + \frac{4P}{RT} \left( y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \right) \right]^{-1/2}
\]

(7.1.24)

where \( y_1 \) and \( y_2 \) are the mole fractions of \( 1 \) and \( 2 \) in the vapour, i.e.

\[
y_i = \frac{n_i}{\sum n_i}
\]

Expansion of the second bracket using the binomial theorem and multiplying out, considering only terms up to those in \( B_{i,j}^2 \) gives

\[
V_i = \frac{RT}{P} + \left[ B_{11} - y_1^2 (B_{11} - 2B_{12} + B_{22}) \right] - \frac{P}{RT} \left[ B_{11}^2 - y_1^2 \left( 4(B_{11} - B_{12})^2 \right. \right.
\]

\[
+ \left. \left. [B_{11} - 2B_{12} + B_{22}] [2B_{11} - 8y_1 (B_{11} - B_{12}) + 3y_1^2 (B_{11} - 2B_{12} + B_{22})] \right) \right]
\]

(7.1.25)
The expression is usually reduced to

$$
\mu_i = \frac{RT}{P} + \left[ B_{ii} + y_i^2 (2B_{j2} - B_{ii} - B_{22}) \right] - \frac{P B_{ii}^2}{RT} \tag{7.1.26}
$$

since the other terms are normally very small and can be neglected.

If equilibrium exists between liquid and vapour then we can write for component \( i \) of the mixture

$$
\mu_i(\text{liq}) (T, P, x_i) = \mu_i(\text{vap}) (T, P, y_i) \tag{7.1.27}
$$

and for pure \( i \)

$$
\mu_i^o(\text{liq}) (T, P^o) = \mu_i^o(\text{vap}) (T, P_i^o) \tag{7.1.28}
$$

where \( T \) is the equilibrium absolute temperature, \( P \) is the observed vapour pressure and \( P_i^o \) is the vapour pressure of pure component \( i \) at the temperature \( T \). In equation (3) the chemical potential of a component in a liquid mixture was given as

$$
\mu_i(\text{liq}) (T, P, x_i) = \mu_i^o(\text{liq}) (T, P) + RT \ln x_i f_i \tag{7.1.29}
$$

G.N. Lewis defined the fugacity of component \( i \), \( f_i \), by the relationships

$$
\frac{P_i^*}{\lambda_i} = \text{constant, } A \tag{7.1.30}
$$
and

\[ \lim_{P \to 0} \frac{P^*_i}{P_i} = 1 \]  \hspace{1cm} (7.1.31)

where \( \lambda_i \) is the absolute activity and \( P_i \) is the partial pressure of component \( i \) and \( P \) is the total pressure.

Then from the definition of the activity of component \( i \), \( \lambda_i \), we have

\[ \mu_i = RT \ln \lambda_i = RT \ln \frac{p^*_i}{A} \] \hspace{1cm} (7.1.32)

where \( A \) is a constant at constant temperature and composition.

Then under these conditions

\[ \frac{\partial \mu_i}{\partial P} = RT \frac{\partial}{\partial P} \ln p^*_i = \nu_i \] \hspace{1cm} (7.1.33)

where \( \nu_i \) is the partial molar volume of component \( i \). We could then write

\[ RT \int \ln p^*_i \, dp = \int \nu_i \, dp \] \hspace{1cm} (7.1.34)

but the constant of integration is difficult to calculate. Consider the definition of partial pressure, \( P_i = y_i P \), then

\[ RT \ln P_i = RT \ln y_i + RT \ln P \] \hspace{1cm} (7.1.35)

and

\[ RT \frac{\partial}{\partial P} \ln P_i = RT \frac{\partial}{\partial P} \ln P = \frac{RT}{P} \] \hspace{1cm} (7.1.36)
thus

\[ RT \frac{\partial}{\partial P} \ln \frac{P_i^*}{P_i} = \nu_i - \frac{RT}{P} \quad (7.1.37) \]

and

\[ RT \lim_{P_0 \to 0} \int_{P_0}^{P} d \ln \frac{P_i^*}{P_i} = \lim_{P_0 \to 0} \int_{P_0}^{P} \left( \nu_i - \frac{RT}{P} \right) dP \quad (7.1.38) \]

but

\[ \lim_{P_0 \to 0} \frac{P_i^*(P_0)}{P_i(P_0)} = 1 \quad (7.1.39), \]

tyhers

\[ RT \ln \frac{P_i^*}{P_i} = \lim_{P_0 \to 0} \int_{P_0}^{P} \left( \nu_i - \frac{RT}{P} \right) dP \quad (7.1.40). \]

The chemical potential of a component of a vapour mixture can be written

\[ \mu_i(vap) (T, P, y_i) = \mu_i(vap)(T \text{ only}) + RT \ln \frac{P_i^*}{y_i} \quad (7.1.41) \]

where \( P_i^* \) is the fugacity of component \( i \) in the vapour and \( \mu_i(vap) \) depends only upon \( T \) once a standard pressure \( P^\dagger \) has been defined. The fugacity \( P_i^* \) of a component \( i \) can be obtained from

\[ RT \ln \frac{P_i^*}{P_i} = \lim_{P_0 \to 0} \int_{P_0}^{P} \left( \nu_i - \frac{RT}{P} \right) dP \quad (7.1.42) \]

where \( \nu_i \) is the partial molar volume of component \( i \) in the vapour, thus
The variation of chemical potential of a component of a liquid with pressure is given by

\[
\mu_i(v_{ap})(T, P, y_i) = \mu_{i}(v_{ap})(T) + RT \ln y_i P + \lim_{P \to 0} \int_{P_0}^{P} \left( u_i - \frac{RT}{P} \right) dP \quad (7.1.43)
\]

Since \( \frac{d\mu_i}{dP} = V_i \) where \( V_i \) is the partial molar volume of component \( i \) in the liquid, then

\[
\mu_i(I_{iq})(T, P, x_i) = \mu_i(I_{iq})(T_p, P, x_i) + \int_{P_0}^{P} V_i dP \quad (7.1.44)
\]

Therefore by substituting into equation (27)

\[
\mu_i(I_{iq})(T, P, x_i) + \int_{P_0}^{P} V_i dP = \mu_{i}(v_{ap}) + RT \ln y_i P + \lim_{P \to 0} \int_{P_0}^{P} \left( u_i - \frac{RT}{P} \right) dP \quad (7.1.45)
\]

and by substituting into equation (28)

\[
\mu_i(I_{iq})(T, P_0) + \int_{P_0}^{P_0} V_i^0 dP = \mu_{i}(v_{ap}) + RT \ln P_0 + \lim_{P \to 0} \int_{P_0}^{P_0} \left( u_i^0 - \frac{RT}{P} \right) dP \quad (7.1.46)
\]

Subtracting equation (47) from (46), and writing in from equation (29)

\[
RT \ln x_i \int_{P_0}^{P_0} = \mu_i(I_{iq})(T, P, x_i) - \mu_i(I_{iq})(T, P_0)
\]
From equation (26) generalised for component $i$ of a binary mixture and also writing $\delta_{ij} = \lambda B_{ij} - B_{ii} - B_{jj}$, clearly

$$u_i - \frac{RT}{P} = B_{ii} + (1 - y_i)^2 \delta_{ij} - \frac{P}{RT} B_{ii}^2$$  \hspace{1cm} (7.1.49)$$

and

$$u_i^o - \frac{RT}{P} = B_{ii} - \frac{P}{RT} B_{ii}^2$$  \hspace{1cm} (7.1.50)$$

then assuming $V_i$ and $V_i^o$ are independent of pressure over the range $P^*$ to $P$ or $P_i^*$, evaluation of the integrals gives

$$RT \ln x_i f_i = RT \ln \frac{y_i P}{P_i^o} + B_{ii} P + (1 - y_i)^2 P \delta_{ij} - \frac{P^2}{2RT} B_{ii}^2$$

$$- B_{ii} P_i^o + \frac{P_i^{o2}}{2RT} B_{ii}^2 - V_i (P - P^*) + V_i^o (P_i^o - P^*)$$  \hspace{1cm} (7.1.51)$$

which on rewriting gives

$$\ln f_i = \ln \frac{y_i P}{x_i P_i^o} + \frac{(B_{ii} - V_i^o)(P - P_i^o)}{RT}$$

$$+ \frac{(V_i - V_i^o)(P^* - P)}{RT} + \frac{B_{ii}^2 (P_i^{o2} - P^2)}{2(2RT)^2} + \frac{(1 - y_i)^2 \delta_{ij} P}{RT}$$  \hspace{1cm} (7.1.52)$$
i.e. an equation for $\ln f_i$ in terms of the compositions of liquid and vapour present at equilibrium together with the vapour pressure, the second virial coefficients, and the partial molar volumes of the liquid. We shall refer to this equation as the full equation for $\ln f_i$ as other workers have used shortened versions of it.

### 7.2 Activity Coefficients as a Series Expansion

In chapter five the use of curve fitting procedures was discussed with regard to fitting excess enthalpy data. The use of the Myers and Scott function will now be explored with the possibility of representing activity coefficients as a series function of composition. If at any fixed temperature $T$ we can write

$$\frac{G^E}{RT} = \sum_{i=0}^{n} \frac{G_i \alpha_i \left( \alpha_i - \alpha_2 \right) \lambda}{\left( 1 - k \left( \alpha_i - \alpha_2 \right) \right)}$$  \hspace{1cm} (7.2.1)$$

then we shall postulate that we may write the logarithms of the rational activity coefficients $\ln f_i$ and $\ln f_2$ as a series of the form

$$\ln f_i = G_0 X_i + \ldots \ldots \ldots \ G_n X_n = \sum_{i=0}^{n} G_i X_i$$  \hspace{1cm} (7.2.2)$$

and
\[ \ln f_x = G_0 y_0 + \cdots + G_n y_n = \sum_{i=0}^{n} G_i y_i \quad (7.2.3) \]

where \( x_i \) and \( y_i \) are functions of \( x_1 \) and \( x_2 \) only. From the definition of \( G^E \), (Equation (7.1.10)), it is clearly seen that

\[ \frac{G^E}{RT} = \sum_{i=0}^{n} G_i x_1 x_2 \left[ \frac{x_i}{x_2} + \frac{y_i}{x_1} \right] \quad (7.2.4) \]

and by comparing the coefficients of the \( G_i \)'s in equations (4) and (1)

\[ \left[ \frac{x_i}{x_2} + \frac{y_i}{x_1} \right] = \frac{(x_1 - x_2)^i}{(1 - k(x_1 - x_2))} \quad \text{for all } i = 0, \ldots, n \quad (7.2.5) \]

In equation (7.1.12) we stated the Gibbs-Duhem relationship which can be applied to this situation to give

\[ \sum_{i=0}^{n} G_i [x_i \frac{d x_i}{d x_1} + x_2 \frac{d y_i}{d x_1}] = 0 \quad (7.2.6) \]

Using the fact that none of the \( G_i \)'s are, in general, zero when \( n \) is number of experimental points, and that \( x_1 + x_2 = 1 \) we can write

\[ \sum_{i=0}^{n} \left( x_i \frac{d x_i}{d x_1} - x_2 \frac{d y_i}{d x_2} \right) = 0 \quad (7.2.6) \]

which must be true for any value of \( n \) and therefore for all
\[ i = 0, \ldots, n \quad x_i \frac{dX_i}{dx_i} - x_j \frac{dY_i}{dx_j} = 0 \] (7.2.7)

Differentiating equation (5) with respect to \( x_i \), and using equation (7)

\[ X_i - Y_i = \left[ (1 - k(x_i - x_2))(2\lambda x_i x_2 (x_i - x_2)^{\lambda - 1} - (x_i - x_2)^{\lambda + 1}) \right. \]
\[ \left. + 2k x_i x_2 (x_i - x_2)^{\lambda} \right] / (1 - k(x_i - x_2))^2 \] (7.2.8)

Then solving equations (5) and (8) simultaneously

\[ X_i = x_2^2 (x_i - x_2)^{\lambda - 1} \left\{ (2\lambda + 1)x_i - x_2 + k(x_i - x_2)(1 - 2\lambda x_2) \right\} / (1 - k(x_i - x_2))^2 \] (7.2.9)

and

\[ Y_i = x_1^2 (x_i - x_2)^{\lambda - 1} \left\{ x_i - (2\lambda + 1)x_2 + k(x_i - x_2)(2\lambda x_2 - 1) \right\} / (1 - k(x_i - x_2))^2 \] (7.2.10)

If \( k = 0 \) then the Myers and Scott function reduces to the Guggenheim function and equations (9) and (10) reduce to

\[ X_i = x_2^2 (x_i - x_2)^{\lambda - 1} \left\{ (2\lambda + 1)x_i - x_2 \right\} \] (7.2.11)

and

\[ Y_i = x_1^2 (x_i - x_2)^{\lambda - 1} \left\{ x_i - (2\lambda + 1)x_2 \right\} \] (7.2.12).
We can therefore write

\[ \ln f_1 = x_1^2 \sum_{i=0}^{n} G_i (x_1 - x_2) i^{-1} \left[ (\lambda i + 1) x_1 - x_2 + k (x_1 - x_2)(1 - 2i x_1) \right] (7.2.13) \]

and

\[ \ln f_2 = x_2^2 \sum_{i=0}^{n} G_i (x_1 - x_2) i^{-1} \left[ x_2 - (\lambda i + 1) x_2 + k (x_1 - x_2)(2i x_2 - 1) \right] (7.2.14). \]

These functions are analogous to those given by Barker (73), Marsh (80) and many other workers.

7.3 Barker's Method of Calculating \( G^E \)

Barker (73) described a systematic method, based upon a least squares procedure, for calculating the rational activity coefficients and the excess Gibbs function of mixing of binary liquid mixtures from total pressure measurements. In this section the method used by Barker will be described in order to outline the procedures which will be used subsequently. The method involves extending the procedure described above, for describing the behaviour of activity coefficients in terms of a series, to the total vapour pressure, \( P \), and calculating the parameters of a Guggenheim \( G^E \) series by an iterative least squares procedure.
Barker took for the logarithms of the rational activity coefficients

\[
\ln \bar{f}_1 = \ln \frac{y_1 P}{x_1 P^o} + \frac{(V_1^o - B_{11})(P^o - P)}{RT} + \frac{P \delta_{12} \cdot y_2}{RT} \tag{7.3.1}
\]

and

\[
\ln \bar{f}_2 = \ln \frac{y_2 P}{x_2 P^o} + \frac{(V_2^o - B_{22})(P^o - P)}{RT} + \frac{P \delta_{12} \cdot y_1}{RT} \tag{7.3.2}
\]

using the notation developed above.

Then defining

\[
\cdot \quad p'_1 = x_1 P^o \exp \left[ \frac{(V_1^o - B_{11})(P - P^o)}{RT} - \frac{P \delta_{12} \cdot y_2}{RT} \right] \tag{7.3.3}
\]

and

\[
\cdot \quad p'_2 = x_2 P^o \exp \left[ \frac{(V_2^o - B_{22})(P - P^o)}{RT} - \frac{P \delta_{12} \cdot y_1}{RT} \right] \tag{7.3.4}
\]

he could write

\[
P = \bar{f}_1 p'_1 + \bar{f}_2 p'_2 \tag{7.3.5}
\]

Expressing the excess Gibbs function for mixing, \( G^E \), by a Guggenheim function

\[
G^E = x_1 x_2 \left[ a + b(x_1 - x_2) + c(x_1 - x_2)^2 + \cdots \right]
\]
he stated that

$$\ln f_1 = A J_1 + B m_1 + C n_1 + \cdots \quad (7.3.6)$$

and

$$\ln f_2 = A J_2 + B m_2 + C n_2 + \cdots \quad (7.3.7)$$

where $J_i$, $m_i$ and $n_i$ are analogous to the functions derived in Section (7.2) and

$$(A, B, C) = (a, b, c) / RT \quad (7.3.8)$$

He continued by assuming that (initially for the first approximation) $B$ and $C$ above were zero, so that

$$A = 4 \ln \left[ \frac{2 P_{12}}{P_1^* + P_2^*} \right]$$

where $P_{12}$ is the vapour pressure when $x_1 = x_2 = 0.5$. This value of $A$ was then used to calculate the vapour compositions from equations (1) and (2), by assuming that the term involving $\delta_{12}$ was small and could be ignored. Since the vapour composition would not be used directly in the calculation of $G^E$ or the activities then any error would not be serious.

Then

$$y_i = x_i P_i^* \int \exp \left[ \frac{(V_i^* - B_i)(P - P_i^*)}{RT} \right] / P \quad (7.3.9)$$
and

\[ y_d = \alpha D p^2 \exp \left[ \frac{(V_d - B_d)(P - P_d^0)}{RT} \right] / P \]  \hspace{1cm} (7.3.10)

where

\[ f_1 = \exp \left[ A_{1,v} + B_{1,m} + C_{1,n} + \ldots \right] \]  \hspace{1cm} (7.3.11)

and

\[ f_2 = \exp \left[ A_{1,v} + B_{2,m} + C_{n,n} + \ldots \right] \]  \hspace{1cm} (7.3.12)

The values of \( p_1' \) and \( p_2' \) could then be calculated from equations (3) and (4), and \( P \) from equation (5) using the values of \( f_1 \) and \( f_2 \) calculated from equations (11) and (12). If the experimentally determined values of \( P \) are \( P_{\text{exp}} \), and those calculated from the coefficients \( A_1, B \) and \( C \) are denoted by \( P_{\text{calc}} \), the pressure residuals \( R = P_{\text{exp}} - P_{\text{calc}} \) may be determined, as may the derivatives

\[ \frac{dP}{dA} = f_1 p_1' + f_2 p_2' \]
\[ \frac{dP}{dB} = m_1 f_1 p_1' + m_2 f_2 p_2' \]
\[ \frac{dP}{dC} = n_1 f_1 p_1' + n_2 f_2 p_2' \]

for each experimental point.
He continued the calculation by determining quantities $S_A$, $S_B$ and $S_C$ which would make

$$\sum_{\text{all points}} \left( R - \frac{dP}{dA} S_A - \frac{dP}{dB} S_B - \frac{dP}{dC} S_C \right)^2.$$

a minimum by solving the set of equations which the minimum condition implied. He added these quantities ($S_A$, $S_B$ and $S_C$) to $A$, $B$ and $C$ respectively to obtain a better approximation and repeated the calculation until $A$, $B$ and $C$ were constant.

### 7.4 Extension of Barker's Method Using Full Equations

The Barker approach has had a great deal of success in calculating $G^E$ from total pressure measurements and it was therefore decided to develop a general computer program to calculate the excess Gibbs function of mixing, $G^E$, from the total vapour pressure without neglecting any terms from the equations used for the activity coefficients, and also to use the most general equation for $G^E$ (i.e. that of Myers and Scott (74)).

The pressure, $P$, is determined as a function of composition, and the values of the constants in the equation for $G^E$ are determined by an iterative procedure since the second pressure derivatives are non-zero.

In section (7.2) an equation for $\ln f_x$ as a function of composition was developed, and we recall that, if
\[
\frac{G^E}{RT} = \sum_{i=0}^{n} \frac{x_i \cdot x_2 \cdot G_{ii}(x_i - x_2)}{(1 - k(x_i - x_2))} \quad (7.4.0.1)
\]

then

\[
\ln f_1 = \sum_{i=0}^{n} \frac{x_i^2 \cdot (x_i - x_2)^{i-1}}{(1 - k(x_i - x_2))^2} \cdot G_{ii} \left( (2i+1)x_i - x_2 + k(x_i - x_2)(1-2x) \right) \quad (7.4.0.2)
\]

and

\[
\ln f_2 = \sum_{i=0}^{n} \frac{x_i^2 \cdot (x_i - x_2)^{i-1}}{(1 - k(x_i - x_2))^2} \cdot G_{ii} \left( (2i+1)x_i - x_2 + k(x_i - x_2)(1-2x) \right) \quad (7.4.0.3)
\]

In section (7.1) the full equation relating \(\ln f_1\) with the vapour pressure and the liquid and vapour compositions was determined enabling us to write

\[
\ln f_1 = \ln \frac{y_1 P}{x_1 P_i} + \frac{(B_{ii} - V_i^* P - P_i^*)}{RT} + \frac{(V_i - V_i^*)(P^+ - P)}{RT}
\]

\[
+ \frac{B_{ii}^2}{2(RT)^2} (P_i^* - P_i^2) + y_i^2 \frac{\delta_{12} P}{RT} \quad (7.4.0.4)
\]

and

\[
\ln f_2 = \ln \frac{y_2 P}{x_2 P_i} + \frac{(B_{ii} - V_i^* P - P_i^*)}{RT} + \frac{(V_i - V_i^*)(P^+ - P)}{RT}
\]

\[
+ \frac{B_{ii}^2}{2(RT)^2} (P_i^* - P_i^2) + y_i^2 \frac{\delta_{12} P}{RT} \quad (7.4.0.5)
\]
Let us define $C_1$ and $C_2$ by

$$C_1 = \left\{ (v_i - b_{ii})(P_i - P_i^*) + (v_i - v_i^*)(P - P^+) + B_{ii} \left( P_i^2 - P_i^{*2} \right) \right\} / RT \quad (7.4.6)$$

and

$$C_2 = \left\{ (v_i^* - b_{ii})(P - P_2^*) + (v_j - v_j^*)(P - P^+) + B_{jj} \left( P_2^2 - P_2^{*2} \right) \right\} / RT \quad (7.4.7)$$

Then the quantities $P_i'$ and $P_2'$, which represent the partial pressures of components 1 and 2 if the liquid obeyed Raoult's Law but the vapour was non-ideal, may be written

$$P_i' = x_i P_i^* \exp \left[ C_i - \frac{\delta_{12}}{RT} y_2 \right] \quad (7.4.8)$$

$$P_2' = x_2 P_2^* \exp \left[ C_2 - \frac{\delta_{12}}{RT} y_1 \right] \quad (7.4.9)$$

Clearly from equations (2) and (3)

$$f_1 = \prod_{i=0}^{n} \exp \left[ \frac{z_i^2 (x_i - x_{12}) \sum_{i=1} \hat{G}_i \left( (2i+1) x_i - z_i + k (x_i - x_{12} X_{12} - 1) \right)}{(1 - k (x_i - x_{12}))^2} \right] \quad (7.4.10)$$

and

$$f_2 = \prod_{i=0}^{n} \exp \left[ \frac{z_i^2 (x_i - x_{12}) \sum_{i=1} \hat{G}_i \left( (2i+1) x_i - z_i + k (x_i - x_{12} X_{12} - 1) \right)}{(1 - k (x_i - x_{12}))^2} \right] \quad (7.4.11)$$
Then using equations (10) and (11), and (6) and (7), and solving equations (4) and (5) for $y_1$ and $y_2$ respectively, and in each case assuming that $\frac{P s_{12}}{RT}$ is negligibly small, we find

$$y_1 = \frac{x_1 P^0}{P} \int_1 \exp[C_1]$$  \hspace{1cm} (7.4.12)

and

$$y_2 = \frac{x_2 P^0}{P} \int_2 \exp[C_2]$$  \hspace{1cm} (7.4.12)

Knowing the values of $y_1$ and $y_2$ (in practice only one vapour composition was calculated), $p_1'$ and $p_2'$ can be evaluated from equations (8) and (9).

The pressure residual $R$ is then determined from a knowledge of the experimental pressure $P_{\text{exp}}$ from the equation

$$R = P_{\text{exp}} - \int_1 p_1' - \int_2 p_2'$$  \hspace{1cm} (7.4.13)

and the $(n+1)$ derivatives are calculated from

$$\frac{\partial P}{\partial G_{i1}} = \int_1 p_1' \left[ x_1^2 (x_1 - x_2) \frac{d^{l+1}}{d^{l+1}} ((2l+1)x_1 - x_2 + k(x_1 - x_2)(1 - 2x_2)) / (1 - k(x_1 - x_2))^2 \right]$$

$$+ \int_2 p_2' \left[ x_2^2 (x_1 - x_2) \frac{d^{l+1}}{d^{l+1}} ((x_1 - (2l+1)x_2 + k(x_1 - x_2)(2l + 1) / (1 - k(x_1 - x_2))^2 \right]$$

where $l = 0, 1, \ldots, n$.  \hspace{1cm} (7.4.14)
If $k$, the "skewing" parameter, is to be obtained by fitting then in addition

$$\frac{\partial P}{\partial k} = \sum_{i=0}^{n} x_i^2 (x_i - x_0)^2 \frac{G_i \left(2(2i+1)x_i - x_0 + (1-2ix_j)(1+k(x_i - x_0)) \right)}{(1-k(x_i - x_0))^3}$$

$$+ \sum_{i=0}^{n} f_{i} x_i^2 (x_i - x_0)^2 \frac{G_i \left(2(x_i - (2i+1)x_0) + (2ix_j - 1)(1+k(x_i - x_0)) \right)}{(1-k(x_i - x_0))^3} \quad (7.4.15)$$

The procedures for calculating the pressure residual $R$ and the values of the $(n+2)$ derivatives are repeated for each of the $N$ experimental points. If there exists $\delta G_0, \delta G_1, \ldots, \delta G_n$ and $\delta k$ such that $G_0 + \delta G_0, G_1 + \delta G_1, \ldots, G_n + \delta G_n$ and also $k + \delta k$ can produce a better fit (that is reduce the sum of the squares of the pressure residuals), then from the condition

$$\sum_{j=1}^{N} \left( R_j - \sum_{i=0}^{n} \frac{\partial P}{\partial G_i} \delta G_i - \frac{\partial P}{\partial k} \delta k \right)^2$$

is a minimum we find the following set of $(n+2)$ simultaneous equations:

$$\sum_{i=0}^{n} \left( \sum_{j=1}^{N} \frac{\partial P}{\partial G_i} \cdot \delta G_j \right) + \sum_{j=1}^{N} \frac{\partial P}{\partial k} \cdot \delta k = \sum_{j=1}^{N} \frac{\partial P}{\partial G_j} \cdot R_j \quad (7.4.16)$$

for all $j = 0, 1, \ldots, n$. 
Solution of these equations provides the $\delta G_i$ and $\delta k$ uniquely. The new values are used to recalculate the rational activity coefficients, the vapour compositions, the pressure residuals and the derivatives, which permit the recalculation of a further set of $G_i$ and $k$ parameters. The second derivatives, $\frac{\partial^2 P}{\partial G_i^2}$ for all $i = 0, 1, \ldots, n$ and $\frac{\partial^2 P}{\partial k^2}$ are in general non-zero, thus several cycles are necessary for convergence. The fit is assumed to be the best available when the Root Mean Square Deviation is constant.

Whilst it is possible to start without any information about the Myers and Scott function in fact it is much quicker to calculate an approximate value for $G_o$ before beginning the first cycle of calculations. As Barker stated if $G_1, G_2, \ldots, G_n$ are zero and $k$ is zero then

$$G_o = 4 \ln \left[ \frac{2P_o}{P_o^* + P_i^*} \right]$$

and this calculation is performed before the iterative procedure is entered.
The input data for the "Barker" Calculation consists of the set of experimental liquid compositions and the corresponding vapour pressures. In Chapter Six we pointed out that using a static method to measure vapour pressure, only the total composition of liquid and vapour was measured.

Initially it is assumed that the number of moles of 0 and 2 in the vapour phase is small compared with the number in the liquid, then the liquid compositions \( x_1 \) and \( x_2 \) are given by

\[
x_i = \frac{N_i}{N_1 + N_2}
\]

Using these values a "Barker" Analysis is used to indicate approximate vapour compositions, which are calculated from the activity coefficients. The liquid compositions can now be recalculated, correcting for the material present in the vapour phase. If \( x_i \), \( y_i \) are the mole fractions of component 0 in the liquid and vapour phases respectively and, \( N_1 \) and \( N_2 \) are the total quantities of 0 and 2 taken, then writing \( n_1 \) and \( n_2 \) for the quantities of 0 and 2 in the vapour phase and using equation (7.1.20) written as a quadratic in \( \frac{n_1 + n_2}{n_1 + n_2} \) we have

\[
\frac{y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}}{V} \left( n_1 + n_2 \right) + \frac{P V}{RT} = 0
\] (7.5.1)
Solution of this equation for \((n_1 + n_2)\) gives

\[
(n_1 + n_2) = -1 + \sqrt{1 + 4 \left( \frac{y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}}{2 (y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22})/V} \right) R/T} \tag{7.5.2}
\]

and from the definition of the partial pressure of component \(i\),

\[
p_i = y_i P = \frac{n_i P}{n_1 + n_2} \tag{7.5.3}
\]

clearly

\[
n_i = y_i \frac{P V}{R T} \left[ 1 + \frac{(n_1 + n_2) (y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22})}{V} \right]^{-1} \tag{7.5.4}
\]

The liquid compositions are then directly determined

\[
\alpha_i = \frac{N_i - n_i}{N_1 + N_2 - (n_1 + n_2)} \tag{7.5.5}
\]

and

\[
\alpha_2 = 1 - \alpha_1 = \frac{N_2 - n_2}{N_1 + N_2 - (n_1 + n_2)} \tag{7.5.6}
\]

Using these new values of \(\alpha_1\) and \(\alpha_2\) the experimental vapour pressures are refitted to the suitable function of composition and the vapour compositions which this "Barker" Analysis produces are
again used to calculate liquid compositions until consistency is achieved.

§7.6 THE EXCESS GIBBS FUNCTION FOR MIXING CALCULATED DIRECTLY FROM ACTIVITY COEFFICIENTS.

If the activity coefficient as a function of composition is available for one component of a binary mixture then it is possible to calculate the excess Gibbs function of mixing directly without using a "Barker" technique. McGlashan and Williamson (78) have employed this basic procedure to calculate the excess Gibbs function of mixing, $G^E$, for the system n-hexane + n-hexadecane with a two parameter Guggenheim function to represent $G^E$. Marsh (80) has used this technique also, but in a more general form when studying mixtures of benzene and carbon tetrachloride with octamethylcyclotetrasiloxane. The method is particularly attractive for mixtures where one component is considerably more volatile than the other.

The method described here is theoretically of general validity with no restriction on relative volatility, and the most rigorous thermodynamic equations will be used. In Section (7.2) it was shown that the logarithm of the rational activity coefficient could be represented at any given temperature and pressure as a function of composition, $F(x_1, x_2)$. Using a Myers and Scott "skewed" equation for $G^E/RT$ we can write
$$\frac{G^E}{RT} = \sum_{i=0}^{n} \frac{x_1 x_2 G_i (x_1 - x_2)^i}{(1 - k(x_1 - x_2))} \quad (7.6.1)$$

and thus

$$\ln f_i = F(x_1, x_2) = \sum_{i=0}^{n} \frac{x_1^2 (x_1 - x_2)^i - G_i (x_1 - (2i+1)x_2 + k(x_1 - x_2)x_2 - 1)}{(1 - k(x_1 - x_2))^2} \quad (7.6.2)$$

If the input data consists of discrete values of \( \ln f_i \) and the corresponding liquid compositions \( x_2 \), then conventional curve fitting procedures can be employed using equation \( (7.6.2) \).

We require \( G_0, G_1, \ldots, G_n \) and \( k \) such that

$$S = \sum_{j=1}^{N} \left( \ln f_j - F(x_{1j}, x_{2j}) \right)^2$$

is a minimum, then \( \frac{\partial S}{\partial G_i} = 0 \) for all \( i = 0, 1, \ldots, n \)

and \( \frac{\partial S}{\partial k} = 0 \), if the skewing parameter \( k \) is to be calculated from the least squares condition.

$$\frac{\partial F}{\partial G_i} = \frac{x_1^2 (x_1 - x_2)^{i-1} [x_1 - (2i+1)x_2 + k(x_1 - x_2)(2i+1)x_2 - 1]}{(1 - k(x_1 - x_2))^2} \quad (7.6.3)$$

for all \( i = 0, 1, \ldots, n \).
\[
\frac{\partial F}{\partial k} = \sum_{i=0}^{N} \frac{x_i^2(x_i-x_s)^i}{(1-k(x_i-x_s))^3} \left[ 2(x_i-(2i+1)x_s) + (2i+x_s-1)(1+k(x_i-x_s))^3 \right]
\]

If there exists \( G_\delta = G_k + \delta G_k \) for all \( \delta = 0, 1, \ldots, n \) and \( k^* = k + \delta k \) such that

\[
F^*(x_i, x_s) = F(x_i, x_s) + \delta F(x_i, x_s)
\]

where

\[
\delta F(x_i, x_s) = \sum_{i=0}^{n} \frac{\partial F(x_i, x_s)}{\partial G_k} \delta G_k + \frac{\partial F(x_i, x_s)}{\partial k} \delta k
\]
yields a better fit to the experimental data, then defining

\[
R_j = \sum_{i=0}^{n} F(x_i, x_s) - F(x_i, x_s)
\]

we can calculate the \( \delta G_k \) and \( \delta k \) which make

\[
\sum_{j=1}^{N} \left( R_j - \sum_{i=0}^{n} \frac{\partial F(x_i, x_s)}{\partial G_k} \delta G_k - \frac{\partial F(x_i, x_s)}{\partial k} \delta k \right)^2
\]
a minimum. That is to say we solve the following \((n + 2)\)
simultaneous equations

\[
\sum_{i=0}^{n} \sum_{j=1}^{N} \frac{\partial F}{\partial G_k} \cdot \frac{\partial F}{\partial G_i} \delta G_i + \sum_{j=1}^{N} \frac{\partial F}{\partial k} \cdot \frac{\partial F}{\partial G_k} \delta k = \sum_{j=1}^{N} R_j \frac{\partial F}{\partial G_k} \tag{7.6.5}
\]

for all \( \delta = 0, 1, \ldots, n \).
\[
\sum_{i=0}^{n} \sum_{j=1}^{N} \frac{\partial F}{\partial \delta_{i,j}} \frac{\partial F}{\partial k} \delta_{G_{i}} + \sum_{j=1}^{N} \frac{\partial F}{\partial k} \frac{\partial F}{\partial k} \delta_{k} = \sum_{j=1}^{N} \frac{\partial F}{\partial k} \delta_{k}
\]  

(7.6.6)

in order to calculate values of the unknowns \( \delta_{G_{i}} \) and \( \delta_{k} \). As \( \frac{\partial^{2} F}{\partial k^{2}} \neq 0 \), in general, when we are fitting for the skewing parameter \( k \) several cycles may be necessary for complete convergence.

A suitable first approximation must be supplied in order that convergence is rapid. Following Barker (73) we assume for the first cycle \( G_{1}, G_{2}, \ldots, G_{n} \) and \( k \) are zero. Then

\[
G_{0} = 4 \ln \left[ \frac{2P_{12}}{P_{10} + P_{20}} \right]
\]

where \( P_{12} \) is the vapour pressure when \( x_{1} = x_{2} = 0.5 \), and \( G_{0} \) provides an acceptable first approximation. Usually \( k \) is only determined in the case when \( n = 0 \), since when further parameters are also included the best fit may occur with \( k \) outside the range \(-1 < k < 1\). The necessary computer program developed to perform these calculations is given in Appendix 3.

\section{7.7 Calculation of Rational Activity Coefficients from Total Composition and Total Vapour Pressure Measurements}

As was pointed out, above, in practice only the total composition has been measured. However the procedure described
for activity coefficient fitting requires the precise liquid composition \( x_2 \). The procedure described below is rigorous provided all the parameters are known. However this may not be true for the virial coefficients \( B_{ij} \) and therefore we shall assume that component \( \Theta \) is the less volatile of the two.

Using the same notation throughout as in Section (7.5), as a first approximation we assume

\[
\begin{align*}
x_1 &= \frac{N_1}{N_1 + N_2} \quad \text{and therefore} \quad x_2 = 1 - x_1, \\
y_1 &= 0, \quad y_2 = 1 - y_1.
\end{align*}
\]

Using equation (7.4.10)

\[
\begin{align*}
f_i &= \prod_{i=0}^{n} \exp \left[ \frac{x_i^2 (x_i - x_i) \gamma G_{ii} ((2i+1)x_i - x_i + k(x_i - x_i)(1 - 2ix_i))}{(1 - k(x_i - x_i))^2} \right],
\end{align*}
\]

the partial pressure of component \( \Theta \) in the vapour, \( p_i \), can be determined from equation (7.1.52)

\[
\begin{align*}
p_i &= x_i f_i \rho_i^0 \exp \left[ \frac{(V_i^0 - B_{ii}) (P - \rho_i^0)}{RT} + \frac{(V_i - V_i^0)(P - \rho_i^0)}{RT} \right] - \\
&\frac{B_{ii}^2 \rho_i^0}{2(\Delta T^2)} \rho_i^2 + \frac{B_{ii}^2 \rho_i^2}{\lambda(\Delta T)^2} \rho_i^2 - y_2^2 \frac{\rho_2 \Delta \rho_2}{RT}
\end{align*}
\]

and therefore we can calculate \( \rho_2 \) from

\[
\rho_2 = P - \rho_i
\]
and the vapour compositions \( y_1 \) and \( y_2 \) from

\[
y_1 = \frac{p_1}{P} \quad \quad \quad y_2 = 1 - y_1
\]

(7.7.6).

Using the equation of state for a gas as written in equation (7.5.2) the total quantity of material in the vapour phase \((n_1 + n_2)\) can be found,

\[
(n_1 + n_2) = \frac{-1 + \sqrt{1 + 4 (y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}) P/RT}}{2 (y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}) / V}
\]

(7.7.7)

Then from the definitions of partial pressure and mole fraction

\[
n_1 = \frac{p_1 V}{V} \left[1 + \frac{(n_1 + n_2) (y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}) RT}{V}\right]^{-1}
\]

(7.7.8)

and

\[
n_2 = \frac{p_2 V}{V} \left[1 + \frac{(n_1 + n_2) (y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}) RT}{V}\right]^{-1}
\]

(7.7.9)

which enables \( y_1 \), \( y_2 \), \( x_1 \) and \( x_2 \) to be recalculated using

\[
y_1 = \frac{n_1}{n_1 + n_2} \quad \quad \quad y_2 = 1 - y_1
\]

(7.7.10)

\[
x_1 = \frac{N_1 - n_1}{N_1 + N_2 - (n_1 + n_2)} \quad \quad \quad x_2 = 1 - x_1
\]

(7.7.11)
The cycle of calculations is repeated until successive values of $p_2$ are constant, then $\ln f_2$ is calculated using equation (7.1.52)

$$
\ln f_2 = \ln \frac{p_2}{x_2 p_2^0} + \frac{(B_{22} - V_2^*) (P - P_2^*)}{RT} + \frac{(V_t - V_t^*)(P_t^+ - P)}{RT}
$$

$$
+ \frac{B_{22}^2}{2(RT)^2} (P_2^+ - P_2^2) + \frac{y_i^2 y_j^2 p}{RT}
$$

(7.7.12).

Initially the system is assumed to be a regular solution i.e., $G_i, G_j, ..., G_n$ and $k$ are zero, and as before

$$
G_o = 4 \ln \left[ \frac{2p_2}{p_1^0 + p_2^0} \right]
$$

When the true liquid composition has been calculated at each experimental point the parameters $G_o, G_i, ..., G_n$ and $k$ are determined using the method described in Section (7.6) and the compositions recalculated using the above procedure until consistency of composition and the Gibbs function is achieved. A computer procedure is shown in Appendix 3 which performs this calculation.

### 7.7.8 TESTING THE COMPUTER PROGRAMS

a) Repeating Barker's Original Calculations

The data of Brown (83) on the system benzene + n-heptane at 80°C was used as a preliminary test of the computer program written to perform the calculations described in Section (7.4). The
results do not agree exactly with those obtained by Barker (73) but were in perfect agreement with those obtained with an earlier program of Morcom and Cole (84), which was neither so general nor so suitable for modern computers as the present program. The results obtained are shown in Table (7.8.1), compared with those obtained by Brown directly from the vapour composition measurements and those obtained by Barker using the method outlined in Section (7.3).

b) Repeating McGlashan and Williamson's Calculation of $G^E$ for the System n-hexane and n-hexadecane, from Activity Coefficient Data.

In table (7.8.2) the results obtained by computer calculation as described in Section (7.6) are compared with those calculated by McGlashan and Williamson (78). The agreement between the two sets of data is good but owing to the unavailability of the vapour space volume it was impossible to test the composition calculation described in Section (7.7).

c) Repeating Gaw and Swinton's Calculations of $G^E$ for the System benzene + hexafluorobenzene, from Total Composition/Total Pressure Measurements.

The results obtained using procedures described in Sections (7.4) and (7.5) are presented in Table (7.8.3) together with those obtained by Gaw and Swinton (59, 60, 85). The data is calculated at three temperatures in order to test the suitability of the program to account for curves which show a pronounced sign inversion. In Table (7.8.4) the values obtained with this system using the procedures described in Sections (7.6) and (7.7) are compared with those obtained by Gaw and Swinton and illustrate
TABLE (7.8.1)
REPEAT OF BARKERS CALCULATION ON THE DATA OF BROWN FOR THE SYSTEM:
BENZENE (1) + n-HEPTANE (2) at 353.15 K,

1) VAPOUR COMPOSITION

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$P_{exp}/N_m$</th>
<th>$y_{exp}$</th>
<th>$y_i$ (Barker)</th>
<th>$y_i$ (This Work)</th>
<th>$G^E/J_{mol}^{-1}$ (This Work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0464</td>
<td>606.110</td>
<td>0.0988</td>
<td>0.0993</td>
<td>0.0998</td>
<td>37.9</td>
</tr>
<tr>
<td>0.0861</td>
<td>634.948</td>
<td>0.1729</td>
<td>0.1734</td>
<td>0.1743</td>
<td>68.2</td>
</tr>
<tr>
<td>0.2004</td>
<td>712.448</td>
<td>0.3473</td>
<td>0.3463</td>
<td>0.3480</td>
<td>144.8</td>
</tr>
<tr>
<td>0.2792</td>
<td>759.258</td>
<td>0.4412</td>
<td>0.4409</td>
<td>0.4437</td>
<td>188.1</td>
</tr>
<tr>
<td>0.3842</td>
<td>817.973</td>
<td>0.5464</td>
<td>0.5458</td>
<td>0.5484</td>
<td>232.3</td>
</tr>
<tr>
<td>0.4857</td>
<td>866.809</td>
<td>0.6304</td>
<td>0.6310</td>
<td>0.6337</td>
<td>258.4</td>
</tr>
<tr>
<td>0.5824</td>
<td>906.246</td>
<td>0.7009</td>
<td>0.7016</td>
<td>0.7054</td>
<td>265.2</td>
</tr>
<tr>
<td>0.6904</td>
<td>944.963</td>
<td>0.7759</td>
<td>0.7749</td>
<td>0.7773</td>
<td>248.0</td>
</tr>
<tr>
<td>0.7842</td>
<td>972.947</td>
<td>0.8384</td>
<td>0.8363</td>
<td>0.8376</td>
<td>207.7</td>
</tr>
<tr>
<td>0.8972</td>
<td>997.865</td>
<td>0.9149</td>
<td>0.9148</td>
<td>0.9154</td>
<td>121.4</td>
</tr>
</tbody>
</table>

2) PARAMETERS IN THE GUGGENHEIM EXPRESSION FOR $G^E/RT$

<table>
<thead>
<tr>
<th></th>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BARKERS VALUES</td>
<td>0.3620</td>
<td>0.0891</td>
<td>0.0261</td>
</tr>
<tr>
<td>THIS WORK</td>
<td>0.3549</td>
<td>0.0952</td>
<td>0.0277</td>
</tr>
</tbody>
</table>
TABLE (7.8.1) (Continued)

3) CALCULATED $G^E$ VALUES

<table>
<thead>
<tr>
<th>$x_i$</th>
<th>$G^E/J \cdot mol^{-1}$</th>
<th>$G^E/J \cdot mol^{-1}$</th>
<th>$G^E/J \cdot mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>81.2</td>
<td>79.4</td>
<td>78.4</td>
</tr>
<tr>
<td>0.2</td>
<td>149.3</td>
<td>147.1</td>
<td>144.6</td>
</tr>
<tr>
<td>0.3</td>
<td>203.8</td>
<td>202.1</td>
<td>198.1</td>
</tr>
<tr>
<td>0.4</td>
<td>242.7</td>
<td>242.8</td>
<td>237.5</td>
</tr>
<tr>
<td>0.5</td>
<td>265.5</td>
<td>266.0</td>
<td>260.5</td>
</tr>
<tr>
<td>0.6</td>
<td>268.0</td>
<td>268.2</td>
<td>264.3</td>
</tr>
<tr>
<td>0.7</td>
<td>247.8</td>
<td>247.8</td>
<td>245.1</td>
</tr>
<tr>
<td>0.8</td>
<td>198.5</td>
<td>199.0</td>
<td>198.3</td>
</tr>
<tr>
<td>0.9</td>
<td>118.8</td>
<td>117.9</td>
<td>118.6</td>
</tr>
</tbody>
</table>
TABLE (7.8.2)

COMPARISON OF THE RESULTS OF McGlashan and Williamson WITH THOSE CALCULATED USING OUR PROGRAM ON THE SYSTEM:

\( \text{n-HEXANE (2) + n-HEXADECANE (1) at} \)

a) 293.15 K

<table>
<thead>
<tr>
<th>(x_2)</th>
<th>(-\ln f_x^{A.G.W.})</th>
<th>(-\ln f_x^{(This\ Work)})</th>
<th>(G^E/J\cdot mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03012</td>
<td>0.09853</td>
<td>0.09868</td>
<td>-7.4</td>
</tr>
<tr>
<td>0.10346</td>
<td>0.08078</td>
<td>0.08063</td>
<td>-23.4</td>
</tr>
<tr>
<td>0.16018</td>
<td>0.07297</td>
<td>0.07295</td>
<td>-33.9</td>
</tr>
<tr>
<td>0.27733</td>
<td>0.05522</td>
<td>0.05522</td>
<td>-50.5</td>
</tr>
<tr>
<td>0.40729</td>
<td>0.03853</td>
<td>0.03858</td>
<td>-61.3</td>
</tr>
<tr>
<td>0.52569</td>
<td>0.02505</td>
<td>0.02503</td>
<td>-64.2</td>
</tr>
<tr>
<td>0.52638</td>
<td>0.02563</td>
<td>0.02564</td>
<td>-64.2</td>
</tr>
<tr>
<td>0.70020</td>
<td>0.01115</td>
<td>0.01111</td>
<td>-55.9</td>
</tr>
<tr>
<td>0.82973</td>
<td>0.00357</td>
<td>0.00356</td>
<td>-38.9</td>
</tr>
</tbody>
</table>

when \(x_1 = x_2 = 0.5\) then

\(G^E = -64.17\ J\cdot mol^{-1} (This\ Work)\)

\(= -65.3\ J\cdot mol^{-1} (Original\ Paper)\)
TABLE (7.8.2) (Continued)

b) 303.15 K

<table>
<thead>
<tr>
<th>( x_2 )</th>
<th>(-\ln k^\circ (A.G.W.))</th>
<th>(-\ln k^\circ (This Work))</th>
<th>( G^E/\text{J. mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02980</td>
<td>0.10336</td>
<td>0.10324</td>
<td>-7.9</td>
</tr>
<tr>
<td>0.10247</td>
<td>0.08681</td>
<td>0.08670</td>
<td>-25.2</td>
</tr>
<tr>
<td>0.15871</td>
<td>0.07718</td>
<td>0.07721</td>
<td>-36.8</td>
</tr>
<tr>
<td>0.27588</td>
<td>0.06146</td>
<td>0.06147</td>
<td>-55.7</td>
</tr>
<tr>
<td>0.40576</td>
<td>0.04225</td>
<td>0.04230</td>
<td>-68.3</td>
</tr>
<tr>
<td>0.52050</td>
<td>0.02848</td>
<td>0.02846</td>
<td>-71.8</td>
</tr>
<tr>
<td>0.52500</td>
<td>0.02768</td>
<td>0.02767</td>
<td>-71.8</td>
</tr>
<tr>
<td>0.69714</td>
<td>0.01128</td>
<td>0.01126</td>
<td>-62.6</td>
</tr>
<tr>
<td>0.82852</td>
<td>0.00332</td>
<td>0.00315</td>
<td>-43.2</td>
</tr>
</tbody>
</table>

when \( x_1 = x_2 = 0.5 \) then

\( G^E = -71.7 \text{ J. mol}^{-1} \) (This Work)

\( = -71.3 \text{ J. mol}^{-1} \) (Original Paper)

c) 313.15 K

<table>
<thead>
<tr>
<th>( x_2 )</th>
<th>(-\ln k^\circ (A.G.W.))</th>
<th>(-\ln k^\circ (This Work))</th>
<th>( G^E/\text{J. mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02939</td>
<td>0.10528</td>
<td>0.10508</td>
<td>-8.2</td>
</tr>
<tr>
<td>0.10116</td>
<td>0.09026</td>
<td>0.09037</td>
<td>-26.4</td>
</tr>
<tr>
<td>0.15670</td>
<td>0.07990</td>
<td>0.07986</td>
<td>-38.5</td>
</tr>
<tr>
<td>0.27324</td>
<td>0.06332</td>
<td>0.06313</td>
<td>-58.7</td>
</tr>
<tr>
<td>0.40341</td>
<td>0.04446</td>
<td>0.04448</td>
<td>-72.4</td>
</tr>
<tr>
<td>0.51264</td>
<td>0.03030</td>
<td>0.03024</td>
<td>-76.4</td>
</tr>
<tr>
<td>0.52314</td>
<td>0.02883</td>
<td>0.02907</td>
<td>-76.4</td>
</tr>
<tr>
<td>0.69254</td>
<td>0.01204</td>
<td>0.01205</td>
<td>-67.2</td>
</tr>
<tr>
<td>0.82682</td>
<td>0.00334</td>
<td>0.00332</td>
<td>-46.5</td>
</tr>
</tbody>
</table>

when \( x_1 = x_2 = 0.5 \) then

\( G^E = -76.3 \text{ J. mol}^{-1} \) (This Work)

\( = -76.3 \text{ J. mol}^{-1} \) (Original Paper)
### TABLE (7.8.2) (Continued)

#### d) 323.15 K

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$\ln ^a(A.G.W.)$</th>
<th>$\ln ^b(This \ Work)$</th>
<th>$G^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02887</td>
<td>0.10827</td>
<td>0.10826</td>
<td>-8.6</td>
</tr>
<tr>
<td>0.09943</td>
<td>0.09226</td>
<td>0.09217</td>
<td>-27.5</td>
</tr>
<tr>
<td>0.15487</td>
<td>0.08286</td>
<td>0.08382</td>
<td>-40.5</td>
</tr>
<tr>
<td>0.27030</td>
<td>0.06463</td>
<td>0.06462</td>
<td>-61.8</td>
</tr>
<tr>
<td>0.39994</td>
<td>0.04483</td>
<td>0.04485</td>
<td>-76.4</td>
</tr>
<tr>
<td>0.50259</td>
<td>0.03180</td>
<td>0.03185</td>
<td>-80.5</td>
</tr>
<tr>
<td>0.52042</td>
<td>0.02940</td>
<td>0.02942</td>
<td>-80.6</td>
</tr>
<tr>
<td>0.68579</td>
<td>0.01248</td>
<td>0.01253</td>
<td>-71.0</td>
</tr>
<tr>
<td>0.82437</td>
<td>0.00345</td>
<td>0.00348</td>
<td>-48.6</td>
</tr>
</tbody>
</table>

when $x_1 = x_2 = 0.5$ then

$G^E = -80.3$ J.mol$^{-1}$ (This Work)

$= -80.5$ J.mol$^{-1}$ (Original Paper)

#### e) 333.15 K

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$\ln ^a(A.G.W.)$</th>
<th>$\ln ^b(This \ Work)$</th>
<th>$G^E$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02823</td>
<td>0.10850</td>
<td>0.10860</td>
<td>-8.7</td>
</tr>
<tr>
<td>0.09726</td>
<td>0.09376</td>
<td>0.09363</td>
<td>-27.9</td>
</tr>
<tr>
<td>0.15172</td>
<td>0.08474</td>
<td>0.08470</td>
<td>-41.2</td>
</tr>
<tr>
<td>0.26621</td>
<td>0.06532</td>
<td>0.06538</td>
<td>-63.4</td>
</tr>
<tr>
<td>0.39614</td>
<td>0.04571</td>
<td>0.04573</td>
<td>-78.9</td>
</tr>
<tr>
<td>0.48843</td>
<td>0.03387</td>
<td>0.03387</td>
<td>-83.3</td>
</tr>
<tr>
<td>0.51730</td>
<td>0.02963</td>
<td>0.02967</td>
<td>-83.5</td>
</tr>
<tr>
<td>0.67878</td>
<td>0.01308</td>
<td>0.01307</td>
<td>-74.3</td>
</tr>
<tr>
<td>0.82110</td>
<td>0.00373</td>
<td>0.00370</td>
<td>-50.9</td>
</tr>
</tbody>
</table>

when $x_1 = x_2 = 0.5$ then

$G^E = -83.5$ J.mol$^{-1}$ (This Work)

$= -83.7$ J.mol$^{-1}$ (Original Paper)
TABLE (7.8.2) (Continued)

f) The parameters calculated from the basic assumption that
\[ \frac{G^E}{R T} = \sum_{i=1}^{2} G_i (x_i - x_1) \cdot x_i \cdot x_i \]
are shown in this section; together with the R,M,S. deviation and the standard deviation (STD), which apply to the activity coefficients.

<table>
<thead>
<tr>
<th>T/K</th>
<th>G₀</th>
<th>G₁</th>
<th>G₂</th>
<th>RMS</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>-0.1053</td>
<td>0.0072</td>
<td>-0.0063</td>
<td>0.0009</td>
<td>0.0011</td>
</tr>
<tr>
<td>303.15</td>
<td>-0.1138</td>
<td>0.0085</td>
<td>-0.0026</td>
<td>0.0011</td>
<td>0.0013</td>
</tr>
<tr>
<td>313.15</td>
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<td>0.0095</td>
<td>-0.0028</td>
<td>0.0010</td>
<td>0.0012</td>
</tr>
<tr>
<td>323.15</td>
<td>-0.1199</td>
<td>0.0073</td>
<td>-0.0006</td>
<td>0.0007</td>
<td>0.0009</td>
</tr>
<tr>
<td>333.15</td>
<td>-0.1205</td>
<td>0.0070</td>
<td>-0.0000</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
</tbody>
</table>
TABLE (7.8.3)

CHECKING THE "BARKER" PROGRAM USING FULL EQUATIONS WITH THE SYSTEM:

HEXAFLUOROBENZENE (1) + BENZENE (2),

1) At 303.15 K

a) Excess Gibbs Function

<table>
<thead>
<tr>
<th>$x_T$</th>
<th>$x_1$</th>
<th>$y_1$</th>
<th>$G_{exp}/N\cdot m^2$</th>
<th>$G^E/J\cdot mol^{-1}$</th>
<th>$G^E/J\cdot mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0942</td>
<td>0.0943</td>
<td>0.0891</td>
<td>15909.4</td>
<td>25</td>
<td>25.3</td>
</tr>
<tr>
<td>0.1846</td>
<td>0.1849</td>
<td>0.1630</td>
<td>15773.4</td>
<td>24</td>
<td>23.6</td>
</tr>
<tr>
<td>0.2734</td>
<td>0.2739</td>
<td>0.2352</td>
<td>15558.7</td>
<td>6</td>
<td>6.3</td>
</tr>
<tr>
<td>0.3638</td>
<td>0.3644</td>
<td>0.3140</td>
<td>15278.7</td>
<td>-20</td>
<td>-19.6</td>
</tr>
<tr>
<td>0.4529</td>
<td>0.4534</td>
<td>0.3999</td>
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<td>-87.6</td>
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<td>-80.5</td>
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<td>-50</td>
<td>-50.4</td>
</tr>
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</table>

b) Curve Fitting Parameters

The parameters determined in this work using

$$\frac{G^E}{RT} = \sum_{i=1}^{n} x_i x_1 G_i (x_i - x_1)^{-1}$$

are given below together with the pressure deviations

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>$G_4$</th>
<th>$G_5$</th>
<th>RMS/N\cdot m^2</th>
<th>STD/N\cdot m^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0732</td>
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<td>-0.2115</td>
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<td></td>
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TABLE (7.8.3) (Continued)

2) At 313.15 K

a) Excess Gibbs Function

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<tr>
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<th>Swinton This Work</th>
</tr>
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<tbody>
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</tr>
<tr>
<td>x_2</td>
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<tr>
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<td>0.7800</td>
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<td>P_{exp}/N\cdot m^2</td>
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<tr>
<td>G^f/J\cdot mol</td>
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<td>RMS/N\cdot m^2</td>
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TABLE (7.8.3) (Continued)

3) At 343.15 K

a) Excess Gibbs Function

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<th>$P_{exp}/N\cdot m^2$</th>
<th>$G^E/J\cdot mol^{-1}$</th>
<th>$G^E/J\cdot mol^{-1}$</th>
</tr>
</thead>
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<td>0.1831</td>
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<td>45.0</td>
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<td>0.2734</td>
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<td>8.1</td>
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<td>-21.4</td>
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<td>-23.9</td>
</tr>
</tbody>
</table>

b) Curve Fitting Parameters

The parameters determined in this work using

$$\frac{G^E}{RT} = \sum_{i=1}^{n} x_i x_i \left(\frac{G_i}{x_i - x_i}\right)^{i-1}$$

are given below together with the pressure deviations

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>$G_4$</th>
<th>$G_x$</th>
<th>RMS/N\cdot m$^2$</th>
<th>STD/N\cdot m$^2$</th>
</tr>
</thead>
<tbody>
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<td>0.0142</td>
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<td></td>
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TABLE (7.8.4)

THE EXCESS GIBBS FUNCTION OF MIXING, $G^E$, FOR THE SYSTEM:
HEXAFLUOROBENZENE (2) + BENZENE (1) BY CURVE FITTING THE
ACTIVITY COEFFICIENTS CALCULATED FROM THE VAPOUR PRESSURE
MEASUREMENTS OF GAW AND SWINTON,

a) At 303.15 K

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0943</td>
<td>0.0891</td>
<td>0.0469</td>
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<td>0.0943</td>
<td>0.0878</td>
<td>0.0134</td>
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<tr>
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<td>0.2444</td>
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<td>-3.0</td>
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<tr>
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<td>-0.0845</td>
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<td>0.3295</td>
<td>-0.0421</td>
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<tr>
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<td>-0.0812</td>
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<td>0.8962</td>
<td>0.8951</td>
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<td>-54.6</td>
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</table>

b) At 313.15 K

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0943</td>
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<td>0.0368</td>
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<td>0.1692</td>
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<tr>
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<td>0.2429</td>
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<td>0.2485</td>
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<td>0.3645</td>
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<td>-7</td>
<td>0.3644</td>
<td>0.3330</td>
<td>-0.0410</td>
<td>-5.7</td>
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### TABLE (7.8.4) (Continued)

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<td>0.6012</td>
<td>0.5682</td>
</tr>
<tr>
<td>0.6892</td>
<td>0.6697</td>
</tr>
<tr>
<td>0.7852</td>
<td>0.7801</td>
</tr>
<tr>
<td>0.8961</td>
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</tbody>
</table>

**c) At 343.15 K**

<table>
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</thead>
<tbody>
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<td>$y_i$</td>
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<td>0.4299</td>
</tr>
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<td>0.5035</td>
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<td>0.5826</td>
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<td>0.7852</td>
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</tr>
<tr>
<td>0.8959</td>
<td>0.8995</td>
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</table>

**d) Curve Fitting Parameters**

The parameters determined in this work using

$$G^E/RT = \sum_{i=1}^{n} x_i x_i \frac{G_i}{J \cdot mol^{-1}}$$

are given below together with the deviations in $\ln f_i$

<table>
<thead>
<tr>
<th>T/K</th>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>$G_4$</th>
<th>RMS</th>
<th>STD</th>
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</thead>
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<td>-0.0329</td>
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<td>0.0009</td>
</tr>
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<td>-0.0566</td>
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</table>
the fact that the method used is not entirely satisfactory when
the components of the mixture are of comparable volatility.

In Table (7,8,5) the results of Gaw and Swinton on the
system hexafluorobenzene + p-xylene are compared in order to test
the program when the volatility of the two components is widely
different. In this case agreement is excellent considering the
entirely different approach to the problem.
TABLE (7.8.5)

THE EXCESS GIBBS FUNCTION OF MIXING, $G^E$, FOR THE SYSTEM:
HEXAFLUOROBENZENE (2) + p-XYLENE (1) BY CURVE FITTING THE
ACTIVITY COEFFICIENTS CALCULATED FROM THE VAPOUR PRESSURE
MEASUREMENTS OF GAW AND SWINTON,

a) At 303.15 K

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
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<td>-0.0191</td>
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</table>

b) At 323.15 K

<table>
<thead>
<tr>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
<th>$x_2$</th>
<th>$y_2$</th>
<th>$\ln f_2$</th>
<th>$\frac{G^E}{J \cdot mol^{-1}}$</th>
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<td>0.0950</td>
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<td>-0.2022</td>
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<td>0.8411</td>
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<tr>
<td>0.5617</td>
<td>0.9086</td>
<td>-0.1078</td>
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<td>0.9086</td>
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<td>-359.5</td>
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</table>
TABLE (7,8,5) (Continued)

<table>
<thead>
<tr>
<th>x₁</th>
<th>y₁</th>
<th>ln(f₁)</th>
<th>Gᵐ⁻¹ J mol⁻¹</th>
<th>Gᶜ⁻¹ J mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6493</td>
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<td>-0.0801</td>
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<tr>
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<td>0.9081</td>
<td>0.9917</td>
<td>-0.0040</td>
<td>-128</td>
<td>0.9081</td>
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</table>

c) At 343.15 K

<table>
<thead>
<tr>
<th>x₂</th>
<th>y₂</th>
<th>ln(f₂)</th>
<th>Gᵐ⁻¹ J mol⁻¹</th>
<th>Gᶜ⁻¹ J mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0925</td>
<td>0.3428</td>
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<td>0.0925</td>
</tr>
<tr>
<td>0.1749</td>
<td>0.5218</td>
<td>-0.2498</td>
<td>-127</td>
<td>0.1748</td>
</tr>
<tr>
<td>0.2552</td>
<td>0.6429</td>
<td>-0.2332</td>
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<td>0.2551</td>
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<td>0.3467</td>
<td>0.7442</td>
<td>-0.2021</td>
<td>-236</td>
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<td>0.4340</td>
<td>0.8170</td>
<td>-0.1649</td>
<td>-274</td>
<td>0.4341</td>
</tr>
<tr>
<td>0.6482</td>
<td>0.9300</td>
<td>-0.0651</td>
<td>-285</td>
<td>0.6482</td>
</tr>
<tr>
<td>0.7401</td>
<td>0.9580</td>
<td>-0.0315</td>
<td>-244</td>
<td>0.7402</td>
</tr>
<tr>
<td>0.8240</td>
<td>0.9761</td>
<td>-0.0121</td>
<td>-184</td>
<td>0.8240</td>
</tr>
<tr>
<td>0.9057</td>
<td>0.9890</td>
<td>-0.0020</td>
<td>-106</td>
<td>0.9057</td>
</tr>
</tbody>
</table>

d) Curve Fitting Parameters

The parameters determined in this work using

\[ \frac{G^c}{RT} = \sum_{i=1}^{n} x_i x_2 G_i (x_i - x_1)^{i-1} \]

are given below together with the deviations in ln

<table>
<thead>
<tr>
<th>T/K</th>
<th>G₁</th>
<th>G₂</th>
<th>G₃</th>
<th>G₄</th>
<th>RMS</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>-0.6818</td>
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<td>0.1471</td>
<td>-0.0034</td>
<td>0.0007</td>
<td>0.0009</td>
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<tr>
<td>323.15</td>
<td>-0.5286</td>
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<td>0.0973</td>
<td>-0.0093</td>
<td>0.0005</td>
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<tr>
<td>343.15</td>
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<td>0.1401</td>
<td>0.0607</td>
<td>0.1277</td>
<td>0.0028</td>
<td>0.0038</td>
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</table>
CHAPTER EIGHT

VAPOUR PRESSURE RESULTS
8.1 PURE HEXAFLUOROBENZENE

The vapour pressure of pure hexafluorobenzene was determined at 303.15, 323.15, 333.15 and 343.15 K as described in Chapter Seven. The results obtained are shown in Table (8.1.1) and are compared with the results of Patrick and Prosser (23), Councell, Green, Hales and Martin (24) and Gaw and Swinton (56) in Table (8.1.2).

The agreement of the present work with the measurements performed by other workers on different samples was taken as an indication that the apparatus was working satisfactorily and also that the Imperial Smelting Corporation Anaesthetic Grade Hexafluorobenzene was sufficiently pure for direct thermodynamic measurements to be made upon it.

8.2 PURE N,N-DIMETHYLANILINE

The vapour pressure of N,N-dimethylaniline, purified as described in Chapter Two, was determined at 323.15 and 333.15 K. The results are shown in Table (8.2.1) and are compared with literature data (86 - 88) in Fig (8.2.1).

Again agreement with the old literature values was considered to be satisfactory, and the use of the twin-manometer cut-off assembly had been fully tested.
**Fig. (8.2.1)**

![Diagram showing vapor pressure vs. temperature relationship with data points labeled: Stull (88), Hartelmann (86), Martin and Collie (87), and This Work.](image)

**The Vapor Pressure of Pure N,N-Dimethylamine**
EXPERIMENTAL VAPOUR PRESSURE RESULTS:

PURE HEXAFLUOROBENZENE

TABLE (8.1.1)

<table>
<thead>
<tr>
<th>NOMINAL TEMPERATURE = 303.15 K</th>
<th>TEMP / K</th>
<th>0/N.m⁻²</th>
<th>1/N.m⁻²</th>
<th>2/N.m⁻²</th>
<th>3/N.m⁻²</th>
<th>4/N.m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303.190</td>
<td>14382.4</td>
<td>14391.7</td>
<td>14398.3</td>
<td>14391.7</td>
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</tr>
<tr>
<td></td>
<td>302.966</td>
<td>14225.1</td>
<td>14230.4</td>
<td>14230.4</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>303.021</td>
<td>14235.6</td>
<td>14240.9</td>
<td>14242.2</td>
<td>14243.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303.087</td>
<td>14288.5</td>
<td>14279.2</td>
<td>14280.5</td>
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</tr>
</tbody>
</table>

VAPOUR PRESSURE AT 303.15 K = 14327 N.m⁻²

<table>
<thead>
<tr>
<th>NOMINAL TEMPERATURE = 323.15 K</th>
<th>TEMP / K</th>
<th>0/N.m⁻²</th>
<th>1/N.m⁻²</th>
<th>2/N.m⁻²</th>
<th>3/N.m⁻²</th>
<th>4/N.m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>323.133</td>
<td>34133.4</td>
<td>34155.9</td>
<td>34132.0</td>
<td>34128.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323.242</td>
<td>34197.9</td>
<td>34216.4</td>
<td>34305.0</td>
<td>34297.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>322.998</td>
<td>33868.5</td>
<td>33864.5</td>
<td>33865.8</td>
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<td></td>
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</tbody>
</table>

VAPOUR PRESSURE AT 323.15 K = 34106 N.m⁻²

<table>
<thead>
<tr>
<th>NOMINAL TEMPERATURE = 333.15 K</th>
<th>TEMP / K</th>
<th>0/N.m⁻²</th>
<th>1/N.m⁻²</th>
<th>2/N.m⁻²</th>
<th>3/N.m⁻²</th>
<th>4/N.m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
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<td>333.040</td>
<td>50000.3</td>
<td>49984.4</td>
<td>49888.0</td>
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<tr>
<td></td>
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<td>50039.3</td>
<td>50116.1</td>
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<td></td>
<td>333.275</td>
<td>50425.3</td>
<td>50430.6</td>
<td>50413.4</td>
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<td></td>
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</tbody>
</table>

VAPOUR PRESSURE AT 333.15 K = 50178 N.m⁻²
Table (8.1.2)

Comparison with other workers' vapour pressure results on hexafluorobenzene

<table>
<thead>
<tr>
<th>TEMP/K</th>
<th>VP/N*m^-2</th>
<th>WORKER</th>
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</thead>
<tbody>
<tr>
<td>303.15</td>
<td>14302</td>
<td>Gaw and Swinton (56)</td>
</tr>
<tr>
<td></td>
<td>14304</td>
<td>Counsell et al. (24)</td>
</tr>
<tr>
<td></td>
<td>14322</td>
<td>Gaw and Swinton (56)</td>
</tr>
<tr>
<td></td>
<td>14327</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>14339</td>
<td>Patrick and Prosser (23)</td>
</tr>
<tr>
<td>323.15</td>
<td>33900</td>
<td>Patrick and Prosser (23)</td>
</tr>
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<td></td>
<td>34076</td>
<td>Gaw and Swinton (56)</td>
</tr>
<tr>
<td></td>
<td>34080</td>
<td>Counsell et al. (24)</td>
</tr>
<tr>
<td></td>
<td>34089</td>
<td>Gaw and Swinton (56)</td>
</tr>
<tr>
<td></td>
<td>34106</td>
<td>This Work</td>
</tr>
<tr>
<td>333.15</td>
<td>50163</td>
<td>Gaw and Swinton (56)</td>
</tr>
<tr>
<td></td>
<td>50164</td>
<td>Gaw and Swinton (56)</td>
</tr>
<tr>
<td></td>
<td>50168</td>
<td>Counsell et al. (24)</td>
</tr>
<tr>
<td></td>
<td>50178</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>50184</td>
<td>Patrick and Prosser (23)</td>
</tr>
</tbody>
</table>
EXPERIMENTAL VAPOUR PRESSURE RESULTS:
PURE N,N-DIMETHYLAMINILINE

**NOMINAL TEMPERATURE = 323.15 K**

<table>
<thead>
<tr>
<th>TEMP / K</th>
<th>0/N.m(^2)</th>
<th>2/N.m(^2)</th>
<th>3/N.m(^2)</th>
<th>4/N.m(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.258</td>
<td>400.5</td>
<td>397.8</td>
<td>397.8</td>
<td>384.6</td>
</tr>
<tr>
<td>323.009</td>
<td>407.1</td>
<td>403.1</td>
<td>408.4</td>
<td>404.4</td>
</tr>
<tr>
<td>323.141</td>
<td>400.9</td>
<td>395.6</td>
<td>400.9</td>
<td>399.6</td>
</tr>
</tbody>
</table>

VAPOUR PRESSURE AT 323.15 K = 401.6 N.m\(^2\)

**NOMINAL TEMPERATURE = 333.15 K**

<table>
<thead>
<tr>
<th>TEMP / K</th>
<th>0/N.m(^2)</th>
<th>2/N.m(^2)</th>
<th>3/N.m(^2)</th>
<th>4/N.m(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.282</td>
<td>729.0</td>
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<td>721.1</td>
<td>723.8</td>
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<tr>
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<td>712.1</td>
<td>712.1</td>
</tr>
<tr>
<td>333.165</td>
<td>717.6</td>
<td>724.4</td>
<td>728.3</td>
<td>720.4</td>
</tr>
</tbody>
</table>

VAPOUR PRESSURE AT 333.15 K = 717.5 N.m\(^2\)
Measurements of the vapour pressure of mixtures of N,N-dimethylaniline and hexafluorobenzene were carried out at 323.15 and 333.15 K over the composition range. The measurements were made in two steps, the first in the N,N-dimethylaniline rich region using the "reversed" manometer and using the conventional cut-off manometer for the hexafluorobenzene rich region. The results obtained are shown in Fig (8.3.1) where it is immediately seen that the calculated vapour pressures show a definite trend to higher values within each series.

The enormous error in these measurements is undoubtedly due to the entry of water into the cell when distillations were in progress. The taps $T_1$ and $T_2$ were of greaseless design (Type Uniform, Messrs. Jencons (Scientific) Ltd., Hemel Hempstead, Hertfordshire) and the one on the "reversed" manometer side of the tank unit was seen to leak slightly during the distillation of the fourth ampoule of hexafluorobenzene. Clearly, the taps are not capable of withstanding the temperature variation imposed upon them by immersing them in the thermostat bath. On the other side of the apparatus the tap was never seen to leak but if the mercury was being wetted through a leaking tap then this could account for the steady upward trend observed in the measurements. However in this case it is not impossible for the excess Gibbs function to show a sign inversion and all that can be said is that these results are inconclusive.
VAPOUR PRESSURE RESULTS FOR
HEXAFLUORBENZENE AND N,N-DIMETHYLAMINE MIXTURES

- Series 1 at 323.15 K
- Series 1 at 333.15 K
- Series 2 at 323.15 K
- Series 2 at 333.15 K

Fig (8.3.1)
The apparatus is to be rebuilt, eliminating the taps $T_1$ and $T_2$ by placing them below the tank and in the interim, whilst the new thermostat tank is being manufactured, taps $T_1$ and $T_2$ are to be replaced by a greaseless design having a mercury seal. The measurements will then be repeated.

§8.4 Calculation of the Excess Gibbs Function, $G^E$, for the System Hexafluorobenzene + N,N-Dimethylaniline

No attempt was made to fit the experimental data given in Fig (8.3.1) to a suitable function for $G^E$, because of the large experimental uncertainty. However those points which are probably reliable, notably (1.1, 1.2, 1.3, 2.1, 2.2) when fitted using the Barker type program described in Chapter Seven gave the results shown in Table (8.4.1) and indicate that the excess Gibbs function for this system is likely to be negative.
TABLE (8.4.1)
THE EXCESS GIBBS FUNCTION FOR MIXING, $G^E$, FOR THE SYSTEM:
HEXAFLUOROBENZENE (2) + N,N-DOMETHYLANILINE (1),

1) At 323.15 K

a) Experimental Results

<table>
<thead>
<tr>
<th>No.</th>
<th>$n_1$/mol</th>
<th>$n_2$/mol</th>
<th>P/N m$^{-2}$</th>
<th>V/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>0.045312</td>
<td>0.005833</td>
<td>4156.5</td>
<td>1.471 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.2</td>
<td>0.045312</td>
<td>0.012358</td>
<td>7079.8</td>
<td>1.492 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.3</td>
<td>0.045312</td>
<td>0.020576</td>
<td>9838.7</td>
<td>1.478 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.4</td>
<td>0.045312</td>
<td>0.031438</td>
<td>19178.2</td>
<td>1.464 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.5</td>
<td>0.045312</td>
<td>0.046678</td>
<td>22319.2</td>
<td>1.462 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.6</td>
<td>0.045312</td>
<td>0.068902</td>
<td>25660.8</td>
<td>1.466 x 10$^{-4}$</td>
</tr>
<tr>
<td>2.1</td>
<td>0.008806</td>
<td>0.004355</td>
<td>9531.2</td>
<td>1.196 x 10$^{-4}$</td>
</tr>
<tr>
<td>2.2</td>
<td>0.008806</td>
<td>0.007143</td>
<td>13142.4</td>
<td>1.236 x 10$^{-4}$</td>
</tr>
<tr>
<td>2.3</td>
<td>0.008806</td>
<td>0.010525</td>
<td>17792.4</td>
<td>1.294 x 10$^{-4}$</td>
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<tr>
<td>2.4</td>
<td>0.008806</td>
<td>0.015823</td>
<td>22596.3</td>
<td>1.187 x 10$^{-4}$</td>
</tr>
<tr>
<td>2.5</td>
<td>0.008806</td>
<td>0.032357</td>
<td>30080.5</td>
<td>1.179 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

b) Barker Analysis, using

$$\frac{G^E}{RT} = \sum_{j=1}^{n} x_j x_2 G_{ij} (x_j - x_2)^{j-1}$$

and experimental points Nos. 1.1, 1.2, 1.3, 2.1, 2.2

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>$G_4$</th>
<th>RMS/N m$^{2}$/STD/N m$^{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1792</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>-0.1250</td>
<td>0.2983</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.1235</td>
<td>0.2948</td>
<td>0.0102</td>
<td></td>
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<tr>
<td>-0.1355</td>
<td>0.1938</td>
<td>0.3445</td>
<td>-0.4218</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>440 492</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>121 156</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>121 191</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>115 257</td>
</tr>
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</table>
TABLE (8.4.1) (Continued)

c) Calculated values for a two parameter fit

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$F_{	ext{calc}}/N\cdot m^{-2}$</th>
<th>$y_1$</th>
<th>$G^E/J\cdot \text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8894</td>
<td>4187.7</td>
<td>0.0805</td>
<td>28.4</td>
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<td>0.7905</td>
<td>7016.9</td>
<td>0.0548</td>
<td>21.5</td>
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<td>-5.7</td>
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<td>0.6906</td>
<td>9745.3</td>
<td>0.0078</td>
<td>-6.5</td>
</tr>
<tr>
<td>0.5726</td>
<td>13117.3</td>
<td>0.0203</td>
<td>-53.7</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$d^E/J\cdot \text{mol}^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>0.9</td>
<td>27.5</td>
</tr>
<tr>
<td>0.8</td>
<td>23.2</td>
</tr>
<tr>
<td>0.7</td>
<td>-3.2</td>
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<tr>
<td>0.6</td>
<td>-42.1</td>
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<tr>
<td>0.5</td>
<td>-83.9</td>
</tr>
<tr>
<td>0.4</td>
<td>-119.1</td>
</tr>
<tr>
<td>0.3</td>
<td>-137.8</td>
</tr>
<tr>
<td>0.2</td>
<td>-130.7</td>
</tr>
<tr>
<td>0.1</td>
<td>-87.9</td>
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</table>
2) At 333.15 K

a) Experimental Results

<table>
<thead>
<tr>
<th>No.</th>
<th>$n_1$/mol</th>
<th>$n_2$/mol</th>
<th>$P$/N.m$^{-2}$</th>
<th>$V$/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>0.045312</td>
<td>0.005833</td>
<td>6128.5</td>
<td>1.489 x 10^{-4}</td>
</tr>
<tr>
<td>1.2</td>
<td>0.045312</td>
<td>0.012358</td>
<td>10401.0</td>
<td>1.520 x 10^{-4}</td>
</tr>
<tr>
<td>1.3</td>
<td>0.045312</td>
<td>0.020576</td>
<td>14533.7</td>
<td>1.524 x 10^{-4}</td>
</tr>
<tr>
<td>1.4</td>
<td>0.045312</td>
<td>0.031438</td>
<td>25925.5</td>
<td>1.534 x 10^{-4}</td>
</tr>
<tr>
<td>1.5</td>
<td>0.045312</td>
<td>0.046678</td>
<td>30490.3</td>
<td>1.552 x 10^{-4}</td>
</tr>
<tr>
<td>1.6</td>
<td>0.045312</td>
<td>0.068902</td>
<td>35341.7</td>
<td>1.567 x 10^{-4}</td>
</tr>
<tr>
<td>2.1</td>
<td>0.008806</td>
<td>0.004355</td>
<td>13971.4</td>
<td>1.248 x 10^{-4}</td>
</tr>
<tr>
<td>2.2</td>
<td>0.008806</td>
<td>0.007143</td>
<td>19180.5</td>
<td>1.307 x 10^{-4}</td>
</tr>
<tr>
<td>2.3</td>
<td>0.008806</td>
<td>0.010525</td>
<td>25704.4</td>
<td>1.213 x 10^{-4}</td>
</tr>
<tr>
<td>2.4</td>
<td>0.008806</td>
<td>0.015823</td>
<td>31827.0</td>
<td>1.301 x 10^{-4}</td>
</tr>
<tr>
<td>2.5</td>
<td>0.008806</td>
<td>0.032357</td>
<td>42727.4</td>
<td>1.325 x 10^{-4}</td>
</tr>
</tbody>
</table>

b) Barker Analysis, using

$$\frac{G^E}{RT} = \sum_{i=1}^{n} x_i x_i G_i (x_i - x_j)^{i-1}$$

and experimental points 1.1, 1.2, 1.3, 2.1, 2.2

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>$G_4$</th>
<th>RMS/N.m$^{-2}$</th>
<th>STD/N.m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1423</td>
<td></td>
<td></td>
<td></td>
<td>505</td>
<td>564</td>
</tr>
<tr>
<td>-0.1036</td>
<td>0.2494</td>
<td></td>
<td></td>
<td>105</td>
<td>135</td>
</tr>
<tr>
<td>-0.1029</td>
<td>0.2477</td>
<td>0.0049</td>
<td></td>
<td>105</td>
<td>166</td>
</tr>
<tr>
<td>-0.1056</td>
<td>0.2124</td>
<td>0.1162</td>
<td>-0.1324</td>
<td>104</td>
<td>232</td>
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</tbody>
</table>
c) Calculated values for a two parameter fit

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$P / N\cdot m^{-2}$</th>
<th>$y_1$</th>
<th>$G^E / J\cdot mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8908</td>
<td>6140.3</td>
<td>0.1031</td>
<td>24.6</td>
</tr>
<tr>
<td>0.7926</td>
<td>10362.1</td>
<td>0.0595</td>
<td>19.3</td>
</tr>
<tr>
<td>0.6951</td>
<td>14390.0</td>
<td>0.0453</td>
<td>-3.7</td>
</tr>
<tr>
<td>0.7008</td>
<td>14151.5</td>
<td>0.0242</td>
<td>-2.0</td>
</tr>
<tr>
<td>0.5831</td>
<td>19171.6</td>
<td>0.0232</td>
<td>-41.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$G^E / J\cdot mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>23.9</td>
</tr>
<tr>
<td>0.8</td>
<td>20.4</td>
</tr>
<tr>
<td>0.7</td>
<td>-2.2</td>
</tr>
<tr>
<td>0.6</td>
<td>-35.7</td>
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<tr>
<td>0.5</td>
<td>-71.7</td>
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<tr>
<td>0.4</td>
<td>-102.0</td>
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<tr>
<td>0.3</td>
<td>-118.3</td>
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<tr>
<td>0.2</td>
<td>-112.2</td>
</tr>
<tr>
<td>0.1</td>
<td>-75.6</td>
</tr>
</tbody>
</table>
CHAPTER NINE

EXCESS VOLUME CHANGE
ON MIXING, $v^e$
69.1 DIRECT V^E MEASUREMENTS AND DILATOMETER DESIGN

Many workers in the past have determined the excess volume of mixing, V^E, by computation from precise density measurements over the whole composition range. This calculation together with the errors involved will be described in Appendix 1, whilst here the technique for measuring the volume change on mixing will be described.

It is only relatively recently that workers have measured V^E directly, using a dilatometer, to a high degree of accuracy (89, 90, 58).

The basic design requirements are fulfilled in the calorimeter vessels described in Chapter Three, and these vessels, equipped with a capillary tube of the type which will be described later, were used for some early measurements on the benzene + cyclohexane system. The principal objection to their continued use was that they were often too small to hold adequate volumes of liquid, especially when there were large differences in sample volume.

In order to increase the volume of liquid taken a new design was prepared as shown in Fig (9.2.1). The limbs were each capable of holding up to 5 x 10^-6 m^3 of liquid and the basic design can be retained even when more sample is required, simply by using a larger vessel. The neck carrying the B10 socket is placed in the lower part of the U-tube in order to facilitate loading. The design is a relatively straight forward development of the
The Dilatometer

Fig (9.2.1)
dilatometer described by Duncan, Sheridan and Swinton (58) but repositioning the filling orifice has made construction easier.

The capillary tube in which the volume change was recorded consists of a length of Veridia precision bore capillary tube (0.5 mm nominal diameter) bent through \( \Pi / 4 \) radians and joined to a B10 cone at its bottom end and having a glass cup fixed to the upper end with Araldite, as shown in Fig (9.2.1).

9.2 CALIBRATION OF THE CAPILLARY

Since it was necessary to determine the change in volume on mixing it was necessary to determine the cross sectional area of the capillary accurately. Two tubes were prepared, one of 0.5 mm nominal diameter and the other of 0.3 mm nominal diameter. The cross sectional area was determined by measuring the length of a mercury thread in the capillary using a travelling microscope followed by weighing of the thread. The room temperature at which the length of the thread was measured was recorded, and the procedure repeated. The results are shown in Table (9.2.1) and the diameters of the two capillaries were taken as 5.085 \( \times 10^{-4} \) m and 3.052 \( \times 10^{-4} \) m for the two tubes, respectively.
CALIBRATION OF CAPILLARY

1) NOMINAL DIAMETER $5 \times 10^{-4} \text{m}$

<table>
<thead>
<tr>
<th>Length of thread/m</th>
<th>Wt. of mercury used/kg</th>
<th>Density of mercury/kg.m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010771</td>
<td>0.010677</td>
<td>0.010592</td>
</tr>
<tr>
<td></td>
<td>0.0002932</td>
<td></td>
</tr>
<tr>
<td>Average length</td>
<td>0.010680 m</td>
<td>13540</td>
</tr>
<tr>
<td>Average diameter of tube</td>
<td>$5.080 \times 10^{-4} \text{m}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Length of thread/m</th>
<th>Wt. of mercury used/kg</th>
<th>Density of mercury/kg.m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010941</td>
<td>0.010930</td>
<td>0.010949</td>
</tr>
<tr>
<td></td>
<td>0.0003015</td>
<td></td>
</tr>
<tr>
<td>Average length</td>
<td>0.010940 m</td>
<td>13540</td>
</tr>
<tr>
<td>Average diameter of tube</td>
<td>$5.089 \times 10^{-4} \text{m}$</td>
<td></td>
</tr>
</tbody>
</table>

True diameter taken to be $5.085 \times 10^{-4} \text{m}$

2) NOMINAL DIAMETER $3 \times 10^{-4} \text{m}$

<table>
<thead>
<tr>
<th>Length of thread/m</th>
<th>Wt. of mercury used/kg</th>
<th>Density of mercury/kg.m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.009792</td>
<td>0.009739</td>
<td>0.009782</td>
</tr>
<tr>
<td></td>
<td>0.000959</td>
<td></td>
</tr>
<tr>
<td>Average length</td>
<td>0.009737 m</td>
<td>13535</td>
</tr>
<tr>
<td>Average diameter of tube</td>
<td>$3.042 \times 10^{-4} \text{m}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Length of thread/m</th>
<th>Wt. of mercury used/kg</th>
<th>Density of mercury/kg.m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.009830</td>
<td>0.009823</td>
<td>0.009839</td>
</tr>
<tr>
<td></td>
<td>0.000980</td>
<td></td>
</tr>
<tr>
<td>Average length</td>
<td>0.009831 m</td>
<td>13534</td>
</tr>
<tr>
<td>Average diameter of tube</td>
<td>$3.062 \times 10^{-4} \text{m}$</td>
<td></td>
</tr>
</tbody>
</table>

True diameter taken to be $3.050 \times 10^{-4} \text{m}$
9.3 THE EXPERIMENTAL TECHNIQUE FOR DETERMINING $V^E$

The dilatometer was cleaned, using concentrated nitric acid, hot freshly prepared chromic acid and then thoroughly washed with deionised water, followed by drying in an air oven at 110°C. The cleaned dilatometer was then evacuated using the apparatus described in Chapter Two for sealing ampoules, Fig (2.2.1), and filled completely with mercury. The liquids were then injected into the appropriate side of the U-tube from weighed hypodermic syringes fitted with bent needles and the precise weight of each component taken was calculated.

The joint of the capillary tube was then lightly greased and the capillary was then pushed hard into the ground glass joint. The mercury was forced up the capillary tube and it was possible to ensure that no air was trapped in the joint. The thermostat used for these measurements was in fact the tank described in Chapter Six for vapour pressure measurements. When the thermostat temperature was below room temperature it was first necessary to fill the reservoir above the capillary with mercury and also to remove all the air from the upper part of the capillary. The mercury level in the capillary tube was finally adjusted by removing the mercury from the upper reservoir. The dilatometer was then removed from the thermostat tank and the excess mercury in the capillary tube expelled by warming the dilatometer with a hot air blower. With practice it was simple to judge how much mercury to remove for any given system.
The dilatometer was replaced in the thermostat and when thermal equilibrium had been achieved the height of the mercury meniscus was measured, using a P.T.I. cathetometer with an accuracy of $\pm 0.01$ mm, relative to a fine scratch made on the capillary. When two successive measurements agreed to within $\pm 0.02$ mm the liquids were mixed by removing the assembly from the thermostat and rotating through $\pi/2$ radians twenty times, in such a way as to ensure that liquids did not contact the ground glass joint. The mixing process was carried out rapidly to ensure that the mercury thread remained within the capillary, care being taken that the ground glass joint was not disturbed.

The vessel was then returned to the thermostat and when thermal equilibrium had been achieved the height of the mercury thread was again measured until successive values agreed to within $\pm 0.02$ mm. The volume change on mixing, $\Delta V_{\text{mix}}$, could then be calculated, and if $\Delta l$ is the change in thread height on mixing clearly

$$
\Delta V_{\text{mix}} = \pi d^2 \Delta l / 4
$$

where $d$ is the diameter of the capillary. Then if $n_1$ moles of component 1 and $n_2$ moles of component 2 were taken

$$
V^E = \frac{\Delta V_{\text{mix}}}{n_1 + n_2}
$$

and

$$
\chi_1 = \frac{n_1}{n_1 + n_2}
$$
With practice it is a relatively easy procedure to determine $V^E$ with an uncertainty of less than $\pm 0.5\%$ and by using larger quantities of sample it should be possible using the same technique to reduce this error to $\pm 0.1\%$.

### 9.4 RESULTS

#### a) The System: Benzene + Cyclohexane at 298.15 K

The results obtained for this system are shown in Table (9.4.1). These measurements were made using a calorimeter vessel as a dilatometer and in view of the small quantity of material used and the purity of the materials they are in excellent agreement with Swinton's measurements (89). These results indicated that both the calibration of the capillary and the technique were satisfactory.

#### b) The System: Hexafluorobenzene + N,N-Dimethylaniline at 323.15 K

The excess volume of mixing was determined at 323.15 K and the experimental results are shown in Table (9.4.2). The results were fitted to an excess function polynomial in the same manner described in Chapter Five and the smooth curve is shown in Table (9.4.2) together with the parameters calculated. In Fig (9.4.2) this curve is presented along with Duncan and Swinton's measurements of $V^E$ for the system hexafluorobenzene + cumene (isopropylbenzene) and hexafluorobenzene + cyclohexane.
The excess volume of mixing, $V_E$, for

**Hexafluorobenzene with**

(i), (ii) and (iii)

---

(i) Cyclohexane at 313.15 K

(ii) Cumene at 313.15 K

(iii) N,N-Dimethylaniline at 323.15 K

---

Fig (9.4.2)
TABLE (9.4.1)

THE EXCESS VOLUME CHANGE ON MIXING, $V^E$, FOR THE SYSTEM:

BENZENE (1) + CYCLOHEXANE (2) AT 298.15 K

<table>
<thead>
<tr>
<th>$w_1$ /kg</th>
<th>$w_2$ /kg</th>
<th>$x_1$</th>
<th>$\Delta \bar{V}$/m</th>
<th>$V^E$/m³·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.067 x 10⁻⁴</td>
<td>5.998 x 10⁻⁴</td>
<td>0.521</td>
<td>4.730 x 10⁻²</td>
<td>6.45 x 10⁻⁷</td>
</tr>
<tr>
<td>6.060 x 10⁻⁴</td>
<td>3.910 x 10⁻⁴</td>
<td>0.625</td>
<td>3.616 x 10⁻²</td>
<td>5.92 x 10⁻⁷</td>
</tr>
<tr>
<td>4.361 x 10⁻⁴</td>
<td>6.852 x 10⁻⁴</td>
<td>0.407</td>
<td>4.302 x 10⁻²</td>
<td>6.37 x 10⁻⁷</td>
</tr>
<tr>
<td>4.751 x 10⁻⁴</td>
<td>4.989 x 10⁻⁴</td>
<td>0.506</td>
<td>3.777 x 10⁻²</td>
<td>6.39 x 10⁻⁷</td>
</tr>
<tr>
<td>3.910 x 10⁻⁴</td>
<td>6.144 x 10⁻⁴</td>
<td>0.407</td>
<td>3.745 x 10⁻²</td>
<td>6.21 x 10⁻⁷</td>
</tr>
<tr>
<td>2.832 x 10⁻⁴</td>
<td>6.960 x 10⁻⁴</td>
<td>0.305</td>
<td>3.268 x 10⁻²</td>
<td>5.58 x 10⁻⁷</td>
</tr>
<tr>
<td>7.836 x 10⁻⁴</td>
<td>3.571 x 10⁻⁴</td>
<td>0.703</td>
<td>3.702 x 10⁻²</td>
<td>5.27 x 10⁻⁷</td>
</tr>
<tr>
<td>7.701 x 10⁻⁴</td>
<td>2.116 x 10⁻⁴</td>
<td>0.797</td>
<td>2.527 x 10⁻²</td>
<td>4.15 x 10⁻⁷</td>
</tr>
<tr>
<td>1.764 x 10⁻⁴</td>
<td>7.447 x 10⁻⁴</td>
<td>0.203</td>
<td>2.324 x 10⁻²</td>
<td>4.25 x 10⁻⁷</td>
</tr>
</tbody>
</table>

R.M.S. Deviation about the curve of
I.A. McLure and F.L. Swinton (89)

= 4.5 x 10⁻⁹ m³·mol⁻¹
TABLE (9.4.2)
THE EXCESS VOLUME CHANGE ON MIXING, \( V^E \), FOR THE SYSTEM:
HEXAFLUOROBENZENE (1) + N,N-DIMETHYLANILINE (2) AT 323.15 K

a) EXPERIMENTAL DATA

<table>
<thead>
<tr>
<th>( w_1 )/kg</th>
<th>( w_2 )/kg</th>
<th>( x_1 )</th>
<th>( \Delta \bar{V} )/m ( ^3 )</th>
<th>( V^E )/m ( ^3 ).mol ( ^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.734 ( \times ) 10 ( ^{-4} )</td>
<td>17.189 ( \times ) 10 ( ^{-4} )</td>
<td>0.1240</td>
<td>-1.766 ( \times ) 10 ( ^{-2} )</td>
<td>-1.381 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>8.744 ( \times ) 10 ( ^{-4} )</td>
<td>12.332 ( \times ) 10 ( ^{-4} )</td>
<td>0.3159</td>
<td>-3.390 ( \times ) 10 ( ^{-2} )</td>
<td>-3.562 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>12.723 ( \times ) 10 ( ^{-4} )</td>
<td>12.640 ( \times ) 10 ( ^{-4} )</td>
<td>0.3928</td>
<td>-3.924 ( \times ) 10 ( ^{-2} )</td>
<td>-4.609 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>14.550 ( \times ) 10 ( ^{-4} )</td>
<td>9.917 ( \times ) 10 ( ^{-4} )</td>
<td>0.4886</td>
<td>-3.712 ( \times ) 10 ( ^{-2} )</td>
<td>-4.711 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>7.959 ( \times ) 10 ( ^{-4} )</td>
<td>4.841 ( \times ) 10 ( ^{-4} )</td>
<td>0.5171</td>
<td>-1.979 ( \times ) 10 ( ^{-2} )</td>
<td>-4.859 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>18.320 ( \times ) 10 ( ^{-4} )</td>
<td>8.360 ( \times ) 10 ( ^{-4} )</td>
<td>0.5880</td>
<td>-3.599 ( \times ) 10 ( ^{-2} )</td>
<td>-4.365 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>21.130 ( \times ) 10 ( ^{-4} )</td>
<td>5.920 ( \times ) 10 ( ^{-4} )</td>
<td>0.6992</td>
<td>-2.609 ( \times ) 10 ( ^{-2} )</td>
<td>-3.263 ( \times ) 10 ( ^{-7} )</td>
</tr>
<tr>
<td>28.920 ( \times ) 10 ( ^{-4} )</td>
<td>3.455 ( \times ) 10 ( ^{-4} )</td>
<td>0.8450</td>
<td>-1.101 ( \times ) 10 ( ^{-2} )</td>
<td>-1.216 ( \times ) 10 ( ^{-7} )</td>
</tr>
</tbody>
</table>

b) CURVE FITTING

1) Method 1, using \( 10^6 \times V^E / x_1 x_2 = \sum_{i=1}^{n} V_i (x_i - x_2)_{i-1} \)

\[
\begin{align*}
V_1 & = -1.923 \\
V_2 & = 0.200 \\
V_3 & = 0.988 \\
V_4 & = 1.103 \\
V_5 & = -1.014 \\
V_6 & = 0.017 \\
RMS & = 0.023 \\
STD & = 0.008 \\
\end{align*}
\]

\[
\begin{align*}
V_1 & = -1.959 \\
V_2 & = 0.619 \\
V_3 & = 1.103 \\
V_4 & = -1.145 \\
V_5 & = 1.683 \\
V_6 & = 0.003 \\
RMS & = 0.012 \\
STD & = 0.006 \\
\end{align*}
\]

\[
\begin{align*}
V_1 & = -1.891 \\
V_2 & = 0.633 \\
V_3 & = 0.166 \\
V_4 & = -3.060 \\
V_5 & = 0.001 \\
V_6 & = 0.003 \\
\end{align*}
\]
TABLE (9.4.2) (Continued)

ii) Method 2, using \( 10^6 \times V^E = \sum_{i=1}^{n} x_1 x_2 V_i (x_i - x_2)^{i-1} \)

<table>
<thead>
<tr>
<th>( V_1 )</th>
<th>( V_2 )</th>
<th>( V_3 )</th>
<th>( V_4 )</th>
<th>( V_5 )</th>
<th>( V_6 )</th>
<th>RMS</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
</tr>
<tr>
<td>-1.815</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.038</td>
<td>0.041</td>
</tr>
<tr>
<td>-1.814</td>
<td>0.286</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.033</td>
<td>0.039</td>
</tr>
<tr>
<td>-1.920</td>
<td>-0.311</td>
<td>0.965</td>
<td></td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.020</td>
</tr>
<tr>
<td>-1.929</td>
<td>-0.602</td>
<td>1.025</td>
<td>0.964</td>
<td></td>
<td></td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>-1.891</td>
<td>-0.622</td>
<td>0.177</td>
<td>1.110</td>
<td>1.657</td>
<td></td>
<td>0.003</td>
<td>0.006</td>
</tr>
<tr>
<td>-1.892</td>
<td>-0.452</td>
<td>0.203</td>
<td>-0.799</td>
<td>1.765</td>
<td>3.070</td>
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</table>

iii) Method 3, using \( 10^6 \times V^E = \sum_{i=1}^{n} x_1 x_2 V_i (x_i - x_2)^{i-1} / (1 - k(x_i - x_2)) \)

<table>
<thead>
<tr>
<th>( V_1 )</th>
<th>( V_4 )</th>
<th>( V_3 )</th>
<th>( V_4 )</th>
<th>( V_5 )</th>
<th>( k )</th>
<th>RMS</th>
<th>STD</th>
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<tr>
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<td>m^3mol^{-1}</td>
<td>m^3mol^{-1}</td>
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<td>m^3mol^{-1}</td>
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<td>2.452</td>
<td>0.082</td>
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</tbody>
</table>
iv) Method 4, using \( 10^6 \times V^E = \sum_{i=1}^{n} V_i \phi_i \)

where the \( \phi_i \) are suitably chosen orthogonal polynomials

<table>
<thead>
<tr>
<th>( V_1 )</th>
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<th>( V_3 )</th>
<th>( V_4 )</th>
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<th>( V_6 )</th>
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</table>
CHAPTER TEN

PRELIMINARY INVESTIGATIONS

USING OTHER TECHNIQUES
610.1 THE APPARATUS

The apparatus used to measure the freezing point of mixtures was of conventional design and is shown in Fig (10.1.1). The sample was stirred by a nichrome wire spiral with reciprocating action which was operated externally by a suitable magnetic drive. The temperature of the sample was measured with a single junction thermopile, one junction of which was placed in a dewar containing melting ice, and its E.M.F. was measured using a Solartron digital voltmeter equipped with a suitable timer and punching out facilities. The use of digital equipment here is extremely useful since it is desirable to record the temperature of the sample accurately every minute or even every thirty seconds over a long period of time (up to 1½ hours). The coolant varied depending upon the freezing temperature, but since the vacuum obtainable was not entirely satisfactory it was impossible to use a very low temperature, and consequently the cooling curves obtained show a marked curvature.

The temperature at which the arrest points in the cooling curve occurred were determined from a large scale graph of temperature against time. Super-cooling of the liquid proved to be small and the effect was easily corrected for by extrapolation.
The Apparatus used to Determine the Solid-Liquid Phase Diagram

Fig (10.1.1)
10.2 OPERATION OF THE APPARATUS

The freezing cell was thoroughly cleaned using chromic acid, then washed with deionised water followed by washing with "Analar" acetone. The cell was then dried and the stirring wire was also washed with "Analar" acetone and dried. The components were then injected, from weighed hypodermic syringes fitted with long needles, into the freezing cell through the stirring wire hole, and the composition of the mixture calculated. The temperature of the liquids was adjusted to a suitable value in the single liquid phase region, the voltmeter switched on and a suitable cooling bath placed around the vessel.

When the temperature was falling steadily readings of the thermocouple E.M.F. and the time were taken at thirty second intervals until both the freezing point and the eutectic point had been reached or until the material was so solid that stirring was impossible. A graph of thermocouple E.M.F. against time was drawn and the arrest points determined by extrapolating the cooling curves to correct for super-cooling. From the E.M.F. at an arrest point it was a simple matter to calculate the corresponding temperature from the calibration of the thermocouple wire. A typical cooling curve for a pure component is shown in Fig (10.2.1a), and in Fig (10.2.1b) a typical cooling curve for a mixture close to the eutectic composition is shown. A number of such determinations over the composition range were carried out for the system hexafluorobenzene + N,N-dimethylaniline and in Fig (10.2.2) the resulting solid - liquid phase diagram for this
Cooling Curve for Pure N,N-Dimethylaniline

Freezing Point = 275.80 K

Fig (10.2.1a)

Cooling Curve for a Mixture of Hexafluorobenzene and N,N-Dimethylaniline with $x_{HF} = 0.0581$

Freezing Point = 273.95 K

Fig (10.2.1b)
The Solid-Liquid Phase Diagram for Hexafluorobenzene and N,N-Dimethylaniline

Fig (10.2.2)
system is shown.

The apparatus was not sufficiently refined to produce very accurate results, the principal sources of error were due to evaporation of the sample through the stirrer orifice and also due to this possibility of water entering the system when the freezing point lay below room temperature. The other major source of error lay in the extrapolation of the cooling curves. The vacuum system available was inadequate for the purpose of evacuating the non-silvered dewar of the apparatus, in fact the rate of cooling was not appreciably affected by its use. However as the measurements were in fact a preliminary investigation prior to a more extensive study in this laboratory they were considered to be satisfactory.

§10.3 THE USE OF FREEZING POINT MEASUREMENTS IN DETERMINING THE EXCESS GIBBS FUNCTION G^E

Although the phase diagram which was given in Section (10.2) has not been used for this purpose it is of interest to note that it is possible to calculate the excess Gibbs function for mixing, G^E, by accurately determining the freezing point of mixtures of known composition (91).

Let us consider a system which shows a single eutectic point in the solid - liquid phase diagram. Provided that the
latent heat of fusion of both the pure components are known as functions of temperature then the rational activity coefficients for the component which separates as the pure solid can be calculated. However this determines the activity coefficients at the corresponding freezing point temperatures and it is therefore necessary to correct them to some standard temperature \( T^\dagger \) and this may be done using experimentally independent excess enthalpy of mixing data. In Chapter Seven we described the calculation of the excess Gibbs function for mixing, \( G^E \), from rational activity coefficient data for either component of the mixture, and this procedure can be applied here to yield values of \( G^E \) from freezing point measurements.

The detailed analysis does not appear to have been set down in completely general terms, and as this forms part of a future project, the mathematical analysis is given below.

On freezing we will assume that one pure component separates from the liquid to the solid phase then

\[
\mu_1^{(liq)} = \mu_1^{(solid)}
\]

and from the definition of the chemical potential of a liquid

\[
\mu_1^{(solid)} = \mu_1^{(liq)} + RT \ln \alpha_1 
\]

writing the Gibbs-Helmholtz equation in the form

\[
\frac{\Delta H}{T^2} = -\frac{1}{T} \left[ \frac{\Delta G}{T} \right]_p
\]

and using this in equation (10.3.2) we find
where \( \Delta H_i \) is the molar latent heat of fusion for component \( i \) at the temperature considered. It has common in the past to assume that \( \Delta H_i \) was constant and obtain an integrated equation

\[
\int_0^T \frac{d \ln \chi, f_i}{d \ln x, f_i} = \frac{\Delta H_i}{R} \int_0^T \frac{dT}{T^2}
\]

i.e.

\[
\ln \chi, f_i = \frac{\Delta H_i}{R} \left[ \frac{1}{T_i} - \frac{1}{T} \right]
\]

However it is unlikely that the latent heat of fusion can be assumed constant and we may therefore consider writing \( \Delta H_i \) as a function of temperature of the form

\[
\Delta H_i = \sum_{j=0}^{m} H_{i,j} (T_i - T)^j
\]

where \( H_{i,j} \) are constants depending only on the material at any fixed pressure.

Integration of equation (10.3.3) can now be performed using a binomial expansion for \( (T_i - T)^j \).
I.e.

\[ (T_1^0 - T)^j = \sum_{k=0}^{j} \binom{j}{k} (-1)^k T_1^0 j^{-k} T^{-k} \quad (10.3.7) \]

where \( \binom{j}{k} \) is the appropriate binomial coefficient.

Therefore

\[
R \ln x_i f_i = \sum_{j=0}^{m} H_{i,j} \left[ \sum_{k=1}^{j} \binom{j}{k} (-1)^k T_1^0 j^{-k} \left[ T^{-k} - T_1^0 k^{-1} \right] - j T_1^0 j^{-1} \ln \frac{T_1^0}{T_1} \right] \quad (10.3.8)
\]

which is obtained by integration of

\[
R \ln x_i f_i = \sum_{j=0}^{m} H_{i,j} \left[ \sum_{k=0}^{j} \binom{j}{k} (-1)^k T_1^0 j^{-k} T^{-k-1} - j T_1^0 j^{-1} T^{-1} \right] dT \quad (10.3.9)
\]

But as was described in Section (7.2) we can express \( \ln f_i \) as a series in \( x_i \) and \( x_2 \) together with the coefficients \( G_{i,j} \) in an expression for \( G^E \) of the type

\[
G^E \quad \frac{\sum_{i=0}^{n} x_i x_2 G_{i,j}(x_i - x_2)^i}{(1 - k(x_i - x_2))} \quad (10.3.10)
\]

Then we have to remember that since \( G^E \) is itself a function of temperature the coefficients \( G_{i,j} \) are functions of temperature and should be themselves represented by a series of the form...
On combining equations (8), (10) and (11) we can describe the section of the freezing point vs. composition curve where pure separates by the equation

\[
\begin{align*}
R \frac{x_z^2}{(1-k(x_z-x_j))^2} & \sum_{j=0}^{n} \sum_{j=0}^{l} F_{i,j} (T^j - T)^j \left[ (a_i+1)x_i - x_j + k(a_i-x_i)(1-2a_i x_j) \right] \\
+ \sum_{j=0}^{m} H_{i,j} \left\{ \sum_{j=0}^{(j^*)} \left( -1 \right)^j T_{i}^{o j-k} \left[ T_{i}^{o k-1} - T^{k-1} \right] + j T_{i}^{o j-1} \right\} \\
= - R \ \mathcal{L}_n \ x_i
\end{align*}
\]

which is an equation involving \( T \) as a function of composition only and the \( (n+2)(1+1) + (m+1) \) parameters involved can all in principle be determined by a conventional least squares treatment.

A similar equation can be written for the section of the phase diagram where pure component \( \oplus \) separates as a solid and this takes the form

\[
\begin{align*}
R \frac{x_z^2}{(1-k(x_z-x_j))^2} & \sum_{j=0}^{n} \sum_{j=0}^{l} F_{i,j} (T^j - T)^j \left[ x_i - (2a_i+1)x_j + k(a_i-x_i)(2a_i x_j - 1) \right] \\
+ \sum_{j=0}^{m} H_{i,j} \left\{ \sum_{j=0}^{(j^*)} \left( -1 \right)^j T_{2}^{o j-k} \left[ T_{2}^{o k-1} - T^{k-1} \right] + j T_{2}^{o j-1} \right\} \\
= - R \ \mathcal{L}_n \ x_j
\end{align*}
\]
By using both equations (12) and (13) together with an adequate number of measurements over the composition range where pure components separate it is possible to calculate the excess Gibbs function, $G^E$, over the same composition range at the standard temperature $T^\dagger$.

However the number of parameters which can be obtained from curve fitting procedures is usually small and therefore it was decided to reduce the number of parameters in equations (12) and (13) by using experimentally independent heat of mixing data. Also having defined the coefficients in the latent heat of fusion series by equation (6) it follows that the latent heats of fusion of the pure components may be expressed by

$$\Delta H_i(T_i^\circ) = H_{i,0}$$  \hspace{1cm} (10.3.14)

and similarly

$$\Delta H_j(T_j^\circ) = H_{j,0}$$  \hspace{1cm} (10.3.15)

and we can usually determine $H_{i,0}$ and $H_{j,0}$ easily, or they may be available in the literature.

Consider the excess enthalpy of mixing, $H^E$, which can be represented by an equation of the type suggested in Chapter Five. As the coefficients are functions of temperature we can write

$$H^E(T) = \sum_{i=0}^{n} \frac{x_i x_j (x_i - x_j)}{(1 - k(x_i - x_j))} \sum_{j=0}^{m} A_{i,j} (T^\dagger - T)^j$$  \hspace{1cm} (10.3.16)
where $T^+$ is some standard temperature. Now if $k$ is used in the manner which Myers and Scott (74) originally suggested then we can represent $\frac{G^E(T)}{RT}$ by a similar series such as

$$\frac{G^E(T)}{RT} = \sum_{i=0}^{n} \frac{x_i x_j G_i(T) (x_i - x_j)^i}{(1 - k (x_i - x_j))}$$ (10.3.17)

From the Gibbs-Helmholtz equation then

$$R \int_{T^+}^{T} \frac{dG^E}{RT} = \int_{T}^{T^+} \frac{H^E(T)}{T^2} dT$$ (10.3.18)

$$R \frac{G^E(T)}{RT} - R \frac{G^E(T^+)}{RT^+} = \sum_{i=0}^{n} \frac{x_i x_j (x_i - x_j)^i}{(1 - k (x_i - x_j))} \sum_{j=0}^{m} A_{i,j} \left\{ \sum_{k=0}^{j} \frac{(i)(-1)^k T^{+j-k}}{(k-1)} \left[ T^{+k-1} - T^{-k-1} \right] + j T^{+j-1} \ln \frac{T}{T^+} \right\}$$ (10.3.19)

Then

$$\frac{G^E(T)}{RT} = \sum_{i=0}^{n} \frac{x_i x_j G_i(T) (x_i - x_j)^i}{(1 - k (x_i - x_j))} = \sum_{i=0}^{n} \frac{x_i x_j (x_i - x_j)^i}{(1 - k (x_i - x_j))} \left[ G_i(T^+) +$$

$$\sum_{j=0}^{m} \frac{A_{i,j}}{R} \left\{ \sum_{k=0}^{j} \frac{(i)(-1)^k T^{+j-k}}{(k-1)} \left[ T^{+k-1} - T^{-k-1} \right] + j T^{+j-1} \ln \frac{T}{T^+} \right\} \right]$$ (10.3.20)
and comparing coefficients of \((x_1 - x_2)^i\)

\[
G_i(T) = G_i(T^+) + \sum_{j=0}^{m} \frac{A_{i,j}}{R} \left\{ \sum_{k=0}^{j} \frac{(j)!(-1)^k}{(k-1)!} T^{j-k} \right\} \left[ T^{k-1} - T^{-k-1} \right] + j T^{j-1} \ln \frac{T}{T^+} \right\} .
\]

(10.3.21)

Then we have, by using equation (21) in place of equation (11) and using a similar argument to that earlier,

\[
\sum_{i=0}^{n} x_2^i G_{i}(T^+) \left[ (2i+1)x_1 - x_2 + k(x_1 - x_2)(2i+1) \right] \frac{J_{m}}{R} \left\{ \frac{1}{T} \right\} + \sum_{j=1}^{m} \frac{H_{i,j}}{R} \left\{ j T^{j-1} \right\}
\]

\[
\ln \frac{T}{T^+} + \sum_{k=0}^{j} \frac{(j)!(-1)^k}{(k-1)!} T^{j-k} \left[ T^{k-1} - T^{-k-1} \right] \right\} = - \ln x_1 + \frac{H_{1,0}}{R} \left\{ \frac{1}{T} \right\}
\]

\[
\sum_{i=0}^{n} x_2^i \left[ (2i+1)x_1 - x_2 + k(x_1 - x_2)(2i+1) \right] \frac{J_{m}}{R} \left\{ \frac{1}{T} \right\} + \sum_{j=0}^{m} \frac{A_{i,j}}{R} \left\{ j T^{j-1} \right\}
\]

(10.3.21)

and also when pure component 2 freezes we can write

\[
\sum_{i=0}^{n} x_1^i G_{i}(T^+) \left[ x_1 - (2i+1)x_2 + k(x_1 - x_2)(2i+1) \right] \frac{J_{m}}{R} \left\{ \frac{1}{T} \right\} + \sum_{j=1}^{m} \frac{H_{2,j}}{R} \left\{ j T^{j-1} \right\}
\]

\[
\ln \frac{T}{T^+} + \sum_{k=0}^{j} \frac{(j)!(-1)^k}{(k-1)!} T^{j-k} \left[ T^{k-1} - T^{-k-1} \right] \right\} = - \ln x_2 + \frac{H_{2,0}}{R} \left\{ \frac{1}{T} \right\}
\]
Therefore we can describe with the aid of equations (21) and (22) the freezing point curve over the entire composition range for which pure components separate and with a number of freezing point determinations at different compositions it is possible to determine the \((n + 1) + 2m\) parameters in the above equations.

These procedures have not yet been tested but outline the work which has been done so far towards using freezing point measurements to determine \(G^E\). The principles of the calculation are well known but the extension to systems which form complexes in the solid phase has not been done yet, although this may provide a method of determining the equilibrium constant of formation of complexes in the liquid phase.
10.4 AIM OF THE WORK

This technique has been used to study various types of complexing and may be carried out in dilute solution (Beaumont and Davis (35) and Beaumont (92)) when studying the formation of the charge transfer complexes between hexafluorobenzene and amines, or in concentrated solution (Scott et al. (93)) when studying the hydrogen bonding between acetone and 1 hydro perfluoro-n-heptane and also when studying the hydrogen bonding between acetone and chloroform (94).

The measurements of Beaumont and Davis are however not strictly compatible with the thermodynamic methods which have been studied in this work. As their N.M.R. and their U.V. spectroscopic work were performed on dilute solutions in n-hexane, the solvent environment of the materials is different to that existing in mixtures when either the fluorocarbon or the amine is in excess.

It was therefore decided to study the complexing in neat solutions of hexafluorobenzene and N,N-dimethylaniline using both fluorine and proton N.M.R. techniques. In practice, however, the work was abandoned due to shortage of time before the proton work had been completed, as the equilibrium constants derived from the spectra were subject to large uncertainty.
Consider an equilibrium of the type

\[ A + D \rightleftharpoons AD \]

with an associated equilibrium constant

\[ K = \frac{x(a + b - x)}{(a - x)(b - x)} \]  \hspace{1cm} (10.5.1)

where \( a \) and \( b \) are the amounts of \( A \) and \( D \) respectively and \( x \) is the amount of complex formed at equilibrium. If an absorption due to the complexed component \( A \) is assumed to occur at frequency \( \nu_{\text{comp}} \) and pure \( A \) shows an observed absorption at \( \nu_a \) then we can postulate that the observed absorption by the solution due to component \( A \) occurs at

\[ \nu_{\text{obs}} = \frac{a - x}{a} \nu_a + \frac{x}{a} \nu_{\text{comp}} \]  \hspace{1cm} (10.5.2)

As \( a \approx 0 \) then \( x \approx 0 \) and \( b \gg a > x \) so

\[ K = \frac{x}{a - x} \]  \hspace{1cm} (10.5.3)

and therefore

\[ \frac{x}{a} = \frac{K}{K + 1} \]  \hspace{1cm} (10.5.4)
and
\[ \frac{a - x}{a} = \frac{1}{K + 1} \]  

(10.5.5).

Then

\[ v_{(a=0)} = \frac{v_0}{K + 1} + \frac{K}{K + 1} v_{smp} \]  

(10.5.6)

From equation (6) together with (2) we can write

\[ v_{obs} = \frac{a - x}{a} v_a + \frac{a}{a} \left[ v_{(a=0)} + \frac{1}{K} (v_{a=0} - v_a) \right] \]  

(10.5.7)

and therefore

\[ x = a \left[ \frac{v_{obs} - v_a}{v_{(a=0)} - v_a} \right] \left[ \frac{K}{K + 1} \right] \]  

(10.5.8).

Writing

\[ W = (v_{obs} - v_a) (v_{(a=0)} - v_a) \]

and

\[ L = \frac{K}{K + 1} \]

then

\[ \frac{L}{1 - L} = \frac{a}{a [1 - WL]} \frac{b - a WL}{[b - a WL]} \]  

(10.5.9)
and writing \[ x_1 = \frac{a}{(a + b)} \]

it is readily shown that

\[ x_1 = \frac{W - 1}{W^2L - 1} \quad (10.5.10) \]

Then it is possible to calculate a suitable value of \( L \) (and hence \( K \)) which makes the experimental data fit equation (10) best.

\section{10.6 EXPERIMENTAL PROCEDURE}

It was decided to use an external reference method, where the standard was to be the pure component, the shift of which was to be observed. Pyrex N.M.R. tubes were prepared by sealing off in the centre and attaching to the open end a length of suitable diameter pyrex tubing. The external reference tubes were fine capillary of a suitable quality and were sealed off at one end. Teflon supports were made which held the reference tube centrally in the N.M.R. tube as shown in Fig (10.6.1).

The reference tubes were prepared by injecting a small quantity of the pure material which was to be used as the reference, from a hypodermic syringe, after which the upper end was sealed.
THE N.M.R. TUBES

Fig (10.6.1)
off with the material frozen in the bottom of the tube. The reference tube was then inserted into the N.M.R. tube and the solution was prepared by injecting the components from weighed hypodermic syringes. The tube was then sealed off after the contents had been frozen in a solid carbon dioxide /acetone cold trap.

The N.M.R. spectra were recorded using a Varian D.A. 60 N.M.R. spectrometer and the spectra calibrated using "side-bands" of known frequency. The temperature of the cell was measured using a single junction thermopile and a suitable potentiometer (Type 4363 E -Auto, Messrs. H. Tinsley and Co. Ltd., London, S.E.25.) and was thermostated using the equipment supplied with the spectrometer. The temperature control was erratic and certainly no better than ± 1 K.

The results obtained are shown graphically in Fig (10.6.2). The large scatter makes the results useless but the best fit value of \( K \) calculated is also shown in Fig (10.6.2).

The causes of this large error may be numerous and steps will be taken to improve the technique. The thermostating of the cell is beyond our control but the external reference can be removed and errors due to diamagnetic susceptibility corrections can be eliminated. The composition errors can be reduced by a more suitable filling technique for volatile and unstable materials.
\[ W = \frac{\nu_{ah} - \nu_0}{\nu_{(a+0)} - \nu_0} \]

**N.M.R. Results for Hexafluorobenzene and N.N-Dimethylamine at**

323 K

**From Dashed Line:**

\[ K = 0.38 \]
CHAPTER ELEVEN

DISCUSSION OF RESULTS
If the discussion of the experimental work described in this thesis is to be based on a model of complex formation it is desirable to consider what the thermodynamic behaviour of such a system should be. If we have an equilibrium of the type

\[ A + D \rightleftharpoons AD \]  

(11.1.1)

\[ a-x \quad b-x \quad x \]

then we can define an equilibrium constant, \( K \), in terms of mole fraction by

\[ K = \frac{x(a+b-x)}{(a-x)(b-x)} \]  

(11.1.2)

where \( a \) and \( b \) represent the initial amounts of \( A \) and \( D \) respectively and \( x \) is the amount of complex in the equilibrium mixture.

Scott (61) has suggested that the Excess Enthalpy of Mixing, \( H^\text{E} \), is composed of at least two contributions; the physical contribution, \( H_p^\text{E} \), which arises due to mixing the fluorocarbon and other material without any complexing stabilisation, and the chemical contribution, \( H_c^\text{E} \), which is that due to complexing. If this procedure is followed then

\[ H^\text{E}_{\text{obs}} = H_p^\text{E} + \frac{x}{(a+b)} \cdot \Delta H_f \]  

(11.1.3)
where $\Delta H_f$ is the enthalpy of formation of one mole of complex.

Further the excess heat capacity,

$$C_p^E = \left( \frac{\partial H^E}{\partial T} \right)_{P_{n_1}, n_2}$$

can be expressed by the equation

$$\frac{\partial H^E}{\partial T} = C_p^E = \frac{\partial H_p^E}{\partial T} + \frac{\Delta H_p}{(a + b)} \frac{dx}{dT}$$

(11.1.4)

if we assume that $\Delta H_f$ is constant over the range of temperature considered. From equation (2) we can write

$$\frac{1}{\partial T} \ln K = \frac{a b (a + b - 2x)}{x (a - x)(b - x)(a + b - x)} \frac{dx}{dT}$$

(11.1.5)

which, on using

$$\frac{1}{\partial T} \ln k = \frac{\Delta H_f}{RT^2}$$

indicates that

$$C_p^E = \frac{\partial H_p^E}{\partial T} + \frac{x (a - x)(b - x)(a + b - x)}{a b (a + b)(a + b - 2x)} \frac{\Delta H_f^2}{RT}$$

(11.1.6)
If charge transfer forces are to have any effect in stabilising the complex then there must be overlap of the donor and acceptor molecular orbitals. This has been investigated for the benzene - hexafluorobenzene type complex and it has been found that the orbital overlap is zero when electrostatic forces are a maximum. The highest energy filled orbitals of benzene (the $\Pi$-bonding levels) and the lowest energy unfilled hexafluorobenzene orbitals (the $\Pi^*$-antibonding ($\Pi^*$) levels) are shown in Fig (11.2.1) and it can be seen that when the $D_{6h}$ symmetry axes are superimposed no favourable overlap of the orbitals is possible. This is expected as no charge transfer bands have been observed with these complexes and the specific interaction has been interpreted in terms of electrostatic interactions such as hydrogen bonding between matching $\text{H}$ and $\text{F}$ atoms (61), dipole - quadrupole interactions of the two molecules (61) and at present in terms of dispersion forces between the molecules (95).

In order to explain the observed charge transfer bands of amine - hexafluorobenzene complexes it is necessary although not sufficient for orbital overlap to occur. The planar skeleton of N,N-dimethylaniline is shown in Fig (11.2.2a,1) and we can apply a standard Hückel molecular orbital calculation to it. Consider the true wave function $\psi$ and the approximate wave function $\Phi$, the latter being a linear combination of a set of known wave functions $\phi_i$. 

611.2 ORBITAL OVERLAP
The Hückel Molecular Orbitals

For Benzene and Hexafluorobenzene

\[ \text{spatial plane}\]

**σ-Bonding**

\[ \text{σ-Bonding}\]

**π* - Antibonding**

\[ \text{π* - Antibonding}\]

Fig (II-2.1)
Fig (11.2.2)

A Diagrammatic Representation of Complex Configuration
\[ E = \int \Phi^* H \Phi \, d\tau / \int \Phi^* \Phi \, d\tau \quad (11.2.2) \]

The best possible \( \Phi \) for any set \( \Phi_j \) may be determined by minimising the energy, and this is when

\[ \frac{\partial E}{\partial c_m} = 0 \quad (11.2.3) \]

for all \( m = 1, 2, \ldots, N \).

Rewriting equation (2) with the aid of equation (1) we find

\[ E = \frac{\sum_{n=1}^{N} \sum_{m=1}^{N} c_n c_m \int \phi_n^* H \phi_m \, d\tau}{\sum_{n=1}^{N} \sum_{m=1}^{N} c_n c_m \int \phi_n^* \phi_m \, d\tau} \quad (11.2.4) \]

and therefore

\[ \frac{\partial E}{\partial c_m} = \frac{\lambda \sum_{n=1}^{N} c_n \int \phi_n^* (H - E) \phi_m \, d\tau}{\sum_{n=1}^{N} \sum_{m=1}^{N} c_n c_m \int \phi_n^* \phi_m \, d\tau} = 0 \quad (11.2.5) \]
and therefore

\[ \sum_{n=1}^{N} c_n \int \phi_n^* (H - E) \phi_m \, d\tau = 0 \quad (11.2.6) \]

for all \( m = 1, \ldots, N \).

If we write

\[ H_{n,m} = \int \phi_n^* H \phi_m \, d\tau \]

and

\[ S_{n,m} = \int \phi_n^* \phi_m \, d\tau \]

then we obtain for all \( n = 1, \ldots, N \)

\[ \sum_{m=1}^{N} c_m (H_{n,m} - ES_{n,m}) = 0 \quad (11.2.7) \]

which represents a set of \( N \) simultaneous linear equations in the \( N \) unknowns \( c_1, c_2, \ldots, c_N \). This set of equations will have a unique solution if and only if the determinant of the coefficients is zero, i.e.

\[
\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\
H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn}
\end{vmatrix} = 0 \quad (11.2.8)
\]
Since the $H_{n,m}$ and $S_{n,m}$ are known then equation (8) is a polynomial of degree $N$ and yields in general $N$ values of $E$, each value having a corresponding set of coefficients $c_1, c_2, \ldots, c_n$. This is a standard method of general validity which we can now apply to the $\Pi$ electrons of our molecule. It was assumed that only overlap between adjacent atoms was significant and the calculations were performed with a suitable computer program made available by Dr. D. McWilliams, whose assistance in this respect is acknowledged.

The highest energy filled orbital of $N,N$-dimethylaniline is shown in Fig (11.2.2,II) along with the lowest energy unfilled orbitals of hexafluorobenzene (III, IV). The most favourable position of the rings is indicated in (V) and significant orbital overlap is possible in this case. The rings are offset to a considerable degree but this is to be expected with the large $NM_2$ group of the $N,N$-dimethylaniline. This configuration reduces the effect of possible electrostatic forces but it would not eliminate them entirely. Thus although charge transfer may and undoubtably does occur (35) it is not necessarily the major stabilising force.

11.3 THE EXCESS ENTHALPY DATA

It is important to consider firstly the magnitude of the endothermic contribution, $H_E^P$. In Chapter One the behaviour of fluorocarbon solutions was briefly discussed and it was pointed out that many fluorocarbon solutions exhibit large positive values for the excess enthalpy, $H_E$, and Gibbs Function, $G_E$. In order to
estimate the likely value of this endothermic contribution to the enthalpy of mixing, $H^E$, a number of systems were considered which were in many ways non-interacting analogues of the hexafluorobenzene + N,N-dimethylaniline system. The analogue of N,N-dimethylaniline chosen was isopropylcyclohexane and this molecule and isopropylbenzene may be compared with the amine in Fig (11.3.1a). The enthalpy of mixing of these systems was determined and the results were presented in Chapter Five. The alternative approach was to consider a fluorocarbon which would not give a specific interaction when mixed with the amines. One possibility was perfluorocyclohexane but as this material has such a short liquid range (m.p. 51°C and b.p. 52°C) it was rejected and perfluoromethylcyclohexane was considered. The physical properties of this compound are acceptable but the initial test tube experiment revealed that two phases were formed at room temperature which persisted above 70°C. This system was therefore typical of the behaviour of non-aromatic fluorocarbons and indicated the reality of the endothermic contribution. The excess enthalpy of mixing for the system hexafluorobenzene + isopropylcyclohexane ($\sim +1300 \text{ J.mol}^{-1} \alpha = \alpha_1 = 0.5$ at $323.15 \text{ K}$) is therefore our only experimental guide to the "endothermic contribution" but the behaviour of the system perfluoromethylcyclohexane + N,N-dimethylaniline may indicate that the amine group considerably effects the non-specific term and that $H^E$ may even be considerably higher.

Other workers have used the value of $H^E$ for the system hexafluorobenzene + cyclohexane ($1517 \text{ J.mol}^{-1} \alpha = \alpha_2 = 0.5$ at $313.15 \text{ K}$) as an indication of the endothermic contribution, however the Excess Enthalpy of Mixing for the cyclohexanes with hexafluoro-
Fig (11.3.1)

(a) \( \text{N}-\text{Dimethylaniline} \)

(b) \( \text{Iso-Propylbenzene (o-xylene)} \)

(c) \( \text{Iso-Propylcyclohexane} \)

The molecular skeletons of:

[Chemical structures are shown with aromatic rings and side chains labeled with methyl (Me) and hydrogen (H) groups.]
benzene does not show a particularly large variation with increasing the number of substituent methyl groupings (57).

If we consider the value of +1300 J.mol⁻¹ as a reasonable indication of the endothermic contribution then from Fig (11.3.2) it can be seen that in every case the observed heat of mixing, \( H^E \), is considerably lower than the endothermic contribution, which is consistent with equation (11.3.1) if \( \Delta H^p \) is fairly large and negative. Also it can be seen from Table (11.3.3) that for each system the excess heat capacity is positive with the exception of the system hexafluorobenzene + pyridine for which \( C^E_p = 0 \). The second term of the right hand side of equation (11.1.6) is always positive whereas the first term is usually negative, for example the system hexafluorobenzene + cyclohexane has \( C^E_p = -2.5 \) J.mol⁻¹.deg⁻¹. The values of \( C^E_p \) are therefore consistent with the simple model even in the case of hexafluorobenzene + pyridine.

Beaumont and Davis (35, 92) have calculated values of the equilibrium constant, \( K \), and the enthalpy of formation \( \Delta H^f \) from their spectroscopic measurements for the systems: hexafluorobenzene + \( \text{N,N-dimethylaniline} \) and hexafluorobenzene + \( \text{N,N-dimethyl-p-toluidine} \). Using these values together with the experimentally determined excess enthalpy of mixing it is possible to calculate the magnitude of the endothermic contribution \( H^E_p \) by using equations (11.1.2) and (11.1.3).

In practice however they did not determine \( K \) at a series of temperatures and obtained the \( \Delta H^f \) from a plot of \( \log K \) against \( T^{-1} \).
The excess enthalpy of mixing, $H^e$

at 323.15 K for hexafluorobenzene

with

iso propyl cyclohexane

triethylamine

pyridine

cumene

2,6 lutidine

N,N-dimethyl-o-toluidine

2,4,6 collidine

N,N-dimethyl aniline

N,N-dimethyl-p-toluidine

N,N-dimethyl-m-toluidine

Fig (11.3.2)
TABLE (11.3.3)  
THE EXCESS HEAT CAPACITIES, $C_p^E$, AT 323.15 K FOR EQUIMOLAR MIXTURES

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>$C_p^E$/J·mol·deg°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexafluorobenzene + N,N-dimethyl-m-toluidine</td>
<td>+11.0</td>
</tr>
<tr>
<td>Hexafluorobenzene + N,N-dimethyl-p-toluidine</td>
<td>+5.0</td>
</tr>
<tr>
<td>Hexafluorobenzene + N,N-dimethylaniline</td>
<td>+4.0</td>
</tr>
<tr>
<td>Hexafluorobenzene + 2,4,6-trimethylpyridine</td>
<td>+4.3</td>
</tr>
<tr>
<td>Hexafluorobenzene + N,N-dimethyl-o-toluidine</td>
<td>+5.6</td>
</tr>
<tr>
<td>Hexafluorobenzene + 2,6-dimethylpyridine</td>
<td>+4.9</td>
</tr>
<tr>
<td>Hexafluorobenzene + pyridine</td>
<td>0</td>
</tr>
<tr>
<td>Hexafluorobenzene + triethylamine</td>
<td>+1.2</td>
</tr>
</tbody>
</table>
but used the Benesi-Hildebrand equation and measurements at only one composition. In Chapter One we wrote

\[
\frac{1}{\text{OD}} = \frac{1}{Kb\varepsilon} \cdot \frac{1}{a} + \frac{1}{b\varepsilon} \tag{11.3.1}
\]

and therefore

\[
-\log K = \log a + \log \left[ \frac{b\varepsilon}{\text{OD}} - 1 \right] \tag{11.3.2}
\]

but

\[
\frac{\partial \ln K}{\partial T} = \frac{\Delta H_f}{RT^2} \tag{11.3.3}
\]

which on integration gives

\[
\ln K = -\frac{\Delta H_f}{RT} + \text{const} \tag{11.3.4}
\]

and on combining equations (2) and (4) we find that if the acceptor concentration \(a\) is constant then

\[
\ln \left[ \frac{b\varepsilon}{\text{OD}} - 1 \right] = \frac{\Delta H_f}{R} \cdot \frac{1}{T} + \text{const} \tag{11.3.5}
\]

and therefore a plot of \(\ln \left[ \frac{b\varepsilon}{\text{OD}} - 1 \right]\) against \(\frac{1}{T}\) should be a straight line of slope \(\frac{\Delta H_f}{R}\). The method is clearly very
bad and open to numerous sources of error. The plots obtained are shown in Fig (11.3.4) together with the values of $\Delta H_f$ obtained. A knowledge of $\Delta H_f$, and the value of $K$ obtained from a conventional Benesi-Hildebrand plot corrected to the mole fraction scale permits the determination of the amount of complex present at equilibrium, i.e.

$$x = \frac{(a+b)}{2} \pm \frac{\sqrt{(K+1)^2(a+b)^2 - 4Kab(K+1)}}{2(K+1)} \quad (11.3.6)$$

Hence it is possible to determine the value of $H_E^*$ from equation (11.1.2). The errors are extremely large in the determination of $\Delta H$ and appreciable in the determination of $K$ which, together with the fact that the spectroscopic work was done in dilute solution, makes comparison of the values difficult. However this procedure gives for the systems:

- hexafluorobenzene + N,N-dimethylaniline $H_E^* = +270 \pm 500 \text{ J.mol}^{-1}$
- hexafluorobenzene + N,N-dimethyl-p-toluidine $H_E^* = +1370 \pm 200 \text{ J.mol}^{-1}$

The latter value is in excellent agreement with the experimentally determined model system: hexafluorobenzene + isopropylcyclohexane (+1300 J.mol$^{-1}$), but in the case of N,N-dimethylaniline the poor agreement is to some extent expected in view of the experimental error and limited temperature range studied as can be seen in Fig (11.3.4)

The curve shapes may be explained in the case of N,N-dimethylaniline and the m- and p- N,N-dimethyltoluidines by complexing of
Calculation of the Heat of Complex Formation, $\Delta H_f$, for:

i) Hexafluorobenzene $+$ N,N-Dimethyl-p-toluidine

\[ \text{Gradient} = -1.795 \times 10^3 \text{ K} \]
\[ \Delta H_f = -14.9 \times 10^3 \text{ J. mol}^{-1} \]
\[ \pm 2.2 \times 10^3 \text{ J. mol}^{-1} \]

Figure (II.3.4)
the amine with hexafluorobenzene in a 1:1 manner, the endothermic contribution being suitably offset, the maximum occurring towards the low fluorocarbon side of the equimolar composition. However we have made a number of assumptions here which need to be considered. Firstly we assumed that the chemical contribution was symmetrical in mole fraction, or in other words the equilibrium constant does not vary with composition. This is unlikely to be true as the solvent environment of the complex is changing as the liquid composition changes and this may well influence complex stability. Also if we assume a symmetrical behaviour for the chemical contribution then we must consider why the endothermic term is offset. Scott has predicted on the basis of solubility parameter theory that the $\Delta^E$ curves should be symmetrical in volume fraction and that when the mole fraction scale is used the curves will be offset as determined by their relative molar volumes. However this rule does not always apply and the curve shapes must remain at present a matter for speculation.

With N,N-dimethyl-o-toluidine the much lower exothermic heat of mixing can be explained by steric interference between the amine grouping and the o-methyl grouping, which causes the C=N bond to twist so that the nitrogen lone pair cannot fully participate in the delocalised $\pi$-molecular orbitals. Furthermore with this non-planar configuration the approach of the hexafluorobenzene would be sterically less favourable and therefore lower complexing results.

The pyridines are of interest because they provide information regarding the configuration of the complex. The observed exothermic
heat of mixing increases with increasing methyl substitution and although no charge transfer bands have been observed this is the trend of the ionisation potentials. A Molecular Orbital calculation carried out in a similar manner to that described in Section 2 shows that although the $\pi$-levels are benzene like their symmetry has been sufficiently distorted to allow small favourable overlap with the orbitals of hexafluorobenzene. Also with 2,6-dimethylpyridine and 2,4,6-trimethylcollidine the heat of mixing, $H^E$, decreases (i.e. becomes more negative), which can be interpreted as indicating $\pi-\pi$ complexing since the nitrogen lone pair would be strongly sterically hindered by the 2 and 6-methyl groups.

Pyridine itself is not in disagreement with this interpretation but its first ionisation potential ($1.51 \times 10^{-18}$ J) is high (96) and there is disagreement as to whether the highest filled orbital is the nitrogen lone pair or the highest energy $\pi$-orbital. The asymmetry of the curves is again consistent with 1:1 complexing provided that the endothermic contribution is suitably offset, having a maximum on the low fluorocarbon side of the equimolar composition. Morcom and Travers (49) interpreted their measurements on the system: carbon tetrachloride + pyridine in terms of a hydrogen bonded structure for pyridine. When a similar argument is applied to the system: hexafluorobenzene + pyridine an offset endothermic contribution is indicated but the curve should be offset in the opposite way to that consistent with 1:1 complexing without solvent effect. The actual curve shapes do not therefore appear to be explainable in terms of a simple qualitative model and the indication of a particularly offset endothermic contribution may be explained equally well by considering 2:1 complexing where one pyridine
molecule is simultaneously involved with two hexafluorobenzene molecules. Whilst this is possible the ionisation potentials are so high that charge transfer stabilisation must be uncertain and as likely a case can be made out for an interaction of the benzene - hexafluorobenzene type without considering charge transfer stabilisation at all.

The system hexafluorobenzene + triethylamine was used to study the effect of a tertiary amine without the possibility of \( \pi - \pi \) interaction. The endothermic contribution to the enthalpy of mixing is likely to be considerably above the approximate value of +1300 J.mol\(^{-1}\) as the molecular shapes are so different. However both the observed excess enthalpy of mixing and the excess heat capacity are consistent with the formation of complexes which must stem from interaction of the nitrogen lone pair with the delocalised \( \pi \) -orbitals of hexafluorobenzene. Despite the low ionisation potential of triethylamine (96) the heat of mixing is consistent with this since overlap between a relatively localised lone pair orbital and a diffuse \( \pi \) -orbital cannot be great although it will always be favourable.

611.4 THE EXCESS GIBBS FUNCTION DATA AND THE EXCESS VOLUME OF MIXING DATA

The experimental determination of the Excess Gibbs Function for mixing, \( G^E \), was not successful but from the experimental results
it is possible to deduce, using only those points which are probably reliable (say the first two from each series of measurements) that \( G^E \) for the system hexafluorobenzene + \( N,N \)-dimethylaniline is predominately negative. This contrasts markedly with the behaviour of many fluorocarbon solutions which show very large positive excess Gibbs Functions for Mixing. In Fig (11.4.1) the calculated value of \( G^E \) is compared with that measured by Gaw and Swinton (56) for the system: hexafluorobenzene + cyclohexane, and this could be used to give an indication of the equilibrium constant for complex formation by applying an associated solution approach to the two sets of data.

This has not been done at this stage because the vapour pressure measurements are to be repeated and then this interpretation may be carried out.

The excess volume of mixing, \( V^E \), is compared with the results of Duncan, Sheridan and Swinton (58) on the systems: hexafluorobenzene + cyclohexane and hexafluorobenzene + isopropylbenzene, in Fig (11.4.2). The volume change on mixing falls rapidly with increasing the electron donor strength and whilst the current trend is to consider other forces as the major stabilisation for the aromatic hydrocarbon - hexafluorobenzene complex, the large deviation from the so-called expected behaviour is not inconsistent with charge transfer complex formation.
The Excess Gibbs Function of Mixing $G^e$ for the Systems:

Hexafluorobenzene + Cyclohexane at

303.15 K

Fig (II.4.1)
The Excess Volume of Mixing, \( V_E \), for
Hexafluorobenzene with
(i) Cyclohexane at 313.15 K
(ii) Cumene at 313.15 K
(iii) N,N-Dimethylaniline at 323.15 K

Fig (11.4.2)
11.5 CONCLUSION

There is overwhelming evidence for a strong specific interaction between hexafluorobenzene and the amines studied in this work. The phase diagram shows that a 1:1 complex is stable in the solid phase to considerably above the melting point of either pure component, but without detailed analysis this cannot be interpreted as indicative of complexing in the liquid phase. However, the charge transfer bands which have been resolved for some of these systems spectroscopically provide sufficient evidence to say that charge transfer does occur in these systems although it may not be the major stabilising force. The thermodynamic properties which have been described in this thesis are also consistent with strong association in the liquid phase and are considerably stronger than those interactions observed with aromatic hydrocarbons. Much further work has yet to be done in this field, spectroscopically, thermodynamically and theoretically before a complete understanding of these mixtures is achieved.
This appendix relates primarily to some work done on water + acetonitrile by the present author in conjunction with other workers in the Department, who were studying spectroscopic and ultrasonic properties of the same system (51).
CHAPTER ONE

THE EXCESS VOLUME OF MIXING, $V^E$, AND THE PARTIAL MOLAR VOLUMES, $V_1$, $V_2$. 
\[ \text{61.1 CALCULATION OF EXCESS VOLUME OF MIXING FROM DENSITY MEASUREMENTS} \]

Many workers have in the past measured the density of binary mixtures. The plot of density against composition which results is a speedy way of determining the composition of an unknown binary mixture. As a result much density data has accumulated in the literature, and if this were of adequate accuracy it would be possible to determine \( V^E \) from it.

Consider a system composed of \( n_1 \) moles of component \( 1 \) and \( n_2 \) moles of component \( 2 \), the molecular weights and molar volumes of \( 1 \) and \( 2 \) being \( M_1 \), \( M_2 \) and \( V_1^o \) and \( V_2^o \) respectively. The density of the mixture, \( \rho \), is given by

\[
\rho = \frac{(n_1 M_1 + n_2 M_2)}{V} \tag{61.1.1}
\]

where \( V \) is the volume of the mixture.

Since we can write

\[
(n_1 + n_2) V^E = V - n_1 V_1^o - n_2 V_2^o \tag{61.1.2}
\]

from the definition of excess volume, then if we denote the densities of pure \( 1 \) and \( 2 \) respectively by \( \rho_1^o \) and \( \rho_2^o \) we find
\[(n_1 + n_2) V^E = \frac{n_1 M_1 + n_2 M_2}{\rho} - \frac{n_1 M_1}{\rho_1^o} - \frac{n_2 M_2}{\rho_2^o} \]  \hspace{1cm} (A1.1.3)

Therefore in terms of the mole fraction

\[x_i = \frac{n_i}{\sum n_i} \]

we can write

\[V^E = x_1 M_1 [1/\rho - 1/\rho_1^o] + x_2 M_2 [1/\rho - 1/\rho_2^o] \]  \hspace{1cm} (A1.1.4)

61.2 ERRORS IN DETERMINATION OF \(V^E\) FROM DENSITY MEASUREMENTS

Excess volumes calculated from density measurements are notoriously inaccurate unless the density measurements are extremely precise. The exact error depends upon the composition and the materials being studied but it is generally true to say that at least five figures must be determined in the density to obtain any significance in the third figure of \(V^E\).

The literature density data for the system acetonitrile + water (97 - 100) was used to calculate \(V^E\) by a computer program which is shown in Appendix III. The resulting excess volumes are
plotted in Fig (A1.2.1) and illustrate that such data is often unreliable.

61.3 USE OF DIRECT TECHNIQUE

It is possible to determine $V^E$ directly, or more sophisticated and precise density measurements may be carried out. For example Franks uses a magnetic float (101, 102) to measure the density of aqueous solutions in the highly aqueous composition region and obtains results of extremely high accuracy and reproducibility (six significant figures), but only over a small range of composition for which his apparatus is designed.

In Chapter Nine of this thesis apparatus for measuring the excess volume of mixing directly was described and illustrated. This apparatus is suitable for relatively large volume changes on mixing and the estimated error on such measurements is $\pm 0.5\%$. Andrews calculated the expected systematic error to be in the order of $\pm 0.2\%$ but this ignores any irreproducible contribution. This error is however considerably below that normally accompanying density measurements and therefore direct measurement of $V^E$ was used in this work.
LITERATURE DENSITY DATA CONVERTED TO EXCESS VOLUMES OF MIXING FOR THE SYSTEM:
WATER + ACETONITRILE,

- Trubé (1897) at 293.15 K
- Othmer et al. (1947) at 298.15 K
+ Maslan et al. (1956) at 298.15 K
* Cunningham et al. (1967) at 298.15 K
The partial molar quantity is defined from the corresponding extensive property by a relationship

$$X_i = \left( \frac{\partial X}{\partial n_i} \right)_{n_j, T, P}$$

which when applied to the volume function gives

$$V_i = \left( \frac{\partial V}{\partial n_i} \right)_{n_j, T, P}$$

where $V_i$ is the partial molar volume of component $i$ in the mixture and $V$ is the volume of the mixture.

For $n_1$ moles of $\circ$ and $n_2$ moles of $\Box$ then we can write

$$V = n_1 \left( \frac{\partial V}{\partial n_1} \right)_{n_2, T, P} + n_2 \left( \frac{\partial V}{\partial n_2} \right)_{n_1, T, P}$$

Therefore for one mole of mixture we have

$$V_m = \frac{V}{n_1 + n_2} = x_1 V_1 + x_2 V_2$$

where the mole fractions $x_1$ and $x_2$ and the partial molar volumes $V_1$ and $V_2$ are as defined above.
The excess volume of mixing $V^E$ is the volume of one mole of mixture minus the volume of the pure components of the mixture and therefore

$$V^E = x_1 (V_1 - V_1^o) + x_2 (V_2 - V_2^o) \quad (1.4.5)$$

The quantities $V_i - V_i^o$ are called the excess or relative partial molar volumes and are often discussed rather than $V_i$ since their calculation is easier as will be seen later.

If we differentiate equation (5) with respect to $x_1$, then

$$\frac{dV^E}{dx_1} = (V_1 - V_1^o) - (V_2 - V_2^o) \quad (1.4.6)$$

and therefore the equation of the tangent to the $V^E$ vs. $x_1$ curve at a point $(x_1', V^E')$ is given by

$$y - V^E' = [(V_1 - V_1^o) - (V_2 - V_2^o)] (x_1 - x_1') \quad (1.4.6)$$

and therefore when $x_1 = 0$

$$y = V_2 - V_2^o \quad (1.4.7)$$

and when $x_1 = 1$

$$y = V_1 - V_1^o \quad (1.4.8)$$
With our normal excess function representation therefore the intercepts which are made by the tangent to the excess function curve at any composition represent the relative partial molar volumes of the two components. The true partial molar volumes may then be obtained from the excess quantities provided that the molar volumes of the pure materials are precisely known at the appropriate temperature.

91.5 Determination of Partial Molar Volume

a) From a Hand Drawn "Best" Curve

It frequently occurs that excess volume curves for aqueous solutions show pronounced points of inflection (103) or other departures from the parabolic behaviour of a regular solution. A method was therefore developed to enable partial molar volumes to be determined with reasonable accuracy from a hand drawn curve. The value of $V^E$ is then read off this smooth curve at regular composition intervals and each small section of the $V^E$ curve used to determine the partial molar volume at the appropriate composition. If the composition interval is sufficiently small then we can regard the curve as parabolic within that interval. Then we can write

$$V^E = ax_i^2 + bx_i + c$$

(91.5a.1)

and from these points we can determine $a$, $b$ and $c$ uniquely.
The equation of the tangent at any composition \((x'_i, V^{E'})\) is given by

\[
y - V^{E'} = (2ax'_2 + b)(x'_i - x'_i) \tag{A1.5a.2}
\]

and therefore when \(x'_i = 0\)

\[
y = V_2 - V_2^o = V^{E'} - (2ax'_2 + bx'_i) = c - ax'_2 \tag{A1.5a.3}
\]

and similarly when \(x'_i = 1\)

\[
y = V_1 - V_1^o = V^{E'} + (2ax'_1 + b)(1 - x'_i) = (V_2 - V_2^o) + 2ax'_1 + b \tag{A1.5a.4}
\]

This procedure is repeated for each composition which is required and the resulting values give a reasonable indication of the behaviour of the partial molar volumes.

b) From a Complete Curve Fit

If the experimentally determined excess volume data can be represented by a smooth curve of the type introduced in Chapter Five of this thesis, then using the most general function (that suggested by Myers and Scott), at any composition \(x'_i, x'_j\) we have

\[
V^{E} = \sum_{i=0}^{n} \frac{x_i x_j \theta_i (x'_i - x'_j)^i}{(1 - k(x'_i - x'_j))} \tag{A1.5b.1}
\]
where the coefficients $A_i$ are determined from the usual least squares condition.

At any point on the $V^E$ vs. $x_1$ curve the gradient (GRAD) is given by

$$\text{GRAD} = \frac{\partial V^E}{\partial x_i} = \sum_{i=0}^{n} \frac{2x_1 x_2 A_i (x_1 - x_2)^{i-1}}{(1-k(x_1 - x_2))} - \sum_{i=0}^{n} \frac{A_i (1-2x_2)^{i+1}}{(1-k(x_1 - x_2))}$$

$$+ \sum_{i=0}^{n} \frac{2k x_1 x_2 A_i (x_1 - x_2)^{i}}{(1-k(x_1 - x_2))^2} \quad (A1.5b.2)$$

Then from the equation of the tangent we have as above

$$V_2 - V_2^o = V^E - x_1 \cdot \text{GRAD} \quad (A1.5b.3)$$

and

$$V_1 - V_1^o = V^E + x_2 \cdot \text{GRAD} = V_2 - V_2^o + \text{GRAD} \quad (A1.5b.4)$$

This procedure is valid at any composition where equation (A1.5b.1) adequately describes the experimental data. The calculation was done by computer and the necessary procedure was built into the curve fitting programs described in Chapter Five of this thesis and presented in Appendix III.

c) By Curve Fitting Small Sections of the $V^E$ Curve

When the curve shape is remarkably distorted it is difficult to adequately represent the entire composition dependance of $V^E$ with an equation of the usual form (A1.5b.1), and such an equation
will represent accurately the experimental points over a limited composition range only. For example in the field of alcohol-water mixtures the highly aqueous region tends to be badly fitted when compositions over the entire range are included. This problem may be overcome by adequately weighting the relevant points or by fitting only that section of the curve which is important. Therefore the procedure is identical with that described in (b) above when applied to the smaller composition range.
CHAPTER TWO

PARTIAL MOLAR VOLUMES AND MAXIMUM DENSITY EFFECTS WITH REFERENCE TO ALCOHOL WATER MIXTURES
4.1 INTRODUCTION TO EARLY WORK

During the course of the aqueous solution work, interest was aroused in maximum density properties of aqueous solutions and the work carried out is outlined in this Chapter.

The presence of a maximum density in liquid water is unique and it has been interpreted in terms of an equilibrium between structurally expanding units and structurally decaying species (103). The effect of added solute has been summarised in the classical "Despretz Law" (104, 105) and it is of interest to note that alcohols do not obey this law.

Frank (106, 107) considered this anomalous behaviour and from his work he was able to conclude that the partial molar volume of the alcohol, $V_2$, should be invariant with temperature, at the composition, $x_2$, at which the change in the temperature of maximum density, $\Delta \Theta$, is a maximum. The underlying thermodynamics was quite satisfactory but there was no experimental evidence to support this view, and Franks and Ives conclude the appropriate section of their review (103) by saying that more numerous and precise density measurements are required.

In a later paper Franks and Watson (108) discuss the effect of dipropylamines and dibutylamines on the temperature of maximum density of water. In their discussion of their experimental data they derived a relationship for the change in the temperature of maximum density by assuming that the expansion of pure water
is governed by a relationship of the form

$$V_i^o = V_i^{o*} \left[1 + \alpha_i (t - 3.98)^2\right]$$  \hspace{1cm} (A1.6.1)

where $V_i^o$ is the molar volume of pure water at some temperature $(t + 273.15)$ K, $\alpha_i$ is the coefficient of expansion of water and $V_i^{o*}$ is the molar volume at $273.15$ K, and that the expansion of the other component is governed by the equation

$$V_2^o = V_2^{oo} \left[1 + \alpha_2 t\right]$$  \hspace{1cm} (A1.6.2)

where $V_i^o$ and $V_2^{oo}$ are the molar volumes of the other component at $(273.15 + t)$ K and $273.15$ K respectively and $\alpha_2$ is the coefficient of expansion of pure component 2. The relationship was then obtained by substituting from equations (1) and (2) into equation (A1.4.4) and differentiating with respect to temperature. They found the condition for a maximum in the property $\Delta \Theta$ was given by

$$\Delta \Theta = \frac{-x_2 \alpha_2 V_2^{oo}}{2 \alpha_1 (1-x_2) V_i^{oo}} - \frac{\partial V^E / \partial T}{2 \alpha_1 (1-x_2) V_i^{oo}}$$  \hspace{1cm} (A1.6.3)

The first term on the R.H.S. of this expression arises from an ideal mixture for which $V^E$ and $\partial V^E / \partial T$ are both zero and the second term which arises from the non-ideality of the solution and can be interpreted in terms of structural effects. They therefore write

$$\Delta \Theta = \Delta \Theta_{\text{ideal}} + \Delta \Theta_{\text{str}}$$
The next step forward in this field came from a visual correlation by N.G. Treloar of this Department when he observed that the relative partial molar volume curves for ethanol in ethanol + water mixtures were seen to pass through one common point at each temperature (109). The partial molar volumes of ethanol in these mixtures are shown in the appropriate composition range and over a wide temperature range in Fig (A1.7.1) and were obtained from the published density data in International Critical Tables (110), by the procedures described in Chapter 1, Sections 1 and 5a. Treatment of literature density data (111 - 113) for some other alcohol water mixtures, namely n-propanol, iso-propanol and t-butanol resulted in clear common points although the data were not so precise in these cases (109). It was observed also that this common point occurred at the same composition in each case as the maximum in $\Delta \Theta_{str}$. 

The occurrence of this phenomenon can be explained by considering the expression obtained by Franks and Watson. They defined

$$\Delta \Theta_{str} = -\frac{\partial V^E / \partial T}{\frac{1}{x_1(1-x_2)} V_i} \tag{A1.7.1}$$

the composition dependence of which will be a maximum when

$$\frac{\partial \Delta \Theta_{str}}{\partial x_2} = -\frac{1}{x_1(1-x_2)} V_i \left\{ \left(1-x_2 \right) \frac{\partial^2 V^E}{\partial x_2 \partial T} + \frac{\partial V^E}{\partial T} \right\} = 0 \tag{A1.7.2}$$
Provided that $x_2 > 0$ we have the condition

$$\frac{\partial}{\partial T} \left[ (1 - x_2) \frac{\partial V^E}{\partial x_2} + V^E \right] = \frac{\partial}{\partial T} \left[ V_2 - V_2^0 \right] = 0 \quad (A1.7.3)$$

since we can write

$$V^E = (1 - x_2) (V_1 - V_1^0) + x_2 (V_2 - V_2^0) \quad (A1.7.4)$$

Thus, at the composition for which $\Delta \Theta_{st}$ is a maximum, the equation

$$\frac{\partial}{\partial T} \left[ V_2 - V_2^0 \right] = 0$$

implies that the value of $V_2 - V_2^0$, the relative partial molar volume of component 2 is a constant independent of the temperature at that particular composition, as was observed. This analysis, which is believed to be original, has now been published.

Furthermore, equation (1) infers that when $\Delta \Theta_{st} = 0$ that $\partial V^E / \partial T = 0$, i.e., the $V^E$ curves at different temperatures should all pass through a common point at the composition at which $\Delta \Theta_{st} = 0$. In Fig (A1.7.2) a large-scale graph of the $V^E$ curves for ethanol + water mixtures is shown and the common point is clearly seen although $\Delta \Theta_{st}$ has not been determined at this particular composition.

The original equation of Franks and Watson may also be used to show the relationship, previously derived by H.S. Frank (106, 107), between the change in the temperature of maximum density, $\Delta \Theta,$
and the behaviour of the alcohol partial molar volume, $V_2$. If we differentiate equation (A1.6.3) with respect to $x_2$ and equate the result to zero to determine the condition for a maximum in $\Delta \theta$ we find

$$\frac{\partial \Delta \theta}{\partial x_2} = 0$$

when

$$\left(1 - x_2\right) \left[V_2^\circ \frac{\partial^2 \Delta \theta}{\partial x_2^2} + \frac{\partial^2 V^E}{\partial x_2 \partial T}\right] = - x_2 V_2^\circ \frac{\partial \Delta \theta}{\partial T} - \frac{\partial V^E}{\partial T}$$

or

$$\frac{\partial}{\partial T} \left[\left(1 - x_2\right) \frac{\partial V^E}{\partial x_2} + V^E\right] = - V_2^\circ \frac{\partial \Delta \theta}{\partial T}$$

Then using equation (A1.7.4) this reduces to

$$\frac{\partial}{\partial T} \left[V_1 - V_2^\circ\right] = - x_2 V_2^\circ$$

and from our original definition of $V_2^\circ$ we find

$$\frac{\partial}{\partial T} V_2^\circ = 0$$

This implies that the partial molar volume of the alcohol should be invariant with temperature at the composition corresponding to the maximum in the change in the temperature of maximum density of the mixture. This has not yet been seen but the cause is probably due to the inadequacies of equation (A1.6.1) which are
less important in the case of the relative partial molar volume condition than for that with the partial molar volume.

Also if we consider the situation when the change in the temperature of maximum density, $\Delta \theta$, is zero then we find

$$\frac{\partial}{\partial T} V^E = -x_2 \alpha_2 V_2^{\infty} \quad (A1.7.9)$$

and therefore since

$$\frac{\partial}{\partial T} V_2^{\infty} = \alpha_2 V_2^{\infty}$$

we can write

$$\frac{\partial}{\partial T} [ V^E + x_2 V_2^{\infty} ] = 0 \quad (A1.7.10)$$

We define the apparent molar volume, $\phi_2$, of component 2 by the relationship

$$\phi_2 = \frac{V^E + x_2 V_2^{\infty}}{x_2} \quad (A1.7.11)$$

and therefore

$$\frac{\partial}{\partial T} [ x_2 \phi_2 ] = 0 \quad (A1.7.12)$$
which implies since $x_z \neq x_z(T)$ that the apparent molar volume $\phi_z$ is invariant with temperature at the composition where $\Delta \Theta$ is zero.
CHAPTER THREE

ACETONITRILE + WATER MIXTURES
Acetonitrile + water mixtures have been used as suitable solvent systems for a number of chemical processes for some time (114, 115) and with the growing interest in how co-solvent molecules disturb the structure of the water it was of interest to investigate some of the properties of these mixtures in greater detail. Much work has been done on the alcohol water mixtures (103) and there is considerable evidence for structural enhancement of the water in the low concentration of alcohol composition region.

The acetonitrile + water system has been investigated in these laboratories by a number of workers using the techniques of thermodynamics, ultrasonics and spectroscopy (51). The initial basis for the work was that these mixtures show an intense ultrasonic sound absorption in a similar manner to that observed in alcohol water mixtures. The composition dependence of the ultrasonic absorption is shown in Fig (A1.8.1). With alcohol water mixtures it was observed that the rapid increase in sound absorption occurred at the same composition as a pronounced minimum in the partial molar volume of the alcohol (116). Acetonitrile + water mixtures show a much larger plateau region, than alcohol + water mixtures, as can be seen by the low sound absorption for this system from Fig (A1.8.1) until the composition of the acetonitrile, \( x_2 \), reaches approximately 0.1. The rise of the absorption is then much slower reaching a maximum at approximately 0.4 mole fraction acetonitrile. It was therefore decided to study the excess volume of mixing for this system in order to determine whether a minimum did occur in the
Comparison of the ultrasonic absorption properties at 70 kHz of methyl cyanide-water mixtures at (a) 0°C and (b) 25°C and t-butyl alcohol-water mixtures at (c) 5°C and (d) 25°C.

Fig (Al. 8.1)
partial molar volume or not as the literature density data (Fig (A1.2.1)) was inadequate to infer anything about the detailed behaviour.

3.2 EXPERIMENTAL DETERMINATION OF $V^E$

The excess volume of mixing, $V^E$, was determined in a similar manner to that described in Chapter Nine of this thesis at two temperatures, namely 298.15 K and 279.15 K. The water used for these measurements was purified by distilling deionised water from alkaline potassium permanganate and in addition to these measurements it was used for the spectroscopic and ultrasonic measurements as well (51). The acetonitrile was purified by drying Koch-Light Puriss Grade acetonitrile with fresh anhydrous phosphorus pentoxide and then twice distilling the residue and collecting only a middle fraction. The resulting material showed no trace of impurity with the Perkin Elmer F11 Gas Chromatograph using either an Apiezon L or Carbowax 1500 column. The liquids were outgassed before loading the dilatometers but were not stored in mercury sealed ampoules.

The experimental results are shown in table form in Table (A1.8.1) and the details of the curve fitting are shown in Table (A1.8.2). The best smooth curves are shown in Fig (A1.8.2) and the relative partial molar volumes are shown in Fig (A1.8.3) calculated from the data obtained at 298.15 K.
The Excess Volume of Mixing, $V^e_m$
for the System: Water + Acetonitrile at,

- $298.15 \text{ K}$
- $279.15 \text{ K}$

Fig (Al 8.2)
Excess Partial Molar Volumes for Water (1) + Acetonitrile (2) Mixtures at 298.15 K
TABLE (A1.8.1)

THE EXCESS VOLUME CHANGE ON MIXING, \( \Delta V^E \), FOR THE SYSTEM:
WATER (1) + ACETONITRILE (2)

a) At 298.15 K

<table>
<thead>
<tr>
<th>( w_1/\text{kg} )</th>
<th>( w_2/\text{kg} )</th>
<th>( x_\lambda )</th>
<th>( \Delta V^E/\text{m} )</th>
<th>( V^E/\text{m}^3 \cdot \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.111 ( \times 10^{-4} )</td>
<td>1.102 ( \times 10^{-4} )</td>
<td>0.0310</td>
<td>-6.241 ( \times 10^{-2} )</td>
<td>-1.464 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>13.141 ( \times 10^{-4} )</td>
<td>1.594 ( \times 10^{-4} )</td>
<td>0.0505</td>
<td>-9.140 ( \times 10^{-2} )</td>
<td>-2.416 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>12.806 ( \times 10^{-4} )</td>
<td>2.046 ( \times 10^{-4} )</td>
<td>0.0655</td>
<td>-11.104 ( \times 10^{-2} )</td>
<td>-2.965 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>7.081 ( \times 10^{-4} )</td>
<td>2.769 ( \times 10^{-4} )</td>
<td>0.1465</td>
<td>-10.832 ( \times 10^{-2} )</td>
<td>-4.778 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>6.924 ( \times 10^{-4} )</td>
<td>6.159 ( \times 10^{-4} )</td>
<td>0.2808</td>
<td>-14.550 ( \times 10^{-2} )</td>
<td>-5.531 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>5.305 ( \times 10^{-4} )</td>
<td>5.656 ( \times 10^{-4} )</td>
<td>0.3187</td>
<td>-11.776 ( \times 10^{-2} )</td>
<td>-5.534 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>4.540 ( \times 10^{-4} )</td>
<td>5.085 ( \times 10^{-4} )</td>
<td>0.3295</td>
<td>-10.373 ( \times 10^{-2} )</td>
<td>-5.605 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>4.485 ( \times 10^{-4} )</td>
<td>5.031 ( \times 10^{-4} )</td>
<td>0.3299</td>
<td>-10.234 ( \times 10^{-2} )</td>
<td>-5.595 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>4.114 ( \times 10^{-4} )</td>
<td>5.103 ( \times 10^{-4} )</td>
<td>0.3525</td>
<td>-9.711 ( \times 10^{-2} )</td>
<td>-5.593 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>3.987 ( \times 10^{-4} )</td>
<td>5.230 ( \times 10^{-4} )</td>
<td>0.3653</td>
<td>-9.560 ( \times 10^{-2} )</td>
<td>-5.569 ( \times 10^{-7} )</td>
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<tr>
<td>3.982 ( \times 10^{-4} )</td>
<td>5.354 ( \times 10^{-4} )</td>
<td>0.3711</td>
<td>-9.583 ( \times 10^{-2} )</td>
<td>-5.538 ( \times 10^{-7} )</td>
</tr>
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<td>3.325 ( \times 10^{-4} )</td>
<td>5.018 ( \times 10^{-4} )</td>
<td>0.3984</td>
<td>-8.341 ( \times 10^{-2} )</td>
<td>-5.522 ( \times 10^{-7} )</td>
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<tr>
<td>6.094 ( \times 10^{-4} )</td>
<td>9.780 ( \times 10^{-4} )</td>
<td>0.4132</td>
<td>-15.419 ( \times 10^{-2} )</td>
<td>-5.433 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>3.003 ( \times 10^{-4} )</td>
<td>5.204 ( \times 10^{-4} )</td>
<td>0.4320</td>
<td>-7.787 ( \times 10^{-2} )</td>
<td>-5.390 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>4.076 ( \times 10^{-4} )</td>
<td>7.710 ( \times 10^{-4} )</td>
<td>0.4536</td>
<td>-10.534 ( \times 10^{-2} )</td>
<td>-5.167 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>3.215 ( \times 10^{-4} )</td>
<td>6.470 ( \times 10^{-4} )</td>
<td>0.4690</td>
<td>-8.652 ( \times 10^{-2} )</td>
<td>-5.229 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>2.656 ( \times 10^{-4} )</td>
<td>6.064 ( \times 10^{-4} )</td>
<td>0.5005</td>
<td>-7.240 ( \times 10^{-2} )</td>
<td>-5.031 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>2.167 ( \times 10^{-4} )</td>
<td>5.160 ( \times 10^{-4} )</td>
<td>0.5110</td>
<td>-5.984 ( \times 10^{-2} )</td>
<td>-4.941 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>1.438 ( \times 10^{-4} )</td>
<td>5.050 ( \times 10^{-4} )</td>
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<td>-4.216 ( \times 10^{-2} )</td>
<td>-4.222 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>2.216 ( \times 10^{-4} )</td>
<td>12.010 ( \times 10^{-4} )</td>
<td>0.7040</td>
<td>-6.685 ( \times 10^{-2} )</td>
<td>-3.268 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>2.093 ( \times 10^{-4} )</td>
<td>14.080 ( \times 10^{-4} )</td>
<td>0.7470</td>
<td>-6.200 ( \times 10^{-2} )</td>
<td>-2.743 ( \times 10^{-7} )</td>
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<tr>
<td>0.635 ( \times 10^{-4} )</td>
<td>7.946 ( \times 10^{-4} )</td>
<td>0.8459</td>
<td>-1.727 ( \times 10^{-2} )</td>
<td>-1.533 ( \times 10^{-7} )</td>
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<tr>
<td>0.910 ( \times 10^{-4} )</td>
<td>13.250 ( \times 10^{-4} )</td>
<td>0.8647</td>
<td>-2.477 ( \times 10^{-2} )</td>
<td>-1.348 ( \times 10^{-7} )</td>
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<tr>
<td>0.448 ( \times 10^{-4} )</td>
<td>26.592 ( \times 10^{-4} )</td>
<td>0.9630</td>
<td>-0.811 ( \times 10^{-2} )</td>
<td>-0.245 ( \times 10^{-7} )</td>
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TABLE (A1.8.1) (Continued)

b) At 279.15 K

<table>
<thead>
<tr>
<th>( w_1/\text{kg} )</th>
<th>( w_2/\text{kg} )</th>
<th>( x_4 )</th>
<th>( \Delta J/\text{m} )</th>
<th>( V^E/\text{m}^3\cdot\text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.738 ( \times 10^{-4} )</td>
<td>0.817 ( \times 10^{-4} )</td>
<td>0.0254</td>
<td>-5.714 ( \times 10^{-2} )</td>
<td>-1.483 ( \times 10^{-7} )</td>
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<tr>
<td>8.066 ( \times 10^{-4} )</td>
<td>0.852 ( \times 10^{-4} )</td>
<td>0.0443</td>
<td>-5.699 ( \times 10^{-2} )</td>
<td>-2.471 ( \times 10^{-7} )</td>
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<tr>
<td>10.174 ( \times 10^{-4} )</td>
<td>2.391 ( \times 10^{-4} )</td>
<td>0.0935</td>
<td>-12.973 ( \times 10^{-2} )</td>
<td>-4.230 ( \times 10^{-7} )</td>
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<td>8.230 ( \times 10^{-4} )</td>
<td>3.272 ( \times 10^{-4} )</td>
<td>0.1485</td>
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<td>4.985 ( \times 10^{-4} )</td>
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<td>0.2388</td>
<td>-10.456 ( \times 10^{-2} )</td>
<td>-5.842 ( \times 10^{-7} )</td>
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<td>3.952 ( \times 10^{-4} )</td>
<td>4.000 ( \times 10^{-4} )</td>
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<td>3.054 ( \times 10^{-4} )</td>
<td>4.990 ( \times 10^{-4} )</td>
<td>0.4176</td>
<td>-8.120 ( \times 10^{-2} )</td>
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<td>7.824 ( \times 10^{-4} )</td>
<td>0.5013</td>
<td>-9.663 ( \times 10^{-2} )</td>
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<td>8.248 ( \times 10^{-4} )</td>
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<td>-7.660 ( \times 10^{-2} )</td>
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<td>6.758 ( \times 10^{-4} )</td>
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<td>-4.208 ( \times 10^{-7} )</td>
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<td>1.306 ( \times 10^{-4} )</td>
<td>11.812 ( \times 10^{-4} )</td>
<td>0.7988</td>
<td>-4.237 ( \times 10^{-2} )</td>
<td>-2.389 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>0.940 ( \times 10^{-4} )</td>
<td>19.650 ( \times 10^{-4} )</td>
<td>0.9017</td>
<td>-2.659 ( \times 10^{-2} )</td>
<td>-1.017 ( \times 10^{-7} )</td>
</tr>
</tbody>
</table>
TABLE (A1.8.2)

CURVE FITTING THE EXCESS VOLUME DATA FOR THE SYSTEM:
WATER (1) + ACETONITRILE (2),

1) At 298.15 K

a) Method 1, using \(10^6 \cdot \frac{V^E}{x_1 x_2} = \sum_{i=1}^{n} V_i (x_i - \bar{x}_i)^{i-1}\)

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<thead>
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<th>(V_i)</th>
<th>(V_\lambda)</th>
<th>(V_3)</th>
<th>(V_4)</th>
<th>(V_5)</th>
<th>(V_6)</th>
<th>RMS</th>
<th>STD</th>
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b) Method 2, using \(10^6 \cdot V^E = \sum_{i=1}^{n} x_1 x_2 V_i (x_i - \bar{x}_i)^{i-1}\)

<table>
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<tr>
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<th>(V_4)</th>
<th>(V_5)</th>
<th>(V_6)</th>
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TABLE (A1.8.2) (Continued)

c) Method 3, using $10^6 \times V^E \sum_{j=1}^{n} \alpha_i \alpha_j V_i (\alpha_i - \alpha_j) \sum_{j=1}^{n} \alpha_i \alpha_j / (1 - k(\alpha_i - \alpha_j))$

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d) Method 4, using $10^6 \times V^E \sum_{j=1}^{n} \nabla_i \nabla_j$

where the $\nabla_i$ are suitably chosen orthogonal polynomials

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<th>$V_1$</th>
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<th>$V_4$</th>
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</table>
TABLE (A1.8.2) (Continued)

2) At 279.15 K

a) Method 1, using \(10^6 \times V^E / \chi_1 \chi_2 \sum_{i=1}^{n} V_i (\chi_i - \chi_2)^{-1}\)

<table>
<thead>
<tr>
<th>(V_1) m(^3).mol(^{-1})</th>
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<th>(V_5) m(^3).mol(^{-1})</th>
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b) Method 2, using \(10^6 \times V^E \times \sum_{i=1}^{n} \chi_1 \chi_2 V_i (\chi_i - \chi_2)^{-1}\)

<table>
<thead>
<tr>
<th>(V_1) m(^3).mol(^{-1})</th>
<th>(V_2) m(^3).mol(^{-1})</th>
<th>(V_3) m(^3).mol(^{-1})</th>
<th>(V_4) m(^3).mol(^{-1})</th>
<th>(V_5) m(^3).mol(^{-1})</th>
<th>(V_6) m(^3).mol(^{-1})</th>
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<td>0.906</td>
<td>0.004</td>
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</table>
TABLE (A1.8.2) (Continued)

c) Method 3, using

\[ 10^6 \times V^E = \sum_{i=1}^{n} \alpha_i \alpha_j V_{k} (\alpha_i - \alpha_j) \alpha_i^{-1} / (1 - k(\alpha_i - \alpha_j)) \]

<table>
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<tr>
<th>(V_1)</th>
<th>(V_2)</th>
<th>(V_3)</th>
<th>(V_4)</th>
<th>(V_5)</th>
<th>(k)</th>
<th>RMS</th>
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d) Method 4, using

\[ 10^6 \times V^E = \sum_{i=1}^{n} V_{ij} \phi_i \]

where the \(\phi_i\) are suitably chosen orthogonal polynomials

<table>
<thead>
<tr>
<th>(V_1)</th>
<th>(V_2)</th>
<th>(V_3)</th>
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<td>-0.304</td>
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</table>
3.3 DISCUSSION

It is interesting to compare the excess enthalpies of mixing for the three systems: water + t-butanol, water + acetonitrile and carbon tetrachloride + acetonitrile (97, 103, 117-119) which are shown in Fig (A1.8.4). The enthalpy of mixing for the system: carbon tetrachloride + acetonitrile is endothermic throughout the composition range and is typical of a system composed of a polar and non-polar liquid. With t-butanol + water the excess enthalpy of mixing varies markedly with composition being exothermic in the water rich region and endothermic in the alcohol rich region. The excess enthalpy of mixing for the system: water + acetonitrile is predominantly endothermic with a small exothermic inversion in the highly aqueous region. This behaviour together with the negative excess volume of mixing at low acetonitrile concentration indicate that either water-water interactions are being enhanced or that hydrogen bonding between the water and acetonitrile is occurring. Infra-red spectroscopy revealed that water-water interactions were the dominant effect with tertiary butanol + water mixtures (51) but with acetonitrile + water mixtures the spectroscopic evidence suggest that hydrogen bonding between water and acetonitrile is the dominant effect. With t-butanol + water the partial molar volume passes through a pronounced minimum at low alcohol concentration which is interpreted in terms of enhanced water-water interaction and the absence of such a minimum with acetonitrile + water mixtures would support the view that water-water interactions are not the dominant feature in this case. This is contrary to the usual behaviour of aqueous
Heats of mixing at 25°C for mixtures of
(a) methyl cyanide and carbon tetrachloride
(b) methyl cyanide and acetone, (c) methyl cyanide
and water, (d) t.-butylalcohol and water.

Fig (AI. 8.4)
solution but the argument is consistent with the observed excess enthalpy (51) and excess volume of mixing, as water structure is being broken down.

With such a balance of forces it would appear likely that there may be a tendency to phase separation (51) and this is observed as an upper critical solution temperature at 272.15 K. This tendency to phase separation is reflected in the intense sound absorption and the compositions at which the maxima in the sound absorption and in the critical solution temperature curves occur are in good agreement. The sound absorption increases rapidly as the temperature approaches the critical value but with tertiary butyl alcohol the system is characterised by a lower critical solution temperature and the sound absorption appears to be more closely related to the behaviour of the partial molar volume.

Much weight has been placed on the theory of ultrasonic sound absorption in recent years (120, 121). The two principal approaches may be summarised as that due to Fixman on the one hand and that due to Romanov on the other. An attempt has been made in these laboratories to describe the behaviour of the acetonitrile + water system in terms of the Romanov Model using thermodynamic data obtained here (51, 122) and from the literature. The results of this analysis (123) have been surprisingly effective in predicting the behaviour towards ultrasonic sound both for the acetonitrile + water system and also for the t-butanol system. The analysis depends upon the second derivatives of the enthalpy, Gibbs Function and volume of mixing and the need here is for extremely accurate thermodynamic data which is capable of undergoing double differentiation with respect to composition.
APPENDIX II

INVESTIGATION OF THE CELL

\[ \text{Cd} / \text{CdCl}_2 \text{ in formamide} / \text{AgCl} / \text{Ag} \]

IN TERMS OF COMPLEX FORMATION
This cell was studied as one of a number of investigations of the behaviour of various electrolytes in formamide carried out in these laboratories by Drs. B.L. Muju and S. Dhabanandana (124, 125). This particular cell was studied with the aim of determining the standard potential of the cadmium electrode in formamide and also the solubility product of cadmium chloride, which is slightly soluble in formamide. The present author's contribution to this work consisted of writing appropriate computer programs and formulating suitable procedures to analyse the experimental results.

This cell has been studied using various solvents instead of formamide (126 – 130). Heiley and Amis, who studied the cell using various compositions of water and ethanol as solvent, determined the standard electrode potentials by assuming that the dissociation of cadmium chloride can be represented by

\[ \text{CdCl}_2 \rightarrow \text{CdCl}^+ + \text{Cl}^- \quad (A2.1.1) \]

and

\[ \text{CdCl}^+ \rightarrow \text{Cd}^{2+} + \text{Cl}^- \quad (A2.1.2) \]

They were able to derive a suitable equilibrium constant for the second dissociation and thus obtain a reliable method for determining \( E^0 \).
Muju (125) attempted to interpret his experimental results in terms of complete dissociation, assuming that the higher dielectric constant of formamide than water would favour complete dissociation. This failed to produce a straight line graph and $E^o$ could not be determined from the resulting curve.

It was then decided to attempt to interpret the results in terms of equilibria describing partial dissociation in the manner described by Hefley and Amis (126). The method will be briefly described together with the results obtained.

The cell reaction can be expressed by

$$ \text{Cd} + 2 \text{AgCl} \rightleftharpoons 2 \text{Ag} + \text{Cd}^{2+} + 2 \text{Cl}^- \quad (A2.2.1) $$

and therefore the E.M.F. of the cell, $E$, by the expression

$$ E = E^o - \frac{RT}{2F} \ln \frac{m_{\text{Cd}^{2+}} \cdot m_{\text{Cl}^-}^2 \cdot Y_\pm^3}{m_A} \quad (A2.2.2) $$

where $E^o$ is the standard E.M.F., $F$ is the Faraday, $m_A$ is the molality of species $A$ and $Y_\pm$ is the mean ionic activity coefficient.

If the dissociation of cadmium chloride is assumed to follow the pattern proposed by Hefley and Amis then if the overall
composition of the solution expressed in terms of the molality of cadmium chloride is \( m \), then the equilibrium concentration of the various ions in solution is

\[
m_{\text{Cd}^{2+}} = \alpha m \quad \text{and} \quad m_{\text{Cl}^-} = m (1 + \alpha) \quad \text{and} \quad m_{\text{CdCl}^+} = m (1 - \alpha)
\]

where \( \alpha \) is the degree of dissociation for the equilibrium described in equation (A2.1.2). The equilibrium constant, \( K \), associated with this equilibrium can therefore be written

\[
K = \frac{\alpha m (1 + \alpha)}{(1 - \alpha)} Y_{\text{Cd}^{2+}}
\]

(A2.2.3)

assuming that \( Y_{\text{Cl}^-} = Y_{\text{CdCl}^+} \), or alternatively we can write

\[
\alpha = \frac{-\left(1 + \frac{K}{m Y_{\text{Cd}^{2+}}}ight) + \sqrt{(1 + \frac{K}{m Y_{\text{Cd}^{2+}}})^2 + 4 \frac{K}{m Y_{\text{Cd}^{2+}}}}}{2}
\]

(A2.2.4)

In order that we may calculate the activity coefficients it is necessary to determine the ionic strength, \( I \), and for this system

\[
I = \sum_i 0.5 m_i z_i^2 = m (2 \alpha + 1)
\]

(A2.2.5)

and we may write for the activity coefficient of \( \text{Cd}^{2+} \), \( Y_{\text{Cd}^{2+}} \)
\[ \log Y_{cd^*} = -A \frac{Z_{cd^*}}{1 + \sqrt{I}} \frac{\sqrt{I}}{1 + \sqrt{I}} = -4A \frac{\sqrt{I}}{1 + \sqrt{I}} \]  

(A2.2.6)

and for \( Y_\pm \)

\[ \log Y_\pm = -A |z_+| \frac{1}{1 + \sqrt{I}} \sqrt{I} + BI \]

\[ = -2A \frac{\sqrt{I}}{1 + \sqrt{I}} + BI \]  

(A2.2.7)

where \( A \) is the Debye-Hückel constant for formamide and \( B \) is a constant.

Using these equations in equation (2) we can write

\[ E = E^0 - \frac{RT}{2F} \sum \alpha m^3(1+\alpha)^2 + \frac{3 \times 2.3026RT}{F} \frac{A\sqrt{I}}{1 + \sqrt{I}} \]

\[ - \frac{3 \times 2.3026RT}{2F} BI \]  

(A2.2.7)

or

\[ E + \frac{RT}{2F} \left\{ \sum \alpha m^3(1+\alpha)^2 - 6 \times 2.3026A\sqrt{I} \right\} = E^0 - \frac{3 \times 2.3026RT}{2F} BI \]  

(A2.2.8)

and if \( \alpha \) and \( I \) are known at various values of \( E \) and \( m \), a plot of \( E' = E + \frac{RT}{2F} \left\{ \sum \alpha m^3(1+\alpha)^2 - 6 \times 2.3026A\sqrt{I} \right\} \) against \( I \)
should be a straight line of gradient \( -\frac{3 \times 2.3026RT}{2F} \). B and intercept \( E^o \).

This depends only upon \( K \) but to include \( K \) in a curve fitting procedure would render the equations very complex and as the second derivatives are in general non-zero the fit would require many cycles. The following procedure was therefore used:

1) A value of \( K \) was chosen and at each experimental point the associated value of \( \alpha \) was determined from equation (4) by assuming that \( Y_{Cd^+} = 1 \).
2) The resulting value of \( \alpha \) was used to determine the ionic strength, \( I \), at each experimental composition from equation (5).
3) The value of \( Y_{Cd^+} \) was then determined for each measurement by using equation (6).
4) Then values of \( \alpha \) and \( I \) were redetermined with the aid of equations (4) and (5).
5) The values of \( \alpha \) and \( I \) were tested for consistency. If this had been achieved the calculation continued, but if it failed the processes (3), (4) and (5) were repeated until consistency was achieved.
6) For each experimental composition the function \( E' \) was determined and the intercept of the best straight line through a plot of \( E' \) against \( I \) (that with the lowest R.M.S. deviation) was taken as a measure of \( E^o \).
7) The process was repeated for various values of \( K \) with the object of obtaining the best fit.
In this section the computer program described above is presented in reference Algol 60.

```algol
begin integer N;
real procedure sum(X,N);
integer N;
real array X;
begin real S;
    integer I;
    S:=0;
    for I:=1 step 1 until N do
        S:=S+X[I];
    sum:=S
end of procedure sum;

real procedure sumprod (X,Y,N);
integer N;
real array X,Y;
begin integer I;
    real SP;
    SP:=0;
    for I:=1 step 1 until N do
        SP:=SP+X[I]*Y[I];
    sumprod:=SP
end of procedure sumprod;

real procedure det2(A,B);
real array A,B;
```
read N;
begin integer I;
    real AC,A1,A2,A3,Z1,R,T,K,APPAL,IOS,GAMMA,Z,ALPHA,K1,C1,G;
    real array E,M,IO,Y,DEV[1:N],A,B,C[1:2];
read AC,A1,A2,A3,R,T;
for I:=1 step 1 until N do
read E[I],M[I];
for Z1:=A1 step A2 until A3 do
begin K1:=10^Z1;
    for I:=1 step 1 until N do
    begin APPAL:=0.5*(-(1+K/M[I])
        +SQRT(((1+K/M[I])^2+4*K/M[I])));
    IOS:=M[I]*(1+2*APPAL);
    L:=GAMMA:=10^(-4*AC*SQRT( IOS)/(1+SQRT(IOS)));
    Z:=K/(M[I]*GAMMA);
    ALPHA:=0.5*(-(1+Z)+SQRT((1+Z)^2+4*Z));
    IO[I]:=M[I]*(1+2*ALPHA);
    if ABS(IO[I]-IOS)<1.0E-6
    then begin K1:=R*T*0.5/96500;
        Y[I]:=E[I]+K1*(LN(ALPHA)*
        (1+ALPHA)^2*M[I]^3)-6*2.3026*
        AC*SQRT(IO[I]))
        end
    else begin IOS:=IO[I];
go to L
    end
end I;
The program and the method was tested by repeating the calculations of Hefley and Amis (120) using their measurements with water as solvent. The results obtained are shown in Table (A2.4.1) and are in satisfactory agreement with the original data.

The program was then used to attempt to interpret the experimental data of B.L. Muju. The results obtained are shown in
TABLE (A2.4.1)
RE-ANALYSIS OF THE DATA OF HEFLEY AND AMIS

SOLVENT: PURE WATER
TEMPERATURE: 298.15 K
EQUILIBRIUM CONSTANT (K) GIVING THE BEST STRAIGHT LINE = 0.1 mol.kg$^{-1}$
STANDARD POTENTIAL ($E^0$) OF THE CELL = 0.5735 V

<table>
<thead>
<tr>
<th>m/mol.kg$^{-1}$</th>
<th>E/V</th>
<th>I/mol.kg$^{-1}$</th>
<th>$E'/V$</th>
<th>$\Delta E'/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>0.8539</td>
<td>0.0014</td>
<td>0.5738</td>
<td>0.0004</td>
</tr>
<tr>
<td>0.0010</td>
<td>0.8300</td>
<td>0.0027</td>
<td>0.5739</td>
<td>0.0004</td>
</tr>
<tr>
<td>0.0020</td>
<td>0.8070</td>
<td>0.0052</td>
<td>0.5737</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.7785</td>
<td>0.0116</td>
<td>0.5733</td>
<td>-0.0002</td>
</tr>
<tr>
<td>0.0029</td>
<td>0.7971</td>
<td>0.0018</td>
<td>0.5753</td>
<td>0.0018</td>
</tr>
<tr>
<td>0.0009</td>
<td>0.8345</td>
<td>0.0024</td>
<td>0.5733</td>
<td>-0.0002</td>
</tr>
<tr>
<td>0.0065</td>
<td>0.7707</td>
<td>0.0145</td>
<td>0.5733</td>
<td>-0.0002</td>
</tr>
<tr>
<td>0.0070</td>
<td>0.7686</td>
<td>0.0154</td>
<td>0.5732</td>
<td>-0.0003</td>
</tr>
<tr>
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<td>0.7585</td>
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<td>0.5730</td>
<td>-0.0005</td>
</tr>
<tr>
<td>0.0103</td>
<td>0.7579</td>
<td>0.0213</td>
<td>0.5722</td>
<td>-0.0013</td>
</tr>
<tr>
<td>0.0162</td>
<td>0.7466</td>
<td>0.0311</td>
<td>0.5741</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.0200</td>
<td>0.7398</td>
<td>0.0371</td>
<td>0.5728</td>
<td>-0.0008</td>
</tr>
<tr>
<td>0.0500</td>
<td>0.7174</td>
<td>0.0802</td>
<td>0.5736</td>
<td>-0.0003</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.7018</td>
<td>0.1457</td>
<td>0.5745</td>
<td>0.0004</td>
</tr>
</tbody>
</table>
Table (A2.4.2) and it can be seen that there is no value of $K$ for which a satisfactory straight line can be derived. As the variation of $E'$ with $K$ depends upon the equilibria postulated it was necessary to reconsider the basic assumption.

6A2.5 INTERPRETATION IN TERMS OF CdCl$_4^{2-}$ COMPLEXES

In order to explain the behaviour of this cell it was considered feasible that interpretation in terms of the higher complexes of cadmium and chlorine may be more suitable. We therefore postulate that dissociation of cadmium chloride in formamide occurs according to the mechanism

$$2 \text{CdCl}_2 \rightarrow \text{Cd}^{2+} + \text{CdCl}_4^{2-} \quad (A2.5.1)$$

$$\text{CdCl}_4^{2-} \rightleftharpoons \text{Cd}^{2+} + 4 \text{Cl}^- \quad (A2.5.2)$$

If the overall quantity of ions in solution expressed in terms of the molality of cadmium chloride is $m$, then writing the degree of dissociation as $\alpha$ we find

$$m_{\text{Cd}^{2+}} = \frac{m}{2} [1 + \alpha], \quad m_{\text{CdCl}_4^{2-}} = \frac{m}{2} [1 - \alpha], \quad m_{\text{Cl}^-} = \lambda m \alpha$$
TABLE (A2.4.2)
ANALYSIS OF MUJU'S RESULTS IN TERMS OF CdCl₂ COMPLEXES

SOLVENT: PURE FORMAMIDE
TEMPERATURE: 298.15 K
EQUILIBRIUM CONSTANT, $K = 10^{-9}$ mol kg⁻¹
STANDARD POTENTIAL OF THE CELL, $E^₀ = 0.4058$ V

<table>
<thead>
<tr>
<th>m/mol kg⁻¹</th>
<th>E/V</th>
<th>I/mol kg⁻¹</th>
<th>E'/V</th>
<th>ΔE'/V</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.9443</td>
<td>0.0001</td>
<td>0.4121</td>
<td>0.0062</td>
</tr>
<tr>
<td>0.0002</td>
<td>0.9125</td>
<td>0.0002</td>
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</tr>
<tr>
<td>0.0004</td>
<td>0.8970</td>
<td>0.0004</td>
<td>0.4001</td>
<td>-0.0059</td>
</tr>
<tr>
<td>0.0006</td>
<td>0.8875</td>
<td>0.0006</td>
<td>0.4010</td>
<td>-0.0051</td>
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<tr>
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<td>0.8770</td>
<td>0.0010</td>
<td>0.4037</td>
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</tr>
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<td>0.0014</td>
<td>0.4054</td>
<td>-0.0009</td>
</tr>
<tr>
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<td>0.8650</td>
<td>0.0018</td>
<td>0.4065</td>
<td>0.0008</td>
</tr>
<tr>
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<td>0.8624</td>
<td>0.0020</td>
<td>0.4071</td>
<td>0.0007</td>
</tr>
<tr>
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<td>0.8585</td>
<td>0.0024</td>
<td>0.4072</td>
<td>0.0007</td>
</tr>
<tr>
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<td>0.8550</td>
<td>0.0028</td>
<td>0.4073</td>
<td>0.0007</td>
</tr>
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</tr>
<tr>
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<td>0.8510</td>
<td>0.0034</td>
<td>0.4093</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.0036</td>
<td>0.8500</td>
<td>0.0036</td>
<td>0.4091</td>
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</tr>
<tr>
<td>0.0040</td>
<td>0.8475</td>
<td>0.0040</td>
<td>0.4089</td>
<td>0.0019</td>
</tr>
<tr>
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<td>0.8451</td>
<td>0.0044</td>
<td>0.4100</td>
<td>0.0029</td>
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<tr>
<td>0.0046</td>
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</tr>
<tr>
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<td>0.8380</td>
<td>0.0060</td>
<td>0.4106</td>
<td>0.0030</td>
</tr>
<tr>
<td>m/mol·kg⁻¹</td>
<td>E/V</td>
<td>I/mol·kg⁻¹</td>
<td>E'/V</td>
<td>ΔE'/V</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>------------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>0.0068</td>
<td>0.8350</td>
<td>0.0068</td>
<td>0.4098</td>
<td>0.0020</td>
</tr>
<tr>
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<td>0.0070</td>
<td>0.4104</td>
<td>0.0025</td>
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<td>0.8295</td>
<td>0.0080</td>
<td>0.4103</td>
<td>-0.0021</td>
</tr>
<tr>
<td>0.0090</td>
<td>0.8251</td>
<td>0.0090</td>
<td>0.4072</td>
<td>-0.0012</td>
</tr>
<tr>
<td>0.0100</td>
<td>0.8225</td>
<td>0.0100</td>
<td>0.4085</td>
<td>-0.0027</td>
</tr>
<tr>
<td>0.0110</td>
<td>0.8200</td>
<td>0.0110</td>
<td>0.4094</td>
<td>0.0004</td>
</tr>
<tr>
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<td>0.0120</td>
<td>0.4063</td>
<td>-0.0030</td>
</tr>
<tr>
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<td>0.8150</td>
<td>0.0130</td>
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<td>-0.0029</td>
</tr>
<tr>
<td>0.0140</td>
<td>0.8125</td>
<td>0.0140</td>
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<td>-0.0031</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.8107</td>
<td>0.0200</td>
<td>0.4125</td>
<td>0.0009</td>
</tr>
</tbody>
</table>
and the equilibrium constant, $K$, for the equilibrium proposed in (2) can be expressed by

$$K = \frac{16 m^4 \alpha^4 (1 + \alpha)}{(1 - \alpha)} \cdot Y^4_{Cl^-} \quad (A2.5.3)$$

assuming that $Y_{cd^{2+}} = Y_{cdCl^{2-}}$

It is now necessary to determine $\alpha$ in terms of $K$ and as the equation involves the fifth power of $\alpha$ this has been done numerically. When $\alpha$ is employed later it is the result of this numerical calculation which is implied. The ionic strength, $I$, may be determined and for the equilibria postulated we find

$$I = \frac{1}{2} \sum_m m \cdot z^2 = m(2 + \alpha) \quad (A2.5.4)$$

and therefore we can determine the activity coefficients

$$\log Y_{Cl^-} = \frac{-A \sqrt{I}}{1 + \sqrt{I}} \quad (A2.5.5)$$

and

$$\log Y_\pm = \frac{-2A \sqrt{I}}{1 + \sqrt{I}} + B I \quad (A2.5.6)$$

Substituting these equations into equation (A2.2.2) as required we find
\[
E' = E + \frac{RT}{2F} \left\{ \ln 2m^3a^2(1+\alpha) - \frac{b \times 2.3026 A \sqrt{T}}{1 + \sqrt{T}} \right\}
\]

\[
= E^0 - \frac{3 \times 2.3026 RT}{2F} B I
\]  

(A2.5.7)

where, if \( K \) describes the system adequately, we should find that a plot of \( E' \) against \( I \) will be a straight line the intercept of which is \( E^0 \).

The procedure involved in the computer calculation is analogous to that described in Section (2) and will not be described again.

A2.6 THE SECOND COMPUTER PROGRAM

The computer program written to interpret the behaviour of the cell in terms of \( CdCl_4^{2-} \) complex ions will be described here and is basically similar to that presented in Section (3). However the equation (A2.5.3) requires numerical solution since it does not factorize easily. The method of Newton is employed here and although it is standard applied mathematics it will be outlined for completeness. Consider writing \( \frac{K}{16 m^4 \gamma_{4+}} = Z \) then

\[
Z = \alpha^4 (1+\alpha)/(1-\alpha)
\]  

(A2.6.1)

and
\[ \frac{dZ}{d\alpha} = \frac{\alpha^3}{(1-\alpha)^2} \left[ (5\alpha + 4)(1-\alpha) + \alpha (1 + \alpha) \right] = 0 \]  
(\text{A2.6.2})

when

\[ \alpha = (1 \pm \sqrt{7})/4 \quad \text{or} \quad 0 \]

then in the range  \( 0 < \alpha < 1 \), \( Z \) does not show a turning point. Also as \( \alpha \to 1 \), \( Z \to \infty \). If we require \( \alpha \) to five significant figures then when \( \alpha = 0.99999 \) we find \( Z = 2 \times 10^5 \), therefore with \( Z \) greater than \( 2 \times 10^5 \) we can assume \( \alpha = 1 \) without error.

The Newton method converges rapidly for a function without turning points and relies upon the derivative of the function being defined, and this is certainly true in the interval \( 0 < \alpha < 1 \).

Consider as a first approximation a value \( \overline{\alpha} \). Then from equation (\text{A2.6.1}), we can determine the corresponding \( Z = \overline{Z} \), and from equation (\text{A2.6.2}) the value of the derivative at \( \overline{\alpha} = \frac{dZ}{d\alpha}(\overline{\alpha}) \).

Applying Taylor's theorem

\[ \left( f(a + h) = f(a) + hf'(a) + h^2 f''(a)/2! + \cdots \right), \]

using only one derivative we find that the value of \( \alpha \) predicted by any \( Z \) is

\[ \alpha = \overline{\alpha} + (Z - \overline{Z}) \left/ \frac{dZ}{d\alpha}(\overline{\alpha}) \right. \]  
(\text{A2.6.3})
The process is then repeated until successive values of \( \alpha \) do not change. The computer program will now be given, in reference Algol 60:

\[
\text{begin integer } N; \\
\text{real procedure sum}(X,N); \\
\text{integer } N; \\
\text{real array } X; \\
\text{begin real } S; \\
\text{integer } I; \\
S:=0; \\
\text{for } I:=1 \text{ step 1 until } N \text{ do} \\
S:=S+X[I]; \\
\text{sum}:=S \\
\text{end;} \\
\text{real procedure sumprod}(X,Y,N); \\
\text{integer } N; \\
\text{real } X,Y; \\
\text{begin integer } I; \\
\text{real } S; \\
S:=0; \\
\text{for } I:=1 \text{ step 1 until } N \text{ do} \\
S:=S+X[I]*Y[I]; \\
\text{sumprod}:=S \\
\text{end;} \\
\text{real procedure det2}(A,B); \\
\text{real array } A,B; \\
\text{real procedure alpha}(Z);
real Z;
begin real X,X1,P,D;
X1:=0;
if Z>2.0 then begin X1:=1;
goto L1
end;
for X:=0.1 step 0.1 until 0.91 do
begin P:=X^4*(1+X)/(1-X);
if P>Z then goto L
end;
X:=0.99999;
L1:P:=X^4*(1+X)/(1-X);
D:=(X^3*(5*X+4)+P)/(1-X);
X1:=X+(Z-P)/D;
if ABS(X-X1)\leq 8 then begin X:=X1;
goto L
end
else goto L1;
L1:alpha:=X1
end;
read N;
begin integer I;
real AC,A1,A2,A3,Z1,R,T,K,IOS,GAMMA,Z,ALF,K1,G,C1;
real array E,M,Y,IO,DEV[1:N],A,B,C[1:2];
read AC,A1,A2,A3,R,T;
for I:=1 step 1 until N do
read E[I],M[I];
for Z1:=A1 step A2 until A3 do
begin K:=10^Z1;
print K;
for I:=1 step 1 until N do
begin
  GAMMA:=1;
  IOS:=0;
  L1:Z:=K/((M[I]*GAMMA)^4);
  ALF:=alpha(Z);
  IO[I]:=M[I]*(2+ALF);
  GAMMA:=SQRT(IO[I]);
  GAMMA:=-AC*GAMMA/(1+GAMMA);
  if ABS(IO[I]-IOS)<1.0^-6 then begin
    K1:=0.5*R*T/96500;
    Y[I]:=E[X]+K1*(LN
      (2*M[I]^3*ALF^2*(1+ALF))+
      6*2.3026*GAMMA)
  end
else begin
  IOS:=IO[I];
  GAMMA:=10^GAMMA;
  go to L1
end;
print Z,ALF,GAMMA
end;
A[1]:=B[2]:=sum(IO,N);
A[2]:=sumprod(IO,IO,N);
B[1]:=N;
C[1]:=sum(Y,N);
C[2]:=sumprod(Y,IO,N);
G:=det2(B,C)/det2(A,B);
C1:=-det2(A,C)/det2(A,B);
print K,C1,G;
for \( I = 1 \) step 1 until \( N \) do
begin \( \text{DEV}[I] = y[I] - (G \cdot IO[I] + C1) \);
        print \( \text{DEV}[I], y[I], IO[I], E[I], M[I] \)
end;
\( G = \sqrt{\text{sumprod}(\text{DEV}, \text{DEV}, N)/N} \);
print \( G \)
end
end;

\( A2.7 \) USING THE PROGRAM DESCRIBED IN \( A2.6 \)

The program was used to obtain a fit on B.L. Mju's data. Initially all the experimental points were studied and suitable trial values of \( K \) were supplied until the value which produced a minimum was found. In Fig (A2.7.1) a plot of the observed E.M.F. against \( M \) is shown and in Table (A2.7.1) that section of computer output which gave the minimum R.M.S. deviation is shown.

The final point was excluded since it is likely to have a considerable tolerance owing to being a saturated solution and the data re-run. The results are shown in Table (A2.7.2).

The fit to the experimental points is extremely good and within the experimental error which exists on the measurements as can be seen from Fig (A2.7.1). The intercept yields the value of \( E^o \) of 0.614 volts which does not change markedly with \( K \).
E.m.f. of Cell III at 25°C plotted against the cadmium chloride molality.

\[ \text{E.m.f. (volts)} \]

\[ m/(\text{mole/kg}) \]

**Fig (A2.7.1)**
TABLE (A2.7.1)
ANALYSIS OF MUJU'S DATA IN TERMS OF CdCl₂ COMPLEXES

SOLVENT: PURE FORMAMIDE
TEMPERATURE: 298.15 K
EQUILIBRIUM CONSTANT = $5.0 \times 10^{-13}$ mol$^4$ kg$^{-4}$
STANDARD POTENTIAL OF THE CELL = 0.6140 V

<table>
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<tr>
<th>m/mol·kg$^{-1}$</th>
<th>E/V</th>
<th>I/mol·kg$^{-1}$</th>
<th>E'/V</th>
<th>ΔE'/V</th>
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R.M.S. DEVIATION = $\sqrt{\frac{\sum(\Delta E')^2}{N}} = 0.0035$
TABLE (A2.7.2)

ANALYSIS OF MITJU'S DATA IN TERMS OF Cd Cl₄⁻ COMPLEXES

SOLVENT: PURE FORMAMIDE

TEMPERATURE: 298.15 K

EQUILIBRIUM CONSTANT = 3.2 x 10⁻¹³ mol⁴ kg⁻⁴

STANDARD POTENTIAL OF THE CELL = 0.6137 V

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R.M.S. DEVIATION = \( \sqrt{\frac{\sum(ΔE')^2}{N}} = 0.0024 \)
APPENDIX III

COMPUTER PROGRAMS
AND PROCEDURES
In this appendix details of the computer programs which have been used in the work on binary mixtures are given. In many cases only the procedures are given as the full programs are unnecessarily long. In such cases the programs are of a trivial nature and were in practice written for each job to call the required procedures. The language used here is reference Algol 60.

\[ A3.1 \text{ PROCEDURES RELATING TO EXCESS VOLUME OF MIXING: } V^E \text{ AND EXCESS PARTIAL MOLAR VOLUMES} \]

a) Mole Fraction from Weight Fraction.

procedure MFFWF(W,N,MA,MB,X,WRITE);

integer N;
real MA,MB;
real array W,X;
boolean WRITE;

begin comment the N values of the weight fraction of species A are stored in the array W and MA and MB hold the values of the molecular weights of A and B respectively. The boolean variable Write controls the printing out of the derived mole fractions which are stored in the array X;

integer I;

for I:=1 step 1 until N do

begin 
X[I]:=W[I]*MB/(MA+W[I] *(MB-MA));

if WRITE then print W[I],X[I]
end I

end of procedure MFFWF;
b) Excess Volume from Density Measurements

```plaintext
procedure EVFDM(X,P,N,MA,MB,VE,WRITE);
    integer N;
    real MA,MB;
    real array X,P,VE;
    boolean WRITE;
    begin comment refering to the pure components as A and B the N
density measurements are stored in the array P in such a way
that P[1] is the density of pure A and P[N] is the density of
pure B. The mole fractions of species A are stored in the
array X in the same order. The boolean variable WRITE controls
the print out of the results which are stored in the array VE;
    integer I;
    for I=1 step 1 until N do
        begin VE[I]:=X[I]*MA*(1/P[I]-1/P[N])+
            (1-X[I])*MB*(1/P[I]-1/P[1]);
            if WRITE then print X[I],P[I],VE[I]
        end I
    end of procedure EVFDM;
```

c) Relative Partial Molar Volumes from Excess Volume Data by
drawing a parabola through successive groups of three points.

```plaintext
procedure RPMVFVND(X,VE,N);
    integer N;
    real array X,VE;
    begin comment the N values of mole fraction and corresponding
    excess volumes are stored in the arrays X and VE;
    integer I,J,M;
    real A,B,C,D,V1,V2;
```
real array T,U,V,W[1:3];
real procedure DET3(D,E,F);
real array D,E,F;
for I:= 2 step 1 until N-1 do
end for M:=1 step 1 until 3 do
   begin J:=I+M-2;
   T[M]:=X[J]*X[J];
   U[M]:=X[J];
   V[M]:=1;
   W[M]:=VE[J];
   end M;
D:=DET3(T,U,V);
if D(1,0)=12 then go to L;
A:=DET3(U,V,W)/D;
B:=-DET3(T,V,W)/D;
C:=DET3(T,U,W)/D;
V1:=C-A*X[I]*X[I];
V2:=V1+B+2*X[I]*A;

comment the values of the relative partial molar volumes at X[I] are now stored in V1 and V2;
print X[I],VE[I],V1,V2;
L: end I

end of procedure RPMVFEVD;
3.2 CURVE FITTING PROCEDURES FOR EXCESS THERMODYNAMIC FUNCTION DATA.

a) Using the function \( \chi^E / \chi \sim \sum_{i=1}^{n} A_i (x_i - x) \).

procedure CFFXEF(X,XE,W,N,K);
integer N,K;
real array X,XE,W;
begin comment N is the number of experimental points included and K is the number of parameters required. The experimental data is stored in the arrays X and XE, X being the mole fraction of one species and XE the corresponding value of the excess function. W contains the weighting of each point;
integer I,J;
real array Y,Z,DEV,DIF,P,P1,V1,V2,U[1:N];
real RMS,STD;
real array A[1:K,1:K],B,C[1:K,1:1];
real procedure SUM(A,K,N);
value K;
integer N,K;
real array A;
begin integer I;
real S;
S:=0;
for I:=1 step 1 until N do
S:=S+A[I] \uparrow K;
comment S now contains the sum of all the A[I] \uparrow K;
SUM:=S
end of real procedure SUM;
real procedure SUMPROD(A,B,K,N);
value K;
integer N,K;
real array A,B;
begi...=0;
for I:=1 step 1 until N do
S:=S+A[I]*B[I]*K;
comment S now contains the required sum of the products;
SUMPROD:=S
end of real procedure SUMPROD;
for I:=1 step 1 until N do
begin Y[I]:=X*[(I)*(1-X[I])]*W[I]*W[I];
Z[I]:=1-2*X[I];
U[I]:=1/(W[I]*W[I])
end I;
for I:=1 step 1 until K do
begin B[I,1]:=SUMPROD(Y,Z,I-1,N);
for J:=1 step 1 until K do
A[I,J]:=SUMPROD(U,Z,I+J-2,N)
end I;
UNSYMDET(K,2,0;37,A,RMS,I,C,FAIL);
UNSYMBSOL(K,1,A,C,B);
comment UNSYMDET and UNSYMBSOL are library procedures used to solve the K simultaneous equations. The solution is written into the array B;
for I:=1 step 1 until N do
begin for J:=1 step 1 until K do
\( \begin{align*}
\text{begin} & \quad P[J]=B[J,1]*Z[I]^{(J-1)}; \\
& \quad P_{1}[J]=(J-1)*B[J,1]*Z[I]^{(J-2)} \\
\text{end} \ J; \\
\text{DIFF}[I]=Z[I]*\text{SUM}(P,1,K)-2*X[I]*(1-X[I])^{*}\text{SUM}(P_{1},1,K); \\
V_{1}[I]=X[I]*(1-X[I]) \quad \star \text{SUM}(P,1,K)-X[I]*\text{DIFF}[I]; \\
V_{2}[I]=V_{1}[I]+\text{DIFF}[I]; \\
\text{DEV}[I]=\text{XE}[I]-X[I] \quad \star (1-X[I])^{*}\text{SUM}(P,1,K) \\
\text{end} \ I; \\
\text{RMS}=\sqrt{\text{SUM} (\text{DEV},2,N)/N}; \\
\text{STD}=\sqrt{N*\text{RMS}^{2}/(N-K)}; \\
\text{print} \ K; \\
\text{for} \ I=1 \ \text{step} \ 1 \ \text{until} \ K \ \text{do} \\
\text{print} \ B[I,1]; \\
\text{print} \ \text{RMS,STD}; \\
\text{for} \ I=1 \ \text{step} \ 1 \ \text{until} \ N \ \text{do} \\
\text{print} \ X[I],XE[I],\text{DEV}[I],V_{1}[I],V_{2}[I]; \\
\text{go to} \ L; \\
\text{FAIL: print 'UNSYMDT FAILED'}; \\
\end{align*} \)

L: end of procedure CFFXEF;

b) Using the function \( X^{E} = \sum_{j=1}^{n} x_{i} x_{j} A_{i} (x_{i} - x_{j})^{i-j} \)

\text{procedure} C2FFXE(X,XE,W,N,K); \\
\text{integer} N,K; \\
\text{real array} X,XE,W; \\
\text{begin} \ \text{comment} \ K \text{ is the number of parameters with which the} N \text{ points} \\
\text{are to be fitted. The experimental data is stored in the arrays} \\
X \text{ and XE, X-containing the compositions and XE the values of} \\
\text{the particular excess function. The array W contains the} \\
\text{statistical weighting of each experimental point;}
integer I,J;
real array Z,Y,U,V1,V2,DEV[1:N],P,P1[1:K],A[1:K,1:K],
B,C[1:K,1:1];
real RMS,STD,X2,V,S,DIFF;
comment real procedures SUM and SUMPROD must also be declared here;
for I:=1 step 1 until N do
begin X2:=1-X[I];
   V:=W[I]*W[I];
   Z[I]:=X[I]-X2;
   X[I]:=X[I]*X2;
   U[I]:=Y[I]*X2/V;
   Y[I]:=Y[I]*Y[I]/V
end I;
for I:=1 step 1 until K do
begin B[I,1]:=SUMPROD(U,Z,I-1,N);
   for J:=1 step 1 until K do
      A[I,J]:=SUMPROD(Y1,Z,I+J-2,N)
end I;
UNSYMDET(K,2.0,-37,A,RMS,I,C,FAIL);
UNSYMSOL(K,1,A,C,B);
for I:=1 step 1 until N do
for J:=1 step 1 until K do
begin P[J]:=B[J,1]*Z[I]^((J-1));
   P1[J]:=(J-1)*B[J,1]*Z[I]^((J-2))
end J;
S:=SUM(P,1,K);
DIFF:=2*Y[I]*SUM(P1,1,K)-S*Z[I];
V1[I]:=X[I]*S-X[I]*DIFF;
\[ V_2[i] := V_1[i] + \text{DIFF}; \]
\[ \text{DEV}[i] := XE[i] - Y[i] \times S \]
\end{I;}
\]
\[ \text{RMS} := \sqrt{\text{SUM(DDEV,2,N)/N}}; \]
\[ \text{STD} := \sqrt{N \times \text{RMS} \times \text{RMS}/(N-K)}; \]
\]
\text{print K;}
\]
\text{for I := 1 step 1 until K do}
\]
\text{print B[I,1];}
\]
\text{print RMS,STD;}
\]
\text{for I := 1 step 1 until N do}
\]
\text{print X[I],XE[I],DEV[I],V1[I],V2[I];}
\]
\text{go to L;}
\]
\text{FAIL; print 'PROCEDURE UNSYMDET FAILED!';}
\]
\text{L: end of procedure C2FFXE;}\]
\]
\text{c) Using the function}
\]
\[ \chi^E = \sum_{i=1}^{n} x_i x_2 A_i (x_i - x_2)^{d-1} / (1 - k(x_i - x_2)) \]
\]
\text{procedure SCFFXE(X1,XE,W,N,SKEWED,PARAMETERS,XE12,VAL,K);}
\]
\text{integer N,PARAMETERS;}
\]
\text{real XE12,K;}
\]
\text{real array X1,XE,W,VAL;}
\]
\text{boolean SKEWED;}
\]
\text{begin comment PARAMETERS is the number of parameters to be}
\text{determined and these values are stored in the array}
\text{VAL, when the skewing parameter, K, is to be determined}
\text{the boolean variable SKEWED must be true. XE12 holds}
\text{the approximate value of } \chi^E \text{ for the equimolar}
\text{composition. The N experimental points are stored in}
\text{the arrays X1 and XE, compositions in the former and}
\text{the values of the excess function in the latter. The}
array W contains the statistical weighting of each experimental point;

integer MINUS,COUNT,PLUS,DIM,I,J;
real X,X2,Z,RMS,RMSLST,XEC,STD;
real procedure SUM(A,K,N);
value K,N;
integer K,N;
real array A;

begin integer I;
  real S;
  S:=0;
  for I:=1 step 1 until N do
    S:=S+A[I-K];
  SUM:=S
end of real procedure SUM;

real procedure SUMPROD(A,K,B,L,N);
value K,L,N;
integer K,L,N;
real array A,B;

begin integer I;
  real SP;
  SP:=0;
  for I:=1 step 1 until N do
    SP:=SP+A[I,K]*B[I,L];
  SUMPROD:=SP
end of real procedure SUMPROD;

MINUS:=PARAMETERS-1;
COUNT:=0;

if SKewed then DIM:=PARAMETERS
else DIM:=MINUS;

PLUS:=DIM+1;
print N, PARAMETERS;
begin real array R[1:N,1:1], DXEDVAL[1:N,0:0:DIM],
A[1:PLUS,1:PLUS], B,C[1:PLUS,1:1],
XECALC,FK[0:MINUS];
VAL[0]:=4*X2^12;
RMS:=0;
for I:=1 step 1 until N do
begin if I=MINUS then VAL[I]:=0;
    print X1[I],X2[I]
end I;
L2: for COUNT:=COUNT+1 do
begin print COUNT;
    for J:=0 step 1 until MINUS do
    print VAL[J];
    print K;
    for I:=1 step 1 until N do
    begin X2:=1-X1[I];
        Z:=X1[I]-X2;
        for J:=0 step 1 until MINUS do
        begin DXEDVAL[I,J]:=X1[I]*X2*
            Z*K/(1-K*Z)*W[I];
            XECALC[J]:=W[I]*VAL[J]*DXEDVAL[I,J];
            FK[J]:=X1[I]*X2*VAL[J]*
                Z*K/(1-K*Z)*K)
        end J;
        XEC:=SUM(XECALC,1,PARAMETERS);
        R[I,1]:=X2-XEC;
        print X1[I],X2[I],XEC,R[I,1];
        if SKEWED then DXEDVAL[I,DIM]=
\[ \text{SUM}(FK, \text{PARAMETERS})/w[i] \]

end I;

RMSLAST := RMS;
RMS := SQRT(SUMPROD(R, 1, R, 1, N)/N);
STD := SQRT(N*RMS*RMS/(N-PLUS));
print RMS, STD;

for X := 0 step 0.1 until 1.01 do
begin X2 := 1 - X;
    Z := X - X2;
    for J := 0 step 1 until MINUS do
        XECALC[J] := X2*VAL[J]*Z^J/(1-K*Z);
    XEC := SUM(XECALC, 1, PARAMETERS);
    print X, XEC
end X;

if ABS(RMS-RMSLAST)<1.0,10 then go to L;
for I := 1 step 1 until N do
    R[I, 1] := R[I, 1]/w[i];
for J := 1 step 1 until PLUS do
begin C[J, 1] := SUMPROD(R, 1, DXEDVAL, J-1, N);
    for I := 1 step 1 until PLUS do
        A[I, J] := SUMPROD(DXEDVAL, I-1, DXEDVAL, J-1, N)
end J;

UNSYMDET(PLUS, 2, 0.1, 37, A, X, I, B, L);
UNSYMSOL(PLUS, 1, A, B, C);

for J := 0 step 1 until MINUS do
    VAL[J] := VAL[J] + C[J+1, 1];
if SKewed then K := K + C[PLUS, 1];
if ABS(K)>10 then go to L;
go to L2
Using the function $X^E = \sum_{j=1}^{n} A_j \phi_j(x)$, where the $\phi_j$ are suitably chosen orthogonal polynomials.

**procedure C3FFXE(X1, XE, N, P, K);**

integer N, K;
real array X1, XE, P;

begin comment the K parameters are determined from the N points using the coefficients of the orthogonal polynomials which are stored in the K x K dimensional array P. The experimental data is stored in the arrays X1 and XE, compositions in X1 and the values of the excess function in XE;

integer I, J, L;
real R, Q;
real array A[1:K, 1:K], B, C[1:K, 1:1];
real procedure PHI(P, X1, L);
integer L;
real X1;
real array P;

begin comment the coefficients of the orthogonal polynomials are stored in the array P and X1 is some particular composition. The procedure computes the value of the polynomial having dimension L;

integer I;
real S;
S := 0;
for I := 1 step 1 until L do
\[ S := S + P[L, I] \times X_{1}^{I} \]  
\[ \text{PHI} := S \cdot (1 - X) \]  
\text{end of real procedure PHI;}

\text{for } I := 1 \text{ step 1 until } K \text{ do}
\begin{align*}
&\text{begin } B[I, 1] := 0; \\
&\text{for } J := 1 \text{ step 1 until } K \text{ do} \\
&\quad A[I, J] := 0
\end{align*}
\text{end for } I;

\text{for } L := 1 \text{ step 1 until } N \text{ do}
\text{for } I := 1 \text{ step 1 until } K \text{ do}
\begin{align*}
&\text{begin } B[L, 1] := B[L, 1] + X_{I} \times \text{PHI}(P, X_{1}^{I}, L); \\
&\text{for } J := 1 \text{ step 1 until } K \text{ do} \\
\end{align*}
\text{end for } I; \text{ end for } L;

\text{for } L := 1 \text{ step 1 until } K \text{ do}
\begin{align*}
&\text{begin for } J := 1 \text{ step 1 until } K \text{ do} \\
&\quad \text{print } A[L, J]; \\
&\quad \text{print } B[L, 1]
\end{align*}
\text{end for } L;

\text{UNSYMDET}(K, 2.0, -37, A, R, I, C, L); 
\text{UNSYMSOL}(K, 1, A, C, B); 
\text{for } L := 1 \text{ step 1 until } K \text{ do} 
\text{print } B[L, 1]; 
\text{Q} := 0; 
\text{for } I := 1 \text{ step 1 until } N \text{ do}
\begin{align*}
&\text{begin print } X_{1}^{I}, (1 - X_{1}^{I}), X_{E}[I]; \\
&\quad R := 0; \\
&\text{for } J := 1 \text{ step 1 until } K \text{ do} \\
&\quad R := R + B[J, 1] \times \text{PHI}(P, X_{1}^{I}, J);
\end{align*}
Thus once the coefficients of the suitably chosen orthogonal polynomials have been determined the procedure above may be used to evaluate the best fit coefficients. The coefficients of the orthogonal polynomials were determined using the procedure given below.

procedure POLYFIT(P,N,WRITE);
integer N;
real array P;
boolean WRITE;
begin comment N is the maximum dimension required for the orthogonal polynomials and P is the array containing the results. The boolean WRITE controls the printing of the polynomial coefficients.
integer I,J,R,S,IJ;
for I:=1 step 1 until N do
begin P[I,1]:=1;
  for J:=2 step 1 until N do
  P[I,J]:=0
end I;

The coefficients obtained with this procedure are given in Table (A3.2.1) and were in exact agreement with those given by Councell (75).
TABLE (A3.2.1)

<table>
<thead>
<tr>
<th>Polynomial</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_1$</td>
<td>1</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>1, -2.00</td>
</tr>
<tr>
<td>$\phi_3$</td>
<td>1, -4.67, +4.67</td>
</tr>
<tr>
<td>$\phi_4$</td>
<td>1, -8.00, +18.00, -12.00</td>
</tr>
<tr>
<td>$\phi_5$</td>
<td>1, -12.00, +45.00, -66.00, +33.00</td>
</tr>
<tr>
<td>$\phi_6$</td>
<td>1, -16.67, +91.67, -220.00, +238.33, -95.33</td>
</tr>
<tr>
<td>$\phi_7$</td>
<td>1, -22.00, +165.00, -572.00, +1001.00, -858.00, +286.00</td>
</tr>
</tbody>
</table>
6A3.3 EVALUATION OF VAPOUR PRESSURE

In this section the program used to calculate the equilibrium vapour pressure of a mixture is presented in reference Algol 60. The contents of the program were described in Section 6 and a section of the output from this program was given in Fig (6.10.3b).

EVALUATION OF VAPOUR PRESSURE;

begin integer I,J,N,CELL,M1,M2;
real MT,RT,TT,H2D,H3D,H5D,MN2,MVAP,U,L,ALPHA,A,B,C,D,R,G,
DENS,P2,P3,P5;
real array H,P1,P4[1:4];
real procedure PHG(T);
real T;
PHG:=13951/(1+T(A+T*(B+T*(C+T*D))));
real procedure EXPCOR(H,T);
real H,T;
begin H:=H*(1+ALPHA*(T-20));
EXPCOR:=H
end of procedure EXPCOR;
read N;
begin integer array INS[1:20*N];
M1:=M2:=1;
ALPHA:=1.96-5;
R:=8.3143;
G:=9.81288;
MN2:=0.028;
MVAP:=0.186;
\(A = 1.81456 \times 10^{-4};\)
\(B = 9.205 \times 10^{-9};\)
\(C = 6.608 \times 10^{-12};\)
\(D = 6.732 \times 10^{-14};\)

\textbf{for } I := 1 \textbf{ step } 1 \textbf{ until } N \textbf{ do}

\begin{verbatim}
begin
INSTRING(INS,M1);
read CELL,MT,RT,TT;
H2D := 0.28;
H3D := 0.15;
H5D := 0.09;
DENS := PEG(TT);
print CELL,G;
OUTSTRING(INS,M2);
print MT,H2D,RT,H3D,TT,H5D,DENS;
for J := 1 \textbf{ step } 1 \textbf{ until } 4 \textbf{ do}
begin
read U,L;
H[J] := U-L;
print H[J],EXPCOR(H[J],RT)
end J;
if CELL = 2 then for J := 1 \textbf{ step } 1 \textbf{ until } 4 \textbf{ do}
H[J] := -H[J];
H3D := H3D - 0.5*H[1];
H5D := H5D - 0.5*H[1];
for J := 1 \textbf{ step } 1 \textbf{ until } 4 \textbf{ do}
begin
P4[J] := H[J]*DENS*G;
print P4[J]
end J;
DENS := PEG(MT);
print DENS;
\end{verbatim}
for J = 1 step 1 until 4 do
begin read U, L;

H[J] := U - L;

print H[J], EXPCOR(H[J], RT)
end J;

H2D := H2D - 0.5 * H[1];
for J = 1 step 1 until 4 do

print P1[J]
end J;
RTi := RT + 273.15;
TTi := TT + 273.15;
P2 := H2D * MN2 * P1[1] * G / (R * RT);
P3 := H3D * RT * P2 / (H2D * TT);
P5 := H5D * MVAP * (P1[1] + F4[1]) * G / (R * TT);
print MN2, MVAP, P2, P3, P5;
for J = 1 step 1 until 4 do

print P1[J]
end J
end I
end

end of evaluation of vapour pressure;
proceedure BARKER(X1,P,N,PARAMETERS,SKEWED,Y1);
integer N,PARAMETERS;
real array X1,P,Y1;
boolean SKEWED;
begin comment the experimental data is stored in the arrays X1 and
P, X1 holding the compositions and P the vapour pressures. N
is the number of points and PARAMETERS is the number of
parameters in the $G^E$ expression to be determined. The boolean
variable SKEWED is used to control the evaluation of the
skewing parameter and the array Y1 is used to store the
calculated vapour compositions. A number of parameters to
this procedure are global but their presence should be clear
from the text.
integer I,J,COUNT,MINUS,PLUS,DIM;
MINUS:=PARAMETERS-1;
if SKEWED then DIM:=PARAMETERS
else DIM:=MINUS;
PLUS:=DIM+1;
print N, PARAMETERS;
begin real array R[1:N,1:1],G,G1,G2,EG1,EG2,FX1,FX2,FK1,
FK2,GEHLC[0:MINUS],DPDG[1:N,0:DIM],A[1:PLUS,1:PLUS],
B,C[1:PLUS,1:1];
real VBPP10,VBPP20,F1,F2,F1D,F2D,X2,Y2,X,GE,RMS,
RMSLAST,X,BBPP10,BBPP20,V1VPP,V2VPP,Z,V1,V2,
real procedure RPMV(V,K,N,X1,V1,V2);
integer N;
real K,X1,V1,V2;
real array V;
begin 
 comment this procedure is used to calculate the relative partial molar volumes \( V_1 \) and \( V_2 \) from the composition \( X_1 \) and the \( N \) parameters in the VE equation \( (V) \) together with the skewing parameter \( K \);
integer I;
real VE,DIFF,X2,Z,CALC;
VE:=DIFF:=0;
X2:=1-X1;
Z:=X1-X2;
for I:=0 step 1 until N-1 do
begin 
CALC:=X1*X2*V[I]*Z^(I-1)/(1-K*Z);
VE:=VE+CALC*Z;
DIFF:=DIFF+2*CALC*(I-Z)/((2*X1*X2)-K*Z/(1-K*Z));
end I;
V1:=VE+X2*DIFF;
V2:=V1-X1*DIFF
end of procedure RPMV;

comment procedures SUM and SUMPROD as given in Section (A3.2(c)) are also used again here;
PST:=101325.0;
G[0]:=4*LN(2*P12/(P10+P20));
K:=RMS:=COUNT:=0;
for I:=1 step 1 until N do
begin if I\leq MINUS then G[I]:=0;
  print X1[I], P[I]
end I;
print T, P10, B11, V10, P20, B22, V20, B12, P12;
L1: for COUNT:=COUNT+1 do
begin print COUNT;
   for J:=0 step 1 until MINUS do
     print G[J];
     print K;
   for I:=1 step 1 until N do
     begin X2:=1-X1[I];
        Z:=X1[I]-X2;
        for J:=0 step 1 until MINUS do
          begin FX1[J]:=X2^2*Z^(J-1)*/((1-K^Z)^2);
          FX2[J]:=X1[I]^2*Z^J*G[J]*
(2*(X1[I]-2*J+1)*X2+KZ*(2*J*X2-1))*/((1-K^Z)^2);
          FK1[J]:=FX1[J]*G[I]*
(2*((2*J+1)*X1[I]-X2)+(1+KZ)*
(1-2*J*X1[I])/*/((1-K^Z)^3);
          FK2[J]:=FX2[J]*G[J]*
(2*(X1[I]-2*J+1)*X2+(1+KZ)*
(2*J*X2-1))/*/((1-K^Z)^3);
          G1[J]:=FX1[J]*G[J];
          G2[J]:=FX2[J]*G[J];
          EG1[J]:=EXP(G1[J]);
EG2[J] := EXP(G2[J]);
GECALC[J] := X1[I]*X2*G[J]*Z\hat{J}/(1-X*Z)

end J;
VBPP10 := (V10-B11)*(P[I]-P10)/(R1*T);
VBPP20 := (V20-B22)*(P[I]-P20)/(R1*T);
BBPP10 := B11*B11*(P[I]-P10)*(P[I]+P10)/ 
(2*(R1*T)^2);
BBPP20 := B22*B22*(P[I]-P20)*(P[I]+P20)/ 
(2*(R1*T)^2);
RPMV(VE,KVE,VEDIM,X1[I],V1,V2);
V1VPP := V1*(P[I]-PST)/(R1*T);
V2VPP := V2*(P[I]-PST)/(R1*T);
COR1 := EXP(VBPP10+BBPP10+V1VPP);
COR2 := EXP(VBPP20+BBPP20+V2VPP);
F1 := PRODUCT(EG1,1,PARAMETERS);
F2 := PRODUCT(EG2,1,PARAMETERS);
Y2 := COR2*F2*P20*X2/P[I];
Y1[I] := 1-Y2;
P1D := X1[I]*P10*COR1*EXP(-P[I]*
D12*Y2*Y2/(R1*T));
P2D := X2*P20*COR2*EXP(-P[I]*
D12*Y1[I]*Y1[I]/(R1*T));
R[I,1] := P[I]-(F1*P1D+F2*P2D);
GE := R1*T*SUM(GECALC,1,PARAMETERS);
print X1[I],P[I],(P[I]-R[I,1]),R[I,1],
Y1[I],GE;
for J := 0 step 1 until MINUS do
DPDG[I,J] := F1*P1D*FX1[J]+F2*P2D*FX2[J];
\( \text{if SKEWED then DPDG}[I, \text{DIM}] := F_1 \cdot P_1 \cdot D \cdot \text{SUM}(F_{K1}, 1, \text{PARAMETERS}) + F_2 \cdot P_2 \cdot D \cdot \text{SUM}(F_{K2}, 1, \text{PARAMETERS}) \)

end I;

RMSLAST := RMS;

RMS := \sqrt{\text{SUMPROD}(R, 1, R, 1, N) / N};

print RMS;

for \( X := 0 \) step 0.1 until 1.01 do
begin

\( X_2 := 1 - X; \)

\( Z := X - X_2; \)

for \( J := 0 \) step 1 until MINUS do

\( \text{GECALC}[J] := X \cdot X_2 \cdot G[J] \cdot Z^J / (1 - K \cdot Z); \)

\( \text{GE} := R_1 \cdot T \cdot \text{SUM}(\text{GECALC}, 1, \text{PARAMETERS}); \)

print \( X, \text{GE} \)

end X;

\( \text{if ABS}(\text{RMS} - \text{RMSLAST}) < 1.0 \cdot 5 \cdot \text{RMS} \) then \( \text{go to L}; \)

for \( J := 1 \) step 1 until PLUS do

begin

\( C[J, 1] := \text{SUMPROD}(R, 1, \text{DPDG}, J - 1, N); \)

for \( I := 1 \) step 1 until PLUS do

\( A[I, J] := \text{SUMPROD}(\text{DPDG}, I - 1, \text{DPDG}, J - 1, N); \)

end J;

\( \text{UNSYMDET}(\text{PLUS}, 2.0, 37, A, X, I, B, L); \)

\( \text{UNSYMSOL}(\text{PLUS}, 1, A, B, C); \)

for \( J := 0 \) step 1 until MINUS do

\( G[J] := G[J] + C[J + 1, 1]; \)

\( \text{if SKEWED then } K := K + C[\text{PLUS}, 1]; \)

\( \text{go to L1} \)

end COUNT

end

end of procedure BARKER;
§ A3.5 CALCULATION OF THE TRUE LIQUID COMPOSITION WHEN USING THE BARKER METHOD

As was emphasised earlier in this thesis it is common practice to measure only the total composition of liquid and vapour. In this section the procedure used in conjunction with procedure BARKER to perform this calculation is presented.

```
procedure CFVP(N1,N2,Y1,P,WWAP,X1);
real N1,N2,Y1,P,WWAP,X1;
begin comment the true liquid composition X1 is determined from
the vapour composition Y1 obtained from procedure BARKER,
N1 and N2 are the amounts of 1 and 2 taken, P is the
vapour pressure and WWAP is the volume of the vapour space;
real TNOOM,V,M1,M2,Z,Y2,RTV,A;
Y2:=1-Y1;
Z:=(B11*Y1*Y1+2*B12*Y1*Y2+B22*Y2*Y2)/WWAP;
RTV:=R1*T/WWAP;
TNOOM:=(-RTV+SQR(TTV*RTV-4*P*RTV*Z))/(2*RTV*Z);
A:=P/(RTV*(1+Z*TNOOM));
M1:=Y1*A;
M2:=Y2*A;
X1:=(N1-M1)/(N1+N2-M1-M2)
end of procedure CFVP;
```
§43.6 CALCULATION OF THE EXCESS GIBBS FUNCTION OF MIXING, $G^E$,
BY CURVE FITTING THE ACTIVITY COEFFICIENTS.

procedure ACTOFIT(LNF2,X2,W,N,G,PARAMETERS,K,SKEWED);
integer N,PARAMETERS;
real K;
real array LNF2,X2,W,G;
boolean SKEWED;

begin comment the activity coefficients are stored as their
natural logarithms in the array LNF2 and the corresponding
compositions in X2. The parameters in the $G^E$ equation at
any time are stored in the array G and the skewing parameter
in K. The boolean variable SKEWED controls when K is
calculated and W contains the statistical weighting of each
point;
integer I,J,DIM,PLUS,MINUS,COUNT;
real X1,Z,X2,LFCALC,GECA,L;
real array R[1:N,1:1];
MINUS:=PARAMETERS-1;
COUNT:=0;
if SKEWED then DIM:=PARAMETERS
else DIM:=MINUS;
PLUS:=DIM+1;
begin real array DLNF2DG[1:N,0:DIM],A[1:PLUS,1:PLUS],
B,C[1:PLUS,1:1];
RMSLAST:=0;
L: for COUNT:=COUNT+1 do
begin print COUNT;
for J:=0 step 1 until MINUS do
print G[J];
print K;
for I:=1 step 1 until N do
begin X1:=1-X2[I];
   Z:=X1-X2[I];
   XZ:=1/(1-K*Z);
   LFCALC:=DLNF2DG[I,DIM];=GECALC:=0;
   for J:=0 step 1 until MINUS do
   begin DLNF2DG[I,J]:=if J=0
         then X1*X1*(1+K)*XZ*XZ
         else X1*X1*Z*(J-1)*(X1-(2*J+1)*
                  X2[I]+K*Z*(2*J*K)-1)*XZ*XZ;
   LFCALC:=LFCALC+G[J]*DLNF2DG[I,J];
   DLNF2DG[I,J]:=DLNF2DG[I,J]/W[I];
   if SKENED
      then DLNF2DG[I,DIM]:=DLNF2DG[I,DIM]+
         X1*X1*G[J]*Z*(J-2*(X1-(2*J+1)*X2[I])+
         (1+K*Z)*(2*J*X2[I]-1))*KZ*XZ*XZ/W[I];
       GECALC:=GECALC+X1*X2[I]*G[J]*Z*J*XZ
   end J;
   R[I,1]:=LNFP2[I]-LFCALC;
   print X2[I],LNFP2[I],LFCALC,R[I,1],
       (RT*GECALC);
end I;

RMS:=SQRT(SUMPROD(R,1,R,1,N)/N);
STD:=SQRT(RMS*RMS*N/(N-PHI));
print RMS,STD;
for I:=1 step 1 until N do
\((319)\)

\[
R[I,1] := R[I,1] / w[I];
\]

for \(X := 0 \text{ step } 0.1 \text{ until } 1.01 \) do
begin
\(X1 := 1 - X;\)
\(Z := X1 - X;\)
\(EZ := 1 / (1 - X * Z);\)
\(LFCALC := GECALC := 0;\)
for \(J := 0 \text{ step } 1 \text{ until } \text{MINUS} \) do
begin
if \(J = 0\) then
\[
LFCALC := LFCALC + X1 * X1 * G[J] * (1 + K) * KZ * KZ
\]
else
\[
LFCALC := LFCALC + X1 * X1 * G[J] *
Z^(J-1) * (X1 - (2 * J + 1) * X + K) *
Z * (2 * J * X - 1) * KZ * KZ;
\]
GECALC := GECALC + X1 * X * G[J] * Z^J * KZ
end J;

print \(X, (GECALC - X * LFCALC) / X1), LFCALC,\)
\(\text{RT} * GECALC)\)
end X;

for \(I := 1 \text{ step } 1 \text{ until } \text{PLUS} \) do
begin
\(B[I,1] := \text{SUMPROD}(R,1,DLNF2DG,I-1,N);\)
for \(J := 1 \text{ step } 1 \text{ until } \text{PLUS} \) do
\(A[I,J] := \text{SUMPROD}(DLNF2DG,J-1,DLNF2DG,I-1,N)\)
end I;

UNSYMDET(PLUS,2,0.1-37,A,X,I,C,L2);
UNSYMSOL(PLUS,1,A,C,B);
for \(J := 0 \text{ step } 1 \text{ until } \text{MINUS} \) do
\(G[J] := G[J] + B[J+1,1];\)
if SKewed then \(K := K + B[\text{PLUS},1];\)
if \(\text{ABS}(\text{RMS-EMSLast}) < \text{RMS} \times 1.0 \times 6\)
then go to L2;
A3.7 CALCULATION OF THE TRUE LIQUID COMPOSITION WHEN USING PROCEDURE ACTOFIT AND TOTAL COMPOSITION MEASUREMENT

In this section the procedure used to determine the true liquid and vapour compositions, and the logarithms of the activity coefficients is presented.

procedure COMPCCALC(N1,N2,P,V,G,PARAMETERS,K,X2,Y2,LNF2);
integer PARAMETERS;
real N1,N2,P,V,K,X2,Y2,LNF2;
real array G;
begin comment the true liquid composition X2, the vapour composition Y2, and the activity coefficient LNF2 are evaluated from the total amounts of materials taken, N1,N2, the total vapour pressure P, the volume of the vapour space V and the parameters of a suitable expression for G, G and K;
integer COUNT,T;
real NV1,NV2,TNMV,X1,Y1,LNF1,Z,K2,P1,P2,P2LAST,YBS;
NV1:=NV2:=X1:=Y1:=P2:=0;
COUNT:=0;
Y2:=1;
print N1,N2,P,V;
TNNV:=P*V/RT;
L: for COUNT:=COUNT+1 do
begin X1:=(N1-NV1)/(N1+N2-TNNV);
    X2:=1-X1;
    Z:=X1-X2;
    K2:=1/(1-K*Z);
    P2LAST:=P2;
    LNF1:=0;
    for I:=0 step 1 until PARAMETERS-1 do
    if I=0 then LNF1:=LNF1+X2*X2*G[0]*(1+K)*KZ*KZ
    else LNF1:=LNF1+X2*X2*G[I]*Z^(I-1)*
        ((2*I+1)*X1-X2*K*Z*(1-2*I*X1))*KZ*KZ;
    P1:=P10*X1*EXP(COR1)*EXP(-Y2*Y2*P*D12/RT)*EXP(LNF1);
    P2:=P-P1;
    Y1:=P1/P;
    Y2:=1-Y1;
    YBS:=1+TNNV*(Y1*Y1*B11+2*Y1*Y2*B12+Y2*Y2*B22)/V;
    NV1:=P1*V/(RT*YBS);
    NV2:=P2*V/(RT*YBS);
    TNNV:=NV1+NV2;
    Y1:=NV1/TNNV;
    Y2:=1-Y1;
    print NV1,NV2,TNNV,Y1,Y2,X1,X2,P1,P2,P;
    if ABS(P2-P2LAST)<0.001
        then go to L2;
        go to L
end COUNT;
L2: \[ \text{LN}(\frac{P_2}{X_2*P_20}) - C_0 + P*D_{12}*Y_1*Y_{1/RT} \]

end of procedure COMPCALC;
(1) E.T. McBEE, V.V. LINDGREN and W.B. LIGETT,

(2) Y. DESIRANT, Bull. classe. sa, Acad. roy. Belg.,
41, 759, (1955)

(3) M. HILLMANN, E. PETERS, W.J. PUMMER and L.A. WALL,


(6) L.A. WALL, M. HILLMAN and W.J. PUMMER, U.S. Patent 2927138,
March 1960

(7) J.M. BIRCHALL, R.N. HASZELDINE and A.R. PARKINSON,

(8) L.A. WALL, J.E. FEARN, W.J. PUMMER and R.E. LOWRY,

(9) R.E. BANKS, J.M. BIRCHALL, R.N. HASZELDINE, J.M. SIM,


(11) K.O. CHRISTIE and A.E. PAVLATH, Ber., 27, 2092, (1964)

(12) J.A. GODSELL, M. STACEY and J.C. TATLOW,
Nature, 178, 199, (1956)

(13) R.E. FLORIN, W.J. PUMMER and L.A. WALL,

(14) B. GETHING, C.R. PATRICK, J.C. TATLOW, R.E. BANKS,

(15) P.L. COE, C.R. PATRICK and J.C. TATLOW,
Tetrahedron, 2, 240, (1960)


(17) P. JOHNCOCK, R.H. MOBBS and W.K.R. MUSGRAVE,

(19) R.D. CHAMBERS, J. HEYES and W.K.R. MUSGRAVE,
    Tetrahedron, 19, 891, (1963)

(20) N.N. VOROZHTSOV JR., V.E. PLATANOV and G.G. YAKOBSON,


(22) G.G. YAKOBSON, V.E. PLANTOV and N.N. VOROZHTSOV JR.,

    60, 700, (1964)

(24) J.F. COUNSELL, J.H.S. GREEN, J.L. HALEs and J.F. MARTIN,

    60, 653, (1964)


(27) R.E. FLORIN, W.J. PUMMER and L.A. WALL,

(28) S.W. CHARLES, J.T. PEARSON and E. WHITTLE,

(29) L.A. WALL, W.J. PUMMER, J.E. FEARN and J.M. ANTONUCCI,

(30) J. BURDON, V.A. DAMODARAN and J.C. TATLOW,


    62, 1082, (1966)

(33) D.V. FENBY, I.A. McLURE and R.L. SCOTT, J. Phys. Chem.,
    70, 602, (1966)
62, 2153, (1965)
(35) T.G. BEAUMONT and K.M.C. DAVIS, J. Chem. Soc. B,
1131, (1967)
65, 688, (1969)
(37) A.W. ANDREWS, Unpublished Work, University of Leicester,
(1969)
(38) J.M. HALL, A. BRACKEN, G. GOLDSTONE and D.S. NEWLAND,
Anaesthesia, 16, 3, (1961)
(41) R.E. FLORIN, L.A. WALL and D.W. BROWN,
(43) F.W. BLOCH, D.R. MCKENZIE and R.H. WISWALL Jr.,
(44) S.L. RUSKIN, U.S. Patent 2944881, July 12th, 1960
1080, 73, (1963)
71, 2703, (1949)
62, 2063, (1966)
(49) K.W. MORCOM and D.N. TRAVERS, Trans. Faraday Soc.,
61, 230, (1965)
(50) D.L. ANDERSON, R.A. SMITH, D.B. MYERS, S.K. ALLEY,
66, 621, (1962)


(57) A.W. ANDREWS, W.A. DUNCAN, J.M. POLLOCK, K.W. MORCOM and F.L. SWINTON, to be published


(64) J.A. LARKIN, Ph.D. Thesis, University of Reading, (1962)


(69) CALVET (1956), in ROSSINI, Ed., Experimental Thermochemistry, Interscience, New York, Chapter 12


(75) J.F. COUNCELL, Unpublished Work, National Physical Laboratory, Teddington, Middlesex

(76) BAXENDALE, ENUSTUN and STERN, Phil. Trans., A243, 169, (1951)


(79) A.G. WILLIAMSON, Ph.D. Thesis, University of Reading, (1957)


(84) A.J. COLE and K.W. MORCOM, Unpublished Work, University of Leicester


(86) KAHLBAUM, Z. physik. Chem., 13, 14, (1894)

and Z. physik. Chem., 26, 577, (1898)


61, 421, (1965)

(90) DESMITER and van der WAALS, Rec. trav. chim.,
27, 53, (1958)

(91) J.R. GOATES and R.J. SULLIVAN, J. Physic. Chem.,
62, 188, (1958)

(92) T.G. BEAUMONT, Unpublished Work, University of Leicester

67, 1182, (1963)

(94) HUGGINS, PIMENTAL and SHOOLEY, J. Chem. Physics.,
23, 1244, (1955)

(95) F.L. SWINTON et.al., Unpublished Work, University of
Strathclyde

(96) V.I. VEDENEYEV, L.V. GURVICH, V.N. KONDRA'TYEV, V.A. MEDVEDEV
and YE.L. FRANKEVICH, Bond Energies, Ionisation Potentials


32, 1175, (1947)

(99) F.D. MASLIN and E.A. STODDARD, J. Physic. Chem.,
60, 1147, (1956)

(100) G.P. CUNNINGHAM, G.A. VIDULICH and R.L. KAY,

12, 538, (1968)

(102) F. FRANKS and H.T. SMITH, Trans. Faraday Soc.,
64, 2962, (1968)

(103) F. FRANKS and D.J.G. IVES, Quart. Revs. Chem. Soc.,
20, 1, (1966)
(106) H.S. FRANK, Unpublished Work, University of Pittsburgh
(107) WEN YANG WEN, Ph.D. Thesis, University of Pittsburgh, (1957)
(121) V.P. ROMANOV and V.A. SOLOVYEV, Akust. Zhur., 11, 84, (1965)
(122) R.W. SMITH, Unpublished Work, University of Leicester

(123) D. WADDINGTON, Unpublished Work, University of Leicester


(125) B.L. MUJU, Ph.D. Thesis, University of Leicester, (1968)

(126) H.S. HARNED and M. FITZGERALD, J. Am. Chem. Soc.,
      58, 2624, (1936)

(127) J.D. Hefley and E.S. Amis, J. Physic. Chem.,
      69, 2082, (1965)


      52, 1583, (1937)

      80, 5048, (1958)