23/3/78

THE CONTINUOUS DILUTION METHOD
EXCESS THERMODYNAMIC PROPERTIES OF BINARY LIQUID MIXTURES CONTAINING HEXAFLUOROBENZENE AND ETHERS

by
Robert Stephen Murray
B.Sc.(Hons.)

A thesis presented for the degree of
Doctor of Philosophy
at the University of Adelaide
April, 1977.

Department of Physical and Inorganic Chemistry

SUMMARY

The continuous dilution method for the measurement of excess thermodynamic properties of binary liquid systems offers considerable economy in both time and materials when compared with other methods. As such its use has won widespread approval in recent years. This thesis describes the use of three continuous dilution devices, two of which were designed, constructed and tested during this work.

An isothermal displacement calorimeter incorporating some new design features has been built and is described in detail. This device has been tested with two systems for which reliable data of high precision are available and is found to reproduce these data with comparable precision.

Few continuous dilution devices have been described which measure the static vapour pressures of binary liquid systems as a function of composition. Such a device, believed to be of simpler construction than those already present in the literature, is described here in detail. The vapour pressures and excess Gibbs free energies of the system *n*-hexane + benzene have been measured and compare favourably with the results of other workers.

Since 1960 considerable attention has been devoted to the ambiguous behaviour of hexafluorobenzene with electron donors. Little work has been done, however, with donors of *n*-electrons. In this work the excess volumes, enthalpies and Gibbs free energies of binary liquid systems containing hexafluorobenzene and ethers have been measured. These results are also ambiguous but the size, shape and polarizability of the carbon backbone incorporating the donor atom would seem to be of overriding importance in determining the resultant thermodynamic properties of these mixtures.

ACKNOWLEDGMENT

It is a pleasure to express my sincere thanks to Dr. M.L. Martin who has helped me as both teacher and friend throughout my postgraduate years. I am also indebted to Dr. P.J. Dunlop, Dr. B.J. Steele and to my fellow students, especially Dr. Michael Yabsley, for giving me the benefit of their knowledge during our many discussions.

The Department of Physical and Inorganic Chemistry at this University is fortunate in counting, amongst its ancillary staff, people who have attained a high degree of excellence in their individual crafts. For their considerable efforts in constructing the various apparatus used in this work, I am especially grateful to Messrs. John Netting, Arthur Bowers, Keith Shepherdson and Gavin Duthie.

The skilful translation of this thesis, from the hieroglyphics of the author into type, was accomplished through the talents of Mrs. Del Hewish and Mrs. Kathy Roberts. I am indebted to my wife Ann, for her careful appraisal of the draft of this thesis.

The process of living with a Ph.D. student may be no less traumatic, at times, than that of doing the work itself. In this respect, I was fortunate to have the unstinting moral support both of my mother and my wife.

I hereby certify that this thesis contains no material which has been accepted for the award of any other degree or diploma in any university, and to the best of my knowledge contains no material previously published or written by any other person, except where due reference is made in the text.

TABLE OF CONTENTS

TABLE OF CONTENTS (contd.)

CHAPTER 4 EXCESS VOLUMES

CHAPTER 5 CALORIMETRY - EXCESS ENTHALPIES

TABLE OF CONTENTS (contd.)

TABLE OF CONTENTS (contd.)

CHAPTER 7 RESULTS AND DISCUSSION

TABLE OF CONTENTS (contd.)

CHAPTER 1

INTRODUCTION

1.1 The continuous dilution method: Investigation of the properties of fluid mixtures normally requires a knowledge of the composition and, for extensive properties, the total mass of the mixture. Composition dependence may be studied in two ways:

(a) Measurements are made on a series of *individually prepared mixtures*, the composition of which is known from analysis, or from the measured amounts, or ratio of amounts, of each component present.

(b) A known amount of one component is successively diluted with smaller known amounts of another component. This process is termed *continuous dilution.*

In many experiments the continuous dilution method offers considerable advantages. It is generally less time consuming and less tedious, allowing the rapid acquisition of a large number of data. The amount of material required is often considerably smaller than that required by other methods, an important consideration when the materials to be studied are costly or difficult to purify. The precision or internal consistency of data acquired by this method is invariably superior to that obtained from individual experiments, especially when systematic errors are small, since the amount of one component is fixed and the materials are of uniform quality. For this work continuous dilution devices were used to measure excess volumes, excess enthalpies and vapour pressures as functions of the composition, x, of binary nonelectrolyte liquid mixtures. Each device requires two experimental "runs" to produce several data over the entire range of composition with small expense of liquid. The amounts of liquid present are calculated from known densities and from volume calibration of the equipment. The congruence of data around the junction of the two runs (shown with all results) may indicate the absence of systematic errors. The composition overlap required for this test is assured by adding a volume of the mobile component greater than that of the static component. These devices and those used by other workers are discussed in chapters concerned with the respective excess thermodynamic functions.

1.2 Binary liquid mixtures containing fluorocarbons: The singular behaviour of liquid mixtures containing perfluorocompounds has been the object of considerable attention and speculation for some time.[1] In particular, studies of the excess thermodynamic properties of binary mixtures containing fluorocarbons have revealed certain trends:

(i) Mixtures of two aliphatic perfluorocarbons are almost ideal, with small excess Gibbs free energies[1,2] (ca. 50 $J.mol^{-1}$).

(ii) Mixtures of the type aliphatic or alicyclic perfluorocarbon + hydrocarbon exhibit unusually large positive deviations from ideality, tending to immiscibility.[1,2] This is especially true when the hydrocarbon is also aliphatic or alicyclic.[2]

e.g.[2,3,4]

n-hexane + perfluoro-*n*-hexane, 298 K, $x = 0.5$

$\bar{G}^E = +1380\ J.mol^{-1}$, $\bar{H}^E = +2160\ J.mol^{-1}$,

$\bar{V}^E = +4.84\ cm^3.mol^{-1}$.

This behaviour has been attributed[5] to the exceeding weakness of the unlike interactions in these systems leading to gross failure of the Berthelot combining rule,

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}}, \qquad (1.1)$$

to predict ε_{12} in the universal binary potential function,

$$\mu_{12}(r) = \varepsilon_{12}f(r/\sigma_{12}). \qquad (1.2)$$

(iii) Mixtures of aromatic fluorocarbons with aromatic hydrocarbons often exhibit negative deviations from ideal behaviour, with apparently strong unlike interaction in some systems and the formation of solid complexes,[1]

e.g.[6,7]

	Freezing point
hexafluorobenzene	278.2 K
1,3,5-trimethylbenzene	221.5 K
1:1 complex	309.2 K

$\bar{H}^E$ (x = 0.5, 313 K) = -2320 J.mol^{-1}.

The behaviour discussed in (iii) above has given rise to some controversy over the nature of observed complex formation involving aromatic fluorocarbons. Much of this speculation has centred around mixtures containing hexafluorobenzene.

1.3 Mixtures containing aromatic fluorocarbons: The observation,[8] in 1960, of the formation of a "weak addition complex" between hexafluorobenzene and aniline was closely followed[9] by the discovery of a series of solid equimolar molecular complexes of hexafluorobenzene with aromatic hydrocarbons. The strongly negative inductive effect of the fluorine atom, reflected in the ionization potentials of fluorobenzenes,[10,11] prompted the authors to regard these complexes to be of the "charge-transfer type". Tentative investigation, however, failed to detect the additional spectral band normally associated with this process.[a] Further spectroscopic work (u.v., n.m.r.)[13] in 1965 with the system hexafluorobenzene + hexamethylbenzene similarly failed to observe a charge transfer band or an appreciable change in the chemical shift of the ^{19}F resonance with changing "donor" concentration.

Crystallographic studies[14] of equimolar complexes of hexafluorobenzene with polycyclic aromatic hydrocarbons revealed structures, of alternate "donor-acceptor" stacking, whose symmetry and unit cell dimensions showed a general resemblance to

---

[a] The charge transfer phenomenon,[12] represented as

$$DT + h\nu \xrightarrow{\text{ca. } 10^{-18}\text{ s}} D^{+}T^{-} \xrightarrow{>10^{-18}\text{ s}} DT + \text{heat, phosphorescence, or fluorescence,}$$

involves the photon-induced transfer of an electron from the highest energy occupied orbital mainly localized on a donor species (D) to the lowest energy unoccupied orbital mainly localized on an acceptor species (T) in the excited state. The electron returns to the donor upon relaxation to the ground state. The species $D^{+}T^{-}$ may contribute to the stability of the ground state of the complex but the broad and often visible charge-transfer absorption ($h\nu$) of organic complexes in solution is intense only when D and T are bound by stronger forces (*e.g.* van der Waals, hydrogen bonding). The lowest energy charge-transfer absorption is normally found at longer wave-lengths (*i.e.* lower energies) than the $\pi \rightarrow \pi^{*}$ bands of aromatic donor molecules.

complexes exhibiting charge-transfer. The weakness of these complexes was, however, implied by their lack of colour and ready loss of hexafluorobenzene.

Experimental phase diagrams for hexafluorobenzene,[6] pentafluorobenzene[15] and other aromatic perfluorocarbons[16] with hydrocarbons indicated the existence of further solid equimolar aromatic complexes as well as three very weak complexes of hexafluorobenzene with cyclohexane[6] possibly, in this case, due to geometric or "packing" phenomena. The continued lack of non-thermodynamic evidence for donor-acceptor interactions in these systems prompted some authors[16] to describe even the congruently melting *aromatic* solids in terms of geometric accident.

The possible extension of the solid state interactions, for these systems, into the liquid phase was investigated by Duncan *et al.*[17] who measured the excess volume of mixtures of hexafluorobenzene with a progression of eight "donor" hydrocarbons (cyclohexane-1,3,5-trimethylbenzene). A correlation between $\bar{V}^E$ and hydrocarbon ionization potential was obtained, but the very small liquid-phase dipole moments of the fluorocarbon in these solvents, confirmed by others,[18,19] implied the extreme weakness of any donor-acceptor complexes in solution.

Extensive measurements, made by Fenby and Scott,[20,21] of the composition and temperature dependence of excess enthalpies for 34 systems of the type $C_6H_mF_{6-m} + C_6H_nF_{6-n}$ produced a striking variety of results which suggested specific interaction in the liquid phase. The observation of positive, negative and sigmoidal composition dependence of $\bar{H}^E$ was discussed in terms of three contributions to observed $\bar{H}^E(x)$ curves:

(i) A large positive and possibly asymmetric contribution from non-specific "physical" interactions commonly observed in fluorocarbon/hydrocarbon mixtures.

(ii) A negative symmetric contribution tentatively ascribed to 1:1 donor-acceptor interaction.

(iii) A negative contribution resulting from C-F/C-H dipole interactions on adjacent rings. This contribution arose from the observation that "lock and key systems" (*e.g.* 1,4-$C_6H_4F_2$ + 1,2,4,5-$C_6H_2F_4$) had algebraically lower excess enthalpies.

Beaumont and Davis[22,23] contrasted the behaviour of hexafluorobenzene with aromatic hydrocarbons and with aromatic amines. This work represented the first study of an aromatic fluorocarbon with *n*-electron donors. Both single and multiple charge-transfer bands were observed in the liquid phase with the amines but not with the aromatic hydrocarbons despite the even lower ionization potentials of the latter. In rationalizing this observation the authors pointed out that donor-acceptor interaction, by no means the only mode of complex formation, may assume a minor role in stabilization of complexes and that quantum mechanical arguments rendered unlikely the simultaneous operation, in the π-donors, of both strong charge-transfer processes *and* strong van der Waals forces. For aromatic amines, however, both types of interaction could occur to a significant extent due to the disposition of the donor orbital. At this stage (1967) it seemed unlikely that hexafluorobenzene, having been observed in one instance[24] as a charge-transfer *donor*, would assume the role of acceptor with any but the strongest donors.

Quantum mechanical calculations by Hanna[25] suggested that charge-transfer is a minor contributor to the ground state stability of these complexes and that most of the observed interaction could be attributed to quadrupole/induced-dipole interactions. This result concurred with earlier experimental results in as much as the interaction would be maximized by a face-to-face configuration of aromatic rings[14] and would account for the parallel[17] between apparent interaction strength in the liquid phase and ionization potentials (π-quadrupole strength) of "donors".

Further study of aromatic amines,[26] this time with chlorofluorobenzenes, detected very weak charge-transfer bands while hexachlorobenzene complexes were noted to be uniformly stronger than those of hexafluorobenzene, contrary to the expected order of acceptor strength. Armitage *et al.*[27] observed, for mixtures of hexafluorobenzene and aromatic amines, large negative excess enthalpies and positive excess heat capacities (*e.g.* C_6F_6 + *m*-$CH_3.C_6H_6.N(CH_3)_2$, $\bar{H}^E$ (x = 0.5, 323 K) = -2860 $J.mol^{-1}$, $\bar{C}_P^E$ (x = 0.5, 323 K) = +11.0 $J.mol^{-1}.K^{-1}$), both attesting to the presence of strong complexes in solution. The relative magnitudes of $\bar{H}^E$ were discussed in terms of steric factors and the disposition and nature of donor orbitals. In this way the apparently weaker interaction with pyridines was reasoned to be of the type earlier postulated[25] for hexafluorobenzene with benzene.

In measuring the excess Gibbs free energies for mixtures of hexafluorobenzene with methyl-substituted benzenes, Gaw and Swinton[28-30] estimated the "excess free energy of complex formation" (ca.-650 $J.mol^{-1}$, 313 K) for the benzene complex in the liquid phase by assuming that the "physical" interactions for this system could be represented by the observed $\bar{G}^E(x)$ for the system hexafluorobenzene + cyclohexane. They incidently observed[30] a persistent double azeotropy (unique amongst non-electrolyte mixtures) the existence of which was later confirmed by others.[31,32] The possible extension of the hexafluorobenzene-benzene interaction to the vapour phase was noted, by Dantzler *et al.*,[33] from the abnormally negative interaction virial coefficient for this system.

In 1970 Swinton *et al.*[7,34,35] presented impressive evidence showing that the magnitude of excess thermodynamic functions for liquid mixtures of fluorocarbons and hydrocarbons is largely determined by the shape of the component molecules. Equimolar excess volume measurements[34] were made on several systems,

series A: hexafluorobenzene + aromatic hydrocarbons (*i.e.* planar fluorocarbon + planar hydrocarbon);

series B: hexafluorobenzene + methyl-substituted cyclohexanes (*i.e.* planar fluorocarbon + globular hydrocarbon);

series C: perfluoromethyl cyclohexane + methyl-substituted cyclohexanes (*i.e.* globular fluorocarbon + globular hydrocarbon),

and the following trends were noted:

(i) For series A an increase in the degree of substitution of alkyl-substituted benzenes led, with more bulky substituents, to an *increase* in $\bar{V}^E(0.5)$.

(ii) $\bar{V}^E(0.5)$ was seen to be linear in n, the number of substituent methyl groups on the hydrocarbon, for each of the above series of mixtures. In addition, these lines were almost parallel and of negative slope.

(iii) The magnitude of $\bar{V}^E(0.5)$ was noted to increase in the sequence series A → series B → series C.

It was reasoned that this behaviour resulted from steric restrictions on the proximity of the component molecules in a mixture, and a consequent modification of the strength of unlike dispersive interactions.[a] The addition of a methyl group to a hydrocarbon produced, in each series, a comparable increase in the polarizability of that molecule leading to enhancement of dispersion forces and a consequent decrease in $\bar{V}^E(0.5)$. That this change was comparable for both aromatic and alicyclic hydrocarbons was deemed evidence for the relative unimportance of the hydrocarbon π-electron system in interaction with the fluorocarbon.

These conclusions were largely substantiated by the additional measurement of equimolar excess enthalpies for series A and series B mixtures.[7] A correlation of the type (ii), outlined above, was obtained with $\bar{H}^E(0.5, 313\ K)$, but the large disparity in line slopes (series A:series B $\simeq$ 3.5:1) implied the presence, in series A, of an additional interaction probably of the type postulated earlier[25] for aromatic hydrocarbons, *viz.* C-F dipole-π-quadrupole interaction). Since such forces could be maximized by face-to-face configuration of aromatic rings resulting in an angle-dependent intermolecular potential, the authors measured gas-liquid critical temperatures for series A and series B mixtures[35] to obtain unlike interaction

---

[a] It may be argued from this that the choice of an essentially globular, alicyclic hydrocarbon to represent the "physical" interactions of a planar aromatic species is a bad one. Estimates of the "chemical" interaction strengths between aromatic fluorocarbons and other aromatic compounds have been made by some authors.[21,29,55,66] These estimates are likely to be high since the "physical" interactions involving, say, benzene are more intense than those involving cyclohexane.

parameters and, using these parameters, correlated the excess thermodynamic functions for these mixtures with a statistical liquid theory incorporating just such an angle-dependent potential function. This analysis "accounted for the thermodynamic properties of a variety of fluorocarbon + hydrocarbon mixtures in an extremely satisfactory manner" and the authors saw no need to invoke the concept of discrete complexes in solution, species for which there was only weak[18,36] evidence.

Subsequent measurements made on mixtures of aromatic fluorocarbons with hydrocarbons[37-48] have been entirely consistent with the conclusions of Swinton *et al.*[7,34,35] Thermodynamic studies of pentafluorobenzene with alicyclic[38] and aromatic[38-40] hydrocarbons have shown that the behaviour of this fluorocarbon closely parallels that of hexafluorobenzene. It forms solid equimolar complexes with methyl-substituted benzenes[40] (but, surprisingly, not with hexamethylbenzene) and the excess enthalpies with hydrocarbons[38,39] appear to exhibit all the trends discussed above. Fenby *et al.*[42,43,66] have measured excess thermodynamic properties of mixtures of cyclohexane and of benzene with fluorocarbons of the type C_6F_5X ($X \equiv H,F,Cl,Br,I,CN$) and have indicated that their results can also be rationalized in terms of molecular shape and polarizability. The last-named fluorocarbon (C_6F_5CN) shows unusual behaviour with benzene. Two congruently melting solid complexes of stoichiometry 1:1 and 5:3 are formed.[67]

Non-thermodynamic evidence of complexes in solution has not been found.[47] Crystallographic studies of solid complexes of hexafluorobenzene with methyl-substituted benzenes[44-46] have confirmed earlier work[14] in revealing structures of alternate hydrocarbon fluorocarbon stacking in infinite columns. Relative twisting of adjacent rings implies the existence of interactions between methyl groups and fluorine atoms which are somewhat stronger than normal van der Waals forces. A recent estimate[48] of the enthalpy of formation of the benzene + hexafluorobenzene 1:1 solid complex (-80 J.mol^{-1}, 291.15 K) from enthalpy of fusion data has confirmed the thermodynamic instability of this species.

The behaviour of hexafluorobenzene with heterocyclic aromatic compounds[27,49-53] is similar to that found with aromatic hydrocarbons. Solid complexes with congruent and incongruent melting points are formed.[49,50] The excess thermodynamic properties (mainly $\bar{H}^E$) of hexafluorobenzene with methyl-substituted pyridines[27,51-53] exhibit the trends found with corresponding aromatic hydrocarbons[7] but suggest weaker unlike interactions in the liquid phase. Gas to solvent shifts of hexafluorobenzene in heterocycles[54] suggest the dominance of van der Waals interactions in these systems, in accord with an earlier suggestion.[27]

Armitage *et al.*[55,56] have studied solid-liquid phase equilibria[56] and u.v. spectra of hexafluorobenzene and of pentafluorobenzonitrile[56] with aromatic amines. These systems exhibit charge-transfer bands,[22,23,56] congruently melting equimolar solid complexes, and large negative enthalpies of complex formation in the liquid phase[55] (estimated spectrophotometrically).

1.4 Hexafluorobenzene and non-aromatic n-electron donors: Until recently (ca. 1974) relatively few measurements have been reported for binary mixtures containing hexafluorobenzene and non-aromatic *n*-electron donors.[22,27,57-59] The liquid mixture with triethylamine exhibits charge-transfer absorption[22] and positive excess heat capacities,[27] both consistent with donor-acceptor complex formation. The excess volumes of hexafluorobenzene with aliphatic ethers[58] and with 1,4-dioxan[57] are all positive but excess enthalpies with the latter[57] are sigmoidal in composition. Infra-red spectra of aliphatic alcohols in hexafluorobenzene[59] suggest that these interact more strongly with the fluorocarbon than with carbon tetrachloride.

More recently Goates *et al.*[60] have measured solid-liquid phase equilibria of hexafluorobenzene with four ethers. Only one instance of complex formation was observed (1,4-dioxan) suggesting weak electrostatic interaction and favourable "packing" geometry. Fenby *et al.*[61-64] have measured excess volumes[61,63] and excess enthalpies[62] for hexafluorobenzene with acetone, di-methyl sulphoxide, di-ethyl ether and tri-ethylamine as well as the excess Gibbs free energy with the amine.[64] With the exception of the excess enthalpy for acetone + hexafluorobenzene, these properties are uniformly positive. The authors have pointed out[63] that the excess volumes for benzene with acetone, di-ethyl ether and di-methyl sulphoxide are *negative* over all or part of the composition range. These observations suggest that liquid-phase complex formation between the fluorocarbon and the *n*-electron donors may be weak or non-existent. Vapour-liquid equilibria and excess volumes for hexafluorobenzene with methanol at a number of temperatures have been measured. The excess volume is positive and the excess enthalpies and Gibbs free energies are small and positive ($\bar{H}^E$ (x = 0.5, 318 K) = 48 J.mol^{-1}, $\bar{G}^E$ (x = 0.5, 318 K) = 81 J.mol^{-1}).

The nature of unlike interactions of hexafluorobenzene with *n*-electron donors remains somewhat ambiguous. As an extension of earlier work[58] the excess volumes, excess enthalpies and excess Gibbs free energies of hexafluorobenzene with ethers have been measured as part of this work. These results and a discussion of their implications are presented in *Chapter 7*.

References

1. Rowlinson, J.S. *Liquids and Liquid Mixtures.* 2nd ed. Butterworths: London 1969
2. McGlashan, M.L. *An. Rep. Chem. Soc.* 1962, 59, 73
3. Williamson, A.G. *Enthalpies of Mixing of Binary Non-Electrolyte Systems.* University of Canterbury: ca. 1970
4. Battino, R. *Chem. Rev.* 1971, 71, 5
5. Scott, R.L.; Fenby, D.V. *An. Rev. Phys. Chem.* 1969, 20, 111
6. Duncan, W.A.; Swinton, F.L. *Trans. Faraday Soc.* 1966, 62, 1082
7. Andrews, A.; Morcom, K.W.; Duncan, W.A.; Swinton, F.L.; Pollock, J.M. *J. Chem. Thermodynamics* 1970, 2, 95
8. Brooke, G.; Burdon, J.; Stacey, M.; Tatlow, J.C. *J. Chem. Soc.* 1960, 1768
9. Patrick, C.R.; Prosser, G.S. *Nature* 1960, 187, 1021
10. Majer, J.R.; Patrick, C.R. *Trans. Faraday Soc.* 1962, 58, 17
11. Bralsford, R.; Harris, P.V.; Price, W.C. *Proc. Roy. Soc. London, Ser. A* 1960, 258, 459
12. Schenk, G.H. *Record of Chemical Progress* 1967, 28, 135
13. Foster, R.; Fyfe, C.A. *Chem. Comm.* 1965, 642
14. Boeyens, J.C.A.; Herbstein, F.H. *J. Phys. Chem.* 1965, 69, 2153
15. Duncan, W.A.; Swinton, F.L.; *J. Phys. Chem.* 1966, 70, 2417
16. McLaughlin, E.; Messer, C.E. *J. Chem. Soc. A* 1966, 1106
17. Duncan, W.A.; Sheridan, J.P.; Swinton, F.L. *Trans. Faraday Soc.* 1966, 62, 1090
18. Baur, M.E.; Horsma, D.A.; Knobler, C.M.; Perez, P. *J. Phys. Chem.* 1969, 73, 641
19. Baur, M.E.; Knobler, C.M.; Horsma, D.A.; Perez, P. *J. Phys. Chem.* 1970, 74, 4594

20. Fenby, D.V.; McLure, I.A.; Scott, R.L. *J. Phys. Chem.* 1966, 70, 602

21. Fenby, D.V.; Scott, R.L. *J. Phys. Chem.* 1967, 71, 4103

22. Beaumont, T.G.; Davis, K.M.C. *J. Chem. Soc. B* 1967, 1131

23. Beaumont, T.G.; Davis, K.M.C. *Nature* 1968, 218, 865

24. Voigt, E.M. *J. Amer. Chem. Soc.* 1964, 86, 3611

25. Hanna, M.W. *J. Amer. Chem. Soc.* 1968, 90, 285

26. Hammond, P.R. *J. Chem. Soc. A* 1968, 145

27. Armitage, D.A.; Morcom. K.W. *Trans. Faraday Soc.* 1969, 65, 688

28. Gaw, W.J.; Swinton, F.L. *Trans. Faraday Soc.* 1968, 64, 637

29. Gaw, W.J.; Swinton, F.L. *Trans. Faraday Soc.* 1968, 64, 2023

30. Gaw, W.J.; Swinton, F.L. *Nature* 1966, 212, 283

31. Kogan, I.V.; Morachevskii, A.G. *Zh. Prikl. Khim.* (Leningrad) 1972, 45, 1888

32. Chinikamala, A.; Houth, G.N.; Taylor, Jr. Z.L. *J. Chem. Eng. Data* 1973, 18, 322

33. Dantzler, E.M.; Knobler, C.M. *J. Phys. Chem.* 1969, 73, 1602

34. Powell, R.J.; Swinton, F.L. *J. Chem. Thermodynamics* 1970, 2, 87

35. Powell, R.J.; Swinton, F.L.; Young, C.L. *J. Chem. Thermodynamics* 1970, 2, 105

36. Steele, D.; Gates, P.N.; Wheatley, W. Paper read before the Chemical Society, Exeter, 1967

37. Ott, J.B.; Goates, J.R.; Reeder, J. *J. Chem. Thermodynamics* 1974, 6, 281

38. Howell, P.J.; Skillerne de Bristowe, B.J.; Stubley, D. *J. Chem. Thermodynamics* 1972, 4, 225

39. Skillerne de Bristowe, B.J.; Stubley, D. *J. Chem. Thermodynamics* 1973, 5, 121

40. Kelly, T.; Swinton, F.L. *J. Chem. Thermodynamics* 1974, 6, 435

41. Komarov, E.V.; Kogan, I.V.; Morachevskii, A.G. *Zh. Prikl. Khim.* (Leningrad) 1973, 46, 1384

42. Fenby, D.V.; Ruenkrairergsa, S. *J. Chem. Thermodynamics* 1973, 5, 227

43. Ruenkrairergsa, S.; Fenby, D.V.; Jones, D.E. *J. Chem. Thermodynamics* 1973, 5, 347

44. Dahl, T. *Acta Chem. Scand.* 1971, 25, 1031

45. Dahl, T. *Acta Chem. Scand.* 1972, 26, 1569

46. Dahl, T. *Acta Chem. Scand.* 1973, 27, 995

47. Bauer, D.R.; Brauman, J.I.; Pecora, R. *J. Chem. Phys.* 1975, 63, 53

48. Ott, J.B.; Goates, J.R.; Cardon, D.L. *J. Chem. Thermodynamics* 1976, 8, 505

49. Goates, J.R.; Ott, J.B.; Reeder, J. *J. Chem. Thermodynamics* 1973, 5, 135

50. Ott, J.B.; Goates, J.R.; Reeder, J.; Shirts, R.B. *J. Chem. Soc., Faraday Trans., 1* 1974, 70, 1325

51. Barlatier, A.; Meyer, R.; Desplanches, H.; Metzger, J. *C.R. Acad. Sci., Ser. C* 1971, 273, 1473

52. Meyer, R.; Barlatier, A.; Vincent, E.J. *C.R. Acad. Sci., Ser. C* 1973, 277, 73

53. Meyer, R. *International Data Series - Selected data on mixtures,* Ser. A 1973, No. 2, pp132-134

54. Cyr, N. *Mol. Phys.* 1972 24, 459

55. Armitage, D.A.; Beaumont, T.G.; Davis, K.M.C.; Hall, D.J.; Morcom, K.W. *Trans. Faraday Soc.* 1971, 67, 2548

56. Armitage, D.A.; Brindley, J.M.T.; Hall, D.J. *J. Chem. Thermodynamics* 1975, 7, 97

57. Andrews, A.W.; Hall, D.; Morcom, K.W. *J. Chem. Thermodynamics* 1971, 3, 527

58. Martin, M.L.; Murray, R.S. *J. Chem. Thermodynamics* 1972, 4, 723 (Bound in at the back of this thesis.)

59. Alekseeva, M.V. *Zh. Fiz. Khim.* 1973, 46, 1060

60. Goates, J.R.; Ott, J.B.; Reeder, J.; Shirts, R.B. *J. Chem. Thermodynamics* 1974, 6, 489

61. Leong, C.Y.; Fenby, D.V.; Jones, D.E. *J. Chem. Thermodynamics* 1974, 6, 611

62. Mattingley, B.I.; Handa, Y.P.; Fenby, D.V. *J. Chem. Thermodynamics* 1975, 7, 169

63. Chand, A.; Fenby, D.V. *J. Chem. Thermodynamics* 1975, 7, 403

64. Handa, Y.P.; Fenby, D.V. *J. Chem. Thermodynamics* 1975, 7, 405

65. Davis, F.T.; Bedsole, A.D.; Taylor, Jr. Z.L. *J. Chem. Thermodynamics* 1975, 7, 611

66. Leong, C.Y.; Jones, D.E.; Fenby, D.V. *J. Chem. Thermodynamics* 1974, 6, 609

67. Hall, D.J.; Morcom, K.W. *J. Chem. Thermodynamics* 1975, 7, 407

CHAPTER 2

MEASUREMENT AND CONTROL OF TEMPERATURE; CATHETOMETRY

2.1 Absolute measurement of temperature: Absolute measurement of the thermodynamic temperature, T, is attended by errors from two sources:

(i) A fundamental error of convention,[1,2] over which the experimenter has no control, exists because of the inequality of the thermodynamic and practical temperature scales. This inequality, up to 0.015 K in the range 0-500 K,[1] is zero only at 273.16 K by definition, and arises from uncertainties in the assignment of fixed reference points (*viz.* phase equilibria) on the thermodynamic temperature scale. This error does not, however, hinder precise comparison of experimental results where due regard is given to the temperature convention used in each measurement. Both International Practical Temperature Scales (IPTS) of 1948 and 1968 occur in literature of current interest and accurate work must recognize the difference between them.

(ii) Despite careful observance of correct procedure, the accuracy of absolute practical temperature measurements in most laboratories probably does not exceed ±0.001 K [3] and may be considerably less where no special precautions have been taken (see *appendix 2.1*). For many purposes an error of order 0.01 K is inconsequential, producing uncertainties in the measured quantity which are far outweighed by other experimental considerations. However, it becomes increasingly important when T is essentially the dependent variable (*e.g.* phase equilibrium studies).

For this work T was measured with bomb calorimeter thermometers of the total immersion type readable to about 0.001 K. These thermometers had a known history and were carefully and frequently calibrated, under the conditions of their use, against a Leeds and Northrup model 8163 platinum resistance thermometer. This had itself been characterized by a national standards laboratory.[3] The ice-point of this instrument was measured using aerated, distilled, de-ionized water (May 1976) and found to differ from the original calibration by 0.0025 K and from a previous measurement made in this laboratory (Dec. 1973) by only 0.0006 K. The most recently measured ice-point was used in all calculations.[3] Independent calibrations of a single thermometer had a reproducibility comparable with the reading error of the scale (*viz.* ±0.001 K). The accuracy of absolute practical temperature measurements obtained from these thermometers during this work is believed to be within ±0.005 K. For the two temperatures employed here, the comparison between IPTS—48 and IPTS—68 is shown below.[1,2]

T_{68}/K	T_{48}/K
283.150	283.154
298.150	298.159

Actual temperatures (IPTS—68) of experiments are stated throughout this work.

2.2 Temperature control: The magnitude and frequency of changes, and the position dependence of absolute temperature in a thermostatted bath, can be readily monitored with high sensitivity (ca. 0.0001 K) for the duration of most experiments. This work made use of electronic temperature regulators which were found to be more reliable than the mercury/toluene relay (see *appendix 2.2*). Initially, temperature control was obtained with a thermistor/Wheatstone bridge circuit and the feedback from a sensitive chart recorder which activated a solid-state relay and a heater (100 W light bulb). Though effective in temperature control, this arrangement produced frequent failure in the servo-potentiometer of the recorder due to constant and rapid motion. It was replaced with a solid state "proportional" temperature controller in which no mechanical links were present. This regulator used the amplified output of a thermistor/Wheatstone bridge circuit to vary the operating phase angle of a silicon controlled rectifier. The heater (100 W light bulb) produced a heating effect commensurate with the deviation of bath temperature from a mean value. The entire circuit was contained in an oil-filled brass cylinder and immersed in the bath of interest. This "temperature feedback" removed drift of the control point caused by changing ambient temperature and its effect on temperature-sensitive circuit elements in the regulator. Temperature control was generally better than ±0.002 K. Those conditions which produced best temperature control in this work are noted in *appendix 2.3*.

2.3 Cathetometry: The relative positions of mercury menisci during experiments were read to 0.001 cm with a telemicroscope[a] mounted on a 1 metre cathetometer scale.[b] Both the scale and meniscus motion were rendered strictly vertical by careful levelling. The telescope was fixed in the horizontal mode using an "artificial horizon" of mercury in a wide U-tube. Menisci were illuminated by small lamps fitted with green translucent shields[4] and adjusted so that only a narrow slit of light appeared over the meniscus crown. This produced sharp images, free from the effects of reflected light. Vibration was

---

[a] Gaertner Scientific Corp., Chicago, U.S.A.

[b] Precision Tool and Instrument Co., Surrey, U.K.

minimized by mounting thermostatted baths on industrial anti-vibration matting. A check of the cathetometer against a calibrated Invar bar[a] mounted in a bath showed that, within experimental error, no differential refractive effects were present. Vapour pressures, measured with a mercury manometer, were obtained from the expression,

$$P = \rho(\mathrm{Hg},T).g_l.\Delta h \qquad 2.1$$

where P is the true vapour pressure (Pa);

$\rho(\mathrm{Hg},T)$ is the density of mercury at temperature T

$\rho(\mathrm{Hg},\ 298.15\ \mathrm{K}) = 13533.6\ \mathrm{kg.m^{-3}})^{4,b}$;

g_l is the local acceleration due to gravity (for this laboratory $g_l = 9.79724\ \mathrm{m.s^{-2}})^{5}$;

Δh is the observed difference in height (metres) of the mercury menisci.

Measurements of the position of both the base and crown of these menisci indicated that capillary corrections[4] were unnecessary (*viz.* less than 2 Pa).

---

[a] Calibrated by the Metrology Section, South Australian Railways, Islington.

[b] *Linear* extrapolation of values at 273.15 K and 293.15 K.

References

1. Division of Physics-National Standards Laboratory, C.S.I.R.O., Sydney *International Practical Temperature Scale of 1968* January 1969
2. Ambrose, D. *J. Chem. Eng. Data* 1976, 21, 139
3. National Standards Laboratory Report on the calibration of a Platinum Resistance Thermometer (serial no. 1793421) 23rd June 1972
4. Weissberger, A.; Rossiter, B.W. *Techniques of Chemistry* Vol. I, Pt. V, Wiley-Interscience 1971
5. Hall, J. McG. Report of the Gravitational Stations in the Metropolitan Area and Salisbury *South Australian Department of Mines, Report 59/89* 1964

CHAPTER 3

MATERIALS

3.1 Introduction: The results of physical measurements on liquids and their mixtures are variously affected by the nature and concentration of impurities. Occasionally one is confronted in the literature by statements concerning purity which range from non-existent to vague or misleading. This is fortunately becoming rare, most laboratories now having access to sensitive instrumental methods of chemical analysis. Assessment of the effect of contaminants on a given measurement is often a complex process which, at best, is only qualitative. When all other experimental considerations have been combined to estimate errors, this element of uncertainty may still exist. A comparison of results obtained with a liquid of varying purity may be the only absolute measure of precision. During this work the number of moles of a liquid present in an experiment was calculated by assuming absolute purity (*i.e.* 100 mol per cent.) of the sample. Without detailed knowledge of impurities (often chemically similar to the major component), this seemed the most valid procedure.

3.2 Gas-liquid chromatography (g.l.c.):[1] G.L.C. is a rapid and extremely sensitive analysis method which is undoubtedly the most popular one for use with organic solvents. This work made use of two such instruments:

(i) A Perkin-Elmer F11 unit equipped with a flame-ionization detector (F.I.D.).

(ii) A Carle 311 unit equipped with both flame-ionization and thermal conductivity detectors (T.C.D.).

The use of the less sensitive thermal conductivity detector was restricted to analysis for water and carbon disulphide since F.I.D. response to both of these compounds is zero.[1] The concentrations of impurities were calculated from peak areas assuming equal detector *mass* sensitivity to each species present.[1] This approximation is essentially valid within certain families of organic compounds which commonly group together as impurities (see *appendix 3.1*). Analyses were conducted under a range of conditions for each liquid. This served the following purposes:

(i) Detection of relatively non-volatile impurities.

(ii) Detection of impurities with retention times close to the major component.

(iii) Disclosure of any thermal degradation of the liquid which may invalidate analysis results.

The conditions and results of final analyses of the liquids used during this work are contained in table 3.1. These analyses represent the condition of each liquid at the time of experimental use.

3.3 Purification: Where possible (or necessary) the liquids I-X, listed below, were purified just prior to experiments. For the liquids I-VI the following sequence of purification steps was carried out *in addition* to those noted below.

(i) Chromatographic analysis of the liquid as supplied by the manufacturer.

(ii) Drying over granulated anhydrous calcium chloride.

(iii) Fractional distillation using 0.25 and 0.45 metre columns of infinitely variable reflux ratio, packed with glass helices and contained in silvered evacuated jackets. Fractions were collected entirely on the

Table 3.1: G.L.C. analyses

liquid	column/column temperature (°C)	Impurity concentration (mass per cent.)		
		$\bar{V}^E$	$\bar{H}^E$	$\bar{G}^E$
benzene	a/55		0.002	0.002
n-hexane	a/60			0.02
cyclo-hexane	b/50		0.03	
carbon tetrachloride	a/30		0.03	
hexafluorobenzene	a/35	0.01-0.02	0.01-0.02	0.005
di-ethyl ether	c/20		0.01	0.005
di-*iso*-propyl ether	b/30		0.04	0.03
di-*n*-butyl ether	b/40		0.21	
di-allyl ether	b/60	0.35		
di-benzyl ether	d/100	0.82		

[a] 4 metre/10 mass per cent. squalane on A.W.-D.M.C.S. Chromosorb W (80/100)

[b] 18 feet/15 mass per cent. Ucon oil on A.W.-D.M.C.S. Chromosorb W (80/100)

[c] 20 feet/28 mass per cent. Carbowax 20M on Varaport 20 (100/120)

[d] 2 metre/10 mass per cent. fluorosilicone oil (F.S. 1265) on A.W.-D.M.C.S. Chromosorb W (80/100)

basis of frequent chromatographic analysis.

(iv) Storage of the pure fractions over clean sodium wire. Molecular sieves (B.D.H. Type 4A) used for drying were from a new batch which had been dried in an air oven (ca. 16 hours, 500°C) and stored in an evacuated desiccator over phosphorus pentoxide.

I *benzene:* "'Univar' A.R. grade benzene" (Ajax Chemicals Ltd. - Sydney/Melb.). Thiophen was first removed by exhaustive treatment with concentrated sulphuric acid.[2]

II *n-hexane:* "'Uvasol' spectroscopic grade Hexan" (E. Merck, Darmstadt). Branched chain and unsaturated hydrocarbons were first removed by exhaustive treatment with chlorosulphonic acid at room temperature.[3]

III *cyclo-hexane:* "'Uvasol' spectroscopic grade cyclohexan" (B.D.H. Chemicals Ltd., Poole, U.K.).

IV *carbon tetrachloride:* "'Analar' A.R. grade carbon tetrachloride (B.D.H. Chemicals Ltd., Poole, U.K.) was dried over anhydrous calcium sulphate.

V *di-ethyl ether:* "'Analar' A.R. grade di-ethyl ether" was first freed of peroxides by standard methods.[2] The liquid was stored in the dark, under dry nitrogen and in the presence of copper gauze.[2]

VI *di-iso-propyl ether:* "B.D.H. 'technical grade' di-*iso*-propyl ether" was treated as for di-ethyl ether. For long term storage purposes 0.005 mass per cent. of hydroquinone ("B.D.H. L.R. grade quinol") was added. It was noted, however, that the ether cannot be stored in the presence of *both* sodium metal and hydroquinone since the two apparently react to form a blue-green radical ion.

VII *di-n-butyl ether:* "Pfaltz and Bauer commercial grade di-*n*-butyl ether" (Flushing, N.Y., U.S.A.) proved difficult to purify by standard methods (see *appendix 3.2*). The liquid was dried over calcium chloride and fractionally distilled under dry nitrogen at reduced pressure (6.67 kPa, 64°C). The distillation was carried out at reflux ratio 5:1 on a 1 metre spinning band column.[a] The pure fraction was stored over clean sodium wire in the dark.

VIII *di-allyl ether:* "Pfaltz and Bauer commercial grade di-allyl ether" (see *appendix 3.3*) was treated with a column of activated alumina[2] and fractionally distilled to give a product containing only two major contaminants. One of these was almost completely eliminated by final drying with molecular sieves.

IX *di-benzyl ether:* "Pfaltz and Bauer commercial grade di-benzyl ether" could not be purified by standard methods (see *appendix 3.4*). The liquid was passed through an alumina column under pressure. This considerably reduced the concentration of three of the five major impurities. The ether was then placed in a flask attached to a high vacuum line and degassed exhaustively by alternate freezing and thawing until the residual pressure over the frozen liquid was about 0.02 Pa. A crude fractional distillation was then conducted using a magnetic stirrer, mild heating and

---

[a] Ernst Haage, Apparatebau u. Laboreinrichtungen, Mülheim-Ruhr.

a receiving vessel cooled in ice. The purest fraction was stored under dry nitrogen with molecular sieves.

X *hexafluorobenzene:* Imperial Smelting Corporation (N.S.C.) Ltd. (Avonmouth, Bristol, U.K.) had supplied two samples of hexafluorobenzene for earlier measurements.[4] At the outset of this work it was necessary to reclaim the pure liquid from two sources:

sample (i): A mixture of high purity hexafluorobenzene with four aliphatic ethers (ca. 50 mol per cent.).

sample (ii): Impure "tailings" of hexafluorobenzene containing other fluorobenzenes (ca. 97 mass per cent.).

sample (i): The mixture was stirred with oleum at room temperature to destroy ethers (see *appendix 3.5*). After separation of the layers and exhaustive washing with sodium bicarbonate solution and distilled water, the liquid was dried over calcium chloride. A rapid distillation produced material of the original purity (ca. 99.99 mass per cent.) with little loss. It was then stored over molecular sieves.

sample (ii): The purification of crude hexafluorobenzene has already been described.[4] The practice of oxidation with potassium permanganate in acetone was found to be objectionable because of the subsequent difficulty in removing the acetone. After 6 extractions with distilled water the sample contained about 10 mass per cent. of the ketone; it was eventually removed by prolonged stirring with 5 portions of concentrated sodium metabisulphite solution.

The work of Evans *et al.*[5] and similar experience in this work suggests that the chemical pre-treatment of crude hexafluorobenzene may be unnecessary. The impurities present do not appear to form solid solutions with the main liquid and are rapidly eliminated by directional freezing. This represents a considerable gain in yield. Rather than removing the unfrozen liquid after each recrystallization, it was the practice during this work to allow the solid to thaw and then to refreeze the undisturbed liquid (a single freezing required about 18 hours). This produced a further gain in the yield of purified material since the unfrozen liquid was only removed after about 10 cycles. At this stage the ratio of impurity concentrations in the unfrozen and bulk liquid was about 25:1.

Where required for vapour pressure measurements, the purest fractions of the above liquids were selected and placed in storage flasks containing molecular sieves. These flasks were fitted with "Kovar" glass/metal seals[a] and "Nupro" 6.35 mm bellows valves.[b] The liquid was crudely degassed by alternate freezing and thawing until the residual pressure over the solid was less than about 1 Pa. After transferring the liquid *in vacuo* to another flask, the molecular sieves were heated under continuous evacuation for some hours. The liquid was then returned and the flask sealed. It is believed that liquids treated and stored in this way are extremely dry ($\leqslant 10^{-4}$ mol per cent.).[6]

3.4 Liquid densities: The densities of liquids used during this work are shown in table 3.2. With the exception of di-allyl ether

---

[a] Jencons (Scientific) Ltd., Hemel Hempstead, Herts. U.K.

[b] Nupro Co., Cleveland, Ohio, U.S.A.

Table 3.2: Liquid densities (ρ/kg.m^{-3})

liquid	ρ(283.150 K)	ρ(298.150 K)
benzene		873.65[4]
n-hexane		654.79[12,a]
cyclo-hexane		773.83[4]
carbon tetrachloride		1584.52[13,a]
hexafluorobenzene	1640.88[4]	1606.88[4]
di-ethyl ether	724.97[4]	707.68[4]
di-*iso*-propyl ether	733.99[10]	718.85[10]
di-*n*-butyl ether	776.64[10]	763.74[10]
di-allyl ether		801.52
di-benzyl ether		1039.53

[a] These densities were not measured by this author.

and di-benzyl ether, these densities are those of liquids of similar purity used in previous work[4,10,12,13] in these laboratories, and compare favourably (±0.008%) with reliable literature values.[2,15] Where necessary, they were corrected to the true temperature of experiments.[2,10] This adjustment was always less than 0.01% of the density.

The densities of di-allyl ether and di-benzyl ether were measured in duplicate by a method previously described.[10] The di-benzyl ether used for density measurements consisted of two samples which were both less pure than that used for experiments:

(i) 96.0 mass per cent. $\rho(298.150\ \mathrm{K}) = 1040.12\ \mathrm{kg.m^{-3}}$

(ii) 98.5_5 mass per cent. $\rho(298.150\ \mathrm{K}) = 1039.65\ \mathrm{kg.m^{-3}}$

The density of this liquid shown, in table 3.2, was obtained by linear extrapolation of the above values to the purity shown in table 3.1. This process yields, for the pure liquid, a density $\rho(298.150\ \mathrm{K}) = 1039.38\ \mathrm{kg.m^{-3}}$ (c.f. 1039.9[2]). The measured density of di-allyl ether compares unfavourably with values calculated from literature (800,[8] 820.6[9]) using $\alpha = 0.0013\ \mathrm{K^{-1}}$.

The degree of aeration of organic solvents has diverse effects on their densities.[11] The results presented in table 3.2 are the densities of liquids which had been partially outgassed by heating to about 30°C above the temperature of measurement. Liquids used for $\bar{V}^E$ and $\bar{H}^E$ measurements were also treated in this manner, while those used for vapour pressure measurements were, of course, rigorously outgassed. The agreement[10] between duplicate measurements and *modern* literature values, however, implies that the liquids used here are not significantly affected in this regard. The precision of all density measurements presented here is believed to be ±0.002%.[10]

3.5 Vapour pressure at 298.150 K: The vapour pressures of liquids used for evaluation of $\bar{G}^E$ are shown in table 3.3. The method of measurement is described in *section 2.3*. Where necessary, the measured pressures (and the literature values with which they are compared) were adjusted ($\Delta T < 0.02$ K) to 298.150 K (IPTS-68) using the Antoine equation.[2] The vapour pressure of each liquid was measured on several occasions and the standard deviation of these observations was added to the error expected from absolute temperature inaccuracy (see *Chapter 2*) to produce the uncertainties shown in the table. In order to assess the effect of contaminants, the vapour pressure of each liquid was measured in the following ways:

(i) A small (ca. 0.1 cm^3) sample was tested. The vapour in equilibrium with this sample (at least 30% of the sample itself) was then swept away into a cold trap and the remaining liquid re-tested.

(ii) A quantity of vapour in equilibrium with the liquid was condensed in the vapour pressure cell and tested.

Although this test is not definitive, any significant difference between the vapour pressure of the bulk liquid and the values obtained in (i) and (ii) above may indicate the presence of non-azeotropic impurities. The vapour pressure of *n*-hexane decreased by about 0.027 kPa to a steady value when vapour in equilibrium with the bulk liquid was successively swept away. For the other liquids tested the maximum difference in vapour pressures between (i) and (ii) above was less than 0.009 kPa. Literature values of the vapour pressure of di-ethyl ether are scattered and, for the most part, dated.[2,16] The discrepancy between the value in reference 14 and that reported here seems too large to be a temperature error (ca. 0.046 K), but may be

Table 3.3: Vapour pressures (kPa) at 298.150 K

liquid	this work	literature
benzene	12.683 ± 0.008	12.691[12]
n-hexane	20.153 ± 0.009	20.161[12]
di-ethyl ether	71.487 ± 0.019	71.622[14]
di-*iso*-propyl ether	19.891 ± 0.008	19.88,[17] 19.952[18,a]
hexafluorobenzene	11.274 ± 0.006	11.260[15,a]

[a] From the Antoine equation.

due to a difference in the purity of the samples used. The agreement between the observed vapour pressure of hexafluorobenzene and that in reference 16 is satisfactory for an extrapolation of the Antoine equation of some 12.3 K.

References

1. McNair, H.M.; Bonelli, E.J. *Basic Gas Chromatography* 5th Ed. Varian-Aerograph, March 1969
2. Riddick, J.A.; Bunger W.B. *Techniques of Chemistry* Vol. II 3rd Ed. Wiley-Interscience 1970
3. Shepard, A.F.; Henne, A.L.; Midgley, Jr. T. *J. Amer. Chem. Soc.* 1931, 53, 1948
4. Martin, M.L.; Murray, R.S. *J. Chem. Thermodynamics* 1972, 4, 723 (Bound in at the back of this thesis.)
5. Evans, F.D.; Bogan, M.; Battino, R. *Anal. Chem.* 1968, 40, 224
6. B.D.H. Laboratory Chemicals Division (Poole, England) *'Union Carbide' molecular sieves for selective adsorption* 3rd Ed. 2nd Imp. (revised)
7. Fuller, G. *private communication* Imperial Smelting Corporation (N.S.C.) Ltd. Avonmouth, Bristol, England. 14th March 1968
8. Hodgman, C.D. (Ed.) *Handbook of Chemistry and Physics* 41st Ed. Chemical Rubber Publishing Co. Ohio 1959-1960
9. Weast, R.C. (Ed.) *Handbook of Chemistry and Physics* 47th Ed. Chemical Rubber Publishing Co. Ohio 1966-1967
10. Murray, R.S. *Honours Report* Physical and Inorganic Chemistry Department, University of Adelaide 1971
11. Battino, R. *Chem. Rev.* 1971, 71, 5
12. Bell, T.N.; Cussler, E.L.; Harris, K.R.; Pepela, C.N.; Dunlop, P.J. *J. Phys. Chem.* 1968, 72, 4693
13. Symons, J.M. *Honours Report* Physical and Inorganic Chemistry Department, University of Adelaide 1971
14. Ambrose, D.; Sprake, C.H.S.; Townsend, R. *J. Chem. Thermodynamics* 1972, 4, 247

15. Counsell, J.F.; Green, J.H.S.; Hales, J.; Martin, J.F. *Trans. Faraday Soc.* 1965, 61, 212

16. Timmermanns, J. *Physico-Chemical constants of Pure Organic Compounds* Elsevier: Amsterdam 1950

17. Ambrose, D.; Ellender, J.H.; Sprake, C.H.S.; Townsend, R. *J. Chem. Thermodynamics* 1976, 8, 165

18. Cidlinsky, J.; Polak, J. *Collect. Czech. Chem. Comm.* 1969, 34, 1317

CHAPTER 4

EXCESS VOLUMES

4.1 Introduction: The excess volume of mixing, $\bar{V}^E(x,T,P)$, may be used, with caution, to study the nature of unlike interactions in liquid mixtures.[1] The magnitude and sign of $\bar{V}^E$ often parallels the strength and nature of intermolecular forces. It may also, however, reflect the relative stability of "quasi-lattice" structures in the pure and mixed liquids resulting from the effects of molecular geometry.[1] $\bar{V}^E$ is a sensitive indicator of the precision of solution theories,[2] and accurate, general predictions of its magnitude are rare. In an experimental sense, $\bar{V}^E$ measurements of high precision are readily accessible with relatively unsophisticated equipment. For these reasons they form a useful adjunct to other thermodynamic measurements.

4.2 Measurement of $\bar{V}^E$: A review, by Battino,[2] of experimental methods of determining $\bar{V}^E$ has been followed by further noteworthy developments:

(i) The adoption of the system cyclohexane + benzene as a test standard for $\bar{V}^E$ has received wide approval.[3,4,5]

(ii) A much cited paper by Stokes *et al.*[3] has pointed to the considerable advantages of a continuous dilution dilatometer. A modified version of this device has previously been used with success in this laboratory.[6]

(iii) Indirect measurements on the above test system using a commercial densimeter have been published by Benson *et al.*[4] Although these results are more scattered than those obtained directly,[3] the agreement between smoothed values is better than 0.6%.

(iv) Bottomley and Scott[7] have produced a tilting dilatometer, based on (ii), in which no tap adjustments are required during experiments. Small errors due to extrusion of grease from taps are thus eliminated. Experience in this and other work[5] has shown that this effect is small and non-reproducible (see *appendix 4.1*).

(v) A continuous dilution dilatometer which operates at constant pressure has been described by Tanaka *et al.*[5] Results obtained for the system (i) with this device were systematically higher (up to 0.004 $cm^3.mol^{-1}$) than those in reference 3 (see *appendix 4.2*).

4.3 Experimental: For this work a modified[8] Stokes-Levien-Marsh dilatometer[3] was used (*figure 4.1*) of the type later described by Reeder *et al.*[9,a] This device is easy to clean and fill and gives trouble-free operation. Liquid contact with all but inert materials is non-existent. Two working days sufficed to produce 30 points over the entire composition range using only about 30 cm^3 of each liquid. The filling and operating procedure is outlined in *appendix 4.3*. For this work $\bar{V}^E$(x, 298 K) was measured for the systems hexafluorobenzene + di-allyl ether and hexafluorobenzene + dibenzyl ether. A computer program was used to calculate results and fit these to a smoothing equation of the form,

$$\bar{V}^E(x) = x(1-x)\sum_{i=0}^{p} a_i x^i \qquad 4.1$$

---

[a] These authors[9] determined the volume of the stationary component by initially removing a weighed amount of mercury from the mixing vessel.

Figure 4.1: Continuous dilution dilatometer: The apparatus consists of a heavy-walled pyrex glass construction mounted on a brass frame, BF, with an adjustable three-point suspension for levelling. T_1, T_2 and T_3 are "Interkey" spring-loaded glass taps[a] lubricated with B.D.H. high vacuum silicone grease. T_2 is operated by a pulley, P, and T_3 by a detachable pulley. T_4 is a P.T.F.E./glass needle valve.[b] T_5 is a "Rotaflo" P.T.F.E./glass stopcock.[c]

C_{1-4} are "Quickfit" B10 ground glass cones.

F_{1-4} are fiducial marks.

The mixing vessel M (ca. 24 cm^3) contains a glass encased magnet, S, for stirring. R is a reservoir for resetting the mercury level in C, a section of "Veridia" precision bore glass capillary (0.075 cm).

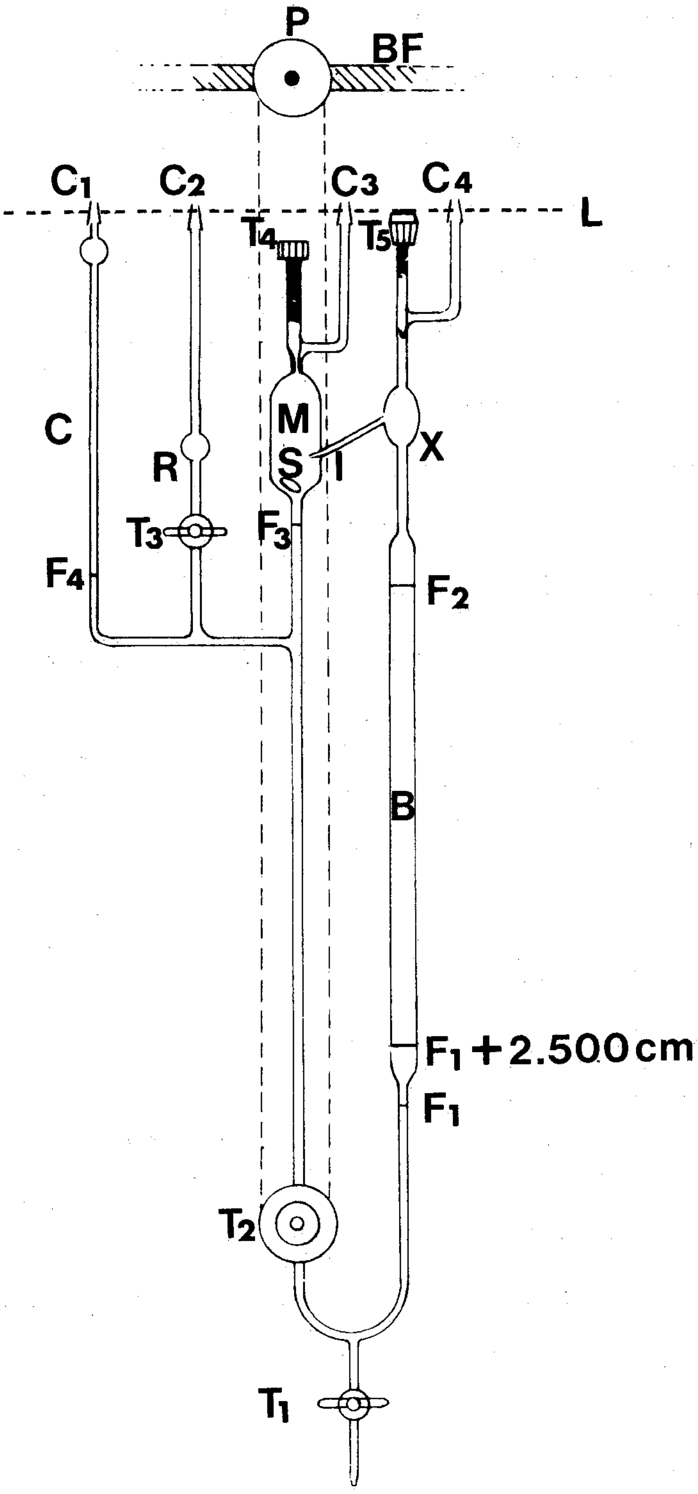
The burette, B, consists of two sections of "Veridia" precision bore glass tubing (0.4, 0.8 cm) with a calibrated cross-over section between F_1 and the imaginary fiducial mark F_1 + 2.500 cm. X is a tapered seat used for filling purposes. The inlet tube, I, has a small bore and a very fine tip in M to give a well-defined junction between the liquids in M and B. B and C are parallel to within 1°. The dashed line L marks bath level during experiments.

---

[a] G. Springham and Co. Ltd., Essex, U.K.

[b] Halu Glass Manufacturers, Croydon, Vic.

[c] Quickfit and Quartz Ltd., Staffordshire, U.K.


P
BF
C1
C2
C3
C4
L
T4
T5
C
M
S
I
X
R
T3
F3
F4
F2
B
F1 + 2.500 cm
F1
T2
T1

Each point was given equal statistical weight and the error in x was taken as zero. The number, p, of parameters, a_i, was chosen such that an increase in p produced no significant reduction of the standard deviation of the fit. The results of these calculations appear in *Chapter 7* with experimental results.

4.4 Compressibility - measurement and use: For dilatometers of the type described here, compressibility corrections are both necessary[3] and useful. They form a diagnostic for the presence of undissolved air which may seriously affect results. Isothermal compressions were measured in this work by observing the dilation, Δh_c, of the meniscus in c (see *figure 4.1*) caused by an external pressure, p_e. This measurement was carried out, for at least four values of p_e, both before and at the end of each half-run. Since the dilation in c also represents a pressure change on the system, the constant, b, referred to in reference 3, is given by

$$b = \left(\frac{\partial \Delta h_c}{\partial p_e}\right)_T / \left(1 - r\left(\frac{\partial \Delta h_c}{\partial p_e}\right)_T\right) \qquad 4.2$$

where r is the ratio of the cross-sectional area of c to that of the mercury in or below the mixing-vessel. The precision of these measurements is believed to be ±2%.[a] In calculating

---

[a] A crude estimate of $\bar{\kappa}^E(x_1)$ was made from the measured values of b.

di-benzyl ether(1) + hexafluorobenzene(2)

$\bar{\kappa}^E(0.4) \approx -8 \times 10^{-7}\ \mathrm{kPa}^{-1}$

di-allyl ether(1) + hexafluorobenzene(2)

$\bar{\kappa}^E(0.4) \approx +1 \times 10^{-7}\ \mathrm{kPa}^{-1}$

$\bar{V}^E$ for each half-run, a linearly interpolated value of b was used.

4.5 Errors: The mismatch of curves and the scatter of points for the system hexafluorobenzene + di-allyl ether are somewhat larger than those normally observed.[6] During experiments a small quantity of a white solid was formed slowly at the mercury/ether interface probably leading to a spurious volume change.

Apart from errors due to the presence of impurities, the factors outlined in *appendix 4.4* combine to produce an overall uncertainty of 0.1-0.2% in $\bar{V}^E(\phi = 0.5)$[a] and of 0.0005 in x. This statment is, however, applicable only to systems having moderate to large excess volumes (*i.e.* $|\bar{V}^E|$ greater than about 0.1 $cm^3.mol^{-1}$). For small values of $\bar{V}^E$ the relative errors may be considerably larger.

---

[a] $\phi \equiv$ volume fraction.

References

1. Duncan, W.A.; Sheridan, J.P.; Swinton, F.L. *Trans. Faraday Soc.* 1966, 62, 1090
2. Battino, R. *Chem. Rev.* 1971, 71, 5
3. Stokes, R.H.; Levien, B.J.; Marsh, K.N. *J. Chem. Thermodynamics* 1970, 2, 43
4. Kiyohara, O.; Benson, G.C. *Can. J. Chem.* 1973, 51, 2489
5. Tanaka, R.; Kiyohara, O.; D'Arcy, P.J.; Benson, G.C. *Can. J. Chem.* 1975, 53, 2262
6. Martin, M.L.; Murray, R.S. *J. Chem. Thermodynamics* 1972, 4, 723 (Bound in at the back of this thesis.)
7. Bottomley, G.A.; Scott, R.L. *J. Chem. Thermodynamics* 1974, 6, 973
8. Dobinson, L. *Honours Report* Physical and Inorganic Chemistry Department, University of Adelaide, 1972
9. Reeder, J.; Knobler, C.M.; Scott, R.L. *J. Chem. Thermodynamics* 1975, 7, 345

CHAPTER 5

CALORIMETRY - EXCESS ENTHALPIES

5.1 *Introduction:* The molar excess enthalpy, $\bar{H}^E(x,T,P)$ is a somewhat more direct guide than $\bar{V}^E$ to the relative strengths of like and unlike molecular interactions in binary liquid mixtures. Large negative or large positive values of $\bar{H}^E$ indicate, respectively, specific interaction or antipathy between the two components.

The molar excess heat capacity,[1] $\bar{C}_p^E(x,T,P)$, given by the relation

$$\bar{C}_p^E = \left(\frac{\partial \bar{H}^E}{\partial T}\right)_{x,p}, \qquad 5.1$$

is conveniently measured by evaluating $\bar{H}^E$ at a series of temperatures. Positive values of $\bar{C}_p^E$ may indicate the presence of specific interactions in mixtures.[2]

5.2 *Measurement of $\bar{H}^E$:* Calorimeters for the experimental determination of binary liquid $\bar{H}^E$ data are of three basic types.[3,4]

(i) In *flow calorimeters* a binary mixture of definite composition is formed by the confluence of two liquids each with a constant, but adjustable, flow rate. The temperature differential produced in the mixing vessel by the enthalpy change is usually annulled (endothermic) or simulated (exothermic) by an electric heater of known power in a separate experiment in which the mixture itself is passed through the device at the same total flow rate. These calorimeters generally consume a relatively large quantity of liquid when $\bar{H}^E(x)$ is studied.

(ii) In *adiabatic calorimeters* the two liquids are mixed in a vessel which is thermally isolated from its surroundings. The enthalpy change is then generally measured as in (i).

(iii) In *isothermal calorimeters* mixing occurs at essentially constant temperature maintained by operation of an electrical heater and/or a thermoelectric cooling device.

The successful use and publication by Van Ness *et al.*[5] of an isothermal dilution calorimeter has established the popularity of this type of instrument for precise $\bar{H}^E$ measurements.[4] While possessing the advantages of continuous dilution devices (see *section 1.1*), the isothermal calorimeter is largely free of the drawbacks peculiar to flow and adiabatic devices.[3,4]

Stokes *et al.*[6,7] have constructed and refined an isothermal displacement calorimeter and established $\bar{H}^E$ for some test systems with exceptional precision. This device is suitable for use with endothermic and with weakly exothermic systems.

Tanaka *et al.*[8] have described a similar device which uses the power balance between a Peltier cell and an electric heater of known power to produce a zero temperature differential between the mixing vessel and the surroundings. This arrangement allows the measurement of both positive and negative enthalpy changes with equal ease.

The distinction between calorimeters of the types (ii) and (iii) is not always clear.[3] Measurement of endothermic heats of mixing in adiabatic calorimeters is often conducted under isothermal conditions, while most isothermal calorimeters have mixing vessels which are thermally isolated from the surroundings, to some degree, to minimize heat losses resulting from temperature fluctuations during mixing.

Accurate determination of $\bar{H}^E$ is beset by a number of practical difficulties.[3] Matters of primary concern in all calorimeters are (a) the absence of a vapour space in the mixing vessel, (b) rapid completion of mixing, (c) rapid and sensitive temperature measurement, (d) constancy of temperature of the surroundings and (e) exchange of heat with the surroundings. This last consideration varies in importance with the design of the calorimeter itself. Significant gains and losses of heat from various sources must be allowed for, and one method of checking the accuracy of these corrections is the "blank" or "dummy" run in which only *one* liquid is used, the corrections are applied, and "$\bar{H}^E$" is evaluated. This process does not, however, reveal contributions arising only when *two* liquids are involved (*e.g.* change in stirrer power with density and viscosity of the mixture), nor does it detect composition errors (*e.g.* from incorrect volume calibration). The definitive test of calorimeters lies in their ability to reproduce reliable data obtained with instruments of different design.

Elliot and Wormald[9] have recently described a precision differential flow calorimeter from which they have obtained $\bar{H}^E(x,T)$ data, for the system benzene + cyclohexane, which are of low scatter ($\sigma \approx 0.2$ J.mol^{-1}) and are in excellent agreement with the results of Ewing *et al.*[7] who employed an isothermal displacement calorimeter.

5.3 *Experimental:* For this work an isothermal displacement calorimeter of a form similar to the dilatometer discussed in *Chapter 4* was designed, built and tested. The various features of this device are shown in *figures 5.1-5.4*.

The calorimeter (*figure 5.1*) is mounted on a brass plate, BP, which is suspended on a heavy brass frame (not shown) provided with a three-point suspension for levelling purposes. A calibrated *burette*, B, consisting of a 40 cm length of "Veridia" precision bore (10 mm) glass tubing, is sealed at the lower end by a spring-loaded ground-glass tap, T_2, and at the top by T_4, a P.T.F.E./glass valve. The reservoir, BR, used for filling purposes, joins the burette above the seat of T_4 and may be sealed at the ground-glass cone, C_1. This burette is used to add liquid to the mixing-vessel, MV, via the *inlet*, I, a 40 cm length of glass capillary (0.4 mm). F_1, F_2 and F_3 are fiducial marks.

The *mixing-vessel assembly* (ca. 51 cm^3, *figure 5.2*) consists of a heavy-walled (3.3 mm) "Pyrex" glass cup, G, with a polished, flat upper rim, sealed by a close-fitting P.T.F.E. gasket, TG, seated in a flanged conical stainless-steel cap, SL, which is threaded to receive a P.T.F.E. needle valve, T_5. This cap is secured by four stainless-steel bolts, SB, which pass through a stainless-steel ring, SR, provided with a shaped polyethylene cushion, PC, and up through a detachable, threaded stainless-steel collar, SC.

A fast-response bead-in-glass *thermistor*, TH, provided with non-inductively wound leads, is mounted on the cap, SL, in a threaded conical socket, SO, via a P.T.F.E. cone, TC, and a nut, SW, which is tightened to give a close seal.

A *heater*, H, formed from a length of "Karma" wire wound

Figure 5.1: Isothermal displacement calorimeter: The burette, B, a 40 cm length of "Veridia" precision bore (10 mm) glass tubing with fiducial marks, F_1, F_2, is sealed with a "Rotaflo" P.T.F.E./glass stopcock[a], T_4, and is filled using the reservoir, BR. Glass inlet, I, and outlet, OU, capillaries (0.4 mm), with fiducial marks, F_3, F_4, support the mixing vessel assembly, MV, which is sealed with the P.T.F.E. valve, T_5, and covered with the removable, dual-walled Dewar, D, which is held down onto the large O-ring, OR, seated in the brass base, BB, by eight bolts, DB, and the Perspex collar, DC. Four solenoids, S, are mounted on D to activate the stirrer. D is evacuated through the vacuum line, VL, and the tube, EV, which carries shielded electrical wires, hermetically sealed[b] through a ground-glass cone at PS, to the thermistor and heater. I, OU and EV are sealed through BB by O-ring seals, OR. A "Veridia" precision bore capillary (0.75 mm), C, with fiducial mark, F_5, and the reservoir, R, allow optional measurements of excess volume to be made. C_{1-3} are B-10 ground glass cones. T_{1-3} are "Interkey" spring-loaded glass taps[c] lubricated with B.D.H. high vacuum silicone grease. T_1 is operated by pulleys, P. The entire apparatus is mounted on a brass plate, BP, attached to a heavy brass frame (not shown). L', L are, respectively, the levels of the thermostat liquid during temperature equilibration of the burette liquid and during experiments.

---

[a] Quickfit and Quartz Ltd., Staffordshire, U.K.

[b] "Sealing rods for glassblower", Jencons (Scientific) Ltd., Herts., U.K.

[c] G. Springham and Co. Ltd., Essex, U.K.

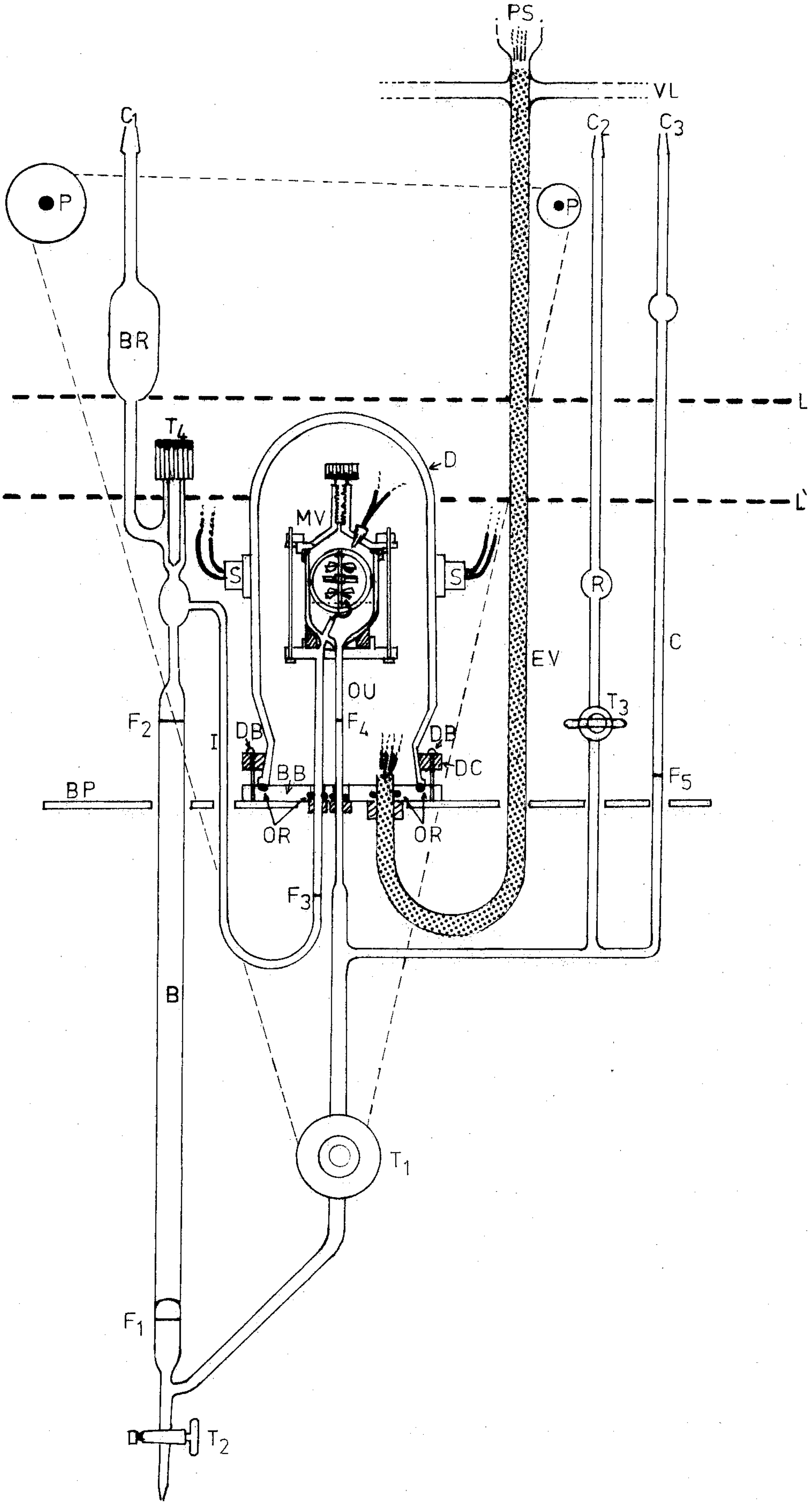

PS
VL
C1
C2
C3
P
P
BR
L
L`
T4
D
MV
S
S
R
EV
C
OU
T3
F2
I
F4
DB
DB
DC
BB
F5
BP
OR
OR
F3
B
T1
F1
T2

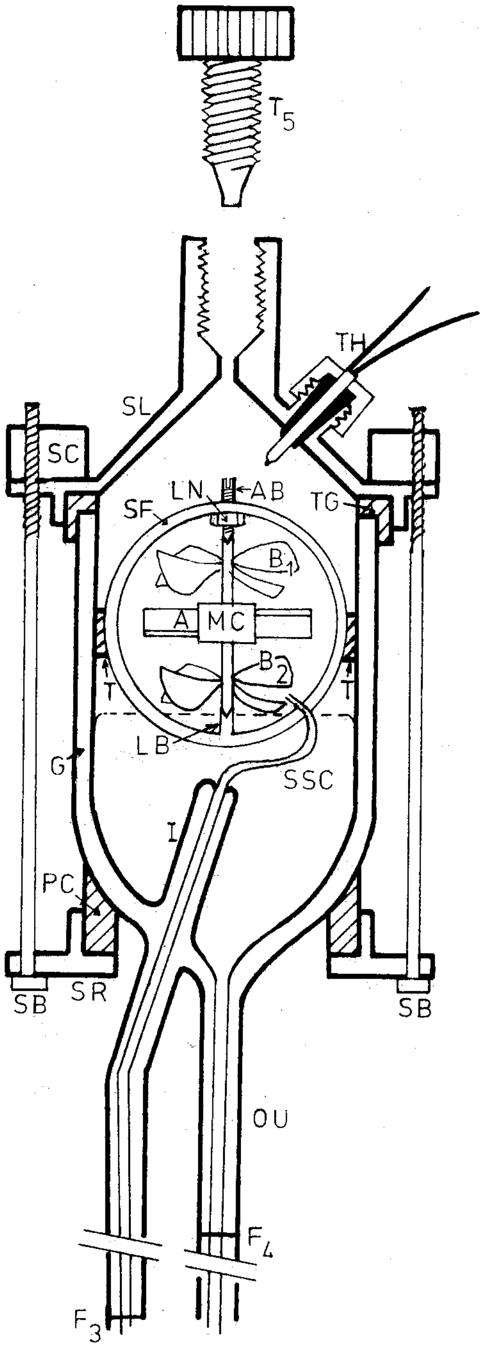
Figure 5.2: Calorimeter mixing-vessel assembly: A heavy-walled (3.3 mm) "Pyrex" glass cup, G, with a polished flat, upper rim is sealed by a close-fitting P.T.F.E. gasket, TG, seated in a conical stainless-steel lid, SL, which is threaded to receive a P.T.F.E. needle valve, T_5. SL is secured by four stainless-steel bolts, SB, which pass through the stainless-steel ring, SR, provided with a shaped polyethylene cushion, PC, and up through a threaded stainless-steel collar, SC. A bead-in-*solid* glass thermistor[a], TH, is sealed through a threaded conical socket, SO (*inset* (b)), with a P.T.F.E. cone, TC, and flanged nut, SW. The heater, H (*inset* (a)), a length of "Karma" wire[b] wound on a curved P.T.F.E. wafer, is supported by two platinum rods which are sealed through SL in the same manner as TH. The stainless-steel stirrer assembly consists of a toroidal frame, SF, with fixed, female, lower, needle bearing, LB, and adjustable male, upper, needle bearing, AB, provided with a locking nut, LN. Two four-blade propellers, B_1, B_2, are mounted on a spindle provided with a collar, MC, through which a two-blade propeller, A, formed from an "Alnico" bar magnet[c], is mounted in a tight fitting P.T.F.E. bush. This assembly is secured against the walls of G by two curved P.T.F.E. studs incorporated in the frame, SF. The mixing vessel assembly is supported by the glass inlet, I, and outlet, OU, capillaries (0.4 mm) with fiducial marks F_3, F_4. The inlet, I, includes the calibrated volume (0.026 cm^3) between F_3 and the tip of the 3.5 cm length of stainless-steel capillary (0.18 mm), SSC, which is sealed in I with a P.T.F.E. film. The volume of the mixing-vessel (ca. 51 cm^3) is calibrated to F_4.

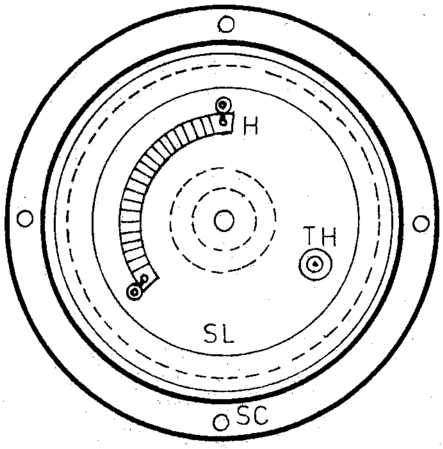
---

[a] Type GB 38 P12. Fenwal Electronics, Framingham, Mass., U.S.A.

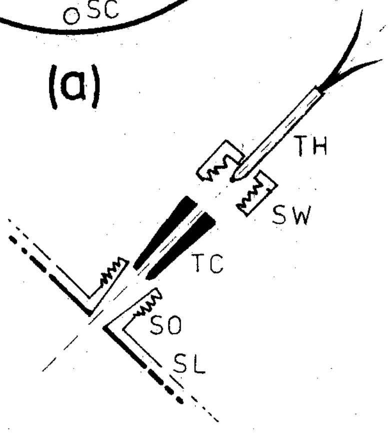
[b] Precision Components, Miranda, N.S.W. (ρ("Karma") $\approx$ 1.3 $\mu\Omega$.m)

[c] James Neill and Co., (Sheffield) Ltd., U.K.


T_5
TH
SL
SC
LN
AB
SF
TG
B_1
A
MC
B_2
T
T
G
LB
SSC
I
PC
SB
SR
SB
OU
F_4
F_3


H
TH
SL
SC

(a)


TH
SW
TC
SO
SL

(b)

on a curved P.T.F.E. wafer is mounted on two platinum rods which are fixed through SL in the same manner as TH.

The stainless-steel *stirrer assembly* consists of a toroidal frame, SF, containing a spindle provided with two four-blade propellers, B_1, B_2, and a collar, MC, in which a two-blade propeller, A, formed from an "Alnico" bar magnet, is mounted through a tight-fitting P.T.F.E. bush. The spindle bearings, a fixed female bearing, LB, and an adjustable male bearing, AB, provided with a locking nut, LN, are arranged to avoid inclusion of air during filling. The entire assembly is removable and is held against the walls of the mixing-vessel by two close-fitting, curved P.T.F.E. studs, T, incorporated in the frame, SF.

The glass inlet, I, is terminated in the mixing-vessel by 3.5 cm of fine stainless-steel capillary (0.18 mm), SSC, at a point very near (ca. 1 mm) to the propeller B_2.

The mixing-vessel (*figure 5.1*), supported only by the capillary inlet, I, and outlet, OU, is covered, during experiments, by a dual walled, silvered *Dewar*, D, provided with a strip window and sliding cover. This Dewar has a flat polished rim which is tightened against a large O-ring, OR, seated in a threaded circular brass base, BB, by eight brass bolts, DB which pass through a thick, split perspex collar, DC. The space between the Dewar and the mixing-vessel may be evacuated via the tube, EV, and the vacuum line, VL, which is connected, through a "Nupro" bellows valve, to an oil backing pump with flexible stainless-steel tubing. The tube, EV, also carries a shielded cable to provide power to the thermistor and heater. These power supply lines are soldered to composite nickel/-tungsten/copper rods which are hermetically sealed through a removable, greased, ground-glass cap at PS. The inlet, I, outlet, OU, and supply tube, EV, are fixed through the base, BB, by O-ring seals, OR. This jacket was evacuated during experiments, to about 2-3 Pa and had an overall leak rate of less than 10^{-3} Pa.s^{-1}.

Four *solenoids*, S, provided with ferromagnetic stainless-steel cores and mounted at 90° intervals around a P.V.C. collar attached to the Dewar, D, are activated by the *stirrer power supply* shown in *figure 5.3*. This device splits a signal of variable frequency from an oscillator into two components, produces a phase shift (90°) between them, then amplifies them before they are separately fed to each diametric pair of solenoids. The result of this arrangement is a rotating magnetic field, in the plane of the bar magnet, A, which drives the stirrer, in either sense, at constant speeds (±0.1%) of up to 10 Hz in steps of 1 Hz. This stirrer design allows the cell to be sealed more completely and obviates the use of a cumbersome rotating horse-shoe magnet outside the Dewar. A negligible level of electrical noise[a] is generated in the thermistor leads by this magnetic field.

The shielded *heater and thermistor circuit* (*figure 5.4*) is powered by a stabilized 7-volt d.c. power supply. A Wheatstone bridge circuit of variable sensitivity containing

---

[a] ±0.1 μV. This noise level was equivalent to a maximum temperature variation of about $\pm 3 \times 10^{-5}$ K and was about 700 times smaller than that present when the thermistor leads were *not* non-inductively wound.

Figure 5.3: Stirrer power supply: A sinusoidal signal is produced by the integrated circuit, IC (*INTERSIL 8038*) and split. A phase shift of 90° is produced between the signals before they are separately amplified by A_1 (*LM310*) and A_2 (*741/T05*), fed to the transistors T_1 (*AY8149*) and T_2 (*AY9149*) and to the solenoids, S. The *discontinuously* variable resistors R_1, which controls the oscillator frequency, and R_2, which maintains the 90° phase shift, are mounted *in tandem* so that, for various stirrer speeds, they have the values shown in the table below.

Stirrer speed/Hz	R_1/kΩ	R_2/kΩ
1	390	820
2	180	470
3	120	330
4	90	220
5	75	180
6	61	150
7	51	120
8	44	100
9	40	82
10	36	82

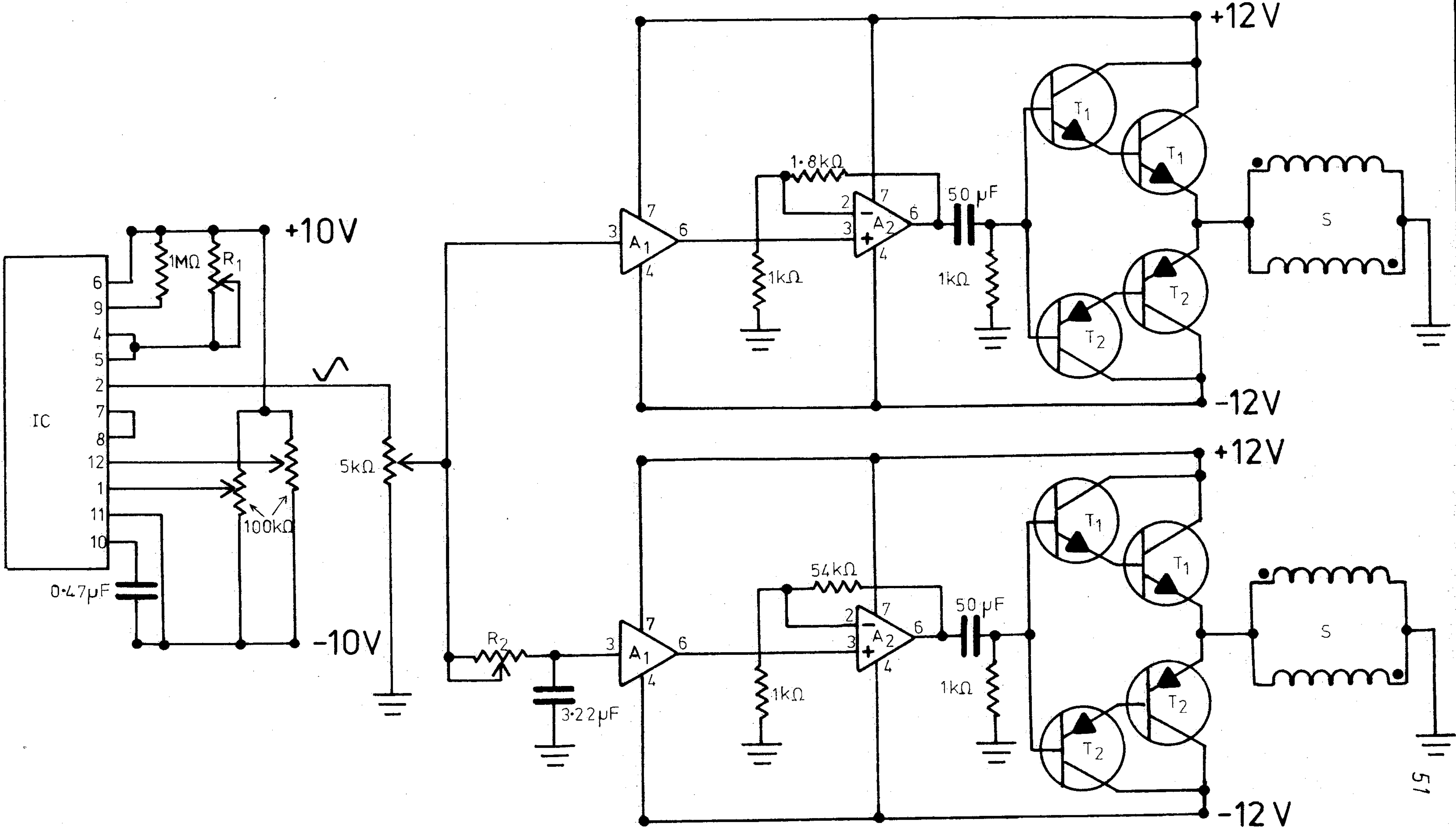

+10V
1MΩ
R1
IC
6
9
4
5
2
7
8
12
1
11
10
100kΩ
0·47μF
−10V
5kΩ
R2
3·22μF
A1
3
6
7
4
A2
2
1·8kΩ
54kΩ
1kΩ
50 μF
T1
T2
S
+12V
−12V

Figure 5.4: Heater and thermistor circuit: A Wheatstone bridge containing the thermistor, TH, decade resistor[a], DR, and precision mica-card resistors[b] (10kΩ) is monitored by the chart recorder[c], CR. The heater circuit contains the "dummy heaters", DH, heater, H (ca. 110Ω), and resistance standard[d], RO. Operation of the heater simultaneously engages the decade counting unit, DT, which is gated at 10^{-4} s. S_1 and S_2 are "double-throw multipole" switches. The potential difference across H and RO is measured by the "auto-ranged digital multimeter"[e], DV. R_1 (500kΩ), R_2 and R_3 (1kΩ) are wire-wound sliding-contact resistors of low temperature coefficient (ca. 20 p.p.m. $°C^{-1}$). RS_1, RS_2 and RS_3 are shunt resistors for use with the micro-ammeter, A. The parallel circuits are powered by a regulated 7 volt d.c. power supply. The diagram shows the circuit in the "standby" mode which might be used for systems with both endothermic and exothermic "lobes" in the excess enthalpies; *i.e.* with the timer *off* but with a steady "base" current passing through the heater.

---

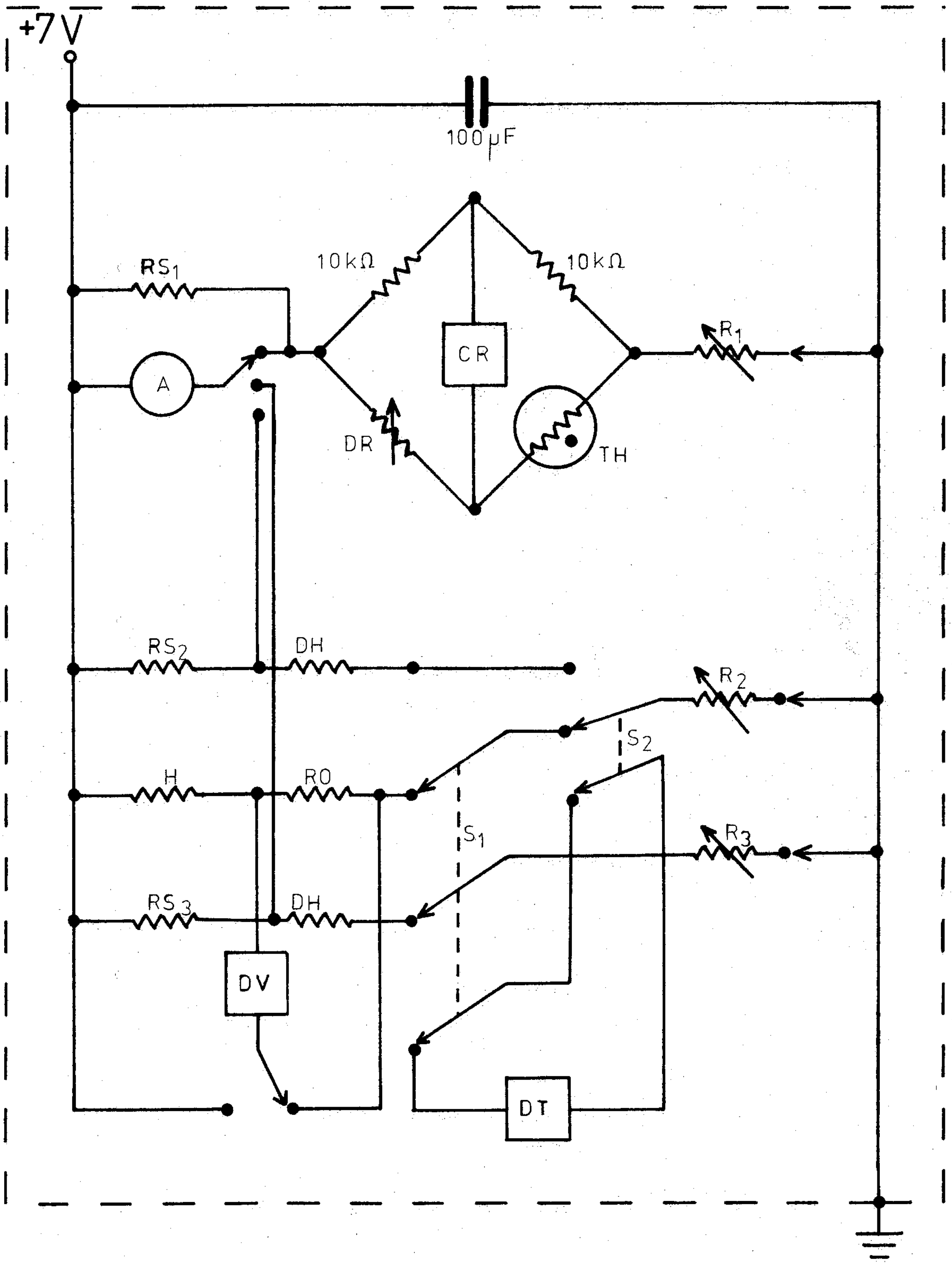
[a] Cambridge Instrument Co. Ltd., U.K.

[b] Precision Components, Miranda, N.S.W.

[c] "Micrograph BD5-686E". Kipp and Zonen, Delft, Holland.

[d] 9.9993 ± 0.0005Ω (20°C). Croydon Precision Instrument Co., Surrey, U.K.

[e] "Model 3500". Data Precision, Wakefield, Mass., U.S.A. (maximum uncertainty in d.c. voltage measurement - ±0.01%).


+7V
100µF
RS1
10kΩ
10kΩ
A
CR
R1
DR
TH
RS2
DH
R2
S2
H
RO
S1
R3
RS3
DH
DV
DT

the thermistor,[a] TH, is monitored by a sensitive chart-recorder, CR.[b] This bridge is operated at null so that the decade resistor, DR, gives the thermistor resistance. The heater circuit is provided with two channels both having a dummy heater, DH, through which the power supply is discharged while the heater is inactive. This use of an independent *base* and *boost* current allows measurements to be made on weakly exothermic systems, although only endothermic systems were encountered in this work. The heater current (0-58 mA) and resistance (ca. 110 Ω) are represented by the potential across the heater leads and across the series standard resistor, RO, (10 Ω) and measured with a sensitive, multi-range digital voltmeter, DV. An electronic timer, DT, is operated by the multi-pole switch controlling the heater current(s).

The mixing vessel outlet capillary, OU, leads (a) down to the pulley-operated tap T_1 which, on opening, allows liquid to be added to the mixing vessel from the burette, and (b) out to the reservoir R and the *precision bore capillary*, C. This capillary allows the optional measurement of excess volumes

---

[a] The maximum power generated in the thermistor was 6 μW. This power level was chosen to maximize the ratio sensitivity:base line width. The thermistor was calibrated against temperature as outlined in *appendix 5.1*.

[b] Resolution 0.2 μV. This recorder was normally operated on the 0.1 mV range. One full-scale deflection was equivalent to 0.017 K at 283 K or to 0.024 K at 298 K.

to be made.[a] F_4 and F_5 are fiducial marks.

The volume of the mixing-vessel was measured (a) before attachment to the calorimeter by weighing it, together with a pycnometer, filled with tri-chloro-ethylene and (b) after attachment to the calorimeter by using a calibrated piston burette filled with *n*-octane. These results agreed to within 0.02%. The thermal relaxation time (ca. 5600 s) and the heat capacity of the empty mixing-vessel (ca. 150 $J.K^{-1}$) were measured as described in *appendix 5.2*.

The *filling procedure* for the calorimeter is as follows:

(i) With C_1, C_2 sealed, T_2, T_4, T_5 closed and T_1, T_3 open, the apparatus is evacuated via a three-way tap (not shown) connected to C_3. A vessel of clean mercury is placed below T_2 which is then opened slightly to bring the mercury level just above it. While pumping continues, T_1 and T_3 are rotated to remove any trapped air.

(ii) T_2 is opened carefully to allow mercury to rise into the apparatus until the level is at a pre-determined mark just below the tip of the capillary, SSC, and just above the tap T_3, which is then closed. T_4 is opened momentarily to allow the mercury to rise just

---

[a] No such measurements of $\bar{V}^E$ were deliberately made for the systems studied here since they had been made more directly in previous work.[10] The observed volume change on mixing must be corrected for (a) compressibility, (b) expansion of the mobile component on entering the mixing-vessel, (c) contraction of mercury leaving the mixing-vessel and (d) changes in the temperature of the mixing-vessel. Such results would, of necessity, be less precise than those measured directly.

above its seat. T_1 and T_2 are closed. C_1, C_2 are unsealed and T_5 and the three-way tap above C_3 are operated alternately to restore atmospheric pressure to all compartments.

(iii) Both liquids are partially degassed, by warming them to about 30°C above the temperature of measurement, and placed in glass syringes. The reservoir, BR, is filled with one liquid and T_2 is opened to fill the burette by draining mercury to a point near F_1. T_4 is removed while the burette is completely filled to exclude air, and is then replaced but not sealed. With T_5 removed, the other liquid is added to the mixing-vessel, MV, until the tip of the capillary, SSC, is covered. T_4 is sealed, the burette is warmed slightly to remove any air from SSC, T_4 is opened again, and the addition of liquid to MV is completed. T_5 is closed and, after a visual inspection for air bubbles in MV, the Dewar, D, is tightened in position.

(iv) Threaded brass extension pieces are screwed onto each of the three-point suspension legs of the brass frame and the calorimeter is lowered into a thermostatted bath to the level L'. When the burette liquid has reached the bath temperature, T_4 is closed, T_3 is opened, the extension pieces are removed and the calorimeter is lowered into the bath to the level L. After electrical connections are made, the Dewar is evacuated and the calorimeter is left overnight to come to temperature equilibrium with the stirrer *off* and the thermistor circuit *on*. The power supply is discharged through the "dummy" heaters at maximum current (ca. 58 mA ≡ 0.37 W).

The enthalpy change on mixing is measured using the following *operating procedure*:[a]

(i) The chart-recorder and stirrer are switched on and the thermistor bridge signal is quickly nulled by operating the decade resistor, DR. This resistance value, which represents the temperature of the surroundings (*i.e.* the water bath), is noted to allow later calculation of the temperature of the mixing-vessel to be made. The recorder trace is then followed for about 10-15 minutes and, from the slope of this trace, the equilibrium temperature of the mixing-vessel is estimated and the calculated amount of energy required to bring the mixing-vessel to this temperature is added with the heater.

(ii) During final temperature equilibration, T_3 is closed (optional) and T_1 is opened *cautiously* to push the inlet mercury thread to a position near F_3. This mercury thread remains intact due to its high surface tension and the small diameter of the glass

---

[a] The procedure described applies to *endothermic* systems. A steady *base* heater current may be employed for *exothermic* systems to raise the mixing-vessel to a higher steady-state temperature. When this current is turned off, the mixing-vessel loses heat energy to the surroundings. Only weakly exothermic systems (less than about 100 $J.mol^{-1}$) may be studied in this way, however, since the mixing-vessel temperature becomes somewhat erratic at high temperature differentials due to stirring imperfections.

inlet capillary, I. At temperature equilibrium the positions of F_1, F_3 and of the mercury levels in B, I and C are determined (see *section 2.3*).

(iii) An addition of liquid is made from burette to mixing-vessel by opening the tap T_1 and the cell temperature is maintained to within ±0.005 K of the equilibrium temperature by operation of the heater. The potential across the standard resistor is noted during this process. At the end of the addition T_1 is closed, the temperature of the mixing-vessel is restored to its previous value and the heating time is noted. The recorder trace is followed for about 30 minutes and then, if necessary, the equilibration time may be shortened by either reducing the stirrer speed or heating. At equilibrium the value of the decade resistor required to null the thermistor bridge signal is read off and the positions of the mercury menisci in B and C are determined. If necessary the position of the meniscus in C is reset to a lower level by opening T_3 and the consequent temperature drop in the cell is compensated electrically. The amount of this compensation is also noted.

(iv) Further additions are made until the mercury level in the cell falls to a position near F_4. The appropriate heater current for each addition is roughly estimated from the average heater power over the previous addition. The potential difference across the active heater leads is noted several times during experimental runs.

(v) The apparatus is removed from the bath, cleaned and filled, with the position of the liquids reversed, for a study of the other side of the composition range.

During this work, studies of the entire composition range, comprising about 20 datum points, required 4-5 days.

5.4 Treatment of observations: For the calorimeter described above, a number of contributions to the energy, E, required to exactly compensate for the heat change on mixing must be considered:

(i) The *positive* energy contribution from the heater, E_H, is calculated from the expression derived in *appendix 5.3*

viz.

$$E_H = V_0^2 . \left(\frac{V_H}{V_0 . R_0} + \frac{\delta R_H}{R_0^2}\right) . t = V_0^2 . f_H . t \qquad 5.2$$

where V_0 is the potential difference across the series standard resistor,

R_0 is the resistance of the standard resistor,

V_H is the potential difference across the heater leads,

δR_H is a small resistance term due to the heater leads,

t is the heating time

and f_H is a constant.

(ii) Because of the temperature differential, ΔT, existing between the burette and mixing-vessel due to the stirrer motion, an addition of liquid to the mixing-vessel results in a *negative* contribution, E_T, to E.

$$E_T = -n . \bar{C}_p . \Delta T \qquad 5.3$$

where n is the number of moles of liquid added

and $\bar{C}_p$ is the molar heat capacity at constant pressure of the added liquid.

The values of $\bar{C}_p$ used in this work are shown in table 5.1.

(iii) During an addition of liquid to the mixing-vessel, the temperature gradients along both the inlet and outlet capillaries are diminished by the flow of liquid through them.[6] This results in the partial inactivity of these heat loss paths during an addition so that some of the heat dissipated by the stirrer remains in the mixing-vessel. It is reasonable to suppose that this *positive* energy contribution, E_R, is linear in ΔT and in the volume, V, of liquid added.

i.e. $$E_R = k_R . V . \Delta T \qquad 5.4$$

The constant, k_R, estimated from "blank" runs, was found to be 0.37 ± 0.1 $J.cm^{-3}.K^{-1}$.

(iv) When the viscosities and/or densities of the two liquids differ appreciably, an addition of liquid to the mixing-vessel results in a change in the power dissipated by the stirrer. The extent of this change is known from the change in the steady-state temperature of the mixing-vessel after an addition (see *appendix 5.2*). If it is assumed that the power dissipation of the stirrer is linear in the volume of liquid added, the additional energy contribution, E_S, is given by

$$E_S = \frac{1}{2} . (w_f - w_i) . t_A \qquad 5.5$$

Table 5.1: Heat capacity ($\bar{C}_p$/J.mol^{-1}.K^{-1}) and viscosity (η/μN.s.m^{-2}) of liquids

liquid	$\bar{C}_p$(283 K)	$\bar{C}_p$(298 K)	η(283 K)	η(298 K)
benzene	-	136[12]	-	603[15]
cyclo-hexane	-	157[12]	-	898[15]
carbon tetrachloride	-	133[12]	-	904[15]
di-ethyl ether	169[13]	173[13]	258[15]	223[15]
di-*iso*-propyl ether	211[14]	216[14]	455[a]	379[15]
di-*n*-butyl ether	247[a]	252[15]	798[15]	644[15]
hexafluorobenzene	219[16]	222[16]	1140[b]	900[17]
mercury	28.0[18]	27.9[18]	1615[18]	1530[18]

[a] Estimated by comparison with the other two ethers.

[b] Estimated by comparison with benzene.

where w_f, w_i are, respectively, the final and initial power dissipations of the stirrer

and t_A is the time elapsed between the start of an addition and the point at which the mixing-vessel temperature has been restored.

(v) The flow of liquid through the capillary inlet, under the influence of the head of mercury existing between the mixing-vessel and the burette, results in the generation of heat from the viscous forces overcome by the liquid. This *positive* contribution, E_η, to E is given by an expression of the form

$$E_\eta = g(\eta_l).f(V) \tag{5.6}$$

where η_l is the viscosity of the liquid,

V is the volume of liquid added

and f and g are functions derived in *appendix 5.4*.

The values of η_l used in this work are shown in table 5.1.

(vi) Changes in the pressure acting on the contents of the mixing-vessel result in temperature changes in the mixture so that an *increase* in pressure during an addition gives rise to a *positive* contribution, E_p, to E. This quantity was found to be given by the relation

$$E_p = k_p(P_f - P_i) \tag{5.7}$$

where P_f, P_i are, respectively, the final and initial pressures acting on the system

and k_p is a constant term evaluated by allowing a pressure imposed on the system to relax and then compensating with the heater for the consequent fall in the temperature of the mixing-vessel contents.

(vii) Deviations of the mixing-vessel temperature from its equilibrium value during an addition result in changes in the power loss from the mixing-vessel to the surroundings. This may be overcome by ensuring that the area swept out by the chart-recorder trace during an addition is symmetric about the baseline and that the fluctuations in the temperature (*i.e.* the amplitude of the trace) are minimal. Any imbalance in these areas produces an additional contribution to E given by,

$$E_A = k\int_0^{t_A} (T_e - T).dt = k.(A_C - A_H) \qquad 5.8$$

where k is the thermal relaxation constant referred to *appendix 5.2*.

t_A is the time elapsed between the start of an addition and the point at which the mixing-vessel temperature has been restored,

T, T_e are, respectively, the temperature and the pre-addition equilibrium temperature of the mixing-vessel,

and A_C, A_H are, respectively, the areas (K.s) included under the hot and cold sides of the temperature-time trace.

(viii) Observation of the chart-recorder trace, after an addition is completed, may indicate that the temperature of the mixing-vessel was not restored *exactly* to its previous equilibrium value, T_e; *i.e.* the trace is extrapolated to some temperature T'_e. This gives rise to an additional contribution, E_C, to E which is given by

$$E_C = C_m \cdot (T_e - T_e') \qquad 5.9$$

where C_m is the heat capacity of the mixing-vessel and its contents.

(ix) Since a calorimeter of the type described here is not strictly isothermal over the duration of an experimental "run" (see (iv)), the measured $\bar{H}^E$ values may not be self-consistent for binary systems which have both (a) numerically large excess heat capacities, $\bar{C}_p^E$, *and* (b) a large range of density and/or viscosity. This effect may be accounted for by the relation

$$\bar{H}^E(x,T_o) \simeq \bar{H}^E(x,T) + \bar{C}_p^E(x,T_o) \cdot (T_o - T) \qquad 5.10$$

where T, T_o are, respectively, the temperature of the mixing-vessel and the temperature at which $\bar{H}^E$ is quoted.

In this work this correction was found to be negligible (<0.02 J.mol^{-1}).

"Blank runs" of 6-10 datum points using benzene, di-ethyl ether and carbon tetrachloride were conducted with both low (0.01 K) and high (0.49 K) temperature differentials, ΔT, between the mixing-vessel and the surroundings. Some examples of these measurements are shown below. *e.g.*

(1) di-ethyl ether, $\Delta T = 0.485$ K, "x" ≈ 0.5

$$\begin{aligned} \Delta H &= E_H + E_T + E_R + E_S + E_\eta + E_P + E_A + E_C \\ &= 15.83 - 20.92 + 4.70 + 0.00 + 0.42 + 0.13 + 0.03 + 0.00 \\ &= 0.19 \text{ J} \end{aligned}$$

$$\text{"}\bar{H}^E\text{"} = 0.38 \text{ J.mol}^{-1}$$

e.g.

(2) carbon tetrachloride, $\Delta T = 0.480$ K, "x" ≈ 0.5

$\Delta H = 11.75 - 17.77 + 4.87 + 0.00 + 0.54 + 0.18 + 0.07 + 0.00$

$= -0.36$ J

$$"\bar{H}^E" = -0.69 \text{ J.mol}^{-1}$$

e.g.

(3) benzene, $\Delta T = 0.016$ K, "x" ≈ 0.5

$\Delta H = 0.00 - 0.65 + 0.16 + 0.00 + 0.54 + 0.26 - 0.18 + 0.00$

$= 0.13$ J

$$"\bar{H}^E" = 0.23 \text{ J.mol}^{-1}$$

The largest observed value of "$\bar{H}^E$" in any blank run was that in example (2) above. For all other measurements "$\bar{H}^E$" did not exceed 0.5 J.mol^{-1}.

5.5 Results: For this work the excess enthalpies for the systems benzene + *cyclo*-hexane (298 K), benzene + carbon tetrachloride (298 K), and hexafluorobenzene + di-ethyl ether, di-*iso*-propyl ether and di-*n*-butyl ether (283 K, 298 K) were measured. Experimental results for the first two systems are presented in table 5.2 and 5.3, while those for the remaining systems appear in *Chapter 7*.

The excess enthalpies for the system benzene + *cyclo*-hexane at 298.15 K appear to have been established to within a range of 2 J.mol^{-1}.[4] In table 5.4 the "smoothed" results of this work[a] are compared with those of other workers; the agreement is within this range.

---

[a] The fact that measurements for this system were made at *298.14 K* is inconsequential; the value of $\bar{C}_p^E(x = 0.5, 298 \text{ K})$[9,11] is about $-2.8 \text{ J.mol}^{-1}.\text{K}^{-1}$.

Table 5.2: Excess enthalpies of benzene (1) + cyclo-hexane(2) at 298.14 K

$$\delta\bar{H}^E = \bar{H}^E_{expt.} - \bar{H}^E_{calc.}$$

Run 1/2

x_1	$\bar{H}^E_{expt.}/J.mol^{-1}$	$\delta\bar{H}^E/J.mol^{-1}$	
0.0012	3.30	-0.28	
0.0028	8.18	-0.45	
0.0054	16.27	-0.36	
0.0080	24.32	-0.09	
0.0111	33.56	-0.29	
0.0174	52.97	0.12	
0.0586	170.80	-0.11	
0.1368	367.59	0.28	
0.2136	524.50	0.10	
0.2911	647.10	-0.19	
0.3675	732.79	-0.24	
0.4426	782.93	-0.02	
0.5164	798.67	0.16	Run 1 ↑
0.5366	797.13	0.21	Run 2
0.5681	789.44	0.09	Run 1
0.5960	777.40	-0.04	Run 2 ↓
0.6551	735.60	-0.06	
0.7144	670.67	-0.04	
0.7732	582.52	-0.19	
0.8310	472.02	-0.11	
0.8873	340.81	0.23	
0.9417	189.49	0.03	
0.9950	17.60	0.31	(contd.)

Table 5.2 (contd.) Run 1/2

$$\bar{H}^E_{calc.}/J.mol^{-1} = \text{equation 4.1}$$

$a_0 = 3090.23$; $a_1 = 143.00$; $a_2 = -33.47$; $a_3 = 307.49$

$\sigma = 0.23$ J.mol^{-1}

Run 3/4

x_1	$\bar{H}^E_{expt.}/J.mol^{-1}$	$\delta\bar{H}^E/J.mol^{-1}$	
0.0441	130.19	-0.26	
0.1163	318.92	0.09	
0.1862	472.22	0.23	
0.2565	596.26	-0.09	
0.3269	691.17	-0.12	
0.3952	754.73	-0.12	
0.4895	796.36	0.11	Run 3 ↑
0.5212	797.86	-0.09	Run 4
0.5289	797.46	0.04	Run 4
0.5435	795.45	0.04	Run 3
0.5681	789.10	0.06	Run 3
0.5832	783.50	0.29	Run 4 ↓
0.6436	745.21	-0.22	
0.7041	683.59	-0.18	
0.7642	598.09	0.11	
0.8230	489.43	0.02	
0.8800	359.28	-0.12	
0.9361	206.72	0.19	
0.9909	31.37	-0.21	
0.9973	9.85	0.22	

(contd.)

Table 5.2 (contd.) Run 3/4

$$\bar{H}^E_{calc.}/J.mol^{-1} = \text{equation 4.1}$$

a_0 = 3084.91; a_1 = 158.23; a_2 = -64.37; a_3 = 336.56

σ = 0.18 J.mol^{-1}

Table 5.3: Excess enthalpies for benzene(1) + carbon tetrachloride(2) at 298.15 K

$$\delta\bar{H}^E = \bar{H}^E_{expt.} - \bar{H}^E_{calc.}$$

x_1	$\bar{H}^E_{expt.}$/J.mol^{-1}	$\delta\bar{H}^E$/J.mol^{-1}	
0.0608	26.66	-0.02	
0.1241	50.34	-0.05	
0.1866	70.00	0.03	
0.2452	85.03	-0.02	
0.3090	97.98	0.06	
0.3757	107.60	0.03	
0.4829	115.14	0.11	Run 1 ↑
0.4882	114.91	-0.23	Run 2
0.5089	115.30	-0.04	Run 2
0.5539	114.75	0.25	Run 1
0.5592	114.21	-0.07	Run 1
0.5849	112.78	-0.09	Run 2 ↓
0.6581	105.52	-0.08	
0.7602	87.05	0.02	
0.8219	70.88	0.10	
0.8948	46.34	0.08	
0.9647	16.86	-0.16	
0.9782	10.54	-0.17	
0.9889	5.37	-0.16	

$\bar{H}^E_{calc.}$/J.mol^{-1} = equation 4.1

$a_0 = 471.24$; $a_1 = -74.98$; $a_2 = 110.69$; $a_3 = -1.75$

$\sigma = 0.13$ J.mol^{-1}

Table 5.4: Comparison of $\bar{H}^E(x_1,\ 298\ K)/J.mol^{-1}$ for benzene(1) + cyclo-hexane(2) with literature

	This work		Literature	
x_1	Run 1/2	Run 3/4	Ewing *et al.*[7]	Van Ness *et al.*[a]
0.02	60.6	60.5	61.1	61.0
0.05	147.1	146.9	148.1	148.0
0.1	279.4	279.0	280.8	280.6
0.2	499.2	498.7	500.7	500.2
0.3	659.1	658.5	660.4	659.4
0.4	758.8	758.3	760.0	758.5
0.5	797.9	797.5	799.3	797.3
0.6	775.3	775.0	776.9	774.6
0.7	688.7	688.7	690.6	688.2
0.8	534.5	534.8	536.4	534.2
0.9	307.4	307.8	308.7	307.3
0.95	164.3	164.6	165.0	164.2
0.98	68.4	68.5	68.7	68.3

---

[a] Reference 10 in the paper by Stokes *et al.*[6]

Table 5.5: Comparison of $\bar{H}^E(x,\ 298\ K)/J.mol^{-1}$ for benzene(1) + carbon tetrachloride(2) with literature

		Literature	
x_1	This work	Stokes *et al.*[6]	Van Ness *et al.*[a]
0.02	9.21	9.25	9.19
0.05	22.22	22.44	22.19
0.1	41.84	42.06	41.82
0.2	73.71	74.10	73.63
0.3	96.32	96.74	95.99
0.4	110.12	110.46	109.41
0.5	115.30	115.54	114.23
0.6	111.77	112.01	110.57
0.7	99.20	99.58	98.21
0.8	76.99	77.66	76.53
0.9	44.29	44.95	44.37
0.95	23.67	24.13	23.84
0.98	9.85	10.07	9.95

---

[a] Reference 10 in the paper by Stokes *et al.*[6]

Stokes *et al.*[6] have measured the excess enthalpies for the system benzene + carbon tetrachloride at 298.15 K with exceptional precision (σ = 0.06 J.mol^{-1}), but point out that some uncertainty exists in respect of other reliable literature values. This system has a large range of density (ca. 710 kg.m^{-3}) and, accordingly, provides a good test of stirring efficiency,[4] a major consideration in calorimetry.[a] In table 5.5 the "smoothed" results of this work are compared with those of other workers; the agreement with those of reference 6 is within 0.7 J.mol^{-1}.

All experimental excess enthalpies were "curve-fitted" in the same way as excess volumes (see *section 4.3*).

5.6 Errors: The numerous corrections outlined in *section 5.4* render the estimation of uncertainties in $\bar{H}^E$ a difficult task. These corrections would appear, from "blank runs" to contribute an uncertainty of about ±0.7 J.mol^{-1} to $\bar{H}^E$. Imperfections in stirring may result in unaccountable heat losses to the surroundings by allowing the formation of transitory hot and cold regions in the mixture. This is particularly so with systems having numerically large excess enthalpies and/or density ranges. This statement is partly substantiated by the increased scatter in results for the systems containing hexafluorobenzene (*Chapter 7*). The comparison (table 5.4) of $\bar{H}^E(x)$ for the system benzene + *cyclo*-hexane with the results of Ewing *et al.*[7] shows a discrepancy of about 2 J.mol^{-1}. Since

---

[a] The system di-ethyl ether + hexafluorobenzene imposes an even more stringent test ($\Delta\rho$ = 900 kg.m^{-3}).

these latter results are in excellent agreement with recent measurements made with an entirely different calorimeter,[9] this discrepancy may be an indication of the experimental error relevant to the work presented here.

In summary, the uncertainty in $\bar{H}^E(x = 0.5)$ is believed to parallel its magnitude, ranging from ±1 to ±2 $J.mol^{-1}$. The uncertainty in x is estimated, from volume calibration errors, to be less than 0.0005.

References

1. Van Ness, H.C. *Ind. Eng. Chem.* 1967, 59, 34
2. Armitage, D.A.; Morcom, K.W. *Trans. Faraday Soc.* 1969, 65, 688
3. Rowlinson, J.S. *Liquids and liquid mixtures* Butterworths, London: 1959
4. Stokes, R.H.; Marsh, K.N. *Ann. Rev. Phys. Chem.* 1972, 23, 65
5. Savini, C.G.; Winterhalter, D.R.; Kovach, L.H.; Van Ness, H.C. *J. Chem. Eng. Data* 1966, 11, 40
6. Stokes, R.H.; Marsh, K.N.; Tomlins, R.P. *J. Chem. Thermodynamics* 1969, 1, 211
7. Ewing, M.B.; Marsh, K.N.; Stokes, R.H.; Tuxford, C.W. *J. Chem. Thermodynamics* 1970, 2, 751
8. Tanaka, R.; Murakami, S.; Fujishiro, R. *Bull. Chem. Soc. Japan* 1972, 45, 2107
9. Elliot, K.; Wormald, C.J. *J. Chem. Thermodynamics* 1976, 8, 881
10. Martin, M.L.; Murray, R.S. *J. Chem. Thermodynamics* 1972, 4, 723 (Bound in at the back of this thesis.)
11. Williamson, A.G. *Enthalpies of Mixing of Binary Non-Electrolyte Systems* University of Canterbury: ca. 1970
12. Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds* Elsevier: Amsterdam 1950
13. Counsell, J.L.; Lee, D.A.; Martin, J.F. *J. Chem. Soc. A* 1971, 313
14. Andon, R.J.L.; Counsell, J.F.; Lee, D.A.; Martin, J.F. *J. Chem. Soc. - Faraday Trans. 1* 1974, 70, 1914
15. Riddick, J.A.; Bunger, W.B. *Techniques of Chemistry* Vol. II,3rd Ed. Wiley-Interscience 1970

16. Counsel, J.F.; Green, J.H.S.; Hales, J.L.; Martin, J.F. *Trans. Faraday Soc.* 1965, 61, 212

17. Mobbs, R.H. *Chemical Processing* April 1967, S5

18. Hodgman, C.D. (Ed.) *Handbook of Chemistry and Physics* 41st Ed. Chemical Rubber Publishing Co.: Ohio 1959-1960

19. Fenwal Electronics (Framingham, Massachusetts) *Thermistor Manual*

CHAPTER 6

EXCESS FREE ENERGIES

6.1 Introduction: The excess Gibbs free energy of mixing defined by the relation,

$$\bar{G}^E = \Delta\bar{G}(\text{experimental}) - \Delta\bar{G}(\text{ideal}) \qquad 6.1$$

where $\Delta\bar{G}(\text{ideal}) = -T\Delta\bar{S}(\text{ideal}) = RT\sum_i x_i \ln x_i$,

and related to other excess thermodynamic functions by

$$\bar{G}^E(x,T,P) = \bar{H}^E(x,T,P) - T\bar{S}^E(x,T,P), \qquad 6.2$$

provides a *direct* indication of the miscibility of liquid pairs. The sign and magnitude of $\bar{G}^E$ reflects, therefore, the nature and relative strength of intermolecular forces in mixtures. Differentiated forms of $\bar{G}^E$ give indirect access to other thermodynamic functions of mixing:

$$\bar{S}^E = -\left(\frac{\partial\bar{G}^E}{\partial T}\right)_{P,x_i} \qquad 6.3$$

$$\bar{H}^E = \left(\frac{\partial(\bar{G}^E/T)}{\partial(1/T)}\right)_{P,x_i} \qquad 6.4$$

$$\bar{V}^E = \left(\frac{\partial\bar{G}^E}{\partial P}\right)_{T,x_i} \qquad 6.5$$

Direct measurements of $\bar{H}^E$ and $\bar{V}^E$ are, however, generally to be preferred for greater precision.[1]

6.2 $\bar{G}^E$ - theory of measurement: The calculation of $\bar{G}^E$ for a binary liquid mixture from experimentally observed quantities is basically more involved than for either $\bar{H}^E$ or $\bar{V}^E$. This calculation makes use of the relations,[2,3]

$$\bar{G}^E(p^*) = x_1\cdot\mu_1^E(p) + x_2\cdot\mu_2^E(p) + (p^*-p)\cdot\bar{V}^E \qquad 6.6$$

$$\mu_i^E(p) = RT\ln(y_i p/x_i\cdot p_i^o) - (p-p_i^o)(\bar{V}_i-B_{ii}) + p\cdot\delta_{ij}y_j^2 \qquad 6.7$$

in which $\mu_i^E(p) = RT\ln f_i$, $\qquad 6.8$

p^* is the pressure at which $\bar{G}^E$ values are quoted (usually about atmospheric pressure),

$\bar{V}^E$ is the excess volume of the mixture,

x_i is the mole fraction of component i in the liquid phase,

p is the experimental total pressure,

$\mu_i^E(p)$ is the excess chemical potential of component i in the system at pressure p,

y_i is the mole fraction of component i in the vapour phase,

p_i^o is the vapour pressure of pure component i,

$\bar{V}_i$ is the molar volume of pure liquid i,

B_{ii} is the second virial coefficient of the pure vapour i,

$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ where B_{ij} is the interaction second virial coefficient for the mixed vapours,

f_i is the activity coefficient of component i,

T is the absolute thermodynamic temperature,

and R is the gas constant (=8.3143 $J.K^{-1}.mol^{-1}$).

The term $(p^*-p)\bar{V}^E$ accounts for the pressure dependence of $\bar{G}^E$ and is negligible in many cases (*e.g.* $(p^*-p)\bar{V}^E \approx 0.1\ J.mol^{-1}$ for $(p^*-p) = 100$ kPa, $\bar{V}^E = 1\ cm^3.mol^{-1}$). Allowance is made, in the last two terms of equation 6.7, for the non-ideality of the vapour phase which, if neglected, may give rise to serious error.[3]

Evaluation of $\bar{G}^E$, therefore, requires a knowledge of p, x, y and T. A simplification of experimental procedure results from solution of the Gibbs-Duhem equation for conditions of constant temperature and pressure.

$$x_1 d\mu_1^E + x_2 d\mu_2^E = 0 \qquad 6.9$$

This enables isothermal p,x data to be used to evaluate y and $\bar{G}^E$ and proceeds as follows.[3,4,5]

(i) As is shown in *appendix 6.1*, equations 6.6, 6.8 and 6.9 may be used to give the relations

$$RT\ln f_1 = \bar{G}^E + x_2\frac{d\bar{G}^E}{dx_1}$$
$$RT\ln f_2 = \bar{G}^E - x_1\frac{d\bar{G}^E}{dx_1} \qquad 6.10$$

(ii) The quantities[3] p_1, p_2 defined as

$$p_i = x_i p_i^o \exp[\{(p-p_i^o)(\bar{V}_i-B_{ii}) - p\delta_{ij}y_j^2\}/RT] \qquad 6.11$$

represent the partial pressures of *non-ideal vapours* resulting from an *ideal liquid mixture*. This gives the total observed vapour pressure as

$$p = p_1f_1 + p_2f_2. \qquad 6.12$$

(iii) $\bar{G}^E$ is given some functional form in x. The choice of this function is largely a matter of finding one which most concisely represents $\bar{G}^E(x)$. A common choice[3,6] is that described by Barker,[4] *viz.*

$$\bar{G}^E/RT = x_1x_2\sum_{k=o}^{n} a_k(x_1-x_2)^k \qquad 6.13$$

although it has been pointed out[5] that this function is inadequate for complex systems in which specific interactions are found. From the relations 6.10, the activity coefficients, f_i, may also now be described as a function of x:

$$f_i = f_i(a_k,x). \qquad 6.14$$

(iv) An initial approximation for a_o may be obtained from an experimental p,x pair (usually at x = 0.5) by setting all other coefficients equal to zero and using equations 6.12 and 6.14. This allows initial estimates of y_i values to be made from equations 6.7 and 6.8 by ignoring the small term $p\delta_{12}y_j^2$.

(v) Initial values of p_i, f_i and $p_{calc.}$ may now be calculated for each x as well as the pressure residuals $\delta p = p_{expt.} - p_{calc.}$, and the derivatives $dp_{calc.}/da_k$. The increments in the coefficients, δa_k, which will minimize $|\delta p|$ are obtained from the least squares solution to the equation

$$\sum_{k=o}^{n} (dp/da_k).\delta a_k = \delta p. \qquad 6.15$$

(vi) Addition of these increments to the initial a_k estimates and repetition of step (v) successively improves the agreement between calculated and experimental vapour pressures until some chosen quantity (usually $\Sigma(\delta p)^2$, the sum of the squares of the pressure residuals) attains a value which is essentially constant.

(vii) A further complication results if there is an appreciable vapour space above the liquid mixture during measurements so that the true liquid composition x is not known exactly. This difficulty is readily overcome by initially executing the steps outlined above using x_i', the total composition of the system as an approximate value of x_i. This yields an estimate of y_i which may be used to compute an improved value of x_i from the relations:

$$x_i(m) = \frac{n_i - y_i(m-1).\Sigma n_v}{n_i + n_j - \Sigma n_v} \qquad 6.16$$

$$\Sigma n_v \simeq \frac{pV/RT}{1+B(x_i).p} \qquad 6.17$$

$$V \simeq V_o - (n_i\bar{V}_i + n_j\bar{V}_j) \qquad 6.18$$

where

$x_i(m), y_i(m-1)$ are, respectively, the m^{th} and $(m-1)^{th}$ approximations to x_i, y_i,

n_i, n_j are the total numbers of moles of each component in the system,

Σn_v is the total number of moles in the vapour phase,

$B(x_i)$ is the second pressure virial coefficient of the vapour mixture, and

V, V_o are respectively the volume of vapour and the total (calibrated) volume of the system.

Equation 6.18 applies under the restraints:

$$\bar{V}^E(x_i) << \bar{V}_i, \bar{V}_j ; \; y_{i(j)} . \Sigma n_v << n_{i(j)}$$

These iterative cycles continue until convergence has been obtained in both modes, *i.e.* until successive values of x_i differ negligibly and the quantity $\Sigma(\delta p)^2$ is minimized.

Although the above process appears tedious, it is readily implemented by modern computing facilities, and the additional step of analysing the vapour phase is useful only if it can be carried out with exceptional accuracy or if the liquids studied form an azeotrope or have similar volatilities.[6]

For this work $\bar{G}^E$, f and y were computed using the method of Barker[4] from isothermal p,x data obtained with a device described in *section 6.4*. A small vapour space correction was applied as described above. The conditions for convergence required that

(i) successive x_i iterations differed by less than 10^{-6},

(ii) successive $\Sigma(\delta p)^2$ values changed by less than 0.01%.

In all cases four iterative cycles were sufficient for convergence. The number of parameters employed to describe $\bar{G}^E(x)$ (equation 6.13) was chosen so that additional parameters did not significantly improve the standard deviation of the fit (σ). The use of a skew factor, due to Myers and Scott,[7] did not reduce the number of parameters required to describe $\bar{G}^E$ with a given value of σ.

The computer program[8] employed for this purpose was tested with the p,x,y data of Brown[9] for benzene + *n*-heptane at 353.15 K. This test revealed numerical errors in reference 4 (see *appendix 6.2*).

6.3 Experimental methods of determining $\bar{G}^E$: Liquid-vapour equilibria have for some time been studied using equilibrium stills[3] in which both the liquid and vapour phases are analysed at constant temperature or at constant pressure. Numerous designs for these stills have appeared in the literature and this itself is partly symptomatic of the difficulties associated with their use.[3] The removal and subsequent analysis of samples which truly represent the liquid and vapour phases requires careful design and a good deal of experimental expertise. These devices remain useful, however, for systems of low volatility.[1]

Isothermal measurement of the total static vapour pressure as a function of liquid phase composition appears to have gained popularity as a method of determining $\bar{G}^E(x)$.[1,6,10] This may be largely due to the availability of high-speed computing facilities and the consequent ease of performing the lengthy calculations outlined in the previous section.

A further refinement has resulted from the extension of the continuous dilution method to these measurements.[11,12] Gibbs and Van Ness[11] have described a device in which static vapour pressures of mixtures produced by twin piston injectors are measured with a differential pressure null indicator/-nitrogen backing line/Bourdon pressure gauge combination. Measurements over the entire composition range are made in a single experimental "run".

Tomlins[12] has described a similar device in which vapour pressures are measured with a nulled capacitance manometer/-servo-operated nitrogen backing line/mercury manometer combination. Two experimental "runs" are required to cover the composition range.

6.4 Experimental: A diagram of a continuous dilution vapour-pressure apparatus[13] used in this work is shown in *figure 6.1*. A Pyrex-glass vacuum line, interposed with "Nupro" bellows valves and "Kovar" glass-to-metal seals, is mounted in a rigid brass framework to which is fitted an adjustable three-point suspension for levelling purposes. A calibrated measuring burette MB of volume about 18 cm^3 consists of two sections of "Veridia" precision-bore (4 mm, 8 mm) glass tubing with three fiducial marks along its length. A bulb B at the lower end of the burette branches down to a mercury reservoir and out to valve 8 through which the burette is filled with liquid from the degassing apparatus (*figure 6.2*). The mercury reservoir is connected via pulley-operated valve 6 either to a vacuum or to a nitrogen supply so that the level of the mercury in the burette can be lowered or raised. A glass bowl surrounding the bulb is filled with ice or liquid nitrogen during distillation of liquid into the burette. A 2 mm bore tube connects the upper part of the burette to pulley-operated valve 4 through which additions of liquid are made to the vapour-pressure cell C. For very fine control and avoidance of side

Figure 6.1: Vapour pressure apparatus: Manometer M constructed from 20 mm "Veridia" precision-bore tubing with fiducial marks F4, F5; cell C, capacity 50 cm^3 containing liquid of known mass introduced through valve 2; platinum coil stirrer PS connected to a sealed glass tube containing soft iron and lifted upwards by solenoid S; 12.7 mm "Nupro"[a] stainless-steel bellows valves, □, 1 to 3; and 6.35 mm "Nupro" stainless-steel bellows valves, ○, 4 to 8, with connexions to the valves through "Kovar"[b] glass-to-metal seals using zytel or teflon ferrules and "Swagelok"[c] fittings; pulleys P1 to P3 to operate valves 4 to 6; mercury reservoirs R1 and R2; Dewar D raised with rod R to surround cell, ice water added through Dewar funnel DF; calibrated measuring burette MB constructed of 4 mm and 8 mm "Veridia" precision-bore tubing with fiducial marks F1 to F3; bulb B surrounded by glass bowl GB, liquid introduced from degassing apparatus through valve 8.

---

[a] Nupro Co., Cleveland, Ohio.

[b] Jencons (Scientific) Ltd., Herts., U.K.

[c] Crawford Fittings, Niagara Falls, Ontario.

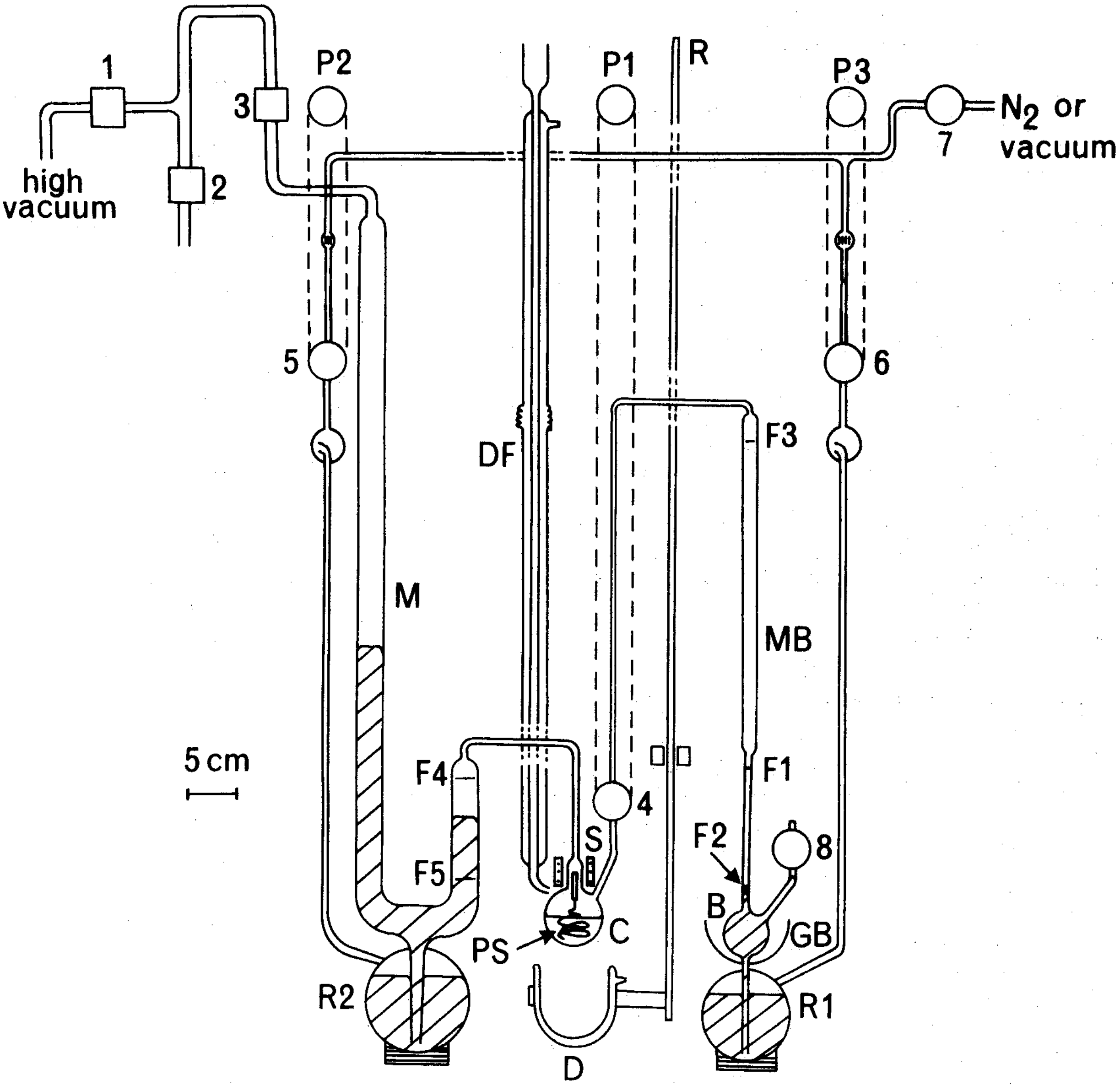
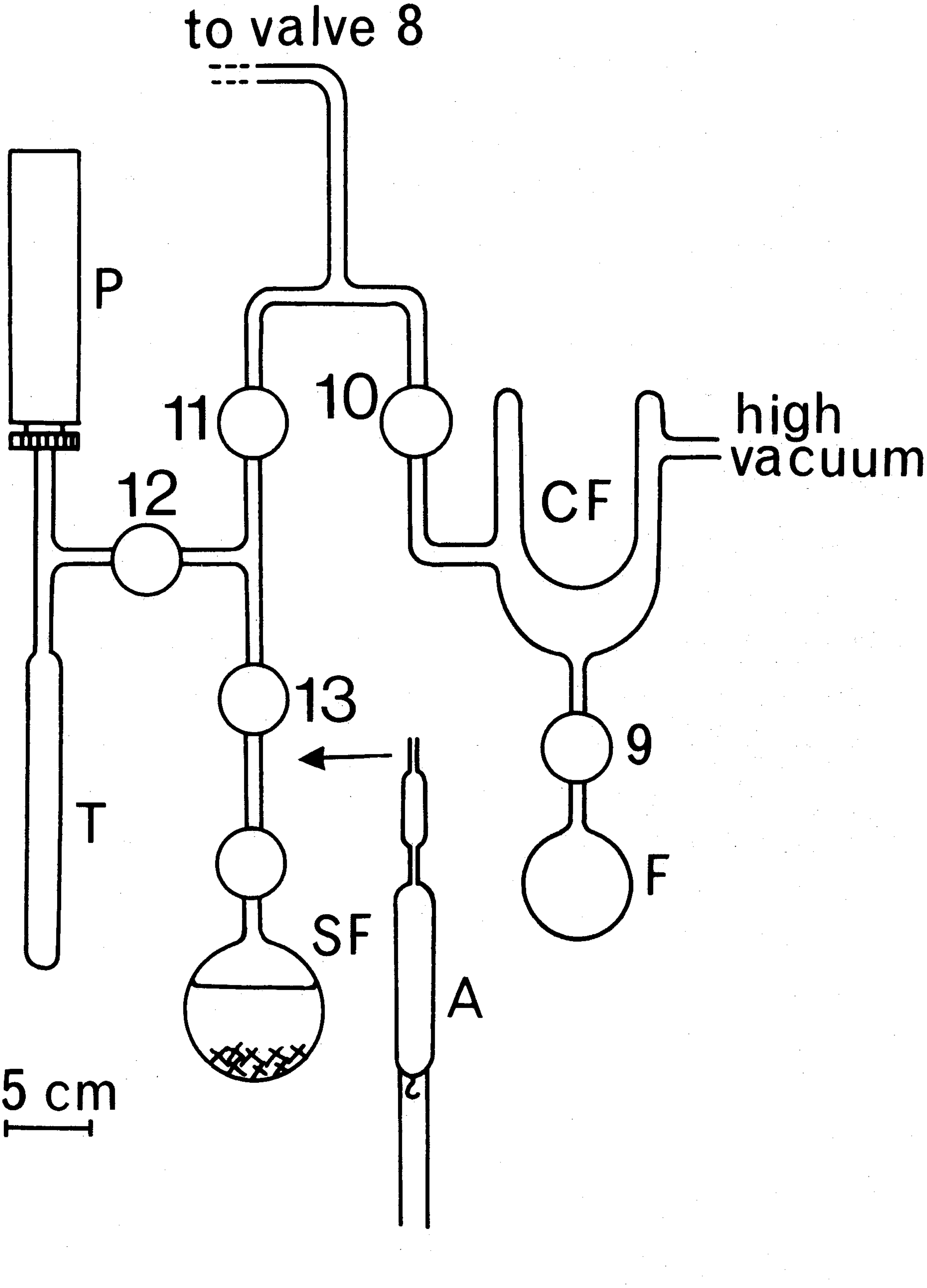

1
3
P2
P1
R
P3
N2 or vacuum
7
high vacuum
2
5
6
F3
DF
M
MB
5 cm
F4
F1
4
S
F2
8
F5
B
GB
PS
C
R2
R1
D

Figure 6.2: Degassing apparatus: Storage flask SF containing liquid and drying agent, sealed with "Nupro" valve; 6.35 mm "Nupro" stainless-steel bellows valves, ◯, 9 to 13; cold finger CF to hold liquid nitrogen; flask F to contain liquid distilled from SF; Pirani gauge head P; trap T to remove vapour used in flushing the apparatus; glass T-tubing connects valves 10 and 11 to valve 8 of the vapour pressure apparatus, replaced by glass U-tubing when degassing the liquid to be distilled into a weighed ampoule or flask; weighed break-seal ampoule A with 6.35 mm "Kovar" glass-to-metal seal for attaching to valve 13. (For connexion to valve 2 of the vapour-pressure apparatus the 6.35 mm glass-to-metal seal is removed from the reweighed filled ampoule and a 12.7 mm "Kovar" glass-to-metal seal is joined at the break-seal end of the ampoule.)


to valve 8
P
11
10
12
high
vacuum
CF
13
9
T
F
SF
A
5 cm

thrusts on the valve 4, a brass bar of adjustable length is interposed between the valve spindle and the pulley shaft. The cell contains a coiled platinum stirrer mounted below a small glass-enclosed magnet which is activated by a solenoid, and is connected to the manometer constructed of calibrated "Veridia" precision-bore (20 mm) tubing and mounted over a mercury reservoir. Mercury levels in the manometer are adjusted as described for the burette. Calibration (by nitrogen compression) of the volume of the cell between fiducial mark F4 and valve 4, about 70 cm^3, enables corrections to be made for vapour space. When necessary, a small Dewar can be raised with a rod to cool the cell and its contents.

The method for degassing liquids has been described by Dunlop *et al.*[14] Using the apparatus shown in *figure 6.2*, liquid is distilled from the storage flask SF into flask F which is cooled with liquid nitrogen. With continuous pumping, the frozen liquid is slowly sublimed on to the liquid-nitrogen-cooled cold finger. Although one sublimation completely degasses most liquids the procedure is always repeated.

The measuring burette is filled with liquid as follows: with liquid in the flask below closed valve 9 the degassing apparatus is connected to the vapour pressure apparatus through valve 8, and both sections, which are maintained under constant vacuum when not in use, are pumped down overnight on the bench to a pressure of less than 10^{-3} Pa. Mild heating of glassware in the early stages of pumping serves to remove adsorbed materials. After closing valve 8, about 25 cm^3 of liquid 1 are thoroughly degassed and then distilled, with valve 4 closed, through re-opened valve 8 into the bulb under the burette, with the mercury level slightly below the glass bowl which is filled with suitable coolant.

Valve 8 is then closed and, after thawing, liquid 1 is forced into the burette[a] by raising the mercury level so that it is finally contained under positive pressure between valve 4 and the mercury meniscus which, ideally, is just below fiducial mark F2. Any excess liquid is bled off through valve 8 before the degassing apparatus is detached.[b] The vapour-pressure apparatus is then transferred to a thermostatted bath to test the effectiveness of the degassing procedure. After re-connecting the apparatus to the pumps with flexible stainless-steel tubing and re-evacuating, the mercury is raised to suitable levels in the manometer arms, and the difference in the meniscus positions is measured to check for correct levelling.[c] A small volume of liquid 1 is admitted to the cell until the mercury meniscus in the burette rises close to the fiducial mark F2. The vapour pressure of liquid 1 is measured as described in *Chapters 2* and *3*. The apparatus is then removed from the bath.

The following procedure is used to admit pure liquid 2

---

[a] Volatile liquids must be *carefully* warmed up to room temperature otherwise contact of the cold liquid with the burette walls may cause a violent pressure change.

[b] When no vapour space exists in the burette and the mercury level is to be withdrawn, *e.g.* at the end of a "run" or if insufficient liquid has been distilled in, care must be taken. *Cavitation* in the liquid is often a sudden and violent process.

[c] This levelling is, of course, a function of the telescope and cathetometer scale only - not of the manometer itself.

of known mass to the vapour pressure cell: with valves 10 and 11 connected with glass tubing, about 25 cm^3 of liquid 2 of known mass are degassed and then sublimed into, and finally sealed in, either a small weighed flask with attached "Nupro" valve or a weighed break-seal ampoule attached to valve 13. The mass of liquid 2 is determined from accurate weighings, to ±0.0001 g, corrected to vacuo. After attaching the ampoule or flask to valve 2 of the vapour pressure apparatus and thoroughly evacuating, the liquid is distilled into the cell cooled with liquid nitrogen. The frozen liquid is pumped on briefly before raising the mercury level into the manometer arms and then allowing thawing to proceed.[a]

The loaded vapour-pressure apparatus is placed in a vibration-free thermostatted bath, reconnected to the pumps, and levelled. After temperature equilibration the positions of F1 and F4 and all mercury menisci are measured. To make an addition of liquid 1 the bath stirrer is switched off, the cell is cooled by adding ice + water to the suitably positioned Dewar, and then a small quantity of liquid is admitted from the burette through valve 4. The ice water remains in position in the Dewar due to its density and, by cooling the cell contents, obviates large pressure changes if the added liquid has a vapour pressure very different from that of the liquid in the cell. (This procedure is also used to bring back into the cell any liquid which has condensed on the mercury surface in the manometer, a problem which occurs with pure

---

[a] For volatile liquids the apparatus must be attended during this process, and heating, if any, should be carried out with *extreme care*.

liquids and sometimes with mixtures.) After temperature equilibration the mercury level in the burette is recorded and the levels in the manometer[a] are read off until, with periodic stirring, the difference is constant. Further additions of liquid are made to complete the remaining half of the mole-fraction range. At the conclusion of the run the contents of the cell are distilled into a weighed flask with attached "Nupro" valve to test for quantitative transfer of liquid 2 and accuracy of burette additions.[b] The second half of the mole-fraction range is covered by a second series of measurements with the positions of the liquids reversed.

It is believed that this apparatus offers some advantages over continuous-dilution methods previously described.[11,12] The relative simplicity of the cell ensures speedy equilibration after an addition is made and, because of its extremely small leak rate (less than 3×10^{-6} Pa.s^{-1}), the vapour pressure of an enclosed liquid remains static within experimental error for long periods. The "mercury piston" type burette allows the introduction of rigorously degassed liquids and their subsequent storage in that condition for indefinite periods.

As transfer and testing of degassed liquids in the apparatus

---

[a] The menisci in the manometer normally require reforming before these readings are taken. This is done by raising them *slowly* by a *small* amount (ca. 2-3 mm).

[b] This removal of liquid from the cell may be conducted *in situ* if the flask contains a small quantity of liquid, with the same or higher vapour pressure, to ballast the high side of the manometer.

require 1-2 days, while measurements of vapour pressures for each half of the composition range take a further day, a complete mixture can normally be studied in 5-6 days.

6.5 Second virial coefficients: As shown in *section 6.2*, the extraction of reliable values of $\bar{G}^E$ from isothermal p,x data requires a knowledge of second virial coefficients for the pure vapours and, ideally, for the mixed vapours also. Experimental values of B_{ii} (and especially B_{ij}) at moderate temperatures (*viz.* below the normal boiling point) are scarce in the literature for all but the most common liquids.

The values of B_{ii} used for all calculations in this work are shown in table 6.1. The assumption was made throughout that $\delta_{ij} = 0$, without some knowledge of B_{ij}, this approximation was necessary.

The vapour pressure apparatus described was used to measure the second virial coefficient for the vapours of diethyl ether, di-*iso*-propyl ether, and hexafluorobenzene at 298.15 K. The results of these measurements and the standard deviation of B are included in table 6.1.

A small quantity of liquid, sufficient to produce *not more than* 70-80% of the saturated vapour pressure, was admitted to the vapour pressure cell C (see *figure 6.1*) and the pressure observed as a function of the position of the mercury meniscus below F4 in the manometer. From the relation,

$$\frac{PV}{RT} = n + \frac{n^2 B}{V} + \ldots \qquad 6.19$$

Table 6.1: Second virial coefficients ($dm^3.mol^{-1}$) of vapours at 298.15 K

vapour	measured - this work	literature	used for $\bar{G}^E$ calculations
benzene	-	-	-1.49^{19}
n-hexane	-	-	-1.98^{19}
di-ethyl ether	-1.187 ± 0.025	-1.176 ± 0.027[15,a]	-1.19
di-*iso*-propyl ether	-2.46 ± 0.83 -2.02 ± 0.30	-2.156[16,b]	-2.14[d]
hexafluorobenzene	-4.93 ± 0.19	-2.662[17,b] -2.530[18,c]	-2.53

[a] From least squares analysis of experimental data obtained over a wide temperature range (293-405 K); $B = -7.625 + 0.032797(T/K) - 0.000037446(T/K)^2$, $\sigma = 0.027\ dm^3.mol^{-1}$.

[b] From the Clapeyron equation, vapour pressures and enthalpy of vaporization data.

[c] From least squares analysis of data obtained both experimentally (498-623 K) and by method b (301-377 K); $B = -3.370 + 0.037766(t/°C) - 0.00016827(t/°C)^2$, $\sigma = 0.032\ dm^3.mol^{-1}$.

[d] Weighted average of values obtained in this work.

the slope[a] and intercept[a] of a plot of (PV/RT) against (1/V) was used to evaluate B. No evidence of curvature was detected in these plots, confirming the accuracy of the cell volume calibration (±0.1%), the absence of adsorption of liquid onto glass, and the relative insignificance of the higher terms in equation 6.19.

The large discrepancy between the measured value and the literature value of B for hexafluorobenzene could not be accounted for in terms of experimental errors. Only for di-ethyl ether could a comparison be made with an experimentally determined value of B; the agreement (ca. 1%) is satisfactory.

6.6 Results: For this work isothermal p,x data was used to calculate $\bar{G}^E$, y and f at 298 K for the systems *n*-hexane + benzene,[b] di-ethyl ether + hexafluorobenzene, di-*iso*-propyl ether + hexafluorobenzene. Experimental results for the first-named system are presented in this chapter (table 6.2)

---

[a] Obtained from least squares analysis. The agreement between this intercept and the number of moles admitted from the burette (0.0002-0.002 mol) was noted to be within experimental error (1-0.2%).

[b] The small discrepancies between the results reported here (table 6.1) and those earlier reported in reference 13 arose from (a) refinement of burette calibrations, (b) rejection of an incongruous point at $x_1 = 0.3320$ in run 1, (c) a misprint ("20.120" kPa should read 20.210 kPa) and (d) the later inclusion (run 4) of the point $x_1 = 0.9999$, $\bar{G}^E = 0.2$ J.mol^{-1}.

Table 6.2: Experimental results for n-hexane(1) + benzene(2) at 298.150 K[a]

δp = p(expt.) - p(calc.)

Run 1
Run 2

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}
0	-	12.679	-	-	-	-
0.0039	0.0133	12.806	0.005	2.1780	1.0000	7.6
0.0107	0.0353	13.017	0.009	2.1416	1.0001	20.6
0.0212	0.0665	13.311	0.003	2.0884	1.0006	40.0
0.0312	0.0939	13.584	0.004	2.0400	1.0012	58.0
0.0398	0.1155	13.807	0.005	2.0007	1.0019	72.9
0.0629	0.1673	14.349	0.000	1.9028	1.0046	111.0
0.1079	0.2475	15.243	-0.005	1.7419	1.0129	176.8
0.1402	0.2936	15.780	-0.006	1.6462	1.0210	217.6
0.1642	0.3237	16.136	-0.006	1.5836	1.0282	244.7
0.1953	0.3583	16.558	0.002	1.5121	1.0386	275.8
0.2247	0.3881	16.903	-0.003	1.4529	1.0497	301.3
0.2599	0.4203	17.287	0.003	1.3908	1.0644	327.1
0.2852	0.4419	17.538	0.007	1.3514	1.0760	342.6
0.3100	0.4621	17.761	0.004	1.3164	1.0880	355.5
------	------	------	------	------	------	------
0.4078	0.5352	18.510	-0.001	1.2070	1.1419	385.0
0.4324	0.5522	18.678	0.005	1.1852	1.1571	387.4
0.4599	0.5716	18.835	-0.008	1.1630	1.1748	387.9
0.4948	0.5951	19.047	0.004	1.1378	1.1985	385.2
0.5332	0.6213	19.244	0.001	1.1135	1.2262	378.1
0.5668	0.6442	19.399	-0.003	1.0949	1.2517	368.5

(contd.)

---

[a] This system has an azeotrope at $x_1 \simeq 0.91-0.92$

Table 6.2 (contd.) Run 2 (contd.)

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}
0.6077	0.6722	19.576	-0.001	1.0751	1.2846	352.7
0.6503	0.7018	19.739	0.002	1.0576	1.3208	331.5
0.7046	0.7412	19.906	-0.003	1.0393	1.3702	297.9
0.7593	0.7824	20.041	-0.003	1.0249	1.4234	256.9
0.8281	0.8378	20.157	-0.003	1.0119	1.4947	195.5
0.8978	0.8986	20.215	0.006	1.0039	1.5709	123.1
0.9346	0.9334	20.211	0.004	1.0015	1.6120	80.9
0.9591	0.9577	20.194	0.000	1.0006	1.6393	51.5
0.9835	0.9826	20.172	0.001	1.0001	1.6665	21.1
1	-	20.152	-	-	-	-

$a_0 = 0.62035$ $a_1 = -0.11622$ $a_2 = 0.03451$ $a_3 = -0.01708$

$\Sigma(\delta p)^2 = 0.00055$ kPa^2

Table 6.2 (contd.)

Run 3
Run 4

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}
0	-	12.685	-	-	-	-
0.0133	0.0430	13.080	-0.003	2.1032	1.0002	25.1
0.0287	0.0865	13.507	0.000	2.0327	1.0009	52.7
0.0463	0.1303	13.958	0.003	1.9575	1.0024	82.8
0.0872	0.2127	14.848	0.000	1.8055	1.0082	146.1
0.1404	0.2938	15.784	-0.001	1.6448	1.0203	216.0
0.1966	0.3601	16.570	-0.002	1.5106	1.0380	275.3
0.2590	0.4200	17.278	0.001	1.3937	1.0629	325.1
0.3243	0.4738	17.880	-0.001	1.2987	1.0942	360.8
0.3735	0.5107	18.267	-0.002	1.2413	1.1210	377.5
0.4094	0.5361	18.531	0.008	1.2057	1.1421	384.4
0.4562	0.5687	18.825	0.004	1.1659	1.1718	387.2
0.4571	0.5696	18.821	-0.005	1.1651	1.1724	387.2
0.5272	0.6174	19.211	-0.003	1.1172	1.2210	378.8
0.6278	0.6868	19.650	-0.010	1.0671	1.2997	343.0
0.6912	0.7315	19.885	0.007	1.0444	1.3550	307.0
0.7441	0.7709	20.028	0.007	1.0296	1.4048	269.5
0.8135	0.8261	20.151	-0.003	1.0152	1.4760	210.5
0.8645	0.8691	20.206	-0.004	1.0079	1.5328	160.4
0.9224	0.9217	20.222	-0.003	1.0026	1.6028	96.6
0.9705	0.9686	20.202	0.008	1.0004	1.6658	38.2
0.9896	0.9889	20.169	-0.002	1.0000	1.6921	13.7
0.9999	0.9995	20.162	0.007	1.0000	1.7067	0.2
1	-	20.154	-	-	-	-

$a_0 = 0.61926$ $a_1 = -0.11516$ $a_2 = 0.03520$ $a_3 = -0.00464$

$\Sigma(\delta p)^2 = 0.00048\ \text{kPa}^2$

Table 6.3: Comparison of the excess Gibbs free energies, $\bar{G}^E$ (J.mol^{-1}), for n-hexane(1) + benzene(2) with the results of Harris and Dunlop[19]

x_1	runs 1/2	runs 3/4	Harris and Dunlop[19]	
			reported	calculated (equation 6.13)
0.09787[a]	163.1	161.3	162.2	162.0
0.17675	257.7	256.0	257.6	257.9
0.29029	345.5	344.3	346.6	347.2
0.36452	376.0	375.1	377.5	377.8
0.37531	378.8	377.9	380.3	380.5
0.48754	386.0	385.3	387.0	386.5
0.59742	357.0	356.6	356.8	355.9
0.69838	302.1	302.2	300.8	300.6
0.79959	222.2	223.2	220.6	221.6
0.90882	110.7	112.2	109.8	111.7

[a] Misprinted in the original paper.[19]

and those for the latter two in *Chapter 7*.

The incongruity of vapour pressures at the junction of each pair of experimental "runs" is satisfactory (<0.01 kPa) for all but the system di-ethyl ether + hexafluorobenzene (ca. 0.06 kPa) which has an unusually large density range (ca. 900 $kg.m^{-3}$). This mixture required a great deal of stirring to produce an apparently steady vapour pressure; mixing may not have been complete. The stirrer design (see *section 6.4*), although effective in breaking the liquid surface may be unsuitable for rapid mixing of liquids with such large density differences.

The system *n*-hexane + benzene at 298.15 K was chosen as a test system for the apparatus and procedures discussed in *sections 6.2* and *6.4*. In table 6.3 a comparison of the values of $\bar{G}^E$ for this system computed from equation 6.13 with the a_i values in table 6.2 is made, both against the originally reported values of Harris and Dunlop[19] and, more directly, against the values calculated from their data fitted to a four parameter equation (6.13) at their mole fractions. The agreement is within experimental error (see *section 6.7*).

6.7 Errors in $\bar{G}^E$: Little comment can be made about the *accuracy* of $\bar{G}^E$ values obtained from p,x measurements without some knowledge of the term δ_{ij} (equation 6.7) and of the effect of contaminants. The experimental *precision* is estimated to be ±2 $J.mol^{-1}$ (see *appendix 6.3*). This estimate is supported by the agreement between duplicate runs and with the results of Harris and Dunlop.[19]

References

1. Van Ness, H.C. *Ind. Eng. Chem.* 1967, 59, 34
2. Scatchard, G.; Raymond, C.L. *J. Amer. Chem. Soc.* 1938, 60, 1278
3. Rowlinson, J.S. *Liquids and liquid mixtures.* Butterworths: London 1959
4. Barker, J.A. *Aust. J. Chem.* 1953, 6, 207
5. Diaz Peña, M. *An. Fis.* 1970, 66, 377
6. Stokes, R.H.; Marsh, K.N. *Ann. Rev. Phys. Chem.* 1972, 23, 65
7. Myers, D.B.; Scott, R.L. *Ind. Eng. Chem.* 1963, 55, 43
8. Based on a FORTRAN program written by Harris, K.R. *Ph.D. Thesis.* Physical and Inorganic Chemistry Department, University of Adelaide, 1970
9. Brown, I. *Aust. J. Sci. Res. A.* 1952, 5, 530
10. McGlashan, M.L. *Ann. Rep. Chem. Soc.* 1962, 59, 73
11. Gibbs, R.E.; Van Ness, H.C. *Ind. Eng. Chem. Fundam.* 1972, 11, 410
12. Tomlins, R.P. Paper presented at the Fifth National Convention of the Royal Australian Chemical Institute, Canberra, 1974
13. Murray, R.S.; Martin, M.L. *J. Chem. Thermodynamics* 1975, 7, 839
14. Bell, T.N.; Cussler, E.L.; Harris, K.R.; Pepela, C.N.; Dunlop, P.J. *J. Phys. Chem.* 1968, 72, 4693
15. Dymond, J.H.; Smith, E.B. *The Virial Coefficients of Gases - a critical compilation* Oxford Science Research papers 2, Clarendon Press: Oxford 1969
16. Andon, R.J.L.; Counsell, J.F.; Lee, D.A.; Martin, J.F. *J. Chem. Soc. - Faraday Trans.* 1, 1974, 70, 1914

17. Counsell, J.F.; Green, J.H.S.; Hales, J.L; Martin, J.F. *Trans. Faraday Soc.* 1965, 61, 212

18. Douslin, D.R.; Harrison, R.H.; Moore, R.T. *J. Chem. Thermodynamics* 1969, 1, 305

19. Harris, K.R.; Dunlop, P.J. *J. Chem. Thermodynamics* 1970, 2, 805

20. Weissberger, A.; Rossiter, B.W. *Techniques of Chemistry* Vol. I, Pt. V, Wiley-Interscience 1971

CHAPTER 7

RESULTS AND DISCUSSION

7.1 Results: Experimental results for the composition dependence of excess thermodynamic functions of binary liquid systems containing hexafluorobenzene and ethers are tabulated on the following pages. Accompanying graphs represent the *smoothed* results obtained from least squares analysis of each data set.

The congruence, at medium composition, of experimental data is clearly shown in each case and may provide an indication of the internal consistency or *precision* of measurements. Pronounced incongruities, evident in some excess enthalpy results, are believed to arise from the large density ranges of the mixtures studied (up to 920 $kg.m^{-3}$), and the consequent reduction of stirring efficiency, a major consideration in calorimetry.[a] This belief is supported by the observations that (a) measurements proceeding from the ether-rich end of the composition range are, for the most part, algebraically smaller than those proceeding from the fluoro-carbon-rich end and (b) that no such mismatch of results appears for the system benzene + *cyclo*-hexane (see *Table 5.2*) which has only a small density range (ca. 100 $kg.m^{-3}$). This effect has little bearing on the discussion of results presented in *Section 7.2*.

---

[a] The incongruity of vapour pressure measurements for the system di-ethyl ether + hexafluorobenzene (*Table 7.9*) is believed to arise in the same way (see *Section 6.6*) but a similar effect with excess volumes for the system di-allyl ether + hexafluorobenzene does *not* originate in this way (see *Section 4.5*).

Table 7.1: Excess volumes for di-allyl ether (1) + hexafluorobenzene(2) at 298.172 K

$$\delta\bar{V}^E = \bar{V}^E_{expt.} - \bar{V}^E_{calc.}$$

x_1	$\bar{V}^E/cm^3.mol^{-1}$	$\delta\bar{V}^E/cm^3.mol^{-1}$
0.0021	0.0068	0.0001
0.0041	0.0134	0.0002
0.0149	0.0490	0.0013
0.0269	0.0877	0.0018
0.0526	0.1694	0.0029
0.1120	0.3461	0.0012
0.1473	0.4440	0.0001
0.1769	0.5207	-0.0014
0.2030	0.5850	-0.0019
0.2376	0.6646	-0.0020
0.2609	0.7141	-0.0019
0.2880	0.7671	-0.0017
0.3173	0.8198	-0.0004
0.3620	0.8888	0.0020
0.3986	0.9348	0.0045
0.4332	0.9690	0.0068
Run 1 Run 2		
0.5405	0.9976	-0.0040
0.5739	0.9913	-0.0038
0.6592	0.9300	-0.0069
0.7502	0.8148	0.0095
0.8392	0.6015	0.0011
0.9310	0.2947	-0.0038
0.9679	0.1450	-0.0022

(contd.)

Table 7.1 (contd.)

x_1	$\bar{V}^E/cm^3mol^{-1})$	$\delta\bar{V}^E/cm^3.mol^{-1}$
0.9975	0.0125	0.0005
0.9995	0.0027	0.0003

$$\bar{V}^E/cm^3.mol^{-1} = \text{equation 4.1}$$

$a_0 = 3.2140$; $a_1 = 2.5951$; $a_2 = -3.1938$; $a_3 = 2.2117$

$\sigma = 0.0037\ cm^3.mol^{-1}$

Figure 7.1

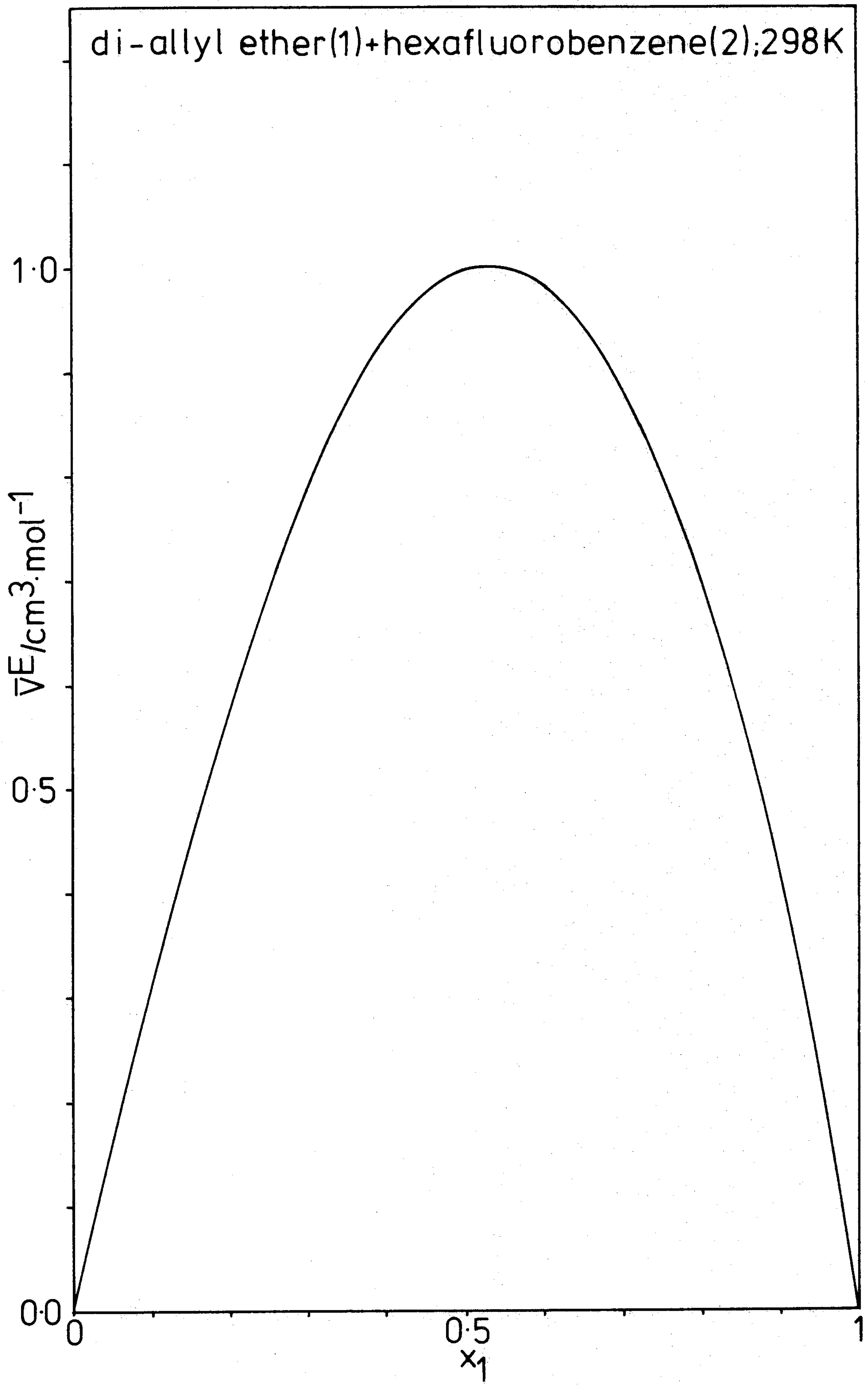

di-allyl ether(1)+hexafluorobenzene(2);298K
$\bar{V}^E$/cm³·mol⁻¹
1·0
0·5
0·0
0
0·5
1
x_1

Table 7.2: Excess volumes for di-benzyl ether(1) + hexafluorobenzene(2) at 298.178 K

$$\delta\bar{V}^E = \bar{V}^E_{expt.} - \bar{V}^E_{calc.}$$

x_1	$\bar{V}^E/cm^3.mol^{-1}$	$\delta\bar{V}^E/cm^3.mol^{-1}$
0.0030	-0.0008	0.0002
0.0107	-0.0031	0.0004
0.0202	-0.0063	0.0004
0.0290	-0.0093	0.0003
0.0416	-0.0132	0.0005
0.0784	-0.0252	0.0000
0.1026	-0.0324	0.0000
0.1371	-0.0421	-0.0006
0.1642	-0.0486	-0.0008
0.1952	-0.0543	-0.0005
0.2222	-0.0581	-0.0001
0.2500	-0.0610	0.0002
0.2863	-0.0627	0.0009
0.3143	-0.0634	0.0008
0.3301	-0.0629	0.0011
Run 1 Run 2		
0.4313	-0.0559	-0.0010
0.4324	-0.0560	-0.0013
0.4685	-0.0492	-0.0006
0.5079	-0.0404	0.0003
0.5499	-0.0310	0.0002
0.6015	-0.0184	0.0005
0.6496	-0.0071	0.0003
0.6923	0.0019	-0.0002

(contd.)

Table 7.2 (contd.)

x_1	$\bar{V}^E/cm^3.mol^{-1}$	$\delta\bar{V}^E/cm^3.mol^{-1}$
0.7230	0.0086	0.0004
0.7866	0.0177	0.0000
0.8265	0.0205	-0.0004
0.8952	0.0201	0.0000
0.9216	0.0175	0.0001
0.9401	0.0143	-0.0002
0.9603	0.0107	0.0001
0.9779	0.0064	0.0001
0.9901	0.0031	0.0001

$\bar{V}^E/cm^3.mol^{-1}$ = equation 4.1

$a_0 = -0.3293$; $a_1 = -0.3939$; $a_2 = 1.8168$; $a_3 = -0.7798$

$\sigma = 0.0005\ cm^3.mol^{-1}$

Figure 7.2

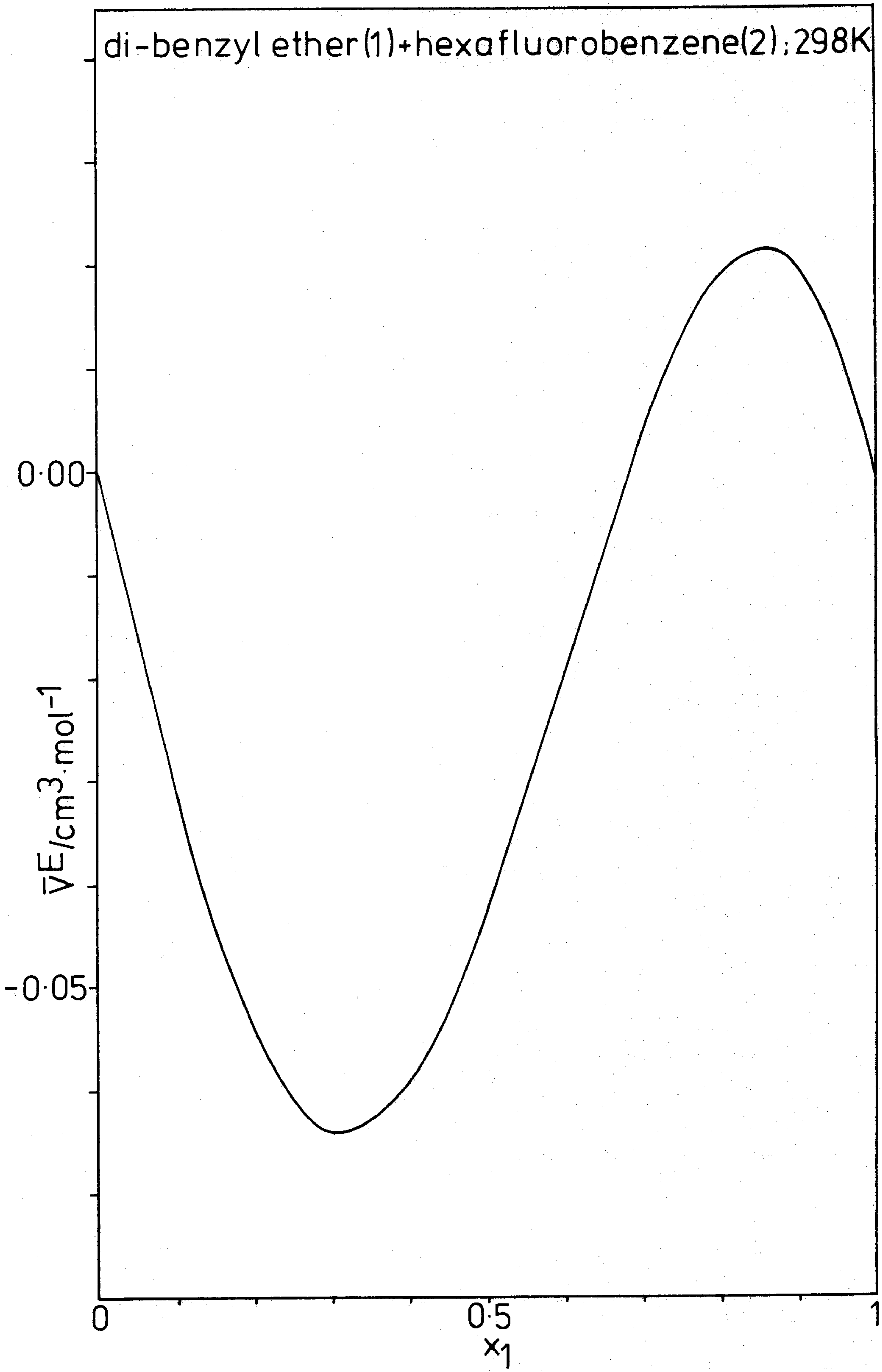

di-benzyl ether(1)+hexafluorobenzene(2); 298K
0·00
-0·05
$\bar{V}^E$/cm^3·mol^{-1}
0
0·5
1
x_1

Table 7.3: Excess enthalpies for di-ethyl ether (1) + hexafluorobenzene (2) at 283.14 K

$$\delta\bar{H}^E = \bar{H}^E_{expt.} - \bar{H}^E_{calc.}$$

x_1	$\bar{H}^E_{expt.}/J.mol^{-1}$	$\delta\bar{H}^E/J.mol^{-1}$	
0.0167	7.30	-0.26	
0.0376	16.40	-0.01	
0.0564	23.99	0.09	
0.0749	30.69	-0.06	
0.1665	58.66	0.11	
0.2564	76.97	-0.02	
0.3368	87.26	-0.13	
0.4006	92.32	0.08	
0.4640	94.56	0.11	Run 1 ↑
0.4988	94.21	-0.44	Run 2
0.5178	94.80	0.33	Run 1
0.5390	93.72	-0.31	Run 2
0.5552	94.07	0.55	Run 1
0.5910	91.71	-0.17	Run 2 ↓
0.6469	87.71	-0.12	
0.7119	80.68	0.03	
0.7678	72.01	-0.01	
0.8198	61.60	0.01	
0.8720	48.33	0.05	

(contd.)

Table 7.3 (contd.)

0.9209	32.84	0.04
0.9631	16.51	-0.13

$\bar{H}^E_{calc.}/J.mol^{-1}$ = equation 4.1

$a_0 = 464.57$; $a_1 = -285.40$; $a_2 = 148.15$; $a_3 = 157.30$

$\sigma = 0.23\ J.mol^{-1}$

Table 7.4: Excess enthalpies for di-ethyl ether(1) + hexafluorobenzene(2) at 298.14 K

$$\delta\bar{H}^E = \bar{H}^E_{expt.} - \bar{H}^E_{calc.}$$

x_1	$\bar{H}^E_{expt.}/J.mol^{-1}$	$\delta\bar{H}^E/J.mol^{-1}$	
0.0567	20.20	-0.06	
0.1140	37.90	0.09	
0.1726	53.03	0.06	
0.2315	65.49	-0.08	
0.2893	75.47	-0.12	
0.3962	88.71	0.15	
0.4759	94.12	0.29	Run 1 ↑
0.4879	94.06	-0.24	Run 2
0.4936	94.51	0.02	Run 3
0.4976	94.31	-0.31	Run 3
0.4984	94.51	-0.13	Run 2
0.5269	95.64	0.39	Run 1
0.5493	95.65	0.27	Run 1
0.5628	94.91	-0.39	Run 3
0.5996	94.76	0.26	Run 2
0.6640	90.32	-0.51	Run 3
0.7130	86.30	0.43	Run 2
0.7922	73.36	0.23	Run 2
0.7931	72.51	-0.43	Run 3
0.8629	56.00	0.29	Run 2
0.8636	55.37	-0.16	Run 3

(contd.)

Table 7.4 (contd.)

0.9355	30.07	-0.34	Run 3
0.9361	30.48	0.31	Run 2

$\bar{H}^E_{calc.}$ J.mol^{-1} = equation 4.1[a]

$a_0 = 384.31$; $a_1 = -99.37$; $a_2 = 100.67$; $a_3 = 151.78$

$\sigma = 0.31$ J.mol^{-1}

---

[a] These results were substantially confirmed by those of Mattingley *et.al.*[1]

viz. $a_0 = 360.7$; $a_1 = -69.8$; $a_2 = 201.2$

$\sigma = 1.07$ J.mol^{-1}

Figure 7.3

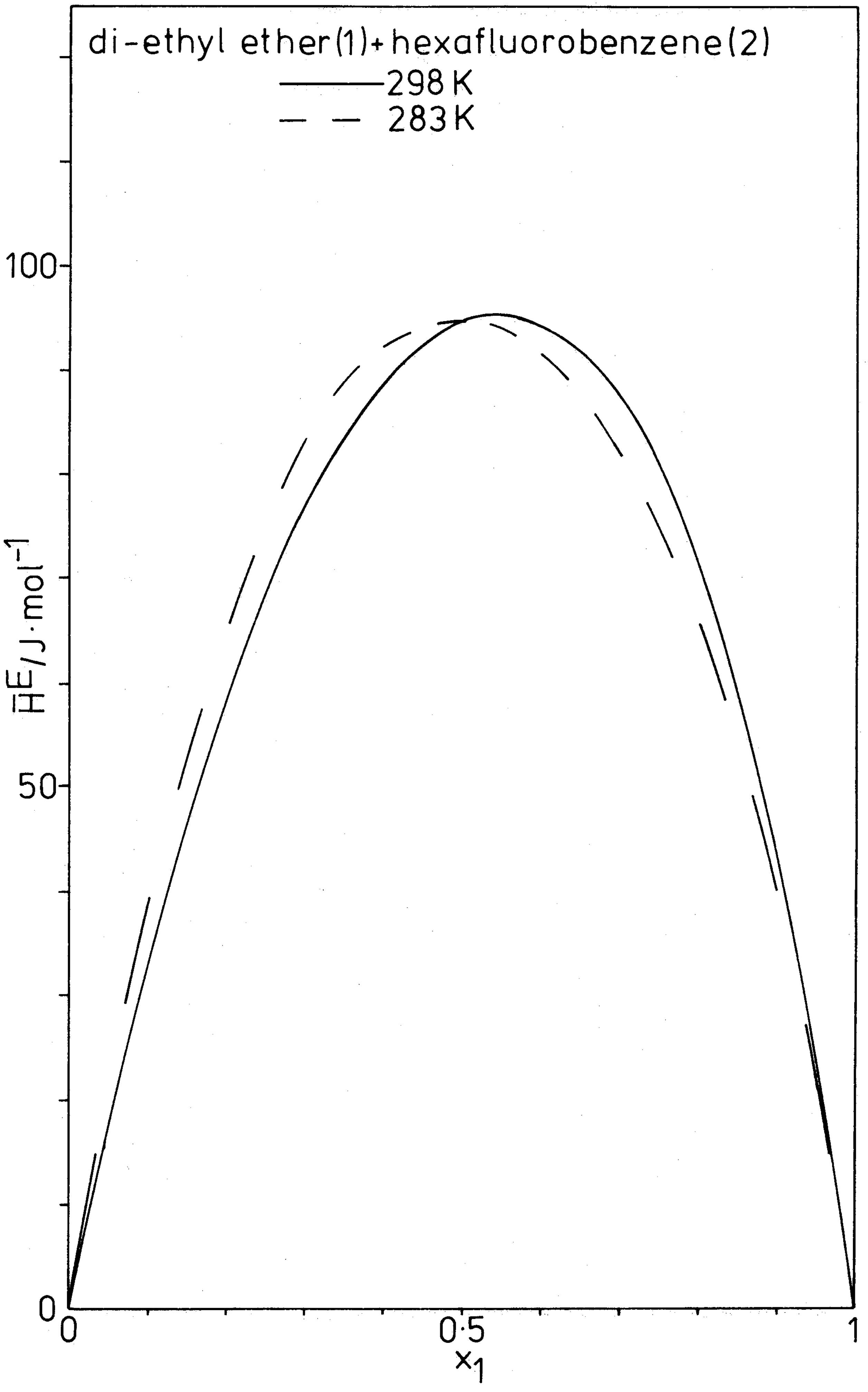

di-ethyl ether(1)+hexafluorobenzene(2)
298 K
283 K
100
50
0
$\bar{H}^E/J\cdot mol^{-1}$
0
0·5
1
x_1

Table 7.5: Excess enthalpies for di-iso-propyl ether (1) + hexafluorobenzene (2) at 283.15 K

$$\delta\bar{H}^E = \bar{H}^E_{\text{expt.}} - \bar{H}^E_{\text{calc.}}$$

x_1	$\bar{H}^E_{\text{expt.}}/\text{J.mol}^{-1}$	$\delta\bar{H}^E/\text{J.mol}^{-1}$	
0.0322	56.30	0.12	
0.0632	105.05	-0.51	
0.1217	188.02	0.66	
0.2247	295.60	-0.28	
0.3180	357.67	-0.39	
0.3538	373.34	-0.12	
0.4014	387.41	0.36	
0.4456	393.65	0.74	
0.4721	394.47	1.05	Run 1 ↑
0.4784	392.00	-1.23	Run 2 ↓
0.5384	384.53	-0.74	
0.6039	364.68	0.05	
0.6783	327.59	0.82	
0.7287	292.17	-0.57	
0.8033	230.50	-0.08	
0.9220	103.24	0.16	
0.9641	49.35	-0.03	
0.9845	21.75	0.04	

$\bar{H}^E_{\text{calc.}}/\text{J.mol}^{-1}$ = equation 4.1

$a_0 = 1818.65$; $a_1 = -546.01$; $a_2 = 17.53$; $a_3 = 131.37$

$\sigma = 0.65\ \text{J.mol}^{-1}$

Table 7.6: Excess enthalpies for di-iso-propylether(1) + hexafluorobenzene(2) at 298.15 K

$$\delta\bar{H}^E = \bar{H}^E_{\text{expt.}} - \bar{H}^E_{\text{calc.}}$$

x_1	$\bar{H}^E_{\text{expt.}}$/J.mol^{-1}	$\delta\bar{H}^E$/J.mol^{-1}	
0.0038	6.51	-0.02	
0.0191	32.30	-0.06	
0.1070	161.32	-0.11	
0.1621	226.40	-0.05	
0.2191	281.56	0.05	
0.2905	333.98	0.21	
0.3273	353.94	0.18	
0.3663	369.91	-0.03	
0.4129	382.40	-0.37	Run 1 ↑
0.4348	386.69	0.31	Run 2
0.4429	386.73	-0.61	Run 1
0.4563	388.67	0.20	Run 2
0.4639	388.53	-0.33	Run 1
0.4991	388.95	0.59	Run 2 ↓
0.5551	379.87	0.01	
0.6334	352.40	-0.13	
0.7128	306.93	-0.08	
0.8162	221.94	0.27	
0.9250	101.01	-0.14	
0.9732	37.57	-0.24	

(contd.)

Table 7.6 (contd.)

$\bar{H}^{E}_{expt.}/J.mol^{-1}$ = equation 4.1

$a_0 = 1736.00$; $a_1 = -456.63$; $a_2 = 198.12$; $a_3 = -32.04$

$\sigma = 0.29\ J\ mol^{-1}$

Figure 7.4

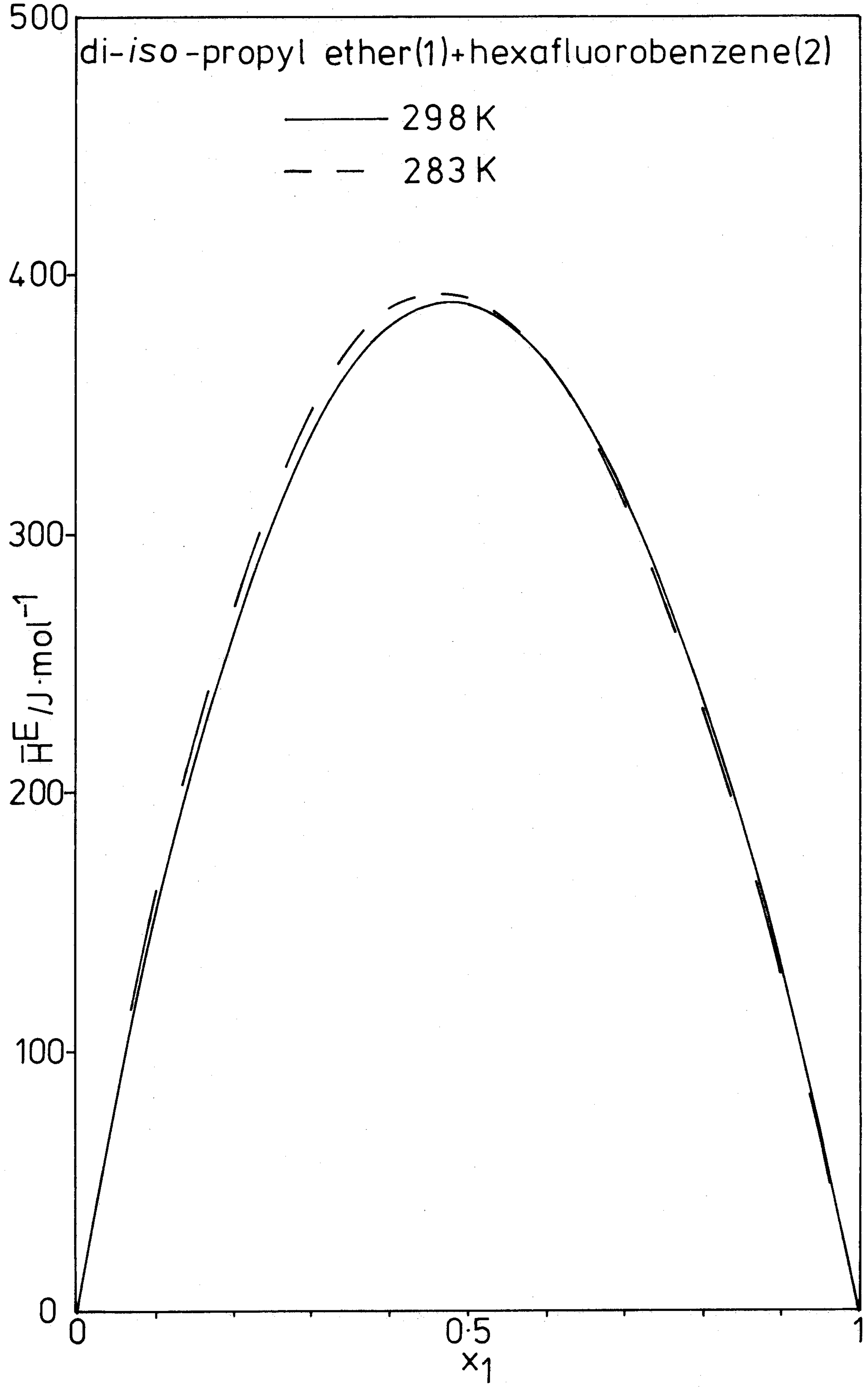

di-*iso*-propyl ether(1)+hexafluorobenzene(2)
298 K
283 K
500
400
300
200
100
0
$\bar{H}^E$/J·mol^{-1}
0
0·5
1
x_1

Table 7.7: Excess enthalpies for di-n-butyl ether(1) + hexafluorobenzene(2) at 283.15 K

$$\delta\bar{H}^E = \bar{H}^E_{expt.} - \bar{H}^E_{calc.}$$

x_1	$\bar{H}^E_{expt.}/J.mol^{-1}$	$\delta\bar{H}^E/J.mol^{-1}$	
0.0257	91.56	0.35	
0.0532	180.92	0.18	
0.0851	274.11	0.04	
0.1415	413.63	-0.09	
0.1863	503.47	-0.10	
0.2299	574.10	-0.31	
0.2761	633.00	-0.09	
0.3264	679.47	0.32	
0.3773	709.55	1.11	Run 1 ↑
0.3815	709.07	-1.04	Run 2
0.3856	710.81	-0.82	Run 2
0.4062	716.64	-1.12	Run 2
0.4231	722.77	1.88	Run 1
0.4257	722.94	1.72	Run 1
0.4519	721.37	-0.99	Run 2 ↓
0.5103	710.53	-0.62	
0.5713	680.08	-0.27	
0.6356	628.10	-0.03	
0.7038	552.01	0.09	
0.7758	449.69	0.20	
0.8525	317.24	0.17	

(contd.)

Table 7.7 (contd.)

0.9363	146.10	-0.40
0.9727	64.64	0.07

$\bar{H}^{E}_{calc.}/J.mol^{-1}$ = equation 4.1

$a_0 = 3708.80$; $a_1 = -2347.72$; $a_2 = 1534.04$; $a_3 = -484.39$

$\sigma = 0.82$ J mol^{-1}

Table 7.8: Excess enthalpies for di-n-butyl ether(1) + hexafluorobenzene(2) at 298.15 K

$$\delta\bar{H}^E = \bar{H}^E_{expt.} - \bar{H}^E_{calc.}$$

x_1	$\bar{H}^E_{expt.}/\mathrm{J.mol^{-1}}$	$\delta\bar{H}^E/\mathrm{J.mol^{-1}}$	
0.0024	8.41	0.05	
0.0067	23.08	-0.19	
0.0120	41.07	-0.58	
0.0514	167.09	0.11	
0.1050	312.78	0.20	
0.1578	430.22	0.27	
0.2076	518.55	-0.19	
0.2557	585.76	-0.37	
0.3054	638.25	0.04	
0.3610	676.94	0.18	Run 1 ↑
0.3784	684.59	-0.25	Run 2
0.3825	686.27	-0.20	Run 2
0.4138	695.95	0.32	Run 1
0.4185	696.11	-0.42	Run 2
0.4226	697.62	0.42	Run 1
0.4527	699.29	0.08	Run 2 ↓
0.5216	686.05	0.57	
0.5976	642.12	-0.54	
0.6827	562.67	-0.24	
0.7746	441.71	0.28	
0.8302	351.00	-0.12	

(contd.)

Table 7.8 (contd.)

0.8411	332.01	-0.02
0.8501	315.67	-0.22
0.8600	298.08	0.46
0.9625	86.98	-0.26

$\bar{H}^E_{calc.}$/J.mol^{-1} = equation 4.1

a_0 = 3525.21; a_1 = -2013.63; a_2 = 1128.03; a_3 = -244.82

σ = 0.33 J.mol^{-1}

Figure 7.5

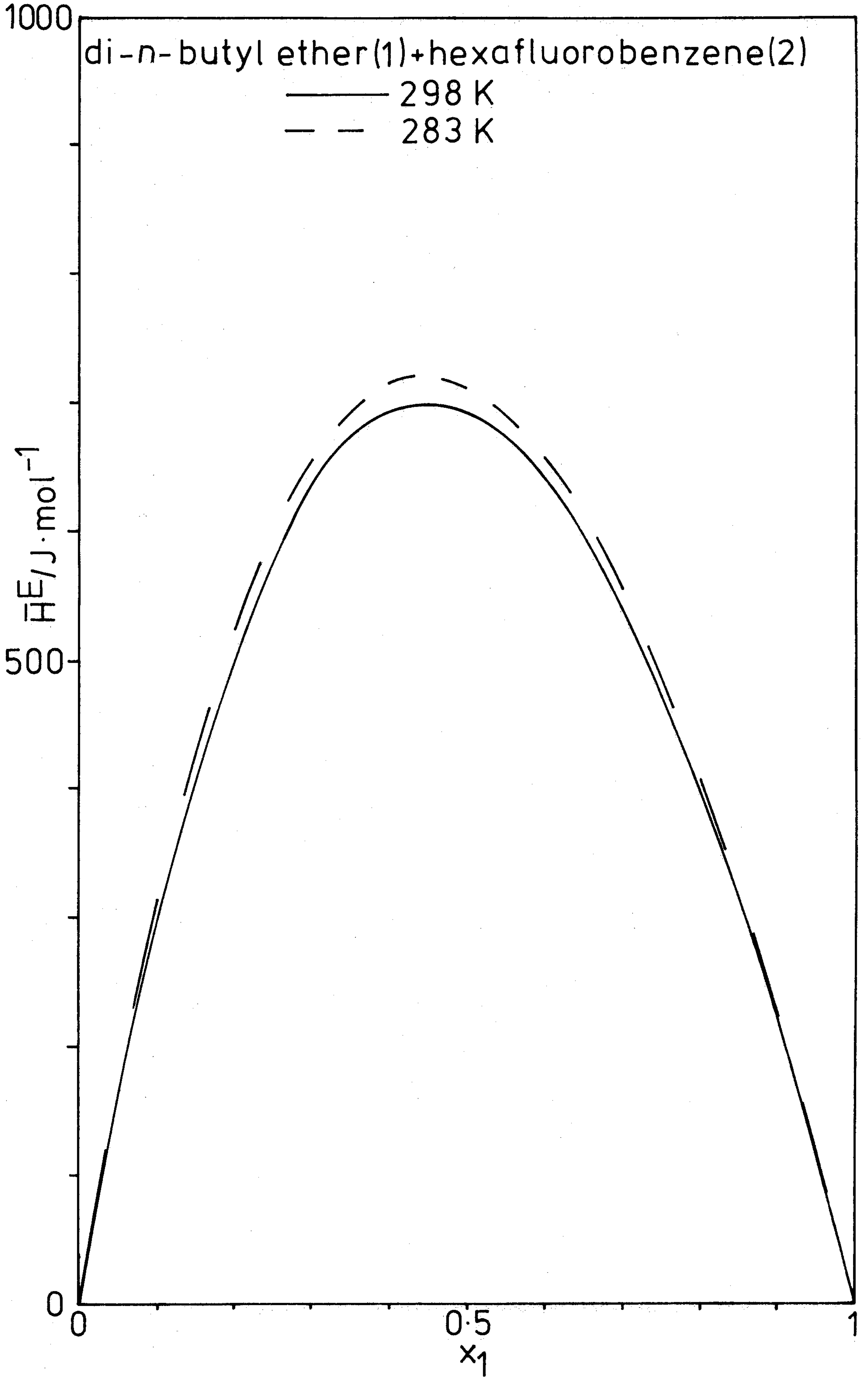

1000
di-n-butyl ether(1)+hexafluorobenzene(2)
298 K
283 K
$\bar{H}^E$/J·mol^{-1}
500
0
0
0·5
1
x_1

Figure 7.6 (see equation 7.1)

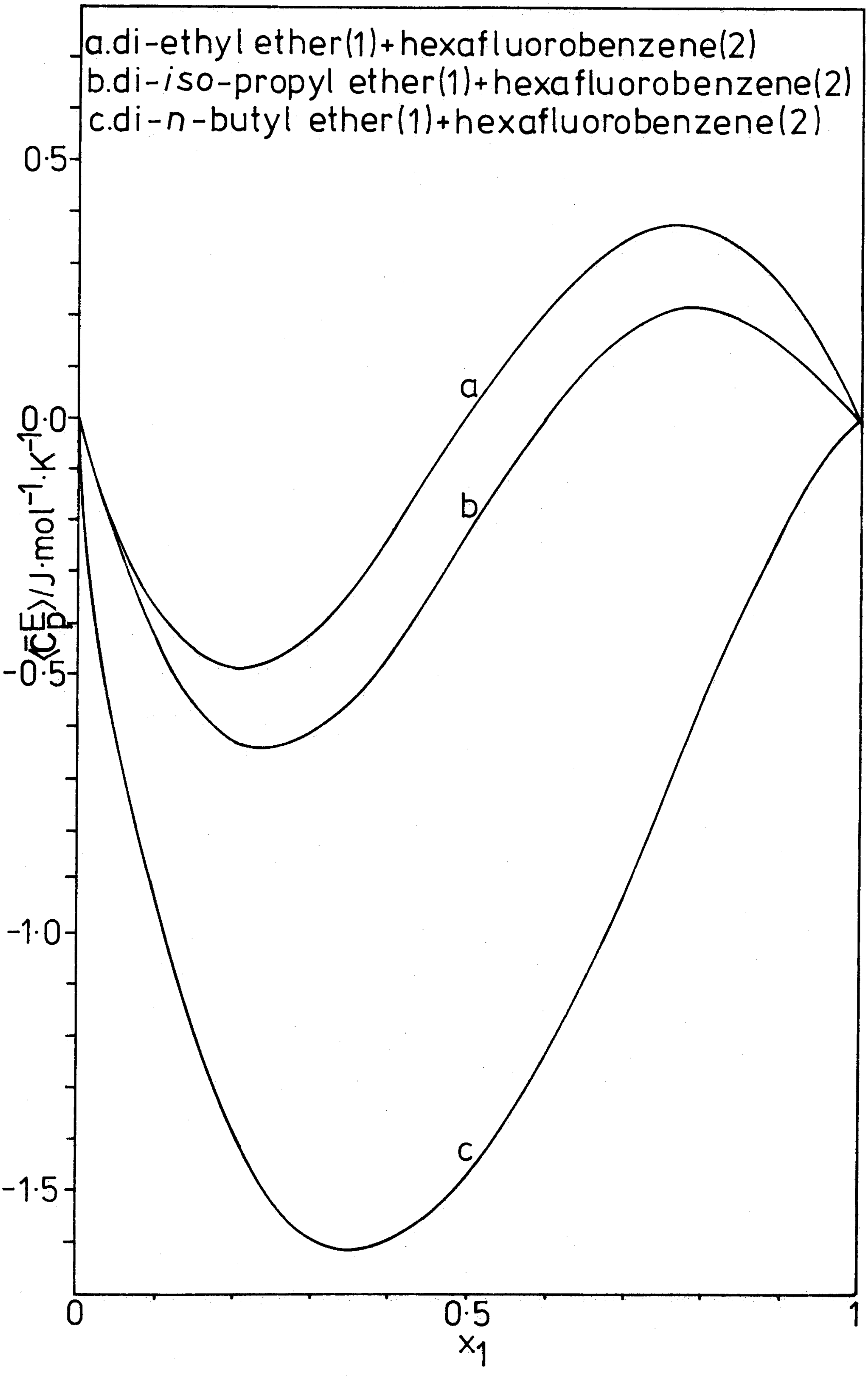


Table 7.9: Excess Gibbs free energies for di-ethyl ether(1) + hexafluorobenzene(2) at 298.131 K

$\delta p = p_{expt.} - p_{calc.}$

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}
0	-	11.264	-	-	-	-
0.0100	0.0726	12.023	-0.010	1.2576	1.0000	5.7
0.0223	0.1493	12.956	-0.013	1.2515	1.0001	12.6
0.0718	0.3674	16.665	0.017	1.2279	1.0010	38.9
0.1138	0.4865	19.670	0.002	1.2089	1.0026	59.3
0.1542	0.5691	22.484	-0.001	1.1917	1.0049	77.2
0.2027	0.6431	25.765	-0.003	1.1720	1.0085	96.5
0.2481	0.6963	28.745	-0.009	1.1546	1.0129	112.3
0.3000	0.7438	32.065	0.000	1.1359	1.0192	127.7
0.3408	0.7746	34.589	-0.008	1.1220	1.0251	137.8
0.3859	0.8033	37.334	-0.002	1.1074	1.0328	146.7
0.4240	0.8241	39.613	0.013	1.0957	1.0403	152.5
0.4575	0.8406	41.564	0.011	1.0860	1.0476	156.1
0.4875	0.8539	43.303	0.023	1.0776	1.0549	158.3

Run 1 ↑

(contd.)

Table 7.9 (contd.)

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}	
0.5006	0.8606	43.997	-0.030	1.0741	1.0583	158.9	Run 2
0.5141	0.8649	44.831	0.034	1.0705	1.0620	159.2	Run 1
0.5228	0.8695	45.259	-0.026	1.0682	1.0644	159.4	Run 2
0.5394	0.8746	46.264	0.043	1.0640	1.0692	159.3	Run 1
0.5521	0.8808	46.898	-0.031	1.0608	1.0730	159.1	Run 2 ↓
0.5783	0.8897	48.375	-0.009	1.0545	1.0814	157.9	
0.6098	0.9003	50.118	-0.005	1.0473	1.0923	155.3	
0.6452	0.9116	52.041	-0.014	1.0398	1.1057	150.7	
0.6926	0.9255	54.608	-0.014	1.0305	1.1258	141.9	
0.7486	0.9402	57.656	0.015	1.0210	1.1532	127.4	
0.8055	0.9547	60.711	0.011	1.0129	1.1855	107.7	
0.8770	0.9719	64.571	0.003	1.0054	1.2336	75.7	
0.9288	0.9838	67.428	0.009	1.0019	1.2746	47.1	
0.9659	0.9923	69.493	0.000	1.0004	1.3076	23.7	

(contd.)

Table 7.9 (contd.)

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}
0.9861	0.9970	70.632	-0.007	1.0001	1.3270	9.9
0.9959	0.9990	71.203	0.002	1.0000	1.3369	3.0
1	-	71.435	-	-	-	-

$\bar{G}^E(x)/RT$ = equation 6.13

$a_0 = 0.25630$; $a_1 = 0.03011$; $a_2 = 0.00701$

$\Sigma(\delta p)^2 = 0.0081\ \mathrm{kPa}^2$

Figure 7.7

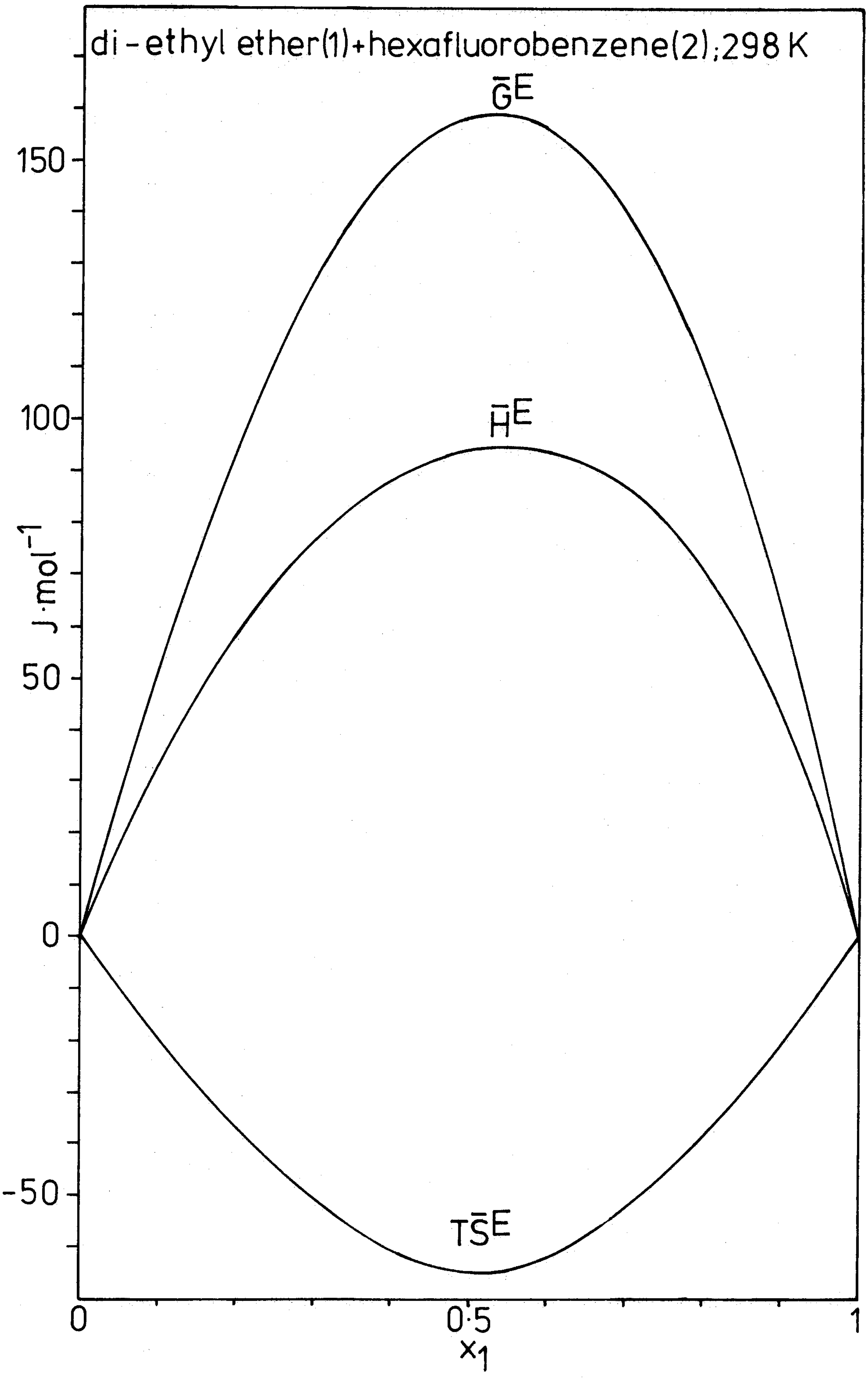

di-ethyl ether(1)+hexafluorobenzene(2);298 K
$\bar{G}^E$
$\bar{H}^E$
$T\bar{S}^E$
150
100
50
0
-50
$J \cdot mol^{-1}$
0
0·5
1
x_1

Table 7.10: Excess Gibbs free energies for di-iso-propyl ether(1) + hexafluorobenzene(2) at 298.131 K

$$\delta p = p_{expt.} - p_{calc.}$$

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E/J.mol^{-1}$
0	-	11.264	-	-	-	-
0.0108	0.0291	11.480	0.000	1.5710	1.0001	12.2
0.0293	0.0754	11.830	-0.008	1.5416	1.0004	32.5
0.0446	0.1102	12.118	-0.001	1.5185	1.0010	48.6
0.0588	0.1403	12.380	0.009	1.4977	1.0018	63.0
0.1142	0.2420	13.267	-0.009	1.4229	1.0066	114.4
0.1562	0.3051	13.890	0.003	1.3726	1.0123	148.3
0.2021	0.3649	14.492	0.001	1.3233	1.0204	180.3
0.2436	0.4124	14.995	0.004	1.2830	1.0295	205.1
0.2874	0.4575	15.475	0.002	1.2448	1.0408	226.7
0.3282	0.4959	15.890	0.001	1.2126	1.0530	242.9
0.3604	0.5243	16.196	0.001	1.1895	1.0637	253.0
0.3938	0.5522	15.492	-0.003	1.1673	1.0759	261.0
0.4191	0.5726	16.704	-0.008	1.1518	1.0858	265.4

Run 1↑

(contd.)

Table 7.10 (contd.)

x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}	
0.4447	0.5921	16.928	0.006	1.1370	1.0965	268.4	Run 2
0.4460	0.5933	16.929	-0.003	1.1363	1.0971	268.5	Run 1
0.4632	0.6062	17.069	0.000	1.1270	1.1046	269.7	Run 2
0.4690	0.6106	17.112	-0.001	1.1239	1.1072	269.9	Run 1
0.4854	0.6227	17.242	0.003	1.1155	1.1149	270.3	Run 2 ↓
0.5098	0.6405	17.421	0.001	1.1038	1.1266	269.7	
0.5426	0.6642	17.645	-0.007	1.0892	1.1434	266.8	
0.5783	0.6891	17.892	-0.001	1.0748	1.1630	261.2	
0.6178	0.7163	18.151	0.005	1.0606	1.1862	251.9	
0.6604	0.7459	18.402	0.001	1.0471	1.2133	238.1	
0.7161	0.7842	18.715	0.003	1.0324	1.2518	214.7	
0.7828	0.8311	19.053	0.003	1.0186	1.3031	178.3	
0.8696	0.8948	19.435	0.003	1.0066	1.3788	117.9	
0.9280	0.9406	19.643	-0.008	1.0020	1.4360	69.1	

(contd.)

Table 7.10 (contd.)

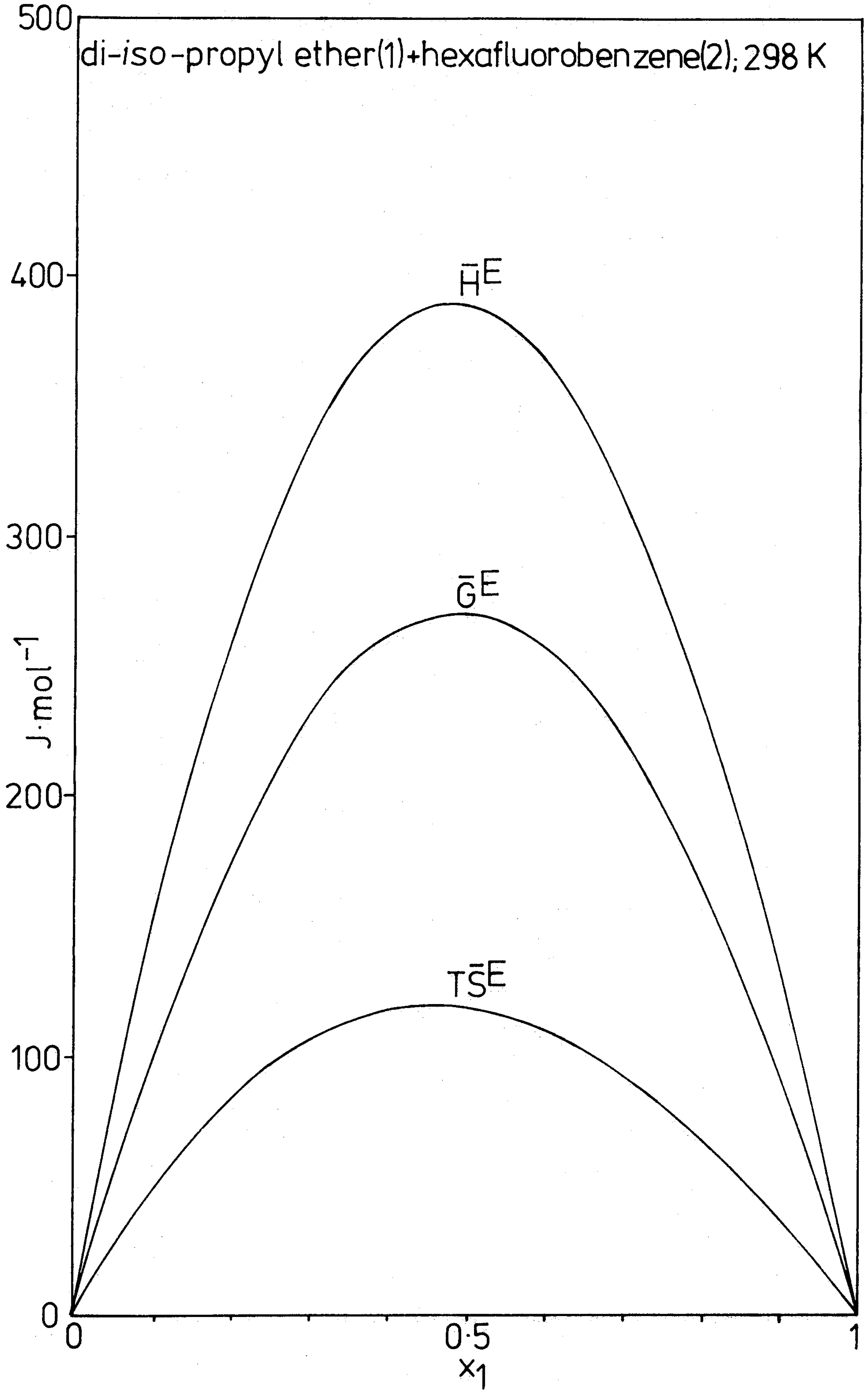
x_1	y_1	p/kPa	δp/kPa	f_1	f_2	$\bar{G}^E$/J.mol^{-1}
0.9496	0.9578	19.720	-0.004	1.0010	1.4585	49.4
0.9745	0.9784	19.800	-0.002	1.0002	1.4855	25.6
0.9924	0.9936	19.852	-0.002	1.0000	1.5055	7.7
1	-	19.874	-	-	-	-

$\bar{G}^E(x)/RT$ = equation 6.13

$a_0 = 0.43575$; $a_1 = -0.02402$; $a_2 = 0.00315$

$\Sigma(\delta p)^2 = 0.00055\ kPa^2$

Figure 7.8


di-*iso*-propyl ether(1)+hexafluorobenzene(2); 298 K
500
400
300
200
100
0
$\mathrm{J \cdot mol^{-1}}$
$\bar{H}^E$
$\bar{G}^E$
$T\bar{S}^E$
0
0·5
1
x_1

7.2 Discussion: The *n*-electron donor properties of ethers are evident in a number of binary systems:

(i) Aliphatic ethers form stable addition compounds with the Lewis acid boron tri-fluoride.[2]

(ii) The predominance of negative excess thermodynamic functions in liquid systems containing ethers and per-halo-methanes is suggestive of specific interaction between oxygen and halogen atoms.[3,4,5]

(iii) Andrews and Morcom[6,7] observed negative excess volumes and enthalpies for some cyclic ethers with benzene and concluded that a weak donor-acceptor interaction is present in these systems.

There is, however, little, if any, evidence in the experimental results of this work indicating the presence of donor-acceptor interaction in systems containing hexafluorobenzene and ethers.

(i) The *excess volumes* for the mixtures containing di-allyl ether (*Table 7.1, Figure 7.1*) are less positive than for those containing di-*n*-propyl ether.[8] This effect may result from the greater polarizability of the unsaturated ether and a consequent enhancement of unlike dispersion force interactions. The predominantly negative, though small, excess volumes for the mixtures containing di-benzyl ether (*Table 7.2, Figure 7.2*) may arise in a similar fashion; the polarizable, and essentially planar, nature of this aromatic ether would also give rise to stronger dispersion forces than those found with aliphatic ethers. The additional operation, in this system, of interactions of the type postulated for hexafluorobenzene + benzene[9] (*viz.* C-F dipole -

(i) (contd.)

π-quadrupole) may produce the observed composition dependence of the excess volume by a contribution which is asymmetric in composition (*i.e.* of stoichiometry 1:2).

(ii) The *excess enthalpies* of di-ethyl ether (*table 7.3, 7.4; figure 7.3*), di-*iso*-propyl ether (*table 7.5, 7.6; figure 7.4*) and of di-*n*-butyl ether (*table 7.7, 7.8, figure 7.5*) with hexafluorobenzene are uniformly positive, and parallel the sequence observed with the excess volumes.[8] In *figure 7.6* is represented the composition dependence of the quantity $<\bar{C}_P^E>$, given by

$$<\bar{C}_P^E> = \frac{\bar{H}^E(x_1 298K) - \bar{H}^E(x_1 283K)}{15} \qquad 7.1$$

This quantity *may* be related to $\bar{C}_P^E(x)$, the molar excess heat capacity, if the molar excess enthalpy, $\bar{H}^E(x,T)$, changes in a monotonic fashion over the temperature range 283-298K. The composition dependence of $<\bar{C}_P^E>$ is similar to the form of $\bar{C}_P^E(x)$ observed for the system 1,4 dioxan + hexafluorobenzene[10] but with the signs reversed. In each case $<\bar{C}_P^E>$ is too large to be an artifact resulting from experimental errors, but is not sufficiently positive to be regarded as firm evidence of specific interaction in these system .

(iii) The *excess Gibbs free energies* of di-ethyl ether (*table 7.9, figure 7.7*) and of di-*iso*-propyl ether (*table 7.10, figure 7.8*) with hexafluorobenzene are uniformly positive. The excess entropy for the mixture containing di-ethyl ether is, however, small and negative over the whole composition range, suggestive of some ordering effect in the mixture.

When considered in isolation, these and other[8] experimental results give little indication of donor-acceptor interactions in the liquid phase.

The modification of the chemical properties of benzene which results from substitution of fluorine for hydrogen atoms is not unexpected. In particular, the high electronegativity of the fluorine atom renders hexafluorobenzene succeptible to nucleophilic attack.[11] Thus, at first, it seems surprising that hexafluorobenzene behaves in such an ambiguous fashion towards organic compounds which are known to exhibit electron-donor properties.

The excess thermodynamic properties of binary liquid mixtures containing hexafluorobenzene and *aliphatic* hydrocarbons have received little attention,[a] but similar work with alicyclic hydrocarbons[13,14] suggests that these systems may also exhibit large positive deviations from ideality:

e.g. *cyclo*-hexane + hexafluorobenzene, $\bar{H}^E(x=0.5,\ 298K) = 1576\ J.mol^{-1}$ $\bar{V}^E(x=0.5,\ 298K) = 2.567\ cm^3.mol^{-1}$.

It seems reasonable, then, to suppose that the observed donor-acceptor activity in mixtures containing hexafluorobenzene is likely to be weak when the donor itself retains at least some of the characteristics of an aliphatic hydrocarbon. In support of this statement, three observations may be made:

---

[a] The only such measurement which could be found in the literature was the isobaric vapour-liquid equilibrium data for the system *n*-hexane + hexafluorobenzene[12] from which $\bar{G}^E(x=0.5,\ 342K) \approx 500\ J.mol^{-1}$.

(i) The excess volumes,[8] enthalpies, entropies and Gibbs free energies of mixtures containing hexafluorobenzene and aliphatic ethers become more positive with increasing chain length despite an opposite trend in the *n*-electron donor strength of the ether from inductive effects.

(ii) For tri-ethylamine mixtures[1,15,16]. The above excess functions are *considerably* more positive at 298K than for di-ethyl ether mixtures in spite of the fact that the ionization potential of the amine[17] (ca. 723 kJ. mol^{-1}) is significantly less than that of the ether[17] (ca. 918 $\mathrm{kJ.mol}^{-1}$).

(iii) The excess volumes and enthalpies of 1,4-dioxan + hexafluorobenzene[10] are *considerably* less positive than those of the system *cyclo*-hexane + hexafluorobenzene.[13-14] It may be significant that such large changes are wrought on the thermodynamic properties of a liquid mixture by replacing two methylene segments with oxygen atoms to produce a molecule of similar shape and size.

In summary, the shape and size of the hydrocarbon chains forming aliphatic *n*-electron donors may be, as with alicyclic and aromatic hydrocarbons,[13,14] an overriding consideration in describing the resultant thermodynamic properties of their mixtures with hexafluorobenzene. The investigation of suitable "reference" mixtures of this fluorocarbon with alkanes (*e.g.* 2,3 di-methyl butane for di-*iso*-propyl ether) may provide an indication of the role of donor-acceptor interaction in these systems.

References

1. Mattingley, B.I.; Handa, Y.P.; Fenby, D.V. *J. Chem. Thermodynamics* 1975, 7, 169
2. Wirth, H.E.; Slick, P.I. *J. Phys. Chem.* 1962, 66, 2277
3. Beath, L.A.; O'Neill, S.P.; Williamson, A.G. *J. Chem. Thermodynamics* 1969, 1, 293
4. Beath, L.A.; Williamson, A.G. *J. Chem. Thermodynamics* 1969, 1, 51
5. Galletly, V.M.; Watson, I.D. *Aust. J. Chem.* 1972, 25, 1125
6. Andrews, A.W.; Morcom, K.W. *J. Chem. Thermodynamics* 1971, 3, 513
7. Andrews, A.W.; Morcom, K.W. *J. Chem. Thermodynamics* 1971, 3, 519
8. Martin, M.L.; Murray, R.S. *J. Chem. Thermodynamics* 1972, 4, 723 (Bound in at the back of this thesis.)
9. Hanna, M.W. *J. Amer. Chem. Soc.* 1968, 90, 285
10. Andrews, A.W.; Hall, D.; Morcom, K.W. *J. Chem. Thermodynamics* 1971, 3, 527.
11. Mobbs, R.H. *Chemical Processing*, April 1967, S5
12. Chinikamala, A.; Houth, G.N.; Taylor, Jr., Z.L. *J. Chem. Eng. Data* 1973, 18, 322
13. Powell, R.J.; Swinton, F.L. *J. Chem. Thermodynamics* 1970, 2, 87
14. Andrews, A.; Morcom, K.W.; Duncan, W.A.; Swinton, F.L.; Pollock, J.M. *J. Chem. Thermodynamics* 1970, 2, 95.
15. Chand, A.; Fenby, D.V. *J. Chem. Thermodynamics* 1975, 7, 403.
16. Handa, Y.P.; Fenby, D.V. *J. Chem. Thermodynamics* 1975, 7, 405.

17. Turner, D.W. *Adv. Phys. Org. Chem.*, 1966, 4, 31.

APPENDICES:

(Literature reference numbers in an appendix correspond to those in the chapter of origin of that appendix.)

APPENDIX 2

Appendix 2.1: Absolute temperature measurements of this accuracy may be obtained only by *constant* and proper[1,3] use of a platinum resistance thermometer which is frequently checked against one or more of the defining fixed points of IPTS. The ice-point of pure, aerated water, used in this work, is a secondary reference only and differs from that of the degassed liquid by ca. 0.0028 K.[4] Triple-point measurements were not accessible at this time.

Calibration of mercury-in-glass thermometers under the exact conditions of their use eliminates the errors cited in reference 4. The bulbs of those used in this work were observed to collapse monotonously (due to the superior external pressure) by up to 0.015 K per year. One thermometer, calibrated both in the vertical mode and tilted at 45°, showed a pressure dependence of 0.0021 $K.kPa^{-1}$. Changes of 1 kPa in barometric pressure are not unusual in Adelaide.

Appendix 2.2: Apart from slow temperature drifts caused by chemical deterioration in these devices, it can readily be shown that the pressure sensitivity of all unsealed mercury/-toluene regulators is a constant fraction of their temperature sensitivity,

viz. 0.00087 K ≡ 1 kPa.

Appendix 2.3: Desirable properties of thermostatted systems observed here are:

bath: Insulated, uncluttered, well-stirred tank of minimum dimensions placed in a draft-free room of stable ambient temperature.

control system: "Proportional" drift-free device devoid of mechanical links. The position of a highly sensitive fast-response probe in relation to a heater of minimum wattage should be studied in view of the stirring pattern. Heat transfer from heater to bath should be instantaneous (incandescent light bulbs approximate to this behaviour).

measuring system: Temperature fluctuations in the system of interest may be minimized in some situations by insulation. In any case, short term changes in bath temperature are seldom realized to their full extent in the system.

APPENDIX 3

Appendix 3.1: The liquids used during this work can be broadly classified as follows:

(i) *Hydrocarbons:* These usually contain other hydrocarbons as impurities. F.I.D. response to virtually all of these compounds is the same (to within ±10%).[1]

(ii) *Carbon tetrachloride:* This liquid was analysed with both F.I. and T.C. detectors and found to contain only two impurities (possibly CH_2Cl_2 and $CHCl_3$). No carbon disulphide was detected.

(iii) *Hexafluorobenzene:* The major contaminants[7] (*viz.* C_6F_5H, $C_6F_4H_2$) of this fluorocarbon could reasonably be expected to produce similar F.I.D. responses.

(iv) *Ethers:* "Hetero-compounds" invariably evoke smaller F.I.D. responses than do hydrocarbons.[1] The main contaminants in aliphatic ethers are peroxides, carbonyl/carboxylic compounds and alcohols derived from the ether.[2] Peroxides are normally removed during purification and are easily detected by F.I.D. They produce a very sharp peak of short retention time due to thermal decomposition. Alcohols produce somewhat smaller F.I.D. responses than the corresponding ether depending on chain length (up to 20% for ethanol/di-ethyl ether). Carbonyl/carboxylic compounds behave in a similar fashion but produce even lower responses.

In summary, the impurity concentrations tabled in *Chapter 3* are least reliable for the ethers.

Appendix 3.2: Di-n-butyl ether: Distillation under dry nitrogen at atmospheric pressure (ca. 142°C) resulted in deterioration of the liquid which assumed a faint yellow colour. No significant improvement was effected by treatments with dilute acid, hot concentrated potassium hydroxide solution, alkaline potassium permanganate solution, columns of activated alumina or B.D.H. 5A molecular sieves.

Appendix 3.3: Di-allyl ether: Information about this ether in the literature seems rare. An attempt to dry some of the liquid with sodium wire resulted in the formation of an orange-yellow mass. This was, presumably, the product of a polymerization reaction through the allyl function. During distillation copper flitters were placed in the receiving vessel to inhibit peroxide formation. The ether appeared to react with the metal (or a compound on its surface) to form a blue-green compound (possibly an "olefin complex"). This colour was rapidly eliminated on an alumina column. Peroxide formation, if any, was seen to be slow and the liquid did not deteriorate significantly on standing. Impurities eliminated in early fractions of distillation seemed to reappear in later ones. This may indicate slow thermal degradation of the ether at its normal boiling point (ca. 94°C).

Appendix 3.4: Di-benzyl ether: The tendency of this relatively viscous liquid to undergo thermal decomposition at temperatures well below the normal boiling point (ca. 288°C) has been noted elsewhere.[2] Attempts to distil the ether under reduced pressure (ca. 0.13 kPa, 95°C) resulted in further decomposition to produce benzaldehyde and toluene (positively identified by g.l.c.

analysis) as well as high molecular weight material. Directional freezing was effective but very slow; after five recrystallizations little improvement was noted. Storage over sodium wire produced a marked increase in the concentration of both benzaldehyde and toluene and a decrease in two other contaminants (unknown). It also imparted a deep red colour to the liquid probably from the formation of a radical ion. Estimation of impurities from g.l.c. (column temperature 100°C, analysis time ca. 4 hours) may have been high because of degradation of the ether during analysis.

Appendix 3.5: Hexafluorobenzene: Treatment of some of the mixture with concentrated sulphuric acid produced a dark flocculent mass of tars and sulphur. Separation of the hexafluorobenzene by filtration was virtually impossible and had to be done with a centrifuge. A subsequent g.l.c. analysis revealed that the fluorocarbon itself had been attacked to produce other fluorobenzenes.

APPENDIX 4

Appendix 4.1: Tabled below are the volume changes which occurred during a "blank" run in which methanol (ca. 12 cm^3) was added to methanol in approximately equal volume steps to give a "composition" of $x \approx 0.5$.

step	cumulative volume change (cm^3)
1	-0.000009
2	+0.000013
3	+0.000013
4	+0.000013
5	+0.000022
6	-0.000026

These volume changes would have contributed less than 0.00015 $cm^3.mol^{-1}$ to $\bar{V}^E$ in the work reported here.

Appendix 4.2: Mention is made in this paper[5] of the *continuous* use of a magnetic stirrer at 200 r.p.m. in the mixing vessel. It seems possible that the power generated by this stirrer may be sufficient to create a significant temperature differential between the mixing vessel and the burette and a consequent artifact in the observed volume change on mixing. For the apparatus described, a temperature differential of 0.01 K would raise the measured $\bar{V}^E$ values by about 0.0006 $cm^3.mol^{-1}$ at $x \approx 0.5$. However, no such "blank" run effect was reported.

Appendix 4.3: The *dilatometer filling procedure* was as follows:

(i) With T_1, T_4, T_5 closed, T_2, T_3 open and R sealed, the apparatus was evacuated through C_1. A vessel of clean mercury was placed under T_1.

(ii) T_1 was opened slightly, to allow mercury to rise just above it, then closed. While evacuation continued, T_2 and T_3 were rotated to remove traces of trapped air.

(iii) After some time, T_1 was opened to allow mercury to rise *slowly* to a position just above T_3. T_1, T_2 and T_3 were then closed, the pump was isolated and C_2 was unsealed.

(iv) By careful manipulation of T_4 or T_5 and a tap above C_1, atmospheric pressure was restored to all compartments.

(v) Both liquids were partially degassed by heating and placed in ground glass syringes. T_4 and T_5 were removed and a small amount of the stationary component was added to the cell to prevent inclusion of air between the glass and mercury.

(vi) With T_2 open the burette was filled by pushing the syringe tip, provided with a conical teflon sleeve, against the seat at X and forcibly displacing mercury up into M. T_2 was then closed, and the filling continued until the liquid in the burette was just above the exit to M and filled the inlet I. The inlet remained filled with liquid because of the small head of mercury above it in M.

(vii) The mixing vessel was rinsed out and stirred with about 5 small portions of the stationary component to remove all traces of the mobile component and was then filled and sealed. The tightening of T_4 pushed some mercury back up into the inlet so that, at the start of measurements, about 0.01 cm^3 of mercury had to be displaced before mixing commenced. The burette was then topped up and T_5 replaced but not sealed.

(viii) The apparatus was placed in a thermostatted bath and, after temperature equilibration, T_5 was sealed. The mercury level in C was adjusted, using T_3, to a suitable position.

During each measurement the position of each fiducial mark and of the menisci in C, M and B were read to constant value (see *section 2.3*). Particular attention was paid to the meniscus in C; this position was read until four or five readings showed no significant trend with intermittent stirring.

Three small additions were made initially to obtain the inlet correction. The number of moles of the stationary component was calculated from the molar volume and the expression,

$$V_S = V_C + (F_3 - M_3)a_3 - V_m - \Delta V \qquad \text{A4.1}$$

where V_S is the volume of the mobile component,

V_C is the calibrated volume of the mixing vessel to F_3,

F_3, M_3 are, respectively, the positions of the fiducial mark and final mercury level beneath the mixing vessel,

a_3 is the calibrated cross-sectional area of the outlet beneath the mixing vessel,

V_m is the volume of mercury displaced into the burette,

and ΔV is the volume of mercury displaced into the excess volume capillary at *constant pressure* so that, for volume changes involving "resetting" of the mercury level in this capillary, the apparent volume change must be corrected for the compressibility of the system.

Appendix 4.4: Sources of error in measuring $\bar{V}^E$*:*

(i) The absolute temperature and pressure dependence of $\bar{V}^E$

$$\left(\left(\frac{\partial \bar{V}^E}{\partial P}\right)_{T,x} = \bar{V}^E(x).\bar{\kappa}^E(x);\ \left(\frac{\partial \bar{V}^E}{\partial T}\right)_{P,x} = \bar{V}^E(x).\bar{\alpha}^E(x)\right)$$

are small enough to be dismissed as a source of significant error. However, *changes* in barometric pressure and especially temperature during an experiment are likely to result in serious error. For the dilatometer described here, a change in temperature of 0.001 K or in pressure of 1 kPa would produce a spurious volume change of 5×10^{-5} cm^3. This might lead, with liquids of high molar volume, to an error of as much as 0.0008 $cm^3.mol^{-1}$ in $\bar{V}^E$. In this work temperature and barometric pressure were noted throughout experiments. Their combined effect would produce an uncertainty in $\bar{V}^E$ of less than 0.0005 $cm^3.mol^{-1}$.

(ii) Errors in the measurement of the compressibility factor, b, and failure to account for its composition dependence in systems with large excess compressibilities, may produce significant uncertainties in $\bar{V}^E$. Compressibility corrections are commonly 1-2% of $\bar{V}^E$ itself. With careful measurement of b, this source of error amounts to a maximum error in $\bar{V}^E$ of 0.05%.

(iii) The cross-sectional area of the excess volume capillary, C, (calibrated with a travelling microscope readable to 0.0001 cm) was established to ±0.05%, an uncertainty directly reflected in $\bar{V}^E$.

(iv) Multiple calibrations of the mixing vessel and the various sections of the burette, established these values sufficiently well to produce an uncertainty in the composition, x, of less than 0.0005.

(v) Random observer errors in establishing the position of the various mercury menisci are unavoidable. Each value was recorded several times and uncertainties from this source are thought to have been small and non-cumulative.

(vi) The error (less than 0.001 cm^3) in establishing the small but variable inlet correction depends inversely upon the magnitude of $\bar{V}^E$ (*i.e.* upon the sensitivity with which it may be measured).

(vii) At various stages during measurements the meniscus in C was reset to a lower position using the reservoir C. This decrease in the pressure acting on the system may have resulted in the injection of a small quantity of liquid (less than 0.0005 cm^3) from the burette to the mixing vessel. This effect may be compensated for if approximate values for the volume and compressibility of the liquid remaining in the burette are known.

APPENDIX 5

Appendix 5.1: Thermistor calibration: This calibration was effected by noting the decade resistor value, R, required to null the Wheatstone bridge circuit, at the same total voltage as that used in experiments, at three temperatures between 283 K and 298 K.

From the relation[19]

$$\frac{d\ln R}{d(1/T)} \approx B(\text{constant}), \qquad \text{A5.1}$$

the constant term, B, was evaluated (3450 K), and this, together with the value of R at the temperature of the bath (measured before each "run"), allowed precise calculation of the temperature differential existing between the mixing-vessel and the surroundings during experiments.

Appendix 5.2: Measurement of the relaxation time and heat capacity of the mixing-vessel: From Newton's law of cooling,

$$\lim_{\Delta T \to 0}\left(-\frac{d\ln\Delta T}{dt}\right) = \frac{1}{\tau}, \qquad \text{A5.2}$$

and the relation,

$$\left(\frac{dH}{dT}\right)_p = C_p, \qquad \text{A5.3}$$

the heat capacity, C_m, and the thermal relaxation time, τ, of the filled mixing-vessel were measured by production of a known steady-state temperature differential above the surroundings with a known heater current which was then switched off to allow the approach to equilibrium to be followed. The heat capacity, C_m^o, of the empty mixing-vessel was then obtained from C_m and the known heat capacity of the contents. This result differed by only 3% from a value obtained by summing the heat capacities of the individual components of the mixing-vessel.

Appendix 5.3: Derivation of equation 5.2: The power, W_H, of the heater carrying a current, i, is given by

$$W_H = i^2 R_H \qquad \text{A5.4}$$

where i is given by

$$i = \frac{V_0}{R_0} \qquad \text{A5.5}$$

and R_H is the *effective resistance* of the active heater. Since the potential, V_H, was taken at a point removed from the heater terminals by leads of accurately known resistance, R_L (ca. 0.42 Ω), the measured resistance ($R_{obs.} = V_H R_0 / V_0$) must be reduced by R_L to give the resistance between the heater terminals.

A further correction, employed by Stokes *et al.*,[4] results from the effective contribution R'_L to the heater resistance from its leads. In this work this contribution was measured by attaching both leads to a single heater terminal and observing the steady-state temperature differential produced by a relatively large current (ca. 1.5 A). The resistance value thus obtained (0.032 Ω) was doubled to give R'_L since, during *this* experiment, only *one* heater terminal could transfer heat into the mixing-vessel.

From these considerations W_H is given by

$$W_H = \left(\frac{V_0}{R_0}\right)^2 . \left(\frac{V_H R_0}{V_0} - R_L + R'_L\right) = V_0^2 \left(\frac{V_H}{V_0 R_0} + \frac{\delta R_H}{R_0^2}\right) = V_0^2 . f_H \qquad \text{A5.6}$$

where $\delta R_H = -R_L + R'_L$ and f_H is a constant term.

Appendix 5.4: Derivation of equation 5.6: The viscous flow of liquid into the mixing-vessel under the influence of a mercury head, p, results in heating of the liquids flowing in both the inlet and outlet capillaries. The total energy, E'_η, generated in this way is given by the relation,

$$E'_\eta = \int_0^V p.dV \qquad \text{A5.7}$$

where V is the volume of liquid added to the mixing-vessel. If the positions of the mercury menisci in the burette and mixing-vessel are known as a function of V, the above expression is readily evaluated.

i.e. $$E'_\eta = f(V) \qquad \text{A5.8}$$

However, only a fraction of this energy finds its way into the mixing-vessel.

The rate of flow, f, of a liquid through a homogeneous tube under the influence of a pressure gradient Δp is given, for streamlined flow, by Poiseuille's equation[18]

viz. $$f = \frac{\Pi}{8}.\frac{\Delta p a^4}{l\eta} \qquad \text{A5.9}$$

where a and l are respectively the radius and length of the tube and η is the viscosity of the liquid.

For a series of connected tubes the flow rate, which must be the same for all, is given by,

$$f = \frac{\Pi}{8}.p.\sum_i\left(\frac{a_i^4}{l_i\eta_i}\right) \qquad \text{A5.10}$$

where p is the total pressure producing flow, and in which the general case of a number of liquids of different viscosity is considered.

Equation A5.10 is relevant to the calorimeter described here since, during an addition, the inlet and outlet tubes carry different liquids. Differentiation of this equation gives,

$$\frac{df}{dp} = \frac{\Pi}{8}.\left(\sum_i \lambda_i \eta_i\right)^{-1} = \text{a constant} \qquad \text{A5.11}$$

where $\lambda_i = l_i/a_i^4$ is a feature of the geometry of each tube.

Experiments in which the flow rates of liquids were measured, as a function of the mercury head in the calorimeter, were carried out with di-ethyl ether, benzene and carbon tetrachloride. The flow rate, f, was found to be strictly linear in p in each case, confirming the presence of essentially streamlined flow. The values of df/dp so obtained were used to evaluate λ_1 for the inlet and λ_2 for the outlet capillary. The simpler expedient of evaluating λ from the geometry of the capillaries was rejected because of the gross uncertainty inherent in the term a^4.

The rate, w_i, at which heat is generated in either capillary is given by,

$$w_i = \Delta p_i . f \qquad \text{A5.12}$$

and so the *fraction*, F_i, of the total heat generated, which appears in each is given by

$$F_i = \frac{\Delta p_i}{p} = \frac{\lambda_i \eta_i}{\lambda_i \eta_i + \lambda_j \eta_j} \qquad \text{A5.13}$$

Since the heat generated in the outlet capillary by mercury flow does not enter the mixing-vessel and since about 97% of the value of λ_1 is accounted for by that section of the inlet within the Dewar, virtually all of the heat generated in the inlet capillary finds its way into the mixing-vessel. This conclusion, together with equations A5.8 and A5.13, gives the total heat energy introduced into the mixing-vessel as

$$E_\eta = f(V).\frac{\lambda_1 \eta_l}{\lambda_1 \eta_l + \lambda_2 \eta_m} = f(V).g(\eta_l) \qquad \text{A5.14}$$

where η_l, η_m are respectively the dynamic viscosities of the liquid in the burette and of mercury.

For the liquids used in this work $g(\eta_l)$ assumed values between 0.48 and 0.68. The function f(V) was obtained from graphical integration. The total correction, E_η, for all experimental runs was in the range 0.42-0.61 J.

APPENDIX 6

Appendix 6.1: Proof of equation 6.9: At constant temperature and pressure

$$\mathrm{RT}\ln f_1 = \mu_1^E = (x_1+x_2).\mu_1^E + x_2.\mu_2^E - x_2.\mu_2^E$$
$$= \bar{G}^E + x_2.(\mu_1^E - \mu_2^E)$$

since

$$\bar{G}^E = x_1.\mu_1^E + x_2.\mu_2^E,$$

and so

$$\frac{d\bar{G}^E}{dx_1} = \mu_1^E + x_1.\frac{d\mu_1^E}{dx_1} + x_2.\frac{d\mu_2^E}{dx_1} - \mu_2^E$$
$$= \mu_1^E - \mu_2^E$$

since

$$x_1.\frac{d\mu_1^E}{dx_1} + x_2.\frac{d\mu_2^E}{dx_1} = 0 \text{ (Gibbs-Duhem relation)}$$

so

$$\mathrm{RT}\ln f_1 = \bar{G}^E + x_2\frac{d\bar{G}^E}{dx_1}$$

A similar relation may be derived for f_2.

Appendix 6.2: Error in reference 4: As a test for the computer program which evaluated $\bar{G}^E$, y and f from isothermal p-x measurements, the p,x,y data of Brown[9] for the system benzene + *n*-heptane at 353.15 K was used. This data was also used by Barker[4] to test a numerical method of evaluating $\bar{G}^E(x)$. The results in table 1 of this reference appear to be incorrect. The corrections are shown below.

Iteration		Reference 4	This work
0	A	0.3859	0.3859
	B	0	0
	C	0	0

(contd.)

Iteration		Reference 4	This work
	A	0.3592	0.3557
1	B	0.0845	0.0948
	C	0.0366	0.0293
	A	0.3620	0.3549
2	B	0.0891	0.0952
	C	0.0261	0.0276
	$\Sigma(\delta p)^2$	0.026 kPa^2	0.016 kPa^2

Iteration 1 was checked by hand calculation. Although the sum of the squares of the pressure residuals is actually smaller than that in reference 4, the experimental values of y are systematically lower (by up to 0.0045) than the calculated values. This may indicate a systematic error in the analysis of the vapour phase.

Appendix 6.3: Precision of $\bar{G}^E(x)$ obtained from p-x measurements: For given values of B_{11}, B_{22} and B_{12} the *precision* of $\bar{G}^E(x)$, obtained by the method described, is determined *only* by the precision of p, x and T measurements,

Errors in p: The largest of these result from temperature fluctuations, incorrect levelling, and observer errors in reading the positions of menisci. Capillary corrections were found to be unnecessary in this work (see *section 2.3*). The vapour pressure, p, is strictly defined as the pressure *immediately* above the liquid surface and so, ideally, the low side of the manometer should be in the same horizontal plane as this surface. A departure from this situation normally causes only a small error, Δp, in p.

$$viz.\ \Delta p \simeq pMgh/RT \qquad A6.1$$

where M is molecular weight (effective molecular weight for mixtures),

and h is the vertical depth of the low side of the manometer *below* the liquid surface.

The largest value of Δp for this work (di-ethyl ether, h = 0.1 m) was only 0.002 kPa.

Weissberger[20] points out that the density of a mercury sample which is clean enough to be used as a manometer fluid is unlikely to differ significantly from that of the pure liquid. The mercury used in this work was "towered" through dilute nitric acid (×3) then deionized water (×3), distilled in an air stream (×1) then distilled in vacuo (×3) and stored in sealed, steam-cleaned glass containers.

In summary the *precision* of vapour pressure measurements made *during "runs"* is believed to be better than $\pm|0.008 + 0.0001\ p/\mathrm{kPa}|$ kPa. The uncertainties in the vapour pressures of the pure liquids (Table 3.3) are somewhat smaller because of the more numerous measurements made on separate occasions leading to smaller observer and levelling errors.

Errors in x: The largest of these result from observer errors in determining the meniscus position in the burette and the calibration of various sections of the burette. This calibration was effected by (a) weighing pure mercury delivered by the burette between measured points and (b) by weighing pure hexafluorobenzene which was added to the vapour pressure cell under experimental conditions, and then distilled into, and sealed in, ampoules. Buoyancy corrections were applied in both (a) and (b) and the agreement between the two methods was better than 0.03%.

The isothermal compressibility of organic liquids is small enough ($\kappa \leqslant 2 \times 10^{-6}$ kPa^{-1}) so that the density of the liquid in the burette was not significantly affected (<0.01%) by subjection to pressures (ca. 150 kPa) above atmospheric.

The experimental error in x is believed to be ±0.0002 at $x \simeq 0.5$ and less elsewhere.

Errors in T: The uncertainties in practical temperature measurement are discussed in *Chapter 2*. The temperature coefficient of $\bar{G}^E$ is $-\bar{S}^E$ (equation 6.3). For the systems studied here $|\bar{S}^E|$ is greatest for *n*-hexane + benzene[19] ($\bar{S}^E(x = 0.5) \simeq 1.7$ J.mol^{-1} K^{-1}), but contributes negligible error to $\bar{G}^E$ (<0.01 J.mol^{-1}).

Precision of $\bar{G}^E$: For the purpose of estimating the *precision* of this method of determining $\bar{G}^E$, equations 6.6 and 6.7 may be combined to give the approximate relation

$$\bar{G}^E/RT \simeq x_1 \ln(py_1/p_1^o x_1) + (1-x_1)\ln(p(1-y_1)/p_2^o(1-x_1)). \qquad A6.2$$

The uncertainty in the terms $x_i(\bar{V}_i - B_{ii})(p_i - p)$, for given B_{ii}, contribute negligible error to $\bar{G}^E$ (<0.1 J.mol^{-1}). Since $\bar{G}^E(x)$ is obtained from a least squares procedure, the overall effect of random errors in p, the total vapour pressure, is probably small. The uncertainty, $\Delta(\bar{G}^E/RT)$, in $\bar{G}^E/RT$ is given, from equation A6.2, by:

$$\Delta(\bar{G}^E/RT) \simeq \frac{\partial(\bar{G}^E/RT)}{\partial x_1}\Delta x_1 + \frac{\partial(\bar{G}^E/RT)}{\partial y_1}\Delta y_1 + x_1\frac{\Delta p_1}{p_1} + (1-x)\frac{\Delta p_2}{p_2} \qquad A6.3$$

where

$$\Delta y_1 \simeq \frac{y_1}{x_1}\Delta x_1.$$

Evaluation of the terms in equation A6.3 for the systems studied in this work gives

$$\Delta(\bar{G}^E) < 2 \text{ J.mol}^{-1}.$$

J. Chem. Thermodynamics **1972**, 4, 723–729

Excess volumes of hexafluorobenzene + aliphatic ethers

M. L. MARTIN and R. S. MURRAY

Department of Physical and Inorganic Chemistry,
University of Adelaide, Adelaide, South Australia, 5001.

(*Received 3 January 1972*)

Excess volumes of hexafluorobenzene with diethyl, di-*n*-propyl, di-isopropyl, and di-*n*-butyl ethers have been measured at 298.15 K using a continuous dilution dilatometer. All systems exhibited positive excess volumes with plots of V^E against volume fraction ϕ_2 of the ether all showing maxima at $\phi_2 = (0.57 \pm 0.01)$.

1. Introduction

In recent years binary systems containing hexafluorobenzene have undergone considerable thermodynamic and spectroscopic investigation with early workers concentrating mainly on systems containing aromatic and alicyclic hydrocarbons. Swinton and his colleagues(1–6) studied these binary systems extensively by examination of their phase diagrams, excess volumes, liquid-phase dipole moments, and vapour pressures. Their work confirmed earlier findings of Patrick and Prosser(7) by showing the existence of a series of well-defined, solid 1-1 molecular complexes between hexafluorobenzene and aromatic hydrocarbons. It was suggested that these complexes could possibly also be present in the liquid state. A correlation between the magnitude of the excess volumes and increasing electron-donating strength of the hydrocarbon was obtained but the unequivocal existence of charge-transfer complexing was not demonstrated.

The positive and negative excess enthalpies of a large number of binary mixtures of fluorinated benzenes resulted in Scott and co-workers(8, 9) postulating that the measured excess function was the sum of three main contributions including an important specific interaction arising from matching hydrogen and fluorine atoms on adjacent rings. No non-thermodynamic evidence of charge-transfer complexing was obtained although spectroscopic evidence of this type of interaction had been reported(10, 11) for some systems containing hexafluorobenzene and suitable aromatic amines.

The observation of positive excess heat capacities and negative excess enthalpies of hexafluorobenzene and suitable aromatic amines was interpreted by Armitage and Morcom,(12) with due regard to molecular orbital theory and steric factors, as arising from the formation of π-type donor complexes. A weaker interaction between hexafluorobenzene and triethylamine was suggested. Recent investigations using 1,4-dioxan as a possible electron-donor have been reported.(13)

Aliphatic ethers,(14) possessing two lone pairs of electrons and a well documented role as *n*-donors with Lewis acids(15) and organic substrates,(16-18) might be expected to show possible charge-transfer complexing with hexafluorobenzene. This paper reports the first findings of investigations on mixtures of hexafluorobenzene + aliphatic ethers.

2. Experimental

The excess volumes were measured with a continuous dilution dilatometer similar to that described by Stokes *et al.*(19) The inclusion of a tap below the U-bend connecting the measuring burette to the mixing vessel enabled the apparatus to be filled with mercury under vacuum and also facilitated both calibration and cleaning procedures. Elimination of occasional minute leakages at the points of sealing the stainless steel connecting tubing to the apparatus shown in figure 1 was achieved by screw-tightening

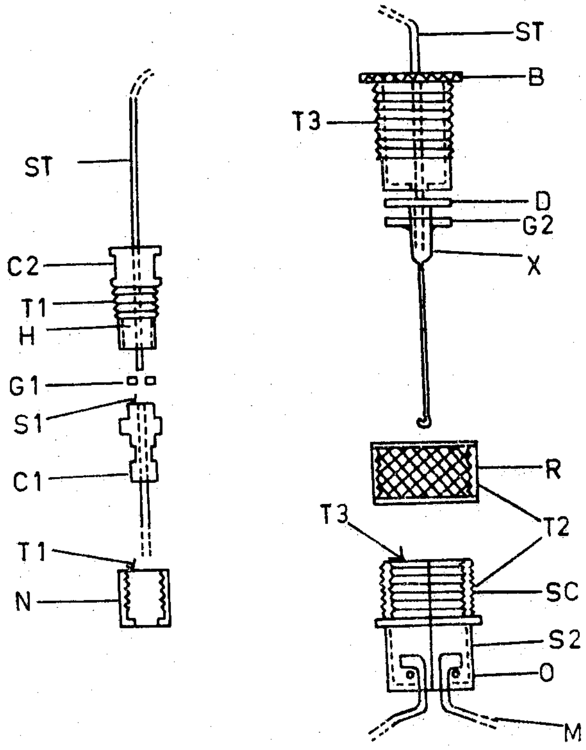


FIGURE 1. Dilatometer sealing attachments. The stainless steel connector C1 on the tubing at the top of the burette is sealed to the stainless steel connector C2 by screwing nut N along the threads T1. This forces teflon gasket G1 into the hole H and on to the flat S1. By screwing brass ring R along threads T2, the split collar SC is fixed below the neoprene O-ring O, placed under the glass head of the mixing vessel M. On rotating bolt B along the threads T3, the stainless steel disk D and teflon gasket G2 are forced on to the flat glass top S2 of the mixing vessel.

connectors, which enclosed flat teflon gaskets, on to both the machined "316" stainless steel surface S_1, at the top of the burette and the flat ground glass surface, S_2, at the top of the mixing vessel. A matching connector on the needle of the syringe was used to introduce one of the liquids to the burette. With the measuring capillary held vertically, the volumes of the mixing vessel and the burette were determined by carefully running pure mercury into tared flasks between suitable points, read with a Precision Tool and Instrument cathetometer fitted with a Gaertner Telemicroscope.(20) Before each run the levelling procedure involved a check on the distance (26.063 cm) between two fiducial marks on the burette. Temperature control to (298.150 ± 0.001) K (IPTS—1948) was achieved with a mercury + toluene regulator. A test of the dilatometer using cyclohexane + benzene yielded values which agreed to within ± 0.001 $cm^3 \, mol^{-1}$ of those found by Stokes *et al.*(19)

3. Materials

The ethers (Fluka puriss, or B.D.H. Analar) were treated with ferrous sulphate + sulphuric acid solutions to remove peroxides,(21) washed exhaustively with distilled water, dried with calcium chloride for 24 h, refluxed for 12 to 15 h over sodium wire, and then slowly fractionally distilled (reflux ratio up to 150) in an atmosphere of nitrogen into a flask containing copper flitters to reduce peroxide formation. Di-isopropyl ether was found to require preliminary shaking with mercury to remove traces of impurities. After purification the ethers were stored over sodium wire, under nitrogen, and in the dark.

Hexafluorobenzene of 96 moles per cent purity from Imperial Smelting Corporation was refluxed with oleum + sulphuric acid followed by washings with sodium carbonate solution and water. After being stirred with a potassium permanganate solution in acetone at room temperature followed by the addition of water, the sample

TABLE 1. Characterization of liquids: gas chromatographic column used, estimated mole fraction purity x, density ρ(298.15 K, IPTS–1948), literature values for comparison

Substance	Gas Chromatographic column	100 x	ρ/g cm^{-3} this work	Literature
benzene	10 mass per cent didecyl phthalate on AW-DMCS Chromosorb W	99.99_9	0.87365	0.87368 (25) 0.87365 (19)
cyclohexane	28 mass per cent carbowax on Varaport 20	99.98	0.77383	0.77389 (25) 0.77388 (19)
diethyl ether	15 mass per cent Ucon oil on A.W. Gas Chrom.	99.97	0.70768	0.70768 (26) 0.70776 (24)
di-*n*-propyl ether	15 mass per cent Ucon oil on A.W. Gas Chrom.	99.92	0.74168	0.74215 (24)[a]
di-isopropyl ether	15 mass per cent Ucon oil on A.W. Gas Chrom.	99.7	0.71885	0.72301 (24)[a]
di-*n*-butyl ether	15 mass per cent Ucon oil on A.W. Gas Chrom.	99.85	0.76374	0.76459 (24) 0.76402 (26)[a]
hexafluorobenzene				
(1)	10 mass per cent squalane on A.W.-DMCS Chromosorb W	99.99_2	1.60688	1.60688 (23)
(2)	10 mass per cent fluorosilicone oil on Chromosorb W	99.99	1.60685	1.60688

[a] Obtained by linear interpolation of literature values at other temperatures.

was treated with sulphur dioxide before being washed exhaustively with water.(22) The liquid was dried over calcium chloride and then B.D.H. 4A molecular sieves before fractional distillation. Last traces of impurities were removed by 15 crystallizations using a directional freezing apparatus based on the design described by Evans *et al.*(23) Samples were stored over 4A molecular sieves.

Benzene (Analar B.D.H.) and cyclohexane (Uvasol, Merck) were purified by standard methods.(24)

All purified liquids were characterized by estimating their purity using a Perkin-Elmer F11 gas chromatograph and by determining their densities in triplicate in single stem pycnometers (volumes about 32 cm^3) using a Mettler B6C 200 balance for weighings. The results are shown in table 1.

The refractive index of hexafluorobenzene, n(D, 298.15 K) = 1.37483 ± 0.00002, obtained by use of a Hilger-Chance instrument,(27) is in excellent agreement with the result 1.37482 of Morris and Davis(28) who obtained their sample by preparative gas-liquid chromatography. The densities of hexafluorobenzene and diethyl ether at 283.150 K (IPTS—1948) were found to be 1.64088 $g\ cm^{-3}$ and 0.72497 (compare 0.72503(26)) $g\ cm^{-3}$ respectively.

4. Results and discussion

The excess volumes V^E are presented in table 2 (a to d) for hexafluorobenzene + each of four aliphatic ethers at 298.150 K and for hexafluorobenzene + diethyl ether at 283.150 K in table 2 (e). An analysis of errors resulting from the calibration of various sections of the dilatometer, the measurements of mercury levels during experiments, and the determination of the compressibility correction,(19) are estimated to lead to a maximum uncertainty of ± 0.15 per cent in a value of V^E. Linear compressions, which lie in the range 9×10^{-6} to 13×10^{-6} $cm\ Pa^{-1}$, are in good agreement with the values calculated from the compressibilities of the liquids, but ignoring contributions from mercury and glass. A useful test of errors is provided by the congruency, in the region of mole fraction 0.5, of the curves representing the two runs which are required to cover the entire composition range. The maximum error in overlap for measurements is 0.002 $cm^3\ mol^{-1}$.

The values of V^E for hexafluorobenzene + aliphatic ether mixtures are all positive (table 2) but this does not of itself negate the existence of any specific interaction between the components.(9, 12) The following trends in the magnitude of V^E may be noted. (a) There is a general increase in V^E with increasing chain length. (b) The excess volumes for the system containing di-isopropyl ether are markedly less than those for the isomeric di-*n*-propyl ether. (c) V^E decreases for the diethyl ether mixture when the temperature is reduced from 298 to 283 K.

The trend in (a) might be expected from the commonly observed "antipathy" between fluorocarbon and hydrocarbon;(29) the endothermic contributions increasingly overshadow effects due to any specific interaction as the chain length is increased. The change in V^E with temperature for diethyl ether mixtures is not dramatic enough to allow any conclusions to be drawn, although it is in the direction that might be expected for increasing complex formation.

TABLE 2. Excess volumes, V^E of hexafluorobenzene + aliphatic ethers (mole fraction x_2) at 298.150 K and + diethyl ether at 283.150 K

x_2	V^E/cm^3 mol^{-1}	x_2	V^E/cm^3 mol^{-1}	x_2	V^E/cm^3 mol^{-1}
(a) Hexafluorobenzene (1) + diethyl ether (2) at 298.150 K					
0.0260	0.0398	0.4221	0.5450	0.6906	0.5918
0.0509	0.0782	0.4496	0.5656	0.7161	0.5748
0.0691	0.1067	0.4769	0.5835	0.7505	0.5443
0.0921	0.1418	0.5010	0.5964	0.7831	0.5065
0.1503	0.2271	0.5315	0.6092	0.8293	0.4380
0.1978	0.2944	0.5340	0.6075	0.8670	0.3670
0.2321	0.3403	0.5581	0.6139	0.9295	0.2193
0.2717	0.3906	0.5789	0.6172	0.9595	0.1326
0.3189	0.4459	0.6053	0.6179	0.9788	0.0712
0.3562	0.4857	0.6403	0.6126		
0.3913	0.5186	0.6617	0.6057		
(b) Hexafluorobenzene (1) + di-*n*-propyl ether (2) at 298.150 K					
0.0186	0.0909	0.3729	1.2890	0.6617	1.2783
0.0375	0.1820	0.3938	1.3196	0.6938	1.2170
0.0714	0.3415	0.4189	1.3504	0.7246	1.1468
0.1160	0.5360	0.4380	1.3692	0.7518	1.0750
0.1716	0.7555	0.4520	1.3821	0.8018	0.9199
0.2185	0.9169	0.4817	1.3980	0.8457	0.7578
0.2605	1.0431	0.5065	1.4036	0.8966	0.5424
0.2918	1.1246	0.5445	1.3987	0.9190	0.4362
0.3206	1.1911	0.5971	1.3646	0.9470	0.2944
0.3475	1.2451	0.6224	1.3365	0.9739	0.1479
(c) Hexafluorobenzene (1) + di-*n*-butyl ether (2) at 298.150 K					
0.0155	0.1055	0.2926	1.3628	0.5744	1.5095
0.0302	0.2033	0.3119	1.4067	0.6171	1.4458
0.0411	0.2737	0.3477	1.4746	0.6597	1.3610
0.0597	0.3893	0.3722	1.5107	0.7149	1.2212
0.1033	0.6354	0.3931	1.5349	0.7640	1.0690
0.1292	0.7678	0.4056	1.5464	0.8069	0.9149
0.1532	0.8814	0.4310	1.5636	0.8759	0.6314
0.1946	1.0552	0.4529	1.5719	0.9125	0.4599
0.2326	1.1915	0.4989	1.5696	0.9466	0.2888
0.2562	1.2655	0.5211	1.5591	0.9649	0.1927
(d) Hexafluorobenzene (1) + di-isopropyl ether (2) at 298.150 K					
0.0320	0.1014	0.3984	0.8984	0.6484	0.9122
0.0675	0.2096	0.4176	0.9167	0.7062	0.8417
0.1384	0.4090	0.4369	0.9328	0.7680	0.7333
0.2103	0.5850	0.4550	0.9447	0.8367	0.5700
0.2807	0.7291	0.4812	0.9577	0.9032	0.3705
0.3159	0.7892	0.5248	0.9676	0.9416	0.2344
0.3594	0.8525	0.5795	0.9589		
(e) Hexafluorobenzene (1) + diethyl ether (2) at 283.150 K					
0.0305	0.0470	0.3086	0.4145	0.5029	0.5629
0.0420	0.0649	0.3361	0.4436	0.5171	0.5662
0.0601	0.0921	0.3524	0.4577	0.5338	0.5679
0.0809	0.1241	0.3832	0.4849	0.5839	0.5762
0.0888	0.1347	0.4098	0.5076	0.6569	0.5653
0.1707	0.2495	0.4266	0.5182	0.7323	0.5215
0.1750	0.2546	0.4643	0.5436	0.8497	0.3722
0.2447	0.3439	0.4725	0.5464	0.9639	0.1136
0.2535	0.3532	0.4950	0.5573		

Armitage and Morcom(12) have suggested the possibility of a weak charge-transfer
complex between hexafluorobenzene and triethylamine acting as an *n*-donor. As
a→ triethylamine exhibits a first ionization potential of 75.7 kJ mol^{-1}, while the values
a→ for ethers are in the range 87 to 96 kJ mol^{-1},(30) the specific interaction between the
lone-pair electrons on the oxygen atom and the π-acceptor orbital of hexafluorobenzene is likely to be fairly weak. In addition there remains the possibility of dipole–dipole interaction between C–H and C–F bonds.

Regular solution theory predicts that for plots of some excess thermodynamic functions of binary liquid mixtures against mole fraction there is a general skewing of the curves in the direction of the component of lower molar volume whereas if volume fractions are used the maximum tends to occur around 0.5. For the mixtures studied in this work the volume fraction ϕ_2 of ether at which the maximum occurs is (0.57 ± 0.01) for all ethers. This is shown in figure 2.

The existence or otherwise of complex formation in these systems has not been demonstrated but other thermodynamic measurements currently being made, together with non-thermodynamic techniques, may provide some insight into the nature and strength of any specific interactions that may be present.

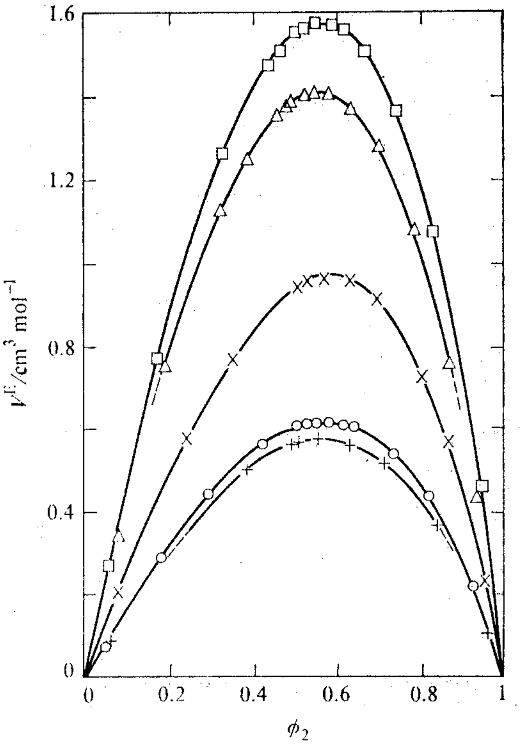


FIGURE 2. Excess volumes V^E of hexafluorobenzene+aliphatic ethers against volume fraction ϕ_2 of ether at 298.15 K. □, di-*n*-butyl ether; △, di-*n*-propyl ether; ×, di-isopropyl ether; ○, diethyl ether (298.15 K); +, diethyl ether (283.15 K).

---

[a] *Error*: the quoted ionization potentials are too *small* by a factor of *10*.

The gift sample of hexafluorobenzene from the Imperial Smelting Corporation, Avonmouth, U.K. is gratefully acknowledged. This research was supported by a grant from the Australian Research Grants Committee.

REFERENCES

1. Duncan, W. A.; Swinton, F. L. *Trans. Faraday Soc.* **1966,** 62, 1083.
2. Duncan, W. A.; Sheridan, J. P.; Swinton, F. L. *Trans. Faraday Soc.* **1966,** 62, 1090.
3. Gaw, W. J.; Swinton, F. L. *Nature* **1966,** 212, 283.
4. Duncan, W. A.; Swinton, F. L. *J. Phys. Chem.* **1966,** 70, 2417.
5. Gaw, W. J.; Swinton, F. L. *Trans. Faraday Soc.* **1962,** 64, 637.
6. Gaw, W. J.; Swinton, F. L. *Trans. Faraday Soc.* **1968,** 64, 2023.
7. Patrick, C. R.; Prosser, G. S. *Nature* **1960,** 187, 1021.
8. Fenby, D. V.; Milure, J. A.; Scott, R. L. *J. Phys. Chem.* **1966,** 70, 602.
9. Fenby, D. V.; Scott, R. L. *J. Phys. Chem.* **1967,** 71, 4103.
10. Beaumont, T. G.; Davis, K. M. C. *Nature* **1968,** 218, 865.
11. Beaumont, T. G.; Davis, K. M. C. *J. Chem. Soc. B* **1967,** 1131.
12. Armitage, D. A.; Morcom, K. W. *Trans. Faraday Soc.* **1969,** 65, 688.
13. Andrews, A. W.; Hall, D.; Morcom, K. W. *J. Chem. Thermodynamics* **1971,** 8, 527.
14. Patai, S. *The Chemistry of the Ether Linkage.* Interscience Publishers: London. **1967.**
15. Wirth, H. E.; Slick, P. I. *J. Phys. Chem.* **1962,** 66, 2277.
16. Beath, L. A.; Williamson, A. G. *J. Chem. Thermodynamics* **1969,** 1, 51.
17. Beath, L. A.; O'Neill, S. P.; Williamson, A. G. *J. Chem. Thermodynamics* **1969,** 1, 293.
18. Battino, R. *Chem. Rev.* **1971,** 71, 5.
19. Stokes, R. H.; Levien, B. J.; Marsh, K. N. *J. Chem. Thermodynamics* **1970,** 2, 43.
20. Gaertner Scientific Corporation, Chicago, U.S.A.
21. Vogel, A. I. *A Textbook of Practical Organic Chemistry* 3rd Ed. Longmans: London. **1962.**
22. Fuller, G. Private communication. Imperial Smelting Corp. Ltd., Bristol, U.K.
23. Evans, F. D.; Bogan, M.; Battino, R. *Anal. Chem.* **1968,** 40, 224.
24. Weissberger, A.; Proskauer, E. S.; Riddick, I. A.; Toops, E. E., Jr. *Technique of Organic Chemistry. Vol. VII. Organic Solvents.* Interscience: New York. **1955.**
25. Bell, T. N.; Cussler, E. L.; Harris, K. R.; Pepela, C. N.; Dunlop, P. J. *J. Phys. Chem.* **1968,** 72, 4693.
26. Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds.* Elsevier: Amsterdam. **1950.**
27. Brown, I.; Lane, J. Private communication. Division of Applied Chemistry, C.S.I.R.O., Melbourne, Victoria.
28. *U.S. Bur. Mines, Rep. Invest.* 6633. **1965.**
29. Rowlinson, J. S. *Liquids and Liquid Mixtures.* Butterworths: London. **1959.**
30. Turner, D. W. *Advan. Phys. Org. Chem.* **1966,** 4, 31.