AN INVESTIGATION OF THE EXCESS VOLUME OF MIXING OF n-ALKANES WITH CYCLOALKANES

A THESIS PRESENTED BY

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This thesis is a record of research carried out in the Department of Physical and Inorganic Chemistry at the University of Adelaide, between January '73 and January '75. To the best of my knowledge and belief it is completely original work, except where due reference is made.

LYNNE DOBINSON

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I

INTRODUCTION

LATTICE THEORIES

- (i) (a) SIMPLE PARTITION FUNCTION
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"Thermodynamics is useful precisely because some quantities are easier to measure than others and that is all."

M.L. McGLASHAN
"Uses & Misuses of the Laws of Thermodynamics"

It is in this context that the excess properties of mixtures are measured, for they can be readily used to examine the validity of the many theoretical models which have been proposed to represent the structure of liquids and their mixtures.

The theories of liquids can be separated into two broad types[1]. Firstly there exists the strict statistical mechanical treatment[2] which utilises the fundamental approach of determining the inter-molecular potential in a hope that this will lead to equations whose solutions describe the structure. However, theories of the other type begin with a simplified description of the structure while omitting the mathematical justification for the treatment. The latter[1] are classified as "lattice" theories. The theoretical treatments considered in this work are of the "lattice" type but they can be seen as being divided into two distinctive sub-types.

The approach of Paul J. Flory[3] and co-workers has its origins in the work of Eyring and Hirschfelder[4] and later that of Prigogine[5]. The basis of all these theories was to formulate a simple partition function, often of the Van der Waals form[6], and relate this equation to the known excess thermodynamic functions. A brief description of this sub-type appears in section (i) of this chapter, together with a more detailed outline of the Flory approach.

In section (ii) there appears an example of the other main sub-type of lattice theories - the semi-empirical form and the Huggins theory[7] is the example described. In this case the interactions between molecules are related in terms of the empirical model and then the parameters derived are associated directly with the excess properties of the mixture. Also no partition function is derived.

Both theoretical treatments predict results by a "curve fitting" method i.e. the experimental results are equated with the expression derived from the model and thus the parameters are obtained. It is hoped that within these results the behaviour of the parameters will enable evidence for the various liquid properties to be obtained.

Much of the early work in these discussions has involved the study of n-alkane mixtures because;

(1) they are the simplest chain molecule to consider and as such are a logical choice after studying the simple spherical molecules,

(2) there is extensive and accurate experimental data available.

Cycloalkane and n-alkane mixtures are of considerable interest as an extension to the studies of n-alkane mixtures to discover if they can also be interpreted within the confines of the same theories.

(i) (a) SIMPLE PARTITION FUNCTION THEORIES[8,9,10].

GENERAL: Below are described the characteristics of the theories which have been developed using a simple partition function as the basis for prediection of the excess thermodynamic functions of mixtures.

The generalised van der Waals[6] equation

$$\frac{PV}{RT} = \phi(y) - \frac{a}{RTV} \quad , \qquad 1.(1)$$

has been used extensively for this treatment, where a is a characteristic attractive constant and $\phi(y)$ is a function of y which can be expressed as

$$y = \frac{b}{4V} \qquad 1.(2)$$

where b = core volume

and V = total volume.

The form of $\phi(y)$ depends on the approach used by the authors concerned. For example, van der Waals used

$$\phi(y) = (1 - 4y)^{-1} \quad , \qquad 1.(3)$$

while Carnahan and Starling[11] used

$$\phi(y) = \frac{1 - y + y^2 + y^3}{(1 - y)^3} \quad . \qquad 1.(4)$$

$\phi(y)$ of the latter type (1.(4)) is used to derive the equation of state for hard spheres.[12]

The calculation of the attractive constant, a, and the core volume, b, for the mixtures involve the use of one of three models. All models combine a and b of the corresponding components and they differ only in their averaging processes.

(i) In the one-fluid model the mixture is considered as one liquid with the values of a and b being composition dependant and thus necessitating an averaging of the molecular parameters.

(ii) In the two fluid model, the mixture is considered as an ideal mixture of two liquids each with its own composition dependant values of a and b.

There is an averaging of both the molecular parameters and the thermodynamic properties.

(iii) The three fluid model considers the addition of all the individual interactions thence averaging the thermodynamic properties.

EXAMPLE - Leland, Rowlinson & Sather[13] considered the mixture as a one-fluid model with

$$a(x) = (1 - x)^2 a_{11} + 2x(1 - x)a_{12} + x^2 a_{22} \qquad 1.(5)$$

$$b(x) = (1 - x)^2 b_{11} + 2x(1 - x)b_{12} + x^2 b_{22} \qquad 1.(6)$$

where x is the mole fraction of the first component.

The values of a and b for the pure component (i.e. a_{11}, a_{22}, b_{11}, b_{22}) are often determined using the properties of the pure liquid s (eg. thermal expansivity). a_{12} and b_{12} are derived from a modified form of the Berthelot equation[14]

$$a_{12} = \xi(a_{11}a_{22})^{\frac{1}{2}} \left(\frac{b_{12}}{b_{11} \quad b_{22}} \right)^{\frac{1}{2}} \qquad 1.(7)$$

$$(b_{12})^{1/3} = \left(\frac{(b_{11}{}^{1/3} + b_{22}{}^{1/3})}{2} \right) \qquad 1.(8)$$

The factor, ξ, can be theoretically determined from the second virial coefficient data. However, it is more usual to obtain ξ by fitting to one of the experimental functions at a single temperature and pressure.

(i) (b) PAUL J. FLORY

Many theories of the simple partition function type have been developed in the past ten years. Perhaps the most noteworthy of these is the treatment of P.J. Flory[3,15-20].

The equation of state is similar to the van der Waals form,

$$PV = \phi(y)RT - \frac{a}{V} \qquad 1.(9)$$

where

$$\phi(y) = (1 - y^{1/3})^{-1} \qquad 1.(10)$$

and

$$y = \frac{b}{4V} \qquad 1.(11)$$

A one fluid model[9] is used to determine a(x) and b(x) for the mixture

$$b(x) = (1 - x)b_{11} + xb_{22} \qquad 1.(12)$$

and

$$a(x) = b(x)\left(\frac{\dfrac{(1-x)^2 a_{11}}{a_{11}^{\ 1/3}} + \dfrac{2x(1-x)a_{12}}{b_{12}^{\ 1/3}} + \dfrac{xa_{22}}{b_{22}^{\ 1/3}}}{(1-x)b_{11}^{\ 2/3} + xb_{22}^{\ 2/3}}\right) \qquad 1.(13)$$

Flory's treatment of chain molecules in terms of the properties of pure liquids has been most successful, not only for these molecules, but, when extended, for other more complex forms.[17,18] The following is an outline of the derivations of the equations used and the assumptions involved therein.

A chain molecule is believed to consist of n repeating units and 2 terminal groups and the difference between these is recognized. The molecule is assumed to have flexibility to adopt various orientations.

A molecule can also be divided into r segments. The number, r, does not have to equal the number of repeating units, n, but, for an homologous series must be linear in n. The total core volume, V^*, is defined as

$$V^* = rv^* , \qquad 1.(14)$$

where v^* is the nett volume of the segments.

The molecular surface, of the molecule is related to the quantity, M, such that —

$$M = rs , \qquad 1.(15)$$

where s is the number of external contact sites per segment of the molecule and

$$rs = r(S_m + S_e) , \qquad 1.(16)$$

where S_m is the number of contact sites for mid-chain segments and S_e is the number of end contact sites.

The oscillatory modes[21] of the isolated molecule can be considered as being either intra- or intermolecular. It is assumed that the former are unaffected by neighbouring molecules, while the latter, which undergo greater perturbation, are considered to exhibit simple translational motion. Added to this are the three degrees of freedom of the molecular centre of gravity. The total number of intermolecular degrees of freedom are,

$$3rc = 3(rc_m + c_e) , \qquad 1.(17)$$

and c, c_m, c_e are factors representing respectively the total number of degrees of freedom per segment, the number of degrees of freedom per middle segments and the number per end segments. When combining equation 1.(14) with the expression for the free length, "ℓ", which is usually associated with the cell model, the following equation can be derived.

$$\ell = \gamma^{1/3}(v^{1/3} - v^{*1/3}) , \qquad 1.(18)$$

where γ is a geometric constant and v is the volume per segment and is represented as

$$v = \frac{V}{rN} , \qquad 1.(19)$$

where N is the number of r type molecules.

A partition function, Z, can now be formulated for a pure liquid, as

$$Z = Z^{\dagger}[\gamma(v^{1/3} - v^{*1/3})^3]^{rNc} \, e^{-E_o/kT} \qquad 1.(20)$$

The combinatorial factor, $Z^{\dagger}$, is specified only as representing various geometric dispositions in space, and is defined to be independant of temperature and volume.

The partition function is identical to that derived by Prigogine, Trappeniers and Mathot[22,23] but the theories differ in their discussion of E°, the intermolecular potential. Flory rejects the cell model interpretation -

> "The energy of interaction between a pair of molecules is a sensitive function of intermolecular distance and relegation of all members of the first shell to the same distance introduces a considerable error in the energy and its dependance on the mean distance."

This error is enhanced by ignoring the eccentric nature of the molecule.

Using the assumption that the correlation factor ($g^{(2)}(r_{12})$) is independent of volume allows E° to be considered as a function of density.[24] By using this approximation the mean intermolecular energy per contact pair, ε, can be expressed as

$$\varepsilon = \frac{-\eta}{v} \qquad 1.(21)$$

where η is the characteristic of the mean interaction between segment pairs.

The intermolecular energy for a pure liquid is given by

$$E_\circ = \frac{-rNs\eta}{2v} \qquad 1.(22)$$

Substituting into the equation for the partition function (Eq. 1.(20)) and using the reduced variables,

$$\tilde{v} = \frac{v}{v^*} \qquad 1.(23)$$

$$\tilde{T} = \frac{T}{T^*} \quad (= 2v^*ckT/\eta s) \qquad 1.(24)$$

he obtained

$$Z = Z^\dagger(\gamma v^*)^{rNc} \; (\tilde{v}^{1/3} - 1)^{3rNc} \; e^{rNc/\tilde{v}\tilde{T}} \qquad 1.(25)$$

The equation of state derived from this expression is

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)} - \frac{1}{(\tilde{v}\tilde{T})} \qquad 1.(26)$$

where $\tilde{p}$, the reduced pressure is expressed as

$$\tilde{p} = \frac{p}{p^*} \qquad 1.(27)$$

and p^*, the characteristic pressure is

$$p^* = \left\{\frac{v^*}{ckT}\right\}^{-1} \qquad 1.(28)$$

This expression has the same form as that derived by Eyring and Hirschfelder,[4] the only difference being due to Flory's inclusion of the factor c. The two expressions are identical when c = 1. In Flory's treatment c is less than unity to allow for the restrictions placed on the precise location of any given segment with respect to its neighbours. i.e. it is restraining the number of degrees of freedom. This is an over-simplified description[3] and lacks rigourous justification.

The reduced volume, temperature and pressure ($\tilde{v}$, $\tilde{T}$, $\tilde{p}$) can be expressed in terms of the properties of the pure liquid. The reduced volume of a mole of segments $\tilde{v}$ $\left(= \frac{v}{v^*}\right)$ can be calculated from the coefficient of thermal expansion, α, using the expression

$$\tilde{v} = \left(\frac{(1 + \frac{4}{3}\alpha T)}{(1 + \alpha T)}\right)^3 \qquad 1.(29)$$

At zero pressure $\tilde{v}$ and $\tilde{T}$ are related by the relation

$$\tilde{T} = \frac{(\tilde{v}^{1/3} - 1)}{\tilde{v}^{4/3}} \qquad 1.(30)$$

and the characteristic pressure is expressed as

$$p^* = \gamma T\tilde{v}^2 \qquad 1.(31)$$

where γ is the thermal pressure coefficient of the pure liquid.

Knowledge of v^*, T^* and p^* enable the calculation of the primary parameters, c and sη. The factor, c, can be written as

$$c = \frac{(\gamma v).(\alpha T)}{k(3 + 4\alpha T)} \qquad 1.(32)$$

while sη is given by

$$s\eta = 2\gamma T v^2 \qquad 1.(33)$$

The absence of order, as considered in the pure liquid, should follow for mixtures of homologous members of a series. The only reservation held is that if the chain length differences are very large, favoured orientations may be possible.

An analogous expression to the intermolecular potential, E°_m, of the mixture is

$$E^\circ_m = \frac{-\bar{r}Np^*v^*}{\tilde{v}} \qquad 1.(34)$$

where $\bar{x}$, the number average, is defined by

$$\frac{\sum r_i N_i}{\sum N_i} = \frac{\sum r_i N_i}{N} \qquad 1.(35)$$

summing over all the species, i, in the mixture. The number average can also be written as

$$\bar{r}^{-1} = \sum \phi_i r_i^{-1} \qquad 1.(36)$$

where ϕ_i is the segment fraction of component i.

Similarly s and c have analogous expressions

$$\begin{aligned} s &= S_m + S_e/\bar{r} \,, \\ &= \sum \phi_i s_i \end{aligned} \qquad 1.(37)$$

and

$$c = \sum \phi_i c_i \quad . \qquad 1.(38)$$

Consider the excess thermodynamic properties of the mixture. The reduced excess volume, $\tilde{v}_E$, is represented as

$$\tilde{v}_E = \tilde{v} - \tilde{v}^\circ \qquad 1.(39)$$

where $\tilde{v}^\circ$ is the ideal reduced volume of the mixture and $\tilde{v}$ is the actual reduced volume of the mixture.

Also,

$$\tilde{v}^\circ = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2 \qquad 1.(40)$$

where ϕ_1 and ϕ_2 are the total segment fractions for the pure liquid. The actual reduced volumes are written as $\tilde{v}_1$ and $\tilde{v}_2$.

Since the characteristic volume of the mixing is given by

$$V^* = x_1V_1^* + x_2V_2^* \,, \qquad 1.(41)$$

where V_1^*, V_2^* are the respective characteristic volumes, it follows that the excess volume

$$V^E = \tilde{v}_E V^* \qquad 1.(42)$$

$$= (x_1V_1^* + x_2V_2^*)(\tilde{v} - \phi_1\tilde{v}_1 - \phi_2\tilde{v}_2) \qquad 1.(43)$$

The expression for excess volume will be expanded upon in Chapter (V).

(ii) SEMI-EMPIRICAL - M.L. HUGGINS

The theory of Maurice L. Huggins[7,25-29] has evolved from a very simple form of the lattice theory, an approach which was specifically designed to represent chain molecules. Huggins' aims were to predict the properties of polymer solutions using data obtained from mixtures of the appropriate small chain molecules.

In a similar manner to that discussed by Flory the molecules are considered to be divided into segments. All segments of the same chemical composition are regarded as acting alike in their interactions with other segments.

This premise, when coupled with the relationship between the intermolecular energies of closest pair interactions and the intermolecularly contacting surface area, is the basis of the model. All contacts that are not due to nearest neighbour interactions are assumed to have negligible contribution to the change in intermolecular energy.

The fundamental assumptions of the theory can be summarised:

1. For each segment the average contacting segment surface area is constant regardless of variations in the types and numbers of segments. Thus if a molecule has n segments of type α and m-segments of type β, then $\sigma_{\alpha\alpha}$, $\sigma_{\beta\beta}$, $\sigma_{\alpha\beta}$ are denoted the average areas of intermolecular contact per mole for the different types of contact and are defined by the combining rules

$$\sigma_\alpha = 2\sigma_{\alpha\alpha} + \sigma_{\alpha\beta} \qquad 1.(44)$$

$$\sigma_\beta = 2\sigma_{\beta\beta} + \sigma_{\alpha\beta} \qquad 1.(45)$$

Here σ_β, σ_α are defined as the intermolecularly contacting surface areas in one mole of substance or mixture.

2. For each kind of segment-segment interaction the average energy per unit area of contact is constant at a given temperature reagardless of variations in the types and areas of other contacts. The average energies per unit contact area for the different types of intermolecular contact are defined as $\varepsilon_{\alpha\alpha}$, $\varepsilon_{\beta\beta}$, $\varepsilon_{\alpha\beta}$.

3. The relative contact areas for the three types of contact as formed by two segment types (α, β) are governed by an equilibrium constant and for each additional type of segment more equilibrium constants are added. The equilibrium constant, K, is related to the contact areas as

$$K = \frac{\sigma_{\alpha\beta}^{2}}{4.\sigma_{\alpha\alpha}\,\sigma_{\beta\beta}} \qquad 1.(46)$$

and the contact energies

$$K = A\,e^{-\Delta\varepsilon/kT} \qquad 1.(47)$$

where $$\Delta\varepsilon = 2\varepsilon_{\alpha\beta} - \varepsilon_{\alpha\alpha} - \varepsilon_{\beta\beta}\,. \qquad 1.(48)$$

Also k (not the Boltzmann constant) is described as depending of the choice of the unit area. The factor, A, is dependant on steric factors, neither A nor k need be evaluated.

These assumptions lead to a series of equations in which the cohesive energy is related to the following

(i) the numbers of different types of segments;

(ii) the contact surface area for each type;

(iii) one or more equilibrium constants depending on the number of different types of contact.

Consider a system in which there is only one type of segment, α. The cohesive energy, E, is then written as

$$E = \sigma_{\alpha\alpha}\,\varepsilon_{\alpha\alpha} \qquad 1.(49)$$

$$= \frac{n_{\alpha}\,\sigma_{\alpha}^{o}\,\varepsilon_{\alpha\alpha}}{2} \qquad 1.(50)$$

where n_α is the number of α segments per molecule and $\sigma_\alpha{}^o$ is the average intermolecularly contact surface area per mole of single segments of the α type. A similar expression can be derived in terms of $\sigma_\beta{}^o$.

If there are two types of segments α and β, then

$$E = \sigma_{\alpha\alpha}\,\varepsilon_{\alpha\alpha} + \sigma_{\beta\beta}\,\varepsilon_{\beta\beta} + \sigma_{\alpha\beta}\,\varepsilon_{\alpha\beta} \qquad 1.(51)$$

and furthermore through use of the combining rules (1.44, 1.45) Huggins obtained,

$$\sigma_{\alpha\alpha} = \frac{\sigma_\alpha}{2} + \frac{(\sigma_\alpha + \sigma_\beta)(1 - (1 + y)^{\frac{1}{2}})}{K^1} \qquad 1.(52)$$

$$\sigma_{\beta\beta} = \frac{\sigma_\beta}{2} \quad \frac{(\sigma_\alpha + \sigma_\beta)(1 - (1 + y)^{\frac{1}{2}})}{K^1} \qquad 1.(53)$$

$$\sigma_{\alpha\beta} = \frac{-\,2(\sigma_\alpha + \sigma_\beta)(1 - (1 + y)^{\frac{1}{2}})}{K^1} \qquad 1.(54)$$

where $$K^1 = 4(\frac{1}{K} - 1) \qquad 1.(55)$$

and $$y = \frac{K^1\,\sigma_\alpha\,\sigma_\beta}{(\sigma_\alpha + \sigma_\beta)^2} \qquad 1.(56)$$

Substitution of these equations into equation 1.(51) yields the molal interaction energy which is the negative of the cohesive energy

$$E = \frac{\sigma_\alpha\varepsilon_{\alpha\alpha}}{2} + \frac{\sigma_\beta\varepsilon_{\beta\beta}}{2} - \frac{(\sigma_\alpha + \sigma_\beta)\Delta\varepsilon}{K^1}\,(1 - (1+y)^{\frac{1}{2}}) \qquad 1.(57)$$

The intermolecular energy of the pure liquid can also be expressed in terms of the enthalpy of vapourisation.

$$\Delta H^o{}_V = \Delta E^o{}_V + P(V_g - V_\ell) \qquad 1.(58)$$

where ΔE^o_V is the change of internal energy on vapourisation and is given by

$$E^o_V = -E + \Delta E_{internal} + \Delta E_{external} \qquad 1.(59)$$

$\Delta E_{internal}$ is the difference between the energies of vibration and rotation of the atoms or groups in the molecule in the gaseous and liquid states and is assumed to be negligible except for chain molecules in which intra-molecula contacts are possible.

$\Delta E_{external}$ is the difference between the energies of translation and rotation of the molecules in the gaseous state and the vibrational and torsional energies in the liquid state. For chain molecules[30]

$$\Delta E_{ext} = -\left(\frac{5}{2}\right) RT, \qquad 1.(60)..a$$

while for spherical molecules

$$\Delta E_{ext} = -\left(\frac{3}{2}\right) RT \qquad 1.(60)..b$$

Thus the intermolecular energy, E, for a chain molecule liquid can be represented as

$$E = -\Delta H^{o}_{V} + P\Delta V^{o} - \left(\frac{5}{2}\right) RT \qquad 1.(61)$$

This allows the calculation of E when all other factors in the equation are known.

Consider now a mixture composed of two liquids. The change in intermolecular energy on mixing is, by approximation, assumed to equal the excess enthalpy of mixing, H^E.

$$\Delta E = E - x_1E_1 - x_2E_2 \qquad 1.(62)$$

where x_1 and x_2 are the mole fractions of components 1 and 2 whose intermolecular energies are given by E_1 and E_2. The intermolecular energy of the mixture is represented as E. Then,

$$H^E = E - x_1E_1 - x_2E_2 \qquad 1.(63)$$

since $$H^E \cong \Delta E \qquad 1.(64)$$

Substituting the expression for the intermolecular energy eq. 1.(57) in eq. 1.(62) and considering a system containing only two types of segments α and β in which there are n α-segments in component 1 and m β-segments in component 2, it can be shown that

$$H^E = -\left(\frac{nx_1\sigma_\alpha{}^{o} + mx_2\sigma_\beta{}^{o}}{K^1}\right)\Delta\varepsilon\left(1-\left(1 + \frac{K^1x_1\sigma_\alpha{}^{o}x_2\sigma_\beta{}^{o}nm}{(nx_1\sigma_\alpha{}^{o}+mx_2\sigma_\beta{}^{o})^2}\right)^{\frac{1}{2}}\right) \qquad 1.(65)$$

where $$x_1\sigma_\alpha^{\ o} = \sigma_\alpha \qquad 1.(66)$$

and $$x_2\sigma_\beta^{\ o} = \sigma_\beta \qquad 1.(67)$$

The expression is simplified when the ratio parameter r is introduced and defined as

$$r = \frac{\sigma_\beta^{\ o}}{\sigma_\alpha^{\ o}} \qquad 1.(68)$$

then

$$H^E = -\frac{\sigma_\alpha^{\ o}\Delta\varepsilon}{K^1}\left\{rm - x_1(rm - n)\right\}\left\{1 - \left(1 + \frac{K^1 rnm(x_1 - x_1^{\ 2})}{(rm-x\ \ (rm-n))^2}\right)^{\frac{1}{2}}\right\} \qquad 1.(69)$$

where $x_1 = 1-x_2$. Huggins then defined the analogous expression for the excess volume of mixing as

$$V^E = -\frac{\sigma_\alpha^{\ o}\Delta v}{K^1}\{ rm - x_1(rm - n)\} \times$$

$$\left\{1 - \left(1 + \frac{K^1 rmn(x_1 - x_1^{\ 2})}{(rm-x_1(rm-n))^2}\right)^{\frac{1}{2}}\right\}, \qquad 1.(70)$$

and the parameters r and K^1 should be consistent for both the excess enthalpy of mixing and the excess volume of mixing of the same mixture. Hence if there is experimental data for one excess property the other excess property can be determined with only one unknown parameter ($\Delta\varepsilon$ or Δv).

Equation 1.(70) will be expanded in the discussion (CH. V) and the experimental data will be analysed within the definitions of the theory.

II

MATERIALS

(a) PURIFICATION

(b) PYCNOMETRY

(c) SUMMARY

(a) PURIFICATION

A PERKIN ELMER F_{11} gas chromatograph with flame ionisation detection was used to analyse the materials at differing stages of treatment. The final purities obtained using various columns are listed in TABLE 1. All liquids were stored over clean dry sodium wire or dried molecular sieves (B.D.H. - type 4A) and were kept in a dark environment whilst not being used.

n-PENTANE[32] (UNIVAR - 99.2 MOLE %)

A sample was fractionally distilled through a 45 cm column packed with glass helices. The column had provision for a variable reflux ratio and the surrounding jacket was internally silvered before evacuation. This apparatus was used for all the simple distillations.

n-HEXANE (B.D.H. - 99.4 mole %, MERK (spectroscopic grade) 99.5 mole %)
n-HEPTANE (B.D.H. - 99.8 mole %, MERK (spectroscopic grade) 99.5 mole %)
n-OCTANE (B.D.H. - 99.7 mole %)

All these n-alkanes[32,33] were treated in an identical manner. The liquids were stirred with chlorosulphonic acid for several days and then exhaustively washed, firstly, with a 10% sodium bicarbonate solution and then with water. After drying over anhydrous calcium chloride they were distilled.

n-NONANE (KOCH-LIGHT - 99.3 mole %)
n-DECANE (KOCH-LIGHT - 99.5 mole %)

The preliminary treatment was the same as for the other n-alkanes, but both samples were distilled at reduced temperature and pressure in a pure nitrogen atmosphere (See fig. (1)). The column was similar to that used for simple distillations but without the added provision of a variable reflux ratio.

The PERKIN ADAPTOR[34] - (a) allowed fractions to be removed while the still remained isolated. The pressure regulator[35] (b) enabled the desired pressure to be obtained (manometer) and also regulated the gas flow to maintain that pressure.

CYCLOHEXANE (MERCK (spectroscopic grade) - 99.9_9 mole %)

Used without further purification

CYCLOHEPTANE[6] (R.N. EMMANUEL - 99.5 mole %)

CYCLOOCTANE[7] (ALDRICH (puriss) - 99.2 mole %, R.N. EMMANUEL - 99.0 mole %)

The cyclic alkanes were shaken with concentrated sulphuric acid until the yellow colour disappeared and were then washed with a 10% sodium bicarbonate solution followed by water. After drying over anhydrous calcium chloride they were distilled at reduced temperature and pressure.

CYCLODECANE (FLUKA - 99.5 mole %)

Because of its expense it was necessary to use the sample without any further purification. Several non-destructive treatments were investigated (eg. molecular sieves, activated carbon and alumina columns), but none produced any significant improvement in the purity.

BENZENE (B.D.H. - 98.0 mole %)

The sample was shaken with concentrated sulphuric acid for several weeks and then washed with a 10% sodium bicarbonate solution followed by water. After drying over anhydrous calcium chloride the sample was distilled and stored over sodium wire.

TABLE 1

HYDROCARBON	COLUMN	PURITY (mole %)
C_5H_{12}	A	99.7
C_6H_{14}	A,B	99.9_5
C_7H_{16}	A,B	99.9_8
C_8H_{18}	A,B	99.9_9
C_9H_{20}	B	99.9_9
$C_{10}H_{22}$	B	99.9_8
C_6H_{12}	A	99.9_9
C_7H_{14}	B	99.9_9
C_8H_{16}	B	99.9_9
$C_{10}H_{20}$	B	99.5
C_6H_6	C	99.9_9

A - 4 metre, 10 mass % Squalane on A.W.-D.M.C.S. CHROMOSORB W.

B - 4 metre, 10 mass % Didecyl phthalate on A.W.-D.M.C.S. CHROMOSORB W.

C - 3 metre, 15 mass % Ucon Oil on A.W.-D.M.C.S. CHROMOSORB W.

DISTILLATION OF CYCLOOCTANE

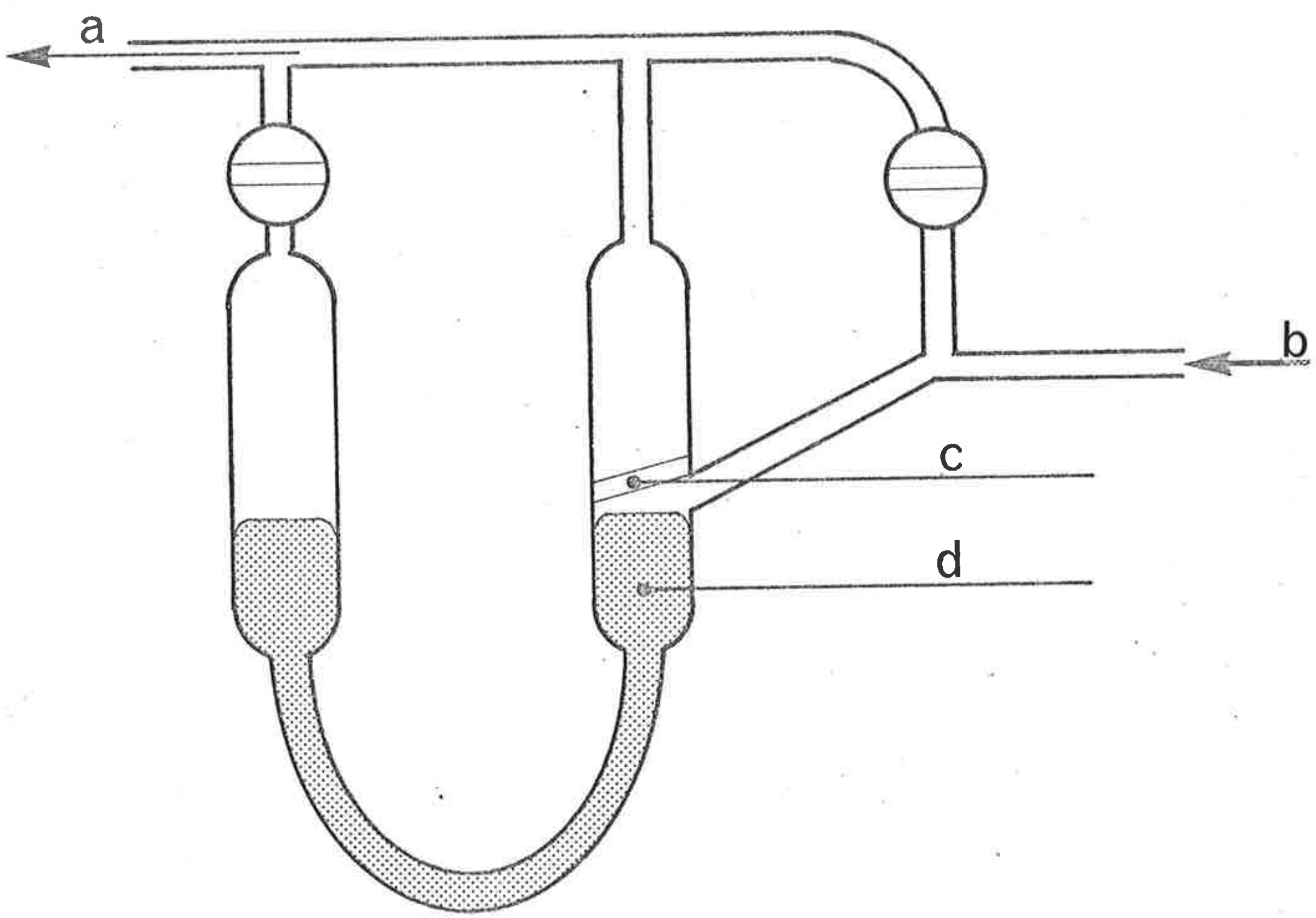
SINTERED GLASS MANOSTAT

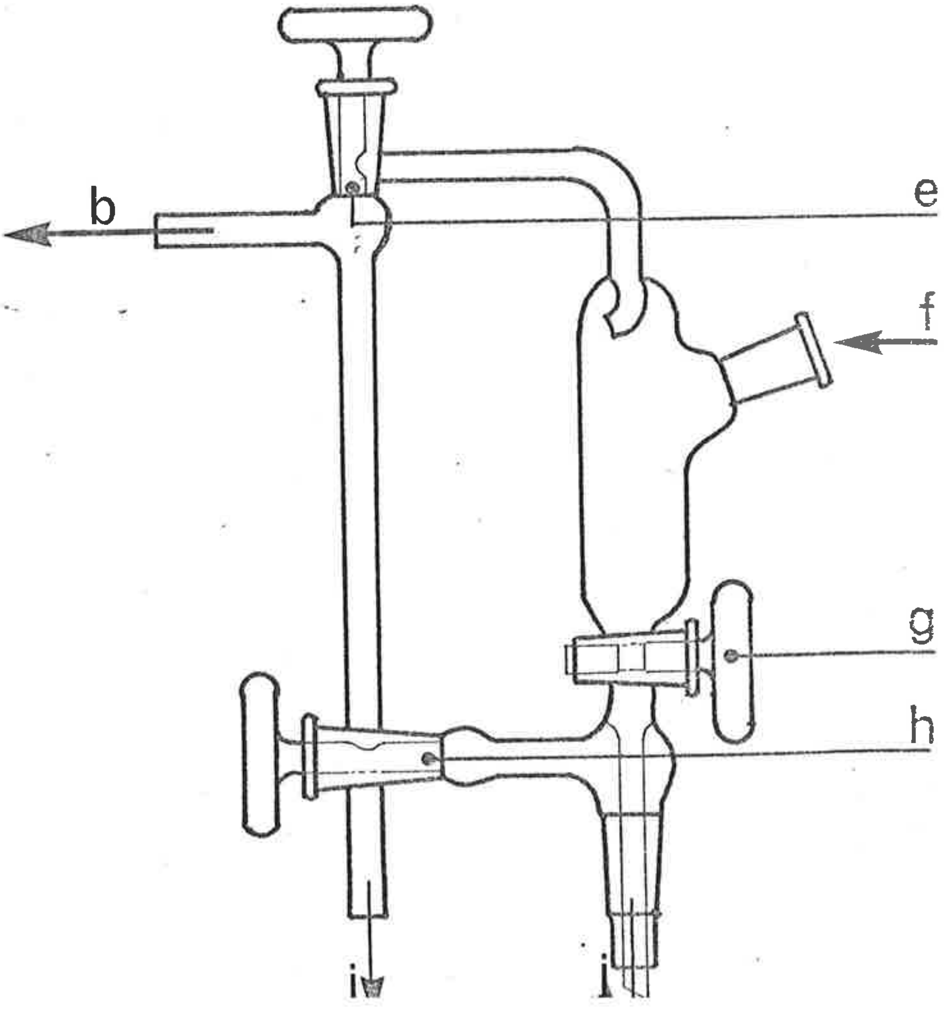
a. Vacuum Pump
c. Glass Sinter
d. Mercury

PERKIN RECEIVER ADAPTER

b. Manometer
e. Open
f. Still
g. Teflon Tap
h. Open
i. Air
j. Collection Flask

(1)





DISTILLATION
OF
CYCLOOCTANE

(b) PYCNOMETRY

The density of each of the hydrocarbons was determined as a final check of their purity. All densities were measured in duplicate. Four single stemmed pycnometers were used, the characteristics of which are summarised in APPENDIX I.

Before use, the pycnometers were cleaned with methanol and dried in a vacuum oven. Using a syringe, the pycnometers were filled with liquid which had been degassed only slightly. The liquids were not rigorously degassed before measuring their density due to the consequent difficulties involved in filling the apparatus with samples of comparable quality.

After allowing the open pycnometers to equilibrate for at least thirty minutes in the water bath (298.150 K ± 0.001K), the menisci were adjusted as close as possible to the reference mark. The capillary above the meniscus was dried and the distance between the reference mark and the meniscus was measured with a cathetometer (PRECISION TOOL & INSTRUMENT CO. LTD., SURREY, ENGLAND).

On removal from the bath the pycnometers were capped, rinsed and gently dried. A sealed water filled tare was treated similarly and placed with the pycnometers in the balance case (METTLER, B6C200 BALANCE) to equilibrate.

The tare and the pycnometers were weighed at intervals of 30-60 minutes over the next 3-4 hours. The ambient conditions - measured with wet and dry bulb thermometers and the barometric pressure - were noted several times and these values were used for calculation of the air density.[38] The tare weight monitored the changes in air density, thus the evaporation from the pycnometers could be measured. Extrapolating to the initial time the pycnometers were placed in the balance case enabled the total vapour loss to be calculated and more accurate weights obtained.[39]

The equation used for density calculations is included in APPENDIX I. All experimental densities together with their literature values are tabulated in Table 2.

TABLE 2

Densities of Liquids at 298.150 K and 1 atm.

HYDROCARBON	THIS WORK (g cm^{-3})	LITERATURE (g cm^{-3})
C_5H_{12}	0.62158 0.62164	0.62137[10]
C_6H_{14}	0.65480,3 0.65479	0.65479[10]
C_7H_{16}	0.67951,2 0.67948,7	0.67949[10]
C_8H_{18}	0.69851 0.69849	0.69847[10]
C_9H_{20}	0.71381,2	0.71379[10]
$C_{10}H_{22}$	0.72611,2,1,4	0.72623[10]
C_6H_{12}	0.77387,4	0.77387[10]
C_7H_{14}	0.80676,3	0.8066[11,2]
C_8H_{16}	0.83200,2 0.83199,8	0.83201[12,3]
$C_{10}H_{20}$	0.85468 0.85470	0.8575,7[13,4]
C_6H_6	0.87364$_5$,5	0.87364$_8$[9,5]

(c) SUMMARY

> "When $\tilde{V}^E$ is determined directly, the purity of the components is not very critical .... The previous comments with respect to purity must be hedged by knowledge to the extent and nature of the impurities."

R. BATTINO[44]

"Volume Changes on Mixing for Binary
Mixtures of Liquids" Chem.Rev. (1971),
71, 5.

There was little analysis of the liquids used in these studies to discover the exact nature of the impurities present. It was thus decided to use samples of very high purity ($\geqslant$ 99.9 mole %) and except for n-pentane and cyclodecane (99.7 mole %, 99.5 mole %) this was achieved.

Results have often been quoted using liquids of purity less than that discussed here and in most cases there appeared to be little effect on these results. However, for systems containing cyclodecane and to a lesser degree n-pentane much less confidence can be had concerning the results than for the other systems.

III

APPARATUS

- (a) INTRODUCTION
- (b) DESIGN
- (c) TEMPERATURE CONTROL
- (d) EXPERIMENTAL
  - (i) PROCEDURE
  - (ii) CALCULATIONS
  - (iii) STANDARD SYSTEM
- (e) SOURCES OF ERROR

(a) INTRODUCTION

The methods[44] that have been most commonly empolyed for determining the excess volumes are pycnometry, magnetic float and single data point per loading dilatometers.

Both pycnometry and magnetic float enable the excess volume to be calculated from density measurements. As these indirect procedures introduce many uncertainties, direct determination of the excess volume using dilatometers are preferred.

Keyes and Hildebrand[45] published details of their dilatometer in 1917 and this formed the basis for modifications by later workers. Two of the more accepted designs were those due to Bellemens[46] and Duncan, Sheridan and Swinton[47], both of which could measure the excess volume of mixing to a precision of better than ± 0.5%. The most serious disadvantage of this and the earlier methods was the time consumed for a single experiment.

To overcome this, a dilatometer capable of making measurements at several different compositions per loading was described in 1937 (Geffken, Kruis and Solana)[48]. The apparatus was unsuitable for use with organic solvents as the components had to pass through a greased tap. Subsequent desgins showed marked improvements although several serious problems were still involved e.g. Demyster and van der Waals[49] (rigorous filling procedure), Beath[50] et. al. (liquid must be weighed for volume determinations).

Stokes et al. (1970)[51] developed a simple continuous dilution dilatometer which overcame many of the previous problems including elimination of the need to weigh and the necessity for only a mild degassing of liquids. The dilatometer used in this work was a modification of the Stokes' design.

(b) DESIGN

Several modifications were made to the dilatometer of Stokes et al.[51] by Martin and Murray (1971).[52] A tap, T_1, was included below the U-bend connecting the burette to the mixing vessel which allowed for simpler cleaning and filling procedures. The sealing assemblies at the top of the mixing vessel and burette were also altered and these underwent further modifications in this work.

Both sealing assemblies were replaced by all-glass fittings, enabling all the liquid to be seen. The burette was sealed by using a ROTOFLOW valve (TF2/C1/13, QUICKFIT & QUARTZ, STAFF., ENGLAND). A threaded glass needle valve (1.25 mm, FISCHER & PORTER, PENN., U.S.A.) sealed the mixing vessel and allowed very fine adjustments of the volume in the mixing vessel. The inlet tube, I, which passed through the side of the mixing vessel eminated from a small reservoir above the large bore burette.

Minor modifications to the dilatometer were made by replacing the pulley operated tap on the reservoir capillary, with an ordinary tap T_3, which was operated by a pulley fitting not attached to the framework. Taps 2 and 3 were SOLVAC spring loaded taps, while Tap 1 was of the INTERKEY spring loaded type. All taps were individually ground into their barrels.

Several advantages of the new design became apparent:

(i) As all liquid could now be seen, the problem of detecting trapped air bubbles was eliminated. If excess liquid was kept in sidearms A and B, any air bubbles could be expelled by opening the respective valve.

(ii) The dilatometer could be filled in the bath.

(iii) The brass frame on which the apparatus was mounted was levelled in a horizontal plane before any $\tilde{V}^E$ measurements were made. The dilatometer was locked in position and only adjustments to align the apparatus had then to be made.

After determining $\tilde{V}^E$ for several systems it was observed that the apparatus allowed no overlapping mole fraction range in the region 0.35 - 0.55 mole fraction. The disparity was of the order of 0.08 - 0.10 mole fraction. The congruency[20,9] of the $\tilde{V}^E$ curves in this region was used as a test of the accuracy of the results. The reason for the absence of cross-over was attributed to the large volume of liquid in the mixing vessel. Subsequently this volume was reduced and a crossover region obtained.

All relevant volume calibrations were determined using distilled mercury. The mercury was weighed in clean, dry flasks on a balance (METTLER - BC1000-H31) in a room in which constant ambient conditions prevailed.[38]

Major errors in the calibrations resulted from the alignment of the dilatometer and the cathetometer (PRECISION TOOL & INSTRUMENT CO., SURREY, ENGLAND) and the error in reading the scale of the cathetometer. These errors coupled with those due to the inability to deduce the position of the meniscus caused by illumination effects. The greatest overall error was estimated to be ± 0.003 cm. A table of the calibrations with estimates of the errors involved appears in APPENDIX II.

(c) TEMPERATURE CONTROL

The apparatus required extremely good temperature control to ± 0.001K or better as small temperature variations would produce contraction or expansion of the liquids in the measuring capillary which leads to a direct error in the volume mixing.

A circuit which gave excellent temperature control of ± 0.0005K was used. The circuit was basically a WHEATSTONE bridge. A mains regulated D.C. bridge was connected in series with a thermistor probe (S.T.C. type F - rated 10 KΩ at 293K) which consisted of a thermistor located in a small pool of mercury in a thin stainless steel cap at the end of a 45 cm. brass tube. The purpose of the mercury was to maintain good thermal contact between the thermistor and the water bath.

Any out of balance signal across the bridge was amplified and fed to a pen-recorder (PHILIPS P.R. 2210A/00). Connected mechanically to the main shaft of the recorder was a potentiometer such that any deflection of the pen about the balance position altered the output of the potentiometer. A 10 KΩ resistance box (W.G. PYE & CO., CAMBRIDGE, ENGLAND) was used to balance the recorder. The temperature was set at the null position (298.000 K) using a total immersion bomb calorimeter thermometer. All thermometers used were checked periodically with a LEEDS & NORTHRUP platinum resistance thermometer and all measurements were made within the region 298.150K ± 0.010K.

The temperature was maintained by connecting the potentiometer to a 100 Watt light bulb immersed in the water bath. When the bulb was illuminated the thermistor was heated, its resistance changed and the out of balance signal amplified and fed to the recorder. The subsequent pen deflection caused the potentiometer output to decrease and the bulb intensity to diminish. The bath temperature eventually fell below the "null" and the thermistor resistance changed. The resulting signal caused an opposite deflection of the potentiometer and the intensity of the illumination increased in proportion to the signal.

An oscillation of temperature around a mean value was thus attained, and the cycle time was dependant on the relative positions of the light bulb and the probe. The optimum cycle time for excess volume measurements was approximately 10 seconds.

During measurements of the excess volume the temperature was controlled to a constancy of better than ± 0.001K. Density measurements were made in the same bath with identical temperature control.

(d) EXPERIMENTAL

(i) PROCEDURE. The dilatometer was evacuated through the $\tilde{V}^E$ capillary and filled with mercury through tap T_1. A syringe with a needle especially adapted to fit into C (figs. 2, 3) was used to introduce component 1 into the burette. The burette was then sealed and the apparatus placed in the water bath.

Liquid in the burette expanded and a small volume entered the mixing vessel through the inlet tube and bubbled up through the mercury. After allowing the apparatus to equilibrate for approximately 30 minutes the liquid in the mixing vessel was removed with a syringe and the mixing vessel rinsed 5 or 6 times with component 2. The mixing vessel was then filled with component 2, allowed to equilibrate and sealed.

The procedure during measurements was very similar to that of Stokes et al.[51]

(ii) CALCULATIONS. If the levels in the mixing vessel and excess volume capillary before and after an addition were M_3, M_4 and $M_3{}^1$, $M_4{}^1$ respectively, the volume could be approximated to

$$\Delta V = (M_4{}^1 - M_4) \, . \, a \text{ cm}^3,$$

where a is the cross-sectional area of the capillary.

However, any change in the level of the mercury in the $\tilde{V}^E$ capillary altered the pressure acting on the system. The expression was modified to include the pressure change which occurred because of the addition.

Thus

$$\Delta V = \{(M_4 - M_4{}^1) + [(M_4{}^1 - M_3{}^1) - (M_4 - M_3)]b\}a.,$$

where b is the compressibility factor.

The compressibility factor, b, was measured before and after each run by plotting the change in mercury level in the $\tilde{V}^E$ capillary against the applied pressure. The gradient obtained from such a plot was equal to b. The factor, b, varied no more than 0.1% between the two sets of measurements.

This alleviated the necessity to measure b at several intermediate points and to interpolate to calulate b for each addition.

Measuring the mercury level in the burette before and after an addition allowed the volume added to the mixing vessel to be calculated. The total volume of component 1 added could then be determined while the volume of component 2 in the mixing vessel was known (total mixing vessel volume - volume change on mixing). The mole fraction corresponding to each addition was determined from the respective volumes added and the molar volumes of the components.

(iii) STANDARD SYSTEM. Cyclohexane-benzene is widely accepted as the reference system[44] for $\tilde{V}^E$ measurements. The present results were compared with those of Stokes et al., which were considered the most acceptable[52] in terms of precision of all the data published recently.

Using the dilatometer which allowed no cross-over the agreement was of the order of ± 0.001 cm^3/mole. However, in the 0.45 - 0.55 mole fraction range the agreement was of the order of 0.0015 cm^3/mole . Despite the disparity in this region there was acceptable random scatter of the points around the least squares curve and the agreement was considered reasonable.

The data obtained using the modified dilatometer was in excellent agreement with that of Stokes, to a precision of better than ± 0.001 cm^3/mole over the entire mole fraction range and again there was good scatter of points.

The smoothing equation used for the least squares plot is included in CHAPTER 4, the coefficients and standard deviations of fit are listed in Table 4.

(e) SOURCES OF ERROR

The possibility of the liquids diffusing through the inlet tube, I, during $\tilde{V}^E$ measurements was the major concern as regards the dilatometer design. The rate of diffusion was measured by observing the meniscus change in the $\tilde{V}^E$ capillary over a period of 6 hours. The results indicated that the volume change attributable to diffusion could be no more than ± 0.002 cm^3.

Misalignment of the apparatus was also a possible source of error. The cathetometer scale (PRECISION TOOL & INSTRUMENT CO., SURREY, ENGLAND) was levelled using a precision spirit levelling device containing a methanol bubble and which was very sensitive to small variations in angle. The telescope was levelled in the horizontal mode by aligning the cross hairs with the menisci in a mercury filled U tube. The dilatometer was aligned vertically using the $\tilde{V}^E$ capillary as a guide with the cathetometer in one plane and a plumb line in the other. All of these settings were checked before each series of excess volume measurements.

Errors involved in the calibration of the dilatometer (APPENDIX II) amounted to less than ± 0.05% of the excess volume. The contribution to the excess volume by any errors in the compressibility factor were negligible (less than 0.1% change over compressibility readings). The main source of error involved in the excess volume determination is the random observer error while making measurements.

CONTINUOUS DILUTION DILATOMETER

a. Pulley Handle

b. Reservoir

c. Reservoir Capillary

d. $\bar{V}_E$ Capillary (0.75 mm)

e. Mixing Vessel (2 mm) Capillary

f. Tap T_3

g. $\ell = F_4$ (Fiducial Mark 4)

h. Pulley

i. Tap T_2 - Pulley Operated

j. Tap T_1

k. Small Bore (4 mm) Burette Section

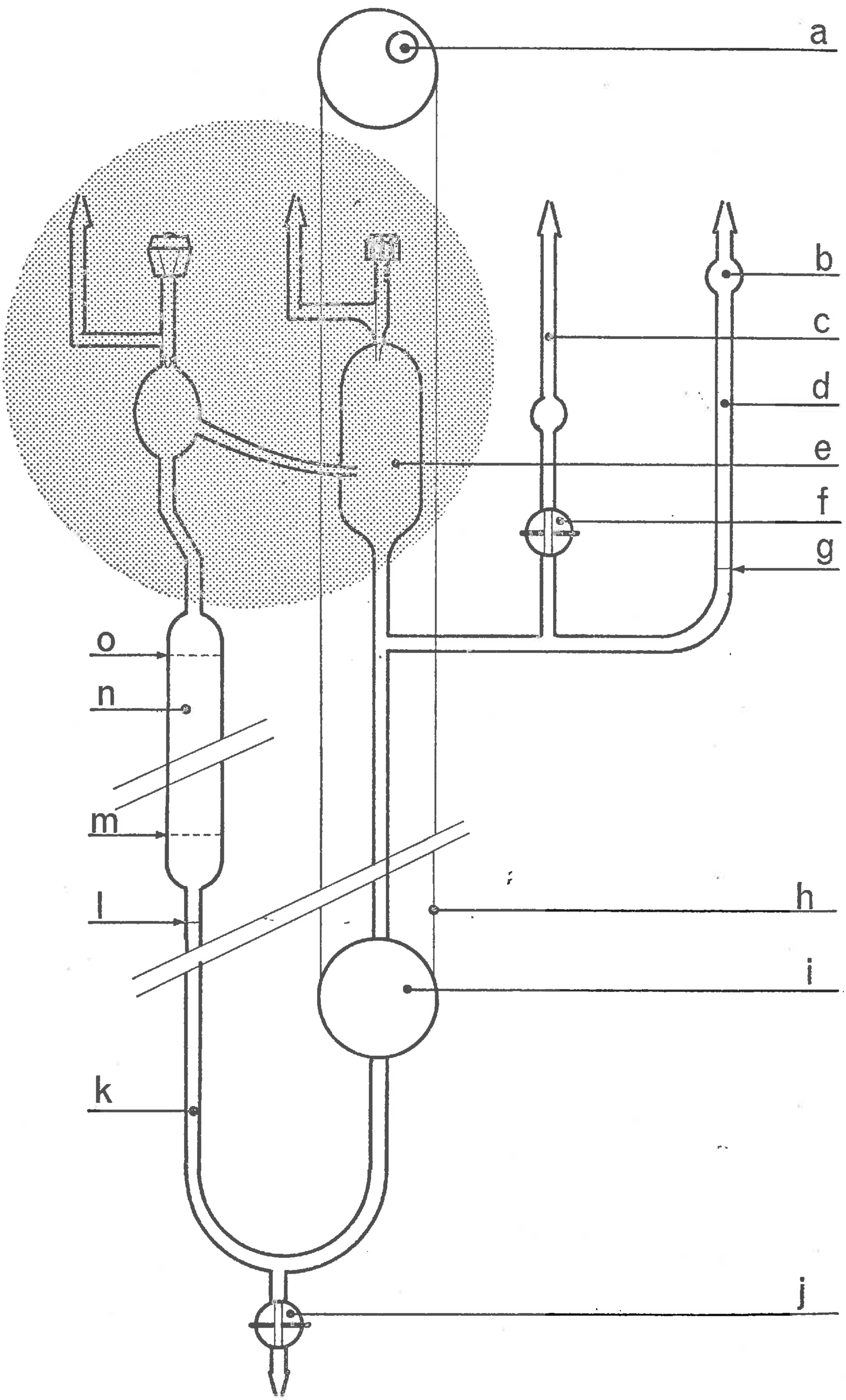
l. $\ell = F_1$ (Fiducial Mark 1)

m. F_1 + 2.500 cms.

n. Large Bore (8 mm) Burette Section

o. $\ell = F_2$ (Fiducial Mark 2)

(2) Continuous Dilution Dilatometer



ENLARGEMENT OF DILATOMETER TOP

(INCLUDING SEALING ATTACHMENTS)

a. Threaded Glass Needle Valve

b. Threaded Inside

c. B

d. Mixing Vessel

e. Inlet Tube

f. Glass Encased Magnet

g. $\ell = F_3$ (Fiducial Mark 3)

h. Attached to Burette

i. C

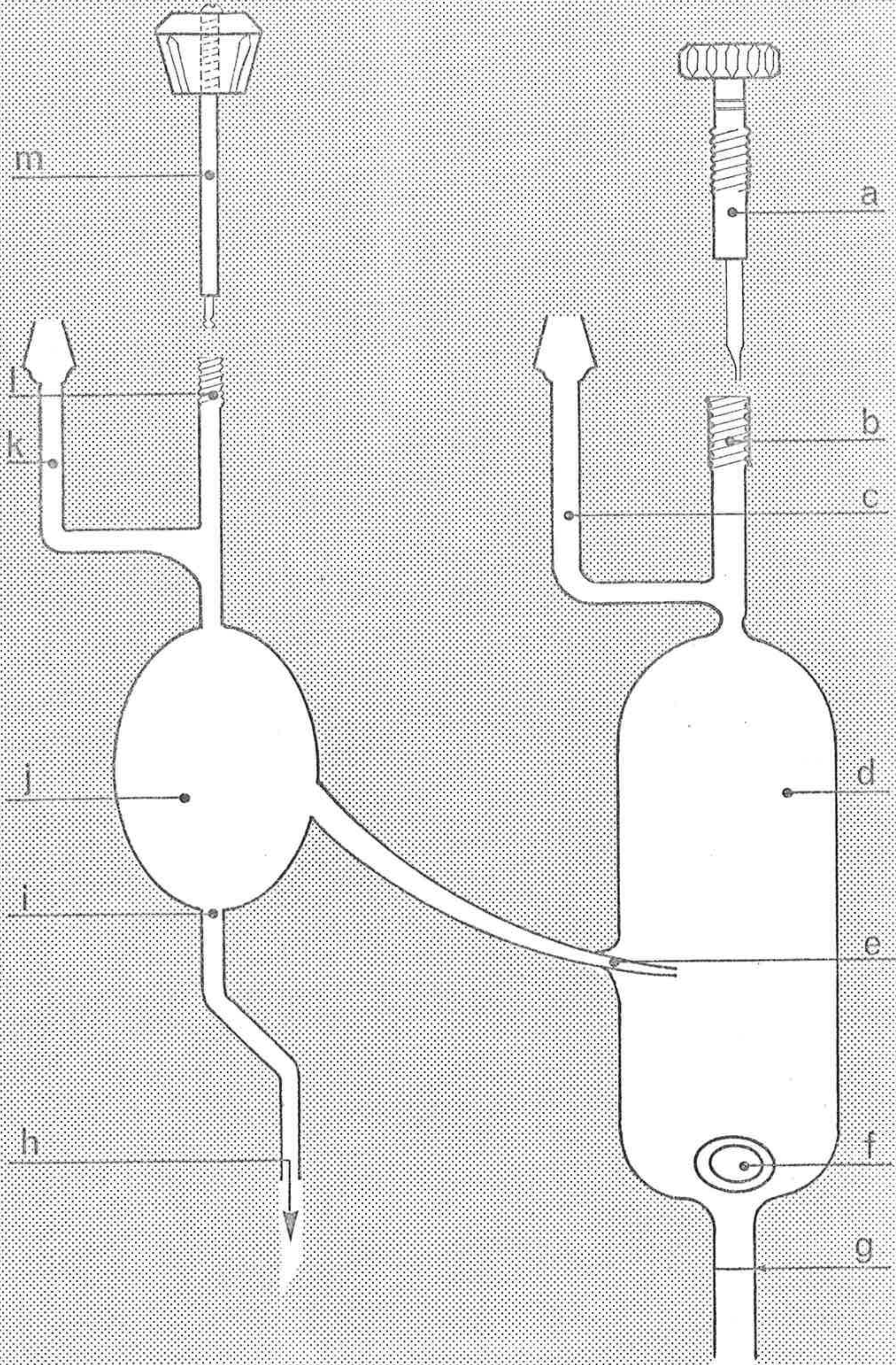
j. Burette Reservoir

k. A

l. Threaded outside

m. Rotaflo Valve

(3)



ENLARGEMENT OF DILATOMER TOP

IV

RESULTS

(a) SMOOTHING EQUATION

The excess volumes for all n-alkane-cycloalkane systems were measured at 298.150K and the results calculated using the appropriate formula (P28), which was incorporated in the computer program "DELTAVE" (APPENDIX IV). The composition dependance of the excess volume is represented graphically at the end of this section for each series of n-alkanes with different cycloalkanes.

SMOOTHING EQUATION

A polynomial of the form

$$\tilde{V}^E = x_1x_2\{A + Bx_1 + Cx_1^2 \ldots\ldots\ldots\ldots\ldots\}$$

$$= x_1x_2 \sum_{j=0}^{n} Ajx_1^j ,$$

was used in the general non-linear least squares program "EXFIT" (APPENDIX IV) The number of terms in x_1, where x_1 is the mole fraction of the n-alkane (or first named component) varied from n = 2-4 as the standard deviation minimised and the random scatter of points maximised.

The least squares method fixed $\bar{V}^E$ at $x_1 = 0$ and $x_1 = 1$, however, the results of several systems indicated a failure of the equation to reproduce data as x_1 approached unity, and the polynomial was probably not correctly weighted in this region.

A summary of the coefficients, Aj, obtained appear in TABLES 3 and 4, together with the standard deviation of the points. The experimentally measured excess volume, the calculated excess volume and the difference between (EXVOL) are tabulated for all systems in APPENDIX III.

TABLE 3

SMOOTHING EQUATION

$$\bar{V}^E = x_1x_2\{A + Bx_1 + Cx_1^2 + Dx_1^3\}\ \mathrm{cm^3\ mol^{-1}}$$

SYSTEMS	A	STANDARD DEVIATION OF A.	B	STANDARD DEVIATION OF B	C	STANDARD DEVIATION OF C	D	STANDARD DEVIATION OF D.	Standard Deviation of Fit
n-PENTANE/ CYCLOHEXANE	-0.120	0.003	-1.074	0.014	0.240	0.014	-	-	0.000_5
n-HEXANE CYCLOHEXANE	1.054	0.002	-1.558	0.018	1.074	0.038	-0.313	0.025	0.000_2
n-HEPTANE/ CYCLOHEXANE	1.990	0.021	-2.545	0.014	2.163	0.300	-0.715	0.194	0.001
n-HEXANE/ CYCLOHEPTANE	0.026	0.015	-2.732	0.104	2.596	0.227	-1.003	0.153	0.001
n-HEPTANE/ CYCLOHEPTANE	0.969	0.016	-3.048	0.113	3.280	0.246	-1.356	0.164	0.001
n-OCTANE/ CYCLOHEPTANE	1.715	0.017	-3.727	0.116	4.207	0.249	-1.885	0.164	0.001
n-HEXANE/ CYCLOOCTANE	-0.811	0.013	-3.101	0.090	2.496	0.195	-1.072	0.131	0.001
n-HEPTANE/ CYCLOOCTANE	0.266	0.014	-3.489	0.100	3.446	0.215	-1.444	0.145	0.001
n-OCTANE CYCLOOCTANE	0.868	0.024	-3.454	0.167	3.765	0.356	-1.680	0.234	0.002
n-NONANE/ CYCLOOCTANE	1.516	0.011	-4.968	0.107	8.774	0.367	-8.389	0.511	0.000_6
n-DECANE/ CYCLOOCTANE	1.388	0.020	-0.794	0.129	-0.377	0.267	0.428	0.173	0.001

TABLE 3

Continued......

n-HEPTANE/ CYCLODECANE	-0.524	0.054	-4.552	0.221	2.051	0.220	-		0.005
n-OCTANE CYCLODECANE	0.021	0.019	-5.720	0.129	6.411	0.279	-2.930	0.188	0.001
n-NONANE/ CYCLODECANE	0.566	0.018	-5.941	0.132	6.911	0.294	-3.001	0.200	0.002
n-DECANE/ CYCLODECANE	1.070	0.034	-6.419	0.242	7.848	0.515	-3.458	0.338	0.003

TABLE 4

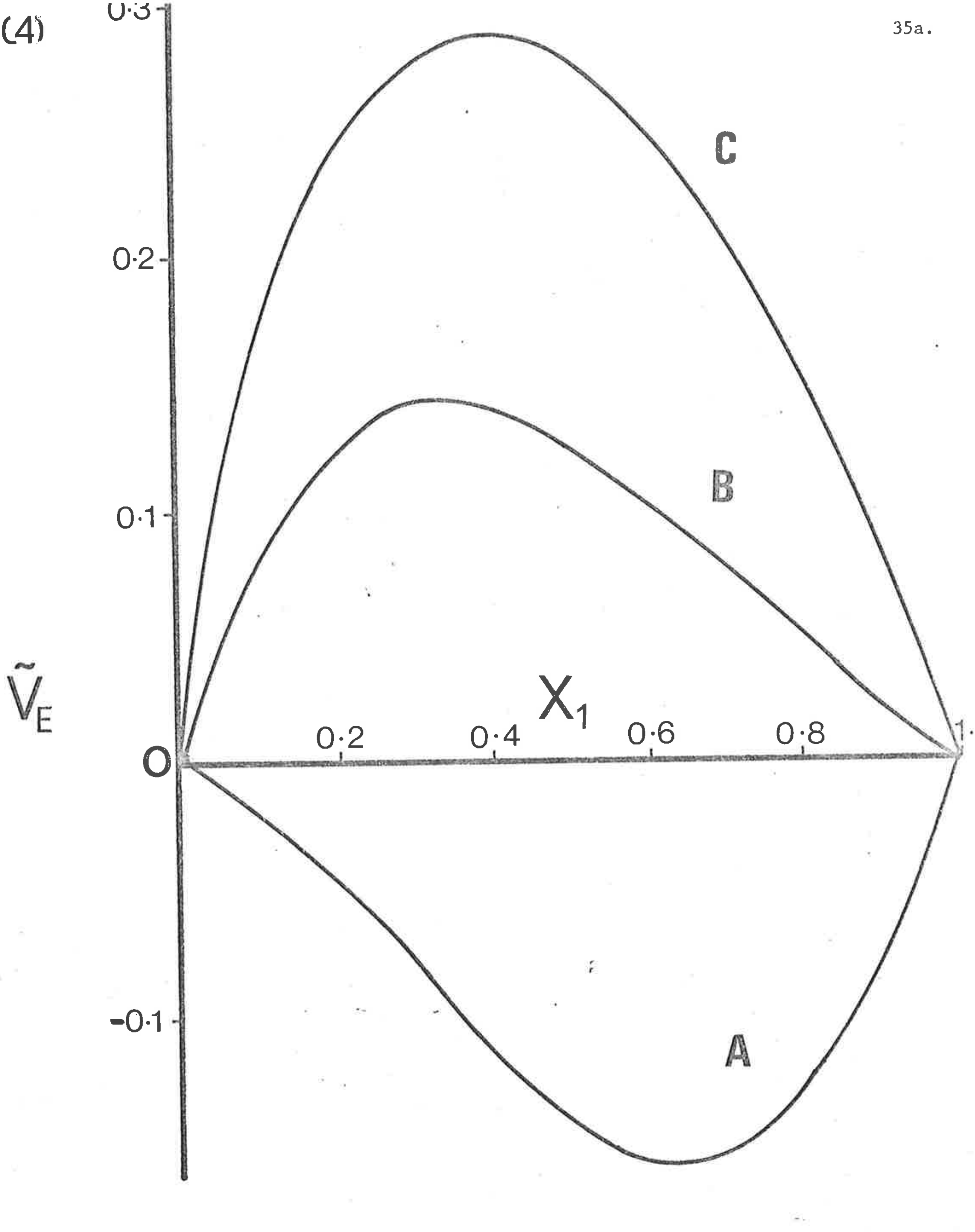
STOKES' DATA

CYCLOHEXANE/BENZENE

$$\bar{V}_E = x_1 x_2 \{A + Bx_1 + Cx_1^2\} \text{ cm}^3 \text{ mol}^{-1}$$

	A		B		C
DILATOMETER 1	2.550	0.044	0.031	-	0.003
STOKES' DATA (n = 2)	2.543	0.084	0.049	-	0.008
STOKES' DATA (n = 3)	2.551	-0.030	0.312	0.121	0.006

(4)

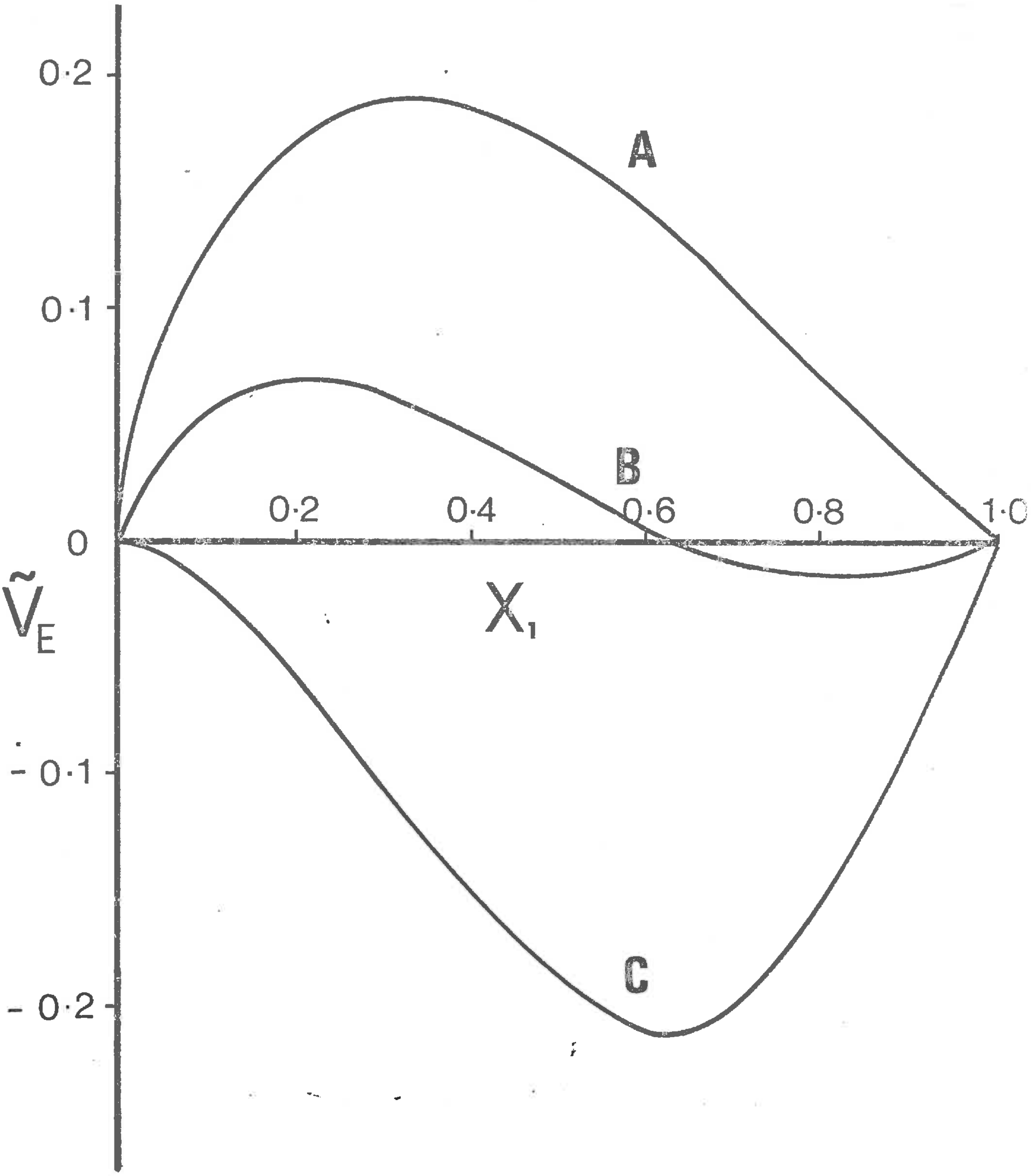


VOLUMES OF MIXING OF CYCLOHEXANE WITH

A N-PENTANE **C** N-HEPTANE

B N-HEXANE

X_1 = MOLE FRACTION OF N-ALKANE



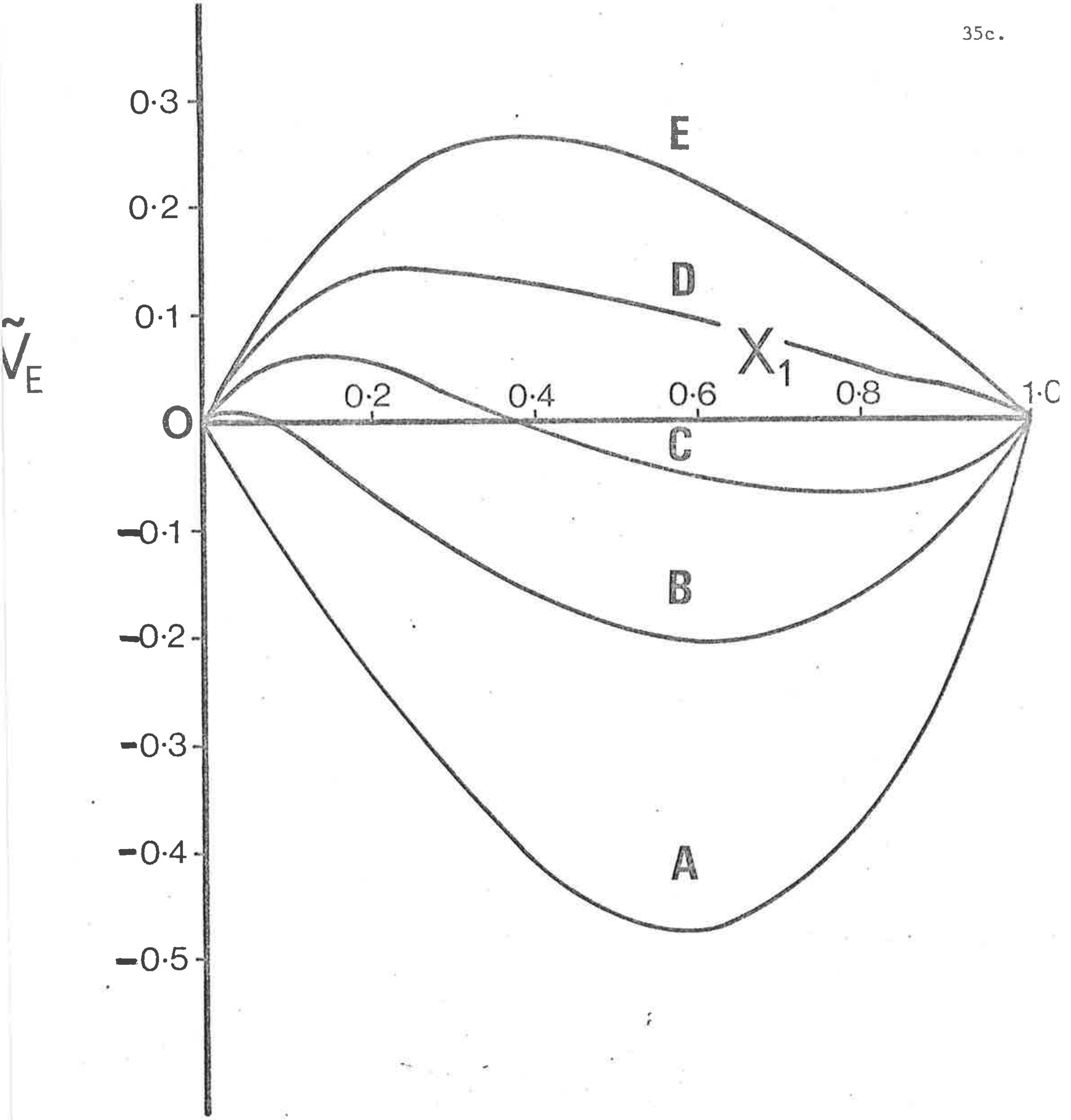
Volumes mixing of cycloheptane with

A N - Octane

B N - Heptane

C N - Hexane

X_1 = mole fraction N - Alkane



VOLUMES OF MIXING OF CYCLO-OCTANE WITH

A N-HEXANE

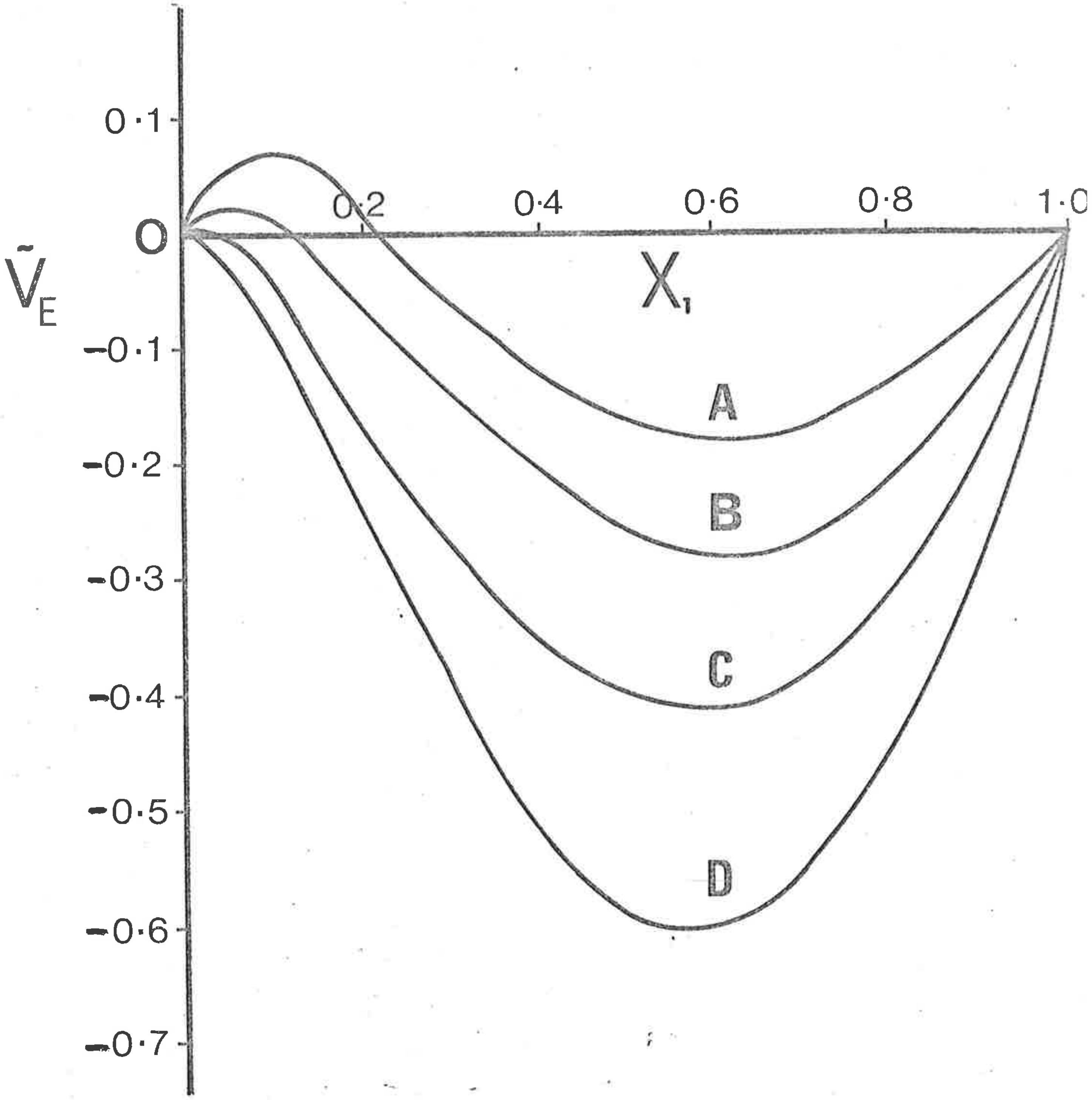
B N-HEPTANE

C N-OCTANE

D N-DECANE

E N-NONANE

X_1 = MOLE FRACTION OF N-ALKANES



Volumes of mixing of cyclodecane with

A Decane
B Nonane
C Octane
D Heptane

X_1 = mole fraction N- Alkane

V

ANALYSIS

(a) INTRODUCTION

(b) HUGGINS' THEORY

(c) FLORY'S THEORY

INTRODUCTION

In the following sections, the results for the various systems are used to test the theoretical models of Flory and Huggins.

Both authors have already studied the thermodynamic properties of simple n-alkane mixtures and have found good agreement between their theoretical equations and the experimental data. A further extension of the theories is an application to the more complex n-alkane-cycloalkane systems that have been studied in this work.

The main purpose of this work was to study the suitability of the theory of Huggins in his application to the n-alkane-cycloalkane series and his treatment will be examined in more detail.

HUGGINS' THEORY

All of the systems studied in this work are considered to be ditonic in that there are only two types of segments present, α and β. However, within this general limitation there are various approaches that can be used to study ditonic systems and these are discussed below:-

(i) Each component of the mixture is considered to be composed only of monotonic molecules. i.e. each molecule is considered to be one segment. Huggins[67] has used this approach for molecules as large as n-hexadecane.

$$\bar{V}^E = \frac{V_\Delta}{K^1}(r-x_1(r-1))\left\{1-\left[1+\frac{K^1 r\ (x_1-x_1^2)}{(r-x_1(r-1))^2}\right]^{\frac{1}{2}}\right\} \qquad 1.(70)$$

where x_1 is the mole fraction of component 1, and V_Δ is the volume parameter.

$$V_\Delta = \sigma_\alpha{}^\circ \Delta v/2 \qquad 4.(1)$$

The equilibrium constant K can be written

$$K = (1 + K^1/4)^{-1}\ , \qquad 1.(55)$$

and the segment ratio r is

$$r = \frac{\sigma_\beta{}^\circ}{\sigma_\alpha{}^\circ} \qquad 1.(68)$$

Thus

$$\bar{V}^E = F(x_1, V_\Delta, R, K). \qquad 4.(2)$$

For a system approaching a situation of complete randomness of contact formation, the equation reduces to

$$\bar{V}^E = \frac{V_\Delta}{2}\{r(x_1-x_1^2)/[r-x_1(r-1)]\} \qquad 4.(3)$$

(ii) Extending this idea to a system in which a component molecules ~~are~~ composed of n α-segments and m β-segments, respectively.

The equation can be written,

$$\bar{V}^E = \frac{V_\Delta}{K^1}(rm-x_1(rm-n))\left[1-\left\{1+\frac{K^1 r.m.n(x_1-x_1^2)}{(rm-x_1(rm-n))^2}\right\}^{\frac{1}{2}}\right] \qquad 1.(70)$$

(iii) The more complex form of the expression for the excess volume of a mixture involves considering a system in which both components have α- or

β—segments. i.e. component 1 has n_1 α-segments and m_1 β-segments and component 2 has n_2 α-segments and m_2 β-segments.

The total number of α-segments is described as

$$Y = A + C \qquad 4.(4)$$

where

$$A = x_1 n_1 \quad \text{and} \quad C = x_2 n_2 \qquad 4.(5)$$

and the total number of β-segments,

$$X = B + D \qquad 4.(6)$$

where

$$B = x_1 m_1 \quad \text{and} \quad D = x_2 m_2 \qquad 4.(7)$$

It follows that

$$\begin{aligned}\bar{V}^E = -\frac{V_\Delta}{K^1}\Bigg\{&(Y + Xr)\left(1 - \left[1 + \frac{YXK^1 r}{(Y+Xr)^2}\right]^{\frac{1}{2}}\right) \\ &- (A + Br)\left(1 - \left[1 + \frac{ABK^1 r}{(A+Br)^2}\right]^{\frac{1}{2}}\right) \\ &- (C + Dr)\left(1 - \left[1 + \frac{C.D.K^1 r}{(C+Dr)^2}\right]^{\frac{1}{2}}\right)\Bigg\}\end{aligned} \qquad 4.(8)$$

Equations 1.(70), 4.(3) and 4.(8) have been used to analyse the experimental excess volume data obtained. The molar excess volume values were studied using a general non-linear least squares program (LCFHT - APPENDIX IV)

The theory predicts that the values of r are consistent for systems in which the types of segments are not altered. Also, if the contacts are random in nature, then K^1 will tend to zero. This work attempted to investigate the nature of these parameters and any trends present.

ANALYSIS

All the systems studied are considered to be ditonic in that only two types of segments are present and, as discussed earlier, can be expressed in one of three basic equations.

1. ONE SEGMENT/ONE MOLECULE

$$\bar{V}^E = -\frac{V_\Delta}{K^1}(r-x_1(r-1))\left[1-\left(1+\frac{K^1 r(x_1-x_1^2)}{(r-x_1(r-1))^2}\right)^{\frac{1}{2}}\right] \qquad 1.(70)$$

This form of the equation assumes that each n-alkane and cycloalkane molecule are monotonic or one segment where $r = \sigma_\beta^\circ / \sigma_\alpha^\circ$. 1.(68)

As a state of complete randomness is approached,

$$\bar{V}^E = \frac{V_\Delta}{2}\,\frac{r(x_1-x_1^2)}{[r-x_1(r-1)]} \qquad 4.(3)$$

Applying this expression for random orientations to the systems n-alkane--cyclohexane, the parameters r and V_Δ were determined. These values together with estimates of the error involved are included in TABLE 9. Similar calculations were made for the n-alkane-cyclooctane system, and these values are tabulated in TABLE 10.

There is no trend apparent for either the r values, which should be consistent, or the V_Δ values. Because of the inability to satisfy the paramete conditions, the cycloheptane and cyclodecane systems were not interpreted using EQ. 4.(3).

If the expanded form of EQ. 4.(3) is used, there is no consistent set of real solutions for any of the cycloalkane systems. The equilibrium parameter, K^1 tends to large negative values ($K^1 < -4$) and causes imaginary terms to be introduced, thus making any real solution impossible.

The "arbitrary" assumptions of the model used, that each molecule is monotonic, could be responsible for this failure. Only for systems which are composed of small molecules, for example the n-hexane or the n-pentane-cyclohexane systems might these assumptions be true. However as the chain length increases and more contacts are possible, differences may be observed.

2. TWO SEGMENTS/ONE MOLECULE

DELETE

Each molecule is considered as being composed of n α-segments and m β-segments so that extending EQ. 4.(3) gives

$$\bar{V}^E = -\frac{V_\Delta}{K^1}(Y+Xr)\left\{1-\left[1+\frac{K^1rYX}{(Y+Xr)^2}\right]^{\frac{1}{2}}\right\} \qquad 1.(70)$$

where,

$$Y = x_1n_1 + x_2n_2 \qquad 4.(4)$$

and

$$X = x_1m_1 + x_2m_2 \qquad 4.(6)$$

EXAMPLE

For the system n-hexane/cyclohexane the number of α-segments in C_6H_{14},

$$n_1 = 4,$$

and the number of β-segments.

$$m_1 = 2$$

In cyclohexane the number of α-segments

$$n_2 = 6$$

and the number of β-CH_3 segments

$$m_2 = 0.$$

Thus

$$Y = 6x_1 + 4x_2$$

and

$$X = 2x_1 + 0.$$

No real solutions of Eq. 1.(70) or its reduced form were found. The two reasons thought to contribute to the inability to determine any real solutions of the equations were:-

(i) As before $K^1 < -4$ and the argument becomes complex. If K^1 were limited to values greater than -4 still no solutions were found and the arguments diverged to increasingly larger values.

(ii) The size of the term Y, would unduly effect the size of $\bar{V}^E$.

EXAMPLE: n-hexane/cyclohexane

$$\begin{aligned} Y &= 6x_1 + 4x_2 \\ &= 6x_1 + 4 - 4x_1 \\ &= 2x_1 + 4. \end{aligned}$$

Hence Y oscillated about the value 4 and on doing so was unsensitive to the mole fraction

$$2 < Y < 4$$

The equation would not converge because of the arbitary nature of Y.

Equation 4.(3) is only an extension of Eq. 1.(70) and as such was thought to have many of the inherent arbitary assumptions associated with it.

3. TWO SEGMENTS/ONE MOLECULE

No solutions of the equation

$$\begin{aligned}\bar{V}^E = -\frac{V_\Delta}{K^1}\Bigg\{&(Y + Xr)\left(1 - \left[1 + \frac{YXK^1r}{(Y+Xr)^2}\right]^{\frac{1}{2}}\right)\\ &- (A + Br)\left(1 - \left[1 + \frac{ABK^1r}{(A+Br)^2}\right]^{\frac{1}{2}}\right)\\ &- (C + Dr)\left(1 \ \left[1 + \frac{C.D.K^1r}{(C+Dr)^2}\right]^{\frac{1}{2}}\right)\Bigg\}\end{aligned} \qquad 4.(8)$$

$A = x_1n_1$, $B = x_1m_1$

$C = x_2n_2$, $B = x_2m_2$

were found. The terms always took imaginary values.

The equations 1.(70), 4.(3) and 4.(8) in the previous discussion were derived by Huggins[25] from earlier work in which he formulated a power series, and the chain length was used as a variable to determine the molar excess volume

It was decided to complete this work investigating the equation for n-alkane-n-alkane mixtures as well as n-alkane-cycloalkane mixtures. Huggins has published details of his analysis using the power series for the excess enthalpy measurements of n-alkane-n-alkane mixtures.

4. POWER SERIES

The total intermolecular energy per mole for an n-alkane is the sum of a series of terms in powers of m, the number of α-type segments.

$$E_{\text{internal}} = am + b + \frac{c}{m} + \frac{d}{m^2} + \frac{d}{m^3}, \qquad 4.(9)$$

where

$$a = \sigma_\alpha{}^\circ\, \varepsilon_{\alpha\alpha}, \qquad 4.(10)$$

$$b = \frac{\sigma_\alpha{}^\circ r}{2}\,(2\varepsilon_{\alpha\beta} - \varepsilon_{\alpha\alpha}), \qquad 4.(11)$$

and r is the surface area of two methyl β-segments divided by $\sigma_\alpha{}^\circ$, thus b can be rewritten

$$b = \sigma_\beta{}^\circ \, \varepsilon_{\beta\beta}, \tag{4.(12)}$$

$$c = -\frac{\sigma_\alpha{}^\circ \, r^2 \, \Delta\varepsilon}{2.K}\,, \tag{4.(13)}$$

$$d = -\frac{\sigma_\alpha{}^\circ \, r^3 \, \Delta\varepsilon}{2\left(\frac{1}{K} - \frac{2}{K^2}\right)}\,, \tag{4.(14)}$$

$$e = -\frac{\sigma_\alpha{}^\circ \, r^4 \, \Delta\varepsilon}{2\left(\frac{1}{K} - \frac{5}{K^2} + \frac{5}{K^3}\right)} \tag{4.(15)}$$

The excess enthalpy of mixing can be represented as

$$H^E = E_{\text{internal}} - (x_1E_1 - x_2E_2) \tag{4.(16)}$$

$$= -K_c c - K_d d \tag{4.(17)}$$

where

$$K_c = \frac{x_1}{m_1} + \frac{x_2}{m_2} - \frac{1}{(x_1m_1 + x_2m_2)}\,, \tag{4.(18)}$$

and

$$K_D = \frac{x_1}{m_1{}^2} + \frac{x_2}{m_2{}^2} - \frac{1}{(x_1m_1 + x_2m_2)^2}\,. \tag{4.(19)}$$

If this relationship is true, and if terms higher than d in the power series are considered negligible, a plot of H^E/K_c versus K_D/K_c should be linear, with the intercept and the slope equal to -c and -d respectively. The points on such a graph should be consistent for various mixtures of n-alkanes at a specific temperature.

Applying Eq. 4.(16) in its similar form for the excess volume for mixtures of n-alkanes at 298.15K plotting V^E/K_c against K_D/K_c for various data, the following values are obtained:-

the slope = 50 ± 30

and the intercept = 3 ± 4.

The values of c and d would not reproduce the experimental results for any system.

CONCLUSION

The equations derived from the theory failed to satisfy any but the simplest data and this would support the idea that the methylene segments of the cycloalkanes differ in the nature of their interactions from those in the n-alkanes.

If this is the case, a tritonic system results in which three different segments are now present. Huggins[67] has derived the equation to represent the system but it has not been applied due to its complexity.

Several other factors which may also contribute to the failure of the theory are:

(i) The possibility of intra-molecular contacts in addition to inter-molecular contacts. The relative proportions of the two types depends both on the respective chain lengths and the concentrations. The longer the chain the more probable this behaviour would occur.

However, the author considers n-hexadecane as monotonic and, although ignoring different segment types and the possiblity of intra-molecular contact, achieves good agreement for his analysis[67] of the excess enthalpy of the system n-hexane with n-hexadecane.

(ii) There is a tendency in systems containing small non-spherical molecules for close packing to occur which would also influence the behaviour of the intermolecular contacts.

(iii) Cycloalkanes of order higher than cyclohexane exhibit a degree of polarity[59] and this could alter their relationship with the non-polar n-alkane molecules.

(iv) All of the above would produce a specific change in the orientation of the molecules. The factor which measures the randomness of the orientation of one segment relative to another is defined as k_3. However, no equation has yet been derived which includes this parameter.

A fundamental error could be due to the direct application of the equations which were formulated for the excess enthalpy of mixing to the excess volume of mixing, although Huggins believes it is a valid procedure. Further work to investigate the excess enthalpy of mixing of the n-alkane-cycloalkane series may solve this problem.

The inability of the 3-parameter Huggins theory to predict the results for these systems, led to further studies using the approach developed by Paul J. Flory.

The following section summarises the theory, treatment procedure, and the results obtained from its application.

PARAMETERS OBTAINED BY FITTING V^E DATA (EQ. 4 (3))

TABLE 9

n-ALKANES/CYCLOHEXANE	r	V_Δ (cm^3 mole^{-1})
n-Pentane -	3.7 ± 0.4	-0.71 ± 0.00
n-Hexane -	0.25 ± 0.1	2.25 ± 0.07
n-Heptane -	4.06 ± 0.01	0.40 ± 0.06

TABLE 10

n-ALKANES/CYCLOOCTANE	r	V_Δ (cm^3 mole^{-1})
n-Hexane -	2.2 ± 0.1	-2.64 ± 0.05
n-Heptane -	0.1 ± 0.05	-4.4 ± 0.9
n-Octane -	2.00 ± 0.00	-0.09 ± 0.04
n-Decane -	2.33 ± 0.06	1.34 0.01

FLORY

The theoretical reduced equation of state[3] for a pure liquid.

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)} - \frac{1}{\tilde{v}\tilde{T}} , \qquad 1.(26)$$

at zero pressure reduces to

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \qquad 1.(30)$$

The reduced variables as have been defined previously

(i) the reduced temperature,

$$\tilde{T} = \frac{T}{T^*} , \qquad 1.(24)$$

where T^* is the characteristic temperature and T is the absolute temperature.

(ii) the reduced volume

$$\tilde{v} = \frac{V}{V^*} , \qquad 1.(23)$$

where V is the molar volume and V^* is the characteristic molar volume. The reduced volume can also be calculated from α, the thermal coefficient of expansion by

$$\tilde{v} = \left\{\frac{(1 + \frac{4}{3} \alpha T)}{(1 + \alpha T)}\right\}^3 \qquad 1.(29)$$

(iii) the characteristic pressure

$$p^* = \gamma T \tilde{v}^2 ; \qquad 1.(31)$$

where γ is the thermal pressure coefficient.

The excess volume of mixing is defined as

$$V^E = V^* \tilde{v}^E \qquad 1.(42)$$

The characteristic volume of the mixture V^*, is described as

$$V^* = x_1 V_1^* + x_2 V_2^* \qquad 1.(41)$$

and the reduced excess volume, $\tilde{v}^E$, is given by

$$\tilde{v}^E = \tilde{v} - \tilde{v}^\circ \qquad 1.(39)$$

the difference between the reduced volume of the mixture, $\tilde{v}$, and the ideal reduced volume of the mixture, $\tilde{v}^{\circ}$.

$$\tilde{v}^{\circ} = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2 \qquad 1.(40)$$

where ϕ_1 and ϕ_2 are segment fractions.

The excess volume of mixing V^E can now be written

$$V^E = (x_1V_1{}^* + x_2V_2{}^*)(\tilde{v} - \phi_1\tilde{v}_1 - \phi_2\tilde{v}_2) \qquad 1.(43)$$

The terms in the above equation can be evaluated as follows:

1. The reduced volumes of the components $\tilde{v}_1$ and $\tilde{v}_2$ can be determined using the equation

$$\tilde{v} = \left(\frac{(1 + {}^4\!/\!_3\ \alpha T)}{(1 + \alpha T)}\right)^3 \qquad 1.(29)$$

[α is the thermal expansion coefficient].

2. The characteristic volumes $V_1{}^*$ and $V_2{}^*$ are defined by the expression

$$V^* = \frac{V}{\tilde{v}} \qquad 1.(23)$$

where V, the molar volume is calculated from the appropriate density and molecular weight.

3. The segment fractions ϕ_1 and ϕ_2 are defined as the ratio of the number of segments per component and the total number of segments in the mixture.

$$\phi_1 = 1 - \phi_2 = \frac{r_1x_1}{(r_1x_1 + r_2x_2)} \qquad 5.(1)$$

where r_1 and r_2 are the respective segment numbers and are defined as

$$r_1 = \frac{V_1{}^*}{v^*}\ , \qquad r_2 = \frac{V_2{}^*}{v^*} \qquad 5.(2)$$

here v^* is the core volume.

Equation 5.(1) can now be written

$$\phi_1 = \frac{x_1}{(x_1 + (\frac{r_2}{r_1})x_2)}\ , \qquad 5.(3)$$

as

$$\frac{r_2}{r_1} = \frac{V_2{}^*}{V_1{}^*} \qquad 5.(4)$$

the equation can be rewritten

$$\phi_1 = \frac{x_1}{\left[x_1 + \left(\frac{V_2^*}{V_1^*}\right)x_2\right]} \qquad 5.(6)$$

4. The reduced temperature of the mixture, $\tilde{T}$, can be shown to be given by

$$\tilde{T} = T\left[\frac{\left(\frac{\phi_1 p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*}\right)}{(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2\chi_{12})}\right] \qquad 5.(7)$$

where p_1^*, p_2^* are the characteristic pressure of each component and can be calculated from the expression

$$p^* = \gamma T\tilde{v}^2 \quad , \qquad 1.(31)$$

if the value of the thermal pressure coefficient, γ is known.

The site fraction θ_2 is defined

$$\theta_2 = \frac{\phi_2}{\left[\phi_2 + \phi_1\left(\frac{s_1}{s_2}\right)\right]} \qquad 5.(8)$$

where $\left(\frac{s_1}{s_2}\right)$ is the ratio of the surface contact sites per segment for the respective sites. This can be expressed in terms of the molecular dimensions of the components (p55), but this extension to the theory is not always necessary, because $\theta_2\chi_{12}$ can be considered a single parameter.

The interaction parameter, χ_{12}, is a constant characterising the difference between the energy of interaction between sites on neighbouring molecules one and two and the average of the interactions in the pure components.

5. The reduced volume of the mixture $\tilde{v}$ is expressed in the formulae

$$\tilde{T} = \frac{(v^{1/3} - 1)}{\tilde{v}^{4/3}} \qquad 1.(30)$$

however there is no explicit solution for $\tilde{v}$.

From the excess volume it is assumed, as a reasonable approximation that[20]

$$\tilde{v}^E = \left(\frac{\partial\tilde{v}}{\partial\tilde{T}}\right)(\tilde{T} - \tilde{T}^\circ) \qquad 1.(9)$$

$$\tilde{v}^E = \frac{v^{o7/3}(\tilde{T} - \tilde{T}^o)}{(4/3 - v^{o1/3})} \qquad 5.(10)$$

and knowing the value of $\tilde{v}^o$ (Eq. 1.(29)) enables the calculation of $\tilde{T}^o$ using the formulae

$$\tilde{T}^o = \frac{(\tilde{v}^{o4/3} - 1)}{\tilde{v}^{o4/3}} \qquad 5.(11)$$

The expression for the molar excess volume of the mixture can now be written

$$\bar{V}^E = \frac{(x_1V_1^* + x_2V_2^*)\tilde{v}^{o7/3}\ (\tilde{T} - \tilde{T}^o)}{(4/3 - \tilde{v}^{o1/3})} \qquad 5.(12)$$

The molar excess volume is now expressed in terms, which depend on the properties of the pure components, density, thermal expansion coefficient and thermal pressure coefficient, and one other parameter, $\theta_2\chi_{12}$.

The usual method[20] of Flory's analysis predicts $\theta_2\chi_{12}$, or χ_{12}, from the molar excess enthalpy measurements of a system and uses this value to calculate the molar excess volume of the same system.

$$\bar{H}^E = x_1p_1^*V_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + x_2p_2^*V_2^*(\tilde{v}_2^{-1} - \tilde{v}_2) + x_1v_1^*\theta_2\chi_{12}\tilde{v}^{-1} \qquad 5.(13$$

The interaction parameter χ_{12} directly influences the excess enthalpy whereas it only enters indirectly into the calculation of the excess volume, in the expression for $\tilde{T}$ of the mixture. Flory's method could not be followed exactly as no excess enthalpy measurements were made in this work.

However, the values of the interaction parameter, which were predicted for a series of n-alkane-cycloalkane mixtures were themselves studied in the belief that any trends observed could be of considerable interest in enabling the prediction of χ_{12} for different n-alkane-cycloalkane mixtures.

The properties of the pure components, which were necessary to enable χ_{12} to be calculated, are tabulated in the following section together with the methods and various sources used for their estimation.

PROPERTIES

(i) DENSITY

All densities were measured experimentally and are listed in TABLE 2.

(ii) THERMAL EXPANSION COEFFICIENT (α, K^{-1}).

Table 5 lists α for the n-alkanes at 298K together with the source of the literature values. All the data cited, with the exception of those due to Flory's work were determined using the formula[53]

$$\alpha = -\frac{1}{\rho}\frac{\partial\rho}{\partial T} \qquad 5.(14)$$

where ρ is the density at any temperature, T.

Flory[19] determined α experimentally at several temperatures and formulated a power series in temperature which enabled the calculation of α at various intermediate temperatures.

The values of α calculated from the work of Young[54] were chosen for use in any further discussions because of the accuracy of the densities recorded.

The thermal expansion coefficients for cyclo-alkanes are listed in TABLE 6, and except for the data of Marsh et al., all values were determined using the above formulae. The data of Marsh[55-57] at 298.15K was considered the most accurate as it was the only direct measurement made and these values were used in all calculations.

THERMAL PRESSURE COEFFICIENT (γ, atm. K^{-1}).

$$\gamma = \frac{\alpha}{\beta} \qquad 5.(15)$$

where β is the isothermal compressibility (atm.$^{-1}$)
Knowing both α and β enables the calculation of γ. The isothermal compressibility has been determined both directly and indirectly for the n-alkanes by several authors and these values when combined with the corresponding α values give the thermal pressure coefficient, γ. The values of γ calculated appear in TABLE 7.

Another indirect method[58] for the determination of γ for n-alkanes, is the application of data relating β to the velocity of sound in the liquid, μ.

$$\beta = \left(1. + \frac{T\alpha\mu^2}{Cp}\right)\frac{1}{\rho\mu^2} \qquad 5.(16)$$

where Cp is the heat capacity at 298K. The speed of sound as a function of temperature is well known[65] and this allowed evaluation of μ at 298K for C_5-C_9,C_{12} n-alkanes. Interpolation of this data allowed μ for n-decane to be calculated.

Combining these values with known heat capacity data[60], β and then γ could be calculated. The values of the thermal pressure coefficient determined by this method were considered the most consistent set of values and were used in all calculations. These values are also included in TABLE 7.

The data for the cycloalkanes was determined indirectly by Benson and Singh[61], and directly by Marsh et.al.[55-57]. The data of Marsh was combined with the corresponding experimentally determined α values and appear in TABLE 8.

TABLE 5

THERMAL EXPANSION COEFFICIENT OF ($\alpha \times 10^3$ K^{-1}) n-ALKANES

n-CHAIN LENGTH	EGLOFF[53]	FLORY[19]	A.P.I.[62]	YOUNG[54]
5	1.56			1.54
6	1.34	1.39		1.39
7	1.24			1.23
8	1.18	1.16		1.16_5
9	1.11		1.09	1.09
10	1.06		1.05	1.03

TABLE 6

CYCLOALKANES (C_nH_{2n})

n-CHAIN LENGTH	BENSON[61]	EGLOFF[53]	MARSH[55-57]
6	1.22		1.21_5
7	1.00		1.06
8	0.99		0.98
10		0.91	

TABLE 7

ISOTHERMAL PRESSURE COEFFICIENT (γ atm. K^{-1})

n-ALKANES

n-CHAIN LENGTH	FLORY[19]	DUNLAP[63]	WESTWATER[64]	BOELHOWER[65]	SOUND
5					7.46
6	8.11	8.01			8.03
7			8.41	8.55	8.40
8	8.76			9.00	8.81
9				9.24	9.07
10			(9.50 extrap.)		9.32

TABLE 8

CYCLOALKANES (C_nH_2n)

n-	BENSON[61]	EXTRAPOLATED	MARSH[55-57]
6	10.54		10.61
7	11.2		11.39
8	12.19		12.06
10		13.6	

ANALYSIS

Knowing the values of the thermal expansion coefficient, α, and the thermal pressure coefficient, γ, it is possible to express an equation for the molar excess volume of mixing with only one parameter $\theta_2 X_{12}$ included.

However, to remain consistent with Flory's analysis[20], the site fraction θ_2 was estimated for each system.

$$\theta_2 = \frac{\phi_2}{\left[\phi_2 + \phi_1\left(\frac{s_1}{s_2}\right)\right]} \qquad 5.(8)$$

The ratio of the surface contact sites per segment for the respective component, $\frac{s_1}{s_2}$, was the only variable in the relationship and was defined as

$$\frac{s_1}{s_2} = \frac{r_2}{r_1} \cdot R \qquad 5.(17)$$

where R is the ratio of the respective surface areas of the molecule. Since

$$\frac{r_1}{r_2} = \frac{V_1^*}{V_2^*} \qquad 5.(4)$$

then

$$\frac{s_1}{s_2} = \left(\frac{V_2^*}{V_1^*}\right) \cdot R \qquad 5.(18)$$

To calculate the surface areas of the molecules it was decided to use Flory's example and consider the cycloalkanes as spheres[21,20], while the n-alkanes were considered as right cylinders.[20,17]

CYCLOALKANES[21,61]

The radius of a molecule

$$r = (KV^*)^{1/3} \text{ A}^\circ, \qquad 5.(19)$$

where

$$K = \left(\frac{7.5}{6.023\ \pi}\right) \qquad 5.(20)$$

and the surface area

$$s = 4\pi(KV^*)^{2/3} \text{ A}^{\circ 2} \qquad 5.(21)$$

n-ALKANES

From crystallographic data[66] the radius has been evaluated as

$$r = 2.49\ A^\circ$$

The characteristic length, ℓ^*,[20] is given by

$$\ell^* = 1.19n + 1.32 \qquad 5.(22)$$

where n is equivalent to the chain length.

Hence the surface area, s, is written

$$s = 4.98\pi\,\{1.19n + 3.81\}\ A^{\circ 2} \qquad 5.(23)$$

The site fraction was calculated for each system and the excess volume of mixing expressed only in terms of the interaction parameter, χ_{12}. For each n-alkane-cycloalkane system χ_{12} was determined by a least squares analysis of the experimental excess volume data. The computer program (FLORY) is included in APPENDIX IV.

All the χ_{12} values and their limits are included in TABLE 11. For each cycloalkane series the relationship between the interaction parameter and the n-alkane chain length, n, is represented graphically (Fig. 5,6).

DELETE

~~The results for the cyclodecane series are presented separately, because of the uncertainty in the value of the thermal pressure coefficient, γ. The interpolation and extrapolation procedures needed to obtain the value for cyclodecane resulted in an uncertainty of the order of 30% in 10.6 ± 3.4.~~

However the general trend of the relationship of the interaction paramete to the chain length, n, is consistent with the other series even if the absolute values are perhaps incorrect.

TABLE 11

INTERACTION PARAMETER (χ_{12} atm.)

SYSTEM	χ_{12}(atm.)	ERROR
CYCLOHEXANE		
n-PENTANE	14.9	±7.9
n-HEXANE	22.0	±7.3
n-HEPTANE	20.9	±7.6
CYCLOHEPTANE		
n-HEXANE	11.15	±4.6
n-HEPTANE	14.15	±5.1
n-OCTANE	21.4	±6.0
CYCLOOCTANE		
n-HEXANE	19.6	±6.4
n-HEPTANE	18.2	±6.6
n-OCTANE	19.1	±6.3
n-NONANE	12.9	±4.4
n-DECANE	20.0	±5.7
CYCLODECANE		
n-HEPTANE	19.2	±7.0
n-OCTANE	18.3	±6.8
n-NONANE	14.7	±5.7
n-DECANE	13.7	±5.6

CONCLUSIONS

From the cycloalkane series studied the interaction parameters, χ_{12} showed a general area of agreement between 5 and 30 atmospheres. This region could be narrowed even further if there were not such a large uncertainty in all the values, usually ± 30%.

If more systems were to be studied it would be interesting to see if an average χ_{12} would be able to predict the excess volumes of mixing for the mixture

Benson and Singh[61] also studied several cycloalkane systems, but considered the excess volume and heats of mixing with benzene and toluene. The behaviour of the interaction parameters as the ring size of the cycloalkane decreased was parabolic and showed a minimum. These results would be less accurate than the values reported here as the properties of the cycloalkanes had not been directly determined when their work was published.

The difference in the behaviour of χ_{12} could also be attributed to the geometry of the molecules studied as toluene and benzene were considered to be spherical molecules while the n-alkanes were treated as right cylinders.

The interaction parameter not only varies from system to system, but, as the mole fraction of the components alters, χ_{12} also varies by its definition. Although the difference has been noted in this work (TABLE 11) no detailed investigation was made. The relative independence of the molar excess volume of mixing predicted with any change in χ_{12} made this unnecessary. The parameter, χ_{12}, only enters the equations for $\bar{V}^E$ indirectly in the expression for the reduced temperature of the mixture,

$$\tilde{T} = T \cdot \left(\frac{\left(\frac{\phi_1 p_1^*}{T_1^*}\right) + \left(\frac{\phi_2 p_2^*}{T_2^*}\right)}{(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 \chi_{12})} \right) \qquad 5.(7)$$

and

$$\bar{V}^E = (x_1V_1^* + x_2V_2^*)(\tilde{T} - \tilde{T}^\circ)(\tilde{v}^{\circ 7/3}(4/3 - \tilde{v}^{\circ 1/3})^{-1} \qquad 5.(12)$$

Flory[19] noticed that for several n-alkane-n-alkane mixtures the interaction parameter needed to change by approximately 100% to alter the excess volume of the mixture by 0.1 cm^3/mole.

It appears that the excess volume of mixing is far more sensitive to any variation in the value of the thermal pressure coefficient, γ. If it is assumed that χ_{12} is small then

$$\frac{\partial\tilde{v}_E}{\partial\ell n\gamma_2} = (\tilde{T}_2 - \tilde{T}_1)\cdot\frac{p_1^*p_2^*}{(p_1^* + p_2^*)^2}\cdot\frac{}{(4 - 3\tilde{v}^{1/3})} \qquad 5.(24)$$

and the sensitivity of $\tilde{v}^E$ with respect to γ_2 is approximately proportional to $(\tilde{T}_2 - \tilde{T}_1)$. A difference in $(\tilde{T}_2 - \tilde{T}_1)$ of 0.015 and an error in γ of 0.5% would alter $\bar{V}^E$ by approximately 0.15 cm^3/mole. Thus any small error in γ would lead to disproportionate values of χ_{12} or $\bar{V}^E$.

For a more detailed discussion of the theoretical model it would be essential to determine accurate values of the thermal pressure coefficients for the cycloalkanes and the n-alkanes. As, in this work they could only be determined from indirect sources such as the sound velocity data.

The measurement of the molar excess enthalpy of mixing $\bar{H}^E$, would allow Flory's treatment ot be followed exactly as, the value of χ_{12} is directly dependant on the enthalpy of mixing.

i.e.

$$\begin{aligned}\bar{H}^E &= x_1p_1^*V_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1})\\ &+ x_2p_2^*V_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1})\\ &+ x_1V_1^*\theta_2\chi_{12}\tilde{v}^{-1} \qquad 5.(13)\end{aligned}$$

The interaction parameter should be estimated from the excess heat of mixing data. This value could then be used to calculate the excess volume of mixing.

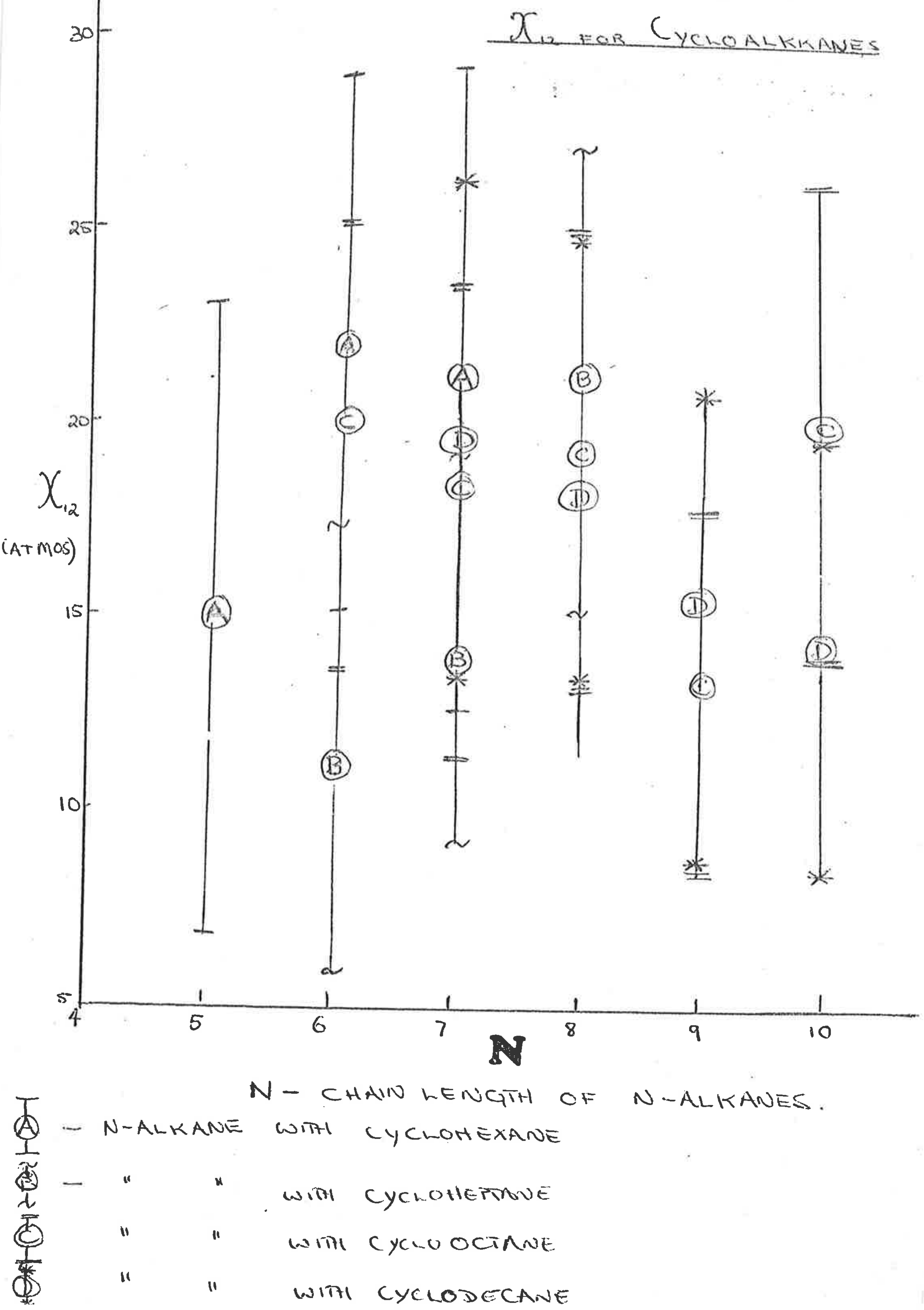
To further reduce the error in χ_{12}, the site fraction θ_2 could be included with χ_{12} and treated as one single parameter. The errors inherent in the assumptions needed to calculate θ_2 would then be avoided.

The theory has much promise in its use of the properties of the pure components to calculate the properties of the mixture. However, the theory proposes only an approximate and simplified equation of state and any failure of the theory can only be attributed to

"................. disparities seem to be caused by limitations inherent in the final scheme of interpretation............."

P.J. FLORY[3]
1972.

(5)


χ_{12} FOR CYCLOALKKANES
30
25
20
15
10
5
χ_{12} (ATMOS)
4
5
6
7
8
9
10
N
N - CHAIN LENGTH OF N-ALKANES.
A
B
C
D
A - N-ALKANE WITH CYCLOHEXANE
B - " " WITH CYCLOHEPTANE
C " " WITH CYCLOOCTANE
D " " WITH CYCLODECANE

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APPENDIX I

DENSITY

PYCNOMETER	Mass (gm.) and Expt. Reproducibility	Volume (cm^3) and Expt. Reproducibility	Stem Calibration (cm^2)
A	24.9384_7 ± 0.00005	32.5247_8 ± 0.00002	0.008766
B	24.9372_4 ± 0.00006	32.5366_1 ± 0.00001	0.008766
C	24.9281_9 ± 0.00004	32.5103_4 ± 0.00002	0.008766
D	24.9380_6 ± 0.00004	32.5054_0 ± 0.00003	0.008766

All pycnometer characteristics were measured at 298 K.

DENSITY FORMULA

$$D = \frac{\beta m\left(1 - \frac{d_A}{d_s}\right) - m_\circ\left(1 - \frac{d_A}{d_p}\right) + V^1 d_A.}{V^1}$$

where β = 1.000018 (the correction factor for the difference between brass and stainless steel weights)

m = Total weight of the pycnometer and liquid

d_A = Density of air

d_s = Density of steel (7.76 $\mathrm{gm \cdot cm^{-3}}$)

d_p = Density of pyrex glass (2.25 $\mathrm{gm \cdot cm^{-3}}$)

V^1 = Total volume of liquid in pycnometer

$m_\circ$ = Mass in vacuo of pycnometer

This equation was incorporated in computer program "DENSITY" (APPENDIX IV).

APPENDIX II

CALIBRATIONS

SECTION	NO. OF CALIBRATIONS	CALIBRATION
Mising Vessel to F_3 (before alteration)	10	29.346 ± 0.002 cm^3
Mising Vessel to F_3 (after alteration)	7	29.393 ± 0.003 cm^3
Large Bore Burette	30	0.4978 ± 0.0001 cm^2
Small Bore Burette	8	0.1277 ± 0.0002 cm^2
Non-Linear Burette Cross-over Section (F_1 + 2.500)	13	0.759 ± 0.002 cm^2
Excess Volume[39] Capillary	3	0.004387 ± 0.000002 cm^2

APPENDIX III

N-PENTANE / CYCLOHEXANE / EXVOL / 25 DEGREES C

MOLE FRACTION	EXVOL(EXP.)	EXVOL(CALC.)	EXVOL(DIFF.)
.0156	-.0017	-.0018	.0001
.0425	-.0059	-.0061	.0002
.0580	-.0094	-.0092	-.0002
.0966	-.0186	-.0188	.0002
.1408	-.0319	-.0320	.0001
.1794	-.0450	-.0450	.0000
.2190	-.0594	-.0591	-.0003
.2586	-.0740	-.0737	-.0003
.2962	-.0877	-.0874	-.0003
.3352	-.1014	-.1013	-.0001
.3765	-.1142	-.1153	.0011
.5257	-.1538	-.1538	-.0000
.5513	-.1581	-.1577	-.0004
.5849	-.1616	-.1614	-.0002
.6320	-.1632	-.1633	.0001
.6789	-.1609	-.1610	.0001
.7119	-.1566	-.1566	-.0000
.7483	-.1488	-.1489	.0001
.7863	-.1371	-.1374	.0003
.8260	-.1214	-.1215	.0001
.8731	-.0972	-.0970	-.0002
.9331	-.0572	-.0569	-.0003
.9549	-.0400	-.0397	-.0003
.9762	-.0212	-.0217	.0005

```
N-HEXANE / CYCLO-HEXANE / 25 DEGREES C  / EXVOL

 MOLE FRACTION        EXVOL(EXP.)         EXVOL(CALC.)         EXVOL(DIFF.)

     .0086               .0091               .0089                 .0002
     .0232               .0226               .0231               -.0005
     .0403               .0381               .0384               -.0003
     .0579               .0526               .0528               -.0002
     .0979               .0804               .0805               -.0001
     .1332               .1000               .0999                 .0001
     .1684               .1153               .1150                 .0003
     .2197               .1304               .1304                 .0000
     .2587               .1377               .1376                 .0001
     .2845               .1406               .1406               -.0000
     .3198               .1426               .1426               -.0000
     .3464               .1427               .1427               -.0000
     .3662               .1420               .1421               -.0001
     .3890               .1406               .1407               -.0001
     .4017               .1397               .1397                 .0000
     .5040               .1252               .1253               -.0001
     .5237               .1216               .1216               -.0000
     .5537               .1155               .1155                 .0000
     .5876               .1081               .1080                 .0001
     .6257               .0992               .0990                 .0002
     .6679               .0885               .0885                 .0000
     .7059               .0787               .0786                 .0001
     .7456               .0683               .0681                 .0002
     .7968               .0538               .0543               -.0005
     .8580               .0376               .0377               -.0001
     .9135               .0226               .0227               -.0001
     .9393               .0160               .0158                 .0002
     .9613               .0100               .0100               -.0000
     .9844               .0047               .0040                 .0007
```

```
N-HEPTANE / CYCLO HEXANE / EXVOL / 25 DEGREES C


MOLE FRACTION       EXVOL(EXP.)       EXVOL(CALC.)       EXVOL(DIFF.)

   .0101              .0198             .0199              -.0001
   .0208              .0402             .0400               .0002
   .0335              .0645             .0624               .0021
   .0462              .0851             .0835               .0016
   .0839              .1384             .1385              -.0001
   .1241              .1856             .1859              -.0003
   .1572              .2172             .2175              -.0003
   .1985              .2480             .2487              -.0007
   .2311              .2675             .2677              -.0002
   .2593              .2809             .2806               .0003
   .2858              .2897             .2900              -.0003
   .3319              .3010             .3008               .0002
   .3579              .3045             .3041               .0005
   .3808              .3066             .3054               .0012
   .4703              .2978             .2986              -.0008
   .4905              .2937             .2947              -.0010
   .5260              .2859             .2860              -.0001
   .5709              .2721             .2719               .0002
   .6110              .2570             .2566               .0004
   .6485              .2406             .2401               .0005
   .6946              .2176             .2173               .0003
   .7446              .1894             .1895              -.0001
   .7946              .1579             .1587              -.0008
   .8516              .1186             .1200              -.0014
   .9157              .0781             .0719               .0062
   .9264              .0618             .0633              -.0015
   .9496              .0430             .0442              -.0012
   .9744              .0184             .0230              -.0046
```

HEXAN / CYCLOHEPTAN / EXVOL

MOLE FRACTION	EXVOL(EXP.)	EXVOL(CALC.)	EXVOL(DIFF.)
.0109	-.0002	.0004	-.0006
.0220	-.0000	.0000	-.0000
.0333	-.0014	-.0011	-.0003
.0434	-.0031	-.0026	-.0005
.0597	-.0068	-.0062	-.0006
.1006	-.0201	-.0198	-.0003
.1435	-.0391	-.0392	.0001
.1837	-.0594	-.0601	.0007
.2272	-.0831	-.0841	.0010
.2680	-.1056	-.1067	.0011
.3040	-.1255	-.1260	.0005
.3383	-.1435	-.1433	-.0002
.3769	-.1624	-.1611	-.0013
.4160	-.1794	-.1770	-.0024
.5723	-.2117	-.2132	.0015
.6107	-.2133	-.2142	.0009
.6407	-.2120	-.2124	.0004
.6831	-.2059	-.2060	.0001
.7268	-.1946	-.1944	-.0002
.7805	-.1742	-.1727	-.0015
.8321	-.1450	-.1440	-.0010
.8875	-.1053	-.1045	-.0008
.9352	-.0622	-.0638	.0016
.9552	-.0430	-.0450	.0020
.9715	-.0282	-.0291	.0009
.9889	-.0106	-.0115	.0009

HEPTAN/ CYCLOHEPTAN / EXVOL

MOLE FRACTION	EXVOL(EXP.)	EXVOL(CALC.)	EXVOL(DIFF.)
.0135	.0135	.0131	.0004
.0263	.0240	.0240	.0000
.0412	.0351	.0350	.0001
.0583	.0457	.0456	.0001
.0791	.0560	.0558	.0002
.1229	.0691	.0696	-.0005
.1738	.0758	.0757	.0001
.2122	.0754	.0753	.0001
.2553	.0716	.0714	.0002
.2985	.0652	.0650	.0002
.3353	.0581	.0583	-.0002
.3736	.0501	.0507	-.0006
.4043	.0434	.0444	-.0010
.4407	.0349	.0368	-.0019
.4810	.0262	.0285	-.0023
.4287	.0417	.0393	.0024
.4577	.0350	.0333	.0017
.4932	.0276	.0261	.0015
.5394	.0180	.0172	.0008
.5888	.0089	.0086	.0003
.6430	-.0010	.0005	-.0015
.7145	-.0073	-.0073	.0000
.7768	-.0107	-.0110	.0003
.8496	-.0109	-.0112	.0003
.8999	-.0080	-.0087	.0007
.9266	-.0073	-.0067	-.0006
.9575	-.0042	-.0040	-.0002
.9814	-.0027	-.0017	-.0010

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OCTAN / CYCLOHEPTAN / EXVOL


 MOLE FRACTION        EXVOL(EXP.)         EXVOL(CALC.)         EXVOL(DIFF.)

    .0148               .0287               .0249                .0038
    .0342               .0572               .0538                .0034
    .0506               .0779               .0752                .0027
    .0700               .0990               .0973                .0017
    .1118               .1321               .1348               -.0027
    .1557               .1604               .1618               -.0014
    .2042               .1804               .1804               -.0000
    .2486               .1897               .1897                .0000
    .2894               .1937               .1932                .0005
    .3277               .1933               .1932                .0001
    .3635               .1914               .1909                .0005
    .4038               .1865               .1860                .0005
    .4404               .1806               .1800                .0006
    .4498               .1788               .1783                .0005
    .3971               .1868               .1870               -.0002
    .4115               .1846               .1849               -.0003
    .4537               .1773               .1775               -.0002
    .4893               .1700               .1700               -.0000
    .5269               .1601               .1610               -.0009
    .5726               .1483               .1487               -.0004
    .6175               .1355               .1354                .0001
    .6763               .1159               .1165               -.0006
    .7395               .0949               .0947                .0002
    .8119               .0694               .0685                .0009
    .8875               .0420               .0407                .0013
    .9184               .0292               .0294               -.0002
    .9545               .0138               .0163               -.0025
```

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N-HEXANE / CYCLO-OCTANE / EXVOL / 25 DEGREES C

 MOLE FRACTION      EXVOL(EXP.)      EXVOL(CALC.)      EXVOL(DIFF.)

    .0168             -.0141            -.0139            -.0002
    .0255             -.0212            -.0216             .0004
    .0397             -.0353            -.0349            -.0004
    .0569             -.0527            -.0520            -.0007
    .0718             -.0683            -.0675            -.0008
    .1176             -.1187            -.1185            -.0002
    .1604             -.1684            -.1685             .0001
    .2037             -.2186            -.2193             .0007
    .2498             -.2703            -.2718             .0015
    .2936             -.3177            -.3187             .0010
    .3249             -.3491            -.3496             .0005
    .3600             -.3815            -.3813            -.0002
    .4018             -.4150            -.4142            -.0008
    .4352             -.4379            -.4363            -.0016
    .4645             -.4546            -.4524            -.0022
    .5539             -.4788            -.4804             .0016
    .5735             -.4807            -.4819             .0012
    .5979             -.4807            -.4813             .0006
    .6269             -.4766            -.4769             .0003
    .6555             -.4686            -.4685            -.0001
    .6862             -.4554            -.4549            -.0005
    .7282             -.4288            -.4281            -.0007
    .7674             -.3950            -.3942            -.0008
    .8058             -.3531            -.3524            -.0007
    .8478             -.2973            -.2965            -.0008
    .8978             -.2153            -.2157             .0004
    .9305             -.1533            -.1541             .0008
    .9441             -.1254            -.1265             .0011
    .9592             -.0933            -.0943             .0010
    .9713             -.0631            -.0675             .0044
    .9831             -.0399            -.0404             .0005
```

HEPTANE / CYCLOOCTANE / EXVOL / 25 C

MOLE FRACTION	EXVOL(EXP.)	EXVOL(CALC.)	EXVOL(DIFF.)
.0148	.0024	.0036	-.0012
.0276	.0076	.0054	.0022
.0437	.0068	.0059	.0009
.0617	.0056	.0046	.0010
.1036	-.0055	-.0051	-.0004
.1465	-.0231	-.0222	-.0009
.1856	-.0430	-.0418	-.0012
.2179	-.0609	-.0598	-.0011
.2603	-.0846	-.0845	-.0001
.2988	-.1069	-.1070	.0001
.3235	-.1209	-.1210	.0001
.3507	-.1357	-.1359	.0002
.3926	-.1564	-.1571	.0007
.4187	-.1664	-.1691	.0027
.4368	-.1754	-.1767	.0013
.5299	-.2077	-.2060	-.0017
.5489	-.2114	-.2097	-.0017
.5769	-.2148	-.2137	-.0011
.6180	-.2164	-.2159	-.0005
.6497	-.2146	-.2147	.0001
.6797	-.2105	-.2111	.0006
.7094	-.2040	-.2049	.0009
.7481	-.1918	-.1931	.0013
.7884	-.1761	-.1759	-.0002
.8366	-.1486	-.1486	-.0000
.8881	-.1112	-.1111	-.0001
.9310	-.0739	-.0733	-.0006
.9505	-.0549	-.0541	-.0008
.9670	-.0374	-.0369	-.0005
.9828	-.0202	-.0196	-.0006

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N-OCTANE / CYCLO-OCTANE / 25 DEGREES C / EXVOL


MOLE FRACTION        EXVOL(EXP.)          EXVOL(CALC.)          EXVOL(DIFF.)

   .0155                .0142                .0137                .0005
   .0301                .0244                .0243                .0001
   .0394                .0294                .0301               -.0007
   .0523                .0361                .0368               -.0007
   .0596                .0394                .0401               -.0007
   .0983                .0511                .0514               -.0003
   .1431                .0551                .0546                .0005
   .1863                .0516                .0509                .0007
   .2213                .0457                .0447                .0010
   .2522                .0383                .0377                .0006
   .2801                .0307                .0305                .0002
   .3126                .0212                .0215               -.0003
   .3365                .0139                .0147               -.0008
   .3681                .0043                .0056               -.0013
   .3964               -.0045               -.0025               -.0020
   .4112               -.0087               -.0066               -.0021
   .4947               -.0214               -.0285                .0071
   .5196               -.0340               -.0343                .0003
   .5613               -.0437               -.0432               -.0005
   .5906               -.0495               -.0486               -.0009
   .6226               -.0544               -.0535               -.0009
   .6541               -.0582               -.0573               -.0009
   .6905               -.0608               -.0602               -.0006
   .7295               -.0614               -.0613               -.0001
   .7751               -.0593               -.0595                .0002
   .8161               -.0539               -.0548                .0009
   .8832               -.0408               -.0407               -.0001
   .9225               -.0273               -.0288                .0015
   .9403               -.0237               -.0227               -.0010
   .9573               -.0173               -.0165               -.0008
   .9778               -.0095               -.0087               -.0008
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NONAN/CYCLOCTAN/EXVOL/25C


 MOLE FRACTION        EXVOL(EXP.)        EXVOL(CALC.)        EXVOL(DIFF.)

     .0057               .0104              .0084               .0020
     .0139               .0204              .0198               .0006
     .0246               .0340              .0336               .0004
     .0364               .0476              .0472               .0004
     .0481               .0596              .0593               .0003
     .0787               .0851              .0852             -.0001
     .1100               .1043              .1042               .0001
     .1563               .1206              .1218             -.0012
     .1944               .1295              .1291               .0004
     .2326               .1320              .1319               .0001
     .2722               .1319              .1312               .0007
     .3006               .1295              .1291               .0004
     .3387               .1243              .1247             -.0004
     .3779               .1175              .1189             -.0014
     .4573               .1053              .1044               .0009
     .4843               .0993              .0989               .0004
     .5116               .0935              .0932               .0003
     .5705               .0805              .0806             -.0001
     .6184               .0698              .0702             -.0004
     .6666               .0596              .0599             -.0003
     .7049               .0519              .0520             -.0001
     .7470               .0435              .0437             -.0002
     .7820               .0374              .0372               .0002
     .8236               .0304              .0301               .0003
     .8638               .0241              .0237               .0004
     .9004               .0178              .0180             -.0002
     .9169               .0155              .0154               .0001
     .9301               .0135              .0133               .0002
     .9435               .0113              .0111               .0002
     .9587               .0087              .0084               .0003
     .9668               .0058              .0069             -.0011
     .9765               .0043              .0050             -.0007
     .9908               .0023              .0021               .0002
```

```
DECAN / CYCLOOCTAN / EXVOL / 25C


 MOLE FRACTION        EXVOL(EXP.)         EXVOL(CALC.)        EXVOL(DIFF.)

    .0154               .0195               .0214              -.0019
    .0430               .0547               .0568              -.0021
    .0683               .0855               .0859              -.0003
    .0946               .1134               .1131               .0003
    .1477               .1607               .1592               .0015
    .2122               .2018               .2010               .0008
    .2833               .2305               .2311              -.0006
    .3434               .2434               .2448              -.0014
    .3946               .2484               .2489              -.0005
    .4385               .2470               .2473              -.0003
    .4725               .2433               .2431               .0002
    .5042               .2379               .2372               .0007
    .5289               .2325               .2312               .0013
    .5474               .2290               .2261               .0029
    .6398               .1904               .1930              -.0026
    .6544               .1847               .1869              -.0022
    .6782               .1752               .1764              -.0012
    .7079               .1623               .1626              -.0003
    .7409               .1475               .1466               .0009
    .7713               .1324               .1313               .0011
    .8105               .1121               .1109               .0012
    .8471               .0921               .0913               .0008
    .8857               .0700               .0699               .0001
    .9235               .0472               .0482              -.0010
    .9558               .0275               .0287              -.0012
    .9751               .0162               .0165              -.0003
    .9918               .0058               .0055               .0003
```

```
HEPTAN/ CYCLODECAN / 25 C / EXVOL


 MOLE FRACTION        EXVOL(EXP.)         EXVOL(CALC.)         EXVOL(DIFF.)

    .0141               -.0056              -.0056               -.0000
    .0290               -.0153              -.0140               -.0013
    .0517               -.0340              -.0311               -.0029
    .0747               -.0605              -.0531               -.0074
    .1352               -.0979              -.1263                .0284
    .1836               -.2056              -.1947               -.0109
    .2429               -.2911              -.2822               -.0089
    .3134               -.3862              -.3823               -.0039
    .3570               -.4392              -.4385               -.0007
    .4092               -.4962              -.4972                .0010
    .4535               -.5347              -.5382                .0035
    .4737               -.5483              -.5538                .0055
    .5697               -.6011              -.5986               -.0025
    .5836               -.6029              -.6006               -.0023
    .6121               -.6023              -.6010               -.0013
    .6580               -.5899              -.5904                .0005
    .6968               -.5684              -.5700                .0016
    .7451               -.5273              -.5290                .0017
    .7914               -.4715              -.4726                .0011
    .8428               -.3898              -.3897               -.0001
    .8717               -.3341              -.3334               -.0007
    .9017               -.2692              -.2676               -.0016
    .9379               -.1798              -.1781               -.0017
    .9504               -.1460              -.1447               -.0013
    .9663               -.1011              -.1004               -.0007
    .9806               -.0586              -.0589                .0003
    .9906               -.0283              -.0289                .0006
```

```
OCTAN / CYCLODECAN / 25 C / EXVOL


 MOLE FRACTION      EXVOL(EXP.)        EXVOL(CALC.)       EXVOL(DIFF.)

    .0158             -.0016             -.0011             -.0005
    .0327             -.0056             -.0050             -.0006
    .0549             -.0147             -.0142             -.0005
    .1039             -.0450             -.0472              .0022
    .1475             -.0869             -.0871              .0002
    .1993             -.1415             -.1416              .0001
    .2439             -.1911             -.1909             -.0002
    .2823             -.2329             -.2328             -.0001
    .3223             -.2745             -.2741             -.0004
    .3641             -.3139             -.3133             -.0006
    .4016             -.3455             -.3441             -.0014
    .4411             -.3729             -.3714             -.0015
    .5602             -.4122             -.4156              .0034
    .5960             -.4152             -.4169              .0017
    .6276             -.4135             -.4133             -.0002
    .6641             -.4043             -.4035             -.0008
    .7002             -.3897             -.3877             -.0020
    .7433             -.3627             -.3610             -.0017
    .7965             -.3170             -.3159             -.0011
    .8409             -.2674             -.2673             -.0001
    .8884             -.2019             -.2038              .0020
    .9318             -.1315             -.1343              .0028
    .9465             -.1056             -.1081              .0025
    .9648             -.0715             -.0734              .0019
    .9864             -.0280             -.0295              .0015
```

```
NONAN / CYCLODECAN / 25 C / EXVOL


  MOLE FRACTION        EXVOL(EXP.)         EXVOL(CALC.)        EXVOL(DIFF.)

      .0145               .0075               .0069               .0006
      .0226               .0105               .0096               .0010
      .0496               .0148               .0136               .0012
      .0567               .0150               .0134               .0016
      .0904               .0077               .0068               .0009
      .1104             -.0005              -.0010               .0005
      .1633             -.0328              -.0318              -.0010
      .2025             -.0631              -.0612              -.0019
      .2577             -.1086              -.1067              -.0019
      .2930             -.1377              -.1361              -.0016
      .3353             -.1704              -.1699              -.0005
      .3704             -.1957              -.1957              -.0000
      .4024             -.2164              -.2167               .0003
      .4191             -.2264              -.2267               .0003
      .5406             -.2697              -.2732               .0035
      .5790             -.2763              -.2778               .0015
      .6163             -.2773              -.2774               .0001
      .6586             -.2724              -.2713              -.0011
      .7014             -.2611              -.2590              -.0021
      .7500             -.2400              -.2378              -.0022
      .7963             -.2118              -.2105              -.0013
      .8427             -.1760              -.1761               .0001
      .8919             -.1317              -.1315              -.0002
      .9313             -.0854              -.0894               .0040
      .9467             -.0671              -.0712               .0041
      .9753             -.0303              -.0347               .0044
      .9867             -.0164              -.0190               .0026
```

```
DECAN / CYCLODECAN / 25 C / EXVOL


 MOLE FRACTION      EXVOL(EXP.)       EXVOL(CALC.)      EXVOL(DIFF.)

     .0077            .0090             .0089             .0001
     .0193            .0217             .0203             .0014
     .0338            .0327             .0314             .0013
     .0515            .0424             .0408             .0016
     .0976            .0460             .0476            -.0016
     .1477            .0342             .0349            -.0007
     .1933            .0123             .0127            -.0004
     .2451           -.0188            -.0185            -.0003
     .2895           -.0438            -.0466             .0028
     .3280           -.0698            -.0702             .0004
     .3591           -.0892            -.0881            -.0011
     .3894           -.1047            -.1042            -.0005
     .5153           -.1523            -.1531             .0008
     .5501           -.1613            -.1609            -.0004
     .5840           -.1664            -.1661            -.0003
     .6178           -.1691            -.1686            -.0005
     .6590           -.1682            -.1680            -.0002
     .7015           -.1625            -.1630             .0005
     .7555           -.1490            -.1497             .0007
     .8124           -.1264            -.1271             .0007
     .8765           -.0932            -.0912            -.0020
     .9279           -.0551            -.0555             .0004
     .9512           -.0378            -.0379             .0001
     .9709           -.0221            -.0227             .0006
     .9869           -.0095            -.0102             .0007
```

APPENDIX IV

```
      PROGRAM DENSITY(INPUT,OUTPUT)
      DS=7.76
      DP=2.25
      B=1.00001178
      A=0.008766
50    READ1,WOVAC,DA,WAIR,VO,DELTAH, TAMB,TBATH,COEFF
      IF (WOVAC.EQ.0.) GO TO 100
1     FORMAT(8F10)
      ANUM=WAIR*B*(1.-DA/DS)-WOVAC*(1.-DA/DP)
      DENOM=VO+A*DELTAH
      TERM=(1.+(TAMB-TBATH)*COEFF)*DA
      DL=ANUM/DENOM+TERM
      PRINT10,DL
10    FORMAT(10X,F10.6)
      GO TO 50
100   STOP $ END
```

```
      PROGRAM FLORY (INPUT,OUTPUT)
      DIMENSION H(100),X(100),Z(1),VCALC(100),VDIFF(100),V(1),C(1,1)
      COMMON/DD/SEG1(40),SEG2(40),G(40),T(40),S(40),TV(40
     C),TM(40),W(40),SI(40),R(40),RVE(40),O(40)
      COMMON/TRY/REV1,REV2,CHV1,CHV2,CHVM,PRES1,PRES2,T1,T2,PI,RATS
      REAL MOLV1,MOLV2
   17 READ 6,L
    6 FORMAT(I1,9X,49H
      IF(L.EQ.0) GO TO 100
      Z=0.
      READ 1,N,LEN,TEMP
    1 FORMAT (2I2,F8)
      READ 7,  ALPH1,ALPH2,GAM1,GAM2,MOLV1,MOLV2,Z1
    7 FORMAT (7F10)
      READ 9, (X(I),I=1,N)
      READ 9, (H(I),I=1,N)
    9 FORMAT (8F10)
      PI = 3.14159265
      REV1   =((1.+(4.*ALPH1*TEMP/3.))/(1.+ALPH1*TEMP))**3
      REV2   =((1.+(4.*ALPH2*TEMP/3.))/(1.+ALPH2*TEMP))**3
      PRINT103,REV1,REV2
      CHV1    =MOLV1/REV1
      CHV2    =MOLV2/REV2
      PRINT103,CHV1,CHV2
      CHVM=CHV1/CHV2
      PRINT 104,CHVM
  104 FORMAT (10X,F10.8)
      PRES1    =GAM1*TEMP*(REV1    **2)
      PRES2    =GAM2*TEMP*(REV2    **2)
      PRINT103,PRES1,PRES2
      T1    =((REV1**0.33333)-1.)/(REV1**1.33333)
      T2    =((REV2**0.33333)-1.)/(REV2**1.33333)
      SA1 = 4.98*(1.19*LEN+3.81)*PI
      SA2=4*PI*((30.*CHV2'(4.*PI*6.023))**0.6666667)
      RATS=((SA1/ SA2)*CHVM)
  103 FORMAT (10X,2E13.6)
      CALL QIKFIT(H,X,N,1,Z,V,C,SD)
      PRINT 6,L
      PRINT 23
   23 FORMAT (///12X,*MOLE FRACTION*,8X,*EXVOL(EXP.)*,9X,*EXVOL(CALC.)*
     C,10X,*EXVOL(DIFF.)*/)
      DO 10 I=1,N
      VCALC(I)=O(I)*RVE(I)
      VDIFF(I)=H(I)-VCALC(I)
      PRINT 11,X(I),H(I),VCALC(I),VDIFF(I)
   11 FORMAT (10X,4(F10.4,10X))
   10 CONTINUE
      PRINT 50,Z(1),V(1)
   50 FORMAT(/////10X,*VALUE OF CHI.≠*,F9.4,10X,*STANDARD DEVIATION OF
     C CHI*,F8.4)
      GO TO 17
  100 STOP $ END
      SUBROUTINE QIKFIT(Y,X,N,M,Z,V,C,SD)
      DIMENSION Y(100),X(100),A(100,1),Z(1),AK(1),L(100),R(100),C(M,M),
     CV(1)
      COMMON/DD/SEG1(40),SEG2(40),G(40),T(40),S(40),TV(40
     C),TM(40),W(40),SI(40),R(40),RVE(40),O(40)
      COMMON/TRY/REV1,REV2,CHV1,CHV2,CHVM,PRES1,PRES2,T1,T2,PI,RATS
      REAL MOLV1,MOLV2,L
      IT =0
   20 IF (IT.GT.20) GO TO 200
      DO 4 I=1,N
```

```
      O(I)=X(I)*(CHV1-CHV2)+CHV2
      SEG1(I)=X(I)*CHVM/(1.-X(I)*(1.-CHVM))
      SEG2(I)=1.-SEG1(I)
      SI(I)=SEG2(I)/(SEG2(I)+(SEG1(I)*SA1/SA2))
      T(I)=SEG1(I)*PRES1
      S(I)=SEG2(I)*PRES2
      G(I)=REV1*SEG1(I)+REV2*SEG2(I)
      W(I)=SEG1(I)*Z(1)*SI(I)
      TM(I)=(T(I)*T1    +S(I)*T2    )/(T(I)+S(I)-W(I))
      TV(I)=((G(I)**0.33333)-1.)/(G(I)**1.33333)
      B(I)=(G(I)**2.33333)/(1.33333-(G(I)**0.33333))
      RVE(I)=B(I)*(TM(I)-TV(I))
      L(I)=1.0
      A(I,1)=(O(I)*B(I)*TM(I)*SEG1(I)/(W(I)-T(I)-S(I)))*SI(I)
      R(I)=Y(I)-O(I)*RVE(I)
    4 CONTINUE
      SUMAK=0.
      DO 3 J=1,M
      DO 5 K=1,M
      P=0.
      DO 2 I=1,N
      P=P + A(I,J)*A(I,K)/L(I)
    2 CONTINUE
      C(J,K)=P
    5 CONTINUE
      D=0.
      DO 6 I=1,N
      D=D + A(I,J)*R(I)/L(I)
    6 CONTINUE
      V(J)=D
    3 CONTINUE
      CALL MATRIX(10,M,M,0,C,M,F)
      DO 11 K=1,M
      XX=0.
      DO 10J=1,M
      XX=XX + C(K,J)*V(J)
   10 CONTINUE
      AK(K)=XX
      SUMAK=SUMAK+AK(K)**2
   11 CONTINUE
      DO 15 I=1,M
      Z(I)=Z(I)-(AK(I))
      IF(I.GT.M) Z(I)=0.
   15 CONTINUE
      PRINT106,Z(1)
  106 FORMAT (10X,F10.5)
      IT = IT +1
      IF (ABS(AK(1)).GT.0.000001) GO TO 20
      S=0.
      DO 70 I=1,N
   70 S=S+R(I)**2/L(I)
      V=0.
      DO 71 K=1,M
      V(K)=SQRT(S/(N-M)*C(K,K))
   71 CONTINUE
      SD=SQRT(S/(N-M))
      RETURN
  200 CALL EXIT
      END
```

```
      PROGRAM EXFIT (INPUT,OUTPUT)
      DIMENSION X(200),Y(100),Z(10),YCALC(100),YDIFF(100),V(10),C(5,5)
      COMMON/DD/B(100),G(100),W(100),U(100)
   17 READ 6,L
    6 FORMAT(I1,9X,49H
      IF(L.EQ.0) GO TO 100
      Z=0.
      READ 1,N,M,K,(Z(I),I=1,3)
   1  FORMAT (3I2,5F10)
      READ 9, (X(I),I=1,N)
      READ 9, (Y(I),I=1,N)
   9  FORMAT (8F10)
   20 DO 16 I=1,6
   16 IF (I.GT.M)Z(I)=0.
      CALL QIKFIT(Y,X,N,M,Z,V,C,SD)
      PRINT 6,L
      PRINT 23
   23 FORMAT (///12X,*MOLE FRACTION*,8X,*EXVOL(EXP.)*,9X,*EXVOL(CALC.)*
     C,10X,*EXVOL(DIFF.)*/)
      DO 10 I=1,N
      YCALC(I)=U(I)*G(I)
      YDIFF(I)=(Y(I)-YCALC(I))
      PRINT 11,X(I),Y(I),YCALC(I),YDIFF(I)
   11 FORMAT (10X,4(F10.4,10X))
   10 CONTINUE
      PRINT 12,(Z(I),I=1,5)
   12 FORMAT (///////10X,*A=*,F10.4,10X,*B=*,F10.4,10X,*C=*,F10.4,10X,
     C*D=*,F10.4,10X,*E=*,F10.4///)
      PRINT 13 ,(V(I),I=1,5)
   13 FORMAT (7X,*SDA=*,F10.4,7X,*SDB=*,F10.4,7X,*SDC=*,F10.4,7X,*SDD=
     C*,F10.4,7X,*SDE=*,F10.4//)
      PRINT 24,SD
   24 FORMAT (10X,*STANDARD DEVIATION OF FIT =*,F10.4//////)
      M=M-1
      IF(M.LE.K) 17,20
 100  STOP $ END
      PRINT 12,VS,FM,VM(1,J)
      SUBROUTINE QIKFIT(Y,X,N,M,Z,V,C,SD)
      DIMENSION Y(100),X(100),A(100,5),Z(5),AK(5),L(100),R(100),C(M,M),
     CV(5)
      COMMON/DD/B(100),G(100),W(100),U(100)
      REAL L
   20 DO 4 I=1,N
      W(I)=(2.*X(I)-1.)
      B(I)=(1.+Z(1)*W(I))
      U(I)=X(I)*(1.-X(I))/B(I)
      G(I)=Z(2)+Z(3)*W(I)+Z(4)*(W(I)**2)+Z(5)*(W(I)**3)
      L(I)=1.
      A(I,1)=+W(I)*U(I)*G(I)/B(I)
      A(I,2)=-U(I)
      A(I,3)=-U(I)*W(I)
      A(I,4)=-U(I)*W(I)**2
      A(I,5)=-U(I)*W(I)**3
      R(I)=Y(I)-(U(I)*G(I))
```

```
    4 CONTINUE
      DO 3 J=1,M
      DO 5 K=1,M
      P=0.
      DO 2 I=1,N
      P=P + A(I,J)*A(I,K)/L(I)
    2 CONTINUE
      C(J,K)=P
    5 CONTINUE
      D=0.
      DO 6 I=1,N
      D=D + A(I,J)*R(I)/L(I)
    6 CONTINUE
      V(J)=D
    3 CONTINUE
      CALL MATRIX(10,M,M,0,C,M,F)
      DO 11 K=1,M
      XX=0.
      DO 10J=1,M
      XX=XX + C(K,J)*V(J)
   10 CONTINUE
      AK(K)=XX
   11 CONTINUE
      DO 15 I=1,M
      Z(I)=Z(I)-AK(I)
      IF(I.GT.M) Z(I)=0.
   15 CONTINUE
      IF (ABS(Z(1)).GT.1.00) Z(1)=0.00
      IF (ABS(AK(1)).GT.0.0001)    GO  TO 20
      S=0.
      DO 70 I=1,N
   70 S=S+R(I)**2/L(I)
      V=0.
      DO 71 K=1,M
      V(K)=SQRT(S/(N-M)*C(K,K))
   71 CONTINUE
      SD=SQRT(S/(N-M))
      RETURN
      END
```

```
      PROGRAM LCFHT (INPUT.OUTPUT)
      DIMENSION H(100).X(100),Z(3).HCALC(100).HDIFF(100),V(3),C(3,3)
      DIMENSION  QO(100),WO(100),UO(100),G1(100),G2(100),G3(100),VCALC
     C(100)
      COMMON/DD/B(100),G(100),W(100).U(100),Q(100),WW(100),UU(100)
      COMMON/TRY/SHAPE,IT,ALON,ALTW.BEON,BETW,ADIF.BDIF
      COMMON/EE/Q1(100).Q2(100),QQ(100),U1(100),U2(100),W1(100),W2(100)
   17 READ 6.L
    6 FORMAT(I1,9X,49H
      IF(L.EQ.0) GO TO 100
      Z=0.
      READ1,N,ALON.ALTW,BEON,BETW.(Z(I),I=1,3)
    1 FORMAT(I2,7F10)
      READ 9, (X(I).I=1,N)
      READ 9. (H(I),I=1,N)
    9 FORMAT (8F10)
      CALL QIKFIT(H,X,N.3,Z,V,C,SD)
      PRINT 6.L
      PRINT 23
   23 FORMAT (///12X.*MOLE FRACTION*,8X,*EXVOL(EXP.)*,9X,*EXVOL(CALC.)*
     C,10X,*EXVOL(DIFF.)*/)
      DO 10 I=1,N
      HCALC(I)=-(Z(1)/Z(2))*((QQ(I)*(1.-G1(I)))-WW(I)*(1.-G2(I))-UU(I)*
     C(1.-G3(I)))
      HDIFF(I)=H(I)-HCALC(I)
      PRINT 11.X(I).H(I).HCALC(I),HDIFF(I)
   11 FORMAT (10X.4(F10.4,10X))
   10 CONTINUE
      PRINT 50.Z(1),V(1),Z(2),V(2),Z(3),V(3)
   50 FORMAT(/////10X.*VALUE OF EPS.≠*,F8.5,10X,*STANDARD DEVIATION OF
     C EPS*.F7.5.//10X.*VALUE OF K=*,F8.5,10X,*STANDARD DEVIATION OF K
     C=*.F7.5,//10X,*VALUE OFRATOB=*,F8.5,10X,*STANDARD DEVIATION OFAAT
     C=*.F7.5)
      GO TO 17
  100 STOP $ END
      SUBROUTINE QIKFIT(Y,X,N,M,Z,V,C,SD)
      DIMENSION Y(100),X(100),A(100,3),Z(3),AK(3).L(100),R(100),C(M,M),
     CV(3)
      DIMENSION  QO(100),WO(100).UO(100).G1(100),G2(100),G3(100),VCALC
     C(100)
      COMMON/DD/B(100).G(100).W(100),U(100),Q(100).WW(100),UU(100)
      COMMON/EE/Q1(100).Q2(100),QQ(100),U1(100),U2(100),W1(100),W2(100)
      COMMON/TRY/SHAPE,IT,ALON,ALTW.BEON,BETW,ADIF,BDIF
      REAL LAMBDA.L
      IT =0
   20 IF (IT.GT.20) GO TO 200
      DO 4 I=1,N
      W1(I)=X(I)*ALON
      W2(I)=X(I)*BEON
      U1(I)=(1.-X(I))*ALTW
      U2(I)=(1.-X(I))*BETW
      Q1(I)=W1(I)+U1(I)
      Q2(I)=W2(I)+U2(I)
      QQ(I)=                (Q1(I)+Q2(I)*Z(3))
      WW(I)=                (W1(I)+W2(I)*Z(3))
      UU(I)=                (U1(I)+U2(I)*Z(3))
      QO(I)=Q1(I)*Q2(I)*Z(2)*Z(3)/(QQ(I)**2)
      UO(I)=U1(I)*U2(I)*Z(3)*Z(2)/(UU(I)**2)
      WO(I)=W1(I)*W2(I)*Z(3)*Z(2)/(WW(I)**2)
      G1(I)=SQRT(1.+QO(I))
      G2(I)=SQRT(1.+WO(I))
```

```
      G3(I)=SQRT(1.+U0(I))
      VCALC(I)=-(Z(1)/Z(2))*((QQ(I)*(1.-G1(I)))-WW(I)*(1.-G2(I))-UU(I)*
     C(1.-G3(I)))
      A(I,1)=-VCALC(I)/Z(1)
      A(I,2)=(VCALC(I)-(Z(1)/(Z(2)*2.))*(Q0(I)*QQ(I)/G1(I)-W0(I)*WW(I)/
     CG2(I)-U0(I)*UU(I)/G3(I)))/Z(2)
      A(I,3)=(Z(1)/Z(2))*(Q2(I)*(1.-G1(I))-W2(I)*(1.-G2(I))-U2(I)*(1.-
     CG3(I))-(1./Z(3))*(Q0(I)*(QQ(I)-2.*Z(3)*02(I)  )/(2.*G1(I))
     C                     -W0(I)*(WW(I)-2.*Z(3)*W2(I)  )/(2.*G2(I))
     C                     -U0(I)*(UU(I)-2.*Z(3)*U2(I)  )/(2.*G3(I))))
      L(I)=1.0
      R(I)=Y(I)+VCALC(I)
    4 CONTINUE
      SUMAK=0.
      DO 3 J=1,M
      DO 5 K=1,M
      P=0.
      DO 2 I=1.N
      P=P + A(I,J)*A(I.K)/L(I)
    2 CONTINUE
      C(J,K)=P
    5 CONTINUE
      D=0.
      DO 6 I=1.N
      D=D + A(I.J)*R(I)/L(I)
    6 CONTINUE
      V(J)=D
    3 CONTINUE
      CALL MATRIX(10,M,M,0,C.M,F)
      DO 11 K=1,M
      XX=0.
      DO 10J=1.M
      XX=XX + C(K.J)*V(J)
   10 CONTINUE
      AK(K)=XX
      SUMAK=SUMAK+AK(K)**2
   11 CONTINUE
      DO 15 I=1,M
      Z(I)=Z(I)-(AK(I))
      IF(I.GT.M) Z(I)=0.
   15 CONTINUE
      PRINT 106,(Z(I),I=1,3)
  106 FORMAT ( 2X,3(E11.4,10X))
      IT = IT +1
      IF (ABS(AK(1)).GT.0.0005)    GO  TO 20
      S=0.
      DO 70 I=1,N
   70 S=S+R(I)**2/L(I)
      V=0.
      DO 71 K=1,M
      V(K)=SQRT(S/(N-M)*C(K,K))
   71 CONTINUE
      SD=SQRT(S/(N-M))
      RETURN
  200 CALL EXIT
      END
```

```
      PROGRAM DELTAVE (INPUT,OUTPUT)
      DIMENSION BM(50,2),VM(50,2),EM(50,2),RESET(50,2),BN(50,2),
     CVOL(50,2) ,SUM(50,2),VB(50,2),S(50,2),X(50,2),EXVOL(50,2)
      DIMENSION XX(50),YY(50)
      AE=0.004387$AS=0.1277$VC=0.759$AL=0.4978$VOLM=24.393$AM=0.03399
 99   READ 1,MM
 1    FORMAT(I1,9X,49H
      IF(MM.EQ.0) GO TO 100
      PRINT 102
 102  FORMAT(1H1)
      PRINT1,MM
      J=0
 70   J=J+1
      READ 17,B,FB,FM,DB,DM,WB,WM,N,M
 17   FORMAT (7F10.2I2)
      KK=N+1
      NPLUSM=N+M
      READ 2,(BM(I,J),I=1,KK)
      READ2,(VM(I,J),I=1,KK)
      READ2,(EM(I,J),I=1,NPLUSM)
      READ2,(RESET(K,J),K=1,M)
 2    FORMAT(8F10)
      XX=0
      K=0 $ L=1
      SEXY=0.
      DO 4 I=1,NPLUSM
      IF(EM(I,J).EQ.0.) GO TO 31
 30   VOL(L,J)=(EM(I,J)-R+(EM(I,J)-VM(L+1,J)-R+V)*B)*AE
      IF(SEXY.EQ.1.AND.L.NE.1) GO TO 40
      SUM(L,J)=XX+VOL(L,J)
 41   L=L+1
      SEXY=0.
 4    CONTINUE
      GO TO 26
 40   SUM(L,J)=SUM(L-1,J)+VOL(L,J)
      XX=SUM(L-1,J)
      GO TO 41
 31   K=K+1
      R=RESET(K,J)
      EM(I,J)=EM(I+1,J)
      V=VM(L,J)
      I=I+1
      SEXY=1.
      GO TO 30
 26   DO 5 I=1,N
      IF  (BM(I+1,J).LT.(FB+1.50))7,8
 7    VB(I,J)=(BM(I+1,J)-BM(I,J))*AS
      GO TO 10
 8    VB(I,J)=(BM(I+1,J)-FB-2.500)*AL+VC+(FB-BM(I,J))*AS
 10   BN(I,J)=VB(I,J)*DB/WB
 5    CONTINUE
      VS=(VOLM-(VM(N+1,J)-FM)*AM-SUM(N,J)-VB(N,J))
      VN=VS*DM/WM
```

```
      PRINT 12,VS,FM,VM(I,J)
   12 FORMAT(10X,3(F10.6))
      DO 20 I=1,N
      S(I,J)=BN(I,J)+VN
      X(I,J)=BN(I,J)/S(I,J)

      IF(J.EQ.2)X(I,J)=1.-X(I,J)
      EXVOL(I.J)=SUM(I,J)/S(I,J)
      IF(J.EQ.1) LL=N
 20   CONTINUE
      IF(J.EQ.1) GO TO 70
      KK=LL+N
      PRINT 80
 80   FORMAT(     8X,*MOLE FRACTION*,9X,*EXCESS VOLUME*/)
      CALL PLOTVOL(X,EXVOL,N,LL,XX,YY,KK)
      GO TO 99
 100  STOP $ END
      SUBROUTINE PLOTVOL(X,Y,N,LL,XX,YY,KK,T)
      DIMENSIONX(50,2),Y(50,2),XX(KK),YY(KK),P(50,2),Q(50,2)
      DO 4 I=1,LL
      YY(I)=Y(I,1)
      XX(I)=X(I,1)
 4    CONTINUE
      DO 5 I=1,N
      K=N-I+1
      P(K,2)=Y(I,2)
      Q(K,2)=X(I,2)
 5    CONTINUE
      DO 6 I=1,N
      L=LL+I
      YY(L)=P(I,2)
      XX(L)=Q(I,2)
 6    CONTINUE
      DO 7 I=1,KK
 7    PRINT 20,XX(I),YY(I)
 20   FORMAT(10X,2(F10.4,10X))
      CALL QIKPLT (XX,YY,KK,-1,15H*MOLE FRACTION*,25H*EXCESS VOLUME OF
     CIXING*)
      RETURN$END
```