EXCESS VOLUMES OF MIXING OF SOME BINARY AQUEOUS-ORGANIC MIXTURES AT PRESSURES UP TO 2.2 kbar

A THESIS
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by

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ABSTRACT

Excess volumes of 2-butanol + water have been determined indirectly from temperatures 5° to 85°C at low pressure. $V^E$ for the same system has also been determined directly from 1° to 85°C at pressures up to 2.2 kbar using a newly developed, low-cost high pressure dilatometer. Excess volumes of ethanol + water and butanone + water have directly been determined at 25° and 50°C, and 30°C respectively.

All three systems studied exhibit negative volume changes on mixing at and near ambient pressures. The alcohol + water mixtures having very low alcohol concentration show positive volume changes at extreme pressures. A similar tendency is found in butanone + water mixtures.

The $V^E$ measurements of 2-butanol + water and ethanol + water have been shown to be consistent with whatever reliable volumetric and LLE data is available. Direct $V^E$ measurements of butanone + water are not in agreement with the only other available data (not very reliable).

The ability of the UNIQUAC equation to describe the volumetric behaviour of 2-butanol + water was tested and as with expressions for excess Gibbs free energy, good $V^E$ fit and good phase equilibrium predictions make inconsistent demands on the values of the adjustable parameters.

The high pressure dilatometer has also been used to determine compressions of pure water, 2-butanol, ethanol and butanone, and the results are found to be in agreement with
the reliable available data. The Tait's and Huddleston's equations have been found to represent the compression data well, though the former seems to do it better than does the latter.
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To My Father and Deceased Mother
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NOMENCLATURE

A  Area
B  Constant
E  Modulus of elasticity
F  Molar Helmholtz free energy
G  Molar Gibbs free energy
H  Molar enthalpy
J  Tait equation constant
K  Compressibility
L  Tait equation constant
M  Molar mass
P  Pressure
R  Universal gas constant
S  Molar entropy
T  Temperature
V  Molar volume
Z  Compressibility factor
χ  Flory constant
A  Differences of energy parameters (i.e. \(g_{ij} - g_{jj}\))
a  Constant in polynomial
b  Constant
c  Constant of elasticity
f  Frequency
g  Energy parameter
k  Compression
ℓ  Length or displacement
m  Mass
n  Number of moles
q  External molecular surface area or number of nearest neighbour sites
r  Radius
v  Volume
w  Interchange energy or mass fraction
x  Mole fraction
α  Non-randomness parameter or linear coefficient of thermal expansion
γ  Activity coefficient
ε  Average intersegment energy
\( \varepsilon_r \) Radial strain
\( \varepsilon_t \) Tangential strain
\( \varepsilon_L \) Longitudinal strain
\( \mu_p \) Chemical potential
\( \mu \) Dipole moment
\( \omega \) Acentric factor
\( \delta \) Solubility parameter
\( \nu \) Poisson's ratio
\( \tau \) Period or as defined in equation (2.3.7.1)
\( \phi \) Volume fraction or as defined in equation (6.1.3.13)

**Superscripts**

E Excess
o Pure component
m Mixing
R Real
' One of the phases
" The other phase
id Ideal

**Subscripts**

c Critical
i Component
j Component
ij Species involved in interaction parameters
INTRODUCTION

The chemical industry is very competitive, and regular efforts are needed to improve the efficiency of various processes, particularly in material and energy utilization, and to increase their range of application. These efforts can have maximum effect when backed up by a thorough understanding of detailed chemical and physical mechanisms involved in a particular process. Reliable prediction of thermal and equilibrium properties of fluid mixtures is of great importance in the design of most chemical engineering unit operations, especially in separation processes like distillation, adsorption and extraction. Chemical thermodynamics provides a means of relating many different aspects of the physical behaviour of systems, so that, in principle, once a few key properties are known, many other properties can be deduced. Mixing rules by which properties of mixtures can be predicted are not well developed because of lack of availability of physical property data, and therefore, lack of understanding of mixture behaviour.

Towards understanding the behaviour of liquid mixtures the concept of the ideal mixture plays a paramount part. Although this idealization has never been realized yet, properties of a hypothetical ideal mixture are introduced into the thermodynamic real mixture to serve as a convenient standard of behaviour. However, there is a certain lack of precision about the definition of an ideal mixture, since it necessarily makes use of the properties of phases, solid, liquid or gas, extrapolated across phase boundaries into regions
of pressure and temperature where they do not exit. One of the simplest definitions of an ideal mixture relates chemical potentials of all components by the following equation:

\[ \mu_a(P, T, x) = \mu^0_a(P, T) + RT \ln x_a \quad (\alpha = 1, \ldots, n) \quad (1) \]

where \( \mu^0_a(P, T) \) is the chemical potential of pure component \( \alpha \) at the same pressure and temperature as the mixture being studied. This equation is supposed to hold good over non-zero ranges of pressure and temperature. But it is not very satisfactory for a liquid mixture on its saturation curve. The vapour pressure of a mixture is usually lower than that of one or more of its components at the same temperature. Some of the \( \mu^0(P, T) \) must therefore refer to liquid states extrapolated to pressures below their vapour pressures and so have no real physical meaning. Nevertheless, the change of \( \mu^0 \) with pressure is small for liquids near their triple point since the liquid molar volumes are much smaller than those of a perfect gas at the same pressure and temperature. In other words, at low vapour pressures the extrapolation needed to obtain \( \mu^0 \) is small enough to be calculated with confidence. But at high vapour pressures, there is no simple standard of normal behaviour.

However, the properties of an ideal mixture are considered as reference states for thermodynamic properties. For example, it is conventional to use excess thermodynamic properties of mixing that are defined as the difference between the thermodynamic properties of a real mixture and those of an ideal mixture of the same components at the same
pressure and temperature.

\[ M_{ij}^E = M_{ij}^R - M_{ij}^id \] \hspace{1cm} (2)

A complete thermodynamic description of a mixture can be given if the molar excess Gibbs energy is known as a function of temperature, pressure and composition which are the most convenient experimental variables. From the appropriate differentiation of an expression for the molar excess Gibbs energy all the excess functions may be deduced as discussed in several text books.

Thus,

\[ \frac{\partial G^E}{\partial P} \mid_{T,x} = V^E \] \hspace{1cm} (3)

\[ \frac{\partial G^E}{\partial T} \mid_{P,x} = -S^E \] \hspace{1cm} (4)

\[ \frac{\partial (G^E/T)}{\partial T} = -\frac{H^E}{T} \] \hspace{1cm} (5)

The excess Gibb's energy, unlike excess enthalpy and excess volume cannot be measured directly. Although a considerable amount of knowledge exists about the temperature and concentration dependence of \( G^E \), very little is known about its pressure dependence which is given by equation 3. Therefore determination of excess volumes as a function of pressure, temperature and composition would provide the information to calculate the pressure dependence of the thermodynamic excess functions \( G^E, H^E, S^E \) etc.

The excess volumes on mixing of binary mixtures can be attributed to structural changes brought about by the mole-
cules of one or both of the components. For most systems volume changes on mixing are negative but in some cases positive excess volumes have been reported. The mechanism involving such changes is not very simple, particularly in aqueous mixtures of polar organics involving hydrogen bonding. Even the detailed structure of water has been a matter of controversy. Many views have been put forward with none offering precise representation of the actual state of affairs. Nevertheless, mostly, pure water has been regarded as a mixture of two structural units in equilibrium:

\[ B \rightleftharpoons D \]  

(6)

The bulky or icelike form of water contains hydrogen bonded clusters, whereas the dense or normal form is composed of monomers or weakly bonded molecules. The bulky form is said to be of lower energy than the dense form. The dense form molecules are situated in between the clusters and also in the cavities in the clusters.

According to Kochner and Khaloimov mixing properties in aqueous mixtures of non-polar organics involving hydrogen bonding are partly due to structural changes of water introduced by the organic molecules. The interaction between the water molecules and non-polar groups of the organic molecules involves on the one hand the manifestation of Van der Waals' interaction between these groups of molecules and surrounding water molecules, and on the other hand the breakdown of the network of hydrogen bonds in
water on the penetration of non-polar groups into the cavities in its structure. With increase in the size of the non-polar group there is an increase in the number of water molecules undergoing Van der Waal's interaction with these groups and also in the number of broken hydrogen bonds in water. Rupture of the hydrogen bonds in water makes it possible to accommodate groups with large dimensions in the cavities by merging of several adjacent cavities in the water lattice to form a single large cavity. In Hvidt's view, for this type of aqueous mixture, negative excess volumes of mixing may be due to the following two effects:

(i) Packing of small water molecules in spaces between organic molecules.

(ii) Formation of dense water structure around polar groups of molecules of organic component.

The positive volume changes on mixing are attributed to the surrounding of non-polar groups in aqueous solutions by bulky water structure.

In order to predict liquid mixture behaviour from pure component properties, a number of theories have been put forward, but very little has been achieved so far. If there were an equation of state capable of application to liquid mixtures under all conditions, there would have been no need to deal with excess properties at all, i.e. the solution properties of interest could be directly calculated.

Experimental excess volumes on mixing of liquid mixtures
are useful in that they provide data to test theories of liquid mixtures and provide a guide for the formulation of new theories. The data are also useful in the chemical and petrochemical industries. At present there are more theories than sets of reliable experimental data to test their applicability.
1.1 Determination of Volume Changes on Mixing

1.1.1 Measurements at Ordinary Pressures

Volume changes on mixing at atmospheric pressure or in the vicinity of atmospheric pressure can be determined in two ways:

a) Indirect Method.

Molar excess volumes \( V^E \) have been, until recently, inferred from precision density measurements. Since density measurements can be performed precisely, they have found general applicability.

Density of a liquid is generally measured relative to the density of a reference material. Mercury, air and water are recommended along with other organic compounds, as reference materials. Use of mercury as a reference material suffers from the disadvantages that the density of mercury is much greater than that of most other liquids and the cleanliness of the apparatus and the purity of mercury greatly affects the contact angle of mercury. Water, because of its availability and the ease with which it can be purified, is normally used as a standard for density measurements. Air, the density of which can be calculated from the perfect gas law is often used for the calibration of
certain types of density meters, at pressures not far removed from ambient.

If the density of a liquid mixture is measured at constant temperature the $V^E$ is deduced according to the following:

$$V^E = \frac{x_1 m_1 + x_2 m_2}{\rho_{12}} - \left( x_1 \frac{m_1}{\rho_1^o} + x_2 \frac{m_2}{\rho_2^o} \right)$$

where $x$, $m$ and $\rho$ denote mole fraction, mass and density respectively.

Density measurements of liquids can be taken by weighing a definite volume of the liquid in a density bottle or pycnometer or by determining the buoyancy acting on a 'sinker' immersed in a liquid (Principle of Archimedes), or by using mechanical oscillator densimeters.

i) Pycnometric Technique

Density measurements using pycnometers are the simplest and least expensive procedure in terms of readily available equipment, but may be the most expensive in terms of time. Filling the pycnometers to obtain reproducibility at a given temperature is a difficult task. The formation of bubbles is a frequent source of error. Wetting of the capillary by the meniscus leads to errors in measurement of the liquid level and calibrating the volume of the pycnometer as a function of temperature gives birth to additional errors. Nevertheless, careful measurements using this classical method can provide an accuracy of about one part in $10^6$ in density.
ii) Magnetic Float Technique

These densimeters\(^5\) work on the principle of balancing the opposing effects of gravity, buoyancy and magnetic field on a float containing a permanent magnet or a soft iron core. This is done by passing current through a solenoid placed below the cell containing the liquid. Density is related to the current at which the float first lifts off from the bottom of the cell. Normally such densimeters can cover only a relatively small density range and require relatively large volumes of the sample for good precision. Such densimeters with an accuracy of 2 ppm and a sensitivity of 0.3 ppm have been reported\(^6,7,8\).

iii) Mechanical Oscillator Densimeter Technique

The measuring principle of such devices\(^9,10\), is based on the variation of the natural frequency of a hollow oscillator when filled with different liquids or gases. The mass and thus the density of the liquid or gas changes this natural frequency due to a gross mass change of the oscillator caused by the introduction of the fluid.

The effective mass \((m)\) of the oscillator is composed of its own unknown mass \((m_o)\) and the well defined, but also unknown mass of the sample of density \('\rho'\) contained in volume \('v'\), and is given by:

\[
m = m_o + v\rho
\]

The usual mode of vibration of the oscillator is of a
bending type and assuming that it can be approximated by that of a mass \( m \) attached to a spring with constant of elasticity, \( c \), and further that the oscillator performs an undamped oscillation, the resonant frequency, \( f \), is given by:

\[
2 \pi f = \left( \frac{c}{m} \right)^{\frac{1}{2}} = \left( \frac{c}{m_0 + \nu_0} \right)^{\frac{1}{2}}
\]

Consequently, the density of the sample is given by:

\[
\rho = -\frac{m_0}{V} + \left( \frac{c}{4 \pi^2 V} \right) \left( \frac{1}{f^2} \right) = A + B \tau^2
\]

where \( \tau \) is the period \((1/f)\) of oscillation, and \( A \) and \( B \) are constants characteristic of the oscillator. As previously mentioned, densities are measured relative to those of a reference material. For a density difference it follows that:

\[
\rho - \rho_0 = B (\tau^2 - \tau_0^2)
\]

where \( \rho_0 \) is the density of the reference material and \( \tau_0 \) is the corresponding period of oscillation. The \( \tau \) values average over the range of \( 10^2 \) to \( 4 \times 10^4 \) periods can be obtained in less than 2 minutes. The effect of the mechanical agitation of the oscillator on liquids has not been evaluated yet, but it should be insignificant in the case of organic liquids and their mixtures. The precision is said to be 1.5 ppm for a relative density measurement of the order of \( 3 \text{ g cm}^{-3} \). Such densimeters are commercially available, and they include the type which can measure densities of flowing liquids as well\(^{10}\).
iv) Other Methods

Methods based on Archimedes' principle depend on determining the reduction in weight of a sinker of known mass and volume as it is immersed in a liquid. Apparatus based on this principle is said to be capable of measuring densities with a precision of 1 ppm or better over a wide range of temperature\textsuperscript{11}. The isopycnic temperature or floatation temperature method\textsuperscript{4,12} depends on the precise variation of the temperature of a solution until its density is identical to that of a calibrated glass diver. This is done by noting the rate of rise or fall of the diver as the temperature is varied. This technique has not been used for determination of excess volumes. A few other techniques for determination of densities of liquids have been discussed by Baver and Lewin\textsuperscript{4}.

v) Precautions in Density Measurements

For density measurements a few precautions are very important, particularly when using pycnometers and mechanical oscillator densimeters. Dissolved gases in liquids are often a source of bubble formation giving rise to erroneous liquid volume measurements. Furthermore, the densities of aerated liquids can differ from those of degassed liquids by as much as 300 ppm\textsuperscript{13}. So it should be explicitly mentioned whether aerated or degassed liquids have been used.
vi) Drawbacks of Density Measurement Method

Molar excess volume on mixing rarely exceeds 2% of the volume of a liquid mixture and it is usually very much less. For most mixtures $V^E$ is usually no greater than 0.3% of the total volume of the mixture. To achieve a reasonable accuracy in estimates of $V^E$, density measurements need to be made to an accuracy approaching one part in $10^5$. To achieve this accuracy on mixtures containing a volatile component is very difficult as the assumption made when applying corrections for evaporation during the preparation and transfer of mixtures are often inadequate. In a number of cases, excess volumes calculated from densities have differed considerably when compared with direct measurements. An example is the liquid and solid system benzene and diphenyl. Duff and Averett\(^{14}\), using the density method, calculated an excess volume of $-0.61 \text{ cm}^3 \text{ mol}^{-1}$ for equimolar mixture at $30^\circ\text{C}$. Kortum and Schrieber\(^{15}\), using a similar technique, obtained a value of $-0.12 \text{ cm}^3 \text{ mol}^{-1}$ at $35^\circ\text{C}$. Direct measurements by Powell and Swinton\(^{21}\) gave $-0.22 \text{ cm}^3 \text{ mol}^{-1}$ at $30^\circ\text{C}$ and $-0.29 \text{ cm}^3 \text{ mol}^{-1}$ at $50^\circ\text{C}$ for a mixture of the same concentration. So there are indications to discourage the density method for determination of excess volumes of mixing, particularly for mixtures containing volatile mixtures, as a difference in density of the order of $20 \times 10^{-6}$ would generate a difference of $0.002 \text{ cm}^3 \text{ mol}^{-1}$ in volume on mixing values\(^{16}\).
b) Direct Method

Although density measurements for the determination of molar excess volumes on mixing can be taken quickly, particularly while using mechanical oscillation densimeters yet, for the sake of greater precision, a more satisfactory method is to measure $V^E$ directly in a dilatometer\textsuperscript{17}. The requirements for measuring excess volumes directly are similar to those for measuring excess enthalpies, except that the presence of a vapour space even as small as $10^{-2}$ or $10^{-3}$ cm$^3$ may lead to considerable error. There are two basic techniques available for direct measurement of $V^E$; (i) single composition, batch dilatometry and (ii) dilution dilatometry.

i) Batch Dilatometry

A basic design employs a vessel having two links and a precision-bore capillary. The vessel is first fitted with mercury. Known masses of each liquid are injected into the limbs of the dilatometer where they remain segregated from each other by the mercury in the lowest part of the vessel. An approximate precision-bore capillary is filled to a certain level in such a way that no air pockets are trapped within the dilatometer. After thermal equilibrium the mercury height relative to a reference is measured. The contents of the dilatometer are mixed by rocking sideways so that the mercury flows into one limb, then the other, thus displacing and mixing the liquids. After thermal equilibrium has been reached the mercury height is recorded again. To confirm that mixing is complete, the rocking process
is repeated until constancy in the mercury height is obtained. A correction in such a design is necessary because the change in height of liquid in the capillary results in a change in pressure on the liquids.

A simple apparatus based on the above lines has been used by Swinton and co-workers\textsuperscript{18}. Their dilatometer is reported to be capable of measuring $V^E$ with an accuracy of 0.001 cm\textsuperscript{3} mol\textsuperscript{-1}.

One of the disadvantages associated with batch dilatometers is the loss due to evaporation of volatile components during injection. Brennan et al\textsuperscript{19} and Ahmed et al\textsuperscript{20} have improved the dilatometers of Swinton\textsuperscript{21} in order to eliminate their source of error. The dilatometer used (with capillary detached) is smaller in size so that it can be weighed directly on the balance pan. Thus, by making three successive weighings on the dilatometer filled with mercury, mercury + component 1, mercury + component 1 + component 2, the precision in composition can be improved greatly. Great importance is attached to compressibility correction in dilatometers where the displacement of mercury meniscus in the capillary has a vertical component. Omission of this correction can lead to errors of 0.5 to 1.0 per cent on $V^E$. Errors arising from other factors are 0.5 per cent for $V^E$ of the order of 0.5 cm\textsuperscript{3} mol\textsuperscript{-1}, from batch temperature fluctuations of .001 and 0.1 per cent from other measurement devices. An excessive amount of grease on the joint where the capillary is attached to the body of the dilatometer, can cause the capillary or the dilatometer to move during the measurements.
and can be an additional source of error. Any attempt to improve the precision of $V^E$ measurements by reducing the bore of the capillary beyond a certain limit can cause the mercury column to separate. Stooky et al$^{22}$ have analysed, at length, the sources of error associated with $V^E$ measurements in batch dilatometers.

ii) Dilution Dilatometers

Dilution dilatometers for measuring excess volumes offer the advantage that the composition range can be covered in two runs and partial molar excess volumes are readily obtained.

The basic design common to most of dilution dilatometers consists of a mixing cell containing a known amount of one component over mercury and a calibrated burette containing the second component also over mercury, the two being connected at the lower end via the mercury column and a greased ground glass stopcock, and at the upper end via a capillary. The level of mercury in the mixing cell is higher than that in the burette. Thus, on opening the stopcock, mercury from the mixing cell flows into the burette thereby forcing the second component through the connecting capillary into the cell. The volume change is obtained by measuring the change in the level of mercury in a calibrated capillary connected to the mixing cell. Measurements are carried out over the entire composition range by making a similar run with the roles of the components reversed.

Van der Waals and Desmyter$^{23}$ described an apparatus
which requires the liquids to be distilled under vacuum before sealing by glass blowing. The operating procedure is complicated. The most conveniently operated version of this type is described by Williamson and colleagues, the construction and operation of which is more or less as described in the previous paragraph. Recent developments have been aimed at making dilatometers with smaller mixing cells, fewer stopcocks or none at all, and at increasing the ease of operation while at the same time improving the precision of the $V^E$ measurements. Some of them have been reviewed by Battino. Stokes et al have described a dilution dilatometer with which they obtained a standard deviation of $0.0008 \text{ cm}^3 \text{ mol}^{-1}$ for the test system cyclohexane & benzene. Martin and Murray have slightly modified the design to facilitate cleaning, filling and calibration procedures.

One of the sources of error associated with dilution dilatometers of the type described above is the greased stopcock. As the stopcock is turned, the mercury flowing through carries some of the grease along with it, and thus changes the volume of the system. This error accumulates every time the stopcock is turned in order to make a new composition in the mixing cell. The effect of this creeping action of the grease on the precision of $V^E$ measurements was studied very carefully by Bottomley and Scott and Tanaka et al. The two studies show that depending upon the characteristic of the stopcock, the operation of turning the greased stopcock can either increase or decrease the volume of the contents of the mixing cell and that grease
gets into the system even when the stopcock is turned without any mercury flowing through it.

Bottomley and Scott\textsuperscript{27} constructed a tilting dilution dilatometer without greased stopcocks in which no stopcock is turned or adjusted during a dilution run. In this dilatometer a known amount of two pure components are injected into the calibrated burette and the calibrated mixing cell respectively. After thermal equilibrium, mixing is done by tilting the dilatometer and volume changes are indicated by the capillary. Although the dilatometer is easy to operate, it has the drawbacks of being difficult to calibrate and being tedious to fill under vacuum. It is limited to the measurement of small volume changes only. McGlashan\textsuperscript{29} has produced an improved version of tilting dilatometer which can be filled under atmospheric pressures, is easier to operate, and can be used to measure $V^E$ of large magnitude as well. Tanaka et al\textsuperscript{28} have produced a dilatometer in which volume changes in the mixing cell are accommodated by a piston controlled by a micrometer which is turned to maintain the same level of the mercury meniscus in the mixing cell and the capillary. Consequently no correction for pressure is needed as it operates at constant pressure. Another rather unconventional dilatometer, which does not use mercury and can be operated at constant pressure has been reported by Tanssens and Ruel\textsuperscript{30}. It has the advantage of no mercury use since some organic liquids are reported to react with mercury\textsuperscript{31}. 
ii) Limitations and Advantages of the Direct Method

Although out of the different direct and indirect techniques for determination of $V^E$, the simplest one with acceptable precision is the mechanical oscillator densimeter, purity of components is critical in any density measurement. Whereas in direct $V^E$ determination the purity of the components is not critical, so the use of more expensive research grade chemicals (99.9 mol per cent or better) is often unnecessary.

The direct measurement of excess volumes at low temperatures imposes severe experimental problems. The expansion method most commonly used involves many potential sources of systematic error. The major source of error is the inaccurate determination of the volume of the cell and the expansion bulbs. As far as the two direct techniques are concerned the batch technique is as accurate as the dilution technique is, if not any better. On the other hand, although the results secured by dilution dilatometry have low standard deviation, they do contain accumulated errors. Dilution dilatometers are faster compared with other techniques but they demand greater operational skill. The point which goes in their favour is that they are very suitable for probing dilute regions. On the other hand, batch dilatometers are preferable for working with expensive materials, since they require from 10 to 15 cc of each component to study the whole composition range, whereas dilution dilatometers need at least 100 cc of each component. Except Tanaka et al. and McGlashan's dilatometers, all other dilution
dilatometers suffer from either compressibility effects or from ambiguities associated with greased stopcocks.

1.1.2 Measurements at Elevated Pressures

Molar excess volumes on mixing at high pressures can be obtained indirectly from compressibilities and densities of mixtures of known composition and of their constituents. The direct method is an extension of the principles used for the same purpose at or near atmospheric pressure. However, the details of design and choice of materials of construction of the apparatus are very different.

a) Indirect Method

A mixture of known composition is made up at atmospheric pressure and the compressibility of the mixture is measured by determining the molar volumes of a set of mixtures at low pressure and selected temperatures and then determining the isothermal compressibilities of these same mixtures at the same selected temperatures. The chief advantages of this method are that several values of $V^E (P, x)$ may be obtained from a single mixture and that the experimental technique is usually simple. The disadvantages of this method are that the results are significantly less accurate than those of the direct method and it is restricted to systems which are completely miscible under all conditions of interest, since it does not employ any means of stirring. For instance, it is not possible to cover the whole concentration range when immiscibility decreases with increasing pressure.
Molar excess volumes at high pressure of a number of binary liquid mixtures have been deduced from compression data by Hamman and Smith\textsuperscript{35}. They also provide their own measurements on several other systems. The effect of pressure on $V^E$ of methylethylketone and water system was calculated from experimental measurements of compressibility by Lamb and Hunt\textsuperscript{36}. Korpela\textsuperscript{37} and Götze\textsuperscript{38} have also published data on various systems obtained from accurate P,V,T data measured on different mixtures and pure components.

b) Direct Method

Weighed amounts of each component are compressed jointly in a device to the required pressure at constant temperature. The components are then mixed and conditions adjusted to the same pressure and temperature. The resulting change of the mixture is observed by some means, e.g. from the displacement of the piston which transmits pressure to the test mixture from the pressure generating system.

This method can yield results of much higher accuracy. Only very limited work has been done on determination of $V^E$ by this technique. The main disadvantage of this method is that each experimental value of $V^E(x)$ has to be obtained from a separate mixing test. Engels and Schneider\textsuperscript{39} were the first to report a high pressure $V^E$ measurement device. The same device has been used by Götze\textsuperscript{40}, and Götze and Schneider\textsuperscript{41} for acquiring more data on pressure and temperature dependence of $V^E$ for various liquid mixtures.
1.2 A Brief Review of Relevant Previous Apparatus for Use in Determination of Excess Volumes on Mixing at High Pressures

1.2.1 Indirect Technique

Extensive work has so far been done on measurement of compressibility of liquids and liquid mixtures. The compressibility data thus obtained can be used to determine excess volumes of mixing. Bridgeman determined compressibilities of a large number of liquids and also the change of many physical properties as a function of pressure. It was he who first developed apparatus which would measure compressibilities up to 690 K bars. The compressibilities were measured in a number of ways, at least two of which had not been used before.

A piston displacement apparatus involved the sample being contained in a cell into which a very narrow diameter rod would slide through a gland which was as leak-proof as possible. On compression of the sample the free space so formed was taken up by the rod moving in. The accuracy was reduced because of difficulties in prevention of leakage across the gland. Another design of apparatus contained the sample in a vessel such that on compression only one of its characteristic dimensions would alter. For this purpose Bridgeman used either a cylinder containing an accurately ground piston or a form of brass bellows. The change in dimension on compression was measured by means of a slide-wire, attached to the sample holder, which moved past a contact. A known current was passed along this wire so that
the change in voltage corresponded to the change in volume of the sample. Thus a continuous method of compressibility measurement was devised.

Liquid compressibilities have been measured by means of Piezometers by several workers. One of the first was that of Richards and Chadwell\textsuperscript{45}, who found the compressibilities of pure water, alcohol and many other liquids as well as binary mixtures of many of these mixtures in the pressure range of 100 to 300 bar at 20°C. The apparatus consisted of a glass piezometer with an electrical contact reaching almost to the bottom of the capillary. Some mercury was placed in the piezometer and pressure was applied until the contact was broken. Then more mercury was added and the process repeated and so on. The mercury was then replaced with the liquid under test and the process repeated. Thus the compressibility of the liquid relative to that of mercury was found.

Adams\textsuperscript{46} used a piezometer which had a capillary rising from the base and into the body of the piezometer. The piezometer was filled with liquid and seated in mercury. As the fluid was compressed the mercury entered through the capillary and collected in the bottom of the piezometer. Thus the volume change was given by the volume of mercury collected.

The method of Gibson and Loeffler\textsuperscript{47} was similar to that of Adams except that the mercury rising up the capillary was observed by means of a microscope. The accuracy of the
compressibility measurement was thus improved since the dis-advantages of Adams' method (where only whole drops of mercury were measured while part-drops adhering to the end of the capillary were undetected) was avoided.

A differential transformer method has been used by Doolittle et al\textsuperscript{48} to measure the compressibility of n-alkanes in the temperature range 20-300°C and pressures up to 4000 bar. The sample was contained in a stainless steel piezometer 0.087 in. diameter and 19 in. long, sealed at the lower end by mercury. A piece of iron was floated on top of the mercury seal. The position of this float could be located by means of external differential transformers and hence the volume change was deduced. The results obtained by this method were claimed to be accurate to four parts in 10000. Boelhower\textsuperscript{49} measured the compressibility of the same type of compounds but combined Bridgeman's bellows method with that of Doolittle's differential transformer. The liquid was contained in the bellows which were attached, by means of a wire, to a piece of iron. The movement of this iron on compression of the liquid was measured by means of a differential transformer. Bellows now find no favour due to uncertainty that $\Delta V \propto \Delta l$.

Eduljee Newitt and Weale\textsuperscript{50} found the compressibility of pure liquids and their mixtures by means of a piezometer which could measure compressibility using a 'digital' form of resistance indicator. The piezometer was a glass tube, closed at one end, and reducing to a smaller diameter at the other. Inside the smaller diameter portion was a high
resistance wire with platinum contacts soldered at intervals along it. The piezometer was filled with the liquid under test and inverted, the open end being immersed in a reservoir of mercury. Compression of the liquid caused the mercury to rise up the piezometer causing changes in the measured current.

Recently, Moriyoshi et al\textsuperscript{51,52,53} have determined compressions of various alcohol water mixtures by employing Adams' method. Their high pressure apparatus consisted of a high-pressure screw pump, a pressure vessel, a pressure exchanger, two pressure gauges (Bourdon gauge and pressure balance), and auxiliary equipment. The pressure vessel was sealed by means of an O-ring and immersed in a thermostat bath. Seven glass piezometers were inverted on an appropriate quantity of distilled mercury in a Teflon container. The container was placed in the pressure vessel. The fluid was separated from hexane in the pressure vessel by means of the pressure exchanger which consisted principally of a mercury column.

Another method to find compressions of various liquids and their mixtures has recently been used by Lamb and Hunt\textsuperscript{36}. They determined compressibilities by placing samples in a stainless steel cylinder closed by a piston of the same material. The piston was sealed with a PTFE O-ring in contact with the liquid mixture backed up by a Viton O-ring. The piston/cylinder arrangement was mounted inside a high pressure vessel filled with petroleum ether. Movement of the piston in the cylinder was monitored by a potentiometer fixed to the cylinder with a wire attached to the piston.
This potentiometer constituted part of a bridge circuit to which it was connected via electrodes which passed through the pressure vessel closure. The bridge circuit was designed to avoid errors due to piezoelectric effects and the effect of pressure on the resistance of the potentiometer.

1.2.2 Direct Technique

For measurement of molar volume change of mixing at elevated pressures this technique is more accurate and has been used by Engels and Schneider. Their mixing device was constructed as a pycnometer. The volume changes of the liquid enclosed in the mixing device were determined by the displacement of a piston in a cylindrical tube of small cross-section, the volume of the cylindrical tube being small relative to the total volume of the mixing device. Inside, the upper part of the vessel was divided into two concentric sections by means of a thin-walled cylinder. The mixing vessel and the tube containing the piston were filled with mercury until the two concentric sections formed chambers which separated one from the other. These chambers were charged with the pure components through sealable openings. The well-fitting piston, which separated the liquid inside the vessel from the pressure transmitting medium, moved freely in the inner tube. Volume changes of the liquid enclosed in the vessel caused the piston to move. Its position was detected from outside the vessel by an inductive coil. The mixing vessel was mounted inside a high-pressure autoclave so that it had to withstand no
pressure difference. For mixing the two liquid components the whole autoclave was turned upside down, thus dislodging the components from the chambers by mercury and giving rise to mixing in the lower part of the vessel.

Although no other equipment is found to have been reported in the literature for direct measurement of volume change on mixing at high pressures yet, some high pressure equipment is mentioned in the literature for the study of phase behaviour of mixtures at high pressures which, with slight modification, can be used for the purpose of determination of excess volumes.

Oeder and Schneider have described an optical cell which could be used for P,V,T measurements up to 400 MPa. They used the cell at moderately low temperatures; nevertheless, the basic design is suitable for use under more extreme conditions of pressure and temperature. Constructed from Cu-Be alloy it was fitted with two sapphire windows. The fluid mixture in the cell could be agitated by a small magnetic stirrer driven from outside by a rotating magnet. The pressure was transmitted to the mixture by flexible bellows. The displacement of the bellows could be detected and measured by a displacement transducer. Alwani and Schneider have described a more complicated optical cell capable of operation up to 400 MPa and 397°C. Constructed from Nimonic 90, fitted with a piston in the base of a thick high pressure tube, and having a moving seal between piston and cylinder made by Viton O'rings, it can be used for P,V,T studies by measuring the displacement of the piston.
Stirring of the fluid mixture was achieved by a magnetic ring in the cell which could be moved backward and forward by making the inner face of the window assembly, first a magnetic north pole and then a south pole and repeating this cycle.

1.3 Some Systems For Which High Pressure Excess Volumes Have Been Determined

Chemical abstracts were searched from the year 1965 (vol. 62) to June 1983 (Vol. 98). Although there is a large number of papers in the literature dealing with investigations on excess volumes of liquid mixtures at atmospheric pressure, measurements of $V^E$ at higher pressures are scarce.

Winnick and Powers determined volume change on mixing from compression measurements, for acetone and carbon disulphide system at 0°C and up to 6.9 kbar pressure, showing large positive deviations from ideality. They found the volume change to decrease with increase in pressure. The maximum was also found to shift towards acetone-rich concentrations during the increase in pressure.

Korpela has calculated $V^E$ from experimentally determined compressions of carboxylic acid and water mixtures at temperatures of 25°C, 40°C and 55°C, and up to 2.5 kbar pressure. Altogether, aqueous mixtures of four carboxylic acids, i.e. formic acid, acetic acid, propanoic acid and isobutyric acid, were studied over the entire composition range. $V^E$ values (found to be negative for all the systems
studied, at the three temperatures and 1 kbar pressure) have been presented.

Hamann and Smith\textsuperscript{35} derived molar excess volumes of mixing from compression measurements for mixtures of 14 organic compounds with water at pressures up to about 1 kbar. In all the cases negative deviations from ideality were observed. In some cases at 1 kbar pressure, for mixtures rich in water, slightly positive volume changes on mixing have been reported. Generally, with increase of pressure $V^E$ increased as well, i.e. the value became less negative. Hamann and Smith also reported positive excess volumes for the pyridine and water system at very high and additionally at very low water concentration at 1 kbar. This could not be confirmed by direct measurements of $V^E$ for the system by Götze\textsuperscript{58}.

Altumin and Konikevich\textsuperscript{59} studied compressibility and volume effects of mixing for solutions of aliphatic alcohols, $(C_4H_9OH + C_3H_7OH$, $C_6H_{13}OH + C_3H_7OH$, $C_8H_{17}OH + C_3H_7OH$ and $C_{10}H_{21}OH + C_3H_7OH$), in the temperature range of $25^\circ$ to $150^\circ$C and pressures up to 2 kbar. For the octanol + propanol system, the volume of mixing increases with increasing pressure and the effect is greater at higher temperatures. At constant pressure the volume changes on mixing decreases as temperature increases and can even be negative at low pressures.

Engels and Schneider\textsuperscript{39} took direct measurements of $V^E$ for water and 3-methylpyridine system at $50^\circ$, $81.5^\circ$ and $95^\circ$C
and pressures up to about 2.5 kbar. The molar excess volumes were negative and their absolute values decreased with increase in pressure. The absolute values of the molar excess volumes also decrease with increase of temperature at a given pressure and composition. For mixtures having very low 3-methylpyridine concentration, the molar excess volumes were found to be slightly positive above 2 kbar pressure.

Götze and Jeschke have reported directly determined $V^E$ of equi-molar aqueous mixtures of acetonitrile, acetone, tetrahydrofurane, methanol, ethanol, 2-propanol, 1,2-ethanediol and pyridine at 25°C and pressures up to 2.5 Kbar. These substances range from molecules with weak H-bonding (e.g. acetonitrile) to molecules which are able to form rather strong H-bonds with water (e.g. pyridine). The excess volumes are negative, in all the cases, and have their greatest absolute value at the lowest pressure (100 bars) at which the measurements were taken. Qualitatively, the effect of increase of pressure on $V^E$ is reported to be the same as that of increase of temperature. Götze and Jeschke also report that for non-aqueous equi-molar mixtures of 2-propanol + heptane (a polar and a non-polar component) and toluene + methylcyclohexane (both non-polar components), the excess volumes are positive. But increase of pressure decreases the absolute value of $V^E$ in the same way as was the case with aqueous mixtures. It is interesting that although the 2-propanol + heptane mixture has one polar component and exhibits greater excess volume at 1 bar than
toluene + methylcyclohexane (with two non-polar components) yet, with increasing pressure, $V^E$ decreases more rapidly for the first than for the second system, so that at the highest pressure (2.5 kbar) the sequence is reversed.

Recently, Götze and Schneider\textsuperscript{41} have reported on the above aqueous systems more fully for temperatures 0°, 25°, 50° and 75°C. They have presented values of excess volumes of mixing up to 2.5 kbar pressure for equi-molar mixtures of water with acetone, tetrahydrofurane, methanol, ethanol, isopropanol and 1,2-ethane diol, and additionally for water + acetonitrile and water + pyridine over the entire composition range. At pressures above 1 kbar the water + acetonitrile system shows positive $V^E$ values at concentrations rich in organic component at 25°, 50° and 75°C, whereas pyridine + water shows positive values of $V^E$ on both water-rich compositions and the pyridine-rich compositions at 50° and 75°C, at a pressure of 2.5 kbar.

Jeschke and Schneider have reported\textsuperscript{61} more fully than Götze and Jeschke on the toluene + methylcyclohexane and 2-propanol + heptane up to 2.5 kbar pressure and at a temperature of 25°C by exploring the whole composition range.

Ohling and Schneider\textsuperscript{62} measured $V^E$ of a typical hydrocarbon + fluorcarbon system, i.e. hexane + tetrafluoro-hexane at 60°C and from 100 bars to 500 bars, over the entire composition range. They reported large positive values of $V^E$ (5.7 cc at 100 bar for equi-molar mixture), which rapidly decrease with increase in pressure.
1.4 Relevant Measurements on Systems Under Study

1.4.1 Excess Volumes of 2-Butanol + Water System

a) At Atmospheric Pressure

The literature survey has revealed that very little data exists on $V^E$ of this system.

Frank and Smith have measured densities of dilute aqueous solutions of isomeric butanols (including 2-butanol), using a magnetic float technique at temperatures of 0.5°, 5°, 25° and 40°. They repeated measurements at every temperature corresponding to a particular concentration of the alcohol in the mixture. Excess volumes from their results of 2-butanol + water have been calculated and are given in Table 1.1.

Friedman and Scheraga measured densities of 2-butanol + water mixtures at 1°, 20°, 40° and 50°C. They also measured densities of various other alcohol-water mixtures using pycnometers which were a modification of the 'type F' form described by Baver. The actual purpose of their experimentation was to find partial molal volumes of various alcohol-water systems. Excess volumes of mixing from their density data for 2-butanol + water solutions have been calculated and tabulated in Table 1.1.

Altsybeeva et al have studied phase equilibria in, and thermodynamic properties of, the 2-butanol + water system. In fact they are the only reference which could be traced in the literature which presented volumes of mixing on the system under consideration. Density measurements taken at
20° and 60°C were secured by the pycnometric technique. The pycnometer used was of 20 cc volume. Their results are presented in Table 1.1.

Nakanishi\textsuperscript{67}, while studying partial molal volume of butyl alcohols and of related compounds in aqueous solutions has reported densities of 2-butanol + water mixtures over a wide range of composition and at 20°C. The device used was a pycnometer and the precision claimed is \( \pm 2 \times 10^5 \) cc per mol.

Some of the available literature volume change on mixing data has been graphed in Figure 6.1. No volume change on mixing of this system which was determined by any direct method has been found described in the literature.

b) At Elevated Pressure

An extensive search of the Chemical Abstracts has revealed no report of volume change on mixing of 2-butanol + water system at elevated pressures, either by direct or by the indirect method.

1.4.2 Excess Volumes on Mixing of Butanone + Water System

a) At Atmospheric Pressure

Two sets of data giving the change of specific gravity, with composition, those of Tarasov et al\textsuperscript{68}, taken at 22°C. and those of Boeke and Hanewald\textsuperscript{69}, taken at 21°C agree well with each other. Volume changes on mixing from these data
have been calculated by Hunt\textsuperscript{70} who studied volume changes on mixing by measuring specific gravities at 21.5\textdegree{}, 30\textdegree{}, 50\textdegree{} and 70\textdegree{}C.

b) At Elevated Pressure

No direct measurements are reported to have been taken at high pressure by anyone so far. Hunt\textsuperscript{70}, however, has calculated excess volumes on mixing from compression data at 30\textdegree{}, 50\textdegree{} and 70\textdegree{}C and at pressures up to about 1.7 Kbars. But his work is restricted to the mixtures of this system which are homogeneous at atmospheric pressure at the three temperatures. Some of the results are shown in Table 1.2.

1.4.3 Excess Volumes on Mixing of the Ethanol + Water System

a) At Atmospheric Pressure

Accurate data on excess thermodynamic function $V^E$ is lacking for the ethanol + water system as well. Friedman and Scheraga\textsuperscript{64}, in order to study partial model volumes of alcohol-water solution, took measurements for densities of ethanol + water mixtures at 1\textdegree{}, 20\textdegree{}, 40\textdegree{} and 50\textdegree{}C with the help of pycnometers.

Kesselman and Onufrier\textsuperscript{71} have calculated excess volumes of mixing, along with other excess thermodynamic functions, over a wide range of temperatures and pressures up to 300 bars from detailed analysis of experimental and tabulated
pressure-volume-temperature-composition data\textsuperscript{72-75}. They suggested an equation to calculate $V^E$ for the water-alcohol system, capable of reproducing the experimental $P,V,T,x$ data with a mean error of 0.1 to 0.2\% in the specific volume of the solution

$$\Delta v = x(1-x) \left[ a_1(T) + b_1(T) P + x \left( a_2(T) + b_2(T) P \right) \right]$$

They give these values of $V^E$ for ethanol-water system in graphical form.

Winnick and Kong\textsuperscript{76} determined excess volumes of mixing of ethanol + water along with a few other binary polar liquid mixtures using pycnometers. They also calculated the excess volumes using a partition function\textsuperscript{77}. However, the excess volumes predicted did not agree well with their experimentally determined values.

b) At Elevated Pressure

Schneider and Götze\textsuperscript{41} have recently measured, dilatometrically, excess volumes of this system at 0°, 25°, 50° and 75°C for a mixture of constant mole fraction of $x = 0.5$ and up to 2.5 kbar pressure. Their direct method of determination of excess volumes has been described in Section 1.2.2. The $V^E$ data at 25° and 50°C is plotted in Fig. 6.2.

Haman and Smith\textsuperscript{35} determined compressions of some organic liquids with water at about 1 kbar at 30°C including ethanol + water mixtures. From their own compression data, and that gathered of other workers, they deduced excess
volumes on mixing. Although Moriyoshi and Inubushi\textsuperscript{52} and Moriyoshi et al\textsuperscript{51} have measured compressions of various aqueous alcohol solutions at 25°C and up to pressure of 1.4 kbars. and 1 kbar respectively, yet no attempt was made by them to calculate excess volumes on mixing from their compression data.

1.5 Liquid-Liquid Phase Equilibrium in the Systems Under Study

For the systems under study, in the pressure and temperature range of interest, it is necessary to know which are miscible regions; otherwise the volume changes on mixing become meaningless.

1.5.1 2-Butanol + Water System

The mutual solubility of 2-butanol + water system has been studied by several investigators, starting before the end of the last century. The first reported data was obtained by Alexjeff\textsuperscript{78}. Then followed Timmermans\textsuperscript{79}, Dolgolenko\textsuperscript{80}, Delcourt\textsuperscript{81} and Jones\textsuperscript{82}. Mutual solubilities of this system were also studied by Boeke and Hanewald\textsuperscript{69}, Altsybeeva et al\textsuperscript{66}, Morachevskii et al\textsuperscript{83} and Moriyoshi et al\textsuperscript{84}. All of the available literature data are graphed in Fig. 1.1.

The mutual solubility of the system 2-butanol + water as a function of pressure was first studied by Timmermans\textsuperscript{79}. The influence of pressure on the mutual solubility of this system was determined by Moriyoshi et al\textsuperscript{84} in the temperature
Fig. 1.1 Solubility of 2-butanol + water at 1 bar
Fig. 1.2 High pressure solubility of 2-butanol + water (cf. Lamb and Bozdag85)
range 10° to 110°. Lamb and Bozdag\textsuperscript{85} have thoroughly studied the phase behaviour of this system at high pressures and in the temperature range of -7° to 99°C. Their data for the mutual solubility of this system as a function of temperature and pressure has been plotted in Fig. 1.2. They have reported that complete miscibility occurred at 0°C and 5°C at 13.8 MN/m\textsuperscript{2}, though tie lines were obtained at the same pressure at -5°C and 10°C. They also found that complete miscibility occurs above 83 MN/m\textsuperscript{2} at any temperature.

1.5.2 Butanone + Water System

Data for this system are available from a large number of sources but only a few of these sets cover the complete temperature range in which the two liquid phases co-exist.

In 1898 Rothmund\textsuperscript{86} first supplied these data and in the same year Bruni\textsuperscript{87} investigated this and other binary liquid system while studying the effect of temperature on partial miscibility. Further data was supplied by Marshall\textsuperscript{88} during his investigation of the various possible types of vapour pressure curves. One pair of points was supplied by Jones\textsuperscript{89} and another pair by Park and Hoffman\textsuperscript{90}. Interest in the relationship between molecular structure and solubility resulted in a further three pairs of points being supplied by Ginnings et al\textsuperscript{91}.

Randall and McKenna\textsuperscript{92} worked on the freezing temperature of the MEK + water system at various compositions. They also
Fig. 1.3 Solubility of MEK + water at 1 bar
FIG. 1.4 H.P. SOLUBILITY OF MEK+WATER AT 30 DEGREE C
provided data for three tie-lines in the liquid-liquid region below 0°C where previously only Rothmund\(^6\) had provided data. Ericksen and Pasquinelli\(^9\) also made their contribution towards such data production. Campbell et al\(^9\) provided the first complete demixing loop since Rothmund and Bruni. Siegelman and Sorum\(^9\) published further data in the temperature range 7.5-88°C. Hunt\(^7\) measured liquid-liquid mutual solubilities in the temperature range 25-100°C. Some of the data are plotted in Fig. 1.3.

Regarding the study of this system at high pressures, Timmermans\(^9\) published part of the only available data in 1911. Later followed a more complete set of data giving upper and lower critical solution temperatures as a function of pressure\(^9\). The constant composition data were in the pressure range 0-150 bars and were available for four compositions only in the immediate vicinity of the upper and lower critical solution temperature. Although these points are on the domed portion of the demixing curve, it is still impossible to obtain any useful tie-line data. In the second set of data the upper and lower critical solution temperatures were found as a function of pressure. The critical pressure was estimated to be 1100 bars at a temperature of 80°C. Hunt\(^7\) explored the immiscibility regions as a function of temperature and pressure. Some of the data are plotted in Fig. 1.4.
CHAPTER 2

RELEVANT THERMODYNAMICS OF FLUIDS AND FLUID MIXTURES

Thermodynamics deals with those laws which govern the transference of energy from one system to another and utilization of energy for useful work in everyday life. Recent developments in energy technology have created interest in vapour liquid equilibria for various systems, especially those containing hydrocarbons and hydrogen at advanced temperature and pressure. For process design, it is often necessary to estimate vapour liquid equilibria and for this purpose it is customary to use an equation of state.

2.1 Equations of State

An equation of state is an algebraic relationship between pressure, temperature and molar volume. Because of the stringent demands for representation of modern high precision data and of the needs of engineers for ever more versatile design tools, complexity is a dominant feature of the newer equation of state. Given the availability of computers, this no longer remains a severe disadvantage, nevertheless there remain incentives for the study of equations of state of relatively simple algebraic form, containing only a few adjustable parameters. Apart from their use as research tools for prediction of equilibrium phenomena, the simpler expressions are commonly employed as bases for the development of more comprehensive equations of state. It has been shown by Abbott\textsuperscript{98} that most of the best known simple equations
of state which are cubic in volume are specialisations of the generic equation:

\[ p = \frac{RT}{V - b} - \frac{\theta}{V^2 + \delta V + \epsilon} \]  \hspace{1cm} \text{(2.1)}

where \( b, \delta \) and \( \epsilon \) are constants for a given liquid and \( \theta \) is an arbitrary function of temperature. Other generic cubic equations are discussed by Hermens and Knapp\(^{99}\) and by Martin\(^{100}\). Many of these specializations give quite reasonable representations of the gross features of real-fluid \( P,V,T \) behaviour, but each of them suffers shortcomings. Attempts at relieving these shortcomings by modifying existing equations so as to obtain new expressions of the same generic type have met with only limited success. A common failing of most cubic equations is their inability to provide simultaneously acceptable predictions of the second virial coefficient \( B \), of the critical compressibility factor, \( Z_C \), and of high pressure volumetric behaviour. All cubic equations of state should satisfy the thermodynamic stability criteria at the critical point,

\[ \left( \frac{dP}{dV} \right)_{T_C} = 0 \] \hspace{1cm} \text{.............. (2.1.1)}

\[ \left( \frac{d^2P}{dV^2} \right)_{T_C} = 0 \] \hspace{1cm} \text{.............. (2.1.2)}

A dependable equation of state should reduce to the ideal gas law as the pressure approaches zero.
2.1.1 General Equations of State for Single Component Systems

The non-ideality of a gas is expressed by its compressibility factor $Z$:

$$Z = \frac{PV}{RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.1.3)$$

where

$V$ = molar volume

$P$ = absolute pressure

$T$ = absolute temperature

$R$ = universal gas constant

For an ideal gas $Z = 1.0$ and for real gases, $Z$ is normally less than unity, except at very high temperature or pressure. Equation 2.1.3 can also be used to define $Z$ for a liquid in which case it is normally much less than unity. The compressibility factor is often correlated with the reduced temperature $T_r$ and Pressure $P_r$ as

$$Z = f(T_r, P_r) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.1.4)$$

where $T_r = T/T_C$ and $P_r = P/P_C$. The function $f(\ )$ can be obtained from $P, V, T$ experimental data. Equation (2.1.4) is a two parameter equation of state, the two parameters are $T_C$ and $P_C$. So for a given fluid it is possible to estimate the volumetric properties at various temperatures and pressures, if one knows $T_C$ and $P_C$. Many suggestions have been offered which have varying degrees of accuracy and applicability. In general, the most successful modifications involve the inclusion of an additional third parameter into the function
expressed by equation (2.1.4). Two types of three-parameter correlations are available. The first type includes those in which \( Z \) is tabulated as a function of \( T_r \) and \( P_r \) with separate tables for various values of \( Z_c \). Edwards and Thodos have used \( Z_c \) in an equation of state to estimate saturated vapour densities of non-polar compounds. The second involves the use of Pitzer acentric factor. This factor is indicative of non-sphericity of a molecule's force field, i.e. a value of \( \omega = 0 \) denotes rare-gas spherical symmetry. The acentric factor is given by

\[
\omega = -\log \frac{P_{\text{vp}}}{P_r} \quad \text{(at } T_r = 0.7) - 1.00
\]

So to obtain values of \( \omega \), the vapour pressure at \( T_r = 0.7 \) is needed as well as the critical pressure. Application of corrections employing the acentric factor should be limited to normal fluids. In no case should such a correlation be used for \( H_2 \), He, Ne or for strongly polar or hydrogen bonded fluids.

Some of the more useful equations of state (well over a hundred equations of state proposed so far) are briefly discussed below:

a) Van der Waals' Equation

The most famous analytical equation of state was suggested by Van der Waals in 1893.

\[
(P + \frac{a}{V^2}) (V - b) = RT \quad \text{........... (2.1.5)}
\]

where \( a \) and \( b \) are specific constants. Applying equations
This equation of state played an important role in the early development of theories of the liquid state and of solutions. It is the simplest form of equation that gives a quantitative and adequate account of the process of condensation and of the properties of the liquid. Its merits are that it is easy to manipulate and that it does not predict physically absurd results. It may be used in theoretical work for a quick qualitative examination of a new problem.

b) Redlich-Kwong Equation

The most successful and widely used in chemical engineering, is the two-parameter equation of state put forward by Redlich and Kwong in 1949. As originally proposed,

\[
p = \frac{RT}{V-b} - \frac{a}{T^5 V(V+b)}
\]

It is clearly based on that of Van der Waals and has much of its simplicity. However, its greater numerical accuracy, particularly when modified to allow for departures from the principle of corresponding states, makes it of great practical value. Like Van der Waals' equation this can be
readily extended to mixtures.

No extensive tabulation of a and b exists for pure compounds, but if equation (2.1.8) is used with equations (2.1.1) and (2.1.2) it is readily shown that:

\[ a = \frac{\Omega_a R T_c^2}{P_c} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.1.9) \]

\[ b = \frac{\Omega_b RT_c}{P_c} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.1.10) \]

where \( \Omega_a \) and \( \Omega_b \) are pure numbers. Thus with the values of the critical temperature and pressure for any material, a and b are easily determined. This equation is often useful in multiple interactive calculations where computation time is important. Its accuracy is good except for polar materials. Prediction of gas-phase volumetric properties are normally not in error by more than 5 percent.

The Redlich-Kwong equation of state, because of its wide reliability, has generated many attempts to improve it by increasing the accuracy and range. The simplest modifications involve the introduction of a deviation function, i.e.

\[ Z = Z_{RK} + \Delta Z \quad \ldots \ldots \ldots (2.1.11) \]

where \( Z_{RK} \) is the value of Z as found with the original Redlich-Kwong equation, and \( \Delta Z \) is a correction term. This procedure makes good predictions possible near the critical point. It was proposed by Redlich et al.\textsuperscript{104,105,106} for gas phase, liquid phase, and vapour-liquid equilibria.
The most successful modifications of Van der Waals' type equation of state involve the assumption of temperature dependence of the parameters a and b. Vogl and Hall\textsuperscript{107} established generalized correlations for the temperature dependence of the constants a and b in the original Redlich-Kwong equation of state. Chaudron et al.\textsuperscript{108} developed a modification of the RK equation by expressing both a and b as polynomials in inverse reduced temperature and by regressing experimental data for pure components.

Another form of modification may be expressed as:

\[
Z = \frac{PV}{RT} = \frac{V}{V - b} - \frac{\Omega_a b}{\Omega_b (V + b) F} \quad \text{(2.1.12)}
\]

where \(\Omega_a\) and \(\Omega_b\) are pure numbers, b is obtained from equation (2.1.10) and F is a variable which depends on the suggested modification. For example, Wilson\textsuperscript{109} suggested \(F = 1 + (1.57 + 1.62\omega)(T_{R}^{-1} - 1)\). His form of the Redlich-Kwong equation of state well predicts enthalpy departures of both polar and non-polar compounds and NH\textsubscript{3} as well.

Soave\textsuperscript{110} closely reproduced the vapour pressure of pure compounds by assuming the parameters a and b in the original Redlich-Kwong equation to the temperature dependent. With the introduction of the acentric factor as a third parameter he derived a generalized correlation for the modified parameter F. This equation applies to all non-polar compounds. He proposed:

\[
F = \frac{1}{T_R} \left[ 1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_R^{0.5}) \right]^2
\]

\[\text{............. (2.1.13)}\]
West and Erbar\textsuperscript{111} have evaluated the Soave relation for light hydrocarbons and find it very accurate when used to predict vapour liquid equilibria and enthalpy departures. The Soave-Redlich-Kwong equation has been superseded by Lee and Kesler's equation\textsuperscript{121} described below because, for example, the Soave-Redlich-Kwong (SRK) equation always predicts specific volumes for the liquid which are greater than the literature values\textsuperscript{111}.

c) Peng-Robinson Equation\textsuperscript{112}

Semi-empirical equations of state generally express pressure as the sum of two terms, a repulsive pressure $P_R$ and an attractive pressure $P_A$ as follows:

$$P = P_R + P_A \quad \text{…………..} \quad (2.1.13)$$

The equations of Van der Waals, Redlich-Kwong-Soave all have the repulsion pressure expressed by the Van der Waals hard-sphere equation, i.e.

$$P_R = \frac{RT}{V - b}$$

The attractive parameter can be expressed as $P_A = -\frac{a}{g(v)}$

Peng and Robinson suggested that by choosing a suitable function for $g(v)$, the predicted critical compressibility factor can be made to approach a more realistic value. So they kept the repulsion parameter constant at its critical point value, while the attraction parameter contains a generalized function of temperature fitted to the vapour pressure. For superheated vapours that function was simply
extrapolated above the critical temperature. The proposed equation is:

\[ P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \quad \text{(2.1.14)} \]

This equation was basically designed for predicting the vapour pressure and volumetric behaviour of non-polar single component systems.

d) Perturbed Hard-Sphere Models

Ishikawa, Chang and Lu have recently put forward a cubic perturbed hard-sphere equation of state for thermodynamic properties and vapour-liquid calculation, which combines the hard-sphere expression of Scott and the empirical attractive term of the Redlich-Kwong equation with the two temperature dependent parameters:

\[ P = \frac{RT(2V + b)}{V(2V - b)} - \frac{a}{T^5 V(V + b)} \quad \text{(2.1.15)} \]

where

\[ a = \frac{\omega_a R^2 T_c^{2.5}}{P_c} \]

\[ b = \frac{\omega_b RT_c}{P_c} \]

The parameters \( \omega_a \) and \( \omega_b \) were evaluated from vapour pressure and saturated liquid densities for twenty-two arbitrarily selected pure compounds, following a procedure similar to that proposed by Chang and Lu. The correlation is satisfactory for the prediction of VLE of non-polar and slightly polar compounds.
e) Benedict-Webb-Rubin Equation

This equation has been extremely valuable in correlating both liquid and vapour thermodynamic, and volumetric data for light hydrocarbons and their mixtures. Expressed in terms of the molar density $\rho$, it is

$$P = RT\rho + (B_0RT - A_0 - C_0/T^2) \rho^2 + (bRT - a) \rho^3 + a\alpha\rho^6 + c\rho^3/T^2 (1 + \gamma\rho^2) \exp(-\gamma\rho^2) \ldots \ldots (2.1.16)$$

The eight constants are normally determined from pure component volumetric data. Some new techniques for this purpose, using multiproperty data have been suggested.

Several tabulations of the BWR constants are available, e.g. Cooper and Goldfrank and Orye.

f) Lee-Kesler Equation

Lee and Kesler have described a modified BWR equation based on Pitzer's three-parameter corresponding state principle. It accurately (within 1 or 2 percent) represents the volumetric and thermodynamic properties of non-polar vapours and liquids as a function of reduced temperature, reduced pressure and acentric factor over the range of $T_R = 0.3$ to $4$ and $P_R = 0$ to $10$. It is a sufficient improvement on the Benedict-Webb-Rubin equation to be the correlation recommended by the American Petroleum Institute. This has led to improved representation of these properties of hydrocarbons and slightly polar materials and their mixtures near the critical region and at low temperatures.
The accuracy is diminished, although to a lesser extent than in the Pitzer correlation, at saturated conditions and near the critical and retrograde regions, when applied to widely boiling mixtures. When used to estimate the liquid density of water at around ambient conditions, the correlation over-estimates volumes by more than 10%.

g) Gmehling-Liu-Prausnitz Equation$^{123}$

Perturbed-hard-chain theory has been extended to polar fluids and to mixtures containing one or more polar components to form the basis of an equation of state. Strong polar-polar interactions are taken into consideration by a chemical equilibrium constant for formation of dimers. The theory is directed primarily at high-pressure phase equilibria where, at present, no other engineering oriented theory is available. At low pressures, classical methods using activity coefficients are more useful. For high pressures, however, the equation of state, coupled with dimerization equilibria, provides an attractive alternative. Using four adjustable molecular parameters, it gives a good representation of the P,V,T properties of polar fluids, including water, alcohols and ketones. For non-polar fluids only three adjustable parameters are required.

\[ Z = Z(\text{repulsive}) + Z(\text{attractive}) \]

where

\[ Z(\text{repulsive}) = 1 + C \left[ \frac{4d_r - 2d_r^2}{(1 - d_r)^3} \right] \quad \ldots \quad (2.1.17) \]
\[ Z \text{ (attractive)} = C \sum_{n=1}^{2} \sum_{m=1}^{5} \frac{m A_{nm}}{T_{r}^{n} V_{r}^{m}} \]  \hspace{1cm} (2.1.18)

where

\[ d_{r} = \text{reduced density} = \frac{\sqrt{2V^{*}}}{6V} = \frac{0.7405V^{*}}{V} \]  \hspace{1cm} (2.1.19)

\[ A_{nm} = \text{dimensionless constants used to calculate} \]
\[ \text{attractive perturbation in Helmholtz's energy} \]

\[ C = \text{one-third of the total number of external degrees} \]
\[ \text{of freedom per molecule} \]

\[ T^{*} = \text{characteristic temperature} \]

\[ V^{*} = \text{hard-core molar volume or close-pack molar volume} \]

\[ \text{Reduced Volume} = V_{r} = \frac{V}{V^{*}} \]

\[ \text{Reduced Temperature} = T_{r} = \frac{T}{T^{*}} = \frac{cK}{q\epsilon} \]

where

\[ q = \text{external molecular surface area} \]
\[ \epsilon = \text{average intersegment energy} \]
\[ V = \text{molar volume per mole} \]

In this treatment a pure fluid is considered to contain monomers (M) and dimers (D), where \( q_{M} \) and \( q_{D} \) depend on temperature and density. For a mixture of monomers and dimers the one-fluid theory was used. It was assumed that two strongly polar molecules tend to form weakly stable dimers and that this tendency can be described through a suitably defined chemical equilibrium constant.

For a pure fluid containing monomers and dimers there are eight parameters which must be found from experimental data. They are: \( V_{M}^{*}, T_{M}^{*}, C_{M}, V_{D}^{*}, T_{D}^{*}, C_{D}, \Delta H^{0}, \Delta S^{0} \). Yet, the following assumptions were made:
The value of $\varepsilon$ was arbitrarily chosen. This value actually designates the molecular segment for which $q = 1$. So any error in $\varepsilon$ is said to be absorbed in $q$. After all these assumptions, $T^*_M$, $V^*_M$, $\Delta H^0$ and $\Delta S^0$ are left with four adjustable parameters.

This, the most promising approach so far, predicts liquid volumes of water, methanol and ethanol over a pressure range of 0.5 to 1000 bar with an average deviation of around 1.5%.

h) Virial Equation

Most analytical equations of state are of a form resembling a polynomial series in inverse volume. It is the same in the case of the virial equation of state

$$p = \frac{RT}{V} + \frac{RTB}{V^2} + \frac{RTC}{V^3} \ldots \quad \ldots \ldots \quad (2.1.20)$$

The parameters $B$, $C$, $\ldots$, are called the second, third, $\ldots$ virial coefficients and are functions only of temperature for a pure liquid. Prausnitz$^{124}$ has reviewed this equation comprehensively. The reason for its popularity is that the coefficients $B$, $C$, $\ldots$, can be related to parameters characterizing the intermolecular potential function. The virial equation is most useful when truncated to retain only the
second virial term and arranged to eliminate the molar volume. If equation (2.1.3) is used in equation (2.1.20) to eliminate \( V \), and the series truncated to retain only in the zeroth or first power in pressure then

\[
Z = 1 + \frac{BP}{RT} \quad \text{............... (2.1.21)}
\]

This equation should not be used if \( P > P_c/2 \). As \( B \) is a function only of temperature this equation predicts that \( Z \) is a linear function of pressure along an isotherm.

A compilation of second virial coefficients is given by Dymond and Smith\(^ {125} \). To estimate values, a number of techniques is available. Most are based on the integration of a theoretical expression relating intermolecular energy to the distance of separation between molecules. Since at present such energies are difficult to determine the corresponding states relations are employed for the estimation of \( B \). Tsonopoulos\(^ {126} \) has modified a simple expansion proposed by Pitzer and Curl\(^ {127} \).

\[
\frac{BP}{RT_c} = f^0 + \omega f^1 \quad \text{............... (2.1.22)}
\]

where

\[
f^0 = 0.1445 - 0.330 \frac{T}{T_r} - 0.1385 \frac{T^2}{T_r^2} - 0.0121 \frac{T^3}{T_r^3} - 0.000607 \frac{T^4}{T_r^4}
\]

\[
f^1 = 0.0637 + 0.331 \frac{T}{T_r} - 0.423 \frac{T^2}{T_r^2} - 0.008 \frac{T^3}{T_r^3}
\]

Equation (2.1.22) is only applicable for non-polar or slightly polar materials. Many modifications have been suggested for polar compounds\(^ {128} \). A simple extension of equation (2.1.22)
was presented by Halm and Stiel\textsuperscript{129}.

Tsonopoulos\textsuperscript{126} suggests that equation (2.1.22) be modified by the addition of another term $f^2$, where

$$f^2 = \frac{a}{T_r^6} - \frac{b}{T_r^8} \quad \text{.......... (2.1.23)}$$

But neither $a$ nor $b$ can be estimated with much accuracy. Nevertheless, $b$ is zero for compounds without hydrogen bonding, in such a case for ketones, aldehydes, nitrites and ethers.

$$a = -2.140 \times 10^{-4} \mu_r - 4.308 \times 10^{-21} \mu_r^8$$

where

$$\mu_r = 10^5 \frac{\mu_p^2 P_C}{T_c^2}$$

where

$\mu_p$ = dipole moment, debyes
$P_C$ = critical pressure, atm.
$T_C$ = critical temperature, K

In hydrogen bonded fluids, i.e. alcohol, water etc. $a$ and $b$ are constants specific for each material. For such fluids $B$ exhibits a strong temperature dependence at low reduced temperature, where the $b/T_r^8$ term predominates.

For pure gas $P,V,T$ properties the virial equation is like the original RK equation, and is less accurate. But being a simple equation it is useful in multiple interative calculation where computing time is important. For non-polar substances its accuracy is good for predictions of gas phase volumetric properties, i.e. normally within 5\%. 
2.1.2 Equation of State for Non-gaseous Fluids

From sub-section 2.1.1 above, which offers comments only on a selection of general equations of state, it is clear that despite the many man-years of effort which have been expended in their development, we still have a long way to go before the volumetric behaviour of complex fluids can be described to acceptable accuracy in the liquid state by equations applicable to liquid, vapour and supercritical states. One must therefore look to the more specialised equations developed specifically for liquids to find more accurate descriptions of liquid P,V,T behaviour.

Many attempts have been made to derive compressibility equations from the molecular theory, but none of them has resulted in a convenient equation expressing the results of experiments within adequate accuracy because the derivation of a P-V relation for a real liquid involves the solution of a very difficult many-body problem, where restriction to pairwise interactions is usually improper. So the best model is only best in a relative sense, i.e. the best of those available for comparison with specific data. It is extremely unlikely that there exists a universal equation of state of a useful degree of simplicity. To meet this need it is necessary to employ some empirical equation, the sole justification for which is that it works.

The two most commonly used equations are those due to Tait and Huddleston.
a) The Tait Equation

Tait formulated an equation to represent the compressibility of sea water, the density of which had been measured from the oceanographic research vessel H.M.S. Challenger;

\[
\frac{V_o - V}{V_o P} = \frac{J}{L + P}
\]............. (2.1.2.1)

where \(V_o\) is the volume at zero pressure and \(J\) and \(L\) are positive parameters. Later this equation was interpreted by Tamann\(^{131}\) as a differential equation which could be written:

\[
\left( \frac{\partial V}{\partial P} \right)_T = -\frac{J'}{L + P}
\]............. (2.1.2.2)

and on integration gives:

\[
V - V_o = J' \ln \left[ \frac{L}{L + P} \right]
\]............. (2.1.2.3)

which, for practical purposes, is usually written as:

\[
\frac{V - V_o}{V_o} = C \log_{10} \left[ \frac{L}{L + P} \right]
\]............. (2.1.2.4)

This modification of the original Tait equation has been found\(^{132}\) not only less accurate but also less convenient than the original Tait equation. Although the equation (2.1.2.2) had no theoretical basis, it was of the form which best fitted the experimental values of the compressibility of sea water measured by Tait on his voyage; yet, Ginell\(^{132}\) has since produced a theoretical justification of the equation from association theory. It is shown that the constant, \(L\), which is temperature dependent, should also
have a small pressure dependence. From the equation for the constants it is shown how the volume of 'holes' in the liquid can be calculated. The general structure of liquids in the light of this equation has been discussed by Ginell as well.

It was Wohl\textsuperscript{133} who first devised a method of evaluating the Tait constants for various liquids, finding that $J$ was independent of temperature. Both Wohl and Carl\textsuperscript{134} found that the Tait equation fitted well the compressibility data of water found by Bridgman\textsuperscript{135} and Amagat\textsuperscript{136}. Apart from water, the Tait equation has been used for many pure hydrocarbons and mixtures of hydrocarbons\textsuperscript{50,137}. In all cases the value of $J$ was kept constant for the class of mixtures being studied. Very recently, Moriyoshi et al\textsuperscript{53} have fitted their compressibility data for $t$-butanol-water mixtures at 25°C and pressures up to 142 MPa to the Tait equation of the form:

$$K = C \ln \left[ \frac{(B + P)}{(B + P_o)} \right]$$

where $B$ and $C$ are constants, and $P_o$ is atmospheric pressure.

The Tait equation leads to zero specific volume at a finite high pressure. Kirkwood\textsuperscript{138} modified it to remove this anomaly as follows:

$$\log \left[ \frac{V_p}{V_o} \right] = \frac{1}{n} \log \left( \frac{A_s - P}{A_s} \right) \quad \text{...... (2.1.2.5)}$$

where $A_s$ is a function of entropy, $1/n$ is a constant, corresponding to $C$ in the original equation, and $V_p$ and $V_o$ are volumes measured along an adiabatic, the subscripts
relating to pressure.

Various equations of a similar type are found in the literature and attempts have been made to identify their constants with properties of simplified intermolecular force fields and to relate them to viscosity and other data\textsuperscript{139,140}.

b) Huddleston Equation\textsuperscript{139}

This equation was based on an intermolecular force law of the form:

\[ f = a (l - l_0) \exp b(l_0 - l) \quad \ldots \quad (2.1.2.6) \]

where

- \( f \) = force between molecules
- \( l \) = distance between molecule centres
- \( l_0 \) = distance at which molecules have no effect on each other
- \( a, b \) = empirical constants

If the distance between the force centres are written as proportional to \( v^{1/3} \) and the force as proportional to \( v^{2/3} \), then the equation becomes:

\[ \log \left( \frac{v^{2/3}P}{(v_0^{1/3} - v^{1/3})} \right) = A + B(v_0^{1/3} - v^{1/3}) \quad \ldots \quad (2.1.2.7) \]

where

- \( v_0 \) = specific volume at atmospheric pressure
- \( v \) = specific volume at pressure \( P \)
- \( A, B \) = constants

A plot of the left-hand side of equation (2.1.2.7) versus \( (v_0^{1/3} - v^{1/3}) \) results in a straight line if Huddleston's
This procedure was used by Cutler et al on the compressibility data of thirteen hydrocarbons. For each liquid straight line plots of equal slope were obtained (i.e. a constant value of B) and different values of A. Similar work was done by Doolittle for a number of n-alkanes and the temperature dependence of Hudderston's parameters was also found. Bett, Weale and Newitt have shown that Hudderston's equation represents liquid (i.e. H₂O, CCl₄ and C₆H₆) compression data at least as accurately as Tait's equation, within certain ranges of pressure.

Hudderston's equation has been widely used to represent some good measurements of the compression of hydrocarbons. For these it is superior to Tait's equation, although it is less accurate for water. It is also less convenient to use than either form of Tait's equation, but this is not important if the fitting is done by computer.

c) Hayward's Review

In a study of compressibility equations for liquids Hayward showed that the equation commonly known as the Tait equation (2.1.2.2) was not the one originally proposed by Tait. The reciprocal of equation (2.1.2.1) when rearranged gives the linear secant-modulus equation as used by Klaus and O'Brien.

\[
\frac{1}{K} = \frac{v_o}{v_o - v_p} \frac{P}{J} = \frac{L}{J} + \frac{P}{J} \quad \ldots \ldots \quad (2.1.2.9)
\]

by putting \( J^{-1} = m \) and \( L/J = K_o \), the equation changes to
\[
\bar{K} = \frac{v_0 P}{v_0 - v_p} = K_o + m p \\
................ (2.1.2.10)
\]

which is the linear secant modulus equation.

Hayward shows how the equations of Tumliez\textsuperscript{145} and Tamman\textsuperscript{146} are of identical form to equation (2.1.2.10) and also that the Huddleston and MacDonald equations are effectively of the same form as equation (2.1.2.2), since allowing for experimental error, the predicted values are the same and are both asymptotic to equation (2.1.2.8) as \( P \to 0 \). He also demonstrates how Tait's original equation well represents the compressibility of water up to 12 kbar. At higher pressures all the compressibility data on water will fit equation (2.1.2.10) if \( \bar{K} \) is modified.

\[
\bar{K} = K_o + m p - n p^2 \\
................ (2.1.2.11)
\]

For organic liquids an equation of the following form will represent its compressive properties up to 12 kbar.

\[
\bar{K} = K_o + m p - n p^2 + q p^3
\]

where

\[ m, n \text{ and } q \text{ are constants} \]

\[ K_o = \text{bulk modulus at zero pressure} = v \left( \frac{2P}{3v} \right)_T \]

d) Davis-Gordon Equation\textsuperscript{147}

Davis and Gordon have compared some equations of state in connection with their own work on mercury at pressures up to 13 kbars and various temperatures. They have presented
an expression for the pressure dependence of the volume which was found best suited for their particular material. All coefficients are expressed in terms of bulk modulus.

\[ \frac{P}{K} = \alpha \Delta v + \frac{\Delta v}{v} \left( K' - 1 \right) (\Delta v/v)^2 + \ldots \]

or

\[ \frac{P}{K} = \mu \left( 1 + \frac{\mu}{2} \right) (K' - 1) w \] 

\[ \ldots \ldots \ldots (2.1.2.13) \]

where

\[ w = \frac{(v_0 - v)}{v} \]

\[ K' = \left( \frac{\partial K}{\partial P} \right)_T \]

Equation (2.1.2.13) is a second degree Davis-Gordon equation. It stems from a truncated Taylor series expansion around \( \frac{v_0}{v} = 1 \), and was used by Bridgman in 1936. Davis and Gordon have also considered Bridgman's second degree Taylor expansion of \( v \) in powers of \( P \) around \( P = 0 \).

\[ v = v_0 + (dv/dP)_{P=0} \cdot P + \frac{1}{2} (d^2v/dP^2)_{P=0} \cdot P^2 \]

\[ \ldots \ldots \ldots (2.1.2.14) \]

where

\[ (dv/dP)_{P=0} = -v_0/K_0 \]

and

\[ (d^2v/dP^2)_{P=0} = v_0 (1 + K'')/K_0^2 \]

The third degree Bridgman equation has been used, without identification of the coefficients with pressure derivations of isothermal bulk modulus, \( K \), by Kell and Whalley\(^{148} \) for fitting their water \( P,V,T \) results; yet, Davis and Gordon do not find Bridgman's equation satisfactory enough, partly because it is not suitable for extrapolation.
e) Grindley-Lind Equation

More recently, Grindley and Lind\textsuperscript{149} have discussed an equation of state, and provided derivatives accurate to 1\% or better for mercury and water, with the background of the hard-sphere model. This model represents the very density-sensitive phenomena arising from the packing of molecules in a dense fluid. Real systems can then be modelled by the addition of terms related to the potential energy which are slowly varying functions of the density.

\[ P = \frac{2}{5} Z_e E_F \left( \frac{N}{V} \right) - \left( \frac{B}{V^{1/3}} \right) + P_h \]

where

- \( P \) = total pressure
- \( \frac{N}{V} \) = number of atoms per unit volume
- \( P_h \) = hard-sphere pressure
- \( E_F \) = Fermi energy of the electron gas
- \( Z_e \) = valence electrons per atom

The first term of the right-hand side of the equation accounts for the contribution to the pressure from the Fermi energy of the electron gas, while the second accounts for the Coulomb, exchange, and correlation energies as well as energy of the lowest state of the valence electrons per atom.

f) Murnaghan Equation\textsuperscript{150}

This non-linear equation has been widely used. Murnaghan was apparently the first to publish although an adiabatic form of the equation was presented earlier by Kirkwood\textsuperscript{138}.
The Murnaghan equation has been found satisfactory at least in the medium pressure range and particularly for water (although not as good as Tait's equation). The equation is as follows:

\[
\frac{v}{v_0} = \left(1 + K_0 \beta_0 P\right)^{-1/K_0}
\]

where \( \beta_0^{-1} = K_0 \)

g) MacDonald's Review

In a review of experimental and theoretical equations of state, MacDonald compared four different polynomial equations and seven non-linear equations, all applicable to both solids and liquids. The equations considered, included those of Tait, Murnaghan, and Davis and Gordon. All these equations were tested on the available compressibility data of water and mercury. In general, he found certain polynomial equations yielded significantly better fits of many different water and Hg data sets than any non-linear equation considered, at least over a limited pressure range. For him the Tait equation seemed to be a "very poor choice" to represent data for water. The mercury data were not represented very well by any of the equations considered.
2.2 Mixing Rules

For pure fluids, a cubic equation of state can provide only a fair representation of thermodynamic properties, as pointed out in a review by Martin\(^{152}\). When the adjustable constants are evaluated to give good agreement in a given density range, agreement in another density range is likely to be poor. In order to study properties of mixtures volumetric properties are related to fugacity coefficients. Fugacity coefficients are sensitive to whatever assumption is made concerning the effect of composition on volumetric properties. This assumption is expressed by mixing rules, i.e. by the variation of equation of state constants with composition. So the more constants the equation of state has, the more mixing rules are required, and therefore, more data is needed for evaluation of the pure component parameters. Thus two-parameter cubic equations of state are often preferred.

Distinction must be emphasized\(^{153}\) between combining and mixing rules. Combining rules are used to estimate binary parameters, related to unlike interaction. A right choice avoids corrective factors. For example, to find \(b_{ij}\), the Lorentz rule was proposed:

\[
b_{ij}^{1/3} = \frac{1}{2} \left( b_{ii}^{1/3} + b_{jj}^{1/3} \right) \quad \text{......... (2.2.1)}
\]

Another expression for \(b_{ij}\) employs the geometric mean of \(b_{ii}\) and \(b_{jj}\). In a general way these recommendations can be looked upon as predictions of \(b_{ij}\). On the other hand,
mixing rules give the choice of a composition dependence law for parameters a or b. But for the second virial coefficient, B, in the virial equation, all the mixing rules are essentially empirical and have resulted after many cut-and-try comparisons of calculated mixture properties with experimental data. Many methods are known with the help of which one may determine equation of state parameters separately for each mixture with a different composition. For example, for the pseudo-critical temperature, $T_{cm}$, a simple mole-fraction average method, called Kay's rule, is usually satisfactory.

$$T_{cm} = \sum_j x_j T_{c,j}$$  \hspace{1cm} \text{(2.2.2)}

In the corresponding states method for mixtures no binary interaction parameters are included in equation (2.2.2) so one may not see any true reflection of mixture properties; yet it gives surprisingly good results. However, if applied to polar substances or those with any tendency to associate into polymers, the results obtained are not so satisfactory.

The pseudo-critical rule (equation 2.2.2) from its linear form, can be modified to a quadratic form:

$$T_{cm} = \sum_i \sum_j \phi_i \phi_j T_{c,ij}$$  \hspace{1cm} \text{(2.2.3)}

where

$$\phi_i = \frac{x_i V_{c,i}}{\sum_j x_i V_{c,j}}$$

and

$$T_{c,ij} = (1 - k_{ij})(T_{c,i} T_{c,j})^{1/2}$$  \hspace{1cm} \text{(2.2.4)}

$k_{ij}$ is a binary interaction parameter which must be found.
from experimental data (values for $k_{ij}$ are back-calculated by the trial-and-error method). For liquids $k_{ij}$ is usually between 0 and 0.2. This method involving the corresponding states approach is reliable for liquid density estimation up to critical temperature and pressure range.

For the cubic equation of state pure component parameters $a_{ii}$ and $b_{ii}$ can be obtained from vapour pressure values and critical conditions, as was done by Soave. For a mixture $a$ and $b$ are usually calculated from pure component parameters, binary parameters $a_{ij}$ and $b_{ij}$, and mixing rules such as:

\[ a = \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} x_i x_j \quad \text{......... (2.2.5)} \]

\[ b = \sum_{i=1}^{n} \sum_{j=1}^{n} b_{ij} x_i x_j \quad \text{......... (2.2.6)} \]

\[ a_{ij} = (a_{ii} a_{jj})^{\frac{1}{2}} \cdot (1 - k_{ij}) \quad \text{......... (2.2.7)} \]

\[ b_{ij} = \frac{b_{ii} + b_{jj}}{2} (1 - k'_{ij}) \quad \text{......... (2.2.8)} \]

where $k_{ij}$ and $k'_{ij}$ take count of differing molecular size or polarity. For hydrocarbon mixtures the corrective factors $k_{ij}$ and $k'_{ij}$ are normally assumed to be zero. The extension to mixtures containing polar compounds has been attempted by adjusting $k_{ij}$ and sometimes $k'_{ij}$ to experimental data or by separating $a_{ii}$ values into polar and non-polar contributions.

Both parameters, $k_{ij}$ and $k'_{ij}$, are temperature dependent and at low temperatures good results could not be obtained. While the introduction of a second binary parameter is help-
ful, it does not abandon the basic assumption of classical quadratic rules, i.e. random mixing meaning that the molecules mix in a completely statistical manner, without preference. In real mixtures molecules may show some preference in choosing their neighbours. For example, in a mixture of H₂O and hexane both components (at ordinary temperature) would surround themselves with molecules of their own type and the random mixing rule does not apply.

However, classical mixing rules imply a quasi-regular behaviour, and unless a thorough revision is made, the method cannot be applied to polar mixtures. It is worth mentioning that the classical mixing rules have a strong tendency towards false phase splitting prediction. It has been proposed that the values of pure-component parameters be modified. Huron and Vidal have recently shown that data correlation can be greatly improved by a local-composition mixing rule. They used Soave's equation of state with their new mixing rule for parameter a and proposed that the close relationship found between the energy parameter \(a/b\) and the excess Gibbs energy \(G^E\) could be extended to other cubic equations of state having the form:

\[
P = \frac{RT}{V-b} - \frac{a(T)}{\psi(v)}
\]

where \(\psi = \text{volume function}\)

However, the mixing rule is not applicable to third parameter equations of state. For such equations mixing rules need to be set for two binary parameters in order to be able to calculate the third one from \(G^E\). Yet, like the choice of a mixing rule, the choice of a model for the
excess Gibbs energy is difficult. The problem of non-randomness in mixing is particularly difficult when one or more of the components in a mixture is strongly polar, leading to segregation. Since a satisfactory theory of non-random mixtures is not likely to become available in the near future, it appears that, for engineering purposes, a combined chemical-physical treatment may provide a useful approximation of those mixtures where molecules have a strong tendency to segregate.  

2.3 Various Approaches Towards Description of Non-ideal Behaviour of Binary Liquid Mixtures

A complete thermodynamic description of a mixture can be given if the molar excess Gibbs free energy is known as a function of T, P and x. Classical thermodynamics offers no clues to the functional forms that may be reasonable for an equation representing $G^E$. Therefore, they must be established either empirically or on the basis of some molecular theory. Since we do not yet possess an accurate statistical mechanical description of a liquid mixture empirical parameters have to be introduced. It is desirable to limit the number of parameters and at the same time develop expressions for an excess thermodynamic function, which are of general applicability. However, the tremendous complexity of various liquid mixtures prevents an accurate representation of many mixture properties by a single mathematical expression having a small number of parameters. In evaluating the usefulness of a given procedure for predicting properties the number of empirical parameters is a key factor. Accurate prediction is
the goal of any technique, however, if accuracy is paid for
in the form of a large number of parameters, its value is
diminished in two ways:

(i) The amount of data needed to evaluate the parameters
increases.

(ii) The reliability of extrapolation often diminishes beyond
the bounds over which data have been taken.

For a binary mixture Gibbs excess free energy is related to
activity coefficients as follows:

\[ \frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \]

and

\[ \gamma(n \frac{G^E}{RT}) = \frac{\ln \gamma_1}{n_1} \]

\[ \text{and} \]

\[ \text{...... (2.3.1)} \]

So, to solve the problem of describing the behaviour of non­
ideal liquid mixtures, activity coefficient analysis has also
been carried out in many different ways. The earliest
efforts\textsuperscript{159,160} were based on empirical relations for homologous
series of solutes and interpreted the results in terms of
group interaction, structural effects, polarity and electron­
donor and electron acceptor capacities. These ideas served
as foundations for the more sophisticated theoretical inter­
pretations. The fundamental approximation used in most of
the theoretical treatments considers the activity coefficients
to be separable into two parts.

\[ \gamma = \gamma_{\text{configuration}} + \gamma_{\text{interaction}} \]
The configurational contribution due to the mixing of molecules of different shapes and sizes can be approximated by simple lattice properties\textsuperscript{161}. A simpler version of the theory originally given by Flory\textsuperscript{162} and Huggins\textsuperscript{163} for solutions of linear polymers gives:

\[ \ln \gamma_1(\text{configuration}) = \ln \left[ \frac{(1 - \phi_3)}{x_1} \right] + (1 - 1/r) \phi_3 \]

\[ \ldots \ldots (2.3.2) \]

where \[ \phi_3 = \frac{rx_3}{(x_1 + rx_3)} = \text{Vol. fraction of long-chain molecules} \]
\[ r = \text{ratio of sites occupied by the long- and short-chain molecules.} \]

The interaction contribution \( \gamma_{\text{int.}} \), is a temperature dependent term associated with the interaction energies between various molecular species present. In the absence of large energy effects, \( \gamma_{\text{int.}} \), has the form\textsuperscript{164}

\[ \ln \gamma_{\text{int.}} = \frac{H^M}{RT} - \frac{S^M}{R} \]

where \( S^M \) is the contribution to the partial molar entropy of mixing from non-configurational terms in the partition function, and \( H^M \) is the partial molar heat of mixing. For small values of \( \ln \gamma_{\text{int.}} \), the contributions are independent of one another, but if large energy effects exist the statistical term, \( \ln \gamma_{\text{conf.}} \), is modified because of higher weighting which must be attached to configurations of lower energy (higher energy of interaction). In fact the form of \( \ln \gamma_{\text{int.}} \) has not been established theoretically with any certainty. It is in the interpretation of this part that various solution theories differ.
2.3.1 Scatchard-Hildebrand Model

This equation in fact is an improvement of Van Laar's theory. Van Laar had calculated the energy change of mixing based on an assumption that both the excess entropy and volume are zero. He then applied the Van der Waals' equation to fluids and fluid mixtures and calculated the internal energy change in the three steps, i.e. (i) energy to evaporate pure liquids to ideal gases; (ii) energy to mix ideal gases; (iii) energy to condense ideal-gas mixture to liquid mixture. Activity coefficients in this case are never less than one, so it gives positive deviations from Raoult's law.

Scatchard and Hildebrand removed the limitation of Van der Waal's equation of state and put forward an equation for Gibbs excess free energy:

\[ G^E = V \phi_1 \phi_2 A_{12} \]  

\[ \phi_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2} \quad \phi_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2} \quad V = x_1 V_1 + x_2 V_2 \]

\[ A_{12} = (\delta_1 - \delta_2)^2 \quad \delta_i = \text{solubility parameter (eqn. 2.3.1.4 below)} \]

Activity coefficients are deduced by differentiation according to equation (2.3.1)

\[ RT \ln \gamma_1 = V_1 \phi_1^2 A_{12} \]  

\[ RT \ln \gamma_2 = V_2 \phi_2^2 A_{12} \]
This theory has been used by many workers to discuss activity coefficients from gas-liquid chromatographic measurements but it did not prove to be very successful. Hildebrand, Scott and Prausnitz put forward the application of an updated version of this theory. The solubility parameters, \( \delta_1 \) and \( \delta_2 \), may be estimated from heat of vaporization (available in turn from the vapour pressure curve and Clausius-Clapeyron equation):

\[
\delta = \left[ \frac{\Delta U_{\text{vap.}}}{V} \right]^{\frac{1}{2}} = \left[ \frac{\Delta H_{\text{vap.}} - RT}{V} \right]^{\frac{1}{2}} \quad (2.3.1.4)
\]

2.3.2 Gugenheim's Model

The quasi-lattice theory of Gugenheim has given birth to a family of equations for excess Gibbs energy. It presents one of the simplest conceptual models of the theory of liquids. A liquid is pictured as a pseudo-crystal, with the assumption that each molecule is located at the intersection point of a regular lattice. Molecules are considered to be of the same size and shape and are interchangeable on the lattice sites. Like Van Laar and Hildebrand-Scatchard, Gugenheim's theory postulates \( S^E \) and \( V^E \) to be zero so that \( G^E = H^E \). The derived equation for the molar excess Gibbs energy is:

\[
\frac{G^E}{RT} = x_1 x_2 \frac{w_{12}}{RT} \quad (2.3.2.1)
\]

where \( w_{12} \) is the interchange energy representing physically the difference between like-pair and unlike-pair interactions. For activity coefficients it gives:
\[ RT \ln \gamma_1 = x_2^2 w_{12} \]  \hspace{1cm} \text{(2.3.2.2)}

\[ RT \ln \gamma_2 = x_1^2 w_{12} \]  \hspace{1cm} \text{(2.3.2.3)}

This theory of the "strictly regular solution" rarely applies to real mixtures. The physical model is too rigid and does not adequately represent real behaviour. Gugenheim extended his quasi-lattice treatment to the mixtures in which each molecule \( i \) consists of \( r_i \) segments, each of which occupies one site on a lattice of coordination number \( Z \). Then

\[
G^E/RT = x_1 \ln \frac{r_1}{x_1 r_1 + x_2 r_2} + x_2 \ln \frac{r_2}{x_1 r_1 + x_2 r_2} \\
+ \frac{1}{2} q_1 Z x_1 \ln \frac{q_1(x_1 r_1 + x_2 r_2)}{r_1(x_1 q_1 + x_2 q_2)} \\
+ \frac{1}{2} q_2 Z x_2 \ln \frac{q_2(x_1 r_1 + x_2 r_2)}{r_2(x_1 q_1 + x_2 q_2)} + \frac{q_1 q_2 x_1 x_2 w_{12}}{(x_1 q_1 + x_2 q_2)KT} 
\]

\hspace{1cm} \text{(2.3.2.4)}

where \( q_1, q_2 \) are the numbers of nearest neighbour sites to molecules 1 and 2. Bruin\textsuperscript{169} and McCann\textsuperscript{170} derived several equations supposedly based on equation (2.3.2.4) by setting \( q_1 \) and \( q_2 \) equal to zero and misinterpreting the parameters \( r_1 \) and \( r_2 \). A non-constant coordination number theory was put forward by Forsyth\textsuperscript{171} in order to relax the requirement of constant coordination number. All coordination numbers may be calculated from hard-sphere radii. Redlich-Kister\textsuperscript{172} determined the interchange energy \( w_{12} \) (eqn. 2.3.2.1) as an empirical measure of two-body interactions. So this equation
provides the leading term in a series expansion, several of which are commonly used.

\[
G^E = (x_1x_2) \left[ A_0 + A_1 (x_1 - x_2) + A_2 (x_1 - x_2)^2 + A_3 (x_1 - x_2)^3 + \ldots \right]
\]

\[
= x_1x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)
\]

\[
\ldots \ldots \ (2.3.2.6)
\]

It can be shown that equation (2.3.2.6) is equivalent to the Margules\textsuperscript{173} expansion. In this type of expression the first term is similar to the pair interchange energy and in a loose sense, higher terms tend to correspond to higher order interactions. The number of parameters \((A_0, A_1, A_2, \ldots)\) which are used to represent the experimental data, depends on the molecular complexity of the solution, on the quality of data and number of data points available. The Redlich-Kister expansion provides a flexible algebraic expression for representing the excess Gibbs energy of a liquid\textsuperscript{172}. Perhaps the greatest disadvantage of the Redlich-Kister equation is its ambiguity in predicting the behaviour of multi-component data from binary data.

2.3.3 Wohl's Model\textsuperscript{174}

Accounting for the interaction between the molecules forming a solution Wohl developed an equation for the excess Gibbs energy which may be put forward for a binary system as follows:

\[
G^E/RT = (q_1x_1 + q_2x_2)(2z_1z_2a_{12} + 3z_1^2z_2^2a_{112} + 3z_1z_2^3a_{122} + 4z_1^3z_2a_{1112} + 4z_1^2z_2^2a_{1222} + 6z_1^2z_2^2a_{1122} + \ldots)
\]

\[
\ldots \ldots \ (2.3.3.1)
\]
where
\[ z_1 \equiv \frac{x_1q_1}{x_1q_1 + x_2q_2} \quad \text{and} \quad z_2 \equiv \frac{x_2q_2}{x_1q_1 + x_2q_2} \]

The q's are effective volumes (cross-section) of the molecules so that \( q_i \) is a measure of the size of molecule \( i \). The ratio of the q's is usually assumed equal to the ratio of the pure component liquid molar volumes. The a's are interaction parameters whose physical significance is somewhat similar to that of virial coefficients. By differentiation according to equation (2.3.1) of the third order Wohl equation the activity coefficients are:

\[ \ln \gamma_1 = z_2^2 \left| A_{12} + 2z_1 \left[ A_{21} \left( \frac{q_1}{q_2} - A_{12} \right) \right] \right| \ldots (2.3.3.2) \]

\[ \ln \gamma_2 = z_1^2 \left| A_{21} + 2z_2 \left[ A_{12} \left( \frac{q_2}{q_1} - A_{21} \right) \right] \right| \ldots (2.3.3.3) \]

Pigford et al.\textsuperscript{175} using the Margules form of Wohl's equation for activity coefficients successfully predicted experimental data. For a wide range of substances, this equation provided a good way of expressing liquid non-ideality, although not without the use of some assumptions resulting in an extra constant.

2.3.4 The Segment Model

Flory\textsuperscript{176} and Higgins\textsuperscript{177}, proceeding from a quasi-lattice model, derived the entropy of mixing of a long, flexible chain molecule (polymer) in solution from statistical geometrical considerations. The chain molecule was considered to be made
up of segments, and these segments, with respect to their size and shape, were assumed interchangeable with the solvent molecules. The solvent molecules were, likewise, approximated as spherical particles. The result of the Flory-Huggins theory is formulated for an athermal mixture (i.e. $H^E = 0$) is as follows:

$$\frac{G^E}{RT} = -\frac{S^E}{R} = x_1 \ln \phi_1/x_1 + x_2 \ln \phi_2/x_2 \quad \ldots \ldots \ (2.3.4.1)$$

where

$$\phi_1 = 1 - \phi_2 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} = \frac{n_1}{n_1 + r n_2}$$

$$r = \frac{V_1}{V_2} = \text{ratio of molar volumes of the solvent and polymer.}$$

Equation (2.3.4.1) serves as a standard of normal behaviour of polymer solution. The actual polymer solutions depart from this standard. The more complete form of the Flory-Huggins theory may be expressed as follows:

$$\frac{G^E}{RT} = x_1 \ln \phi_1/x_1 + x_2 \ln \phi_2/x_2 + x \phi_1 \phi_2 \ (x_1 + r x_2) \quad \ldots \ldots \ (2.3.4.2)$$

where $\chi$ is the Flory interaction parameter determined by intermolecular forces in a solution. For activity coefficients:

$$\ln \gamma_1 = -\ln (n_1 + r x_2) + (1 - 1/r) \phi_2 + \chi \phi_2^2 \quad \ldots \ldots \ (2.3.4.3)$$

$$\ln \gamma_2 = -\ln (1/r x_1 + x_2) + (1 - r) \phi_1^2 + r \chi \phi_1^2 \quad \ldots \ldots \ (2.3.4.4)$$
2.3.5 Local Composition Models

Wilson\textsuperscript{178} postulated that the local concentration in the neighbourhood of a central molecule can differ from the bulk (overall) concentrations. It means that if a given molecule is chosen as the central one, then the number, nature and position of the molecules in the nearest neighbourhood shell are influenced by certain properties of the central molecule.

Renon and Prausnitz\textsuperscript{179} combined the local mole fraction concept with the Scott's two-liquid theory, in order to overcome the limitations of Wilson's equation which fails to predict phase separation of liquid mixtures. The two-liquid theory of Scott postulates that molecules in a liquid mixture do not, in general, distribute themselves in a random manner, but exhibit a tendency to segregate due to the influence of a central molecule. It suggests that the ordering or disordering effect of a central molecule diminishes rapidly beyond the first neighbouring shell. In other words, it sees a single molecule in a liquid being surrounded by a cage or cell of adjacent molecules. Tassios\textsuperscript{180} has shown that the local mole fractions in N.R.T.L. model are not consistent with the overall composition of the mixture.

Heil and Prausnitz\textsuperscript{181} have given an equation for polymer solutions with interactions between like and unlike molecules. In fact it is a combination of Wilson's equation and the N.R.T.L. equation. Vetere\textsuperscript{182} has suggested a modification to Heil's equation by introducing a non-randomness parameter.
Orye\textsuperscript{183} presented an equation, which is based on Wilson's theory; yet, it is capable of predicting phase separation without the need of a third parameter.

Local composition equations can be generalized in one mathematical expression:

\begin{equation}
\frac{G^E}{RT} = -q \left[ x_1 \ln \left( x_1 + x_2 A_{21} \right) + x_2 \ln \left( x_2 + x_1 A_{12} \right) \right] \\
+ p x_1 x_2 \left[ \frac{\tau_{21} A_{21}}{x_1 + x_2 A_{21}} + \frac{\tau_{12} A_{12}}{x_2 + x_1 A_{12}} \right] + r x_1 x_2 \frac{a_{12} \tau_{12} + a_{21} \tau_{21}}{(x_1 + x_2 A_{21}) (x_2 + x_1 A_{12})} \\
\end{equation}

where

\[ A_{ij} = \rho_{ij} \exp (-\alpha_{ij} \tau_{ij}) \]

\[ \tau_{ij} = (g_{ij} - g_{jj})/RT \]

\( \rho_{ij} \) and \( \alpha_{ij} \) are defined in the following table for various equations.

<table>
<thead>
<tr>
<th></th>
<th>( p )</th>
<th>( q )</th>
<th>( r )</th>
<th>( \rho_{ij} )</th>
<th>( \alpha_{ij} )</th>
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<td>1</td>
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<tr>
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<td>0</td>
<td>1</td>
<td>C</td>
</tr>
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</table>
2.3.6 Continuous Linear Association Model (CLAM)

Renon and Prausnitz\textsuperscript{184}, starting with Flory's\textsuperscript{176} theory of polymer solutions, derived an equation giving activity coefficients for hydrocarbon + alcohol systems. The model is suitable for solutions rich in alcohol. For dilute solutions or for high temperatures, where the degree of association is small, the assumptions used by Flory do not apply, and the model fails. The CLAM equation for activity coefficients is given below:

\[
\ln \gamma_a = \ln \phi_a/x_a + \phi_b (1 - V_a/V_b) + K_c V_a/V_b \phi_b \phi_{b1} + \beta/RT V_a \phi_b^2
\]  
\[\cdots \cdots \quad (2.3.6.1)\]

\[
\ln \gamma_b = \frac{\ln \phi_{b1}^*}{\phi_{b1}^* x_b} + \phi_a (1 - V_b/V_a) + K_c (\phi_b \phi_{b1} - \phi_{b1}^*) + \beta/RT V_b \phi_a^2
\]  
\[\cdots \cdots \quad (2.3.6.2)\]

where

- $\phi_b$ = apparent volume fraction of alcohol
- $\phi_{b1}^*$ = volume fraction of alcohol monomer in pure alcohol (reference state)
- $\phi_{b1}$ = the (true) volume fraction of molecular species $b_1$
- $\beta$ = physical interaction parameter (temperature independent)
- $K_c$ = chemical equilibrium constant for alcohol association reaction
- $V_b$ = molar volume of alcohol

According to this model the Gibbs excess free energy can be given by:

\[
G^E = G^E_{\text{chem.}} + G^E_{\text{phy.}}
\]  
\[\cdots \cdots \quad (2.3.6.3)\]
where
\[
g_{\text{chem}} = x_a \ln \frac{\phi_a}{x_a} + x_b \left[ \frac{\ln \phi_{b1}}{\phi_{b1}^{*} x_b} \right] + K_c x_b \left( \phi_{b1}^{*} - \phi_{b1}^{*} \right)
\]
and
\[
g_{\text{phy}} = \beta \phi_a \phi_b (x_a \nu_a + x_b \nu_b)
\]

where
\[ x_b = \text{apparent mole fraction of species } b, \text{ i.e. alcohol.} \]

For solutions of alcohols in aliphatic and aromatic hydrocarbons which exhibit pronounced non-ideality, generally attributed to the effects of linear association (the hydrogen-bonded-polymer formation), a good agreement between this theory and both VLE and \( H^E \) data has been shown by Renon and Prausnitz.

Hanks, O'Neil and Christensen\textsuperscript{185} used CLAM to extend the method of predicting VLE data for multicomponent mixtures of aliphatic and aromatic hydrocarbons with one alcohol. The predicted VLE data for 35 hydrocarbon + alcohol mixtures was found to be with 10% standard deviation, averaging 5.5% for all the systems. It appears to account properly for pronounced deviations from ideal solution behaviour (large \( H^E \)) which are due to alcohol association.

2.3.7 UNIQUAC Model\textsuperscript{186}

The Universal quasi chemical (UNIQUAC) model is applicable to a wide range of mixtures, even though only two adjustable parameters per binary are required. Put forward by Abrams
and Prausnitz, and based on Guggenheim's quasi-chemical analysis, through introduction of the local area fraction, as the primary concentration available, it can effectively be applied to both partly or completely miscible systems. It can well represent liquid-liquid as well as vapour-liquid equilibria for binary and multicomponent systems, containing a variety of non-electrolyte components, such as hydrocarbons, ketones, esters, amines, alcohols, nitrates, etc. and water. Extension to multicomponent systems requires no ternary or higher parameters. The effect of molecular sizes and shapes is introduced through structural parameters obtained from pure component data and through Stavermans' combinatorial entropy as a boundary condition for athermal mixtures. The UNIQUAC equation for $G^E$ is as follows:

$$G^E = x_1 \ln \phi_1/x_1 + x_2 \ln \phi_2/x_2 + Z/2 \left[ q_1 x_1 \ln \theta_1/\phi_1 + q_2 x_2 \ln \theta_2/\phi_2 \right] - q_1 x_1 \ln (\theta_1 - \theta_2 \tau_{21}) - q_2 x_2 \ln (\theta_2 + \theta_1 \tau_{12})$$

... (2.3.7.1)

where

$$\tau_{12} = \exp \left[ -\frac{g_{21} - g_{11}}{RT} \right], \quad \tau_{21} = \exp \left[ -\frac{g_{12} - g_{22}}{RT} \right]$$

$\phi$ is the average segment fraction

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}, \quad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$r_1, r_2, q_1, q_2$ are pure-component structural parameters, which can be predetermined from bond angles and bond distances.
Equation (2.3.7.1) can be reduced to many of several well-known equations, including those of Wilson, Margules, Van Laar and N.R.T.L., by the introduction of well-defined simplifying assumptions.

The activity coefficients are obtained by differentiation of equation (2.3.7.1) according to equation (2.3.1) as follows:

\[
\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + \ell_i - \frac{\phi_i}{x_i}
\]

\[
(x_1 \ell_1 + x_2 \ell_2) + q_i \left| \begin{array}{c}
1 - \ln \left(\frac{\theta_1^\tau_{11}}{\theta_1^\tau_{11} + \tau_{22}^\theta_2}\right)
\end{array} \right.
\]

\[
- \frac{\theta_1^\tau_{11}}{\theta_1^\tau_{11} + \tau_{22}^\theta_2} - \frac{\theta_2^\tau_{22}}{\theta_1^\tau_{12} + \tau_{22}^\theta_2}
\]

\[
\ell_n \gamma_2 \text{ is detained by rotation of subscripts } 1 \leftrightarrow 2 \leftrightarrow 1
\]

While various physical models for excess Gibbs energy (such as UNIQUAC) usually give a reasonable representation of experimental activity coefficients, highly accurate representation can often not be achieved, particularly when there is extensive solvation and/or association in the mixture.

Which model for GE is the best? There is no simple answer. It all depends on the type of mixture, and also on the quantity of experimental data that may be available. The model chosen for GE may not be adequate for the available data. The binary parameters obtained depend upon the method
used for data reduction and, what is worse, regardless of what data-reduction method is used, many sets of binary parameters can equally well reproduce the data within experimental uncertainty. Although this may not effect seriously prediction about a binary system, yet, when binary parameters are used to predict activity coefficients in multicomponent systems, the choice of binary parameters necessarily affects the predictions. The same is true for multicomponent liquid-liquid equilibria for which extreme care has to be exercised in the choice of binary parameters\textsuperscript{187}.

A useful procedure for estimating binary parameters (when no experimental binary data is available) is provided by the concept of group contributions. The groups are considered as structural units, such as -CH\textsubscript{3}, -OH etc., which, when added, form the parent molecule. Instead of considering a liquid mixture as a solution of molecules, it is considered to be a solution of groups. So the activity coefficients are determined by the properties of groups.

A group contribution method based on Wilson's equation, called ASOG (Analytical Solution of Groups) was developed at Shell. A recent monograph by Kojima and Tochigi\textsuperscript{188} summarizes this method. Another group contribution method based on UNIQUAC, called UNIFAC (Universal Functional Group Activity Coefficient) was presented by Fredslund\textsuperscript{189}. A further revision and extension of the UNIFAC parameter tables was carried out by Rasmussen\textsuperscript{190} et al. For many mixtures the accuracy of estimation is good, but some mixtures are not
as well represented as the others, particularly at high dilution.

In practice, UNIFAC is usually preferred to ASOG, because UNIFAC parameters are more readily available and because UNIFAC parameters, unlike those of ASOG are assumed to be temperature independent.
CHAPTER 3

DESCRIPTION OF APPARATUS

3.1 The Low Pressure Density Meter and Ancillaries

For determination of excess volumes of mixing at atmospheric pressure, through density measurements, a DMA 40 density meter, made by Anton Paar of Austria, was employed.

The density meter contained a mechanical oscillator, consisting of a hollow elastic glass 'U' tube which, when excited electronically, vibrated at its resonant frequency which is influenced by the mass of any fluid filling the bore of the tube. The frequency of the oscillator was only influenced by that fraction of the liquid which was actually present in the vibrating part of the sample tube. The borosilicate glass oscillator (sample tube) was mounted in the centre of a double walled cylinder closed at both ends. The space between sample tube and the inner wall of the cylinder was filled with helium, a gas of high thermal conductivity. A thermostatically controlled liquid flowed between the outer and inner walls of the enveloping cylinder.

The 'U' tube described above was rigidly mounted on a heavy metal block representing the counter-mass for the oscillator. The filling of the sample tube could be observed through a window on the front plate.

A built-in pump provided a stream of filtered air to
dry the sample tube after cleaning.

The electronic part of the instrument provided for excitation of the oscillator at constant amplitude via an exciter coil and an armature attached to the 'U' tube. A second magnetic armature attached to the 'U' tube provided feed-back to the circuitry designed to sustain the oscillator via a second (pick-up) coil. A built-in quartz crystal timer accurately determined the period of oscillation in about two seconds. The electronically measured time-frequency was digitally displayed on the front of the density meter.

There were no special requirements regarding the location or installation of the DMA 40 density meter, i.e. it was not necessary to place the instrument on a vibration-proof mounting, as in the case of precision balances. However, the density meter had to be protected, during operation, from severe shocks and vibrations.

The instrument required connections to an external thermostat in order to achieve the desired temperature control within the density meter. According to the manufacturers, for accurate measurements, a recirculating system with a minimum flow rate of six litres per minute and a temperature constancy of ±0.05°C was needed. Accordingly, a large thermostat bath filled with water, and controlled to ±0.05°C was set up, with a circulating system to the density meter, delivered an adequate water flow. All the connections were made from rubber tubing
and were properly insulated with glass wool.

Two high quality, calibrated, mercury-in-glass thermometers were connected, one near the inlet and another close to the outlet at the rear of the density meter. Provision was also made to measure temperatures at the two points with the help of a platinum resistance thermometer.

3.2 The High Pressure System

3.2.1 Pressure Generator

Pressure was generated by a hand pump, manufactured by Pressure Products, Duriron Company Inc., and transmitted through a steel pipe to a high pressure dilatometer. The pump was capable of generating pressures up to 4750 bars. In order to prevent transmission of torsion or strain to piping, and reduce high pressure joint leakage, all fittings and the gauge were mounted on a rigid steel upright. The pressure was displayed on a Bourdon tube gauge claimed to be accurate to about 10 bars or better by the manufacturers.

A distilled water and methanol mixture was used as a pressure transmitting fluid. The presence of methanol in the mixture rendered any leakage past the piston more susceptible to detection (by gas-liquid-chromatography). Also, it reduced the compressibility of the hydraulic fluid which helped achieve pressures of higher degree. The presence of methanol in the water depressed the freezing point of the hydraulic fluid to below the lowest temperature at which experiments were carried out.
Fig. 3.1a A typical cone connection

Fig. 3.1b The temperature control circuit
3.2.2 Piping and Valves

a) Piping

The tubing used for conveying the pressures was made of 316 stainless steel (cold drawn bright finished), and had 6 mm external and 2 mm internal diameter. The maximum working pressure of the tubing was 5200 bars at 40°C. It was manufactured by Autoclave Engineers Inc.

Any long runs of tubing were securely clamped to obviate the danger of tubing 'whipping' in the event of a failure while under pressure.

From the pump the high pressure pipe led to an isolating valve and then via a 'T' to a three-way-two-stem manifold valve. The lower access was fitted with a length of high pressure tubing and was used for testing leaks in the dilatometer assembly prior to its immersion in the heating medium. The top access was connected with the dilatometer assembly after it was immersed in the heating medium.

All pipe connections were of the A.E. cone type. A typical connection is shown in Figure 3.1a. All ends of the tubings were externally coned at an angle of 58°. Threaded with a left-hand thread the tubings had collars screwed on all ends. An internal cone was machined at an angle of 60° to the part where the high pressure connection was made. These male and female (External and Internal) cones, machined at slightly different angles, bear on each
other through what is essentially a line contact. Thus the metal to metal sealing contact area is reduced to a minimum. Adequate stress for effective sealing was provided by moderate tightening of a gland nut placed behind the collar. All joints in the high pressure pipe-line were carefully tested for leaks before the start of experimental operation.

b) Valves

For safety reasons all valve spindles were so positioned that they did not point towards any person or object susceptible to damage.

Different body style valves with AE-cone connections and manufactured by Autoclave Engineering Inc., and by Pressure Products Inc., were used. These two-piece needle stem valves could be safely used up to 4137 bars pressure. All the valves had mounting holes for rigid installation, as well as a locking device to prevent unthreading of the packing gland.

3.3 The Constant Temperature Bath

a) Description

The tank was constructed from a 2 mm mild steel plate. The dimensions of the tank were 60 x 43 x 45 mm, and it contained approximately 50 litres of heating medium. The tank was insulated with glass wool in order to minimize heat losses. The walls of the tank carried two supports
for the two knife-edge bearings of the rocking plate which held the dilatometer. A stirrer and motor was also bolted to one side of the tank.

b) Heating medium

Shell oil 'Diala oil B' was used as the heating medium. Use of water as heating medium was avoided because of electrical connections of Linear Variable Differential Transformer, immersed in the heating medium.

c) Control of temperature

All temperatures were controlled with a mercury contact thermometer, and a control circuit which switched the power input to electrical heaters installed in the tank. These heaters had to be of low heat flux to avoid cracking of the heat transfer oil. The temperature control circuit is shown in Figure 3.1b. The power was turned on and off to the heater at zero voltage points avoiding radio frequency interference to other equipment. Closing the switch on the control thermometer, disconnected power to the heater. The role of the thermometer was that of a switch providing an on-off temperature control.

Temperatures below ambient were reached using a laboratory refrigeration unit manufactured by Townson and Mercer Ltd., England.
3.4 The High Pressure Dilatometer

3.4.1 Design and Construction

For a device to be constructed for direct determination of excess volumes of mixing at high pressures, there were certain design requirements:

(i) The device should be handy and inexpensive.

(ii) Means must be provided for filling and keeping two liquids apart during the first stage of an experiment.

(iii) Some way of stirring must be provided to achieve adequate mixing, while the device is still pressurised.

(iv) Separation of the hydraulic fluid and the system under study must be ensured since any leakage of hydraulic fluid into the system under study would alter its composition.

(v) The change in volume on isothermal, isobaric mixing must be measurable to high accuracy.

(vi) Perfect sealing of the apparatus must be ensured.

A high pressure dilatometer was designed and constructed to satisfy these requirements. The dilatometer basically consisted of a stainless steel block, an elbow and four tubes. The maximum working pressure of the dilatometer was 4137 bars. The block and elbow were made of annealed 316 stainless steel, whereas the tubes were made of 'superpressure' quality type 304 stainless steel. All of these fittings had A.E.-cone connections and were manufactured by Autoclave Engineers Inc.
Fig. 3.2 The dilatometer, a schematic diagram
Necessary design alterations were carried out in the Chemical Engineering workshop. The dilatometer is shown in Figures 3.2 and 3.3. Two tubes (1,2) each up to 300 mm in length, of 14 mm o.d. and 4.6 mm i.d., were connected to two sides of the stainless steel block (3) at right angles to each other. The other end of each of these two tubes was tightly closed with an end piece (4,5). A third tube (6) of about 80 mm length, 9 mm o.d. and 3 mm i.d. was connected to the block so that the three tubes were mutually orthogonal. The other end of the third tube was connected to a fourth tube (8) through a 90° elbow (7). This tube differed from the third only in its greater length. The bore and length of this tube were chosen to accommodate a piston and armature (see below). The bore of this tube was lapped to a high polish. The open end of this fourth tube was reduced to the size 6 mm o.d. used for connection to the pump by a reducing coupling (9) which, in turn, was connected to an isolating valve (11) via a short, right-angled length of 6 mm o.d. tubing (10).

3.4.2 The Piston

In order to provide a seal to keep separate the hydraulic fluid from the system under study a piston was placed in tube (8) of the dilatometer. To make the piston (Figure 3.4) a brass rod (1) of about 1.4 mm diameter and about 10.5 mm length was threaded on both ends. A length of silicone rubber (2) of 1 mm i.d. and slightly over 3 mm o.d., obtained from Scientific Suppliers Ltd., was placed near to
Fig. 3.3 The completely assembled dilatometer
1 brass rod
2 silicone rubber
3,3' stainless steel washers
4,4' leather washers
5,5' stainless steel nuts
6,6' stainless steel nuts
7 armature

Fig. 3.4. The piston
one end of the brass rod. An arrangement of leather packing (3,3') and stainless steel washers (4,4') was placed at each side of the silicone rubber. One end of the rod was fitted with two stainless steel 12 BA size nuts (5,5') and on the other end a magnetic core was placed (for use in locating the position of the piston by a displacement transducer set on the outside of tube (8) of Figure 3.3. The core was held against the back face of the piston by screwing two stainless steel nuts (6,6') on the other end of the brass rod.

3.4.3 Dilatometer Holders

A 38 mm x 38 mm steel plate with carefully positioned fittings was made to hold the dilatometer assembly (Figure 3.3). The basic idea was to rock the assembly through a small angle, about a horizontal axis, in order to mix the two liquids contained in two limbs of the dilatometer. The plate could pivot on knife-edges resting on supports attached to walls of the constant temperature bath. A big hole in the middle of the plate was also cut to be in a position to see through and to be able to reach tube (8) of the dilatometer, while the whole assembly was immersed in a constant temperature bath.

Two extremely useful stands, one for holding the semi-assembled dilatometer in a particular position, while assembling it and another for holding the plate upright while attaching the dilatometer to it (Figure 3.3), were also designed and constructed.
3.5 Measurement Devices

a) Displacement

Displacement of the magnetic core (about 10 cm long and made from soft Ni 48-52 alloy), attached to the piston in tube (8) of the dilatometer was detected by a Linear Variable Differential Transformer manufactured by Electro Mechanisms Ltd. The transducer could slide over tube (8) of the dilatometer. For primary excitation a constant voltage of 6 volts with sine waveform and 2.5 KHz frequency was recommended. This was provided by using a model 3310A function generator manufactured by Hewlett-Packard Ltd. With this instrument selection of output waveform, voltage and frequency could be made. The function generator has an operating temperature 0-55°C and is a high quality device giving good long-term stability of output.

The output from the LVDT was gathered on a digital voltmeter type 7144 manufactured by Solartron. Such voltmeters employ triple-slope conversion in which integration time is 100 ms and they have excellent immunity to interference at 50 Hz, 60 Hz and all other multiples of 10 Hz. The voltmeter could display output voltage correctly to ±.1 mV.

b) Temperature

All temperature measurements were taken through high grade, precalibrated mercury-in-glass thermometers. A platinum resistance thermometer was also employed but due to lack of sensitivity of the available resistance measuring
device, it did not prove to be any better than the mercury-in-glass thermometer.

c) Pressure

High pressure measurements were recorded from a Bourdon tube gauge manufactured by Astra Products. Safe working range of the gauge was 4137 bars and it was calibrated and checked to 1/4 percent or better accuracy of the range at a minimum of five points by the manufacturers. The gauge had to be mounted in a vertical plane in order to be properly zeroed. Ambient pressures were measured with a Fortin barometer.

3.6 Gas Chromatograph

Analysis of 'pure components' and some of their mixtures (to check suspected contamination caused by any leak) was carried out on a Hewlett Packard 5100 gas chromatographic unit equipped with a thermal conductivity detector. The signal from the detector was continuously recorded as a function of time on a strip-chart recorder. The peak area for each component peak was also measured by a Pye Unicam DP88 computing integrator. The chromatograph was fitted with two columns packed with different materials suitable for analysis of a particular liquid or liquid mixture. The column used was a 3000 mm spiral stainless steel tube of 3mm i.d. packed with 80/100 mesh Porapack Q. Helium was used as a carrier gas at a constant flow rate for each system. The samples were introduced into the gas chromato-
<table>
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<tbody>
<tr>
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</tr>
<tr>
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<td>2872 2</td>
</tr>
<tr>
<td>35</td>
<td>887210 3</td>
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Fig. 3.5 Typical pure component chromatograms with peak area values
Fig. 3.5 Typical pure component chromatograms with peak area values
graphic column through a silicone rubber septum by means of a plunger-operated injection needle. A careful injection technique was needed as the injection needle was delicate and susceptible to damage even by slight mishandling. Also high pressure at the injection port could blow the plunger out. The optimum working temperatures at the injection port, in the oven and detector block were found by trial and error and are given in the following table for all the systems studied.

<table>
<thead>
<tr>
<th>Injection port</th>
<th>Oven</th>
<th>Detector block</th>
<th>Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>T°C</td>
<td>T°C</td>
<td>T°C</td>
<td>ml/min</td>
</tr>
<tr>
<td>200</td>
<td>156</td>
<td>200</td>
<td>50</td>
</tr>
</tbody>
</table>

Some of the (actual) chromatographs for the systems studied, together with corresponding integrator output, are shown in Figure 3.5.
4.1 Atmospheric Pressure Density Determination

Densities of liquids and liquid mixtures were measured using an Anton Paar DMA 40 density meter. The apparatus has been discussed in section 3.1. The solutions were prepared with special care in stoppered bottles of small mass to attain maximum accuracy in determination of their mass compositions. Enough solution was kept in each bottle to ensure that it was nearly filled to the top in order to minimise evaporation of the liquid components. The experimental setup as well as the solutions were protected from exposure to a source of extreme heat such as sunlight. The temperature fluctuation within the density meter was found to be not more than ±0.05°C.

Air and water were used as reference materials. As soon as the power was switched on, the sample tube in the density meter started oscillating. After a certain time, depending upon the sample density, the display showed a number which represented the period of oscillation. The displayed value drifted until temperature equilibrium was reached. Then it only fluctuated ± one digit. Sometimes greater variations were encountered which meant either complete temperature equilibrium of the measuring cell had not been reached or the sample tube had not been loaded fully. At higher temperatures degassing can occur resulting in a drift in the display value.
At the start the sample tube was filled with air. Adequate time for its thermal equilibrium was allowed. The light with the help of which one may see through the sample tube was switched off to avoid any risk of disturbing the thermal equilibrium. Once the displayed frequency stayed constant, within the limits of its sensitivity, it was recorded as $T_{air}$. Distilled water was then injected into the lower opening of the sample tube using a plastic-tipped hypodermic syringe. Filling could be observed through the window in the front panel after turning on the illumination. The sample tube was completely filled. While leaving the hypodermic syringe in position, the upper inlet was closed off with a teflon plug. Overfilling did not effect the measurement because the vibrating volume, inside the sample tube, was always the same. Therefore it was not necessary to make separate volume measurements. Nevertheless, about 0.7 cc of liquid was needed to fill the tube completely.

Again some time was allowed for the system to attain thermal equilibrium, i.e. until constant frequency reading was observed. After that the 'Teflon' plug was removed and the sample in the tube was withdrawn into the syringe. The sample tube was then rinsed with acetone. At this stage, the air hose was connected to the upper inlet of the sample tube. With the air pump switched on, the flow of air was continued for some time. Once the tube was again clean and dry, the original 'T' value for air reappeared on the display. Failing this, the tube was once again rinsed and dried with air until it was ensured that the sample tube had become clean and dry. Test samples of unknown density
were then introduced into the sample tube in the same way as is described for water.

It was found necessary to recheck 'T' values for air and water from time to time, particularly if the measuring temperature was changed. It guaranteed that the effect of any insoluble substance left in the sample tube from previous measurements was taken into account. Care was also exercised during filling of the sample tube. Too fast filling could entrap air bubbles which yielded erroneous results. Each sample was tested with more than one measurement. If the same 'T' value was not repeated on the display existence of, even invisible, bubbles could be suspected and a re-run was found necessary.

4.2 Direct Determination of Excess Volumes of Mixing at High Pressures

The high pressure dilatometer described in section 3.4 was utilized for direct determination of excess volumes of mixing of various binary mixtures, at high pressure.

4.2.1 Calibration of the Measurement Devices

The thermometers used were checked for zero degree centigrade against ice, specially prepared from distilled water, crushed and kept in equilibrium with a small amount of water, in order to ensure zero degree centigrade temperature. Calibration for 100°C was made against condensing steam and no discrepancy in thermometer readings were found.
For pressure measurements the Bourdon gauge was calibrated by the manufacturers and described as accurate to about 10 bars or better.

The Stanton balance used for mass determination was checked by an expert from time to time during the course of the experimental work and was found reading correctly up to \(10^{-4}\)g.

Calibration of the displacement transducer was carried out with a micrometer capable of measuring to \(0.01\) mm. The magnetic core was placed in the dilatometer tube, positioned horizontally on a desk in a state of rest. The core could slide within this tube when pushed by a non-magnetic rod fixed to the micrometer. The transducer was set in a fixed position around the dilatometer tube, and was then connected with the signal generator and the multi voltmeter. With the magnetic core just completely inside the transducer, readout on the meter was noted for a constant input of 6 volts and 2.5 kHz frequency supplied by the signal generator. From that point onwards the output on the voltmeter was noted, each time, after displacing the core further inside by an exact distance of 1 mm, until it nearly reached the other end of the displacement transducer. The calibration thus obtained, for change of output in milli volts per millimetre displacement of the core, for a constant input of 6 volts and 2.5 kHz frequency is shown in Table 2.1. It was found necessary, while working, to ensure that no magnetic material be present in the immediate vicinity of the core. Output from the transducer was found not to be appreciably effected by temperature changes.
4.2.2 Determination of Cross-sectional Area of High Pressure Dilatometer Tube

Precise measurement of the internal cross-sectional area of the H.P. dilatometer tube, in which the piston moved, was of utmost importance. To achieve this, a piston with the armature attached to it, was packed inside the tube. The other end of the tube was sealed with a length of silicone rubber. A hypodermic needle was fixed through this silicone rubber seal. The space between this rubber seal and the piston was completely filled with mercury. Then, the piston end of the tube was connected to the pressure generating system by an adapter.

Very mild pressure, generated by a gentle operation of the hand pump moved the piston forward, thus forcing mercury out through the hypodermic needle. Each exhausted batch of mercury was weighed and the corresponding displacement of the piston (detected by the LVDT set around the tube) was recorded.

For a particular run the volume of the exhausted mercury was calculated from the knowledge of its density (from literature) and its mass. Then using the relationship:

\[ \text{Volume} = \ell \cdot A \]

and from the knowledge of \( \ell \) (Piston displacement), cross-sectional area \( A \), of the tube was easily calculable.

Several runs covering the full length of the tube were made and only negligible variations of the apparent
cross-sectional area were found. These were as likely to have arisen through measurement error as through genuine variations in the tube bore.

4.2.3 Preparation of the Apparatus

a) Packing of the piston

Packing of the piston in the dilatometer tube was a job demanding great care. With any damage, caused by a sharp or uneven stainless steel tube bore, the rubber piston did not provide a perfect seal. Therefore the bore of the tube was highly polished before the piston was gently and slowly pushed inside. Leather packings were used to protect both ends of the rubber piston from being chewed up (while under pressure) by the stainless steel backing washers. A piston not sufficiently pre-compressed could allow leakage of hydraulic fluid into, or out of, the system under study, whereas too tight a packing caused lost motion of the piston (due to greater friction between the rubber piston and the inner walls of the tube), even at pressures higher than the lowest, at which H.P. experimental measurements were carried out. Skill in selecting the right sized packing was gained by practice. Care was duly taken to ensure that the armature was tightly attached to the piston because any gap (between the two) would result in erroneous displacement measurements. Any possible uneveness inside the bore of the tube was accounted for by flexibility of the rubber piston itself. The brass rod used in the piston assembly (Figure 3.4) was sprayed with a lacquer to prevent
it being attacked by mercury.

b) Filling of the dilatometer

In order to prepare mixtures of a known composition
the block (3) of the dilatometer (Figure 3.2) with limbs
(1) and (2), disconnected from the rest of the apparatus,
was turned upside down. It was then filled with mercury
by means of a hypodermic syringe with a stainless steel
needle. The assembly was tapped, a number of times, to
ensure that the two limbs were completely filled with mer­
cury, i.e. no air remained trapped inside the system.
After making sure that this system was full of mercury,
the closed end of limb 1 was raised so that the filling
hole was situated at a lower position than the limb itself.
The desired quantity of one of the pure components was then
injected into it by using a hypodermic syringe with a long
stainless steel needle. While keeping limb 1 in the same
position, the closed end of limb 2 was then similarly raised
and the second component was injected into it using another
hypodermic syringe with a stainless steel needle. It was
ensured that there was enough mercury left to keep the two
pure components segregated. The mass of each component
(injected) was determined by weighing the syringes before
and after the injections. Later the rest of the apparatus
(dilatometer parts) was assembled and filled with mercury.
The position of the piston was then adjusted to establish
an initial position.

The whole procedure was carried out in a specially
built 60 x 60 mm tray, with raised edges, to avoid any spillage of mercury.

c) Assembly of the apparatus

The assembly of the dilatometer was a gradual process accompanied by the filling process. The fully assembled dilatometer was attached to the rocking plate, as shown in Figure 3.3. After checking for leaks, the whole apparatus was lowered in the oil bath and supported in the heat transfer fluid in the tank in such a way that the elbow (7) occupied the lowest position relative to the rest of the assembly. This ensured continued segregation of the two liquids while thermal equilibration took place. Finally, the dilatometer was connected to the pressure generating system.

After each experimental run the dilatometer was cleaned, dismantled and thoroughly washed with acetone to remove traces of oil still sticking to various parts of it. Filtered compressed air was then blown through various parts of the dilatometer to ensure its dryness before refilling and assembling it again.

4.2.4 Experimental Procedure

In order to check for leaks, the dilatometer was attached to the pressure generating system. With all electrical circuitry properly connected, pressure was gradually raised to the maximum of the range in which
experimental measurements were to be taken. A display of constant output on the digital voltmeter from the transducer, mounted on the limb (8) containing the armature, ascertained a leak proof system. The dilatometer was then depressurised, disconnected from the pressure generating system and lowered in the constant temperature tank. Enough time was allowed for the dilatometer to reach thermal equilibrium. A display of constant output on the voltmeter made certain that the temperature constancy had been reached.

From the previous knowledge of its calibration the transducer was then clamped firmly so that the armature was approximately 30 mm below the magnetic centre (zero output region). The voltmeter reading as a function of the pressure was noted and the corresponding piston displacement was found from the calibration; see Table 4.1. The lowest pressure at which the experimental measurements were taken was 69 bars. All pressure increases were slowly made and after each increment, some time was allowed for the system to restore its thermal equilibrium.

Finally, with the needle valve (11) closed, the pump was isolated. Mixing was carried out by raising and lowering the ends of the limbs. Mercury in the two limbs functioned as a stirrer. When the system eventually reached a constant volume, a further continuation of the mixing operation caused no noticeable change on the voltmeter reading. The dilatometer was then returned to its normal position and original thermal equilibrium as well as mechanical and pressure conditions were restored. The voltmeter reading
was recorded again.

Pressures were then raised to the same levels to which they were elevated prior to the mixing process, and as before, corresponding displacement of the core was recorded.

To check repeatability, the experimental procedure was repeated, for mixture of a particular composition, under the same conditions of temperature and pressures. Overall agreement in piston displacement was found to be within 0.1 percent.

Any leak of the hydraulic fluid into, or out of, the system under study, was easily detectable on depressurising as the magnetic core did not revert to its original position. A layout of the experimental set-up is shown in Figure 4.2.

4.3 Materials

For the study of excess volumes of mixing distilled, commercially available ('Analar') organic materials, with no significant impurities detectable by gas liquid chromatographic analysis, were used. Some specifications of the test materials are given in the following table.

For the sake of maintaining a high degree of purity, the chemicals were kept in small containers with very little empty space on top (to avoid oxidation or absorption from air). Distilled water was degassed before any use.

The mercury, used, was clean and free from any contamination. After each experimental run it was thoroughly washed with acetone and then filtered twice before being considered reusable.
Fig. 4.1 Layout of the experimental apparatus

1. Primary pump
2. Reservoir
3. High pressure pump
4. Non-return valve
5. Bourden gauge
6. Needle valve
7. Three-way-two-stem valve
8. The dilatometer assembly
<table>
<thead>
<tr>
<th>Material</th>
<th>This work</th>
<th>As supplied by the manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>density (g/cm³) at 20°C</td>
<td>refractive index n²⁰</td>
</tr>
<tr>
<td>2-butanol</td>
<td>.80666</td>
<td>1.3962</td>
</tr>
<tr>
<td>butanone</td>
<td>-</td>
<td>1.3775</td>
</tr>
<tr>
<td>ethanol</td>
<td>-</td>
<td>1.362</td>
</tr>
<tr>
<td>water</td>
<td>-</td>
<td>1.3331</td>
</tr>
</tbody>
</table>

* by gas-liquid chromatography as in section 3.6.
CHAPTER 5

TREATMENT OF RESULTS

The main objective of the whole experimental exercise was the determination of volume changes on mixing as a function of composition, temperature and pressure. For the fulfilment of this objective experiments were carried out, under isothermal and isobaric conditions, on mixtures of various compositions. As a consequence volumes of various mixtures and pure components were also obtained which have been utilized to deduce compressions.

5.1 At Atmospheric Pressure

5.1.1 Density

For density determination using an oscillating densitometer, we may consider the system to be represented by a hollow body of mass $m$, which is suspended on a spring with an elasticity constant $c$, and its volume $v$, filled with a sample of density $\rho$. The natural frequency of this system will then be:

$$f = \frac{1}{2\pi} \sqrt{\frac{c}{\rho \cdot v \cdot m}}$$  \hspace{1cm} (5.1.1.1)

Therefore, the period

$$T = 2\pi \sqrt{\frac{\rho \cdot v \cdot m}{c}}$$  \hspace{1cm} (5.1.1.2)

By taking the square of equation (5.1.1.2) and substituting

$$A = \frac{c}{4\pi^2 v}, \quad B = \frac{4\pi^2 m}{c}$$
FIG. 5.1 DENSITIES OF 2-BUTANOL AT 1 BAR
we obtain
\[ \rho = A(T^2 - B) \] ........ (5.1.1.3)

It is obvious that A and B can be regarded as apparatus constants which may be determined from two calibration measurements using samples of known density (e.g. air and water).

If the samples have densities \( \rho_1 \) and \( \rho_2 \) with corresponding time periods, \( T_1 \) and \( T_2 \), then:

\[ A = (\rho_1 - \rho_2)/(T_1^2 - T_2^2) \] ........ (5.1.1.4)

\[ B = (\rho_1 T_2^2 - \rho_2 T_1^2)/(\rho_1 - \rho_2) \] ........ (5.1.1.5)

The chosen calibration materials were air and water. The density of air was calibrated by the following equation\(^{191}\):

\[ \rho_{\text{air}} = \frac{0.0012930}{1 + 0.00367 \times t} \times \frac{P}{760} \text{ g/cm}^3 \]

where \( P \) is in mm of Hg and \( t \) in °C, and the density of water was chosen from reliable sources\(^{191,192}\). Densities of pure 2-butanol at various temperatures are listed in Table 3.1 and are plotted in Figure 5.1.

5.1.2 Excess Volumes of Mixing

The actual molar volume, \( V_{\text{act}} \), of a mixture (at constant temperature and composition), by the definition of density, can be related by:

\[ V_{\text{act}} = \frac{M_1 x + M_2 (1 - x)}{\rho_{\text{mix}}} \] ........ (5.1.2.1)

where

\( M_1, M_2 = \text{Molar masses of components 1 and 2} \)
\( \rho_{\text{mix}} = \text{Density of the mixture containing components 1 and 2} \)
**FIG. 5.2a** EX. VOL. OF 2-BUTANOL+WATER AT 1 BAR
FIG. 5.2b EX. VOL. OF 2-BUTANOL+WATER AT 1 BAR
\[ x = \text{Mole fraction of component 1} \]
\[ (1-x) = \text{Mole fraction of component 2} \]

The ideal molar volume, \( V_{id} \), under the same conditions is given by:
\[ V_{id} = xV_1 + (1-x)V_2 \] ........... (5.1.2.2)

where
\[ V_1, V_2 = \text{the molar volumes of pure components 1 and 2 at a given temperature.} \]

The values of \( V_1 \) and \( V_2 \) at the same conditions can be found from the respective density measurements of the pure components 1 and 2. Equation (5.1.2.2) then becomes:
\[ V_{id} = x \frac{M_1}{\rho_1} + (1-x) \frac{M_2}{\rho_2} \] ........... (5.1.2.3)

The molar excess volume of mixing is defined as the difference between the actual molar volume and the ideal molar volume, as is equated below:
\[ V^E = V_{act} - V_{id} \]

Therefore subtraction of equation (5.1.2.3) from equation (5.1.2.1.) yields the desired excess volumes of mixing at atmospheric pressures. A copy of the computer programme, used to calculate \( V^E \) is presented in Appendix 1.

The values of excess volumes of mixing for 2-butanol + water system at temperatures from 5°C to 85°C (at intervals of 5°C) are presented in Table 3.2 and some of the data is plotted in Figure 5.2.
5.2 At High Pressures

5.2.1 Excess Volumes of Mixing of Binary Mixtures

The molar excess volumes, \( V^E \), can be obtained from piston displacements as follows:

\[
V^E = \frac{\text{Change in volume of a mixture}}{\text{Total no. of moles present in the mixture}} = \frac{\Delta v}{N} \quad \ldots (5.2.1.1)
\]

where

\[
\Delta v = A \ell \quad \ldots \ldots (5.2.1.2)
\]
\[
N = \frac{m_1}{M_1} + \frac{m_2}{M_2} \quad \ldots \ldots (5.2.1.3)
\]

\( m_1, m_2 \) = masses of components

\( M_1, M_2 \) = molar masses of components

\( A = \) area of cross-section of the piston

\( \ell = \) displacement of the piston caused by mixing process.

Substituting the values from equation (5.2.1.2) and equation (5.2.1.3) into equation (5.2.1.1) we get:

\[
V^E = \frac{\ell A M_1 M_2}{m_1 M_2 + m_2 M_1} \quad \ldots \ldots (5.2.1.4)
\]

Excess volumes of mixing of the systems 2-butanol + water, butanone + water, and ethanol + water (under various conditions of temperature and pressure) were calculated according to equation (5.2.1.4) using a computer programme. The high pressure \( V^E \) data is listed in Table 3.3 and some of it is plotted in Figure 5.3.
Fig. 5.3a High pressure excess volumes of 2-butanol + water at 10°C
Fig. 5.3b High pressure excess volumes of 2-butanol + water at 25°C
Fig. 5.3c  High pressure excess volumes of 2-butanol + water at 55°C
Fig. 5.3d High pressure excess volumes of 2-butanol + water at 85°C
Fig. 5.3e High pressure excess volumes of ethanol + water at 25°C
Mass fraction ($w$) ethanol

Fig. 5.3f High pressure excess volumes of ethanol + water at 50°C
Mass fraction (w) butanone

Fig. 5.3g High pressure excess volumes of MEK + water at 30°C
5.2.2 Effects of Temperature and Internal Pressure on a Hollow Cylinder

In a hollow cylindrical vessel with closed-ends (analogous to the dilatometer), the change in volume as a result of change in temperature and pressure can be caused by a change in area of cross-section and a change in length of the cylinder.

As a result of temperature and internal pressure changes, from a datum of \( t_0 \) and \( p_0 \), the new cross-sectional area can be obtained by:

\[
A = A_0 + \int_{t_0}^{t} \frac{dA}{dt} \cdot dt + \int_{p_0}^{p} \frac{dA}{dp} \cdot dp \quad \ldots \ldots \quad (2.2.2.1)
\]

where

\[
\frac{dA}{dt} = A \cdot 2\alpha \quad \ldots \ldots \quad (2.2.2.2)
\]

\[
\frac{dA}{dp} = A \cdot 2\varepsilon_r / dp \quad \ldots \ldots \quad (2.2.2.3)
\]

\( \alpha \) = linear coefficient of thermal expansion

\( \varepsilon_r \) = radial strain

The radial strain, \( \varepsilon_r \), can be calculated, using Lame's theorem, from the following expression:

\[
\varepsilon_r = -\frac{p}{E(q^2 - 1)} \left[ \frac{r_i^2}{r_o^2} (1 - \nu) - (1 - 2\nu) \right] \ldots \ldots \quad (2.2.2.4)
\]

which is appropriate to a cylinder which is unconstrained axially.

where \( E \) = modulus of elasticity

\( q \) = radius ratio \( r_o / r_i \)

\( \nu \) = Poison's ratio
A change in length as a result of internal pressure, $P$, is given by longitudinal strain:

$$\varepsilon_\ell = \frac{\varepsilon_r + \varepsilon_t}{2} \quad \cdots \quad (2.2.2.5)$$

where $\varepsilon_t$ (the tangential strain) = \(-\frac{P}{E(q^2 - 1)} \left[r_0^2/r_1^2 (1 + \nu) + (1-2\nu)\right]\) (2.2.2.6)

Substituting the values from equation (2.2.2.6) and equation (2.2.2.4) in equation (2.2.2.5), we get:

$$\varepsilon_\ell = \frac{P}{E(q^2 - 1)} (1 - 2\nu) \quad \cdots \quad (2.2.2.7)$$

Longitudinal and radial strains were worked out for the dilatometer tube (made of stainless steel 316). For a length of 10 cm (the maximum piston displacement observed over the most extreme experimental conditions of temperature and pressure), the longitudinal strain was found to be negligible. The change in cross-sectional area of the dilatometer tube as a function of temperature and pressure, calculated according to equation (2.2.2.1), was accounted for in the computer programme used to calculate molar excess volume of mixing. The computer programme is listed in Appendix 1.

5.2.3 Estimate of Accuracy

Errors in experimentally determined $V^E$ at high pressures could have been introduced because of possible uncertainties in the following:

i) Determination of mass of liquid components.

ii) Determination of cross-sectional area of the dilatometer tube in which the piston moved.
(iii) Determination of piston displacements due to limitations of the transducer calibration and failure to return conditions to the pressure of the unmixed system when mixing was complete.

Because of the complex interplay of the experimental variables it is not feasible to obtain a single estimate of errors which could be applied to all the $V^E$ measurements (as a function of $x, T, P$). The certainty in determination of mass of a liquid was estimated by finding the standard deviation of repeated weighings of a certain sample, over a time scale which was generally needed to fill the dilatometer (thus also taking into account any possible losses due to evaporation). The standard deviation in the measured values of area of cross-section of the dilatometer tube was estimated from the calibration measurements. The variance associated with piston displacement measurements, $\Delta l$, due to pressure repeatability, was found from the values of replicate runs, performed over the entire pressure range, on fluids of a single composition. But towards finding gross-standard deviation of $\Delta l$, the sensitivity of the measurement devices was an important factor as well. The possible error in displacement measurement with respect to the output on the milli-voltmeter was estimated as $\pm 0.0054$ mm.

The error of a dependent variable, $y$, is related to the errors of the independent variables, $x_i$ ($i = 1,n$), by the expression:
\[ \sigma^2_y = \sum_{i=1}^{n} \left( \frac{\partial f}{\partial x_i} \right)^2 \sigma^2_{x_i} \] 

\[ \ldots \ldots \quad (5.2.3.1) \]

where

\[ y = f(x_1, x_2, \ldots, x_n) \]

which in this case becomes:

\[ \sigma^2_{V^E} = \left( \frac{\Delta \ell}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} \right)^2 \sigma^2_A + \left( \frac{A}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} \right)^2 \sigma^2_{\Delta \ell} + \left( -\frac{1}{M_1} \cdot \frac{A \Delta \ell}{\left( \frac{m_1}{M_1} + \frac{m_2}{M_2} \right)} \right)^2 \sigma^2_{m_2} \] 

\[ \ldots \ldots \quad (5.2.3.2) \]

Error analysis for mixtures (2-butanol + water) of two different concentrations at 85°C was found to be as follows:

Example 1.

The following values for the parameters in equation (5.2.3.2) were used:

Piston displacement as a function of pressure, \( \Delta \ell = 3.5 \text{ mm} \)

Area of cross-section of the tube, \( A = 7.5672 \text{ mm}^2 \)

Mass of component 1 (2-butanol), \( m_1 = 0.8191 \text{ g} \)

Mass of component 2 (water), \( m_2 = 1.5701 \text{ g} \)

Molar mass of component 1, \( M_1 = 74.12 \)

Molar mass of component 2, \( M_2 = 18.016 \)

Standard deviation of area cross-section \( \sigma_A = 0.037 \text{ mm}^2 \)

Standard deviation of total displacement measurement, \( \sigma \Delta \ell \), was obtained from the following two factors:

a) due to displacement measurement devices = 0.0054 mm
b) due to pressure measurement = .0385 mm

Standard deviation attached to mass of component 1, $\sigma_{m_1} = .0002$ g.

Standard deviation attached to mass of component 2, $\sigma_{m_2} = .0002$ g.

By putting all the above values in equation (5.2.3.2) we get:

\[
\sigma_{VE}^2 = \left( \frac{3.5}{.0982} \right)^2 (.037)^2 + \left( \frac{7.5672}{.0982} \right)^2 (.049)^2 + \left[ \frac{-1}{74.12} \cdot \frac{26.4852}{(.0982)^2} \right]^2 (.0002)^2
\]

or

\[
\sigma_{VE} = 3.28 \text{ mm}^3 \text{ mol}^{-1}
\]

Example 2.

Following are the values used for various parameters in equation (5.2.3.1).

\[
\Delta \ell = 3.6 \text{ mm}
\]

\[
A = 7.5672 \text{ mm}^2
\]

\[
m_1 = .5859 \text{ g.}
\]

\[
m_2 = 2.6297 \text{ g.}
\]

\[
M_1 = 74.12
\]

\[
M_2 = 18.016
\]

\[
\sigma_A = .037 \text{ mm}^2
\]

\[
\sigma_{\Delta \ell} = .0054 \text{ mm (} .03 \text{ mm}
\]

\[
\sigma_{m_1} = .0002 \text{ g.}
\]

\[
\sigma_{m_2} = .0002 \text{ g.}
\]
Equation (5.2.3.2) then becomes:

\[
\sigma_{E}^{2} = \left( \frac{3.6}{.15387} \right)^{2} \cdot (.037)^{2} + \left( \frac{7.5672}{.15387} \right)^{2} \cdot (.03)^{2} + \left( \frac{-1}{74.12} \cdot \frac{27.2419}{(.15387)^{2}} \right)^{2} \\
\cdot (.0002)^{2} + \left[ - \frac{1}{18.016} \cdot \frac{27.2419}{(.15387)^{2}} \right]^{2} (.0002)^{2}
\]

\[\therefore \sigma_{E} = 1.711 \text{ mm}^{3} \text{ mol}^{-1}\]

Whereas example 2 can almost be regarded as a standard case, example 1 is more or less an extreme case. The degree of accuracy attached to \(V_{E}^{E}\) values pertaining to the various systems studied is in the following order:

Ethanol > Butanone > 2-Butanol

5.2.4 Compressions of Pure Liquids

Two quantities are commonly used to express the amount of contraction of a substance under pressure.

(i) Compressibility

This represents the rate of fractional contraction with increasing pressure and can be written as follows:

\[K = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T} \quad \text{ ............ (5.2.4.1)} \]

(ii) Compression

It denotes the total fractional contraction brought about by a pressure increase, say from \(P^0\) to \(P'\) and it
may be expressed as follows:

\[
\frac{\Delta V}{V_o} = \frac{V_0 - V}{V_o} = \frac{1}{V_o} \int_{P_o}^{P} vK \, dP \quad \ldots \ldots (5.2.4.2)
\]

where \( V_o \) is the volume of the substance at pressure \( P_o \) usually taken as 1 atmosphere. \( v \) is the volume of the substance at pressure \( P \).

The majority of high pressure measurements have been reported as compressions.

As a first step towards determination of compressions of liquids or liquid mixtures, using the present equipment the volume change of the rubber piston as a function of temperature and pressure had to be determined.

This was achieved by compressing pure mercury under specific conditions of temperature and pressure. The mercury was then recovered from the dilatometer and its mass was determined. From knowledge of the density, the volume of the mercury at atmospheric pressure was calculated. Grindley and Lind's\textsuperscript{149} data for the density of mercury, at various temperatures and pressures, was used to compute the volume change (as a function of temperature and pressure) in the rubber piston. The computer programme used for this purpose is attached in Appendix 1.

The dilatometer was then filled with the liquid (to be studied) and some mercury, and the piston displacement at various pressures was recorded. Experiments were done on 2-butanol, butanone and ethanol at 25°C and 55°C, 30°C, and
FIG. 5.4a COMPRESSIONS OF WATER AT 25, 30 AND 55 DEGREE C
FIG. 5.4b COMPRESSIONS OF ETHANOL AT 25 AND 50 DEGREE C
FIG. 5.4c COMPRESSIONS OF 2-BUTANOL AT 25 AND 55 C
FIG. 5.4d COMPRESSIONS OF MEK AT 30 DEGREE C
25°C and 50°C respectively and at pressures up to 2.2 kbar.

In each case, because of friction up to 69 bar pressure, some loss of motion of the piston was noticed. This was accounted for by regressing every set of experimental results and thus finding the loss of motion due to friction.

Compressions for the pure liquids were then computed. The computer programme used for this purpose is attached in Appendix 1.

Because of many assumptions described above, the compression values are not claimed to be of very high precision. The accuracy (by comparison with literature data) is nevertheless better than 1%. The compressions of various liquids obtained at various temperatures and pressures are given in Table 3.4 (a,b,c,d) and are plotted in Figure 5.4.

5.3 Data Reduction

If there were any tolerably successful general predicting methods for estimating liquid state volumetric properties, these might offer some guidance on how to reduce data with the aid of a few adjustable parameters which might be determined empirically. However, as was discussed at length earlier, no such methods exist and so one is left with the purely empirical methods which have met with some success in the past plus any modifications which may suggest themselves.
1. Polynomial fits

Whereas polynomial fits of the form

\[ V^E = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i \]  \hspace{1cm} (5.3.1)

have been successfully used by certain researchers to represent experimental \( V^E \) as a function of \( x \), for various organic systems, such an expression has not been found capable of adequately representing unsymmetric experimental \( V^E \) data at constant temperature and pressure, e.g. systems showing an inflection in \( V^E \) values. Equally unsuccessful is the following type of expression:

\[ V^E = x_1 x_2 \left[ A_0 + A_1 (x_1 - x_2)^5 + A_2 (x_1 - x_2)^{13} \right] \]  \hspace{1cm} (5.3.2)

2. The quasi-chemical approach

The inadequacy of a theoretical mixing rule suggests that a quasi-chemical approach may provide an answer to the problem.

Let us make the assumption that in a binary liquid system the following equilibria exist:

\[ A + A \ \overset{k_{11}}{\longrightarrow} \ A_2 \]
\[ A + B \ \overset{k_{12}}{\longrightarrow} \ AB \]
\[ B + B \ \overset{k_{22}}{\longrightarrow} \ B_2 \]

Also assume that all the five species (\( A, B, AB, A_2, B_2 \)) have different molar volumes and that they form an ideal
solution. Let the number of moles of these five species in an equilibrium mixture be \( n_1, n_2, n_{11}, n_{12}, n_{22} \) respectively, giving:

\[
\text{total moles } n_T = n_1 + n_2 + n_{11} + n_{12} + n_{22} \quad \ldots \quad (5.3.3)
\]

\[
\text{total volume } V_T = n_1 v_1 + n_2 v_2 + n_{11} v_{11} + n_{12} v_{12} + n_{22} v_{22}
\]

\[
\ldots \ldots \quad (5.3.4)
\]

For equilibrium:

\[
n_{11} n_T = k_{11} n_1 n_{11}
\]

\[
n_{12} n_T = k_{12} n_1 n_{12}
\]

\[
n_{22} n_T = k_{22} n_2 n_{22}
\]

So the number of moles of monomer present are

(for A) \[
n_{10} = n_1 + 2n_{11} + n_{12} \quad \ldots \quad (5.3.8)
\]

\[
n_{20} = n_2 + 2n_{22} + n_{12} \quad \ldots \quad (5.3.9)
\]

Before mixing the volume of A would be

\[
V_1^O = m_1 v_1 + m_{11} v_{11}
\]

\[
\ldots \ldots \quad (5.3.10a)
\]

where

\[
n_{10} = m_1 + 2m_{11}
\]

\[
\ldots \ldots \quad (5.3.11a)
\]

and

\[
m_{11}(m_1 + m_{11}) = k_{11} m_1^2
\]

\[
\ldots \ldots \quad (5.3.12a)
\]

Similarly, for B

\[
V_1^O = m_2 v_2 + m_{22} v_{22}
\]

\[
\ldots \ldots \quad (5.3.10b)
\]

\[
n_{20} = m_2 + 2m_{22}
\]

\[
\ldots \ldots \quad (5.3.11b)
\]

\[
m_{22}(m_2 + m_{22}) = k m_2^2
\]

\[
\ldots \ldots \quad (5.3.12b)
\]
So the volume change on mixing, $V^E$, can be given by:

$$V^E = V^T - (V_1^0 - V_2^0) \quad \ldots \ldots \ldots \ldots (5.3.13)$$

Equation (5.3.12a) can be rewritten as:

$$m_{11}^2 + m_2m_{11} - k_1m_1^2 = 0$$

or

$$m_{11} = m_1 \left[ (k_{11} + 0.25)^{\frac{1}{2}} - \frac{1}{2} \right]$$

Now replacing $(4k_{11} + 1)^{\frac{1}{2}}$ by $\phi_1$ we get

$$m_{11} = \frac{m_1}{2} (\phi_1 - 1) \quad \ldots \ldots \ldots (5.3.14a)$$

From equations (5.3.14a) and (5.3.10a) we get

$$n_{10} = m_1 + 2m_{11}$$

$$= m_1(\phi_1 - 1 + 1)$$

$$= m_1 \phi_1 \quad \ldots \ldots \ldots (5.3.15a)$$

From equations (5.3.15a) and (5.3.11a) we can write

$$m_{11} = \frac{n_{10}}{2} \left[ 1 - \frac{1}{\phi_1} \right] \quad \ldots \ldots \ldots (5.3.16a)$$

and it can be shown that from equations (5.3.15a), (5.3.16a) and (5.3.10a) we can write:

$$\frac{V_1^0}{n_{10}} = \frac{v_1}{\phi_1} + \frac{v_{11}}{2} \left[ 1 - \frac{1}{\phi_1} \right] \quad \ldots \ldots \ldots (5.3.17a)$$

Likewise, an expression for molar volume of component 2 can be found. So volume change on mixing now becomes:

$$V^E = n_1v_1 + n_2v_2 + n_{11}v_{11} + n_{12}v_{12} + n_{22}v_{22} -$$

$$n_{10} \left[ \frac{v_1}{\phi_1} + \frac{v_{11}}{2} \left( 1 - \frac{1}{\phi_1} \right) \right] - n_{20} \left[ \frac{v_2}{\phi_2} + \frac{v_{22}}{2} \left( 1 - \frac{1}{\phi_2} \right) \right] \quad \ldots \ldots \ldots (5.3.18)$$
So, in principle, $V^E$ can be written as a function of $v_1$, $v_2$, $v_{11}$, $v_{12}$, $v_{22}$, $k_{11}$, $k_{12}$ and $k_{22}$ for any known values of $n_{10}$ and $n_{20}$ as the values of $n_1$, $n_2$, $n_{11}$, $n_{12}$ and $n_{22}$ can be eliminated via equations (5.3.5), (5.3.6), (5.3.7), (5.3.8) and (5.3.9).

Given a set of experimental $V^E$, i.e. $V^E_{\text{exp}, i} = f_{\text{exp}}(n_{10i}, n_{20i})$, one can seek values of the volume and equilibrium parameters which give the best fit. Furthermore, experimental measurements of molar volumes $V^0_1$ and $V^0_2$ can be used either to reduce the number of adjustable parameters required or as additional pieces of experimental evidence to be incorporated into the objective of the fitting routine.

**Preliminary considerations for the model**

i) $V^E$ is negative for alcohol-water mixtures at low (near ambient) pressures.

ii) It is known that water as a hydrogen-bonded structure is less dense than in monomeric form at a given temperature. So $v_{11} > 2v_1$.

iii) Despite what is said above with respect to water it is expected to be more generally the case that 'dimers' will be more compact than the parent monomers. So $v_{22} < 2v_2$.

iv) In view of the above, if the concept of dimer formation is to be at all successful in describing the $V^E$ behaviour one has to assume
\[ v_{12} < v_1 + v_2 \]
and perhaps \[ v_{12} < \frac{1}{2} (v_{11} + v_{22}) \]

v) In non-interacting systems one can visualise a population of two different sizes being able to pack more closely (in same size ratios) than single size populations. This is of marginal relevance but justifies \[ v_{12} < \frac{1}{2} (v_{11} + v_{22}) \].

vi) In a model as complex as equation (5.3.18) there must be many sets of the parameters which give a 'fair fit' to the experimental measurements but many will be implausible, e.g. negative equilibrium constants and mole fractions, \[ v_{ii} < v_i \] etc. Care should be exercised when accepting a set of parameters as 'fitting' the experimental data. Poor fits can arise through:

a) the search on the parameters converging on an incorrect solution;
b) the model being so unrealistic as to be incapable of describing the physical reality;
c) the experimental data incorporating serious errors; systematic errors are obviously worse than random errors.

vii) Any supporting evidence or information indicating the magnitude of any adjustable parameter should be built into the model and suitably weighted in accordance with its credibility.

Preliminary Calculations

The model was employed to calculate excess volumes of
Fig. 5.5 Comparison of experimental and calculated excess volumes of 2-butanol + water at 20°C and at 1 bar
mixing for the 2-butanol + water system at atmospheric pressures and 20°C. The calculated and experimental values of $V^E$ are plotted in Figure 5.5. Careful consideration of the calculated values leads to the conclusion that probably the model is inadequate; it being incapable of giving values of $V^E$ close to those experimentally determined for any plausible set of values of the semi-empirical volumes and equilibrium constants. Nevertheless, the model has some merit in that it gives a simple 'ideal' method of describing $V^E$ curves of asymmetric shape with inflections.

In short, the model can qualitatively produce results conforming with $V^E(x)$ observed experimentally but not quantitatively.

It was thought unrealistic to refine the model, at this stage, to take into account higher order interactions (e.g. 'poly-water') as there are insufficient data to estimate the larger number of parameters involved.

3 Application of the UNIQUAC model

This model was selected as a possible basis for a description of $V^E(P,T,x)$ as it is typical of a large family of semi-empirical models which have been used relatively successfully to describe non-ideal behaviour in a wide range of mixtures, though not, it has to be admitted, as a function of pressure.
As excess volumes of mixing can be related to the excess Gibbs' energy through a simple expression:

\[ V^E = \frac{\partial G^E}{\partial P} \]

differentiation of the UNIQUAC equation for \( G^E \), equation (2.3.7.1), with respect to pressure, yields the following expression:

\[ V^E \text{ (resid.)} = \frac{q_1 x_1 \theta_2 \tau_{21} \frac{\partial \Delta g_{21}}{\partial P}}{(\theta_1 + \theta_2 \tau_{21})} + \frac{q_2 x_2 \theta_1 \tau_{12} \frac{\partial \Delta g_{12}}{\partial P}}{(\theta_2 + \theta_1 \tau_{12})} \quad \ldots (5.3.19) \]

The basis of the UNIQUAC equation (2.3.9.1) implies that \( \frac{\partial r_1}{\partial P} \) and \( \frac{\partial q_1}{\partial P} \) are both zero or negligible and from this it follows that \( V^E \) arises only from the interaction energy (\( \Delta g \)). By rearranging equation (5.3.19) we get:

\[ V^E = x_1 q_1 x_2 q_2 \left[ \frac{\tau_{21}}{x_1 q_1 + x_2 q_2 \tau_{21}} \cdot \frac{\partial (\Delta g_{21})}{\partial P} + \frac{\tau_{12}}{x_2 q_2 + x_1 q_1 \tau_{12}} \cdot \frac{\partial (\Delta g_{12})}{\partial P} \right] \quad \ldots \ldots (5.3.20) \]

Equation (5.3.20) was used to fit experimentally obtained values of \( V^E \) at 25°C, 55°C and 85°C, and at atmospheric as well as high pressure (2068.44 bars).

The evidence of LLE\(^{193}\) is that:

\[ \frac{\partial (\Delta g_{12})}{\partial P} < 0 \]

and

\[ \frac{\partial (\Delta g_{21})}{\partial P} \geq 0 \]

but equation (5.3.20) needed the opposite sign for \( \frac{\partial (\Delta g_{12})}{\partial P} \) and so provided inconsistent results.
FIG. 5.6a EXP. AND CALC.(UNIQUAC) EX. VOLS. AT 1 BAR
EXCESS VOLUME CC/MOL

EXPERIMENTAL EX. VOL. (55 DEGREE C)

CALCULATED EX. VOL. (55 DEGREE C)

FIG. 5.6b EXP. AND CALC. (UNIQUAC) EX. VOL. AT 2068 BAR
FIG. 5.7a TAIT EQ. CONST. J (FOR WATER) vs T
FIG. 5.7b TAIT'S EQ. CONT. L (FOR WATER) vs T
Some $V_{\text{calc.}}^E$ values are compared with $V_{\text{exp.}}^E$ values in Figure 5.6. Similar inconsistencies arise when other expressions for $G^E$ such as Van Laar's equation are similarly used suggesting that this is not a fruitful line to pursue.

4. Application of the Tait$^{130}$ and Huddleston equations$^{139}$

The compression data (Table 3.4) at various temperatures and pressures up to 2206.336 bars for pure water, ethanol, MEK and 2-butanol was fitted to the Tait and Huddleston equations, i.e. equations (2.1.2.1) and (2.1.2.7) respectively, whereas it is found that the Tait's equation fits the data slightly better (i.e. lower standard deviation) than the Huddleston equation.

For water at $25^\circ\text{C}$, $30^\circ\text{C}$, $50^\circ\text{C}$ and $55^\circ\text{C}$, and pressures up to 2206.336 bars, both the Tait equation constants, $J$ and $L$, are found to be non-linear functions of temperature. Figure 5.7 shows the change of $J$ and $L$ with temperature. It can be said that the values of both these constants are indicative of the behaviour of compressibility (as a function of temperature) of water. This may find a theoretical justification on the basis of Ginell's$^{132}$ model where he, while theoretically deriving the Tait equation, has related $J$ with empty spaces between the molecules of a liquid and $L$ with the temperature.
6.1 Consistency

6.1.1 Internal Consistency

a) Atmospheric pressure results

The excess volumes of mixing of the 2-butanol + water system computed from the densities in the homogeneous range of composition for temperatures ranging from 5°C to 85°C with intervals of 5°C, were found to be negative both at lower and higher concentrations of 2-butanol. At higher concentrations the absolute values of $V^E$ decrease with increasing temperature. In other words, the solution tends to behave more ideally as the temperature goes up. At lower concentrations of 2-butanol the behaviour shows interesting variance. Below 30°C the $V^E - w$ curves (at $w < 0.12$) are convex upwards. At around 30°C an inflection becomes apparent so that for mass fractions above the point of inflection the curve is convex downwards. At higher temperatures the curvatures weaken so that $V^E - w$ curves become nearly linear. The minimum $V^E$ is at about $w = .69$. All the density and $V^E$ values are smooth functions of composition and temperature with low scatter (cf. Figures 5.1 and 5.2).

b) Elevated pressure results

i) 2-butanol + water system

Values of excess volumes (cf. Figure 5.3) measured at
$1^\circ$, $25^\circ$, $55^\circ$ and $85^\circ$C and pressures up to 2206 bars are negative except at very low 2-butanol concentrations (mass fraction < .07) where they are positive at extreme pressures. The excess volumes increase with increasing pressure. The rate of increase is more marked at lower pressures than it is at higher pressures. At 2206 bars the $V^E$ at equimolar concentration of 2-butanol and water is reduced to about 1/3 of the value at 69 bars (at all the four temperatures). The maximum is at about $w = .67$ and does not seem to shift either with $T$ or $P$. The increase of temperature has a reducing effect on the absolute values of $V^E$ at all pressures and concentrations. Good repeatability (section 5.2.3) and low scatter are prominent features of the measured values.

ii) Ethanol +water system

$V^E$ values (cf. Figure 5.3) determined at $25^\circ$ and $50^\circ$C and at pressures up to 2206 bars are found to be negative at all but very low ethanol concentrations (mass fraction < .07) where the values are positive at and above 1930 bars pressure. The variation of $V^E$ as a function of temperature and pressure shows the same features as the 2-butanol + water system, i.e. $V^E$ increases with increasing pressure, and with increase of temperature the absolute values of $V^E$ decrease at all concentrations and pressures. At equimolar concentration of ethanol and water this system exhibits significantly greater excess volumes than those in the case of 2-butanol +water at all pressures and both the temperatures. Although the effect of temperature appears to be somewhat less marked than that in the case of 2-butanol +
water system yet both the cases present qualitatively the same picture of an alcohol+water system.

iii) MEK + water system

For this system \( V^E \) values (cf. Figure 5.3) at 30°C and up to 2206 bars are found to be negative and their absolute values decrease with increasing pressure. Apparently there is a tendency in the \( V^E \) to turn positive at extremely low MEK concentrations (mass fraction <.04) at around 2070 bars. The values are a smooth function of pressure and have a low scatter.

iv) Compressions of pure liquids

Compression values determined for water and pure 2-butanol, ethanol and methylethylketone at various temperatures and pressures up to 2206 bars (cf. Figure 5.4) are smooth functions of pressure. For ethanol and 2-butanol compression values are higher at higher temperatures. In the case of water, compressions at 50°C have the lowest values.

6.1.2 External Consistency

Excess volumes of mixing of ethanol + water and 2-butanol + water systems have been found consistent with what little published data there are whose quality is not suspect.

At atmospheric pressure and temperatures of 20°C and 60°C excess volumes of 2-butanol + water mixtures were determined
by Altsybeeva\textsuperscript{66}. The present work, under the same conditions of temperature and pressure, compares well with that of the above mentioned, and also has much lower scatter. No data at higher pressure is available for comparison of the 2-butanol + water $V^E$ values obtained during this work. Comparison of Altsybeeva's data on $V^E$ and that of the present work is drawn in Figure 6.1.

Excess volumes of mixing, at high pressures, of equimolar mixtures of ethanol and water at 25°C and 50°C have been reported by Götze and Schneider\textsuperscript{38}. The $V^E$ values of the same system determined during the present work under the same conditions of temperature and pressure are in excellent agreement with those of the above mentioned. Comparison of the two works is shown in Figure 6.2.

Lamb and Hunt\textsuperscript{33} reported positive volumes of mixing for MEK + water systems at 30°C, 50°C and 70°C and at pressures greater than 690 bars, both at very low and very high MEK concentrations. These positive values of $V^E$ could not be confirmed by the present work carried out at 30°C under the same conditions of pressure. The method used by Lamb and Hunt is not expected to lead to accurate estimates, so it is felt that more confidence should be placed in the present measurements.

Compressions of water, at temperatures of 25°C, 30°C, 50°C and 55°C and pressures up to 2206 bars agree within about 1% of the data of Grindley and Lind\textsuperscript{49}. The MEK compression data at 30°C obtained during this work disagrees considerably with
EXCESS VOLUME CC/mol

MOLE FRACTION (x) 2-BUTANOL

0.00 0.20 0.40 0.60 0.80 1.00

-0.80 -0.60 -0.40 -0.20 -0.00

THIS WORK (20 DEGREE C)
FRIEDMAN AND SHERAGA (20 DEGREE C)
ALTSYBEEVA (20 DEGREE C)
BOEKE AND HANEWALD (21 DEGREE C)

FIG. 6.1 COMPARISON OF EX. VOL. OF 2-BUTANOL+WATER AT 1 BAR
This work
Ref. 41

Fig. 6.2 Excess volumes of ethanol + water (x = .5) at 25° and 50°C
FIG. 6.3 COMPRESSIONS OF WATER AT 50 DEGREE C
that of Hunt. No compression data on 2-butanol is available for comparison. Compressions of ethanol at 25° and 50°C and up to 2206 bars agree well within 1% of the data of Moriyoshi and Inubushi. Figures 6.3 and 5.4b compare the compressions of water and ethanol obtained during this work with those of the other workers mentioned above. Good fits (Table 3.4) by the Tait and Huddleston equations of the compression data of various liquids also show consistency of the data. It has been found that Tait's equation provides a better fit to the compression data of water, ethanol, 2-butanol and MEK at various temperatures and pressures up to 2206 bars than does Huddleston's equation.

6.1.3 Thermodynamic Consistency

a) Qualitative

Opportunities present themselves for comparing \( V^E \) with other thermodynamic functions such as \( \frac{\partial G^E}{\partial P} \), \( T \), \( x \) or \( \frac{\partial H^E}{\partial P} \). An approach that has been used in the past was to estimate \( G^E \) at pressures above normal from \( G^E \) at atmospheric pressure by integrating \( V^E \).dP. Accurate prediction of conjugate compositions at high pressures by this method gives a good indication that the \( V^E(P) \) measurements are of reasonable quality. However, this approach is only applicable where there are good data on \( G^E(x) \) at some fixed pressure and at relevant temperatures, and where miscibility data are available. No such data is available in the case of 2-butanol + water and MEK + water systems.
b) Qualitative

For 2-butanol + water rather sparse VLE experimental measurements by Altsybeeva\textsuperscript{66} and Boeke and Hanewald\textsuperscript{69} allow one to deduce $\Lambda_{\text{mix}}^G(x)$ curves. These curves show curvatures such that $\phi' > \phi'' > 0$, where $\phi = [\phi^2(\Lambda_{\text{mix}}^G)/\phi^2]_{\text{T,P}}$ and the superscripts denote two conjugate phases. Bozdag and Lamb\textsuperscript{85} using their own LLE measurements and VLE data on $H^E$ of Altsybeeva have endorsed the above relationship.

The effect of pressure on the mutual solubility of 2-butanol + water is most clearly indicated in Figure 1.2. It is evident that the increase of pressure increases mutual solubility under all conditions. As suggested by Rowlinson\textsuperscript{194}, expressions relating the effect of pressure on miscibility gap to volume of mixing can be developed. Making appropriate substitutions in Rowlinson's expressions results in:

$$\left( \frac{\partial x}{\partial P} \right)_T = \left[ \frac{1}{\phi'} \right] \left[ \left( \frac{\partial V^E}{\partial x} \right)_T, P \right] - \frac{(V_{E''} - V_{E'})}{(x'' - x')}$$  \hspace{1cm} (6.1.3.1)

$$\left( \frac{\partial x}{\partial P} \right)_T = - \left[ \frac{1}{\phi''} \right] \left[ \left( \frac{\partial V^E}{\partial x} \right)_T, P \right] - \frac{(V_{E''} - V_{E'})}{(x'' - x')}$$  \hspace{1cm} (6.1.3.2)

Bozdag's work\textsuperscript{193} has shown that $(\partial x/\partial P)_T'$ is positive for all the pressure and temperature ranges explored except at $-7^\circ$C and low pressures and that $(\partial x/\partial P)_T''$ is negative under all the conditions studied. The $V^E$ data at 1 atmosphere obtained during the present work give the approximate gradients shown in the following table.
<table>
<thead>
<tr>
<th>T°C</th>
<th>$\left(\frac{\partial V^E}{\partial x}\right)'$ cm$^3$ mol$^{-1}$</th>
<th>$\left(\frac{\partial V^E}{\partial x}\right)''$ cm$^3$ mol$^{-1}$</th>
<th>$(V''^E - V'^E)/(x'' - x')$ cm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-6.9</td>
<td>-0.3</td>
<td>-0.8</td>
</tr>
<tr>
<td>35</td>
<td>-5.4</td>
<td>-0.3</td>
<td>-0.9</td>
</tr>
<tr>
<td>20</td>
<td>-6.6</td>
<td>-0.4</td>
<td>-0.9</td>
</tr>
</tbody>
</table>

This table indicates that at 20°, 35° and 50°C

$$
\left(\frac{\partial V^E}{\partial x}\right)'_{T,P} < \left(\frac{\partial V^E}{\partial x}\right)''_{T,P} < \left(\frac{\partial V^E}{\partial x}\right)''_{T,P}
$$

In the above relationships the second relation is nearly an equality. This, coupled with the observation that the absolute magnitudes of $\left(\frac{\partial x}{\partial P}\right)'_T$ and $\left(\frac{\partial x}{\partial P}\right)''$ are similar (Fig.1.2) leads to the conclusion that $\phi' > \phi'' > 0$ at ordinary pressures and around 25°C. So the $V^E$ measurements obtained during this work are found to be consistent with other experimental observations relating to phase equilibria.

Very few measurements of mixture properties at high pressures have been made, often only liquid phase equilibria for immiscible systems are available. A few thermal measurements at low pressure have also been reported. If excess enthalpy at atmospheric pressure ($H^E_{P_0}$) is available then it is possible to calculate excess enthalpy at a higher pressure ($H^E_P$), through the following relationship:
\[ H^E_p = H^E_{p_o} + \int_{p_o}^P (\frac{\partial H^E}{\partial P})_{T,x} \cdot dP \quad \ldots \ldots \quad (6.1.3.3) \]

or, more approximately

\[ H^E_p \approx H^E_{p_o} + (\frac{\partial H^E}{\partial P})_{T,x,p} \cdot (P - P_o) \quad \ldots \ldots \quad (6.1.3.4) \]

where

\[ (\frac{\partial H^E}{\partial P})_{T,x} = V^E - T(\frac{\partial V^E}{\partial T})_{p,x} \quad \ldots \ldots \quad (6.1.3.5) \]

and \( p \) is an appropriate mean pressure.

Using high pressure \( V^E \) measurements of 2-butanol + water system and Altsybeeva's atmospheric pressure \( H^E \) data\(^6\), \( H^E \) at 276 bar and 25\(^\circ\)C has been calculated. In order to be able to use equation \( (6.1.3.4) \), \((\frac{\partial H^E}{\partial P})_{T,x} \) was found by regressing \( V^E \) (2-butanol + water) against \( T \) at various compositions. So from

\[ V^E = a_0 + a_1T + a_2T^2 + a_3T^3 \quad \ldots \ldots \quad (6.1.3.6) \]

and \(-T \cdot \frac{\partial V^E}{\partial T} = -a_1T - 2a_2T^2 - 3a_3T^3 \quad \ldots \ldots \quad (6.1.3.7) \]

where \( a_0, a_1, a_2 \) and \( a_3 \) are constants, one can write

\[ V^E - T(\frac{\partial V^E}{\partial T}) = a_0 + a_1(1-1)T + a_2(1-2)T^2 + a_3(1-3)T^3 \]

\[ \therefore (\frac{\partial H^E}{\partial P})_{T,x} = a_0 - a_2T^3 - 2a_3T^3 \quad \ldots \ldots \quad (6.1.3.8) \]

The experimental\(^6\) \( H^E_{p_o,25^\circ C} \) along with the calculated \( H^E_{p,25^\circ C} \) (276 bars) have been plotted in Figure 6.4. The actual values are too raw to draw any quantitative conclusions but the figure clearly shows that close to the 2-butanol+water
Fig. 6.4 Excess enthalpies of 2-butanol + water at 25°C
critical region (assuming that $H_P^E$ is an analytic function)

$$(\frac{\partial^2 H^E}{\partial x^2})_{T_c,P_c} > 0 \quad \ldots \ldots \quad (6.1.3.9)$$

Also the plot of $V^E$ and $x$ (for the same system under the same conditions of $P$ and $T$), is convex downwards meaning that

$$(\frac{\partial^2 V^E}{\partial x^2})_{T_c,P_c} > 0 \quad \ldots \ldots \quad (6.1.3.10)$$

As shown by Rowlinson$^{194}$ the pressure dependence of the critical temperature can be given as follows:

$$\frac{dT_c}{dP} = \lim_{P = P_c, T = T_c} \left[ \frac{T_c \left( \frac{\partial^2 V^E}{\partial x^2} \right)_{T_c,P_c}}{\left( \frac{\partial^2 H^E}{\partial x^2} \right)_{T_c,P_c}} \right] \quad \ldots \ldots \quad (6.1.3.11)$$

From relations (6.1.3.9) and (6.1.3.10) it follows that around 25°C and 276 bars equation (6.1.3.11) requires $dT_c/dP$ to be positive. $dT_c/dP$ has been shown to be positive (a lower critical solution temperature which increases with pressure) by two independent sets of measurements$^{84,193}$.

Taking an approach analogous to that in equation (6.1.3.1) and equation (6.1.3.2), it can be shown that

$$\left( \frac{\partial x}{\partial T} \right)_P' = \left[ \frac{1}{T \phi'} \right] \left[ \left( \frac{\partial H^E}{\partial x} \right)_T,P' - \frac{(H^E'' - H^E')}{(x'' - x')} \right] \quad \ldots \ldots \quad (6.1.3.12)$$

and

$$\left( \frac{\partial x}{\partial T} \right)_P'' = \left[ \frac{1}{T \phi''} \right] \left[ \left( \frac{\partial H^E}{\partial x} \right)_T,P'' - \frac{(H^E'' - H^E')}{(x'' - x')} \right] \quad \ldots \ldots \quad (6.1.3.13)$$

where \( \phi = \left[ \frac{\partial^2 (\Delta G_{mix})}{\partial x^2} \right]_{T,P} \)
As stability of the equilibrium mixture requires $\phi$ to be positive for all miscible combinations$^{194}$, so the sign of $(\partial x/\partial T)_p$ is determined by the sign of second factor in equations (6.1.3.12) or (6.1.3.13). From the excess enthalpy of 2-butanol + water (Figure 6.4) calculated at high pressure (276 bars) and 25°C using $V^E$ measurements taken during this work it is estimated that:

$$(\partial HE/\partial x)' << \frac{H^{E''} - H^{E'}}{x'' - x'} < (\partial HE/\partial x)'' \quad \ldots \ldots \ (6.1.3.14)$$

From relation (6.1.3.14) it follows that around 25°C and at high pressure, equation (6.1.3.12) requires $(\partial x/\partial T)'$ to be negative and equation (6.1.3.13) requires $(\partial x/\partial T)''$ to be positive. Independent LLE measurements$^{84,193}$ confirm this.

It seems, then, that the present results are in complete accordance with other available experimental measurements except the suspect measurements on butanone + water.

6.2 Physical Interpretations

Quantitative explanations of the excess volumes of mixing, of the systems studied, in basic physical terms are not yet possible due to limited understanding of the complex interactions between molecules of different shapes and electronic charge distributions. However, some qualitative interpretation is possible.

A plausible qualitative explanation of the excess volumes of aqueous non-electrolyte systems as a function
of composition, pressure and temperature can be based on
the structure of water. The structure of water may it­
self be considered as a mixture of dense (monomeric) and
bulky (polymeric) forms in equilibrium with each other.
The hydrogen bonded bulky form of water may be regarded
as "ice-like" or else as "clusters" of water molecules
with big void spaces in between.

Frank and Evans\textsuperscript{195} suggested that non-polar groups
(-R) or molecules in aqueous solutions are surrounded by
low energy, bulky water molecules. This idea may be ex­
pressed in the form of a solvation equilibrium.

\[
-R + n \text{H}_2\text{O} \rightleftharpoons -R(\text{H}_2\text{O})_n \quad \text{dense} \leftrightarrow \text{voluminous} \quad \text{(6.2.1)}
\]

Recent research on this subject\textsuperscript{2} including infrared
spectroscopic analysis\textsuperscript{1} of various organic + water mixt­
ures supports the view of Frank and Evans.

As far as the negative $V^E$ values of the systems studied
are concerned, these can be partly attributed to a break­
down of water structure, i.e. shifting of the equilibrium
in equation (6.2.1) towards the left-hand side. It can be
justified in two ways:

It can be postulated that the solute (organic) mole­
cules are accommodated in the large cavities between water
"clusters" and some of the released monomeric water mole­
cules involve themselves in hydrogen bonding. With further
addition of the solute the stabilization of the water
structure soon reaches a saturation state where no more
solute can be accommodated in the cavities, but where water-alcohol hydrogen bonding may become significant thus causing a reduction in the total volume of the system.

Another explanation can be based on the interaction between water and the polar group of the non-polar molecules which give rise to water-organic hydrogen bonding and thus formation of dense water structure around the polar part of the molecule. Also packing of small water molecules in relatively large void spaces between the organic molecules (as indicated by the large compression values of the organic liquids) can cause a significant reduction in volume.

An increase of temperature increases the kinetic energy of the molecules and the penetration of water molecules into the appropriate cavities becomes increasingly less significant. Thus a decrease in the absolute values of negative excess volumes results as a consequence of rise in temperature.

An explanation of the decrease in the values of negative $V^E$, with an increase of pressure, can be related to the effect of pressure on the structure of water and the organic molecules. As pressure is increased it causes a breakdown of the tetrahedral structure of water. A pressure increase also causes a more compact molecular placing by the formation of new and denser skeletons in both the liquids. Such a situation will leave less room for penetration of molecules into appropriate cavities thus leading to a decrease in the absolute value of negative $V^E$. 
Both the alcohol + water systems studied during the course of this research show positive deviations from the overall negative volume change on mixing at the water-rich end of the composition, indicating that the non-polar group is solvated by the water molecules and has acted as a structure promotor. This enhanced formation of the bulky-water structure gives rise to the positive volumes of mixing.

The 2-butanol + water system exhibits more pronounced positive volume changes, due to solvation effect, than does the ethanol + water system. This is because the bigger the non-polar group, the more solvation effect it will have\(^1\) and therefore the more positive would be the volume change. Whether the solvation process involves only Van der Waals' forces between the non-polar group and the water molecules or whether it involves water-water hydrogen bonding, increase of temperature would decrease the solvation effect, i.e. it would shift the equilibrium towards the left-hand side of equation (6.2.1). The decrease observed in the positive deviation of excess volumes with increasing temperature for dilute solutions of the organic component is due to the fact that a temperature increase increases the thermal motion of the molecules. This effects both Van der Waals' forces and hydrogen bonding in a negative way as both bond lengthening and bond breaking are endothermic processes.

From the consideration of atmospheric pressure excess volumes (calculable from literature density data) of various
aqueous alcoholic mixtures, it can be postulated that the more compact alkyl groups give a greater reduction in volume on mixing with water than do their more extended isomers. The reason may be that a more compact alkyl group fits more readily into the interstices, present in the structure of water, than does the more extended group.

6.3 Conclusions

a) It is clear that the P,V,T behaviour of the systems studied here is by no means simple. Until understanding of the structural behaviour of aqueous solutions of non-electrolytes is more complete it is futile to attempt to advance "explanations" of P,V,T behaviour.

b) The tendency of $V^E$ towards positive values for the system 2-butanol + water at higher pressures is not so great as to lead one to expect large positive values which would suggest the possibility of high values of $G^E$ leading to phase separation as is the case with 3-methylpyridine + water.

c) What this thesis offers is, primarily, a set of experimental measurements which have been shown to be consistent, in so far as tests can be carried out, both among themselves and when compared with other available information.

d) This primary achievement depended upon the development of an accurate and reliable high pressure mixing dilatometer.
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APPENDIX 1

LIST OF COMPUTER PROGRAMMES
1 REM-CALCULATES EXCESS VOLUMES OF MIXING FROM DENSITY & COMPOSITION
2 REM
3 REM
5 DIM X1(90),X2(90),W1(90),W2(90),D(91),VO(91),V(91),W3(90),W4(90),W5(90),V1(91)
6 PRINT "GIVE INPUT FILE NAME"
7 INPUT A:
8 PRINT "GIVE OUTPUT FILE NAME"
9 INPUT B:
10 DEFINE FILE #1=A:
11 DEFINE FILE #2=B:
15 WS='---###-###' '---###-###'
20 READ * #1,X1(0),X2(0),W1(0),W2(0),D(0),VO(0),V(0),W3(0),W4(0),W5(0),V1(0)

21 XI(0)=1
22 X2(0)=0
23 W1(0)=1
24 W2(0)=0
25 X1(N+1)=0
26 X2(N+1)=1
27 W1(N+1)=0
28 W2(N+1)=1
30 VO(0)=M1/D1
40 VO(N+1)=M2/D2
41 D(C)=D1
42 D(N+1)=D2
50 FOR I=1 TO N
51 READ * #1,W3(I),W4(I),W5(I),D(I)
60 W1(I)=(W5(I)-W4(I))/(W5(I)-W3(I))
70 W2(I)=1-W1(I)
80 NEXT I
100 FOR I=0 TO N+1
110 XI(I)=W1(I)/(W1(I)+W2(I)*M1/M2)
120 X2(I)=1-X1(I)
130 VO(I)=X1(I)*VO(0)+X2(I)*VO(N+1)
140 V(I)=1/(W1(I)/M1+W2(I)/M2)/D(I)
150 W1(I)=V(I)-VO(I)
160 NEXT I
181 PRINT"EXCESS VOLUMES OF 2-BUTANOL-WATER MIXTURES AT"
183 PRINT "AT ";T;"C AND ";P;"BARS ABS."
184 PRINT "FROM ";CS;"(DATE)"
185 PRINT
186 PRINT
189 PRINT" W X V(ID) V(ACJ) V(EXCESS)"
200 PRINT
210 FOR I=0 TO N+1
220 PRINT USING WS, W1(I):
221 PRINT TAB(10):
222 PRINT USING WS, X1(I):
223 PRINT TAB(20):
224 PRINT USING WS, VO(I):
225 PRINT TAB(30):
226 PRINT USING WS, V(I):
227 PRINT TAB(40):
228 PRINT USING WS, V1(I)
229 WRITE #2, T,P,W1(I),X1(I),VO(I),V(I),V1(I),CS
230 NEXT I
700 STOP
C FRCG * * * * * * * 7 0  C A L C U L A T E  EX. VOLS. AT H IG H  P R E S U R E S * * * * * *

C

C REAL TITLE(8), PRESS(25), DEL(25), K(25), DELCAL(25), X(9), P, SIDE, ACC
1 , DELU(25), DELM(25), M BUT, KH2O, M1, M2, TEMP, KCLFRN, H, W(25)
2 , DELMIX, MOL, KA
INTEGER NDATA, N, IR, IW
DATA M1, M2 / 74.12, 18.016 /, KA / .07504 /
IR = 5
IW = 6
C
C READ DATA
C
30 READ(IR, 101, END = 9999)(TITLE(I), I = 1, 8)
101 FORMAT (BA4)
   READ(IR, *) TEMP, M BUT, KH2O
   READ(IR, *) NDATA
   DO 200 I = 1, NDATA
      READ(IR, *) PRESS(I), DELU(I), DELM(I)
   200 CONTINUE
   READ(IR, *) DELMIX
   MOL = MBUT / (M1 + KH2O / M2)
   DO 300 I = 1, NDATA
      K(I) = KA * (1.0 + (TEMP - 22.5) * 32.0E-6 + PRESS(I) * 10.04E-6)
      DELM(I) = DELMIX(I) + DELMIX
      DEL(I) = DELU(I) - DELM(I)
      DELCAL(I) = DEL(I) * K(I) / (10 * MOL)
   300 CONTINUE
C
C MOLFRN = MBUT / (MBUT + M1 / K2 * KH2O)
C WRITE(IW, 101) TITLE
C WRITE(IW, 501) TEMP, MOLFRN
501 FORMAT(// 'TEMP = ', F6.2, 6X, 'MOL FRN. COMPT. 1 = ', F8.5, //)
C WRITE(IW, 503)
503 FORMAT(// 'PRESS DELTA L UNM. DELTA L MIX. DL MIXING 1', 'VOL. OF MIXING (CC/MOL)',//)
   DO 600 I = 1, NDATA
      WRITE(IW, 601) PRESS(I), DELU(I), DELM(I), DEL(I), DELCAL(I)
   600 CONTINUE
601 FORMAT (6E14.6)
9999 STOP
END
100 REM CALCS COMPRESSION OF RUBBER PISTON WITH HG
110 DIM L(20), V1(20), V2(20), V3(20)
120 T=30
130 M1=176.345
140 M2=0.0678
150 DEFINE FILE \"I\"='HG.DAT'
160 L(0)=0
170 FOR I=0 TO 16
180 IF I=0 GOTO 200
190 READ I,R,L(I)
200 P1=2000*I
210 P=0.068946*P1
220 CCUSUB2000
230 V1(I)=M1/D
240 V2(I)=0.075705*(1+1.6E-6*(T-22.5)+2*5.02E-8*P1)*L(I)/10
250 V3(I)=V1(0)*(1+1.6E-6*P1)-V2(I)-V1(I)
260 PRINT P1,V1(I),V2(I),V3(I)
270 NEXT I
999 STOP
2000 REM SUBROUTINE TO CALC DENSITY OF HG AS A FUNCTION
2010 REM OF TEMP AND PRESS FROM DATA OF GRINDLEY, T &
2020 LIND, J.E., J. CHEM. PHYS 54(1971)3983.
2030 A=(-2.12921E-3*T+.1450404)*T+.378265E3
2040 B=(5.464785E-2*T+.684101)*T-.277069E5
2050 C=(-.3624357*T-.58.65276)*T+.421727F5-P
2060 D=(SQR(B*B-4*A*C)-B)/(A+A)
2070 RETURN
100 REM CALCULATE VOLUMES AND COMPRESSIONS OF A FLUID OVER HG
101 REM IN A STEEL DILATOMETER WITH SILICONE RUBBER SEAL
110 DIM L(20),V1(20),V2(20),V3(20),V4(20)
120 INPUT 'DATAFILE',AS
130 DEFINE FILE #1=AS
140 READ #1,AS
150 READ / /1,T
160 READ h,R3
165 READ 3 '1,M2,M1,M7
170 L(0)=0
171 PRINT LIN(3);'*** ';AS;' ***',LIN(2)
172 PRINT 'PRES/Psi SPECIFIC VOLUME/Cm G-1 DELTA V/VC'
173 PRINT
180 FOR I=0 TO 16
185 IF I=0 GOTO 195
190 READ i!,L(I)
195 READ V2(I)
197 V2(I)=V2(I)*M2
198 REM V2 NOW VOLUME CHANGE OF RUBBER PISTON
200 P1=2000*1
210 P=0.068946*P1
220 GOSUB2000
230 V1(I)=M1/D
231 REM V1 NOW ACTUAL VOLUME OF MERCURY
240 V3(I)=0.075705*(1+2*16E-6*(T-22.5)+2*5.02E-8*P1)*L(I)/10
241 REM V3 VOLUME CHANGE REGISTERED BY DISPLACEMENT OF PISTON
242 IF I<I0 GOTO 250
243 V0=V1(O)+M3/R3
250 V4(I)=V0*(1+.1E-6*P1)-V3(I)+V2(I)-V1(I)
255 GOTO 265
260 PRINT V1(I),V2(I),V3(I),V4(I)
262 GOTO 270
265 PRINT P1,V4(I)/M3,(V4(O)-V4(I))/V4(O)
270 NEXT I
280 REM CHANGE IN VOLUME OF 1 GRM OF RUBBER AT VARIOUS PRESSURES AND 30C
290 REM AT 2000 PSI INTERVALS
300 REM 30C DATA 0,.017,.052,.048,.063,.079,.092,.102,.109,.114,.121,.124,.133
310 REM 30C DATA .140,.144,.149,.152
320 DATA 0,.018,.032,.044,.057,.067,.078,.089,.097,.105,.112,.117,.123
330 DATA .130,.133,.137,.142
340 REM 50 AND 55C DATA 0,.017,.032,.045,.056,.066,.075,.082,.089,.096,.100,.105
350 REM DATA .109,.115,.119,.123,.128
390 STOP
399 REM SUBROUTINE TO CALC DENSITY OF HG AS A FUNCTION
400 REM OF TEMP AND PRESS FROM DATA OF GRINDLEY,T &
400 REM LIND, J.E., J. CHEM. PHYS 54(1971)3993.
400 REM A=(-2.129211E-2*T+.1450404)*T+5.378285E3
404 REM B=(5.464785E-2*T+5.684101)*T-1.277089E5
405 REM C=(-3624357*T-58.65276)*T+7.421727E5-P
406 REM D=(SQR(B*B-4*A*C)-B)/(A+A)
407 RETURN
Table 1.1 Excess volumes of 2-butanol (1) + water (2) (at 1 bar) of some workers

<table>
<thead>
<tr>
<th>Boeke &amp; Hanewald(^{69})</th>
<th>Altsybeeva(^{66})</th>
<th>Friedman &amp; Scheraga(^{64})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_1)</td>
<td>(V^E/\text{cm}^3\text{mol}^{-1})</td>
<td>(x_1)</td>
</tr>
<tr>
<td>.0040</td>
<td>-.0273</td>
<td>.003</td>
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<tr>
<td>.0081</td>
<td>-.0537</td>
<td>.005</td>
</tr>
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<td>.010</td>
</tr>
<tr>
<td>.0214</td>
<td>-.1586</td>
<td>.015</td>
</tr>
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<td>-.1947</td>
<td>.020</td>
</tr>
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<td>.0310</td>
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<td>.038</td>
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<td>.600</td>
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<td>.800</td>
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<td>.900</td>
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<tr>
<td>.8251</td>
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</table>
Table 1.2 Excess Volumes of MEK(1) + Water(2) at 30°C and at pressures up to 1724 bar

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>( w_1 = 0.5 )</th>
<th>( w_1 = 0.10 )</th>
<th>( w_1 = 0.15 )</th>
<th>( w_1 = 0.91 )</th>
<th>( w_1 = 0.94 )</th>
<th>( w_1 = 0.97 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.104</td>
<td>-0.227</td>
<td>-0.364</td>
<td>-0.609</td>
<td>-0.427</td>
<td>-0.294</td>
</tr>
<tr>
<td>345</td>
<td>-0.076</td>
<td>-0.190</td>
<td>-0.274</td>
<td>0.135</td>
<td>0.187</td>
<td>0.415</td>
</tr>
<tr>
<td>689</td>
<td>-0.028</td>
<td>-0.100</td>
<td>-0.206</td>
<td>0.442</td>
<td>0.611</td>
<td>0.730</td>
</tr>
<tr>
<td>1034</td>
<td>-0.004</td>
<td>-0.118</td>
<td>-0.223</td>
<td>0.031</td>
<td>0.866</td>
<td>0.092</td>
</tr>
<tr>
<td>1379</td>
<td>0.047</td>
<td>-0.031</td>
<td>-0.077</td>
<td>0.549</td>
<td>0.663</td>
<td>0.637</td>
</tr>
<tr>
<td>1724</td>
<td>0.159</td>
<td>0.046</td>
<td>0.045</td>
<td>0.635</td>
<td>0.750</td>
<td>0.562</td>
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</table>
Table 2.1 Calibration of the displacement transducer

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<th>Range II</th>
<th>Range III</th>
</tr>
</thead>
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<td>Core displacement (mm)</td>
<td>Output (mV)</td>
<td>Core displacement (mm)</td>
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<tr>
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<td>121.0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>137.9</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>154.8</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>171.7</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>188.6</td>
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<tr>
<td>5</td>
<td>205.4</td>
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<tr>
<td>6</td>
<td>222.2</td>
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<td>238.9</td>
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<td>288.6</td>
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<td>337.0</td>
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<td>352.4</td>
<td>14</td>
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<td>367.1</td>
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<td>16</td>
<td>381.6</td>
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<td>409.3</td>
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<tr>
<td>19</td>
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<td>20</td>
<td>435.3</td>
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<td>447.6</td>
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<td>515.1</td>
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<td>34</td>
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</table>
Table 3.1 Densities of 2-butanol at various temperatures and at 1 bar

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Density g cm⁻³</th>
<th>Temperature °C</th>
<th>Density g cm⁻³</th>
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</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.81868</td>
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</tr>
<tr>
<td>10.0</td>
<td>0.81476</td>
<td>50.0</td>
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<tr>
<td>15.0</td>
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<td>20.0</td>
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<tr>
<td></td>
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</table>
Table 3.2 Densities and excess volumes of 2-butanol (1) + water (2) at various temperatures and 1 bar

<table>
<thead>
<tr>
<th>$w_1$</th>
<th>$x_1$</th>
<th>$\rho$/g cm$^{-3}$</th>
<th>$\gamma^E$/cm$^3$mol$^{-1}$</th>
<th>$w_1$</th>
<th>$x_1$</th>
<th>$\rho$/g cm$^{-3}$</th>
<th>$\gamma^E$/cm$^3$mol$^{-1}$</th>
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<tbody>
<tr>
<td><strong>5°C</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
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</tr>
<tr>
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<td>.9196</td>
<td>.7355</td>
<td>.83590</td>
<td>-.4363</td>
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<tr>
<td><strong>10°C</strong></td>
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<td></td>
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| 276                                           | -.8112 | -.6808 | -.4723 |
| 414                                           | -.7315 | -.6029 | -.4065 |
| 552                                           | -.6756 | -.5492 | -.3606 |
| 689                                           | -.6318 | -.4925 | -.3318 |
| 827                                           | -.5817 | -.4550 | -.3079 |
| 965                                           | -.5429 | -.4301 | -.2904 |
| 1103                                          | -.5107 | -.4099 | -.2774 |
| 1241                                          | -.4815 | -.3877 | -.2647 |
| 1379                                          | -.4479 | -.3654 | -.2527 |
| 1517                                          | -.4295 | -.3510 | -.2406 |
| 1655                                          | -.4024 | -.3338 | -.2334 |
| 1793                                          | -.3869 | -.3196 | -.2269 |
| 1931                                          | -.3748 | -.3047 | -.2200 |
| 2068                                          | -.3560 | -.2967 | -.2000 |
| 2206                                          | -.3404 | -.2874 | -.1956 |</p>
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Table 3.3 continued (butanone + water)

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| MASS FRAC | 0.149 | 0.232 | 0.412 | 0.075 | 0.062 | 0.136 | 0.151 |
| COOL FRAC | 0.054 | 0.080 | 0.150 | 0.200 | 0.279 | 0.367 | 0.423 |

**Note:** The table continues with similar entries for different pressures, mass fractions, and cool fractions.
TABLE 3.4 PURE LIQUIDS' VOLUMETRIC DATA

a) 2-Butanol at 25°C \( (m_b = 2.3849, m_m = 87.3556\, g, m_{rub} = 0.0718\, g) \)

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<th>( \Delta \ell_{\text{corr}} ) (mm)</th>
<th>( \frac{(v_0 - v)}{v_0} ) \text{ exp}</th>
<th>( \frac{(v_0 - v)}{v_0} ) \text{ Tait}</th>
<th>( \frac{(v_0 - v)}{v_0} ) \text{ Hud.}</th>
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* \( m_b \) = mass of butanol, \( m_m \) = mass of mercury, \( m_{rub} \) = mass of rubber piston
Table 3.4 continued

b) 2-Butanol at 55°C ($m_b = 2.3849 \text{ g}$, $m_m = 87.3556 \text{ g}$, $m_{rub} = .0718 \text{ g}$)

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* $m_b =$ mass of butanol, $m_m =$ mass of mercury, $m_{rub} =$ mass of rubber piston
Table 3.4 continued

c) Butanone at 30°C ($m_k = 2.3627$ g, $m_m = 90.1124$ g, $m_{rub} = .0725$ g.)*

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<th>$\Delta \ell_{\text{corr}}$ (mm)</th>
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* $m_k$ = mass of butanone, $m_m$ = mass of mercury, $m_{rub}$ = mass of rubber piston
Table 3.4 continued

d) Ethanol at 25°C ($m_e = 2.3564$, $m_m = 88.8562$ g, $m_{rub} = 0.690$ g) *

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* $m_e$ = mass of ethanol, $m_m$ = mass of mercury, $m_{rub}$ = mass of rubber piston
Table 3.4 continued

e) Ethanol at 50°C (m_e = 2.3564 g, m_m = 88.8562 g, m_rub = .0690 g)*

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<th>[(v_o - v)/v_o]_{\text{Tuit}}</th>
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* m_e = mass of ethanol, m_m = mass of mercury, m_rub = mass of rubber piston
Table 3.4 continued

f) Water at 25°C (m_w = 2.9986 g, m_m = 89.8316 g, m_rub = .0748 g)*

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<th>[(v_o - v)/v_o]_{Tait}</th>
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* m_w = mass of water, m_m = mass of mercury, m_rub = mass of rubber piston
Table 3.4 continued

g) Water at 30°C ($m_w = 2.9986$ g, $m_m = 89.8316$ g, $m_{rub} = .0748$ g)*

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<th>$\Delta \ell_{\text{corr}}$ (mm)</th>
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* $m_w$ = mass of water, $m_m$ = mass of mercury, $m_{rub}$ = mass of rubber piston
Table 3.4 continued

h) Water at 50°C \((m_w = 2.9986 \text{ g}, m_m = 89.8316 \text{ g}, m_{rub} = .0748 \text{ g})\)

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<th>(\Delta l_{\text{corr}} ) (mm)</th>
<th>([ (v_o - v)/v_o ]_{\text{exp}} )</th>
<th>([ (v_o - v)/v_o ]_{\text{Tait}} )</th>
<th>([ (v_o - v)/v_o ]_{\text{Hud.}} )</th>
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* \(m_w = \text{mass of water}, m_m = \text{mass of mercury}, m_{rub} = \text{mass of rubber piston} \)
Table 3.4 continued

i) Water at 55°C ($m_w = 2.9986$ g, $m_m = 89.8316$ g, $m_{rub} = .0748$ g)

<table>
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<th>Pressure (bar)</th>
<th>$\Delta \ell$ $\text{exp}$ (mm)</th>
<th>$\Delta \ell$ $\text{corr}$ (mm)</th>
<th>$[(v_o - v)/v_o]_{\text{exp}}$</th>
<th>$[(v_o - v)/v_o]_{\text{Tait}}$</th>
<th>$[(v_o - v)/v_o]_{\text{Hud.}}$</th>
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* $m_w$ = mass of water, $m_m$ = mass of mercury, $m_{rub}$ = mass of rubber piston
APPENDIX 3

ESTIMATION OF DEMIXING CURVE OF A BINARY SYSTEM USING THE DILATOMETER
APPENDIX 3

Estimation of Demixing Curve of Partially Miscible Liquids
by Piston Displacement Method

As described in section 4.2.4, in order to determine experimentally $V^E$ of a binary liquid mixture (at constant $T$ and $x$) the two pure liquids were first compressed under various conditions of pressure. Mixing was then carried out and the mixture was compressed to the same pressures as before.

The mixture was then stepwise depressurised and the change in piston displacement was noted. It was found that the piston displacement gradually increased with each 138 bar decrease of pressure until there came a point where any further drop in the pressure caused a greatly increased change in the piston displacement as is evident from Figure 1. This sudden increase in the volume of the mixture, it is thought, was caused by demixing of the two liquids at that temperature pressure and composition. Thus a rough idea about the demixing envelope of MEK + water was formed at 30°C (cf. Figure 2). The values are not too different from those obtained by Hunt\textsuperscript{70}.

A better estimate of pressure dependence of miscibility loop of any partially miscible binary system may be made by reducing the pressure in smaller steps. The dilatometer used for high pressure $V^E$ and compression measurements can thus be used for a rough estimation of the demixing envelope as well.
FIG. 1 PISTON DISPLACEMENT vs PRESSURE
FIG. 2  ESTIMATED MISCIBILITY LOOP OF MEK+WATER AT 30 C
A similar approach has been used\textsuperscript{70} in the past by Steiner and Schadow, who used their dielectric constant measurements to estimate MEK + water demixing curve. The results thus obtained could only be considered approximate.