THE BEHAVIOUR OF THE PARTIALLY
MISCIBLE LIQUID-LIQUID SYSTEM
METHYL ETHYL KETONE/WATER
AT ELEVATED PRESSURES

A THESIS
PRESENTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

A. F. HUNT
1977
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>viii</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>xiii</td>
</tr>
</tbody>
</table>

## CHAPTER 1  A brief review of the relevant previous work on the study of partially miscible liquid systems

1.1 Equilibrium Data

1.1.1 At atmospheric pressure  
1.1.2 At high pressure  
1.1.3 The methyl ethyl ketone/water system at atmospheric pressure  
1.1.4 The methyl ethyl ketone/water system at high pressure

1.2 Compressibility Data

1.2.1 Historical introduction  
1.2.2 A brief review of the practical aspects of previous work  
1.2.3 Available equations of state for liquid compressibilities  
   a) Tait equation  
   b) Huddleston equation  
   c) MacDonald's review  
   d) Hayward's review  
1.2.4 Previous experimental work  
   a) Pure liquids  
   b) Liquid mixtures

## CHAPTER 2  A review of the available equations for the prediction of phase equilibrium data and the circumstances under which they can be applied

2.1 The Thermodynamics of Phase Equilibria

2.1.1 The phase equilibrium problem
2.1.2 The Gibbs-Duhem equation
2.1.3 The ideal solution
2.1.4 The activity
2.1.5 The activity coefficient
2.1.6 The Gibbs free energy
2.1.7 Excess functions

### 2.2 Expressions for the Excess Free Energy in Terms of Composition

#### 2.2.1 Two parameter semi-empirical equations
a) the Wohl equation
b) the van Laar equation
c) the Margules equation
d) Scatchard Hamer equation

#### 2.2.2 Other semi-empirical equations
a) Black's equation
b) Redlich-Kister equation

#### 2.2.3 Comparison of the equations resulting from the Wohl equation

#### 2.2.4 Suitability of the semi-empirical equations for representing the Methyl-Ethyl-Ketone/water system

#### 2.2.5 Quasi-chemical equations
a) Flory-Huggins equation
b) Wilson equation
c) the Segment interaction equation
d) the non-random two liquid equation
e) the Orye equation

### 3.1 The High Pressure System

#### 3.1.1 The pressure generator
#### 3.1.2 The pressure vessel
#### 3.1.3 Piping
a) general
b) sealing of capillary tubing
3.2 The Constant Temperature Bath

3.2.1 Description

3.2.2 Heating and control system

3.3 Sample Holders

3.3.1 Equilibrium data sample holder
   a) description
   b) description of the sampling system

3.3.2 Compressibility data sample holder
   a) the vessel
   b) the linear displacement transducer
   c) transducer power supply and reference circuit
   d) pressure and temperature effects on the accuracy of the measurements

3.4 The Gas Chromatograph

3.4.1 General

3.4.2 The column

3.4.3 Calibration

CHAPTER 4 Experimental technique

4.1 Specific Gravity Measurements

4.1.1 Apparatus

4.1.2 Experimental method
   a) preparation of apparatus
   b) water calibration of pyknometers
   c) temperature equilibrium and level adjustment
   d) drying and weighing
   e) preparation of solutions
   f) determination of the specific gravity of the solutions

4.2 Determination of the Liquid-Liquid Equilibrium Data

4.2.1 Preparation of the apparatus
   a) filling of sample holder
   b) assembly of the apparatus
4.2.2 Experimental method
   a) attainment of equilibrium
   b) measurements at atmospheric pressure
   c) method of sample removal

4.3 Determination of Compressibility Data

4.3.1 Preliminary measurements
   a) vessel volume
   b) calibration of transducer
   c) zeroing transducer

4.3.2 Apparatus-general assembly

4.3.3 Experimental method
   a) filling and assembly of sample holder
   b) attainment of thermal equilibrium
   c) the measurement of compressibility

4.4 Investigation of Individual Systems

4.4.1 Compressibility of water

4.4.2 Compressibility of methyl ethyl ketone

4.4.3 Compressibility of methyl ethyl ketone/water mixtures

CHAPTER 5 Treatment of results.

5.1 Specific Gravity Measurements

5.1.1 Calculation of the specific gravity and density of the mixtures

5.1.2 Calculation of the volume change on mixing

5.1.3 Comparison with other workers

5.2 Equilibrium Data Measurements

5.2.1 Measurements at atmospheric pressure
   a) testing technique
   b) determination of empirical constants
   c) temperature dependence of the constants
   d) prediction of tie line data
   e) dependence of constants on composition
5.2.2 Determination of constants at high pressure

5.3 Compressibility Measurements

5.3.1 Expression of compressibility

5.3.2 Expression of compressibility in terms of pressure

5.3.3 Determination of the coefficient of isothermal compressibility

5.3.4 Calculation of the volume change on mixing at high pressure

5.3.5 Correction of the results for the inherent inaccuracy in the method

5.3.6 The use of volumetric measurements to show phase splitting

CHAPTER 6 Discussion of results.

6.1 Equilibrium Data

6.1.1 Atmospheric pressure results
a) comparison with other data
b) back-calculation of experimentally obtained data

6.1.2 Results obtained at high pressure
a) comparison with other results
b) demixing loops
c) derived empirical constants

6.2 Volumetric Data

6.2.1 Volume changes on mixing at atmospheric pressure
a) comparison with other data
b) the sign of \( vE \)
c) data obtained at atmospheric pressure

6.2.2 Accuracy and presentation of compressibility data
a) accuracy of the method
b) correlation of data

6.2.3 Volumetric changes on mixing at high pressure
a) general observations from the data
b) empirical expressions for vE
   i) Redlich-Kister equation
   ii) van Laar equation
   iii) Black's equation
   iv) Margules equation
c) local composition equations

CHAPTER 7 Conclusions.

BIBLIOGRAPHY

APPENDIX I Flushing of a two way valve.

APPENDIX II Flushing of a capillary tube.

APPENDIX III Accuracy of the excess volume.

APPENDIX IV Presentation of the compressibility data - choice of polynomial order

APPENDIX V Table of results.
APPENDIX V

Table of Results

5-1 Specific gravity and density of MEK/H₂O mixtures. 182
5-2 Specific gravity and density of MEK/H₂O mixtures at 21.5°C. 183
5-3 Volumetric data of MEK/H₂O mixtures at 21.5°C. 183
5-4 MEK/H₂O liquid-liquid equilibrium data at atmospheric pressure. 184
5-5 The constants at atmospheric pressure for the van Laar, NRTL, Heil and Orye equations obtained from the data of various workers. 185
5-6 Coefficients for the polynomials to represent the van Laar, NRTL, Heil and Orye constants at various temperatures and 1 atm. 188
5-7 The van Laar, NRTL, Heil and Orye constants at various pressures and temperatures up to 100°C. 189
5-8 Coefficients for the polynomials to represent the Orye constants at various pressures and at fixed temperatures. 191
5-9 Compressibility of MEK, H₂O and their mixtures at 30°C. 192
5-10 Compressibility of MEK, H₂O and their mixtures at 50°C. 193
5-11 Compressibility of MEK, H₂O and their mixtures at 70°C. 194
5-12 Coefficients of the compressibility polynomial for MEK, H₂O and their mixtures at 30, 50 and 70°C. 195
5-13 Isothermal compressibility of MEK, H₂O and their mixtures at different pressures and at 30, 50 and 70°C. 196
5-14 Volume changes on mixing for MEK/H₂O mixtures at pressures up to 25000 psi and at 30°C. 197
5-15 Volume changes on mixing for MEK/H₂O mixtures at pressures up to 25000 psi and at 50°C. 198
5-16 Volume changes on mixing for MEK/H₂O mixtures at pressures up to 25000 psi and at 70°C. 199
ACKNOWLEDGEMENT

My most sincere thanks must first go to Dr. J.A. Lamb, whose constant guidance, help and encouragement have been invaluable throughout the course of this work; Professor S.R. Tailby, for allowing the facilities for carrying out this work; and the Science Research Council for financing the project.

I am also very grateful to Mr. Pat O'Sullivan and his technicians for applying their special skills to overcome the practical problems involved, and the University of Surrey Computing Unit for their help in the analysis of the results obtained.

Finally, I must thank my friends and colleagues for their frequent advice and practical help.
SUMMARY

Equilibrium compositions of conjugate liquid phases in the system methyl ethyl ketone (MEK) - water (H₂O) have been measured over a range of temperatures from 25°C to 100°C and at pressures up to 17,500 psi extending considerably the range of conditions previously investigated. This method of investigation, which relies on the analysis of equilibrium phases, gives results which are not entirely consistent with the previous methods used. These earlier methods involve the location of the boundary of the two phase envelope in the pressure - temperature - composition (P-T-x) space by detecting some discontinuity in \( \frac{\partial Z}{\partial p} \) or \( \frac{\partial Z}{\partial T} \) or \( \frac{\partial Z}{\partial T} \) where Z is the measured property.

The densities of a range of methyl ethyl ketone water mixtures which are homogeneous at atmospheric pressure have been determined and their compressibilities measured at three temperatures and pressures up to 30,000 psi.

The applicability of a number of simple solutions of the Gibbs-Duhem equation to the observed behaviour of this binary system has been examined but none was found to describe the system's equilibrium and volumetric behavior adequately.
<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAPTER 1</td>
</tr>
<tr>
<td>1-1 The MEK/H2O system - equilibrium data of various workers</td>
</tr>
<tr>
<td>CHAPTER 3</td>
</tr>
<tr>
<td>3-1 Method of sealing the capillary into the high pressure nipple</td>
</tr>
<tr>
<td>3-2 Temperature bath heating and control circuits</td>
</tr>
<tr>
<td>3-3 Detail of the assembly of the equilibrium cell</td>
</tr>
<tr>
<td>3-4a Exploded view of the equilibrium cell</td>
</tr>
<tr>
<td>3-4b Exploded view of the compressibility cell</td>
</tr>
<tr>
<td>3-5 General arrangement of the equilibrium cell and valves</td>
</tr>
<tr>
<td>3-6 Schematic arrangement of the sampling valve system</td>
</tr>
<tr>
<td>3-7 Detail of the assembly of the compressibility cell</td>
</tr>
<tr>
<td>3-8 Circuit diagram of the transducer power supply</td>
</tr>
<tr>
<td>3-9 Circuit diagram of the transducer reference circuit</td>
</tr>
<tr>
<td>3-10 An actual chromatogram: water/acetone/MEK system</td>
</tr>
<tr>
<td>CHAPTER 4</td>
</tr>
<tr>
<td>4-1 Sprengel pyknometer</td>
</tr>
<tr>
<td>4-2 Micrometer used for the calibration of the transducer</td>
</tr>
<tr>
<td>4-3 A typical transducer calibration curve</td>
</tr>
<tr>
<td>4-4 Arrangement of the compressibility cell before insertion into the pressure vessel</td>
</tr>
</tbody>
</table>
CHAPTER 5

5-1 Comparison of the volume change on mixing data obtained at 21.5°C with that of other workers 100

5-2 Liquid-liquid equilibrium data for the MEK/Water system at 1 atm 103

5-3 The van Laar constants vs. temperature at 1 atm 105

5-4 The NRTL constants vs. temperature at 1 atm (α=0.3) 106

5-5 The Heil constants vs. temperature at 1 atm 107

5-6 The Orye constants vs. temperature at 1 atm 108

5-7 Method of prediction of the line data 109

5-8 Variation in liquid composition with pressure for the MEK/water system 110

5-9 Variation of the Orye constants with pressure at various temperatures 111

5-10 Tie line data interpolated by the Orye equation at 1 atm 112

5-11 V/V₀ vs. pressure for MEK/water mixtures at 30°C 118

5-12 V/V₀ vs. pressure for MEK/water mixtures at 50°C 119

5-13 V/V₀ vs. pressure for MEK/water mixtures at 70°C 120

5-14 The coefficient of isothermal compressibility for MEK/water mixtures at 30°C 123

5-15 The coefficient of isothermal compressibility for MEK/water mixtures at 50°C 124

5-16 The coefficient of isothermal compressibility for MEK/water mixtures at 70°C 125
<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-17</td>
</tr>
<tr>
<td>5-18</td>
</tr>
<tr>
<td>5-19</td>
</tr>
<tr>
<td>5-20</td>
</tr>
<tr>
<td>CHAPTER 6</td>
</tr>
<tr>
<td>6-1</td>
</tr>
</tbody>
</table>
**NOMENCLATURE**

\[ f \] \quad \text{fugacity}

\[ g \] \quad \text{molar Gibbs free energy}

\[ g^E_i \] \quad \text{molar Gibbs excess free energy of component } i

\( (g_{ij} - g_{ii}) \) \quad \text{empirical energy term}

\[ h_i \] \quad \text{enthalpy of pure } i \text{ in ideal gas state}

\[ \bar{h}_i \] \quad \text{partial molar enthalpy of component } i

\[ h_{\text{pure } i} \] \quad \text{enthalpy of pure liquid } i

\[ i \] \quad \text{component}

\[ j \] \quad \text{component}

\[ m \] \quad \frac{v_2}{v_1} \text{ the ratio of molar volumes of the polymer and the solvent}

\[ n_i \] \quad \text{number of moles of component } i

\[ s \] \quad \text{molar entropy}

\[ v^E \] \quad \text{molar excess volume change on mixing}

\[ \bar{v}_i \] \quad \text{partial molar volume of component } i

\[ v_{\text{pure } i} \] \quad \text{molar volume of pure } i

\[ x_i \] \quad \text{mole fraction of component } i

\[ x^1_i \] \quad \text{mole fraction of component } i \text{ in the second phase}

\[ A \] \quad \text{constant}

\[ B \] \quad \text{constant}

\[ C \] \quad \text{constant}

\[ D \] \quad \text{constant}

\[ E \] \quad \text{original Tait equation constant}

\[ G \] \quad \text{Gibbs free energy}

\[ H \] \quad \text{enthalpy}

\[ J \] \quad \text{Tait equation constant}
\[ L \quad \text{Tait equation constant} \\
M \quad \text{thermodynamic property} \\
P \quad \text{pressure} \\
S \quad \text{entropy} \\
T \quad \text{absolute temperature} \\
U \quad \text{internal energy} \\
V \quad \text{volume} \\
\beta \quad \text{coefficient of isothermal compressibility} \\
\gamma_i \quad \text{activity coefficient of component } i \\
\varepsilon_{11} \quad \text{local volume fractions} \\
\varepsilon_{12} \quad \text{subscripts referring to the components} \\
\varepsilon_{22} \quad \text{in the locality} \\
\tilde{\kappa} \quad \text{average bulk modulus over pressure range considered} \\
\lambda_{ij} \quad \text{parameter characteristic of the } ij \text{ interaction in the NRTL equation} \\
\pi \quad \text{original Tait equation constant} \\
\mu_i \quad \text{chemical potential of species } i \\
\mu^0_B \quad \text{chemical potential of species } B \text{ and } C \text{ in} \\
\mu^0_C \quad \text{their standard state} \]
CHAPTER 1

A Brief Review of the Relevant Previous Work on the Study of Partially Miscible Liquid Systems
Chapter 1
A brief Review of the Relevant Previous Work - The Study of Partially Miscible Liquid Systems

1.1. Equilibrium Data

1.1.1. At Atmospheric Pressure

The phenomenon of partial miscibility in the liquid phase has been the subject of considerable study which began towards the end of the last century.

The first studies were concerned with the effect of temperature on mutual solubility, Alexejeff (1) being the first to carry out such studies. He used a visual technique to determine the onset of phase separation or complete homogeneity, a technique used by many subsequent workers. Using similar techniques, Rothmund (2), soon after, studied thirteen partially binary systems, one of which was MEK/H₂O. Since then the liquid-liquid equilibrium data of many partially miscible systems have been obtained. Francis (3) lists over 5000 partially miscible systems, 1100 being non-hydrocarbon mixtures with 2000 exhibiting lower critical solution temperature. This critical solution temperature is less common than an upper critical solution temperature. Many systems show signs of forming a lower consolute point, but the two phases freeze before the point is reached.

1.1.2. At High Pressure

In 1899 Kuenen (4) became perhaps the first to study the effect of external pressures on partially miscible liquid systems. While studying the vapour-liquid equilibrium in three binary systems which are formed when ether is mixed with either ethanol, n-propanol, or n-butanol, he observed the appearance of two liquid phases near the
critical temperature of pure ethane. He determined the pressure-dependence of the lower critical solution temperature at constant composition $\frac{\partial T_c}{\partial P}$ for these systems and also for methanol-propane, methanol-isopentane and methanol-ethane.

The next important contributor was Timmermans who began his study of liquid mixtures at high pressures in 1911. By 1923, when he published a summary of this aspect of his work (5) he had studied sixty-five liquid systems in the pressure range 0-1000 Kg/cm$^2$ and had classified them into five different categories.

Similar work was done by Poppe (6) who obtained $\frac{\partial T_c}{\partial P}$ for twenty-nine partially miscible liquid systems using pressures up to 100 atm.

The last two workers were the main contributors to this topic. More recently Hildebrand et al., (7) found $\frac{\partial T_c}{\partial P}$ for two binary liquid systems, one component of each being a fluorocarbon, and also found that negative absolute pressure raised the upper critical solution temperature linearly.

Lower critical solution temperatures for simple liquid-liquid systems, e.g. CH$_4$/C$_6$H$_{14}$, were first found by Rowlinson & Davenport (8). Previously only hydrogen bonding systems, e.g. Et$_3$N + H$_2$O, had been found to display this phenomenon. Twenty-four systems were investigated, one component in each being liquid methane. Data have also been provided by Myres (9) who found critical solution temperatures for nine systems during his studies in fluorocarbon chemistry.

Working pressures were raised substantially by Winnick & Powers (10), who, while studying the phase separation of the
acetone-CS$_2$ system (normally completely miscible at atmospheric pressure) used pressures up to 100,000 psi at a temperature of 0°C.

Data such as the above have enabled Schneider (11) to thoroughly review the possible behaviour of liquid mixtures under pressure. While Rowlinson (12), making use of both high pressure vapour liquid equilibrium data and solid, liquid, vapour equilibrium data has classified comprehensively the phase diagrams of liquid mixtures at high pressure.

The workers mentioned so far all used observation of the onset of opalescence to determine phase separation. Recently Kanda (13) has devised a method by which density is dynamically measured as a function of temperature, the onset of immiscibility being indicated by an inflection in the density/temperature curve. Density/composition isotherms were also used to delineate phase boundaries. The dynamic method was found particularly suitable for systems having a domed solubility curve where a small change in temperature produces two widely differing compositions and hence density changes.

Very few attempts have been made to obtain liquid-liquid solubility data by means of a direct sampling method, but it is this technique which is beginning to be used more widely. First to take samples from high pressure systems in order to verify visual observations were Elgin & Wienstock (14). For a total of 26 ternary liquid systems,
each of which separated into two phases, they first observed
the relative proportion of each phase at various pressures.
Their observations were then verified by withdrawing samples
of each layer into cartridges inside the pressure vessel.
The apparatus was then dismantled to obtain the samples
which were then analysed. All readings were taken at 15°C
and the maximum pressure employed was 1000 psi.

Methods have now been devised which enable samples to
be withdrawn from the system by means of valves, and
dismantling of the apparatus is unnecessary. This is an
obvious improvement since data can be obtained far more
quickly. However, the only work done using this method
has been mainly on vapour - liquid equilibrium. For example
Fleck & Prausnitz (15) used a magnetic pump to circulate
both gas and liquid phases for the systems ethylene/n-propyl
alcohol and water/n-propyl alcohol/ethylene. The maximum
pressure employed was 1000 psi. and the samples were
analysed by gas-liquid chromatography. The ternary system
investigated was one of the systems first studied by
Elgin & Wienstock (14) and the results were in reasonable
agreement.

Most recently Rodgers & Prausnitz (16) have investigated
the vapour-liquid equilibrium of the argon-neopentane system,
again withdrawing samples of each phase and analysing by means
of gas-liquid chromatography. In this work the maximum
pressure was raised to 1000 atm. and the temperature was in
the range -50 to 150°C.
Data for this system are available from a total of 13 sources, many sets of data resulting from work in other fields of physical chemistry. As a result only a few of these sets cover the complete temperature range in which the two liquid phases co-exist. In fact some workers only supply the compositions at each end of one tie-line. Data of all workers are shown in Fig. (1-1)

From 1898, when Rothmund (2) first supplied these data, until 1932 when Park & Hoffman (20) used a different approach, only a visual method had been used to provide liquid-liquid equilibrium data for this system. During this period Rothmund (2) and in the same year Bruni (17), investigated this and other binary liquid systems while studying the effect of temperature on partial miscibility. Further data were supplied by Marshall (18) during his investigation of the various possible types of vapour pressure curves. One pair of points was supplied by Jones (19) and another pair by Park & Hoffman (20) during the latter's study of the suitability of aliphatic ketones as solvents.

Interest in the relationship between molecular structure and solubility resulted in a further three pairs of points being supplied by Ginnings, Plonk & Carter (21). While investigating the use of the Fischer method to determine the water content of organics, Berkengetm (22) used the MEK/H2O system as one of his systems, thus providing more data and an indication that this method was unsuitable for the accurate analysis of water in the ketone.
Randall & McKenna (23) worked on the freezing temperatures of the MEK/H₂O system at various compositions. They also provided data for three tie-lines in the liquid-liquid region below 0°C where previously only Rothmund (2) had provided data. Analysis was made using the hydroxylamine method of Marasco (25).

Doing similar work to Ginnings et al (21), Ericksen (26) provided three further points at the same temperatures, and in 1957 Pasquinelli (27) provided four more points during his work on the use of electric and magnetic properties of liquids to predict partial miscibility.

In 1958 Campbell, Kartzmark & Falconer (28) provided the first complete demixing loop since Rothmund & Bruni as part of their work on the ternary system water-nicotine-MEK. Compositions were measured by means of refractive index and densities of the samples, but near the critical point a visual method was used.

Finally, in order to clear up discrepancies in the data that had accumulated up until 1960, Siegelman & Sorum (29) published further data in the temperature range 7.5 - 88°C (omitting the domed portion of the curve). At the lower end of the temperature range they used the method due to Hill (30), and at higher temperatures, a visual method.
FIGURE (1-1) The MEK/H₂O system - equilibrium data of various workers

Timmermans
1  10.00 bars
2  43.55 "
3  78.22 "
4  113.78 "
5  150.00 "

- Temperature °C
- Wt % MEK

Campbell et al 28
Ginnings et al 21
Randall et al 23
Siegleman et al 29
Bruni 17
Marshall 18
Jones 19
Park and Hoffmann 20
Berkengetum 22
Shell Chem Co 5
Rothmund 2

- Campbell et al 28
- Ginnings et al 21
- Randall et al 23
- Siegleman et al 29
- Bruni 17
- Marshall 18
- Jones 19
- Park and Hoffmann 20
- Berkengetum 22
- Shell Chem Co 5
- Rothmund 2
1.1.4. The MEK/H$_2$O system at high pressure

Timmermans (31) published part of the only available data in 1911. These were obtained by observing the upper and lower critical solution temperatures of a mixture of known composition at different pressures. Later followed a more complete set of data giving the upper and lower critical solution temperatures as a function of pressure (5).

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 temperatures. 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 functions of pressure. The critical pressure was estimated to be 1100 bars at a temperature of 80°C.

1.2. Compressibility Data

1.2.1. Historical Introduction

The first experiments at high pressure on liquids concerned themselves with ascertaining whether or not water was compressible. In fact the early experiments during the 18th and 19th centuries were to investigate the volume changes of liquids at different pressures, and in 1898 Amagat (32) produced some of the first reliable compressibilities for a number of liquids including water. A review of the historical development of this work is well discussed in Bridgman's (33) book.
It was Bridgman who did so much to develop the experimental technique required in this type of work, developing apparatus which would measure the compressibility of liquids, and also solids, up to pressures of 1,000,000 psi.

1.2.2. A Brief review of the practical aspects of previous work

Bridgman, during the course of his work, measured the compressibility of many pure liquids (34) and solids (35), and also the change of many physical properties with pressure (36). The liquid compressibilities were measured in a number of different ways at least two of which had not been used before. The piston displacement method involved the sample being contained in a cell into which a very narrow diameter rod would slide through a gland which was as leak-tight as possible. On compression of the sample the free space so formed was taken up by the rod moving in. Since the diameter of the rod was small, the movement of the rod was large. However, the prevention of the leaks around the gland was impossible and the accuracy reduced. The other method was to contain the sample in a vessel such that on compression only one of its characteristic dimensions would alter. For this purpose Bridgman 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 slidewire, 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 & Chadwell (37) who found the compressibility of pure water, an alcohol, ethyl ether, benzene and methyl acetate; and also binary mixtures of these liquids in the pressure range 100 to 300 bar and at a temperature 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 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 (38), during his work on the compressibility of various salt solutions in water, 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 rose up 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 & Loeffler (39) 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 measurements was thus improved since the disadvantage of Adam's 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, (40) 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" diameter and 19" long, sealed at the lower end by mercury. A piece of iron floated on top of the mercury seal. The position of this float could be located by means of 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 (41) measured the compressibility of n-alkanes by using a combination of Bridgman's bellows and 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.

Eduljee, Newitt & Weale (42) 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 step changes in the measured current.
1.2.3. Available Equations of State for Liquid Compressibilities

a) The Tait Equation

The most well known equation, and one that has been the most widely used, is that due to Tait (43). Its most common form is:

\[ \frac{\partial v}{\partial p} \bigg|_T = \frac{J}{L+P} \]  \hspace{1cm} \text{(1.2-1)}

which on integration becomes:

\[ \frac{V}{V_0} = 1 - \frac{J}{V_0} \cdot \ln \left( \frac{L+P}{L+P_0} \right) \]  \hspace{1cm} \text{(1.2-2)}

Although equation (1.2-1) had no original theoretical justification, it was of the form which best fitted the experimental values of the compressibility of sea water measured by Tait on his voyage. Ginnett (44) has produced a theoretical derivation of equation (1.2-2). Its derivation made use of association theory and from the equation for the constants, the volume of holes in a liquid could be calculated.

It was Wohl (45) who first devised a method of evaluating the Tait constants for various liquids, finding that J was independent of temperature. Both Wohl and Carl (46) found that the Tait equation fitted well the compressibility data of water found by Bridgman (47) and Amagat (32). Gibson et al (48) fitted Tait's equation to Adam's (38) water data and the values found for L and J at 25°C when substituted into equation (1.2-2) give:

\[ -\Delta V = 0.3071 \ln(2.923 + P) - 0.1430 \]  \hspace{1cm} \text{(1.2-2a)}
The units of pressure were kilobars.

Apart from water the Tait equation has been used for many pure hydrocarbons and mixtures of hydrocarbons (39) (42) (49). In all cases the value of J kept constant for the class of mixtures being studied.

b) The Hudleston Equation (50)

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

\[ f = a(l-l_0) \exp(l_0-l) \]  \hspace{1cm} (1.2-3)

where:

- \( f \) = force between molecules
- \( l \) = distance between molecular centres
- \( l_0 \) = distance at which molecules have no effect on each other.
- \( a \) = empirical constant

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

\[ \log[v^{2/3}P/(v_o^{1/3}-v^{1/3})] = A + B(v_o^{1/3} - v^{1/3}) \]  \hspace{1cm} (1.2-4)

where:

- \( v_o \) = specific volume at atmospheric pressure
- \( v \) = specific volume at pressure \( P \)
- \( A \) & \( B \) = constants

A plot of the right hand side of equation (1.2-4) versus \( (v_o^{1/3}-v^{1/3}) \) results in a straight line if Hudleston's equation applies.

This procedure was used by Cutler et al. (49) 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 has been done by Doolittle for a number of n-alkanes.
and the temperature dependance of the Hudleston parameters also found.

c) MacDonald's Review

In a review of experimental and theoretical equations of state, MacDonald (51) compared four different polynomial equations and seven non-linear equations (all applicable to solids and liquids) both theoretically and analytically. The equations considered included those of Tait, Murnaghan (52), and Davis & Gordon (53) (this last was used to correlate the compressibility of mercury). All these equations were tested on the available compressibility data of water and mercury. For water MacDonald decided that the data were best represented by a polynomial, rather than one of the non-linear equations, at least over a limited pressure range. The Tait equation did not represent the data well. The mercury data was not represented very well by any of the equations considered.

d) Hayward's Review

In a study of compressibility equations for liquids, Hayward (54) showed that the equation commonly known as the Tait equation (1.2-1) was not that originally proposed by Tait, which was:

\[
\frac{V - V_0}{PV_0} = \frac{E}{\pi + \frac{P}{V_0}}
\]  \hspace{1cm} (1.2-5)

The reciprocal of equation (1.2-5), when rearranged, gives the linear secant-modulus equation, as used by Klaus & O'Brien (55).

\[
\tilde{K} = \frac{V_0 P}{V_0 - V} = K + mP
\]  \hspace{1cm} (1.2-6)
Hayward shows how the equations of Tumirz (56) and Tamman (57) are of the identical form to equation (1.2-6), and also that the Hudleston and MacDonald equations are effectively of the same form as equation (1.2-5), since allowing for experimental error, the predicted values are the same, and are both asymptotic with equation (1.2-5) at \( P = 0 \). He also demonstrates how equation (1.2-5) well represents the compressibility of water up to 12 kbar. At higher pressures all the compressibility data on water will fit equation (1.2-3) if \( \tilde{K} \) is modified:

\[
\tilde{K} = K + mP - nP^2
\]  

(1.2-7)

For organic liquids an equation of the form of equation (1.2-8) will represent its compressive properties up to 12 kbar.

\[
\tilde{K} = K + mP - nP^2 + qP^3
\]  

(1.2-8)

where \( K, m, n \) and \( q \) are constant.

1.2.4 Previous Experimental Work

a) Pure Liquids

After approximately two centuries of occasional experiments on liquid compressibility (33) the first worker to set about the task methodically was Amagat (32) who determined the compressibility of twelve liquids in the pressure range 0-3000 atm. It is his values for the compressibility of water which are generally accepted as the most accurate of the early attempts (54) although relatively small in number. This century Bridgman has carried out by far the most extensive study of the subject, measuring liquid compressibilities of 82 pure liquids at various temperatures and pressures up to 50,000 atm. All his results, except
one, are published in the Proceedings of the American Academy of Arts and Science and are all comprehensively listed by Hamann (58).

Gibson & Loeffler (39) found the compressibility of benzene and four of its derivatives at pressures up to 1000 bars. The Tait equation was fitted for each liquid, the value of J being kept constant at 0.2159.

The compressibilities of n-hexane, n-heptane and n-octane have been measured by Eduljee, Newitt & Weale (42) at pressures up to 5000 atm. and various temperatures. The Tait equation was fitted with J kept constant at 0.2172. Boelhouwer (41) found the relative volumes of five alkanes in the temperature range 30-120°C and pressures up to 1200kg/cm^2, and found that the Hudleston equation represented the relative volumes well. Cutler et al (49) found that both the Tait and Hudleston equations fitted well their compressibility data of the thirteen hydrocarbons that they studied at pressures up to 1000 bars. When fitting the Tait equation the value of J was not kept constant as previously done by other workers (42) (49) but was made a function of the liquid volume at atmospheric pressure. The relationship was

\[ J = 0.2058 V_0 \]

b) Liquid Mixtures

(i) Non-Aqueous Mixtures

Eduljee, Newitt and Weale (42) carried out compressibility studies on binary and ternary mixtures of the same alkanes which they studied in the pure state.
The compressibility of aniline-benzene, aniline-chlorobenzene and aniline-nitrobenzene mixtures were found by Gibson and Loeffler (39) in order to ascertain whether the compressibility of liquid mixtures was an additive property of the pure components. Similar experiments have been done by Newitt & Weale (59) on chloroform-acetone and ethanol-propanol and all were found linear in mole fraction, except aniline-benzene which showed negative deviations from linearity.

(ii) Aqueous Mixtures

The compressibility of aqueous inorganic salt solutions has been studied by Adams (38), who studied the NaCl/H₂O system, and Gibson and Loeffler who obtained data on many aqueous salt systems (60) (61).

Various workers have obtained compressibility data for aqueous solutions of organic compounds. Richards and Chadwell (37) measured the compressibility of aqueous solutions of ethyl alcohol, benzene and methylacetate at a temperature of 20°C and pressures up to 300 bar. Newitt and Weale (59) have obtained similar data for the propanol-water and acetone-water systems; Gibson and Loeffler (48) for the methanol-water system; and Moesveld (62) for the ethanol-water system. Stutchbury (63) has found the compressibility of aqueous mixtures of isopropyl alcohol, ethyl alcohol, tert-butyl alcohol, acetone and pyridine at a temperature of 30°C and pressures up to 1000 atm. In all these aqueous systems the curve of compressibility vs. composition
exhibits a minimum at low concentrations of the organic component.

Holder & Whalley (64) have measured the compressibility of pure benzene, carbon tetra-chloride and cyclo-hexane. Also they measured the compressibility of the near ideal systems formed by binary mixtures of these liquids and calculated the excess compressibilities at 1 atm.
CHAPTER 2.

A Review of the Available Equations for the Prediction of Phase Equilibrium Data and the Circumstances Under which they can be applied.
CHAPTER 2.

A Review of the available equations for the prediction of phase equilibrium data and the circumstances under which they can be applied.

2.1 The Thermodynamics of Phase Equilibrium.

2.1.1. The Phase Equilibrium Problem.

The essence of the problems that phase equilibrium thermodynamics sets out to solve is best illustrated by an example. Consider the system Acetone, Chloroform, Methanol at equilibrium, at a fixed temperature the composition of each component in both the liquid and vapour phases is fixed, as is the total pressure of the system. What, if the temperature was altered, would the new compositions of the equilibrium vapour and liquid phases be at the same pressure? Alternatively, given the composition of the liquid phase and the temperature, what is the composition of the vapour phase and at what pressure? Such is the problem which may be concerned with combinations of many other variables.

By describing such a problem in abstract, mathematical terms, it is sometimes possible to obtain a simple answer, but not always in terms of immediate physical reality. Thermodynamics provides the mathematical language in which an abstract solution of the phase equilibrium problem is readily obtained.

The method of solution can be divided into three parts:
a) Translation of the problem into an abstract mathematical form.
b) Solution of the mathematical problem.
c) Translation of the result into physically meaningful terms.

Gibbs (65) in 1875 defined the chemical potential which facilitated the transformation of the physical problem into mathematical terms. The mathematical solution results from the fact that at equilibrium the chemical potential of the two phases is equal. The great problem is to get the result of step (b) into physically meaningful terms.

In finding laws of equilibrium for systems the effects of surface tension and tensile effects, acceleration and change of position in a potential field, and chemical and nuclear reactions are neglected. What remains is the classical problem of phase equilibrium in which the internal equilibrium with respect to the following processes is considered;
a) Heat transfer between any two phases within the heterogeneous system.
b) Displacement of a phase boundary.
c) Mass transfer of any component in the system across a phase boundary.

The governing potential in (a) and (b) are temperature and pressure respectively. The third potential is susceptible to a variety of definitions and classical thermodynamics provides appropriate chemical potentials for various situations.

With particular regard to the highly complex MEK/water system, it would, of course, be unrealistic to expect that a mathematical expression, which contained no more than two or
three adjustable parameters, could describe adequately the deviations of the system's behaviour from ideality. While the expressions discussed in this chapter are in many cases based on some physical concept involving the interaction of like and unlike molecules, their applicability to the MEK/water system is considered only from the standpoint of practicability; that is whether or not they provide a convenient way of correlating the observed behaviour of the system.

2.1.2. The Gibbs-Duhem Equation.

The intensive state of each phase present in a heterogeneous system at equilibrium may be characterized by the temperature and pressure of each species present along with its chemical potential. However, these are not all independent as shown by the Gibbs-Duhem equation below.

First consider a homogeneous closed system. Its internal energy, \( U \), can be considered as a function of its entropy, \( S \), and its volume, \( V \).

\[
U = U(S,V) \quad (2.1 - 1)
\]

In an open system the number of moles of the various species present \( (n_1, n_2 \text{ etc}) \) must also be considered.

\[
U = U(S,V,n_1, n_2, \cdots, n_m) \quad (2.1 - 2)
\]

where \( n \) is the number of species and \( n_i \) the number of moles of the \( i \)-th component present.

Total differentiation of equation (2.1 - 2) gives:

\[
dU = \left( \frac{\partial U}{\partial S} \right)_{V,n_1} dS + \left( \frac{\partial U}{\partial V} \right)_{S,n_1} dV + \sum_i \left( \frac{\partial U}{\partial n_i} \right)_{V,n_j} dV_{n_i} \quad (2.1 - 3)
\]
using the identities for a closed system:

\[
\left(\frac{\partial U}{\partial S}\right)_{V,n_i} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -P
\]

and defining \( \mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} \)
equation (2.1-3) becomes:

\[
dU = TdS - PdV + \sum_i \mu_i \, dn_i
\] (2.1-4)
equation (2.1-4) is the fundamental equation for an open system.

Now consider a phase within the heterogeneous system as an open homogeneous system. In this case equation (2.1-4) applies. Integrate this equation from a state of zero mass \((U=S=V=n_i = n_2 = \ldots = n_m = 0)\) to a state of finite mass at constant temperature, pressure and composition. Along this path all coefficients are constant

\[
U = TS - PV + \sum_i \mu_i n_i
\] (2.1-5)
since \(U\) is a state function the result of equation (2.1-5) is independent of the path of integration.

Differentiating equation (2.1-5) gives:

\[
dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i
\] (2.1-6)

Comparing equations (2.1-4) and (2.1-6):

\[
SdT - VdP + \sum_i n_i d\mu_i = 0
\] (2.1-7)

This is one of the Gibbs-Duhem equations. It is a fundamental equation in the thermodynamics of solutions which restricts the simultaneous variation of temperature, pressure and chemical potential in a single phase.
2.1.3. The Ideal Solution.

An ideal solution is defined as one, in which at constant temperature and pressure, the fugacity is proportional to some suitable measure of the composition, usually the mole fraction, \( x \). Thus for any component, \( i \), in an ideal solution,

\[
\tilde{f}_i^L = Cx_i^i \quad (2.1-8)
\]

where \( C \) is a proportionality constant dependent on temperature and pressure. Setting the fugacity equal to the partial pressure and \( C \) equal to the total pressure of the system yields Raoult's Law. In many cases the proportionality between the fugacity and the composition holds for only small values of \( x_i \). Such systems are known as ideal dilute solutions and Henry's Law applies.

For a solution obeying Raoult's Law at any temperature and pressure:

\[
f_i(T,P) = f_{\text{pure}i}(T,P) \cdot x_i \quad (2.1-9)
\]

Substitution of equation (2.1-9) into the thermodynamic relations

\[
\frac{\partial \ln f_i}{\partial T}_{P,x} = -\frac{\tilde{h}_i - h_i}{RT^2}, \quad \frac{\partial \ln f_{\text{pure}i}}{\partial P}_{T,x} = -\frac{(h_{\text{pure}i} + h_i)}{RT^2}
\]

and

\[
\frac{\partial \ln f_i}{\partial P}_{T,x} = \frac{\tilde{v}_i}{RT}, \quad \frac{\partial \ln f_{\text{pure}i}}{\partial P}_{T,x} = \frac{v_{\text{pure}i}}{RT} \quad (2.1-10)
\]

and

\[
\frac{\partial \ln f_i}{\partial T}_{P,x} = \frac{\tilde{v}_i}{RT}
\]

and

\[
\frac{\partial \ln f_{\text{pure}i}}{\partial T}_{T,x} = \frac{v_{\text{pure}i}}{RT} \quad (2.1-11)
\]

gives

\[
\tilde{h}_i = h_i \quad (2.1-12)
\]

\[
\tilde{v}_i = v_i \quad (2.1-13)
\]

since these two partial molar quantities are equal both in the pure state and in an ideal solution, it follows that formation of an ideal solution occurs without any changes in volume and enthalpy.
2.1.4. The Activity.

The activity is defined (66) as the ratio of the fugacity of a component in a given state to the fugacity of the same component at the same temperature in some standard state.

\[ a_i = \frac{f_i}{f_i^0} \quad (2.1 - 14) \]

where \( a_i \) = activity of component \( i \)
\( f_i \) = fugacity of the component \( i \) in the given state
\( f_i^0 \) = fugacity of component \( i \) in the standard state and at the same temperature.

The numerical value of the activity depends largely on the choice of standard state as shown by equation (2.1 - 14). Therefore it is necessary to choose a suitable standard state for the solution of a given problem. For solutions of non-electrolytes the most convenient standard state is that of the pure constituent at the temperature and pressure of the system. Thus the activity of the pure substance is always equal to unity:

\[ (a_i)_{x_i = 1} = 1 = \frac{f_i^0}{f_i^0} = 1 \quad (2.1 - 15) \]

and the activity of a component in an ideal solution is always equal to its mole fraction, since from Raoult's Law:

\[ x_i = \frac{f_i}{f_i^0} = a_i \quad (2.1 - 16) \]

2.1.5 The Activity Coefficient.

It is defined as the ratio of the activity of a component to its mole fraction:

\[ \gamma_i = \frac{a_i}{x_i} \quad (2.1 - 17) \]
A comparison of equations (2.1 - 15) and (2.1 - 16) shows that for an ideal solution the activity coefficient is equal to unity:

\[ \gamma_i = \frac{a_i}{x_i} = \frac{x_i}{x_i} = 1 \quad (2.1 - 18) \]

Now that deviations from ideality are represented by the one quantity, \( \gamma_i \), then equations for ideal systems can be used for real systems once modified by the activity coefficient.

2.1.6. The Gibbs Free Energy.

For a closed system the Gibbs free energy is defined as:

\[ dG = VdP - SdT \quad (2.1 - 19) \]

This is a very useful function for any system since its two primary variables are temperature and pressure, two very easily measured quantities. The Gibbs free energy change on mixing is of primary interest in the study of mixtures. Consider the change in this quantity in mixing pure liquid constituents, \( b \) moles of component B, \( c \) moles of component C etc. at constant temperature and pressure, to form a solution:

\[ bB + cC + \ldots = [bB + cC + \ldots] (2.1 - 20) \]

where the left hand side of equation (2.1 - 20) represents the number of moles of each component separate from each other and the right hand side represents the ideal solution. The change in the Gibbs free energy for this process is given by:

\[ \Delta G_{\text{mix}} = b\mu_B + c\mu_C + \ldots - b\mu_B^0 - c\mu_C^0 \]

\[ = b(\mu_B - \mu_B^0) + c(\mu_C - \mu_C^0) + \ldots \quad (2.1 - 21) \]

The difference in molar free enthalpy (chemical potential) between an actual and standard state is given by:

\[ \mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0} = RT \ln a_i \quad (2.1 - 22) \]
Substitution of equation (2.1-22) into equation (2.1-21) gives:

\[ \Delta G_{\text{mix}} = bRT \ln a_B + cRT \ln a_C + \ldots \]
\[ = bRT \ln x_B + cRT \ln x_C + \ldots \]
\[ + bRT \ln \gamma_B + cRT \ln \gamma_C + \ldots \]
\[ = \sum n_i RT \ln x_i + \sum n_i RT \ln \gamma_i \]  

(2.1-23)

Since for an ideal solution the activity of each component is equal to unity the second term on the right hand side of equation (2.1-23) vanishes:

\[ \Delta G_{\text{mix}}^{id} = \sum n_i RT \ln x_i \]  

(2.1-24)

Equation (2.1-24) gives the molar Gibbs free energy change of mixing for an ideal solution.

2.1.7. Excess Functions.

These are thermodynamic properties of solutions which are in excess of those for ideal solutions at the same temperature and pressure. For the thermodynamic property, \( M \):

\[ M_i^E = M_i - M_{i}^{id} \]  

(2.1-25)

where \( M_i \) and \( M_{i}^{id} \) are the actual and ideal values respectively. Excess functions for ideal systems are zero.

Relations between excess functions are the same as those between the total functions:

\[ H^E = U^E + PV^E \]  

(2.1-26)

\[ G^E = H^E - TS^E \]  

(2.1-27)

\[ A^E = U^E - TS^E \]  

(2.1-28)

Similarly the partial derivatives are:

\[ \left( \frac{\partial G^E}{\partial T} \right)_{P,x} = -S^E \]  

(2.1-29)
Excess functions can be either positive or negative. Positive values classify positive deviations from ideality, negative values negative deviations.

As mentioned in Section 2.1.5 the activity coefficient is a measure of the deviation of a solution from ideality, the partial molar excess Gibbs free energy is another. These two variables are related by the equation:

\[ \frac{\partial E_i}{\partial n_i} = RT \ln \gamma_i \]  \hspace{1cm} (2.1 - 32)

Thus knowledge of either \( E_i \) or \( \gamma_i \), in terms of a property of the solution, will yield a quantitative measure of the deviation from ideality of a given solution. The most useful quantity to use for this purpose is the composition of the phase, the mole fraction \( x_i \). A further exact thermodynamic relationship is:

\[ \ln \gamma_i = \left[ \frac{\partial}{\partial n_i} \left( \frac{E_i}{RT} \right) \right]_{T,P,n_j} \]  \hspace{1cm} (2.1 - 33)

which will find considerable use during this chapter.

2.2. Expressions of the excess free energy in terms of composition.

2.2.1. Two-parameter semi-empirical equations.

a) Wohl Equation

Wohl (68) expressed the excess Gibbs free energy of a solution as a power series in \( z_i, z_j, z_k \) etc., the effective volume fractions of the components.
\[
\frac{g}{RT} = \sum_{i} q_i x_i + \sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \ldots (2.2-1)
\]

$q_i, q_j, q_k, q_l \ldots$ are constants called the effective molar volumes of the constituents $i, j, k, l \ldots$ and $z_i, z_j, z_k, z_l \ldots$ are effective volumetric fractions of the constituents. The effective volumetric fraction of any constituent, $i$, is defined by the relation:

\[
z_i = \frac{q_i x_i}{\sum_{j} q_j x_j} (2.2-2)
\]

The empirical constants $a_{ij}, a_{ijk}, a_{ijkl}$ measure the interactions in various groups of molecules, $ij, ijk, ikl$.

The first summation in equation (2.2-1) gives the sum of the products of the volumetric fractions ($z_i, z_j$) of all pairs of dissimilar constituents that can be chosen from the given $n$ - component system, where each product is multiplied by a constant $a_{ij}$, which is related to the force interactions between the corresponding pair of molecules. Similarly the second summation takes into account the force interactions of all triplets of volumetric fractions, etc.

It is a method by which some physical significance can be given to the parameters.
b) The van Laar Equation

i) Derivation

van Laar considered the energy change when two pure liquids were mixed at constant temperature and pressure. He assumed that there was no volume change \( E(\Delta v_{\text{mix}} = 0) \) and that the excess entropy of mixing was also zero \( (S^E_{\text{mix}}=0) \). He then constructed a three step thermodynamic cycle in which the pure liquids were:

a) vapourized to some arbitrary low pressure.
b) mixed at this low pressure.
c) recompressed to the original pressure.

Since the energy is a state variable, independent of the path, the total energy change was given by the sum of the energy changes of the three steps. Using rigorous thermodynamic equations, and assuming the volumetric properties of the pure liquids were given by the van der Waal's equations, the energy changes in steps (a) and (c) were obtained. The energy change during step (b) was taken as zero since the isothermal mixing of the ideal gases proceeds with no energy change. He found the total energy change to be:

\[
E^E = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2} \left( \frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 \tag{2.2-3}
\]

where \( a \) and \( b \) are the van der Waals constants the subscripts referring to components.

Differentiation according to equation (2.1-33) yields the activity coefficient.
In the above two equations the constants $A$ and $B$ are given by:

$$A = \frac{b_1}{RT} \left( \frac{\sqrt{a_{11}}}{b_1} - \frac{\sqrt{a_{22}}}{b_2} \right)^2$$  \hfill (2.2 - 6)

$$B = \frac{b_2}{RT} \left( \frac{\sqrt{a_{11}}}{b_1} - \frac{\sqrt{a_{22}}}{b_2} \right)^2$$  \hfill (2.2 - 7)

Two properties of the van Laar equation emerge:

1) The logarithms of the activity coefficients are inversely proportional to the absolute temperature. This is a consequence of assuming a regular solution ($s^E=0$)

2) The activity coefficients predicted are never less than unity, thus positive deviations from Raoult's Law are always predicted. This results from the assumption that the inter-reaction forces between the two dissimilar molecules in the mixture can be expressed in terms of the inter-reaction forces between two like molecules by:

$$\sqrt{a_{\text{mix}}} = x_1 \sqrt{a_1} + x_2 \sqrt{a_2}$$  \hfill (2.2 - 8)

ii) Examples of its use

Considering a binary solution of two components which are not too dissimilar chemically but differ in molecular size, and considering only the first term of Wohl's equation (2.2-1) one obtains:

$$\frac{g^E}{RT} = \frac{2a_{12} x_1 x_2 q_1 q_2}{x_1 q_1 + x_2 q_2}$$  \hfill (2.2 - 9)
Differentiating equation (2.2 - 9) according to equation (2.1 - 33) an expression for $\gamma_1$ is obtained in terms of $x_1$ and $x_2$.

\[
\ln \gamma_1 = \frac{A}{1 + \frac{A}{B} \frac{x_1}{x_2}} \tag{2.2 - 4}
\]

\[
\ln \gamma_2 = \frac{B}{1 + \frac{B}{A} \frac{x_2}{x_1}} \tag{2.2 - 5}
\]

where $A = 2q_1a_{12}$ and $B = 2q_2a_{12}$

Equations (2.2 - 4) and (2.2 - 5) are van Laar's (69) equations.

The derivation suggests that the van Laar equation should be used for solutions whose constituents differ in molecular size but where their interactions are weak. In practice this equation can be used for far more complex systems, and in such cases as these the constants lose what little physical significance they might have and become purely empirical constants based on a thermodynamically consistent equation.

When the van Laar equation is applied to the vapour equilibria of partially miscible systems, previous work has suggested (70) that separate pairs of constants be derived for each liquid miscible phase and the composition of the vapour above it calculated. This method requires a previous knowledge of the vapour liquid equilibrium data of the system. When such data are not available only one pair of constants can be used which may be found from tie-line data of the partially miscible phase. This approach was first suggested by Robinson & Gilliland (71).
c) Margules Equation (76)

For a binary solution, the components of which do not differ greatly in molecular size, and neglecting terms greater than the fourth power in equation (2.1-32), the four suffix Margules equation is obtained:

\[ \ln y_i = A x_2^2 + B x_2^3 + C x_2^4 \] (2.2-10)
\[ \ln y_2 = (A+\frac{3}{2}B+2C)x_1^2-(B+\frac{3}{2}C)x_1^3+Cx_1^4 \] (2.2-11)

where:

\[ A = q(2a_{12}+6a_{112}-3a_{123}+12a_{1112}-6a_{1122}) \] (2.2-12)
\[ B = q(6a_{122}-6a_{112}-24a_{1112}-8a_{1222}+24a_{1122}) \] (2.2-13)
\[ C = q(12a_{1112}+12a_{1222}-18a_{1122}) \] (2.2-14)

Usually the experimental data is sufficiently scarce not to justify the use of a three parameter equation, therefore, the constant C is set equal to zero. Equations (2.2-10) and (2.2-11) now become:

\[ \ln y_1 = A x_2^2 + B x_2^3 \] (2.2-15)
\[ \ln y_2 = (A+\frac{3}{2}B)x_1^2-Bx_1^3 \] (2.2-16)

Although the equations have been derived on the assumption that the molecular sizes of each component are equal, it can represent well the data of many systems which do not conform to this requirement. The advantage that this equation has over van Laar's is that it can predict maxima in the activity coefficient vs. composition curves, although these systems are not common.

Margules originally derived the equation by expressing the logarithm of the activity coefficient in terms of an exponential series:

\[ \ln y_i = \sum_{k=1}^{\infty} \alpha_k x_2^k \] (2.2-17)
d) Scatchard-Hammer Equation

On truncating equation (2.2-1) after the third order terms and assuming:

\[
\begin{align*}
q_1 &= v_1 \\
q_2 &= v_2
\end{align*}
\]

where \(v_1\) and \(v_2\) are the molar volumes of the pure liquids at the temperature of the solution, the Wohl equation now becomes:

\[
\begin{align*}
\ln \gamma_1 &= A z_2^2 + B z_2^3 \\
\ln \gamma_2 &= (A + \frac{3}{2} B) \frac{V_2}{V_1} + \frac{BW_2}{V_1} z_2^3
\end{align*}
\]

where:

\[
\begin{align*}
A &= v_1 (2a_{12} + 6a_{112} - 3a_{122}) \\
B &= v_1 (6a_{122} - 6a_{112})
\end{align*}
\]

The equations predict values of \(\gamma_i\) between those of van Laar and Margules when the same constants are being used.

2.2.2 Other semi-empirical equations.

a) Black's Equation

Association of like molecules increases the activity coefficient while interassociation of unlike molecules decreases the activity coefficient. In the van Laar equation these two effects sometimes cancel out and the data is well represented, on other occasions this is not the case and the van Laar equation makes poor predictions.

Black (79) modified the van Laar equation by the addition of another constant \(C\):
\[
\ln \gamma_1 = \frac{A}{(1+A x_1) B x_2} + C_{12} \quad (2.2 - 23)
\]
\[
\ln \gamma_2 = \frac{B}{(1+B x_2)^2 A x_1} + C_{21} \quad (2.2 - 24)
\]
where \(C_{12} = C_{21}\).

If \((\ln \gamma_1)^{0.5}\) vs.\((\ln \gamma_2)^{0.5}\) is plotted the van Laar equation predicts a straight line, whereas experimental data often give a curve. The constant \(C_{12}\) is to correct for this discrepancy. If experimentally obtained values are plotted on the above graph, and form a curve, then a tangent is drawn to this curve such that the difference between the intercept of the experimental curve and the intercept of the tangent equal on both ordinate and abscissa. This is necessary since \(C_{12} = C_{21}\).

On squaring the difference in intercepts the value of \(C_{12}\) is obtained.

The systems to which Black applied his equation were:

a) Propylene - propane.

b) Ethanol - 2,2,4 Trimethylpentane

c) Methanol - Benzene

d) Chloroform - ethanol

e) Acetone - water

f) Water - furfural

In all these systems, except (a) the components show high degrees of association or interassociation, either in the pure state or when mixed with each other. The equation's superiority over the two suffix van Laar equation is readily shown when applied to system (b). Although this system is extremely non-ideal it remains completely miscible in the liquid phase.
at 50°C. Black's equation represents the vapour-liquid equilibrium data well, however, the van Laar equation not only gives a poor representation of the data but predicts partial miscibility in the liquid phase.

b) Redlich-Kister Equation

A requirement for any expression for $g^E$ in a binary system is that

$$g^E = 0 \text{ when } x_1 = 0$$

and

$$g^E = 0 \text{ when } x_1 = 1$$

An expression that fulfills the above requirements and which is sufficiently flexible to accommodate complex systems is that attributed to Redlich-Kister:

$$g^E = x_1 x_2 [A' + B' (x_1 - x_2) + C' (x_1 - x_2)^2 + D' (x_1 - x_2)^3 + ...] \quad (2.2 - 25)$$

since $RT \ln \gamma_i = g^E_i = \frac{3n_1 g^E}{\rho \bar{n}_i} T, P, n_j$ \quad (2.2 - 26)

then:

$$RT \ln \gamma_1 = A_1 x_1^2 + B_1 x_1^3 + C_1 x_1^4 + D_1 x_1^5 + \text{ .......} \quad (2.2 - 27)$$

and

$$RT \ln \gamma_2 = A_2 x_1^2 + B_2 x_1^3 + C_2 x_1^4 + D_2 x_1^5 + \text{ .......} \quad (2.2 - 28)$$

This expansion provides a convenient means of classifying different types of liquid mixtures. As shown by Redlich, Kister & Turnquist (94). Plots of $\ln \gamma_1/\gamma_2$ vs. $x_1$ of experimentally obtained activity coefficient data can be represented by the joint use of equations (2.1 - 32) and (2.2 - 25) which yields the expression:

$$RT \ln \frac{\gamma_1}{\gamma_2} = A' (x_2 - x_1) + B' (6x_1 x_2 - 1) + C' (x_1 - x_2) (8x_1 x_2 - 1)$$

$$+ D' (x_1 - x_2)^2 (10x_1 x_2 - 1) + \text{ .......} \quad (2.2 - 29)$$

They showed that the complexity of the binary liquid mixture dictates the number of non-zero parameters required in equation (2.2 - 29) to give adequate representation of the
experimental data. For example, for a binary mixture of two non-interacting components being of similar molar volumes, then in equation (2.2 - 29) \( B = C = D = 0 \) and a plot of \( \ln \gamma_1/\gamma_2 \) is a straight line which is typical behaviour for this type of mixture.

More complicated mixtures which have components of different molecular volumes, for example benzene/iso-octane exhibits a curve when \( \ln \gamma_1/\gamma_2 \) is plotted against \( x_1 \) and two or more parameters are required to represent these data adequately. As the complexity of the system increases, so the number of parameters required in equation (22 - 29) increases. In systems where there are strong interactions between either like or unlike components, together with the effects of molecular size, affecting the shape of the \( \ln \gamma_1/\gamma_2 \) plot then as many as four or more parameters are required to represent the data adequately.

2.2.3 Comparison of the equations arising from Wohl's Equation.

Carlson & Colburn (84) were among the first to study the relative merits of the van Laar, Margules and Scatchard-Hamer equations. For the van Laar and Margules equations they found that the logarithm of the activity coefficients at infinite dilution gave the values of \( A \) and \( B \). Also they found that the molecular size of the pure components was a clue to choosing the most suitable equation. These equations were used to predict the activity coefficient data of five systems:

a) Iso-propyl ether - isopropyl alcohol.
b) n - propyl alcohol - water.
c) Acetone - chloroform.
d) Chloroform - ethyl alcohol.
e) n - butyl alcohol - water.
In (a), (b) and (c) van Laar's equation fitted the experimental data well; while (d) was well represented by the Margules equation, because of the similarity in molecular size of the two components. The fifth, (e), which is partially miscible in the liquid phase, was only poorly represented by the van Laar equation. The Scatchard-Hamer equation predicted activity coefficients similar to those of either the van Laar equation or the Margules equation depending on the molecular size of the two components.

Aspects of the behaviour of the Margules and Scatchard-Hamer equations which make them less satisfactory than the van Laar equation were observed by Brian (85). These were shown by the partially miscible systems:

a) Aniline - water.
b) Isobutyl alcohol - water.
c) 1-butanol - water.
d) Phenol - water.
e) Propylene oxide - water.

For system (e), the predictions of both van Laar and Margules were in close agreement. However for the other four systems, Margules predicted values of the activity coefficient less than unity, while the van Laar equation predicted reasonable values. Examination of a number of solutions showed that this behaviour occurred in highly asymmetric systems where the ratio of component 1 in one phase to component 2 in the second phase is far removed from unity. Van Laar's equation is of such a mathematical form that it prevents the activity coefficient from crossing unity and is satisfactory for highly asymmetric systems. The Margules equation adjusts to the necessary equilibrium condition.
\( \gamma_1 x_1 = \gamma_1^1 x_1^1 \), by adjusting \( \gamma_1 \) to impossible limits.

The Scatchard-Hamer equation permits the activity coefficients to cross unity but none the less gives similar results to the van Laar equation in (a) to (d), apparently high values of \( v_1/v_2 \) compensate for low values of \( x_1/x_1^1 \). However this delicate balance is upset when \( v_1/v_2 \) approaches unity and the equation will fail since it now becomes identical to the Margules equation.

2.2.4 Suitability of the semi-empirical equations for representing the MEK/H2O system.

In all the solutions to the Gibbs-Duhem equations considered so far it is possible to take into account the complexities of the mixture by increasing the number of parameters in each equation until the predicted result matches the experimental result. The danger arising from increasing the number of constants, until an acceptable fit is obtained, is that experimental data is often too scarce or inaccurate to justify the use of many parameters. Thus the van Laar, Margules and Scatchard Hamer equations in their familiar 2 constant form have only two empirical constants which is a result of truncating the Wohl expansion after the first term in the case of the van Laar equation and the third term is the case of the Margules and the Scatchard-Hamer equations. As described previously it is the intention during this work to restrict the number of parameters used in any equation to define the system, to two. The three suffix van Laar equation would be expected to be suitable for this system since it has been derived from the Wohl expansion assuming that the molar volumes of the two components are dissimilar. In the particular
case of the MEK/H\textsubscript{2}O system the molar volumes are in the approximate ratio of 5:1. A useful means of judging the suitability of the van Laar equation for a particular system is to rearrange into the following form:

\[
\frac{x_1^2 \ln \gamma_1}{x_2^2 \ln \gamma_2} = \frac{B}{A} = \text{constant} \quad (2.2 - 30)
\]

A plot of the left hand side of this equation, as calculated from experimental data, against \(x_1\) will be linear, if the equation is suitable.

The three suffix Margules equation would be less likely to represent the system well since it is derived from the Wohl expansion assuming that the molar volumes of both components are equal. Rearrangement of the Margules equation again provides a means by which an objective decision may be reached.

\[
\frac{\ln \gamma_1}{x_2^2} + \frac{\ln \gamma_2}{x_1^2} = B-A = \text{constant} \quad (2.2 - 31)
\]

Again, a plot of experimentally obtained values of the left hand side of the equation against \(x_1\) will be linear if the equation is suitable. Regrettably the only means available by which values of the activity coefficients may be obtained from the tie line data obtained in this work is via the chosen algebraic function which automatically presupposes its suitability to a certain extent.

The accuracy of the calculation of activity coefficient data from mutual solubilities is very sensitive to the algebraic function chosen to represent the excess Gibbs energy. As shown by Brian (85) the Margules equation performs poorly, compared with the van Laar equation, when used for strongly
asymmetric systems, that is to say in systems where the ratio of the mole fraction of component 1 is the first phase to mole fraction of component 2 in the second phase is far removed from unity. For the MEK/H₂O system at 1 atm and 100°C this ratio is approximately 11, the inference being that the van Laar would be the more suitable equation of the two.

The Scatchard-Hamer equation is similar in form to the three suffix Margules equation, the differences being that the mole fraction x is replaced by the volume fraction, z, and also the ratio of the molar volumes for the two components are included in the expression for ln γ_i while A and B remain the only two adjustable parameters a third parameter is present, namely v_2/v_1, which while it is not adjustable, must be determined for each set of temperature and pressure conditions. As shown in the previous section the Scatchard-Hamer equation, like the van Laar equation, performs well with highly asymmetric systems, but because of the presence of the third parameter v_2/v_1, its use has not been considered further.

Finally, the Redlich-Kister equation is considered. Section 2.2.2.b shows that this equation is capable of representing complex systems by the expedient of adding terms as the complexity of the mixture increases. The MEK/H₂O system has features which make it a complex mixture: the ketone can act as a weak proton acceptor, water has a tendency to form hydrogen bonds, also the large difference in the molar volumes of the two components will be of significance.

It was shown in Sect. 2.2.2.b how the binary mixture benzene/isooctane, complex only in that the ratio of molar volumes was 1.86 at 25°C, required two parameters in equation
(2.2 - 29) to represent the mixture's characteristics adequately (94). Again, unfortunately, the tie line data obtained in this work cannot be utilized to establish the number of parameters required in the Redlich-Kister equation to represent the MEK/H₂O system satisfactorily. It may be concluded, however, that since this system has tendencies towards hydrogen bonding, proton accepting and also differences in molar volumes, then more than two parameters would be required in the Redlich-Kister equation which will, therefore, not be considered further.

2.2.5 Quasi-chemical Equations

a) The Flory Huggins Equation

This equation was derived for liquid mixtures where the molecules of one component differ greatly in size from those of the other component, for example polymers in liquid solvents.

A definition of the Gibbs free energy is:

\[ G = H - TS \]  \tag{2.2 - 32}

The regular solution theory concerned itself with accounting for the enthalpy term in equation (2.2 - 32) and assumed that the entropy of mixing was zero. When dealing with polymer solutions, the entropy of mixing is considered and the heat of mixing assumed to be zero. Such solutions are called athermal and the following equation was derived independently by FLORY (87) and HUGGINS (88) to describe their behaviour:

\[ \frac{\Delta G_{\text{mix}}}{RT} = \Delta S_{\text{mix}} = - n_1 \ln \phi_1 - n_2 \ln \phi_2 \]  \tag{2.2 - 33}

where: \( \phi_1 = \frac{n_1}{n_1 + mn_2} \) volume fractions.

\( \phi_2 = \frac{mn_2}{n_1 + mn_2} \)

\( n_1 = \) number moles of solvent

\( n_2 = \) number moles of polymer

\( m = \frac{v_2}{v_1} \), the ratio of molar volumes of the polymer and the solvent.
Since polymer solutions are not athermal, equation (2.2 -33) is corrected for use on real systems by adding a semi-empirical term for the enthalpy of mixing which is set proportional to the volume of the solution and the product of the volume fractions:

\[
\frac{\Delta G_{\text{mix}}}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + x_1\phi_1(x_1 + x_2) (2.2. - 34)
\]

where \(X = \text{Flory interaction parameter, determined by intermolecular forces between molecules in the solution.}\)

b) **Wilson Equation.** (89)

The case was considered where the molecules of the components differed, not only in size, but also in their intermolecular forces. The idea of local composition was introduced whereby the probability was considered of finding molecules of one type relative to a central molecule of the other type. On this basis local volume fractions were defined and were substituted into the Flory-Huggins equation (2.2 - 33), and the modified Flory-Huggins equation becomes:

\[
\frac{E_{\text{mix}}}{RT} = x_1 \ln(x_1 + Ax_2) + x_2 \ln(Bx_1 + x_2) (2.2 - 35)
\]

where: \(A = \frac{v_2}{v_1}\exp\left[-\frac{(\lambda_{12} + \lambda_{1i})}{RT}\right] (2.2 - 36)\)

and \(B = \frac{v_1}{v_2}\exp\left[-\frac{(\lambda_{12} - \lambda_{22})}{RT}\right] (2.2 - 37)\)

where \(\lambda_{ij}\) is related to the potential energy of a pair of molecules consisting of one of type (i) and one of type (j).

The activity coefficients are given by:
The equations provide good representations of excess Gibbs energies for a variety of miscible mixtures, particularly asymmetric systems. Data analysed by Orye (90) for many systems showed that Wilson's equation represented the data well and in many cases better than the van Laar or Margules equations. The latter two equations must be modified with a third constant to fit these systems, particularly asymmetric ones.

Wilson's equation cannot represent activity coefficient data which have a maximum or minimum, neither can it predict partial miscibility. From equation (2.2 - 35) the mixture will be close to separation as the constants approach unity, but in this limit the excess free energy becomes equal and opposite to the ideal free energy of mixing, therefore the free energy of mixing becomes equal to zero at all compositions. Therefore Wilson suggested multiplying the right hand side of equation (2.2. - 35) by a constant (89) when this modified equation was used on the partially miscible butyl alcohol-water system, the solubility loop fitted the experimental data fairly well. (77)

The Enthalpic Wilson equation is a further modification of the original Wilson equation. It is derived on the basis of a regular solution (i.e. assuming $S^E=0$) and the following equation results:

\[
\frac{g^E}{RT} = \frac{x_2 \ln AB}{(x_1+Ax_2)(x_2+Bx_1)} \tag{2.2. - 40}
\]
Differentiating the above equation yields the activity coefficient:

$$\ln \gamma_1 = -x_2 \ln AB \frac{[1+x_1\left(1-x_1B(x_1+Bx_1)(x_2+Bx_2)-(x_1+Bx_2)(x_2+Bx_1)\right)]}{(x_1+Bx_2)(x_2+Bx_1)} \tag{2.2 - 41}$$

The use of this equation has been investigated by Bruin (72) and also McCann (73).

c) The Segment Interaction Equation - Heil's equation. (93)

An equation was proposed for solutions of polymers with interactions between like and unlike molecules. The Flory-Huggins equation is unsatisfactory for this application since the parameter X is a strong function of composition. The segment interaction equation makes use of the local volume concept of Wilson by considering the local volume fractions about molecules of the same component and molecules of different components. The resulting equations reduce to the Flory-Huggins equation when the difference in the interaction energy parameters is small. The resulting equation is:

$$\frac{\Delta g_{\text{mix}}}{RT} = x_1 \ln \epsilon_{11} + m x_2 \ln \epsilon_{12} + (1-m) x_2 \ln \phi_2 + x_1 \epsilon_{21} \frac{(g_{12}-g_{11})}{RT} + m x_2 \epsilon_{12} \frac{(g_{12}-g_{22})}{RT} \tag{2.2 - 42}$$

The equation was tested against the experimental data of polystyrene dissolved in mixed solvents:

a) Acetone - toluene
b) Acetone - benzene
c) Methanol - benzene
d) Methanol - ethyl acetate.
e) Acetone - methylcyclohexane.
Values of the interaction energies were obtained from data of the necessary binary systems. The experimental data of (a), (b) and (c) were well represented by the equation, but in (d) and (e) the prediction was only fair.

d) The Non-random Two liquid equation.

Two types of cells were considered to be present in a binary mixture. The first has a molecule of 1 at its centre which is surrounded by molecules of components 1 and 2. The other has a molecule of 2 at its centre similarly surrounded with molecules of components 1 and 2. The Gibbs energies were assumed to be related to the local mole fractions and parameters characteristic of the interactions between the molecules 1 and 2. The molar Gibbs excess energy was found by considering the change in residual Gibbs free energy which results from transferring \( x_1 \) moles of component 1 from pure component 1 to cells of the mixture, likewise for component 2. Renon (92) assumed local mole fractions similar to Wilson's assumption except that the parameter \( \alpha \) was included in the exponential part. This accounts for the tendency of the molecules not to mix in a completely random fashion.

The excess Gibbs energy is given by:

\[
\frac{G^E}{RT} = x_1 x_2 \left[ \frac{\tau_{21} G_{21}}{x_1 + x_2} + \frac{\tau_{21} G_{12}}{x_2 + x_1 G_{12}} \right] \quad (2.2. - 43)
\]

where 
\[
\tau_{12} = \frac{(g_{12} - g_{22})}{RT} \quad (2.2. - 44)
\]

\[
\tau_{21} = \frac{(g_{21} - g_{11})}{RT} \quad (2.2. - 45)
\]

\[
G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (2.2. - 46)
\]

\[
G_{21} = \exp(-\alpha_{21} \tau_{21}) \quad (2.2. - 47)
\]
and the activity coefficients are given by:

\[
\ln \gamma_1 = x_2^2 \left( \frac{\tau_{12} \exp(-\alpha_{12} T_{12})}{[x_1 + x_2 \exp(-\alpha_{12} T_{12})]^2} + \frac{\tau_{12} \exp(-\alpha_{12} T_{12})}{[x_2 + x_1 \exp(-\alpha_{12} T_{12})]^2} \right)
\]

\[(2.2. - 48)\]

\[
\ln \gamma_2 = x_1^2 \left( \frac{\tau_{12} \exp(-\alpha_{12} T_{12})}{[x_2 + x_1 \exp(-\alpha_{12} T_{12})]^2} + \frac{\tau_{12} \exp(-\alpha_{12} T_{12})}{[x_1 + x_2 \exp(-\alpha_{12} T_{12})]^2} \right)
\]

\[(2.2. - 49)\]

On considering a symmetric system, comparison of the NRTL, with two different values of \(\alpha_{12}\), the van Laar, Heil and Wilson equations showed that for the same system different excess Gibbs free energies were predicted by these equations. The Gibbs energy of mixing curve showed a maximum and two minima for the van Laar, NRTL (with \(\alpha_{12}=0.25\)) and Heil equations and so predicted phase splitting. The mutual solubilities are small in the case of van Laar and are larger with the NRTL (\(\alpha_{12}=0.25\)) and Heil equations. Thus the local composition equations compared with the van Laar equation have a lower maximum for the excess Gibbs energy and thereby reduce the tendency toward phase splitting. The same tendency was observed for nonsymmetric systems.

In an attempt to represent accurately the binary vapour liquid equilibria of strongly non-ideal systems, the vapour liquid equilibrium data of sixty binary systems were calculated and compared with experimental results. During the course of this work the systems were divided into eight groups depending on the chemical nature of the two components.

It was found that the NRTL equation gave the best fit for all types of system considered, provided a proper value of \(\alpha_{12}\) was chosen. Since the value of \(\alpha_{12}\) flattens the excess
Gibbs energy curve, it can represent the system accurately and not predict false phase splitting. A value of $\alpha_{12}$ may be chosen according to the type of system, as specified in the above reference, or if the experimental data are sufficiently plentiful and accurate, $\alpha_{12}$ may be left to float and a three parameter equation results.

A study of twelve partially miscible binary liquid-liquid systems (one component polar, the other a hydrocarbon) showed that both the Heil and NRTL equations could be used for this type of system. The parameters of these two equations were found to be linear functions of temperature and consistent with parameters derived from the vapour liquid equilibrium data for the system. Therefore the vapour liquid equilibrium data can be predicted from the liquid-liquid data.

e) Drye Equation

Drye (75) obtained an expression for the excess Gibbs free energy as follows:

$$
\frac{\Delta_{E}}{RT} = -x_1 \ln(x_1 + Ax_2) - x_2 \ln(x_2 + Bx_1)
$$

and, on differentiating this equation according to equation (2.1. - 33) the activity coefficient is obtained:

$$
\ln \gamma_1 = - \ln (x_1 + Ax_2) + x_2 \left[ \frac{A}{(x_1 + Ax_2)} - \frac{B}{(x_2 + Bx_1)} \right]
$$

$$
- \frac{x_1 \ln AB}{(x_1 + Ax_2)(x_2 + Bx_1)} \left[ 1 + x_1 \left( 1 - \frac{1}{(x_1 + Ax_2)} \right) - \frac{B}{(x_2 - Bx_1)} \right]
$$

(2.2 - 51)
Bruin (72) has examined the use of this equation on vapour-liquid equilibrium data for sixteen different binary systems.

McCann (73) derived a modified version of the original Orye equation which effectively involves the multiplication of the third term on the right hand side of equations (2.2 - 50) and (2.2 - 51) by a constant $K$. When tested on the vapour-liquid data of forty nine different binary systems it was found that the Wilson, NRTL and modified Orye equations all performed with a similar amount of success.

The value of $K$ was determined for six aqueous, partially miscible vapour-liquid systems. Such systems were chosen since $K$ was thought to be significant in systems showing a large degree of non-randomness. An average value for $K$ of 0.1 was deduced for the six systems considered.
CHAPTER 3

Description of Apparatus
CHAPTER 3

Description of Apparatus

3.1. The High Pressure System

3.1.1. The Pressure Generator

A hand pump, manufactured by Pressure Products Inc. (U.K.) Ltd., was used, the maximum pressure attainable being 75,000 psig. The pressures were displayed on a Burdon gauge. No pressure intensifier was required to obtain pressures in the above range. The pressure transmitting fluid was petroleum ether of boiling fraction 120 - 160°C. This fluid was chosen because:

a) It has a very high electrical resistance, the conductivity given in the International Critical Tables as being in the order $10^{-15}$ to $10^{-18}$ ohm$^{-1}$ cm$^{-1}$.

b) It has a high freezing pressure which is necessary to prevent the solidification of the pressure transmitting fluid within the apparatus. It is a reasonable general assumption that the freezing point of the fluid increases by 25°C/1000 atm.

3.1.2. The Pressure Vessel

The pressure vessel was manufactured by Autoclave Engineers Inc., its working pressure being 60,000 psig. at 400°F. It was sealed by means of a viton 'O' ring and P.T.F.E. back-up ring which were retained by a large gland nut. After several unsuccessful attempts to seal the vessel the back-up ring was dispensed with and the 'O' ring was then found to seal satisfactorily at all pressures.
The vessel had an outside length of 11.25 inches and an outside diameter of 6 inches; the interior had a diameter of 2 inches and a maximum depth of 5 inches. Electrical access to the interior was by means of three "Kovac" electrodes which were secured into the cover by means of core type fittings. The pressure transmitting fluid entered through a connection in the base of the vessel, and sample tubes left by way of a similar hole and connection through the axis of the cover.

3.1.3. Piping
   a) General

   Seamless 304 stainless steel high pressure tubing, manufactured by Autoclave Engineers Inc. was used. The outside and inside diameters were 0.250 inches and 0.083 inches respectively and its working pressure was 60,000 psig. at 100°F.

   From the pump the high pressure pipe ran to an isolating valve and then to a cross. The bottom access to the cross was plugged with a standard fitting; the top access was connected to the base of the pressure vessel by a 2.75 inch nipple. The fourth access was fitted with a length of high pressure tubing which was bent at a right angle to rise above the top of the pressure vessel, and terminated in a bursting disc holder. The bursting disc was rated at 62,000 psig. at a temperature of 72°F.

   All pipe connections were of the AC cone type. The tube was chamfered at an angle of 58°, threaded with a left hand thread and a collar screwed on. A gland nut behind the collar forced the chamfered part of the tube into an angle of
60° in the part to which it was to be connected. The knife edge formed when these two slightly different angles were forced together formed a joint capable of containing the maximum pressure used in these experiments.

b) Sealing of Capillary Tubing

Stainless steel capillary tubing was chosen to withdraw samples from within the pressure vessel since its narrow bore would assist in controlling the volume of liquid taken and have minimum hold-up. The two capillaries left the pressure vessel along the interior of two short lengths of high pressure tubing which were terminated by two valves. Details of this arrangement are given in Section (3.3.1.b).

It was necessary to seal the capillary somewhere in the high pressure tubing, before the valve, in order to prevent hydraulic fluid from leaking into the sample being drawn off. Contamination of the sample with hydraulic fluid would not only cause considerable inconvenience during its analysis on the gas chromatograph but would also alter the equilibrium portions of MEK and water when in the presence of the third component. It was found most convenient to make the seal where the tubing entered the valve. Of the several methods tried the most successful is illustrated in Fig.(3-1). Brass bushes drilled axially with a hole just large enough for the capillary to pass through, were soldered into each end of the tube. The capillary was then soldered to the brass bush at each end. This arrangement was found to provide a satisfactory seal to the maximum pressure used in these components.

From the sample holder up to this seal the capillary was surrounded by hydraulic fluid at the same pressure, so that there was no pressure difference across the wall. However in the space between the two brass bushes the capillary experiences the full pressure of the system across
FIGURE (3-1) Method of sealing the capillary into the high pressure nipple
its walls, but since the ratio of the outside diameter to
the inside diameter is 3:1 (the same as the 0.250 inch
pressure tubing), it was considered that the capillary
would not burst. During the course of the experiments
there was no evidence to prove this assumption wrong.

3.2. The Constant Temperature Bath

3.2.1. Description

The tank was fabricated from 0.25 inch thick mild
steel plate with a large lip around the top to catch any
spillage that occurred on removing articles from the tank.
The dimensions of the tank were 12" x 18" x 3' deep and
contained approximately 25 gallons of shell SAE 30 motor
oil. The extra depth was allowed for the inclusion of
extra equipment if required. A valve at the base of the
tank allowed the oil level to be kept constant during
alterations in the temperature of the oil. The outside
four sides of the tank were lagged with glass wool and
enclosed in a hardboard box. A framework of welded, one
inch angle iron rested on the bottom of the tank and
supported the pressure vessel, electric immersion heater
and stirrer motor. The tank was fitted with a jib and
hoist which assisted with the lifting of the frame,
together with all its attachments, from the tank.

3.2.2. Heating & Control System

This system is shown schematically in Fig. (3-2).
A mercury contact thermometer in the oil bath acted as a
simple on-off device and fed back to a relay which supplied
current to a 5kw immersion heater. This heater was mounted
so that the heater elements hung vertically in the oil bath.
The oil was stirred by a constant rated 0.25 hp, electric
FIGURE (3-2) Temperature bath heating and control circuits
motor running at 940 rpm. The stirrer shaft was fitted with two impellers, one at the base and the other half way up, and adequate movement of the oil was achieved.

A surface thermostat was clamped to the outside of the tank and was set at 120°C. It fed back to the relay and would shut off the heater if the primary control system failed.

Using the above system it was found, by means of a copper-constantin thermocouple, placed in a specially made well in the wall of the pressure vessel, in conjunction with a chart recorder, that the temperature of the bath varied by 0.1°C at 50°C.

3.3. Sample Holders

3.3.1. Equilibrium Data Sample Holder

a) Description

In designing this part of the equipment a number of requirements had to be fulfilled:

i) Means must be provided for samples of both phases to be removed while the apparatus is still pressurised.

ii) Since samples were to be removed from it, its volume must be able to change.

iii) It must be completely leak proof since any leakage of hydraulic fluid inwards would change the equilibrium composition of the two phases.

iv) For equilibrium to be attained in reasonable time its contents must be stirred.

v) The whole apparatus must fit into a space 2 inches diameter and 5 inches at its maximum length.

A Number of unsuccessful attempts at designing and
building apparatus to the above requirements eventually resulted in the final successful version as shown in Fig(3-3).

The main body of the vessel (1) was turned from a piece of austenitic stainless steel rod. This rod was almost completely bored out to a diameter of 1.312", except for a thin diaphragm(2) approximately 0.020" thick, which supported a narrow bore tube (3) which acted as the exit for samples of the top layer and as a guide for the stirrer shaft (4). To the end of this tube was attached the capillary (7) which took the top sample. This connection was made by drilling a square bottomed hole in the end of (3) and tapping it 2BA. A brass connector (5) was soldered on to the end of the stainless steel capillary (7) (0.011 inches O.D. and 0.004" I.D.) and was tightly held by a modified hexagonal-headed, 2BA brass bolt (6), against the sharp shoulder formed at the base of the square-bottomed hole. Distortion of the brass connector, which resulted from the tightness of the bolt (6), against the shoulder, ensured a leak free point. The capillary (7) was sheathed with 0.011" I.D. P.T.F.E. sheathing (not shown) to prevent any short circuiting between the two electrodes (17). A stainless steel piston (8), fitted with two BS.025 P.T.F.E. 'O' rings (12), sealed the other end of the cylinder. Samples of the lower layer were withdrawn through a capillary (9) which was attached to the piston in the same way as that at the top, except that the connector (10) was made from stainless steel as was the OBA retaining bolt(11). Although the piston and cylinder were designed to B.S. 1806 leakage still occurred past the 'O' rings. To overcome this difficulty a stainless steel liner (13) was made to fit inside the
FIGURE (3-3). Detail of the assembly of the equilibrium cell.
pressure vessel and around the sample holder. This container was filled with mercury (14) to approximately the level shown and as the piston rose up the cylinder, on removing the samples, the mercury filled the empty space created. Any leakage of mercury past the 'O' rings would then not upset the equilibrium of the sample. In anticipation of mercury leaking into the cylinder, the capillary (9) was allowed to protrude about 0.5 inches above the connector (10), preventing any mercury being removed with the sample. To prevent the soldered joints on this connector being attacked by mercury, the solder was smeared with a protective layer of Autostic adhesive. Strain on the capillary (9) was minimised, when the piston rose, by allowing plenty of slack, in the form of a coil, below the piston.

The coil (15) was made from highly permeable radio metal 60 and enclosed a toroidally wound copper coil (16) which was wrapped in P.T.F.E. tape to act as insulation. This coil was connected to two of the electrodes (17) by insulated flexible copper wires (18) which were soldered to the electrodes, these joints being covered by shrinkable sheathing (19). An intermittent current was supplied to the coil. This current was interrupted by fitting a micro switch in the line which carried it. The micro switch was operated by a cam rotated by a chart recorder motor. The arrangement allowed four electrical pulses per minute to reach the coil, each of five seconds duration. Two holes were drilled in the core (15), one acting as an exit for leads from the coil, the other as an anchor for a tommy bar when tightening the core.
The stirrer consisted of a 1/16 inch diameter stainless steel shaft (4) near the top of which was soldered a thin (0.030 inch) disc (20) of radio metal 60 and secured at the other end of the shaft was a P.T.F.E. disc (21), perforated with 1/16 inch diameter holes. This disc was held between two 10BA nuts (22) and washers (23) and locked off with a 10BA locking nut (24). The stirrer rested on a P.T.F.E. circlip (25) set into a groove machined in the wall of the cylinder and the top of the shaft was guided by (3). The intermittent current attracted the high permeability disc (20) and subsequently let it fall back through the liquid to rest on the circlip (25). This circlip was set at effectively half way up the cylinder and by filling the cylinder with equal volumes of each phase, the reciprocating action of the stirrer constantly disturbed the interface of the two layers.

This sample holder was attached to the two arms of a supporting frame (25) by four stainless steel, 6BA counter sunk screws (27). The supporting frame itself was held to the cover of the pressure vessel (28) by three 3/16 inch BSF counter sunk screws (not shown).

An exploded view of the sample holder is shown in Fig.(3-4A) and the complete assembly in Fig.(3-5). For clarity the stainless steel mercury reservoir has been omitted in these two Figures.

b) Description of the Sampling System

In addition to the apparatus already described a system of valves was needed to control the withdrawal of samples. In order to ensure that the sample taken was representative of the contents of the sample holder under the conditions
FIGURE (3-4a)
Exploded view of the equilibrium cell

FIGURE (3-4b)
Exploded view of the compressibility cell
FIGURE (3-5) General arrangement of the equilibrium cell and valves
existing within the pressure vessel, it was necessary to:

i) flush out the fluid already in the capillary with some
of the contents of the sample holder.

ii) flush this liquid from the body of the valve which holds
back this fluid.

A system of valves was devised which enabled these two
procedures to be carried out and it is shown schematically
in Fig.(3-6). The capillary tubes from the sample holder
left the pressure vessel and were then threaded through a
2½" long high pressure nipple (8) which connected the 'Y'
block (1) to the pressure vessel cover. Connected to the
'Y' block by means of two more nipples were a pair of high
pressure three way valves (2) and connected to each of these
valves was a high pressure (although this was not necessary)
two-way valve (3). The capillaries were led through as far
as the upper ends of (4) where their ends were sealed
(details in Sect 3.1.3. b) flush with the end of this nipple.
Nipple five was connected by a silicone rubber tube to a
separating funnel containing acetone. This funnel was
mounted approximately six feet above the apparatus. Air
entering this separating funnel first passed through a 'U'
tube filled with self-indicating silica gel to ensure that the
acetone remained dry. Any liquid moved from the system left
by a 0.030" internal diameter capillary tube (6) and was
collected in a small test tube (7) sealed with a serum cap.
FIGURE (3-6) Schematic arrangement of the sampling valve system
3.3.2. Compressibility Data Sample Holder (Fig 3-7).

a) The Vessel

A cylinder (1), closed at one end, was bored out from a piece of solid stainless steel rod. The inside face of the closed end was finished flat and smooth and the whole length of the bore was polished. Into this was fitted a brass piston (2) which retained two B.S. 025 P.T.F.E. 'O' rings (3). Both cylinder and piston were designed to B.S. 1806.

The piston had a 5° lead so that if the piston should become tilted little damage would result to the bore of the cylinder. Brass was chosen for the piston since any contact between the piston and the cylinder would result in damage to the piston and not the cylinder. The inside face of the piston was machined as shown to assist with the removal of air bubbles which occur on filling the cylinder. The sample was introduced through the axial hole in the piston which was tapped 4BA. After filling this hole was sealed with a hexagonal headed brass bolt (4) which tightened onto a brass washer (5) and a P.T.F.E. washer (6). The head of the bolt was drilled and tapped 8BA and into it screwed the shaft (7) of a linear displacement transducer (13). The transducer was held by a beryllium copper spring clip (9) which was soldered (10) to a stainless steel support (11) screwed to the cylinder by four 6BA countersunk screws (12).

This apparatus was supported in the pressure vessel in the same manner as shown in Fig.(3-3), and the leads (8) from the transducer were soldered to the three electrodes in the cover of the pressure vessel.
b) **Linear Displacement Transducer**

This device was specially designed for use in compressibility measurements. The transducer was 1 inch long and 0.25 inch square, the shaft having a maximum travel of 0.75 inches. Anodised nichrome resistance wire (0.001 inch diameter) was wound on a stainless steel former and the resistance of the resulting coil was 2K.ohm. A wiper was fixed to the shaft in such a manner that the shaft was free to rotate, which enabled it to be easily attached to the piston. The windings and wiper were enclosed in a thin sheet metal casing.

It is estimated that the transducer could measure to within 0.13% of full scale.

c) **Transducer Power Supply & Reference Circuit**

The power supply circuit is shown in Fig.(3-8). It is a standard circuit consisting of a 240/12 volt transformer and rectifier bridge. The output voltage is stabilized by two 12 volt Zener diodes and is supplied across the 2K.ohm transducer the wiper of which is connected to one side of a Pye null detector.

The reference unit is shown in Fig.(3-9) where the ten turn potentiometer can be seen. The wiper of this potentiometer is connected to the other side of the null detector. This potentiometer was fitted with a null detector. This potentiometer was fitted with a dial which displayed the number of turns through which the adjusting knob had been turned. The dial was divided into one hundred equal divisions, thus the potentiometer could be read to one thousandth part of its total travel.
Changes in volume of the sample holder result in movements of the transducer shaft and a consequent change in the voltage across the null detector. The ten turn potentiometer is then adjusted to restore the voltage balance across the null detector. From the reading on the potentiometer the distance moved by the piston can be deduced (Sect 4.3.1.b)

d) Pressure and Temperature effects on the accuracy of the measurements.

Since each set of measurements was made under isothermal conditions, temperature is of no importance, displacements of the piston being measured from the reference position when $P=0$ at the temperature in question. Also, the thermal coefficient of the resistance is compensated by the use of a bridge circuit and thermo-electric emfs cancel due to the symmetry of the circuit.

Similar remarks apply to the effect of pressure except where the pressure affects the transducer coil and wiper, and also the dimensions of the cylinder itself. However, the compressibility of the metals used is very much less than the compressibility of fluids and, therefore, the changes in dimensions of the apparatus with pressure, whilst real, will have no significant effect on the experimentally obtained values of compressibility.
FIGURE (3-7) Detail of the assembly of the compressibility cell
FIGURE (3-8) Circuit diagram of the transducer power supply

- Lamp
- Sw1
- Transformer (12-0-12V)
- Rectifier Bridge
- Z1 (12V)
- Z2 (12V)
- 240V ac
- Transducer
- To Null Detector
FIGURE (3-9) Circuit diagram of the transducer reference circuit
3.4. The Gas Chromatograph

3.4.1. General

The instrument used was a Pye Panchromatograph with twin 0.125 inch inside diameter glass columns, both five feet in length with thermal conductivity detector, chart recorder and an integrator supplied by Gas Chromatography Ltd.

3.4.2. The Column

The column was required to separate water acetone and methyl ethyl ketone. Of these three components, the water presented a problem since the trailing edge of its peak always tails. The Porapak range of column packings give sharp, symmetrical peaks with polar compounds, such as water, and for this reason Porapak P-S (80 mesh) was chosen as the column packing with helium as carrier gas. After analysis of the above three component mixture at several temperatures an optimum column temperature of 137.5°C was found to give complete separation and a short elution time, with a gas rate of 50ml/min. Elution times for each component are shown below:

- Water 60 sec
- Acetone 154 sec
- MEK 300 sec
- Total 390 sec

An actual chromatograph is shown in Fig. (3-10).

3.4.3. Calibration of the Chromatograph.

For meaningful results to be obtained from this instrument, its response must be a linear function of sample size passing through the origin. Samples varying in size from 1 to 10µl were injected into the column and the volumes injected plotted against the response after it had
FIGURE (3-10) An actual chromatogram: water/acetone/MEK system
been corrected to a constant value of attenuation. Initial experiments using nitrogen as a carrier gas proved unsuccessful as the plot obtained was markedly curved. As pointed out by Littlewood (67) this is to be expected. If a carrier gas and sample vapour have comparable molecular dimensions then non-linearity is likely to occur at relatively small vapour concentrations. Organic vapours with molecular weights of between 50 and 100 i.e. containing between two and six carbon atoms give a non-linear response with heavy carrier gases, for example, nitrogen and argon. The use of hydrogen or helium as the carrier gas restores linearity to the response curve and changing the carrier gas to helium did indeed result in a straight line being obtained.

Using a micro syringe fitted with a chaney adapter, which ensured that the volume injected each time was constant, ten 1µl samples of pure methyl ethyl ketone and ten of water were injected into the column and the average response for each calculated. From a knowledge of the temperature of the pure components (taken as the ambient temperature) and their densities at this temperature, the mass, M, of 1µl of pure component could be calculated. The response produced by this mass of component, at an attenuation, A, was

\[ R = M \times A. \]

Since the response had been shown to be linear with sample size in the range 1-10µl, the above identity applies to any sample size in this range and can be written in the form of the equation for a straight line passing through the origin:
\[ y = mx \]

or in the current notation:

\[ RA = mM \]

\[ \therefore M = \frac{RA}{m} \]

The value of \( m \) was found from the response data of 1\( \mu l \) of each pure component.

i.e. \[ m = \frac{RA}{mass \ 1\mu l \ pure \ component} \]

Thus the mass of component in any sample is a simple function of response and attenuation.
CHAPTER 4.

Experimental Technique.
CHAPTER 4.

Experimental Technique.

4.1 Specific Gravity Measurements.

4.1.1 Apparatus.

Sprengel pyknometers of twenty five millilitre capacity and manufactured from borosilicate glass were used. This type was chosen since the contents of the pyknometer could be completely sealed from the atmosphere and this enabled the pyknometer to be dried in a dessicator, prior to weighing, without loss of any of the aqueous component. The pyknometers were weighed using a Stanton balance capable of weighing accurately to one part in 10000.

A pyknometer is illustrated in Fig. (4 - 1) where caps, identification tag and graduation mark are shown.

4.1.2 Experimental Method

a) Preparation of Apparatus

All glass apparatus was soaked in chromic acid, rinsed with tap water and then distilled water, rinsed with acetone, dried with compressed air and finally roasted in an oven for one hour at 200°C. The balance was zeroed before any weighings were made.

b) Water Calibration of Pyknometers.

The clean pyknometers (with caps) were weighed empty on the Stanton balance. They were then filled with distilled water. This was done by attaching one end of a narrow bore rubber tube to the capillary which entered the base of the pyknometer, the other end of the rubber tube being immersed
FIGURE (4-1) Sprøngel pyknometer
in a beaker of distilled water. A knock-out pot was attached by another length of rubber tubing to the other capillary of the pyknometer. Air was sucked, by mouth, from the pyknometer through the knock-out pot, which resulted in the distilled water being drawn into the pyknometer. This process was continued until the pyknometer was approximately filled to the calibration mark.

c) Temperature equilibrium and level adjustment.

The filled pyknometers were suspended in a well stirred, constant temperature water bath, so that only the ends of the capillaries protruded above the water level of the bath. They were left in this bath for eight hours to allow the contents of each pyknometer to attain the temperature of the bath along with the consequent change in volume.

With the pyknometer remaining in the bath the knockout pot was attached to its top limb. The contents of the pyknometer were subjected to gentle pressure (using the mouth) and the contents left the pyknometer, drop by drop from the other limb. Each of the drops was removed from the end of the limb by a piece of filter paper. The graduation mark on the upper limb, which was submerged below the water level of the bath, was observed by means of a dentist's mirror. When the level of liquid in the upper limb became level with this mark the pyknometer contained a volume of liquid which was accurately and easily reproducible. The same procedure was repeated for the other pyknometers.

After this procedure the pyknometers were left in the bath for a further hour when their volumes were again checked. The caps were then fitted and the pyknometers were removed for drying.
d) **Drying and Weighing.**

The water adhering to the pyknometers had to be removed before any accurate weighings could be made. The pyknometers chosen were of a type which allowed them to be dried in a dessicator containing anhydrous calcium chloride, without any effect on their contents. Initially the pyknometers were dried until their weights ceased to change as shown by repeated weighings. It was found that a period of 24 hours drying led to the pyknometers being completely dry and this drying time was consequently adopted. Once dry the pyknometers were weighed and the weight of liquid contained by each found.

e) **Preparation of Solutions.**

A technique was used which prevented any of the volatile methyl ethyl ketone from being lost once it had been weighed out.

A clean 250 ml. conical flask, fitted with a rubber serum cap, was weighed. Since the solutions were being made up on a weight per cent basis, the most convenient quantity to make up at a time was 100 ml., which was sufficient to fill three pyknometers. Using a 20 ml. glass syringe fitted with a stainless steel hypodermic needle, the required weight of each component was injected through the seal. By this means solutions could be made up very close to the desired composition without loss by evaporation.

f) **Determination of the Specific Gravity of the Solutions.**

Specific Gravity is defined as the weight of a given volume of the liquid divided by the weight of an equal volume
of water at the same temperature.

The specific gravity of each solution was found three times and the average taken. The pyknometers, once calibrated with water and marked with a removable tag, were filled with the solutions. The procedure followed for the water calibration was repeated at the same temperature. Thus the weight of the solution contained in a pyknometer divided by the weight of water contained by the pyknometer at the same temperature gave the specific gravity of the solution at that temperature.

4.2 Determination of the Liquid-Liquid Equilibrium Data.

4.2.1 Preparation of the Apparatus.

a) Filling of the Sample Holder.

The sample holder with the vessel cover and 'Y' block attached was inverted and held in a retort stand. By loosening the bolt in the centre of the piston the capillary tube was removed. Equal quantities of each layer of a solution of MEK/water, made up at room temperature, were injected into the sample holder using a hypodermic syringe. The capillary was then replaced and its retaining bolt tightened.

When filling the sample holder after a previous experimental run, it was necessary, after removing the capillary, to draw the piston back down the cylinder, since the piston moved up the cylinder as samples were withdrawn. A simple tool was used which evenly drew the piston to the bottom of the cylinder and resulted in no damage to the bore.

b) Assembly of the Apparatus.

Once the sample holder was filled the stainless steel cylinder liner was inserted into the pressure vessel and
approximately 75 ml. of mercury were poured in by means of a funnel connected to a length of polythene tubing. The sample holder together with the vessel cover and 'Y' block, was then lowered into the vessel and the closing nut screwed down until almost tight. The two pairs of valves were then attached and hydraulic fluid gently pumped into the vessel until it seeped out around the closing nut. The return valve to the hydraulic reservoir was opened and the closing nut tightened, forcing excess hydraulic fluid back to the reservoir and ensuring that no air was trapped within the vessel.

Each time the sample holder was removed from the pressure vessel to be refilled, it was necessary to separate the hydraulic fluid which had contaminated the mercury. The liner was removed by inserting two aluminium welding rods, hooked at one end, into the two holes provided for this purpose, near the top of the liner, and then withdrawing the liner containing the mercury and the hydraulic fluid. The contents of the liner were poured into a separating funnel and the lower mercury layer drawn off and returned to the liner for further use.

4.2.2. Experimental Method.

a) Attainment of Equilibrium.

Before the apparatus was assembled the oil bath was allowed to reach a constant temperature. Once the sample holder was fixed inside the pressure vessel, the electrical connections to the stirrer were made and the magnetic stirrer was set in operation at the control box. The pressure was adjusted in the vessel to the required value and then half an hour was allowed for any heat of compression to be dissipated. The pressure was then adjusted, if required, and the vessel isolated from the pump by means of a valve to prevent any loss
of pressure due to leakage of hydraulic fluid past the non
return valves in the pump.

After twenty-four hours the first sample of each layer
was taken and analysed three times on the gas chromatograph,
an average of the three readings being taken, which usually
varied by $\pm 0.5\%$. Further samples were taken at six hourly
intervals until the composition was found to be consistent
with the previous result. By this method equilibrium was
found to be obtained usually after 36 hours.

Once equilibrium had been attained the pressure was
altered, as described above, and the process repeated.

b) Measurements at Atmospheric Pressure.

Although for high pressure runs samples were taken at
constant temperature and at various pressures (this was
most convenient since pressure equilibrium was achieved
more rapidly than temperature equilibrium) the first set of
data was taken at a constant pressure of 1 atm. and at various
temperatures in the range 25 - 100°C. These data, on comparison
with published liquid-liquid data for the methyl ethyl ketone
system, give an indication of the precision with which liquid-
liquid equilibrium data could be found using this apparatus.
The results obtained compare well with those of CAMPBELL,
KARTZMARK & FALCONER (28) and the less numerous results of
GIMMINGS, PLONK & CARTER(21). The success achieved with
these initial readings increased the confidence in those yet
to be taken at elevated pressures.

c) Method of Sample Removal.

With the system pressurised valve (2) in Fig. (3-6) was
slowly opened and a quantity of liquid removed from the
capillary to flush out the whole length of the capillary (Appendix II), valve (2) was then closed and valve (3) opened allowing acetone to run through valve (2). When approximately 20 ml. of acetone had been collected valve (3) was closed and valve (2) was assumed only to contain acetone (Appendix II). Valve (2) was then opened slowly and approximately 0.5 ml. of liquid was allowed to run out of the capillary (6). This sample was collected in a 4 ml. test tube (7) sealed with a rubber serum cap. The sharpened end of the capillary (6) was forced through this seal prior to the sample being removed, thus the sample was collected with no losses due to evaporation. The acetone not only served to flush the previous sample from the valve, but also to act as a mutual solvent for the new sample should it split into two phases at ambient conditions.

Removal of the contents of the sample holder resulted in a drop in pressure throughout the system. However if the samples were removed sufficiently slowly, it was easy to maintain the pressure at a constant value by pumping in more hydraulic fluid as the sample was removed. Thus the composition of the two layers did not change as the pressure attempted to drop. Also, should any pressure change occur during this operation, it was expected that the resulting composition change would be negligible, bearing in mind the time taken for the sample to reach equilibrium in the first place.

Samples of the system at atmospheric pressure were removed in exactly the same manner, except that the hydraulic pump was used to generate just sufficient pressure to force the samples through the capillaries. The required pressure was so low that it did not register on the Bourdon gauge.
4.3 Determination of Compressibility Data.

4.3.1 Preliminary Measurements.

a) Vessel Volume.

The internal dimensions of the cylinder and the dimensions of the piston were measured to ± 0.001 inches using micrometers. The internal volume of the cylinder was then calculated with the base of the piston flush with bottom of the cylinder.

b) Calibration of Transducer.

The shaft of the transducer was fully extended and its end clamped in a holder normally used for a micrometer-pipette, Fig. (4-2), leaving the body of the transducer free to move. The terminals of the transducer were connected to the power supply and the voltage drop across the transducer balanced by adjusting the variable resistor (10 turn potentiometer). With the transducer shaft fully extended a null point was not obtained until the potentiometer was at the limit of its range.

The micrometer head was then adjusted until it just touched the base of the body of the transducer, this was best observed by watching the null detector. Using the potentiometer a null point was again found. The readings on the micrometer head and potentiometer were noted. The micrometer head was then screwed down by increments of 0.025". This had the effect of pushing the body of the transducer up the shaft. On each occasion the null detector was balanced and the potentiometer reading noted. This process was continued until the transducer had reached the end of its travel. At this point the potentiometer was at the
FIGURE (4-2) Micrometer used for the calibration of the transducer
limit of the other end of its range. A calibration chart was then plotted of distance moved by the transducer shaft against the number of turns of the potentiometer required to achieve a null point. Thus from this curve the distance moved by the piston could easily be found by reference to the potentiometer. This calibration chart, Fig. (4-3) was found to be linear for the most part but substantial deviations from linearity occurred at each end of the shaft's travel.

c) Zeroing of the Transducer.

To enable the volume of the sample holder to be accurately determined at any temperature and pressure, a reference point for the piston and the transducer had to be found. A knowledge of the position of the transducer shaft when the base of the piston is flush with the bottom of the cylinder would be most useful. Using a fly press the piston (refer to Fig. 3-7) was gently pushed into the cylinder until its base was flush with the bottom of the cylinder. The apparatus shown in Fig. (4-4) was then assembled (a detailed description of this procedure is given below). Once assembled the terminals of the transducer were connected to the power supply, the null point found and the reading on the potentiometer noted. The knowledge of this quantity enabled the true volume of the contents of the cylinder to be calculated should there be any change in volume due to thermal expansion once enclosed within the pressure vessel.

4.3.2. Apparatus - General Assembly.

The assembly that fitted inside the pressure vessel is shown in Fig. (3-7). This was attached to the cover of the
A typical transducer calibration curve
pressure vessel by exactly the same means as those by which
the equilibrium data sample holder was held. For these
experiments the sampling valves and 'Y' block were removed
and the cover of the vessel sealed with a plug. The whole
assembly is shown in Fig. (4-4).

4.3.3. Experimental Method.

a) Filling and assembly of sample holder.

The cylinder and piston were cleaned with detergent,
thoroughly rinsed with tap water, then distilled water and
finally dried. Using a fly press and a suitable spacer the
piston was pushed into the cylinder until its base was
approximately 0.250" inside the cylinder. The cylinder was
then filled with the liquid under test by injecting it with a
hypodermic syringe through the hole in the centre of the piston.
The sample holder was then vigorously knocked on the bench
until no more air bubbles appeared at the hole in the piston.
It is felt that from the experience of removing trapped air
bubbles from the pyknometers, that this method was satisfactory
in removing the air bubbles adhering to the wall of the cylinder.
Once the air had been removed the hole in the piston was sealed
using the P.T.F.E. and brass washers and securing them with
the 4BA bolt. The cylinder was then attached to the cover of
the vessel by screwing it to the supporting frame attached to
the cover. Next, the transducer shaft was screwed into its
locating hole, its support clipped round it and the support
screwed to the vessel.

This assembly was then placed in the pressure vessel,
the power supply connected to the three electrodes, and the
pressure vessel closed as described in Sect. 4.2.1.b.
FIGURE (4-4) Arrangement of the compressibility cell before insertion into the pressure vessel
b) Attainment of thermal equilibrium.

Once inside the pressure vessel the liquid under test expanded until it had reached the same temperature as that of the oil bath. This expansion resulted in a downward movement of the piston (the reason why the piston was initially pushed some distance into the cylinder) which could be observed by the deflection of the null detector. Using the potentiometer the null point was found once again. The process was continued until the null detector ceased to show any further deflection. During this time the return valve to the hydraulic reservoir was open. It was then that the liquid under test was considered to have attained thermal equilibrium and the potentiometer reading was noted. From this potentiometer reading and the one obtained during the "zeroing" procedure the initial volume of the sample could be accurately calculated.

c) The Measurement of Compressibility.

Compressibilities were measured up to pressures of 25,000 psi, at intervals of 2,500 psi.

The return valve to the hydraulic reservoir was closed and the pressure in the vessel raised to 2500 psi. The movement of the piston was determined by adjusting the potentiometer until the null point was obtained. The apparatus was left for 15 minutes during which time any heat generated as a result of the compression of the hydraulic fluid, was dissipated, resulting in a drop in pressure and a slight downward movement of the piston. A continual upward movement of the piston (observed from the null detector) indicated leakage of fluid past the 'O' rings.

Normally these pressure changes were hardly noticeable between the 2500 psi intervals, however, if this procedure
was not followed the cumulative effect would lead to considerable inaccuracies in the region of the maximum pressure used. When necessary the pressure was adjusted to the required value and the null detector finally zeroed. During this operation, care was taken to ensure that in approaching the null point (and finally locating it) the potentiometer was always turned in an anti-clockwise direction. By this means the backlash in the potentiometer was always taken up and could not cause inaccuracies between one reading and the next (the same procedure was followed when calibrating the transducer). The pressure and potentiometer readings were noted. This procedure was repeated at each pressure up to the maximum.

Once the maximum pressure had been achieved the pressure was lowered in steps of 2500 psi. 15 minutes were again allowed for thermal equilibrium to be achieved and after final adjustments to pressure and potentiometer their values were noted. On reaching atmospheric pressure the final reading of the potentiometer was compared with its initial reading. These two readings being equal indicated that no leakage had occurred past the 'O' rings in either direction. In practice ± 0.05% of full scale of the potentiometer dial was considered acceptable. If the difference was greater than this requirement then the results were considered insufficiently accurate and the run was repeated.

The above procedure was used to obtain the compressibility of pure water, pure Methyl ethyl ketone and mixtures of these two components at temperatures of 30, 50 and 70°C.

4.4.1 Compressibility of Water.

The compressibility of water was measured by the method described above and the results obtained compared with Bridgman's data for the compressibility of water. Fig. (4-5) compares the two sets of data.

The dashed line represents Bridgman's data and the continuous line represents the results obtained during this work. At the three temperatures considered the respective points virtually lie on the same curve. The points obtained in this work lie on another curve. Inspection of Fig. (4-5) shows that there appears to be a systematic error in the method used to obtain the compressibilities in this work. In all cases the error is +0.003.

For the calculation of the volume change on mixing at high pressures the compressibility data are required relative to the temperature under consideration, and the values obtained in this work have been calculated on that basis. Bridgman presents his data relative to the volume of water at 0°C and, therefore, it was necessary to convert his data, relative to the temperature at which it was obtained for use in Fig. (4-5). This conversion was achieved by using the water density data from the Smithsonian Tables (Table 287 for 30°C and Table 290 for 50 and 70°C). The compressibility at temperature, $T$, was that found from the formula:

$$\frac{V}{V_0} = \left( \frac{\rho_T}{\rho_0} \right) \times \frac{\rho}{\rho_0}$$

where: $V/V_0$ = compressibility referred to temperature, $T$. 
FIGURE (4-5) Comparison of the water compressibility obtained in this work with that of Bridgman.
4.4.2 Compressibility of Methyl Ethyl Ketone.

The compressibility of methyl ethyl ketone was measured by the method described above at the same temperatures as water. Since there are no previous data with which to compare them, and also considering the future use of their values, they were calculated with respect to their volume at atmospheric pressure and the temperature under consideration.

4.4.3 Compressibility of Methyl Ethyl Ketone/Water Mixtures.

The compressibilities were measured at the same temperatures and by the same method as previously described. The mixtures chosen were in the range 0 to 15 wt.% methyl ethyl ketone and 90 to 100 wt% methyl ethyl ketone. At these compositions, as seen from the phase diagram, Fig. (1-1), no phase splitting would occur at these temperatures.

Six mixtures were investigated. Their approximate compositions were 5, 10, 15, 90, 94 and 97 wt.% methyl ethyl ketone and were made up using the same method as that described in Sect. 4.1.2.e.

The actual compositions used in the following compressibility work were:

<table>
<thead>
<tr>
<th>wt.% MEK</th>
<th>Mole fraction MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.067</td>
<td>0.013</td>
</tr>
<tr>
<td>10.025</td>
<td>0.027</td>
</tr>
<tr>
<td>15.190</td>
<td>0.043</td>
</tr>
<tr>
<td>91.022</td>
<td>0.717</td>
</tr>
<tr>
<td>94.092</td>
<td>0.799</td>
</tr>
<tr>
<td>97.129</td>
<td>0.894</td>
</tr>
</tbody>
</table>
CHAPTER 5

TREATMENT OF RESULTS
5.1. Specific Gravity Measurements

5.1.1. Calculation of the Specific Gravity and Density of the Mixtures

The results obtained (Sect. 4.1.2.f) for each pykrometer, first containing water, and then a methyl ethyl ketone/water mixture, readily enabled the calculation of the specific gravity of the mixtures, since:

\[ \text{s.g.} = \frac{\text{Weight of a volume of mixture at temp } T}{\text{Weight of an equal volume of water at temp } T}. \]

The specific gravity was calculated at 30\(^\circ\), 50\(^\circ\) and 70\(^\circ\)C by this method, from three experiments for each composition, and the mean of these three results taken. Multiplication by the density of water at the same temperature, given by the Smithsonian Tables (93) converts the specific gravity to the density, the units of which are gm/ml. These results are summarised in Table (5-1).

5.1.2. Calculation of the Volume change on mixing

At constant temperature and composition, the actual molar volume, \( V_{\text{act}} \), of the mixture is, from the definition of the density,

\[ V_{\text{act}} = \frac{72.12x_1 + 18.02 (1-x_1)}{\rho_{\text{mix}}} \]  

(5.1-1)

where \( x_1 \) is the mole fraction of the ketone.

The ideal molar volume, \( V_{\text{id}} \), under the same conditions is given by:

\[ V_{\text{id}} = x_1 V_{\text{MEK}} + (1-x_1) V_{\text{H}_2\text{O}} \]  

(5.1-2)
where: \( V_{MEK} \) = the molar volume of pure MEK at temp T. 
\( V_{H2O} \) = the molar volume of pure water at temp T.

Thus with the measured values of the specific gravity of MEK, at a given temperature, the value of \( V_{MEK} \) is easily found from the definition of the density. Similarly the value of \( V_{H2O} \) at the same temperature is found from the water density data (95) and equation (5.1-2) becomes:

\[
V_{id} = x_1 \frac{72.12}{\rho_{MEK}} + (1-x_1) \frac{18.02}{\rho_{H2O}}
\]

where \( \rho_{MEK} \), \( \rho_{H2O} \) are the densities of MEK and H\(_2\)O respectively at the relevant temperature.

The excess volume of mixing is defined as the difference between the actual volume and the ideal volume. Conversion of the composition from weight per cent to mole fraction and subtraction of equation (5.1-3) from equation (5.1-1) yields the excess volume of mixing. The values at 30, 50 and 70°C are shown in Tables (5-14) to (5-16).

5.1.3 Comparison with other Workers

Two sets of data giving the variation of the specific gravity with composition, those of Tarasov et al. (96) taken at 22°C and those of Boeke and Hanewald (97) taken at 21°C, agree well with each other, and also with those taken at 21.5°C during this work.

From the specific gravity data obtained at 21.5°C during this work, shown in Table (5-2), the volume changes on mixing were calculated, and are shown in Table (5-3). They are plotted together with those calculated from the specific gravity data of Tarasov et al and Boeke & Hanewald in Fig.(5-1). The values of \( \Delta V \) at temperatures of 30, 50 and 70°C
FIGURE (5-1) Comparison of the volume change on mixing data obtained at 21.50°C with that of other workers.
are shown plotted in Fig. (5-20).

Landholdt & Bornstein (98) state that the density of methyl ethyl ketone is well represented in the temperature range 0-50°C by:

\[ \rho = 0.82511 - 1.022 \times 10^{-3} T - 0.46 \times 10^{-6} T^2 \]  \hspace{1cm} (5.1-4)

Below are shown the values of the density of methyl ethyl ketone calculated from this equation at temperatures of 30, 50, and 70°C, compared with the values obtained in this work. At 30 and 50°C the agreement is good, at 70°C, however, the agreement is rather poor, possibly due to the fact that this temperature is out of the temperature range of equation (5.1-4).

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Landholdt &amp; Bornstein</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.79444</td>
<td>0.7944</td>
</tr>
<tr>
<td>50</td>
<td>0.77326</td>
<td>0.7728</td>
</tr>
<tr>
<td>70</td>
<td>0.75172</td>
<td>0.7486</td>
</tr>
</tbody>
</table>
5.2. Equilibrium Data Measurements

5.2.1. Measurements at Atmospheric Pressure

a) Testing Technique

Six samples of the upper and lower layer were removed and analysed, as described in Sect.4.2.2., in the temperature range 25 - 100°C. The results are shown in Table (5-4). Their values are in good agreement with Campbell, Kartzmark and Falconer (28) and also with the less extensive data of Ginnings, Plonk and Carter (21). The results of this work compared with the data of the above two workers are shown in Fig. (5-2).

b) Determination of Empirical Constants

The data obtained above, together with the data of other workers, (21) (23), (28) and (29), were used to determine the constants in the van Laar, NRTL (α fixed at 0.3), Heil and Orye equations for each individual pair of data points, i.e. individual tie-lines.

For equilibrium between two partially miscible phases it is a necessary thermodynamic condition that the activity of a component in both phases is equal

\[ a_i = a_i^1 \]  \hspace{1cm} (5.2-1)

therefore, from equation (2.1-17)

\[ x_i = x_i^1 \]  \hspace{1cm} (5.2-2)

This equality was used in a computer programme to calculate values of A and B for each of the above mentioned equations which best fitted the experimentally obtained data. The above-mentioned solutions to the Gibbs Duhem equation may be expressed by the general term:

\[ \ln \gamma_i = f(x_1, x_2, A, B) \]  \hspace{1cm} (5.2-3)

Taking antilogs of equation (5.2-3) and substituting into equation (5.2-2) gives:
FIGURE 5-2) Liquid-liquid equilibrium data for the MEK/water system at 1 atm
\[ x_1 \cdot \exp[f(x_1, x_2, A, B)] = x_1 \cdot \exp[f(x_1, x_2, A, B)] \quad (5.2-4) \]

The selection of suitable values of A and B yields a calculated value of \( x_1 \) from equation \((5.2-4)\), using experimentally obtained values of \( x_1, x_2, x_1^i \) and \( x_2^i \).

The equation for the calculated value of \( x_1 \) is obtained from equation \((5.2-4)\):

\[ x_1 \text{ calculated} = x_1 \cdot \exp[f(x_1, x_2, A, B) - f(x_1^i, x_2^i, A, B)] \quad (5.2-5) \]

The difference between the experimental and calculated values of \( x_1 \) may either be positive or negative, but squaring this difference will always yield a positive value. This procedure is repeated for each pair of values of \( x_1 \) and \( x_1^i \) and then with each pair of experimentally obtained values of \( x_2 \) and \( x_2^i \). The sum of the squared differences obtained is minimised by adjusting the values of A and B.

Thus the resulting values of A and B obtained are specific to one tie-line at the corresponding temperature. Table (5-5) shows the values of the constants obtained.

c) Temperature dependence of the constants.

The constants derived as described above are shown plotted in Figs. (5-3), to (5-6) against temperature. To each of these curves a second order polynomial in temperature was fitted, and in each of the above figures the solid line represents the best fit. The polynomial used in each case was of the form:

\[ A = a_{10} + a_{11}T + a_{12}T^2 \quad (5.2-6) \]

and the values of the coefficients, \( a_{10}, a_{11}, \) and \( a_{12} \), corresponding to each equation are tabulated in Table (5-6).
FIGURE (5-3) The van Laar constants vs temperature at 1 atm
FIGURE (5-4) The NRTL constants vs temperature at 1 atm (α=0.3)
FIGURE (5-5): The Heil constants vs temperature at 1 atm
FIGURE (5-6) The Orye constants vs temperature at 1 atm
FIGURE (5-7) Method of prediction of tie-line data
FIGURE (5-8) Variation in liquid composition with pressure for the MEK/water system
FIGURE (5-9) Variation of the Orye constants with pressure at various temperatures
FIGURE (5-10) Tie line data interpolated by the Orye equation at 1 atm
d) Prediction of tie-line data

With a knowledge of the variation of each constant with temperature it is possible to predict tie-line data at various temperatures, utilizing one of the four equations.

During the following treatment the activities of the components in the two phase region are fictitious but are considered to be continuous. The activities in the two-phase region have no physical significance but are generated only by the particular empirical expression for $g^E$ or $\ln Y$.

The activities of the two components of a partially miscible binary system, when plotted against mole fraction, have the form shown in Fig. (5-7). Both curves exhibit a maximum and a minimum. When an empirical fit is used their exact form is decided by the algebraic expression used to represent $g^E$ and hence the activity.

For equilibrium between the two liquid phases the activities must be equal. Referring to Fig. (5-7), for equilibrium of component (i) between the two phases of compositions represented by the points C and D, or A and B, then $a_1 = a_1^\dagger$. Similarly for component (ii), $a_2 = a_2^\dagger$.

The requirements of these two equalities are met separately by the points U and V which lie in the two phase region, but both are not normally satisfied simultaneously. To avoid these two points being found rather than A, B, C and D, a feasible region of search is determined. The miscibility gap includes the region between the maxima of curves (i) and (ii), the values of $(\partial a_1/\partial x_1)_{T,P}$ and $(\partial a_2/\partial x_2)_{T,P}$ changing in sign at these points. At the two maxima the differentials are equal to zero which is the conditions for incipient instability.
Thus the working ranges lie between \( x_1 = 0 \) and the maximum of curve (i) and \( x_1 = 1 \) and the maximum of curve (ii) and are located by searching for the maximum of each curve by using a simple search technique. Having found these two working ranges the search for \( x_1 \) and \( x_1^1 \) etc. is confined only to them.

The value of \( x_1^1 \) at point B is found by first assuming a value of \( x_1 \), at point A, and then using an equation of the form given by equation (5.2-5) to calculate the value of \( x_1^1 \). The concentration of the second component, at point C, is:

\[
x_2^1 = 1 - x_1^1 \quad (5.2-7)
\]

Using this value of \( x_2^1 \) the above procedure is repeated to find the value of \( x_2 \) at point D. The value obtained should be given by

\[
x_2 = 1 - x_1 \quad (5.2-7a)
\]

but if equation (5.2-7a) is not satisfied the value of \( x_1 \) is adjusted and the procedure repeated.

A demixing curve for the MEK/water system, obtained using the above method and the Orye equation as the empirical expression for the activity coefficient, is shown in Fig. (5-10). It is the Orye equation that performs best in this application.

e) Dependence of constants on composition

The tie-lines obtained as functions of temperature and pressure have been used to obtain the dependence of various two parameter equations over the boundaries of the two-phase region. If, however, two parameters are inadequate then they themselves will be functions of composition.

Examination of vapour-liquid equilibrium data at atmospheric pressure yields different value of \( x \) (together with the appropriate composition in the vapour phase), at an almost constant temperature of around 70° C. From such data values
of $g_{RT}^E$ can be derived and then fitted by the equations used for the liquid-liquid equilibrium data.

The vapour-liquid equilibrium data of Siegleman & Sorum (78), Othmer & Benenati (80), Other, Chudgar & Levi (81) and Ellis & Garbett (86) was used to derive values of $g_{RT}^E$ for which the best fits were found for the various equations. The parameters found for these data do not agree well with the parameters found from the liquid-liquid equilibrium data at 70°C. This is not surprising, however, since values of $g^E$ derived from the vapour-liquid equilibrium data show considerable scatter, especially at low concentrations of MEK where some of the values are negative.

5.2.2. Determination of constants at high pressure

The equilibrium data determined at high pressure and various temperatures, plotted in Fig. (5-8), were used in exactly the same manner as the atmospheric pressure data in order to determine the values of the empirical constants at various pressures but at constant temperature. The values of the constants of the van Laar, NRTL ($\alpha$ fixed at 0.3), Heil and Orye equations at different pressures and in the temperature range 25 - 100°C are shown in Table (5-7).

Of the four equations the Orye equation is of the most interest. The variation of the Orye constants with pressure at various temperatures is shown plotted in Fig. (5-9) from which it can be seen that these sets of points at the various temperatures lie on a series of curves. These curves are well represented by a quadratic function in pressure. The coefficients of the equation found for each of these curves are shown in Table (5-8) and the curves are drawn on Fig. (5-9). It may well be possible to relate these pressure coefficients to
temperature, perhaps by means of polynomials in temperature, and thereby obtain an expression for the simultaneous variation of the Orye constants with temperature and pressure. Such a line of approach has not been further pursued in this work since it is felt that the final results would be somewhat tenuous.
5.3. Compressibility Measurements

5.3.1. Expression of Compressibility

The compressibilities obtained in this work were expressed as \( V/V_0 \), where \( V \) is the volume of the liquid, at a given pressure and fixed temperature, and \( V_0 \) is the volume of the liquid at atmospheric pressure and the same temperature. This form of expression was preferred to that of Bridgman, who made \( V_0 \) equal to the volume at one atmosphere and \( 0^\circ C \), since at atmospheric pressure (effectively 0 psi) the curves of \( V/V_0 \) vs. \( P \) pass through the point \((1, 0)\) which brings clarity to the initial appearance of the results and also simplifies the subsequent curve fitting and calculation of \( v^E \) from them. Values of \( V/V_0 \) are shown in Tables (5-9) to (5-11) plotted in Figs. (5-11) to (5-13).

5.3.2. Expression of the compressibilities in terms of Pressure

Each of the eight curves obtained for each temperature was fitted to polynomials in pressure, obtained, once again, using a least squares method. The fit was of the form:

\[
\frac{V}{V_0} = a_1 + a_2 P + a_3 P^2 + a_4 P^3 \tag{5.3-1}
\]

where \( a_1, a_2, a_3 \), and \( a_4 \) are coefficients.

Fits were found for both second and third order forms of equation (5.3-1). Variances were calculated for each of the curves, and the average of the twenty four variances taken. The second order fit was found to give an average variance of \( 3.1 \times 10^{-8} \), while the third order curve had an average variance of \( 1.3 \times 10^{-8} \).
FIGURE (5-11) V/V₀ vs pressure for MEK/water mixtures at 30°C

P x 10³ (psi.)
FIGURE (5-12) \( V/V_0 \) vs pressure for MEK/water mixtures at 50°C

\( P \times 10^{-3} \) (psi)
FIGURE (5-13) \( V/V_0 \) vs pressure for MEK/water \( P \times 10^{-3} \) (psi.) mixtures at 70°C.
The third order form of equation (5.3-1) was chosen to represent the \( V/V_0 \) vs. \( P \) curves. Although more complicated than the second order form, it could predict liquid compressibilities more accurately, and this was considered a great advantage since the calculation of \( v^E \) essentially involves finding the difference between two similar numbers which may differ very slightly. The greater complexity of this equation was no disadvantage since the calculation of \( v^E \) was to be done by means of an electronic computer.

The coefficients for equation (5.3-1) which were found by the fitting procedure for each compressibility curve are shown in Table (5-12).

5.3.3. The determination of the Coefficient of Isothermal Compressibility

The coefficient of isothermal compressibility defined as

\[
\beta = -\frac{1}{V_0} \cdot \frac{\partial V}{\partial P} \quad (5.3-2)
\]

at constant temperature.

It is this quality which shows well the decrease in the compressibility of water on the addition of small quantities of an organic second component. It is easily found for each temperature and composition in the range studied, and also any pressure over which the polynomials apply. Each compressibility is represented by an equation of the form:

\[
\frac{V}{V_0} = a_1 + a_2 P + a_3 P^2 + a_4 P^3 \quad (5.3-1)
\]

Differentiation of equation (5.3-1) with respect to \( P \) yields \( \beta \) in terms of pressure since:

\[
\frac{\partial}{\partial P} \left( \frac{V}{V_0} \right) = \frac{1}{V_0} \cdot \frac{\partial V}{\partial P} = -\beta = a_2 + 2a_3 P + 3a_4 P^2 \quad (5.3-3)
\]
The results of this operation are plotted in Figs. (5-14) to (5-16) and tabulated in Table (5-13).

From these graphs can be seen the decrease in compressibility of water on small additions of the organic component and also the much larger decrease in the compressibility of MEK on small additions of water.

5.3.4. Calculation of $v^E$ at high pressure.

The calculation of $v^E$ at elevated pressures is by a similar means to that used to calculate $v^E$ at atmospheric pressure, except that the compressibilities of both the pure components and the mixture must be considered.

The definition of the excess volume change of mixing is:

$$v^E = V_{\text{actual}} - V_{\text{ideal}} \quad (5.3-4)$$

At atmospheric pressure the values of $V_{\text{actual}}$ and $V_{\text{ideal}}$ may be calculated from equations (5.1-1) and (5.1-3). At elevated pressure $V_{\text{actual}}$ and $V_{\text{ideal}}$ are calculated by multiplying equations (5.1-1) and (5.1-3) by the corresponding compressibility. These equations therefore become (writing $V_a$ for $V_{\text{actual}}$ and $V_i$ for $V_{\text{ideal}}$):

$$V_a^P = \frac{72.12x_1 + 18.02(1-x_1)}{\rho_{\text{mix}}} \left(\frac{V}{V_0}\right)_{\text{mix}} \quad (5.3-5)$$

and

$$V_i^P = x_1 \frac{72.12}{\rho_{\text{MEK}}} \left(\frac{V}{V_0}\right)_{\text{MEK}} + (1-x_1) \frac{18.02}{\rho_{\text{H}_2\text{O}}} \left(\frac{V}{V_0}\right)_{\text{H}_2\text{O}} \quad (5.3-6)$$

where the superscript indicates elevated pressure, and the subscripts mix, MEK and H$_2$O refer to the mixture, MEK and water.

$$v^E = \frac{72.12x_1 + 18.02(1-x_1)}{\rho_{\text{mix}}} \left(\frac{V}{V_0}\right)_{\text{mix}}$$

$$- x_1 \frac{72.12}{\rho_{\text{MEK}}} \left(\frac{V}{V_0}\right)_{\text{MEK}} \quad (1-x_1) \frac{18.02}{\rho_{\text{H}_2\text{O}}} \left(\frac{V}{V_0}\right)_{\text{H}_2\text{O}} \quad (5.3-7)$$
FIGURE (5-14) The coefficient of isothermal compressibility for MEK/water mixtures at 30°C.
FIGURE (5-15) The coefficient of isothermal compressibility for MEK/water mixtures at 50°C
FIGURE (5-16) The coefficient of isothermal compressibility for MEK/water mixtures at 70°C.
For each of the mixtures studied and at each of the
three temperatures, \( v^E \) was calculated from equation (5.3-7)
at intervals of 5000 psi, up to 25000 psi. The results were
plotted in Figs. (5-17) to (5-19) and tabulated in Tables
(5-14), (5-15) and (5-16).

5.3.5. Correction of the Compressibility results for the
inherent inaccuracy in the method

As shown in Fig. (4-5), the method employed in this
work gave values for the compressibility of water + 0.003
in excess of the values obtained for water by Bridgman. To
compensate for this error, 0.003 must be subtracted from the
values of compressibility found at all pressures within the
range investigated.

When determining the isothermal coefficient of
compressibility (\( \beta \)), the first differential of \( V/V_0 \) with
respect to pressure is being determined i.e. the slope of
the compressibility curve at various pressures. The pressure
polynomials only deviate appreciably from the experimentally
determined values in the pressure range 0-5000 psi, since
the curve fits have been forced through the point (0,1)
instead of (0,1.003). The slopes of the curves at pressures
above 5000 psi will be little affected by the initial
inaccuracy.

Subsequent examination of the data indicated that the
error arose because the only experimental measurements of
the movement of the piston, which were used in the
calculations of the compressibilities, were those obtained
whilst the pressure was being increased. If the results
obtained firstly while increasing the pressure and secondly
FIGURE 5-17: Volume changes on mixing for MEK/water mixtures at 30°C and pressures up to 25000 psi.
FIGURE (5-18) Volume changes on mixing for MEK/water mixtures at 50°C and pressures up to 25000 psi
FIGURE (5-19) Volume changes on mixing for MEK/water mixtures at 70°C and pressures up to 25000 psi
FIGURE (5-20) Volume changes on mixing of MEK/water mixtures at 1 atm
while decreasing the pressure had been averaged, this error would have been largely eliminated.

It can be imagined that as the pressure was increased the transducer wiper lagged behind the movement of the piston, i.e. for a small initial increase in pressure no movement was registered by the null detector. Thus all the subsequent piston movements measured were less than the true value and the $V/V_0$ vs. $P$ curve was displaced upwards. This resulted in the curve passing above the point (0,1) when extrapolated back to zero. On reducing the pressure the wiper was again imagined to lag behind the piston and the calculated compression results were displaced downwards resulting in the $V/V_0$ vs. $P$ curve crossing the ordinate below the point (0,1). Averaging these two sets of results would have considerably reduced the error incurred.
5.3.6. The use of volumetric measurements to show phase separation

Using the vapour-liquid equilibrium data of other workers (78), (80), (81), (86), the free energy of mixing at atmospheric pressure may be found from the equation

\[ g_{\text{mix}} = \sum_{i} x_i \ln x_i \gamma_i \]

To find the free energy of mixing at elevated pressure account must be taken of the change in the free energy of mixing in raising the pressure from atmospheric pressure to some pressure \( P \). Since:

\[ \left( \frac{\partial g}{\partial P} \right)_{T,x} = \sqrt{\frac{\left[ \frac{\partial g_{\text{mix}}}{\partial P} \right]_{T,x}}{\partial P}} = v_{\text{mix}} \]

Then, at constant temperature and composition:

\[ g_{\text{mix}}^{P} = \int_{0}^{p} v_{\text{mix}} \, dP + g_{0}^{\text{mix}} \]

Considering the volumetric data obtained at 70\(^{\circ}\)C values of \( g_{\text{mix}} \) were obtained by the graphical integration of \( v \) between atmospheric pressure and pressure \( P \) (from 5000 to 25000 p.s.i.) for each of the experimentally used compositions. Thus the addition of the two free energy of mixing terms yields the free energy of mixing at the composition and pressure under consideration.

The resulting values are all negative and either exhibit, or infer the existence of, two minima and one maximum in the range \( x = 0 \) to 1 for each pressure considered. The turning points of each of the minima indicate the composition of each end of each tie-line. The values obtained by this method compare very badly with the experimentally obtained values at this temperature.
By a very similar method $g^E/RT$ has been deduced at 70°C and at the pressures and compositions under consideration. The excess free energy at one atmosphere was calculated from the vapour-liquid equilibrium data by using:

$$g^E = \sum_{i}^{0} x_i \ln Y_i$$

Account of the excess free energy change, due to the changes in pressure, was again taken by integrating the excess volume change of mixing as appropriate. To the resulting $g^E/RT$ vs. $P$ curves, at various pressures, the Redlich-Kister equation was fitted. It was found that to fit the vapour-liquid equilibrium data, 4 parameters were required. The values obtained for the tie-line ends, derived from the Redlich-Kister equation, were in very poor agreement with the experimentally obtained values. The apparent failure of the Redlich-Kister equation is not surprising since in order to reach these results it has been necessary to differentiate twice some rather suspect free energy data.
CHAPTER 6

DISCUSSION OF RESULTS
6.1. Equilibrium Data

6.1.1. Atmospheric Pressure Results

a) Comparison with other data

Liquid-liquid mutual solubilities were measured in the temperature range 25-100°C by the method described in Sect. 4.2.2. The results were found to agree closely with the data of Campbell, Kartzmark and Falconer (28) and also with the less extensive data of Ginnings, Plonk and Carter (21) as shown in Fig. (5-2). These data, together with the data of Siegleman and Sorum (29) and Randall and McKenna (23) were used to find the constants in the van Laar, NRTL, Heil and Orye equations at constant temperature. Since each of the equations have only two constants, each tie-line gives an estimate of the values of the constants, subject, of course, to the experimental errors.

b) Back-calculation of the experimentally obtained data

All the values of each constant were fitted by a third order polynomial in temperature (Sect.5.2.1.c) and this polynomial was then used to calculate the demixing curve for the MEK/H₂O system, as described in Sect. 5.2.1.d. In Fig. (5-10) the demixing curve at 1 atmosphere as predicted by the Orye equation is shown. Whilst the van Laar, NRTL and Heil equations predict the almost vertical portions of the curve, they fail to predict the upper or lower consolute points. However, Fig. (5-10) shows that the Orye equation predicts the experimentally obtained de-mixing for this system very well.
Since there is no reason in principle why the Orye equation should perform any better in this application than the other equations considered, a possible explanation is that the temperature dependence of the Orye constants is simpler than those of the other equations.

6.1.2. Results obtained at high pressure

a) Comparison with previous results

The only available data for this system, for the purpose of comparison with the results obtained at high pressure from this work, are those of Timmermans (5). It was he who found the UCST and LCST for MEK/H₂O mixtures at fixed pressures and compositions using a visual method. His results are summarised with the other available equilibrium data for this system in Fig. (1-1).

The demixing loops of pressure vs. mole fraction (P vs. x) at constant temperature obtained by the method described in Section 4.3.3. are shown in Fig. (5-8). The upper critical solution pressure obtained at each temperature by interpolation is plotted against temperature in Fig (5-8f) together with the data obtained by Timmermans (5). It can be seen from this graph that this work predicts a higher maximum critical solution pressure and suggests a narrower range of demixing temperatures at atmospheric pressure (effectively 0 psia) however, the data are too sparse to give much weight to the latter observation.
Steiner and Schadow (99) used visual and a dielectric constant method to study the high pressure equilibrium behaviour of the MEK/H$_2$O system at 30°C. The maximum critical solution pressure obtained by the sampling technique was higher than that obtained by the visual method. Therefore, maximum critical solution pressures obtained in this work, which are higher than those obtained by Timmermanns, may possibly be attributed to the different technique employed.

b) Demixing loops

The upper critical solution composition appears to remain constant with temperature as found by Timmermanns, however, at all the temperatures chosen, with the possible exception of 69.5°C, the demixing loop becomes wider before narrowing. The upper critical solution pressure increases in the temperature range 25-69.5°C but at 100°C it has reduced.

Referring to Fig. (5-8f): the critical solution pressures are plotted against the temperature at which they occurred (solid line), these data being obtained from the preceding Figs. (5-8a) to(5-8e), and the dashed line represents Timmermanns' data. The maximum pressure occurs at 75°C, compared with 80°C found by Timmermanns, and the maximum pressure found in this work is 18000 psi, compared with 16000 psi, found by Timmermans. At 75°C the demixing loop is at its widest at atmospheric pressure.

With increasing pressure the demixing loops do not expand uniformly, or, more precisely, the two liquid layers
do not become either richer or leaner in MEK, but rather the composition of one phase alters while the composition of the other phase stays substantially the same. This is best illustrated at 25 and 100°C. However, at the upper critical solution pressure both liquid compositions of each layer approach the critical composition rapidly.

c) Derived Empirical Constants

From the experimentally obtained high pressure data, constants for the van Laar, NRTL, Heil and Orye equations were obtained at the temperatures and pressures measured. The values obtained are shown in Table (5-7). Of the most interest are the values obtained for the Orye equation which are plotted in Fig (5-9). It can be seen that when the values obtained are plotted against pressure at constant temperature, what appears to be a family of curves is formed for both constants. Also, at the top of the temperature range considered the variation of these constants with pressure is small. Bearing in mind the success achieved in using the Orye equation to back-calculate the experimentally obtained liquid-liquid equilibrium data at atmospheric pressure (which was due considerably to the constants only being weak functions of temperature) it may well be possible to back-calculate the equilibrium data obtained at high pressure, particularly in the upper range of temperatures considered. However, at lower temperatures the constants become stronger functions of temperature and, therefore, the second order polynomials in pressure fitted to the constants at various temperatures also need to be functions of temperature. It is not felt that this extra sophistication is justified by the number of data points available.
6.2. Volumetric Data

6.2.1. Volume change on mixing at Atmospheric Pressure

a) Comparison with other data

Although no actual volume changes have been published as such, specific gravity data for a range of compositions are available from several sources. Volume changes on mixing were calculated by the method described in Sect 5.1.2. from the specific gravity data of Tarasov et al (96) and Boeke and Haneward (97), since these two sets of data are the most extensive available, and are also taken at almost the same temperature, 21 and 22°C respectively. The $v^E$ calculated from these two sets of data are shown plotted in Fig. (5-1). Also shown are the $v^E$'s calculated from the specific gravity measurements taken at 21.5°C which were obtained experimentally in this work. These results are shown in Table (5-2). From Fig. (5-1) it can be seen that the results obtained agree closely with the results calculated from the data of the two other workers.

b) The sign of $v^E$

Two liquids are completely miscible if the following is obeyed:

$$\Delta g^\text{mix} < 0 \quad (6.1-1)$$

$$\left(\frac{\partial^2 \Delta g^\text{mix}}{\partial \chi^2}\right)_{T,P} > 0 \text{ for all compositions (6.1-2)}$$

From equation (2.1-19) it can be seen that $\Delta g^\text{mix}$ is a function of pressure and thus changes in pressure can affect the miscibility of the system. A quantity related closely to both pressure and $\Delta g^\text{mix}$ is the volume change on mixing $\Delta v^\text{mix}$. 
The relation is: \[ \left( \frac{\partial \Delta g_{\text{mix}}}{\partial P} \right)_{T,x} = \Delta v_{\text{mix}} \] (6.1-3)

For an incompletely miscible liquid system at atmospheric pressure the requirement of equation (6.1-2) is not satisfied. If the system also has a negative volume change on mixing then from equation (6.1-3) an increase in pressure will lower \(\Delta g_{\text{mix}}\) and at high pressure the variation of \(\Delta g_{\text{mix}}\) with \(x\) may well satisfy equation (6.1-2) and complete miscibility will result.

The evidence supplied by the results obtained in this work supports the theoretical predictions: from the equilibrium data it is found that the system becomes completely miscible at elevated pressures, and from the volumetric studies the excess volume changes of mixing are, at the lower pressures, negative.

c) **Data Obtained at Atmospheric Pressure**

Specific gravity data were obtained for the mixtures at temperatures of 30, 50 and 70°C and the volume changes on mixing calculated were of primary use in the calculation of \(v^E\) at various pressures as shown in Section 5.3.4. These values of \(v^E\) are plotted in Fig. (5-20) and tabulated in Tables (5-14) to (5-16). From Fig. (5-20) it appears that \(v^E\) is not a strong function of temperature, i.e. \(\frac{\partial v^E}{\partial T}\)\(\neq 0\)

The values obtained at 70°C for the MEK rich layer deviate from the points obtained at 30 and 50°C and indicate the influence of temperature on \(v^E\).
6.2.2 Accuracy and Presentation of Compressibility Data

a) Accuracy of the Method

The method chosen for the measurement of compressibilities was continuous and rapid. Only the time required for the dissipation of the heat generated during compression limited the speed of the experiments. Also, inaccuracies in the readings due to changes in electrical properties of the measuring systems were eliminated.

The accuracy of these measurements was limited by the available apparatus. A large volume of sample (approximately 50 ml) was contained in a vessel the maximum effective length of which was 2.25 inches. The maximum travel of the piston in the pressure range considered was approximately 0.25 inches. If, for example, apparatus similar to that of Doolittle (40) had been used far greater movements would have resulted for the same pressure changes and the accuracy improved. A more delicate transducer construction, i.e. finer windings (although less than the 0.001 inch diameter used is probably impracticable) and finer wiper construction, would have assisted in the accurate location of the piston. However, in spite of the above criticism of the method it is shown in Appendix III that the method used is still accurate.

b) Correlation of Data

As explained in Section 5.3.2 the points obtained for each mixture and temperature were fitted to a third order
polynomial in $P$, as suggested by Hayward (54). For organic liquids Hayward suggested a fourth order polynomial to express their compressibilities, however, as shown in Appendix IV the accuracy of the data obtained did not warrant the fitting of a fourth order polynomial, since the method used produced data with an inaccuracy sufficiently large to cause changes in the third decimal place of the compressibility.

From Figs. (5-11) to (5-13) the compressibilities at constant temperature and various compositions appear to form a family of curves. It is possible that the pressure coefficients of the polynomials which fit the experimental data are themselves related to composition in a similar manner as the constants of the van Laar, NRTL, Heil and Orpe equations could be related to temperature.

Fig. (4-5) which compares the results obtained in this work for the compressibility of water with results obtained by Bridgman, shows that for the range of pressures considered the values obtained in this work are consistently higher than those obtained by Bridgman by $+0.003$. It has been concluded, therefore, that the apparatus used in this work has an inherent error of $+0.003$. Since the volume changes on mixing at elevated pressures have been calculated from the actual experimental results, their correction was a simple matter. The polynomials, expressing the compressibility, have been calculated ignoring the inherent error mentioned above. This omission, as explained in Section 5.3.5,
will only cause inaccuracy in the calculation of the isothermal compressibility at pressures below 5000 psi.

Using a polynomial to express the compressibility easily enabled the isothermal compressibility, \( \beta \), to be found by simply differentiating the polynomial for \( V/V_0 \) with respect to \( P \). Because of the miscibility gap only points at the two composition extremes may be obtained, but even so, some conclusion may be drawn. As found by other workers (48), (59), (62), (63) the compressibility of water is decreased by small additions of an organic phase. This causes the curve of \( \beta \) vs. \( x \) to pass through a minimum at about 10\% (wt) MEK at all three temperatures considered. At the other end of the composition range small additions of water cause a spectacular decrease in the value of \( \beta \), this effect becoming more noticeable at higher temperatures.

6.2.3 Volume Changes on Mixing at High Pressure

a) General Observations from the Data

The excess molar volumes of mixing deduced directly from the density measurements are tabulated in Tables (5-14) to (5-16) and plotted in Figs. (5-17) to (5-19). Also shown are the excess molar volumes of mixing at elevated pressures, calculated from the molar volumes at 1 atm and the measured compressions of the mixtures. Reference to Figs. (5-17) to (5-19) shows that the excess
molar volumes at each temperature considered, exhibit two maxima and one minimum. At high concentrations of MEK $v^E$ is positive, but towards the miscibility gap $v^E$ decreases and can be imagined to cross the line $v^E = 0$ somewhere in the two phase region. At low concentrations of MEK $v^E$ is negative but towards $x = 0$, $v^E$ appears to become positive again.

The excess molar volume changes of mixing have been calculated from 'unsmoothed' data. By expressing the compressibility data, at various compositions by, for example, a polynomial in $P$, and then expressing the constants obtained in each polynomial as a function of the composition, smoothed $v^E$ vs. $x$ curves would be obtained. This method would prejudge, to some extent, the shape of these curves. Also, the polynomials would have to be sufficiently flexible to provide a good fit at the sharp curvature near $x = 0$ and $x = 1$ which would require them to be of such a high degree as to exhibit a number of maxima and minima within the miscibility gap.

A similar shape $v^E$ vs. $x$ curve at high pressures has been reported by Stutchbury (63) for the pyridine - water system, although this latter pair of components do not show a miscibility gap.

The small range of temperature considered has no great effect on $v^E$. Temperature seems to have more affect on $v^E$ at elevated pressures than at atmospheric pressure, also
the MEK rich end of the composition range is more affected than the aqueous end.

Referring to Figs. (5-17) to (5-19) it is possible to infer the existence of a second two phase region at pressures outside the range used in this work. Positive values of the excess molar volume change of mixing occur mainly in the MEK rich solutions at all the temperatures considered and also at the majority of the pressures used. Small positive values are also observed in weak solutions of MEK, towards the upper end of the pressure range, at 30 and 50°C. However, at compositions approaching each side of the miscibility gap the indication is that the values of $v^E$ decrease and, when continued through the miscibility gap (shown with dashed lines, which although fictitious are considered to exist for the purposes of this discussion) actually become negative.

The behaviour of the excess molar volume change of mixing on approaching the miscibility gap is in accordance with theory. For the miscibility gap at a given temperature to get narrower with increasing pressure, $g^E$ must become less positive. Since

$$\left( \frac{\partial g^E}{\partial P} \right)_T = v^E$$

(2.1-31)

and, therefore, $v^E$ must be negative, at least near the immiscible region, for the gap to narrow. At pressures above the critical the negative portions of these curves approach the line $v^E = 0$, indicating that at some high pressure,
probably above the maximum pressure used in this work, a
two phase region may again be formed since at these
elevated pressures the inference is that $g^E$ may become
increasingly positive.

b) **Empirical Expressions for $v^E$**

It is hoped to describe the volumetric behaviour of the
MEK/H$_2$O system by using a derivative of one of the
expressions for $g^E$ which were considered for representing
the liquid-liquid equilibrium data.

As pointed out earlier (Section 2.2.4) the MEK/H$_2$O
system is complex, due to various intermolecular inter-
actions, the various solutions for the Gibbs-Duhem equation
are not intended to be adequate for such applications. The
van Laar equation, for example, assumes in its derivation
that $v^E = 0$, but since when many solutions of the Gibbs-
Duhem equation are used for the representation of equilibrium
data the original meaning of the parameters disappears, and
they become only empirical parameters, then it is possible
that one of the equations will be suitable for the represen-
tation of the volumetric behaviour of the MEK/H$_2$O system.

(i) **Redlich-Kister Equation**

The Redlich-Kister equation may be written (section
2.2.2b)

$$
g^E/RT = x_1x_2[A' + B'(x_1-x_2) + C'(x_1-x_2)^2 + ...] \tag{6.2-4}
$$
which, from equation (2.1-31) becomes:

\[ \frac{v^E}{RT} = x_1x_2 \left[ \frac{\partial A'}{\partial P} + \frac{\partial B'}{\partial P} (x_1 - x_2) + \frac{\partial C'}{\partial P} (x_1 - x_2)^2 + \ldots \right] \] (6.2-5)

In order to produce the general shape of the \( v^E \) vs \( x \) curves at least three adjustable parameters are required, their derivatives with respect to pressure being non-zero.

On fitting the three parameter form of equation (6.2-5) to the experimental results it was found that, while the general shape of the curve was described, the actual fit was poor. Increasing the number of adjustable parameters improved the fit, but maxima and minima were often formed in the miscibility gap.

b) Van Laar Equation

The expression for \( g^E \) from the van Laar equation is

\[ g^E_{RT} = \frac{ABx_1x_2}{Ax_1 + Bx_2} \] (6.2-6)

Differentiating with respect to pressure gives:

\[ \frac{v^E}{RT} = x_1x_2 \frac{(A^2x_1^2 + B^2x_2^2 + 3A)}{(Ax_1 + Bx_2)^2} \] (6.2-7)

The right hand side of this equation can show a single sign change if \( \left( \frac{\partial A}{\partial P} \right) \left( \frac{\partial B}{\partial P} \right) < 0 \) but cannot show two roots in \( v^E \) for \( 0 \leq x \leq 1 \).
(iii) **Black's Equation**

Black's expression for $g^E$ in a binary mixture is:

$$\frac{g^E}{RT} = \frac{ABx_1x_2}{Ax_1 + Bx_2} + Cx_1x_2(x_1 - x_2)^2 \quad (6.2-8)$$

which, on differentiation with respect to pressure, gives the following expression for $v^E$:

$$\frac{v^E}{RT} = x_1x_2 \left( \left( A^2x_1 + B^2x_2 \right) \frac{\partial A}{\partial P} + \left( 2A^2 + 2B^2 \right) \frac{\partial B}{\partial P} + \left( A^2 + B^2 \right) \frac{\partial C}{\partial P} \right) (x_1 - x_2)^2 \quad (6.2-9)$$

The first term in the square brackets is identical to the van Laar equation for $v^E$. Although the second term cannot change sign over the range $0 \leq x \leq 1$, on combination with the first, it is possible to obtain curves showing the same characteristics of those obtained experimentally. Examination of equation (6.2-9) reveals that it contains four independent parameters, namely $B/A$, $\frac{\partial A}{\partial P}$, $\frac{\partial B}{\partial P}$ and $\frac{\partial C}{\partial P}$. In order to give curves having two maxima and one minimum for the range $0 \leq x \leq 1$, it is necessary for $B/A$ to be positive, $\frac{\partial A}{\partial P}$ and $\frac{\partial B}{\partial P}$ must each be negative and $\frac{\partial C}{\partial P}$ must be positive.

The attempts at using equation (6.2-9) to fit the experimentally obtained high pressure results have resulted in poor fits which were no better than the results obtained when the three parameter Redlich-Kister expression for $v^E$, equation (6.2-5), was fitted. The $v^E$ values found at 30°C
and atmospheric pressure were approximated quite well by
equation (6.2-9).

iv) Margules Equation

The three parameter form of the equation is:

\[
\frac{E}{RT} = x_1 x_2 (A x_2 + B x_1 - C x_1 x_2) \tag{6.2-10}
\]

which on differentiation with respect to pressure gives:

\[
\frac{\nu^E}{RT} = x_1 x_2 \left( \frac{\partial A}{\partial P} x_2 + \frac{\partial B}{\partial P} x_1 - \frac{\partial C}{\partial P} x_1 x_2 \right) \tag{6.2-10a}
\]

Equation (6.2-10a), like the three parameter Redlich-Kister
equation, can give roots at \( x = 0 \) and \( x = 1 \) and also at two
concentrations in the range \( 0 < x < 1 \). A plot of \( \nu^E \) vs \( x \),
therefore, may cross the line \( \nu^E = 0 \) at two points in this
range and can represent the behaviour of the system quanti-
tatively. The fit will be no better than that for the three-
constant Redlich-Kister equation (6.2-5) since, on equating
this equation with equation (6.2-10) and equating coefficients
(namely powers of \( x \) ) it is found that the two equations are
identical when:

\[
A'_1 M = A'_1 R - A'_2 R + A'_3 R \tag{6.2-11}
\]

\[
A'_2 M = A'_1 R + A'_2 R + A'_3 R \tag{6.2-12}
\]

\[
A'_3 M = A'_3 R \tag{6.2-13}
\]
The second suffixes, M and R, in equations (6.2-11), (6.2-12) and (6.2-13) denote Margules and Redlich-Kister.

c) Local Composition Equations

Three of the local composition equations, namely the Orye, NRTL and Heil, have been mentioned earlier during the study of the liquid-liquid equilibrium for the system. Below are considered the applicability of these three equations for representing the volumetric behaviour of the system along with other local composition equations which may be summarised as:

\[
\frac{E}{RT} = -p\left[x_1 \ln(D_{12}) + x_2 \ln(D_{21})\right] + qx_1x_2\left[\frac{\tau_{21}G_{21} + \tau_{12}G_{12}}{D_{21}}\right] + rx_1x_2\frac{\ln(G_{12}G_{21})}{D_{12}D_{21}}
\]

(6.2-14)

where:

\[D_{12} = x_1 + x_2 G_{21},\]

and

\[D_{21} = x_2 + x_1 G_{12}.\]

The table below shows how this general expression reduces to various local composition equations when the appropriate values of p, q, r, pij and αij are chosen.

In differentiating equation (6.2-14) with respect to pressure it has been assumed that αij is independent of
\[
\frac{V^E}{RT} = p x_1 x_2 \left( \frac{G_{21}}{D_{12}} + \frac{G_{12}}{D_{21}} \frac{\partial \tau_{12}}{\partial P} \frac{\partial (\ln p_{12})}{\partial P} \right) + \frac{\partial \tau_{12}}{\partial P} \frac{\partial (\ln p_{12})}{\partial P} \frac{\partial (\ln p_{12})}{\partial P}
\]

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>r</th>
<th>( \frac{V_i}{V_j} )</th>
<th>( \alpha_{ij} )</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>( \frac{V_i}{V_j} )</td>
<td>1</td>
<td>Wilson</td>
<td>6.2-15</td>
<td>89</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>( \frac{V_i}{V_j} )</td>
<td>1</td>
<td>Modified Wilson</td>
<td>6.2-16</td>
<td>89</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>( \frac{V_i}{V_j} )</td>
<td>1</td>
<td>Enthalpic Wilson</td>
<td>6.2-17</td>
<td>72</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>( \frac{V_i}{V_j} )</td>
<td>1</td>
<td>Orye</td>
<td>6.2-18</td>
<td>75</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>( \frac{V_i}{V_j} )</td>
<td>1</td>
<td>Modified Orye</td>
<td>6.2-19</td>
<td>73</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>C</td>
<td>NRTL</td>
<td>6.2-20</td>
<td>92</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>( \frac{V_i}{V_j} )</td>
<td>1</td>
<td>Heil</td>
<td>6.2-21</td>
<td>93</td>
</tr>
</tbody>
</table>

Pressure although account has been taken of the possible variation of \( p_{ij} \) with pressure. The general expression for the excess volume of mixing is given by:

\[
\frac{V^E}{RT} = p x_1 x_2 \left( \frac{G_{21}}{D_{12}} \frac{\partial \tau_{21}}{\partial P} \frac{\partial (\ln p_{21})}{\partial P} + \frac{G_{12}}{D_{21}} \frac{\partial \tau_{12}}{\partial P} \frac{\partial (\ln p_{12})}{\partial P} \right)
\]

\[
+ q x_1 x_2 \left( \frac{G_{21}}{D_{12}} \frac{\partial \tau_{21}}{\partial P} \tau_{21} \frac{\partial (\ln p_{21})}{\partial P} + \frac{G_{12}}{D_{21}} \frac{\partial \tau_{12}}{\partial P} \tau_{12} \frac{\partial (\ln p_{12})}{\partial P} \right)
\]

\[
+ \frac{G_{12} \frac{\partial \tau_{12}}{\partial P} \tau_{12}}{D_{21}} \left( \frac{\partial (\ln p_{12})}{\partial P} \right)
\]

\[
+ \frac{x_1 x_2 \alpha_{12}}{D_{12}^2} \left( \frac{\partial \tau_{21}}{\partial P} \tau_{21} + \frac{G_{21} \left( \tau_{21} + \tau_{21} \right)}{D_{12}} \frac{\partial \tau_{21}}{\partial P} \tau_{21} \frac{\partial (\ln p_{21})}{\partial P} \right)
\]

\[
+ \frac{\partial \tau_{12}}{\partial P} \left( \frac{G_{12} \left( \tau_{12} + \tau_{12} \right)}{D_{21}} \frac{\partial \tau_{12}}{\partial P} \tau_{12} \frac{\partial (\ln p_{12})}{\partial P} \right)
\]
The differentiation of the various forms of equations (6.2-15) to (6.2-21) with respect to pressure yields expressions for the volume change on mixing designated equations (6.2-22) to (6.2-28) respectively.

Examination of the first five of these equations namely (6.2-22) to (6.2-26) shows that each of these can give just one sign change in the range 0 < x < 1. Since these curves pass through (0, 0) and (1, 0) then only one maximum and one minimum can be exhibited in the range 0 < x < 1. It is evident, therefore, that the local composition equations that have been considered so far are unable to describe the volumetric behaviour of the MEK/H₂O system.

The remaining two equations, namely the Heil and the NRTL equations, are capable of showing two maxima and one minimum in the range 0 < x < 1 provided that the values of α_{ij} τ_{ij} are sufficiently large and positive and also that the two ∂τ_{ij}/∂P terms are positive. For example, in a symmetrical system with the NRTL equation (6.2-27) two maxima and one minimum are always found if ατ exceeds about 1.28 and the ∂τ/∂P's are positive. The shapes of the curve given by this equation for several values of ατ in a symmetrical system are shown sketched in Fig. (6-1). Similar curves result from Heil's equation (6.2-28). Initially the curves exhibited by these equations look promising but examination shows that at low pressure the v^E vs x curves corresponding to very high values of ατ in Fig. (6-1) are
FIGURE (6-1) Excess volume for symmetrical NRTL equation for positive \( \alpha \tau \)
found, while at higher pressures, curves corresponding to lower values of $\alpha$ are obtained. It is, therefore, a requirement of the experimental evidence that the quantity $\partial \sigma / \partial P$ has two conflicting properties. The first is that it is negative, to allow $\alpha$ to decrease with increasing pressure; the second is that it is positive, to enable the $v^E$ vs. $x$ curves, according to equations (6.2-19) or (6.2-20), to show one minimum and two maxima rather than one maximum and two minima.
CHAPTER 7

CONCLUSIONS
CONCLUSIONS

Using the specially designed equilibrium cell it was possible to investigate the liquid-liquid phase behaviour of the MEK/H₂O system at atmospheric pressure. The data obtained was found to agree well with the results of other workers who used various other methods.

The atmospheric data obtained in this work, together with some of the other available atmospheric data, yielded values for the constants of the van Laar, NRTL, Heil and Orye equations. The constants obtained were found to be quite simple functions of temperature. The temperature dependence of all these constants could be represented by an equation of the form:

\[ A \text{ or } B = a_1 + a_2T + a_3T^2 \]

Attempts to back calculate the demixing loops for the system at atmospheric pressure, using the above equations, succeeded only in the case of the Orye equation, the other equations failing to predict the closed part of the loop. Each set of A and B was fitted up to the term in \( T^2 \) in the above equation and since the Orye equation gave the best overall fit to the loop, it may be inferred that the Orye constants are the least temperature sensitive. For example

\[ \left( \frac{\partial A}{\partial T} \right)_{\text{Orye}} < \left( \frac{\partial A}{\partial T} \right)_{\text{van Laar}} \quad \text{or} \quad \left( \frac{\partial A}{\partial T} \right)_{\text{NRTL}} \quad \text{or} \quad \left( \frac{\partial A}{\partial T} \right)_{\text{Heil}} \]
Liquid-liquid equilibrium data for the system obtained at high pressure compares reasonably well with that of Timmermanns, especially when the difference in method is considered. From the results obtained in this work it can be seen that the demixing surface forms the shape of a dome, its highest point occurring at 18000 psi and 75°C, compared with Timmermanns' values of 16000 psi and 80°C.

The constants for the van Laar, NRTL, Heil and Orye equations have been found at high pressure and it has further been found that the variations of the Orye constants with pressure appears quite simple at constant temperature. The Orye constants were well represented by the equation:

\[ A \text{ or } B = a_1 + a_2 P + a_3 P^2 \]

Measurements of the compressibility of MEK/H₂O mixtures at 30, 50 and 70°C show that the compressibility may be expressed as a second order polynomial in pressure as suggested by Hayward (54). The isothermal compressibilities of the mixtures obtained from the polynomials show the expected minimum at low concentrations of MEK.

The excess molar volumes are found to be functions not only of composition but also of temperature and pressure. An examination of the semi-empirical two parameter solutions to the Gibbs-Duhem equation has not yielded a version which can adequately represent the volumetric behaviour of the system. Various features of the ketone-water system give rise to complications, since assumptions made when deriving the equations are no longer applicable. It has been clearly
shown that these semi-empirical solutions to the Gibbs-Duhen equation are not capable of representing the volumetric behaviour of the system. Thus, the hope of discovering at least one solution, although theoretically inappropriate has not been fulfilled, failing even to provide a quantitative representation of this system's behaviour.

The quasi chemical theory has given rise to two equations, the NRTL and Heil equations, which at least give a qualitative representation of the experimentally obtained data. To enable these two equations to represent the volumetric data at both high and low pressures, it is necessary for the parameters to vary in completely different ways in order to enable the experimental evidence to be satisfied.

In conclusion, the hope of finding a suitable two-parameter solution to the Gibbs-Duhem equation which could represent quantitatively the behaviour of the MEK-water system has not on the whole been fulfilled. However, the NRTL and the Heil equations can represent qualitatively the volumetric behaviour of the system. Also the Orye equation lends itself to a fitting procedure which enables experimental liquid-liquid equilibrium data, at various temperatures and pressures, to be used to predict similar data under other conditions of temperature and pressure.
Bibliography

2. ROTHMUND, V. Z.F. Physical Ch. 26, 459 (1898).
4. KUENEN, J.P. Z.F. Physical Ch. 38, 361 (1899).
17. BRUNI, G. - Gazz. chim. Ital. 28, 508 (1898).
35. BRIDGMAN, P.W. " " " " 74, 21, (1940).
36. BRIDGMAN, P.W. " " " " 77, 129 (1949).
       **63**, 898 (1941).
60. GIBSON, R.E. & LOEFFLER, O.H., Jour. Am.Chem.Soc.59, 1521 (1937)
63. STUTCHBURY, J.E. Australian Jour. Chem. 9, 356, (1956).
69. Van LAAR, Z. Physik. Chem. 72, 723 (1910), 63, 599(1913)


82. SHELL CHEMICAL CO., "Methyl Ethyl Ketone", 1938.


84. CARLSON, H.C., & COLBURN, A.P., IEC 34, 581 (1942).


96. TARASOV, V.V., BERING, V.P. & SIDROVA, A.A.


99. STEINER, R. & SCHADOW, E. Zeitschrift für Physikalische
APPENDIX I

Flushing of a two way valve.

This simple initial experiment was performed in order to establish the quantity of acetone required to flush away completely the remaining previous sample of methyl ethyl ketone-water from the valve.

With the valve closed it was filled with distilled water and then a 5 ml. syringe, filled with acetone, was connected to one side of the valve using a specially made adaptor. Using the syringe, 0.2 ml. of acetone at a time was injected into the valve and the liquid forced out of the other side of the valve was collected and analysed on the gas chromatograph. This procedure was continued until the whole of the 5 ml. of acetone had been injected.

Below is shown a summary of the results obtained in this experiment. It can be seen that, for practical purposes, the water is removed from the valve when between 4 and 5 ml. of acetone has flowed through it. A graph of these results is plotted in Fig. (I-1).
<table>
<thead>
<tr>
<th>Vol. of acetone injected (ml.)</th>
<th>Mean area under water peak.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1200</td>
</tr>
<tr>
<td>0.4</td>
<td>1130</td>
</tr>
<tr>
<td>0.6</td>
<td>637</td>
</tr>
<tr>
<td>0.8</td>
<td>86</td>
</tr>
<tr>
<td>1.0</td>
<td>29</td>
</tr>
<tr>
<td>2.0</td>
<td>4</td>
</tr>
<tr>
<td>3.0</td>
<td>3</td>
</tr>
<tr>
<td>4.0</td>
<td>2</td>
</tr>
<tr>
<td>5.0</td>
<td>0</td>
</tr>
</tbody>
</table>

Attenuation 200; sample size 1 µl.
FIGURE (I-1) Determination of the quantity of acetone required for the complete flushing of a two way valve.
APPENDIX II.

Flush of the capillary tubing.

In order to obtain a representative sample of the contents of the sample holder it was necessary to flush the remains of the previous sample from the capillary tubing. Initially it was attempted to find this quantity experimentally in a manner very similar to that used in Appendix I, however, it was found impossible to force liquid through an appreciable length of 0.0004" diameter bore tubing using a syringe. For this reason the problem was approached theoretically:

Assume laminar flow and constant viscosity. If the capillary is initially full of liquid A, and has a bore of $2r_0$, a length $\ell$ and, for the purpose of this analysis, a constant flow rate $q$, then:

$$q = \pi r_0^2 \frac{\hat{u}}{2}$$

and

$$\hat{u} = \hat{u} \left[1 - \left(\frac{r}{r_0}\right)^2\right]$$

where: $\hat{u}$ = maximum velocity of the fluid

$u$ = velocity of the fluid at radius $r$.

In time $t$, the first trace of liquid B appears at the centre line of the exit of the capillary, then

$$t_1 = \frac{\ell}{\hat{u}}$$

and at time $t > t_1$, the radius of the A/B interface, $r_1$ will be given by:

$$\hat{u} \left[1 - \left(\frac{r_1}{r_0}\right)^2\right] = \frac{\ell}{t}$$
but \( t = \frac{Q}{q} \), where \( Q \) is the volume of fluid taken off

\[
(Q = \pi r_0^2 \hat{u} = \frac{\pi}{2} r_0^2 \hat{u})
\]

so \( \hat{u} [1-(\frac{r_i}{r_0})^2] = \frac{q}{Q} = \frac{\pi r_0^2 \hat{u}}{2Q} \).

i.e. \( (\frac{r_i}{r_0})^2 = 1 - \frac{\pi r_0^2 \hat{u}}{2Q} \).

Now at the time when the interface at the exit is at \( r_i \), the volume flow rate of \( B \) is:

\[
\int_0^{r_i} \hat{u} [1-(\frac{r}{r_0})^2] 2\pi r \, dr = 2\pi \hat{u} \left( \frac{r_i^2}{2} - \frac{r_i^4}{4r_0^2} \right)
\]

and the total volume flow rate is:

\[
\int_0^{r_0} \hat{u} [1-(\frac{r}{r_0})^2] 2\pi r \, dr = 2\pi \hat{u} \frac{r_0^2}{4}
\]

So the instantaneous concentration of \( B \)

\[
= \frac{\text{volume flowrate of } B}{\text{total volume flowrate}}
\]

\[
= \frac{\frac{r_i^2}{r_0^2} [2-(\frac{r_i}{r_0})^2]}{\frac{r_0^2}{2}}
\]

\[
= (1-\pi r_0^2 \hat{u}) (1+\pi r_0^2 \hat{u}) \frac{1}{2Q} \frac{1}{2Q}
\]

\[
= 1- \frac{(\pi r_0^2 \hat{u})^2}{2} = x \text{ (say)}
\]

So, to get an instantaneous composition, \( x \), one needs to reject a volume:

\[
Q = \pi r_0^2 \hat{u} \frac{1}{2(1-x)^{\frac{1}{2}}}
\]

Selecting typical values for the apparatus used, namely

\( r_0 = 0.0051 \text{ cm and } l = 50 \text{ cm} \), and assuming that the required purity of fluid \( B \) is 99%, then the necessary quantity of fluid
to be removed from the capillary is found by substitution into the above equation:

\[
Q = \pi \times 26 \times 10^{-6} \times \frac{50}{2 \times 0.1} = 0.02 \text{ ml.}
\]

Therefore, before taking each new sample, the capillary was flushed with 0.5 ml. from the sample holder in order to obtain a representative sample.
Accuracy of the Excess Volumes

The effect of experimental error on the excess volume of mixing is estimated below. A region of particular interest is at compositions around 5% by weight of MEK as it is at around this composition that a small maximum in the curve of $v^E$ versus composition appears to occur. The estimate of the standard error in $v^E$ is therefore a guide as to how much credence to place on the existence of this apparent maximum.

In arriving at an estimate of the standard error of $v^E$, the general formula for the propagation of error,

$$(\Delta y)^2 = \sum_{i=1}^{n} \left( \frac{\partial y}{\partial x_i} \Delta x_i \right)^2 \quad (III-1)$$

was applied where $y = y(x_1, x_2, \ldots, x_n)$

- $x_i = \text{an experimental variable (i=1 to n)}$
- $\Delta x_i = \text{the standard error associated with variable i}$
- $\Delta y = \text{the standard error on y}$

Table III-1 lists the relevant experimental variables and their estimated standard errors which were taken into account in calculating the standard error on $v^E$ measured at a mole fraction of MEK of 0.013 at 50°C and 20,000 psi.
### TABLE III-1 Experimental Errors in $v^E$

<table>
<thead>
<tr>
<th>INTERMEDIATE VARIABLE</th>
<th>RELATED EXPERIMENTAL VARIABLE</th>
<th>ERROR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar composition of test mixture</td>
<td>Mass of flask 65g</td>
<td>65x$10^{-4}$g</td>
</tr>
<tr>
<td></td>
<td>Mass of flask + ketone 70g</td>
<td>70x$10^{-4}$g</td>
</tr>
<tr>
<td></td>
<td>Mass of flask + ketone + water 170g</td>
<td>170x$10^{-4}$g</td>
</tr>
<tr>
<td>Density of water</td>
<td>From tables</td>
<td>10$^{-4}$g/cc</td>
</tr>
<tr>
<td>Density of solutions</td>
<td>Mass of pyknometer 20g</td>
<td>20x$10^{-4}$g</td>
</tr>
<tr>
<td></td>
<td>Mass of pyknometer + solution 45g</td>
<td>45x$10^{-4}$g</td>
</tr>
<tr>
<td>Compressibility</td>
<td>Volume of sample 50cc</td>
<td>0.02cc</td>
</tr>
<tr>
<td></td>
<td>Volume change of sample 2cc</td>
<td>0.02cc</td>
</tr>
<tr>
<td></td>
<td>Pressure charge 20000psi</td>
<td>200psi</td>
</tr>
</tbody>
</table>

When the combined effect of these errors is allowed for in equation III-1 the resulting value of the standard error on $v^E$ is estimated to be 0.05cc per mole. It can therefore be concluded that the features of the $v^E$ versus $x$ curves given in this work are generally correct, though the accuracy of the values ascribed to $v^E$ is not high.
Appendix IV  Presentation of Compressibility data.

Choice of Polynomial Order.

Below are listed the experimentally obtained compressibility data for M.E.K. water and their mixtures at various temperatures and pressures. Also are listed the values predicted from 3rd and 4th order polynomials fitted to the experimentally obtained points. It can be seen that the effect of adding the fourth term to the polynomial is to alter the value of the compressibility at the third or fourth decimal place. Since it has been shown previously in Appendix (III) that the maximum error in the experimentally obtained values can affect the third decimal place, only a third order polynomial was chosen to represent the experimentally obtained values.
<table>
<thead>
<tr>
<th>System Temp(°C)</th>
<th>Pressure (psi)</th>
<th>Experimental Compressibility</th>
<th>from 3rd order</th>
<th>from 4th order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0002</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9879</td>
<td>0.9874</td>
<td>0.9871</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9740</td>
<td>0.9751</td>
<td>0.9751</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9642</td>
<td>0.9634</td>
<td>0.9637</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9420</td>
<td>0.9427</td>
<td>0.9422</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9412</td>
<td>0.9413</td>
<td>0.9413</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0003</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9874</td>
<td>0.9870</td>
<td>0.9875</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9624</td>
<td>0.9619</td>
<td>0.9618</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9524</td>
<td>0.9522</td>
<td>0.9521</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9416</td>
<td>0.9423</td>
<td>0.9420</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9336</td>
<td>0.9332</td>
<td>0.9335</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0005</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9884</td>
<td>0.9878</td>
<td>0.9881</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9762</td>
<td>0.9762</td>
<td>0.9759</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9633</td>
<td>0.9639</td>
<td>0.9639</td>
</tr>
<tr>
<td></td>
<td>19300</td>
<td>0.9540</td>
<td>0.9544</td>
<td>0.9541</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9425</td>
<td>0.9423</td>
<td>0.9420</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9325</td>
<td>0.9324</td>
<td>0.9327</td>
</tr>
<tr>
<td>5% MEK</td>
<td>30</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9890</td>
<td>0.9880</td>
<td>0.9876</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9763</td>
<td>0.9771</td>
<td>0.9764</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9665</td>
<td>0.9673</td>
<td>0.9670</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9580</td>
<td>0.9587</td>
<td>0.9590</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9523</td>
<td>0.9512</td>
<td>0.9518</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9463</td>
<td>0.9448</td>
<td>0.9453</td>
</tr>
<tr>
<td>System Temp(°C)</td>
<td>Pressure (psi)</td>
<td>Experimental from 3rd order poly</td>
<td>Experimental from 4th order poly</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td></td>
</tr>
<tr>
<td>5% MEK</td>
<td>50</td>
<td>1.0000 1.0005 1.0005</td>
<td>1.0000 1.0003 1.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9892 0.9881 0.9881</td>
<td>0.9882 0.9877 0.9878</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10100</td>
<td>0.9759 0.9761 0.9761</td>
<td>0.9757 0.9759 0.9760</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9647 0.9653 0.9652</td>
<td>0.9650 0.9649 0.9650</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9546 0.9549 0.9549</td>
<td>0.9546 0.9546 0.9546</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9452 0.9451 0.9452</td>
<td>0.9452 0.9451 0.9451</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9368 0.9360 0.9361</td>
<td>0.9362 0.9364 0.9363</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>14.7</td>
<td>1.0000 1.0003 1.0001</td>
<td>1.0000 0.9996 1.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9882 0.9877 0.9878</td>
<td>0.9885 0.9875 0.9870</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9757 0.9759 0.9760</td>
<td>0.9753 0.9765 0.9756</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9645 0.9665 0.9659</td>
<td>0.9645 0.9665 0.9659</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9550 0.9544 0.9542</td>
<td>0.9550 0.9544 0.9542</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9516 0.9499 0.9505</td>
<td>0.9516 0.9499 0.9505</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9445 0.9431 0.9441</td>
<td>0.9445 0.9431 0.9441</td>
<td></td>
</tr>
<tr>
<td>10% MEK</td>
<td>30</td>
<td>14.7</td>
<td>1.0000 0.9997 0.9999</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9886 0.9882 0.9891</td>
<td>0.9886 0.9882 0.9891</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9728 0.9736 0.9732</td>
<td>0.9728 0.9736 0.9732</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9623 0.9621 0.9619</td>
<td>0.9623 0.9621 0.9619</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9519 0.9516 0.9517</td>
<td>0.9519 0.9516 0.9517</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9341 0.9339 0.9341</td>
<td>0.9341 0.9339 0.9341</td>
<td></td>
</tr>
<tr>
<td>System Temp(°C)</td>
<td>Pressure(psi)</td>
<td></td>
<td>Compressibility from 3rd order poly</td>
<td>Compressibility from 4th order poly</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------</td>
<td>---</td>
<td>----------------------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>10% MEK 70</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9863</td>
<td>0.9866</td>
<td>0.9867</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9675</td>
<td>0.9670</td>
<td>0.9672</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9629</td>
<td>0.9622</td>
<td>0.9624</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9512</td>
<td>0.9514</td>
<td>0.9514</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9411</td>
<td>0.9414</td>
<td>0.9413</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9321</td>
<td>0.9323</td>
<td>0.9321</td>
</tr>
<tr>
<td>15% MEK 30</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9996</td>
<td>1.0003</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9879</td>
<td>0.9877</td>
<td>0.9872</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9759</td>
<td>0.9766</td>
<td>0.9759</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9652</td>
<td>0.9663</td>
<td>0.9660</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9573</td>
<td>0.9569</td>
<td>0.9572</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9494</td>
<td>0.9482</td>
<td>0.9489</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9408</td>
<td>0.9404</td>
<td>0.9409</td>
</tr>
<tr>
<td>50</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9996</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9860</td>
<td>0.9863</td>
<td>0.9862</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9737</td>
<td>0.9737</td>
<td>0.9736</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9621</td>
<td>0.9620</td>
<td>0.9619</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9471</td>
<td>0.9470</td>
<td>0.9472</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9410</td>
<td>0.9413</td>
<td>0.9414</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9328</td>
<td>0.9323</td>
<td>0.9324</td>
</tr>
<tr>
<td>70</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0003</td>
<td>1.0001</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9866</td>
<td>0.9862</td>
<td>0.9863</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9727</td>
<td>0.9731</td>
<td>0.9732</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9609</td>
<td>0.9608</td>
<td>0.9609</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9497</td>
<td>0.9495</td>
<td>0.9495</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9393</td>
<td>0.9391</td>
<td>0.9390</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9292</td>
<td>0.9297</td>
<td>0.9295</td>
</tr>
<tr>
<td>System Temp(°C)</td>
<td>Pressure (psi)</td>
<td>Experimental Compressibility</td>
<td>from 3rd order poly</td>
<td>from 4th order poly</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
<td>-----------------------------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>91% MEK</td>
<td>30</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td></td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9991</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td>50000</td>
<td>0.9748</td>
<td>0.9753</td>
<td>0.9749</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9529</td>
<td>0.9539</td>
<td>0.9531</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9346</td>
<td>0.9348</td>
<td>0.9343</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9182</td>
<td>0.9182</td>
<td>0.9182</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9043</td>
<td>0.9039</td>
<td>0.9044</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.8928</td>
<td>0.8920</td>
<td>0.8928</td>
</tr>
<tr>
<td>94% MEK</td>
<td>30</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9969</td>
</tr>
<tr>
<td></td>
<td>50000</td>
<td>0.9762</td>
<td>0.9772</td>
<td>0.9755</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9559</td>
<td>0.9590</td>
<td>0.9557</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9394</td>
<td>0.9423</td>
<td>0.9400</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9263</td>
<td>0.9271</td>
<td>0.9271</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9167</td>
<td>0.9135</td>
<td>0.9157</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9053</td>
<td>0.9014</td>
<td>0.9046</td>
</tr>
<tr>
<td>System Temp(°C)</td>
<td>Pressure(psi)</td>
<td>Experimental Compressibility from 3rd order poly</td>
<td>Experimental Compressibility from 4th order poly</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>91% MEK 30</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9975</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9717</td>
<td>0.9732</td>
<td>0.9721</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9494</td>
<td>0.9513</td>
<td>0.9491</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9298</td>
<td>0.9317</td>
<td>0.9302</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9143</td>
<td>0.9145</td>
<td>0.9145</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9025</td>
<td>0.8997</td>
<td>0.9012</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.8890</td>
<td>0.8873</td>
<td>0.8895</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1.0000</td>
<td>0.9973</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.9686</td>
<td>0.9691</td>
<td>0.9675</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9408</td>
<td>0.9439</td>
<td>0.9410</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9190</td>
<td>0.9219</td>
<td>0.9199</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9031</td>
<td>0.9030</td>
<td>0.9030</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.8896</td>
<td>0.8873</td>
<td>0.8894</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.8760</td>
<td>0.8747</td>
<td>0.8777</td>
</tr>
<tr>
<td>97% MEK 30</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9995</td>
<td>1.0005</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9760</td>
<td>0.9756</td>
<td>0.9749</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9537</td>
<td>0.9547</td>
<td>0.9537</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9355</td>
<td>0.9368</td>
<td>0.9364</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9224</td>
<td>0.9220</td>
<td>0.9224</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.9114</td>
<td>0.9103</td>
<td>0.9112</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.9028</td>
<td>0.9016</td>
<td>0.9023</td>
</tr>
<tr>
<td>50</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9974</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9705</td>
<td>0.9720</td>
<td>0.9707</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9470</td>
<td>0.9490</td>
<td>0.9466</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9266</td>
<td>0.9266</td>
<td>0.9269</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.9108</td>
<td>0.9107</td>
<td>0.9107</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.8970</td>
<td>0.8954</td>
<td>0.8971</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.8853</td>
<td>0.8827</td>
<td>0.8851</td>
</tr>
<tr>
<td>System Temp(°C)</td>
<td>Pressure (psi)</td>
<td>Experimental</td>
<td>from 3rd order poly</td>
<td>from 4th order poly</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
<td>--------------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>97% MEK 70</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9975</td>
<td>1.0005</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9652</td>
<td>0.9666</td>
<td>0.9651</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>0.9385</td>
<td>0.9394</td>
<td>0.9365</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9134</td>
<td>0.9160</td>
<td>0.9140</td>
</tr>
<tr>
<td></td>
<td>20000</td>
<td>0.8945</td>
<td>0.8963</td>
<td>0.8963</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.8800</td>
<td>0.8804</td>
<td>0.8824</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.8771</td>
<td>0.8683</td>
<td>0.8712</td>
</tr>
<tr>
<td>MEK 30</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9993</td>
<td>1.0002</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9670</td>
<td>0.9676</td>
<td>0.9663</td>
</tr>
<tr>
<td></td>
<td>9900</td>
<td>0.9411</td>
<td>0.9421</td>
<td>0.9417</td>
</tr>
<tr>
<td></td>
<td>14300</td>
<td>0.9232</td>
<td>0.9241</td>
<td>0.9238</td>
</tr>
<tr>
<td></td>
<td>22600</td>
<td>0.8966</td>
<td>0.9028</td>
<td>0.9049</td>
</tr>
<tr>
<td></td>
<td>27000</td>
<td>0.8898</td>
<td>0.8981</td>
<td>0.8967</td>
</tr>
<tr>
<td>50</td>
<td>14.7</td>
<td>1.0000</td>
<td>1.0004</td>
<td>1.0001</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9662</td>
<td>0.9654</td>
<td>0.9657</td>
</tr>
<tr>
<td></td>
<td>9700</td>
<td>0.9375</td>
<td>0.9378</td>
<td>0.9380</td>
</tr>
<tr>
<td></td>
<td>14700</td>
<td>0.9139</td>
<td>0.9141</td>
<td>0.9139</td>
</tr>
<tr>
<td></td>
<td>19600</td>
<td>0.8965</td>
<td>0.8966</td>
<td>0.8962</td>
</tr>
<tr>
<td></td>
<td>24800</td>
<td>0.8842</td>
<td>0.8841</td>
<td>0.8853</td>
</tr>
<tr>
<td>70</td>
<td>14.7</td>
<td>1.0000</td>
<td>0.9930</td>
<td>0.9970</td>
</tr>
<tr>
<td></td>
<td>4900</td>
<td>0.9647</td>
<td>0.9593</td>
<td>0.9554</td>
</tr>
<tr>
<td></td>
<td>9800</td>
<td>0.9327</td>
<td>0.9302</td>
<td>0.9261</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>0.9059</td>
<td>0.9046</td>
<td>0.9046</td>
</tr>
<tr>
<td></td>
<td>19900</td>
<td>0.8881</td>
<td>0.8854</td>
<td>0.8894</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.8723</td>
<td>0.8705</td>
<td>0.8745</td>
</tr>
<tr>
<td></td>
<td>30000</td>
<td>0.8581</td>
<td>0.8608</td>
<td>0.8568</td>
</tr>
</tbody>
</table>
Appendix \textit{V}

Tables of Results.
TABLE (5-1) SG. & density of MEK/H₂O mixtures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>wt%</th>
<th>Specific Gravity</th>
<th>Density gm/ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>5.066</td>
<td>0.9929</td>
<td>0.9886</td>
</tr>
<tr>
<td></td>
<td>10.025</td>
<td>0.9865</td>
<td>0.9822</td>
</tr>
<tr>
<td></td>
<td>15.190</td>
<td>0.9802</td>
<td>0.9760</td>
</tr>
<tr>
<td></td>
<td>91.022</td>
<td>0.8197</td>
<td>0.8162</td>
</tr>
<tr>
<td></td>
<td>94.092</td>
<td>0.8122</td>
<td>0.8087</td>
</tr>
<tr>
<td></td>
<td>97.129</td>
<td>0.8056</td>
<td>0.8021</td>
</tr>
<tr>
<td></td>
<td>100.000</td>
<td>0.7978</td>
<td>0.7944</td>
</tr>
<tr>
<td>50°C</td>
<td>5.066</td>
<td>0.9923</td>
<td>0.9805</td>
</tr>
<tr>
<td></td>
<td>10.025</td>
<td>0.9849</td>
<td>0.9732</td>
</tr>
<tr>
<td></td>
<td>15.190</td>
<td>0.9768</td>
<td>0.9651</td>
</tr>
<tr>
<td></td>
<td>91.022</td>
<td>0.8049</td>
<td>0.7953</td>
</tr>
<tr>
<td></td>
<td>94.092</td>
<td>0.7966</td>
<td>0.7871</td>
</tr>
<tr>
<td></td>
<td>97.129</td>
<td>0.7902</td>
<td>0.7807</td>
</tr>
<tr>
<td></td>
<td>100.000</td>
<td>0.7821</td>
<td>0.7728</td>
</tr>
<tr>
<td>70°C</td>
<td>5.066</td>
<td>0.9905</td>
<td>0.9685</td>
</tr>
<tr>
<td></td>
<td>10.025</td>
<td>0.9813</td>
<td>0.9595</td>
</tr>
<tr>
<td></td>
<td>15.190</td>
<td>0.9718</td>
<td>0.9502</td>
</tr>
<tr>
<td></td>
<td>91.022</td>
<td>0.7896</td>
<td>0.7721</td>
</tr>
<tr>
<td></td>
<td>94.092</td>
<td>0.7802</td>
<td>0.7629</td>
</tr>
<tr>
<td></td>
<td>97.129</td>
<td>0.7726</td>
<td>0.7555</td>
</tr>
<tr>
<td></td>
<td>100.000</td>
<td>0.7656</td>
<td>0.7486</td>
</tr>
</tbody>
</table>
TABLE (5-2) SG. & density of MEK/H₂O mixtures @ 21.5°C.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>wt%</th>
<th>Specific Gravity</th>
<th>Density gm/ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5</td>
<td>4.605</td>
<td>0.9930</td>
<td>0.9918</td>
</tr>
<tr>
<td></td>
<td>13.444</td>
<td>0.9811</td>
<td>0.9799</td>
</tr>
<tr>
<td></td>
<td>13.222</td>
<td>0.9838</td>
<td>0.9826</td>
</tr>
<tr>
<td></td>
<td>23.342</td>
<td>0.9681</td>
<td>0.9669</td>
</tr>
<tr>
<td></td>
<td>11.903</td>
<td>0.9824</td>
<td>0.9812</td>
</tr>
<tr>
<td></td>
<td>87.970</td>
<td>0.8280</td>
<td>0.8288</td>
</tr>
<tr>
<td></td>
<td>92.074</td>
<td>0.8232</td>
<td>0.8122</td>
</tr>
<tr>
<td></td>
<td>96.856</td>
<td>0.8118</td>
<td>0.8270</td>
</tr>
</tbody>
</table>

TABLE (5-3) Volumetric data of MEK/H₂O mixtures @ 21.5°C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Mole fraction</th>
<th>Actual Vol. ml.</th>
<th>Ideal Vol. ml.</th>
<th>ΔV²E ml/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5</td>
<td>0.0119</td>
<td>18.7965</td>
<td>18.8968</td>
<td>-0.1003</td>
</tr>
<tr>
<td></td>
<td>0.0374</td>
<td>20.4273</td>
<td>20.7230</td>
<td>-0.2957</td>
</tr>
<tr>
<td></td>
<td>0.0367</td>
<td>20.3789</td>
<td>20.6735</td>
<td>-0.3195</td>
</tr>
<tr>
<td></td>
<td>0.0707</td>
<td>22.5927</td>
<td>23.1162</td>
<td>-0.5235</td>
</tr>
<tr>
<td></td>
<td>0.0327</td>
<td>20.1660</td>
<td>20.3856</td>
<td>-0.2442</td>
</tr>
<tr>
<td></td>
<td>0.8850</td>
<td>81.2722</td>
<td>81.5700</td>
<td>-0.2928</td>
</tr>
<tr>
<td></td>
<td>0.7438</td>
<td>70.6556</td>
<td>71.4300</td>
<td>-0.5745</td>
</tr>
<tr>
<td></td>
<td>0.6463</td>
<td>64.0674</td>
<td>64.4327</td>
<td>-0.4427</td>
</tr>
</tbody>
</table>
TABLE (5-4)

Methyl ethyl Ketone/water Liquid-Liquid Equilibrium Data at Atmospheric Pressure.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>x₁ wt.%</th>
<th>x₂ wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>25.43</td>
<td>89.18</td>
</tr>
<tr>
<td>39.7</td>
<td>20.05</td>
<td>88.40</td>
</tr>
<tr>
<td>55.0</td>
<td>17.84</td>
<td>87.80</td>
</tr>
<tr>
<td>69.5</td>
<td>17.02</td>
<td>86.50</td>
</tr>
<tr>
<td>81.0</td>
<td>17.22</td>
<td>84.19</td>
</tr>
<tr>
<td>100.0</td>
<td>19.50</td>
<td>79.82</td>
</tr>
</tbody>
</table>
from the data of various workers.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$x_1$ wt.%</th>
<th>$x_2$ wt.%</th>
<th>Van Laar</th>
<th>NRTL($\alpha=0.3$)</th>
<th>Heil</th>
<th>Drye</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>280.7</td>
<td>0.329</td>
<td>0.854</td>
<td>6595</td>
<td>3776</td>
<td>5648</td>
<td>1357</td>
<td>-23.5</td>
</tr>
<tr>
<td>282.7</td>
<td>0.323</td>
<td>0.851</td>
<td>6680</td>
<td>3760</td>
<td>5675</td>
<td>1382</td>
<td>17.7</td>
</tr>
<tr>
<td>284.2</td>
<td>0.311</td>
<td>0.871</td>
<td>6763</td>
<td>3973</td>
<td>5683</td>
<td>1565</td>
<td>-13.6</td>
</tr>
<tr>
<td>284.2</td>
<td>0.289</td>
<td>0.890</td>
<td>6880</td>
<td>4172</td>
<td>5672</td>
<td>1795</td>
<td>3.5</td>
</tr>
<tr>
<td>291.2</td>
<td>0.286</td>
<td>0.901</td>
<td>7056</td>
<td>4439</td>
<td>5716</td>
<td>2032</td>
<td>-33.2</td>
</tr>
<tr>
<td>291.7</td>
<td>0.283</td>
<td>0.876</td>
<td>7120</td>
<td>4085</td>
<td>6009</td>
<td>1600</td>
<td>9.8</td>
</tr>
<tr>
<td>303.7</td>
<td>0.240</td>
<td>0.914</td>
<td>7719</td>
<td>4775</td>
<td>6250</td>
<td>2246</td>
<td>152</td>
</tr>
<tr>
<td>308.7</td>
<td>0.224</td>
<td>0.912</td>
<td>7987</td>
<td>4772</td>
<td>6541</td>
<td>2180</td>
<td>262</td>
</tr>
<tr>
<td>313.2</td>
<td>0.211</td>
<td>0.910</td>
<td>8250</td>
<td>4782</td>
<td>6824</td>
<td>2125</td>
<td>362</td>
</tr>
<tr>
<td>318.2</td>
<td>0.210</td>
<td>0.869</td>
<td>8400</td>
<td>4593</td>
<td>7121</td>
<td>1845</td>
<td>448</td>
</tr>
<tr>
<td>329.2</td>
<td>0.188</td>
<td>0.893</td>
<td>8941</td>
<td>4644</td>
<td>7696</td>
<td>1761</td>
<td>641</td>
</tr>
<tr>
<td>335.2</td>
<td>0.186</td>
<td>0.887</td>
<td>9125</td>
<td>4617</td>
<td>7940</td>
<td>1658</td>
<td>701</td>
</tr>
<tr>
<td>344.2</td>
<td>0.176</td>
<td>0.884</td>
<td>9498</td>
<td>4662</td>
<td>8344</td>
<td>1599</td>
<td>818</td>
</tr>
<tr>
<td>356.2</td>
<td>0.175</td>
<td>0.840</td>
<td>9819</td>
<td>4169</td>
<td>9202</td>
<td>794</td>
<td>1090</td>
</tr>
<tr>
<td>Temperature $T_K$</td>
<td>$x_1$ wt%</td>
<td>$x_2$ wt%</td>
<td>Van Laar</td>
<td>NRTL($\alpha=0.3$)</td>
<td>Heil</td>
<td>Drye</td>
<td>$R_f$</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>----------</td>
<td>-------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>293.2</td>
<td>0.273</td>
<td>0.884</td>
<td>7218</td>
<td>4190</td>
<td>6053</td>
<td>1699</td>
<td>110</td>
</tr>
<tr>
<td>298.2</td>
<td>0.256</td>
<td>0.883</td>
<td>7480</td>
<td>4205</td>
<td>6340</td>
<td>1642</td>
<td>213</td>
</tr>
<tr>
<td>303.2</td>
<td>0.241</td>
<td>0.882</td>
<td>7731</td>
<td>4224</td>
<td>6613</td>
<td>1593</td>
<td>309</td>
</tr>
<tr>
<td>270.6</td>
<td>0.369</td>
<td>0.869</td>
<td>6117</td>
<td>3877</td>
<td>5004</td>
<td>1658</td>
<td>-248</td>
</tr>
<tr>
<td>264.6</td>
<td>0.397</td>
<td>0.869</td>
<td>5842</td>
<td>3837</td>
<td>4713</td>
<td>1704</td>
<td>-346</td>
</tr>
<tr>
<td>254.6</td>
<td>0.450</td>
<td>0.859</td>
<td>5545</td>
<td>3557</td>
<td>4532</td>
<td>1492</td>
<td>-437</td>
</tr>
<tr>
<td>261.8</td>
<td>0.438</td>
<td>0.868</td>
<td>5596</td>
<td>3860</td>
<td>4632</td>
<td>1621</td>
<td>-480</td>
</tr>
<tr>
<td>278.2</td>
<td>0.343</td>
<td>0.870</td>
<td>6428</td>
<td>3948</td>
<td>5324</td>
<td>1629</td>
<td>-149</td>
</tr>
<tr>
<td>298.2</td>
<td>0.255</td>
<td>0.884</td>
<td>7486</td>
<td>4220</td>
<td>6340</td>
<td>1655</td>
<td>211</td>
</tr>
<tr>
<td>323.2</td>
<td>0.206</td>
<td>0.871</td>
<td>8576</td>
<td>4261</td>
<td>7581</td>
<td>1372</td>
<td>611</td>
</tr>
<tr>
<td>338.2</td>
<td>0.183</td>
<td>0.858</td>
<td>9236</td>
<td>4211</td>
<td>8406</td>
<td>1101</td>
<td>882</td>
</tr>
<tr>
<td>358.2</td>
<td>0.186</td>
<td>0.839</td>
<td>9736</td>
<td>4217</td>
<td>9087</td>
<td>838</td>
<td>1008</td>
</tr>
<tr>
<td>388.2</td>
<td>0.211</td>
<td>0.769</td>
<td>10225</td>
<td>3896</td>
<td>10310</td>
<td>-101</td>
<td>1236</td>
</tr>
<tr>
<td>413.2</td>
<td>0.317</td>
<td>0.598</td>
<td>9876</td>
<td>3796</td>
<td>10887</td>
<td>-302</td>
<td>1167</td>
</tr>
</tbody>
</table>

$R_f$
<table>
<thead>
<tr>
<th>Temperature $\alpha_K$</th>
<th>$x_1$ wt%</th>
<th>$x_2$ wt%</th>
<th>Van Laar A</th>
<th>Van Laar B</th>
<th>NRTL($\alpha=0.3$) A</th>
<th>NRTL($\alpha=0.3$) B</th>
<th>Heil A</th>
<th>Heil B</th>
<th>Orye A</th>
<th>Orye B</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.2</td>
<td>0.254</td>
<td>0.892</td>
<td>7221</td>
<td>4213</td>
<td>6255</td>
<td>1799</td>
<td>178</td>
<td>3232</td>
<td>-1998</td>
<td>4390</td>
</tr>
<tr>
<td>312.9</td>
<td>0.201</td>
<td>0.864</td>
<td>8366</td>
<td>4303</td>
<td>7259</td>
<td>1593</td>
<td>567</td>
<td>3233</td>
<td>-1905</td>
<td>4421</td>
</tr>
<tr>
<td>328.2</td>
<td>0.178</td>
<td>0.878</td>
<td>9024</td>
<td>4356</td>
<td>7994</td>
<td>1413</td>
<td>792</td>
<td>3302</td>
<td>-1895</td>
<td>4527</td>
</tr>
<tr>
<td>342.7</td>
<td>0.170</td>
<td>0.865</td>
<td>9508</td>
<td>4320</td>
<td>8631</td>
<td>1188</td>
<td>964</td>
<td>3329</td>
<td>-1889</td>
<td>4597</td>
</tr>
<tr>
<td>354.2</td>
<td>0.172</td>
<td>0.842</td>
<td>9800</td>
<td>4162</td>
<td>9167</td>
<td>815</td>
<td>1098</td>
<td>3279</td>
<td>-1862</td>
<td>4580</td>
</tr>
<tr>
<td>373.2</td>
<td>0.195</td>
<td>0.798</td>
<td>10017</td>
<td>3957</td>
<td>9826</td>
<td>236</td>
<td>1291</td>
<td>3180</td>
<td>-1865</td>
<td>4578</td>
</tr>
</tbody>
</table>
TABLE (5-6)

Coefficients for the polynomials to represent the van Laar, NRTL(α=0.3), Heil and Orye constants at various temperatures and 1 atm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$a_{10}$</th>
<th>$a_{11}$</th>
<th>$a_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>van Laar A</td>
<td>-7.3130</td>
<td>6.0142x10^{-2}</td>
<td>-8.5222x10^{-5}</td>
</tr>
<tr>
<td>van Laar B</td>
<td>-1.3323</td>
<td>2.1951x10^{-2}</td>
<td>-3.9158x10^{-5}</td>
</tr>
<tr>
<td>NRTL(α=0.3) A</td>
<td>11000.41</td>
<td>69.11207</td>
<td>-0.03690</td>
</tr>
<tr>
<td>NRTL(α=0.3) B</td>
<td>-13406.31</td>
<td>103.5369</td>
<td>-0.17665</td>
</tr>
<tr>
<td>Heil A</td>
<td>-9457.03</td>
<td>48.5993</td>
<td>-0.05425</td>
</tr>
<tr>
<td>Heil B</td>
<td>-5528.66</td>
<td>51.7357</td>
<td>-0.07506</td>
</tr>
<tr>
<td>Orye A</td>
<td>-1676.82</td>
<td>-2.4502</td>
<td>4.73699x10^{-3}</td>
</tr>
<tr>
<td>Orye B</td>
<td>4834.46</td>
<td>52.2689</td>
<td>-0.07151</td>
</tr>
<tr>
<td>Temperature (°K)</td>
<td>Pressure (Psi)</td>
<td>$x_1$ (wt%)</td>
<td>$x_2$ (wt%)</td>
</tr>
<tr>
<td>----------------</td>
<td>---------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>298.2</td>
<td>2500</td>
<td>20.97</td>
<td>88.27</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>20.56</td>
<td>78.05</td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>24.72</td>
<td>70.65</td>
</tr>
<tr>
<td>312.9</td>
<td>3000</td>
<td>22.42</td>
<td>87.80</td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>21.97</td>
<td>87.83</td>
</tr>
<tr>
<td></td>
<td>8500</td>
<td>21.55</td>
<td>79.12</td>
</tr>
<tr>
<td></td>
<td>10400</td>
<td>24.24</td>
<td>57.96</td>
</tr>
<tr>
<td>328.2</td>
<td>3100</td>
<td>20.27</td>
<td>87.87</td>
</tr>
<tr>
<td></td>
<td>7000</td>
<td>20.36</td>
<td>86.02</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>22.03</td>
<td>83.95</td>
</tr>
<tr>
<td></td>
<td>13500</td>
<td>24.22</td>
<td>73.77</td>
</tr>
<tr>
<td></td>
<td>14000</td>
<td>24.16</td>
<td>70.65</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>Pressure (Psi)</td>
<td>$x_1$ wt%</td>
<td>$x_2$ wt%</td>
</tr>
<tr>
<td>----------------</td>
<td>---------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>342.7</td>
<td>5750</td>
<td>21.88</td>
<td>86.81</td>
</tr>
<tr>
<td></td>
<td>9600</td>
<td>22.36</td>
<td>84.38</td>
</tr>
<tr>
<td></td>
<td>13500</td>
<td>23.89</td>
<td>83.94</td>
</tr>
<tr>
<td></td>
<td>17000</td>
<td>25.10</td>
<td>76.53</td>
</tr>
<tr>
<td>373.2</td>
<td>3200</td>
<td>20.11</td>
<td>84.09</td>
</tr>
<tr>
<td></td>
<td>6500</td>
<td>2102</td>
<td>87.07</td>
</tr>
<tr>
<td></td>
<td>9500</td>
<td>21.67</td>
<td>81.69</td>
</tr>
<tr>
<td></td>
<td>12500</td>
<td>24.28</td>
<td>67.57</td>
</tr>
</tbody>
</table>
at various pressures and at fixed temperatures.

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Orye A</th>
<th></th>
<th>Orye B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_{10}$</td>
<td>$a_{11}$</td>
<td>$a_{12}$</td>
<td>$a_{10}$</td>
</tr>
<tr>
<td>298.2</td>
<td>-1985.99</td>
<td>0.0763</td>
<td>$1.34197 \times 10^{-6}$</td>
<td>4396.94</td>
</tr>
<tr>
<td>312.9</td>
<td>-1980.60</td>
<td>$-3.2476 \times 10^{-3}$</td>
<td>$3.70810 \times 10^{-6}$</td>
<td>4520.67</td>
</tr>
<tr>
<td>328.2</td>
<td>-1960.06</td>
<td>-0.0181</td>
<td>$3.04331 \times 10^{-6}$</td>
<td>4615.00</td>
</tr>
<tr>
<td>342.7</td>
<td>-1951.77</td>
<td>-0.0333</td>
<td>$2.37467 \times 10^{-6}$</td>
<td>4678.49</td>
</tr>
<tr>
<td>373.2</td>
<td>-1931.91</td>
<td>-0.0606</td>
<td>$3.96793 \times 10^{-6}$</td>
<td>4705.23</td>
</tr>
<tr>
<td>MEK</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pressure (psi)</strong></td>
<td><strong>Comp.</strong></td>
<td><strong>Pressure (psi)</strong></td>
<td><strong>Comp.</strong></td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>0.9670</td>
<td>5000</td>
<td>0.9879</td>
<td></td>
</tr>
<tr>
<td>9900</td>
<td>0.9411</td>
<td>10000</td>
<td>0.9740</td>
<td></td>
</tr>
<tr>
<td>14300</td>
<td>0.9232</td>
<td>15000</td>
<td>0.9642</td>
<td></td>
</tr>
<tr>
<td>22600</td>
<td>0.9052</td>
<td>20000</td>
<td>0.9420</td>
<td></td>
</tr>
<tr>
<td>27000</td>
<td>0.8966</td>
<td>25000</td>
<td>0.9412</td>
<td></td>
</tr>
<tr>
<td>30000</td>
<td>0.8898</td>
<td>30000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5% MEK</th>
<th>10% MEK</th>
<th>15% MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure (psi)</strong></td>
<td><strong>Comp.</strong></td>
<td><strong>Pressure (psi)</strong></td>
</tr>
<tr>
<td>5000</td>
<td>0.9890</td>
<td>5000</td>
</tr>
<tr>
<td>10000</td>
<td>0.9763</td>
<td>10000</td>
</tr>
<tr>
<td>15000</td>
<td>0.9665</td>
<td>15000</td>
</tr>
<tr>
<td>20000</td>
<td>0.9580</td>
<td>20500</td>
</tr>
<tr>
<td>25000</td>
<td>0.9523</td>
<td>25000</td>
</tr>
<tr>
<td>30000</td>
<td>0.9463</td>
<td>30000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>91% MEK</th>
<th>94% MEK</th>
<th>97% MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure (psi)</strong></td>
<td><strong>Comp.</strong></td>
<td><strong>Pressure (psi)</strong></td>
</tr>
<tr>
<td>5000</td>
<td>0.9786</td>
<td>5000</td>
</tr>
<tr>
<td>10000</td>
<td>0.9580</td>
<td>10000</td>
</tr>
<tr>
<td>15000</td>
<td>0.9418</td>
<td>15000</td>
</tr>
<tr>
<td>20000</td>
<td>0.9290</td>
<td>20000</td>
</tr>
<tr>
<td>25000</td>
<td>0.9199</td>
<td>25000</td>
</tr>
<tr>
<td>30000</td>
<td>0.9119</td>
<td>30000</td>
</tr>
</tbody>
</table>
TABLE (5-10) Compressibility of MEK, H₂O & their mixtures at 50°C.

<table>
<thead>
<tr>
<th>MEK</th>
<th></th>
<th>Water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psi)</td>
<td>Comp.</td>
<td>Pressure (psi)</td>
<td>Comp.</td>
</tr>
<tr>
<td>5000</td>
<td>0.9662</td>
<td>5000</td>
<td>0.9874</td>
</tr>
<tr>
<td>9700</td>
<td>0.9375</td>
<td>12500</td>
<td>0.9683</td>
</tr>
<tr>
<td>14700</td>
<td>0.9139</td>
<td>15000</td>
<td>0.9624</td>
</tr>
<tr>
<td>19600</td>
<td>0.8965</td>
<td>20000</td>
<td>0.9524</td>
</tr>
<tr>
<td>24800</td>
<td>0.8842</td>
<td>25000</td>
<td>0.9416</td>
</tr>
<tr>
<td>30000</td>
<td>0.8767</td>
<td>30000</td>
<td>0.9336</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5% MEK</th>
<th>10% MEK</th>
<th>15% MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psi)</td>
<td>Comp.</td>
<td>Pressure (psi)</td>
</tr>
<tr>
<td>5000</td>
<td>0.9892</td>
<td>5000</td>
</tr>
<tr>
<td>11000</td>
<td>0.9759</td>
<td>10000</td>
</tr>
<tr>
<td>15000</td>
<td>0.9647</td>
<td>15000</td>
</tr>
<tr>
<td>20000</td>
<td>0.9546</td>
<td>20000</td>
</tr>
<tr>
<td>25000</td>
<td>0.9452</td>
<td>25000</td>
</tr>
<tr>
<td>30000</td>
<td>0.9368</td>
<td>30000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>91% MEK</th>
<th>94% MEK</th>
<th>97% MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psi)</td>
<td>Comp.</td>
<td>Pressure (psi)</td>
</tr>
<tr>
<td>5000</td>
<td>0.9748</td>
<td>5000</td>
</tr>
<tr>
<td>10000</td>
<td>0.9529</td>
<td>10000</td>
</tr>
<tr>
<td>15000</td>
<td>0.9346</td>
<td>15000</td>
</tr>
<tr>
<td>20000</td>
<td>0.9182</td>
<td>20000</td>
</tr>
<tr>
<td>25000</td>
<td>0.9043</td>
<td>25000</td>
</tr>
<tr>
<td>30000</td>
<td>0.8928</td>
<td>30000</td>
</tr>
</tbody>
</table>
### TABLE (5 - 11) Compressibility of MEK, H₂O and their mixtures at 70°C.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4900</td>
<td>0.9647</td>
</tr>
<tr>
<td>9800</td>
<td>0.9327</td>
</tr>
<tr>
<td>15000</td>
<td>0.9059</td>
</tr>
<tr>
<td>19900</td>
<td>0.8881</td>
</tr>
<tr>
<td>25000</td>
<td>0.8723</td>
</tr>
<tr>
<td>30000</td>
<td>0.8581</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>0.9884</td>
</tr>
<tr>
<td>9900</td>
<td>0.9762</td>
</tr>
<tr>
<td>15000</td>
<td>0.9633</td>
</tr>
<tr>
<td>19300</td>
<td>0.9540</td>
</tr>
<tr>
<td>25000</td>
<td>0.9425</td>
</tr>
<tr>
<td>30000</td>
<td>0.9325</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Comp.</th>
<th>Pressure (psi)</th>
<th>Comp.</th>
<th>Pressure (psi)</th>
<th>Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>0.9882</td>
<td>5000</td>
<td>0.9863</td>
<td>5000</td>
<td>0.9868</td>
</tr>
<tr>
<td>10000</td>
<td>0.9757</td>
<td>10000</td>
<td>0.9675</td>
<td>10000</td>
<td>0.9727</td>
</tr>
<tr>
<td>15000</td>
<td>0.9650</td>
<td>20000</td>
<td>0.9512</td>
<td>20000</td>
<td>0.9497</td>
</tr>
<tr>
<td>20000</td>
<td>0.9650</td>
<td>15000</td>
<td>0.9629</td>
<td>15000</td>
<td>0.9609</td>
</tr>
<tr>
<td>25000</td>
<td>0.9452</td>
<td>25000</td>
<td>0.9411</td>
<td>25000</td>
<td>0.9393</td>
</tr>
<tr>
<td>30000</td>
<td>0.9362</td>
<td>30000</td>
<td>0.9321</td>
<td>30000</td>
<td>0.9292</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Comp.</th>
<th>Pressure (psi)</th>
<th>Comp.</th>
<th>Pressure (psi)</th>
<th>Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>0.9691</td>
<td>5000</td>
<td>0.9686</td>
<td>5000</td>
<td>0.9652</td>
</tr>
<tr>
<td>10000</td>
<td>0.9458</td>
<td>10000</td>
<td>0.9408</td>
<td>10000</td>
<td>0.9385</td>
</tr>
<tr>
<td>15000</td>
<td>0.9273</td>
<td>15000</td>
<td>0.9190</td>
<td>15000</td>
<td>0.9134</td>
</tr>
<tr>
<td>20000</td>
<td>0.9112</td>
<td>20000</td>
<td>0.9031</td>
<td>20000</td>
<td>0.8945</td>
</tr>
<tr>
<td>25000</td>
<td>0.8991</td>
<td>25000</td>
<td>0.8896</td>
<td>25000</td>
<td>0.8800</td>
</tr>
<tr>
<td>30000</td>
<td>0.8927</td>
<td>30000</td>
<td>0.8780</td>
<td>30000</td>
<td>0.8771</td>
</tr>
</tbody>
</table>
### TABLE (5 - 12) Coefficients of the Compressibility polynomial for MEK, H₂O and their mixtures at 30°C, 50 & 70°C.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Composition wt% MEK</th>
<th>( a_1 ) x10⁻⁶</th>
<th>( a_2 ) x10⁻¹¹</th>
<th>( a_3 ) x10⁻¹⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0</td>
<td>1.00025</td>
<td>-2.76588</td>
<td>3.01891</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.00074</td>
<td>-2.86902</td>
<td>4.89027</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.00064</td>
<td>-2.95903</td>
<td>5.00078</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.00036</td>
<td>-2.84687</td>
<td>4.54521</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>1.00049</td>
<td>-4.94123</td>
<td>7.49415</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>1.00046</td>
<td>-5.61268</td>
<td>13.07037</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>1.00059</td>
<td>-5.61667</td>
<td>10.03879</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.00033</td>
<td>-7.84376</td>
<td>22.08963</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>0.99997</td>
<td>-2.46822</td>
<td>-5.86643</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.00057</td>
<td>-2.57789</td>
<td>1.54006</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.99998</td>
<td>-2.98668</td>
<td>3.32512</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.99997</td>
<td>-2.88240</td>
<td>2.38907</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>0.99999</td>
<td>-5.36290</td>
<td>7.14773</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>0.99991</td>
<td>-6.11310</td>
<td>11.43516</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>1.00005</td>
<td>-6.46093</td>
<td>12.38670</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.00025</td>
<td>-7.40185</td>
<td>9.55517</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
<td>1.00019</td>
<td>-2.37431</td>
<td>-9.90492</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.00019</td>
<td>-2.54447</td>
<td>1.23796</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.99988</td>
<td>-2.70815</td>
<td>1.26647</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.00017</td>
<td>-2.84024</td>
<td>1.38399</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>0.99967</td>
<td>-6.48386</td>
<td>11.54206</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>1.00060</td>
<td>-7.35511</td>
<td>15.42782</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>1.00063</td>
<td>-7.89456</td>
<td>16.31242</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.99718</td>
<td>-10.07472</td>
<td>34.06757</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>Composition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>2.766</td>
<td>2.330</td>
<td>2.228</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.869</td>
<td>2.049</td>
<td>1.508</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.959</td>
<td>2.101</td>
<td>1.528</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.847</td>
<td>2.104</td>
<td>1.693</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>4.941</td>
<td>3.529</td>
<td>2.291</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>5.613</td>
<td>3.500</td>
<td>2.388</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>5.617</td>
<td>3.834</td>
<td>2.499</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>7.844</td>
<td>4.231</td>
<td>2.230</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>2.468</td>
<td>2.443</td>
<td>2.133</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.578</td>
<td>2.280</td>
<td>2.006</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.987</td>
<td>2.380</td>
<td>1.932</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.868</td>
<td>2.424</td>
<td>2.048</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>5.363</td>
<td>4.052</td>
<td>2.978</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>6.113</td>
<td>4.158</td>
<td>2.889</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>6.461</td>
<td>4.345</td>
<td>2.957</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>7.402</td>
<td>5.665</td>
<td>4.275</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
<td>2.374</td>
<td>2.035</td>
<td>2.204</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.544</td>
<td>2.311</td>
<td>1.990</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.708</td>
<td>2.478</td>
<td>2.109</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.840</td>
<td>2.586</td>
<td>2.194</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>6.484</td>
<td>4.361</td>
<td>2.611</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>7.355</td>
<td>4.726</td>
<td>3.011</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>7.895</td>
<td>5.069</td>
<td>3.122</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8.383</td>
<td>5.520</td>
<td>3.525</td>
</tr>
</tbody>
</table>
TABLE (5 - 14)  Volume changes on mixing for MEK/H₂O mixtures at pressures up to 25000 psi and at

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>91%</th>
<th>94%</th>
<th>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>5000</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>10000</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>15000</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>20000</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>25000</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>
</tr>
</tbody>
</table>
TABLE (5 - 15) Volume changes on mixing for MEK/H₂O mixtures at pressures up to 25000 psi and a

<table>
<thead>
<tr>
<th>Pressure psi</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>91%</th>
<th>94%</th>
<th>97%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.118</td>
<td>-0.248</td>
<td>-0.369</td>
<td>-0.638</td>
<td>-0.403</td>
<td>-0.318</td>
</tr>
<tr>
<td>5000</td>
<td>-0.052</td>
<td>-0.211</td>
<td>-0.302</td>
<td>-0.080</td>
<td>0.000</td>
<td>0.076</td>
</tr>
<tr>
<td>10000</td>
<td>-0.048</td>
<td>-0.163</td>
<td>-0.248</td>
<td>0.418</td>
<td>0.489</td>
<td>0.557</td>
</tr>
<tr>
<td>15000</td>
<td>0.170</td>
<td>0.035</td>
<td>-0.030</td>
<td>0.053</td>
<td>0.009</td>
<td>0.095</td>
</tr>
<tr>
<td>20000</td>
<td>0.195</td>
<td>0.066</td>
<td>0.049</td>
<td>0.830</td>
<td>0.941</td>
<td>0.978</td>
</tr>
<tr>
<td>25000</td>
<td>0.161</td>
<td>0.035</td>
<td>0.021</td>
<td>0.607</td>
<td>0.935</td>
<td>0.721</td>
</tr>
</tbody>
</table>
TABLE (5 - 16) Volume changes on mixing for MEK/H₂O mixtures at pressures up to 25000 psi and a

<table>
<thead>
<tr>
<th>Pressure (Psi)</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>91%</th>
<th>94%</th>
<th>97%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.109</td>
<td>-0.230</td>
<td>-0.350</td>
<td>-0.708</td>
<td>-0.382</td>
<td>-0.186</td>
</tr>
<tr>
<td>5000</td>
<td>-0.076</td>
<td>-0.182</td>
<td>-0.286</td>
<td>-0.369</td>
<td>0.020</td>
<td>-0.054</td>
</tr>
<tr>
<td>10000</td>
<td>-0.051</td>
<td>-0.170</td>
<td>-0.226</td>
<td>0.142</td>
<td>0.201</td>
<td>0.351</td>
</tr>
<tr>
<td>15000</td>
<td>0.005</td>
<td>-0.119</td>
<td>-0.104</td>
<td>0.607</td>
<td>0.483</td>
<td>0.330</td>
</tr>
<tr>
<td>20000</td>
<td>0.018</td>
<td>-0.107</td>
<td>-0.107</td>
<td>-0.794</td>
<td>0.697</td>
<td>0.403</td>
</tr>
<tr>
<td>25000</td>
<td>0.025</td>
<td>-0.112</td>
<td>-0.083</td>
<td>0.999</td>
<td>0.844</td>
<td>0.395</td>
</tr>
</tbody>
</table>