LIQUID-LIQUID PHASE EQUILIBRIUM
AT HIGH PRESSURE

A THESIS
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by

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ABSTRACT

Mutual solubilities of 3 methyl 2 butanone-water have been determined analytically for temperatures from -8°C to 180°C at low pressure and from -8°C to 90°C at pressures up to 350 MN/m². It is found that this system shows a phase behaviour at elevated pressure similar to that of the homologous system 2 butanone-water. The phase behaviour of the ternary system 3 methyl 2 butanone-water-propanone was studied analytically and optically at ambient pressure at 0°C and 40°C.

Liquid-liquid equilibria of the binary system 2 butanol-water were thoroughly studied as a function of temperature and pressure. An hitherto unknown immiscibility phenomenon shown by this system was observed at 13.8 MN/m² isobar in which a domed curve with an U.C.S.T. is followed by a closed solubility loop having a L.C.S.T. and an U.C.S.T.

The phase behaviour of the binary system propanone-carbon disulfide was investigated at -12°C and -14°C up to a pressure of 362 MN/m². The results support an earlier investigation carried out at -2°C which indicates that increasing pressure, raises the critical solution temperature. For each system above the relations existing among the consolute solution properties are discussed in the light of the observed results.

The mutual solubility of the binary system thiodipropionitrile-toluene was studied at atmospheric pressure by a light transmission method. It appears that the demixing curve of this system exhibits a L.C.S.T. inbetween two U.C.S.T.'s over a small concentration range in an open miscibility loop.
CHAPTER 1 Liquid-Liquid Equilibrium: Review of Previous Work

1.1 Determination of liquid-liquid equilibria

1.1.1 Atmospheric Pressure Measurements

a) Synthetic method
b) Volumetric method
c) Analytical method

1.1.2 High Pressure Measurements

a) Synthetic method
b) Analytic method

1.2 A Brief Review of Relevant Previous Apparatus Used in the Determination of Mutual Solubility at Elevated Pressure

1.2.1 Optical Observation Cells

1.2.2 Autoclaves for Determination of Conjugate Composition

1.3 Measurement of Excess Volume

1.3.1 Atmospheric Pressure Measurements

a) Direct method
b) Indirect method
1.3.2 High Pressure Measurements
   a) Direct method 26
   b) Indirect method 27

1.4 Liquid-Liquid Phase Equilibria in the 3 Methyl 2 Butanone-Water System
   1.4.1 At Atmospheric Pressure 28
   1.4.2 At Elevated Pressure 28

1.5 2 Butanol-Water System
   1.5.1 Measurements at Atmospheric Pressure 30
   1.5.2 Measurements at Elevated Pressure 32

CHAPTER 2 Relevant Thermodynamics

2.1 Thermodynamics of Partially Miscible Liquids 33
   2.1.1 Equilibrium Conditions 33
   2.1.2 Stability Condition 34
   2.1.3 Determination of Equilibrium Phase Compositions 36
   2.1.4 Identification of a Consolute Point 38
      a) Condition of upper and lower critical solution temperature 39
      b) Condition for upper and lower critical solution pressure 40
      c) Condition for an hyper-critical solution point 42

2.2 Excess Properties of Solutions 42

2.3 Empirical and Semiempirical Expressions for the Excess Gibbs Energy
   2.3.1 Van Laar Equation 47
   2.3.2 Scatchard-Hildebrand Equation 49
2.3.3 Gugenheim's Equation 50
2.3.4 N.C.2 Equation 52
2.3.5 Redlich-Kister Equation 53
2.3.6 Wohl's Equation 55
2.3.7 The Flory-Huggins Equation 57
2.3.8 Wilson's Equation 58
2.3.9 N.R.T.L. Equation 60
2.3.10 Heil's Equation 63
2.3.11 Orye's Equation 64
2.3.12 Generalized Local Composition Equation 65
2.3.13 Uniquac Equation 66

2.4 Determination of the Empirical Parameters of the Equation for $G^E$
   2.4.1 Vapour-Liquid Equilibrium Data 68
   2.4.2 Liquid-Liquid Equilibrium Data 69
   2.4.3 Infinite-Dilution Activity Coefficient Data 71
   2.4.4 Sedimentation Equilibrium 72

CHAPTER 3 Description of the Apparatus

3.1 The High Pressure System 74
   3.1.1 The Pressure Generator 74
   3.1.2 The Pressure Vessel 74
   3.1.3 Piping
       a) General 76
       b) Sealing of capillary tubes 77

3.2 The Constant Temperature Bath
   a) Description 78
b) Heating medium 79

c) Control of temperature 79

3.3 Sample Holders 79

3.3.1 Design Requirements 79

3.3.2 Piston-Cylinder Arrangement 81

3.3.3 Double Cylinder Arrangement 83

3.4 Gas Chromatograph 86

3.4.1 Apparatus 86

3.4.2 Calibration 86

CHAPTER 4 Experimental Technique 87

4.1 Determination of Mutual Solubility Data at Atmospheric and Slightly Elevated Pressure 90

4.1.1 Analytical Method 90

a) At atmospheric pressure 91

b) At slightly elevated pressure 92

4.1.2 The Light Transmission Method 93

a) Application of the light transmission method 94
to a binary system

b) Application of the light transmission method to a ternary system 95

4.2 Determination of Liquid-Liquid Equilibrium Data at High Pressure 98

4.2.1 Preparation of the Apparatus 98

a) Filling the piston-cylinder holder 98

b) Filling the double-cylinder holder 98

4.2.2 Assembly of the Apparatus 98

4.2.3 Experimental Procedure 99

a) Attainment of equilibrium 99
b) Method of withdrawing samples

4.3 Materials

CHAPTER 5 Treatment of Results

5.1 The Mutual Solubility of the Binary System 3 Methyl 2 Butanone-Water

5.1.1 Atmospheric Pressure Measurements

5.1.2 The Ternary System 3 Methyl 2 Butanone-Water-Propanone

5.2 The Mutual Solubility of the Binary System 2 Butanol-Water

5.2.1 Atmospheric Pressure Measurements

5.2.2 High Pressure Measurements

5.3 The phase Behaviour of the Propanone-Carbon Disulfide System at High Pressure

5.4 The Mutual Solubility of the Thiodipropionitrile-Toluene System

5.5 Correlation and Prediction of the Conjugate Compositions

CHAPTER 6 Discussion of Results

6.1 Equilibrium Data of the System 3 Methyl 2 Butanone-Water

6.1.1 Atmospheric Pressure Measurement Results

6.1.2 High Pressure Results

6.1.3 The Ternary System 3 Methyl 2 Butanone-Water-Propanone

6.2 Liquid-Liquid Equilibrium of the 2 Butanol-Water System

6.2.1 Atmospheric Pressure Results

6.2.2 High Pressure Results
<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3 The Propanone-Carbon Disulfide System</td>
<td>147</td>
</tr>
<tr>
<td>6.4 The Mutual Solubility of the Thiodipropionitrile-Toluene System</td>
<td>148</td>
</tr>
<tr>
<td>6.5 Back-Calculation of the Experimentally Obtained Liquid-Liquid Equilibrium Data</td>
<td>149</td>
</tr>
<tr>
<td><strong>CHAPTER 7 Conclusions</strong></td>
<td></td>
</tr>
<tr>
<td>7.1 3 Methyl 2 Butanol-Water</td>
<td>151</td>
</tr>
<tr>
<td>7.2 2 Butanol-Water</td>
<td>151</td>
</tr>
<tr>
<td>7.3 Propanone-Carbon Disulfide</td>
<td>152</td>
</tr>
<tr>
<td>7.4 Thiodipropionitrile-Toluene</td>
<td>152</td>
</tr>
<tr>
<td>7.5 General Remarks</td>
<td>153</td>
</tr>
</tbody>
</table>

**REFERENCES**                                                          | 154      |

**APPENDIX 1 Tables of Results**                                        | 161      |

**APPENDIX 2 Empirical Constants**                                      | 172      |

**APPENDIX 3 Accuracy of Conjugate Compositions**                       | 186      |

**APPENDIX 4 High Pressure Dilatometer**                                | 192      |
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LIST OF FIGURES

INTRODUCTION

I.1 Schematic representation of temperature-composition isobars 3
I.2 Pressure dependence of consolute temperature of binary system 7
I.3 Schematic representation of the multiplicity of the consolute temperatures 9

CHAPTER 1

1.1 Apparent region of immiscibility of 3 methyl 2 butanone-water 29
1.2 Liquid-liquid equilibrium data of various workers for the 2 butanol-water system 31

CHAPTER 2

2.1 Composition dependence of Gibbs energy and its derivatives 37
2.2.a Enthalpy of binary mixtures 41
2.2.b Consolute temperature of binary mixtures 41

CHAPTER 3

3.1 General layout of the experimental apparatus 76
3.2 External-internal cone connection 78
3.3 Method of sealing the capillary into the high pressure nipple 78
3.4 a) Temperature control circuit 80
   b) 12 Power supply 80
3.5 Detail of the piston-cylinder equilibrium cell 82
3.6 An exploded view of equilibrium cells 84
3.7 Double cylinder equilibrium cell 87
3.8 General arrangement of the equilibrium cell and valves 88
3.9 Chromatograms of 3 methyl 2 butanone-water-propanone 88
CHAPTER 4

4.1 Analytical cell for determination of the mutual solubility at temperatures above the boiling point of the mixture 92
4.2 Optical cell for the measurements of the light transmission method 92
4.3 Optical cell for cloud point observation 96
4.4 Optical cell for 'cloud point' observation 97
4.5 Schematic arrangement of the sampling valves 101

CHAPTER 5

5.1 Miscibility isobars for system 3 methyl 2 butanone-water 104
5.2 Miscibility isotherms for system 3 methyl 2 butanone-water 106
5.3 P, T, x space of the system 3 methyl 2 butanone-water 107
5.4 Liquid-liquid equilibria at 40°C and natural pressure in the system 3 methyl 2 butanone-water-propanone 108
5.5 Mutual solubility of the system 2 butanol-water at various pressure 110
5.6 Miscibility isotherms for the system 2 butanol-water 112
5.7 Miscibility isotherms for the system 2 butanol-water 112
5.8 P, T, x space of the system 2 butanol-water 114
5.9 Miscibility isotherms of the system propanone-carbon-disulfide 116
5.10 P, T, x space of the system propanone-carbon-disulfide 117
5.11 P, T, x space of the system 2 butanol-water 119
5.12 Mutual solubility of the system thiodipropionitrile-toluene 119
5.13 Pressure dependence of the Van Laar constants of the system 3 methyl 2 butanone-water at various temperatures 122
5.14 Pressure dependence of the Heil constant of the system 3 methyl 2 butanone-water at various temperatures 123
5.15 Pressure dependence of the Orye constants of the system 3 methyl 2 butanone-water at various temperatures 124
5.16 Pressure dependence of the Uniquac constants of the system
3 methyl 2 butanone-water at various temperatures

5.17 Temperature dependence of the Van Laar constants of the system
3 methyl 2 butanone-water at various pressures

5.17 Temperature dependence of the Heil constants of the system
3 methyl 2 butanone-water at various pressures

5.18 Temperature dependence of the Orye constants of the system
3 methyl 2 butanone-water at various pressures

5.19 Temperature dependence of the Uniquac constants of the system
3 methyl 2 butanone-water at various pressures

5.20 The variation of the Van Laar constants of the system 2 butanol-
water with temperature at various pressures

5.21 The variation of the Heil constants of the system 2 butanol-water
with temperature at various pressures

5.22 The variation of the Orye constants of the system 2 butanol-water
with temperature at various pressure

5.23 The variation of Uniquac constants of the system 2 butanol-water
with temperature at various pressure

5.24 Tie-line data interpolated by the Orye equation for the system
3 methyl 2 butanone-water at various pressures

5.25 Tie-line data interpolated by the Orye equation for the system
2 butanol-water at various pressures

CHAPTER 6

6.1 Consolute line of the system 3 methyl 2 butanone-water

6.2 Comparison of the mutual solubilities of 2 butanol-water at low
temperature end

6.3 The critical line connecting the consolute points of the system
2 butanol-water.
NOMENCLATURE

A  Constant
B  Area
C  Heat Capacity
E  Molar internal energy
F  Molar Helmholtz free energy
G  Molar Gibbs free energy
H  Molar enthalpy
M  Molecular weight
P  Pressure
R  Universal gas constant
S  Molar entropy
T  Temperature
X  Flory constant
Y  Either temperature or pressure
Λ  Differences of energy parameters (i.e. g_{ij} - g_{jj})
V  Molar volume
a  constant of polynomial
c  defined in Eq. 2.3.18
d  density
δ  solubility parameters
f  fugacity
g  energy parameter
k  defined in Eq. 2.3.39
n  number of moles
x  liquid phase mass fraction
y  vapour phase mass fraction
γ  activity coefficient
ε  energy parameter
w  interchange energy
α  non-randomness parameter
q  defined in Eq. 2.3.17 and 2.3.25
r  molar volume ratio in Eq. 2.3.35 and radius in Eq. 2.4.19
u  energy parameters
ϕ  defined in Eq. 2.3.9 and 2.3.48
τ  defined in Eq. 2.3.40
ω  angular rotation rate

Superscripts

E  excess
o  pure component
r  reference
∞  infinitely dilute
-  partial
'  one of the phases
"  the other phase

Subscripts

c  critical
i  component
j  component
ij, ji  species involved in interaction parameters
HP  hyper-critical
s  self
INTRODUCTION

The study of phase behaviour of a liquid mixture is of considerable theoretical and practical interest, since the phase behaviour is one of the most fundamental properties of a mixture. For instance the differences of composition between liquid phases are exploited in order to separate substances (e.g. liquid-liquid extraction or extractive distillation). In addition to its practical importance in separation processes, knowledge of the phase behaviour is a prerequisite for other types of studies of a mixture, as it establishes the pressure-temperature-composition (P.T.X.) boundaries which define the limit of existence and coexistence of separate phases.

The phenomenon of partial miscibility, is, very important as a stringent test of any theory of solutions, since liquid-liquid immiscibility is a manifestation of strong non-idealities in the liquid mixture. It is also possible to deduce much of the information about thermodynamics of a mixture from its phase behaviour, even in the ranges of temperature and pressure, where calorimetric and volumetric measurements are difficult.

The purpose of the experimental work described here was to provide a more complete set of measurements for three selected systems: 3 methyl 2 butanone-water, 2 butanol-water and propanone-carbon disulfide. Phase behaviour of pairs of liquids is highly variable ranging from complete miscibility under all conditions (e.g. n.hexane-n.octane), to almost complete immiscibility under all conditions (e.g. water-mercury). The phase rule of Gibbs provides the framework for the description of phase diagrams. This rule expressed by the equation $f = c + 2 - p$ gives the number of independent variables, $f$, as a function of the number of components, $c$, and the number of phases, $p$, in a system at equilibrium.
For a binary system separated into two phases the application of the phase rule gives two degrees of freedom. Temperature and pressure are usually chosen as independent variables. For condensed phases the effect of pressure is often ignored so that \( f = c - p + 1 \). This is justifiable for narrow ranges of pressure but not where the pressure ranges from a few bars to several kilobars.

In the study of binary liquid-liquid equilibrium either one of the independent variables (\( T \) or \( P \)) is kept constant and the influence of the other is observed, or both of the independent variables are kept constant and the compositions of equilibrated phases are determined. In other words, there are three common methods used in the study of liquid-liquid equilibrium.

I  Isobaric Study of Liquid-Liquid Systems

An enormous amount of experimental and theoretical work has already been done in the thermodynamic investigation of mixtures at constant pressure, especially at ambient pressure. Most of the experimental work on the mutual solubilities of binary and multicomponent systems has been compiled in books by Timmermans (1) Stephens and Stephens (2), Seidel (3), Landolt-Börnstein (4) and cited by Francis (5), Hicks (6) and Chemical Abstracts.

In Fig. I.1 the different types of temperature-mole fraction isobars are schematically represented. The temperature at which the two liquid phases merge is called the critical solution temperature (C.S.T.). The maximum C.S.T. is called the upper critical solution temperature (U.C.S.T.) or upper consolute temperature and the minimum C.S.T. is called the lower critical solution temperature (L.C.S.T.) or lower consolute temperature.
Fig. 1.1 Schematic Representation of Temperature - composition isobars.
The most common form of behaviour is for mutual solubility to increase with temperature (Fig. I.1.a) and, unless the boiling point or liquid-vapour critical point occurs first, increase of temperature usually brings about complete miscibility. L.C.S.T.'s are much less common, (Fig. I.1.b) but many examples also exist. Although many liquid systems show an increase in the mutual solubility, with decreasing temperature, the L.C.S.T. is usually masked by the occurrence of a solid phase. Very few examples exist of systems showing both types of consolute point (Fig. I.1.c). For instance water-4 methyl piperidine has a closed solubility loop over a range of about 100°C within which partial miscibility occurs.

There are some unusual systems which show rather different behaviour. For instance some sulphur-aromatic hydrocarbon systems (e.g. sulphur-benzene, -toluene, p-xylene, -thriphenylmethane) have a L.C.S.T. at a significantly higher temperature than the U.C.S.T. (Fig. I.1.e). Yet an other less common demixing curve shows a waist as in Fig. I.1.f but does not exhibit any consolute points (e.g. water-diethylether).

At a specific isobar the upper and lower consolute temperatures of some systems merge at a single point which is so called hyper critical solution temperature. In this case the immiscibility loop usually consists of a single point (Fig. I.1.d) or has the shape of Fig. I.1.g).

II Isothermal Study of Liquid-Liquid Equilibrium.

In spite of extensive investigation of temperature's effect on the liquid-liquid equilibria the pressure variable has been widely neglected, although in the first decades of this century lively interest in the topic was shown in the Netherlands. However with the recent rapid development
of high pressure technique, study of the influence of pressure as a
variable on fluid mixtures has intensified in the last decades.

From the classical thermodynamic standpoint temperature and pressure
are in principle equivalent variables. Experimental findings of various
workers which have been reviewed in several papers by Schneider (7-10),
Prausnitz (11), and in books by Weale (12), Tsiklis (13), Rowlinson, (14),
Prausnitz (15) show that the shapes of isothermal pressure-composition
diagrams correspond to the temperature-composition diagram for constant
pressure. All of the known types of pressure-composition diagrams are schemat-
ically depicted in Fig. I.1. Definitions of consolute and hypercritical
solution pressures are similar to those for temperature.

III Pressure Dependence of Critical Solution Temperature in Binary Systems

The determination of a C.S.T. as a function of pressure was carried
out before the turn of the century by Kohnstamm (16), Roozeboom (17),
Kuenen (18) and Timmermans (19). Since then it has attracted more attention,
since some thermodynamic information can be deduced from the pressure
derependence of a C.S.T.

Timmermans (19) especially has made an extensive study of the effect
of pressure on U.C.S.T. and L.C.S.T. With only a few exceptions early
measurements were limited to the pressure range below 20 MN/m². In spite
of the limited pressure range of these measurements some of the general
rules discussed below, about the pressure dependence of C.S.T.'s were
deduced by Timmermans.

With the aid of modern experimental high pressure techniques, however,
a great deal of progress has been made during recent decades in the
investigation of fluid systems at pressures up to 700 MN/m². In addition
to Timmerman's findings, some new types of pressure dependence of immiscibility phenomena were observed.

In Fig. 1.2 all types of presently known C.S.T. are schematically plotted against pressure for mixtures with \( x = \text{constant} = x_c^{\text{UCST}} \) or \( x_c^{\text{LCST}} \) at atmospheric pressure. If the system does not exhibit any consolute points at atmospheric pressure \( x = \) rectilinear composition. Since the critical concentrations depend only slightly on pressure for liquid-liquid equilibria, these \( T(P) \) sections for constant composition are also characteristic for critical \( T_c(P) \) curves themselves.

U.C.S.T.'s may either rise with increasing pressure (Fig. 1.2.a₁), may remain constant within a limited pressure range, run through a temperature minimum (Fig. 1.2.a₃) or decline (Fig. 1.2.a₂). L.C.S.T.'s may also either rise with increasing pressure (Fig. 1.2.b₁), run through a temperature maximum (Fig. 1.2.b₃) or decline (Fig. 1.2.b₂). Of course there is also a possibility for U.C.S.T.'s to run through a maximum (Fig. 1.2.a₄) and for L.C.S.T.'s to run through a minimum (Fig. 1.2.b₄), but no examples of such a behaviour are presently known.

For closed solubility loops in \( T_c(P) \) sections several kinds of interesting pressure dependence have been found. In some systems, with increasing pressure the C.S.T.'s approach each other and finally merge completely at a hyper-critical solution point (Fig. 1.2.c₁). In some other systems a solubility loop reappears with further increase of pressure (Fig. 1.2.c₂) or it only appears at sufficiently high pressure (Fig. 1.2.c₃), and then disappears completely with further increase of pressure (Fig. 1.2.c₄). Fig. 1.2.c₅ and 1.2.c₆ show other types of pressure dependence of closed loops. With increasing pressure the U.C.S.T. and L.C.S.T. approach each
Fig. 1.2 Pressure Dependence of Consolute Temperature of binary System.
other then either merge at a hyper critical point and diverge with further increase of pressure (Fig. I.2.c₅) or do not merge completely but diverge with further increase of pressure again (Fig. I.2.c₆).

The influence of pressure on a system exhibiting a demixing curve as shown in Fig. I.1.e either reduces the region of complete miscibility and brings about a hyper-critical point (Fig. I.2.e₁) or brings about the behaviour of Fig. I.2.e₂. By contrast the system with a diagram as in Fig. I.1.f, may exhibit the opposite behaviour. In this case increasing pressure increases the region of complete miscibility and brings about a hyper-critical point. Further increase in pressure gives rise to an U.C.S.T. and a L.C.S.T. There is also a possibility for phase behaviour such as shown in Fig. I.2.h₁, h₂ and h₃.

There is some rather scanty evidence in the literature that certain systems may show two distinct consolute points of the same type in the same miscibility loop at either constant pressure or temperature. For instance the binary system 2,2 thiodipropionitrile-toluene studied by Skinner (20) was reported to have two separate U.C.S.T.'s within a small concentration range, at atmospheric pressure (Fig. I.3.a).

The 3 methyl 2 butanone-water system studied at high pressure by Steiner and Schadow (21) shows two upper critical solution pressures and yielded results which imply two separate L.C.S.T.'s at elevated pressure (Fig. I.3.b).

Winnick and Powers (22) in their measurements of the miscibility of carbon disulphide-propanone at -2°C as a function of pressure presents results which may possibly show two lower critical solution pressures, the inverse of the reported behaviour of 3 methyl 2 butanone-water mixture. Winnick and Powers make no comment on this aspect of their work.
Fig. I.3 Schematic Representation of the Multiplicity of the Consolute-Temperatures.
Published data on the phase behaviour of 2-butanol-water system at atmospheric pressure (Fig. 1.2) suggests that this system also might have two U.C.S.T.'s under certain conditions, but, unlike the three systems alluded to above, these U.C.S.T.'s occur in separate miscibility loops (Fig. 1.3.c).

Experiments at high pressure (23,24) have shown that there are analogies between the influence of pressure and of dissolved salt concentration on the immiscibility phenomena in liquid systems. For instance addition of KCl at atmospheric pressure to a mixture of 1-butanol-water system with a constant mass ratio creates similar effect to a change in pressure. In fact, when the pressure-concentration diagram is compared with the concentration of mixture-decreasing salt concentration diagram there is a perfect analogy.

The phase behaviour of aqueous solutions with added salts under high pressures can be extremely complicated. The ethanol-water system with a constant mass ratio of $(\text{NH}_4)_2\text{SO}_4$ added exhibits four consolute points, which imply two separate immiscibility loops, each having one U.C.S.T. and one L.C.S.T. (Fig. 1.3.d).

Theoretical consideration shows that the existence of the two separate miscibility gaps is consistent with thermodynamic principles, since the only restriction on a consolute temperature is $\frac{\partial^2 G}{\partial x^2} = 0$. 

CHAPTER 1

LIQUID-LIQUID EQUILIBRIUM

REVIEW OF PREVIOUS WORK

1.1 Determination of Liquid-Liquid Equilibria

1.1.1 Atmospheric Pressure Measurements

For the investigation of the liquid-liquid equilibria at atmospheric pressure or in the vicinity of atmospheric pressure, there are various methods. None of them requires experimentation of any complexity. Three of these methods have found general applicability:

a) Synthetic Method

This is the oldest method initiated by Alexzeff (25). In this method weighed quantities of the two liquid components are sealed in a glass tube to prevent changes in composition by evaporation. The tube is then immersed in a heating bath and heated to a temperature at which the two liquid phases are completely miscible or cooled until the single phase separates into two phases. The critical solution temperature is then associated with the appearance or disappearance of a turbidity which results from the difference in refractive index of the coexisting phases.

The method is simple to perform and is very suitable for the measurements in the vicinity of a consolute point but not at conditions far away from it where the absolute value of $\frac{\partial T}{\partial X_p}$ may be very big or infinite. This method has a number of other disadvantages which may be cited as follows:

i) It does not yield experimental points at the same temperature for conjugate compositions.
ii) The vapour pressure in the dead space above the liquid mixture in the sealed tube may affect the equilibrium solubility, though not necessarily in all systems.

iii) The presence of a trace of sparingly soluble impurities in the mixture may cause a turbidity which could be confused with the actual critical solution temperature (26).

iv) The observation of a C.S.T. could also be confused by occurrence of an iso-optic condition in which the refractive indices of the liquid phases are equal for some wavelength in the visible spectrum. In general the lower the refractive index difference between the two pure components, the less accurate the result is.

A further difficulty may arise when the densities of the two phases are equal; the phases do not stratify into separate layers, but remain as a stable emulsion of large globules. This phenomenon is called barotropy which is in a sense inverse of azeotropy (e.g. in azeotropy the composition of the coexisting phases is the same, but densities are different. Here the situation is reversed).

One other difficulty, which is inherent in any method, is that one has to infer from the set of experimental points the 'best' co-ordinates of the consolute point.

Several versions of the synthetic method have been suggested. They all stem from the fact that the coexisting phases have the same temperature and pressure, but differ in density, concentration and other related physical properties. If one determines the variation of any of these properties with temperature at constant pressure or vice versa, the discontinuity of the property as a function of the independent variable yields the critical solution temperature and pressure. For instance the density of one of the
coexisting phases as a function of temperature is dynamically measured around a C.S.T. From the inflection point in the density-temperature curve the C.S.T. is deduced (27). For the precise measurement of the temperature dependence of density, descriptions of several magnetic densitometers have recently appeared in the literature (28,29). In the magnetic densitometric method the current needed to maintain the float at a given level is used as a measure of the density of the medium. The float is calibrated using a number of liquids of known density.

In a similar way, the C.S.T. of a synthetic mixture may be deduced from the measurement of dielectric constant (21), refractive index (30) and sound velocity (31).

The C.S.T. of a synthetic mixture may also be deduced from differential thermal analysis. Although this method still lacks application for the study of liquid-liquid equilibria, it may prove to be useful, since some information about the heat of mixing may also be deduced.

b) Volumetric Method

The method was initially employed for the measurement of mutual solubility by Hill (32). It consists of mixing known volumes of pure liquids and measuring the volume of the two phases after equilibrium has been attained. In order to calculate the mutual solubility, several measurements have to be carried out with different initial volume ratios. From two parallel experiments with m and m' mass of one of the components, volume a, b and a', b' of the phases, the equilibrium concentration x and y' can be calculated using the mass balance \( ax + by' = m \) and \( a'x + b'y' = m' \).
Centrifugation of the whole unit improves phase separation and eliminates possible errors caused by retention of liquid on the vessel's walls or by emulsification (33). If the two liquids have similar densities, centrifugation becomes mandatory.

One other method for determination of a C.S.T. is the titration method of Hertz (34). Here one of the pure liquids is added to the other, up to point of saturation at constant temperature. The accuracy of this method is considered to be poor. It may be improved in the aqueous solution of organic solvents by dispersing a water-insoluble dye in water and adding the organic solvent dropwise, until the excess dissolves the organic dye (35), though the presence of dye as solute may itself disturb the equilibrium.

c) Analytical Method

For the determination of the mutual solubility of a binary system at a chosen temperature below the boiling point of the mixture a heterogeneous mixture is made up in a test tube and immersed in a constant temperature bath. The contents of the test tube are stirred by some means to ensure equilibrium. Then the phases are allowed to reach complete separation by gravity. Representative samples of each phase are extracted and analysed. For the measurement at a temperature above the boiling point of the mixture, the experiment has to be carried out in a sealed device to prevent complete evaporation. Again samples from each phase are withdrawn and analysed.

Since gas-liquid chromatography provides a simple and accurate method of analysis, this method is becoming the most favoured.
The composition of coexisting phases may also be determined by measuring two physical properties. Curves representing the behaviour of any two physical properties with respect to composition make possible the analysis of any mixture, when plotted on a triangular diagram. In this method in order to get accurate results, it is necessary that curves should intersect sharply.

In this method, the only problem arising from the type of phase involved is the necessity of allowing sufficient agitation and contact time to attain equilibrium without formation of a stable emulsion and sufficient time to ensure that only one phase is being sampled at a time.

1.1.2 High Pressure Measurements

There are two methods commonly used for obtaining high pressure liquid-liquid equilibrium data. The synthetic method and the analytical method. These methods are extensions of the principles used at or near atmospheric pressure. However the details and materials of construction of the apparatus are often very different.

a) The Synthetic Method

There are two common versions of this method. The first is usually called the "optical method" in which a known composition of mixture is made up at atmospheric pressure by mass. The critical solution point is associated with a cloud point. Pressure is the preferred variable, since varying pressure is, in general, more convenient than temperature. This method fails where the absolute value of \( \frac{\partial P}{\partial T} \) is very big or infinite. It is equally possible to vary the temperature at constant pressure. This method fails where the absolute value of \( \frac{\partial P}{\partial T} \) is very small or zero.
The second version of the synthetic method, is similar to that at atmospheric pressure. Here the variation of a physical property with one of the independent variables is determined. From the discontinuity in the relationship between the independent variable and that physical property, critical solution point is deduced. Although at atmospheric pressure the temperature is the unique variable, here either temperature or pressure may be varied. In determining a critical solution point on the consolute envelope the measurements of properties such as volume (36), dielectric constant (21), electrical conductivity (37) have found some application.

The synthetic method has a number of advantages and disadvantages:

**Advantages**: The method is particularly suitable for measurements near a consolute point. Barotropic systems (i.e., systems with equal density but with different compositions) can also be studied.

Simultaneous determination of P.V.T. data is possible. The high pressure cell can be comparatively small and inexpensive. A whole T(p) isopleth can be obtained with one filling. Usually the experimental procedure is easy and quick.

**Disadvantages**: The method is not suitable for measurements far away from consolute points, where the absolute values of \( \frac{\partial T}{\partial x} \) or \( \frac{\partial p}{\partial T} \) are big or infinite. Visual observation is inconclusive for iso-optic systems. The method is not very convenient for multicomponent systems. The study of phase behaviour is impossible when more then two phases are present.

b) The Analytical Method

The vessel is charged with the mixture of approximately known overall composition such that two equilibrium layers of more or less equal volumes form at the required conditions. Then the system is brought to
the required conditions. The contents of the sample holder are stirred to equilibrate the phases. Once the equilibrium condition has been reached the concentration of each phase is determined by withdrawing samples from each layer and analysing them outside the autoclave. In principle it is of course possible to determine the concentration of coexisting phases within the vessel under the existing conditions by an appropriate physico-chemical method of analysis.

This method has also a number of advantages and disadvantages:

**Advantages**: Several isotherms (or isobars) can be measured with one filling. Multicomponent systems can be studied. Tie-lines are determined directly. Results are free from subjective errors.

**Disadvantages**: The method is not suitable near consolute points or for barotropic systems where the equilibrating phases do not separate well. Reliable sampling can be difficult especially if the substances under investigation show very different volatility (e.g. gas-gas equilibria). Additionally, the samples have to be small and the volume of the mixture confined within the holder large in order to avoid fluctuation in equilibrium resulting from pressure change during the sampling procedure. A great internal volume however requires heavy and expensive autoclaves. The increase of viscosity with increasing pressure may retard the complete separation of phases. It may be difficult to ensure that equilibrium is effectively reached. Contamination of one phase by the other may cause considerable errors. The co-ordinates of the consolute point or the hyper-critical point have to be inferred from the set of experimental points. This difficulty is probably inherent in any other method for determination of the mutual solubility at elevated pressure.
1.2 A Brief Review of Relevant Previous Apparatus Used in Determination of Mutual Solubility at Elevated Pressure

1.2.1 Optical Observation Cells

A great number of optical cells described in the literature have been used by numerous authors for the investigation of all kinds of fluid two-phase equilibria. The study has been started by Kohnstamm (16), Roozeboom (17), Timmermanns (19), Kuenen (18) and many others. The original references of these earlier workers are very difficult to obtain and very little information is available about their experimental apparatus, though some of them made measurements at pressures up to 300 MN/m² as early as 1912.

Several high pressure optical cells have been described in the literature. Most of these use synthetic sapphire windows, since the behaviour of glass under pressure is unpredictable.

Schneider (38) has described a very simple high pressure cell which can be used to study liquid-liquid immiscibility up to 500 MN/m². The contents of the cell were agitated by a small magnetic stirrer driven from outside the vessel by a rotating magnet and were viewed through two sapphire windows. Pressure was conveyed to the system by a moving p.t.f.e. piston.

Ehrlich and Kurpen (39) have described another simple high pressure cell which was used to study phase equilibria of polymer-solvent systems. They used large windows (25 mm) made from pyrex or plate glass which were sealed by two sets of neoprene 'O' rings. The cell operated up to 60 MN/m².

Connolly (40) described an apparatus to determine solubility of hydrocarbon in water up to a pressure of 80 MN/m². It consists of a stainless steel vessel with three injection points, one each for mercury, water and
hydrocarbon. The topmost portion of the cell is viewed through a prism and window arrangement. Mixing is accomplished by a magnetically driven steel ball.

The cell is loaded with a known amount of water and brought to required temperature. Mixing is started and hydrocarbon is injected until either a cloud point or a small portion of a second phase appears at the top of the cell. Then mercury is injected to change the pressure and more hydrocarbon is injected and so on.

Oeder and Schneider (41) described a slightly more complicated optical cell for measurements up to 300 MN/m². The cell, intended for low temperature working, was constructed from copper-beryllium and was fitted with two sapphire windows. The liquid mixture in the cell was agitated by a small magnetic stirrer driven from outside the cell by a rotating magnet. The pressure was transmitted to the mixture by a flexible bellows. Displacement of the bellows could be detected and measured by a displacement transducer. This enables the cell to be used for P.V.T. measurements as well.

Another optical cell was described by Arons and Diepen (42). The fluid mixture is enclosed in a glass pyknometer that is mounted in an autoclave. Mercury is used as an intermediate fluid to prevent pressure transmitting fluid coming in contact with the mixture under test. The phase equilibrium in the neck of the pyknometer could be viewed through two windows of safety glass. The mixture is stirred by a small permanent magnet which is driven from outside the pyknometer by a second permanent magnet fastened to an iron tube. The second magnet was actuated by a solenoid mounted at the outside of the vessel. The cell was used up to 200 MN/m².
Lentz (43) used a horizontally positioned hollow cylinder for observation of a critical solution point at high pressure and P.V.T. measurements. The contents of cell could be viewed through a sapphire window positioned at one end. A piston fitted to the other end with a platinum mirror conveys pressure to the system. The mixture confined within the cell is agitated by a magnetic stirrer. The displacement of the piston can be read on a linear scale viewed through another optical window.

A more complicated apparatus has been described by Buback and Franck (44). The sample holder is a cylinder of synthetic sapphire, pressed on a steel plug, thus providing a seal for the high pressure space using Poulter's principle. A gold-platinum bellows is attached to the sapphire by a compression seal. The position of the bellows can be determined by an external inductive detector. Through the sapphire window the phase equilibria can be observed. With slight modification the cell can also be used for P.V.T. or conductivity measurements.

Another complicated optical cell for studying phase behaviour which can operate up to 220 MN/m² and 400°C has been developed by Alwani and Schnieder (45). The cell was constructed from 'Nimonic 90'. The phase transitions in the cell are observed through a single window. The light for observation is focused into the cell by a mirror and reflected on an internal platinum mirror. The pressure is transmitted to the fluid mixture by a piston. The displacement of the piston could be determined by a displacement transducer enabling the cell to be used for P.V.T. studies. The contents of the cell were stirred by a permanent ring magnet which could be moved back and forth by making the top of the window plug alternately a magnetic north and south pole. This change in polarity is achieved by passing a direct current of slowly alternating polarity.
through a large solenoid attached to the window plug. Liphard and Schneider (46) described an optical cell which is made of non-magnetic stainless steel. The cell is sealed by a copper ring compressed by a special flange. A piston with 'O' rings fitted to the centre of the flange conveys pressure to the mixture under test. The liquid mixture in the cell is stirred by a magnetic stirrer operated from outside the cell. In order to improve mixing a coil was attached to the stirrer. All phase transitions in the cell can be viewed through two sapphire windows. The apparatus has been used up to 1000 bar and 150°C.

Steiner and Schadow (21) have reported a manually stirred optical cell with two sapphire windows which can operate up to 130 MN/m². One other optical cell was described by Winnick and Powers (22) which can operate up to 700 MN/m², it does not have provision for stirring.

1.2.2 Autoclaves for Determination of Conjugate Compositions at Elevated Pressure

An apparatus for the investigation of gas-gas equilibria up to pressures of 20 k-bar has been described by Kricheuskii and Tsiklis (47). The apparatus consists of a high pressure cylinder containing a piezometer in which the mixture of known composition is compressed over mercury. The top of the piezometer is connected to a sampling valve at the top of high pressure cylinder. The bottom of the cylinder is connected to a manganin resistance pressure gauge and pressure intensifier.

The piezometer is filled with the mixture at a predetermined pressure and temperature where only one phase is possible. Then the system is brought to the required heterogeneous condition and allowed to separate. When separation of phases was judged to be complete, first, the upper phase, later, the lower phase was forced out through a valve
and analysed. The phases were driven out by pumping mercury up into
the piezometer. The pressure was kept constant by pumping more liquid
into the system. One of the disadvantages of this system is that it
does not have any provision for stirring.

Tsiklis (48) has also designed a piezometer which incorporates a
stirrer and solenoid. The incorporation of stirrer allows for sub-
sequent experiments at lower pressures than the first experiment.

Tsiklis and Maslenikova (49) have described an apparatus which
does not employ mercury and can operate up to 600 MN/m² and 500°C. The
equilibrium vessel consists of a thick-walled cylinder made from stain-
less steel. An electromagnetic stirrer is mounted within the vessel which
has two accesses to outside, one at the top the other at the bottom. The
top access is terminated in a sampling valve. The bottom access connected
to a cross to which, the pressure intensifier, manganin manometer and
sampling valve are connected. The manganin manometer is insulated from
the fluid under test by a bellows filled with dry kerosene. When the cell
contents are equilibrating, the pressure intensifier is isolated by means
of a valve. After equilibrium is established, the pressure is measured
and samples are withdrawn for analysis. The drop in pressure is compensated
by adding one of the liquid components of the mixture.

Elgin and Weinstock (50) devised an apparatus to withdraw a sample
from the high pressure system in order to verify visual observations.
Samples of each layer were withdrawn into cartridges inside the pressure
vessel. The apparatus was then dismantled to recover the samples which
were analysed.
A neater solution to the sampling problem was devised by Moruyoshi et al. (51) who used a modified glass syringe. This syringe was charged with mixture and then immersed in hydraulic fluid in a pressure vessel and connected to the exterior of the vessel via a capillary terminated in a needle valve. The contents of the syringe were stirred by rocking the vessel so that a glass ball within the syringe rolled from end to end. A sample of the denser phase could be withdrawn when the capillary connection was at the bottom of the syringe. Inversion of the assembly then permitted a sample of the upper layer to be withdrawn.

Hunt (52) used a different method. The equilibrium cell consisted of a stainless steel cylinder closed by a piston of the same material. Stainless steel capillary sample lines, were connected to the head of the cylinder and to the piston. The contents of the equilibrium cell were stirred by a drop-stirrer actuated magnetically. Provision was made for introducing a flushing solvent into the sampling valves which terminated the capillaries.

Most of the apparatus in the literature used to study vapour liquid equilibria at high pressure may be used with or without minor changes to study liquid-liquid equilibria. For instance a typical rocking autoclave has been used for vapour-liquid equilibria at high pressure by Bolshakova and Lindschits (53). The apparatus consists of a steel vessel closed by a steel head fitted to a valve for withdrawing sample from one of the phases. A high pressure cross connected to the middle of the vessel. A valve for removing sample of the other layer and a pressure gauge fitted to the cross. The whole unit is submerged in a liquid thermostat so that its axis is horizontal. The cell is pivoted at the middle and can be rocked by an eccentric drive at one end. Stirring is effected by a rolling steel ball in the cell.
A similar apparatus to that of Bolshakovawas designed by Lindroos and Dodge (54) which incorporates a drop-stirrer actuated from outside by a solenoid.

These last two apparatuses can be used without modification for liquid-liquid equilibrium study. First the vessel is charged with one of the pure components. Later the other component is used as a pressure transmitting fluid and forced into the system up to a specified pressure. After having established equilibrium, samples of each phase are withdrawn and analysed.

An elegant apparatus for high-pressure vapour-liquid equilibrium has recently been described by Rogers and Prausnitz (55). This apparatus can be used without any modification for liquid-liquid equilibrium study at elevated pressure.

A compilation of experimental techniques in the field of high pressure fluid-fluid phase equilibria is presented in books by Tsiklis (13,56), Weale (12), and Rowlinson (14). Several review articles have also recently been published by Schneider (57), Young (58), Street (59).

1.3 Measurement of Excess Volume

The excess thermodynamic properties of binary non-electrolyte mixtures have gained much importance in recent years in connection with the theory of liquid mixtures. They provide data to test theories and provide a guide for the formulation of new theories.

If one determines one of the molar excess quantities as a function of temperature T, pressure P, and composition x, then the variation of all thermodynamic functions may be deduced using the well-known thermo-
dynamic relations which have been discussed in several text books (14, 15, 60). Thus the problem of the thermodynamics of mixtures reduces to
the knowledge of one of the excess quantities as a function of $T$, $P$, $x$.

There exist various methods of measuring temperature dependence
of excess functions which have recently been throughly reviewed by
Marsh (61). An extensive bibliography has also been reported on the
available literature of excess functions by Hicks (6). However, very
little has been achieved to determine the pressure dependence of excess
functions. The excess volume is, so far, the only thermodynamic excess
function which may be measured accurately under high pressure. It can
be easily shown that the following relations hold for the pressure dependence
of the excess functions:

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E$$  \hspace{1cm} 1.3.1

$$\left(\frac{\partial H^E}{\partial P}\right)_{T,x} = V^E - T\left(\frac{\partial V^E}{\partial T}\right)_{P,x}$$  \hspace{1cm} 1.3.2

$$\left(\frac{\partial S^E}{\partial P}\right)_{T,x} = -\left(\frac{\partial V^E}{\partial T}\right)_{P,x}$$  \hspace{1cm} 1.3.3

$$\left(\frac{\partial C_P^E}{\partial P}\right)_{T,x} = -T\left(\frac{\partial^2 V^E}{\partial T^2}\right)_{P,x}$$  \hspace{1cm} 1.3.4

It can be seen from this that the pressure derivatives of all molar
excess functions are completely described by the molar excess volume $V^E$
as a function of $T$, $P$, $x$. The excess functions themselves can be obtained by
integration. For instance, the molar excess Gibbs energy by

$$G^E(P) = G^E(P^r) + \int_{P^r}^{P} V^E \, dp \hspace{1cm} \text{for constants } T \text{ and } x \hspace{1cm} 1.3.5$$

where $P^r$ is the reference pressure and $G^E(P^r)$ is the value of $G^E$ at that
pressure.

There are two principal methods to determine volume change on mixing at atmospheric and high pressure.

1.3.1 Atmospheric Pressure Measurements

a) Direct method: In this method pure liquids are mixed in a dilatometer and the resulting volume change is observed. The composition of the mixture is determined by weighing each component before mixing. All of the apparatus developed for direct measurement of $V^E$ employs mercury to confine and segregate the pure liquids before mixing. The resulting volume change is determined from the mass or volume of mercury displaced by the isothermal, isobaric mixing process. Most of the apparatus described in the literature have been thoroughly reviewed by Battino (62) and Marsh (61).

b) Indirect method: Here the density of liquid mixtures is measured at constant temperature and $V^E$ is deduced according to

$$V^E = \frac{x_1 M_1 + x_2 M_2}{d_{12}} - \left( x_1 \frac{M_1}{d_1^0} + x_2 \frac{M_2}{d_2^0} \right)$$  \hspace{1cm} 1.3.6

There are various methods for determining density at atmospheric pressure such as pycknometry, dilatometry, buoyancy, and hydrostatics. The work in this field has recently been thoroughly reviewed by Bauer and Lewin (63).

1.3.2 High Pressure Measurements

a) Direct method: A weighed amount of each component is compressed to the required pressure at constant temperature in question and mixed. The resulting volume change of mixing is observed by some means.
Direct measurement of excess volume was recently begun by Engels and Schneider (64). They have devised a high pressure dilatometer which consists of two chambers and a moving piston. Pure liquids are segregated within the chambers by mercury. When the required conditions are attained, the whole system is inverted to achieve mixing. The volume change of mixing is calculated from the determination of the displacement of the piston which transmits pressure to the test mixture from the hydraulic pressure-generating system. The main disadvantage of this method is that each experimental value of $V^E(x)$ has to be obtained from a separate mixing test.

b) Indirect method: A mixture of known composition is made up at atmospheric pressure and the compressibility of the mixture is measured. Then the excess volume at high pressure is deduced using the compressibilities of the pure components according to

$$V^E = V_P - x V_{1,P}^0 - x V_{2,P}^0$$

The chief advantages of this method are that several values of $V^E(P,x)$ may be obtained from single mixture and that the experimental technique is usually simple.

The disadvantage of this method is that the results are significantly less accurate than those of the direct method. It is restricted to systems which are completely miscible under all conditions of interest, since it does not employ any means of stirring. For instance it is not possible to cover whole concentration range when immiscibility decreases with increasing pressure.

Excess volumes at high pressure of a number of binary liquid mixtures may be deduced from compression data in the literature (65). Hammann and
Smith (66) have collected some of these and derived $V^E$ data. They also provide their own measurements on several other systems. The effect of pressure on the excess volumes for propanone-carbondisulfide system was calculated from experimental measurements of compressibility correlated by the Tait equation by Winnick and Powers (67).

Recently Lamb and Hunt (68), Korpela (69), Götze (70) published data on various systems obtained from accurate P.V.T. data measured on different mixtures and all pure components.

1.4 Liquid-Liquid Phase Equilibria in the 3 Methyl 2 Butanone-Water System

1.4.1 At Atmospheric Pressure

A literature survey has revealed that very little data exists on the mutual solubility of this system and that this lies within a small temperature range.

Ginnings et al. (71) determined conjugate compositions at 20°C, 25°C and 30°C, when they systematically investigated aqueous solubilities of some aliphatic ketones to find a relationship between solubilities and molecular structure. The saturated water content of the ketones at 10°C, 30°C and 50°C has been given by Gross et al. (72). All of these results are given in Table 1.1 and graphed in Fig. 5.1.

1.4.2 At Elevated Pressure: The mutual solubility of this system at 30°C, 45°C, 60°C and pressures up to 110 MN/m² have been studied by the synthetic method described in Sec. 1.1.2.a by Steiner and Schadow (21). Their experimental apparatus consisted of a small cell of 0.67 ml volume equipped with two sapphire windows and a manually operated stirrer. Pressure was transmitted from the hydraulic fluid to the mixture under test, through a piston.
Fig. 1.1 Apparent region of immiscibility of 3 methyl 2 butanone-water from Ref. (21) (Schematic only).
Qualitatively the results of Steiner and Schadow are represented by the sketch of Fig. 1.1 in which the region of immiscibility is indicated by cross hatching. Fig. 1.1 shows two upper critical solution pressures and a lower critical solution pressure in any open miscibility loop. A T-x diagram in the plane P = P', then, corresponding to section ABCD of the T-P-x space has the form as stated earlier and indicated by Fig. I.3.b.

Extrapolation of the P(x) curves for the three temperatures given by Steiner and Schadow suggests that at ambient pressures the consolute temperatures may lie around -10°C and +20°C. Such a system would show interesting properties over the temperature range between two L.C.S.T.'s.

1.5 2-Butanol-Water System

1.5.1 Measurements at Atmospheric Pressure

The mutual solubility of 2-butanol-water system has been studied by several investigators, starting before the end of last century. The first reported data were obtained by Alexjeff (25) by the synthetic method as described in Section 1.1.2. Following Alexjeff, Timmermans (73), Dolgolenko (74), Delcurt (75), Jones (76) have provided further points on the demixing curve.

Mutual solubilities of this system were also studied by Boeke and Hanewald (77) using Hertz's method; that is adding one pure liquid to the other up to saturation point at constant pressure and temperature. Directly determined tie-lines have also been obtained by an analytical method based on refractometric measurements by Altzybeeva et al. (78), Moracheuskii et al. (79) and Moriyoshī et al. (51).
Fig. 1.2 Liquid-Liquid Equilibrium Data of Various Workers for the 2-Butanol-Water System.
All of the available literature data are graphed in Fig. 1.2.

1.5.2 Measurements at Elevated Pressure

The mutual solubility of the system 2 butanol-water as a function of pressure was firstly studied in an optical cell by Timmermans (73) who has determined an isopleth with a mixture of "middle range composition" (the exact value of composition is uncertain), while Schneider and Russo (23), studying the influence of added salt on the mutual solubility of this system, have obtained an isopleth with a mixture of 36.5% by weight 2 butanol. Their observation was effected in an optical cell.

The influence of pressure on the mutual solubility of this system was determined analytically by Moriyoshy et al. (51) in the temperature range 10 to 110°C. Their experimental apparatus is described in Sec. 1.2.1.b.
CHAPTER 2

RELEVANT THERMODYNAMICS

2.1 Thermodynamics of Partially Miscible Liquids

2.1.1 Equilibrium Conditions

The basic thermodynamic equations of state for a closed system are:

\[ dH = TdS + VdP \]  \hspace{1cm} (2.1.1)

\[ dG = VdP - SdT \]  \hspace{1cm} (2.1.2)

\[ dF = -SdT - PdV \]  \hspace{1cm} (2.1.3)

\[ dE = -PdV + TdS \]  \hspace{1cm} (2.1.4)

The thermodynamic requirement or criterion that must be satisfied for an equilibrium state to exist is that one of the four equations above must be zero, when appropriate independent variables are held constant (80). Each of these four criteria with different sets of constraints for equilibrium in a closed system is sufficient by itself. They are all equivalent and each has an equal claim to be regarded as fundamental. Since \( T \) is a more convenient independent variable than \( S \) and \( P \) is a more convenient variable than \( V \), the criterion

\[ dG = 0, \hspace{0.5cm} dT = 0, \hspace{0.5cm} dP = 0 \]  \hspace{1cm} (2.1.5)

is most useful, but in no way more fundamental than the others. It shows that at constant temperature and pressure Gibbs energy tends towards an extremum in an actual or irreversible process in a closed system and remains constant in a reversible process.

More useful criteria may be obtained (15) in terms of the intensive
quantities T, P and \( \mu_1 \). In order to have thermal and mechanical equilibrium in the system temperature and pressure must be uniform throughout the whole system. If \( \mu_1 \) is the intensive potential governing mass transfer, it should also have a uniform value throughout the whole heterogeneous system at equilibrium with respect to this process.

\[
\begin{align*}
T' &= T'' = T''' \quad 2.1.6 \\
p' &= p'' = p''' \quad 2.1.7 \\
\mu_1' &= \mu_1'' = \mu_1''' \quad 2.1.8
\end{align*}
\]

2.1.2 Stability Condition

The stability condition for a binary mixture may be established by considering a stable binary system at constant temperature and pressure \((G, n, x)\). If one divides this system into two neighbouring phases by a virtual process, one being \((G + \Delta G', n', x + \Delta x')\), the other \((G + \Delta G'', n'', x + \Delta x'')\), then the following argument may be carried out:

The neighbouring condition, requires the mass and energy conservation, therefore the stability criteria can be written

\[
\begin{align*}
\Delta G &= n'\Delta G' + n''\Delta G'' > 0 \quad 2.1.9 \\
n &= n' + n'' \quad 2.1.10 \\
nx &= n'(x + \Delta x') + n''(x + \Delta x'') \quad 2.1.11 \\
n'\Delta x' + n''\Delta x'' &= 0 \quad 2.1.12
\end{align*}
\]

considering \( G \) as analytic (i.e. continuous function of \( x \) through stable and unstable phases), it can be expressed in a Taylor series expanded around the critical point (or a point on the critical line or surface).
\[ \Delta G' = \frac{\partial G}{\partial x} \Delta x' + \frac{1}{2} \left( \frac{\partial^2 G}{\partial x^2} \right) \Delta x'^2 + \ldots \quad 2.1.13 \]

In a similar way

\[ \Delta G'' = \frac{\partial G}{\partial x} \Delta x'' + \frac{1}{2} \left( \frac{\partial^2 G}{\partial x^2} \right) \Delta x''^2 + \ldots \quad 2.1.14 \]

Substituting \( \Delta x'' = -\frac{n'}{n''} \Delta x' \)

\[ \Delta G'' = -\frac{n'}{n''} \frac{\partial G}{\partial x} \Delta x' + \frac{1}{2} \left( \frac{n'}{n''} \right)^2 \left( \frac{\partial^2 G}{\partial x^2} \right) \Delta x'^2 + \ldots \quad 2.1.15 \]

The substitution of Eq. 2.1.13 and Eq. 2.1.15 into Eq. 2.1.9 gives

\[ \Delta G = \frac{n'n}{2n'} \frac{\partial^2 G}{\partial x^2} (\Delta x')^2 + O(\Delta x')^3 > 0 \quad 2.1.16 \]

Hence as \( \Delta x' \to 0 \)

\[ \frac{\partial^2 G}{\partial x^2} > 0 \quad 2.1.17 \]

This inequality has a simple geometric interpretation. If for a given value of \( T \) and \( P \), \( G \) is plotted as a function of \( x \), then this equation expresses the fact that for the system to be stable, the curve must be convex downwards. On the other hand, if the system can achieve a lower Gibbs energy by forming two phases between certain values of \( x \), than by forming a single phase, the system ceases to be stable and splits into two phases. In that concentration range \( G(x) \) curve must be convex upwards, unless there are said to be metastable conditions.
2.1.3 Determination of Equilibrium Phase Compositions

The compositions of the two phases that will result from the separation of the mixture of overall composition $x$ may be calculated in the following manner: since the chemical potentials are partial molar quantities, one may write in view of Eq. 2.1.8

$$\mu'_1 = G' - x'_2 \left( \frac{\partial G}{\partial x_2} \right)'_{P,T} = \mu''_1 = G'' - x''_2 \left( \frac{\partial G}{\partial x_2} \right)''_{P,T} \quad 2.1.18$$

$$\mu'_2 = G' + x'_1 \left( \frac{\partial G}{\partial x_2} \right)'_{P,T} = \mu''_2 = G'' + x''_1 \left( \frac{\partial G}{\partial x_2} \right)''_{P,T} \quad 2.1.19$$

Subtraction of these equations gives

$$\left( \frac{\partial G}{\partial x_2} \right)'_{P,T} = \left( \frac{\partial G}{\partial x_2} \right)''_{P,T} \quad 2.1.20$$

and substitution in Eq. 2.1.18 gives

$$\frac{G' - G''}{x'_2 - x''_2} = \left( \frac{\partial G}{\partial x_2} \right)_{P,T} \quad 2.1.21$$

These last two conditions have a geometrical significance. The two compositions representing the limits of complete miscibility $x'_1$, $x''_1$ have a common tangent to the function $G(x)$ at constant $T$ and $P$. The Gibbs energy of the system with two phases of different composition is given by the tangent line which clearly represents a condition of lower Gibbs energy than any single phase of intermediate composition. This is schematically depicted in Fig. 2.1. Along the tangent line, the system exists as two equilibrium phases of compositions $x'_1$ and $x''_1$ determined by points of tangency. As the miscibility gap narrows and the consolute point is approached, these two points approach each other and finally
Fig. 2.1 Composition Dependence of Gibbs Energy and its Derivatives.
merge at the consolute point, as do the two points of inflection A and B.

From this it can be seen that phase splitting occurs whenever the $G(x)$ curve has points of inflection. This condition has been discussed by several authors (7,14,60,80) and requires that the second and third derivatives are zero at a consolute point, but the fourth derivative is positive:

\[
\frac{\partial^2 G}{\partial x^2} = 0, \quad \frac{\partial^3 G}{\partial x^3} = 0 \quad 2.1.22
\]

\[
\frac{\partial^4 G}{\partial x^4} > 0 \quad 2.1.23
\]

2.1.4 Identification of a Consolute Point

In the identification of a consolute point, one of the simplest methods consists of considering the sign of slope of the stability curve around the consolute point. The expression for the slope of the demixing curve may be obtained by considering a point on the stability curve near the consolute point $(y_k, x_k)$, where $y = P$ or $T$

\[
y - y_k = \Delta y \quad x - x_k = \Delta x \quad 2.1.24
\]

Then expanding the function $y(x)$ and $\frac{\partial^2 G}{\partial x^2}(y,x)$ of the stability curve around that point into a Taylor series, one obtains

\[
\Delta y = \left(\frac{dy}{dx}\right) \Delta x + \frac{1}{2!} \left(\frac{d^2y}{dx^2}\right) \Delta x^2 + \quad 2.1.25
\]
\[ \Delta \frac{\partial^2 G}{\partial x^2} = \left( \frac{\partial^3 G}{\partial x^3} \right)_C \Delta x + \left( \frac{\partial^3 G}{\partial x^2 \partial y} \right)_C \Delta y + \\
+ \frac{1}{2!} \left| \left( \frac{\partial^4 G}{\partial x^4} \right)_C \Delta x^2 + 2 \left( \frac{\partial^4 G}{\partial x^3 \partial y} \right)_C \Delta y \Delta x + \left( \frac{\partial^4 G}{\partial x^2 \partial y^2} \right)_C \Delta y^2 \right| = 0 \quad 2.1.26 \]

The derivatives \( \frac{dy}{dx}, \frac{d^2 y}{dx^2} \) are along the stability curve, and the partial derivatives of \( G \) with respect to \( x \) are subject to the condition either \( dT = 0 \) or \( dP = 0 \).

At the consolute point \( \frac{dy}{dx} = 0 \), so from Eq. 2.1.25 and Eq. 2.1.26 one obtains

\[ \left( \frac{\partial^2 y}{\partial x^2} \right)_C = - \frac{\left( \frac{\partial^4 G}{\partial x^4} \right)_C}{\left( \frac{\partial^3 G}{\partial x^2 \partial y} \right)_C} \quad 2.1.27 \]

a) Condition of upper and lower critical solution temperature.

If one replaces \( y \) with \( T \) in Eq. 2.1.27, the denominator is equal to \( \left( \frac{\partial^2 S}{\partial x^2} \right) \) in the light of Eq. 2.1.2

\[ \frac{d^2 T}{dx^2} = \frac{\left( \frac{\partial^3 G}{\partial x^3} \right)_C}{\left( \frac{\partial^2 S}{\partial x^2} \right)} \quad 2.1.28 \]

Differentiation of the equation which defines the molar Gibbs energy \( G = H - TS \) gives

\[ \left( \frac{\partial^2 G}{\partial x^2} \right)_{T,P} = \left( \frac{\partial^2 H}{\partial x^2} \right)_{T,P} - T \left( \frac{\partial^2 S}{\partial x^2} \right)_{T,P} \quad 2.1.29 \]

In view of Eq. 2.1.22, this equation is equal to zero at a consolute
point. It is seen from Eq. 2.1.28 and Eq. 2.1.29 that the following relations hold at an U.C.S.T.

\[
\frac{d^2 T}{dx^2} < 0, \quad \left(\frac{\alpha^2 S}{\partial x^2}\right)_C < 0, \quad \left(\frac{\alpha^2 H}{\partial x^2}\right)_C < 0 \quad 2.1.30
\]

and at a L.C.S.T.

\[
\frac{d^2 T}{dx^2} > 0, \quad \left(\frac{\alpha^2 S}{\partial x^2}\right)_C > 0, \quad \left(\frac{\alpha^2 H}{\partial x^2}\right)_C > 0 \quad 2.1.31
\]

These conditions relate the nature of the critical solution temperature to the curvature of the enthalpy-composition diagram. In case of an U.C.S.T. one has a curve such as in Fig. 2.2 a which is concave; while for a L.C.S.T. one has a curve such as a which is convex. In principle, of course, the curves can have more complicated shapes such as Fig. 2.2 a', a2 in which the curvature changes with concentration.

If one compares T(x) curves with H(x) curves in Fig. 2.2, one may well say that the curve a1 corresponds to b1, a2 to b2 and so on. In this respect Skinner's (20) and Steiner's (21) results have some theoretical backing.

b) Condition for upper and lower critical solution pressure

Replacing y with P in Eq. 2.1.27 and evaluating the value of the denominator in Eq. 2.1.27 from Eq. 2.1.2

\[
\frac{d^2 P}{dx^2} = - \frac{\left(\frac{\partial^2 G}{\partial x^2}\right)_C}{\left(\frac{\partial^2 V}{\partial x^2}\right)_C} \quad 2.1.32
\]
Fig. 2.2a  ENTHALPY OF BINARY MIXTURE

Fig. 2.2b  CONSOLUTE TEMPERATURE OF BINARY MIXTURE
Therefore at an upper critical solution pressure in an isothermal $P(x)$ diagram

\[ \left( \frac{\partial^2 y}{\partial x^2} \right)_c > 0 \]

at a lower critical solution pressure

\[ \left( \frac{\partial^2 y}{\partial x^2} \right)_c < 0 \]

2.1.33

2.1.34

c) Condition for an hyper-critical solution point

An hyper-critical solution point (H.P.) is defined as a point in a T,$x$ isobar or in a P,$x$ isotherm at which an upper and a lower consolute point merge together. As sketched in Fig. 1.d and g, there are two kinds of hyper-critical points in an isobar (H.C.T.1 and H.C.T.2) and in an isotherm (H.C.P.1 and H.C.P.2). The thermodynamic requirement at a hyper-critical point may be deduced from the simultaneous fulfilment of the criteria for the consolute solution points in question. In the deduction of these requirements one should also specify whether the H.P. is the beginning or the end of the immiscibility. The conditions for eight possible types of hyper-critical solution point were deduced and discussed by Schneider (7).

2.2. Excess Properties of Solutions

The degree of deviation of a non-ideal solution from the ideal solution is expressed by the excess properties. An excess property is defined as the difference between an actual property and the property that would be calculated at some standard state by the equations for an ideal solution. Thus, by definition, the molar thermodynamic properties of a binary mixture are related to those of excess properties.
\[ V = x_1 v_1^0 + x_2 v_2^0 + v^E \quad \text{(2.2.1)} \]
\[ H = x_1 h_1^0 + x_2 h_2^0 + h^E \quad \text{(2.2.2)} \]
\[ S = x_1 s_1^0 + x_2 s_2^0 - R(x_1 \ln x_1 + x_2 \ln x_2) + s^E \quad \text{(2.2.3)} \]
\[ G = x_1 u_1^0 + x_2 u_2^0 + RT(x_1 \ln x_1 + x_2 \ln x_2) + g^E \quad \text{(2.2.4)} \]

The excess properties of a solution are thermodynamic properties in their own right and are functions of temperature, pressure and composition which are the favoured experimental variables. Their use requires a clear specification of the standard state to which they refer.

Excess properties may be expressed in terms of auxiliary functions such as activity coefficient. One of the most convenient definitions of activity coefficient is

\[ \mu_1 = \mu_1^0 + RT \ln x_1 y_1 \quad \text{(2.2.5)} \]

The total Gibbs energy of a binary mixture is given

\[ G = x_1 u_1 + x_2 u_2 \quad \text{(2.2.6)} \]

Substitution of Eq. 2.2.5 into Eq. 2.2.6 gives

\[ G = x_1 u_1^0 + x_2 u_2^0 + x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln y_1 + x_2 \ln y_2 \quad \text{(2.2.7)} \]

Comparison of Eq. 2.2.4 and Eq. 2.2.7 yields

\[ \frac{G^E}{RT} = x_1 \ln y_1 + x_2 \ln y_2 \quad \text{(2.2.8)} \]

By multiplying this equation by \( n (= n_1 + n_2) \) and differentiating at constant temperature and pressure one obtains

\[ d \left( \frac{n G^E}{RT} \right) = n_1 d \ln y_1 + n_2 d \ln y_2 + t \ln y_1 d n_1 + t \ln y_2 d n_2 \quad \text{(2.2.9)} \]
Under the condition of constant T and P, the first two terms on the right-hand side are zero as follows from the well-known Gibbs-Duhem equation, therefore

\[ \frac{\partial (nG^E/RT)}{\partial n_1} \bigg|_{T,P,n_2} = \ln \gamma_1 \]

2.2.10

This equation suggests that \( \ln \gamma_1 \) is related to \( G^E/RT \) as a partial molar property.

The upper and lower critical solution temperature points of a binary solution may be defined in terms of the behaviour of the excess functions. The differentiation of Eqs. 2.2.1-4 with respect to \( x \) yields the following equations:

\[ \frac{\partial^2 \gamma}{\partial x^2} \bigg|_{T,P} = \left( \frac{\partial^2 \gamma^E}{\partial x^2} \right)_{T,P} \]

2.2.11

\[ \frac{\partial^2 H}{\partial x^2} \bigg|_{T,P} = \left( \frac{\partial^2 H^E}{\partial x^2} \right)_{T,P} \]

2.2.12

\[ \frac{\partial^2 S}{\partial x^2} \bigg|_{T,P} = -\frac{R}{x(1-x)} + \left( \frac{\partial^2 S^E}{\partial x^2} \right)_{T,P} \]

2.2.13

\[ \frac{\partial^2 G}{\partial x^2} \bigg|_{T,P} = \frac{RT}{x(1-x)} + \left( \frac{\partial^2 G^E}{\partial x^2} \right)_{T,P} \]

2.2.14

Since for a phase to be stable \( \frac{\partial^2 G}{\partial x^2} \) must be positive, it also follows that at the critical composition but at a temperature just above the U.C.S.T. or just below the L.C.S.T.
that is, the curvature of \( G(x) \) is less than \( \frac{RT}{x(1-x)} \) at the critical point. This criterion is rigorous, but experimentally inaccessible.

From Eq. 2.1.29, Eq. 2.2.12 and 2.2.14 one obtains:

\[
\left( \frac{\partial^2 G}{\partial x^2} \right)_{T,P} = \left( \frac{\partial^2 H}{\partial x^2} \right)_{T,P} - T \left( \frac{\partial^2 S}{\partial x^2} \right)_{T,P} \tag{2.2.16}
\]

In view of Eq. 2.1.22, Eqs. 2.2.11-14 and Eq. 2.2.16, the following conditions hold at an U.C.S.T.

\[
\left( \frac{\partial^2 H}{\partial x^2} \right)_{c} < 0 , \quad \left( \frac{\partial^2 S}{\partial x^2} \right)_{c} = \left( \frac{\partial^2 H}{\partial x^2} \right)_{c} + \frac{RT}{x(1-x)} > 0 \tag{2.2.17}
\]

and at a L.C.S.T.

\[
\left( \frac{\partial^2 H}{\partial x^2} \right)_{c} > 0 , \quad \left( \frac{\partial^2 S}{\partial x^2} \right)_{c} > \frac{R}{x(1-x)} > 0 \tag{2.2.18}
\]

In a similar way from Eq. 2.1.33, 2.1.34 and Eq. 2.2.11 the condition for a consolute pressure may be deduced. Thus at an U.C.S.P.

\[
\left( \frac{\partial^2 V}{\partial x^2} \right)_{c} > 0 \tag{2.2.19}
\]

and at an L.C.S.P.

\[
\left( \frac{\partial^2 V}{\partial x^2} \right)_{c} < 0 \tag{2.2.20}
\]
2.3 Empirical and Semiempirical Expressions for the Excess Gibbs Energy

A complete thermodynamic description of a mixture can be given if the molar excess Gibbs energy is known as a function of temperature, pressure and composition which are the most favoured experimental variables.

From the appropriate differentiation of the expression for the molar excess Gibbs energy all of the excess functions may be deduced as discussed in several text books (14,60). Thus

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

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

\[
\left| \frac{\partial (G^E/T)}{\partial T} \right| = -\frac{H^E}{T} 
\]

when the values of excess properties are deduced, any molar thermodynamic property can be obtained by simple addition of appropriate ideal property.

Although classical thermodynamics imposes certain general requirements on equations used to represent $G^E$, it offers no clues as to the functional forms that might be reasonable for such equations. Therefore they must be established either empirically or on the basis of some molecular theory. Since we do not yet possess an accurate statistical mechanical description of a liquid mixture, in either case empirical parameters have to be introduced. From both a practical and a theoretical standpoint, it is desirable to limit the number of parameters used and at the same time develop expressions for $G^E$ which are of general applicability. However the tremendous complexity and variety of liquid mixtures prevents an accurate representation of many mixture properties by a single mathematical expression containing
a small number of parameters.

In evaluating the usefulness of a given procedure for predicting properties, discerning the number of empirical parameters is the key. Accurate prediction is the goal of any technique. However, when this accuracy must be paid for with a large number of empirical parameters its value is diminished in two ways. First, the amount of data needed to evaluate the parameters increases rapidly with their number, second, the reliability for extrapolation often diminishes beyond the bounds over which data have been taken.

Numerous attempts have been made to predict solution behaviour from pure component properties only. Very little has been achieved so far. If there were an equation of state capable of application to liquid mixtures under all conditions, there would be no need to deal with excess properties at all; the solution properties of interest could be directly calculated.

2.3.1 Van Laar Equation (81)

To calculate the energy change of mixing Van Laar constructed a three-step isothermal thermodynamic cycle, by assuming that both the excess entropy and volume are zero. He then applied the Van der Waals equations to fluids and fluid mixtures and calculated the internal energy change in each step. Thus

\[ \Delta E^E = \Delta E_1 + \Delta E_2 + \Delta E_3 \]  \hspace{1cm} 2.3.4

where

\( \Delta E_1 \) is the energy to evaporate pure liquids to ideal gases
\( \Delta E_2 \) is energy to mix ideal gases
\( \Delta E_3 \) is energy to condense ideal-gas mixture to liquid mixture
Here \( \Delta E_2 = 0 \), and \( \Delta E_1 \) and \( \Delta E_3 \) may be found if the functional dependence of volume \( V \) on the internal energy \( E \) is known

\[
\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P
\]

2.3.5

This equation was applied to both pure components and to the mixture using the usual empirical mixing rules for the Van der Waals constants \( a \) and \( b \), and the result for the excess Gibbs energy is given as

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

2.3.6

This form of the Van Laar equation is given by Carlson and Colburn (82) it gives a relationship for calculating activities in solution from pure component properties only. Unfortunately it works rather badly in practice. Redefining the parameters as

\[
A_{12} = \frac{b_1}{b_2}, \quad A_{21} = \frac{b_1}{R} \left( \frac{\sqrt{a_1}}{b_1} + \frac{\sqrt{a_2}}{b_2} \right)^2
\]

2.3.7

Activity coefficients are obtained by differentiating according to Eq. 2.2.10

\[
\ln \gamma_1 = \frac{x_2 A_{21}}{T(A_{12} x_1 + x_2)}, \quad \ln \gamma_2 = \frac{x_1 A_{12} A_{21}}{T(A_{12} x_1 + x_2)}
\]

2.3.8

As a consequence of the assumption that \( S^e = 0 \), the logarithms of the activity coefficient are inversely proportional to the absolute temperature. According to Van Laar's theory the activity coefficients
are never less than unity; hence this theory always predicts positive deviations from Raoult's Law. If one regards $A_{12}$ and $A_{21}$ as adjustable parameters then the Van Laar's equations are useful empirical relations to correlate experimental activity coefficients for many binary systems.

2.3.2 Scatchard-Hildebrand Equation (83,84)

Van Laar's method formed a basis for the development of the Scatchard-Hildebrand regular solution theory. They improved Van Laar's theory by removing the limitation of Van der Waals equation of state. The resulting equation for $G^E$ has the following form

$$G^E = V \phi_1 \phi_2 A_{12}$$  \hspace{1cm} 2.3.9

where

$$\phi_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2}, \quad \phi_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2}, \quad V = x_1 V_1 + x_2 V_2$$

$$A_{12} = (\delta_1 - \delta_2)^2$$

Activity coefficients are deduced by differentiation according to Eq. 2.2.10

$$RT \ln \gamma_1 = V \phi_1^2 A_{12}$$  \hspace{1cm} 2.3.10

$$RT \ln \gamma_2 = V \phi_2^2 A_{12}$$  \hspace{1cm} 2.3.11

The application of an updated version of this theory was given by Hildebrand Prausnitz and Scott (85). The solubility parameters, $\delta_1$ and $\delta_2$, may be estimated from heat of vaporization (available in turn from the vapour pressure curve and Clausius-Clapeyron equation)

$$\delta = \left( \frac{\Delta U_{vap}}{V} \right)^{\frac{1}{2}} = \left( \frac{\Delta H_{vap} - RT}{V} \right)^{\frac{1}{2}}$$  \hspace{1cm} 2.3.12
Regular solution treatment always gives positive deviations from Rault's law. In general for non-polar systems, the predictions made by these equations from pure component data only are in qualitative agreement with experiment.

As pointed out by Lambardo (86) the values of $\phi_{1c}$ (volume fraction at a consolute point) are restricted to the middle third of composition range, whereas those of $x_{1c}$ are not restricted. This result implies that demixing curve would tend to be more symmetrical in terms of volume fractions.

A modification of the regular solution theory is given by Gonsalves and Leland (87)

$$G^E = V_1 \phi_2 A_{12} + 2m_{12} \delta_1 \delta_2$$

where $m_{12}$ takes account of the unlike pair interactions.

2.3.3 Gugenheim's Equation

One of the families of equations for excess Gibbs energy stemmed from the quasilattice theory of Gugenheim (88) which is one of the simplest conceptual models of the theory of liquids. The liquid is pictured as a pseudocrystal. It is assumed that each molecule is located at the intersection point of a regular lattice. Molecules are considered to be of the same size and shape and are interchangeable on the lattice sites. It is assumed further that $S^E$ and $V^E$ are both zero so that $G^E = H^E$. The derived equation for the excess Gibbs energy is:

$$G^E = x_1 x_2 w_{12}$$
where $w_{12}$ is the interchange energy representing physically the
differences between like-pair and unlike-pair interactions. It
follows that

$$RT\ln \gamma_1 = x_2^2 w_{12}$$  \hspace{1cm}  2.3.15

$$RT\ln \gamma_2 = x_1^2 w_{12}$$  \hspace{1cm}  2.3.16

This theory of "strictly regular solution" rarely applies to real
mixtures. The physical model is literally too rigid and does not
adequately represent real behaviour.

Gugenheim extended the quasi-lattice treatment to the mixtures in
which each molecule i consists of $r_i$ segments each of which occupies
one site on a lattice of co-ordination number $z$. Then

$$G^E \over RT = x_1 \ln \frac{r_1}{x_1 r_1 + x_2 r_2} + x_2 \ln \frac{r_2}{x_1 r_1 + x_2 r_2}$$

$$+ \frac{1}{2} q_1 z x_1 \ln \frac{x_1 r_1 + x_2 r_2}{r_1 (x_1 q_1 + x_2 q_2)}$$

$$+ \frac{1}{2} q_2 z x_2 \ln \frac{x_1 r_1 + x_2 r_2}{r_2 (x_1 q_1 + x_2 q_2)}$$  \hspace{1cm}  2.3.17

$$+ \frac{q_1 q_2 x_1 x_2 w_{12}}{(x_1 q_1 + x_2 q_2)kT}$$

where $q_1$, $q_2$ are the numbers of nearest neighbour sites to molecules
1 and 2. Bruin (89) and McCann (90) derived several equations supposedly
based on Eq. 2.3.17 by setting $q_1$ and $q_2$ to zero and misinterpreting the
parameters $r_1$ and $r_2$.
2.3.4 N.C.Z. Equation

One attempt to relax the requirement of constant co-ordination number was made by Forsythe (90). The N.C.Z. (non-constant co-ordination number) equation for $G$ is given in its simplest form as

$$G^E = - c_1 x_1 \ln (x_1 + A_{21} x_2) - c_2 x_2 \ln (x_2 + A_{12} x_1)$$

$$+ c_3 x_1 (1 - c_1) e^{-\varepsilon_{11}/kT} + x_2 (1 - c_2) e^{-\varepsilon_{22}/kT}$$

where

$$c_1 = \frac{z_1}{z_{12}}, \quad c_2 = \frac{z_2}{z_{12}}, \quad c_3 = \frac{z_s}{2}$$

$$A_{21} = \frac{z_2}{z_1} e^{-\varepsilon_{12}/kT}, \quad A_{12} = \frac{z_1}{z_2} e^{-\varepsilon_{12}/kT}$$

Activity coefficients are obtained by differentiation according to Eq. 2.2.10

$$RT \ln \gamma_1 = c_1 \left[- \ln (x_1 + A_{21} x_2) + x_2 \left(\frac{x_1 (1 - A_{21})}{x_1 + A_{21} x_2}\right) + \frac{c_2 x_2 (1 - A_{12})}{c A_{12} x_1 + x_2}\right]$$

$$+ \left[\frac{z_s}{2} (1 - c_1) e^{-\varepsilon_{11}/kT}\right] + (c_1 - 1) \ln x_1 + (c_1 - c_2) x_2$$

$\ln \gamma_2$ is obtained by interchanging the subscripts. Here $z_1$ and $z_2$ are the co-ordination numbers of components 1 and 2 in the mixture. $z_{12}$ is average co-ordination number $Z_s$ is the self co-ordination number, considered to be the same for both of the components. All co-ordination numbers may be calculated from hard sphere radii, $w_{12}$ is the interchange energy.
2.3.5 Redlich-Kister Equation (91)

If the interchange energy in Eq. 2.3.14 is not taken as a quantity determined from intermolecular forces, but merely as an empirical measure of two-body interactions, Eq. 2.3.14 provides the leading term in a series expansion, several of which are commonly used.

\[ G^E = (1 - \Delta^2)(A_0 + A_1\Delta + A_2\Delta^2 + A_3\Delta^3 + \text{etc.}) \]  

2.3.20

where \( \Delta = 2x - 1 \)

Activity coefficients are obtained according to Eq. 2.2.10

\[ RT\ln\gamma_1 = (1 + \Delta)^2[A_0 + A_1(2\Delta - 1) + A_2(3\Delta - 2)\Delta \]
\[ + A_3(4\Delta - 3)\Delta^2 + \text{etc.} \]  

2.3.21

\[ RT\ln\gamma_2 = (1 - \Delta)^2[A_0 + A_1(2\Delta + 1) + A_2(3\Delta + 2)\Delta \]
\[ + A_3(4\Delta + 3)\Delta^2 + \text{etc.} \]  

2.3.22

It can be shown by simple algebra that Eq. 2.3.20 is equivalent to the Margules (92) expansion.

In this type of expression the first term is similar to the pair interchange energy and in a loose sense, higher terms tend to correspond to the higher order interactions. The number of parameters \( (A_0, A_1, \ldots) \) which should be used to represent the experimental data depends on the molecular complexity of the solution, on the quality of data and number of data points available.

The Redlich-Kister expansion provides a flexible algebraic expression for representing the excess Gibbs energy of a liquid mixture (15). The first term in the expansion is symmetric in \( x \) and gives a parabola when \( G^E \) is plotted against \( x \). The odd-powered correction terms are asymmetric in \( x \) and therefore tend to skew the parabola either to the left or right.
The even-powered correction terms are symmetric in \( x \) and tend to flatten or sharpen the parabola. When \( G^E - x \) curve is sharply skewed Eq. 2.3.20 needs an excessive number of parameters. Myer and Scott (93) suggested a preselected skewing constant \( B \), where \(-1 < B < 1\) and Eq. 2.3.20 is divided by \( 1 - B(1 - 2x) \). Kehlen (94) has recently suggested an expression for \( G^E \), which is in some sense a modification of the Redich-Kister equation.

It has the following form

\[
G^E(T,\Delta) = c'B \tau
\]

where

\[
\begin{align*}
\Delta & \quad \Delta^2 & \quad \ldots & \quad \Delta^n \\
1 & \quad \lambda & \quad \ldots & \quad \lambda^n \\
\end{align*}
\]

\[
B = \begin{pmatrix}
g_0 & h_0 & c_0 & d_0 \\
g_1 & h_1 & c_1 & d_1 \\
g_2 & h_2 & c_2 & d_2 \\
\vdots & \vdots & \vdots & \vdots \\
g_n & h_n & c_n & d_n \\
\end{pmatrix}
\]

\[
\tau = \frac{T}{T^r}
\]

\( c \) is concentration vector (\( c' \) is the transpose of \( c \))

\( t \) is temperature vector

\( B \) is the specific matrix of the system

\( x \) is the concentration of one of the components

\( \tau \) is a reduced temperature which is referred to \( T^r \)

\( h_i, c_i, d_i \) are specific parameters of the system. They are deduced from values of \( H^E, c_p^E, D^E \) (\( D^E \) is the temperature coefficient \( \frac{\partial c_p^E}{\partial T} \)) when data are available. Then it is straight-forward to obtain \( g_0, g_1, g_2 \ldots g_n \). Since the excess properties are usually (if not always) scarce, it is usually assumed that \( c_i = d_i = 0 \). Then it is assumed further that either \( h_i = 0 \) (i.e. \( H^E = 0 \)) or \( h_i = g_i \) (i.e. \( H^E = G^E, S^E = 0 \)). Estimation of parameters \( g_i \) may be made from the demixing curve.
Activity coefficients are obtained on differentiation:

\[
\begin{align*}
RT\ln\gamma_1 &= \frac{a't}{t}, & RT\ln\gamma_2 &= \frac{b't}{t} & \text{(2.3.24)}
\end{align*}
\]

When the temperature in question is taken to be the reference temperature \( (\tau = 1) \), this equation reduces to the Redlich-Kister equation.

Perhaps the greatest disadvantage of the Redlich-Kister equation is its ambiguity in predicting the behaviour of multicomponent data from binary data.

2.3.6 Wohl's Equation

Taking into consideration the interaction between the molecules forming a solution Wohl (95) developed an equation for the excess Gibbs energy which may be written for a binary system as follows

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

\[
2.3.25
\]

where

\[
z_1 \equiv \frac{x_1q_1}{x_1q_1 + x_2q_2} \quad \text{and} \quad z_2 \equiv \frac{x_2q_2}{x_1q_1 + x_2q_2}
\]

This equation contains two types of parameter. The q's are effective volumes (or cross sections) of the molecules so that \( q_1 \) is a measure of
the size of molecule i. The ratio of the q's is usually assumed equal to the ratio of the pure component liquid molar volumes. The a's are interaction parameters whose physical significance is, in a loose sense similar to that of virial coefficients. The activity coefficients are deduced for the third order Wohl's equation by differentiation according to Eq. 2.2.10

$$\ln \gamma_1 = z_1^2 \left[ A_{12} + 2z_1 \left( A_{21} \frac{q_1}{q_2} - A_{12} \right) \right]$$  \hspace{1cm} 2.3.26

$$\ln \gamma_2 = z_2^2 \left[ A_{21} + 2z_2 \left( A_{12} \frac{q_2}{q_1} - A_{21} \right) \right]$$  \hspace{1cm} 2.3.27

where

$$A_{12} = q_1(2a_{12} + 3a_{122}) \hspace{0.5cm}, \hspace{0.5cm} A_{21} = q_2(2a_{12} + 3a_{112})$$

Wohl, in his original paper does not give comparisons with experimental data. Pigford et al. (96) have tested Wohl's theory by comparing ternary data predicted by Wohl's equation from the constituent binary data with experimental ternary data. It was found that this type of equation without an additional constant is unable to describe adequately the observed behaviour of ternary systems (i.e. solely in terms of the binary interactions).

When appropriate assumptions are introduced, Eq. 2.3.25 yields some of the well-known equations e.g.

$$\frac{q_2}{q_1} = \frac{V_2}{V_1} \hspace{2cm} \text{Scatchard-Hamer (97)}$$

$$\frac{q_{21}}{q_{12}} = \frac{A_{21}}{A_{12}} \hspace{2cm} \text{Van Laar (81)}$$

$$\frac{q_2}{q_1} = \left| \frac{A_{21}}{A_{12}} \right| \hspace{2cm} \text{Van-Laar-Null (98)}$$

$$\frac{q_2}{q_1} = 1 \hspace{2cm} \text{Margules (92)}$$
2.3.7 The Flory-Huggins Equation

Proceeding from a quasi-crystalline lattice model, Flory (99) and Huggins (100) were able to derive the entropy of mixing of a long, flexible chain molecule in solution from statistical geometrical considerations. This chain molecule is considered to be made up of segments, and these segments, with respect to their geometry (i.e. their size and spherical shape), are interchangeable with the solvent molecules which are likewise considered spherical particles in a first approximation.

The result of the Flory-Huggins theory is formulated for an athermal mixture (i.e. $H^E = 0$) as follows

$$
\frac{G^E}{RT} = -\frac{S^E}{R} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \tag{2.3.28}
$$

where

$$
\phi_1 = 1 - \phi_2 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2} = \frac{n_1}{n_1 + r n_2}
$$

$$
r = \frac{V_1}{V_2}
$$

the ratio of molar volumes of the solvent and the polymer.

Eq. 2.3.28 serves as the standard of normal behaviour for polymer solutions. Real polymer solutions depart significantly from this standard. The more complete form of the Flory-Huggins theory may be expressed in terms of excess Gibbs energy:

$$
\frac{G^E}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \chi \phi_1 \phi_2 (x_1 + r x_2) \tag{2.3.29}
$$

where $\chi$ called the Flory interaction parameter is determined by intermolecular forces between the molecules in the solution. The activity coefficient for the solvent follows from differentiation according to Eq. 2.2.10
\[ \ln \gamma_1 = - mn(x_1 + r x_2) + (1 - \frac{1}{r}) \phi_2 + \phi_2^2 \]  

2.3.30

and for the polymer

\[ \ln \gamma_2 = - \ln \left( \frac{1}{r} x_1 + x_2 \right) + (1 - r) \phi_1 + r \phi_1^2 \]  

2.3.31

2.3.8 Wilson's Equation

Wilson (101) has proposed an expression for the molar excess free energy which differs from the usual Wohl expansion. He postulated that the local concentrations in the neighbourhood of a central molecule can differ from the bulk (overall) concentrations. By local it is specifically meant that if a given molecule is chosen as the central one, then the number, nature and position of the molecules in its nearest neighbouring shell is influenced by certain properties of the central molecule. To account for the ordering (or disordering) effects of a central molecule Wilson suggested the following equation

\[ \frac{x_{12}}{x_{11}} = \frac{x_2 \exp(-g_{12}/RT)}{x_2 \exp(-g_{11}/RT)} \]  

2.3.32

This equation may be interpreted as the probability of finding a molecule of type 2 compared to finding a molecule of type 1 about a central molecule of type 1. Using the definition embodied in Eq. 2.3.32, Wilson has empirically redefined the volume fractions of the Flory-Huggins equation (Eq. 2.2.28) calling them the local volume fractions. The resulting equation for the excess Gibbs energy is

\[ \frac{G^E}{RT} = - x_1 \ln(x_1 + A_{21} x_2) - x_2 \ln(x_2 + A_{12} x_1) \]  

2.3.33
where

\[ A_{12} = \frac{V_1}{V_2} \exp -\frac{(g_{12} - g_{22})}{RT} \]

\[ A_{21} = \frac{V_2}{V_1} \exp -\frac{(g_{21} - g_{11})}{RT} \]

The activity coefficients are given by

\[ \ln \gamma_1 = -\ln(x_1 + A_{21} x_2 + x_2) \left( \frac{A_{21}}{x_1 + A_{21} x_2} - \frac{A_{12}}{x_1 x_2} \right) \]

\[ \ln \gamma_2 \text{ is obtained by rotation of subscripts } 1 \rightarrow 2 \rightarrow 1 \]

A study by Orye (102) indicated that Wilson's equation is in many respects very useful and directly applicable to strongly non-ideal mixtures. However as pointed out by Wilson it fails to predict phase separation of liquid mixtures. For partially miscible systems, Wilson suggested that the equation be multiplied by an arbitrary constant \( c \) which depends on the binary system. The three-parameter Wilson equation is applicable to partially miscible systems. Renon and Prausnitz (103) have shown that the three parameters Wilson equation can be obtained by introducing the local mole fraction concept into Scott's two-liquid theory. One of the most important advantages of this equation is that it can be straight-forwardly generalized to multicomponent mixtures, without the need for ternary (or higher) parameters.

The derivation of this equation contains two essentially arbitrary steps: the relations between the local-molefraction equations and the introduction of local compositions into the Flory-Huggins equation. The Flory-Huggins equation is based on the athermal solution theory (i.e. \( H^E = 0 \)) so the Wilson equation is supposedly for "athermal solutions and Eq. 2.3.33 supposedly only takes into account entropy effects. However
\[ \frac{\partial}{\partial t} \left( \frac{G^E}{RT} \right) = \frac{H^E}{RT^2} \]

so if \( H^E = 0 \)

\[ \frac{\partial}{\partial T} \left( \frac{G^E}{RT} \right) = 0 \]

\[ \frac{\partial}{\partial T} \left( \frac{G^E}{RT} \right) = -R \left[ \frac{x_1}{x_1 + x_2 A_{12}} \frac{g_{12} - g_{22}}{RT^2} A_{21} + \frac{x_2}{x_2 + x_1 A_{12}} \frac{g_{21} - g_{11}}{RT^2} A_{12} \right] \]

and, as \( A_{21} \neq 0 \) and \( A_{12} \neq 0 \) and \( T \neq \infty \), the only situation where this expression gives athermal behaviour for all values of \( x \) is when

\[ g_{12} - g_{22} = g_{21} - g_{11} = 0 \]

that is ideal!

If one recalls Eq. 2.3.28 and writes in the following form

\[ \frac{G^E}{RT} = -x_1 \ln(x_1 + r x_2) - x_2 \ln(\frac{1}{r} x_1 + x_2) \]

2.3.35

Comparison of Eq. 2.3.35 and Eq. 2.3.35 shows that Wilson arbitrarily multiplied the molar volume ratios \( r \) and \( \frac{1}{r} \) by

\[ \exp - \frac{g_{12} - g_{22}}{RT} \quad \text{and} \quad \exp - \frac{g_{21} - g_{11}}{RT} \]

respectively.

The assumption, \( H^E = 0 \) results that \( r \) is independent of temperature. So Wilson's equation is inconsistent with its initial postulate of \( H^E = 0 \).

2.3.9 N.R.T.L. Equation

To overcome the limitation of Wilson's equation Renon and Prausnitz (104), combined the local mole fraction concept with the Scott's two-liquid theory. The two-liquid theory of Scott postulates that molecules in a liquid mixture do not in general distribute themselves in a random manner but exhibit a tendency to segregate due to the influence of a
central molecule. It considers that the (ordering or disordering) effect of a central molecule diminishes rapidly beyond the first neighbour shell. In other words, it envisages a single molecule in the liquid being surrounded by a cage or cell of adjacent molecules. Two different cells are hypothesized on the molecular level. The properties of cell 1 are due to average of 1-1 and 1-2 interactions and the properties of cell 2 are determined by 2-2 and 2-1 interactions.

Considering the residual Gibbs energy (i.e. compared with the ideal gas at the same P,T,x) of each of the two kinds of cell Renon and Prausnitz wrote the following equation for the molar excess Gibbs energy

\[ G^E = x_1 x_2 (g_{21} - g_{11}) + x_2 x_1 (g_{12} - g_{22}) \]  \hspace{1cm} 2.3.36

where \( g_{12}, g_{21} \) is the configurational free energy of a hypothetical fluid in which there are only unlike pair interactions. \( g_{11}, \) and \( g_{22} \) are equal to configurational free energies of the pure liquids. \( x_1, x_2 \) are mole and \( x_{12}, x_{21} \) are local mole fractions. Local compositions are experimentally inaccessible numbers. For a completely random mixture, they will be equal to the overall mole fractions. Therefore a promising way of defining local compositions is to use the overall compositions, but there is no clue as to what sort of relation that would be. It is implicitly assumed that \( \frac{x_{ji}}{x_{ii}} \) is proportional to \( \frac{x_i}{x_{ii}} \), thus

\[ \frac{x_{ji}}{x_{ii}} = k_{ji} \frac{x_i}{x_{ii}} \quad (i, j = 1,2 \quad i \neq j) \]  \hspace{1cm} 2.3.37

Bearing in mind the mass constraint equations

\[ x_{ji} + x_{ii} = 1 \]

one can write for a binary mixture
\[
x_{21} = \frac{x_{2} k_{21}}{x_{1} + x_{2} k_{21}}, \quad x_{12} = \frac{x_{1} k_{12}}{x_{2} + x_{1} k_{12}}  \quad 2.3.38
\]

Defining the proportionality constant \( k_{ji} \) as

\[
k_{ji} = \exp \left( \alpha_{ij} \frac{(g_{ji} - g_{ij})}{RT} \right) \quad (i, j = 1, 2 \ i \neq j) \quad 2.3.39
\]

where \( \alpha_{12} = \alpha_{21} \)

Substitution of Eq. 2.3.38 and Eq. 2.3.39 into Eq. 2.3.36 yields the N.R.T.L. equation

\[
\frac{G}{RT} = x_{1} x_{2} \left[ \frac{\tau_{21} A_{21}}{x_{1} + x_{2} A_{21}} + \frac{\tau_{12} A_{12}}{x_{2} + x_{1} A_{12}} \right] \quad 2.3.40
\]

where \( \tau_{21} = \frac{g_{21} - g_{11}}{RT} \), \( \tau_{12} = \frac{g_{12} - g_{22}}{RT} \)

\[
A_{12} = \exp \left( -\frac{\alpha_{12} (g_{12} - g_{22})}{RT} \right) \quad A_{21} = \exp \left( -\frac{\alpha_{21} (g_{21} - g_{11})}{RT} \right)
\]

Activity coefficients are obtained by differentiation

\[
RT \xi \nu_{1} = x_{2}^{2} \left[ \frac{\tau_{21} \exp (-\alpha_{12} \tau_{12})}{[x_{1} + x_{2} \exp (-\alpha_{12} \tau_{21})]^{2}} + \frac{\tau_{12} \exp (-\alpha_{12} \tau_{12})}{[x_{2} + x_{1} \exp (-\alpha_{12} \tau_{21})]^{2}} \right]  \quad 2.3.41
\]

\( \xi \nu_{2} \) is obtained by rotation of subscripts \( 1 \rightarrow 2 \rightarrow 1 \).

Eq. 2.3.40 has one preselected \( \alpha_{12} \) and two adjustable parameters \( (g_{12} - g_{22}) \) and \( (g_{21} - g_{11}) \). Renon and Prausnitz (105) recommended the use of a value between 0.2-0.47 for \( \alpha \). However Marina and Tassios (106) showed that a single value of \( \alpha = -1 \) yielded correlations of accuracy comparable to that of the recommended value of \( \alpha \). The energy parameters \( g_{11} \) and \( g_{22} \) may be calculated from pure component's latent heats.
\[ g_{ii} = -(\Delta U_{V_1} - RT) \]  

2.3.42

\( g_{ii} \) values carry a negative sign, since they are cohesive energies.

Relating \( g_{12} \) to \( g_{11} \) and \( g_{22} \) through an assumption, (e.g. assuming \( g_{12} \) is the arithmetic or geometric mean of \( g_{11} \) and \( g_{22} \)), one may predict mixture properties from pure component data only. For a given \( \alpha \), determination of the adjustable parameters \( g_{12} - g_{22} \) and \( g_{21} - g_{11} \) from the miscibility data can give rise to different solutions depending upon the initial guess, when a search method is used (107). Mattelino and Verhoeve (108) have shown how to predict the exact number of sets of energy parameters at any value of \( \alpha \) and to select physically significant sets of parameters. Tassios (109) has shown that the stability criterion for complete miscibility is not always met by the N.R.T.L. equation. McDermott and Ashton (110) pointed out that local mole fractions are not consistent with the overall composition of the mixture. Certain restraining conditions must be fulfilled when Eq. 2.3.40 is extended to ternary and higher system (111).

2.3.10 Heil's Equation

An equation was proposed for solutions of polymers with interactions between like and unlike molecules by Heil and Prausnitz (112). When the number of segments is considered to be unity, Heil's equation can be used for binary non-electrolyte systems. It has the following form

\[
\frac{G^E}{RT} = -x_1 \ln(x_1 + A_{21}x_2) - x_2 \ln(x_2 + A_{12}x_1) \\
+ x_1 x_2 \left[ \tau_{21} \frac{A_{21}}{x_1 + x_2 A_{21}} + \frac{\tau_{12} A_{12}}{x_2 + x_1 A_{12}} \right] 
\]

where

\[
\tau_{21} = \frac{g_{21} - g_{11}}{RT}, \quad \tau_{12} = \frac{g_{12} - g_{22}}{RT}
\]
The activity coefficient are given by

\[
A_{21} = \frac{V_1}{V_2} \exp \left[-\frac{(g_{12} - g_{22})}{RT} \right], \quad A_{12} = \frac{V_2}{V_1} \exp \left[-\frac{g_{21} - g_{11}}{RT} \right]
\]

\ln y_1 \quad \text{is obtained by interchanging subscripts 1-2. In Eq. 2.3.43 first two terms constitute Wilson's expression, the last has the same form as the N.R.T.L. equation. So the first part of Eq. 2.3.43, supposedly, only takes into account the entropy effect. The derivation of the second part uses the residual Gibbs energy, therefore it should combine in one expression enthalpic and entropic terms. In effect the entropic contribution to } G^E \text{ arises partly through the term explicitly introduced by Heil to account for the excess entropy of mixing and partly through the Wilson-type term as mentioned earlier.}

\begin{align*}
\ln y_1 &= x_2^2 \left[ \frac{\tau_{21} A_{21}^2}{(x_1 + x_2 A_{21})} + \frac{\tau_{12} A_{12}}{(x_2 + x_1 A_{12})^2} \right] - \ln (x_1 + A_{21} x_2) \quad 2.3.44 \\
&+ x_2 \left[ \frac{A_{21}}{(x_1 + x_2 A_{21})} - \frac{A_{12}}{x_2 + x_1 A_{12}} \right]
\end{align*}

Vetere (113) has suggested a modification of Eq. 2.3.43 by introducing the nonrandomness parameters.

2.3.11 Orye's Equation

Orye (114), taking the approach of Wilson, has derived an equation which contains the entropic and enthalpic contributions to the Gibbs energy of mixing. The excess Gibbs energy is given by a relation of the form

\[
\frac{G^E}{RT} = -x_1 \ln (x_1 + A_{21} x_2) - x_2 \ln (x_2 + A_{12} x_1) \quad 2.3.45
\]

\[
-\frac{x_1 x_2 \ln A_{12} A_{21}}{(x_1 + A_{21} x_2)(x_2 + A_{12} x_1)}
\]
The last term on the right hand side of this equation represents an approximation to the enthalpic contribution to the Gibbs energy of mixing. If one ignores this term, Wilson's equation results.

The derivation of this equation has the same arbitrary steps as the Wilson equation. It conserves the advantages of the Wilson equation and is capable of predicting phase separation without need of a third parameter.

On differentiation of Eq. 2.3.45, according to Eq. 2.2.10, the activity coefficients are obtained:

\[
\ln y_1 = -\ln(x_1 + A_{21}x_2) + x_2 \left[ \frac{A_{21}}{x_1 + A_{21}x_2} - \frac{A_{12}}{x_2 + A_{12}x_1} \right] - \frac{x_1 \ln A_{12} A_{21}}{(x_1 + A_{21}x_2)(x_2 + A_{12}x_1)} \left[ 1 + x_1 \left( 1 + x_1 \left( 1 - \frac{1}{x_1 + A_{21}x_2} + \frac{A_{12}}{x_2 + A_{12}x_1} \right) \right) \right]
\]

2.3.12 Generalized Local Composition Equation

Local composition equations may be written in one mathematical scheme

\[
\frac{G}{RT} = -q[x_1 \ln(x_1 + x_2 A_{21}) + x_2 \ln(x_2 + x_1 A_{12})]
\]

\[
+ p x_1 x_2 \left[ \frac{\tau_{21} A_{21}}{x_1 + A_{21}x_2} + \frac{\tau_{12} A_{12}}{x_2 + x_1 A_{12}} \right] + r x_1 x_2 \left[ \frac{\alpha_{12} \tau_{12} + \alpha_{21} \tau_{21}}{(x_1 + x_2 A_{21})(x_2 + x_1 A_{12})} \right]
\]

where \( A_{ij} = p_{ij} \exp(-\alpha_{ij} \tau_{ij}) \)

\[
\tau_{ij} = (g_{ij} - g_{jj})/RT
\]
**ρ**<sub>ij</sub> = see the following table

**α**<sub>ij</sub> = see the following table

<table>
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<tr>
<th></th>
<th></th>
<th></th>
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<th><strong>α</strong>&lt;sub&gt;ij&lt;/sub&gt;</th>
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</thead>
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<td>0</td>
<td>( \frac{v_i}{v_j} )</td>
</tr>
<tr>
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<td>1</td>
<td>0</td>
<td>( \frac{v_i}{v_j} )</td>
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<td>1</td>
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<tr>
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<td>0</td>
<td>1</td>
<td>1</td>
<td>( \frac{v_i}{v_j} )</td>
</tr>
<tr>
<td>N.R.T.L.</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

### 2.3.13 Uniquac Equation (115)

Abrams and Prausnitz have recently proposed an equation for the Gibbs energy. They have generalized Guggenheim's quasi-chemical analysis through introduction of the local area fraction, as the primary concentration variable. The equation has the following form

\[
\begin{align*}
G^F &= x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{z}{2} \left( q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2} \right) \\
&\quad - q_1 x_1 \ln (\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln (\theta_2 + \theta_1 \tau_{12}) \\
&\quad \text{2.3.48}
\end{align*}
\]

where \( \tau_{12} = \exp \left( - \frac{u_{12} - u_{11}}{RT} \right) \), \( \tau_{21} = \exp \left( - \frac{u_{12} - u_{22}}{RT} \right) \).
\( \phi \) is the average segment fraction

\[
\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}
\]

This equation contains four pure-component structural parameters \( r_1, r_2, q_1, q_2 \) which are predeterminable from bond angles and bond distances and two adjustable binary parameters which must be determined from experimental data.

The activity coefficients are obtained by differentiation according to Eq. 2.2.10

\[
\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta}{\phi_1} + \ln \frac{\phi_1}{x_1} (x_1 \xi_1 + x_2 \xi_2)
\]

\[
+ q_1 \left[ 1 - \ln (\theta_{11} + \theta_{21}) - \frac{\theta_{11} \tau_{11}}{\theta_{11} + \tau_{21} \theta_{21}} - \frac{\theta_{12} \tau_{12}}{\theta_{11} + \tau_{21} \theta_{21}} \right]
\]

\[2.3.49\]

\[
\ln \gamma_2 = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad i = 1, 2
\]

\( \ln \gamma_2 \) is obtained by interchanging subscripts 1 and 2.

Eq. 2.3.48 works for a wide range of mixtures of polar and non-polar liquids such as hydrocarbons, ketones, esters, amines, alcohols, nitriles and water. It can, unlike Guggenheim's model, handle mixtures whose molecules differ appreciably in size and shape. When well-defined simplifying assumptions are introduced into Eq. 2.3.48, it reduces to any one of the several well-known equations, including the Wilson, Margules, Van Laar and N.R.T.L. equations.
2.4 Determination of the Empirical Parameters of the Equations for $G^E$

One of the main uses of solution thermodynamics is to predict equilibrium properties such as mutual solubility via the Gibbs energy. However, due to lack of adequate theory, the procedure is usually reversed and the Gibbs energy is estimated from equilibrium data and used as a means of data reduction, because it is often a relatively simple matter to obtain equilibrium data experimentally. To calculate the excess Gibbs energy from equilibrium data, a particular arbitrary function for $G^E$ is chosen and its empirical parameters are evaluated. There are four common procedures to calculate parameters. These are based on the following equilibrium knowledge.

2.4.1 Vapour-Liquid Equilibrium Data

For binary vapour-liquid equilibria the measured properties are pressure $P$, temperature $T$, liquid phase composition $x$ and vapour phase composition $y$. According to the phase rule any two of the measured properties are sufficient to describe the equilibrium system. At equilibrium, the fugacity of each component in the vapour phase is equal to its corresponding fugacity in the liquid phase; this requirement yields the thermodynamic relations (15)

\[ y_1 \phi P = x_1 \gamma_1 f^r_1 \]  \hspace{1cm} 2.4.1

\[ y_2 \phi P = x_2 \gamma_2 f^r_2 \]  \hspace{1cm} 2.4.2

where

\[ \gamma_1 = \gamma_1^r \exp \left( \frac{\bar{V}_1 P}{RT} \right) \]  \hspace{1cm} 2.4.3

\[ \gamma_2 = \gamma_2^r \exp \left( \frac{\bar{V}_2 P}{RT} \right) \]  \hspace{1cm} 2.4.4
These equations are subject to mass constraints

\[ x_1 + x_2 = 1 \]  \hspace{2cm} 2.4.5
\[ y_1 + y_2 = 1 \]  \hspace{2cm} 2.4.6

Expressions for the fugacity coefficient, \( \phi \) and the liquid phase activity coefficient, \( \gamma \), are chosen and then the parameters of the liquid phase activity coefficients are evaluated either by a least square fit, (116,117) for instance on

\[ \frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = f(x,T,A_{11},1,m) \]  \hspace{2cm} 2.4.7

or by solving Eq. 2.4.3 and Eq. 2.4.4 with the appropriate expression for the reference state activity coefficient inserted:

\[ \ln \gamma_1 = f(x^r,T,A_{12},A_{21}) \]  \hspace{2cm} 2.4.8
\[ \ln \gamma_2 = f(x^r,T,A_{21},A_{12}) \]  \hspace{2cm} 2.4.9

This latter method is restricted to a maximum of two parameters as only two equations are available.

2.4.2 Liquid-Liquid Mutual Solubility Data

For partially miscible systems parameters of an equation for \( G^E \) may be obtained from mutual solubility data as follows: if \( G^E \) is written as a function of \( x_1 \) and \( x_2 \) and two adjustable parameters \( A_{12} \) and \( A_{21} \)

\[ G^E = G^E(x_1,x_2,A_{12},A_{21}) \]  \hspace{2cm} 2.4.10

then, using a symmetrical convention for the activity coefficients, they may be written
\[ \gamma_1 = \gamma(x_1, x_2, A_{12}, A_{21}) \quad 2.4.11 \]
\[ \gamma_2 = \gamma(x_1, x_2, A_{21}, A_{12}) \quad 2.4.12 \]

Substitution of the last two equations into Eq. 2.1.8 gives a pair of simultaneous equations which may be written in the following form

\[ F_i = x_i' \gamma_i' - x_i'' \gamma_i'' = 0 \quad 2.4.13 \]
\[ F_2 = x_2' \gamma_2' - x_2'' \gamma_2'' = 0 \quad 2.4.14 \]

Since conjugate compositions have a fixed value at a given temperature and pressure, solution of these simultaneous equations provides a means of estimating \( A_{12} \) and \( A_{21} \). The procedure consists in searching for parameters which satisfy Eq. 2.4.13 and Eq. 2.4.14. Simultaneously by minimizing the objective function, \( F \), by a search method (117), where

\[ F(A_{12}, A_{21}) = F_1^2 + F_2^2 \quad 2.4.15 \]

The efficiency of the procedure depends on the initial guess of the parameters and frequently convergence to different sets of parameters was observed (107). To avoid the very high negative values of the parameters Mattelin and Verhoeye (108) proposed the following objective functions

\[ F(A_{12}, A_{21}) = \left( \ln \frac{x_1' \gamma_1'}{x_1'' \gamma_1''} \right)^2 - \left( \ln \frac{x_2' \gamma_2'}{x_2'' \gamma_2''} \right)^2 \quad 2.4.16 \]

An equivalent formulation of simultaneous equations may be based on Eq. 2.1.20 and Eq. 2.1.21 namely

\[ \frac{\partial G}{\partial x_1} \bigg|_{x_1'} = \frac{\partial G}{\partial x_1} \bigg|_{x_1''} = \frac{1}{x_1'' - x_1'} \left\{ G \bigg|_{x_1'} - G \bigg|_{x_1''} \right\} \quad 2.4.17 \]
where the free energy of mixing $G$ is given by

$$G = RT(x_1 \ln x_1 + x_2 \ln x_2) + G^E(x_1, x_2, A_{21}, A_{12})$$

2.4.3 Infinite-Dilution Activity Coefficient Data

The concept of infinite dilution activity coefficient was introduced into thermodynamics by Gautreaux (118). As the mole fraction of one of the components in binary mixture approaches to zero, its activity coefficient approaches to a definite limit. Aside from the statistical significance of the infinite dilution activity coefficient $\gamma^\infty$ it has great practical importance, because one of the characteristics of separation or purification processes is that most costly portion of purification occurs in the region approaching infinite dilution where relatively pure material is converted to material meeting specifications of high purity. This is also the region where the non-ideal mixture differs greatly from ideality.

The activity coefficient is a measure of the deviation of the behaviour of a component in a mixture from ideality. It can be directly measured at finite concentration. A number of reviews and discussions on this measurements have appeared in the literature (119,120).

When $\gamma^\infty_1$ and $\gamma^\infty_2$ are measured or available the evaluation of parameters of a two-constant equation for $G^E$ is relatively simple matter, since the mathematical expression for activity coefficients has its simplest form at infinite dilution. The expression for $\ln \gamma^\infty_1$ in a binary mixture is derived as $x_2 \to 0$ for those equations discussed in Sec. 2.3 and are given below
### 2.4.4 Sedimentation Equilibrium

Cullinan and Lenzyk (121) have recently proposed the phenomenon of sedimentation equilibrium as a basis for a practical experimental technique for the determination of the liquid solution thermodynamic properties. He has developed an experimental technique for the direct determination of chemical potential composition derivatives in liquid systems.

The method involves spinning the liquid sample in a centrifuge followed by analysis of composition against radial position in the centrifuge field. Separation on the basis of molecular weight difference is opposed by random motion and intermolecular attractions. The driving force for diffusion of species 1 in a 1-2 binary mixture subjected to a

<table>
<thead>
<tr>
<th>Equation</th>
<th>( \ln y_1^\infty = \lim_{x_1 \to 0} \ln y_1 )</th>
<th>( \ln y_2^\infty = \lim_{x_2} \ln y_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular Solution</td>
<td>( A_{12} )</td>
<td>( A_{12} )</td>
</tr>
<tr>
<td>Van Laar</td>
<td>( A_{12} )</td>
<td>( A_{21} )</td>
</tr>
<tr>
<td>Redich-Kister</td>
<td>( 4(A_{0-3A_1}^0) )</td>
<td>( 4(A_{0+3A_1}^0) )</td>
</tr>
<tr>
<td>Wilson</td>
<td>( 1-\ln A_{12} - A_{21} )</td>
<td>( 1-\ln A_{21} - A_{12} )</td>
</tr>
<tr>
<td>Flory-Huggins</td>
<td>( 1-\ln n - \frac{1}{r} + \chi )</td>
<td>( 1+\ln r + r(\chi-1) )</td>
</tr>
<tr>
<td>N.R.T.L.</td>
<td>( \tau_{12}^G + \tau_{12}^G )</td>
<td>( \tau_{12}^G + \tau_{21}^G )</td>
</tr>
<tr>
<td>Orye</td>
<td>( 1-\ln A_{12} - A_{21} )</td>
<td>( 1-\ln A_{21} - A_{12} )</td>
</tr>
<tr>
<td>Heil</td>
<td>( 1+\tau_{12}^G + A_{12} (\tau_{12}^G - 1) - \ln A_{21} )</td>
<td>( 1+\tau_{12}^G + A_{21} (\tau_{21}^G - 1) - A_{12} )</td>
</tr>
</tbody>
</table>
A plot of $x_1$ against $r^2$ was found to be linear in their case. The chemical potential derivatives being determined from the value of slope.

In order to circumvent the problem posed by the integral method, Sethy (122) made use of Wilson equation as a form for chemical potential. The two empirical parameters were then determined by regression.
CHAPTER 3

DESCRIPTION OF APPARATUS

3.1 The High Pressure System

3.1.1 The Pressure Generator

Pressure was generated by a hand pump manufactured by Pressure Products Inc. and transmitted to the bottom of a pressure vessel along a steel pipe. The pump was capable of generating pressures up to 475 MN/m². The pressures were displayed on a Bourdon tube gauge described by the maker as accurate to 1.2 MN/m², if hysteresis effects are allowed for. The pressure transmitting fluid used was distilled water containing sufficient methanol to depress the freezing point below the lowest temperature used.

3.1.2 The Pressure Vessel

The equipment consisted of a thick-walled stainless steel cylinder manufactured by Autoclave Engineers Inc., its working pressure being 420 MN/m² at 200°C. It was sealed by means of a Viton 'O' ring set into a groove in the metal plug which formed the closure. This plug was retained by a large gland nut. The vessel had an outside length of 280 mm, an outside diameter of 160 mm and an internal cavity of 130 mm long by 50 mm bore. Hydraulic fluid was introduced through an inlet at the base of the vessel.

The vessel bolted into a frame provided with pivots at the centre of balance. The frame could be mounted in a constant temperature tank
where it was suspended by the pivots bearing on recesses on either side of the tank. When the vessel is isolated from the pressure generator, it is free to move from a vertical position to the horizontal position or vice versa.

3.1.3 Piping

a) General: The tubing used for conveying the pressure was 9 mm o.d. and 3 mm i.d and made of 316 stainless steel (cold worked bright finished) manufactured by Autoclave Engineers Inc. Its working pressure was 520 MN/m² at 40°C.

From the pump the high pressure pipe ran to an isolating valve and then to a 'T' (Fig. 3.1). The top access was connected to the base of the pressure vessel by a short nipple. The third access was fitted with a length of high pressure tubing which was bent at a right angle to rise above the surface of the heating medium and terminated in a bursting disc holder. The prebulged bursting disc was rated at 435 MN/m² at a temperature of 22°C.

All pipe connections were of the A.E. cone type. A typical connection is shown in Fig. 3.2. The tube was externally coned at an angle of 58°, threaded with a left hand thread and a collar screwed on. An internal cone was machined at an angle of 60° to the part where the high pressure connection was made. The external and internal cones machined to slightly different angles, bear on each other through what is essentially a line contact. Thus, the metal to metal contact area is reduced to a minimum. Adequate stress for effective sealing was provided by moderate tightening of a gland nut placed behind the collar. Each joint in the high pressure pipe-line was carefully tested for leaks before it was covered by the heating medium.
Fig. 3.1 General layout of the experimental apparatus
b) Sealing of Capillary Tubing: Samples of the two layers were withdrawn from the sample holders (c.f. 3.3 below) through a pair of capillary tubes (0.3 mm od. and 0.1 mm id). The small diameter capillary tubing allows samples to be withdrawn at a low volume flow rate, but with a high velocity of flow inside the line, so that there are no problems of fractionation as the sample is taken. The small diameter of the capillary also reduces the liquid hold-up (dead volume) to a minimum.

Each capillary was soldered to high pressure tubing just before the valve to prevent hydraulic fluid from leaking into the sample being drawn off (Fig. 3.3). Contamination of the sample with hydraulic fluid (which was water-methanol mixture) would greatly upset the equilibrium condition. The capillary tube was subjected virtually to the same internal and external pressure, except through the soldered part where it experiences the full pressure of the system across its wall. It was also subjected to some external pressure, while samples were being withdrawn.

3.2 The Constant Temperature Bath

3.2.1 Description

The tank was constructed from 3 mm mild steel plate. The dimension of the tank was 800 x 350 x 400 mm and it contained approximately 90 litres of heating medium. The tank was insulated with glass wool to reduce the heat transfer. The wall of the tank served also as a support for the recess of the pivots bearings and pneumatic pump.
Fig. 3.3 Method of sealing the capillary into the high pressure nipple.

Fig. 3.2 The External-internal cone connection.
3.2.2 Heating Medium

Shell motor oil "Diala oil B" was used as the heating medium in the temperature range 0°C and 100°C. For temperatures below 0°C a methanol-water mixture was used, and at above 100°C "Shell thermal oil 3S".

3.2.3 Control of temperature

In the range 0°C and 200°C temperatures were controlled with a mercury contact thermometer and monitored by a good grade mercury-in-glass thermometer. At temperatures below 0°C temperature was controlled by a thermistor temperature controller (Fig. 3.4).

The thermistor sensor is used as a part of a resistor bridge network with a 741 operational amplifier as a buffer and a micro amperemeter (µA) to give an indication of temperature. As the temperature changes the thermistor resistance changes and the output accordingly. This output is fed to another operational amplifier used as a comparator. The other input to the comparator is connected to a potentiometer which is calibrated to set temperature control. The output from the comparator controls a triac via a transistor. The triac gives ON-OFF control of 240 V, 50 Hz to a heater as the input varying with temperature passes the reference voltage from the potentiometer. The circuit operates from a 12 V supply given from a transformer, rectifier bridge and 78 L12 regulator.

3.3 Sample Holders

3.3.1 The Design Requirements

In designing this part of the equipment a number of requirements had to be fulfilled:
a) Means must be provided for samples of both phases to be withdrawn while the apparatus is still pressurised.

b) Since samples were to be withdrawn from it, its volume must be able to change.

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

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

e) The whole apparatus must be fitted into a cavity 50 mm diameter and 130 mm in length.

3.3.2 Piston-Cylinder Arrangements

The main body of the vessel for high pressure studies was constructed from a piece of stainless steel bar. This bar was bored out to a diameter of 35 mm leaving a substantial end as closure. A stainless steel piston was fitted to the other end of the cylinder. The piston was sealed by two 'O' rings; that in contact with the mixture being of 'p.t.f.e.' and the other 'neoprene'.

To withdraw samples from the top layer, a capillary was attached to the centre of the closed end as shown in Fig. 3.5. Samples of the lower layer were withdrawn via capillary which was attached to the piston through an angled insert with a backing nut. This capillary was allowed to protrude about 15 mm above the connector. A 'L' stop was inserted into the end of the piston to protect the capillary tube. To minimize strain on the capillary, when the piston rose, plenty of slack was allowed in the form of a coil.
Fig. 3.5 Detail of the Piston-Cylinder Equilibrium Cell.
The inside face of the piston was machined as shown in Fig. 3.5 to assist with the removal of air bubbles which collect on filling the cylinder. When filling the sample holder after a previous experimental run, the piston was withdrawn from the cylinder by jacking bolts, the use of which prevents damage to the cylinder walls.

The sample holder was attached to two arms of a supporting frame by four counter-sunk screws. The supporting frame itself was held to the cover of the pressure vessel by three counter-sunk screws. An exploded view of the sample holder is shown in Fig. 3.6.a.

3.3.3 Double Cylinder Arrangements

The second vessel developed for the high pressure studies consisted of a pair of concentric stainless steel cylinders. Each cylinder was machined from a short length of stainless steel bar leaving a thick end closed. A cap was threaded to the open end of each of the cylinders.

A filling hole was drilled in the cap of the inner cylinder which was coned as shown in Fig. 3.7 to assist the removal of air bubbles. The inner cylinder had a side hole at the bottom end which, in use, is always covered by mercury contained by the outer cylinder. To withdraw samples of both of the coexisting phases, two capillary tubes entered into the system through the bottom hole. One of them was extended right to the top to withdraw samples from the upper layer. The position of the other capillary was determined by a trial-error approach to withdraw samples from the lower layer.

At the capped end of the outer cylinder a hole 3 mm in diameter was drilled to admit the hydraulic fluid and capillaries. This hole was slotted to the top edge to enable the capillaries to be removed without detachment.
Fig. 3.6 An exploded view of equilibrium cells
Fig. 3.7 Double Cylinder Equilibrium Cell.
from the inner cylinder. Both of the capillaries passed through the port of the plug to its own three-way high pressure valve situated outside the vessel. An exploded view of this holder is shown in Fig. 3.6.b and the complete assembly in Fig. 3.8.

3.4. Gas Chromatograph

3.4.1 Apparatus

Analysis of each mixture was carried out on a Hewlet Packard 5700 gas chromatographic unit with a thermal conductivity detector. The signal obtained from the detector was continuously recorded as a function of time on a strip-chart recorder. The area of each of the component peaks was measured by a Pye Unicam DP88 Computing Integrator. The column was a 3000 mm spiral stainless steel tube of 3 mm ID packed with 80/100 mesh Porapack Q. Helium was used as a carrier gas at a constant flow rate for each system.

The samples were introduced into the gas chromatographic column through a silicon rubber septum by means of a plunger-operated injection needle. The standard injection techniques described by Schupp (123) were followed. The optimum working temperature at the injection port, in the oven and detector block were found by a trial and error approach, and are given in the following table for each mixture. Some of the actual chromatograms of 3 methyl 2 butanone-propanone mixture are shown in Fig. 3.9, together with corresponding integrator output.

3.4.2 Calibration

A number of synthetic mixtures were made up by weight and analysed to calibrate the detector response. The area correction factors were then calculated using one of the components as a reference. Water in the aqueous
<table>
<thead>
<tr>
<th>Time</th>
<th>Area</th>
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<th>Area</th>
<th>Time</th>
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<td>202</td>
<td>202</td>
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<td>263</td>
<td>262</td>
<td>262</td>
<td>262</td>
<td>270922</td>
</tr>
</tbody>
</table>

Fig. 3.9 Chromatograms of 3 methyl 2 butanone-water
<table>
<thead>
<tr>
<th>Mixture</th>
<th>Injection Port T°C</th>
<th>Oven T°C</th>
<th>Detector Block T°C</th>
<th>Flow Rate ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 methyl 2 butanone-water</td>
<td>200</td>
<td>220</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>2 butanol-water</td>
<td>200</td>
<td>215</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Carbondisulfide-propanone</td>
<td>150</td>
<td>165</td>
<td>150</td>
<td>30</td>
</tr>
</tbody>
</table>

Mixtures and propanone in the propanone-carbondisulfide mixture were respectively used as the reference component.

Area correction factors (C.F.) are calculated by comparing the response of each component to the reference of each system considered.

\[ CF = \frac{B_r}{B_i} \times \frac{X_i}{X_r} \]  

In an analysis run, the area of each component is multiplied by its C.F. to find the corrected area. Then the ratio of the corrected area of each component to the whole corrected area was taken to find the actual composition of the mixture. (see appendix 3).
4.1 Determination of the Mutual Solubility Data at Atmospheric and at Slightly Elevated Pressure

4.4.1 Analytical Method

a) At Atmospheric Pressure:

Equal volumes of about 20 ml of each of the components of binary mixture to be investigated were placed in a test tube which was immersed in a constant temperature bath. The test tube was equipped with a stopcock through which samples of both layers could be extracted with a syringe. To ensure equilibrium, the liquid phases were mixed thoroughly for a certain length of time with a glass stirrer driven by an electrical motor, then allowed to reach complete separation confirmed analytically.

Samples were taken from both layers at the same time by two hypodermic syringes. Each sample was put into a vial which already contained enough solvent (propanone) to prevent phase separation. The syringes were washed out several times by taking the whole content of the vial into the syringe and flushed back to reduce the resulting errors due to wetting and to ensure uniform mixing. The system was then further stirred and the above procedure was repeated until at least two successive analytical results were found to be the same.

For the ternary system the third component was added in small amounts at constant temperature and pressure until the critical solution composition was reached. After each addition of the third component, the mixture was
treated exactly like a binary system except that the solvent used to maintain homogeneity of the samples was dry methanol.

b) At Slightly Elevated Pressure

To extend the temperature range upwards, it is necessary to maintain a total pressure which is greater than or equal to the vapour pressure of the system. To achieve this the simple equilibration apparatus of Fig. 4.1 was devised.

The main body of the vessel was machined from a piece of stainless steel bar of 50 mm diameter. This bar was bored out leaving a substantial end as a closure. Then a thick stainless steel plate was welded on the open end. A thermocouple boss-head was threaded to the centre of the plate. Two stainless steel capillary tubes passed through the boss-head. One of them extended to the bottom of the cylinder, the other was allowed to protrude about 25 mm into the vessel to avoid sampling the vapour phase. Both of the capillaries were silver-soldered to the boss-head by sweating and each communicated with its own three-way high pressure valve.

The mixtures were made up to approximately known over-all compositions, such that two equilibrium layers of more or less equal volumes would form at the temperature in question. One fifth of the volume of the vessel was left as vapour space. The vessel was immersed into a constant temperature bath and allowed to reach the bath temperature. Mixing was carried out by raising and lowering one end of the vessel. Establishment of complete separation of the coexisting phases and attainment of equilibrium were confirmed by sampling at one hourly intervals, until the composition was found to be consistent with the previous result. Samples were withdrawn as described in Section 4.2.3.b and analysed by gas chromatography.
Fig. 4.1 Analytical Cell for Determination of the Mutual Solubility of Temperatures Above the Boiling Point of the Mixture.
4.1.2 The Light Transmission Method

In order to eliminate the subjectivity of the commonly used 'cloud method' in the determination of the critical solution temperature of a binary system and the critical solution composition of a two-phase multi-component system, a light transmission method has been devised. The method relies upon the development of optical turbidity when a second phase separates out at a critical point. This turbidity results from the difference in refractive index between the dispersed and continuous phases. It consists of stirring vigorously a synthetic mixture contained in a test tube or closed glass cell and passing through the sample a parallel beam of light. The intensity of light transmitted by the mixture from a stabilised voltage tungsten lamp was measured with a photo-cell. The discontinuity in the relationship between temperature and photo-cell output was found both on heating and on cooling. The average of these two values was taken to correspond to the C.S.T. of the mixture.

a) Application of the Light Transmission Method to a Binary System

At temperatures where the vapour pressure of the system is low, the experiment was carried out in a stop-cocked glass test tube immersed in a glass tank. The contents of the test tube were stirred by a glass stirrer driven by an electrical motor.

To extend the temperature to the vicinity of the normal boiling point of the mixture or above, the cell of Fig. 4.2 was constructed. It was made from a short length of buttress-end boroslicate glass tube (100 mm in length and 25 mm in diameter). The ends were each closed by a flange with asbestos inserts, bolted to a metal plate. Full-face 'Teflon' gaskets provided the effective sealing. The cell had an internal propeller driven by an external magnet.
Fig. 4.2 Optical Cell for the Measurements of the Light Transmission Method.
Two other optical cells were constructed with the hope of closing the demixing curve of the 3 methyl 2 butanone-water system. The first consisted of a short length of glass tubing closed by two thick metal plates fastened by means of three bolts. Effective sealing was provided by a pair of teflon 'O' rings conforming with BS1806 let into the end plates as shown in Fig. 4.3. The contents of the cell were stirred manually by rotating the cell end-over-end.

The second cell is shown in Fig. 4.4, it allows the free expansion of glass tubing. Graphite impregnated string was employed as packing. It was stirred manually by repeatedly inverting the cell.

The temperature in each cell was measured with a sheathed copper-constantan thermocouple within the cell. An air bath with two glass windows was used to heat up the mixture. The critical solution temperature in the last two cells was determined by observing the disappearance of a cloud point while heating and by the appearance of traces of turbidity while cooling. The average of these two values is taken to be the critical solution temperature.

b) Application of the Light Transmission Method to a Ternary System

A similar technique was used to determine critical solution composition of a two-phased ternary system at constant temperature and pressure. The third component was added step-wise into vigorously stirred mixture of known amounts of the other two components. At each step, the amount of the component added was determined by weighing the hypodermic syringe before and after. The discontinuity found in the relationship between solvent added and photo-cell output was taken to correspond to the critical concentration of the mixture.
Fig. 4.3 Optical Cell for 'Cloud Point' Observation.
Fig. 4.4 Optical Cell for 'Cloud Point' Observation.
4.2 Determination of Liquid-Liquid Equilibrium Data at High Pressure

4.2.1 Preparation of the Apparatus

a) Filling the Piston-Cylinder Holder

The sample holder with the vessel cover and valve system attached was inverted and held in a rotor stand. By loosening the bolt in the centre of the piston the capillary tube was removed. The sample holder was loaded with a mixture that would form more or less equal volumes at the conditions of interest. The capillary was then replaced and its retaining bolt tightened.

b) Filling the Double-Cylinder Holder

The liner was filled with sufficient mercury to cover the bottom hole of the sample container. The sample holder together with the capillaries inserted and fixed was lowered into the liner. Then it was filled with a mixture that would form roughly equal volumes of each phase at the conditions in question. The filling hole was closed with a bolt and compression washer. The sample container was fixed so that the pressure transmitting holes were diagonally opposite. More mercury was added and the liner was closed. The liner was attached to the supporting arms of the vessel cover so that when the whole unit was brought to the horizontal position the liner hole was positioned upwards.

4.2.2 Assembly of the Apparatus

The sample holder together with the vessel cover was lowered into the vessel and the closing nut screwed down until almost tight. Then the pressure transmitting liquid was gently pumped into the vessel by means of
a priming pump, 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 into the reservoir and so ensuring that no air was trapped within the vessel.

4.2.3 Experimental Procedure

a) Attainment of equilibrium

Before the apparatus was assembled the oil bath was set to the required temperature. The required pressure was slowly built up so that enough time was allowed for the heat of compression to dissipate. Then the vessel was isolated from the pressure generator by closing an isolating valve. The rise in pressure due to the reduction of volume caused by the advancing valve spindle, was so small that it was not registered on the pressure gauge.

When mixing of the sample under test was required, the pressure generator was isolated and the pressure vessel was rotated to a horizontal position. The vessel was then rocked by an arm connecting the frame holding the vessel to a pneumatic pump of which stroke and speed were controllable. The contents of the sample holder were stirred by the movement of a non-porous ceramic ball which acted as a stirrer. Raising and lowering the head of the vessel caused the ceramic ball to roll from end to end of the sample holder.

After adequate mixing to achieve equilibrium, the mixture was stood to allow segregation of the two phases. Samples of the two layers were then withdrawn through a pair of capillary tubes as described in the following subsection. The length of time to reach complete separation of the co-existing phases and for the attainment of equilibrium was determined by
sampling at hourly intervals up to eight hours, with this system. For the 3 methyl 2 butanone-water system equilibrium conditions were reached after four hours stirring and complete separation took six hours. For the 2 butanol-water system stirring and settling time were found to be two and four hours respectively.

The propanone-carbon disulfide is homogeneous at ambient conditions and separates out into phases at high pressure; it was found that the stirring of this system to equilibrate the phases is unnecessary. The complete separation of the coexisting phases of this system was found to take not less than twelve hours.

b) Method of Withdrawing Samples

When the required conditions were established, the three-way high pressure valve (4) in Fig. 4.5 was slowly opened. About 0.5 ml of liquid was removed through each capillary to purge it (See Appendix III). Then valve (4) was closed and washed out with a solvent. The valve (4) was again opened slowly and approximately 0.5 ml of representative sample was allowed to drip into 1 ml of solvent in a small stopped vial. The valve was then closed. The whole content of the vial (7) was withdrawn into a hypodermic syringe (5) and flushed out several times to bring about a homogeneous mixture.

The solvent used for aqueous mixtures was propanone which ensured homogeneity. Although propanone-carbon disulphide is homogeneous at ambient conditions, carbon tetrachloride was used as a washing solvent in the sample valves to prevent contamination with previous samples.

Samples could be taken roughly isobarically by injecting hydraulic fluid into the system as the samples were withdrawn. At least two successive samples were withdrawn from each layer and analysed by gas chromatography.
Fig. 4.5 Schematic Arrangement of the Sampling Valve.
as described in Sec. 3.4. No trace of methanol was found which would indicate an inleak of hydraulic fluid.

4.3 Materials

Unless specifically stated otherwise, materials used for phase equilibrium studies were distilled products which showed no impurities detectable by gas chromatographic analysis.
CHAPTER 5

TREATMENT OF RESULTS

5.1 The Mutual Solubility of the Binary System 3 Methyl 2 Butanone-Water

5.1.1 Atmospheric Pressure Measurements

Table 1.1 summarises the results obtained analytically at atmospheric and low pressure at various temperatures. Thirteen tie-lines were determined as described in Sec. 4.1.1.a at atmospheric pressure in the temperature range -8°C and 90°C. A solid phase separates out just below -8°C. Tie-lines in the temperature range 110°C to 180°C were obtained under the vapour pressure of the system as described in Sec. 4.1.1.b. Limitations of the heating oil used, precluded working at temperatures above 180°C.

Although various optical cells were constructed as described in Sec. 4.1.2 with the intention to determine the critical solution temperatures, none of them could withstand the vapour pressure of the system at the supposed critical composition of the system. Only the three critical solution temperatures given in Table 1.1, were observed.

All of the analytical and optical results are plotted on Fig. 5.1 together with the available literature data.

5.1.2 High Pressure Measurements

The influence of pressure on the mutual solubility of the 3 methyl 2 butanone-water system was investigated up to a pressure of 345 MN/m² at
Fig. 5.1 Miscibility isobars for system 3 methyl 2 butanone-water
at 69 MN/m² intervals. The design of the experimental apparatus used precluded working at pressures above about 360 MN/m². Within the constraints of the apparatus the shape of nine isothermal miscibility loops were determined analytically. The results obtained are given in Table 1.2 in terms of mass fraction of 3 methyl 2 butanone. T-x isobars are plotted in Fig. 5.1 together with atmospheric pressure results. P-x isotherms and T-P-x diagram are also graphed in Fig. 5.2 and Fig. 5.3 respectively. Some of the isotherms or isobars are omitted in Fig. 5.1 to Fig. 5.3 for clarity.

To investigate the existence of any anomalous tie-line, each isothermal experiment was repeated with several different overall compositions. Analytical results have shown that mixtures with different overall compositions resulted at the same temperature and pressure in the same conjugate compositions within experimental error (See Appendix III).

5.1.3 The Ternary System 3 Methyl 2 Butanone-Water-Propanone

The liquid-liquid phase equilibrium behaviour of this system was examined at 0°C and 40°C at atmospheric pressure. Tie-lines were determined as described in Sec. 4.1.1 at 0°C and 40°C and are given in Table 1.4. Critical solution concentrations of this system determined by the light transmission method as described in Sec. 4.1.2.b are given in Table 1.5. The results obtained by both of these methods at 40°C are graphed in Fig. 5.4. The consolute envelope at 25°C for the homologous system 4 methyl 2 butanone-water-propanone reported by Othmer et al. 124) is also shown in Fig. 5.4.
Fig. 5.2 Miscibility Isotherms for the System 3 Methyl 2 Butanone-Water.
Fig. 5.3 P, T, x space of the system 3 methyl 2 butanone-water
KETONE A = 3 methyl 2 butanone  ○ Analytical  ● Synthetic (optical), 40°C
KETONE A = 4 methyl 2 pentanone  ■ Synthetic (optical), 25°C

Fig. 5.4 Liquid-liquid equilibria at 40°C and natural pressure in the system 3 methyl 2 butanone-water-propanone (miscibility loop of 3 methyl 2 pentanone-water-propanone at 25°C (124) also shown).
5.2 The Mutual Solubility of the Binary System 2 Butanol-Water

5.2.1 Atmospheric Pressure Measurements

There are several different published sets of observations made on the 2 butanol-water system at atmospheric pressure as summarised in Sec. 1.5 and graphed in Fig. 1.2. The literature data reported on the mutual solubilities of this system at temperatures below 10°C show a great deal of disagreement, although all of the results below 10°C were obtained by the optical method. However, the general shape of the demixing curve in Fig. 1.2 suggests that this system may exhibit a waist at around 0°C.

In order to clarify the actual behaviour of the mutual solubilities of this system at low temperatures, tie-lines were analytically determined at 1°C intervals in the temperature range -7°C to 5°C. A solid phase separates out around -9°C. To make comparison with the available literature data, the determination of tie-lines was extended up to 99°C as described in Sec. 4.1.1. The results obtained are given in Table 1.6 and plotted in Fig. 5.5.

Critical solution temperatures of eight synthetic mixtures were also determined by the light transmission method, as described in Sec. 4.1.2 in the region where this method is more convenient and probably more accurate than the analytical method. The results are given in Table 1.7 and are also shown in Fig. 5.5.

5.2.2 High Pressure Measurements

The pressure dependence of the mutual solubility of the binary system 2 butanol-water, was thoroughly investigated in the temperature range -7°C to 99°C. The analytical results are given in Table 1.8 in terms of mass
Fig. 5.5 Mutual Solubility of the System 2-Butanol-Water of Various Pressures
fraction of 2 butanol. The T,x isobars and P,x isotherms of the T,P,x space are graphed in Fig. 5.5, Fig. 5.6 and Fig. 5.7. To emphasise the pressure dependence of the mutual solubilities especially at low temperature, part of the P,T,x space is plotted in Fig. 5.8.

Experimentation has shown that complete miscibility occurs at 0°C and 5°C at 13.8 MN/m², though tie-lines were obtained at the same pressure at -5°C and 10°C. It is also found by experimenting with several mixtures of different overall composition that complete miscibility occurs at 83 MN/m² at any temperature.

5.3 The Phase Behaviour of the Propanone-Carbondisulfide System at High Pressure

Although the propanone-carbondisulfide system is completely miscible at ambient conditions, it shows immiscibility at low temperatures with a U.C.S.T. at about -45°C and atmospheric pressure. Winnick and Powers (22) found experimentally that this system shows an immiscibility at -2°C at pressures above 420 MN/m². The indication of this experiment is that increasing pressure raises the U.C.S.T.

The limit of experimental high pressure apparatus used here precluded working at pressures above 362 MN/m². In order to investigate the phase behaviour of this system analytically within the limitation of the apparatus a temperature lower than that used by Winnick and Powers was chosen. The highest temperature at which the occurrence of phase separation was observed was -12°C. Because the system is homogeneous at ambient conditions and separates out into layers at elevated pressure, it is unnecessary to stir the mixture for the attainment of the equilibrium conditions, unless the demixing curve is sharply skewed (i.e. the sign of the slopes of the
Fig. 5.6 Miscibility Isotherms for the System 2 Butanol-Water.
Fig. 5.7 Miscibility Isotherms for the System 2 Butanol-Water.
Fig. 5.8 $P, T, x$ space of the system 2 butanol-water.
demixing curve at both ends of a tie-line are the same) and separation of phases is virtually instantaneous with increase of pressure.

The trend of the demixing curve was found within a small pressure range by determining two tie-lines at -14°C. The same tie-lines were redetermined without stirring and the same conjugate compositions were found. It was then concluded that the stirring for the attainment of equilibrium was unnecessary.

To explore the possibility of the existence of multiple lower critical solution pressures, the cell was loaded with mixtures of different overall compositions. Then representative samples of each layer were withdrawn at the conditions of interest. Analytical results have shown that the tie-lines are independent of overall compositions, under the same conditions of temperature and pressure so that the same tie-lines were obtained.

The results obtained are tabulated in Table 1.10 and graphed in Figure 5.9 to 5.11.

5.4 The Mutual Solubility of the Thiodipropio-nitrile-Toluene System

The mutual solubility of the thiodipropio-nitrile-toluene was determined at atmospheric pressure by the light transmission method as described in Sec. 4.1.2. The results are given in Table 1.11 and graphed in Fig. 5.12 together with the only literature data provided by Skinner (20).

Materials. Toluene: B.D.H. 'Analar' toluene was used as it was received. Thiodipropio-nitrile: Liquid thiodipropio-nitrile was crystallised. The crystals were washed with distilled water and melted. The liquid was dried
Fig. 5.9 Miscibility Isotherms of the System Propanone–Carbon Disulfide.
Fig. 5.10 Mutual miscibilities of propanone-carbon disulfide at various pressure
Fig. 5.11  P, T, x space of the system propanone-carbon disulfide
Fig. 5.12 Mutual Solubility of the System Thiodipipionitrile-Toluene at Atmospheric Pressure.
by purging with nitrogen at 100°C. Further drying was carried out with anhydrous sodium sulfate. This procedure was repeated three times.

The thiodipropio-nitrile is too involatile to be analysed by gas chromatography. Elemental analysis was carried out by micro-analysis and the results are given in Table I.12 together with Skinner's results.

5.5. Correlation and Prediction of the Conjugate Compositions

It is always desirable to express the experimental results of equilibrium studies in analytical form. The obvious benefit of such data reduction is communication of the results in a compact form which permits:

a) interpolation between discrete points,

b) extrapolation of fragmentary data to conditions in which no data exist,

c) Extrapolation or prediction of the behaviour of systems on which no experimental data is available under any condition.

Four of these equations for $G^E$ discussed in Sec. 2.3 are chosen to represent the systems 3 methyl 2 butanone-water, and 2 butanol-water studied as a function of temperature and pressure. The parameters of these equations (e.g. Van Laar, Orye, Uniquac,Heil) are computed from liquid-liquid equilibrium data as described in Sec. 2.4. The results are tabulated in Appendix 2.

The parameters of each equation chosen are found to be a function of temperature and pressure. Temperature and pressure dependence of each set of parameters for 3 methyl 2 butanone-water system are graphed in
Figs. 5.12-19. Temperature dependence of parameters for 2 butanol-water system are also plotted in Figs. 5.19-23.

To each of these curves a second order polynomial was fitted. In each of the above figures the solid line represents the best fit. The polynomial in each case was of the form

\[ A = a_0 + a_1 Y + a_2 Y^2 \]

With the knowledge of the variation of each constant with temperature and pressure, it is possible to interpolate isothermal and isobaric tie-lines for the systems 3 methyl 2 butanone-water and 2 butanol-water. There are various methods for prediction of conjugate compositions through an expression for \( G^E \) (98), when the values of parameters are known at the conditions of interest. All of these methods are based on either finding the common tangent to the total Gibbs energy of mixture or solving the simultaneous Eqs. 2.4.13-14. Demixing curves for the 3 methyl 2 butanone-water and 2 butanol-water systems obtained through the Orye equation are shown in Fig. 5.24 and Fig. 5.25 respectively.

The reduction of experimental liquid-liquid equilibrium data to a set of mathematical equations presents a unique set of problems. It is not possible to test the data for thermodynamic consistency for two main reasons as follows:

a) the data give the ratio of activity coefficients, instead of yielding their individual values,

b) the data do not extend over a continuous composition range; since consistency tests (14,15,125) require either integration or differentiation, they cannot be applied to such data.
Fig. 5.12 Pressure dependence of the Van Laar constants of the system 3 methyl 2 butanone-water at various temperatures.
Fig. 5.13 Pressure dependence of the Heil constants of the system 3 methyl 2 butanone-water at various temperatures.
Fig. 5.14 Pressure dependence of the Orye constants of the system 3 methyl 2 butanone-water at various temperatures.
Fig. 5.15 Pressure dependence of the Uniquac constants of the system 3 methyl 2 butanone-water at various temperatures.
FIG. 5.16 Temperature dependence of the Van Laar constants of the system 3 methyl 2 butanone-water at various pressures.
Fig. 5.17 Temperature dependence of Heil constants of the system 3 methyl 2 butanone-water at various pressures.
Fig. 5.18 Temperature dependence of the Orye constants of the system 3 methyl 2 butanone-water at various pressures.
Fig. 5.19 The temperature dependence of the Uniquac constants of the system 3 methyl 2 butanone-water at various pressures.
Fig. 5.20  The variation of the Van Laar parameters with temperature at various pressures.
Fig. 5.21 The variation of the Heil constants of the system 2 butanol-water with temperature at various pressures.
Fig. 5.22 The variation of the Orye constants of the system 2 butanol-water with temperature at various pressures.
Fig. 5.23 The variation of the Uniquac constants of the system 2-butanol-water at various pressures.
Mass fraction of 3 methyl 2 butanone

Fig. 5.24 Tie-line data interpolated by the Orye equation for the system 3 methyl 2 butanone at various pressures.
Fig. 5.25 Tie-line data interpolated by the Orye equation for the system 2 butanol-water.
6.1 Equilibrium Data of the System 3 Methyl 2 Butanone-Water

6.1.1 Atmospheric Pressure Measurement Results

As it is seen from Fig. 5.1, the demixing curve at natural pressure tends to form a closed immiscibility loop. However freezing masks the lower critical solution temperature. Extrapolation of Steiner and Schadow's (21) results suggests that complete miscibility occurs at temperatures around \(-10^\circ C\) and their demixing curves show two minima and a maximum in between. Experimentation has shown that the tie-lines are independent of overall composition and complete miscibility does not occur above the freezing temperature of the mixture.

A literature survey has revealed that there is no set of data which spans a wide temperature range comparable with the present results. Only three tie-lines by Ginnings et al. (71) at 20°C, 25°C, 30°C and three saturation concentrations of ketone in water provided by Gross et al. (72) are available. As can be seen from Table 1.1 and Fig. 5.1 there is good agreement between the literature and the present results. Good agreement was also found between critical solution temperatures determined by the light transmission method and the results obtained by the analytical method.
6.1.2 High Pressure Results

At elevated pressure the conjugate compositions measured here show that at all temperatures between -8°C and 90°C increase of pressure caused increase in mutual solubility, but this increase was considerably less than that found by Steiner and Schadow. Although the pressure was raised to levels three times higher than those used hitherto for this system, there was no sign of complete miscibility occurring below 345 MN/m² nor were any apparently anomalous samples taken which might correspond to a segment of miscibility loop lying between two upper critical solution pressures.

It can be seen from the T, x section (Fig. 5.1) that the present system has a U.C.S.T. at low pressure, but its L.C.S.T. seems to be masked by freezing. With increasing pressure the U.C.S.T. falls, the L.C.S.T. becomes apparent, and then rises, indicating that further increase of pressure will merge the U.C.S.T. and L.C.S.T. at a hyper critical point to form a dome of immiscibility.

There is no firm evidence in the literature that the optical and analytical results differ greatly, because the measurements in the neighbourhood of the critical point are complicated by the occurrence of some pitfalls, such as opalescence phenomena and colorations (126). Therefore, the disagreement between the results obtained here and Steiner and Schadow's results should not originate from the different method used.

It is worth emphasising the design of their apparatus in which the pressure was transmitted from hydraulic fluid to the test mixture confined within a cell of 0.7 ml volume via a piston. The most likely source of error is the small undetected leak of hydraulic fluid into the test mixture during their observation. Of course any leakage into the test mixture would
change the entire phase diagram, since the consolute point is very sensitive to the presence of any impurity. This sensitivity is even used as an analytical method to check the purity of some substances (26).

The other likely sources of error in their measurements are the ineffective stirring in the cell and difficulties of ensuring accurate measurement of the overall composition of the samples placed in the test cell.

It appears that the phase behaviour of this system is similar to that of its homologue 2 butanone–water studied by Hunt and Lamb (127), in which the closed solubility loops contract with increasing pressure and disappear completely at a limiting point, the so-called hyper-critical solution point.

The position of the hyper-critical solution temperature could not be exactly determined partly due to the constraints of the apparatus used, partly due to the nature of the experimental method used. Tie-lines in $P(x)$ isotherms and in $T(x)$ isobars are extrapolated via Orye's equation (Eq. 2.3.45). Then consolute temperature and pressure are estimated by assuming that $T, x$ isobars in Fig. 5.1 and $P, x$ isotherms in Fig. 5.2 follow satisfactorily the rectilinear diameter law of Cailletet and Mathias (128) represented by the following equation

$$\frac{1}{2}(x'_1 + x'_2) = a_0 + a_1 Y$$

6.1

The pressure dependence of the consolute temperature is given in Table 1.3 and a critical line connecting the consolute temperature and pressure is graphed in Fig. 6.1.

No attempt was made to evaluate the pressure dependence of consolute composition, from which only very little information can be deduced, since the expression in question is one of the most cumbersome equations of thermodynamics (60, 80, 129):
Figure 6.1 Consolute line of the system 3 methyl 2 butanone-water.
\[
\frac{dx}{dP} = \lim_{T\to T_c} \lim_{P\to P_c} \frac{\partial S}{\partial x} \frac{\partial V}{\partial x^2} - \frac{\partial S}{\partial x^2} \frac{\partial V}{\partial x^2} \tag{6.2}
\]

From the observed pressure dependence of consolute temperatures (and compositions) some knowledge of the thermodynamic functions of this system may be deduced as follows: the pressure dependence of a consolute temperature has been given as \((60, 80, 129)\)

\[
\frac{dT_c}{dP} = \lim_{T\to T_c} \lim_{P\to P_c} \frac{\partial S}{\partial x^2} \frac{\partial V}{\partial x^2} \tag{6.3}
\]

comparison of this equation with Eq. 2.1.30 and 2.1.31 shows that for an U.C.S.T. the sign of \(\frac{dT_c}{dP}\) is opposite to that of \(\frac{\partial^2 V}{\partial x^2}\) \(T, P\), while for a L.C.S.T. \(\frac{dT_c}{dP}\) and \(\frac{\partial^2 V}{\partial x^2}\) \(T, P\) have the same sign. At the hyper-critical temperature (Fig. 6.1) \(\frac{dT_c}{dP} = \mp \infty\) and \(\frac{\partial^2 S}{\partial x^2} = 0\). That is mixing leads to a decrease of volume up to the hyper-critical temperature and then causes to increase of volume.

Since this system exhibits a miscibility loop, according to Eq. 2.1.30 and 2.1.31 the \(H(x)\) curve must change sign between the U.C.S.T. and the L.C.S.T.

With the assumption that the excess functions are free from inflection points, at constant temperature and pressure Eq. 6.3 may be approximately written as

\[
\frac{dT_c}{dP} \approx \frac{T \frac{\partial V}{\partial P}}{H_c} \tag{6.4}
\]

It is seen from this that \(H_c^E > 0\) at the U.C.S.T. and \(H_c^E < 0\) at the L.C.S.T. and \(H_{HP}^E = 0\) at the hyper-critical point. Within the validity of the above
assumption the excess volume of this system also changes sign from negative to positive with increasing pressure. The excess volume at atmospheric pressure is deduced according to Eq. 1.3,6 from the density measurements of Ginnings et al. (71). The change of sign of \( V^E(x) \) from negative to positive has recently been verified for the homologous system 2 butanone-water by Lamb and Hunt (68). It is very likely that this system behaves similarly.

The observed increase in mutual solubility with increase in pressure suggests that \( G^E \) is positive at low pressure, but becomes less and less positive as pressure increases. It is likely that reduction in \( G^E \) would give rise to an increase in mutual solubility.

6.1.3 The Ternary System 3 methyl 2 Butanone-Water-Propanone

Although extrapolation of Steiner and Schadow's results for solutions containing 40% by weight of ketone suggests that a homogeneous system might be achieved at around ambient pressure and temperature, two phases persisted when a 40% mixture was stirred at normal pressure and cooled to its freezing point around -8°C.

It was with the hope that all of the three consolute solution temperatures inferred from the high pressure results of Steiner and Schadow were masked by the system freezing that the three component system 3 methyl 2 butanone-water propanone was examined. It was hoped that the presence of the third component as solvent would bring about behaviour analogous to that resulting from increase of pressure.

As is seen from Fig. 5.4, no anomalous behaviour was observed and the general shape of the curve conforms with that of its homologue 4 methyl 2 pentanone-water-propanone reported by Othmer et al. (124).
6.2 Liquid-Liquid Equilibria of the 2 Butanol-Water System

6.2.1 Atmospheric Pressure Results

It is seen from Fig. 5.5 at temperatures above 5°C the immiscibility region first widens with increasing temperature, then at temperatures higher than 60°C, it narrows to disappear completely at an U.C.S.T. The so called "rectilinear diameter" was plotted. The U.C.S.T. was found to be 112°C and the lower consolute composition 36 weight per cent 2 butanol. Below 5°C the unusual behaviour occurs; the demixing curve forms a waist. Thus the immiscibility region becomes greater again with further decreasing temperature. Results of this work are compared in Fig. 6.2 with the available literature data in a low temperature range.

The occurrence of a waist was also qualitatively confirmed. A mixture with a composition of 40% mass 2 butanol was equilibrated at 0°C and allowed to reach complete separation of the coexisting phases. Rapid heating or cooling of this mixture causes cloudiness in each layer, in either case.

6.2.2 High Pressure Results

As is seen from Figs. 5.5-5.7 at all temperatures, the mutual solubility of this system increases with elevating pressure. Consequently the waist of the demixing curve exhibited at atmospheric pressure, shrinks with increasing pressure. Then it disappears completely giving rise to two separate loops the upper one being a closed loop, showing an U.C.S.T. and L.C.S.T. and the lower one showing an U.C.S.T. (Fig. 5.5). This indicates that the existence of a hyper-critical solution point of the type H.C.T.2 shown in Fig. I.l.g, at an isobar between 10.3 MN/m² and 13.8 MN/m² in the T,x diagram. The U.C.S.T. shown at low temperature goes beyond the visible region with further increase of pressure, so that the
Fig. 6.2 Comparison of the mutual solubilities of 2 butanol-water at low temperature end.
system has only an upper and lower critical solution temperature on a closed immiscibility loop at pressures higher than 17.2 MN/m². With increasing pressure the U.C.S.T. falls and the L.C.S.T. rises so that the closed solubility loops become smaller and smaller and then disappears completely at another hyper-critical solution point of type H.C.P.1 in Fig. 1.2.d.

The position of the hyper critical points could not be exactly determined due to the nature of the experimental method used. It is estimated from the critical line connecting the consolute points. This line was obtained using the same assumptions as the similar line for 3 methyl 2 butanone-water described in Sec. 6.1.2.

Sets of consolute values thus obtained are tabulated in Table 1.9. The critical line connecting the consolute points is shown as the P,T projection in Fig. 6.3 together with the values of Moriyoshy et al. (51). In Fig. 6.3 the results of Timmermans (73) measurements are also shown, though the values of consolute compositions are uncertain. The T,P curve determined by Schneider and Russo (23) for a mixture of 36.5 mass per cent 2 butanol was compared with the corresponding values deduced from our results and found to be in good agreement.

The gist of this observation is that this system exhibits two different types of hyper-critical solution temperature. Consequently the T_c(P) section of the T,P,x space is not symmetrical about the rectilinear diameter passing through the point H.C.T.1 in Fig. 6.3 as widely accepted. As is seen from Fig. 6.3, T,P curve has an other extremum in temperature, H.C.T.2 in addition to a maximum, H.C.T.1. The exhibition on the immiscibility surface, a maximum and a minimum (or a saddle point) in the T,P,x space is
Fig. 6.3 The Critical Line Connecting the Consolute Points of the System 2 Butanol-Water.
an hitherto unknown phenomenon, for this system.

A similar pattern to that of the T,P section with constant composition in Fig. 6.3 has been found in the effect of ionic surfactants (additives) instead of pressure on the miscibility of some alcohols (23, ).

It has been known for a long time that quite a number of systems show immiscibility phenomena in which L.C.S.T.'s are higher than U.C.S.T.'s. From the thermodynamic standpoint, there is no restriction that these immiscibility curves should not be closed. The existence of two consolute points of the same kind in two separate immiscibility loops has been predicted qualitatively by the Ising liquid theory developed by Lacombe and Sánchez (130).

From the phase diagram some knowledge about the thermodynamic function of this system may be deduced as follows: comparison of Eq. 6.3 with 2.1.30 and 2.1.31 shows that for an U.C.S.T. the sign of \( \frac{dT_c}{dP} \) is opposite to that of \( \frac{\partial^2 V}{\partial x^2} \), while for a L.C.S.T. \( \frac{dT_c}{dP} \) and \( \frac{\partial^2 V}{\partial x^2} \) have the same sign. So it may be concluded from Fig. 6.3, the second derivative of the molar volume with respect to composition \( \frac{\partial^2 V}{\partial x^2} \) is positive along the critical line. The same conclusion may also be deduced from Eq. 2.1.32: since the critical line in Fig. 6.3 is the line connecting the U.C.S.P.'s of the system \( \frac{\partial^2 P}{\partial x^2} < 0 \), so according to Eq. 2.1.32, \( \frac{\partial^2 V}{\partial x^2} \) > 0 at any point on the critical line. Although at the hyper-critical points (e.g. H.C.P.1 and H.C.P.2 in Fig. 6.3) the second derivatives of T, H, S with respect to composition are zero as can be seen from Eqs. 2.1.30-31, but \( \frac{\partial^2 V}{\partial x^2} \) > 0.
This indicates that the pressure and temperature dependence of the mixture molar properties are far from simple. Until there are more experimental measurements for the pressure and temperature dependence of the mixture properties, it is fruitless to speculate on the qualitative values of them, because classical thermodynamic argument of solutions itself grounds on the assumption that G is analytical. It has however been shown that the assumption of G being analytical at a critical point is doubtful; for an explicit critical discussion (14,131).

Excess volume of this system at atmospheric pressure is deduced from density measurements of Nakanishi (132) according to Eq. 1.3.6 and has negative value in the whole range of composition. A similar concentration dependence of the excess volume is seen for aqueous solutions of other aliphatic alcohols (60) and ketones (133).

The negative excess volume of aqueous mixtures may be due, primarily to a packing of the small water molecules in void volumes between organic molecules (134). Another negative contribution to the excess volume of aqueous mixture may be due to a formation of local structures around polar groups of the molecules of the non-aqueous component in the same manner as in the mixture of tert. butyl alcohol with water (135). However recent review articles on water and aqueous solutions stress the fact that there does not exist an adequate theory by which the concentration dependence of the thermodynamic quantities of dilute aqueous solutions of non-polar solutes can be established (136).

6.3 The Propanone-Carbon Disulfide System

The phase behaviour of the binary system propanone-carbon disulfide was investigated at -12°C and -14°C up to pressures 362MN/m².
The results within the constrains of the apparatus used support the earlier investigation carried out at \(-2^\circ\text{C}\) by Winnick and Power (22). They indicate that increasing pressure raises the upper critical solution temperature.

No anomalous samples were taken which would support the view that this system shows two minima and a maximum in an open P-x loop at elevated pressure. Therefore the apparent existence of two lower and an upper critical solution pressures in Winnick and Powers observations (Fig. 5.9) must be attributed to experimental error.

Winnick and Power (137) have also calculated the excess volume of this system at \(0^\circ\text{C}\) as a function of pressure and composition from experimental measurements of compressibility correlated by the Tait equation. It has been found that the excess volume has positive values in the whole range of composition at all pressures studied, but its value decreases with increasing pressure. These authors were able to show quantitative agreement between the observed phase equilibria and their volumetric measurements.

6.4 The Mutual Solubility of the Thiodipropionitrile-Toluene System

As is seen in Fig. 5.12, it appears that this system shows a demixing curve with two U.C.S.T.'s and a L.C.S.T. in between, over a small concentration range. Critical solution temperatures determined by Skinner are much higher than those found here. The discrepancy may be due to an impurity in the materials used by Skinner (most probably water which greatly decreases the mutual solubility). The purity of the materials involved is compared in Table 1.12.

Both the demixing curves in Fig. 5.12 are obtained by the optical method in which some pitfalls are likely to be encountered. Therefore the
results obtained here do not provide clear-cut evidence for the multipl-
city of consolute points over a small concentration range in an open
miscibility loop, though such behaviour is theoretically possible, it is
said to be improbable (140).

6.5 Back-Calculation of the Experimentally Obtained Data

The constants pertaining to the various semi-empirical expressions for
$G^E$ were fitted by a third or fourth order polynomial in temperature and
pressure. These polynomials were then used to calculate the demixing curves
for the system 3 methyl 2 butanone-water and 2 butanol-water. In Figs.5.24
and 5.25 the demixing loops calculated from Orye's constants are shown.
With the exception of the Uniquac equation applied to 2-Butanol-water, where
computational difficulties were encountered in estimating the constants,
possibly due to the existence of multiple solutions to the equation as
described by Heidemann and Mandhane (107), the Van Laar, Heil, and Uniquac
equations describe the almost vertical portions of the loop, but they fail
to extrapolate to the upper and lower portions of the consolute points.
However Fig.5.24 shows that the Orye equation interpolates the experimentally
obtained conjugate compositions of the system 3 methyl 2 butanone-water very
well, though it does not lend itself to the extrapolation of tie-lines or
for the prediction of consolute points for this system.

Fig. 5.25 shows the tie-lines predicted by the Orye equation for the
system 2 butanol-water. There is good agreement between experimental and
predicted values at temperatures higher than 20°C at any pressure considered.
At lower temperatures the semi-empirical equations tested seem unable to
describe satisfactorily the more complex solution behaviour of this system.

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 and pressure dependence of the
Orye equation is simpler than those of the other equations.
In view of the relatively unsatisfactory way in which the semi-empirical expressions for the systems studied, it would be a dubious step to attempt to derive such other functions as $V^E$ and $H^E$ from $G^E$ by equations such as Eqs. 2.3.1 and 2.3.3.
CHAPTER 7

CONCLUSIONS

The liquid-liquid phase behaviour of the systems 3 methyl 2 butanone-water, 2 butanol-water, propanone-carbon disulfide were studied at high pressure by using two specially designed equilibrium cells. The mutual solubility of the system thiodipropionitrile-toluene was also studied at atmospheric pressure. The following conclusions are drawn for each individual system investigated.

7.1 3 Methyl 2 Butanone-Water

The mutual solubility of 3 methyl 2 butanone-water system was studied up to pressures three times higher than hitherto used in a much wider temperature range. Results obtained here do not support the earlier report that this system shows a lower critical solution pressure in between two upper critical solution pressures over a concentration range.

It is concluded that this system shows similar behaviour to that of its homologue 2 butanone-water system in which increasing pressure contracts the miscibility loop. Thus, with increasing pressure the upper critical solution pressure falls, the lower critical solution pressure rises. This behaviour supports the view that this system would form a closed miscibility dome in the T, P, x space if the freezing did not occur at low temperature and pressure.

7.2 2 Butanol-Water

The mutual solubilities of the 2 butanol-water system were thoroughly studied as a function of temperature and pressure by the equilibrium cell
designed for the purpose. The data obtained were found to agree well with the results of the most of the other workers who used various other methods. An hitherto unknown immiscibility phenomenon for this system was observed, namely that the immiscibility surface in T, P, x space shows a minimum (or a saddle point) in addition to a maximum. Consequently this system exhibits consolute points of the same kind in two separate miscibility loops in an open T, x isobar.

7.3 Propanone-Carbon Disulfide

The influence of pressure on the mutual solubility of the system propanone-carbon disulfide system was studied analytically at -12°C and -14°C up to pressures 362 MN/m². The results obtained indicate that increasing pressure reduces the range of mutual solubility. No anomalous tie-lines were obtained. It is therefore concluded that the indications of the existence of two lower critical solution pressures and one upper critical solution pressure given by earlier workers result from small experimental errors. It has been found that the shape of demixing curve at high pressure conforms with the generally encountered form of phase behaviour.

In the light of the results obtained for the propanone-carbon disulfide system one might suggest that the application of pressure may be useful as a separation process in industry, although it is rather unlikely that this separation technique can compete with the other well-established separation processes such as distillation and extraction, it might be valuable in the separation of expensive products, where the other techniques fail.

7.4 Thiódipropionitrile-Toluene

The mutual solubility of the binary system thiódipropionitrile-toluene was studied at atmospheric pressure by a light transmission method. It
appears that this system shows two U.C.S.T.'s and a L.C.S.T. over a small concentration range.

7.5 General Remarks

It is worth emphasizing that no experimental evidence was found to support the view that the binary systems 3 methyl 2 butanone-water and propanone-carbon disulfide show an anomalous behaviour at high pressure. No adequate theory has been found to describe the phase behaviour of the systems 3 methyl 2 butanone-water and 2 butanol-water.
REFERENCES


6. Hicks, C.P., Chemical Thermodynamics (Chemical Society Specialist Reports) 2, 275 (1977).


34. Hertz, Berl. Berl. 31, 2669 (1898).
61. Marsh, K.N., Chemical Thermodynamics (Chemical Society Specialist Reports) 1, 2 (1977).
73. Timmermans, J., J. de Chimie Physique, 20, 491 (1923).
Table 1.1 Conjugate Compositions for 3 Methyl 2 Butanone (1)-Water (2) at Atmospheric Pressure

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<th>Temp °C</th>
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<th>Ref. 72</th>
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<td>$x_1''$</td>
<td>$x_1'$</td>
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* Determined by light transmission method with solutions under their own va our ressures.
Table 1.2 Conjugate Compositions for 3 Methyl 2 Butanone (1)-Water (2) as Functions of Temperature and Pressure

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<tr>
<th>Temp (°C)</th>
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<th>Mass frn. 1 lower layer</th>
<th>Mass frn. 1 upper layer</th>
<th>Temp (°C)</th>
<th>Press (MN/m²)</th>
<th>Mass frn. 1 lower layer</th>
<th>Mass frn. 1 upper layer</th>
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Table 1.3 Consolute Points of the System 3 Methyl 2 Butanone-Water extrapolated by the Orye equation.

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Table 1.4 Conjugate solutions in the system 3 methyl 2 butanone - water - propanone at normal pressure.

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Table 5 Critical compositions of solutions of 3 methyl 2 butanone - water - propanone at normal pressures and 40°C determined by optical method.

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<th>Mass fraction C₅ ketone</th>
<th>Mass fraction water</th>
<th>Mass fraction C₅ ketone</th>
<th>Mass fraction water</th>
<th>Mass fraction C₅ ketone</th>
<th>Mass fraction water</th>
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<td>0.5065</td>
<td>0.6516</td>
<td>0.0978</td>
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<tr>
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<tr>
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<tr>
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Table 1.6 Compositions of Conjugate Solutions of 2 Butanol (1) and Water (2) at Natural Pressure

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<tr>
<th>Temp °C</th>
<th>Mass frn. 1 $x'_1$</th>
<th>Mass frn. 2 $x''_1$</th>
<th>Temp °C</th>
<th>Mass frn. 1 $x'_1$</th>
<th>Mass frn. 2 $x''_1$</th>
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Table 1.7 Critical Solution Temperature of 2 Butanol-Water Determined by the Light-Transmission Method with Solutions Under Their Own Vapour Pressure

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Table 1.8 Mutual Solubilities of the System 2 Butanol (1)-Water (2) at Elevated Pressure

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<th>Temp °C</th>
<th>Press MN/m²</th>
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<th>Temp °C</th>
<th>Press MN/m²</th>
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Table 1.9  Consolute Points of the System 2 Butanol-Water.

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* Calculated from differences.

The results are within 0.30% absolute.

Table 13 The Physical Properties of Thiodipropionitrile

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APPENDIX 2

EMPIRICAL CONSTANTS
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* Data of Ref. (71).
Table 2.2 The Variation of the Hel constants of the System 3 Methyl 2 Butanone-Water with Temperature and Pressure

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* Data of Ref. (71)
Table 2.3  The Variation of Orye's Constants of the System 3-Methyl 2 Butanone-Water with Temperature and Pressure

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**Table 2.8** The Variation of the Heil Constants of the System 2 Butanol (1) - Water (2) with T and P
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<td>80</td>
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<td>-809</td>
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APPENDIX 3

ACCURACY OF THE CONJUGATE COMPOSITIONS
In the determination of liquid-liquid equilibrium data at elevated pressure, error may originate from two principal sources: gas chromatography and uncertainties in representative sample. The effect of experimental error from each source on the conjugate composition is estimated below. In arriving at an estimate of the standard error of conjugate composition, the following general formula for the propagation of error was applied

\[
(\Delta y)^2 = \sum_{i=1}^{n} \left( \frac{\partial y}{\partial x_i} \Delta x_i \right)^2
\]

where

- \( y = y(x_1, x_2 \ldots x_n) \)
- \( x_i \) = an experimental variable
- \( \Delta x_i \) = the standard error associated with variable \( i \)
- \( \Delta y \) = the standard error on \( y \)

### A.3.1 Estimation of the Standard Error in the Analytical Method

After having established the optimum conditions for the system of interest, the detector response is calibrated by a series of synthetic mixtures. It has been found that the detector response is linear with sample size within the range 0.5 \( \mu \)l and 5 \( \mu \)l and correction factor (Eq. 3.4.1) is independent of composition for each system considered.

The Table below lists the relevant experimental variables and their estimated standard errors which were taken into account in calculating the standard error on mutual solubility determined at 75°C and 206.8 MN/m² for the system 3 methyl 2 butanone-water.
<table>
<thead>
<tr>
<th>Intermediate variable</th>
<th>Related experimental variable</th>
<th>Value</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation of synthetic mixture</td>
<td>Mass of vial (gr)</td>
<td>12</td>
<td>$12 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Mass of vial + ketone (gr)</td>
<td>21.5</td>
<td>$21.5 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Mass of vial + ketone + water (gr)</td>
<td>2?</td>
<td>$22 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Ketone mass fraction</td>
<td>0.95</td>
<td>$2.71 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Area of ketone (units)</td>
<td>48500</td>
<td>$48500 \times 10^{-3}$*</td>
</tr>
<tr>
<td></td>
<td>Area of water (units)</td>
<td>4200</td>
<td>$4200 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>C.F. (Eq. 3.4.1)</td>
<td>1.645</td>
<td>0.00311</td>
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<tr>
<td>Unknown mixture</td>
<td>Area of water (units)</td>
<td>7107</td>
<td>$7107 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Area of ketone (units)</td>
<td>39328</td>
<td>$39328 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Corrected area of ketone</td>
<td>64694.6</td>
<td>138.37</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>71802</td>
<td>138.55</td>
</tr>
<tr>
<td>Mass fraction of ketone</td>
<td></td>
<td>0.91</td>
<td>0.0029</td>
</tr>
<tr>
<td>Percentage error</td>
<td></td>
<td>0.32%</td>
<td></td>
</tr>
</tbody>
</table>

* found by the statistical tests.
A.3.2 Uncertainties in the Representative Samples

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. Since the capillary had a bore of 0.1 mm, it was impossible to force the dead liquid through an appreciable length and detect it experimentally. Therefore the problem was approached theoretically.

Assume a stream-line flow and constant viscosity. If the capillary is initially full of liquid A and has a diameter \( r \), a length \( l \) and for the purpose of this analysis a constant flow rate \( q \), then:

\[
q = \pi r^2 u = \frac{1}{2} \pi r^2 \hat{u} \tag{A.3.2}
\]

and

\[
u_s = \hat{u} \left(1 - \frac{s^2}{r^2}\right) \tag{A.3.3}
\]

where

\( u \) = average velocity of the fluid
\( \hat{u} \) = maximum velocity of the fluid
\( u_s \) = velocity of the fluid at a distance, \( s \), from the axis.

The time required for the first trace of liquid to appear at the centre of the exit of the capillary \( t_1 \)

\[
t_1 = \frac{\hat{u}}{u_s} \tag{A.3.4}
\]

The time \( t_2, (t_2 > t_1) \) to form a radius of the interface, \( s \), will be given by

\[
t_2 = \frac{\hat{u}}{u_s} \tag{A.3.5}
\]
The amount of fluid withdrawn, $Q$, in time $t = t_2 - t_1$

$$Q = (t_2 - t_1)q$$  \[A.3.6\]

From the above equations one obtains

$$\frac{s^2}{r^2} = 1 - \frac{\pi s^2}{2Q}$$  \[A.3.7\]

Now at the time when the interface at the exit is, $s$, the volume flow rate of $B$ is $Q_1$

$$Q_1 = \int_0^s \frac{1}{d} \left(1 - \frac{s'^2}{r^2}\right) 2\pi s \ ds = \pi d \left(s^2 - \frac{s^4}{2r^2}\right)$$  \[A.3.8\]

and total flow rate, $Q_2$

$$Q_2 = \int_0^r \frac{1}{d} \left(1 - \frac{s'^2}{r^2}\right) 2\pi s \ ds = \frac{1}{2} \pi r^2$$  \[A.3.9\]

so the instantaneous concentration of $B$, $x$ (say)

$$x = \frac{Q_1}{Q_2} = \frac{s^2}{r^2} \left(2 - \frac{s^2}{r^2}\right)$$  \[A.3.10\]

substitution of Eq. A.3.7 into Eq. A.3.10 gives

$$x = 1 - \left|\frac{\pi s^2 k}{2Q}\right|^2$$  \[A.3.11\]

so, to get an instantaneous composition, $x$, one needs to reject a volume:

$$Q = \frac{\pi s^2 k}{2(1-x)^{\frac{1}{2}}}$$  \[A.3.12\]
Selecting typical values for the apparatus used, namely \( r = 0.005 \text{ cm} \) 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 from Eq. A.3.12 to be approximately 0.02 ml. Since before taking each new sample, the capillary was flushed with 0.5 ml from the sample holder in order to obtain a representative sample, it is therefore considered the representative sample is free from previous samples. So conjugate compositions are only affected by the errors originated in gas chromatography analysis. When the combined effect of the errors is allowed for in Eq. A.3.1, the resulting value of the standard error on conjugate composition is estimated to be 0.3\%. It can therefore be concluded that the features of the mutual solubility data given in this work are generally correct.
APPENDIX 4

THE HIGH PRESSURE DILATOMETER
The High Pressure Dilatometer

The equipment described here is intended to be used for the isothermal isobaric mixing of two liquids.

A.4.1 Apparatus:

To determine the excess volume of a binary mixture as a function of pressure and temperature by the direct method the apparatus of Fig. A.4.1 (the high pressure dilatometer) is designed and constructed. The apparatus basically consists of a stainless steel block, and elbow and four nipples. The block (3) connects orthogonally three of the nipples. One end of two of these nipples is closed. The third nipple (4) is connected to the fourth nipple (6) through a 90° elbow (5). Limbs 1 and 2 serve as reservoirs for pure components which are segregated by mercury before mixing. Mercury also prevents hydraulic fluid from coming in contact with the liquids under test and provides a medium on which a magnetic core floats in limb 6.

The whole unit is mounted in a frame in which it can rotate about the axis of the lowest nipple 4, though rotation is restricted so that limb 6 is always above the lowest point of the tube 4. The axis of tube 4 is inclined to the horizontal so that the elbow 5 is slightly lower than block 3. After isolating the pressurised apparatus from the pressure generator at valve (8), it can be detached and rocked in such a way that mixing of the contents of limbs 1 and 2 is achieved while tube 4 and elbow 5 remained full of mercury at all times. The displacement of the magnetic core floating on the mercury within the column 6 is determined by a linear differential transformer (7).

While working with dilute or rich concentrations, the length of one of the limbs is varied during the course of experiment in order to avoid the use of excess mercury.
Fig. A4.1 The high pressure dilatometer.
A.4.2 Filling the Dilatometer

To prepare a mixture of known composition the block 3 with limb 1 and 2 is separated from the rest of the apparatus and turned upside down. It is then filled with mercury by means of a syringe with a flexible stainless steel needle. When limbs are full with mercury the ends of the limbs are raised, so that the filling hole is situated at a lower position than the limbs. The desired quantity of pure, degassed components is then injected into each limb. It is ensured that there is enough mercury left to segregate the pure components. The amount of each component injected may be determined by weighing the syringes before and after. The masses of pure components may be confirmed by weighing the mercury displaced. Later the rest of the apparatus is connected and loading of mercury is continued with simultaneous gradual return of the dilatometer to the normal position where the elbow 5 stays at the lowest position. Finally the dilatometer is connected to the high pressure pump.

A.4.3 The Experimental Procedure

The filled dilatometer is immersed into a constant temperature bath and allowed to attain the bath temperature. The required pressure is then generated and the apparatus is allowed to reach thermal equilibrium. The magnetic centre is then found by sliding the transformer which is mounted on the limb 6, containing mercury until the magnetic core is located. The transformer is then clamped so that the magnetic centre is approximately 10 mm above or below the zero output region according to the findings of the previous runs. Finally the needle valve 8 is closed and the pump is isolated. Mixing is carried out by raising and lowering the ends of limbs. Since the system eventually reaches a constant volume, the mixing operation is
continued until there is no noticeable change observed on the voltmeter reading. That is to say the system is stirred for a while. The dilatometer is then returned to its normal position to establish original mechanical equilibrium. The voltmeter reading was noted. This procedure is repeated until at least two successive equal readings are obtained. Finally the displacement of the core is found from the calibration curve of the transformer and the excess volume is calculated according to

\[
V^E = \frac{hA m_1 m_2}{m_1 M_1 + m_2 M_2}
\]

where

- \( h \) is the displacement of the core
- \( A \) = cross-section area
- \( M_1, M_2 \) = molar masses of pure components
- \( m_1, m_2 \) = masses of pure components

The linear displacement transducer is calibrated against a high precision micrometer. The cross-section area of the mercury collector is calibrated by means of the transformer by determining the movement of the armature corresponding to the addition of measured quantities of mercury.

In the reduction of data, it is necessary to make two kinds of corrections. The first is due to changes in the cross-sectional area of the mercury collector due to increasing pressure and varying temperature. The second is due to changes in the inductance with changes in the float length/diameter ratio.

It was hoped that this apparatus would enable us to measure the pressure dependence of excess volume with high accuracy, because the
displacement of the mercury level could be detected with a precision of 0.01 mm. An unforeseen problem arose that the core of the transformer did not float freely on the mercury because of the surface tension effects. Attempts to circumvent this problem have failed. Therefore no experimental measurements could be performed. However it is believed that a spherical armature, which can "roll" along the wall of limb 6 will obviate this problem, though this requires the use of a different design and different transformer.