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PHASE EQUILIBRIUM STUDIES AT MODERATE PRESSURES

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Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

October 1992

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SUMMARY

The theory of vapour-liquid equilibria is reviewed, as is the present status of prediction methods in this field. After discussion of the experimental methods available, development of a recirculating equilibrium still based on a previously successful design (the modified Raal, Code and Best still of O'Donnell and Jenkins) is described. This novel still is designed to work at pressures upto 35 bar and for the measurement of both isothermal and isobaric vapour-liquid equilibrium data.

The equilibrium still was first commissioned by measuring the saturated vapour pressures of pure ethanol and cyclohexane in the temperature range 77-124 °C and 80-142 °C respectively. The data obtained were compared with available literature experimental values and with values derived from an extended form of the Antoine equation for which parameters were given in the literature.

Commissioning continued with the study of the phase behaviour of mixtures of the two pure components as such mixtures are strongly non-ideal, showing azeotropic behaviour. Existing data did not exist above one atmosphere pressure. Isothermal measurements were made at 83.29 °C and 106.54 °C, whilst isobaric measurements were made at pressures of 1 bar, 3 bar and 5 bar respectively.

The experimental vapour-liquid equilibrium data obtained are assessed by a standard literature method incorporating a thermodynamic consistency test that minimises the errors in all the measured variables. This assessment showed that reasonable x-P-T data-sets had been measured, from which y-values could be deduced, but that the experimental y-values indicated the need for improvements in the design of the still.

The final discussion sets out the improvements required and outlines how they might be attained.

Keywords: Equilibrium still, Experimental determination, Moderate pressures, Saturated vapour pressure, Vapour-liquid equilibrium.

Dedication

I dedicate this thesis to my parents, my parents-in-law, my wife Frances, my daughter Haneen-Arabella, my niece Majd, Alhakeem, my sisters Badeeá, Fatina and Suheir, my brothers Ashraf, Nader and Sáed, my brother in-law Dr Jihad Mashal and my cousin Usamah.

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Contents

		Summary	2
Chapter	1:	Introduction	12
Chapter	2:	Theoretical Background	14
	2.1	Introduction	14
	2.2	Criteria for Equilibrium	14
	2.3	Activity	17
	2.4	The Equilibrium Relationship	17
	2.5	The Gibbs-Duhem Equation	21
	2.6	Models for the Vapour Phase	22
		2.6.1 The Indirect Model	22
		2.6.2 The Direct Models	23
	2.7	The Liquid Phase Models	24
		2.7.1 Liquid Phase Models based on the Regular Solution Approach	26
		2.7.2 Liquid Phase Models based on the Athermal Theory	29
		2.7.3 Other Liquid Phase Models	32
		2.7.4 Comparison of the Liquid Phase Activity Coefficient Models	34
	2.8	Thermodynamic Consistency Tests	36
		2.8.1 Area Tests	36
		2.8.2 Slope Tests	37
		2.8.3 Statistical Tests	38
		2.8.4 Barker-Type Tests	41
Chapter	3:	Methods of Predicting Phase Equilibria	43
	3.1	Introduction	43
	3.2	The Solubility Parameter Approach	43
	3.3	The Equation-Of-State Approach	44
	3.4	The Group-Contribution Approach	
		3.4.1 The UNIQUAC Model	45
		3.4.2 The UNIFAC Equation	46
		3.4.3 An Evaluation of the UNIFAC Method	50

3.4.4 Uses of UNIFAC 52
3.4.5 The Temperature-Dependence of the UNIFAC Model 53
3.4.6 The SUPERFAC Model 62
3.4.7 The Modified UNIFAC Model, Larsen (1985) 63
3.5 The Group-Contribution Equation-Of-State Approach 66
3.5.1 The PFGC Equation 66
3.5.2 The Group-Contribution Equation of State of Skjold-Jorgensen (1984) 67
3.6 The Extension of UNIFAC to Higher Pressures 67
3.6.1 The Use of the Non-Quadratic Mixing Rules due to Vidal (1978) 68
3.6.2 Discussion of the Gupte and Daubert (1986) Contribution 69

Chapter 4: Review of Experimental Methods for Vapour-Liquid Equilibria 71
4.1 Introduction 71
4.2 Differential Distillation Methods 72
4.3 Circulation Methods 72
4.3.1 Vapour Recirculation Methods 73
4.3.2 Condensate Recirculation Methods 75
4.3.2.1 Othmer Still and its Modifications 76
4.3.2.2 Jones Still and its Modifications 84
4.3.3 Liquid Phase And Vapour Condensate Recirculation Methods 86
4.4 Static Methods 107
4.5 Total Pressure Methods 109
4.5.1 Introduction 109
4.5.2 Experimental Techniques 109
4.6 Flow Methods 114
4.7 Other Methods 119

Chapter 5: Development of an Equilibrium Still to Work at Moderate Pressures up to 35 Bar 122
5.1 Introduction and Background 122
5.2 The Development of the Equilibrium Cell of the Zain and Jenkins Still (Mark I) 122

	5.3	The Development of the Equilibrium Cell of the Zain and Jenkins Still (Mark II)	125
	5.4	The Development of the Equilibrium Still	125
Chapter	6:	Experimental Work`	131
	6.1	Introduction	131
	6.2	Materials	131
	6.3	Temperature Control and Measurement	131
	6.4	Pressure Control and Measurement	132
	6.5	Analysis	132
	6.6	Mode of Operation of the Equilibrium Still	134
Chapter	7:	Discussion of Results	136
	7.1	Saturated Vapour Pressure Measurements for Pure Ethanol and Pure Cyclohexane	136
	7.2	Initial Vapour-Liquid Equilibrium Data Screening	136
	7.3	Application of Consistency Tests to the Experimental Vapour-Liquid Equilibrium Data	138
	7.4	Ethanol-Cyclohexane at 83.29°C	142
	7.5	Ethanol-Cyclohexane at 106.54°C	144
	7.6	Ethanol-Cyclohexane at 1 bar	144
	7.7	Ethanol-Cyclohexane at 3 bar	146
	7.8	Ethanol-Cyclohexane at 5 bar	148
	7.9	Ethanol-Cyclohexane Azeotrope Compositionaa as a Function of Pressure	148
	7.10	Review of Ethanol-Cyclohexane Vapour-Liquid Equilibrium Data	148
Chapter	8:	Conclusions and Recommendations	150
	8.1	Conclusions	150
	8.2	Recommendations	150
	Nomenclature		153
	References		156

Appendices

Appendix	1:	Heater Calibrations	165
Appendix	2:	Calibration of Thermocouples	167
Appendix	3:	Analysis	168
Appendix	4:	Data	170
Appendix	5:	Data Reduction	173
Appendix	6:	Constants for an Extended Antoine Equation	181
Appendix	7:	Operation of the Equilibrium Still	182

List of Figures

Figure	2.1	The Problem to be Solved
Figure	4.2	Principle of Operation of Vapour Recirculation Method
Figure	4.2	Principle of Operation of Vapour Condensate Recirculation Method
Figure	4.3	The Othmer (1928) Still
Figure	4.4	Modification of the Othmer (1928) Still, (I)
Figure	4.5	Modification of the Othmer (1928) Still, (II)
Figure	4.6	Boiling Flask Suitable for Use with External Electrical Heating (Othmer)
Figure	4.7	Internal Heater (Othmer)
Figure	4.8	Kortüm Still
Figure	4.9	Bukala and Majeski (1952) Two-Plate Still
Figure	4.10	Jones, Schoenborn and Colburn (1943) Still
Figure	4.11	Modification of the Jones Still (due to Amick et al., 1951)
Figure	4.12	Bar-David and Dodge (1959) Still
Figure	4.13	Othmer and Morley (1946) Still
Figure	4.14	Swietoslawski Ebulliometer
Figure	4.15	Principle of Operation of Liquid Phase Vapour Condensate Recirculation Method
Figure	4.16	Rogalsk and Co-workers (1977, 1980) Ebulliometer
Figure	4.17	Lee (1931) Still
Figure	4.18	Gillespie (1946) Still
Figure	4.19	Fowler-Norris Still
Figure	4.20	Otuski-Williams Still
Figure	4.21	Brown (1952) Still
Figure	4.22	Rose-Williams Still
Figure	4.23	Ellis (1952) Still
Figure	4.24	Röck and Sieg Still
Figure	4.25	Stage and Müller Still
Figure	4.26	Dvorak and Boublik (1963) Still
Figure	4.27	Raal, Code and Best (1972) Still
Figure	4.28	Raal and Brouckaert (1992) Still
Figure	4.29	Jenkins and O'Donnell (1980) Modified Raal, Code and Best Still
Figure	4.30	Colburn Flow Still
Figure	4.31	Cathala (1960) Flow Still

Figure 5.1 Diagrammatic Cross-Section of the Equilibrium Chamber of the O'Donnell and Jenkins Still (1980)
Figure 5.2 Diagrammatic Cross-Section of the Equilibrium Chamber of the Zain and Jenkins Still (Mark I)
Figure 5.3 Diagrammatic Cross-Section of the Equilibrium Chamber of the Zain and Jenkins Still (Mark II)
Figure 5.4 Diagrammatic Elevation and Plan of the Mark II Zain and Jenkins Equilibrium Cell
Figure 5.5 Diagrammatic Representation of the Zain and Jenkins Still
Figure 6.1 Pressure Control System
Figure 7.1 Plot of log P against 1/T for Pure Ethanol
Figure 7.2 Plot of log P against 1/T for Pure Cyclohexane
Figure 7.3 Plot of (y - x) against x for Ethanol-Cyclohexane at 83.29°C
Figure 7.4 Plot of (y - x) against x for Ethanol-Cyclohexane at 106.54°C
Figure 7.5 Plot of (y - x) against x for Ethanol-Cyclohexane at 1 bar
Figure 7.6 Plot of (y - x) against x for Ethanol-Cyclohexane at 3 bar
Figure 7.7 Plot of (y - x) against x for Ethanol-Cyclohexane at 5 bar
Figure 7.8 Plot of Azeotrope Composition against Temperature for Ethanol-Cyclohexane
Figure 8.1 Proposed Method for Adequate Mixing of the Condensate in the Condensate Receiver and in the Sample Volume

List of Tables

7.1 Saturated Vapour Pressures of Pure Ethanol (Scatchard, 1964)

7.2 Saturated Vapour Pressures of Pure Ethanol (NPL)

7.3 Saturated Vapour Pressures of Pure Ethanol (This work)

7.4 Calculated Saturated Vapour Pressures of Pure Ethanol (An extended Antoine equation)

7.5 Saturated Vapour Pressures of Pure Cyclohexane (Scatchard, 1964)

7.6 Saturated Vapour Pressures of Pure Cyclohexane (This work)

7.7 Calculated Saturated Vapour Pressures of Pure Cyclohexane (An extended Antoine equation)

7.8 Azeotrope Composition-Temperature Data for Ethanol-Cyclohexane

A2.1 Calibration Data for the Central Thermocouple

A3.1 Densimeter and Refractometer Calibration Data for Ethanol-Cyclohexane

A3.2 Gas Chromatograph Calibration Data for Ethanol-Cyclohexane

A4.1 Vapour-Liquid Equilibrium for the Binary Mixture Ethanol-Cyclohexane at 83.29°C

A4.2 Vapour-Liquid Equilibrium for the Binary Mixture Ethanol-Cyclohexane at 106.54°C

A4.3 Vapour-Liquid Equilibrium for the Binary Mixture Ethanol-Cyclohexane at 1 bar

A4.4 Vapour-Liquid Equilibrium for the Binary Mixture Ethanol-Cyclohexane at 3 bar

A4.5 Vapour-Liquid Equilibrium for the Binary Mixture Ethanol-Cyclohexane at 5 bar

A5.1 Measured Variables and Estimates of their True Values for Ethanol-Cyclohexane at 83.29°C

A5.2 Measured Variables and Estimates of their True Values for Ethanol-Cyclohexane at 106.54°C

A5.3 Measured Variables and Estimates of their True Values for Ethanol-Cyclohexane at 1 bar

A5.4 Measured Variables and Estimates of their True Values for Ethanol-Cyclohexane at 3 bar

A5.5 Measured Variables and Estimates of their True Values for Ethanol-Cyclohexane at 5 bar

A5.6 Calculated Parameters for UNIQUAC for Ethanol-Cyclohexane

A5.7 Results of the Fit of the Data of Keshpande and Lu (1963) at 760 mmHg

A6.1 Constants for the Extended Antoine Equation (Appendix 6)

Distillation is one of the more expensive separation processes and in the present energy-saving world the running and capital costs for a given separation must always be determined, even if only to justify on economic grounds the use of alternative separation processes. Design of any distillation column requires a knowledge of vapour-liquid equilibrium data, either from experimental sources or from prediction methods. For the "leaner, harder" designs (Rush, 1980) needed in today's energy-conscious society, the data have to be of high accuracy. Recent advances in the energy integration of distillation columns into the overall heat flows within the process (e.g. Linnhoff et al., 1983) require columns to be operated at pressures away from the conventional atmospheric pressure. Hence vapour-liquid equilibrium data are needed at higher pressures both for testing prediction methods and for the operation of distillation columns at these pressures. In addition the direct measurement of vapour-liquid equilibrium data remains an important source of information concerning the equilibrium properties of fluid mixtures. For a given application data may not be available in the literature, or may be of dubious reliability, or, if available and reliable, not at the desired conditions.

In general, when a process for the separation of close-boiling components or for high purity products is to be designed, high accuracy vapour-liquid equilibrium data are indispensable and in most cases new reliable and accurate measurements should be made.

This thesis describes work carried out to develop a novel equilibrium still to work at moderate pressures up to 35 bar. The work is set against the theoretical background of vapour-liquid equilibria, and in the context of general reviews of both prediction methods and experimental vapour-liquid equilibrium methods, the latter review focussing on recirculating equilibrium stills.

The development of the new still from its antecedents is set out. Its commissioning over a range of temperatures and pressures up to 5 bar on mixtures of ethanol-cyclohexane is described. This mixture was chosen as a text mixture since accurate data exist in the literature below atmospheric pressure, the mixture is strongly non-ideal, having an azeotrope, and historically data had been required for flow-boiling research on mixtures, data at 5 bar not being available at that time (Jenkins, 1992a). When the compositions of ethanol-cyclohexane mixtures are expressed in group-terms, the mixtures contain only two groups. Data on such mixtures of only a few groups are useful for investigating the temperature behaviour of prediction methods such as UNIFAC (Fredenslund et al., 1975), especially when considering conditions removed from near-atmospheric.

Finally the experimental data are assessed by a standard literature method, that of Prausnitz et al. (1980), conclusions drawn as to the quality of the data and recommendations set out for further development of the still's design.

Chapter 2: Theoretical Background

2.1 Introduction

The first and second laws of thermodynamics are the fundamental relationships which are used to derive further expressions which relate the concentrations of a given component in each phase of an equilibrium vapour-liquid mixture. These expressions are used to correlate and consistency-test experimental data, as well as extrapolating data to new conditions. They also provide a basis for both theoretical and semi-empirical prediction methods of vapour-liquid equilibrium data from a minimum of information.

2.2 Criteria for equilibrium

A combined expression of the first and second laws of thermodynamics gives:

$$dU = TdS - PdV \tag{2.1}$$

The definition of the Gibb's energy is:

$$G = H - TS \tag{2.2}$$

Differentiation and substitution into equation 1 gives:

$$dG = VdP - SdT \tag{2.3}$$

For a system of variable composition we may express G generally as:

$$G = G\ (P,\ T,\ n_i,\ n_j \ldots\ldots) \tag{2.4}$$

On partial differentiation we get:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \Sigma\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\ (i \neq j)}} dn_i \tag{2.5}$$

By inspection of equations (2.3) and (2.5), we see that:

$$\left(\frac{\partial G}{\partial T}\right)_{P,ni} = -S, \left(\frac{\partial G}{\partial P}\right)_{T,ni} = V \tag{2.6}$$

We now define μ_i, the chemical potential of the i^{th} species by:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\,(j\neq i)}} \tag{2.7}$$

Therefore, for a system of variable composition we get:

$$dG = VdP - SdT + \Sigma\mu_i dn_i \tag{2.8}$$

If we consider two phases A and B, which represent two systems in contact at thermal and mechanical equilibrium ($P^A = P^B$ and $T^A = T^B$) and let δn_i moles of component i transfer from A to B, then for phase A and phase B we get:

$$dG_A = \mu_i^A\left(-|\delta n_i|\right) \tag{2.9}$$

$$dG_B = \mu_i^B\left(+|\delta n_i|\right) \tag{2.10}$$

respectively. Overall we have:

$$dG = dG_A + dG_B = 0 \tag{2.11}$$

$$\mu_i^A\left(-|\delta n_i|\right) + \mu_i^B\left(+|\delta n_i|\right) = 0 \tag{2.12}$$

Rearranging, we have:

$$|\delta n_i|\left(\mu_i^B - \mu_i^A\right) = 0 \tag{2.13}$$

δn_i has a finite value, hence the result:

$$\mu_i^A = \mu_i^B \tag{2.14}$$

is obtained.

To be of practical use, the chemical potential must be transformed from its abstract form into one dependent on pressure, temperature and phase concentrations. The problem is set out well by Prausnitz (1981) in diagram form as in Figure 2.1. Equation (2.14) is represented by Step 2. Steps 1 and 2 present little or no problem due to the work of Gibbs (1861) who first defined the chemical potential. The real problem arises in step 3 where the transformation from abstract terms into real world mathematical functions is made.

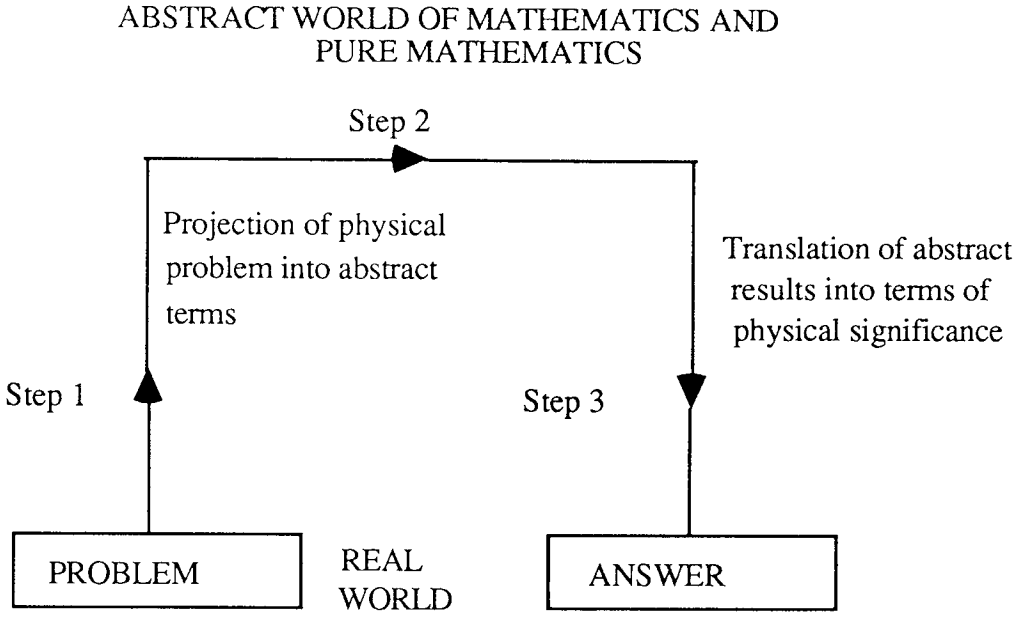

Figure 2.1 The problem to be solved.

Lewis (1901) defined fugacity as:

$$d\mu_i = RTd\ln f_i \quad (dT = 0) \tag{2.15}$$

where f_i is the fugacity of the i^{th} component. On integration the expression

$$\mu_i = RT\ln f_i + \theta_i \tag{2.16}$$

is obtained, where θ_i is a constant dependent only on temperature. At equilibrium, the temperature is uniform throughout all phases of a system hence the result:

$$f_i^A = f_i^B \tag{2.17}$$

is obtained. Equation (2.17) is another way of expressing the criteria for equilibria but it is practically more useful than equation (2.14). The fugacity can be thought of as a thermodynamic "pressure" which has been corrected for certain non-idealities.

2.3 Activity

The activity is defined by Lewis (1907) as the ratio of the fugacity of the constituent in the given state to the fugacity of this constituent at the same temperature in some standard state:

$$a_i = \frac{f_i}{f_i^o} \tag{2.18}$$

where a_i denotes the activity of the i^{th} constituent and f_i^o the fugacity in the standard state at the same temperature.

On combining equations (2.18) and (2.16) it follows that the activity is a measure of the difference of the chemical potentials in the given and standard states.

$$\mu_i - \mu_i^o = RT \ln \frac{f_i}{f_i^o} \tag{2.19}$$

The numerical value of the activity depends among other things on the choice of standard state, since if f_i^o is changed, a_i^o also changes according to equation (2.18). It is therefore necessary to consider which standard state is suitable for the solution of a given problem. For solutions of non-electrolytes, we choose as the standard state that of the pure constituent at the temperature and pressure of the system. Thus the activity of the pure substance is always equal to unity.

$$(a_i)_{x_i=1} = \frac{f_i^o}{f_i^o} = 1 \tag{2.20}$$

The activity coefficient γ_i is defined as the ratio of the activity to the mole fraction of the i^{th} constituent:

$$\gamma_i = a_i / x_i \tag{2.21}$$

It can be shown that the activity coefficient for a component in an ideal solution is equal to unity and thus the activity coefficient can be regarded as a correction factor for non-idealities in real solutions.

2.4 The equilibrium relationship

There are two basic methods of representing the equilibrium relationship, both derived from the criteria for equilibrium,

$$f_i^A = f_i^B \tag{2.17}$$

The first method of expressing the equilibrium relationship uses fugacities calculated from the pressure-volume-temperature (PVT) data through:

$$\ln\left(\frac{f_i}{p_i}\right)_{p=p'} = \int_o^{p'} \left(\frac{\bar{v}_i}{RT} - \frac{1}{P}\right) dP \tag{2.22}$$

For use with equations of state explicit in volume, the equivalent relationship due to Beattie (1949);

$$\ln\left(\frac{f_i}{p_i}\right) = \frac{1}{RT}\int_v^{\infty} \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{v}\right] dv - \ln Z \tag{2.23}$$

can be used for both phases.

The second method uses an equation of state for the vapour phase only. A fugacity coefficient ϕ_i is defined to relate the vapour phase fugacity to the mole fraction y_i and the total pressure P, hence:

$$\phi_i = \frac{f_i}{y_i P} \tag{2.24}$$

is obtained, and Beattie's equation is then represented by:

$$\ln\phi_i = \frac{1}{RT}\int_v^{\infty} \left[\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{v}\right] dv - \ln Z \tag{2.25}$$

Equations (2.18) and (2.21) can be combined to give the results:

$$f_i = \gamma_i x_i f_i^o \tag{2.26}$$

where f_i^o is the standard state fugacity, hence from equations (2.17), (2.24) and (2.26) we have:

$$\gamma_i x_i f_i^o = \phi_i y_i P \tag{2.27}$$

Equation (2.27) is a key equation for the calculation of vapour-liquid equilibria.

For liquids at low pressures, it is usual to use an alternative approach. Equation (2.19) is replaced by,

$$\mu_i - \mu_i^* = RT \ln a_i \qquad (2.28)$$

where a_i is the activity of component i, and μ_i^* is the chemical potential for pure liquid. The actual experimental data can be reduced to give the activity coefficients and these can then be expressed as functions of concentrations. Using this alternative approach;

$$f_i^L = f_i^V \quad ; \qquad (2.29)$$

but $$f_i^L = \gamma_i x_i f_i^{*L} \quad ; \qquad (2.30)$$

and $$f_i^V = \phi_i y_i P \quad ; \qquad (2.31)$$

therefore $$\gamma_i x_i f_i^{*L} = \phi_i y_i P \qquad (2.32)$$

But the standard states for the two phases are not the same and so the value of f_i^{*L} has to be established with respect to the standard of the vapour phase. We choose the vapour standard state to be the one more commonly used, i.e. that at which the fugacity of the pure component is one atmosphere. We can relate f_i^{*L} (pure i at T and P of mixture) to f_i^{oV} ($f_i^{oV} = 1.0$) in two steps.

Writing the relationship for pure saturated vapour i in equilibrium with pure saturated liquid i at the temperature of the mixture, we have:

$$f_i^L\left(T, p_i^{sat}\right) = f_i^V\left(T, p_i^{sat}\right) = \phi_i\left(T, p_i^{sat}\right) p_i^{sat} \qquad (2.33)$$

$$\gamma_i x_i \phi_i\left(T, p_i^{sat}\right) p_i^{sat} \frac{f_i^{*L}(T,P)}{f_i^{L}(T, p_i^{sat})} = \phi_i\left(T, p_i^{sat}\right) y_i P \qquad (2.34)$$

Now,

$$RT\, d\ln f_i = \overline{V}_i dP \qquad (2.35)$$

Hence,

$$RT\, d\ln f_i^L = v_i^L dP \qquad (2.36)$$

$$\ln \frac{f_i^{*L}(T,P)}{f_i^{L}(T, p_i^{sat})} = \frac{1}{RT} \int_{p_i^{sat}}^{P} v_i^L dP \qquad (2.37)$$

v_i^L, the specific volume of the pure liquid i is often regarded as being independent of pressure, hence,

$$\gamma_i x_i \phi_{i\left(T,p_i^{sat}\right)} p_i^{sat} \exp\left(\frac{v_i^L}{RT}\left(P - p_i^{sat}\right)\right) = \phi_{i(T,P)} y_i P \qquad (2.38)$$

(Note that since Prausnitz et al. (1980) uses a standard state of zero pressure for the liquid phase, the exponential term becomes

$$\exp\left(v_i^L \frac{P}{RT}\right).)$$

This term is often neglected since for pressures below about ten atmospheres it is negligible.)

Equation (2.38) can be simplified. At pressures close to one atmosphere (and perhaps upto five atmospheres),the fugacity coefficients cancel out and, neglecting the pressure term, we have:

$$\gamma_i x_i p_i^{sat} = y_i P \qquad (2.39)$$

If we define the relative volatility ratio by,

$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} \qquad (2.40)$$

Then equation (2.38) for both i and j gives:

$$\alpha_{ij} = \frac{\gamma_i p_i^{sat}}{\gamma_j p_j^{sat}} \qquad (2.41)$$

The relative volatility is not as strong a function of concentration as the equilibrium ratio. Similarly, the equilibrium ratio can be expressed rigorously as:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i \phi_i^{sat} \exp\left(\frac{v_i^L}{RT}\left(P - P_i^{sat}\right)\right)}{\phi_i P} \qquad (2.42)$$

Expressing the equilibrium ratio in this way brings out the possibility of predicting the equilibrium data on right hand side only ϕ_i and γ_i are functions of composition. Note that for the equation-of-state approach the equilibrium ratio is given by:

$$K_i = \frac{\phi_i^V}{\phi_i^L} \tag{2.43}$$

2.5 The Gibbs-Duhem Equation

The Gibbs-Duhem Equation is developed from a fundamental equation in terms of U for a system of variable composition:

$$dU = TdS - PdV + \Sigma_i \mu_i dn_i \tag{2.44}$$

Integrating this from a state of zero mass to one of finite mass at constant composition gives:

$$U = TS - PV + \sum_i \mu_i n_i \tag{2.45}$$

Differentiating equation (2.45) gives a general expression for dU comparable with equation (2.44):

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \tag{2.46}$$

and on comparison with equation (2.44) we get:

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \tag{2.47}$$

Equation (2.47) is the Gibbs-Duhem Equation, sometimes used in its restricted form:

$$\sum_i n_i d\mu_i = 0 \tag{2.48}$$

Great care must be exercised when using the restricted form due to the fact that the two omitted terms are related to the heat and volume change on mixing, which are not always negligible. Two further useful thermodynamic relationships which are used to evaluate the two left hand terms of equation (2.47) are:

$$\left(\frac{\partial \left(\frac{\mu_i}{T} \right)}{\partial T} \right)_{P,n_i,n_j} = \frac{-\overline{H}_i}{T^2} \tag{2.49}$$

and $$\left(\frac{\partial(\mu_i)}{\partial P}\right)_{T,n_i,n_j} = \overline{V}_i \qquad (2.50)$$

where $\overline{H}_i$ and $\overline{V}_i$ are the partial molar enthalpy and partial molar volume of component i in the mixture.

2.6 Models for the Vapour Phase

The vapour phase is represented by two types of models, the indirect and the direct models.

2.6.1 The Indirect Model

The indirect model already encountered in the definition of fugacity:

$$d\mu_i = RTd\ln f_i \quad (dT = 0) \qquad (2.15)$$

is in its integrated form

$$\mu_i = RT\ln f_i + \theta_i \qquad (2.16)$$

On defining a standard state for the vapour phase this becomes:

$$\mu_i - \mu_i^o = RT\ln\frac{f_i}{f_i^o} \qquad (2.19)$$

where f_i^o and μ_i^o are the fugacity and chemical potential of the reference state, usually defined as one standard atmosphere.

Further we have the limit $\frac{f_i}{p_i} \to 1.0 \quad \text{as} \quad p \to 0 \qquad (2.51)$

Equation (2.19) is usually written as

$$\mu_i - \mu_i^o = RT\ln f_i \qquad (2.52)$$

The indirect models are of direct use in transforming the abstract chemical potential of the vapour phase into the more meaningful fugacity of the vapour phase. In the case of a single ideal gas, equation (2.52) becomes:

$$\mu_i = \mu_i^o + RT\ln P \qquad (2.53)$$

2.6.2 The Direct Models

The direct vapour phase models are the equations of state which are used in the calculation of vapour phase fugacity coefficients. The first of these is the ideal gas law (PV = n RT) whose only use is as a starting point. The earliest real gas equation is due to Van der Waals who introduced two constants into the ideal gas law to allow for the attractive forces between molecules and the volume of the molecules themselves.

The most used equation of this type is due to Redlich and Kwong, it is:

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \qquad (2.54)$$

where a and b may be expressed as functions of the critical properties. The results from this equation show a great improvement over the Van der Waals equation although it has its limitations. Consequently many workers have attempted to improve the equation. The improvements include making the constants a and b functions of temperature, and relaxing the nature of the proportionality constants, which relate the constants a and b to the critical properties, then fitting the equation to available data. These modifications have been successful and have produced very good fits to experimental PVT data (Prausnitz, 1969)

An alternative approach is that of the Virial equation,

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots \qquad (2.55)$$

where B, C and D are the second, third and fourth virial coefficients respectively and are, for pure components, each functions of temperature only. Z is the compressibility factor. Equation (2.55) is the volume form of the virial equation.

The pressure form is:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \ldots \qquad (2.56)$$

B', C' and D' are related to B, C and D.

The physical significance of second virial coefficient B is that it takes account of deviation from ideality resulting from interactions involving two molecules. The third virial coefficient C deals with three molecules effect and so on. Since third virial coefficients are

scarce and fourth virial coefficients are rarely available, the virial equation is often used in a truncated form:

$$Z = 1 + \frac{BP}{RT} \tag{2.57}$$

The virial coefficients are either obtained from fitting the equation to experimental data or by using a correlation of the corresponding states type. One frequently used, is that of Pitzer and Curl, (1955, 1957). It is better to use experimental data to give the virial coefficients but good volumetric data for the mixture in question are not always available and thus correlations of the Pitzer and Curl type have to be used. Fortunately vapour-liquid equilibrium data at moderate pressures are not very sensitive to vapour phase fugacity coefficients and virial coefficients of limited accuracy introduce little error into phase equilibrium calculations, while their use is better than the assumption of ideal behaviour. Virial coefficients in a mixture are calculated using the relationship:

$$B_{MIX} = \sum_i \sum_j y_i y_j B_{ij} \tag{2.58}$$

Beattie (1949) developed an expression which can be used to obtain fugacity coefficient.

$$\ln\phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{v} \right] dv - \ln Z \tag{2.25}$$

This equation needs the substitution of a suitable equation of state to be of practical use, for example using the truncated virial equation we have:

$$\ln\phi_i = \frac{2}{v} \sum_i y_i B_{ij} - \ln Z \tag{2.59}$$

2.7 The Liquid Phase Models

The liquid phase can be represented in two ways. The first way treats the liquid phase in the same manner as the vapour phase and calculates the fugacity of the liquid phase directly by substitution of an equation of state into equation (2.22). This method has the advantage of not having to use a standard state, however, it has seen little use at low to moderate pressures due to the inadequacy of the earlier equations of state to perform suitably over a range of densities. In the light of this we need to discuss an alternative approach to vapour-liquid equilibrium which involves a relationship between the excess Gibbs function

(or free energy) and the activity coefficient. In this, the liquid phase is represented by defining an activity coefficient as used in calculating liquid phase fugacities:

$$f_i = \gamma_i x_i f_i^* \tag{2.60}$$

where f_i^* is the fugacity of the standard state. The value of the activity coefficient depends on the composition, pressure and temperature of the liquid solution and also on the standard state chosen. The choice of standard state will determine the normalisation of the activity coefficient. For condensable components which can exist as pure liquids at the temperature of the solution, the normalisation $\gamma_i \to 1$ as $x_i \to 1$ is used, whereas for non-condensable components, the normalisation $\gamma_i \to 1$ as $x_i \to 0$, $x_r \to 1$ is the most convenient, r stands for some reference solvent.

As previously stated, the activity coefficient is a variable which is used to account for all non-idealities of the liquid phase for each component. The activity coefficient can be related to another function which expresses the non-ideality of a solution, the excess Gibbs energy G^E.

$$G_{MIXTURE} = \sum_i n_i \mu_i^{REAL} = \sum_i n_i \mu_i^* + \sum_i n_i RT \ln x_i + RT \sum_i n_i \ln \gamma_i \tag{2.61}$$

But for an ideal mixture the Gibbs function is clearly the first two terms in the expression on the right hand side, so

$$G^E = G_{MIXTURE} - G_{MIXTURE}^{IDEAL} = RT \sum_i n_i \ln \gamma_i \tag{2.62}$$

Dividing by the total number of moles we get:

$$g^E = RT \sum_i x_i \ln \gamma_i \tag{2.63}$$

For a binary mixture this becomes:

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{2.64}$$

Prausnitz (1969) and others have shown that any individual activity coefficient γ_i is related to the molar excess Gibbs energy by:

$$RT\ln\gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_{j\,(i\neq j)}} \qquad (2.65)$$

where n_i is the number of moles of the i^{th} component and n_T is the total number of moles. Many equations have been proposed to express g^E as a function of composition. The form of the equation has usually been based on some simple theory of the nature of liquids and of liquid mixtures; often just an assumption about the energy required to replace one molecule of the solvent by one molecule of solute. There have been two lines of approach to this. It is noted that,

$$g^E = h^E - Ts^E \qquad (2.66)$$

The first approach is to assume that the non-ideality lies entirely in the enthalpy term, i.e., $s^E = 0$ and no volume change occurs on mixing. This is the approach of the theory of regular solutions.

$$g^E = h^E \qquad (2.67)$$

The second approach is to assume that the non-ideality is due entirely to the entropy of mixing, i.e. $h^E = 0$ and

$$g^E = -Ts^E \qquad (2.68)$$

This is the athermal solution approach. In both cases, the only justification for the use of any equation is that:

(a) it represents the experimental data well; and

(b) it is of use, by virtue of its accuracy and generality, in the correlation (and to a lesser extent the prediction) of vapour-liquid equilibrium data.

2.7.1 Liquid phase models based on the regular solution approach

The work of Van Laar was a particular landmark, as it was the first non-ideal solution model. The non-ideality of the solution expressed as the excess internal energy, U^E, is calculated by assuming a thermodynamic cycle in which two liquids are expanded isothermally at a low pressure and then mixing them ideally. The mixture is then cooled isobarically. Van Laar calculated the energy change during each step, assuming that the volumetric properties were given by the Van der Waals equation of state.

He obtained the well known Van Laar equations:

$$\log \gamma_1 = \frac{A}{\left[1 + \frac{A}{B}\frac{x_1}{x_2}\right]^2} \qquad (2.69)$$

$$\log \gamma_2 = \frac{B}{\left[1 + \frac{B}{A}\frac{x_2}{x_1}\right]^2} \qquad (2.70)$$

The constants A and B are functions of the Van der Waals constants, R the gas constant and absolute temperature.

Agreement between experimental activity coefficients and those calculated from equations (2.69) and (2.70) is poor due to the dependence of the Van Laar equation on the Van der Waals equation. Reasonable data have been obtained on considering A and B as adjustable parameters and evaluating them by fitting to experimental data (e.g. O'Donnell, 1980).

The main disadvantage of the activity coefficient models mentioned so far is that they are difficult to extend to multi-component mixtures and that there is no attempt to account for variations in temperature and pressure.

Another equation, due to Margules (1895), has received wide-spread use in vapour-liquid equilibrium data correlation:

$$\log \gamma_1 = x_2^2[A + 2x_1(B - A)] = x_2^2(2B - A) + 2x_2^3(A - B) \qquad (2.71)$$

$$\log \gamma_2 = x_1^2[B + 2x_2(A - B)] = x_1^2(2A - B) + 2x_1^3(B - A) \qquad (2.72)$$

With symmetrical systems for which A = B, both the Margules and Van Laar equations further simplify to the common form:

$$\log \gamma_1 = Ax_2^2 \quad , \quad \log \gamma_2 = Ax_1^2 \qquad (2.73)$$

Their extension to ternary and higher order mixtures requires the evaluation of ternary and higher order interaction parameters and so they become cumbersome and tedious. This disadvantage encountered in the regular solution approach was overcome by Scatchard in 1949 and Hildebrand in 1950.

The Hildebrand solubility parameter approach is based on a simple theory of liquid mixtures. Basically, the parameter employed, the solubility parameter, is related to the energy required to take a molecule from an ideal gas state to the liquid state. The parameters are combined in a way which models crudely the interactions between any molecule and the cloud of average molecules around it.

$$RT\ln\gamma_1 = v_1 z_2^2[\delta_1 - \delta_2]^2 \tag{2.74}$$

$$RT\ln\gamma_2 = v_2 z_1^2[\delta_1 - \delta_2]^2 \tag{2.75}$$

Here δ is the solubility parameter, and is given by:

$$\delta = \sqrt{\left(\frac{\Delta E_i}{v_i}\right)} \tag{2.76}$$

i.e. the square root of an energy density, for temperatures below the critical this is given by:

$$\Delta E_i = \Delta H_i^V - RT \tag{2.77}$$

where E_i is the energy required to vaporise one mole of i to infinite volume.

The solubility parameters δ_1 and δ_2 are temperature dependent but the difference (δ_1 - δ_2) is nearly independent of temperature and the equations hold good for moderate temperature ranges:

$$\delta_1 = \left(\frac{\Delta u_1^v}{v_1}\right)^{\frac{1}{2}}, \quad \delta_2 = \left(\frac{\Delta u_2^v}{v_2}\right)^{\frac{1}{2}} \tag{2.78}$$

$\overline{\delta}$ is the volume average solubility parameter for the liquid mixture and is given by:

$$\overline{\delta} = \sum_i z_i \delta_i \tag{2.79}$$

z_1, z_2 and z_i are the volume fractions of component 1, component 2 and component i in the mixture, where z_i is given by:

$$z_i = \frac{x_i v_i}{\sum_i x_i v_i} \tag{2.80}$$

assuming that no volume change occurs on mixing.

The problem of extension to multi-component mixtures is also overcome because the only constants required are the solubility parameters for each component of a mixture.

2.7.2 Liquid phase models based on the athermal theory

Flory (1942) and Huggins (1942) working independently, used the lattice theory of fluids in deriving an expression for the Gibbs free energy of a liquid mixture, where the molecules of the components are not of a similar size. It was found advantageous to assume that in such mixtures the enthalpy of mixing is zero and all the non-ideality arises from the entropy produced.

This assumption leads to the athermal solution theory of liquids:

$$g^E = -Ts^E \tag{2.68}$$

The derivation of the Flory-Huggins equations follows from a number of well chosen assumptions, concerning the behaviour of polymer molecules in solution and judicial use of statistical mechanics:

$$\frac{g^E}{RT} = \sum_i x_i \ln \frac{z_i}{x_i} \tag{2.81}$$

Wilson (1964) modified the equations of Flory and Huggins by introducing the local mole fraction concept. This arises due to the knowledge that molecules in a mixture do not arrange themselves randomly, but partially segregate due to the effect of intermolecular forces. Thus the composition at a point in the mixture will not be equal to the overall mole fraction. The local mole fraction x_{12} is related to the overall mole fraction by the relationship:

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp(-\lambda_{12}/RT)}{x_1 \exp(-\lambda_{11}/RT)} \tag{2.82}$$

Also, the local mole fraction x_{21} is related to the overall mole fraction by the relationship:

$$\frac{x_{21}}{x_{22}} = \frac{x_1 \exp(-\lambda_{21}/RT)}{x_2 \exp(-\lambda_{22}/RT)} \tag{2.83}$$

The exponential terms are Boltzman factors and the λs are proportional to the 1-1 and 1-2 interaction energies.

Wilson converted his expressions for local mole fractions into expressions for local volume fractions, substituting this into the Flory-Huggins expression and differentiating, he obtained:

$$\ln\gamma_k = \ln\left(\sum_j x_j \Lambda_{kj}\right) + 1 - \sum_i \frac{x_i \Lambda_{ik}}{\sum_j x_i \Lambda_{ij}} \qquad (2.84)$$

and for a binary mixture

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(\frac{-(\lambda_{12} - \lambda_{11})}{RT}\right) \qquad (2.85)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(\frac{-(\lambda_{21} - \lambda_{22})}{RT}\right) \qquad (2.86)$$

where the $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ are the adjustable parameters, usually obtained by fitting to experimental data.

Equation (2.84) has been proved to produce good representation for the behaviour of many mixtures and its extension to multi-component mixtures is relatively simple due to the fact that only binary parameters are needed. However, the Wilson equation does not produce a good representation of mixtures which exhibit partial miscibility. Wilson (1964) tried to overcome this problem by the introduction of a third parameter but he encountered difficulties. One good feature of the Wilson equation is that the adjustable parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ are only weakly temperature dependent and thus can be extrapolated over a wide temperature range.

In general this equation gives a better fit than the Van Laar or Margules equations and can handle a wide range of mixtures than either of these.

The derivation of the Wilson equation assumes a random distribution of molecules around a central molecule. In a real liquid, this can hardly be true since differences in molecular size and shape, besides any specific interactions, will create some order in the liquid. Such considerations led to the Non-Random Two Liquid (NRTL) equation of Renon and Prausnitz (1968). This equation, besides two binary energy interaction parameters, contains a shape factor which expresses the non-randomness element.

Theoretically, this shape factor can only take on a limited range of values, but in practice for many mixtures, a good representation of their behaviour can only be obtained when the third parameter is allowed to take on any value.

In its binary form, the expression for g^E is:

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{2.87}$$

where

$$\tau_{12} = \frac{G_{12}}{RT} \quad ; \quad \tau_{21} = \frac{G_{21}}{RT} \tag{2.88}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \quad ; \quad G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{2.89}$$

with

$$G_{12} = (g_{12} - g_{22}) \tag{2.90}$$

$$G_{21} = (g_{21} - g_{11}) \tag{2.91}$$

and α_{12} is the binary adjustable parameter.

The activity coefficients forms are:

$$\ln\gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{2.92}$$

$$\ln\gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{2.93}$$

Note that g_{ij} have a similar significance to λ_{ij} in the Wilson equation, i.e. a Gibbs energy parameter, characteristic of the i-j interactions.

The adjustable parameters of the NRTL equations are (g_{12} - g_{22}), (g_{21} - g_{11}) and α_{12}. If α_{12} is set to zero, then the equations reduce to the form of the two suffix Margules equations, and the mixture is completely random. Renon and Prausnitz indicate that from the reduction of the experimental data for a large number of binary mixtures, α varies between 0.20 and 0.47 and thus for mixtures where little experimental data are available, the value of α can be set to one obtained for similar mixtures.

: advantage that the NRTL equations have over the Wilson equation, is that they are able of producing good data fits both for miscible and partially miscible systems. The ameters (g_{12} - g_{22}) and (g_{21} - g_{11}) are highly temperature dependent.

selineau and Renon (1970) have assumed linear relationships for the parameters, iving at a six-parameter NRTL equation:

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15) \qquad (2.94)$$

$$g_{12} - g_{22} = C_2 + D_2(T - 273.15) \qquad (2.95)$$

$$\alpha_{12} = \alpha^o + \alpha^T(T - 273.15) \qquad (2.96)$$

'he C-parameters represent the value of the NRTL parameters at 0°C and the D-parameters iven their dependence upon temperature.

A nine-parameter equation has also been proposed by Nagata (1973) which assumes a quadratic temperature dependence of the parameters.

Bruin and Prausnitz (1971) modified the NRTL equations to introduce the local volume fractions rather than the local mole fraction. This improved the fitting of aqueous mixtures but very little else.

2.7.3 Other liquid phase models

One general expression for representing the excess Gibbs energy as a function of composition, which does not rely on assumptions of regular or athermal solutions, was proposed by Redlich and Kister (1948) who produced a series expansion in composition:

$$g^E = x_1x_2\left[A + B(x_1 + x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + ...\right] \qquad (2.97)$$

The constants A, B, C, D, etc., are all temperature dependent and are obtained by fitting of the equation to experimental data. Chao (1959) modified the Redlich-Kister equation to obtain the relationship:

$$\log\left(\frac{\gamma_1}{\gamma_2}\right) = a + b(x_2 - x_1) + C(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + ... \qquad (2.98)$$

ermination of the constants is difficult due to an indeterminately condition. Ochi (1977) further modified the equation of Chao to facilitate the evaluation of these ıts. Klaus and Van Ness (1967) proposed that G^E could be represented as a ›n of composition using orthogonal functions. Christiansen and Fredenslund (1975) 'ed this problem and used the method of orthogonal collocation.

ns and Prausnitz (1975) developed Guggenheim's quasi-chemical analysis and ded the local area fraction concept to produce the UNIQUAC (Unified Quasi- ıical) equation. It is similar to the Wilson and NRTL equations in that it is based on ɔcal composition concept. With only two interaction parameters for each binary it can ɛsent both vapour-liquid and liquid-liquid equilibria.

. expression for the activity coefficients contains two parts, a combinatorial part which ɛs into account differences in the size and shape of the molecules and a residual part, ich account for energetic interactions:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{2.99}$$

here γ_i^C is the combinatorial part and γ_i^R the residual part.

The combinatorial part is given by:

$$\ln\gamma_i^C = \ln\frac{\phi_k}{x_k} + \frac{Z}{2}q_k\ln\frac{\theta_k}{\phi_k} + l_k - \frac{\theta_k}{x_k}\sum_j x_j l_j \tag{2.100}$$

where

$$l_k = \frac{Z}{2}(r_k - q_k) - (r_k - 1),\ Z = 10 \tag{2.101}$$

θ_k and ϕ_k are volume and surface fractions respectively, r_k and q_k are measures of Van der Waals group volumes and surface areas respectively and are determined from values given by Bondi (1968).

The residual contribution is given by:

$$\ln\gamma_i^R = q_i\left[1 - \ln\left(\sum_j \theta_j\tau_{ij}\right) - \frac{\sum_j\left(\theta_j\tau_{ij}\right)}{\sum_k \theta_k\tau_{jk}}\right] \tag{2.102}$$

where

$$\tau_{ij} = \exp\left[\frac{\mu_{ij} - \mu_{ii}}{RT}\right] \qquad (2.103)$$

The adjustable parameters (μ_{ij} - μ_{ii}) are obtained by fitting to experimental data.

Although the UNIQUAC equation has been used extensively for representing liquid-liquid equilibrium data, it shows little or no improvement over the Wilson equation for miscible systems. Maurer and Prausnitz (1975) modified the UNIQUAC by the introduction of a third parameter. However, little improvement was obtained by the use of a three-parameter equation. Maurer and Prausnitz have commented that, "Although UNIQUAC is a useful two-parameter equation for the excess Gibbs energy, it cannot claim as much theoretical foundation as was hoped originally".

2.7.4 Comparisons of the liquid phase activity coefficient models

In the equations which have been discussed the number of adjustable constants per binary is typically two or three. Use of equations with a large number of parameters can only be justified if the experimental data are numerous and of very high quality for just one temperature. If the binary mixture is only moderately non-ideal, then all equations using about two binary parameters represent the data well. The earlier equations (Margules, Van Laar) are mathematically more tractable than the later equations (Wilson, NRTL, UNIQUAC).

For strongly non-ideal behaviour in binary mixtures such as alcohol/hydrocarbon mixtures, the Wilson equation remains probably the most useful. This stems from the fact that it has only two adjustable parameters for each binary, and is simpler mathematically than the UNIQUAC equation. The earlier equations will probably not represent the data well, particularly at low alcohol concentrations. The Wilson equation performs well at these concentrations.

Since the NRTL and UNIQUAC equations are applicable to both vapour-liquid and liquid-liquid equilibria, mutual solubility data can be used to determine the values of their parameters (this is not the case with the Wilson equation). While the UNIQUAC equation is mathematically more complete than the NRTL, it is more advantageous due to the following:

(1) it has only two, rather than three adjustable parameters, and they can be determined uniquely from mutual solubility data,

(2) it has a better theoretical background and so its parameters ought to be less temperature-dependent, and

(3) the major concentration variable is a surface fraction rather than mole fraction, so it can be used for solutions containing small or large molecules including polymers.

Counsell and Hicks (1976) used the data on water and ethanol mixture as obtained by Larkins and Pemberton (1976) to test the equations of Redlich-Kister, Van Laar, Wilson, NRTL and UNIQUAC. The temperature dependent forms of the above equations were also tested together using a fixed and variable α parameter in the NRTL equation. The NRTL equation with a variable α was discovered to produce the best fits, although the UNIQUAC equation was found superior to models representing g^E instead of g^E/RT.

When considering non-temperature dependent equations, the equations of Redlich-Kister, Van Laar and Wilson were discovered to produce superior fits. Counsell and Hicks (1976) further tested the above equations using another ten binary mixtures covering a wide range of mixture types. They concluded that the temperature dependent forms of the equations proved superior to the originally proposed equations, but the Wilson, NRTL and UNIQUAC equations fit the data twice as well as the Van Laar or Redlich-Kister equations. The Wilson equation has the disadvantage that it cannot fit partially miscible mixtures and therefore the modified NRTL and UNIQUAC equations are to be preferred. The last has the disadvantage of requiring extra parameters, but they can be estimated from pure component information.

Monfort and Rojas (1978) tested the accuracy of the Wilson, UNIQUAC and NRTL equations using 34 binary and 9 ternary mixtures. They concluded that the UNIQUAC equation was slightly better than the other two for binary mixtures. The Wilson equation proved superior for alcohol-hydrocarbon and chloroform-polar component mixtures. For ternary mixtures, no equation could clearly be considered superior as all gave similar results.

Wilkinson (1979) compared the abilities of the Wilson and NRTL equations to predict vapour-liquid equilibria from heats of mixing data. He concluded that both equations performed satisfactorily for mixtures with heats of mixing less than 120 calories per gram-mole but above the value, the NRTL equation performed better than the Wilson equation although both methods produced poor data. This work together with the work of Murthy and Zudkevitch (1979) casts doubts at the general usefulness of heats of mixing data for the calculation of vapour-liquid equilibria.

2.8 Thermodynamic consistency tests

The basic aim which all thermodynamic consistency tests seek to achieve, whatever the form, is to assess whether or not the data obeys the Gibbs-Duhem equation. If it does, the data is considered thermodynamically consistent. If it does not, then the data is thermodynamically inconsistent. The Gibbs-Duhem equation as previously derived is:

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \qquad (2.47)$$

For general application of consistency test, Ljunglin and Van Ness (1962) expanded this to the form:

$$\sum_i x_i d\ln f_i + \left((h - h^*)/RT^2\right)dT - (v/RT)dP = 0 \qquad (2.104)$$

and from this general equation for the coexistence of a liquid and vapour for binary mixtures was deduced:

$$AdP + BdT = (y_1 - x_1)d\ln\left(\frac{\gamma_{1V}}{\gamma_{2V}}\right) + \left(\frac{y_1 - x_1}{y_1 y_2}\right)dy_1 \qquad (2.105)$$

where

$$A = \left(\Delta v_V + x_1 v_V + x_2 v_{2V} - v_L\right)/RT \qquad (2.106)$$

and

$$B = -\left(\Delta h_V + x_1 h_{1V} + x_2 h_{2V} - h_L\right)/RT^2 \qquad (2.107)$$

Other equations have been proposed by Tao (1969) and Lee et al. (1969), but the equations presented above have proved to be the most frequently used.

Consistency tests can be grouped into the following four types:

1. Area tests
2. Slope tests
3. Statistical tests
4. Barker type tests

2.8.1 Area tests

These consistency tests are based on an integral form of the Gibbs-Duhem relationship in its simplest form, derived by Herington (1947) and Redlich and Kister (1948).

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2}.dx = 0 \qquad (2.108)$$

and it is used by applying the fact that the curve of $\ln(\gamma_1/\gamma_2)$ versus x crosses the $\ln(\gamma_1/\gamma_2)=0$ line and if the data is consistent the areas above and below the line should be equal. Many variations of this test have been proposed by Herington (1951), Broughton and Brearly (1955) and McDermot and Ellis (1965) but they all have the disadvantage that errors above and below the $\ln(\gamma_1/\gamma_2)=0$ line tend to cancel out. In performing the area test on real data, the integral in equation (2.108) will not come out to be exactly equal to zero, thus a criterion must be stated so that the data can be compared with it and a judgement can then be made as to whether a set of data is consistent or not. It is usually agreed that a set of data is considered consistent if it obeys the relationship

$$0.02 > \left(\frac{\text{AREA ABOVE x - AXIS - AREA BELOW x - AXIS}}{\text{AREA ABOVE x - AXIS + AREA BELOW x - AXIS}}\right) \qquad (2.109)$$

although the value on the left hand side of equation (2.109) will depend on how non-ideal the mixture is. If it is very non-ideal, the value can be raised and vice versa.

2.8.2 Slope tests

The slope method was proposed to provide a more stringent method of consistency testing. According to Prausnitz (1969), if a set of data was to "pass" the slope test, then it will automatically pass the area test, although the converse is not necessarily true.

For a binary mixture at moderate pressures, the Gibbs-Duhem equation can be written as:

$$x_1\frac{d\ln\gamma_1}{dx_1} = x_2\frac{d\ln\gamma_2}{dx_2} \qquad (2.110)$$

Plots of $\ln\gamma_1$ versus x_1 and $\ln\gamma_2$ versus x_2 are prepared and the slopes measured at regular intervals and substituted into equation (2.110) to see whether or not the relationship is obeyed. If it is, the data are consistent. The problem here, is that in practice, the slopes are hard to measure to any degree of accuracy and thus the method has not seen much use, although it provides a quick test to see if the data are very consistent. Van Ness (1964) and Van Ness and Mrazek (1959) have developed a method which uses a value Q defined as:

$$Q = \frac{\Delta G^E}{RT} = \sum_i x_i \ln \gamma_i \qquad (2.111)$$

and is plotted against x. The slopes of these plots are not so steep and thus the slopes are more easily evaluated.

Techo (1963) produced a further extension to the slope test and he used orthogonal polynomials to represent certain functions, but the curves produced were liable to develop extraneous inflection points which would result in false indications of consistency and inconsistency and thus the method is unreliable.

2.8.3 Statistical tests

In experimental vapour-liquid equilibrium data, two basic errors are always present:

1. Random errors associated with analytical procedures.
2. Systematic errors arising from erroneous operation or poor equipment design.

The problem is distinguishing whether a particular error in the data is due to random or systematic sources. An error analysis on the data will indicate uncertainty arising from random errors, whereas a consistency test will indicate the magnitude of the sum of both systematic and random errors. Rarely are both an error analysis and consistency testing carried out together. This fact was noticed by Ulrichson and Stevenson (1972), who used a local area test of the Stevenson and Sater type (1966), where the Gibbs-Duhem equation is integrated from a given data point a to the adjacent data point b. The test due to Stevenson and Sater is:

$$f(x) = \int_a^b \sum_i x_i d \ln \gamma_i + \int_a^b \frac{\Delta h_m}{RT^2} dT - \int_a^b \frac{\Delta v_m}{RT} dP \qquad (2.112)$$

Ulrichson and Stevenson improved this method by considering that although for consistent data f (x) = 0, in reality, this will never happen and some means for determining

acceptable bounds should be proposed. They did this by using the trapezoidal rule in the integration and then applying the propagation of error formulae.

Using the trapezoidal rule we have:

$$f(a,b) = \sum_i \frac{x_{ia} + x_{ib}}{2}\left(\ln\gamma_{ib} - \ln\gamma_{ia}\right) + \int_a^b \frac{\Delta h_m}{RT^2}dT - \int_a^b \frac{\Delta v_m}{RT}dP \qquad (2.113)$$

The propagation of error formulae are then applied and confidence areas are set up, if data points occur outside the confidence limits then it is most probably that large systematic errors are present in the data. If all data falls within the confidence limits, then there is a high probability that only random errors in the data exist. Although how accurate the data actually is depends on where the confidence limits are set.

Ulrichson and Stevenson concluded that an error analysis provides valuable additional information as well as improving the consistency tests. The additional information is as follows:

1. It provides a quantitative meaning to the consistency test rather than just a comparison with the null value.
2. It provides a means for determining whether the data are adequately represented by a liquid-phase activity coefficient model and may avoid misrepresentation of good data and excessively complex representation of poor data.
3. It provides a means for assessing the importance of non-ideal vapour phase behaviour and the heat and/or volume change of mixing.
4. It illustrates that the consistency test does not effectively detect random measurement errors in the liquid composition, nor in the vapour composition near an azeotrope.

This work casts doubts as to the value of previous consistency tests and Ulrichson and Stevenson proposed that the words consistent and inconsistent should no longer be applied to experimental data due to the fact that only exact solutions to the Gibbs-Duhem equation may be considered consistent. They further stated that data should either be said to satisfy or to not satisfy the Gibbs-Duhem equation, within certain experimental uncertainty. Data which do not satisfy the Gibbs-Duhem equation will then have excessive random error, or systematic error present, or both.

A similar procedure called the maximum likelihood procedure (Box, 1970) was used by Sutton and MacGregor (1977) to study 50 data sets, they concluded that this approach proved superior to previous methods. This was also the conclusion in the work of Anderson et al. (1978) and Fabries and Renon (1975).

In the maximum-likelihood analysis (see, for example, Prausnitz et al., 1980), it is assumed that all the measured data are subject to random errors. If each experiment were replicated many times, the average value derived from all the replicated experimental points would, in the limit, approach some true value. Usually the distribution of a measured variable about its true value is approximated by the normal distribution, characterised by an associated variance. If there is any coupling between the measurement method (e.g. measurements of overlapping peaks on a chromatograph), then there are also associated covariances between these measured variables. These variances and covariances must be known or estimated, although covariances are almost always assumed to be negligible. The variances are ideally obtained from replicated experiments, but they may be estimated from experience associated with a particular type of experimental apparatus. It is customary to assume that the random errors in different experiments are uncorrelated.

For each experiment, the true values of the measured variables are related by one or more constraints. Because the number of data points exceeds the number of parameters to be estimated, all constraint equations are not exactly satisfied for all experimental measurements. Exact agreement between theory and experiment is not achieved due to random and systematic errors in the data and to "lack of fit" of the model used to the data. Optimum parameters and true values corresponding to the experimental measurements must be found by satisfaction of an appropriate statistical criterion.

If this criterion is based on the maximum-likelihood principle, it leads to those parameter values that make the experimental observations appear most likely when taken as a whole. The likelihood function is defined as the joint probability of the observed values of the variables for any set of true values of the variables, model parameters, and error variances. The best estimates of the model parameters and of the true values of the measured variables are those which maximise this likelihood function with a normal distribution assumed for the experimental errors.

The maximum-likelihood method is not limited to phase equilibrium data. It is applicable to any type of data for which a model can be postulated and for which there are known random measurement errors in the variables. P-V-T data, enthalpy data, solid-liquid adsorption data, etc., can all be reduced by this method. The advantages indicated here for vapour-liquid equilibrium data apply also to other data.

The maximum-likelihood method, like any statistical tool, is useful for correlating and critically examining experimental information. However, it can never be a substitute for that information. While a statistical tool is useful for minimising the required experimental effort, reliable calculated phase equilibria can only be obtained if at least some pertinent and reliable experimental data are at hand. It will be seen below that this approach was used in assessing the data of this work, in particular as a variant of the classical Barker test.

2.8.4 Barker-type tests

It is well known that when obtaining x, y, P and T data for a mixture, only three out of the four variables are needed for data reduction. Van Ness et al. (1973), building on the approach of Barker (1953), proposed that the fourth variable may be compared with calculated variables obtained from the reduced data. This provided a very stringent test of thermodynamic consistency.

The method of Barker (1953) is used to enable the value of the redundant fourth variable to be calculated from the reduced data. The most general approach was developed by Abbot and Van Ness (1975) who used Barker's method to reduce P, x, T data and used y in the consistency test. Calculated y (exp) - y (calc) and P (exp) - P (calc) data are plotted versus x and a consistent set of data is obtained when Δy and ΔP values are small and randomly distributed around the $\Delta y = 0$ and $\Delta P = 0$ axis. This method uses an activity coefficient model such as the Wilson or NRTL equations to represent the liquid phase behaviour and data could be erroneously discovered inconsistent due to misrepresentation of the liquid phase activity coefficients by the chosen model. This disadvantage has been overcome by Christiansen and Fredenslund (1975) who avoided the use of liquid phase activity coefficient models and used orthogonal collocation to solve for G^E, and hence obtained

activity coefficients to predict y values. The resultant y (exp) - y (calc) versus x data was used in a screening test.

Jenkins and Gibson-Robinson (1978) used experimental data from a modified Cathala still to examine the consistency tests of Ulrichson and Stevenson (1972), of Samuels et al. (1972), of Van Ness et al. (1973), and of Wan and Prausnitz (1973) and Christiansen and Fredenslund (1975). They concluded that for consistency tests to be of use, forty to fifty data points per binary mixture must be used if any reasonable assessment of the data was to be obtained. A further conclusion was that use of the Barker method would be unwise in mixtures where association occurs, unless a suitable association model was to be used.

Chapter 3: Methods of Predicting Phase Equilibria

3.1 Introduction

A large part of chemical engineering design is concerned with separation operations. For the design of separation processes such as distillation, extraction, etc., quantitative information on the phase equilibria of binary and multi-component systems is required, primarily as a function of composition and temperature.

Data on multi-component mixtures are often not available, particularly for new processes. They are difficult and expensive to measure under all conditions of temperature, pressure and composition. Furthermore, in many cases, experimental information may be available for some, but certainly not all, of the possible binary mixtures. In this situation, the design engineer can only make a reasonable guess, often with large uncertainty. To reduce the uncertainty, a rational, accurate, and flexible prediction method may be used, particularly for the prediction of fluid-phase equilibria.

The prediction of vapour-liquid equilibrium data can be carried out, depending on the nature and the thermodynamic conditions of the mixture concerned, by the use of one of the following main approaches:

(1) The solubility parameter approach.
(2) The generalized equation-of-state approach.
(3) The group-contribution approach.
(4) The group-contribution equation-of-state approach.

3.2 The Solubility Parameter Approach

The solubility parameter approach is mainly used when choosing solvents for extractive distillation. Many methods based on this approach exist in the literature, typically those of Hildebrand and Scott.(1959); Weimer and Prausnitz (1965); Weihe and Bagly (1967) and Helpinstill and Van Winkle (1968). The method as set out by Null et al. (1970) , is only useful for screening solvents and not for reliable process design.

3.3 The Equation-of-State Approach

For the equation-of-state approach the interaction parameters must be known for all the possible binaries in the multi-component mixture of interest. The use of this approach is useful when for the final design:

(1) Data parameters are not available for all the binaries involved in a multi-component, and

(2) The two components of the mixture of interest to be separated are minor constituents but an exact specification has to be met as to their concentration level at top, bottom or in any side-stream.

In principle, applying the relationship: equilibrium ratio, K_i

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V}$$

(where ϕ_i^V and ϕ_i^L are the fugacity coefficients of component i in the vapour and liquid phase respectively), and using an equation of state for both the liquid and vapour phase, has several advantages. One needs not to specify the standard state fugacity of component i, f_i^o; continuity at the critical point is guaranteed, and all needed thermodynamic properties may be derived from the same model.

Generally speaking:

1. Equations of state may be used to represent the vapour phase but these are not predictive in nature.
2. At high pressures, vapour-liquid equilibrium are usually modelled using equations of state.
3. Excellent prediction results for hydrocarbon systems may be obtained using cubic equations of state with quadratic mixing rules. These mixing rules are empirical in nature. While vapour-liquid equilibrium data for systems containing non-hydrocarbon components can not be predicted using common equations of state (e.g. cubic equation of state). Hence, successful extensions of the Soave Redlich-Kwong equation to mixtures with polar components necessitated the development of new mixing rules (the Vidal (1978) Non Quadratic Mixing Rules).
4. A combination of the Soave Redlich-Kwong equation with chemical theory (Baumgärtner et al. (1979)), has proved successful.

In practice, for many types of mixtures containing for example strong polar, complex or polymer molecules, it is not yet possible to calculate a liquid-phase fugacity by means of an equation of state. Instead, activity coefficients models are used.

We now consider the various group contribution approaches.

3.4 The Group-Contribution Approach

The group-contribution approach is based on the solution-of-groups concept which has been successful for estimating a variety of pure-component properties such as liquid densities and heat capacities. The basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups which constitute these compounds is much smaller. Therefore, the liquid mixture is considered to be a solution of structural groups like CH_3, OH, and others which when added form the parent molecules. The properties of the mixture are then calculated from the properties of the groups rather than from the properties of the molecules.

Estimation of group contributions was first suggested by Langmuir (1925) who stated that physical (Van der Waals) interactions between polyfunctional molecules may be estimated by summing interactions between the functional groups that constitute the molecules. He also stated that if it was possible to characterise quantitatively the physical interactions between such groups, it should be possible to estimate inter-molecular interactions and finally, with a suitable model, to estimate thermodynamic properties; in particular, activity coefficients. Redlich et al. (1959) and Derr and Papadopoulos (1959) used this concept to correlate heats of mixing. Wilson and Deal (1962) developed the solution of groups method for activity coefficients. This work was expanded by Derr et al. (1969) with the analytical solution of groups (ASOG) method and by Ronc and Ratcliff (1971). The success of this work together with the introduction of the local composition concept by Wilson (1964), the NRTL model due to Renon and Prausnitz (1968), and the UNIQUAC model due to Abrams and Prausnitz (1975), encouraged Fredenslund et al. (1975) to combine the solution of functional groups concept with the molecular activity coefficients to give the UNIFAC model.

3.4.1 The UNIQUAC Equation

When non-electrolyte liquids are mixed at constant temperatures and pressures remote from critical conditions, there is little volume change. Scatchard (1937) has shown that even small volume changes could have a significant effect on the entropy of mixing and

on the enthalpy of mixing but to a good approximation, these effects tend to cancel in the excess Gibbs energy. Therefore, when attention is restricted to mixtures of non-electrolyte liquids at low or moderate pressure, the excess Helmholtz energy of mixing at constant temperature and volume can be substituted for the excess Gibbs energy of mixing at constant temperature and pressure (Hildebrand and Scott (1949)). This substitution was the basis for the theory of Guggenheim's Quasichemical Lattice Model (Guggenheim, 1952) which in its original form was restricted to small molecules of the same size.

In the work of Abrams and Prausnitz (1975) to develop the UNIQUAC model, they succeeded in extending Guggenheim's model to mixtures of different size and shape by utilising the local-composition concept introduced by Wilson (1964). The UNIQUAC model gives the excess Gibbs energies of multi-component liquid mixtures of non-electrolytes. This model, using only two adjustable parameters per binary, gives good representation of vapour-liquid and liquid-liquid equilibria for a wide variety of mixtures. The utility of this model follows from its semi-theoretical basis which gives consideration to molecular size and shape through structural parameters and to deviations from random mixing through application of the local composition concept.

The UNIQUAC model contains a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interaction between the molecules in the mixture.

3.4.2 The UNIFAC Model

The UNIFAC (UNIQUAC function group activity coefficients) group-contribution method is a reliable and fast method for predicting liquid-phase activity coefficients in non-electrolyte non-polymeric mixtures at low to moderate pressures in the range 1-10 bar and temperatures between 300 and 425 K. In UNIFAC as well as in ASOG, the excess Gibbs free energy of a solution is assumed to be the sum of two contributions - one associated with the differences in molecular size and shape and the other with energetic interactions between the group. As a consequence of this assumption, the logarithm of the activity coefficiencies, γ_i may be written as :

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$$

where γ_i^C is the combinatorial or size or entropy part, and γ_i^R is the residual or interaction or enthalpy part.

The method incorporates a number of parameters, as set out below.

1. Group volume parameters, R_k and group surface area parameters, Q_k. These are obtained from the Van der Waals group volumes and surface areas V_{wk} and A_{wk} given by Bondi (1968):
   $R_k = V_{wk} / 15.17$ and $Q_k = A_{wk} / 2.5 \times 10^9$,
   while the normalisation factors 15.17 and 2.5×10^9 are those given by Abrams and Prausnitz (1975).

2. The group interaction parameters a_{mn} and a_{nm} between groups m and n. These must be evaluated from the reduction of thermodynamically consistent vapour-liquid equilibrium data through the application of one of the minimisation methods. In practice, only binary vapour-liquid equilibrium (VLE) and to some extent activity coefficients at infinite dilution γ_∞ were used for determining these interaction parameters. The possibility of using γ_∞ from gas-liquid chromatographic (GLC) data has been investigated by Rizzi and Huber (1981), Alessi et al. (1982a,b,c), and Bastos et al. (1985). Information referring to activity coefficients at infinite dilution (γ_∞) of solutes in potential solvents for extractive distillation processes was collected and a computerised data bank was established by Bastos et al. (1985). They concluded that the use of UNIFAC and vapour-liquid equilibrium Group Interaction Parameters was still the best approach in solvent selection. Novotnã et al. (1986) presented ebulliometrically determined infinite-dilution activity coefficients in some systems to fill some gaps or blanks in the UNIFAC vapour-liquid equilibrium-group interaction parameter matrix. Weidlich et al. (1985, 1986) showed that headspace gas chromatographic analysis was suitable for measuring vapour-liquid equilibrium data in particular for the study of mixtures whose components can chemically react either with themselves or with other compounds present in the mixture. They used this technique to enlarge the data basis for the fitting of new interaction parameters for the UNIFAC method.

<u>UNIFAC Equations (Fredenslund et al., 1975)</u>

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$$

$$\ln\gamma_i^C = (\ln\varphi_i / x_i + 1 - \varphi_i / x_i) - \frac{1}{2} Z q_i (\ln\varphi_i / \Theta_i + 1 - \varphi_i / \Theta_i)$$

$$\varphi_i = x_i r_i / \sum_j x_j r_j \qquad \Theta_i = x_i q_i / \sum_j x_j q_j$$

(Here summation is over all components.)

$$r_i = \sum_k \nu_{ki} R_k \qquad q_i = \sum_k \nu_{ki} Q_k$$

(Here summation is over all groups.)

R_k = volume parameter for group k

Q_k = surface area parameter for group k

ν_{ki} = number of groups of type k in molecule i

x_i = liquid mole fraction of component i

Z = co-ordination number = 10

$$\ln\gamma_i^R = \sum_k \nu_{ki}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right)$$

(Here summation is over all groups.)

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk}\right) - \sum_m \left(\Theta_m \Psi_{km} / \sum_n \Theta_n \Psi_{nm}\right)\right]$$

$$\Psi_{nm} = \exp(-a_{nm}/T)$$

$$\Theta_m = Q_m X_m / \sum_n Q_n X_n$$

$$x_m = \frac{\sum_j \nu_{mj} x_j}{\sum_j \sum_n \nu_{nj} x_j}$$

a_{mn} = group interaction parameter for the interaction between groups m and n.

As previously mentioned, the UNIFAC method was originally developed by Fredenslund et al. (1975). Later this was revised and its range of applicability extended. The establishment of the vapour-liquid equilibrium Data Bank at the University of Dortmund in 1976/1977 and the updating of this data bank allowed these revisions and extensions to be carried out. These were done by Fredenslund et al. (1977 a,b) Skjold-Jorgensen et al. (1979); Gmehling et al. (1982); and Macedo et al. (1983). Further, but small extensions, were done by Macedo et al. (1984); Weidlich et al. (1985, 1986); and Novotnã et al. (1986). According to Fredenslund and Rasmussen (1986), a new revision and extension of the UNIFAC-vapour-liquid equilibrium group interaction parameter matrix was under preparation. The UNIFAC method, at present, handles 43 main functional groups. Of the 903 possible pairs of groups interaction parameters, 417 have been estimated in the temperature range 300 to 425 K for non-electrolyte systems. Only binary vapour-liquid equilibrium data and to some extent activity coefficients at infinite

dilution, $\gamma\infty$, data were used for determining these interaction parameters. At this point, it is important to review the revisions and extensions mentioned.

(i) Fredenslund et al. (1975)

In the work of Fredensleund et al. (1975), 18 functional groups were considered. The functional group volumes and surface area parameters were given as well as the group interaction parameters. They used a non-linear, least squares data reduction scheme.

(ii) Fredenslund et al. (1977 a,b)

Here, the same group (Fredenslund et al., 1977 (a,b)) presented a revised table of group-interaction parameters based on a large vapour-liquid equilibrium database for roughly 2500 binary systems chosen from a data set of more than 4000 binary systems stored on magnetic tape and collected at the University of Dortmund, Gmehling and Onken (1977) (see above). The number of the main functional groups considered was 25. Here, the Ketone, Ester, Ether, Secondary Amines and Alcohol groups were redefined by the addition of another methylene group. Furthermore, organic acids, secondary alcohols, methanol, additional chlorinated hydrocarbons, carbon disulphide, and compounds with the nitro group were considered. In their reduction of the vapour-liquid equilibrium data, the Nelder-Mead Search Method due to Nelder and Mead (1965) was used.

(iii) Skjold-Jorgensen et al. (1979)

Skjold-Jorgensen et al. (1979) revised and extended the UNIFAC Group-interaction parameter table by including experimental vapour-liquid equilibrium data published upto the middle of 1978 and collected at the University of Dortmund. The number of the main functional groups considered was 34. As a result of this work, some of the not available parameters have been eliminated, while new groups have been added, some parameters have been revised based on experimental data too. Of great importance, a new alcohol group has been empirically defined. This is the (OH) Group which was found to be much more flexible than the old one (CCOH). This improvement was achieved through the optimisation of the group volume and surface area for the alcohol group. This new group is not able to distinguish between isomers.

(iv) Gmehling et al. (1982a)

In the work of Gmehling et al. (1982a) the number of the main functional groups considered was 40 introducing seven new groups not previously covered by UNIFAC. The old alcohol group was dropped in favour of the new group OH. Dimethyl sulfoxide, acrylonitrile, trichloroethylene, and dimethyformamide were included, each as one separate group. Most of the group interaction parameters presented in this work were

estimated using the Nelder-Mead Search Method and some of the group-interaction parameters were estimated using a parameter estimation programme based on the principle of maximum likelihood and described by Skjold-Jorgensen (1980).

(v) Revision and extension due to Macedo et al. (1983).

A revision and extension due to Macedo et al. (1983) presented new UNIFAC parameters for interaction with ClC and ClCC Groups. They recommend that these parameters replace the parameters given by Gmehling et al. (1982). They also presented parameters for a flexible Ester Group (COO) and recommended the use of such a group only when it is not possible to use the CCOO Group.

Further small extensions were presented by Herskowitz and Gottlieb (1981); Macedo et al. (1984); Wedlich et al. (1985, 1986); and Novotnã et al. (1986). Herskowitz and Gottlieb (1981) presented two new main functional groups, SiO and SiH_2. Macedo et al. (1984) presented new UNIFAC interaction parameters between the groups ACH/HCOO, $ACCH_2$/HCOO and CH_2CO/HCOO. Their experimental binary (VLE) data were reduced by means of a maximum likelihood procedure. Wedlich et al. (1985, 1986), through the use of headspace gas chromatographic analysis, presented new UNIFAC interaction parameters between the groups CIC/CHO, ACH/CHO and $ACCH_2$/CHO. Novotnã et al. (1986) presented new UNIFAC interaction parameters between the groups Br/CCN and Br/CCl_3 through the reduction of ebulliometrically determined infinite-dilution activity coefficients data for some binary mixtures.

Gmehling et al. (1986) extended their database to include excess enthalpies of mixing H^E, activity coefficients at infinite dilution, γ_∞ as well as vapour-liquid equilibrium data for fitting the required group interaction parameters. They state that the present parameter matrix of their modified UNIFAC Model (Gmehling et al., 1986) will be extended using the total information in the Dortmund data bank.

3.4.3 An Evaluation of the UNIFAC Method

In evaluating the UNIFAC method we note the following:

(1) Kehiaian (1983) states, "The many revisions and extensions proposed, for the UNIFAC Method, were all empirical, but the effort appears to be worthwhile". This is true, since the UNIFAC Group contribution method is based on the Local Composition Concept. Therefore, this method is somewhat empirical in nature, and can be improved. The effort is certainly worthwhile, bearing in

mind that these revisions and extensions reported in this work, succeeded in increasing the range of the applicability, flexibility, and accuracy of the UNIFAC method.

It is also worth mentioning the fact that without the continuous updating of the Dortmund data bank, DDB, and in particular, the extensive reliable vapour-liquid equilibrium data, such revisions and extensions would not have been possible. Again, many more reliable experimental (VLE) data are still needed not only to fill the gaps in the UNIFAC vapour-liquid equilibrium group interaction parameter matrix and to revise further this matrix, but also to include more main functional groups in this parameter matrix. The UNIFAC method remains the most established group contribution method.

(2) The concept of a solution of groups is the basic assumption in the group-contribution approach for the prediction of activity coefficients. It implies that the functional groups which add together to form the molecules in the mixture, are independent from one another and thus do not know which were their neighbouring groups in the parent molecules. In effect:

i. The group contribution models, UNIFAC included, are still unable to distinguish between details in the molecular structures as in isomers, for example, xylenes.

ii. Kehiaian (1979, 1983) pointed out the fact that the new group contribution methods (UNIFAC among them) should attempt to handle the so called "proximity effect" which is the presence of strong functional groups on neighbouring carbon atoms. Due to this effect, Skjold-Jorgensen et al. (1979) could not predict the properties of mixtures with glycols using 2-alcohol-OH groups. As a result it was necessary to introduce a special glycol group.

(3) As far as non-electrolyte systems are concerned activity coefficients are normally used to describe phase equilibria at low to moderate pressures in the range 1 to 10 bar. This itself is a limitation which is important in any attempt to extend the UNIFAC Model to higher pressures up to 35 bar. This limitation is due basically to the lack of a general and reliable method for predicting vapour-phase fugacity coefficients at pressures above, say, 10 bar. This will be discussed further when we report the work of Gupte and Daubert (1986) on the extension of UNIFAC to higher pressures and illustrates the need for reliable experimental methods for routine determinations upto 35 bar.

(4) The lack of flexibility in the UNIFAC functional expression can be set out as follows:

i. Separate group interaction parameter tables have had to be developed for vapour-liquid and liquid-liquid equilibrium data calculations, (Magnussen et al., 1981).

ii. The group-interaction parameter table have been estimated from the available experimental vapour-liquid equilibrium data. As a result, predictions of liquid-liquid equilibrium and excess heat of mixing data based on these parameters are qualitatively reasonable but a quantitative and simultaneous representation of both vapour-liquid equilibrium data and liquid-liquid equilibrium data from the same parameters was not feasible, Fredenslund et al. (1977 a,b) and Skjold-Jorgensen et al. (1982).

iii. The original UNIFAC Model (Fredenslund et al., 1975) uses temperature independent group-interaction parameters. This limits the temperature range in which UNIFAC may be applied and hinders simultaneous, and accurate predictions of vapour-liquid equilibrium data and H^E data extensively.

We will deal with the lack of flexibility of the UNIFAC functional expression when we report and discuss the various attempts to overcome such limitations, Skjold-Jorgensen et al. (1980); Kikic et al. (1980); Skjold-Jorgensen et al. (1982); Jensen (1984); Aim et al. (1984); Larsen (1985) and Gmehling and Weidlich (1986), resulting in the following models:

a. The SUPERFAC model - Jensen (1984)

b. The modified UNIFAC - Larsen (1985)

c. The modified UNIFAC model due to Gmehling and Weidlich (1986).

3.4.4 Uses of UNIFAC

We may set out the uses of UNIFAC as below:

1. Application of UNIFAC to vapour-liquid equilibria, (Fredenslund et al., 1975)
2. Application of UNIFAC to liquid-liquid equilibria, (Magnussen et al., 1981)
3. Application of UNIFAC to solid-liquid equilibria, (Gmehling and Herskowitz., 1978)
4. Estimation of solvent effects on chemical reaction rates, (Lo and Paulaitis., 1981)

5. Estimation of flash points of flammable liquid mixtures, (Gmehling et al., 1982b)
6. Choosing of solvents for extraction purposes, (Tegtmeier and Misselhorn., 1981)
7. Representation of petroleum fractions, (Ruzicka et al., 1983)
8. Description of phase equilibria of polymer solutions, (Gottlieb and Herskowitz., 1981)
9. Calculation of gas solubilities in pure and mixed solvents, (Sander et al., 1983)
10. Prediction of pure component vapour pressures, (Jensen et al., 1981) and prediction of heats of vaporisation, (Yair and Fredenslund, 1983)
11. Prediction of retention data, Weidlich (1985). This is useful for selecting stationary phases for separation problems using gas-chromatography.
12. The prediction of Henrys' constants in single solvents, (Antunes and Tassios, 1983)
13. Prediction of excess enthalpies of mixing, Rupp et al. (1984); Stathis and Tassios (1985); and Dang and Tassios (1986).
14. Prediction of the binary parameters of a cubic equation of state, Schwartzentruper et al. (1986).

On the temperature dependence of the interaction energy parameters, Kehiaian (1983) clearly states that:

(1) A perfect statistical model should be able to express the free energy and the functions derived there from in terms of temperature-independent interaction ASOG, UNIFAC, which are models based on the local composition concept, and Nitta et al. (1977); Kehiaian (1977, 1979) models based on Guggenheim's quasichemical approximation.

(2) The intermolecular interactions depend not only on the distances but also on the angles at which the molecules are orientated to each other, especially at the short distances encountered in liquids. Kehiaian (1983) also states that because of the physical and mathematical difficulties in operating with an exact expression of the configurational energy, the interaction parameters in his model are more or less temperature dependent.

3.4.5 The Temperature-Dependence of the UNIFAC Model

An improved temperature-dependence of UNIFAC may be introduced empirically in two different approaches:

I. One way is to assume that the co-ordination number, Z, depends on temperature, T. This was investigated by Skjold-Jorgensen et al. (1980).

II. The second approach is to assume that the group interaction parameters are temperature-dependent. This was investigated by Malanowski et al. (1989); Jensen (1984); Larsen (1985); Aim (1984); Fredenslund and Rasmussen (1985); and Gmehling et al. (1986).

The contribution of Skjold-Jorgensen et al. (1980) was directed towards the improvement of the UNIFAC model, and considered the temperature dependence of the coordination number.

A physically realistic model of the liquid state should allow simultaneous representation of the excess Gibbs energy and excess enthalpy of liquid mixtures. If the model is physically significant, then it should be possible to derive other types of thermodynamic information from the expression for the excess Gibbs energy, G^E. An expression for excess enthalpy, H^E, can immediately be obtained from any model for G^E,

$$H^E = -RT^2\left(\frac{\partial\left(G^E/RT\right)}{\partial T}\right)_{P,x} \qquad \text{or:} \qquad \frac{G^E}{T} = \frac{G_o^E}{T_c} - \int_{T_c}^{T} \frac{H^E}{T^2}\,.dT$$

Generally speaking, local composition models in their original forms fail to achieve this. This is true for the UNIQUAC/UNIFAC models, since the sets of interaction parameters used to represent the excess Gibbs energy, G^E for a specific mixture or system are, in many cases, not in close agreement with those used to represent the excess enthalpy, H^E. Therefore, these models lack the ability to describe physical reality. Here, Skjold-Jorgensen presented a modification of the UNIQUAC/UNIFAC models in which the co-ordination number, Z, which is the number of nearest neighbours in the lattice structure, was considered to be dependent on temperature.

This modification permitted cross-correlation of the excess enthalpy and Gibbs energy in mixtures of non-associating and non-solvating components to be achieved with accuracy. For such mixtures, Skjold-Jorgensen et al. (1980) obtained an empirical equation representing the variation of the co-ordination number, Z(T), by optimising this parameter over a wide temperature range, using both vapour-liquid equilibrium and H^E data:

$$Z = 35.2 - 0.1272\,T + 0.00014\,T^2$$

limited to the following temperature range, $253 \leq T \leq 454$ K, which corresponds to $12 \geq Z \geq 6$, where ($Z = 12$) relates to close packing and corresponds to a temperature of 253 K and ($Z = 6$) relates to loose packing and corresponds to a temperature of 454 K. Therefore this equation should be applied strictly to a mixture that solidifies at 253 K.

This modified UNIFAC model contains the same number of adjustable parameters as the original UNIFAC of Fredenslund et al. (1975), i.e., two interaction parameters for each pair of groups.

According to Skjold-Jorgensen et al. (1980):

(1) The temperature extrapolation of (VLE) information over wide temperature ranges (318.5 - 413.5 K) has been improved considerably by means of the general temperature dependent co-ordination number.

(2) The prediction of excess enthalpies from information from experimental H^E data was possible by means of the modified models. Such an attempt leads to very poor results with the original local composition models with and without the introduction of temperature dependent parameters.

(3) The prediction of excess enthalpies from information for only one isothermal set of vapour-liquid equilibrium data was possible.

Edulijee (1932) has shown that this empirical equation of Skjold-Jorgensen et al. (1980) corresponds closely to predictions based on Fürth's (1964) mathematical treatment of Bernal's (1964) model for the liquid state. This provides a theoretical basis for the Skjold-Jorgensen equation. The essential feature of Bernal's model, briefly, is that liquids are "Homogeneous, coherent and essentially irregular assemblages of molecules containing no crystalline regions nor, in their low temperature form, holes large enough to admit another molecule". According to Vera and Vidal (1984), this proposal of Skjold-Jorgensen et al. (1980) has not been included in more recent modifications of the UNIFAC method, see Jensen et al. (1982).

At this point, it is relevant to report the work of Rupp et al. (1984); Stathis and Tassios (1985) and Dang and Tassios (1986).

Rupp et al. (1984) compared three contribution models in the correlation and prediction of enthalpies of mixing;

(1) The analytical group solution model, (AGSM) of Derr and Deal (1969) adapted for enthalpies of mixing by Ratcliff et al. (1974);

(2) The original UNIFAC model of Fredenslund et al. (1975); and

(3) The modified UNIFAC model due to Skjold-Jorgensen et al. (1980).

Rupp et al. (1984) concluded that the modified UNIFAC model of Skjold-Jorgensen provided the best correlation and prediction results. They also presented values for 19 pairs of primary (CH_2/G) interaction parameters where G represents a functional group. For systems with no strong hydrogen bonding, and in the temperature range of 0 - 100°C, the typical correlation and prediction results were within 5 - 15%.

For systems containing alcohols, Stathis and Tassios (1985) proposed a UNIFAC association model by including a "chemical contribution" term that accounts for the alcohol polymerisation. Typical errors for such systems were in the range 5-15%.

In their study, Dang and Tassios (1984) used the Gibbs-Helmholtz equation:

$$\frac{\Delta H^m}{RT^2} = - \left(\frac{\partial (G^E / RT)}{\partial T} \right)_{P,x}$$

, ΔH^m : Enthalpy of mixing,

In conjunction with the UNIFAC model modified by Skjold-Jorgensen et al. (1980), they presented the interaction parameters matrix for 136 new group pairs and included those values of Rupp et al. (1984) and Stathis and Tassios (1985).

The interaction parameter table includes 172 pairs. Water was not included because it needed to have both association and solvation effects accounted for.

Dang and Tassios (1986) claim that correlation results were very good with errors less than 10% and that prediction results were also very good with errors below 15% in most cases.

The following two points may be made about work of Dang and Tassios (1986):

(1) They state that the original UNIFAC model of Fredenslund et al. (1975) used temperature-dependent interaction parameters. This is simply untrue, since it is well known that this model used temperature-independent interaction parameters.

(2) Relevant to the above point, it would have been more beneficial if they applied the modified UNIFAC of Larsen (1985) not only for the purpose of comparison but also for the establishment of the group interaction parameter matrix. Doing so would be of interest, since the work of Larsen (1985) was the outcome of

extensive work by Kikic et al. (1980); Skjold-Jorgensen et al. (1982); Jensen (1984); Aim et al. (1984) and Larsen (1985).

The introduction of temperature-dependent group-interaction parameters is the second way to improve empirically the temperature dependence of the UNIQUAC/UNIFAC parameters. This is vitally important bearing in mind:

(1) The UNIFAC model was considered for the prediction of enthalpies of mixing by Fredenslund et al. (1977b). They concluded that the use of temperature-independent parameters failed to provide predictions of heats of mixing.

(2) The temperature-dependent co-ordination number, Z, approach of Skjold-Jorgensen et al. (1980) is quite good but limited to mixtures of non-associating components and not applicable to all temperatures.

Several investigators like Messow et al. (1977); Dohnal et al. (1979); Nagata and Ohta (1978) and others introduced temperature-dependent interaction parameters in local composition models in order to represent the temperature dependence of the G^E function correctly. Forms of temperature dependency were presented, such as:

$$a_{nm} = A_{nm} + B_{nm} \cdot T$$

or:

$$a_{nm} = A_{nm} + B_{nm} / T$$

These increased the flexibility of the model. The empirical constants, A_{nm} and B_{nm} need to be determined by a fit of data over a temperature range. The second equation was found to be better when wide temperature ranges were used.

Further investigations on the temperature dependency of the UNIFAC group interaction parameters will be reported and discussed when dealing with the SUPERFAC Model (Jensen, 1984); the modified UNIFAC Model (Larsen, 1985) and the newly modified UNIFAC Model (Gmehling et al., 1986).

The original UNIQUAC Model of Abrams and Prausnitz (1975) and the original UNIFAC (Fredenslund et al., 1975) which uses the UNIQUAC Model for the representation of group activity coefficients were not in general able to represent simultaneously vapour-liquid and liquid-liquid equilibrium data with satisfactory results. For some highly non-ideal mixtures like tert-butanol (1) - water (2) at 1atm, the original UNIFAC with parameters from Skjold-Jorgensen et al. (1979) erroneously predicted a phase split for this mixture.

For mixtures such as ethanol (1) - heptane (2) and iso-propanol (1) - heptane (2) the original UNIQUAC was unable to represent well activity coefficient versus concentration curves. The deviation between the experimental and calculated activity coefficients were quite large and systematic.

When vapour-liquid equilibrium and liquid-liquid equilibrium data for hexane(1) - methanol(2) at 298.15 K were correlated simultaneously the liquid-liquid equilibrium data were poorly represented when high priority was placed on the vapour-liquid equilibrium data and vice versa.

Skjold-Jorgensen et al. (1982) state that the above examples and others indicated the need for developing an improved model for describing the concentration dependence of the group activity coefficient in UNIFAC. Work was done in this direction and one can present such work carried out with two modifications:

(1) The chemical theory was used to take into account association and solvation effects. This work was done by Nagata and Kawamura (1977).

(2) The second approach was based on the assumption of concentration dependent interaction energies. Solvation-like effects and association-like effects were taken into account. The findings of this work, as we shall see later, were taken up by Jensen (1984) and Aim et al. (1984).

Nagata and Kawamura (1977) combined the chemical theory of Mecke (1948) and Kretschmer and Weibe (1954) with the UNIQUAC model of Abrams and Prausnitz (1975) to represent binary vapour-liquid equilibrium data for different alkane-alcohol systems, but applied the chemical theory only to the combinatorial part of UNIQUAC.

For binary systems, the resulting model has three parameters, the equilibrium constant, K, is assumed to be independent of the degree of association and two interaction parameters. Association of alcohol takes place according to:

$$A_n + A_1 \Leftrightarrow A_{n+1}$$

According to Skjold-Jorgensen et al. (1982), in some cases only marginal improvements compared with the original UNIQUAC model were achieved. Also, the range of values of the equilibrium constant K where there was an improvement may be rather small.

The chemical theory is only applied to the combinatorial part of UNIQUAC. In the derivation of UNIQUAC, the combinatorial term arises as a high-temperature limit taking into account differences in size and shape only. Here, no association or solvation exists. This may make the combination of the chemical theory to the combinatorial part of the UNIQUAC inconsistent with the derivation of UNIQUAC.

Skjold-Jorgensen et al. (1982)

Skjold-Jorgensen et al. (1982) examined the normalisation problem in the UNIQUAC and UNIFAC models and shown that it was of substantial importance for the definition of functional groups. As far as the UNIQUAC model was concerned, they have shown the normalisation factors used for the molecular surface and molecular volume parameters, q_i and r_i, to be acceptable. They have also found that the normalisation factors used for the group surface area and volume parameters, Q_k and R_k, in the original UNIFAC model gave rise to some numerical problems and that, in general, it would be better to use double values of Q_k and R_k. This, for UNIFAC, would make the fits using the small functional groups like CO and OH of the same quality as the fits obtained by means of the old definition, i.e., CH_2CO and CH_2CH_2OH. This enhances the flexibility of the UNIFAC model.

Their main task in this work was to modify the UNIFAC model due to the shortcomings and limitations of the chemical theory approach. The modification was based on the assumption of concentration-dependent interaction energies. They also took into account association-like effects as well as solvation-like effects to improve the simultaneous correlation of the vapour-liquid equilibrium and liquid-liquid equilibrium data. They expressed the interaction energy between two like segments by:

$$U_{jj} = U^*_{jj} + \alpha_j \theta_j^E + \sum_{k \neq j} \beta_{kj} \theta_k$$

where the exponent E, based on experience, was chosen to have the value 0.25,

U_{jj}	The interaction energy between two like segments;
U^*_{jj}	A reference quantity
$\alpha_j \theta_j^E$	This term accounts for association effects for each segment,
$\sum_{k \neq j} \beta_{kj} \theta_k$	This term accounts for solvation effects between segment j and all neighbouring segments k.

On the other hand, the interaction energy between two unlike segments, U_{ij} was considered to be independent of concentration since the solvation effects have already been accounted for, once, in the expression for U_{jj} and U_{ii}

Skjold-Jorgensen et al. (1982) obtained a modified UNIQUAC model using the two-fluid theory by a derivation parallel to that of the original UNIQUAC model by Maurer and Prausnitz (1978). For the modification of UNIFAC the group activity coefficient, Γ_K was given by:

$$\ln \Gamma_K = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \theta_m \Psi_{km} / \sum_n \theta_n \Psi_{nm} \right]$$

$$+ \frac{1}{T} \left(\bar{U}_{kk} - \bar{U}^{(u)}_{kk} \right) + \frac{1}{Q_K} \Sigma ____ \theta_j \left(___ \right))$$

The modified UNIFAC model was tested on a data base containing binary vapour-liquid equilibrium data and liquid-liquid equilibrium data. The original UNIFAC method gave a poor simultaneous representation of liquid-liquid equilibrium and vapour-liquid equilibrium data. While the predictions of ternary liquid-liquid equilibrium systems by means of UNIFAC parameters based on binary vapour-liquid equilibrium and liquid-liquid equilibrium data gave qualitatively correct results with the modified method. They claim, that in some cases, the results were quantitatively acceptable too.

Their findings were taken up and followed up by the work of Jensen (1984) and Aim et al. (1984) in developing the SUPERFAC model.

The establishment of vapour-liquid equilibrium, liquid-liquid equilibrium and H^E data bank has allowed Kikic et al. (1980) to evaluate various expressions for the combinatorial term.

For alkane-alkane mixtures, the residual contribution may be expected to be zero. For such mixtures, the evaluation of the combinatorial contribution is of great importance when evaluating the molecular activity coefficients using UNIQUAC and the group activity coefficients using UNIFAC. UNIFAC uses the same combinatorial expression as the UNIQUAC model. This combinatorial contribution is due to the size and shape differences between molecules and consists of two terms; the Flory-Huggins term

$$\ln \gamma_i^{FH} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}$$

and the Stavermann-Guggenheim term,

$$\ln \gamma_i^{SG} = -\frac{1}{2} Zq_i \left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{x_i} \right]$$

where:

ϕ_i is the volume fraction, $= \dfrac{r_i x_i}{\sum_j r_j x_j}$ and θ_i is the area fraction $= \dfrac{x_i q_i}{\sum_j x_j q_j}$

Kikic et al. (1980) proposed to use the following two modifications in the Flory-Huggins term, replacing the volume fraction ϕ_i with a modified volume fraction Φ_i

(1) $$\Psi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}}$$

With this modification, it is not possible to distinguish between isomers if the Van der Waals volumes r_i are calculated from the group volumes.

(2) $$\Psi_i = \frac{x_i v_i^{2/3}}{\sum_j x_j v_j^{2/3}}$$

This modification can distinguish between isomers but it requires the knowledge of the molar volume v_i.

This modification followed the approach of Donohoe and Prausnitz (1975). The exponent 2/3 was chosen on the basis of comparison with experimental results for a large number of mixtures of aliphatic hydrocarbons. Kikic et al. (1980) have shown that the use of the first modification was specially advantageous for the representation of infinite-dilution activity coefficients. In fact, Alessi et al. (1982b) concluded that it was possible to obtain reliable group-interaction parameters from infinite-dilution activity coefficients data alone when the Kikic et al. (1980) modification of UNIFAC was used.

The finding of Kikic et al. (1980) were used in developing the SUPERFAC model (Jensen, 1984); Aim et al. (1984) and the modified UNIFAC model due to Larsen (1985). Also, Gmehling et al. (1986) used a similar modification except the fact that 3/4 was used instead of Kikic's 2/3 term.

3.4.6 The SUPERFAC Model

The model-changes evolving from the findings of Kikic et al. (1980); Skjold-Jorgensen et al. (1980, 1982) and the extensive research work at the Technical University of Denmark, by Jensen (1984) and Aim et al. (1984), have resulted in a new model termed SUPERFAC.

This model represents the extensive work in dealing with the implications of the lack of flexibility of the UNIFAC functional expression. For example, separate group-interaction parameters tables had to be developed for vapour-liquid equilibrium and liquid-liquid equilibrium calculations (correlation and prediction). This was the case with Skjold-Jorgensen et al. (1982). Also the use of temperature-independent interaction parameters limits the temperature range in which UNIFAC may be applied and hinders simultaneous and accurate predictions of vapour-liquid equilibrium data and H^E data .

The following modifications were used:

(1) The Kikic et al. (1980) modification of the combinatorial term of the activity coefficient.

(2) The use of concentration dependent interaction parameters to improve the simultaneous correlation of vapour-liquid equilibrium and liquid-liquid equilibrium data. This was possible through the use of the findings of Skjold-Jorgensen et al. (1982) on taking into account the association and solvation effects.

(3) To assume the group-interaction parameters, and the association and solvation parameters to be temperature dependent to correlate vapour-liquid equilibrium and H^E data.

Evaluation of this model led to the conclusion that the model was a good correlative model but a bad predictive model. This was the case when predicting for multi-component mixtures from binary mixtures data. For example, when non-zero values of the association and solvation parameters were used, the SUPERFAC model correlated simultaneously vapour-liquid equilibrium, H^E and liquid-liquid equilibrium data over a wide range of temperatures when six parameters were fitted to the data for the binary mixtures in question, while prediction was very bad when non-zero association and solvation parameters were used. In comparison, SUPERFAC was better than UNIFAC when predicting vapour-liquid equilibrium data and H^E data for systems with zero solvation and association parameters.

Fredenslund and Rasmussen (1985) reported that Jensen (1984) had found that the association parameter, a, for polar groups was dependent on the mixture under investigation. Therefore, this parameter could not be described on a group-contribution basis. Also, the solvation parameter ß, was found to give erratic prediction of multi-component systems from parameters based on binary data only. When r and q values not corresponding to physical reality were used, most notably for mixtures with water, the Stavermann-Guggenheim term was found to give limiting activity coefficients much larger than unity. This caused erratic multi-component predictions.

3.4.7 The Modified UNIFAC Model, Larsen (1985)

After the SUPERFAC model was tested, it was recommended that:

(1) the association and solvation parameters be dropped;

(2) the Stavermann-Guggenheim term be dropped.

These findings were used and more extensive work was carried out by Larsen (1985) which led to the following changes:

(a) The Stavermann-Guggenheim term was dropped from the combinatorial expression; while $r^{2/3}$ was used, i.e.

$$\ln \gamma_i^c = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i} \qquad \text{where } \omega_i = \frac{r_i^{2/3}\, x_i}{\sum_j x_j\, r_j^{2/3}}$$

(b) The group interaction parameters were assumed temperature dependent according to:

$$\alpha_{mk} = \alpha_{mk,1} + \alpha_{mk,2\,(T-T_o)} + \alpha_{mk,3}\left[T \ln\left(\frac{T_o}{T}\right) + T - T_o\right]$$

(m, k are groups m and k)

T_o : reference temperature (= 298.15 K),

$\alpha_{mk,1}$, $\alpha_{mk,2}$, $\alpha_{mk,3}$ are temperature coefficients.

Information about G^E as well as the first two temperature derivatives of G^E are required, to establish all three temperature coefficients. To achieve this, one of the following two approaches may be used:

I. The availability of G^E information at three different temperatures is enough. One should use very accurate and reliable vapour-liquid equilibrium data.

II. One can base the six adjustable parameters required for one binary group combination, on vapour-liquid equilibrium and H^E data measured at different temperatures. The first, second and third coefficients of the temperature function $\alpha_{mk,1}$, $\alpha_{mk,2}$, and $\alpha_{mk,3}$ are related to G^E, H^E, and C_p^E respectively. The term containing $\alpha_{mk,3}$, can be dropped if H^E data are only known at one temperature.

The outcomes were:

(1) The modified UNIFAC model gave slightly better vapour-liquid equilibrium predictions than UNIFAC.

(2) It gave better qualitative vapour-liquid equilibrium predictions than did UNIFAC.

(3) It predicted much better activity coefficients (at infinite-dilution) of alcohols in various solvents than with UNIFAC.

The equation set is given below:

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^R$$

$$\ln\gamma_i^c = \ln\omega_i / x_i + 1 - \omega_i / x_i$$

$$\omega_i = r_i^p x_i / \sum_j r_j^p x_j; \qquad p = 2/3$$

$$r_i = \sum_k \nu_k^{(i)} R_k$$

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)} \left[\ln\Gamma_k - \ln\Gamma_k^{(i)} \right]$$

$$\ln\Gamma_k = \frac{Z}{2} Q_k \left(1 - \ln\left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \left(\Theta_m \Psi_{km} / \left(\sum_n \Theta_n \Psi_{nm} \right) \right) \right)$$

$$\Theta_i = x_i q_i / \sum_j x_j q_j \qquad q_i = \sum_k \nu_k^{(i)} Q_k$$

$$R_k = V_{w,k} / \left(15.17 \text{cm}^3 / \text{mol} \right) \qquad \text{(as in UNIFAC).}$$

Indices i, j refer to components; k, m and n to groups.

Contrary to the UNIFAC model, the modified UNIFAC model needs no information about both the lattice co-ordination number Z and the group surface area Q_k, as they appear only as the product (Z/2 Q_k). The normalisation is chosen in such a way that

$$S_k \equiv Z/2\ Q_k = A_{w,k}/\ (25.10^9\ cm^2/\ mol)$$

This gives the same normalisation for S_k as used for Q_k in the UNIFAC model.

$$\Psi_{mk} = \exp(-a_{mk}\ /\ T)$$

The group-interaction parameters are unsymmetrical $(a_{mk} \ddagger a_{km})$ and temperature-dependent according to:

$$a_{mk} = a_{mk,1} + a_{mk,2}(T - T_0) + a_{mk,3}(T\ \ln(T_0\ /\ T) + T - T_0)$$

where the reference temperature T_0 is 2948.15 K.

Gmehling et al. (1986) carried out an investigation on alkane-alcohol systems through the use of a newly modified UNIFAC method. This new version of the UNIFAC correlation was used for predicting the behaviour of systems including alkanes, alkenes, aromatics, alcohols and ketones. The newly modified UNIFAC was established through the use of:

(1) A modification of the temperature-independent combinatorial part similar to that of Kikic et al. (1980) except the fact that the term 3/4 was used instead of Kikic's 2/3 term.

(2) Temperature-dependent interaction parameters to describe the residual part of the activity coefficient UNIFAC model, using the following equation: $u_{nm} = a_{nm} + b_{nm}T + c_{nm}T^2$, but no information on the parameters a_{nm} , b_{nm} and c_{nm} was given by them.

(3) An extended database which included vapour-liquid equilibrium, H^E and $\gamma\infty$ data for fitting the required group-interaction parameters. Data on mixtures with very large molecules were used in establishing the parameters.

(4) Slightly modified values for the relative Van der Waals volumes and surface areas were used.

They state that very good vapour-liquid equilibrium predictions were obtained for 16 different alkane-alcohol systems, and much better activity coefficients at infinite-dilution predictions were obtained for 16 different alkane-alcohol systems.

3.5 The Group-Contribution Equation-of-State Approach

This approach incorporates the advantage inherent in both the equation-of-state approach and the group contribution methods. To illustrate this approach the following group-contribution equations of state will be briefly discussed:

(1) The PFGC equation due to Cunningham (1974).

(2) The group contribution equation of state due to Skjold-Jorgensen (1984).

(3) The group contribution equation of state due to Gupte and Daubert (1986).

3.5.1 The PFGC Equation

The Parameters From Group Contribution (PFGC) equation was developed by Cunningham (1974) and Moshefeghian et al. (1979). It is based on empirical extensions of a local-composition model for the excess Gibbs function, G^E, by method of the hole theory. A description of the Helmholtz energy of a liquid lattice structure with holes can be set out as:

$$A^{PFGC} = A^{FH} + A^{W}$$

where A^{FH} is a Flory-Huggin contribution (entropy effect), and A^{W} is an intermolecular interaction term (enthalpy effect). It is assumed that all the expressions for the Helmholtz energy are analogous to expressions for the excess Gibbs energy. Hence, any activity coefficient expression may in principle be used for A^{W}, and Cunningham uses a modified Wilson equation to describe the interactions between the molecules themselves.

The PFGC equation contains three parameters per pure group i :

(i) The interaction between groups i, E_{ii} ;

(ii) The volume of one mole of groups i, b_i ;

(iii) A parameter proportional to the external degrees of freedom per group i, S_i; and for mixtures;

(iv) Interaction coefficient per binary, a_{ij}.

$$E_{ij} = \tfrac{1}{2} a_{ij}\left(E_{ii} + E_{jj}\right), \qquad \left(a_{ij} = a_{ji}\right)$$

The PFGC equation can simultaneously predict the thermodynamic properties of liquid and vapour phases. It does not satisfy the critical conditions and therefore, it should not be applied to the critical region, i.e. (T_r = reduced temperature > 0.95).

Cunningham applied successfully the PFGC equation to hydrocarbon systems over a wide range of pressures and with components ranging from C_1 to C_{32}. Vapour-liquid equilibrium data for mixtures with polar components were predicted with good results, for example hexane-methanol and decane-propionaldehyde. Moshefeghian et al. (1979) revised and extended the PFGC parameter table and carried out calculations for a large number of systems, including systems with large hydrocarbons and polar components.

3.5.2 The Group-Contribution Equation of State of Skjold-Jorgensen (1984)

The Skjold-Jorgensen equation of state (Skjold-Jorgensen, 1984) was developed for polar as well as non-polar components. This equation is based on the generalised Van der Waals partition function with mixing rules based on density-dependent mixing rules. The mixing rules chosen are based on an NRTL-like expression for A^E (Renon and Prausnitz, 1968).

This method requires the group compositions of the components and the critical pressure and temperature of the pure components. The critical pressure P_c and the critical temperature, T_c are chosen for the calculations of the hard-sphere diameter according to:

$$d_c = \left(0.08943\ R\ \frac{T_c}{P_c} \right)^{1/3}$$

when the critical compressibility factory, Z_c is equal to 0.358956.

Skjold-Jorgensen (1984) states that the hard-sphere diameter should be fitted to vapour pressure information whenever the critical point is somewhat inaccurate or when non-randomness plays an important role. He showed the overall presentation of water-alcohol mixtures to be fair and the GC-EOS to predict correctly liquid-phase immiscibility for isobutanol-water and total miscibility for ethanol-water. This GC-EOS covers wide ranges of temperature and pressures below ~ 25 MPa. In most cases, the accuracy of K-values lay within 15%. Larger errors were encountered for Henry constants in multi-component mixtures containing large amounts of water.

3.6 The Extension of UNIFAC to Higher Pressures

One of the important limitations of the group contribution method, UNIFAC, is that of the activity coefficient approach. Activity coefficients are normally used to predict vapour-liquid equilibrium data at low to moderate pressures in the range of 1 to about 10 bar. At higher pressures, the UNIFAC method is not applicable. The limitation here is

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lack of a general, consistent and reliable method for predicting vapour-phase non-alites.

ıpte and Daubert (1986) investigated this problem and succeeded in extending the NIFAC-vapour-liquid equilibrium method to higher pressures through the use of ɔthermal as well as isobaric vapour-liquid equilibrium data of polar and non-polar 'stems measured at pressures ranging from 7 to 67 bar. This extension was developed y incorporating the UNIFAC model of Fredenslund et al. (1975) in an equation-of-state :amework using the non-quadratic mixing rules due to Vidal (1978).

The equation of state used here was the PSU Soave equation. This equation was chosen ɔy Gupte and Daubert (1986) for its predictive nature through the acentric factor ω_i. The following equations represent their equation for pure fluids:

$$\left(P+\frac{a(T)}{v+(v+b)}\right)x(v-b)=RT$$

where a is the energy size parameter and b is the molecular size parameter. Here

$b_{ii}=\dfrac{0.08664\ RT_{ci}}{P_{ci}}$, where b_{ii} is the molecular size parameter, and

$$a_{ii}=0.42747\frac{R^2T_{ci}^2}{P_{ci}}\left[1+S_i\left(1-\sqrt{T_{rc}}\right)\right]^2$$

where a_{ii} is the energy size parameter, and $S_i = 0.48508 + 1.55171\ \omega_i - 0.15615\ \omega_i^2$.

3.6.1 The Use of the Non-Quadratic Mixing Rules due to Vidal (1978)

The non-quadratic mixing rules of Vidal (1978) were used with the group contribution method, UNIFAC, to improve the predictions for non-electrolyte mixtures.

Vidal (1978) had suggested the following mixing rules:

$$b=\sum_{i=1}^{n}x_ib_i$$

$$a=b\left[\sum_{i=1}^{n}\frac{x_ia_i}{b_i}-\frac{g_E^{\infty}}{\ln 2}\right]$$

where g_E^∞ is the excess free energy at infinite pressures. Gupte and Daubert (1986) obtained g_E^∞ using the UNIFAC model, since this model is predictive in nature, from:

$$g_E^\infty = RT\sum_i^n x_i \ln\gamma_i^{UNIFAC}$$

The Vidal mixing rules were applied to both liquid and vapour phases. For each phase, g_E^∞ was obtained from the UNIFAC-vapour-liquid equilibrium model using the respective phase compositions, here,

$$\ln \gamma_i^{UNIFAC} = \ln\gamma_i^c + \ln\gamma_i^R$$

γ_i^c and γ_i^R are the combinatorial and residual activity coefficients respectively. The combinatorial contribution, $\ln\gamma_i^c$ consists of two terms, the first is the Flory-Huggins term and the second is the Stavermann-Guggenheim term. As pointed out by Whiting et al. (1982), the Flory term already exists in an equation of state. The Stavermann-Guggenheim term can not be derived from an equation of state. This is because no relation is available between Z and the segment volume U_o (Mollerup, 1981). However, when evaluating their results, Gupte and Daubert (1986) considered both taking and not taking into account the combinatorial term in the above equation. They also considered the use of regular quadratic mixing rules and the non-quadratic mixing rules of Vidal (1978) to study the significance of such mixing rules when applied to the mixtures of interest. They also drew a comparison between their approach and the original UNIFAC model with the Hayden-O'Connell virial equation. This was important because systems of low pressure data were studied too.

When evaluating their results, they concluded that the quadratic mixing rules were useful when dealing with polar-polar systems which are nearly ideal. They also concluded that the best model was encountered when using the Vidal mixing rules with g_E^∞ obtained from the full UNIFAC-vapour-liquid equilibrium model.

Gupte and Daubert (1986) state that the development of a group contribution equation of state based on UNIFAC-density dependent-DDLC mixing rules was under development.

3.6.2 Discussion of the Gupte and Daubert (1986) Contribution

In evaluating the excess free energy at infinite pressures, g_E^∞, Gupte and Daubert used group interaction parameters based on vapour-liquid equilibrium data measured at or

near atmospheric pressure. This assumes that the excess free energy is independent of pressure. This assumption is inherent in the UNIFAC-vapour-liquid equilibrium model but one must obtain and use UNIFAC parameters from higher pressure vapour-liquid equilibrium data through the mixing rules of Vidal (1978) to obtain accurate evaluation of g_E^{∞}. This approach presents the most favourable way of utilising experimental data obtained at higher pressures.

Also the use of temperature dependent UNIFAC parameters will lead to more accurate predictions.

Chapter 4: Review of Experimental Methods for Vapour-Liquid Equilibria

4.1 Introduction

Despite many attempts in recent years to predict accurately vapour-liquid equilibrium data using various proposed models of phase behaviour, it is still not possible to achieve this using pure component property data alone. An accurate prediction of phase equilibrium data must therefore, at some stage, use experimental data for the evaluation of parameters in the appropriate models.

Experimental data can be obtained in many different ways, and can take the form of vapour and liquid phase compositions, pressure and temperature and sometimes heats of mixing. The most frequent forms of experimental data presented in the literature are either liquid and vapour phase compositions together with the equilibrium temperatures at the isobaric mixture pressure, or liquid and vapour phase compositions together with the equilibrium pressures at the isothermal mixture temperature, although recently total pressure methods have brought the presentation of isothermal pressures and liquid-phase compositions as experimental data sets, the vapour compositions being predicted through the Gibbs-Duhem relationship.

The design and construction of equilibrium stills can be a source of various errors, which need not have the same importance in all mixtures, since the errors which arise are to a certain extent also dependent on the nature of the mixture concerned (relative volatility, heat of vaporisation, etc.). So far, it has not been possible to construct a still which would yield thermodynamically completely consistent data for all mixtures.

The methods for the direct determination of equilibrium data can be classified into the following groups:

(i) Differential distillation methods
(ii) Circulation methods
(iii) Static methods
(iv) Total pressure methods
(v) Flow methods
(vi) Other methods

This discussion will include the most important and recent developments in determining vapour-liquid equilibrium data. More general reviews of the methods are available in

bbott (1986), Marsh (1978) and Malanowski (1982a&b). A review of the older :velopments can be found in Hala et al. (1967).

.2 Differential Distillation Methods

)ifferential distillation methods are the oldest method of direct experimental determination)f vapour-liquid equilibrium data. In this technique which has been used by Taylor (1900) ınd Rayleigh (1902), a small amount of liquid is distilled off from the boiling flask which :ontains a large amount of the mixture. This method is very simple but it has marked disadvantages in that it requires a large quantity of the mixture under consideration and permits the withdrawing of only a very small sample of condensate for analysis, since the composition of the liquid phase must remain essentially constant. Large errors can also be caused by condensation of vapour on the cold walls of the distillation flask at the beginning of the experiment. This method is now obsolete.

4.3 Circulation Methods

The circulation method has been the most widely used method. It is convenient to use at both medium and low pressures. Although the various equilibrium stills with simple circulation differ significantly from one another in their construction details, they are all based on a common principle. Vapours evolved from a boiling mixture in a distilling flask, when completely condensed, collect in a receiver. After filling the receiver, the condensate returns to the distilling flask. If the still is started with the receiver empty, at the instant when it first fills, its contents are richer in the more volatile constituent than is the vapour phase over the boiling mixture in the distilling flask. With further operation of the still, the contents of the distillation flask become richer in the more volatile component and the receiver becomes poorer. This process continues until the steady state is attained, in which the compositions in both vessels no longer change with time. Both compositions are determined analytically.

According to Malanowski (1982a), the following conditions, which are based on those formulated previously by Fowler (1948) and complemented by Hala et al. (1967), should be fulfilled by a properly designed recirculating still:

(1) The still should have a simple form.
(2) Small amounts of materials should be required for measurements.
(3) Facilities should be incorporated allowing accurate determinations of equilibrium pressure and temperature.

(4) A short time should be required to achieve steady-state operation after start or after any change of equilibrium parameters.

(5) Neither partial condensation of vapour on the temperature-measuring sensor nor overheating in the vicinity of the latter should occur.

(6) No liquid drops should appear in the vapour stream leaving the equilibrium chamber after separation from the liquid phase.

(7) The recirculated vapour or its condensate should be perfectly mixed with the liquid phase to obtain uniform composition and to prevent secondary evaporation during mixing.

(8) There should be no fluctuations of the recirculated streams' composition and flow.

(9) No pockets should be present allowing accumulation of substances outside the recirculation pathways of the apparatus.

(10) It should be possible to introduce and withdraw samples without interruption of steady-state boiling.

Circulation stills can be classified, according to the number of recirculated streams and their thermodynamic conditions, into the following groups:

(A) Vapour recirculation methods;

(B) Condensate recirculation methods:

  (i) Liquid condensate recirculation;

  (ii) Revaporised condensate recirculation;

(C) Recirculation of liquid phase and vapour condensate.

4.3.1 Vapour Recirculation Methods

The vapour recirculation method was first proposed by Inglis (1906) in an attempt to overcome the uncertainty in attaining the steady state in flow methods. The principle of the vapour recirculation method is illustrated in Figure 4.1. A pump (Pu) recirculates the vapour through the stationary liquid by way of a heat-interchange system (thermostat) until the steady state is attained. Then, the temperature, pressure and the compositions of the liquid and vapour phases are measured.

Although this technique appears simple, numerous complications are encountered in practical applications. In order to attain steady-state operation, the total volume, the system pressure and temperature must remain constant or the quantities, and consequently compositions, of the vapour and liquid phases will vary. However, pressure fluctuations are present in the system, caused by pumping of the vapour stream through the liquid

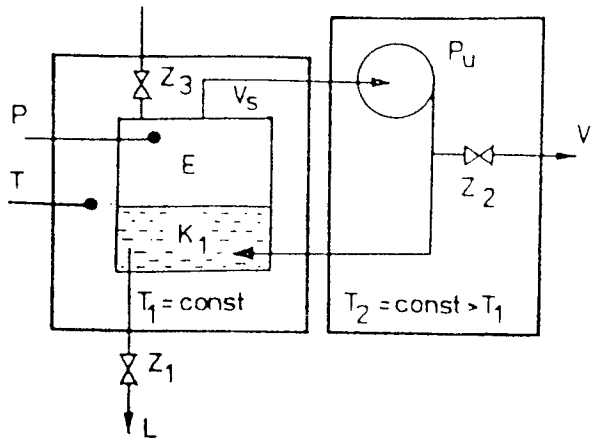


Figure 4.1 Principle of Operation of Vapour Recirculation Method: E, equilibrium chamber; K_1, liquid phase container; P, pressure gauge; P_u, vapour pump; T, thermometer; T_1, T_2, constant-temperature baths; V_s, vapour stream; Z_1, liquid phase (*L*) sampling valve; Z_2, vapour phase (*V*) sampling valve; Z_3, valve for still degassing.

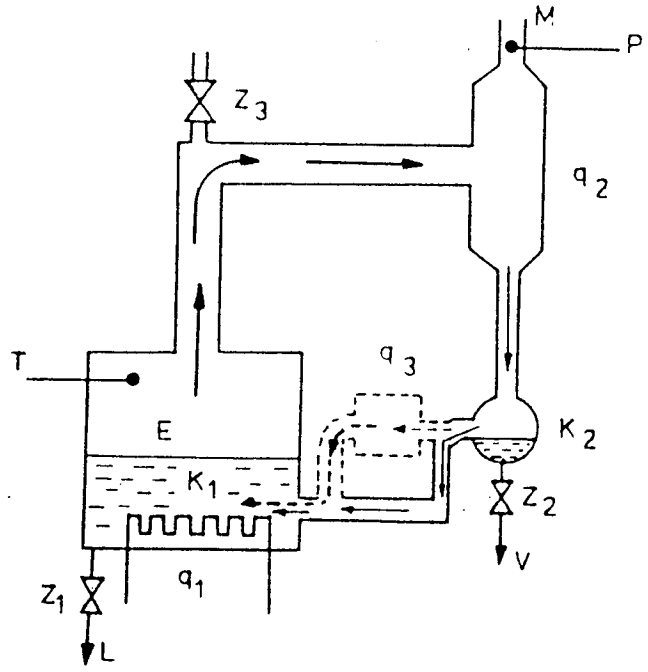


Figure 4.2 Principle of Operation of Vapour Condensate Recirculation Method; dotted lines denote the alternative flow of condensate in the case when it enters the equilibrium chamber as vapour: K_2, vapour condensate container; M, to pressure-stabilising system; q_1, heater for boiling liquid; q_2, cooler for condensing vapour; q_3, heater for flash vaporisation of condensate; other notation as in Figure 4.1.

lthough these can be minimised by perfecting the pump design. Lowering the vapour 'elocity decreases the pressure differences existing in the equilibrium cell due to the ıydrostatic head of liquid, and reduces the possibility of liquid entrainment in the vapour ;tream. The change of vapour phase composition due to this small pressure difference is generally not significant, although the error introduced may be large in the critical region when the vapour is very compressible. In order to minimise liquid entrainment, special separators can be placed in the vapour space of the still. Any condensation of vapour during recirculation must also be prevented. This may be accomplished by placing only the equilibrium chamber in the constant-temperature bath and maintaining the rest of the system at a temperature higher than the vapour dew-point. Isobaric conditions must be maintained during sampling, since vapour samples are removed without condensation, the quantity of sample removed may be too small for accurate analysis unless the operating pressure is high.

Owing to the above limitations, exact equilibrium conditions cannot be achieved by vapour phase circulation methods; however, influence of pressure and composition fluctuations can be neglected when the still is operated at pressures above 0.5 MPa. For pressures in the range 1-50 MPa, vapour phase recirculation methods are considered to be among the most accurate for obtaining vapour-liquid equilibrium data and are widely used especially at cryogenic temperatures. Numerous papers on the development and applications of the vapour phase recirculation method have been published since the method was first proposed. The most recent review was published by Eubank et al. (1980).

4.3.2 Condensate Recirculation Methods

In the condensate recirculation method, the vapour leaving the equilibrium chamber is condensed and the hydrostatic head of the condensate provides the required pressure differential. Two operational modes can be used. In the first, the vapour condensate re-enters the equilibrium chamber as liquid; in the second, the condensate is revaporised in a heater and re-enters the chamber as vapour. The principle of operation of all stills employing circulation of the vapour phase condensate is illustrated in Figure 4.2. The liquid sample in the equilibrium chamber E is boiling. Heat is delivered continuously by the heater q_1. Vapour is condensed in the cooler q_2 and returns to the equilibrium chamber via the condensate container K_2. The valve Z_3 is used for removing inert gases (air) from the still in the early stage of operation. The steady state is achieved after about 30 minutes, when the liquid and vapour in the chamber E are of equilibrium composition. The composition of the vapour is identical to that of the condensate in the container K_2. The

ıe necessary to achieve the steady state depends on the volume of condensate in the ntainer K_2.

ter the steady state has been achieved, boiling is stopped at once, for example by creasing the pressure in the stabilising system M, to prevent non-equilibrium distillation . the container K_2. Samples of the liquid and vapour condensate are withdrawn for ıalysis from the containers K_1 and K_2, through valves Z_1 and Z_2 respectively. After /ithdrawal of the samples, the still can be filled with a new sample and the entire rocedure repeated.

The main drawbacks of this method are:

(1) There is partial condensation of vapour after bringing the apparatus to standstill;
(2) Accurate determination of the equilibrium temperature is not possible;
(3) It is not possible to obtain uniform composition in container K_1.

4.3.2.1 Othmer Still and its Modifications

The first still with circulation of the condensate was proposed by Jamaguchi (1913) and Sameshima (1918), but the first equilibrium still which functioned satisfactorily was constructed by Othmer (1928) (Figure 4.3). Othmer, in an effort to remove some of the weaknesses of his still (see the main drawbacks of the condensate recirculation methods), proposed two further modifications, shown in Figures 4.4 and 4.5. The working procedure is the same and the modifications differ only in certain constructional details (Othmer, 1932, 1943 and 1948). By shortening and contracting the neck of the distillation flask, the heat losses and thus the possibility of partial condensation are diminished. The volume of the receiver was also decreased. For decreasing the period required for obtaining steady state, it is desirable to use a receiver of minimal volume, with due regard to the requirement of the analytical method employed. Othmer used both a micro-burner and an electrical heater for heating the liquid. The second method was shown to be more advantageous.

The special external heater shown in Figure 4.6 proved very successful. It is essentially a simple U-tube sealed to the bottom of the distillation flask, whose narrower arm is wound with a heating wire. Bubbles of vapour generated in this arm thoroughly mix the boiling liquid in the main flask. The small protruding tube o forces the inflow of condensate to the boiling flask to mix the bulk of the liquid and prevents its immediate penetration into the heated part of the instrument. Figure 4.7 shows the commonly used internal heating

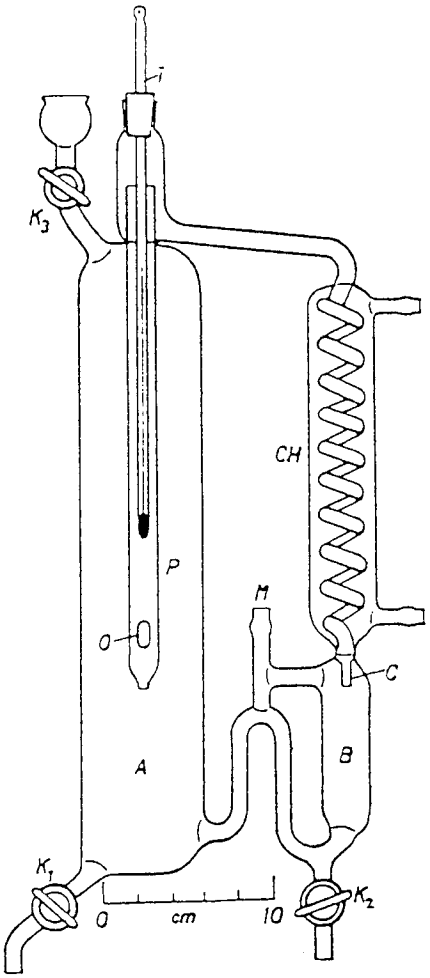


Figure 4.3 The Othmer (1928) Still.

A = boiling vessel; B = receiver; K_1, K_2 = sampling cocks; K_3 = vent cock; T = thermometer; CH = cooler; P = vapour tube; O = inlet; C = drop counter; M = to manostat.

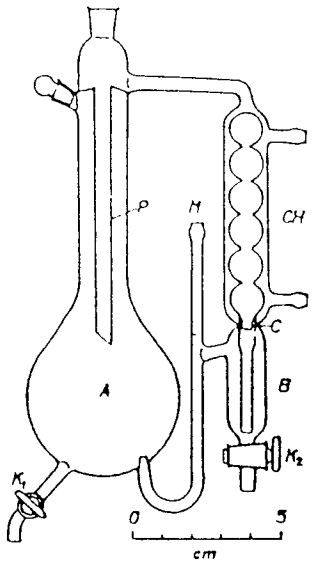


Figure 4.4 Modification of the Othmer (1928) Still, (I)

A = boiling flask; B = receiver; CH = cooler; P = vapour tube; C = drop counter; K_1, K_2 = cocks; M = to manostat.

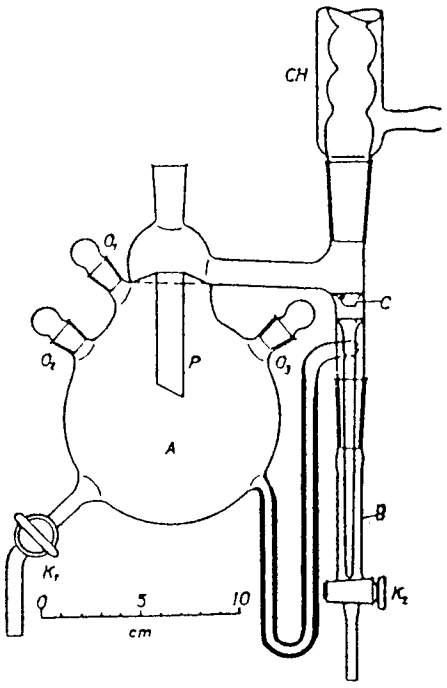


Figure 4.5 Modification of the Othmer (1928) Still, (II)

A = boiling flask; B = receiver; CH = cooler; C = drop counter; P = vapour tube; K_1, K_2 = cocks; O_1 = filling neck; O_2, O_3 = necks for internal heating.

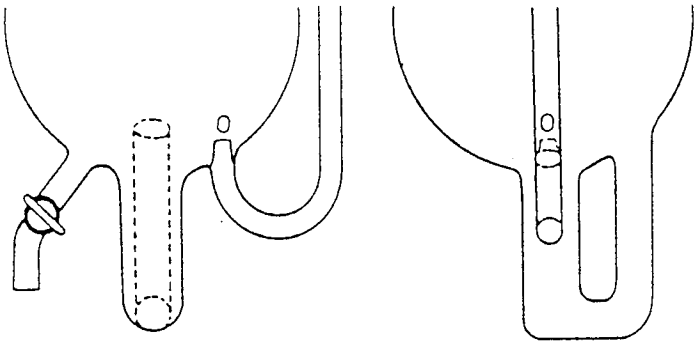


Figure 4.6 Boiling Flask Suitable for Use with External Electrical Heating (Othmer)

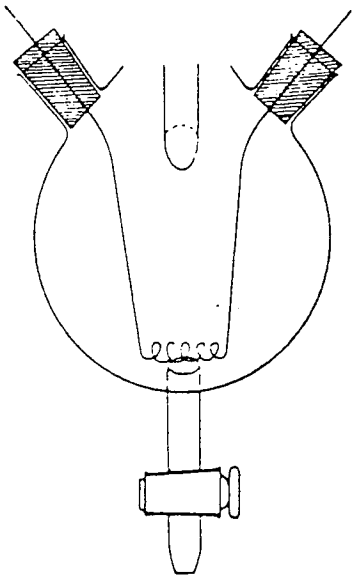


Figure 4.7 Internal Heater (Othmer)

system. The cooler of the still shown in Figure 4.5 was installed so that it returned hot condensate to the receiver, thus diminishing the possibility of dissolving gases (air) in the condensate. Since there is hot condensate in the receiver and it is desirable to return cold condensate to the boiling flask, Othmer recommended the addition of a small Liebig cooler to the return line.

Imprecise measurements of temperature remained, however, the chief drawback of these modifications. The instruments proposed by Othmer have been further improved by various authors. One of the most successful of these modifications is the Kortüm et al. (1953) depicted in Figure 4.8. The working procedure is very simple. The solution to be tested is poured into the boiling flask (the level of the liquid should reach just to the thermocouple T_1) and is brought to the boil by hot liquid which circulates in the glass jacket around the entire distillation flask. The temperature of the hot bath should be maintained at most 0.6°C above the boiling point of the solution. This measure is intended to eliminate all partial condensation and at the same time any superheating of the vapour phase. The vapour space is closed above with a ground stopper which carries the sampling capillary, the thermocouple leads and the heater leads. The internal heater (platinum winding) compensates for both the thermal losses and the losses arising from the continuous flow of cold condensate into the boiling flask and at the same time generates vapour bubbles, which also help to mix the boiling liquid thoroughly. The magnetic mixer serves to eliminate completely any remaining concentration gradients.

The vapour condensing in the cooler flows through a funnel fitted with an iron ring into the receiver whence it returns to the boiling flask. In order not to interrupt the circulation during sampling, the funnel can be swung to the side with an electromagnet so that the condensate flows directly into the boiling flask instead of into the receiver. This arrangement is especially suitable for checking the steady state. At given time intervals, it is possible to remove very small samples of distillate and to test whether its composition is still changing. The sampling opening shown in Figure 4.8 is used to remove the samples.

Bukala and Majeski (1952) adapted the Othmer still to produce a two-plate still, as shown in Figure 4.9. This still proved useful for mixtures having a low relative volatility. One recent modification of the Othmer still was proposed by Paul (1976) who used a silvered evacuated jacket on the upper part of the vessel to prevent heat losses and consequent partial condensation. He also used a thermosyphon reboiler to improve the mixing characteristics of the still.

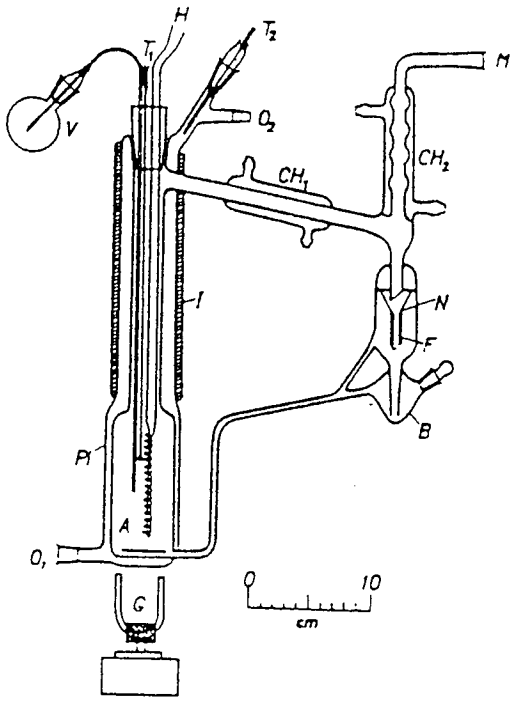


Figure 4.8 Kortüm Still

A = boiling flask; B = receiver; G = magnetic mixer; Pl = jacket; O_1, O_2 = inlet and outlet of heating liquid; V = liquid sampler; T_1, T_2 = thermocouples; H = internal heater; CH_1, CH_2 = coolers; N = movable funnel; F = iron ring; I = insulation; M = to manostat.

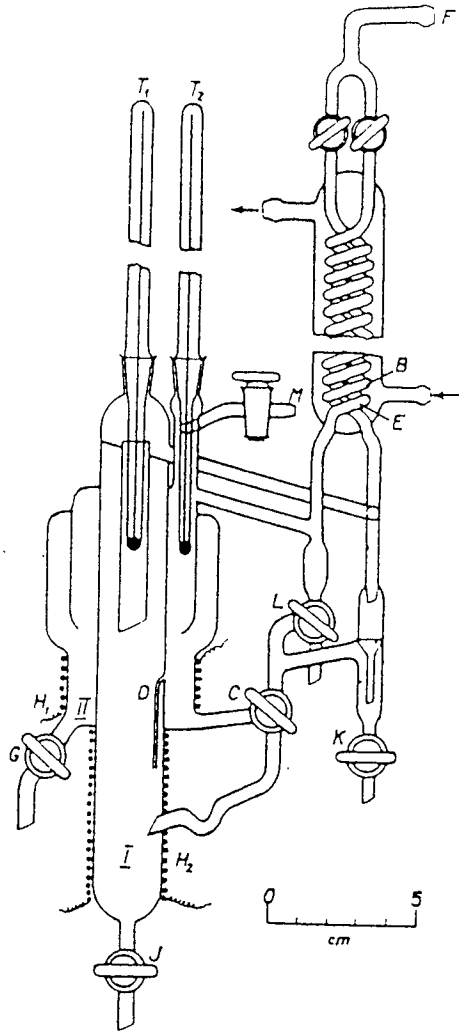


Figure 4.9 Bukala and Majeski (1952) Two-Plate Still

I, II = boiling vessels; C, L = three-way cocks; G, J, K = sampling cocks; M = to manostat; B, E = cooling spirals; H_1, H_2 = heating; T_1, T_2 = thermometers.

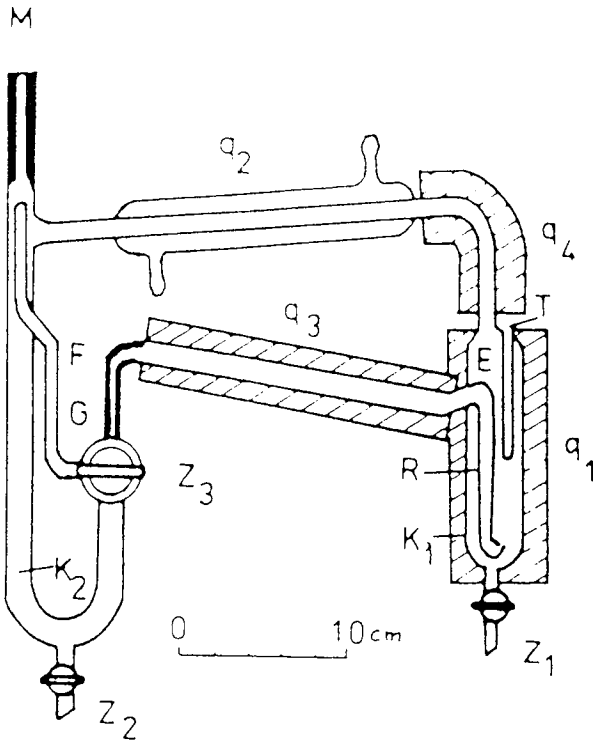


Figure 4.10 Jones, Schoenborn and Colburn (1943) Still: F, tube for pressure equalisation for sample withdrawal; G, capillary for smoothing flow of condensate to vaporiser q3; q4, heater for overheating vapour stream; R, tube for bubbling vapour stream through residue chamber K_1; Z_3, valve for maintaining vacuum during withdrawal of samples; other notation as in Figures 4.1 and 4.2

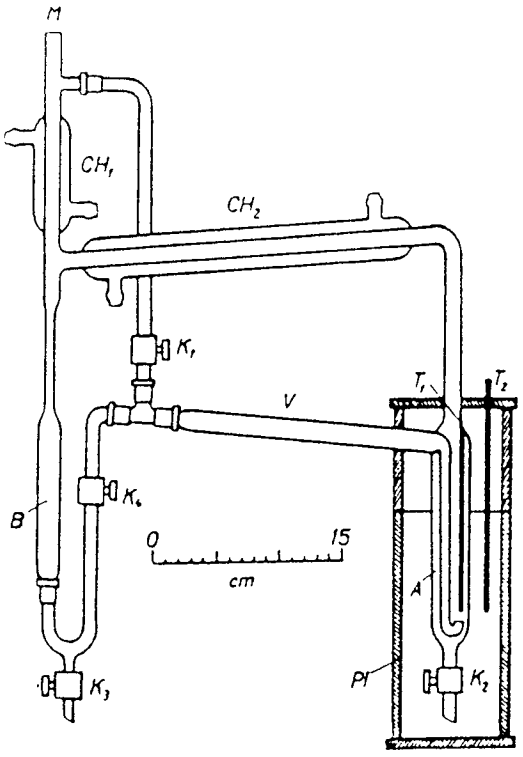


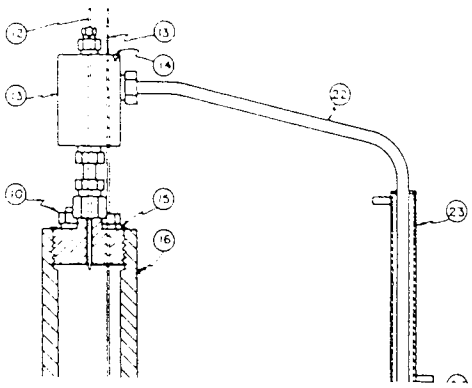
Figure 4.11 Modification of the Jones Still (due to Amick et al, 1951)

A = supply vessel; B = receiver; Pl = jacket; K_1 to K_4 valves; T_1, T_2 = thermometers; CH_1, CH_2 = coolers; M = to manostat; V = vaporiser.

4.3.2.2 Jones Still and its Modifications

The second operational principle i.e., vaporisation of vapour condensate, was applied for the first time in a still described by Chilton (1935), and its mode of operation is again shown in Figure 4.2. This type of still was further developed by Jones et al. (1943). The high accuracy of the data obtained by the Jones still led to many subsequent modifications. The basic Jones still, shown in Figure 4.10, consists of a heated residue-chamber K_1, and overhead condenser q_2 leading to a condensate chamber K_2 and a flash vaporiser q_3. The condensate flows under its own hydrostatic pressure through a three-way stopcock Z_3 and a capillary into the vaporiser q_3, which is a heated tube connecting K_1 and Z_3. The liquid level in K_2 remains constant. The capillary G is present to smooth the flow into K_2 and to prevent fluctuations in the vaporisation rate. The temperature in q_3 is maintained slightly above the equilibrium temperature. The vapour generated enters K_1 almost at its base via a tube R which directs the vapour stream upwards through the liquid and against the thermometer well T. This ensures agitation of the residue liquid and allows measurement of temperature. The residue chamber K_1, is heated. The heater q_1 compensates for heat losses so that the quantity of vapour leaving K_1 is the same as that entering. The vapour flowing from K_1 to the condenser q_2 is slightly superheated in the heater q_4 in order to prevent condensation and refluxing of the condensate. The condensate flowing from q_2 to K_2 is recycled and when steady-state conditions have been obtained liquid and vapour samples are withdrawn from the residue (K_1) and condensate (K_2) chambers. The stopcock Z_3 allows vacuum to be maintained and the liquid to be sucked back during sample withdrawal. Careful supervision is required in controlling the heat input into this still. The chief difficulty encountered with this equipment appears to be the balancing of the heat losses from the residue chamber K_1, and owing to this difficulty proper operation of the still is difficult to achieve. The bubbling of the vapour through the liquid leads to pressure drop within the still and thus diminishes the accuracy of the pressure and temperature determinations. Because of this, methods involving recirculation of the vaporised condensate have become less popular among experimental thermodynamicists. Another defect of most such recirculating devices is that they are tedious to operate and require some hours to achieve equilibrium (Williamson, 1975).

Amick et al. (1951) made several small changes in the Jones still and thus substantially simplified its operation. His instrument is shown in Figure 4.11. This instrument is made from glass in combination with metal (valves), which allows it to be adapted for work at higher pressures.



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25. Line to pressure gages, vent, evacuation line
26. Condensate chamber
28. $\frac{9}{16} \times \frac{9}{16} \times \frac{1}{4}$ inch tee
29. Vapor sample line

Figure 4.12 Bar-David and Dodge (1959) Still

Barr-David and Dodge (1959) proposed an apparatus of a similar type. They measured vapour-liquid equilibria for the binary mixture ethanol-water at pressures up to 200 bar. Their equilibrium still is shown in Figure 4.12. Omitted from Figure 4.12 for the sake of clarity are the insulation, electrical windings, and supports.

In the reboiler, 7, the liquid is heated by means of an external heater winding surrounding the leg. Thorough mixing of the returning liquid and liquid in the still is ensured by the circulation pipe and collar, 8. The vapour formed passes up through the main body, 9, in which any entrained liquid settles out. The vapours leave the top of the still and pass into a two-section condenser, which can be cooled by air or water. The main body of the still and the top fittings are maintained 2°C or 3°C above the vapour temperature to ensure adiabatic operation of the still and prevent refluxing. The condensed vapour collects in the condensate chamber, 26, flows through a check valve, 19, and returns by the vapour-condensate return line, 17, to the reboiler. A vent pipe from the check valve to the main vapour space was added to prevent siphoning of the liquid from the condensate chamber to the still. The reboiler, 7, main body, 9, and top plug, 15, were constructed from AISI 4130 steel. The rest of the equipment was made from stainless steel. The operation of the still was checked by a study of the 200°C ethanol-water vapour-liquid isotherm and a comparison of the results with the work of Griswold et al. (1943). According to Bar-David and Dodge, the y-x data showed excellent agreement.

Othmer and Morley (1946) modified the Othmer still so as to measure high pressure vapour-liquid equilibria and developed the instrument shown in Figure 4.13. Data on the binary mixtures methanol-water and acetone-water were reported at pressures up to 15 bar (absolute). This still was made from stainless steel and high-pressure valves were used. The apparatus is attached at the flange G to a vessel fitted with a Bourdon pressure gauge and connected by a reducing valve to a nitrogen bomb. The measurements were carried out in an inert atmosphere of nitrogen and it was found that at pressures up to 15 bar the errors caused by the solubility of nitrogen in the cold condensate were negligible. Similar instruments have been proposed by other workers such as Othmer et al. (1951) and Othmer et al. (1952).

4.3.3 Liquid Phase And Vapour Condensate Recirculation Methods

Stills based on this principle were at first used for the determination of boiling points. Around 1910 Cottrell introduced, for undergraduate courses at the University of California, an ebulliometer with a thermal lift pump used to deliver the stream of boiling liquid to a thermometer (Cottrell, 1919). This apparatus was further developed by

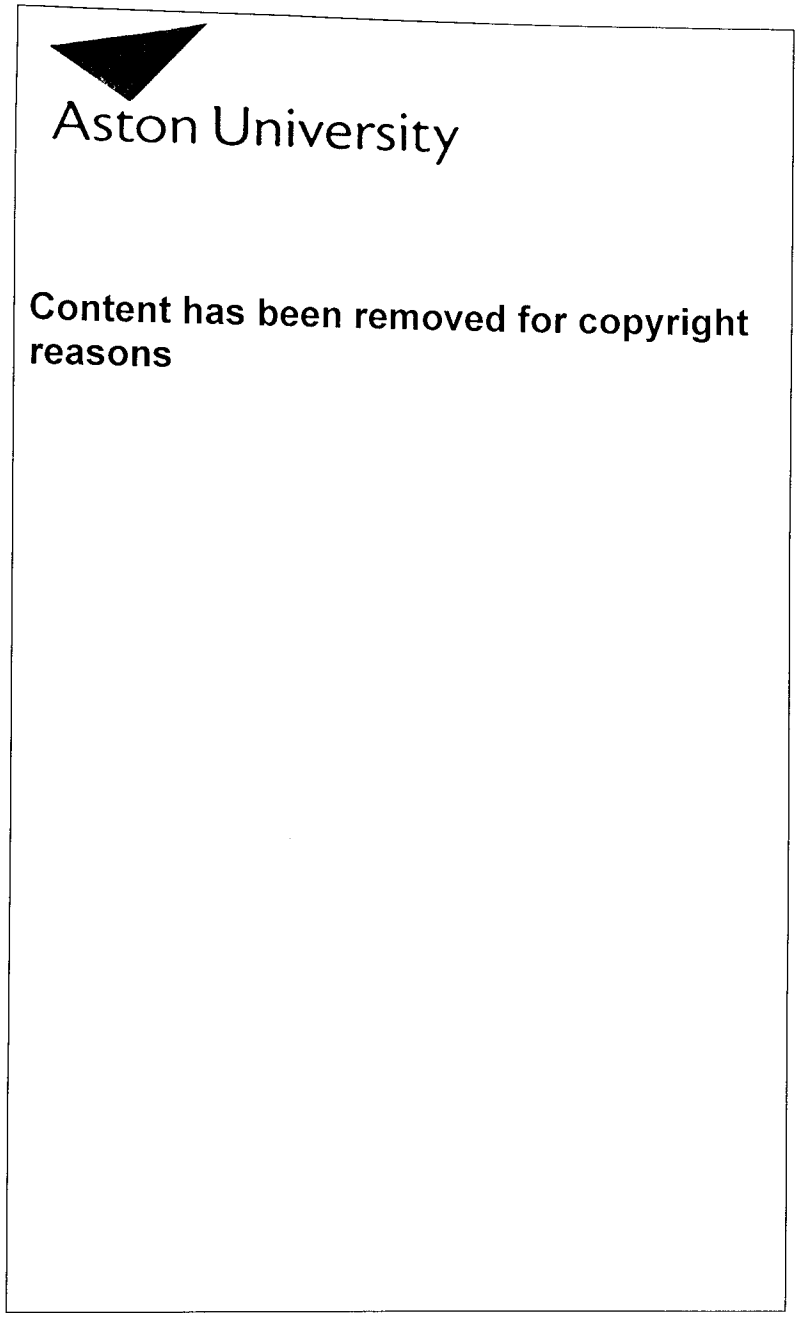

Figure 4.13 Othmer and Morley (1946) Still

A = boiling flask; B = receiver; P = weir; T = thermometer; V_1 to V_4 = valves; CH_1, CH_2 = coolers; G = flange to pressure bomb.

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Figure 4.14 Swietoslawski Ebulliometer, original design (Swietoslawski and Romer, 1924): A, heated bulb providing thermal lift of Cottrell pump; B, equilibrium chamber; C, tube preventing heat losses; D, condenser; I, Cottrell-pump tube; II, condensate and liquid down-stream tube; a-a, liquid level.

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Figure 4.15 Principle of Operation of Liquid Phase and Vapour Condensate Recirculation Method: A, mixer for uniform mixing of vapour condensate and liquid streams; C, condenser; E, equilibrium chamber; H_1, heater providing thermal lift to Cottrell pump; H_2, heater for overheating vapour stream; K, flow meter (drop counter); L, liquid level when operation is stopped; M, to pressure-stabilising system; P, pressure gauge; S_1, vapour condensate container; S_2, liquid phase container; T, thermometer; V_1, valve for introducing samples to still; V_2, valve for drainage of still; W, tube delivering (on thermal-lift principle) mixture of vapour and overheated liquid from H_1 to E; Z_1, vapour condensate sampling valve; Z_2, liquid phase sampling valve.

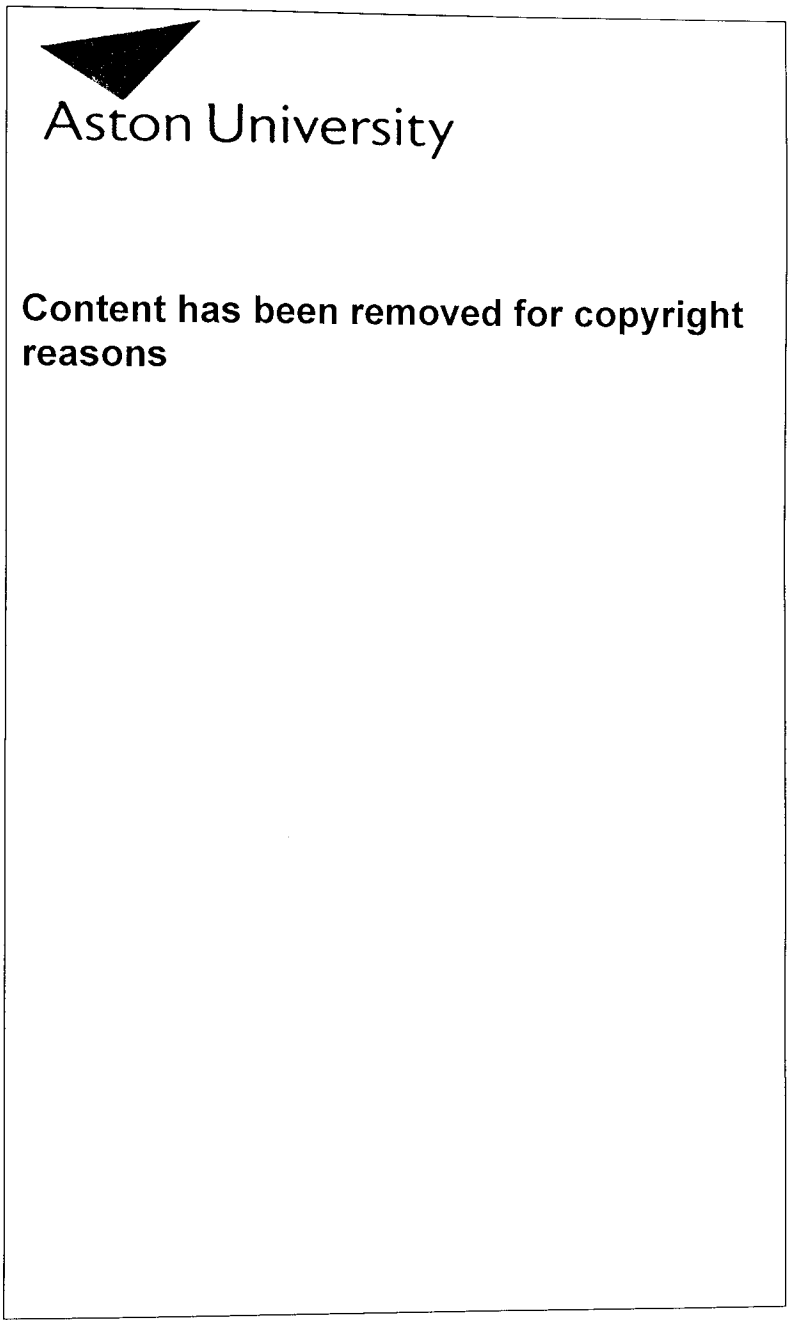

Figure 4.16 Rogalsk and Co-workers (1977, 1980) Ebulliometer: A, B, mixers for uniform mixing of vapour condensate and liquid streams; J, vacuum jacket preventing heat exchange; max, min, maximum and minimum levels of liquid in non-operating ebulliometer; other notation as in Figure 4.15.

Washburn (1919). The apparatus was further modified and considerably simplified by Swietoslawski and Romer (1924), and is considered to be the most accurate for the determination of boiling temperature in the pressure range 5-200 kPa (Leslie and Kuehner, 1968). The original Swietoslawski ebulliometer is shown in Figure 4.14 and its operational principle in Figure 4.15.

A Cottrell pump is a device which throws a mixture of vapour and liquid slugs at equilibrium onto a thermocouple or thermometer well, thus enabling very precise equilibrium temperature measurement.

The high accuracy of vapour pressure data obtained using the Swietoslawski ebulliometer pointed to this apparatus as a natural base for further development (Rogalski and co-workers, 1977, 1980). The apparatus proposed as shown in Figure 4.16. This represents an ebulliometer for simultaneous determination of pressure, temperature and the composition of both phases. The mixture boils in an electrically heated container H_1. Powdered glass is sintered on the inside walls of this container, providing an activated surface to obtain steady boiling. The vapour generated provides gas lift via a Cottrell pump in the tube W, and the continuous stream, consisting of vapour and overheated liquid, is delivered into the equilibrium chamber E. This stream hits a thermometer well T. The expansion caused by the impact results in the equilibrium temperature being established on the outside wall of the thermometer well. In order to minimise heat losses, the equilibrium chamber is placed inside a vacuum jacket J. The liquid and vapour streams separate in the equilibrium chamber E. The vapour stream leaves E through a large-bore tube leading to a condenser, when it is totally condensed. This large-bore tube is heated using the heater H_2 above the equilibrium temperature, to prevent partial condensation and refluxing, which may affect the composition of the condensate leaving the condenser C2. The condensate then flows through a drop counter (flow meter) K and condensate container S_1 to the mixing chamber A, where it is mixed with the liquid flowing from the equilibrium chamber E via the liquid container S_2. Perfect mixing is very important for minimisation of boiling-temperature fluctuations. Each still is equipped with two mixing devices, A and B. The mixed stream of uniform composition re-enters the Cottrell pump H_1 where it is partly evaporated.

Rogalski and Malanowski (1980) used the above ebulliometer to obtain very accurate determinations of the vapour-liquid equilibrium of the binary mixture chlorobenzene-hexane at 338.15 K. The present modifications of the Swietoslawski ebulliometer are very useful for vapour-liquid equilibrium measurements, and allow operation at pressure from 5

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Figure 4.17 Lee (1931) Still: notation as in Figure 4.15.

Figure 4.18 Gillespie (1946) Still: C_1, vapour condenser; C_2, cooler; R, separator for liquid and vapour phases; other notation as in Figure 4.15.

to 300 kPa when the apparatus is made of glass. A steel ebulliometer operates well for pressures to ~3.5 MPa (Zieborak, 1966).

Gutsche and Knapp (1982) used the modified Swietoslawski ebulliometer (Rogalski and Malanowski, 1980) to obtain isothermal vapour-liquid equilibrium data for 1-chlorobutane with n-hexane and n-heptane at three temperatures and for 1, 2-dichloroethane with n-heptane at two temperatures.

The first circulating still with a Cottrell pump and having the capability for withdrawal of liquid and condensate samples after temporary cessation of circulation by pressure increase was proposed by Lee (1931). This apparatus is shown in Figure 4.17. Two important modifications, the separator for the liquid and condensate streams and the facilities for withdrawing samples without interruption of boiling (Figure 4.18), were introduced by Gillespie (1946). This still has the basic arrangement of the Swietoslawski ebulliometer, and gained high popularity after it was found by Coulson et al. (1948) to be greatly superior to stills with vapour condensate circulation (Othmer, 1943) and even to those modified with an additional Cottrell pump (Scatchard et al., 1938). Its main advantage is the accurate measurement of boiling points. The possibility of partial condensation in this still is very slight since the vapour and liquid are maintained in close contact as far as the equilibrium chamber. Concentration gradients are eliminated since the cold condensate mixes with the hot residual liquid before entering the boiling flask and because the vapour bubbles formed on the internal heater ensure perfect mixing.

Gillespie himself pointed out the one serious error in this apparatus, namely that the samples withdrawn from the boiling flask do not correspond to the liquid which is in true equilibrium with the vapour leaving the separator. Since this error can become quite large with certain mixtures having particularly large relative volatility, the original Gillespie still was modified. Simple modifications were proposed by Fowler and Norris (1955) and further modifications were made by Otsuki and Williams (1953). The instruments and their functioning should be clear from Figures 4.19 and 4.20. They mainly differ in the special collector placed in the return liquid line from the separator. A sample withdrawn here represents a liquid that is in true equilibrium with the vapour leaving the chamber.

Brown (1952) modified the Gillespie still as shown in Figure 4.21. The electrically controlled valves are very useful as they permit the withdrawal of samples of liquid and condensate without causing interruption of the circulation. This arrangement also eliminates the error arising from partial evaporation of the condensate after connecting the instrument with the external atmosphere and simultaneously prevents the contamination of

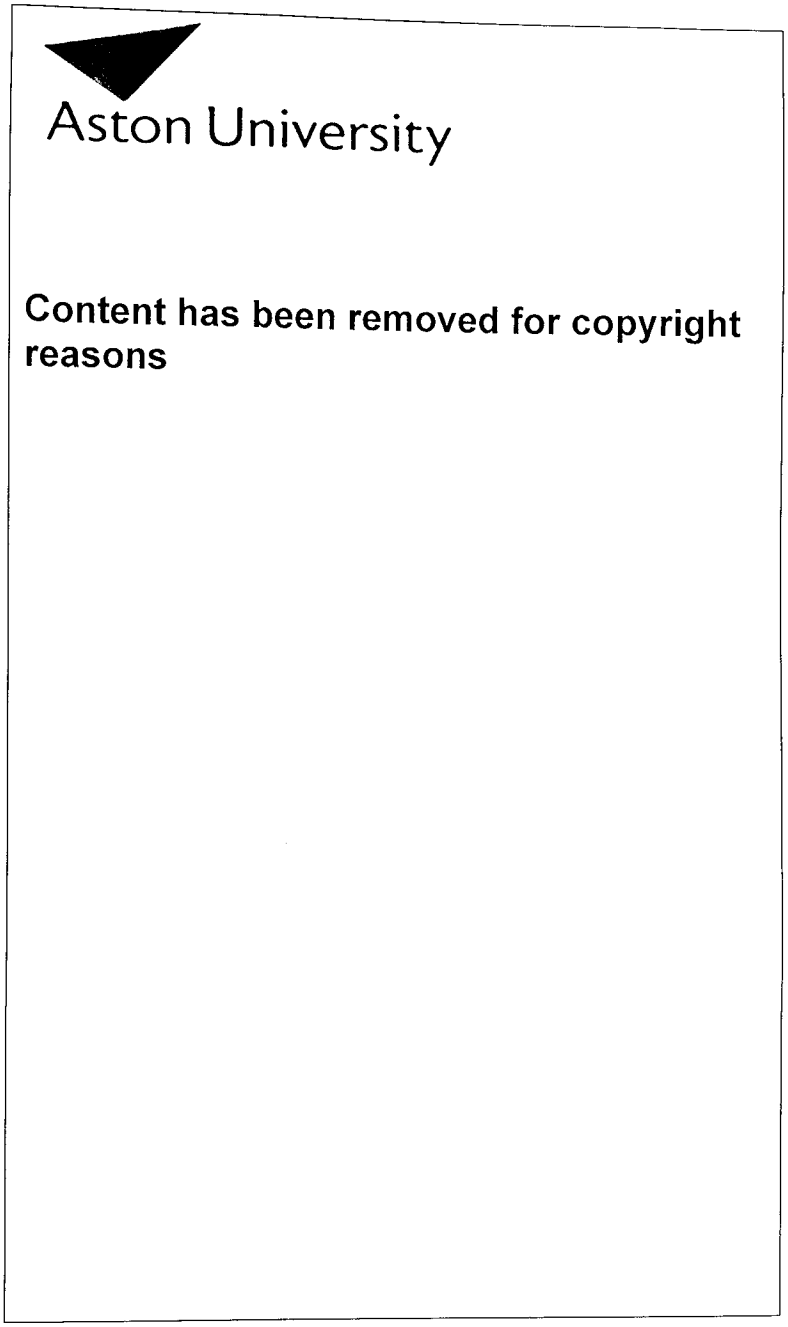

Figure 4.19 Fowler-Norris Still.

A = boiling flask; B, C = receivers for collecting condensate and liquid; R = equilibrium chamber; CH_1 = cooler; P = Cottrell pump; H = internal heater; T = thermometer; K_1 and K_4 = cocks.

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Figure 4.20 Otuski-Williams Still.

A = boiling flask; H = internal heater; P = Cottrell pump; T = thermometer well; R = droplet separator; P! = jacket; J = liquid sampler; Z = return line; CH_1, CH_2 = coolers; K_1 to K_3 = sampling cocks.

Figure 4.21 Brown (1952) Still: C_1, vapour condenser; C_2, cooler; C_3, liquid cooler; other notation as in Figure 4.15.

Figure 4.22 Rose-Williams Still.

A = boiling flask; B, C = liquid and vapour samplers; P = Cottrell pump; T = thermometer; H = internal heater; CH = cooler.

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Figure 4.23 Ellis (1952) Still: C_1, vapour condenser; C_2, cooler; R, separator for liquid and vapour phases; other notation as in Figure 4.15.

the contents of the receivers with liquid flowing down the walls after stopping the still. The small cooler C_3 serves to cool the residual liquid returning from the droplet separator before its union with the condensate stream from the receiver. This completely eliminates the possibility of non-equilibrium vaporisation in the distilling chamber. This instrument gives very precise results even with mixtures having a high relative volatility. Its most important drawbacks are the very long time, up to 4 hours, necessary to achieve steady-state operation, and the large sample size required (200 cm^3).

Rose and Williams (1955) modified the Gillespie still and proposed the still shown in Figure 4.22 which insures reliable results. A novel feature is its specially modified liquid and vapour samplers, which permit the removal of samples under any conditions, without interrupting the operation of the apparatus.

Another apparatus provided good results, as a result mainly of its simplicity and similarity to the still of Lee (1931), was proposed by Ellis (1952) and is shown in Figure 4.23. The heterogeneous mixture flows through the glass spiral of several turns which functions as the Cottrell pump and spurts on the thermometer well. The still is charged with about 250 ml of the mixture and equilibrium is reached after operating for one hour. The attainment of equilibrium was judged by the constancy of the thermometer readings and when the distillation rate is such that 40-70 drops per minute of condensate fell from the finger condenser. This still has the same disadvantages as the Brown still, but owing to its simplicity is much easier to operate. Ellis tested his still with four types of mixtures formed by close-boiling or wide-boiling components. In both cases, mixtures close to ideality and strongly non-ideal were tested. The resulting data were compared with those measured by Othmer (1943) and Fenske et al. (1947), and were found to correlate more favourably with the Gibbs-Duhem equation than was the case for the data from other stills.

In an effort to prevent condensation of the vapour phase, Röck and Sieg (1955) fitted their apparatus with a thermostated jacket. The functioning of their still is apparent from Figure 4.24. Gmehling et al. (1980) measured accurate isothermal (30°C) and isobaric (700 mmHg) vapour-liquid equilibrium data for the binary mixtures diethyl ether-halothane, halothane-methanol, and diethyl ether-methanol by using a recirculation still proposed by Röck and Sieg.

Schmelzer et al. (1983) used a modified Röck and Sieg (1955, 1956) recirculation apparatus and measured accurate vapour-liquid equilibrium data for the binary mixtures ethanol-undecane and 1-propanol-undecane at 333.15 and 353.15 K, 1-butanol-undecane at 353.15 and 373.15 K, and 1-dodecanol-undecane and 1-tetradecanol-undecane at

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Figure 4.24 Röck and Sieg Still.

A = boiling flask; B = Cottrell pump; C = cooler; D = droplet separator; E = receiver for collecting liquid; F = receiver for collecting condensate; H = heater; T = thermometer wells.

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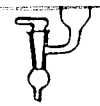

Figure 4.25 Stage and Müller Still.

A = boiling flask; B = Cottrell pump; C_1, C_2 = coolers; D = droplet separator; E = receiver for collecting liquid sample; F = receiver for collecting condensate sample; M_1, M_2 = electrmagnetic valves; T = thermometer wells; Z = supply flask.

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Figure 4.26 Dvorak and Boublik (1963) Still: C_1, vapour condenser; C_2, cooler; "L", liquid stream; "L" + "V", vapour condensate and liquid stream; N_1, N_2, magnetic stirrers; R, separator for liquid and vapour phases; "V", vapour stream; other notation as in Figure 4.15.

Figure 4.27 Raal, Code and Best (1972) Still.

Raal and Brouckaert (1992) proposed a recirculating equilibrium still for the determination of vapour-liquid equilibrium data for mixtures with partial liquid miscibility. The design shown in Figure 4.28 differed only in detail from the Raal, Code and Best still. Capillary tubes were introduced in the condensate return line and in the liquid return line from the vapour-liquid disengagement chamber as shown. Rapid and effective stirring, particularly important in regions of partial liquid miscibility, was introduced in the condensate and boiling chambers. A split downcomer in the condensate receiver has subsequently been adopted for partially miscible mixtures.

Jenkins and O'Donnell (1980) developed a modified version (Mark I) of the Raal et al. (1972) still shown in Figure 4.29. This still was designed to run at pressures of one bar and less. A charge of about 100 ml of the desired equilibrium mixture is placed into the still via the pressure system connection. On heating, a vapour liquid mixture rises up tube A and into the outer chamber of the still. This outer chamber is an annulus with about 3 mm between the walls. The vapour liquid mixture forms a Cottrell pump in this annulus and the mixture is propelled up and onto the spiral surrounding the thermocouple well. The spiral promotes good vapour-liquid contact with the thermocouple well, and the temperature is measured using a chromal-alumel thermocouple. The liquid then drains down into the agitated mixing chamber via tube B. The vapour enters the inner chamber, where it is bubbled through small holes near the bottom, through the liquid sample in the middle chamber and out onto the condenser via tube D. The liquid sample in the middle chamber is formed by some of the vapour partially condensing on the walls of the still. The liquid comes to equilibrium with the vapour bubbling through it, and can be withdrawn through the sampling valve. The vapour after leaving the still is totally condensed and passes through a drop counter into the vapour sample collector where it is sampled. Excess condensate runs over a weir, down tube C and into the agitated mixing chamber. The mixture from the agitated mixing chamber enters the heater and the process is repeated. The Cottrell pump surrounding the still maintains the inner and middle chambers at a uniform temperature. The still and tube D are both lagged and the still is isolated from draughts. Equilibrium is achieved after approximately one and a half hours (O'Donnell, 1980). The main differences between this still and the one proposed by Raal, Code and Best are:

(1) The heater has been separated from the main body of the still and replaced by a quartz sheathed immersion heater. This prevents thermal stresses being set up in the still and hence breakage.

(2) An agitated mixing chamber was inserted to provide a well-mixed feed to the heater.

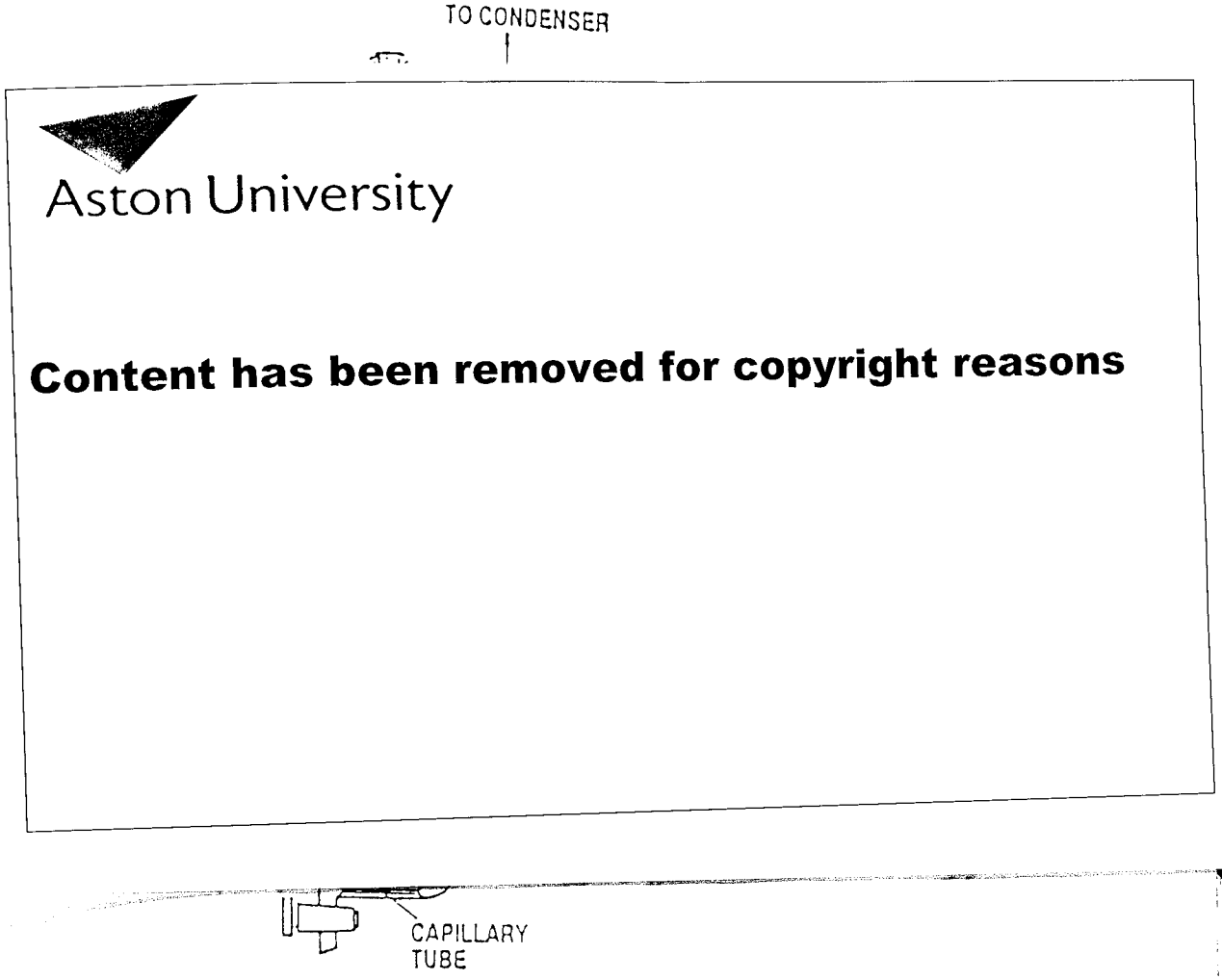

Figure 4.28 Raal and Brouckaert (1992) Still.

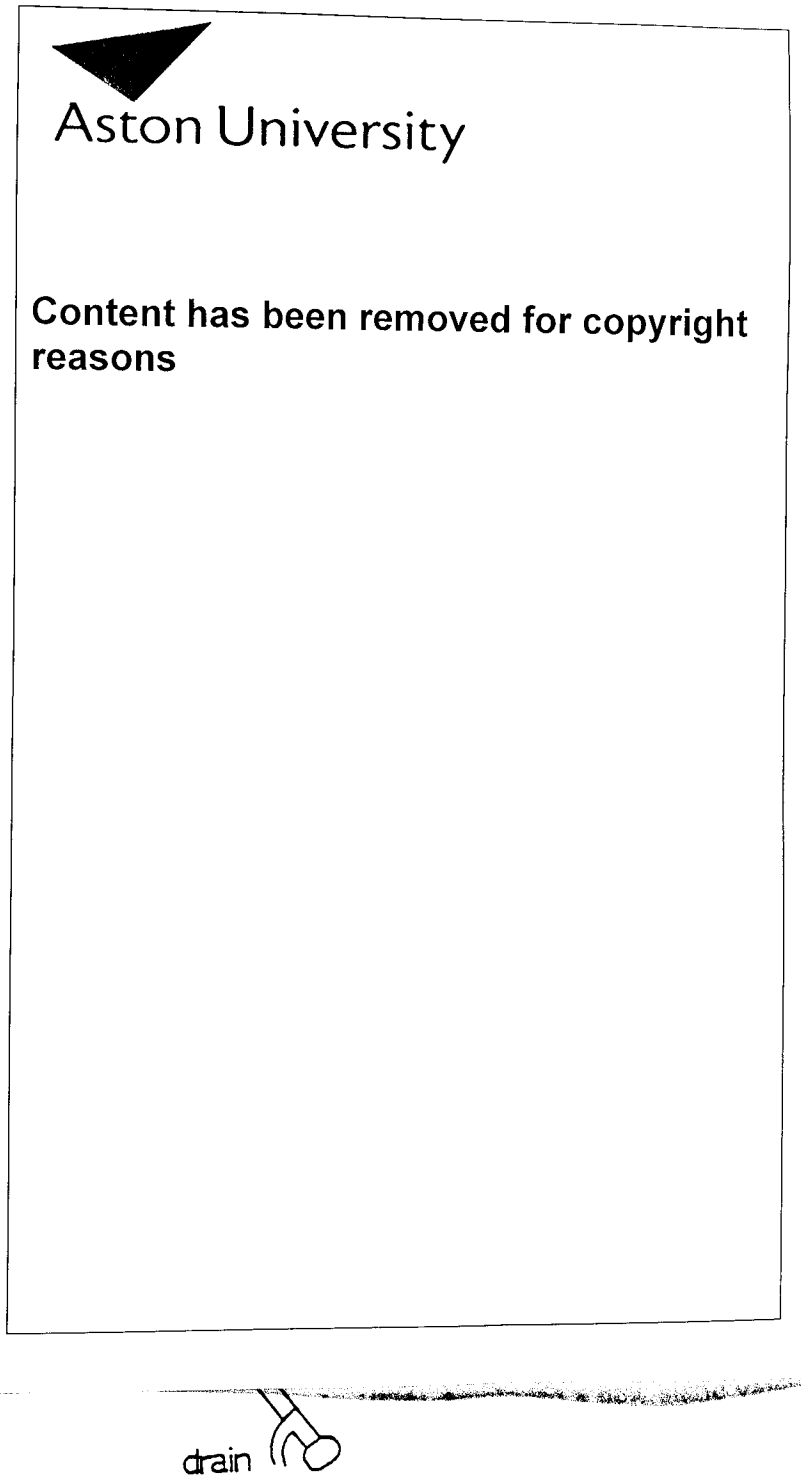

Figure 4.29 Jenkins and O'Donnell (1980) Modified Raal, Code and Best Still.

(3) The thermocouple well has a glass spiral on its outer wall and this gives a longer contact time and an accurate measurement of temperature.

(4) The greaseless ball and cap joints used in the structure relieve any stress set up on heating.

This still has been used successfully to obtain vapour-liquid equilibrium data on a number of binary mixtures.

4.4 Static Methods

In static methods of direct experimental determination of vapour-liquid equilibrium data the vapour and liquid phases of a mixture are maintained in contact within an evacuated chamber which is immersed in a thermostatically-controlled water bath. The two phases are vigorously agitated and sampled for analysis. The method sounds simple but removing even a small sample for analysis affects the equilibrium. The problem is reduced by the use of chromatographic methods for analysis but difficulties arise when taking the vapour sample from the equilibrium chamber. Another disadvantage is the extensive and careful degassing of the components required.

Wichterle and Hala (1963) used a still based on the static method to carry out semi-microdetermination of vapour-liquid equilibrium data in multi-component mixtures at isothermal conditions. Their method was based on the sampling of very small volumes of the vapour phase which were then analysed by gas chromatography; the method makes possible the determination of equilibrium data on a fairly small amount of liquid mixture, about 2 ml for one value. The quantity of substance in the sample is proportional to the peak area; it is therefore possible to calculate the relative volatility from the chromatograms directly by comparing the ratios of the peak areas of components in the two phases. It is not even necessary to reach the equilibrium partial pressures because it is sufficient to measure the concentration ratios of components in order to determine the relative volatility. The very small vapour samples make it possible to obtain a large set of analytical data while leaving the concentrations in the liquid phase unchanged.

In 1975 Inoue and co-workers (Inoue et al., 1975) developed a new static vapour-liquid equilibrium apparatus which consists of five units; an equilibrium unit, a temperature control bath, a vapour pressure measuring unit and an argon purification unit. To attain an equilibrium with sufficient amounts for the vapour component analysis which follows, two large flasks with about 44 litre capacities are connected in series with a small bulb of

200 ml capacity. The latter was immersed in a temperature controlled bath regulated to within ± 0.01°C at the given temperature and the vicinity of the two flasks was surrounded by an air thermostat regulated to 0.5°C at a temperature 1.0°C higher than the temperature of the water bath to avoid condensation of the vapour phase. The three vessels were connected in series by glass tubing through glass pumps and glass valves to agitate the gas phase and to separate the vapour phase from the liquid phase. A pure liquid in a sample bulb was thoroughly degassed by repeated freezing, pumping and melting. Finally an appropriate amount was distilled into the main bulb. A stirrer in this bulb was coupled magnetically to an external rotor, this arrangement assists in attaining equilibrium. After equilibrium was achieved, the total pressure was measured with the aid of a quartz Bourdon gauge which is balanced against purified argon. Then the glass valves are closed to separate vapour and liquid phases. These phases are collected separately by vacuum distillation into the separate bulbs which are cooled in liquid nitrogen, and the concentrations of the components are determined. This apparatus was used to obtain vapour-liquid equilibrium data on a benzene-cyclohexane mixture (Inoue et al., 1975).

Work has also been done in this field by Mihkelson et al. (1978) using an equilibrium still to measure the boiling temperature at a fixed pressure with an amount of solution of less than 1 ml. The boiling temperature in the still is measured by a special thermistor (Mihkelson, 1964). The samples of the liquid mixture are prepared by weighing out the pure components and transferring them successively into the equilibrium cell using a syringe. The apparatus is connected with a barostat which keeps the pressure at the desired value. In this apparatus the equilibrium is achieved within approximately 15 minutes and the experiment to measure the resistance of the thermistor for one solution at four fixed pressures requires about four hours.

Kassmann and Knapp (1986) developed a static cell technique in which they employed two cells to measure vapour pressures as a function of temperature and also to measure differential pressures between two solutions of different compositions. The apparatus is built in glass and stainless steel. The cells have a capacity of 25 ml. Liquid substances can be added by injection through a septum at the top of the cell. The cell could be isolated by a valve and removed or replaced by means of a quick-connect device. The liquid is placed in the cell where it is degassed by evacuating the cell while stirring thoroughly with a magnetically agitated stirrer. The amount of liquid in the cell is determined gravimetrically. The cells are then connected to the apparatus. The shut-off valves at the cells are opened after the tubing system of the apparatus had been evacuated. The vapour pressure of the liquids in the two cells can be measured. The vapour pressures should be equal and the differential pressure should be zero.

A small amount of the degassed second component is injected with a gas-tight syringe. The differential pressure is measured as a function of the concentration of the second component.

4.5 Total Pressure Methods

4.5.1 Introduction:

One method which eliminates the need for separating the liquid and vapour phases and their analysis is that based on the Total Pressure approach, sometimes abbreviated to P-T-x. This involves the direct determination of temperature, pressure and liquid phase composition in a static cell. The composition of the equilibrium vapour phase is obtained by calculations from observed saturated pressures as a function of liquid phase composition, thus eliminating two of the major sources of errors in the vapour-liquid equilibrium data measurements. The P-T-x approach has earned its popularity for vapour-liquid-equilibrium measurements as it is a fast and efficient method, although most suitable only for binary systems. The essential feature of this method is that the total pressure of the mixture is measured as a function of composition at a constant temperature. Since total pressure data are measured in a static cell where no boiling takes place, the total pressure method eliminates the bumping and unsteady boiling frequently found with stills operating at low pressures. It is nearly always possible to obtain low pressure vapour-liquid equilibrium data by this method.

4.5.2 Experimental Techniques

Early experimental work using the total pressure approach was performed on two different types of apparatus, a form of isoteniscope and a circulating still technique using an ebulliometer.

Holtzlander and Riggle (1955) modified the Smith and Menzies (1910) isoteniscope by decreasing the vapour volume in relation to the liquid volume to minimise changes in liquid composition caused by vaporisation of the more volatile component during operation. A stopcock was added to the outlet of the isoteniscope to give a better control of the apparatus and a magnetic stirrer was incorporated in the bulb to give improved mixing characteristics. The isoteniscope was connected via glass tubing to a degassing unit which was based on the freezing-evacuating-thawing cycle. The apparatus was used to take

pressure against temperature readings on a fixed charge to the bulb, over the pressure range of 2 mmHg to 20 mmHg absolute.

The ebulliometer method was used by Redlich and Kister (1949) and Prengle and Palm (1957), although the method was initially developed by Swietoslawski in 1928. The method consisted of a circulating still, where the condensed vapour is returned immediately to the liquid phase and the main concern is the precise measurement of the boiling point of the liquid. The vapour pressure is measured relative to an identical unit working with only a pure component boiling at the same temperature. Prengle and Palm (1957) used the ebulliometer as a device to determine the boiling temperatures of a given mixture as a function of pressure. They designed the apparatus such that three ebulliometers could be operated concurrently at the same total pressure, thereby speeding the accumulation of the desired data. However, this method has since been proved inaccurate.

Jakubrowsky and Norman (1969) described a total pressure still based on the modified Swietoslawski (1928) ebulliometer of Prengle and Palm with the condensate hold-up reduced to a minimum. The technique provides to a limited accuracy both isothermal and isobaric vapour-liquid equilibrium data without the analysis of either phase. The liquid composition is adjusted gravimetrically and assumes constant during operation. The technique assume vapour phase ideality. The ebulliometric method in general has the disadvantage that it can produce spurious results when the mixture consists of widely differing boiling points.

Most of the methods mentioned above did not produce data with the desired rapidity as a separate experiment was required for each measured vapour pressure because pure degassed liquids were distilled directly into the equilibrium chamber.

In an interim development Ljunglin and Van Ness (1962) used an apparatus in which an equilibrium glass measuring cell was almost completely filled with the liquid. A miniature pressure transducer was used to measure the pressure in order to keep the cell light and portable. The entire apparatus was submerged in a temperature-controlled bath. The degassing of pure components was carried out by intermittent withdrawals of vapour from a storage flask over the period of a week. The pure degassed materials were then transferred to the measuring cell by distillation under vacuum. Since the cell was light and portable, successive weighings of the cell allowed determination of amounts of pure materials added and hence the composition of the solution formed. The vaporisation of the liquid phase did not significantly affect its composition as the vapour space above the

liquid was minimal. The apparatus was used to take temperature against pressure data at a fixed composition. The disadvantage of this method was that only one data point per run could be obtained and this made the method time consuming and tedious.

A new breed of total pressure apparatus was developed by Gibbs and Van Ness (1972). In this new method degassed liquids were first transferred into evacuated piston and cylinder devices where they were stored for subsequent injections into the equilibrium cell. Solutions of known compositions were formed in the test cell and the composition was varied by metering the pure liquids volumetrically from these dispensing devices. The entire composition range for a binary mixture could be covered in two runs and it was possible to produce a complete pressure trace based on 20 to 30 vapour pressure measurements in one day. The equilibrium cell was made from a stock end piece of Corning industrial glass pipe with a capacity of 100 ml which was submerged in the constant temperature water bath. The equilibrium cell was connected to a Texas Instruments fused quartz Bourdon pressure gauge which measured the vapour pressure directly. The line connecting the test cell with the Bourdon gauge was insulated and heated to a temperature above that of the cell to prevent condensation of vapour. This mode of operation could not be used above 45°C.

In a subsequent version a differential pressure transducer was interposed between the equilibrium cell and the pressure gauge as a null device. The transducer was also heated to a temperature above that of the cell to prevent vapour condensation. The cell is kept constantly stirred using an internal mechanical stirrer driven via an external rotating magnet.

Gibbs and Van Ness used an evacuation, freezing and thawing under reflux followed by evacuation cycle for degassing of pure liquids. This technique although acceptable at the time has two major drawbacks, it is very time consuming and there is no direct way of determining whether degassing is complete.

Jenkins and Smith (1975) developed a total pressure apparatus to obtain vapour-liquid equilibrium data on mixtures when one component is present in very small concentrations. A glass cell was used and the liquids were metered into the cell using burettes with floating pistons. These had a small piston inserted within the burette on which was engraved a vernier scale. The main apparatus comprised of an equilibrium cell with the connection for the introduction of degassed components being made from the sides near the top. The cell was placed in a water bath inserted into another water bath and the temperature measured with a platinum resistance thermometer. The pressure measurement system was quite

different from that of Gibbs and Van Ness. As the apparatus was developed for vapour-liquid equilibrium data measurements at low concentrations of one component, high precision pressure measurements and control are required as the absolute pressure may be only of the order of 10 mmHg, and differences in pressures were of greater interest than the absolute pressures. Jenkins and Smith achieved the required pressure measurements and control by means of a metallic diaphragm whose position is detected by a transducer. The diaphragm was positioned across the top of the equilibrium cell giving a definite volume to the cell. The diaphragm transducer was used as a null detector, a high precision Texas Instruments quartz Bourdon gauge measuring an equalising pressure supplied to the top of the diaphragm. The voltage output from the transducer, zero at rest, is used to drive a pressure control system. A modified Texas Instruments Bourdon gauge was used in both a controlling mode and a measuring mode, simultaneously. Jenkins and Smith used a self-built diaphragm transducer which was used in conjunction with the Bourdon gauge. Their apparatus had some features which led to errors in vapour-liquid equilibrium data measurements, especially in the pressure. Firstly, a self-built transducer was used as a null device, with consequent disadvantages. Secondly the transducer diaphragm sat across the top of the cell. This arrangement introduced errors caused by the condensation of vapour on the bottom surface of the diaphragm, thus giving a false null. On the whole this apparatus was demonstrated to be superior to existing isothermal techniques in:

a) its rapidity, producing more than 30 data points in one experimental run, and,

b) its ability to produce data at low concentrations.

The full composition range to infinite dilution at both ends of the binary could be covered by two experimental runs. The data was obtained in the form of liquid volumes and the total pressure at a given temperature. A computational technique was developed to reduce the experimental data to P-T-x-y form (Smith, 1975).

Ronc and Ratcliffe (1976) developed a semi-continuous total pressure static equilibrium cell based on that of Gibbs and Van Ness (1972) and Jenkins and Smith (1975). They used an absolute pressure transducer placed in the centre of the cell lid. It is a flush diaphragm transducer which is mounted with the diaphragm in the same plane as the surface of the lid. The main modifications of Ronc and Ratcliffe apparatus over that of Gibbs and Van Ness design are:

a) The temperature is measured inside the cell.

b) There is no upper temperature limitation due to the pressure gauge, and the pressure readings are direct and instantaneous.

c) Stainless steel is widely used in the construction.

The pure degassed components were introduced into the cell through two accurate volumetric piston injectors. The equilibrium cell made from an end piece of 2 inch diameter thick glass tubing and sealed off to form a cell of 120 ml capacity, was placed in a constant temperature water bath. The cell temperature was measured with a thermistor placed in an housing compartment of the test cell. Although this apparatus was claimed to be more accurate than that of Gibbs and Van Ness there is still one drawback. As the transducer diaphragm is actually sitting across the top of the cell, any vapour condensation on the bottom surface of the diaphragm would lead to erroneous pressures.

Young et al. (1977) further modified the Gibbs and Van Ness apparatus to obtain vapour-liquid equilibrium data on cyclohexane with benzene, octane-1, m-xylene and n-heptane. They employed a different degassing technique in which they repeatedly froze the pure component then evacuated the space above the solid. The assumption was made that the gases were insoluble in the solids. The frozen solid was then allowed to melt with intermittent evacuation of the flask. This method of degassing has the disadvantage in that it is tedious and also that residual gases are always partially reabsorbed in the solid phase, even if the crystalline layer is formed under evacuation (Aim, 1978). A pressure transducer was used as a null device between the equilibrium cell and the pressure gauge. The pressure in the cell was directly measured with a Texas Bourdon gauge and the absolute temperature was measured with a platinum resistance thermometer.

Aim (1978) used a similar method to that of Gibbs and Van Ness. The samples to be tested were held in ampoules attached to a vacuum line, the seals were broken when the sample was ready to be charged into the cell. The ampoules were made up prior to experimentation and were then connected to the vacuum line, each one being sealed. Mixtures of known composition were prepared synthetically in a thermostatic equilibrium cell by weight from pure degassed components and the total pressure was measured by a quartz Bourdon gauge. The entire composition range for a binary mixture at three temperature values could be covered in two experimental runs. The equilibrium cell was a flat bottomed cylindrical glass vessel with a total capacity of 48 ml.

Mentzer, Greenkorn and Chao (1982) developed a high pressure version of the total pressure apparatus based on the original design of Gibbs and Van Ness (1972). Several improvements have been made over the previous design, the most notable being the design of the equilibrium cell. The cell was constructed from stainless steel with a copper gasket providing a leak-tight seal between the body of the cell and the lid. Pure liquids enter through the sides of the cell rather than the top, to ensure good mixing. Two pure liquids were degassed and then transferred by distillation to the piston injectors. The composition

of the liquid phase was directly determined from the volume of the material transferred to the cell, except for a small correction to account for that which vaporises. The piston injectors used were volumetric metering pumps, made by Ruska Instruments Corporation, with a capacity of 100 ml.

The pistons on each pump are then advanced to compress the fluids to a pressure sufficiently larger than each component's vapour pressure to ensure that a single phase is present. The pressure exerted on the fluid was 582 kPa. The entire composition curve is obtained in one day.

Vapour-liquid equilibrium data have commonly been measured using a circulating still which involves separation of the phases and then analysing them using any of the standard analytical techniques. On the other hand the total pressure approach involves the measurements of total pressure exerted in a static cell as the liquid composition is varied. The analysis of either of the phases is avoided and in general total pressure-liquid compositions measurements are easier than the equilibrium vapour composition measurements, especially for solutions of high relative volatilities and for solutions which are difficult to analyse. It has been suggested that since the data can be collected much more rapidly using the total pressure method, it is an effort wasted carrying out careful and sophisticated analysis of the vapour phase. Instead it is prudent to spend time improving techniques of measuring pressure-liquid composition data and use several of the computational techniques available to calculate the vapour phase compositions. There is however an advantage to be gained from the experimental measurements of vapour phase composition. These values can be used in a consistency test to check the integrity and quality of the data deduced from using a computational method.

All the total pressure methods mentioned above depend on the availability of a suitable computation technique to reduce the P-x data to give y values.

4.6 Flow Methods

The dynamic flow methods, in contrast to the circulation methods, have the feed entering the equilibrium chamber as a steady stream of constant composition which can be either in the liquid or in the vapour phase or a combination of both. These stills are mainly used for systems of limited miscibility in the liquid phase or a reacting mixture, or where a high speed of determination, with some loss in accuracy, is required.

The flow methods for direct experimental determination of vapour-liquid equilibrium data were developed from a need to obtain steady state within an equilibrium still in a short period of time. The first still developed using this method was proposed by Colburn et al. (1943). The Colburn still, shown in Figure 4.30 is a simple type of still, with the feed entering as a steady stream of vapour of given composition, the stream being made up by mixing the pure vapours. The liquid sample through which the feed bubbles is formed by partial condensation of the vapour on start-up as well as a small amount being injected through the capillaries before start-up. The still was designed to determine the vapour-liquid equilibrium of partially miscible liquids. During its operation a constant flow of saturated vapour was bubbled through 25 ml of liquid contained in an adiabatic contacting unit. The contactor was surrounded by a vapour jacket and a dead air jacket. Vapour-liquid equilibrium was considered to have been reached when a constant liquid level and a temperature variation of less than 0.1°C was observed.

Another flow still was designed by Vilim et al. (1954). The liquid was placed in a reservoir below which there was a float mechanism. The float established a constant level in the vaporiser. The boiling liquid-vapour mixture leaving the vaporiser impinged on a thermometer in the disengager unit. The phases separated, were condensed, cooled and sampled. The heat input to the vaporiser was adjusted to give a liquid-to vapour-ratio of 1:1. 300 ml of liquid was placed in the reservoir when large samples were required but generally a charge of 50 to 100 ml of liquid was sufficient. Each equilibrium determination took between 10 to 15 minutes.

Ruis et al. (1959) have designed a flow still specifically for reacting mixtures. The reactants, stored in reservoirs, were mixed at the correct rate in an agitator and fed at 50 ml per minute to a 10 cm long vaporiser. The heating time of the liquid took about 30 seconds. The boiling mixture was fed into a contactor which was contained in a Dewar flask. The phases separated by gravity, were condensed, cooled and sampled. The time for each determination was about 15 minutes and equilibrium was achieved when a constant temperature was reached.

Cathala (1950) constructed a still for reacting mixtures which differs considerably from the previously described flow stills. Basically, the vapour and the preheated liquid were mixed in a contacting chamber. The mixture passed up into an equilibrium chamber. It was proposed to investigate the vapour-liquid equilibrium of the thermally unstable sulphuric acid-nitric acid-water mixtures in the still. Marek (1955, 1956) slightly modified Cathala's original still to investigate the vapour-liquid equilibrium of the various tertiary mixtures in the hydrolysis scheme of acetic anhydride. The major modifications were that

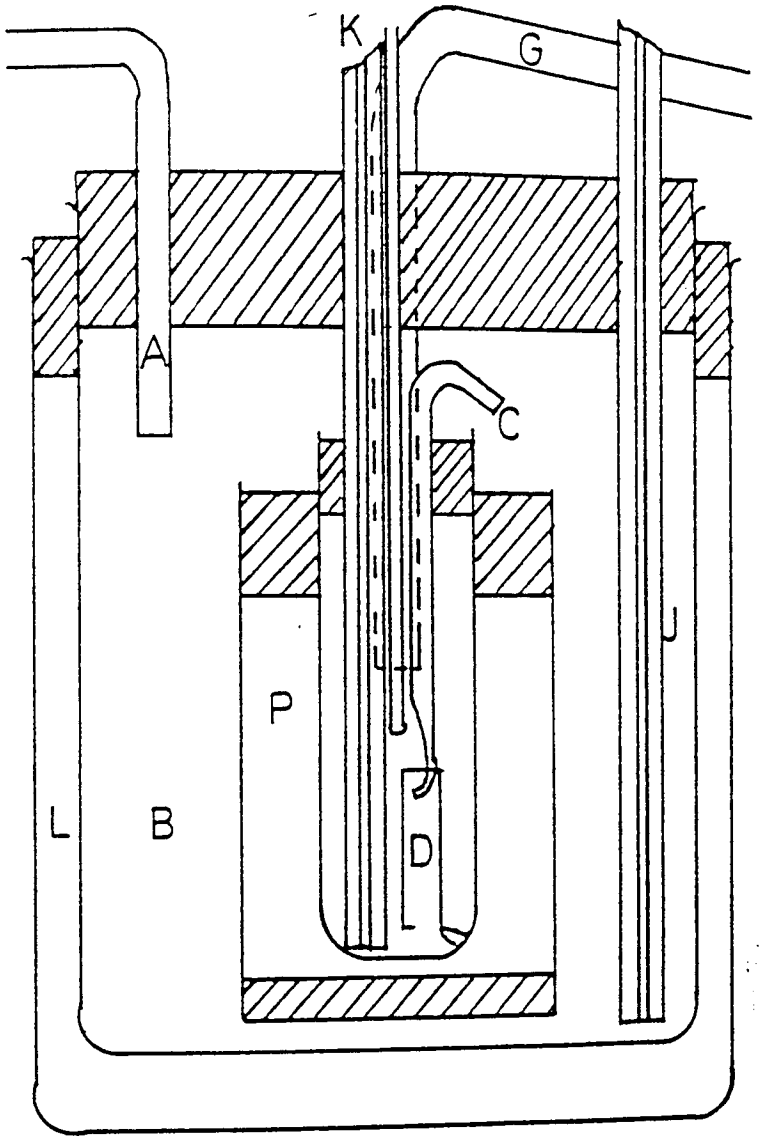

Figure 4.30 Colburn Flow Still.

L, protective jacket, B thermostatting vessel, P, air jacket, A, inlet tube, C, tube for introducing vapour into the equilibrium chamber, G, outlet tube, D, circulating tube, J, K, capillaries.

the whole of the equilibrium chamber was enclosed in a silvered evacuated jacket to help maintain adiabatic conditions and the contacting chamber was made detachable from the equilibrium chamber. The equilibrium temperature was measured by a copper-constantan thermocouple and equilibrium was reached after 10 to 20 minutes when the steady state temperature changes were less than ± 0.05°C. For the investigations, a feed rate of 0.5 to 0.6 g per minute under an operating pressure of 400 mmHg was used (Davies, 1971).

Cathala (1960) developed a second version of his flow still (see Figure 4.31). In this case the equilibrium chamber, the de-entrainer, the contactor and the vaporiser was constructed as one unit. The liquid level in the vaporiser was controlled and a magnetic stirrer was incorporated to promote regular boiling and mixing whilst an air bleed was used to facilitate low pressure work. The contacting chamber and equilibrium chamber were lagged and thermocouples were used to measure the temperature to an accuracy of 0.05°C. Equilibrium was reached after 15 to 20 minutes. The accuracy of the still was checked by measuring the composition of the ethyl acetate-water azeotrope and the worst error was found to be ± 0.158 mol percent. Liquid entrainment was estimated by boiling a solution containing potassium dichromate and analysing the vapour phase. It was concluded that entrainment was very small (Cathala, 1960).

A major modification to the Cathala still was made by Mamers (1965) who separated the vaporiser from the equilibrium chamber unit. As in the case of Marek's design (1955) the equilibrium chamber was surrounded by an evacuated jacket and the still was well lagged with asbestos tape and a resistance wire heater. Mamers (1965) concluded that the vaporiser design of both Cathala (1960) and Marek (1955) was unsatisfactory due to the large hold-up and thus with the lack of flexibility the flow would be difficult to control. Hence a falling film vaporiser containing stainless steel Oldershaw packing to increase the surface area together with a superheater which was inclined at 15 degrees were used. The hold-up in the preheater and the vaporiser was calculated to be between 2 and 3 minutes which was considerably less than the hold-up of the Cathala still.

Davies (1971) and Gibson-Robinson (1977) further modified the Cathala still. The vaporiser is once more separated from the body of the still and a super-heater is also used. Another modification is the silvered evacuated jacket, used to reduce heat losses by radiation and convection. O'Donnell (1980) used the modified Cathala still of Gibson-Robinson (1977) to investigate the mixtures, ethyl acetate-n-butanol, acetic acid-n-methanol, acetic acid-ethanol and acetic acid-n-butanol, all at 760 mmHg and acetic acid-n-butanol at 119°C. The operation of the still requires the mixing of a superheated vapour and a preheated liquid, prior to entry into the still. It is an advantage to have each stream,

Figure 4.31 Cathala (1960) Flow Still

itself a mixture of the feed components, straddling the expected equilibrium composition, and thus the feed system to the still consists of two parts, each supplying both components.

The liquid is cooled by a water cooler and passes into a sampling section, where sampling by syringe is made. It then flows upwards, back through the cooler, and over an overflow device situated at a level just above the base of the still. This is to enable a liquid level to be maintained in the still and prevent bypassing of the vapour through the liquid cooler. The liquid then flows down into a 25 litre collection reservoir. The vapour stream flows through a condenser and then a condensate cooler, where it passes a sampling point, and flows to the collection reservoir (O'Donnell, 1980).

The flow stills have one disadvantage, large quantities of the feed components are needed although this disadvantage is offset by the fact that equilibrium can be reached in a relatively short time.

4.7 Other Methods

Although most comprehensive low pressure vapour-liquid equilibrium experimentation is done with circulation stills or with static cells, special techniques are also available.

Dew-point and bubble point methods have been used for a long time (Ramsay and Young, 1885; Feller and McDonald, 1950; Malanowski, 1982b). In its idealised form, a dew-point and bubble-point apparatus consists of a calibrated piston/cylinder assembly immersed in a constant temperature bath. A mixture of known composition is introduced to the apparatus, and the pressure of the system is determined as a function of volume. The dew-point and the bubble-point are found from breaks in the pressure against volume trace; the co-ordinates of the breaks define the molar volumes of the coexisting phases. Although dew-point and bubble-point methods are used primarily for high pressure equilibrium data, low pressure applications have been proposed. Dixon and McGlashan (1965) suggested a variation on the idealised procedure, in which the composition is not measured, but is instead calculated as part of the data reduction. The major drawback of the method is the difficulty of accurately measuring bubble-point pressures, because of their extreme sensitivity to even small amounts of dissolved gases. Dew-point pressure determinations, if the composition is also measured, constitute a related but alternative procedure. Brewster and McGlashan (1973, 1977) have applied this technique to mixtures at low pressure.

Kato et al. (1970) developed a completely new version of the dew- and bubble-point method. Their method is applicable to tertiary mixtures and is based on two relationships:

1. The bubble point of the liquid composition is equal to the dew-point of the equilibrium vapour mixture.
2. The condensation point of the liquid composition is the bubble-point of the equilibrium vapour composition.

An apparatus was constructed, which utilises a unique flow system through three stills where the bubble-points and dew-point condensation points are measured at a steady state. Kato et al. (1971& 1972) have used the technique on several mixtures.

Dew- and bubble-point methods used for measuring high pressure vapour-liquid equilibrium data have been reviewed by Schneider (1975), Young (1978) and Eubank et al. (1980).

Christian and his co-workers have explored novel ways of measuring low pressure vapour-liquid equilibrium data. Christian et al. (1960) used a static method incorporating a vapour density balance, obtaining isothermal p-y data. No sampling is required; liquid compositions are found by integration of the Gibbs-Duhem equation. Tucker and Christian (1979) devised an automated apparatus which produced isothermal p-y data. Sample addition is computer-activated; pressure measurements are made every three minutes, and when successive measurements agree to within 0.7 Pa, accurately reproducible quantities of a liquid are deliverable to the system through a chromatograph valve. A complete experiment, covering about half the liquid-composition range, takes about two hours.

A procedure known as gas chromatographic head-space analysis was originally proposed by Wichterle and Hala (1963), which was also used by Hachenberg and Schmidt (1977); more recently this method was applied by Shaw and Anderson (1983). The development of gas chromatography as a quantitative analytical tool has inspired a few recent designs in which the vapour phase is sampled directly. In gas chromatographic head-space analysis, precisely reproducible volumes of vapour are sampled from a closed container containing vapour in equilibrium with a liquid phase. Liquid compositions are determined gravimetrically, and peak areas are measured. Provided that the detector is operated in a linear range and that sampling procedures and operating conditions are carefully reproduced, the activity of species i in the liquid phase is approximately equal to the ratio

of peak areas $A_i / A_i^{'}$, where $A_i^{'}$ is determined for a vapour sample in equilibrium with pure liquid i. To the extent that vapour-phase non-ideailities can be ignored in the data reduction, the liquids need not be degassed. Sample sizes are small, and a complete binary mixture can be studied in a day (Abbott, 1986).

Chapter 5: Development of an Equilibrium Still to Work at Moderate Pressures up to 35 Bar

5.1 Introduction and background

Vapour-liquid equilibrium data are needed at higher pressures both for testing prediction methods such as UNIFAC and for the operation of distillation columns at higher pressures, especially for energy-integrated distillation schemes.

Equilibrium cells can be used to obtain vapour-liquid equilibrium data at higher pressures but, they require extensive back-up equipment largely for degassing the pure components, and the cell, and for charging the cell. To withdraw a vapour sample without condensation tends to upset the equilibrium state unless sampling is of very small arrangements. It was decided to use an equilibrium still based on a successful equilibrium still (the modified Raal, Code and Best still) of O'Donnell and Jenkins (O'Donnell (1980)) designed to run at pressures of one bar and less. This still was earlier discussed in some detail in chapter 4. Forced circulation of both liquid and vapour phases overcomes problems associated with natural convection at higher pressures. The problems of degassing the pure components and the cell, and for charging the cell do not arise with the liquid and condensate recirculation still.

Figure 5.1 shows a diagrammatic cross-section of the equilibrium chamber of the O'Donnell and Jenkins still. The success of this earlier still was due to the use, first, of an external Cottrell pump, which also acted as an insulating jacket, and second, to the fact that the liquid sample was produced by condensation as vapour from the equilibrium disengaging chamber bubbled through liquid in an internal annular chamber in the body of the still.

5.2 The development of the equilibrium cell of the Zain and Jenkins still (Mark I)

As in the earlier still, the equilibrium cell is made from borosilicate glass. As the equilibrium cell has to be contained in a steel pressure bomb (vessel), mounting the cell in the bomb would be made easier if the vapour left the bomb at its base. To do this in this early design an external vapour jacket surrounds the Cottrell pump annulus of the low pressure design, and a bottom connection to this forms the vapour line to the condenser and vapour sampling system. The residence time of vapour in the Cottrell pump was

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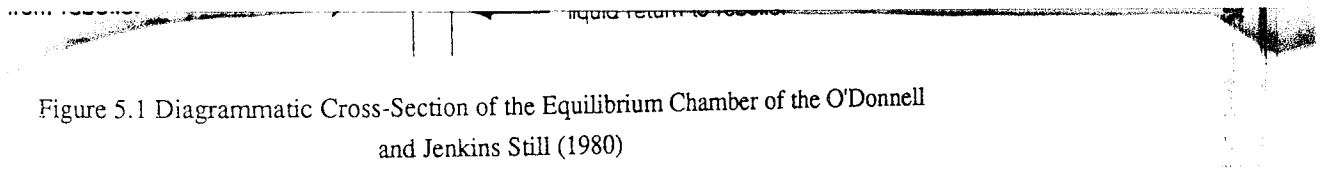

Figure 5.1 Diagrammatic Cross-Section of the Equilibrium Chamber of the O'Donnell and Jenkins Still (1980)

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Figure 5.2 Diagrammatic Cross-Section of the Equilibrium Chamber of the Zain and Jenkins Still (Mark I)

increased by providing a spiral of glass up the inner wall of the annulus forming the Cottrell pump. In constructing the cell, the most difficult criterion to meet was that of a small clearance between the two walls of this annulus and providing a spiral made this less critical. This equilibrium cell is shown in Figure 5.2.

5.3 The development of the equilibrium cell of the Zain and Jenkins still (Mark II)

Following the glass blowing of the Mark I equilibrium cell, inspection showed that modifications to this cell were necessary. This led to the design of the equilibrium cell (Mark II) shown in Figure 5.3. The modifications were:

(1) The arms of the cell were no longer at the same level. This avoids the difficulty in using the rotulex clips.

(2) The external vapour jacket was removed to make glass blowing easier.

(3) The annular gaps in the cell were to be smaller than those in the previous design.

(4) A simple feed arrangement was adopted at the base, again to simplify glass blowing.

The excess clearance both in the Cottrell pump and across the top of the cell would have jeopardised the proper functioning of the equilibrium cell, both in temperature measurement and in reaching equilibrium compositions. Figure 5.4 shows a diagrammatic cross-sectional elevation and plan of the Mark II Zain and Jenkins equilibrium cell.

5.4 The development of the equilibrium still

Figure 5.5 shows a diagrammatic representation of the Zain and Jenkins still. Natural convection to provide circulation through the still is not used. Instead, a small graphite gear pump capable of working at pressures up to 35 bar is used to feed the reboiler. This pump is supplied with low voltage DC power from a constant current power source to give a steady flow. The reboiler is annular in construction and made of 316 stainless steel. The central tube contains a cartridge heater of a nominal 210 wattage.

The flange at the base of the pressure bomb is made of 316 stainless steel. This has four holes through which connection to the still is made. Each hole has a bored-through NPT to Swagelok connector in it. The appropriate line passes through each and then is connected (for the liquid/vapour feed, the vapour and liquid offtake lines) to a Cajon glass-

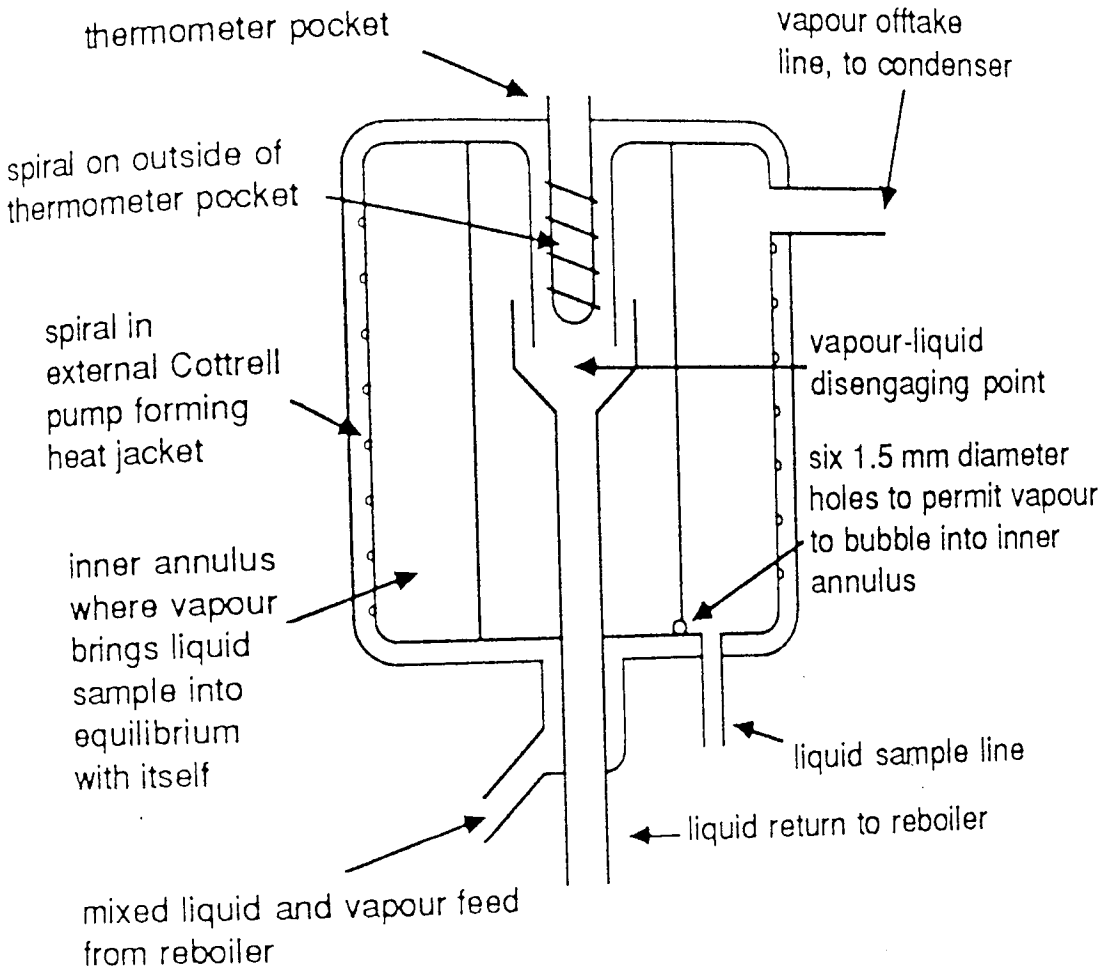

Figure 5.3 Diagrammatic Cross-Section of the Equilibrium Chamber of the Zain and Jenkins Still (Mark II)

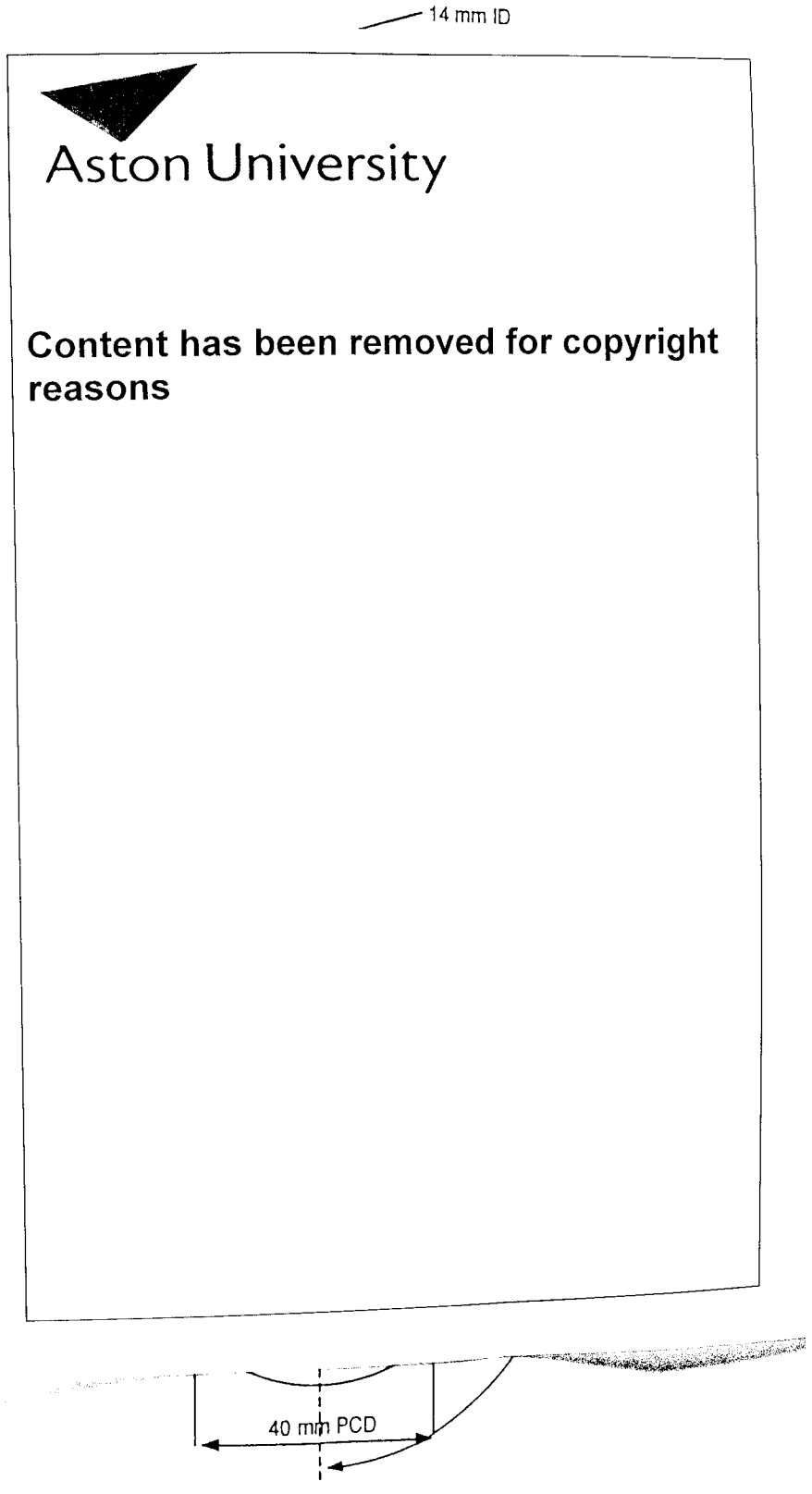

Figure 5.4 Diagrammatic Elevation and Plan of the Mark II Zain and Jenkins Equilibrium Cell

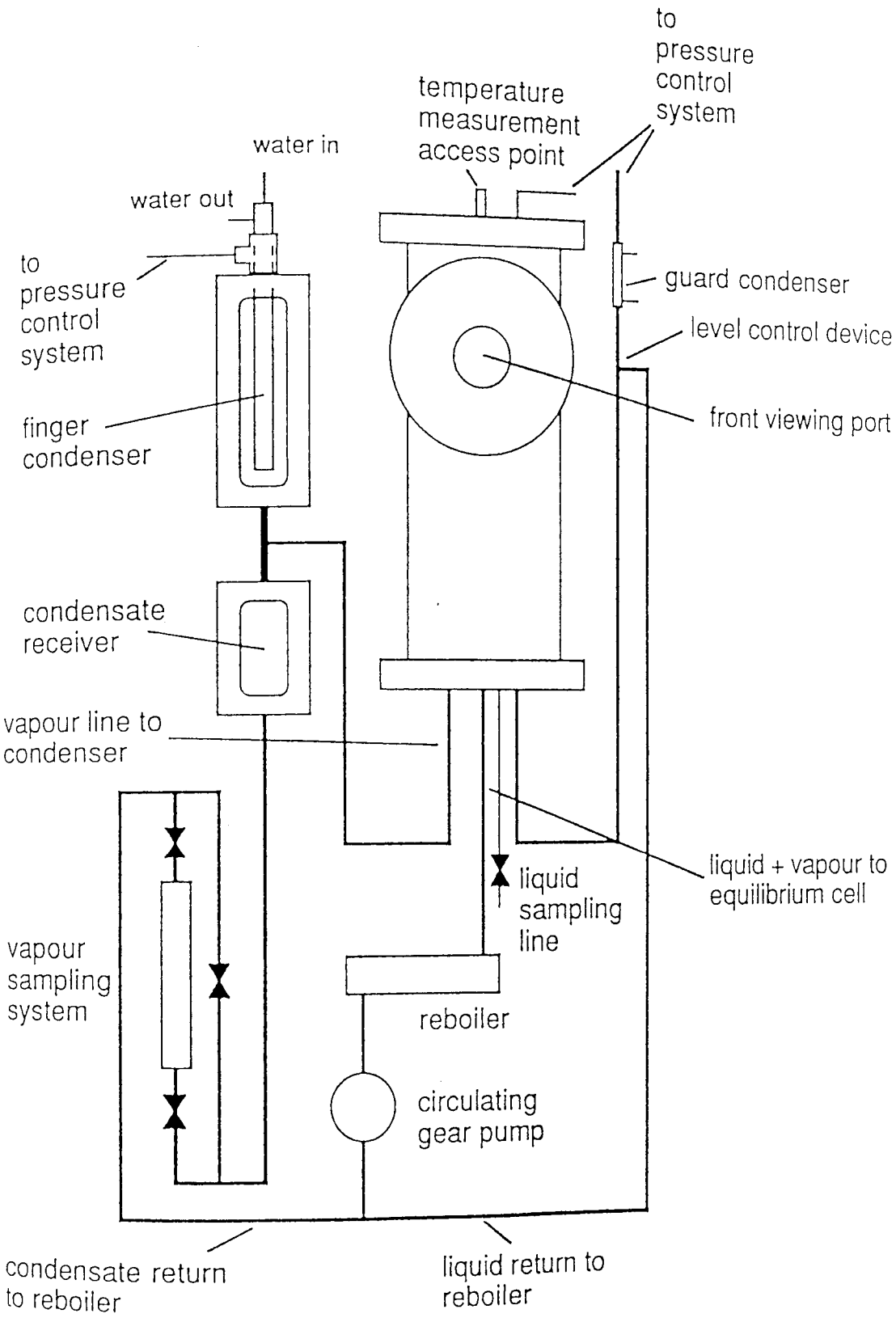

Figure 5.5 Diagrammatic Representation of the Zain and Jenkins Still

metal flexible connectors via standard Swagelok couplings. Each glass portion ends in a Rotulex cup which makes with the appropriate ball joint on the equilibrium cell.

The top flange of the pressure bomb is again made of 316 stainless steel. This flange has five holes to make it possible to connect the pressure bomb to the controlled pressure source and four thermocouples. Three of these measure the temperature in the pressure bomb below the equilibrium cell, near to it and above. The fourth, central thermocouple measure the boiling temperature in the equilibrium cell.

The condenser is a cold finger inside a Jergusen transparent gauge, and a smaller Jergusen transparent gauge below it acts as a condensate receiver and reservoir. These gauges are made of 316 stainless steel, with tempered glass sight glasses on both sides to permit the passage of light with an unobstructed view of practically the entire contents. The larger gauge is 184.2 mm long and the visible glass length is 146 mm, while the smaller gauge is 133.5 mm long and the visible glass length is 95.3 mm. From the condensate receiver and reservoir, the condensed vapour goes to a sampling loop before joining the liquid recycle from the overflow device. They then together flow to the circulating gear pump. This sampling loop is made of:

(i) The sampling chamber which is made of 316 stainless steel,

(ii) five Whitney valves, and

(iii) $^1/_8$ inch O.D 316 stainless steel tube from the condensate receiver to the circulating gear pump.

The final liquid sample is withdrawn through a 316 stainless steel capillary which runs up into the liquid sample chamber in the equilibrium cell. The sample is withdrawn through a small bore tube immersed in an ice bath into a sampling device. The vapour sample (as condensate) is trapped inside its sampling chamber and is then removed from the still for analysis.

The guard condenser prevents any escape of vapour into the pressure system from the liquid overflow from the equilibrium cell. The level control device is a 316 stainless steel T-piece used to provide a simple weir-type overflow. It is arranged so that the free liquid surface in the vapour-liquid separating cup in the equilibrium cell is at a suitable height, i.e. neither falling below the constant temperature zone in the equilibrium cell nor overflows into the central volume of the equilibrium cell, where it could be blown into the liquid sample annulus in the equilibrium cell.

One constant problem in equilibrium still work is knowing exactly what is happening inside the still. For example, in our case, if the still inventory is too large, then liquid may carry over from the disengaging device below the thermocouple pocket and mix with the liquid sample in contact with the vapour stream. Therefore we need to be able to see the liquid levels inside the equilibrium cell, something which also helps in following the progress of the run. To do this two windows are provided at the sides of the pressure bomb, but since these must not run at the temperature of the equilibrium cell itself, they are at the ends of the side arms, with further internal dividing glasses, close to the inner ends of the arms, reducing heat transfer by convection into the side arms. The bomb contents are viewed by placing a source of light (lamp) in front of a window at one side of the pressure bomb, and looking at the equilibrium cell through the window at the other side of the pressure bomb.

If the only heat source were the reboiler, the still would never come to equilibrium because of the high thermal capacity of the pressure bomb. So three Hedin electrical mat heaters each of a nominal 310 wattage are provided along the vertical length of the pressure bomb. These electrical heaters are suitable for continuous operation at any surface temperature up to 200°C. Their energy outputs are controlled separately through the use of three Variacs (contained in a panel) which were previously calibrated by measuring the voltage and the corresponding current at a particular Variac setting between 0 and 100. The load resistance (power) was then graphed as a function of Variac setting for these heaters (see Appendix 1). The heaters are lagged using Contronic Corporation mouldable wet felts (mats) and then sprayed with chrome aluminium spray paint. This insulation material provides a lightweight resilient and highly efficient thermal insulation. As noted earlier, three chromel-alumel thermocouples measure the temperature profile up the pressure bomb; and the heaters outputs are adjusted to maintain a nearly constant temperature profile, a degree or so above the equilibrium temperature measured in the equilibrium cell. The vapour line is also heated along its length to prevent condensation and the consequent high pressure drop in the line to the condenser. This is achieved by wrapping the vapour line around with a silicone-rubber encapsulated heating tape of a nominal 250 wattage. The heating tape is lagged using woven ceramic rope over-wrapped with woven ceramic self-adhesive tape. The reboiler is lagged using a mouldable wet mat and then sprayed with chrome aluminium spray paint. These heaters were also calibrated (see Appendix 1). The energy outputs of the vapour line heater and the reboiler heater are controlled separately through the use of two more Variacs.

Chapter 6: Experimental Work

6.1 Introduction

The experimental work has involved determination of vapour pressure data for pure ethanol and pure cyclohexane in the temperature range 77-124°C and 80-142°C respectively, using the developed equilibrium still. This equilibrium still was then used to investigate the binary mixture ethanol-cyclohexane isothermally at 83.29°C and 106.54°C; and isobarically at 1, 3 and 5 bar. As noted in chapter 1 the reasons for choosing the binary mixture ethanol-cyclohexane are:

(i) This binary mixture is a good model for looking at the temperature dependency of the UNIQUAC model.

(ii) It is an azeotropic mixture.

(iii) Boiling studies have been carried out using ethanol-cyclohexane mixture at 5 bar, but accurate vapour-liquid equilibrium data were not available at the time at this pressure (Jenkins, 1992a).

(iv) No comparable vapour-liquid equilibrium data can be found in the literature for the ethanol-cyclohexane mixture at pressures above 1 bar.

6.2 Materials

The ethanol used in this investigation was supplied by James Burrough (F.A.D.) Ltd. This was B.P. absolute alcohol 100 (ethyl alcohol 99.86% v/v minimum). The cyclohexane used in this investigation was supplied by Aldrich (99.9%, HPLC grade) with a water content of less than 0.01%. Prepared mixtures of different compositions of the binary mixture ethanol-cyclohexane were stored in 400 ml storage bottles over 4 A molecular sieves for dehydration.

6.3 Temperature control and measurement

The boiling temperature in the equilibrium cell is measured by a central thermocouple calibrated to ±0.02 K against a platinum resistance thermometer with a discrimination of 0.001 K. This in turn may be periodically checked against an RF bridge, (with a precision of ±0.0001 K) using a platinum resistance thermometer calibrated at the National Physical Laboratory to IPT'68. For details of the calibration of the central thermocouple and the other three thermocouples see Appendix 2. In outline, by using a Croydon Precision

Instruments Potentiometer type P3, a Guildline digital platinum resistance thermometer with a precision of ±0.001 K and a Grant Instruments (Cambridge) Ltd heater/stirrer, the central thermocouple was calibrated and a calibration graph of temperature/°C against the electromotive force/mV was plotted on an A2 graph paper to provide greater resolution in the interpolation of the equilibrium temperature (see Appendix 2).

6.4 Pressure control and measurement

The pressure control system is represented diagrammatically in Figure 6.1. For operating pressures below 3.5 bar, the pressure was measured by a Druck digital pressure indicator (DPI 140) and controlled using a Fairchild pressure regulator to an accuracy of two parts in 10000 of a bar using a vibrating cylinder sensor with accuracy of ±0.015% of full scale. For operating pressures above 3.5 and up to 35 bar (g), the pressure was measured and controlled by a Druck digital pressure indicator/controller (DPI 500) accurate to ±0.01 bar. The accuracy of this controller may be checked at any time by an on-line air-operated Budenburg dead weight tester also accurate to ±0.01 bar. For this weights are placed on the piston pan of the gauge to give the desired pressure when the piston is riding high in the cylinder. Thus with the weights on the piston floating free and spinning (to nullify frictional forces) in the cylinder, then two nitrogen cylinders are used, one for pressures up to 3.5 bar and the other for pressures above 3.5 bar. The two sides of the pressure system are connected together. The pressure system was connected to three points on the equilibrium still, at the top flange of the pressure bomb, to the finger condenser and to the guard condenser. The connections between the pressure bomb and the condenser were $^3/_8$ inch O.D tubing as against $^1/_4$ inch O.D. tubing used in the pressure system to ensure that the bomb pressure and that supplied to the glass equilibrium cell were never appreciably different.

6.5 Analysis

Density measurement is used as an analytical method for determination of the composition of liquid phase and vapour phase samples. For this purpose, calibration mixtures of ethanol and cyclohexane were prepared by successive weighing of pure components. Then, their densities were determined at 25°C using an Anton Paar densimeter (DMA 60) with two DMA 602 cells (with a potential precision of better than 1 in 10^6). The temperature of the densimeter measuring cells was controlled to ±0.01 K using a heater/controller (Heto Birkerod Denmark). The densimeter calibration data for the binary mixture ethanol-cyclohexane are reported in Appendix 3. The data were plotted on an A1 graph paper to provide greater resolution in the interpolating of composition. The plot

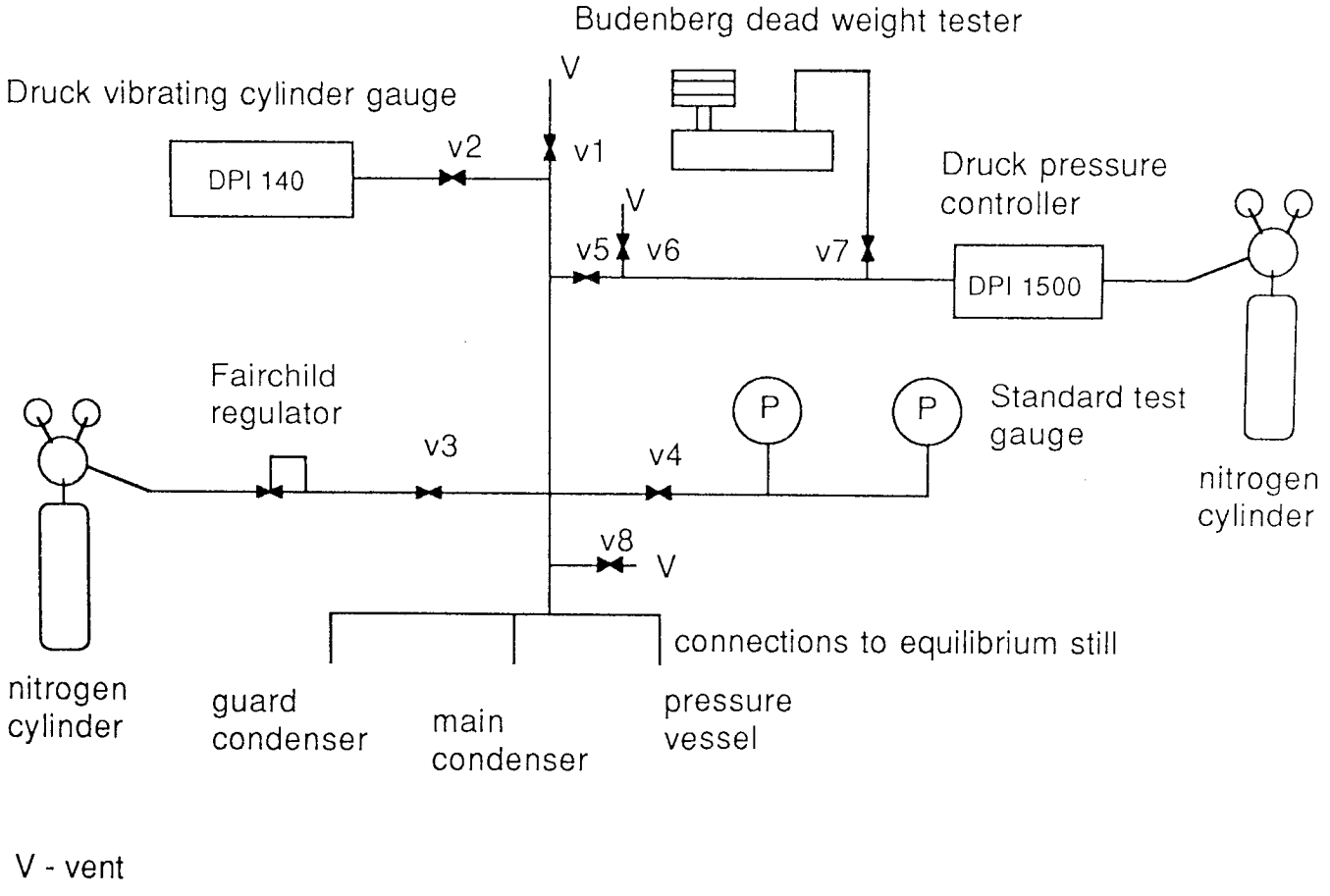

Figure 6.1 Pressure control system.

outer annulus (within the glass spiral) (these acting as part of the Cottrell pump) and flows across the top of the cell, where it impinges on the thermometer pocket and runs down the spiral mounted on it. The liquid then separates from the vapour in the disengaging cup and flows out of the cell through the overflow device and then rejoins the recycled condensate. The vapour passes between the inner surface of the disengaging cup and the vapour shield around the thermometer pocket, and then bubbles through six small holes at the bottom of the central chamber into the middle annulus. Liquid trapped in this annulus is brought to equilibrium with the vapour bubbling through it, and provides the final liquid sample. The vapour leaves this annulus and passes to the total condenser, and then to the condensate receiver.

It should be noted that the desired operating state is that the condensate level is maintained within the visible part of the condensate receiver. Further, during the development stage, the level of the overflow device was adjusted so as to maintain the liquid level inside the cell visible in the lower part of the disengaging cup. Note that this level also depends on the rates at which the liquid phase is circulated and the boil-up rate used, i.e., the proportion of the liquid feed which is vaporised, see discussion below.

Outline operating instructions are given in Appendix 7.

Chapter 7: Discussion of Results

7.1 Saturated Vapour Pressure Measurements for Pure Ethanol and Pure Cyclohexane

In order to assess the capability of the new equilibrium still, saturated vapour pressures for pure ethanol at 77.58, 96.50, 108.50, 117.48 and 124.43°C; and pure cyclohexane at 79.95, 105.08, 120, 132.58 and 141.42°C have been determined. The vapour pressure data of this work are reported for pure ethanol and pure cyclohexane in Table 7.3 and Table 7.6 respectively. Table 7.1 lists saturated vapour pressures of pure ethanol (Scatchard, 1964) and Table 7.5 lists saturated vapour pressures of pure cyclohexane (Scatchard, 1964); both measured at 5, 20, 35, 50 and 65°C. Saturated vapour pressures of pure ethanol (Larkins and Pemberton, 1976) at 25, 35 and 50°C are reported in Table 7.2. An extended form of the Antoine equation (Appendix 6) was used to give calculated saturated vapour pressures of both pure ethanol and cyclohexane in the temperature ranges (15-130°C) and (15-143°C) respectively, they are listed in Tables 7.4 and 7.7.

The saturated vapour pressures at the different conditions for pure ethanol and cyclohexane were plotted in the form of log P against (1/T) (see Figure 7.1 and Figure 7.2). The calculated values for pure ethanol gave a line through all the points, whilst in the plot for pure cyclohexane, the calculated saturated vapour pressures which were outside the declared range of the Antione equation used did not lie on a straight line through all the data points.

Table 7.1 Saturated vapour pressures of pure ethanol (Scatchard, 1964)

Temperature/°C	Saturated vapour pressure/mmHg
5	16.798
20	43.990
35	103.210
50	221.200
65	437.724

7.2 Initial data screening

For each experimentally determined data set, initial screening of the data was carried out by using a (y - x) against x plot. While these data plots could not be compared with similar

Table 7.2 Saturated vapour pressure of pure ethanol (Larkins and Pemberton, 1976).

Temperature/°C	Saturated vapour pressure/mmHg
25	59.378
30	79.176
50	216.653

Table 7.3 Saturated vapour pressures of pure ethanol (this work)

Temperature/°C	$\left(\frac{1}{T}.10^3\right)/K^{-1}$	Vapour pressure/bar	log P
77.58	2.8512	1.0016	0.00069
96.50	2.7053	2.0293	0.30735
108.50	2.6202	3.0357	0.48226
117.48	2.5599	4.10	0.61278
124.43	2.5152	5.00	0.69897

Table 7.4 Calculated vapour pressures of pure ethanol using an extended form of the Antoine equation (see Appendix 6)

Temperature/°C	$\left(\frac{1}{T}.10^3\right)/K^{-1}$	Vapour pressure/bar	log P
15	3.4704	0.0431	-1.36552
40	3.1934	0.1791	-0.74690
55	3.0474	0.3732	-0.42806
70	2.9142	0.7222	-0.14134
85	2.7921	1.3120	0.11793
100	2.6799	2.2579	0.35370
110	2.6099	3.1583	0.49945
120	2.5436	4.3354	0.63703
130	2.4805	5.8502	0.76717

Table 7.5 Saturated vapour pressures of pure cyclohexane (Scatchard, 1964)

Temperature/°C	Saturated vapour pressure/mmHg
5	36.457
20	77.511
35	150.641
50	271.960
65	461.259

Table 7.6 Saturated vapour pressures of pure cyclohexane (this work)

Temperature/°C	$\left(\frac{1}{T}.10^3\right)/K^{-1}$	Vapour pressure/bar	log P
79.95	2.8321	0.9872	-0.00559
105.08	2.6439	2.0018	0.30142
120.00	2.5436	3.0045	0.47777
132.58	2.4647	4.09	0.61172
141.42	2.4121	5.09	0.70672

plots due to the lack of such data in the literature, they identified a number of points which would need special consideration in the data reduction process.

Both these plots and initial reduction of the data (for details see below) showed that it was probable that the y-values were not of high an accuracy as the x-P-T data. This consideration was confirmed by the thermodynamic consistency test described below. Thus the final data sets produced from this work are essentially x-P-T sets, with y-values deduced during the data reduction process.

7.3 The application of a consistency test to the experimental vapour-liquid equilibrium data

In the data reduction the default standard state liquid fugacity curve was not used, instead either an extended form of the Antoine equation was used or a two-constant Antoine fitted manually to the experimental saturated vapour pressures of this work. The extended

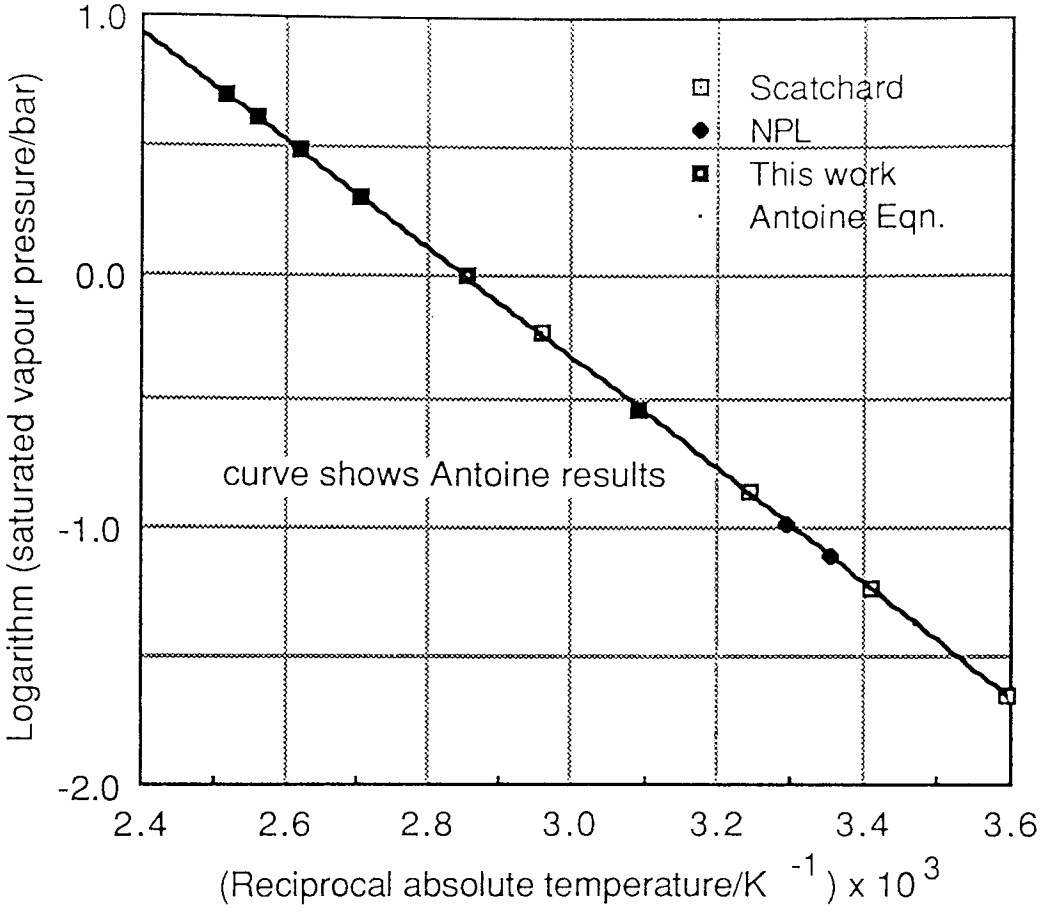

Figure 7.1 Plot of log P against 1/T for pure ethanol.

Antoine approach was used for ethanol as a comparison of the results obtained using the parameters reported by Prausnitz et al. (1967) with the experimental data reported here showed good agreement, even at 5 bar (see Figure 7.1). This was not true for cyclohexane and so for each data set a fresh pair of Antoine constants were determined (see Figure 7.2). For the set at 1 bar the extended Antoine equation was retained as this was within the quoted range of the equation (Prausnitz et al., 1967).

Table 7.7 Vapour pressure of pure cyclohexane using an extended form of the Antoine equation

Temperature/°C	$\left(\frac{1}{T}.10^3\right)/K^{-1}$	Vapour pressure/bar	log P
15	3.4704	0.0812	-1.09044
40	3.1934	0.2459	-0.60924
60	3.0017	0.5184	-0.28534
75	2.8723	0.8489	-0.07114
90	2.7537	1.3257	0.12245
110	2.6099	2.2589	0.35389
115	2.5763	2.5550	0.40739
125	2.5116	3.2346	0.50982
130	2.4805	3.6215	0.55889
135	2.4501	4.0422	0.60662
138	2.4322	4.3115	0.63463
143	2.4029	4.7900	0.68034

The experimental vapour-liquid equilibrium data sets at 83.29°C, 106.54°C, 1 bar, 3 bar and 5 bar have all been tested for thermodynamic consistency by use of the Barker method (Barker, 1953; Prausnitz et al., 1980). The basis of the Barker method is that an integrated form of the Gibbs-Duhem equation (e.g. the UNIQUAC equation) is used to relate the liquid-phase activity coefficients to the mole fractions in a binary mixture. In the usual Barker method, the parameters in the integrated form of the Gibbs-Duhem equation used are adjusted by a non-linear least-squares fitting procedure until a minimum error between the experimental and calculated total pressures is obtained. In essence, the Barker method uses only the x-P-T data and assumes that the T and x measurements are error free.

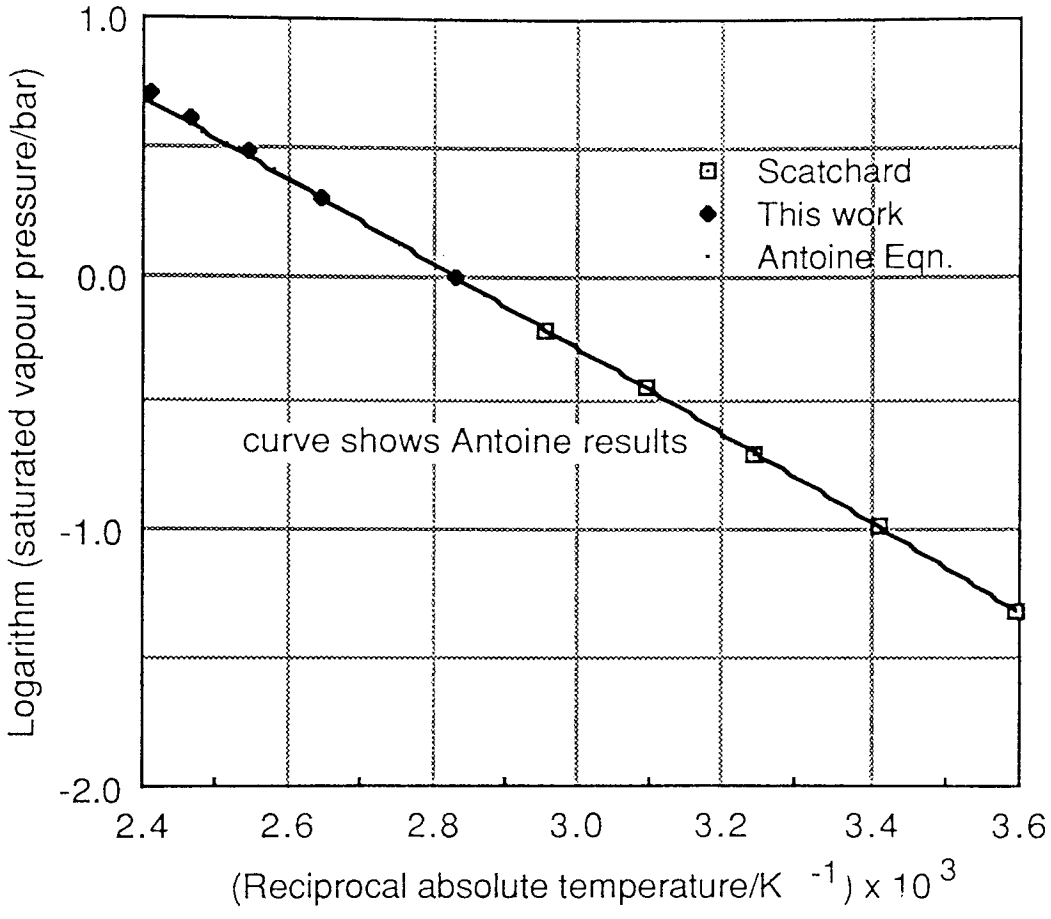

Figure 7.2 Plot of log P against 1/T for pure cyclohexane.

Since experimental uncertainty is likely to be greater for y (Van Ness et al., 1973), prudence suggests that the preferred procedure for data reduction is one based on just the x-P-T data. Values of y calculated from the correlation can then be compared with measured values as a check on the thermodynamic consistency of the vapour-liquid equilibrium data. Thus it was decided to correlate all the x-P-T data using the UNIQUAC equation (Abrams and Prausnitz, 1975) to represent the liquid-phase non-ideality, but to vary the procedure slightly by minimising the differences between estimated and measured values for x, P and T, not just for the pressures. As noted earlier, the original equation has two adjustable binary parameters. The two adjustable binary parameters were estimated by a non-linear regression method based on the maximum-likelihood principle (Anderson et al., 1978) as set out in Prausnitz et al. (1980). The computer program used was VPLQFT which is capable of correlating binary vapour-liquid equilibria at low to moderate pressures. The most important feature of the maximum-likelihood principle is that it attempts properly to account for all measurement errors.

7.4 Ethanol-cyclohexane at 83.29°C

In the data reduction of the isothermal data at 83.29°C, none of the experimental points were discarded since the (y - x) versus (x) plot (Figure 7.3) did not indicate strongly that any should be. The plot shows the existence of an azeotrope as would be expected. The experimental points between $x_{meas} = 0.1687$ and 0.8195 lie almost on a straight line. The composition of the azeotrope (y = x) can not be estimated accurately since there is more than one possibility for drawing a straight line crossing the x-axis. An approximate value for the azeotrope is 0.517(4). The temperature of the azeotrope is 83.29°C since the vapour-liquid equilibrium data were measured at 83.29°C. From Table A5.1, it can be seen that the pressure fit is good and its root mean squared deviation has the value 4.5 mmHg; and the temperature fit is also good with R.M.S. deviation of 0.52°C whilst the ethanol liquid composition has an R.M.S. deviation of 0.0062. The vapour-phase composition fit is clearly not as good.

This confirms the decision to regard the data as being a reasonable x-P-T set and reporting only the y-values estimated in this fit. The x-P-T set was fitted quite well by the two-parameter UNIQUAC equation. The fitting package used was not developed in this programme and on using it, a hither-to undetected bug was disclosed in that attempts to use modelling equations with more than two parameters cause the program to fail. Time did not permit resolution of this problem.

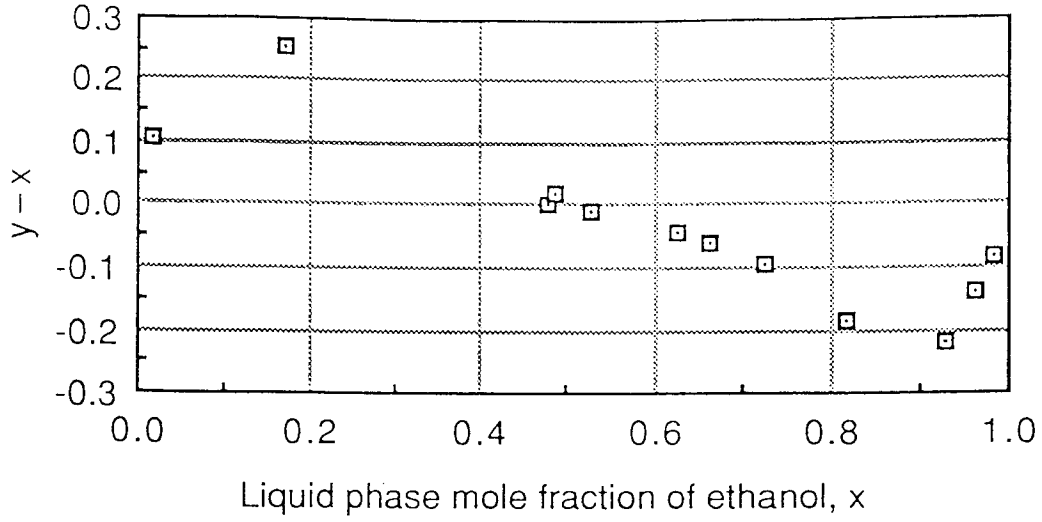

Figure 7.3 Plot of (y - x) against x for ethanol-cyclohexane at 83.29 °C

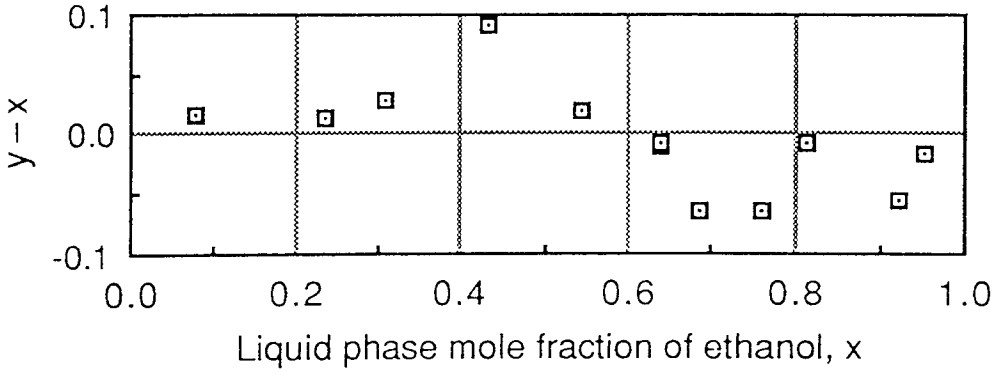

Figure 7.4 Plot of (y – x) against x for ethanol-cyclohexane at 106.54 °C

7.5 Ethanol-cyclohexane at 106.54°C

Three experimental points were discarded as suggested by the (y - x) versus (x) plot (Figure 7.4). These correspond to ethanol mole fractions in the liquid phase of 0.2350, 0.3087 and 0.8135. The distribution of the (y - x) versus (x) points shows the existence of an azeotrope. The experimental points corresponding to x_{meas} 0.4338, 0.5475 and 0.6900 give the best straight line across the middle points. An approximate value of the azeotrope composition is 0.5670 at 106.54°C. From Table A5.2, it can be seen that the pressure fit is good and has an R.M.S. deviation of 3.7 mmHg. The temperature fit is reasonably good (an R.M.S. deviation of 0.68°C). The ethanol liquid-phase mole fraction deviations were very small except those of x_{meas} of 0.0795, 0.9238 and 0.9530 which gave an R.M.S. deviation of 0.0200. Again the vapour-phase composition fit is not good (see Table A5.2). The vapour R.M.S. deviation is 0.0399 and the individual vapour-phase deviations were all except one higher than the criterion $\Delta y < 0.01$. However, the x-P-T set again appears reasonable.

7.6 Ethanol-cyclohexane at 1 bar

None of the experimental points were discarded, as suggested by Figure 7.5, the plot of the (y-x) versus (x). From Figure 7.5, it can be seen that all the experimental points could lie on a reasonably smooth curve. It can also be seen that none of the vapour-phase deviations met the criterion $\Delta y < 0.01$ (Table A5.3). The root mean squared deviation for the vapour-phase composition is 0.0674. Generally, the individual liquid-phase composition deviations and the R.M.S. deviation (= 0.00054) indicate a very good fit for the measured liquid phase composition values. The equilibrium temperature fit is also good since the R.M.S. deviation is equal to 0.20°C. The operating pressure fit is equally good and has an R.M.S. deviation value of 2.74 mmHg. In Figure 7.5, the points corresponding to the ethanol liquid mole fractions 0.4337, 0.5155, 0.6820, 0.8480 and 0.8752 lie quite well on a straight line. The azeotrope composition has an approximate value of 0.478(9). The temperature of the azeotrope is about 64.0°C. Again the results of the fit show that a reasonable x-P-T set has been determined.

Keshpande and Lu (1963) determined vapour-liquid equilibrium data for ethanol-cyclohexane at 760 mmHg. Table A5.6 lists the results of a fit of the data using the same correlating procedures (Jenkins, 1992b). The azeotrope composition was 0.4310 at an equilibrium temperature of 64.77°C. Also, in their data, a y-value of 0.4310 (the same as that of the azeotrope) corresponded to an x-value of 0.4030. The vapour-phase compositions of Keshpande and Lu data were generally less accurate than the liquid-phase

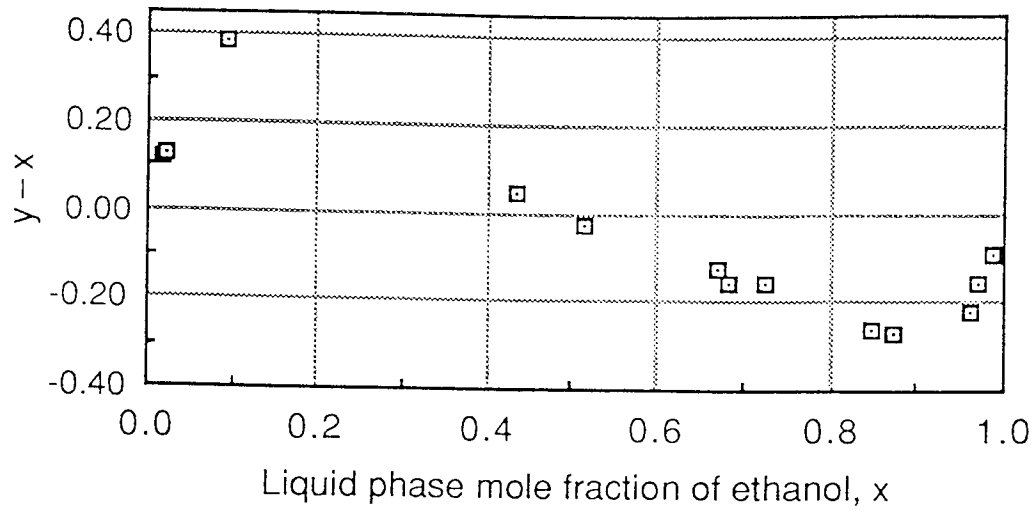

Figure 7.5 Plot of (y – x) against x for ethanol-cyclohexane at 1 bar.

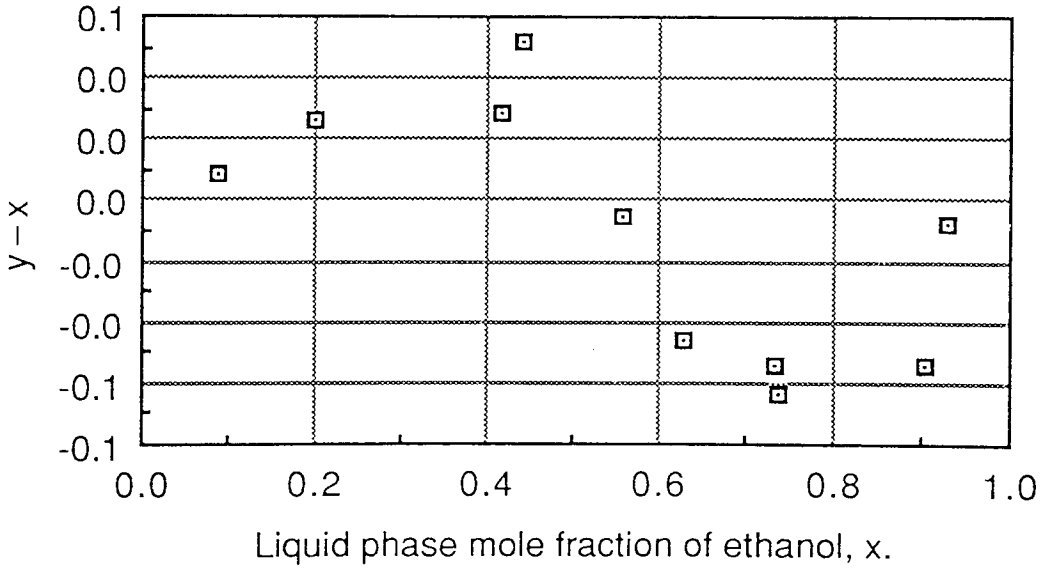

Figure 7.6 Plot of (y – x) against x for ethanol-cyclohexane at 3 bar

compositions, a pattern observed in our work. Greater accuracy in both the vapour-phase and liquid-phase compositions tends to be obtained in the middle range of the data. This pattern is also observed in the data of this work.

7.7 Ethanol-cyclohexane at 3 bar

Two experimental points were discarded for the 3 bar pressure data. These correspond to x_{meas} = 0.4436 and 0.9307. Figure 7.6 shows the distribution of the (y - x) versus (x) values. From Table A5.4, it can be seen that the root mean squared deviations for the ethanol liquid composition and vapour composition values have not met the general criterion of $\Delta x < 0.01$ and that of $\Delta y < 0.01$. These values were 0.133 and 0.1040 respectively. The equilibrium temperature fit was not good and has an R.M.S. deviation value of 1.22°C which is high. The operating pressure fit was bad and has an R.M.S. deviation value of 63.44 mmHg. Figure 7.6 shows the existence of an azeotrope whose composition is difficult to estimate from the plot. An approximate value of the azeotrope composition is 0.539(4) at an approximate equilibrium temperature of 96.3°C.

Table 7.8 Azeotrope composition-temperature data for ethanol-cyclohexane

Operating condition	Estimated azeotrope composition (Ethanol) (x = y)	Temperature (°C)
1 bar	0.478(9)	64.0*
83.29°C	0.517(4)	83.29
3 bar	0.539(4)	96.3*
5 bar	0.586(0)	114.8*
106.54°C	0.567(1)	106.54

* Estimated temperature

Evaluation of the operating procedure and a check on the raw data do not suggest how this bad fit has arisen. It may be that fitting with a more complex model would enable a better fit to be obtained but, as noted above, this is not feasible at the moment.

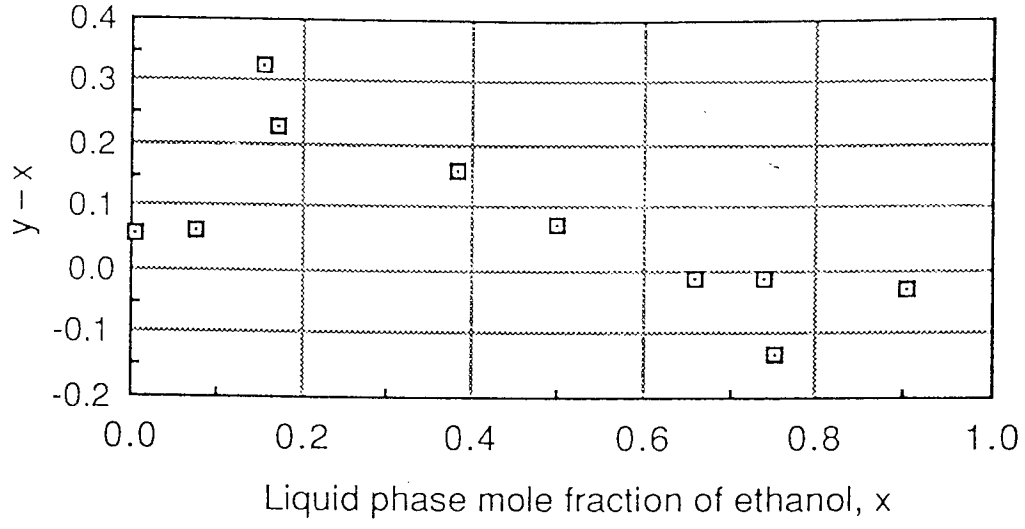

Figure 7.7 Plot of (y – x) against x for ethanol-cyclohexane at 5 bar.

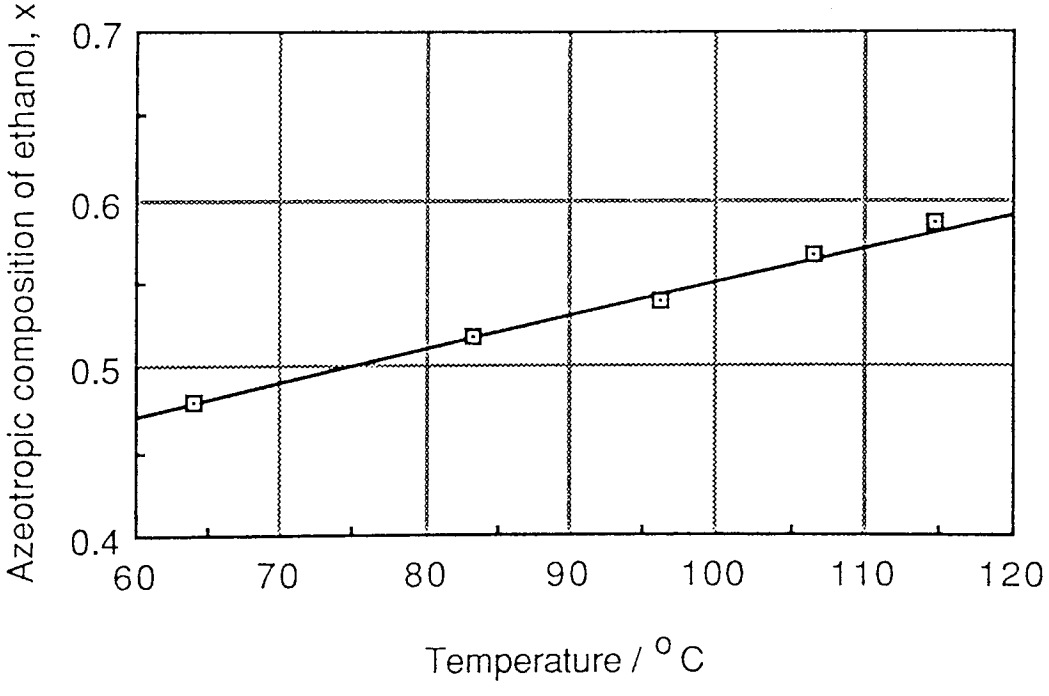

Figure 7.8 Plot of azeotrope composition against temperature for ethanol-cyclohexane.

7.8 Ethanol-cyclohexane at 5 bar

Two experimental points were discarded for the 5 bar pressure data. These correspond to x_{meas} = 0.1725 and 0.9048. Figure 7.7 shows the distribution of the (y - x) versus (x) values. An almost straight line could be drawn through the points corresponding to the measured ethanol liquid-phase composition values 0.1563, 0.3837, 0.5005 and 0.7505. Figure 7.7 shows an azeotrope which has an approximate composition of 0.586(0). The equilibrium temperature of this azeotrope at the operating pressure (5 bar) is approximately 114.8°C. From Table A5.5, it can be seen that the operating pressure fit and the equilibrium temperature fit are both good. The root mean squared deviations are 2.04 mmHg and 0.56°C. Overall, the ethanol liquid-phase composition fit is good and has an R.M.S. deviation value of 0.0041 whilst that of the vapour-phase is 0.06 which indicates that the vapour-phase composition fit is once again not good. Again we deduce that a reasonable set of x-P-T data have been determined.

7.9 Ethanol-cyclohexane Azeotope Compositions as a Function of Pressure

Table 7.8 lists the estimated azeotrope compositions of ethanol-cyclohexane mixtures and their corresponding boiling temperatures.

Figure 7.8 shows a plot of the estimated azeotrope composition of ethanol-cyclohexane against temperature. All the points lie on or close to a smooth curve.

7.10 Review of the Ethanol-cyclohexane Vapour-Liquid Equilibrium Data

Overall we can state that of the five data-sets, four provide reasonable x-P-T data. That reliable y-values were not obtained is unfortunate; a review of the construction of the equilibrium cell and the operating conditions suggest reasons why this outcome was obtained. These are discussed below.

A review of the still design and operation brought out the following points:

(i) In the cell as built, the clearance between the vapour shield around the thermocouple pocket and the vapour-liquid disengaging cup was only a millimetre or so. As a result only quite low liquid and vapour flows could be used without liquid being carried over from the the disengaging cup.

(ii) The still as a whole has a large inventory, of the order of 200 ml of liquid.

(iii) No means of stirring either the condensate receiver or the sample volume were provided.

Points (i), (ii) and (iii) together suggest that the $1^1/_4$ to $1^1/_2$ hour equilibrium period, based on experience with the one atmosphere pressure still, was too short. The one atmosphere still operates with much higher flows of vapour and liquid and has a lower inventory (about half). Further, experience in other laboratories (Jenkins, 1992c) suggests that pressure equipment in any case takes longer to reach equilibrium. In a subsequent section we discuss how these problems may be overcome.

Chapter 8: Conclusions and Recommendations

8.1 Conclusions

Saturated vapour pressures for pure ethanol at 77.58, 96.50, 108.50, 117.48 and 124.43°C; and for pure cyclohexane at 79.95, 105.08, 120.00, 132.58 and 141.42°C have been determined in order to assess the capability of the new equilibrium still. The initial measurements on the saturated vapour pressures of pure ethanol and cyclohexane showed that accurate boiling points could be determined.

Of the five sets of vapour-liquid equilibrium data measured for ethanol-cyclohexane (at 83.29°C, 106.54°C, 1 bar, 3 bar and 5 bar), four (the two isothermal, and those at 1 bar and 5 bar) when assessed by the Principle of Maximum Likelihood (Prausnitz et al., 1980) appeared to provide reasonable x-P-T sets but not x-y-P-T sets, the y-values giving much higher standard deviations. This outcome is satisfactory at this stage of the development of the equilibrium still. The design modifications identified below should enable consistent x-y-P-T sets to be obtained. No reason has been found which account for the rogue data-set at 3 bar. While one would expect such a data-set to be the result of consistent error in experimental technique, this seems unlikely as these data were measured piece-meal amongst the rest (see above).

As noted in Chapter 7, the failure to obtain vapour compositions was due to insufficient time allowed for the vapour sample to reach the final equilibrium value. This in the present design is in part due to the higher material inventory in this still as opposed to the atmospheric still and the lower rates of vapour and liquid circulation achievable due to the small clearances in the disengaging cup. The lack of any means to stirring the contents of the condenser receiver and the sampling volume added to the problem, thus the following recommendations are made.

8.2 Recommendations

(1) The use of a stirring loop to provide adequate mixing of the condensate.
(2) The use of larger clearances within the disengaging cup in the equilibrium cell.

These suggestions should shorten the length of time required to reach vapour-liquid equilibrium in the still. One suggested idea is detailed in Figure 8.1. Here an additional

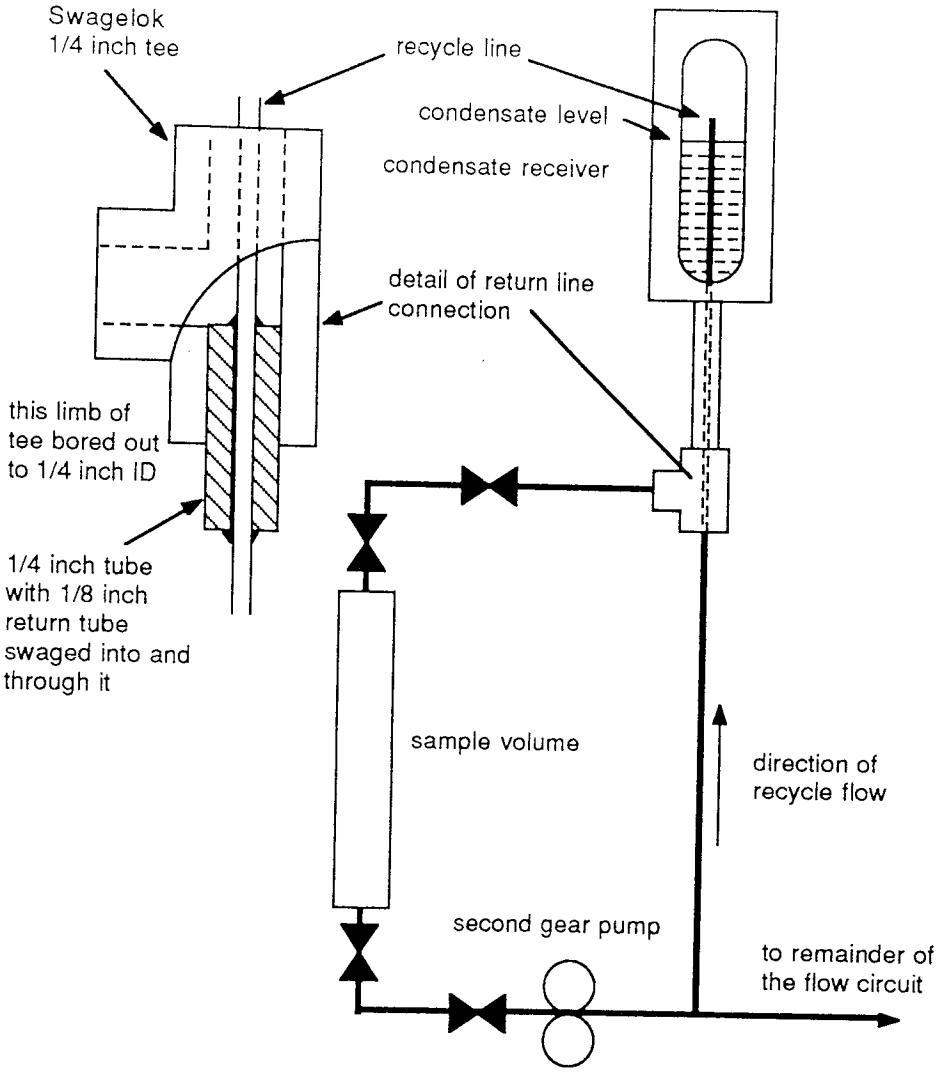

Fig. 8.1 Proposed method for adequate mixing of the condensate in the condensate receiver and in the sample volume.

gear pump circulates liquid rapidly through the condensate receiver and the sample volume. The construction should be such as to eliminate any dead spaces (see details in Figure 8.1). That equilibrium is being attained could be monitored by the use of the Anton Paar densimeter on-line, any one run could then be continued until a constant density was achieved . Operation of the still would be made easier by mounting one or more thermocouples on the vapour line to measure the temperature of the line, so as to avoid burnout of the heater on this line. The use of miniature platinum resistance thermometers instead of thermocouples is another possible development, especially if operation under computer control is contemplated.

For future work on the same binary mixtures, more points (up to, say, 20) for each set of conditions should be measured, this will enable the behaviour of the mixture close to the azeotrope to be examined in more detail. It is recommended that other types of mixtures are investigated after the recommended modifications.

Nomenclature

a – Van der Waals constant a

a_i – Activity of component i

a_{ii} – Energy size parameter

a_{12} – Interaction parameters

a_{112} – Interaction parameters

a_{mn} – UNIFAC group interaction parameter for groups m and n

A, B – Adjustable parameters in Van Laar and similar equations

A – First virial coefficient

A_K – Van der Waals group surface area

A_{nm} – Constant in temperature-dependence expression for UNIFAC

b – Van der Waals constant

b_{ii} – Molecular size parameter

B – Second virial coefficient

B_{ij} – Mixture cross second virial coefficient for components i and j

B_{nm} – Constant in temperature-dependence expression for UNIFAC

C – Third virial coefficient

C, D – Adjustable parameters in Margules and similar equations

D – Fourth virial coefficient

E_i – Energy required to vaporize one mole of component to infinite volume

f_i – Fugacity of component i

f_i^o – Standard state fugacity of component i

f_i^L – Fugacity of component i in liquid phase

f_i^V – Fugacity of component i in vapour phase

f_i^* – Standard state fugacity of component i in liquid phase

g – Interaction energy in NRTL equation

g^E – Molar Gibbs excess energy

G – Gibbs free energy

G – Parameter in NRTL equation

G^E – Excess Gibbs energy

h^E – Molar excess enthalpy

h_i – Molar enthalpy of component i

h^* – Standard state enthalpy

H – Enthalpy

H^E – Excess enthalpy

$\overline{H}_i$ – Partial molar enthalpy of component i

K_i – Equilibrium ratio

l – Auxiliary relationship in UNIQUAC equation

n_i – Number of moles of component i

n_T – Total number of moles

P – Pressure

P_{Ci} – Critical pressure of component i

p_i^{sat} – Saturated vapour pressure of component i

p_i – Partial pressure of component i

q – Heat exchange

q_i – Pure component molecular surface area of component i in UNIQUAC equation

q_1 – Effective volume, surface solubility parameter for component 1

q_2 – Effective volume, surface solubility parameter for component 2

q_k – Van der Waals group surface area

Q_i – Group surface area parameter of group i in UNIFAC equation

r_k – Van der Waals group volume

R – Universal gas constant

R_i – Group volume parameter of group i in UNIFAC method

S – Entropy

S^E – Excess entropy

s^E – Molar excess entropy

T – Temperature

T_C – Critical temperature

T_R – Reduced temperature

U – Internal energy

U_{jj} – Interaction energy between two like segments in UNIFAC

v – Volume

v_i – Molar volume of i'th component

v_i^L – Specific volume of pure liquid i

V_{wk} – Van der Waals group volume for group k

V_i – Partial molar volume of i'th component

x_i – Mole fraction of component i in liquid phase

x_{12} – Local mole fraction in liquid phase

X_i – Group fraction of group i in liquid phase

y_i – Mole fraction of component i in vapour phase

z – Coordination number

z_1 – Volume fraction of component 1 in liquid phase

z_2 – Volume fraction of component 2 in liquid phase

Z – Compressibility factor

Z_C – Compressibility factor at critical point

Greek letters

α – Parameter in NRTL equation

α_{ij} – Relative volatility

α_{12} – Binary adjustable parameter

γ_i^C – Combinational activity coefficient

γ_i^R – Residual activity coefficient

γ_i – Activity coefficient

Γ_k – Residual activity coefficient of group k

Γ_{ki} – Residual activity coefficient of group k in reference solution of type i only

δ_i – Solubility parameter

δ – Average solubility parameter

Δh_m – Enthalpy change on mixing

Δv_m – Volume change on mixing

θ – Surface area fraction for UNIQUAC equation

Θ – Group surface area fraction for UNIFAC method

λ_{ij} – Boltzman factor parameter

Λ – Adjustable parameter in Wilson equation

μ_i – Chemical potential of i'th component

μ_i^o – Standard state chemical potential in gaseous phase

μ_i^* – Standard state chemical potential in liquid phase

ν_{ki} – Number of groups of type k in molecule i

ϕ – Fugacity coefficient

φ – Interaction parameter

φ – Volume fraction for UNIFAC method

Ψ – Binary parameter for Wilson equation in the UNIFAC method

τ – Parameter in NRTL and UNIQUAC equations

ω – Acentric factor

Ω_a – Proportionality constant in Redlich-Kwong equation of state

Ω_b – Proportionality constant in Redlich-Kwong equation of state

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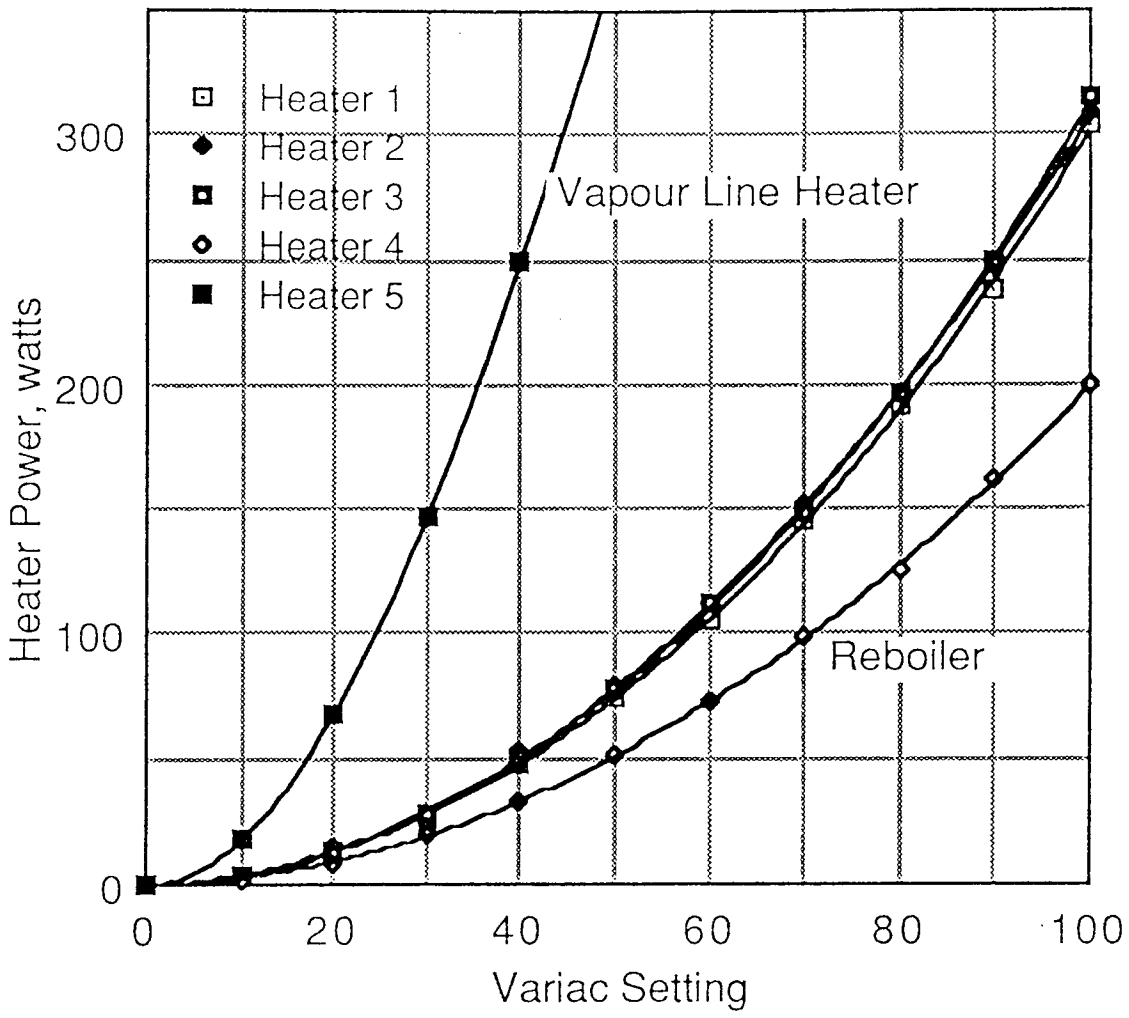
Appendix 1: Heater Calibrations

The energy outputs of heaters 1, 2, 3, 4 and 5 are controlled separately through the use of five Variacs (contained in a panel). These heaters were previously calibrated by measuring the voltage and the corresponding current at a particular Variac setting between 0 and 100. The load resistance (power) was then graphed as a function of Variac setting for these heaters. This is presented in Figure A1.1.



KEY: Heater 1 is Upper Heater Heater 2 is Middle Heater
Heater 3 is Lower Heater

Figure A1.1 Heater Calibrations

Appendix 2: Calibration Of Thermocouples

The calibration of the central thermocouple was carried out by comparing the potentiometer reading (Croydon Precision Instruments Potentiometer type P3) with the temperature indicated by a Guildline digital platinum resistance thermometer. About six litres of silicone oil were heated and stirred in a metal container using an immersed Grant Instruments (Cambridge) Ltd heater/stirrer. The tips of the central thermocouple and the other thermocouples were placed next to the tip of the platinum resistance thermometer and were all immersed in the oil. Finally, the oil was well stirred and heated at a constant temperature. At this temperature, the value of the electromotive force/mV and the temperatures/^{o}C corresponding to the central thermocouple were recorded. The temperature readings of the other thermocouples were read using a digital read out device (Cropico Ltd, NORMA D1401) connected to a Comark (1694F) multiposition thermocouple switch. Then the control point was increased and another constant temperature obtained. The temperature range used in calibrating the thermocouples was 50.321 to 149.271^{o}C. Table A2.1 lists the operating temperatures and the corresponding potentiometer readings. As noted above, a calibration graph of temperature/^{o}C against electromotive force/mV for the central thermocouple was plotted on A2 paper to provide greater resolution in the interpolation of the equilibrium temperatures.

Table A2.1 The central thermocouple calibration data

Potentiometer Reading (mV)	Temperature (°C)
2.032	50.321
2.335	57.575
2.634	64.829
2.958	72.698
3.287	80.558
3.615	88.441
3.902	95.393
4.241	103.578
4.540	110.838
4.848	118.410
5.192	126.872
5.438	132.912
5.763	141.078
6.09	149.271

Appendix 3: Analysis

As noted earlier in Chapter 6, density measurement is used as an analytical method for determination of the composition of liquid phase and vapour phase samples. For this purpose, calibration mixtures of ethanol and cyclohexane were prepared by successive weighing of pure components. Then their densities were determined at 25°C using an Anton Paar densimeter (DMA 60) with two DMA 602 cells. The temperature of the densimeter measuring cells was controlled to ±0.001 K using a heater/controller (Heto Birkerod Denmark). Table A3.1 lists the densimeter calibration data and the refractometer calibration data for the binary mixture ethanol-cyclohexane. Table A3.2 lists the gas chromatograph calibration data for the above binary mixture.

Table A3.1: Densimeter and refractometer calibration data for the binary mixture ethanol-cyclohexane.

Mole fraction ethanol	Phase lock loop	Refractive index
0.00000	1.941812	1.42287
0.05333	1.941302	1.42079
0.10966	1.941054	1.41823
0.15436	1.940941	1.41662
0.21195	1.940850	1.41325
0.30048	1.940823	1.40762
0.35004	1.940888	1.40601
0.41116	1.940960	1.40245
0.48648	1.941152	1.39825
0.55063	1.941423	1.39403
0.58835	1.941577	1.39159
0.69394	1.942324	
0.78882	1.943366	
0.90396	1.945319	
1.00000	1.947990	

Table A3.2 Gas chromatograph calibration data for the binary mixture ethanol-cyclohexane.

Mole fraction ethanol	Peak area of ethanol	Peak area of cyclohexane	Peak area of ethanol / Peak area of cyclohexane
0.10479	4631	174961	0.026
0.17058	7935	169612	0.047
0.44108	25565	140587	0.182
0.53979	32134	124278	0.259
0.65143	41234	101965	0.404

Appendix 4: Data

The experimental isothermal vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 83.29 and 106.54°C are listed in Table A4.1 and Table A4.2 respectively. Tables A4.3, A4.4 and A4.5 list the experimental isobaric vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 1, 3 and 5 bar respectively.

Table A4.1: Vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 83.29°C

Mole fraction of ethanol		Equilibrium Pressure P/bar	y - x
in liquid x	in vapour y		
0.0153	0.1195	1.309	0.1042
0.1687	0.4230	1.646	0.2543
0.4775	0.4788	1.867	0.0013
0.4863	0.5053	1.942	0.0190
0.5255	0.5183	1.978	-0.0072
0.6267	0.5850	1.953	-0.0417
0.6638	0.6010	1.934	-0.0628
0.7275	0.6333	1.842	-0.0942
0.8195	0.6355	1.823	-0.1840
0.9293	0.7113	1.688	-0.2180
0.9620	0.8205	1.508	-0.1415
0.9835	0.9020	1.389	-0.0815

Table A4.2: Vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 106.54°C

Mole fraction of ethanol		Equilibrium Pressure P/bar	y - x
in liquid x	in vapour y		
0.0795	0.0950	2.353	0.0155
0.2350	0.2471	2.813	0.0121
0.3087	0.3373	3.189	0.0286
0.4338	0.5245	3.820	0.0907
0.5475	0.5655	3.974	0.0180
0.6405	0.6298	3.994	-0.0107
0.6407	0.6325	3.930	-0.0082
0.6900	0.6260	3.850	-0.0640
0.7620	0.6970	3.736	-0.0650
0.8135	0.8050	3.446	-0.0085
0.9238	0.8679	3.249	-0.0559
0.9530	0.9355	3.022	-0.0175

Table A4.3: Vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 1 bar

Mole fraction of ethanol		Operating Pressure P/bar	Equilibrium Temperature t/°C	y - x
in liquid x	in vapour y			
0.0150	0.1370	1.009	74.75	0.1220
0.0215	0.1455	1.004	67.83	0.1240
0.0938	0.4755	1.005	64.95	0.3817
0.4337	0.4813	1.001	64.13	0.0476
0.5155	0.4845	1.009	64.25	-0.0310
0.6820	0.5275	0.999	64.30	-0.1545
0.6693	0.5445	1.007	64.20	-0.1248
0.7238	0.5655	0.999	64.69	-0.1583
0.8480	0.5838	1.003	66.45	-0.2642
0.8752	0.6015	0.999	66.45	-0.2737
0.9604	0.7360	1.004	70.44	-0.2244
0.9704	0.8120	1.003	72.63	-0.1584
0.9867	0.8920	1.003	74.75	-0.0947

Table A4.4: Vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 3 bar

Mole fraction of ethanol		Operating Pressure P/bar	Equilibrium Temperature t/°C	y - x
in liquid x	in vapour y			
0.0855	0.0940	3.000	116.10	0.0085
0.2011	0.2268	3.000	110.13	0.0257
0.4175	0.4463	2.999	101.80	0.0288
0.4436	0.4949	3.000	97.54	0.0513
0.5584	0.5525	3.000	96.89	-0.0059
0.6292	0.5832	2.994	96.53	-0.0460
0.7325	0.6780	3.006	98.93	-0.0545
0.7378	0.6745	3.002	98.80	-0.0633
0.9045	0.8498	3.000	103.90	-0.0547
0.9307	0.9230	2.999	105.93	-0.0077

Table A4.5: Vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 5 bar

Mole fraction of ethanol		Operating Pressure P/bar	Equilibrium Temperature t/°C	y - x
in liquid x	in vapour y			
0.0060	0.0615	5.011	140.50	0.0555
0.0763	0.1395	4.999	130.76	0.0632
0.1563	0.4810	4.990	122.21	0.3247
0.1725	0.3993	5.003	126.30	0.2268
0.3837	0.5412	5.009	116.20	0.1575
0.5005	0.5775	5.004	115.04	0.0770
0.6595	0.6470	4.999	114.65	-0.0125
0.7375	0.7280	4.994	116.73	-0.0095
0.7505	0.6165	5.000	115.03	-0.1340
0.9048	0.8740	5.000	120.79	-0.0308

Appendix 5: Data Reduction

For the binary mixture ethanol-cyclohexane, the measured isothermal vapour-liquid equilibrium data at 83.29 and 106.54°C, estimates of the true values corresponding to the measurements, and deviations of the measured values from the UNIQUAC model predictions are listed in Table A5.1 and Table A5.2 respectively. Tables A5.3, A5.4 and A5.5 list the measured isobaric vapour-liquid equilibrium data at 1, 3 and 5 bar, together with similar estimated values and deviations. Table A5.6 lists calculated adjustable binary parameters for the 2-parameter original UNIQUAC equation from the experimentally-determined vapour-liquid equilibrium data. Table A5.7 gives the communicated results of the data-fit carried out on the one atmosphere data of Keshpande and Lu (1963).

TABLE A5.1

Measured variables and estimates of their true values for the binary mixture ethanol-cyclohexane at 83.29°C

Pressure, mmHg			Temperature, °C			Liquid composition, mole fraction x			Vapour composition, mole fraction y		
Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev
989.05	977.16	4.89	83.29	83.65	-0.36	0.0153	0.0341	-0.0188	0.1195	0.1749	-0.0554
1234.80	1241.45	-6.65	83.29	82.62	0.67	0.1687	0.1595	0.0092	0.4230	0.4231	-0.0001
1400.10	1404.24	-4.14	83.29	82.79	0.50	0.4775	0.4773	0.0002	0.4788	0.5522	-0.0734
1456.70	1452.81	3.89	83.29	83.77	-0.48	0.4863	0.4865	-0.0002	0.5053	0.5556	-0.0503
1483.80	1476.46	7.34	83.29	84.21	-0.92	0.5255	0.5257	-0.0002	0.5183	0.5614	-0.0431
1465.10	1460.22	4.88	83.29	83.90	-0.61	0.6267	0.6265	0.0002	0.5850	0.5704	0.0146
1450.40	1447.31	3.09	83.29	83.67	-0.38	0.6638	0.6636	0.0002	0.6010	0.5734	0.0276
1381.60	1387.62	-6.02	83.29	82.57	0.72	0.7275	0.7283	-0.0008	0.6333	0.5784	0.0549
1367.50	1371.79	-4.29	83.29	82.78	0.51	0.8195	0.8217	-0.0022	0.6355	0.6019	0.0336
1266.20	1265.50	0.70	83.29	83.37	-0.08	0.9293	0.9275	0.0018	0.7113	0.6972	0.0141
1131.30	1131.90	-0.60	83.29	83.23	0.06	0.9620	0.9647	-0.0027	0.8205	0.7932	0.0273
1042.10	1041.95	0.15	83.29	83.30	-0.01	0.9835	0.9826	0.0009	0.9020	0.8748	0.0272
Root Mean Squared Deviations											
		4.50			0.52			0.0062			0.0405

Dev = Meas - Calc

TABLE A5.2

Measured variables and estimates of their true values for the binary mixture ethanol-cyclohexane at 106.54°C

Pressure, mmHg			Temperature, °C			Liquid composition, mole fraction x			Vapour composition, mole fraction y		
Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev
1765.30	1772.01	-6.71	106.54	105.74	0.80	0.0795	0.0281	0.0514	0.0950	0.1506	-0.0556
2865.20	2865.41	-0.21	106.54	106.49	0.05	0.4338	0.4337	0.0001	0.5245	0.5726	-0.0481
2980.60	2976.75	3.85	106.54	107.41	-0.87	0.5475	0.5480	-0.0005	0.5655	0.5984	-0.0329
2995.80	2991.42	4.38	106.54	107.54	-1.00	0.6405	0.6402	0.0003	0.6298	0.6165	0.0133
2948.00	2945.79	2.21	106.54	107.03	-0.49	0.6407	0.6406	0.0001	0.6325	0.6157	0.0168
2888.10	2888.42	-0.32	106.54	106.47	0.07	0.6900	0.6901	-0.0001	0.6260	0.6257	0.0003
2802.40	2805.67	-3.27	106.54	105.82	0.72	0.7620	0.7638	-0.0018	0.6970	0.6463	0.0507
2437.40	2441.61	-4.21	106.54	105.71	0.83	0.9238	0.944	-0.0202	0.8679	0.8099	0.0580
2266.40	2269.63	-3.23	106.54	105.94	0.60	0.9530	0.9762	-0.0232	0.9355	0.8976	0.0379
Root Mean Squared Deviations											
		3.70			0.68			0.0200			0.0399

Dev = Meas - Calc

TABLE A5.3

Measured variables and estimates of their true values for the binary mixture ethanol-cyclohexane at 1 bar

Pressure, mmHg			Temperature, °C			Liquid composition, mole fraction x			Vapour composition, mole fraction y		
Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev
756.69	757.23	-0.54	74.25	74.22	0.03	0.0150	0.0075	0.0075	0.1370	0.1801	-0.0431
752.69	750.66	2.03	67.83	67.96	-0.13	0.0215	0.0286	-0.0071	0.1455	0.3274	-0.1819
753.81	753.66	0.15	64.95	64.96	-0.01	0.0938	0.0939	-0.0001	0.4755	0.4021	0.0734
750.77	754.61	-3.84	64.13	63.85	0.28	0.4337	0.4337	0.0000	0.4813	0.4471	0.0342
756.59	759.49	-2.90	64.25	64.04	0.21	0.5155	0.5155	0.0000	0.4845	0.4540	0.0305
749.76	752.16	-2.40	64.30	64.13	0.17	0.6820	0.6823	-0.0003	0.5275	0.4761	0.0514
755.50	755.63	-0.13	64.20	64.19	0.01	0.6693	0.6693	0.0000	0.5445	0.4737	0.0708
749.83	753.61	-3.78	64.69	64.41	0.28	0.7238	0.7246	-0.0008	0.5655	0.4870	0.0785
751.94	754.34	-2.40	66.45	66.27	0.18	0.8480	0.8499	-0.0019	0.5838	0.5544	0.0294
749.29	746.24	3.05	66.45	66.67	-0.22	0.8752	0.8721	0.0031	0.6015	0.5769	0.0246
752.69	747.18	5.51	70.44	70.85	-0.41	0.9604	0.9464	0.0140	0.7360	0.7209	0.0151
751.94	750.23	1.71	72.63	72.76	-0.13	0.9704	0.9647	0.0057	0.8120	0.7877	0.0243
752.20	750.88	1.32	74.75	74.85	-0.10	0.9867	0.9811	0.0056	0.8920	0.8680	0.0240
Root Mean Squared Deviations											
		2.74			0.20			0.0054			0.0674

Dev = Meas - Calc

TABLE A5.4

Measured variables and estimates of their true values for the binary mixture ethanol-cyclohexane at 3 bar

Pressure, mmHg			Temperature, °C			Liquid composition, mole fraction x			Vapour composition, mole fraction y		
Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev
2250.50	2290.01	-39.51	116.10	115.45	0.65	0.0855	0.0647	0.0208	0.0940	0.1871	-0.0931
2250.30	2318.88	-68.58	110.13	108.89	1.24	0.2011	0.1778	0.0233	0.2268	0.3895	-0.1627
2250.20	2268.41	-18.21	101.80	101.44	0.36	0.4175	0.4154	0.0021	0.4463	0.5953	-0.1490
2250.70	2161.30	89.40	96.89	98.58	-1.69	0.5584	0.5615	-0.0031	0.5525	0.6548	-0.1023
2245.90	2154.02	91.88	96.53	98.28	-1.75	0.6292	0.6304	-0.0012	0.5832	0.6737	-0.0905
2254.90	2232.07	22.83	98.93	99.37	-0.44	0.7325	0.7324	0.0001	0.6780	0.6947	-0.0167
2252.10	2226.43	25.67	98.80	99.30	-0.50	0.7378	0.7376	0.0002	0.6745	0.6953	-0.0208
2250.60	2339.97	-89.37	103.90	102.05	1.85	0.9045	0.9254	-0.0209	0.8498	0.7507	0.0991
Root Mean Squared Deviations											
		63.44			1.22			0.0133			0.1040

Dev = Meas - Calc

TABLE A5.5

Measured variables and estimates of their true values for the binary mixture ethanol-cyclohexane at 5 bar

Pressure, mmHg			Temperature, °C			Liquid composition, mole fraction x			Vapour composition, mole fraction y		
Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev	Meas	Calc	Dev
3758.40	3758.17	0.23	140.50	140.55	-0.05	0.0060	0.0106	-0.0046	0.0615	0.0614	0.0001
3749.60	3750.46	-0.86	130.76	130.56	0.20	0.0763	0.0660	0.0103	0.1395	0.2720	-0.1325
3743.00	3742.57	0.43	122.21	122.32	-0.11	0.1563	0.1587	-0.0024	0.4810	0.4377	0.0433
3757.10	3756.76	0.34	116.20	116.29	-0.09	0.3837	0.3841	-0.0004	0.5412	0.5797	-0.0385
3753.10	3751.58	1.52	115.04	115.46	-0.42	0.5005	0.5011	-0.0006	0.5775	0.6111	-0.0336
3749.20	3747.27	1.93	114.65	115.18	-0.53	0.6595	0.6594	0.0001	0.6470	0.6423	0.0047
3745.70	3750.66	-4.96	116.73	115.36	1.37	0.7375	0.7394	-0.0019	0.7280	0.6610	0.0670
3750.60	3749.32	1.28	115.03	115.38	-0.35	0.7505	0.7499	0.0006	0.6165	0.6640	-0.0475
Root Mean Squared Deviations											
		2.04			0.56			0.0041			0.0600

Dev = Meas - Calc

Table A5.6 Calculated parameters for UNIQUAC equation for the vapour-liquid equilibrium data for the binary mixture ethanol-cyclohexane at 83.29 and 106.54°C and 1, 3 and 5 bar.

	$u_{12} - u_{21}$	$u_{21} - u_{22}$
83.29°C	761.90	-46.02
106.54°C	795.45	-93.29
1 bar	1492.97	-96.33
3 bar	311.71	96.66
5 bar	723.20	-75.82

Table A5.7 Results of the Fit of the Data of Keshpar de and Lu (1963)

Pressures, mmHg			Temperatures, °C			Compositions, Mole Fractions Liquid			Vapour		
Meas'd	Calc'd	Diff	Meas'd	Calc'd	Diff	Meas'd	Calc'd	Diff	Meas'd	Calc'd	Diff
760.00	760.95	-0.95	73.99	73.93	0.06	0.0200	0.0102	0.0098	0.1750	0.1884	-0.0134
760.00	759.88	0.12	69.08	69.09	-0.01	0.0300	0.0304	-0.0004	0.3020	0.3093	-0.0073
760.00	758.69	1.31	66.54	66.63	-0.09	0.0650	0.0663	-0.0013	0.3580	0.3687	-0.0107
760.00	758.53	1.47	66.08	66.18	-0.10	0.0810	0.0819	-0.0009	0.3630	0.3801	-0.0171
760.00	761.89	-1.89	66.37	66.24	0.13	0.0860	0.0849	0.0011	0.3650	0.3821	-0.0171
760.00	760.10	-0.10	65.59	65.58	0.01	0.1250	0.1250	0.0000	0.3880	0.3983	-0.0103
760.00	758.76	1.24	65.23	65.32	-0.09	0.1510	0.1512	-0.0002	0.3960	0.4049	-0.0089
760.00	760.28	-0.28	65.12	65.10	0.02	0.2060	0.2060	0.0000	0.4080	0.4148	-0.0068
760.00	759.87	0.13	64.93	64.94	-0.01	0.2580	0.2580	0.0000	0.4150	0.4214	-0.0064
760.00	759.77	0.23	64.87	64.89	-0.02	0.2830	0.2830	0.0000	0.4180	0.4242	-0.0062
760.00	759.94	0.06	64.84	64.84	0.00	0.3150	0.3150	0.0000	0.4260	0.4276	-0.0016
760.00	759.86	0.14	64.78	64.79	-0.01	0.3660	0.3660	0.0000	0.4300	0.4327	-0.0027
760.00	759.96	0.04	64.77	64.77	0.00	0.4030	0.4030	0.0000	0.4310	0.4365	-0.0055
760.00	760.02	-0.02	64.77	64.77	0.00	0.4310	0.4310	0.0000	0.4310	0.4394	-0.0084
760.00	760.12	-0.12	64.78	64.77	0.01	0.4440	0.4440	0.0000	0.4380	0.4409	-0.0029
760.00	760.21	-0.21	64.81	64.79	0.02	0.5000	0.5000	0.0000	0.4430	0.4476	-0.0046
760.00	760.24	-0.24	64.88	64.86	0.02	0.5570	0.5570	0.0000	0.4550	0.4558	-0.0008
760.00	760.22	-0.22	65.01	64.99	0.02	0.6130	0.6130	0.0000	0.4600	0.4661	-0.0061
760.00	759.79	0.21	64.99	65.01	-0.02	0.6210	0.6210	0.0000	0.4580	0.4677	-0.0097
760.00	759.80	0.20	65.25	65.26	-0.01	0.6780	0.6780	0.0000	0.4750	0.4823	-0.0073
760.00	758.36	1.64	65.56	65.68	-0.12	0.7380	0.7375	0.0005	0.5050	0.5038	0.0012
760.00	760.04	-0.04	66.03	66.03	0.00	0.7630	0.7630	0.0000	0.4960	0.5161	-0.0201
760.00	757.61	2.39	65.93	66.11	-0.18	0.7760	0.7750	0.0010	0.5150	0.5225	-0.0075
760.00	761.09	-1.09	66.40	66.32	0.08	0.7810	0.7815	-0.0005	0.4980	0.5265	-0.0285
760.00	761.23	-1.23	66.90	66.81	0.09	0.8090	0.8097	-0.0007	0.5450	0.5455	-0.0005
760.00	759.87	0.13	67.26	67.27	-0.01	0.8330	0.8329	0.0001	0.5780	0.5645	0.0135
760.00	761.26	-1.26	67.98	67.89	0.09	0.8530	0.8541	-0.0011	0.5950	0.5857	0.0093
760.00	760.67	-0.67	68.86	68.81	0.05	0.8810	0.8818	-0.0008	0.6230	0.6203	0.0027
760.00	759.79	0.21	69.44	69.46	-0.02	0.8980	0.8977	0.0003	0.6530	0.6450	0.0080
760.00	760.52	-0.52	70.11	70.07	0.04	0.9090	0.9098	-0.0008	0.6780	0.6669	0.0111
760.00	761.10	-1.10	71.42	71.34	0.08	0.9290	0.9312	-0.0022	0.7250	0.7135	0.0115
760.00	759.08	0.92	72.48	72.55	-0.07	0.9510	0.9488	0.0022	0.7780	0.7623	0.0157

Table A5.7 Results of the Fit of the Data of Keshpar de and Lu (1963)

Pressures, mmHg	Temperatures, °C	Compositions, Mole Fractions	
		Liquid	Vapour

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Appendix 6: An Extended Antoine Equation

ble A6.1: Constants for the extended Antoine equation given by Prausnitz et al. (1967).

Appendix 7: Operation of the Equilibrium Still

The equilibrium still is operated using the pressure system illustrated in Figure 6.1.

1. Prior to start-up, prepare mixtures of appropriate compositions by weighing in storage bottles for the binary mixture ethanol-cyclohexane of desired compositions.
2. Turn on heaters 1, 2, and 3 to a Variac setting of around 75 to heat up the pressure bomb.
3. Switch on the potentiometer to warm up.
4. Place crushed ice in the thermocouple cold junction vacuum flask.
5. Using a syringe, place mixture (~ 170 ml) into still via the feeding connection above the condenser.
6. Turn on water to condensers.
7. Turn on heaters 4 and 5 to Variac settings of around 50 and 20 respectively.
8. Turn on pump to a setting of around 5V.
9. Standardise potentiometer.
10. Close valves 1, 6 and 8 and open valve 4.
11. For pressures up to 3.5 bars, close valve 5, open valve 2, switch on Druck vibrating cylinder gauge (DPI 140) and open valve 3. Turn on pressure system and set desired pressure if an isobaric data point is to be determined, set pressures initially to near atmospheric and use Fairchild pressure regulator to adjust pressure. For pressures above 3.5 bars, close valves 2 and 3 and open valves 5 and 7. Switch on Druck pressure controller (DPI 1500). Turn on pressure system and set desired pressure (above 3.5 bar) if an isobaric data point is to be determined.
12. When circulating of both phases has started to occur, monitor boiling temperature. During this time erratic boiling may need to be eliminated by adjustment of the heater control. If an isothermal data point is to be determined, adjust either pressure controllers until the exact potentiometer reading corresponding to the desired temperature is achieved.
13. After 1 1/2 hours has elapsed and the boiling temperature (potentiometer reading) has been steady, take samples (as described earlier) and record temperature and pressure.