PHASE EQUILIBRIUM STUDIES AT NORMAL PRESSURES

BY

MOHAMMED RAFAQUAT

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY

THE UNIVERSITY OF ASTON IN BIRMINGHAM

DECEMBER 1991

The University of Aston in Birmingham

Phase Equilibrium Studies at Normal Pressures

MOHAMMED RAFAQUAT

Doctor of Philosophy December 1991

SUMMARY

A total pressure apparatus has been developed to measure vapour-liquid equilibrium data on binary mixtures at atmospheric and sub-atmospheric pressures. The method gives isothermal data which can be obtained rapidly. Only measurements of total pressure are made as a direct function of composition of synthetic liquid phase composition, the vapour phase composition being deduced through the Gibbs-Duhem relationship. The need to analyse either of the phases is eliminated. As such the errors introduced by sampling and analysis are removed.

The essential requirements are that the pure components be degassed completely since any deficiency in degassing would introduce errors into the measured pressures. A similarly essential requirement was that the central apparatus would have to be absolutely leak-tight as any leakage of air either in or out of the apparatus would introduce erroneous pressure readings.

The apparatus was commissioned by measuring the saturated vapour pressures of both degassed water and ethanol as a function of temperature. The pressure-temperature data on degassed water measured were directly compared with data in the literature, with good agreement. Similarly the pressure-temperature data were measured for ethanol, methanol and cyclohexane and where possible a direct comparison made with the literature data .

Good agreement between the pure component data of this work and those available in the literature demonstrates firstly that a satisfactory degassing procedure has been achieved and that secondly the measurements of pressure-temperature are consistent for any one component; since this is true for a number of components, the measurements of both temperature and pressure are both self-consistent and of sufficient accuracy, with an observed compatibility between the precision/accuracy of the separate means of measuring pressure and temperature.

The liquid mixtures studied were of ethanol-water, methanol-water and ethanol-cyclohexane. The total pressure was measured as the composition inside the equilibrium cell was varied at a set temperature. This gave P-T-x data sets for each mixture at a range of temperatures. A standard fitting-package from the literature was used to reduce the raw data to yield y-values to complete the x-y-P-T data sets. A consistency test could not be applied to the P-T-x data set as no y-values were obtained during the experimental measurements. In general satisfactory agreement was found between the data of this work and those available in the literature. For some runs discrepancies were observed, and further work recommended to eliminate the problems identified.

Key words: Atmospheric Pressure, Experimental Determination, Isothermal, Saturated Vapour Pressure, Sub-Atmospheric Pressure, Total Pressure, Vapour-Liquid Equilibrium, .

Dedication

In the fondest memories of my late father,
Raja Munsabdar, and my late grandfather,
Raja Barkhurdar.

Acknowledgements

The Author would like to express his gratitude to the following people :

Dr J. D. Jenkins for his friendly guidance and encouragement throughout the course of this research programme.

Mr I. Murkett and Mr M. Santoro for their assistance in the construction of the experimental apparatus.

Mr Colin Sudlow and Mr K. K.Yin for their good friendship and advice on the use of word-processing packages.

Dr J. Bickerton of Allied Colloids Ltd for his constructive comments.

Mrs Wendy Overton for typing part of the thesis.

The author would also to express his thanks to many friends for their moral support.

Warm and kind thanks to my close family members, and in particular my mother, for their love and support throughout my student days.

Last but not least, I take pleasure in expressing my warmest gratitude to my fiancé, Sania for her support and encouragement.

Contents

List of Figures

List of Tables

Chapter 1: Introduction

The need for accurate vapour-liquid equilibrium data for use in the design of separation equipment for the process industry cannot be overestimated. Despite the existence of extensive collections of vapour-liquid equilibrium data, such as the vapour-liquid equilibrium data collection of Gmehling and Onken (1982 and continues) there is still a need to obtain accurate vapour-liquid equilibrium data. In particular, much of the existing data has been obtained on equipment of questionable performance. Typically data have been obtained from the use of circulation stills in which after a certain period of equilibration the vapour phase and the liquid phase are sampled and then analysed, a procedure that introduces random and systematic errors; consequently the final results do not represent the true compositions of the equilibrium phases. In the light of this, the attention of experimentalists has been focussed on finding methods which would avoid the use of sampling and analysis. Typical of such methods is that developed by Gibbs and Van Ness (1972) based on the measurement of total vapour pressure exerted by the mixture inside an equilibrium cell as the composition was varied.

In this department Smith (1975) had developed a total pressure apparatus based on that of Jenkins (1963) to measure vapour-liquid equilibrium data for binary mixtures. His apparatus used ordinary glass burettes as dispensing devices and a home-made pressure transducer. In his recommendations Smith suggested that improvements could be made in the design of equilibrium cell, in that of the degassing unit, in that of the systems for the dispensing and storage of pure component, of the pressure measurement system and of the vacuum system. Further work was carried out by O'Donnell but not reported by him (Jenkins, 1991). It was with these objectives in mind that this work was undertaken. In this research programme emphasis was placed on developing an experimental technique to measure total vapour pressure inside a cell as a direct function of the liquid phase composition at a set temperature. The PTx data so obtained were then reduced to determine the values of the vapour phase composition, y. A data reduction program,

developed by Gibson-Robinson (1975) and O'Donnell (1980) and further modified by Jenkins (1991), was used to deduce the y values.

An important aspect of the total pressure method is that small pressure changes may be involved and therefore the system for measurement and control of pressure would need to be of high sensitivity and reproducibility. A system was developed to both measure and control the pressure exerted inside the cell. For the measurement a pressure transducer was used as a null device, its sensitivity matches that of the control system. The balancing pressure could in the event be controlled and measured to a precision of $\pm$ 0.00001 bar and an accuracy of $\pm$0.0001 bar.

An essential pre-requisite of any total pressure method is that the pure components must be free from any dissolved air as the vapour pressure is measured as a direct function of composition and any dissolved air in the liquid would give a false reading. Similarly it was vital to ensure that the central apparatus was completely leak-tight.

Temperature measurements were carried out using a Guildline platinum resistance thermometer and temperature was controlled to $\pm$0.001 K.

The apparatus designed and developed in this work was commissioned initially by investigating ethanol-water mixtures. This system was chosen because a large body of data was already available from the work by Larkin and Pemberton (1976) at the National Physical Laboratory (NPL). On establishing the integrity of the apparatus work was done on two further binaries, namely, methanol-water and cyclohexane-ethanol.

The apparatus developed is suitable for measuring vapour-liquid equilibrium data on binary mixtures at isothermal conditions. The measurements could be made at a maximum temperature of 70°C. The method gives total pressure–liquid composition measurements and the equilibrium vapour compositions are deduced from these data via a suitable model for activity coefficients. Several methods are available (Barker 1953, Christian 1960, Redlich and Kister 1948). In general, these methods involve evaluations of either the constants of equations representing the liquid activity coefficients as a

function of composition or equilibrium vapour compositions directly by means of a step-wise integration procedure. All methods involve, however, the use of either integrated form of the Gibbs-Duhem equation or direct integration of the equation itself.

In this work the Barker method has been used, it is based on the use of a suitable expression relating excess Gibbs functions to composition.

The procedure is to seek through regression a set of values for the parameters in the correlating expression for the Gibbs function that minimises the sum of squares of the differences between experimental values for P and the corresponding values calculated from the expression used. An optimisation routine is used to minimise the error in the pressures by seeking the optimal parameter set. The final values of the parameter permit accurate values of the y_i to be calculated.

Chapter 2: Theoretical Background

2.1 Introduction

The first and second laws of thermodynamics are the fundamental relationships 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 test experimental data for thermodynamic consistency as well as extrapolating data to new conditions. They also provide a basis for both theoretical and semi-empirical prediction methods for vapour-liquid equilibrium data from a minimum of information.

2.2 Criteria for equilibrium

Equilibrium implies a situation in which there is no macroscopic change with respect to time. In thermodynamics where attention is focussed upon a particular quantity of material, there must not be a change in the properties of the material with time. Equilibrium requires a balance of all potentials capable of causing a change. In other words the necessary and sufficient condition of equilibrium in a closed system with n different components at temperature T, and pressure P is that the Gibbs energy G for a mixture is at a minimum.

The first law of thermodynamics states that:

$$dU = q + w \qquad - 2.1$$

where dU is the infinitesimal increase in internal energy linked with an infinitesimal amount of work w done on the system and the heat added being the infinitesimal amount q. The second law may be expressed as,

$$dS = \frac{q}{T} = 0 \qquad - 2.2$$

for the system and its surrounding for a reversible (i.e., equilibrium) process. Combining First and Second Laws gives the expression:

$$dU = T\,dS - P\,dV$$

i.e. $$dU - T\,dS + P\,dV = 0 \qquad - 2.3$$

Equation (2.3) implies that the system is characterised by the two independent variables or degrees of freedom S and V where S is the entropy and V is volume. In order to reformulate the expression with P and T as the independent variables, the Gibbs free energy G is defined as:

$$G = H - T\,S \qquad - 2.4$$

where H is the enthalpy, given by the expression,

$$H = U + P\,V \qquad - 2.5$$

and therefore,

$$G = U + P\,V - T\,S \qquad - 2.6$$

Differentiating at dT = 0, dP = 0, for a system at equilibrium gives:

$$dG = dU + P\,dV - T\,dS \qquad - 2.7$$

Comparing equation (2.7) with equation (2.3) shows that at equilibrium $dG_{T,P} = 0$

Differentiating equation (2.6) gives:

$$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT \qquad - 2.7a$$

Substitution with equation (2.3) gives:

$$dG = V\,dP - S\,dT \qquad - 2.8$$

for a closed system.

If we now open the system, we introduce another set of variables, the mole number of each component present, thus

$$G = f(P, T, n_i, n_j, \ldots.) \qquad - 2.9$$

After partial differentiation we get

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j} dn_i \qquad - 2.10$$

Comparing equation (2.10) with equation (2.8) we recognise that:

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_i} = V \qquad - 2.11$$

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S \qquad - 2.12$$

We now define μ_i, the chemical potential of the *i* th species by,

$$\mu_i = \left(\frac{\partial G}{\partial T}\right)_{P, T, \sum_j n_j} \qquad (i \neq j) \qquad - 2.13$$

Thus, for a system of variable composition we get:

$$dG = V\,dP - S\,dT + \sum_i \mu_i\, dn_i \qquad - 2.14$$

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 n_i moles of component *i* transfer from A to B, then for phase A and phase B we get the following:

$$dG_A = \mu_i^A\left(-\left|\delta n_i\right|\right) \qquad - 2.15$$

$$dG_B = \mu_i^B\left(+\left|\delta n_i\right|\right) \qquad - 2.16$$

Overall we have,

$$dG = dG_A + dG_B = 0 \qquad - 2.17$$

$$\mu_i^A\left(-\left|\delta n_i\right|\right) + \mu_i^B\left(+\left|\delta n_i\right|\right) = 0 \qquad - 2.18$$

and rearranging,

$$\left|\delta n_i\right|\left(\mu_i^{B} - \mu_i^{A}\right) = 0 \qquad - 2.19$$

now δn_i has a finite value, hence

$$\mu_i^{A} = \mu_i^{B} \qquad - 2.20$$

i.e., the chemical potential of a species *i* in phase A and B at equilibrium is the same.

To be of practical use, the chemical potential must be transformed from its abstract form into one dependent on pressure, temperature and the phase concentrations.

To do this Lewis (1901) defined fugacity as:

$$\mu_i = \mu_i^{o} + R\,T \ln \frac{f_i}{f_i^{o}} \qquad - 2.21$$

rewriting:

$$\mu_i - \mu_i^{o} = R\,T \ln f_i - R\,T \ln f_i^{o} \qquad - 2.22$$

Equation (2.22) illustrates that as long as

$$\mu_i^{o} = R\,T \ln f_i^{o} \qquad - 2.23$$

we can use any standard state we like. The f_i value can be determined by using any of the following equivalent expressions. The fugacity coefficient ϕ_i is defined as the ratio f_i/P_i and it goes to one as P goes to zero.

$$\phi_i = \frac{f_i}{P_i} \qquad - 2.24$$

$$\ln\left(\frac{f_i}{P_i}\right)_{P = P'} = \int_0^{P'} \left(\frac{\overline{V_i}}{R\,T} - \frac{1}{P}\right) dP \qquad - 2.25$$

where,

$$\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{P\,T\,n}$$

Other equivalent forms of equation (2.25) are available in the literature.

The partial differential term suggests that equations of state could be used to determine fugacity values for gases and liquids both for pure substances and for mixtures, from experimental data.

For liquids at low pressures it is usual to use an alternative approach. Equation (2.21) is replaced by,

$$\mu_i = \mu_i^* + R\,T \ln a_i \qquad - \ 2.26$$

with a_i the activity of component *i*, and μ_i^* is the chemical potential for pure liquid.

$$a_i = x_i \gamma \qquad - \ 2.27$$

$$\mu_i = \mu_i^* + R\,T \ln x_i \gamma_i \qquad - \ 2.28$$

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;

$$f_i^L = f_i^V$$

$$\gamma_i x_i f_i^{*L} = f_i^V \qquad - \ 2.29$$

Substituting,

$$f_i^v = \phi_i y_i P \qquad - \ 2.30$$

and therefore:

$$\gamma_i x_i f_i^{*L} = \phi_i y_i P \qquad - \ 2.31$$

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 state of the vapour phase. We chose 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^{0V}(where f_i^{0V} =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:

$$f_i^{L}\left(T, P_i^{Sat}\right) = f_i^{V}\left(T, P_i^{Sat}\right) = \phi_i\left(T, P_i^{Sat}\right) P_i^{Sat} \qquad - \ 2.32$$

$$\gamma_i x_i \phi_i\left(T, P_i^{Sat}\right) P_i^{Sat} \frac{f_i^{*L}(T, P)}{f_i^{L}\left(T, P_i^{Sat}\right)} = \phi_i\left(T, P_i^{Sat}\right) y_i P \qquad - \ 2.33$$

Now,

$$R\,T \ln f_i = \overline{V}_i\, dP$$

Hence,

$$R\,T\, d \ln f_i^{L} = V_i^{L} dP$$

$$\ln \frac{f_i^{*L}(T, P)}{f_i^{L}\left(T, P_i^{Sat}\right)} = \frac{1}{R\,T} \int_{P_i^{Sat}}^{P} V_i^{L} dP \qquad - \ 2.34$$

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

$$\gamma_i x_i \phi_i\left(T, P_i^{Sat}\right) P_i^{Sat} \exp\left(\frac{v_i^{L}}{R\,T}\left(P - P_i^{Sat}\right)\right) = \phi_{i(T, P)} y_i P \qquad - \ 2.35$$

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

$$\exp\left(v_i^{L} \frac{P}{R\,T}\right) .)$$

Often this term is neglected since for pressures below about ten atmospheres it is negligible.

Equation (2.35) can be simplified. At pressures close to one atmosphere (and perhaps up

to five atmospheres) the fugacity coefficients cancel out and, neglecting the pressure term, we have:

$$\gamma_i x_i P_i^{Sat} = y_i P \qquad - 2.36$$

If we define the relative volatility ratio by,

$$\alpha_{ij} = \frac{y_i x_i}{x_i y_i} \qquad - 2.37$$

Then equation (2.35) for both i and j gives:

$$\alpha_{ij} = \frac{\gamma_i P_i^{Sat}}{\gamma_i P_j^{Sat}} \qquad - 2.38$$

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

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i x_i \phi_i^{Sat} P_i^{Sat} \exp\left(\frac{V_i^L}{R T}\left(P - P_i^{Sat}\right)\right)}{\phi_i P} \qquad - 2.39$$

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:

$$K_i = \frac{\phi_i^V}{\phi_i^L} \qquad - 2.40$$

2.3 The Gibbs-Duhem Equation

Combining equations (2.7a) and (2.14) gives:

$$dU = T\,dS - P\,dV = \sum_i \mu_i\,dn_i \qquad - 2.41a$$

Integrating equation (2.15) from a state of zero mass to infinite mass at constant composition gives:

$$U = T\,S - P\,V + \sum_i n_i\,\mu_i \qquad - 2.41b$$

Differentiating equation (2.41b) and comparing with equation (2.15) gives:

$$S\,dT - V\,dP + \sum_i n_i\,d\mu_i = 0 \qquad - 2.42$$

Equation (2.42) is the Gibbs-Duhem equation and is sometimes used in its restricted form

$$\sum_i n_i\,d\mu_i = 0 \qquad - 2.43$$

Two further useful thermodynamic relationships which are used to evaluate the two left hand terms of equation (2.42) are

$$\frac{\partial\left(\frac{\mu_i}{T}\right)_{P\,n_i}}{\partial T} = -\frac{\overline{H_i}}{T^2} \qquad - 2.44$$

and,

$$\frac{\partial \mu_i}{\partial P}_{T\,n_j} = -\overline{V_i} \qquad - 2.45$$

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

2.4 Models for the Vapour Phase

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

2.4.1 Indirect model

The indirect model has already been encountered through the definition of fugacity by,

$$\mu_i = R\,T\,d\ln f_i \qquad - \ 2.22$$

and on defining a standard state for the vapour phase this becomes:

$$\mu_i - \mu^{o}_{i} = R\,T\,d\ln \frac{f_i}{f_i^{o}} \qquad - \ 2.22a$$

where f_i^{o} and μ_i^{o} are the fugacity and chemical potential of the reference state, usually defined as 1 standard atmosphere. Also,

$$\frac{f_i}{p_i} \rightarrow 1 \text{ as } P_i \rightarrow 0$$

Equation (2.22a) is usually written as

$$\mu_i = \mu^{*}_{i} + R\,T\ln f_i \qquad - \ 2.46$$

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 (2.46) becomes

$$\mu_i = \mu^{*}_{i} + R\,T\ln P \qquad - \ 2.47$$

2.4.2 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 ($PV = nRT$) whose only use is as a starting point. The earliest real gas equation is due

to van der Waals who introduced two terms to allow for the attractive forces between molecules and the volume of the molecules themselves:

$$\left(P + \frac{a}{v^2}\right)(v - b) = R\,T \qquad - \ 2.48$$

for one mole of gas.

Many variations on equation (2.48) have been proposed but by far the most successful using two adjustable constants is that due to Redlich and Kwong (1949).

$$P = \frac{R\,T}{v - b} - \frac{a}{T^{0.5}\,v\,(v + b)} \qquad - \ 2.49$$

As with van der Waals equation a and b can be related to the critical temperature $T_ç$ and the critical pressure P_c by

$$a = \frac{\Omega_a\,R^2\,T_c^{2.5}}{P_c}, \qquad b = \frac{\Omega_b\,R\,T_c}{P_c} \qquad - \ 2.50$$

where Ω_a and Ω_b are proportionality constants

Equation (2.49) combines simplicity with reasonable accuracy. Since it is a cubic equation it can be solved analytically rather than by trial and error.

Many modifications have been made to the Redlich-Kwong equation to improve its performance. The improvements include making the constants a and b function of temperature and relaxing the nature of the proportionality constants, and then fitting the equation to available data. These modifications have been successful and have produced very good fits to experimental PVT data (Prausnitz, 1969)

Another approach is that of the virial equation which uses the exact relationship between the virial coefficients and the intermolecular potential describing the forces between molecules. The equation is:

$$Z = \frac{P\,v}{R\,T} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots. \qquad - \ 2.51$$

where B, C and D are the second, third and fourth virial coefficients respectively and are for pure components, each functions of temperature only. As there is a theoretical relation between them and the intermolecular potential it is possible to extend the use of the equation to gas mixtures and for these the virial coefficients depend on the composition in an exact and particularly simple manner. The equation is often truncated after the third term and then;

$$B = \lim_{\rho \to 0} \left|\frac{\partial Z}{\partial \rho}\right|_T , \quad C = \lim_{\rho \to 0} \frac{1}{2}\left|\frac{\partial^2 Z}{\partial \rho^2}\right|_T \qquad - \ 2.52$$

where $\rho = \frac{1}{V}$

Equation (2.51) can be expressed in the alternative pressure form,

$$Z = 1 + B'P + C'P \qquad - \ 2.53$$

Coefficients B and C can be obtained from PVT data for low pressures along an isotherm and use to predict the PVT data along the same isotherm at high pressures (Pitzer and Curl, 1955, 1957). This form is good up to half the critical density. Experimental methods and theory do not yet permit D and higher coefficients to be measured accurately or predicted, and this prevents the equation being applied to higher densities. The physical significance of the second virial coefficient B is that it takes into account deviations from ideality which result from collision or interactions that involve two molecules. The third deals with three molecule effects 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:

$$Z = 1 + \frac{B\,P}{R\,T} \qquad - \ 2.54$$

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 calculation, while their use is better than the assumptions of ideal behaviour. Virial coefficients in a mixture are calculated using the relationship:

$$B_{mix.} = \sum_{i}^{n} \sum_{j}^{n} y_i y_j B_{ij} \qquad - \ 2.55$$

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

$$\ln \phi_i = \frac{1}{R T} \int_{v}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,v,n_j} - \frac{R T}{v} \right] dv - \ln Z \qquad - \ 2.56$$

This is a version of equation (2.25) and equation (2.56) needs the substitution of a suitable equation of state to be of practical use, for example using the truncated virial equation we have

$$\ln \phi_i = \frac{2}{v} \sum_{v}^{n} y_i B_{ij} - \ln Z \qquad - \ 2.57$$

2.5 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 (2.25). 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:

$$f_i = \gamma_i x_i f_i^{o} \qquad - \ 2.58$$

where f_i^{o} 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 $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ is used, whereas for non-condensables components the normalisation $\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$, $x_r \rightarrow 1$ 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, and can be related to another function which expresses the non-ideality of a solution, the excess Gibbs energy G^E.

$$G_{mixture} = \sum_i n_i \mu_i^{real} = \sum_i n_i \mu_i^{*} + \sum_i n_i R T \ln x_i + \sum_i n_i \ln \gamma_i$$

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

$$G^E = G_{mixture} - G_{mixture}^{ideal} = R T \sum_i n_i \ln \gamma_i \qquad - \ 2.59$$

dividing by the total number of moles we get:

$$g^E = R T \sum_i^N x_i \ln \gamma_i \qquad - \ 2.60$$

For a binary mixture this becomes,

$$g^E = R T \left(x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \qquad - \ 2.61$$

Prausnitz (1969) and the others have shown that individual activity co-efficient is related to the molar excess Gibbs energy by,

$$R T \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T,P,n_{i \neq j}} \qquad - \ 2.62$$

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,

$$g^E = h^E - TS^E \qquad - 2.63$$

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

The second approach is to assume that the non-ideality is due entirely to the entropy of mixing, i.e. $h^E = 0$ and $g^E = -TS^E$, 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 (b) it is of use, by virtue of its accuracy and generality, in the correlation (and to a lesser extent the prediction) of VLE data.

2.5.1 Liquid phase models based on the regular solution approach

The work of Van Laar historically is of particular significance 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 isothermally. 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:

$$\ln \gamma_i = \frac{A'}{\left[1 + \frac{A'}{B'}\frac{x_1}{x_2}\right]^2} \qquad - 2.64a$$

$$\ln \gamma_2 = \frac{B'}{\left[1 + \frac{B'}{A'}\frac{x_2}{x_1}\right]^2} \qquad - 2.64b$$

The constants A' and B' are functions of the van der Waals constants and R, the gas

constant.

Agreement between experimental activity co-efficients and those calculated from equations (2.64a) and (2.64b) is poor due to the dependence of the Van Laar equation on the van der Waals equation. Reasonable results 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, has received a wide-spread use in VLE data correlation and is:

$$\log \gamma_1 = x_2^2\left(a + 2x_1(B - A)\right) = x_2^2(2B - A) + 2x_2^3(A - B) \quad - \ 2.65a$$

$$\log \gamma_2 = x_1^2\left(B + 2x_2(A - B)\right) = x_1^2(2A - B) + 2x_1^3(B - A) \quad - \ 2.65b$$

If as well as A = B (ie. the system is symmetrical) we obtain:

$$\log \gamma_1 = A x_2^2, \qquad \log \gamma_2 = A x_1^2 \quad - \ 2.66$$

Their extension to ternary and higher order mixtures require 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.

$$\ln \gamma_i = V_i \frac{\left(\delta_i - \bar{\delta}\right)^2}{RT} \qquad - 2.67$$

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

$$\delta = \sqrt{\left(\frac{\Delta E_i}{V_i}\right)} \qquad - 2.68$$

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

$$\Delta E_i = \Delta H_{v_i} - RT \qquad - 2.69$$

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

δ is the volume average solubility parameter for the liquid mixture and is given by

$$\bar{\delta} = \sum_i^N Z_i \delta_i \qquad - 2.70a$$

where

$$Z_i = \frac{x_i v_i}{\sum x_i v_i} \qquad - 2.70b$$

assuming that no volume change occurs on mixing.

Erdos (1955) developed a similar expression, but his models were based on the surface characteristics of intermolecular forces, thus he obtained surface solubility parameters:

$$RT \ln \gamma_1 = S_1 \theta_2^2 (q_1 - q_2)^2 \qquad - 2.71a$$

$$RT \ln \gamma_2 = S_2 \theta_1^2 (q_1 - q_2)^2 \qquad - 2.71b$$

where q_1 and q_2 are the surface solubility parameters, S_1 and S_2 are the molar surfaces and θ_1 and θ_2 are the surface fractions of components 1 and 2 respectively.

2.5.2 Liquid phase models based on the athermal theory

In this approach it is assumed that the excess enthalpy of mixing, h^E, is zero; thus,

$$g^E = T S^E$$

This model was originally proposed by Flory (1942) and Huggins (1942) as a basis for their treatment of the thermodynamic properties of polymer solutions. They set:

$$\frac{g^E}{RT} = \sum_i x_i \ln \frac{Z_i}{x_i} \qquad - 2.72$$

where,

$$Z_i = \frac{x_i v_i}{\sum_i x_i v_i}$$

This again assumes that there is no volume change on mixing. The approach was based on a simple model of the structure of liquids. In this the distribution of molecules around a central molecule is assumed to be given by equation (2.73) where x_{12} is the local mole fraction of species 2 around a molecule of 1.

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp\left(\frac{-\lambda_{12}}{RT}\right)}{x_1 \exp\left(\frac{-\lambda_{11}}{RT}\right)} \qquad - 2.73a$$

and for species 1 around 2

$$\frac{x_{21}}{x_{22}} = \frac{x_1 \exp\left(\frac{-\lambda_{21}}{RT}\right)}{x_2 \exp\left(\frac{-\lambda_{22}}{RT}\right)} \qquad - 2.73b$$

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

Wilson converted expressions (2.73a) and (2.73b) for local mole fractions into an expression for local volume fractions. Substituting this into the Flory-Huggins

expression and differentiating he obtained:

$$\ln \gamma_k = \ln\left(\sum_j x_j \Lambda_{kj}\right) + 1 - \sum \frac{x_i \Lambda_{ik}}{\sum_j x_i \Lambda_{ij}} \qquad - 2.74$$

where for a binary mixture

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(\frac{-\left(\lambda_{12} - \lambda_{11}\right)}{RT}\right) \qquad - 2.75a$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(\frac{-\left(\lambda_{21} - \lambda_{22}\right)}{RT}\right) \qquad - 2.75b$$

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

Equation (2.74) has been proved to provide good representation for the behaviour of many systems and its extension to multi-component mixtures is relatively simple due to the fact that only binary parameters are needed. However the Wilson equation cannot produce a good representation for systems 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 parameter (Λ_{12}) and (Λ_{21}) 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 wider range of systems 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

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{12} G_{12}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \qquad 2.76$$

where

$$\tau_{12} = \frac{g_{12}}{RT} \quad , \quad \tau_{21} = \frac{g_{21}}{RT}$$

$$\ln G_{12} = -\alpha_{12} \tau_{12} \quad , \ln G_{21} = -\alpha_{12} \tau_{21}$$

with $G_{12} = (g_{12} - g_{22})$, $G_{21} = (g_{21} - g_{11})$

and α_{12} the binary adjustable parameter.

The form of the activity coefficient is:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad - 2.77$$

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

We have seen that the adjustable parameters of the NRTL equations are α_{12}, $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$. 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 systems α varies between 0.20 and 0.47, and thus for a system where little experimental data is available , the value for α can be set to one obtained for similar systems.

One advantage that the NRTL equations have over the Wilson equation, is that they are capable of producing good data fits both for miscible and partially miscible systems. The

parameters ($g_{12} - g_{22}$) and ($g_{21} - g_{11}$) are highly temperature dependent. Asselineau and Renon (1970) assumed linear relationships for the parameters, arriving at a six-parameter NRTL equation:

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15) \quad - 2.78a$$

$$g_{12} - g_{22} = C_2 + D_2(T - 273.15) \quad - 2.78b$$

$$\alpha_{12} = \alpha^{0} + \alpha^{T}(T - 273.15) \quad - 2.78c$$

The C-parameters represent the values of the NRTL parameters at 0 °C and the D-parameters given their dependence upon temperature.

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

2.5.3 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 solution approach, was proposed by Redlich and Kister (1948) who produced a series expansion in composition

$$g^E = x_1 x_2 \left[A + B\,(x_1 + x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + ... \right] \quad - \ 2.79$$

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:

$$\log\left(\frac{\gamma_1}{\gamma_2}\right) = a + b(x_2 - x_1) + c(6\,x_1 x_2 - 1) + d(x_2 - x_1)(1 - 8\,x_1 x_2) + ... \quad - \ 2.80$$

Ochi and Lu (1977) further modified the equation of Chao to facilitate the evaluation of constants which were otherwise difficult due to an indeterminately condition.

Klaus and Van Ness (1967) proposed that G^E could be represented as a function of composition using orthogonal functions. Christiansen and Fredensland (1975) reviewed this problem and used the method of collocation.

The appearance of the UNIQUAC (Unified QUAsi-Chemical) equation due to Abrams and Prausnitz (1975) is a recent and most significant advance in liquid phase models. Like the Wilson and NRTL equations, it is based on a local composition concept and with just two interaction parameters per binary is able to represent both vapour-liquid and liquid-liquid equilibria.

In this model the excess Gibbs function and hence the activity coefficient are given by two contributions, one accounting for size and shape effects and the other intermolecular interactions (energetic interactions).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad - \ 2.81$$

where γ_i^C is the combinational part and γ_i^R the residual part. The combinational part is given by:

$$\ln \gamma_i^C = \ln \frac{\phi_k}{x_k} + \frac{Z}{2} q_k \ln \frac{\theta_k}{\phi_k} + l_k - \frac{\phi_k}{x_k} \sum_j x_j L_j \quad - 2.82$$

where,

$$l_k = \frac{Z}{2}(r_k - q_k) - (r_k - 1) \ , \ Z = 10 \quad - 2.83$$

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 combinational part takes into account liquid phase non-ideality due to differences in molecular size and shape. Such a term is needed to handle non-ideality in non-interacting (e.g. alkane-alkane) systems. The residual contribution is given by:

$$\ln \gamma_i^k = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ij} \right) \frac{\sum_j (\theta_j \tau_{ij})}{\sum_k \theta_k \tau_{jk}} \right] \quad - 2.84$$

where,

$$\tau_{ij} = \exp \left[\frac{\mu_{ij} - \mu_{ii}}{R T} \right] \quad - 2.85$$

The adjustable parameters $(\mu_{ij} - \mu_{ii})$ are obtained by fitting to experimental data. The residual part allows for non-ideality due to intermolecular interactions. It resembles the Wilson equation, but the composition variable is surface area fraction rather than mole fraction. This is reasonable since such interactions take place across surfaces.

2.5.4 Comparisons of the liquid phase activity co-efficient models

In the equations which have been discussed the number of adjustable constants per binary is typically two or three. With more constants the data can be represented better, but this also requires extra and more reliable experimental data points. Extensive and highly accurate experimental data are required to justify more than three empirical constants for a

binary mixture at a fixed temperature.

For moderately non-ideal binary mixtures, all equations for g^E containing two or more binary parameters give good results, however, the older ones (Margules, Van Laar) are mathematically easier to handle than the more recent ones (Wilson, NRTL, UNIQUAC). The simple (one parameter) Margules is applicable only to simple mixtures where the components are similar in chemical nature and size of the molecule.

For strongly non-ideal binary mixtures such as alcohol + hydrocarbons, the Wilson equation is probably most useful since unlike the NRTL equation, it has only two adjustable parameters, it is also simpler mathematically than the UNIQUAC equation. The older equations are likely to be significantly less successful in representing the data, especially at low alcohol concentrations, here the Wilson equation is particularly useful.

The Redlich-Kister equation is mathematically identical to the various forms of the Margules equation.

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 because:

(1) it has only two, rather than three, adjustable parameters

(2) since it has a better theoretical basis, its parameters often have a smaller dependence on temperature and

(3) because the major concentration variable is a surface fraction rather than mole fraction, 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 with 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 (1977) further tested the above equations using another ten binary systems covering a wide range of system 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 better than the Van Laar or Redlich-Kister equations. The Wilson equation has the disadvantage that it cannot fit partially miscible systems and thus the modified NRTL and UNIQUAC equations are to be preferred, the UNIQUAC method has the disadvantage of requiring extra parameters, but these can be estimated from pure component information.

Monford and Rajos (1978) tested the accuracy of the Wilson, UNIQUAC and NRTL equations using 34 binary and ternary systems. They concluded that the UNIQUAC equations were slightly better for binary systems and that the Wilson equation was superior for alcohol-hydrocarbon and chloroform-polar component systems. In the case of ternary systems no equation could distinctively be considered superior as all produced similar results.

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

Chapter 3: Methods for Vapour Liquid Equilibrium Data Determination

3.1 Introduction

Experimental methods for the determination of vapour-liquid equilibrium data have been developed since the early 1900s when the foundations were laid from work on positive and negative deviations from Raoult's Law. Zawidski (1900) carried out such work which provided a basis for a theoretical treatment of non-ideality. Just, in 1901, worked on the solubility of various gases in water and many organic solvents. Later, McDanial in 1911 investigated hydrocarbon gases and solvents while Kunerth (1922) did further work on the solubility of carbon dioxide and nitrous oxide in various solvents.

While the work mentioned above was valuable as a beginning, it was limited to comparatively few systems and the accuracy was not high by modern standards. More extensive work was not carried out until the need was realized for reliable data for industrial design.

Many of the early results were not checked for thermodynamic consistency and later workers have shown the earlier techniques and data to be unreliable. As a result many improved techniques have been evolved over the years and the important ones are reviewed in this chapter.

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. For accurate prediction of phase equilibrium data, some experimentally obtained data must be used for the evaluation of parameters in the appropriate models.

Vapour-liquid equilibrium data take the form of the liquid- and vapour- phase compositions, pressure and temperature. Direct determination of these data normally

involves the separation of samples of liquid and vapour in true equilibrium and analysis of the two phases when separated. The separate determinations can be carried out either at constant temperature (isothermal) or constant pressure (isobaric), though the former is normally preferable as isobaric data are inconvenient for theoretical analysis since excess functions based on such results are complicated functions of temperature and composition.

When equilibrium stills are used, errors in the measured data can be produced by the details of the design and construction of the stills themselves. The sources of these errors are inherent in the various designs but the errors are not of the same importance in every mixture investigated since their magnitude is to some extent dependent on the properties of the mixture, i.e. relative volatility, heat of vaporisation.

The methods available for the determination of equilibrium data fall largely into the following classes :

i) Differential distillation methods

ii) Circulation methods

iii) Flow methods

iv) Static methods

v) Total pressure methods (but for discussion on these see Chapter 4)

vi) Special methods

This discussion will include the most important and recent developments, a review of the methods is available in Abbott (1976) and Marsh (1978). A review of the older methods can be found in Hala et al. (1963).

3.2 Differential Distillation Methods

In differential distillation methods, the oldest method, a small amount of liquid is distilled off from a boiling flask containing a large charge (Hala *et al*, 1963). Although very simple, the method has marked disadvantages of requiring a large liquid sample while only a small vapour sample can be taken for analysis, since the liquid composition must remain substantially constant. Large errors can also be caused by condensation of vapour on the cold walls of the flask at the beginning of the determination. This method has been largely abandoned today. However, Ramalho (1961) proposed a technique for obtaining equilibrium data quickly based on this method. In principle a simple distillation is performed with continuous determination of the concentration of either the liquid or the vapour. One stream is analysed and the composition of the other is found by a material balance.

3.3 Circulation Methods

Circulation methods are the most widely used methods. They are convenient for use at low and medium pressures. Although there are many different equilibrium stills which employ simple circulation, they are all in principle alike. In the circulation stills, a liquid mixture is charged to a distilling flask and brought to the boil. Evolved vapours are condensed into a receiver; the vapour condensate returns to the distilling flask where it mixes with the boiling liquid. Compositions of the boiling liquid and the vapour condensate change with time, eventually attaining steady values. In a properly functioning still, these are the true equilibrium liquid and vapour compositions.

A common principle of all circulation methods is the continuous separation of the vapour phase from the liquid phase under steady state conditions, measurements of the thermodynamic parameters, characterising the equilibrium state, and recirculation of the vapour stream back to the liquid phase. Either all the thermodynamic parameters (temperature, pressure and the composition of the co-existing phases) are measured simultaneously or only those sufficient for the determination of the equilibrium conditions.

Generally the following conditions should be met by a properly designed circulating still (Hala et al. 1963):

1) The still should be simple in design.

2) Small amounts of substances should be required for measurements.

3) Facilities should be incorporated allowing accurate determination of equilibrium pressure and temperature.

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

5) Neither partial condensation of vapour on the temperature-measuring sensor nor over-heating 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) 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 stream's composition and flow.

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

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

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

A) Vapour circulation methods;

B) Condensate recirculation methods; two types

(i) Liquid condensate recirculation;

(ii) Revaporised condensate recirculation;

C) Circulation of liquid phase and vapour condensate.

In this discussion emphasis will be placed on the B and C types of equilibrium stills and for more detailed information on these and type A stills see the review by Malanowski (1982a). Figures 3.1 to 3.11 have been reproduced from the review by Malanowski (1982a).

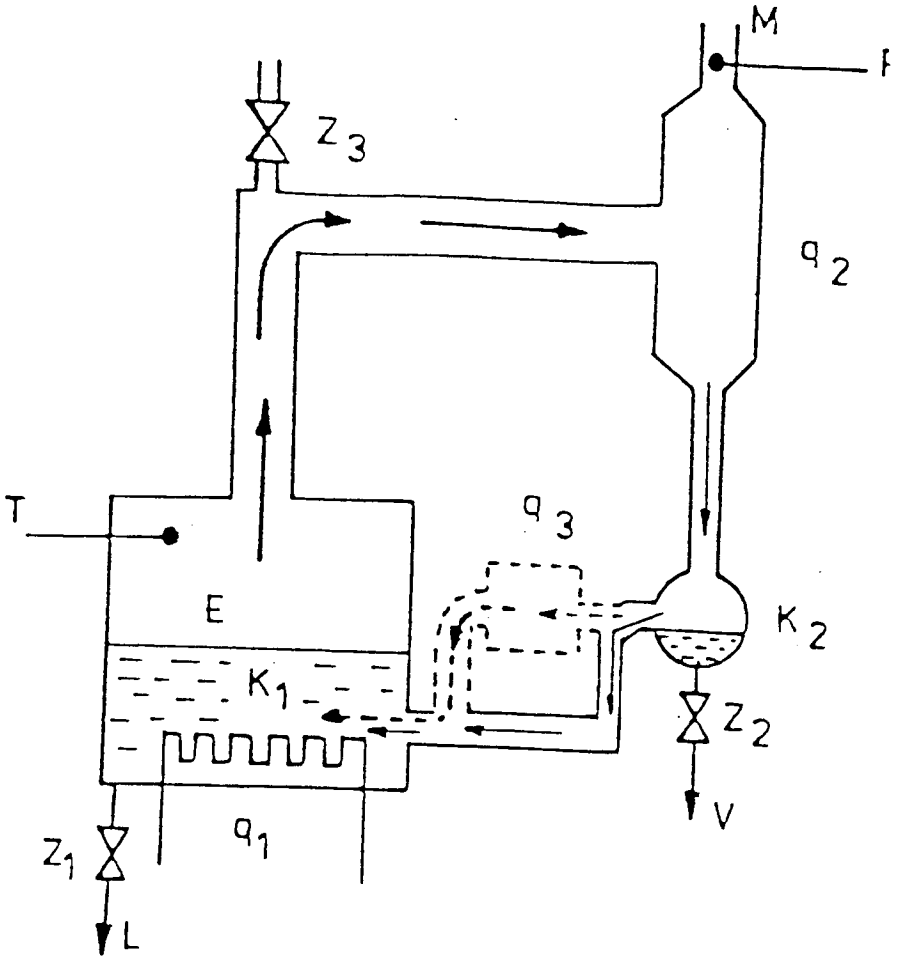
3.3.1 Stills with circulation of the vapour phase only

Equilibrium stills with circulation of the vapour phase only have two distinct operational modes. In the first, the vapour arising from the heated liquid is condensed and re-enters the equilibrium chamber as liquid; in the second, condensate is revaporised by the heater and re-enters the chamber as vapour.

The working principle of these stills is illustrated in Figure 3.1. The liquid sample in the equilibrium chamber E is brought to the boil by the continuous heat from 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 the 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 time necessary to achieve the steady state depends mainly on the volume of the condensate in K_2.

After the steady state has been achieved, boiling is terminated at once, for example by increasing the pressure in the stabilizing system M, to prevent non-equilibrium distillation to the container K2. Samples of the liquid and vapour condensate are withdrawn for analysis from the container K_1 and K_2 through the valves Z_1 and Z_2 respectively. After

Figure 3.1: *Principles of Operation of Vapour Condensate recirculation Method*



Dotted lines denote the alternative flow of the condensate in the case when it enters the equilibrium chamber as vapour: E, Equilibrium Chamber; K_1, Liquid Phase Container; K_2, Vapour Condensate Container; P, Pressure Gauge; T, Thermocouple; M, Pressure Stabilising System; q_1, Boiling Water Heater; q_2, Condensing Water Cooler; q_3, Flash Vapourisation Heater for Condensate; Z_1 and Z_2, Valves; Z_3, Degassing Valve; L and V, Sampling Points.

withdrawal of the samples the still can be filled with a new sample and the entire procedure repeated.

The main drawbacks of this method are:

(1) There is partial condensation of the vapour after bringing the apparatus to a standstill;

(2) Accurate determination of the equilibrium temperature is not possible;

(3) It is not possible to obtain uniform composition in the container K_1.

Numerous modifications of the Othmer apparatus were introduced by different workers to eliminate these drawbacks. This aim was not achieved, and analysis of the thermodynamic consistency of the data obtained by this method indicate low accuracy (Malanowski, 1982). One of the latest versions of the Othmer apparatus (Othmer, 1948) is shown in Figure 3.2. Bukala and Majewski (1952) adapted the Othmer still to produce a two-plate still useful for systems having a low relative volatility and Paul (1976) used a silvered evacuated jacket on the upper part of the vessel to prevent heat losses and consequent partial condensation.
The second operational principle.(i.e., vaporisation of the vapour condensate) and its mode of operation is shown in Figure 3.1 as the alternative configuration. This type of still was developed by Jones (1943) and is shown in Figure 3.3. It consists of a heated residue-chamber K_1, an 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 ensure agitation ofhe residue liquid and allows

Figure 3.2: *The Othmer (1948) Still*

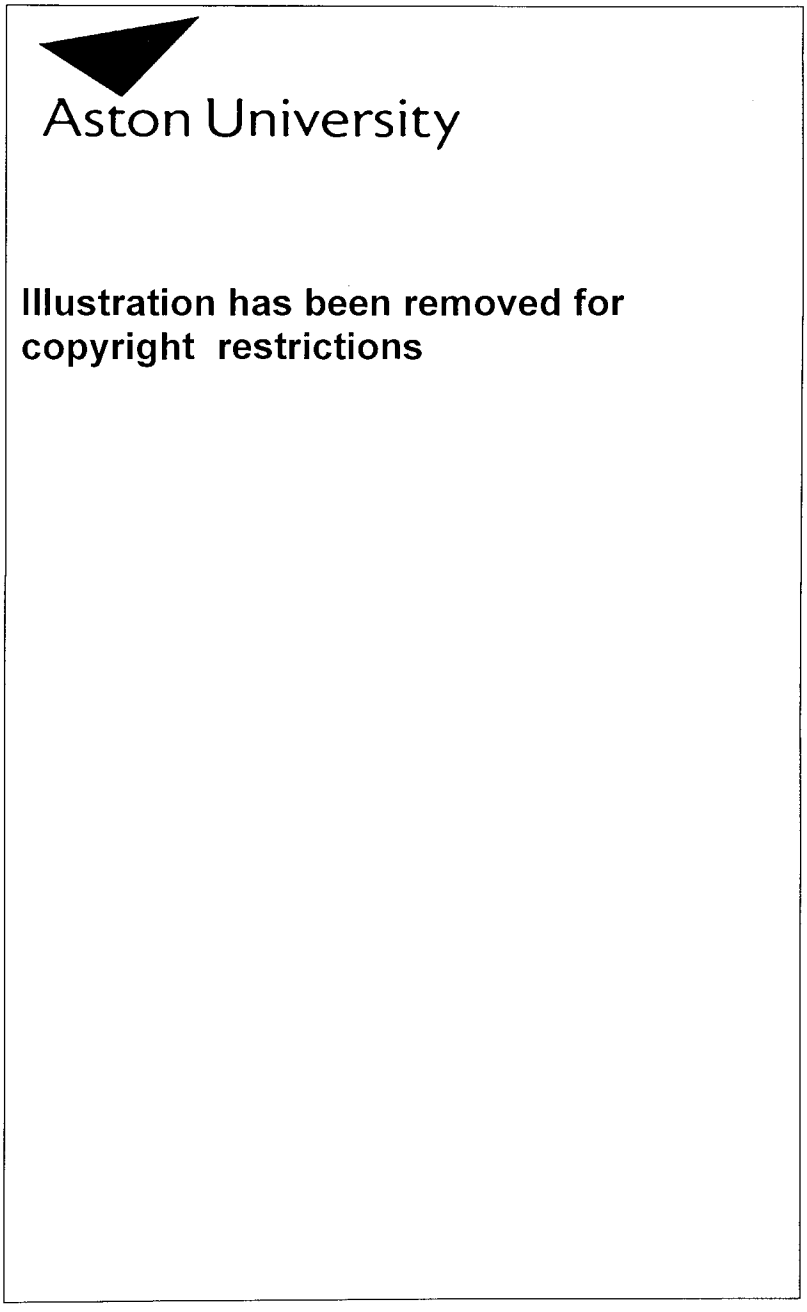
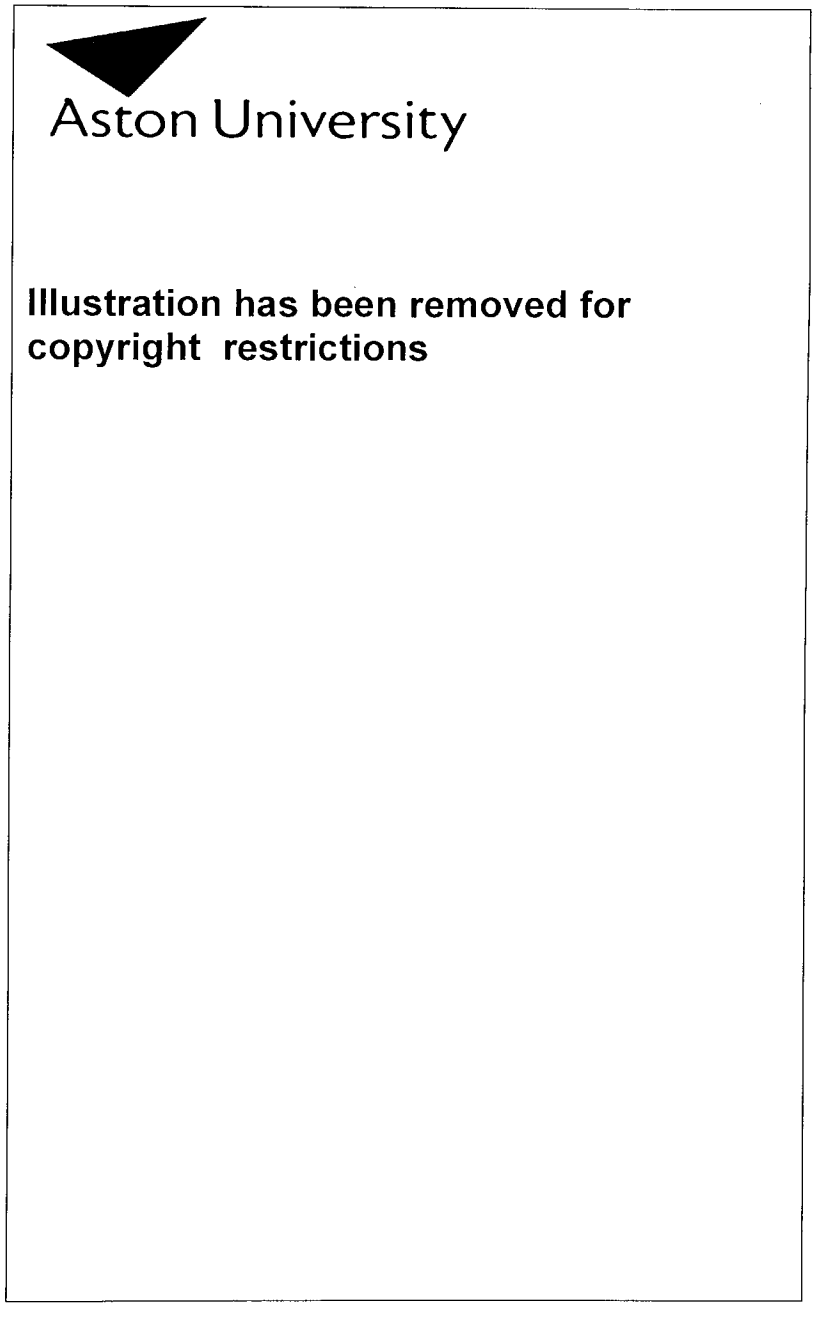


Figure 3.3: *Jones, Schoeborn and Colburn Still (1943)*



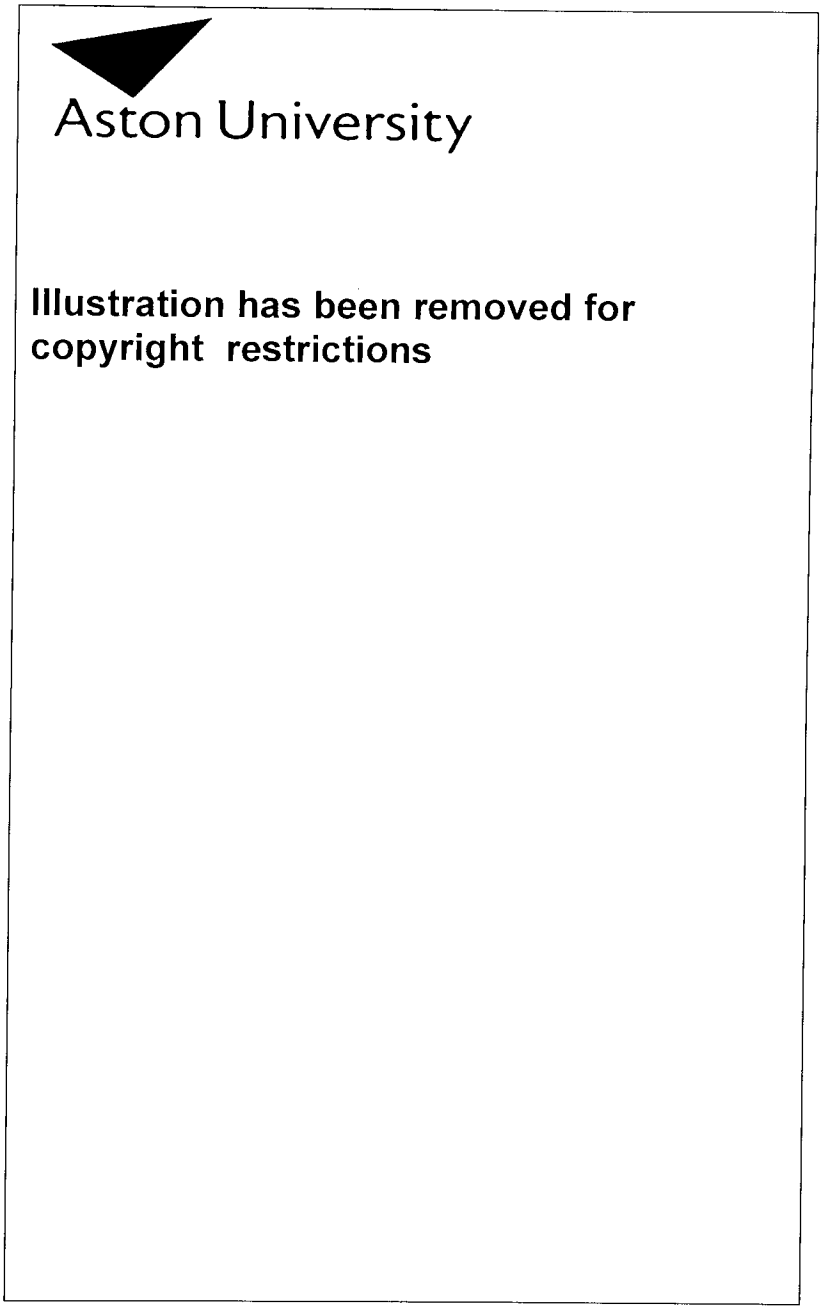
measurement of the temperature. The residue chamber K_1 is heated. The heater q_1 compensates for heat losses so that the quantity of vapour leaving K_1 is the same as that entering. The vapour flowing from K_1 to the condenser q_2 is slightly superheated in the heater q_4 in order to prevent condensation 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 drops 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. Another defect of most such recirculating devices is that they are tedious to operate and require some hours to achieve equilibrium (Williamson 1975).

Kassmann and Knapp (1986), see Figure 3.4, developed a modified version of the Kortum (1953) still in which the vessels are jacketed and the temperature of the liquid which is circulated through the jacket is regulated very close to the boiling temperature of the mixture. Only a little energy has to be added for the operation of the Cottrel pump. Temperature fluctuations caused by boiling are reduced and thermally sensitive substances are not over-heated.

3.3.2 Stills with circulation of both liquid and vapour phases

In stills with circulation of both liquid and vapour phases both phases are circulated through the equilibrium chamber. The Cottrel pump is used, a device which throws a mixture of vapour and liquid slugs at equilibrium onto a thermocouple pocket, thus enabling a very precise temperature measurement. The first circulating still with a Cottrel pump and having the capability for withdrawal of liquid and condensate samples after

Figure 3.4: *Kassmann and Knapp Still (1986)*



temporary cessation of circulation by pressure increase was proposed by Lee (1931). Two important modifications, the separator for the liquid and condensate streams and the facilities for withdrawing samples without interruption of boiling were introduced by Gillespie (1946). This still has the basic arrangement of the Swietoslawski ebulliometer, and gained high popularity after it was found (Coulson, 1948) to be greatly superior to stills with vapour condensate circulation (Othmer, 1943) and even to those modified with an additional Cottrel pump (Scatchard, 1938). Many further modifications of the Gillespie apparatus were introduced, most importantly by Brown and Ewald (1950) who realised that samples taken from the boiler H_1 do not represent the liquid equilibrium composition and that a liquid trap S_2 should be added beneath the separator R on the liquid return line to the boiler H_1.

Owing to certain operating difficulties encountered with this still, Brown (1952) introduced further modifications. He found that the evaporation of a small amount of condensate from the vapour trap, after the still was vented for sampling, led to errors in vapour composition determinations, and he therefore redesigned the sample traps. He further found that if the relative volatility of the system studied is high, flashing occurs when the condensate is mixed with hot circulating liquid. To eliminate this Brown modified the still by adding a condenser C_3 for cooling the liquid return before it mixes with the condensate vapour. The modified still is shown in Figure 3.5. The Brown still allows very accurate results to be obtained. Its most important drawbacks are the very long time, up to four hours, necessary to achieve steady-state operation, and the large sample size required (200 ml).

Another apparatus providing good results, arising mainly from its simplicity and similarity to the still of Lee (1931), was proposed by Ellis (1952) and is shown in Figure 3.6. It 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 systems close to ideal and strongly non-ideal were tested. The resulting data were compared with those measured by Othmer (1943) and Fenske (1947), and were found to correlate more reliable than was the case for the

Figure 3.5: *Brown Still (1952)*

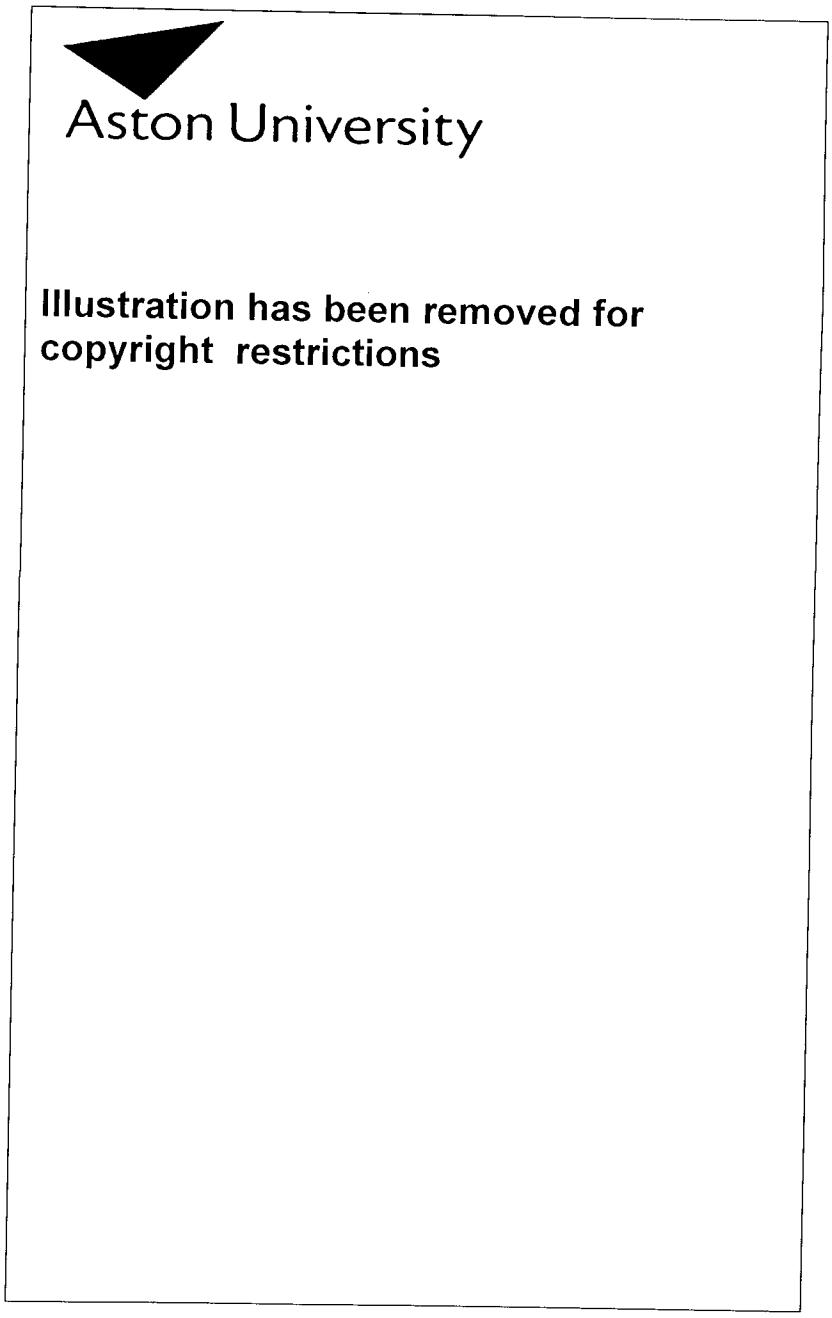
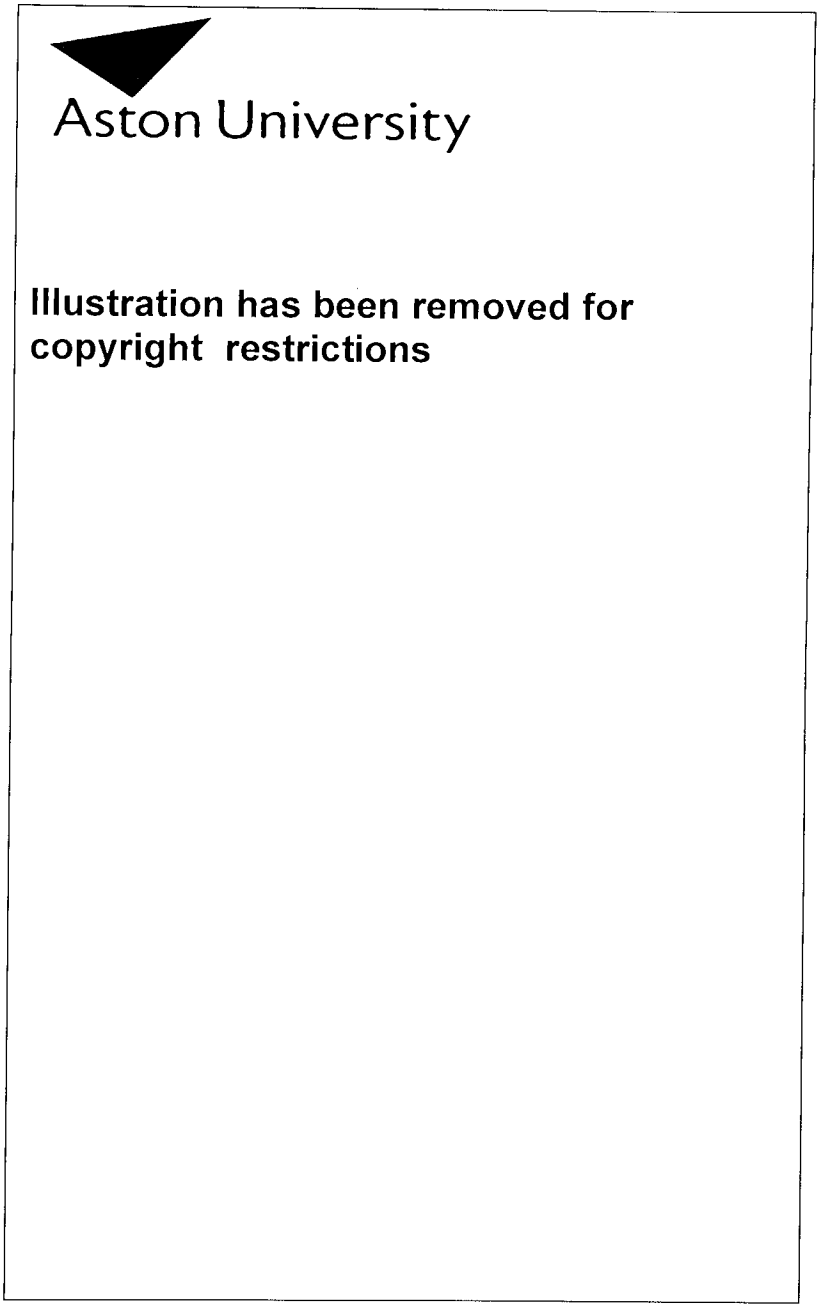


Figure 3.6: *Ellis Still (1952)*



data from other stills.

An interesting apparatus suitable even for systems of very high relative volatility was proposed by Dvorak and Boublik (1963) and is shown in Figure 3.7. They emphasised the importance of thorough stirring, in both the liquid and the condensate receivers.

One of the most advanced stills in this group was proposed by Raal, Code and Best (1972). This still has excellent mixing characteristics and utilizes a novel adaptation of the Cottrel pump to provide accurate temperature measurement and ensure adiabatic operation of the equilibrium chamber. The Cottrel pump forms the annulus between the inner chambers and the outer wall, where a mixture of liquid and vapour is propelled over the thermocouple well. The vapour liquid mixture in the outer annulus maintains the inner equilibrium chamber at the boiling temperature. The liquid sample, collected in the inner equilibrium chamber, is produced by condensation of some of the vapour and comes into equilibrium with the vapour bubbling through it.

Jenkins and O'Donnell (1980) developed a modified version of the Raal *et al* still shown in the Figures 3.8a and 3.8b. 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. This 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

Figure 3.7: *Dvorak and Boublik Still (1963)*

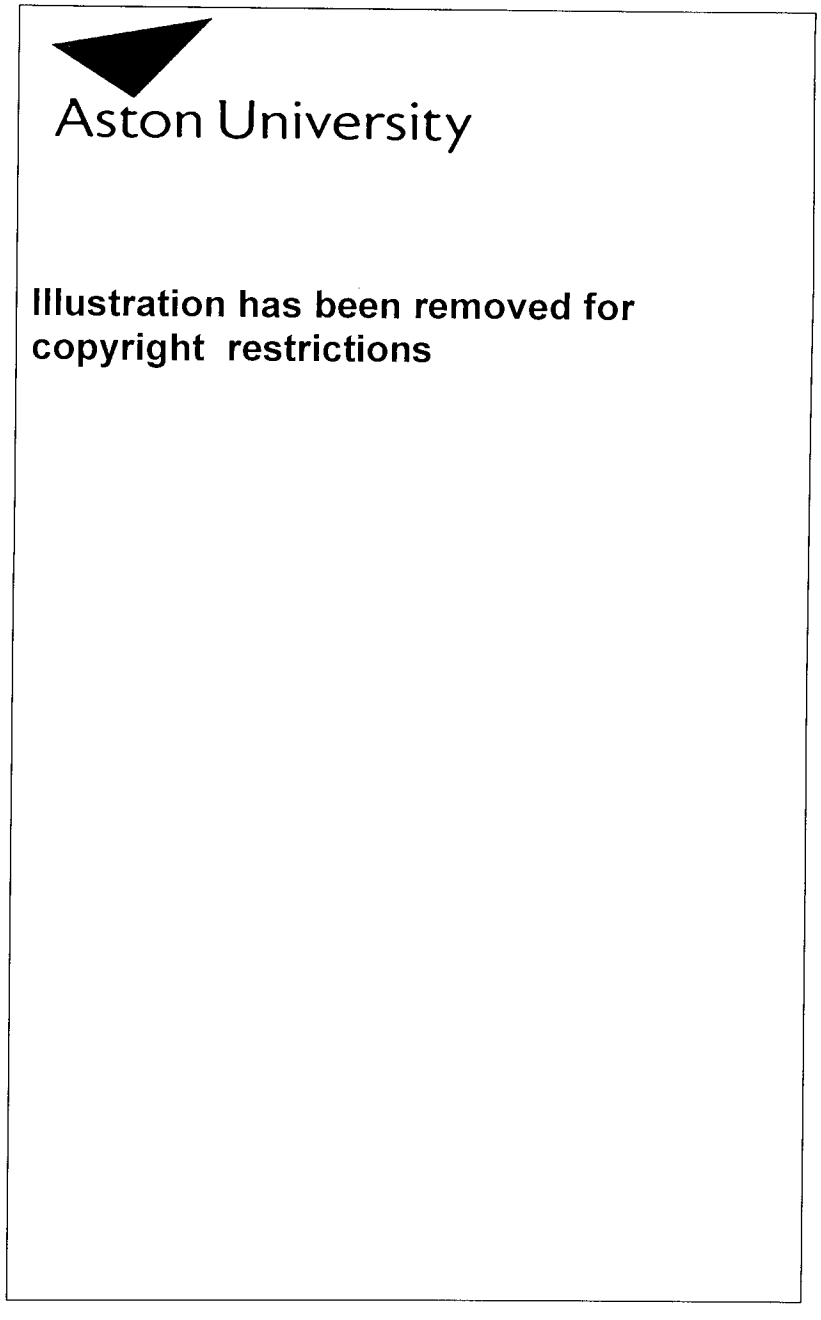
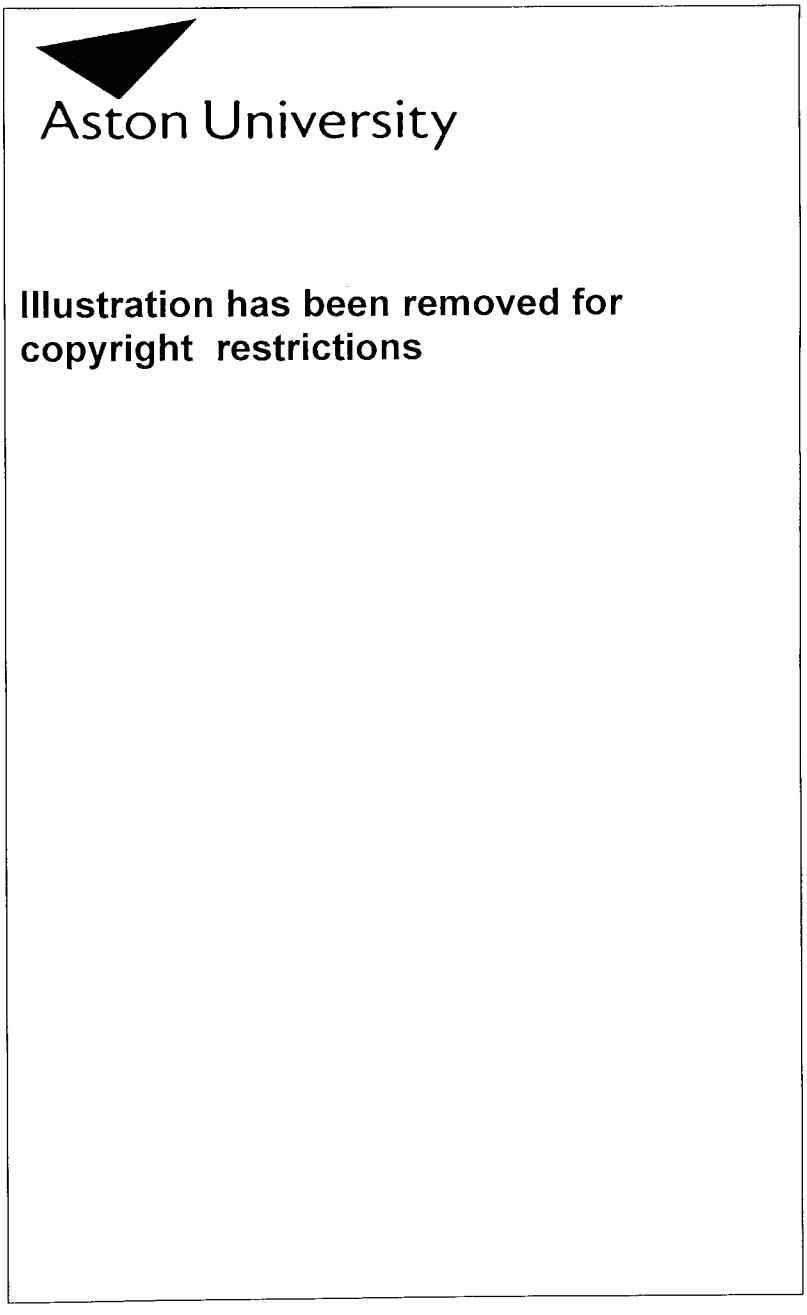


Figure 3.8a: *Line Diagram of Modified Raal, Code and Best Equilibrium Still (1972)*

Figure 3.8b: *Equilibrium Cell of Modified Raal, Code and Best Equilibrium Still (1972)*



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 Cottrel pump surrounding the still maintains the inner and middle chambers at a uniform temperature. The still and the tube D are both lagged and the still is isolated from draughts. Equilibrium is achieved after approximately one and half hours (O'Donnell, 1980). It is similar in design to the original still, the main differences are as follows:

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

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

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

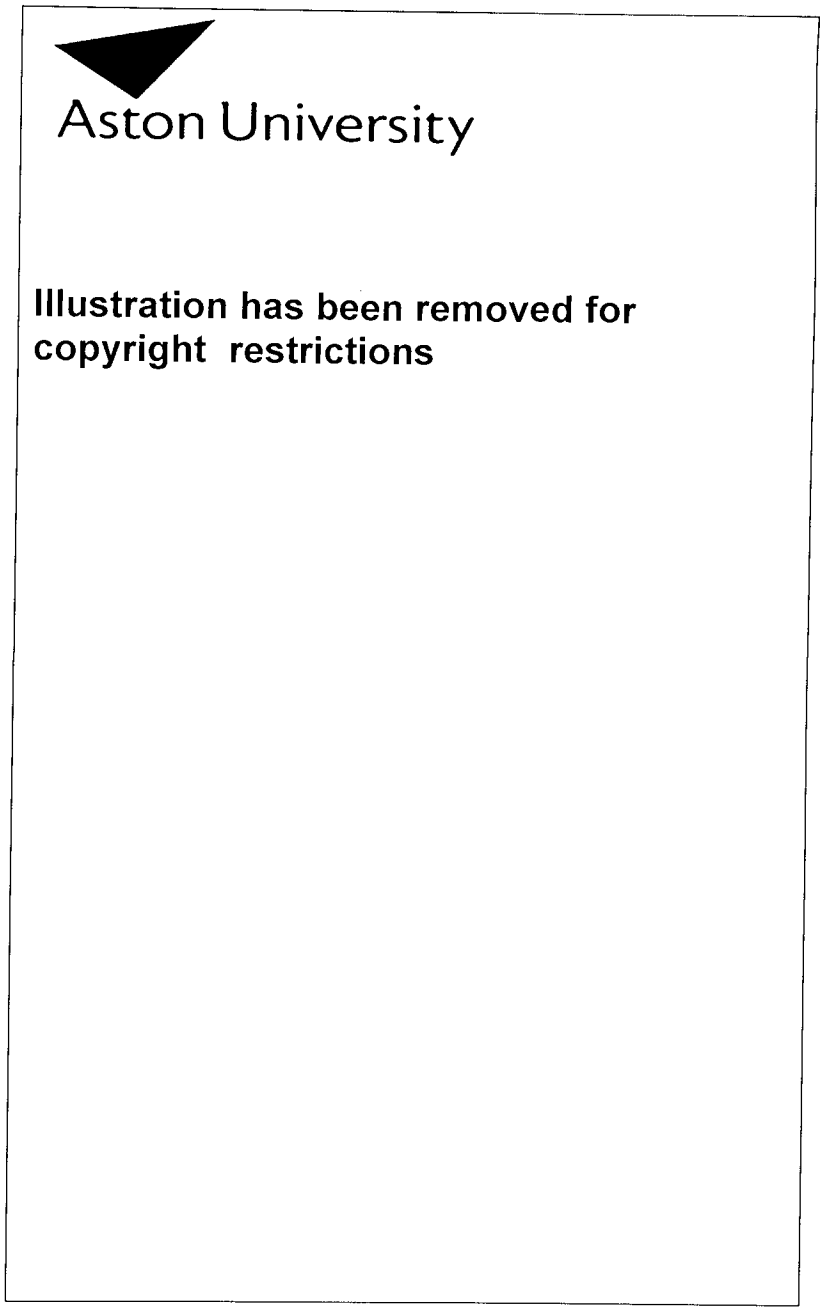
d) The greaseless ball and cup joints used in the structure relieve any stress set up on heating.

The modified apparatus has been used successfully to obtain vapour-liquid equilibrium data on a number of systems. The liquid phase and the vapour phase may be analyzed using gas liquid chromatography and other techniques such as refractive index (Jenkins and Rafaquat, 1988).

Jenkins and Zain (1990) have developed a moderate pressure still based on the O'Donnell and Jenkins modified Raal, Best and Code still with a number of modifications and it is shown in Figure 3.9.

As the equilibrium cell has to be contained in a steel bomb, mounting the cell in the bomb is made easier if the vapour leaves the bomb at its base. To do this an external vapour jacket surrounds the Cottrel pump annulus of the low pressure design, and a bottom

Figure 3.9: *Jenkins and Zain (1990) Modified Raal, Code and Best Equilibrium Still to Work at Moderate Pressures*



connection to this forms the vapour line to the condenser and vapour sampling system.

The second modification is that the residence time of vapour in the Cottrel pump is increased by providing a spiral of glass up the inner wall of the annulus forming the pump. In constructing the cell, the most difficult criterion to meet is that of a small clearance between the two walls of this annulus and providing a spiral makes this less critical. An overflow/weir system has also been incorporated to maintain the vapour/liquid interface inside the isothermal region of the cell body.

Another change is that natural convection is not used to provide circulation through the still. A small graphite gear pump capable of working at pressures up to 35 bar feeds the reboiler. The type of pump used gives a very steady flow if supplied with low voltage DC power from a constant current power source.

Only the equilibrium cell is constructed from glass, the remainder of the apparatus is made from 316 grade stainless steel. Two windows are provided at the sides of the pressure bomb to enable observation of the flows in the equilibrium cell.

The liquid sample is withdrawn through a stainless steel capillary which runs up into the sample chamber in the 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. This equilibrium still is potentially capable of producing data at up to 35 bar.

3.4 Flow Methods

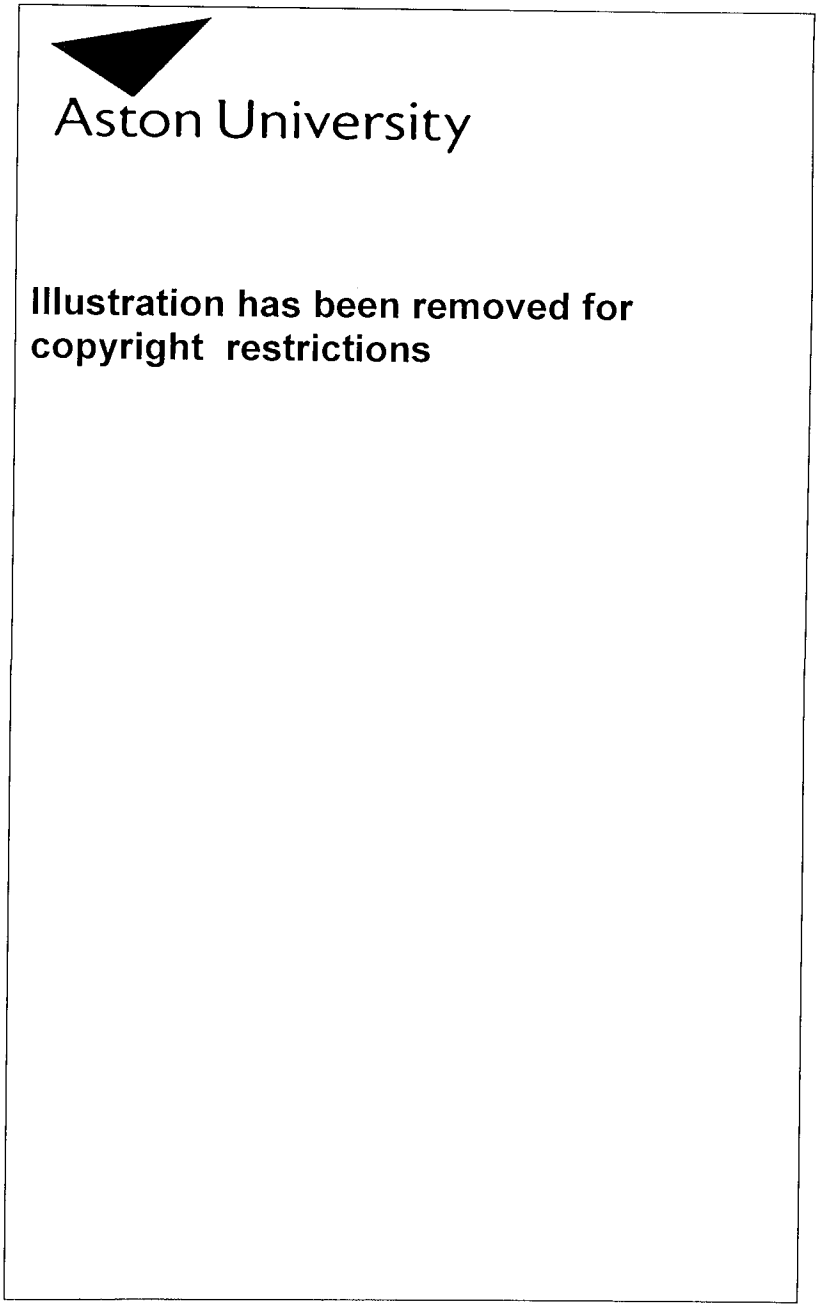
The dynamic flow methods, in contrast to the circulation methods, have the feed entering the equilibrium chamber as a steady stream of constant composition which can be either in the liquid or in the vapour phase or a combination of both. These stills are mainly used for systems of limited miscibility 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* (1953). The Colburn still, shown in Figure 3.10 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 cont actor 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.

Rius *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.

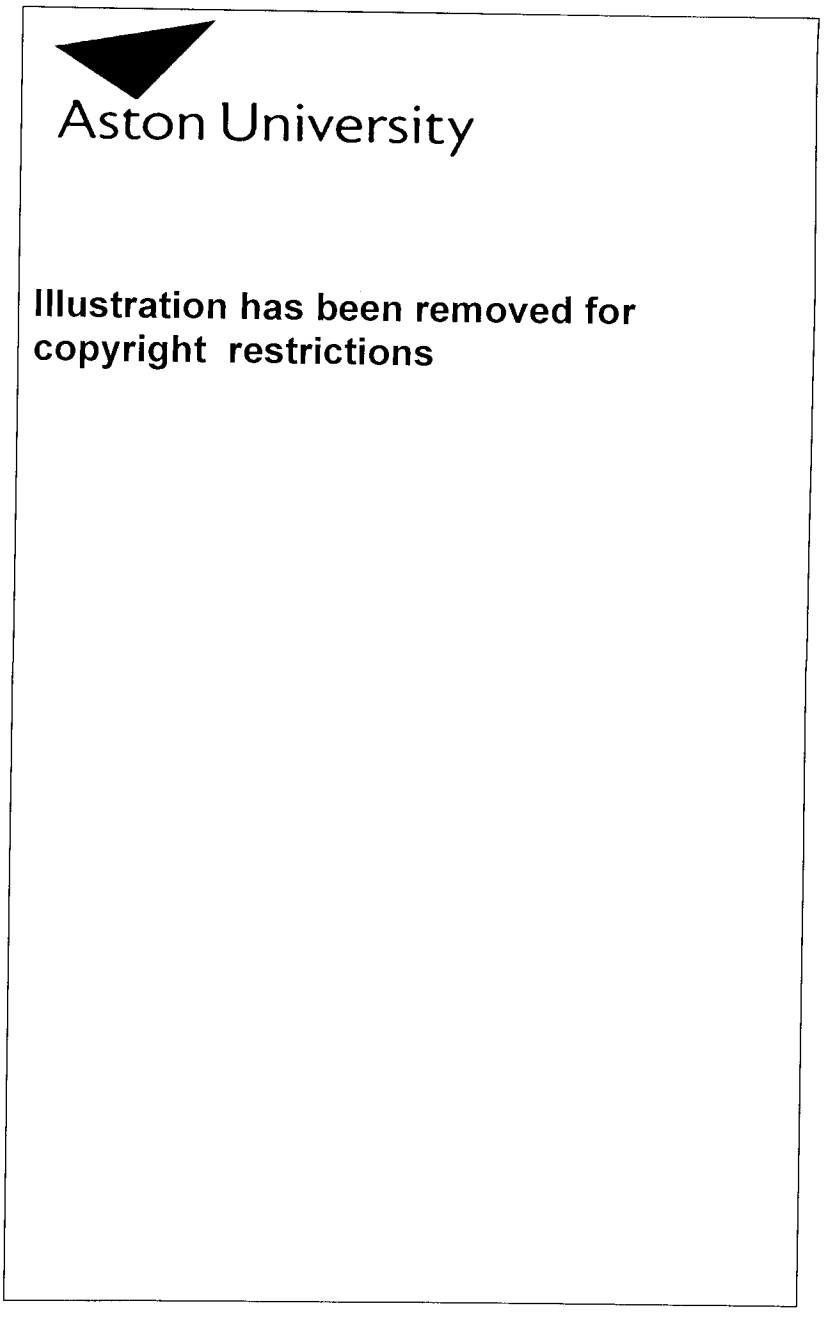
Figure 3.10: *Colburn Still (1953)*



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 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 3.11). In this case the equilibrium chamber, the de-entrainer, the contactor and the vaporiser were 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

Figure 3.11: *Cathala Modified Still (1960)*



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 holdup 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 holdup in the preheater and the vaporiser was calculated to be between 2 and 3 minutes which was considerably less than the holdup 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-methanol, acetic acid-ethanol and acetic acid-n-butanol, all at 760 mm Hg 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, 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.

3.5 Static Methods other than Total Pressure Methods

In static methods of direct experimental determination of vapour-liquid equilibrium data the vapour and liquid phases of a system 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.

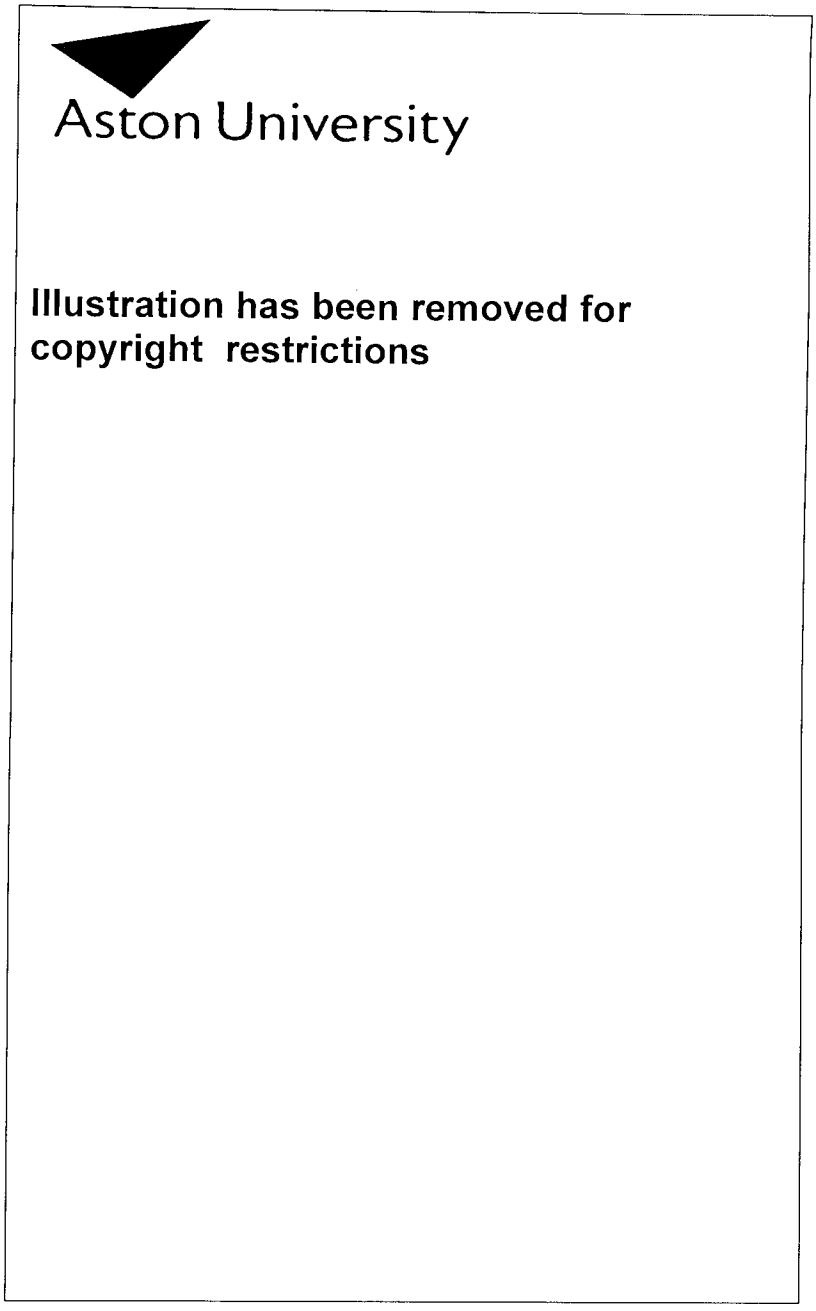
Wichterle and Hala (1963) used a still based on the static method to carry out semi-microdetermination of vapour-liquid equilibrium data in multicomponent systems at isothermal conditions. Their method was based on the sampling of very small volumes of the vapour phase which were then analysed by gas 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 $\pm$ 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).

Tomlins and Marsh (1976) developed another new static apparatus which is shown in Figure 3.12. The purified liquids are degassed in the vacuum sublimation vessel H and introduced by injection through the microvalve J into the glass pressure cell A. The cell was connected through the valve E to the sensing head B of the Granville-Phillips capacitance manometer which was used as a null device, backed by an automatic pressure controller. The pressure in the backing line was controlled so that the pressure differential across the diaphragm was less than 0.7 Pa. The capacitance manometer is used as a null device, the variation in capacitance which occurs when the diaphragm is deflected is the error signal to the servo-system. The backing line pressure was measured with a mercury manometer. Dry nitrogen was stored in a 35 litre reservoir L and admitted through the motorized valve C into the backing line as required. The gas pressure in the reservoir is maintained at about 2.7 kPa above the backing line pressure by a Matheson vacuum regulator M. To achieve optimum control, gas is continuously removed from the backing line through an Edwards Speedivac needle valve D. The temperature of the liquid and vapour in the pressure cell is measured with a platinum resistance thermometer (Marsh, 1978).

Figure 3.12: *Tomlin and Marsh Static Apparatus (1976)*



1978).

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.

3.6 Special 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 idealized 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 coordinates 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 idealized 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 systems 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 systems 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 utilizes 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 systems.

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

Christian and his coworkers 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-z 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 delivered to the system through a chromatograph valve. A complete experiment, covering about half the liquid-composition range, takes about two hours.

The isopiestic method can be used for mixtures containing a single volatile component. An apparatus described by Herskowitz and Gottlieb (1984) is representative. It consists of five silver cups placed in holes drilled in a large copper plate. Three cups are loaded with non-volatile standards and with the non-volatile substance being studied. Weights of the non-volatile substance are determined, and some volatile substance is added gravimetrically to each of the cups. The copper plate with cups is placed in a desiccator, air is pumped out, and the entire assembly allowed to equilibriate in a constant-temperature bath. At equilibrium, the chemical potential of the volatile substance is the same in the sample solution as in the standard solutions; gravimetric determination of equilibrium compositions allows one to compute (from the known behaviour of the standard solutions) the activity of the volatile substance in the samples. No pressure measurements are required, but the non-volatile substances must be truly non-volatile. Equilibriation times can be very long; Herskowitz and Gottlieb allowed one to three days for each of their determinations.

A method which determines composition by measuring density in situ has been used by Hall and Eubank (1975) and is known as the method of intersecting isochores.

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 repreduced, 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-idealities can be ignored in the data reduction, the liquids need not be degassed. Sample sizes are small, and a complete binary system can be studied in a day (Abbott, 1986).

A high pressure method for PVT measurements has been developed by Ashcroft and Shearn (1990). This method enables the measurements of high pressure PVT properties, vapour-liquid equilibrium data, densities, bubble points, and viscosities. Its operating ranges are for pressure, 3 to 690 bars and for temperature, 5 to 150°C and it has been used to study pure hydrocarbons, carbon dioxide, crude oils, natural gases and natural gas liquids.

The equilibrium cell has an internal volume of 900 ml. The materials are transferred by displacement with mercury from high pressure sample bottles to the equilibrium cell where they are confined between mercury and a hydraulic oil-operated piston. A double-acting high pressure pump allows the mixture under test to be moved, without change of pressure, through a capillary-viewing section in order to identify the phases. Small samples of liquid and vapour can be withdrawn through a sampling valve for direct injection into the carrier gas of a gas chromatography system.

Chapter 4: Review of the Techniques Based on the Total Pressure Approach

4.1 Introduction

Most of the equilibrium stills mentioned in the proceeding chapter are subject to errors due to partial condensation of equilibrium vapour or superheating of vapour in the vapour jacket, occurrence of concentration gradients in the boiling liquid, imperfect mixing of cold condensate with boiling liquid, entrainment of liquid droplets with the vapour and the presence of concentration gradient in the condensate receiver. The reliability of these equilibrium stills is further hampered by the fact that they involve sampling and analysis of both liquid and vapour phases. One method which eliminates the need for separating the liquid 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.

4.2 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 minimize 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 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 assumed constant during operation. The technique assume vapour phase ideality. The ebulliometric method in general has the disadvantage that it can produced spurious results when the mixture consists of widely

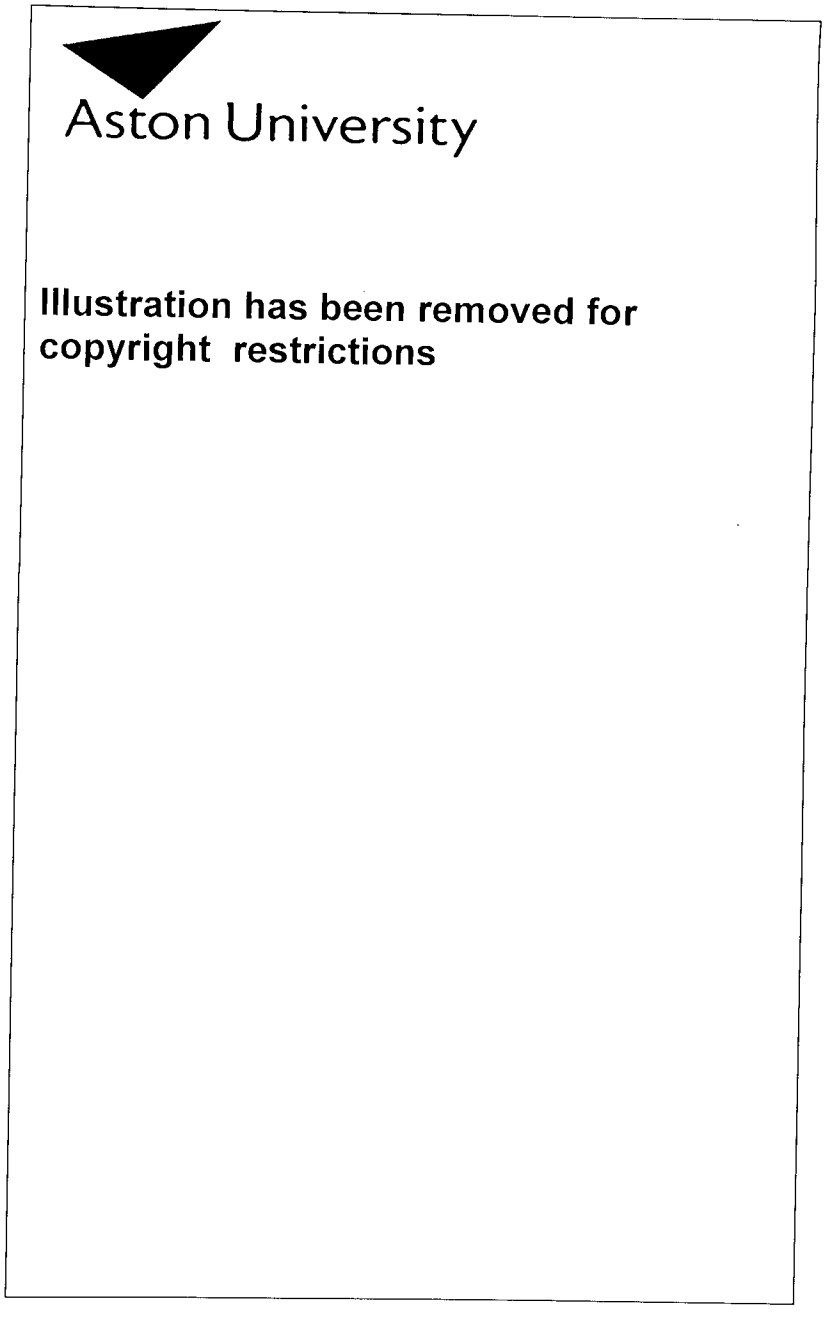
differing boiling points.

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 were carried 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) as shown in Figure 4.1. 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 system could be covered in two runs and it was possible to produced 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

Figure 4.1: *Total pressure VLE cell of Gibbs and Van Ness (1972)*



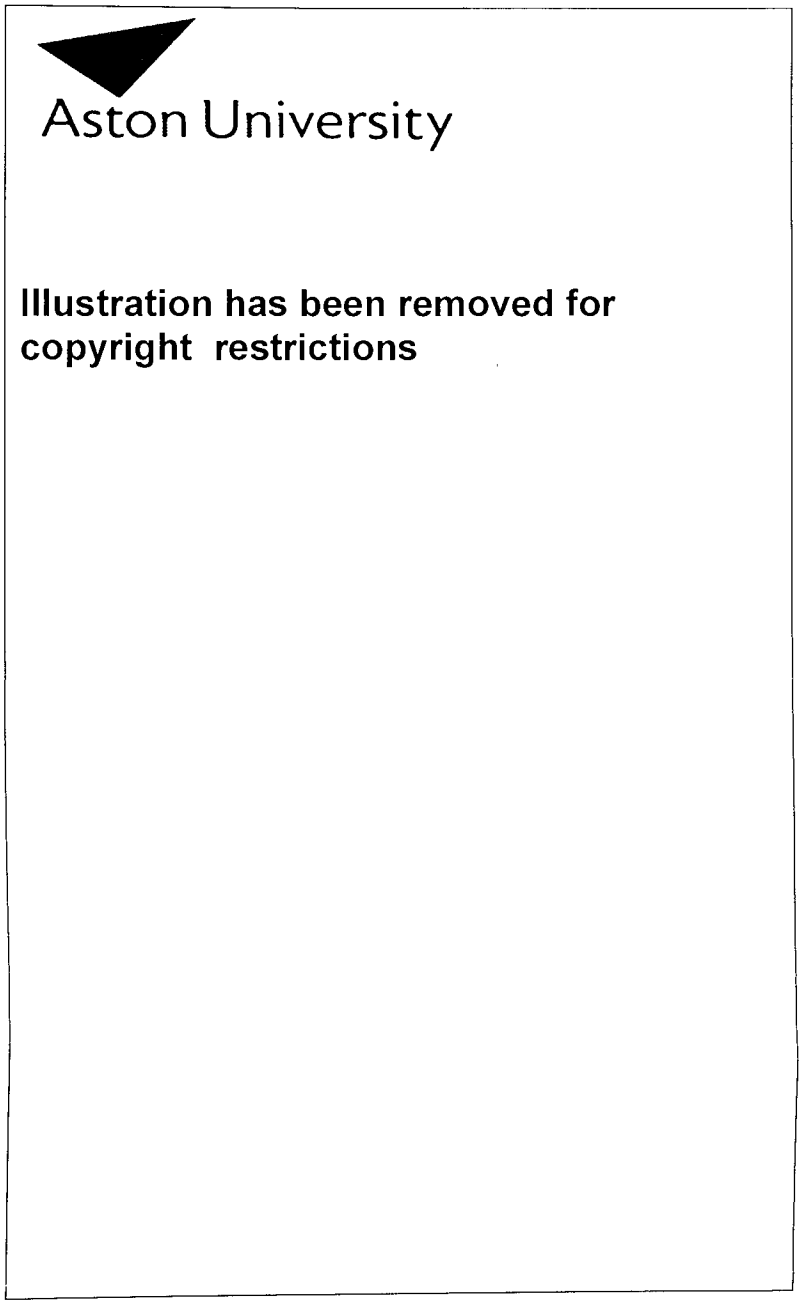
Instruments fused quartz Bourdon pressure gauge which measured the vapour pressure directly. The line connecting the test cell with the Bourdon gauge was insulated and heated to a temperature above that of the cell to prevent condensation of vapour. This mode of operation could not be used above 45°C

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 systems 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 embossed a vernier scale. As shown in Figure 4.2 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 to 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

Figure 4.2: *Total pressure apparatus of Jenkins and Smith (1975)*



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 equalizing 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,

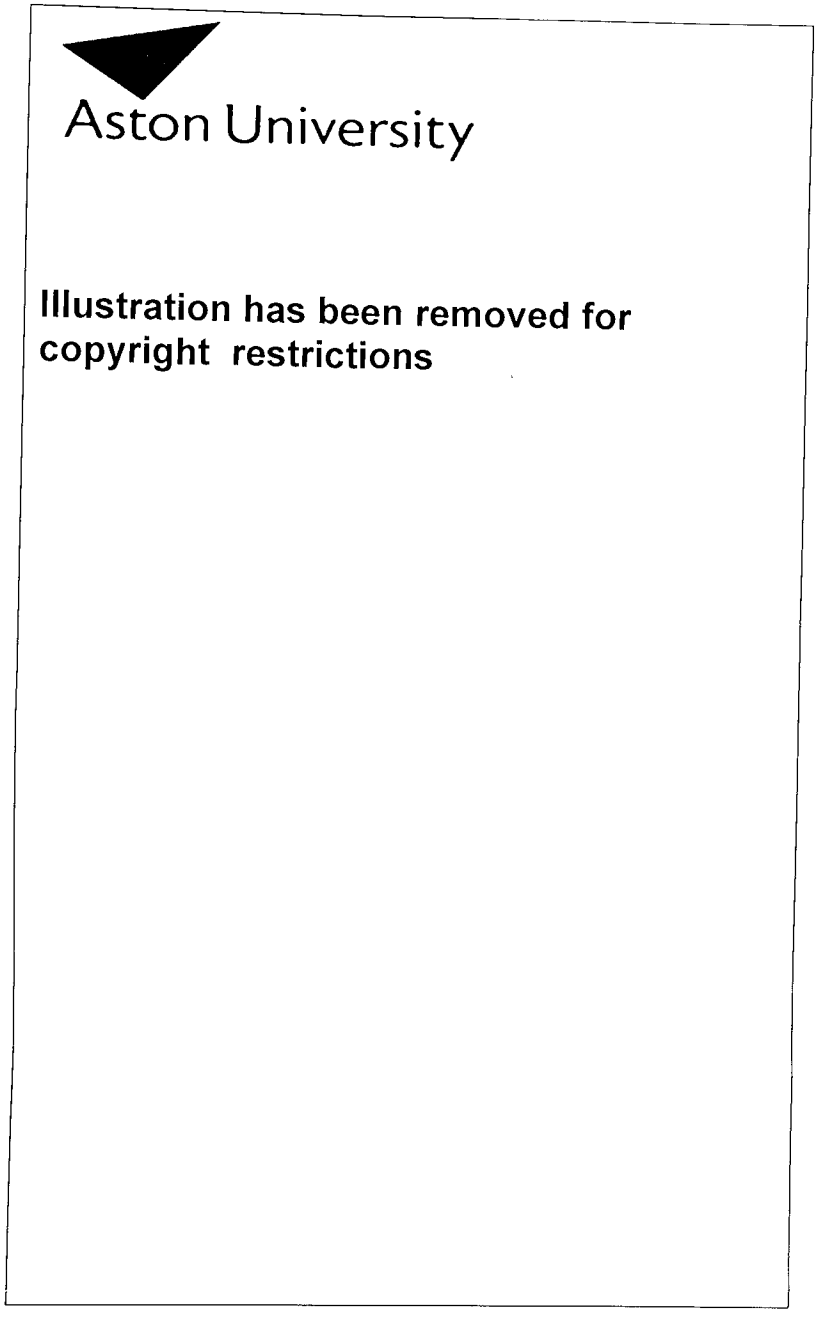
b) its ability to produce data at low concentrations.

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). The main apparatus is shown in Figure 4.3. They used a 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.

Figure 4.3: *Total pressure apparatus of Ronc and Ratcliffe (1976)*



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 system 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. The main apparatus is shown in Figure 4.4.

Maher and Smith (1979a&b) developed a new version of the total pressure apparatus with one design objective in mind, that is to obtain the vapour-liquid equilibrium measurements of three pressure versus liquid mole fraction, x, isotherms for a given binary system within five working days. As shown in Figure 4.5 fifteen small cells were loaded with two pure components and thirteen intermediate binary mixtures. The cells were loaded by adding the desired amounts of liquid to each one and weighing after each addition. After loading the fifteen cells were attached to the vacuum line. The liquids in the cells were degassed by successive freezing, evacuation and thawing cycles. After degassing the manifold with the attached cells was placed in a temperature-controlled bath and connected to the pressure transducer. The P versus x isotherm at the bath temperature was obtained by opening each cell in turn to the pressure transducer. With this arrangement it was sometime possible to measure two isotherms in the same day. The cells were in the liquid bath but the manifold was in the air bath which is kept about 5 K warmer than the liquid to prevent condensation in the valves, manifold, pressure transducer and the connecting lines. The pressure measurements were made by opening each cell in turn to the pressure transducer.

With this method the rate of data accumulation was rapid as compared with the titration device where one component is put into the cell and the second component is added in small increments to change the composition. One drawback of this method is that it is only suitable for chemically stable systems. Another problem with this apparatus is that build up of pressure due to leakage and desorption occurs over a four days period from the last degassing cycle.

Mentzer, Greenkorn and Chao (1982) developed a high pressure version of the total

Figure 4.4: *Total pressure apparatus of Aim (1978)*

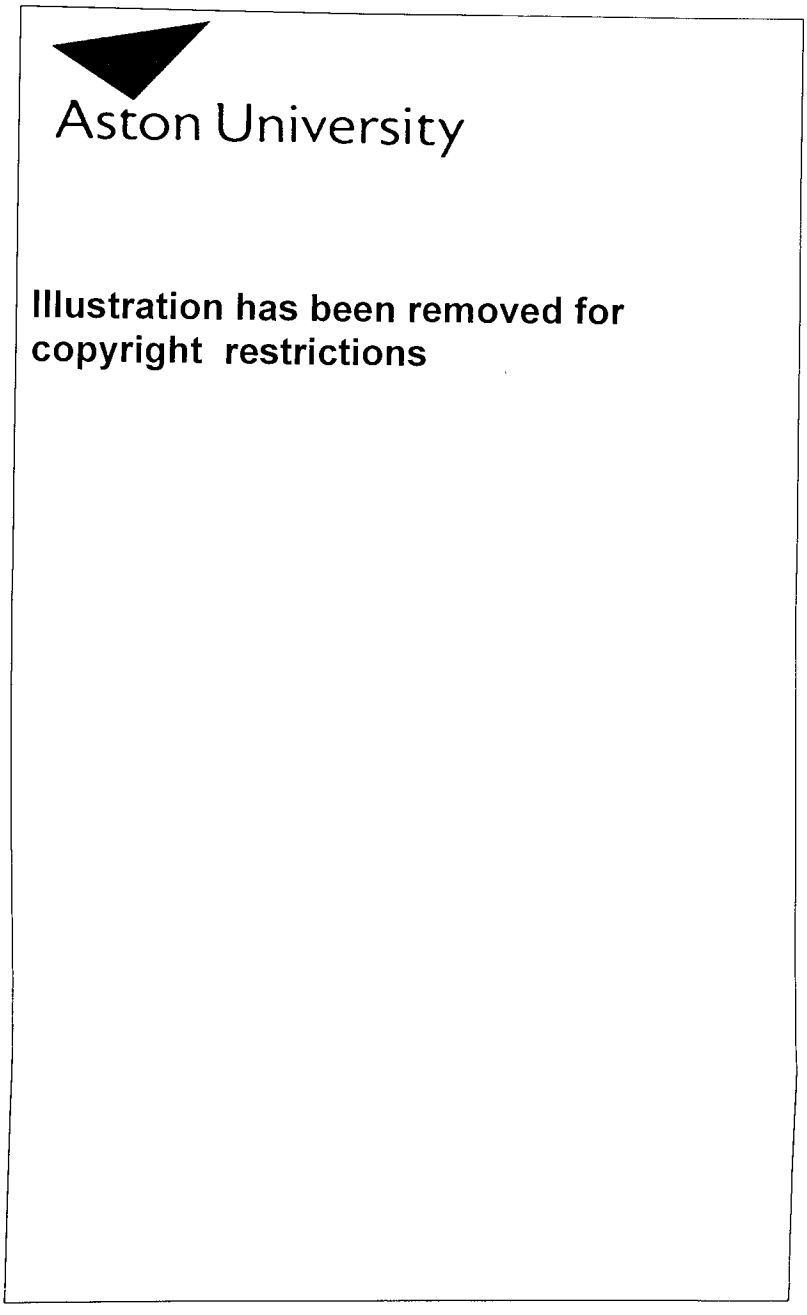
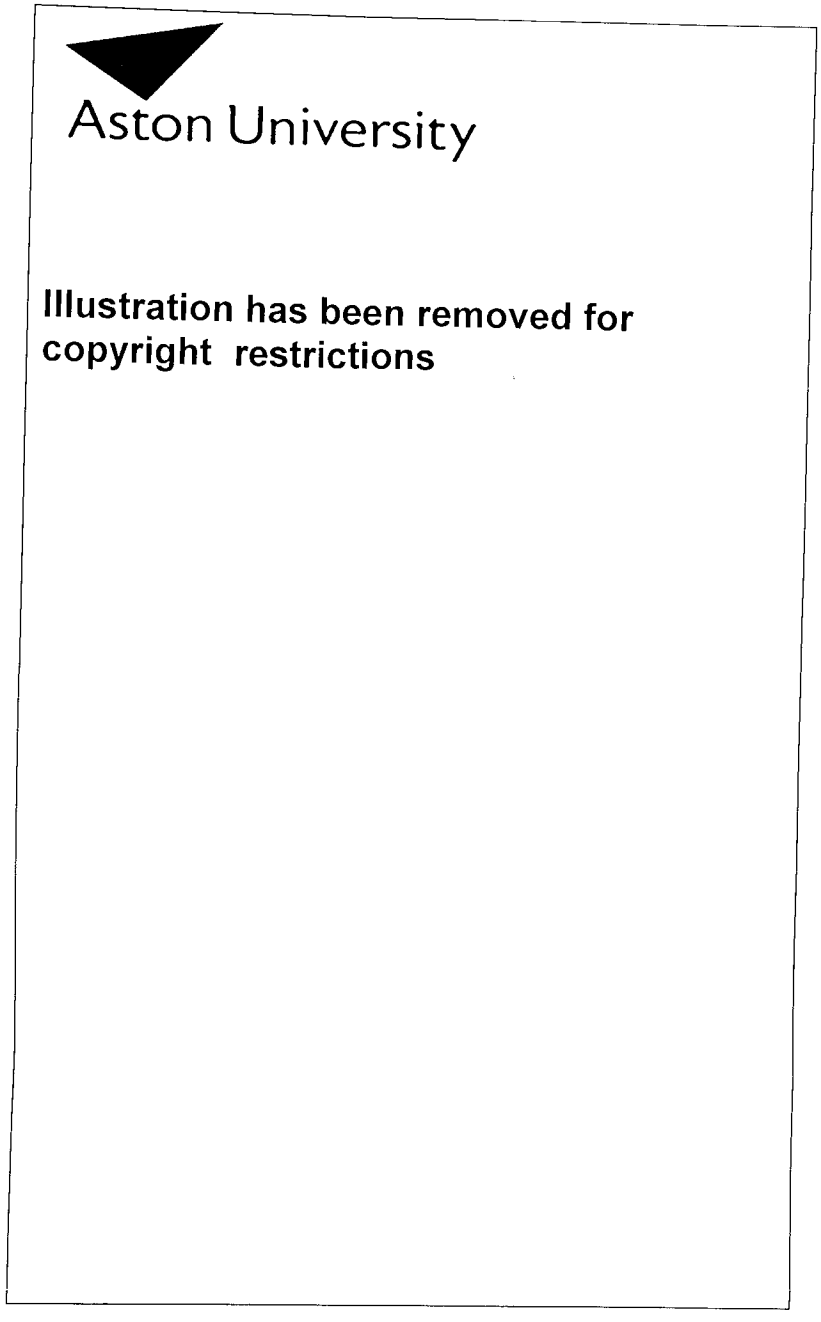


Figure 4.5: *Total pressure apparatus of Maher and Smith (1979)*



A, Manifold Assembly; B, Baffle Tank; C, Impeller; D, Impeller Motor; E, Auxillary Heater; F, Auxillary Cooling Coils; G, Control Heater; H, Cells; I, Nulling Transducer; J, Air Bath Blower; K, Openings for Air Flow; L, Air Bath Heaters.

pressure apparatus based on the original design of Gibbs and Van Ness (1972) as shown in Figure 4.6. 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 vapourises. 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.

Gillespie, Cunningham and Wilson (1985), see Figure 4.7, developed another version of the total pressure apparatus in which they constructed an equilibrium cell from 304 stainless steel with a capacity of 296 ml. The cell was equipped with a charging and sampling line, a thermowell and a pressure tap. The temperature of the cell was measured with a thermocouple and the pressure with a mercury manometer and a cathetometer. Both temperature and pressure were measured within the accuracy of $\pm$ 0.05 K and $\pm$ 10 Pa. This apparatus differs from those mentioned above in that it employs a charging cylinder rather than a piston burette as a means of introducing degassed components in to the equilibrium cell. The composition of the charge in the cell was measured by weight change of a charging cylinder for each increment. The fluids in the charging cylinder were stored under a pressure of 174 kPa.

Alessi, Fermeglia and Kikic (1986) developed an apparatus based on that of Gibbs and Van Ness (1972) to determine the activity coefficients at infinite dilution for binary systems. The apparatus consisted of two cells and operated according to the principle

Fig. 4.6 Total pressure apparatus of Mentzer, Greenkorn and Chao (1982)

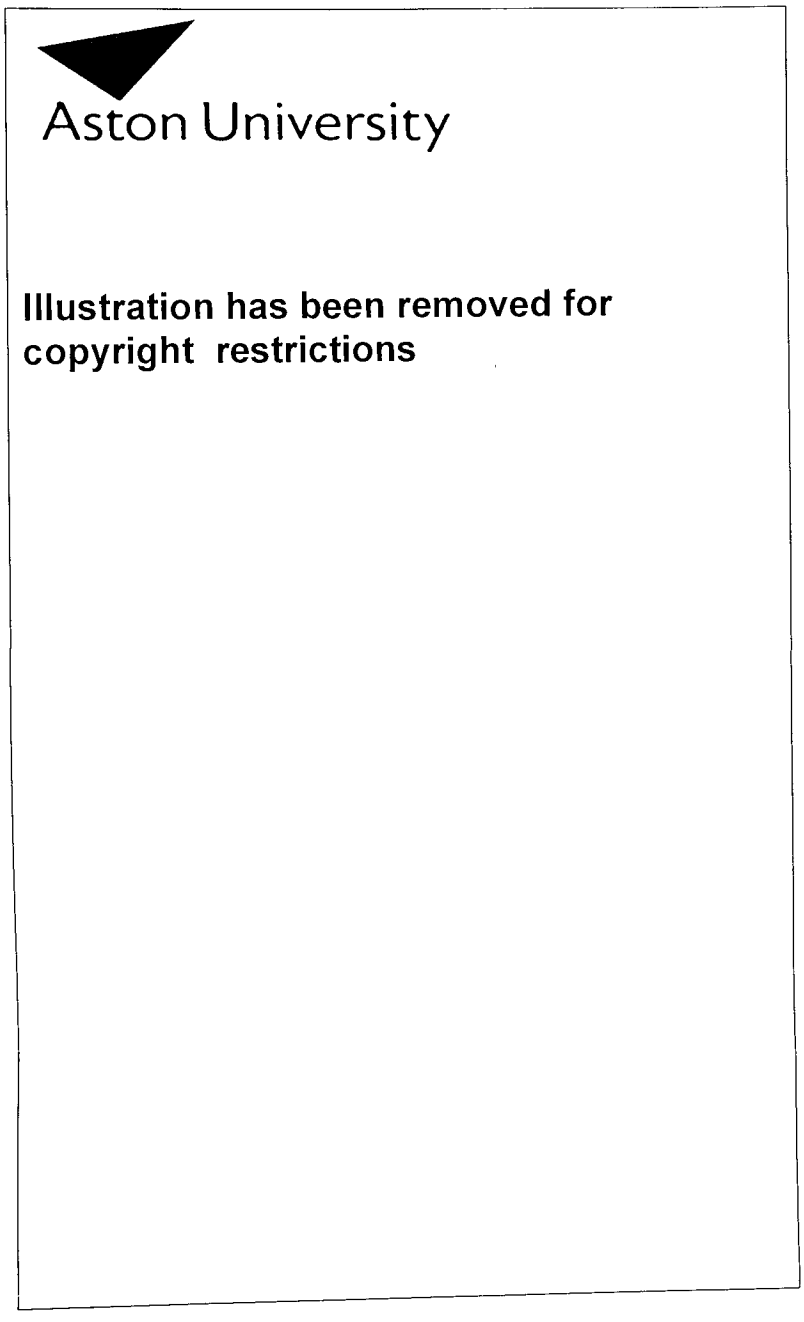
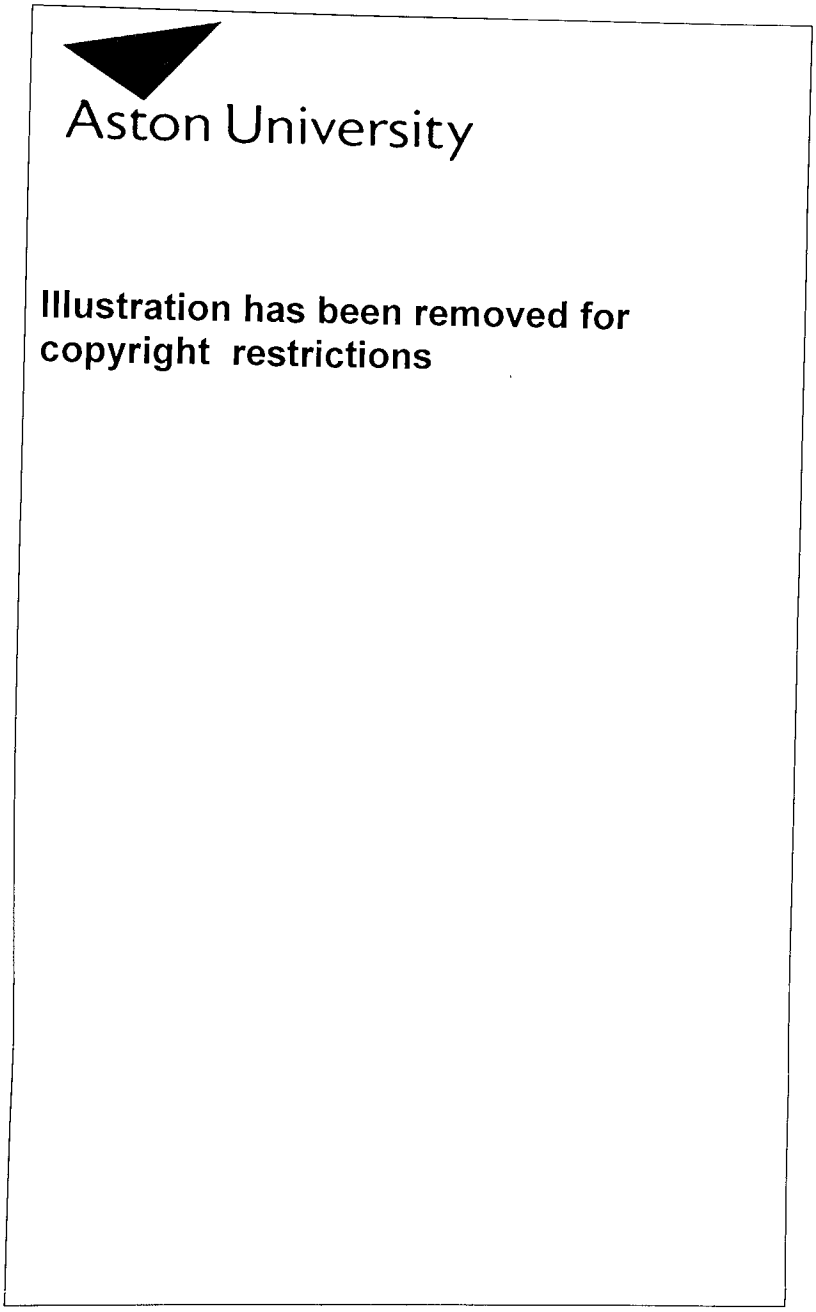


Figure 4.7: *Total pressure apparatus of Gillespie, Cunningham and Wilson (1985)*



proposed by Gibbs and Van Ness, except, as shown in Figure 4.8, two cells, A and B, were used and that the component which was present in small concentration (solute) was injected into the cell A, containing a known amount of the solvent, by means of a gas-tight syringe. The second cell, B, contained only the solvent and therefore could be considered as the reference cell. Difference in pressure at constant temperature were then determined for additions of known amount of the solute in the cell A. The total pressures above the liquids in the cells A and B were measured by pressure gauges. The two cells were identical they were constructed in 316 grade stainless steel and they had a volume of 53 ml each.

The procedure for degassing was essentially that proposed by Hermsen and Prausnitz (1963) and consists of distillation under vacuum at total reflux and a programmed sampling of the top product by means of two solenoid valves. Complete degassing was normally achieved in 20 to 25 hours of continuous running.

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 technique. 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.

Figure 4.8: *Total pressure apparatus of Alessi, Fermeglia and Kikic (1986)*

All the total pressure methods mentioned above depend on the availability of a suitable computational technique to reduced the P-x data to give y values and the method developed in this work is no exception. Use of a data reduction program has been made involving a suitable activity coefficient model for the liquid phase to deduce y values.

4.3 Data Reduction

Data reduction is somewhat complex, as potentially a number of methods are available (Barker, 1953; Ljunglin and Van Ness, 1962; Hala et al., 1967, Mixon et al., 1965; Abbott and Van Ness, 1975). These methods involve the evaluation of liquid activity coefficients, partial pressures and equilibrium vapour compositions from the total pressure-liquid composition measurements. In general, these methods involve evaluations of either constants of equations representing the liquid activity coefficients or of equilibrium vapour compositions directly by means of a step-wise integration procedure. All methods involve the Gibbs-Duhem equation in an integrated form.

The most straight forward approach is due to Barker (1953) in which the adjustable parameters in any desired integrated form of Gibbs-Duhem relationship (such as any of the extended forms of the Margules equation or the UNIQUAC equation) are found by optimising the fit between the experimental and calculated values of the total pressure. The y values can then be deduced for the experimental x values at the measured temperature and total pressure, since the activity coefficients may now be calculated. The only drawback of this approach is if the equation chosen can not in fact represent the actual behaviour of the mixture, especially at the extremes of the concentrations.

In doing this fit in this work we need to apply a correction to each x, P, T point for the material present in the vapour phase, since we only know the total volume of the cell. Ignoring the change in volume on mixing will give still a good estimate of the vapour phase volume, and so of the mole numbers in the vapour phase, if we know the vapour composition (which at first we do not). So the first Barker fit uses the assumption that all

the material is in the liquid phase. The resulting y values may then be used to correct this assumption and generate corrected liquid phase compositions (the corrections are in fact very small at sub-atmospheric pressures).

This procedure automatically generates the parameters for the fitting equation used. Parameters for other equations can be found by repeating the Barker fits.

The Barker method is based on the assumption that the excess free energy G^E can be represented as a suitable function of composition. It is the availability of such a suitable analytical expression, for relating G^E to x that is capable of producing a fit to the data within the limits of experimental uncertainty, is that the only requirement of the Barker approach. Abbott and Van Ness (1975) have developed an empirical approach to meet this requirement and they proposed the use of extended four-suffix Margules equation. Details of general thermodynamic equations used can be found in Van Ness et al. (1973) .

If,

$$g = \frac{G^E}{RT} \qquad - 4.1$$

and we may write the following equations for an i , j binary system:

$$g = x_i \ln \gamma_i + x_j \ln \gamma_j \qquad - 4.2$$

and,

$$P = \frac{x_i P_i^{Sat}}{\phi_i} \exp\left(g + x_j \frac{dg}{dx_i}\right) + \frac{x_j P_j^{Sat}}{\phi_j} \exp\left(g - x_i \frac{dg}{dx_i}\right) \qquad - 4.3$$

where:

$$\gamma_i = \frac{y_i P}{x_i P_i^{Sat}} \phi_i \qquad - 4.4$$

and,

$$\phi_i = \frac{\exp\left(B_i i - V_i^{l}\right)\left(P - P_i^{Sat}\right) + P y_i^{2} \gamma_{ij}}{R T} \qquad - 4.5$$

Since the terms on the right-hand side of equation (4.3) represent the partial pressures, $y_i P$ and $y_j P$, the y's are calculated by division of the values of these terms by the calculated value of P. Barker's method is carried out through application of equation (4.3) in conjunction with a correlating expression for g, using five-suffix Margules equation:

$$\frac{g_i}{x_1 x_2} = A_{21} x_1 + A_{12} x_2 - \left(\lambda_{21} x_1 + \lambda_{12} x_2\right) x_1 x_2 \qquad - 4.6$$

The procedure is to seek through regression a set of values for the parameters in the correlating expression for g that minimises the sum of the squares of the differences between the experimental values of P and the corresponding values calculated by equation (4.3). Since the y's are not known initially, calculation of ϕ_i values requires an iterative process.

Chapter 5: Development of the Total Pressure Apparatus

5.1 Introduction

The experimental apparatus described in this section was developed for measuring vapour-liquid equilibrium data at atmospheric and subatmospheric pressure. The method is principally based on the measurements of the total saturated vapour pressure as a direct function of the composition of the binary mixture. The method produces isothermal data for binary mixture over the full composition range with the need of sampling and analysis stages eliminated for both phases. It is suitable for obtaining vapour liquid equilibrium data at very low concentrations of one component.

5.2 Practical Considerations

The final apparatus consists of a number of sections each having a different function. Their design and construction are discussed below:

1) The degassing units

2) The dispensing devices

3) The equilibrium cell

4) Auxillary equipment

5.2.1 Degassing units

The removal of all the air and gases from the mixture components is an essential pre-requisite to ensure that the cell pressure is a function of the temperature and the mixture vapour composition only. Failure to completely degas the components is often the cause of the largest experimental error present in total pressure techniques and is severely critical in methods where pressure differences may be of the order of only 10 mmHg.

Various degassing techniques have been reported in the literature. Most popular procedures involve the pure components being degassed by freezing, evacuating and thawing cycles. This procedure is, however, tedious and time consuming. An improved procedure was adopted by Jenkins and Smith (1975) where the pure components were degassed by refluxing under vacuum followed by condensation.

The apparatus used in this work was closely modelled on the Jenkins and Smith (1975) design, comprised of three parts A, B and C as shown in Figure 5.1.

Part A is a 250 ml three necked glass round bottom flask which is connected to the double surface condenser and to the reboiler unit, B, while the third branch provides the inlet for the feed. The section C is the reservoir which is used to store the degassed liquids. The entire apparatus is connected to a vacuum pump. The vacuum is used to remove the vapour built up during refluxing of the liquids. High quality vacuum taps are used and efforts were made to ensure that there was minimal leakage of air into the apparatus.

The most important part of the degassing unit is the reboiler which is of 50 ml capacity. As seen in Figure 5.2 there are two arms which connect the round flask to the heating element compartment. One arm leads from the bottom of the flask and connects to the bottom of the heating element compartment while the other branches off immediately from the top of the flask and connects to the mouth of the heating compartment. The dimensions of the heating compartment were such that the heating element of the hot rod is fully immersed in the liquid. This heats the liquid more efficiently as there is a good contact between the hot rod and the liquid surrounding it.

Part C is the 50 ml round bottom flask with a long neck, one side of which is connected to the reboiler unit via a glass-bodied valve while the other side is connected to the vacuum line. Once the liquid is judged to have been degassed it is transferred to the reservoir where it is stored for subsequent introduction in to the equilibrium cell. This is the most crucial stage of the degassing apparatus as it is here where the degassed pure component is kept, sometimes for a week, over which the actual pressure measurements may be carried out.

Figure 5.1: *Degassing apparatus*

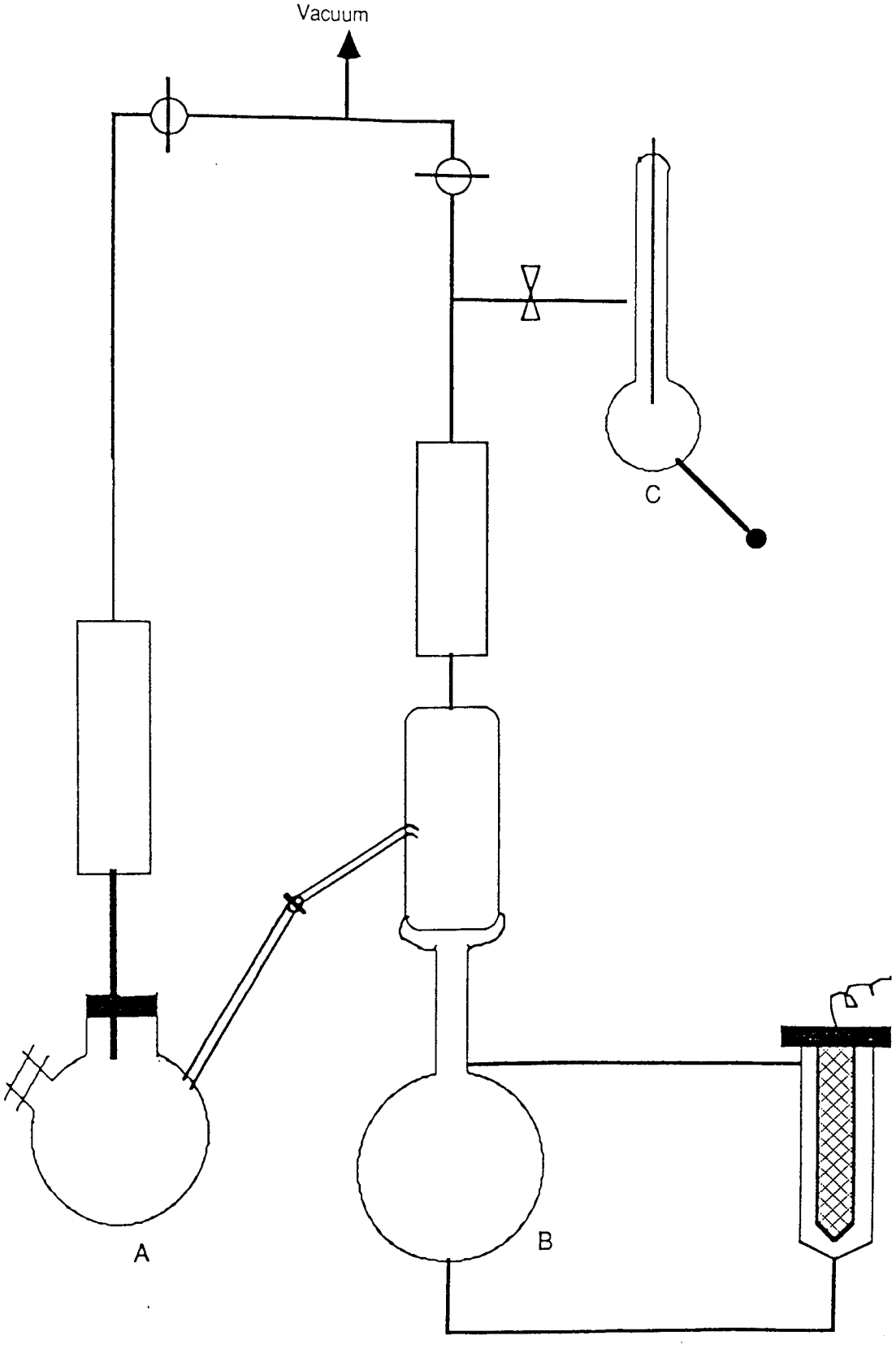
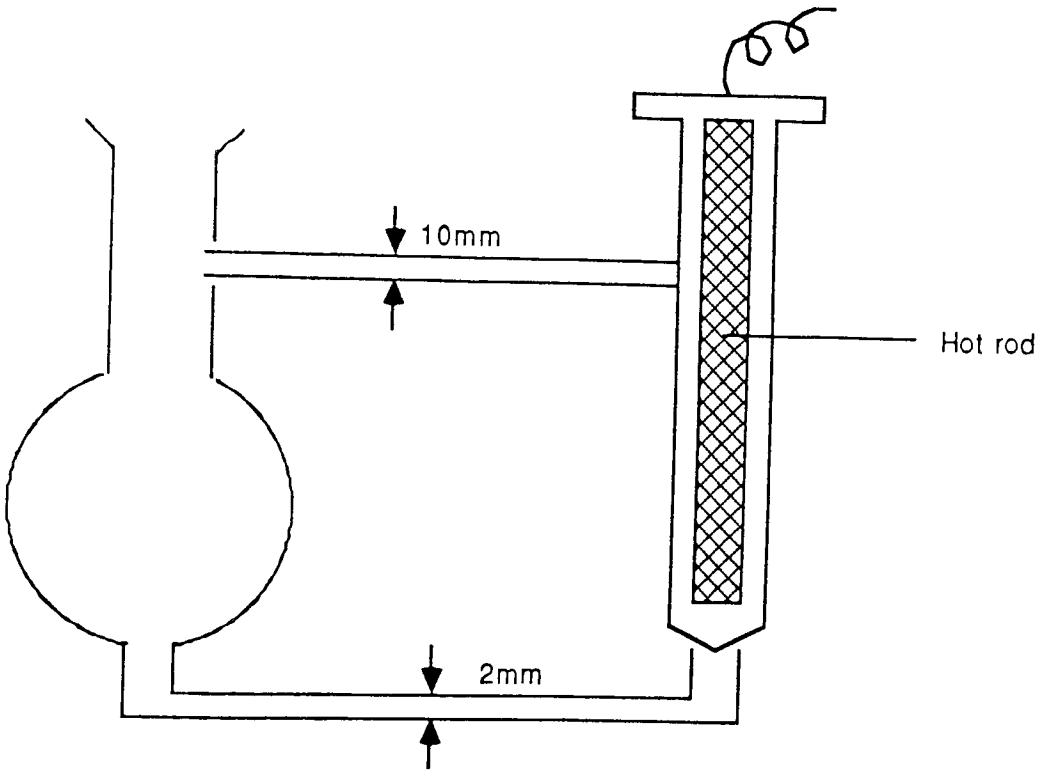


Figure 5.2: *Reboiler unit*



It is therefore necessary that the reservoir be leak tight and that the pure component could be stored for the duration of the experiment. To achieve this the reservoir unit was designed as shown in Figure 5.3.

It has a cold finger sealed on to its neck (in the O'Donnell (1980) version this had been inserted through a glass-screw joint) and is connected to the capillary tube leading from the dispensing device via a Rotulex joint with a PTFE sheathed O-ring. On the both sides of the reservoir are the glass bodied valves which are known to give a good seal. In order to establish that the reservoir was capable of holding the pure liquid with little air leakage a series of experiments were carried out with ethanol and water as discussed in Section 6.4.2a. It was shown that the pure degassed liquid could be stored in the reservoir for one week before observing significant changes in its vapour pressure.

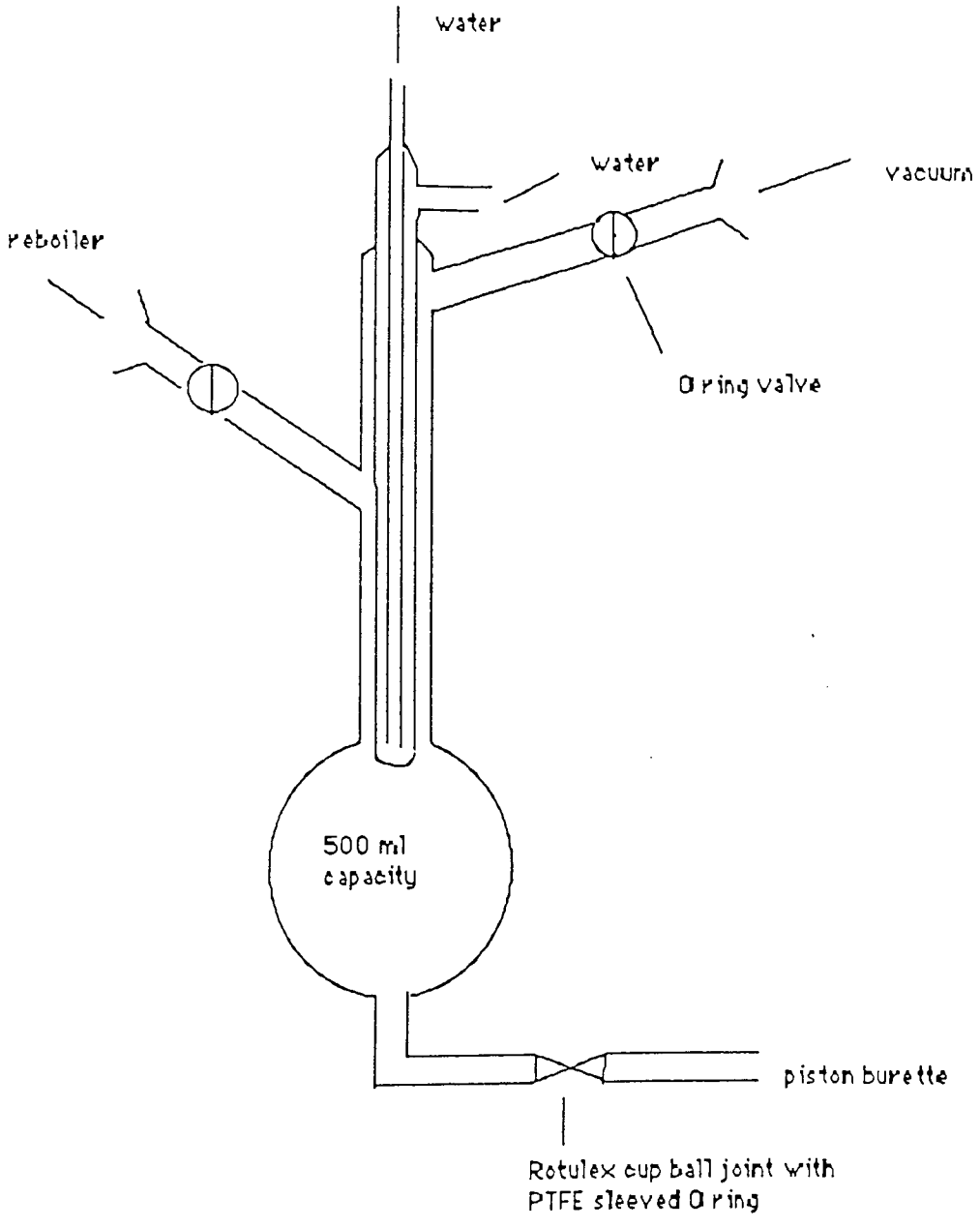
All the degassing assembly was constructed from borosilicate glass and the taps and valves used were high quality vacuum types.

5.2.2 Dispensing device

Gibbs and Van Ness (1972) developed a total pressure apparatus in which they used a dispensing device. The pure components were degassed and then stored for subsequent introduction into the equilibrium cell. This was the first device of its kind to be used in a total pressure apparatus. Figure 4.1 shows a semi-schematic drawing of the essential features of one piston injector used in their original apparatus. The piston M is advanced by a precision lead screw D and the displaced volume is indicated by a travelling marker on a hub graduated to 0.01 ml. Jenkins and Smith (1975) in their apparatus had used conventional burettes where the degassed liquids were stored before introduction to the equilibrium cell.

A new injection device was used in this research programme based on the piston head principle with the central shaft carrying the piston head attached to a manual driven mechanism. The quantity of liquid introduced into the cell could be measured accurately.

Figure 5.3: *Reservoir unit for Storage of Degassed Liquid*

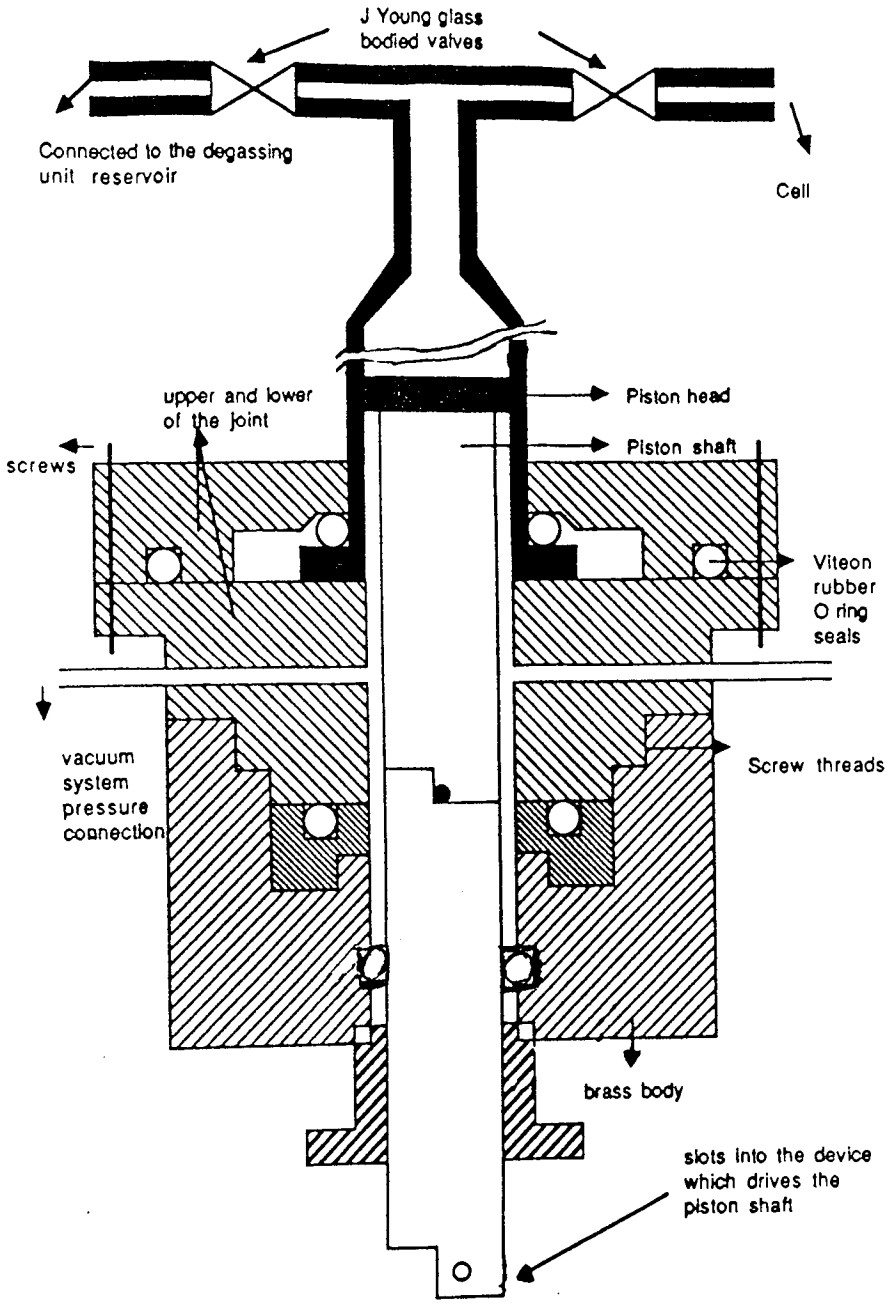


The problem associated in using the piston head burette in its orginal form is that if the pressure above the piston is less than that below, then leakage of gas into the degassed liquid may occur, therefore them unsuitable for use in the pressure measurements. Too, since there is a pressure difference across the piston head movement of the piston shaft becomes difficult.

The new device was constructed in such a way that any possibility of air leakage from the dead space below the piston head was eliminated. This was achieved by building an extension onto the piston burette. As shown in Figure 5.4 an extension was made of brass and attached to the base of the glass burette. Further down this extension a seal is made between the central metal shaft, bearing the piston head, and the casing. A vacuum line was built into the extended burette body to evacuate the dead space below the piston head, and this space was opened to vacuum during the operation in such a way that there was no pressure gradient across the burette piston. This procedure prevented any leakage of air into the degassed component . Further down at the bottom of the metal burette an other seal was put in to prevent air leaking into the dead space.

One of the essential requirements of this method is that the pure component must be free of any air and that a complete degassing of the liquids had been carried out before introducing them into the equilibrium cell. The most crucial part of the apparatus is the line between the reservoir and the cell. This line consists of the dispensing burette, one side of which is connected, via a cup-ball joint, to the reservoir and the other side is connected to a capillary tube leading to the cell. The line from the reservoir end to the cell forms a critical part of the apparatus and every precautions had been taken to ensure that there was no leak at any point along this path. The glass capillary connecting the reservoir to the piston burette and eventually to the equilibrium cell was a 2 mm bore capillary tube. This minimised the amount of liquid retained in the line.

Figure 5.4: *Extension built onto the piston burette.*



There are two glass bodied valves one on each side of the burette. These are glass-bodied with one PTFE. ring which seals against the capillary tube and an O-ring which provides a double seal.

It is thought that PTFE surfaces absorb organic liquids thus introducing errors in the quantity of pure component entering the cell. The use of a glass-body for the valves minimise errors attributable to adsorption and to diffusion of air through them. The use of two O-rings reduces the possibility of any dust preventing an effective seal.

5.2.3 Equilibrium cell

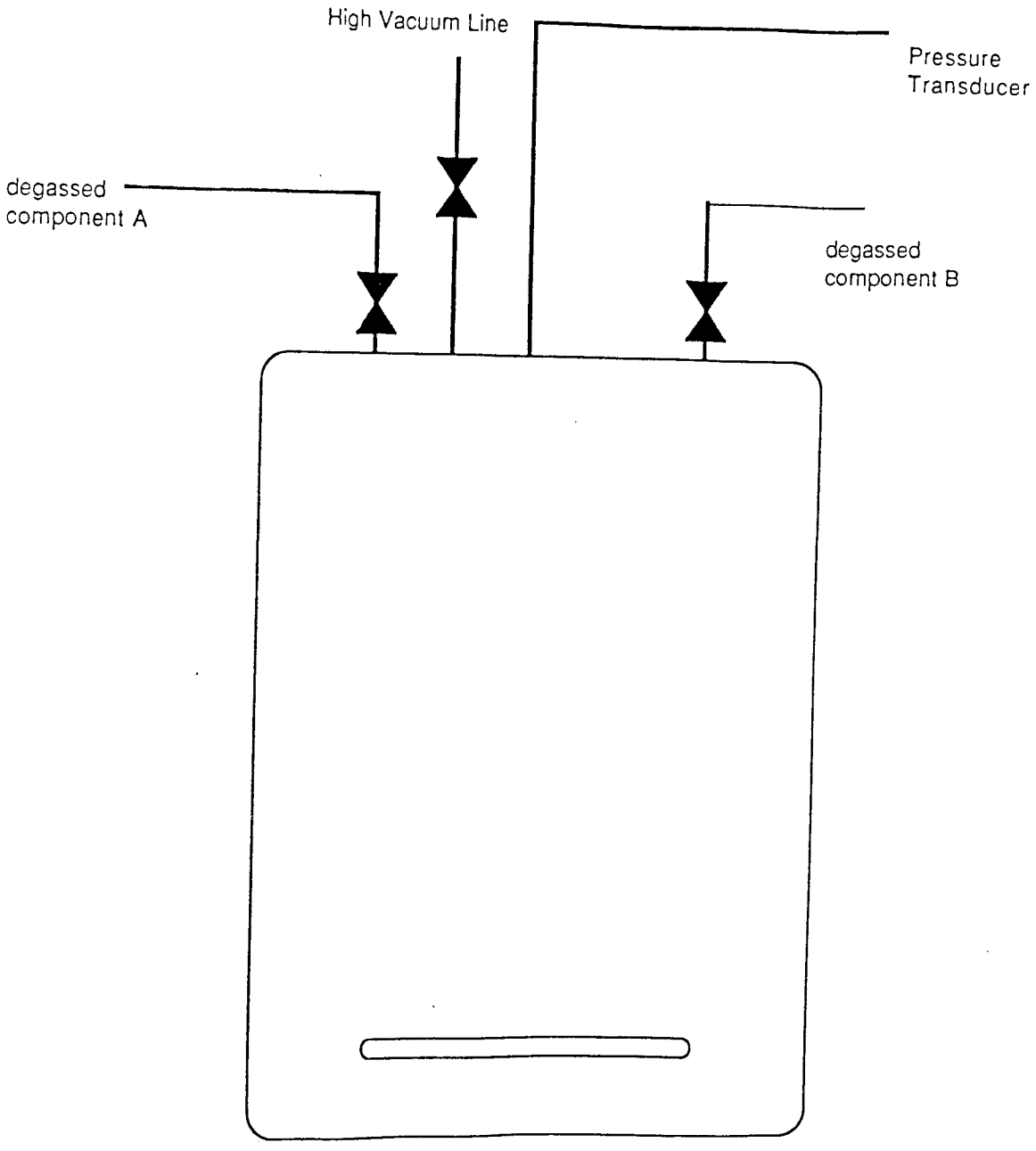
An equilibrium cell, made from borosilicate glass, was constructed to give a total capacity of 50 ml. As shown in Figure 5.5 there are four capillary arms situated at the top of the cell to provide connections. The central branch is connected to a stainless steel line via a Rotalux cup-ball joint. The remaining three are located at the circumference of the cell, two for each of the two pure components and the third one provides a connection to the vacuum line. The cell is connected to each of capillary tube leading from the dispensing device via a rotulex joints with a PTFE sleeved O-ring. The joints are held secure by Rotulex clips.

To isolate the cell from the rest of the apparatus glass-bodied valves were used for the reasons discussed earlier; once again a number of other valves were tried which were found to be unsatisfactory.

One important criterion is that the cell is completely leak-free, as any air diffusing into the cell would introduce errors in the total pressure measurements. Accordingly a considerable time was spent establishing the integrity and suitability of these valves and the associated joints for use in this apparatus.

When designing the equilibrium cell it was decided to make the two capillary arms for the pure components upright, of 80 mm length and 2 mm bore. This ensured a good drainage of liquid into the cell. The vacuum line of 1/4 inch diameter was connected to the cell again via a Rotalex joint. The two lines carrying the degassed pure liquids from the piston

Figure 5.5: *Schematic Diagram of an Equilibrium Cell*



burettes to the cell were of 2 mm bore and their length was kept as short as practically possible to minimize the dead space. The cell connection to the pressure transducer was made through the central branch via a glass-stainless steel Rotalex joint. The capillary leading from this point was a stainless steel narrow bore, 1/16 inch, again for a similar reason.

A magnetic follower, coated with glass, was placed inside the cell. The stirring action made the mixture attain equilibrium more quickly. An external electric magnet was used to drive the stirrer.

5.2.4 Other requirements

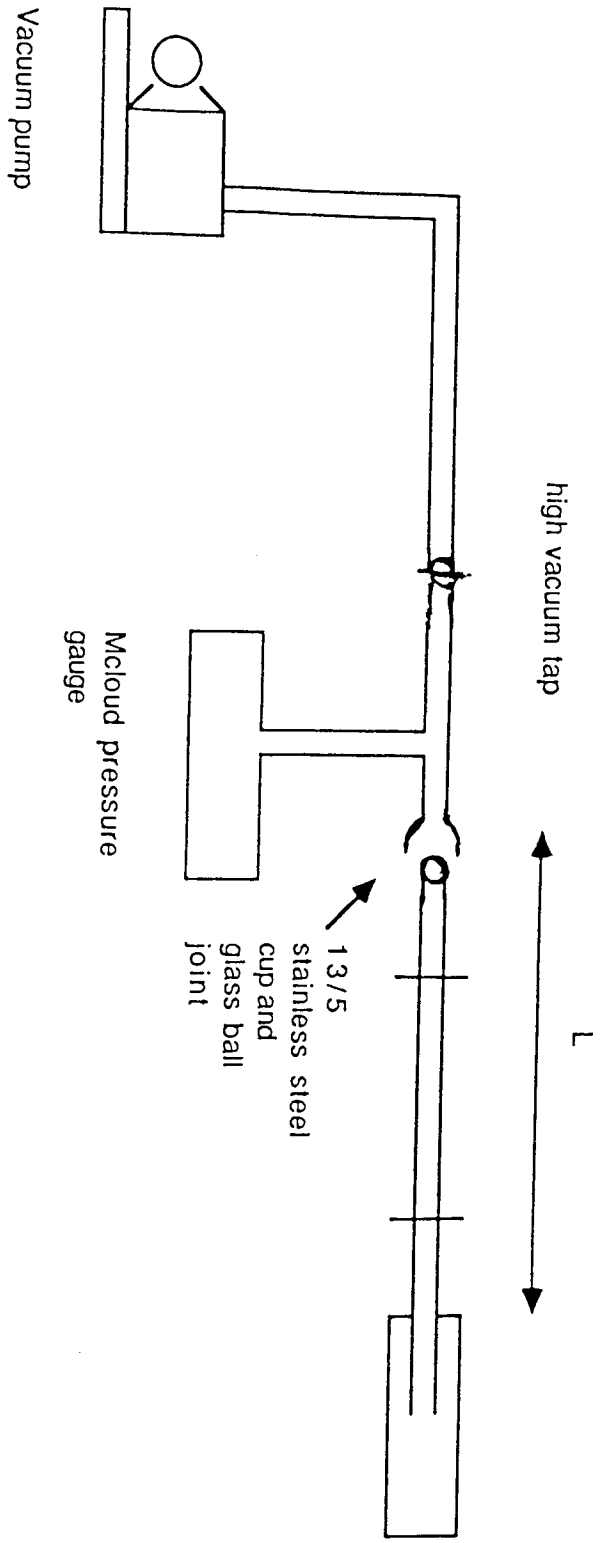
Vapour inside the cell travels up the capillary tube and impinges onto the surface of the transducer's diaphragm. The capillary tube carrying this vapour must have several features incorporated into it. These features include the following:

1) It must be as short and as narrow as practically possible. This was achieved by having a 3 cm long arm from the cell connected onto a 2 cm long 1/4 inch stainless steel tube which was in turn connected to the 1/16 inch bore tube via a Swagelok reducer fitting. This capillary was then connected to the pressure transducer. A special fitting was made in the department for this purpose.

2) It must be completely leak tight as any air entering into the capillary tube would adversely affect the pressure. A considerable time was spent in order to develop a leak-free line. Great care was taken to ensure that the Swagelok connection fittings formed well sealed joints. A thin layer of PTFE tape was used on the threads of the connectors. The joints were then sprayed with a silicon vacuum leak sealant. This aerosol forms a thin film of polymeric resin which does not flake or crack.

A series of experiments were carried out to detect and quantify the leaks along the entire length of the capillary tube connecting the equilibrium cell to the pressure transducer. One such experiment involved the set-up as out lined in Figure 5.6.

Figure 5.6: *Leak Testing the Capillary Line Connecting the Equilibrium Cell to the Pressure Transducer*



The vacuum pump capable of reducing to the pressure to below 0.01 mmHg was used to evacuate the entire length, L, with its transducer connecting end blocked. Once a pressure of 0.01 mmHg was attained in the line the pump was isolated. Any pressure increase in the line was monitored with a MacLeod pressure gauge. The presence of leaks at any point along the length was detected by using Leak-Tec vacuum leak detector, this foam-like substance was applied to the suspect joints. In the presence of a leak the foam formed an indentation. All the joints along the line were tested for the presence of leaks in a similar manner. The faulty joints were then dismantled, a little more PTFE tape was applied to the screwthreads and the joint was securely assembled. The joints were treated with the aerosol vacuum sealant. Further coats of the sealant were applied every 24 hours, in total 4 to 5 coats were applied.

After one week the capillary tube was pumped down to a pressure of 0.01 mmHg and it was then isolated from the pump as before. A rise in pressure was measured with the gauge over a period of 8 hours. Despite exhaustive efforts it was found that there was an unacceptable leakage at some of the joints. Several more coats of the sealant was applied but no improvements were observed, even an ordinary hair spray was tried.

Since the capillary connecting the equilibrium cell to the pressure transducer forms a most important part of the apparatus and a successful attainment of leak-free joints would determine the fate of the project, there was now a need to take more drastic steps in order to achieve the set objectives. By this time it had been established that stainless steel Swagelok fittings were not able to hold the vacuum and that the silicon vacuum sealant was ineffective for the stainless steel joints. The only feasible option was to silver solder the entire joints on to the stainless capillary. After soldering the entire capillary length was tested for the leak as before. At last, the mission was successful in that once the capillary was evacuated and isolated from the pump the rise in pressure observed over a period of 8 hours proved did not prove to be significant, see Appendix 1.

Having checked that the capillary length was leak-tight it was now decided to investigate if any leakage occurred when the equilibrium cell was connected to the line, i.e., at the joint

between the cell and the stainless steel cup, and all the joints situated in the vicinity of the cell, as even a small amount of leakage could introduce large errors into the total pressure measurements. For this investigation the following set-up was used and any leak was detected with the Leak-Tec vacuum leak detector and its rate was monitored on the McLeod gauge.

As shown in Figure 5.7 the vacuum pump was connected to one of the cell's arms via a Rotalux joint and the central arm was connected to the capillary tube with its end blocked as before. In this operation the tap, T_3, was opened whilst taps T_1 and T_2 were closed. The equilibrium cell and the line to the pressure transducer were evacuated to 0.01 mmHg. The vacuum pump was isolated by shutting tap V and the pressure was monitored as before. The vacuum sealant was applied to the glass joints, this subsequently being found to form a good seal. With the vacuum pump isolated it was seen that the pressure did not change significantly with time, see Appendix 2.

Having achieved a leak-free situation between the cell and the pressure transducer the next task was to check if any leakage occurred at the other two joints linking the cell with the two piston burettes. The central connection to the capillary tube was dismantled and the cell was blocked with a glass tube having a Rotalex cup at one end and the other end sealed. Again with the valves T_1, T_2 closed and the central arm blocked the cell was pumped down and the pressure was observed, with pump isolated, as a function of time.

3) As mentioned earlier the vapour from the liquid in the cell acts on the bottom surface of the transducer diaphragm. If the capillary tube carrying the vapour is at a temperature below that of the cell then the vapour would condense onto the walls before reaching the diaphragm. This would obviously give untrue pressures. In order to eliminate any condensation of vapour an encasing was developed to house the capillary tube as shown in Figure 5.8. A 4 cm length of copper pipe was wrapped around with a heating tape and then insulated with an inch thick glass fibre lagging. Heating tape was used to heat the pipe, as the capillary tube was placed inside the pipe, the temperature inside the pipe was controlled by positioning a temperature

Figure 5.7: *Leak Testing the Cell and Associated Capillary*

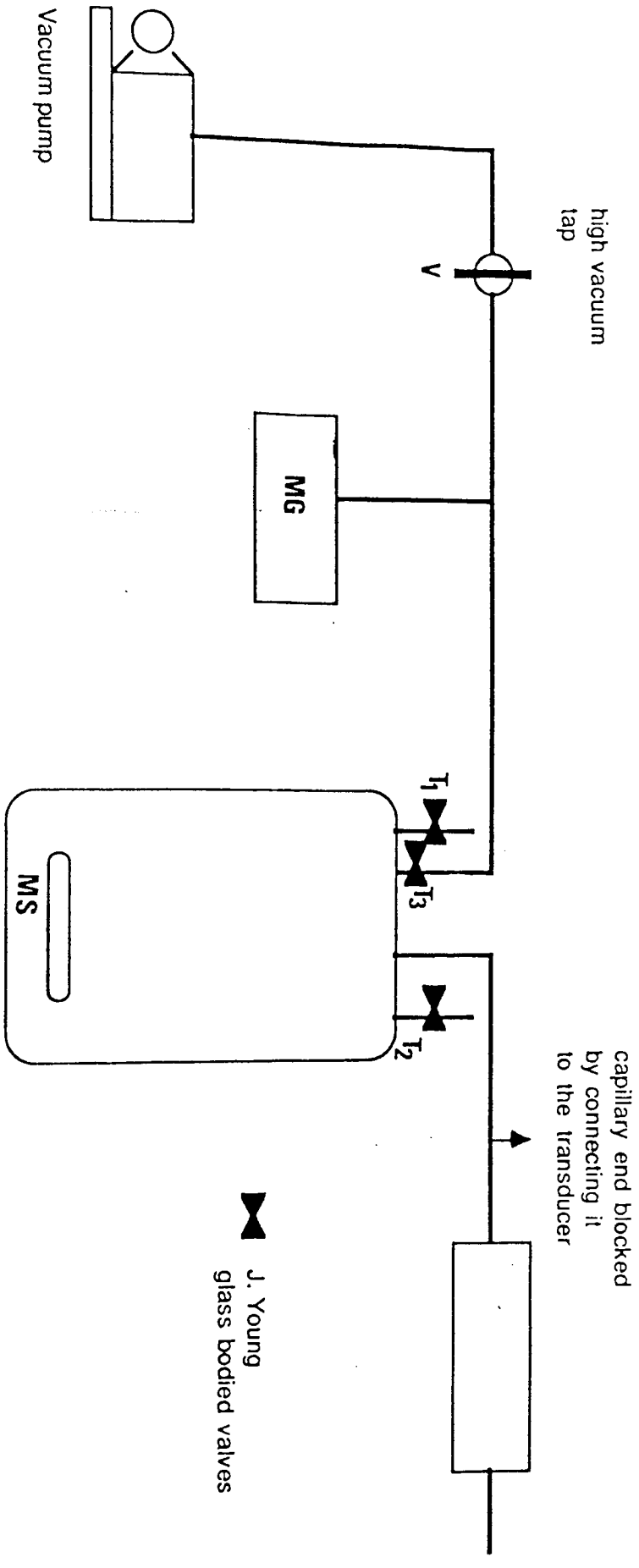
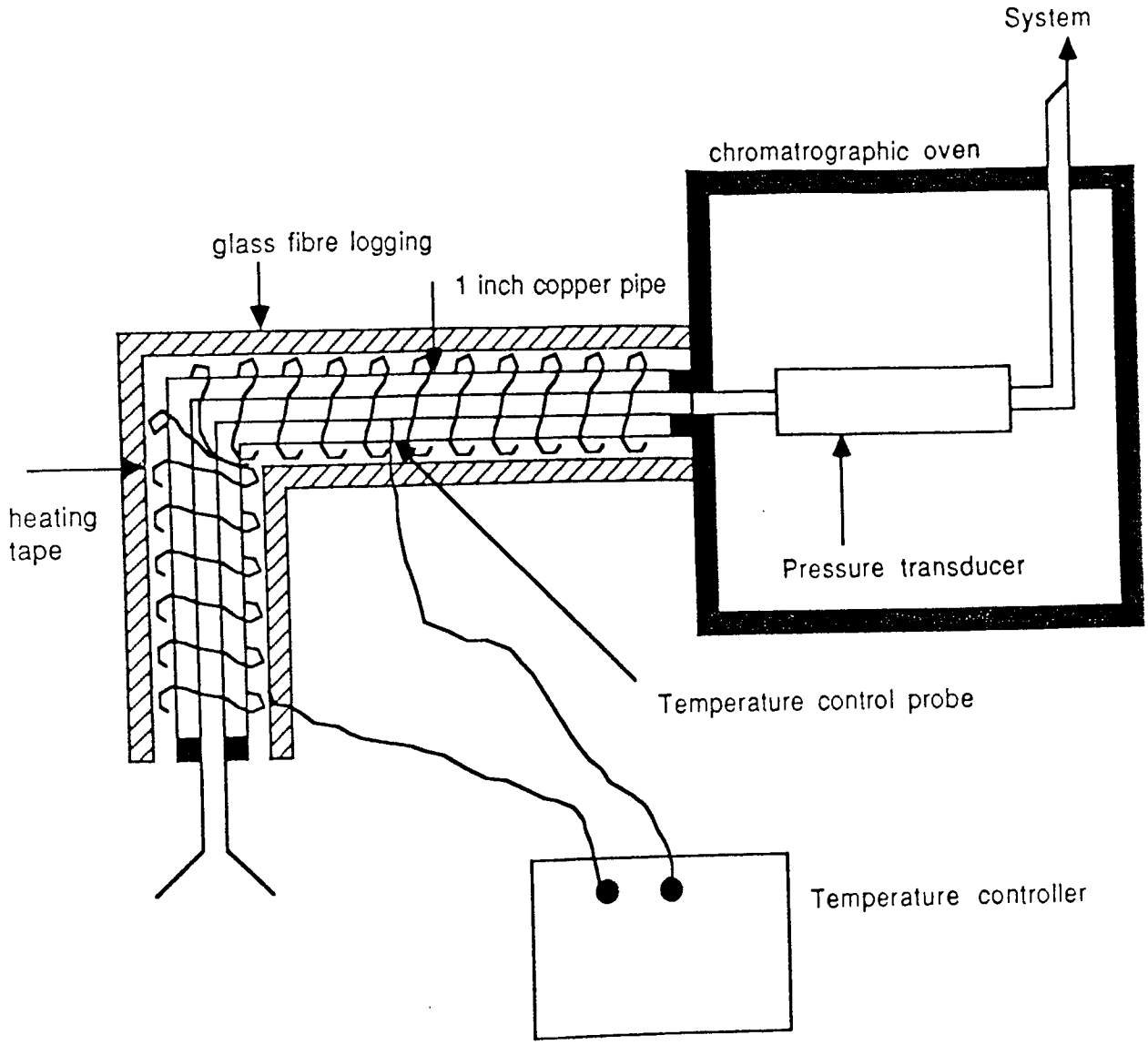


Figure 5.8: *Diagram Showing the Capillary Tube Linking the Cell to the Pressure Transducer*



control probe in this vicinity.

This assembly ensured that the capillary line could be maintained at a temperature slightly higher than that of the equilibrium cell thus preventing the condensation of vapour.

5.2.5 Pressure measurement and control

The accuracy and control of the pressure system of the apparatus is determined by the performance of the transducer. In this work a Druck differential pressure transducer, type PDCR 10/L, was used. As stated earlier the cell pressure is transmitted to a transducer via a capillary tube and this pressure causes a deflection of the transducer's diaphragm. The transducer was placed in a chromatograph oven at a distance from the equilibrium cell. With this procedure it was possible to keep the transducer at a temperature slightly above that of the cell, thus eliminating the possibility of vapour condensing on to the surface of the diaphragm. The transducer requires an excitation voltage of 10 volts and a millivoltmeter was used as a read-out device. The balancing side was connected via a 1/4 inch copper pipe to the system reservoir. The reservoir is made from an empty gas cylinder with three connections at the top (as is the vacuum reservior). It was connected to the compressed air supply from which air passed through a drying chamber containing silica gel. The output line from the gauge was the system line. With the Bourdon gauge connected in this way it was used both as a pressure measuring device as well as a pressure controller by applying an equalizing pressure. When the pressure on both sides of the diaphragm is equal, a null position, i.e., a zero read-out, is obtained. Since the transducer is, in effect, being used as a null detector it must provide both the required sensitivity and reproducibility of the null position.

While the balancing pressure system was to be sometimes subjected to vacuum no very good vacuum had to be achieved, so this system was biult up from copper tubing and fittings, with some reinforced PVC lines.

A vent valve was incorporated in the system line so that excess pressure could be

dissipated.

As mentioned earlier the system reservoir cylinder has three connection lines such that the central line goes to all the way to the bottom of the cylinder while the other two are inserted such that they are at different levels inside the cavity, thus exploiting the full volume and uncoupling the three connections (see Figure 5.9). The reservoirs serve to eliminate pressure fluctuations thereby maintaining a smooth pressure in the line.

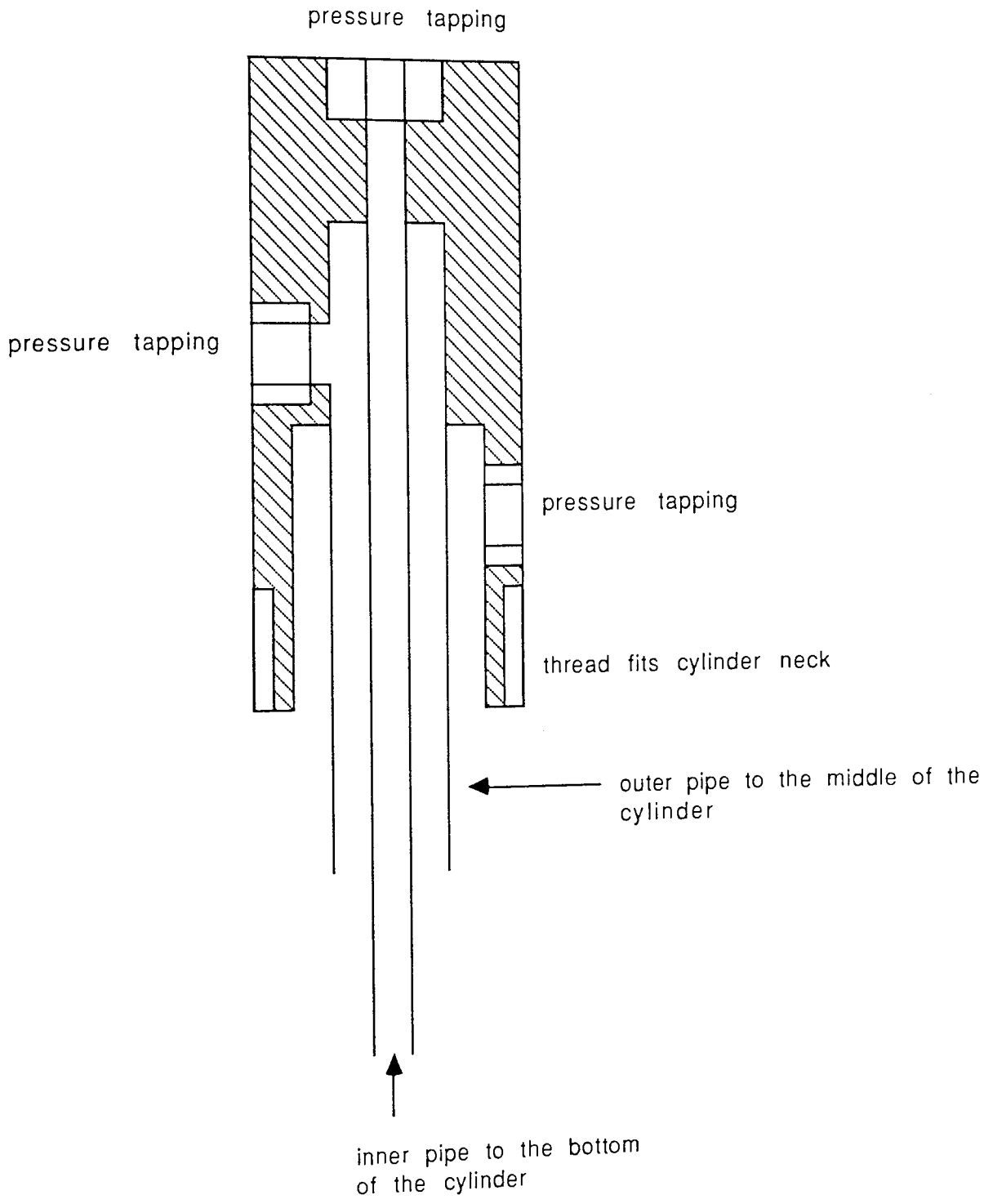
The Bourdon gauge controller was used to both measure and control the pressure. There are three connections to the gauge, one the pressure input line carrying compressed air which had been passed through the drying chamber. The second line is the pressure balancing system line and the third is the vacuum supply.

Together with the Bourdon gauge another pressure measuring device was used. This was a Druck digital pressure indicator, model DPi 140. Since small pressure changes were involved the sensitivity and accuracy of the pressure measuring system was of paramount importance. With the set up as described above it was found possible to control and measure the pressure to an accuracy of two parts in 10,000 of a bar.

A series of experiments were carried out to establish the reproducibility of the null position. These involved evacuation of the equilibrium cell and isolating it and then opening the balancing side of the transducer diaphragm to vacuum. The shift in the null position was observed as a function of time. A small drift in the null point was seen which was within the expected precision of the experiment.

In another experiment an equal and controlled pressure was applied on both sides of the diaphragm and the null position noted over a period of time. The procedure was repeated at different pressures. The performance of the transducer was found to be consistent and reproducible.

Figure 5.9: *Construction of the Reservoir Cylinder*



5.2.6 Vacuum system

One most essential pre-requisite of the total pressure technique is that the cell must be completely air-free. This requirement imposes severe technical difficulties in that the line leading from the vacuum pump to the pressure cell must be leak-free and once the vacuum pump is isolated from the line the vacuum is maintained. This requirement was achieved finally having spent a considerable amount of time and also selecting the right kind of fittings and tubing to construct the line.

The vacuum system was designed to meet three requirements:

a) Vacuum needed for the degassing procedure.

b) Vacuum needed for the balancing side.

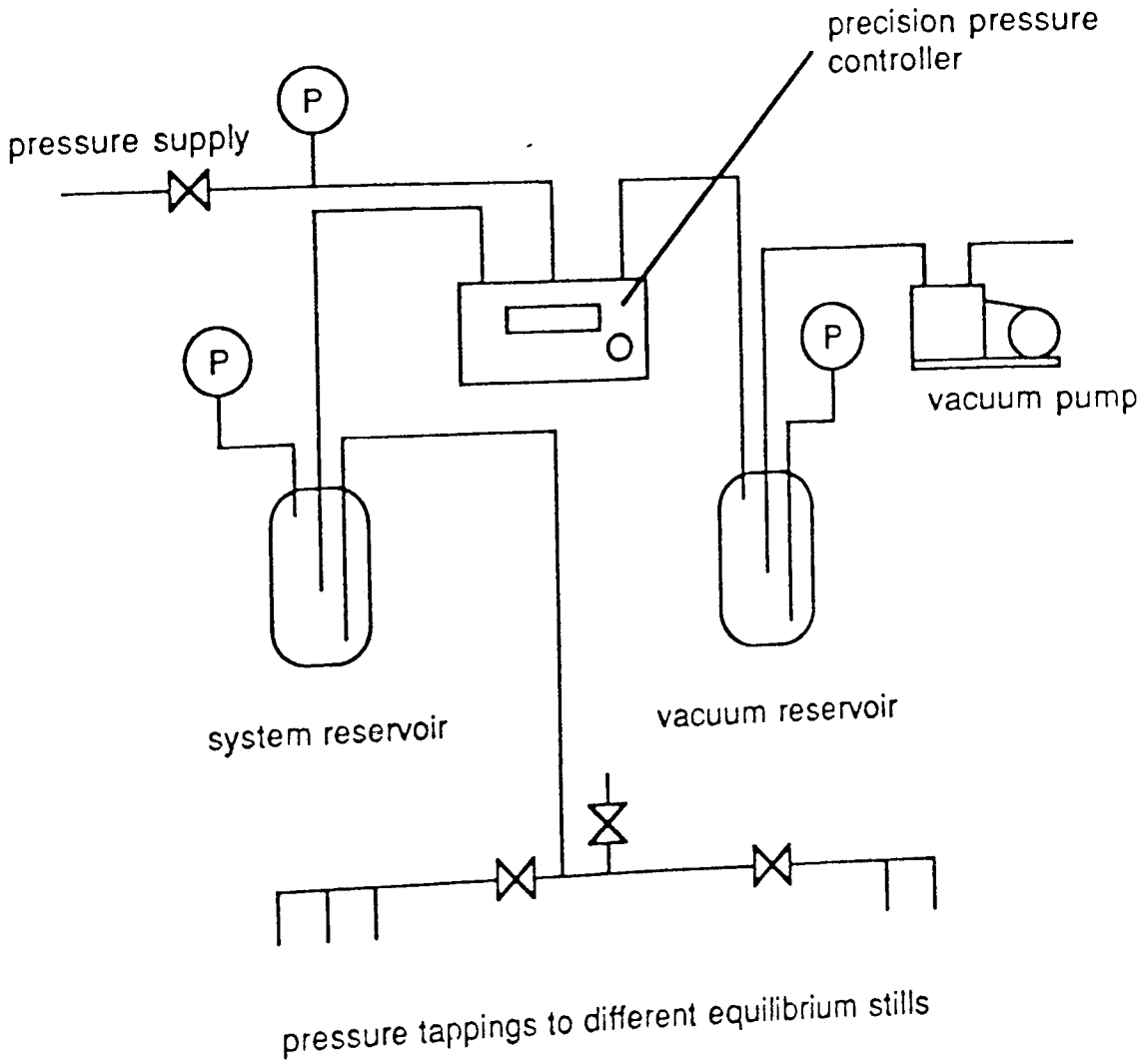
c) High vacuum needed to pump down the cell and the associated capillaries.

All three are essential in the total pressure technique and in practical terms they conflict with each other. In order to achieve (a) and (b) above the vacuum system was designed to pull the pressure to about 2 to 3 mmHg where as in the case of (c) an absolute pressure of less than 0.001 mmHg was needed. These objectives were achieved by having the vacuum system in two halves, the low vacuum side, which would be satisfactory for degassing and the balancing side, and the high vacuum side which were used to evacuate the equilibrium cell and the associated capillary line in its vicinity.

Initially the lines in the vacuum system were constructed from 1/4 inch OD copper pipes and 1/4 ID reinforced PVC tubing and the joints were brass connectors. On testing this set up it was found possible to obtain a vacuum low enough to meet the requirements of degassing and the balancing of the pressure. However, a more sophisticated set up was necessary to achieve the high vacuum criterion.

Figures 5.10 and 5.11 show the vacuum system used. An Edward's rotary vacuum pump was used for both the high and the low vacuum sides.

Figure 5.10: *Pressure Control System*



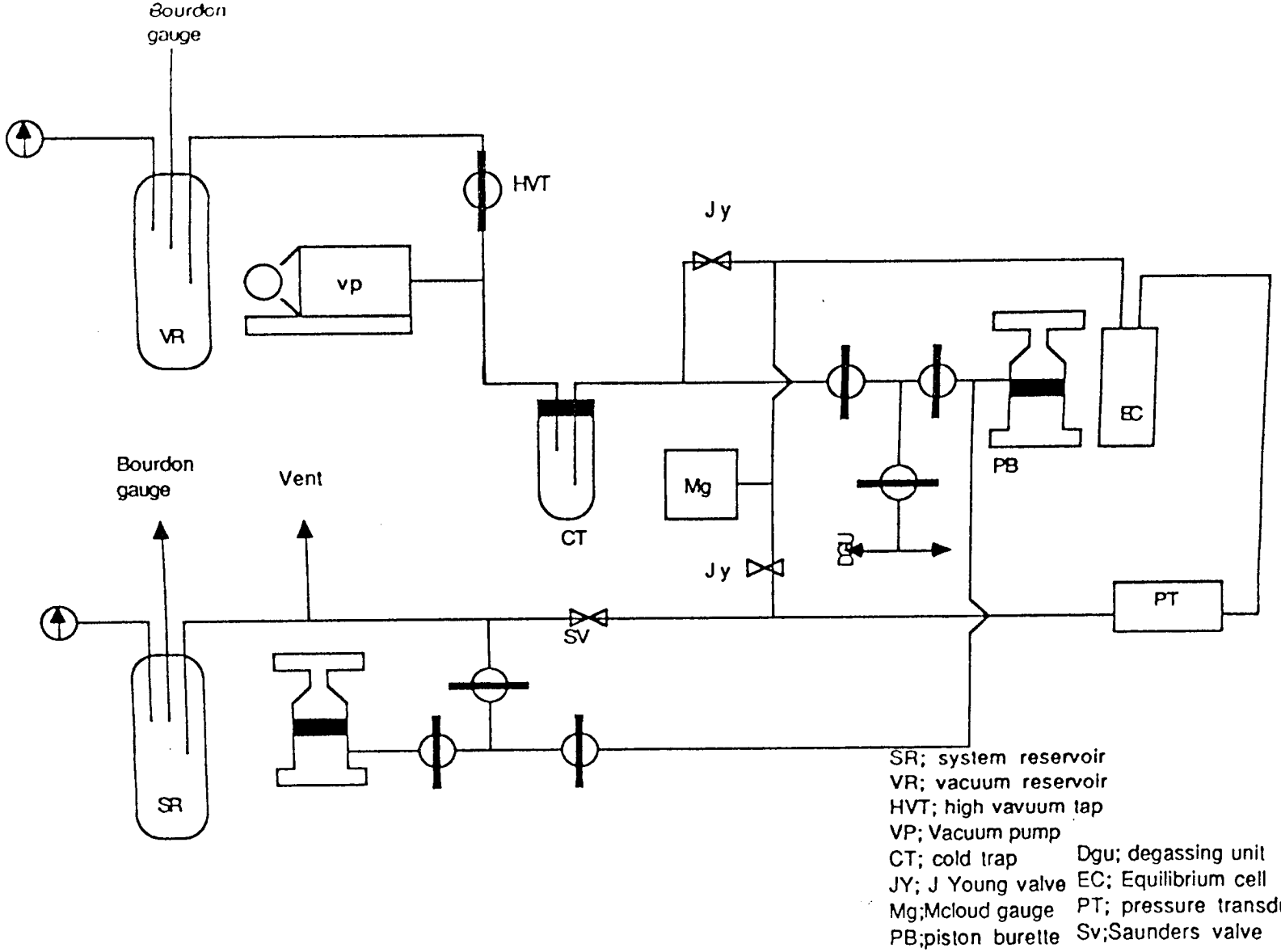


Figure 5.11: *Vacuum System*

5.2.6.1 High vacuum side

The high vacuum side was constructed in the following way. Half-inch bore reinforced PVC tube leading from the pump was connected to a cold trap and the degassing unit via a glass tee-piece. A cold trap was positioned immediately upstream of the pump to remove any condensables from the vapour entering the pump. The trap contained dry ice with a small amount of acetone. The line forming the critical path of the vacuum system was constructed from half-inch bore glass tube and the Rotulex cup- and -ball joints with PTFE sleeved O-rings. These joints were tested and proven capable of pulling and holding high vacuum. The pump and the pressure balancing line could be isolated from the critical path with the aid of two glass bodied valves.

A considerable time was spent in achieving the high vacuum needed for a complete evacuation of the cell. High vacuum was also needed to evacuate the piston burettes and the associated capillaries before they are charged with the degassed liquids. All the taps and valves used in this side of the vacuum system were of good integrity.

5.2.6.2 Low vacuum side

This side of the vacuum system serves both the degassing units and the pressure control system to demonstrate a null. In both cases a pressure of 2 to 3 mmHg was required. As noted above it was found possible to achieve this by constructing the line with PVC reinforced pipe and copper tubing while less crucial every effort was made to minimize the factors responsible for leakage.

Low vacuum was also applied continuously to evacuate the dead space beneath the piston heads in the burettes. This procedure removes any air trapped in this space which would otherwise leak past the piston head and into the degassed liquid. Also the pressure on both sides of the piston head was balanced and this facilitates the operation of the dispensing device.

As with the pressure system, an empty gas cylinder was used as a reservoir in the vacuum line to provide a smooth supply to the pressure controller.

5.2.7 Temperature control and measurement

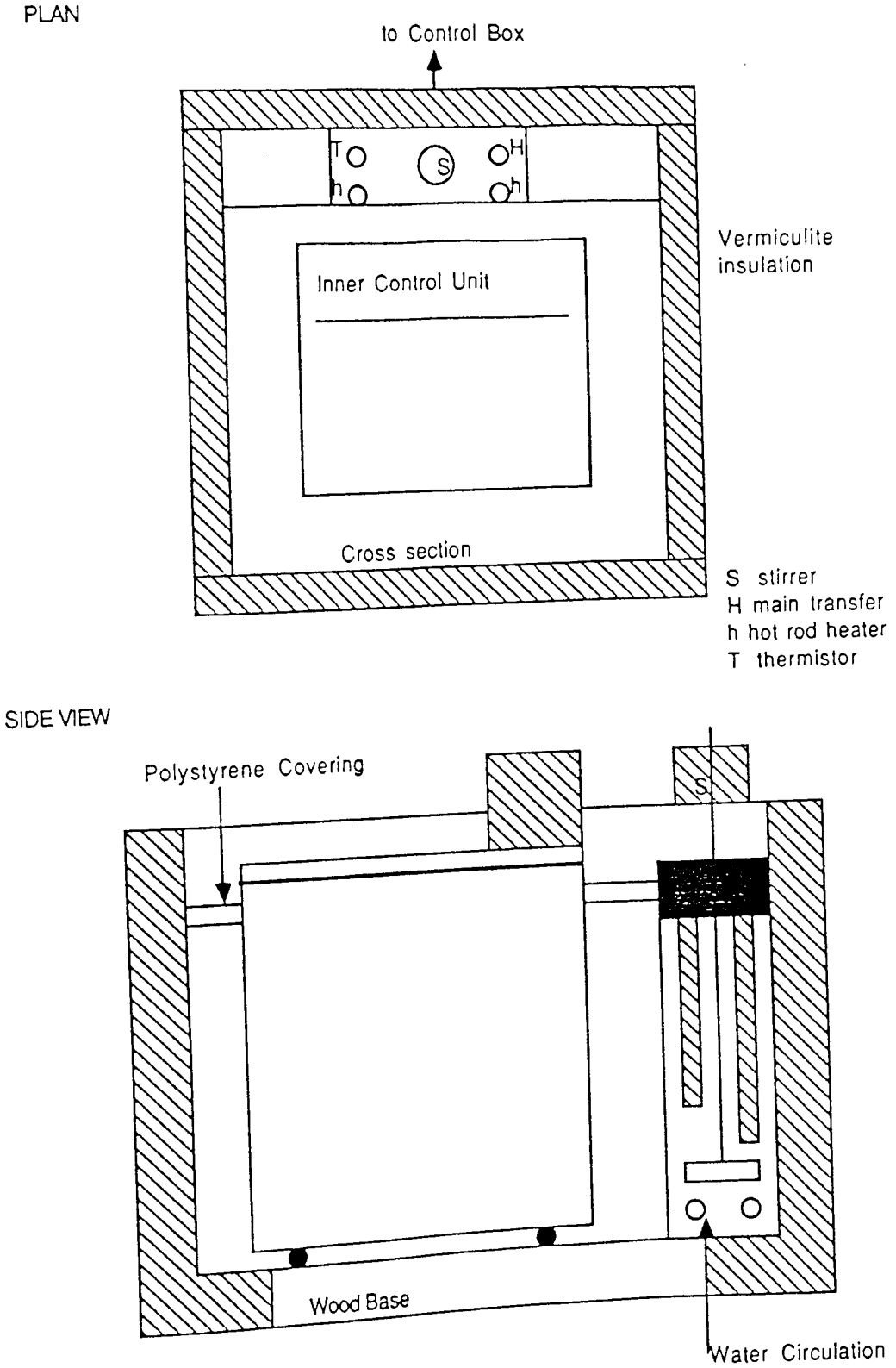
The thermostatically controlled water bath comprises inner and outer controlled compartments. The outer compartment was controlled to within ± 0.02 K with the inner compartment providing the necessary control to ± 0.001 K. The control bath for the apparatus is shown in Figure 5.12.

The control unit for the inner compartment is a proportional control unit by Heto-therm. The outer compartment is governed by an externally situated proportional control unit connected to the detector and heater h. This control unit was designed and constructed in the department. The other two (boost) heaters aid the initial water heat up. This control section is compactly constructed to produce a well stirred intimate contact between the water, heater and the detector. The detector had been a thermister but was replaced by a platinum resistance thermometer because of a tendency to drift over long periods. Water is taken into the section via a weir arrangement and returned to the main section via exit holes at the bottom.

The outer compartment is surrounded by a 30 mm thick insulation of vermiculite and is mounted on a wooden base. The bath is constructed from stainless steel with float glass windows on the front of both compartments so that the equilibrium cell can be observed as well as its associated joints and capillariy lines. The water surface is covered with polystyrene balls during operation to reduce heat losses through evaporation.

The bath has been tested satisfactorily at temperatures up to 80°C with a thermocouple whose potential difference was measured with a potentiometer. Consistent and comparable temperatures were observed with no detectable variations. During operation, the outer compartment is maintained slightly below the controlled temperature to aid the performance of the inner unit. The inner bath temperature temperature was measured using a Guildline platinum resistance thermometer.

Figure 5.12: *Thermostatic Control Bath*



Chapter 6: Description of Apparatus and Experimental Procedure

6.1 Introduction

The apparatus developed in this research programme is essentially a total pressure method of obtaining vapour-liquid equilibrium data on binary systems. In principle the total pressure above the liquid phase in a static cell is measured as the composition of the mixture is varied. The data were obtained isothermally over a range of temperatures.

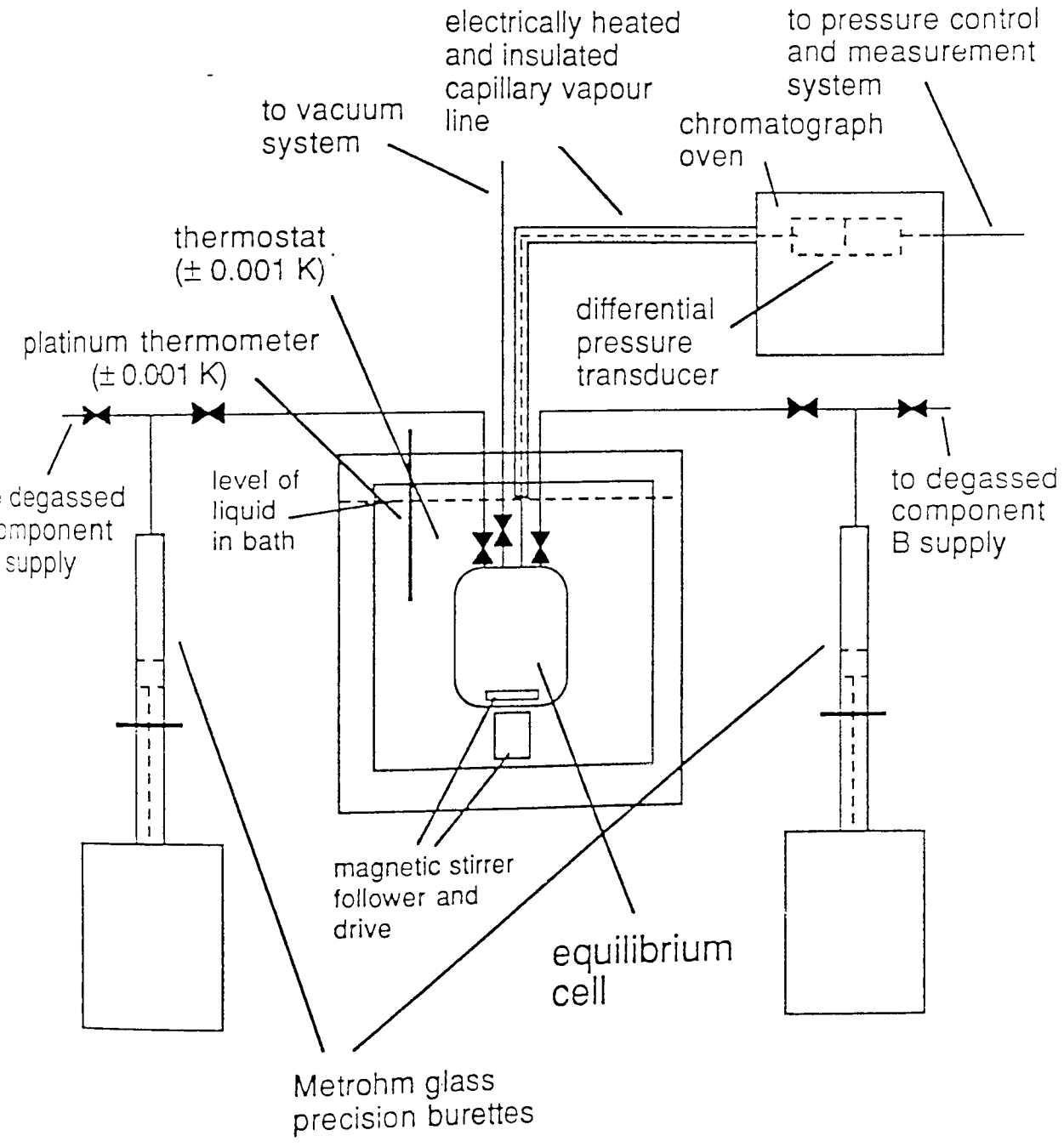
6.2 Temperature Measurement and Control

The vapour pressures are extremely sensitive to temperatures and since small vapour pressures are measured as a function of composition it is necessary to be able to control and measure the temperature within ± 0.001 K. As shown in section 5.6.2 a double water bath was used in this experiment with thermostats controlling the temperatures of the outer and inner compartments to within ± 0.02 K and ± 0.001 K respectively. The temperature was monitored by a Guildline platinum resistance thermometer to a precision of ± 0.001 K.

6.3 Pressure Measurement and Control.

The accuracy of the pressure system is determined by the performance of the pressure transducer. As stated previously the pressure developed in the cell is transmitted, along a capillary tube, to the transducer which is placed in a chromatographic oven.The method of measuring the pressure in the cell is designed to utilise to their full capabilities both the differential transducer and the pressure-controller and pressure gauge.

Figure 6.1: *Diagrammatic Representation of the Total Pressure Equilibrium Cell*



The differential transducer is not optimal, it was used because it was immediately available from the previous project; it has a differential range of -1 to 7 bar gauge. However, it has infinite resolution, and by using it as a null transducer, whose balance point can be checked before and after each run, most of the effects associated with strain-gauge silicon diaphragm transducers, and which degrade their accuracy, are eliminated.

The transducer was connected to a constant voltage source to provide 10 volts to provide the excitation for the strain gauge bridge. The null position of the diaphragm was detected by having a read-out device attached to the bridge out put. A millivoltmeter was used as an indicator with a range of 0 to 1 mV. When the pressure on both sides of the diaphragm is equal, the indicator reads zero, giving the null point, as the pressure on either side changes the null position on the indicator is lost. With the aid of the Bourdon gauge operating in the control mode the pressure is adjusted, increased or decreased depending which direction the indicator needle has drifted, until the read-out device reads zero, i.e., the null point, again.

The Texas Instruments Bourdon gauge, when used in the control mode, was capable of controlling the pressure within ± 0.0002 bar. The read-out from the controller gave the system pressure but as there is some doubt about the hysterisis effect in the gearing of the gauge mechanism, an additional pressure gauge has been added to the system, a Druck vibrating cylinder gauge, with an accuracy of the same order as the precision of the controller. This gauge has a range of 0 to 3.5 bar.

6.4 Degassing Apparatus and its Operation

One of the essential requirements of this method is that the pure components must be thoroughly degassed as it is the vapour pressure due to the liquid itself which is measured. In this research programme a degassing procedure of reflux evacuation, condensation and evacuation has been used for both the organic liquids and water.

As illustrated in Figure 5.1 the degassing apparatus consists of three individual interconnecting units and the following procedure was adopted to degas pure liquids for use in this research project.

In the first stage the liquid was contained in a 250 ml three necked flask with a double surface condenser. The liquid was heated with the aid of an isomantle and brought to boil. The vapour arising from the liquid condensed onto the surface of the condenser and fell back into the flask. This was allowed to continue for three hours during which the vacuum was applied, at 10 minute intervals, to remove the buildup of noncondensables, air being the major component.

In the second stage the liquid was transferred, drop by drop under the influence of vacuum, into the main reboiler unit which was designed and built for the purpose of this research project, see Figure 5.2. The liquid was heated with a Electrothermal Hot-rod and the vapour arising was condensed onto the double surface condenser and returned into the reboiler flask. This reflux operation was allowed to continue for 10 to 24 hours depending on the liquid, water takes longer than organic liquids to reach satisfactory degassing. During this stage essentially all the degassing was carried out. Once the liquid becomes depleted with the air it starts to make a characteristic cracking noise as the bubbles collapse against the wall of the reboiler. This cracking noise becomes more distinct as the degassing progresses and it was observed to be more subtle with the organic liquids.

Finally the vapour was allowed to escape into the next chamber, the reservoir, where it condensed to liquid by impinging onto the walls of the cold finger. Once again during the condensation stage a little vacuum was applied to remove any residual air from the system. The degassed liquid was stored for use in the experimental measurements.

6.4.1 Degassing procedure

The degassing apparatus described above is shown in Figure 6.2 and was used to degas both organic liquids and water. The procedure of the degassing operation is as follows:

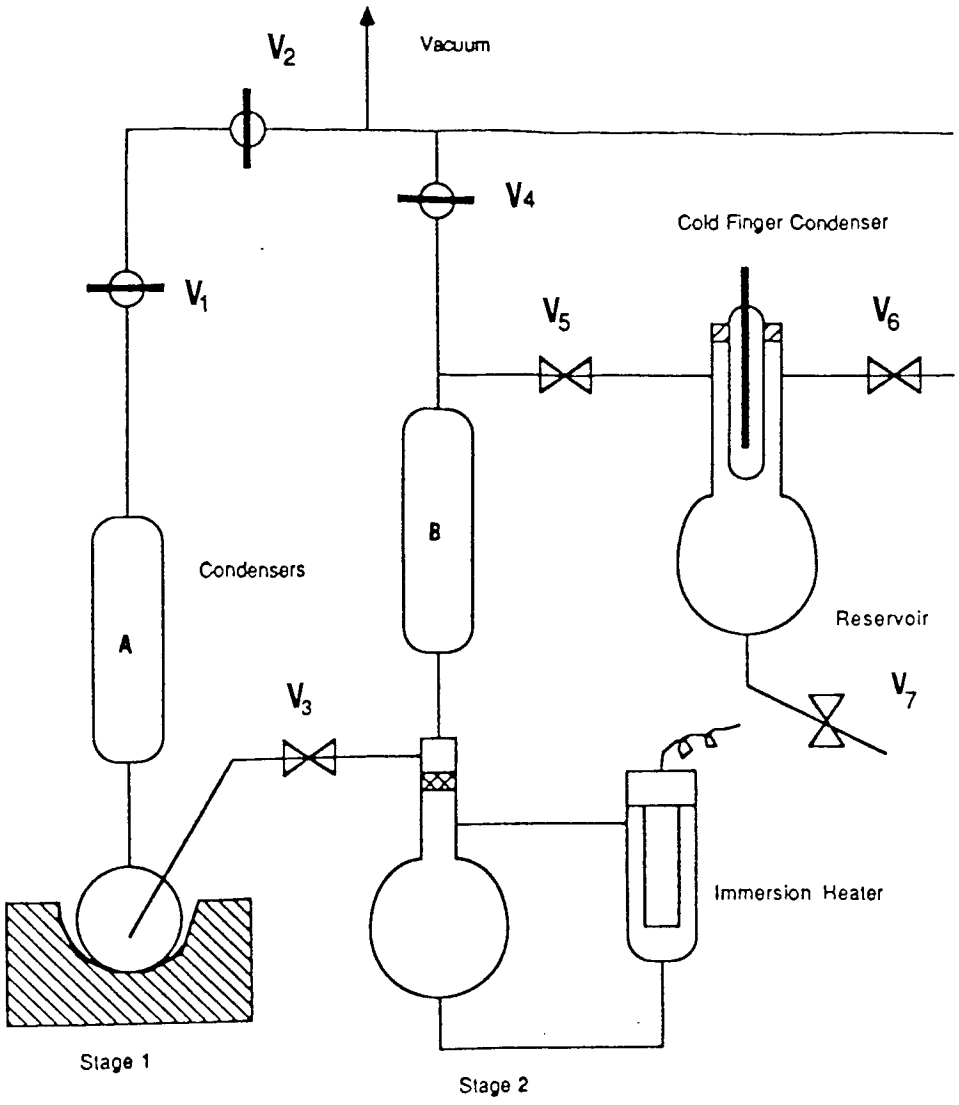
The pure liquid was poured into the 250 ml three necked flask through the inlet which was then closed with a stopcock, a little vacuum grease was applied to the stopcock to ensure a good seal. The valves V_1, V_2 and V_3 were closed and the vacuum pump switched on. Valve V_1 was opened to evacuate the space above the liquid. This was done for 20 minutes and condenser A might then be turned on to remove the vapour as the liquid starts to boil under vacuum. Then valve V_1 was closed and the isomantle energised to heat the liquid in the flask.

As the liquid boiled the vapour arising condensed and fell back into the flask. By opening valve V_1 vacuum could be applied to remove the air and other noncondensables. Care was be taken when applying vacuum as a large flux of liquid could rise and be drawn into the condenser, also a large quantity of liquid may be flushed out of the flask. This was the first stage of the degassing operation and took about three hours.

With valves V_1, V_2, V_4 and V_5 closed, valve V_3 was cracked open and the liquid allowed to drip into the reboiler unit. The condenser B was turned on and valve V_4 cracked open to introduce a small amount of vacuum as the liquid continued to drip across. Once the reboiler flask was nearly full then the heating rod was energised and valves V_3 and V_4 closed. The liquid was allowed to boil under reflux and a vacuum introduced intermittently until a characteristic cracking noise could be heard, with a good vacuum in the system this could be achieved in the first stage of the operation.

Once the liquid was judged to have been degassed (this requires some experience) it was then transferred into the reservoir via a condensation process on the cold finger.

Figure 6.2: *Water Degassing Apparatus*



Condenser B was turned off and valves V_4, V_6 and V_7 closed and valve V_5 opened. This permited the vapour to impinge on to cold finger condenser. Valve V_6 was cracked open to withdraw any noncondensables. Once most of the liquid from the reboiler unit had been transferred into the reservoir the heating rod was switched off and valves V_5 and V_6 firmly closed. The cold finger condenser was turned off and the liquid stored in the reservoir and was ready to be charged into the piston burette for subsequent introduction into the equilibrium cell.

As mentioned earlier the ability to judge that a good degassing has been achieved requires some experience and it was found that the technique improved as more experience was gained. This was particularly the case with water which required longer and rigorous treatment. Experience with this technique showed that the organic liquids could be degassed in 10 hours whereas water needed about 24 hours to reach complete degassing.

6.4.2 Commissioning of degassing apparatus

The degassing method developed in this research project was commissioned on a number of well known binary systems. Components such as ethanol and water were chosen to establish the performance of the apparatus, because data on these components were available to enable a direct comparison to be made. The commissioning programme was conducted in two stages:

a) To verify whether the degassing could be achieved to a degree comparable to that achieved by the other workers who used different and more tedious procedures.

b) That once degassed the pure liquid could be stored in a well sealed reservoir to allow the experimental measurements to be carried out over a period of one week.

6.4.2.1 To check that degassing had been achieved

By this stage of the project extensive tests had been carried out to ensure that the equilibrium cell and the associated capillary connections were all leak tight because any

leakage either at the cell connections or capillary tube connections would have disastrous effect on pressure measurements in that false readings would be obtained.

The detailed experimental procedure will be described in Section 6.7. Saturated vapour pressures of absolute ethanol and water were measured at different temperatures and the values obtained were compared with those obtained by the National Physical Laboratories (NPL) (Larkin and Pemberton 1976).

Since it is generally accepted that water is more difficult to degas than any organic liquid, it was decided to degas water first to measure its vapour pressure. In the first experiment the vapour pressure of degassed distilled water was measured at a fixed temperature as a function of the volume added to the cell. This experiment was repeated at different temperatures. The results obtained were compared with the NPL and the steam tables data on water. The results are shown below:

Table 6.1: *Distilled water at 25.00°C*

Volume of Water Added (ml)	Experimental Pressure (bar)	NPL Pressure (bar)	Steam Table Data Pressure (bar)
5	0.03180	0.03169	0.031670
10	0.03183	0.03169	0.031670
10	0.03183	0.03169	0.031670
10	0.03184	0.03169	0.031670

The experiment was repeated at 30.00°C ,35.00°C, 40.00°C, 44.00°C and 50.00°C. The results obtained were compared with those of NPL and the steam table data (see Appendix 5).

Dry Ethanol

Absolute ethanol was degassed in a similar fashion to water except instead of 24 hours only 12 hours were needed to reach an equivalent degassing. As with the previous experiment the volume of pure degassed ethanol added to the cell was varied and the saturated vapour pressure measured after each addition. Measurements were carried out at different temperatures.

Table 6.2: *Ethanol at 25.00°C*

Volume of Ethanol Added (ml)	Experimental Pressure (bar)	NPL Pressure (bar)
5	0.07896	0.07893
10	0.07895	0.07893
10	0.07893	0.07893
10	0.07896	0.07893

The experiment was repeated at 30.00°C, 35.55°C, 40.54°C and 50.00°C and the results are shown in Appendix 9. Taking the average of the pressure values for each of the temperature examined and comparing the experimental pressures with those of NPL the following is observed:

Temperature (°C)	25.00	30.00	50.00
Experimental Pressure (bar)	0.07896	0.10470	0.28756
NPL Pressure Data (bar)	0.07893	0.10428	0.29507

The experimental results obtained with distilled water and ethanol show that as the volume of liquid into the cell was increased there was no significant change in the vapour pressure and this compares well with the NPL data. The results suggest that several very important experimental pre-requisites have been achieved namely:

(a) The water and ethanol have been degassed completely using the technique developed otherwise insufficient degassing would lead to increased pressure values on addition of more pure liquid into the cell.

(b) That a well sealed central apparatus, the equilibrium cell and the associated capillaries, have been achieved.

(c) By the fact that the results obtained are close to those of NPL means that the pressure measurements and control are working well to a high accuracy.

6.4.2.2 Storage of degassed components

Once the liquid was judged to have been degassed it was stored in the reservoir for subsequent use in the experiment. It is essential from a practical view point that the storage of liquid is possible for at least one week duration before the air re-enters the liquid thus making it unsuitable for use in the experiment. This enables the experimental measurements to be made in the week following degassing operation. To elucidate whether or not this was possible extensive work was undertaken to determine if the saturated vapour pressure values were affected with time, that is to see if any air had reentered the liquid.

The experiment was carried out firstly with water and ethanol. For water two days were taken for degassing and on third day the water from the reboiler unit was transferred into the reservoir where it was stored overnight. On the fourth day the equilibrium cell, piston burettes and the associated capillaries were pumped down using the high vacuum facility. After evacuating the system for three hours 5 ml of water were introduced into the cell and the contents were stirred for twenty minutes to allow equilibrium to be established inside the cell before the vapour pressure of pure water was measured. Three measurements were taken at ten minutes interval. A second quantity of water, again 5 ml, was charged to the cell as before and its vapour pressure measured. The experiment was repeated until the cell was nearly full. The cell contents were flushed out and the experiment was repeated the

following day. The experiment was interrupted by the weekend following which two further measurements were taken. The results and the experimental layout are shown in Appendix 11.

In a similar experiment absolute ethanol was degassed and stored in the reservoir. It took ten hours to completely degas ethanol. On the second day the system was pumped down as before and the vapour pressure of ethanol was measured on 5 ml increments until the cell was nearly full. The pressure measurements were repeated over five days to establish the integrity of the degassing apparatus, see Appendix 12 for fuller details.

The data obtained on water and ethanol showed that both liquids can be stored in the reservoir for up to seven days before a noticeable pressure change was observed. After this period air entered the reservoir and redissolved in the liquids thus rendering them unsuitable for further experimental measurements.

A considerable time was spent investigating ethanol and water because the literature data on these was available for direct comparison. The most important source of vapour-liquid equilibrium data on ethanol and water mixture was the National Physical Laboratory (NPL). Once a direct comparison had been made between the data from NPL and the data of this work and a satisfactory agreement obtained between the two, vapour pressure measurements were made on ethanol-water, methanol-water, and ethanol-cyclohexane mixtures.

6.5 Dispensing Device and its Operation

The pure degassed liquid contained in the reservoir of the degassing apparatus was transferred into the piston head glass burette for subsequent introduction to the cell. The design details can be found in Section 5.2.2.

6.5.1 Mode of operation

The glass burettes and the associated capillaries were thoroughly evacuated with the high vacuum pump. The space immediately below the piston head was opened to a similar vacuum to remove any air which enters the cavity. This procedure also eliminates pressure differential across the piston head and therefore facilitating the movement of the piston.

For charging the burette the piston was pushed up to the maximum with valves V_1 and V_2 in a closed position, see Figure 6.3. V_1 was opened and the piston shaft pulled downwards. The liquid was sucked into the burette. When the piston head had reached its lowest position, V_1 was closed while the piston was slowly pushed upwards until the glass burette was full of liquid. The valve V_1 was opened and the piston head was pulled downwards again until liquid continuity was obtained. V_1 was closed and the piston was pushed up again until it was locked against the the liquid. The valve V_2 was cracked open and V_1 and V_3 closed, then the piston was moved upwards to push the liquid into the capillary connected to the cell. At this stage it was essential that no air bubbles be present in this capillary tube. As the liquid entered the tube the piston was kept pushed up until further movement was not possible. This procedure ensured that the liquid in the capillary line was stored under pressure.

To introduce the pure liquid into the cell, V_3 was cracked opened while valves V_4 and V_5 were firmly shut. The piston head was pushed upwards and at the same time V_3 was opened a little more so that the liquid was charged into the cell under pressure. Once the required volume of liquid had been placed in the cell V_3 was closed off and the position of the piston head noted on the vernier scale. Further charging of the pure liquid into the burette and its subsequent introduction into the cell was carried out in a similar fashion.

Since the material was dispensed by the upward movement of the piston, any pressure necessary to load the material into the cell could be easily generated thus enabling successive quantities of liquid to be introduced into the cell which would otherwise be hampered as the pressure inside built up.

6.6 Initial Preparations and Cleaning of the Apparatus

It was an essential pre-requisite that the pure components under investigation were free from any species which are capable of interfering with the true vapour pressure. Ethanol, methanol and cyclohexane were all Analytical grade from BDH. As soon as these chemicals were purchased they were analysed using a gas liquid chromatography to see if there were any impurities present, particularly water. Small traces of water were detected. The chromatograph of absolute ethanol showed a prominent peak due to the presence of water. Similarly methanol and cyclohexane appeared to contain a small trace of moisture. 500 ml portions of these liquids were taken into a flask and were stored on molecular sieves. These flasks were placed in a desiccator. A small quantity of the liquids under investigation was removed with the aid of a syringe and put into the gas liquid chromatography column. This analysis was repeated every two days until all traces of water had been removed. The storage time was about two weeks.

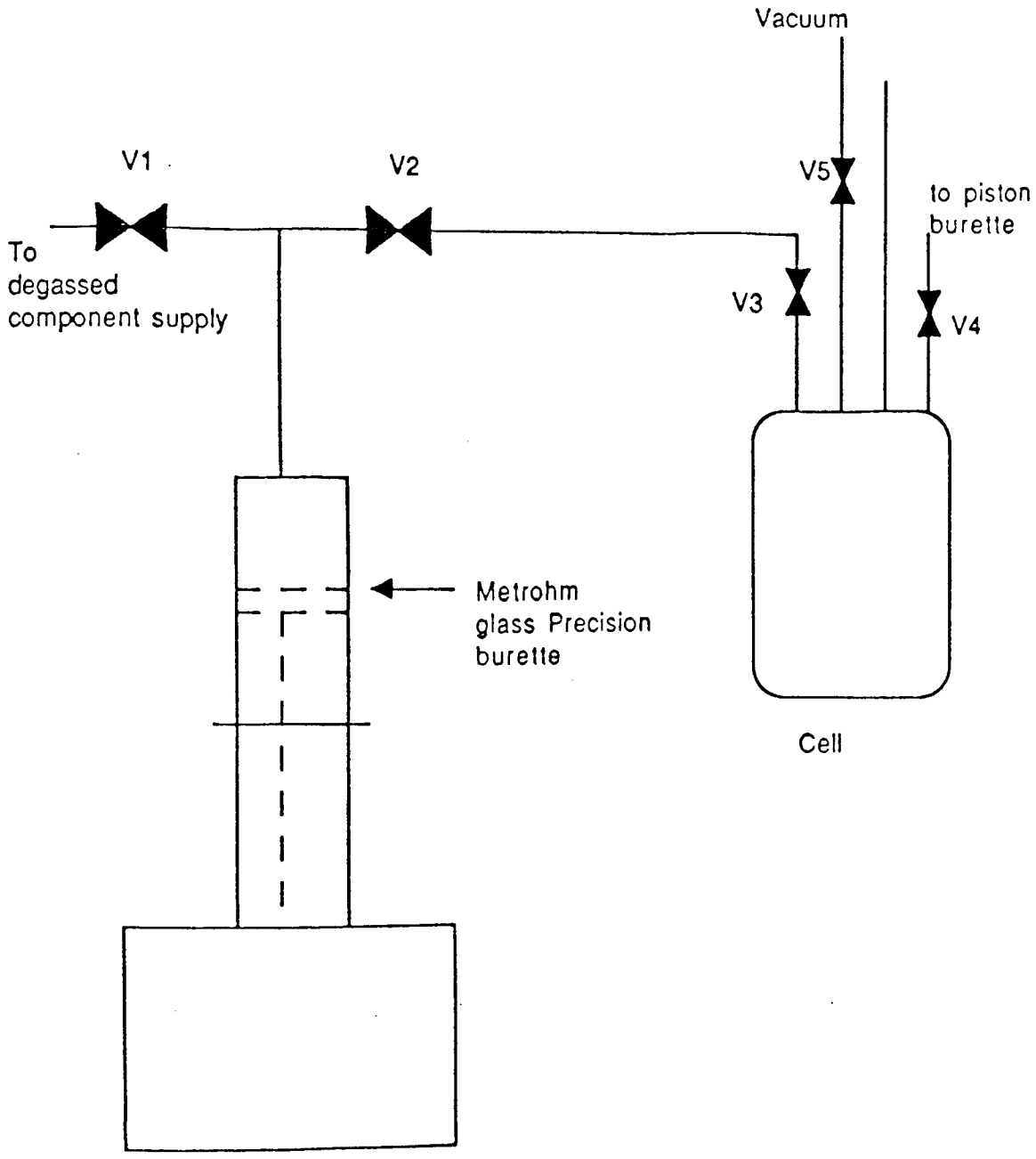
6.6.1 Cleaning of the glass apparatus

The parts of apparatus made from glass were soaked in soap and water overnight and thoroughly rinsed to remove any traces of detergent. They were then dried by placing them in a dry oven set at 110°C over night before being assembled.

6.7 Data Acquisition and Experimental Procedure

The pure components under investigation were degassed and stored in the reservoir until such time that the parts which form the critical path of the apparatus were well evacuated. The critical path entails from the base of the reservoir and all the way to the connection to the pressure transducer. The critical path was pumped down to a pressure of less than

Figure 6.3 Showing the procedure of introducing the liquids into the cell.



0.01 mmHg. Once a satisfactory pumping down of the the equilibrium cell and the connecting capillaries had been achieved, the cell was isolated from the system by shutting off the valves V_3, V_4 and V_5 shown in Figure 6.3.

Before a desired quantity of liquid was placed in the cell a null point was established by subjecting both sides of the transducer diaphragm to equal pressure, 0.01 mmHg in this case. The pressure on the balancing side of the transducer was controlled by the Texas Bourdon gauge pressure controller. In this set up the position of the indicator needle of the transducer read out device was noted.

The pure liquid from the burette into the cell was transferred using the following approach; with the capillary line filled with the liquid (as described in Section 6.5.1) and the valves V_4 and V_5 closed and the position of the piston head on the vernier scale noted and called the initial volume V_i, the valve V_3 was cracked opened and almost simultaneously the piston shaft was moved upward. The liquid rushed into the cell and the pressure on the liquid was maintained by having the piston head well pressed against the liquid. While having the piston head pressed against liquid the valve V_3 was closed off. The position of the piston head was noted on the vernier scale and this was called the final volume V_f.

As the liquid charge was placed in the cell the vapour pressure inside the chamber changed due to the vapour pressure of the liquid and this offset the balance point. The pressure control knob on the Bourdon gauge was adjusted until the null position was regained. The pressure controller works by applying positive or negative pressure on the system until a null is found. The amount of pressure (positive or negative) applied by the Bourdon gauge on the system in order to re-establish the null on the indicator was equal to the vapour pressure exerted by the liquid charge inside the cell. Before the pressure readings were taken the charge in the cell was stirred electrically by an external magnet and the contents were kept stirred until a thermal equilibrium with the surrounding had been attained and that the indicator needle became steady suggesting that an equilibrium exits between the liquid and the vapour arising from that liquid.

A second quantity of the same liquid was introduced in exactly the same manner and its vapour pressure measured. Three measurements were taken at an interval of ten minutes and as these values appeared consistent a known volume of second component was charged into the cell in the same fashion as before. The second component was added in increments and the total pressure inside the cell was measured after each addition from the pressure required to regain the balance position of the transducer diaphragm. When the cell was nearly full its contents were pumped out by opening it to the high vacuum facility. Once the cell had been pumped down to a pressure of less than 0.01 mmHg the experimental measurements were carried out in the reverse order to cover the second half of the composition-pressure curve.

The experimental measurements were the incremental volume of liquid introduced into the cell, the total pressure inside and the total pressure exerted as a result of liquid additions and an operating temperature. The thermostat controlling the temperature of the water bath was set to a different temperature and the total vapour pressure inside the cell was measured as a function of volume of liquid placed in the cell.

6.8 Data Reduction

In this work, as already noted in Chapter 4 , the Barker method was adopted as the means by which the experimental data would be manipulated to give values of x and y in equilibrium. As pointed out above, in the Barker method a liquid phase activity co-efficient model is chosen and its parameters adjusted using an optimisation scheme until a minimum error is achieved between the experimental and calculated total pressures. Values of y are produced during this process.

In this work, the first set of liquid mole fractions are computed assuming all the moles added to the cell are in the liquid phase. Whilst in practice these values are very close to the true liquid mole fractions, the first set of calculated y values is used, using the ideal gas law and a simple mass balance, to give corrected values of the liquid mole fractions. Whilst

this procedure could be repeated until the liquid mole fraction did not change on subsequent passes, in practice the charge is so small that only one correction is necessary.

A computer package was available for this purpose. It had been developed from a programme written by O'Donnell (1980), this programme carried out Barker method consistency tests on complete experimental x-y-P-T data set. A front end had been added which reads in the experimental data from the total pressure method, and then processes these for passing to the Barker method. The y values returned by this were then used in the mass balance already referred to, and the Barker method used on the adjusted liquid mole fractions. The results were printed from both Barker fits so that the degree of adjustment could be checked.

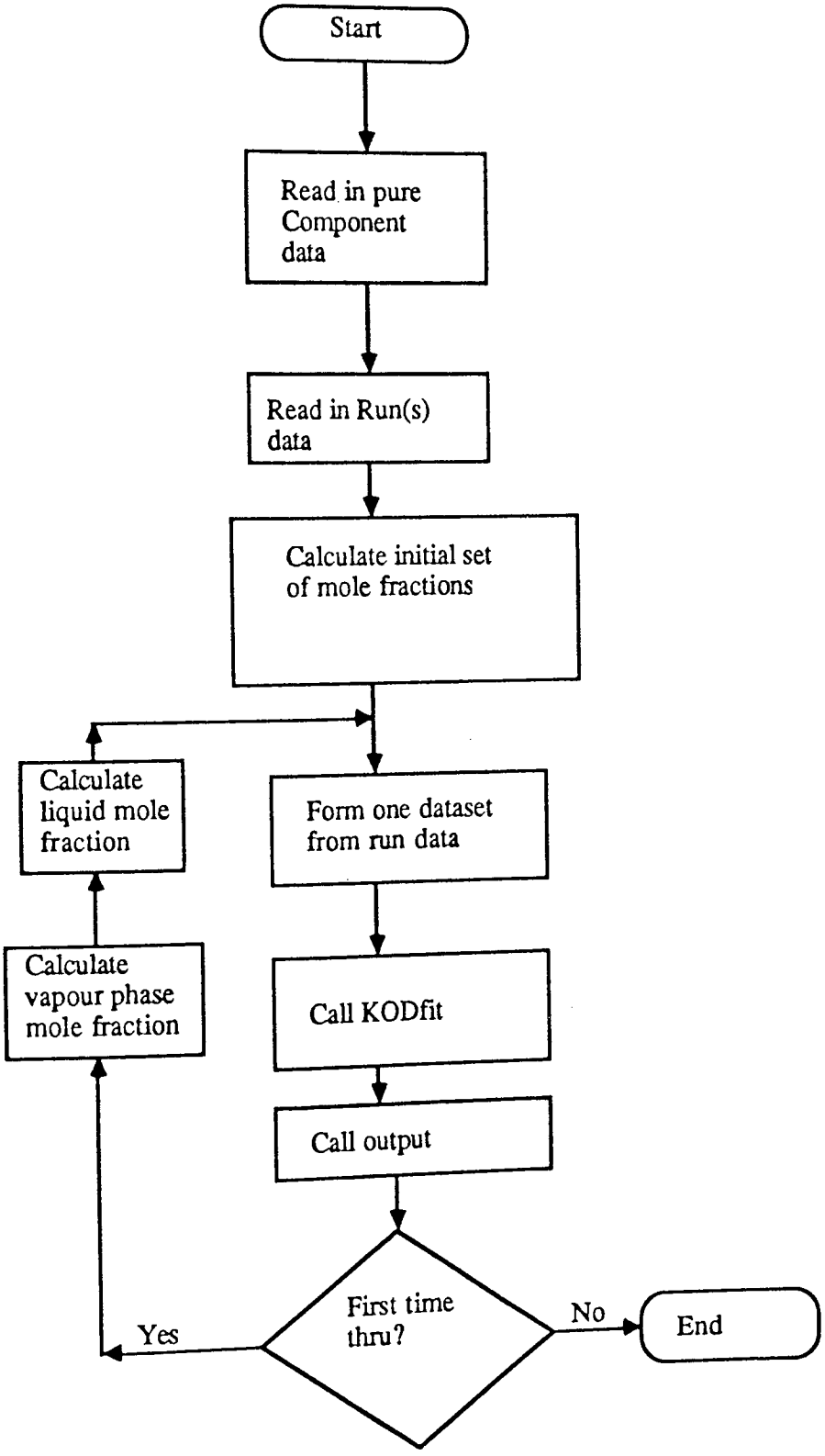
Had an excessive change occurred, the programme could then be run with an additional pass through the Barker fit. The flow diagram for this front end is given in Figure 6.4.

An alternative package was also available which, while it did not contain the front end as discussed above, also enabled integrated forms of the Gibbs-Duhem equation to be fitted to both experimental x-y-P-T and x-P-T data. This was an implementation of the computer programme presented by Praunitz et al. (1980) in their monograph. The distinctive feature of this package relevant to this work is that the fit used is not a Barker-fit as such but a maximum likelihood fit to all the experimental data presented rather than to just the x-P-T data. When only x-P-T data are used then this approximates to a Barker-fit.

Initially the first programme was used to give the y-values, and in general using the only fitting equation implemented in this version, a fifth order Margules, good fits were found to the experimental x-P-T data. However, an initial comparison of the values so obtained with experimental data from other sources showed large discrepancies. In view of the good fits obtained, massive experimental error was considered unlikely, which left the possibility that the package was in fact giving erroneous values (Jenkins, 1991), a point returned to below. Hence the data were reduced on the Prausnitz-derived package, the x-values deduced in the first package being used as input together with the measured

pressures and temperatures. The correlating equation used was the UNIQUAC equation with only two adjustable parameters. Values of vapour phase composition much closer to those of other workers were observed and these are the values discussed below. It is opined (Jenkins, 1991) that with a five-parameter equation the degree of flexibility is such that multiple solutions are possible and which one is found depends on the starting values used for the adjustable parameters. In principle this could have been examined by repeating the fits using different estimates of the starting values in a systematic way to identify the nature of the problem. But such a purely computational exercise was both precluded by the time available and outside the nature of this research programme. It was sufficient for this project for a satisfactory fit to be obtained using a well proven equation such as the UNIQUAC, since multiple solutions are both virtually impossible and in practice not observed with this equation (Jenkins, 1991).

Figure 6.4: *Flow Chart*



Chapter 7: Data Analysis and Discussion of Results.

The total pressure method relies on the measurements of total vapour pressure exerted inside a static cell as the liquid composition is varied. As already mentioned earlier the method gives pressure, temperature, and liquid phase mole fractions, the PTx data. The mole fractions of the components present in the vapour phase have to be determined by means of a suitable computational technique. Since the method almost entirely relies on the measurements of P as x is varied, there are several essential requirements which have to be met. These being (a) good degassing procedure (b) high vacuum integrity, i.e no-leakage situation (c) accurate measurement and control of both temperature and pressure and (d) a data-reduction package must be available.

Despite the above requirements the total pressure method is still widely used in the measurements of vapour-liquid equilibrium data. Its credibility and popularity have arisen from the fact that both the sampling and analysis stages of the measurements are avoided; thus eliminating two of the major sources of error in phase equilibria studies. Since it is the sampling and analysis stages which can be cumbersome, eliminating these allows data to be collected more rapidly than is possible with other methods which involve analysis of the phases.

Having built an apparatus with all the technical requirements in hand, it was commissioned using well studied systems. The experimental programme was designed to make measurements of vapour-liquid equilibrium on three mixtures; namely ethanol/water, methanol/water, and ethanol/cyclohexane. These were chosen because data on all three mixtures were available in the literature.

In screening the raw data to obtain an indication of performance and integrity of the experimental apparatus pure component data were examined on their own and a direct comparison of these data was made with those from the literature. Where possible multiple

sets of data were obtained from the literature for each pure liquid. The pure liquid data were available as saturated vapour pressures.

7.1 Ethanol-Water Mixtures.

Saturated vapour pressures of pure water and pure ethanol were measured over a range of temperatures and a comparison of this data was made with the literature values.

7.1.1 Pure Water.

Both from the literature review on degassing techniques for water and from the experience gained from this work, it is clear that generally water is more difficult to degas than organic liquids, requiring a more rigorous treatment typically 24 hours as against 10 hours for the organics.

Saturated vapour pressures of water were measured at a range of temperatures and these were compared with data from Larkin and Pemberton (1976), McGlashan and Williamson (1976), Jenkins and O'Donnell (1980), d'Avila and Silva (1970),standard steam tables data from Perry and Chilton (1973) and data obtained from the correlation of Prausnitz et al (1967).

On plotting pressures against temperatures our data showed good agreement with those of other workers, see Figure 7.1. A clearer fit was obtained when ln P against 1/T was plotted, see Figure 7.2. For the reasons of clarity only a few data sets are plotted on the graphs.

Note that these plots contain not only the initial pure water measurements but those taken at the beginning of runs involving the initial addition of water. So it is clear that (1) satisfactory degassing was achieved (2) the measurements of temperature and pressure are at least consistent within themselves and since good agreement is reached for other pure liquids (see below) that they are accurate to within the level of precision. See table 7.1 below.

Table 7.1: *Showing data for pure water.*

Saturated Vapour Pressures in mmHg					
Temp / °C	**Measured**	**During run**	**NPL**	**Correlation**	**Steam Table**
25	23.1750		23.7675	23.7770	23.775
30	31.2675	32.130	31.8375	31.8220	31.800
35	41.2125	43.563		42.1720	42.2013
40	54.3300	55.077		55.3220	55.3500
50	93.7890	93.844	92.5875	92.5149	92.5500
60	152.2100	152.076		149.381	151.302

Figure 7.1: *Plot of Pressure against Temperature for Water.*

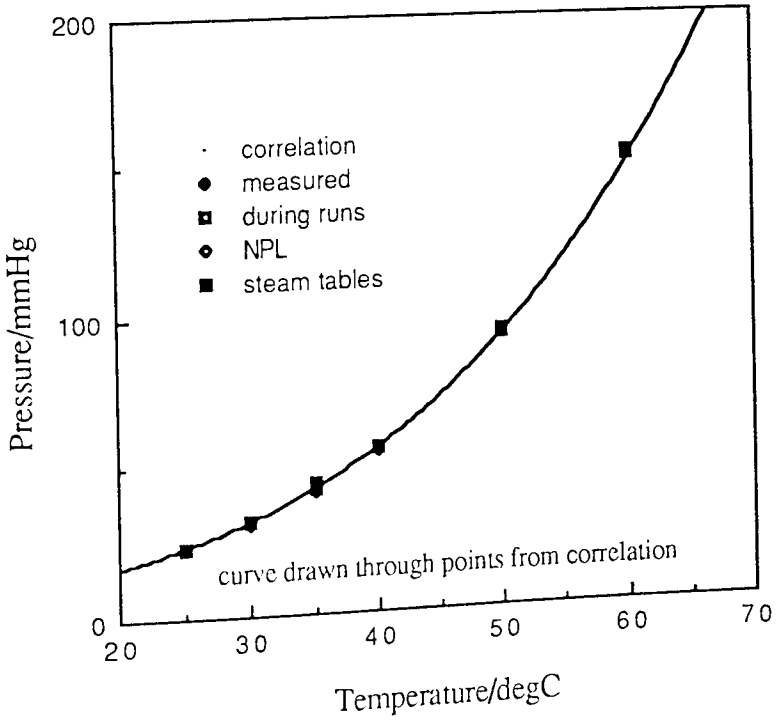
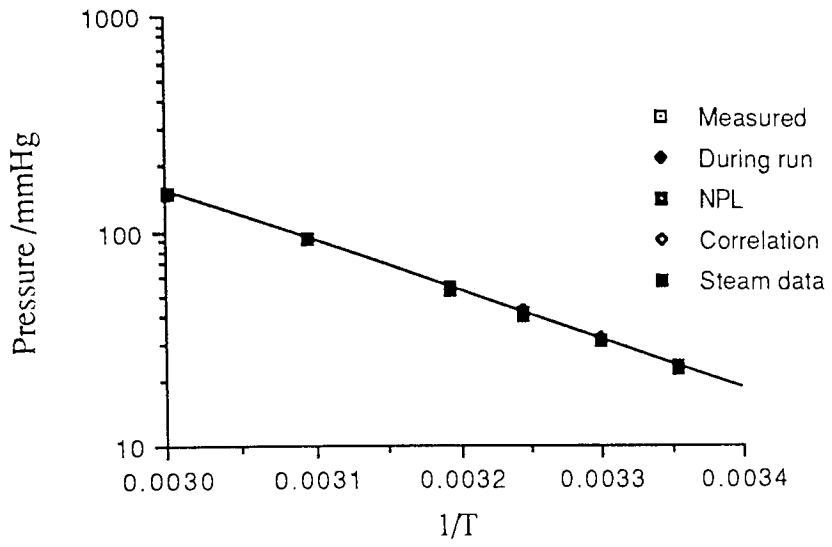


Figure 7.2: *Plot of ln P against 1/T for pure Water.*



7.1.2 Pure Ethanol.

The vapour pressure of pure ethanol was measured at a range of temperatures. As before these data were compared with the literature data, Larkin and Pemberton (1976), the correlation of Prausnitz et al. (1967) and the data of Scatchard et al. (1964), Ronc and Ratcliffe (1976) and Maher and Smith (1979). For the reason mentioned above only a few data sets are presented graphically and it should be noted that as well as the initial data for pure ethanol the vapour pressures measured for ethanol in the beginning of the runs on mixtures are also compared with the initial P-T data.

As shown in Figures 7.3 and 7.4 a good agreement exists between our experimentally measured data and those from other sources. This again illustrates that a satisfactory degassing has been achieved as well as reinforces the points made above on the measurements of pressure and temperature.

7.1.3 Ethanol-Water Mixtures

After having checked the apparatus with pure water and pure ethanol mixtures of the two

were examined. The data obtained were isothermal and most of the measurements were carried out at the high water dilution end. The vapour liquid equilibrium data were obtained over a range of temperatures.

For all the mixtures studied, an initial check was carried out on the calculation from the raw experimental data of the liquid phase mole fractions. A simple mass balance calculation assuming all the material in the cell was in the liquid phase gave an initial liquid phase composition. The first data reduction package echoed this step but then used the first estimates of vapour phase compositions to give corrected values. But since the amount of material present in the vapour phase proved to be so small, in practice rarely was any difference noted between the manual calculation and the corrected ones from the package. As noted above these values were then used as input to the Prausnitz derived package, to give the vapour phase compositions as well as an indication of the consistency of the data. One output of the Prausnitz derived package is an estimate of the least square (LSQ) error in the measured data. For data of high consistency, the calculated LSQ error should be

Table 7.2: *Showing data for pure ethanol.*

Pressure in mmHg					
Temp / °C	Measured	During run	Correlation	NPL	Scatchard
25	59.430		59.3120	59.378	
30	79.540		79.2177	79.176	80.235
30.5	84.892	83.805	80.672		
35.5	111.758	108.750	106.558		
40.5	143.655	145.500	138.157		
42.5	158.460		157.390		
45	174.210		173.159		
50	222.330	225.150	221.120	216.653	221.200

Figure 7.3: *Plot of Pressure-Temperature for Pure Ethanol.*

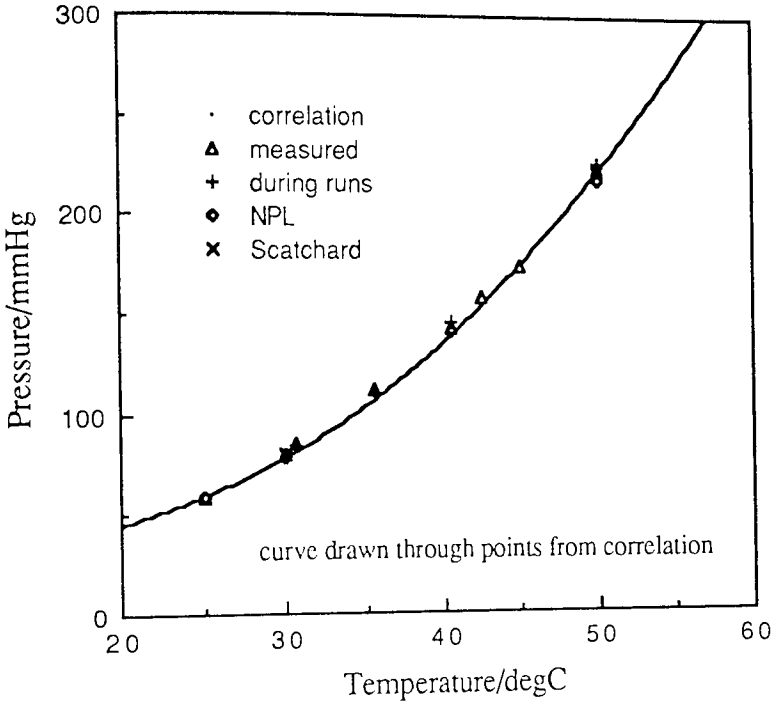


Figure 7.4: *Plot of ln P against 1/T for Pure Ethanol*

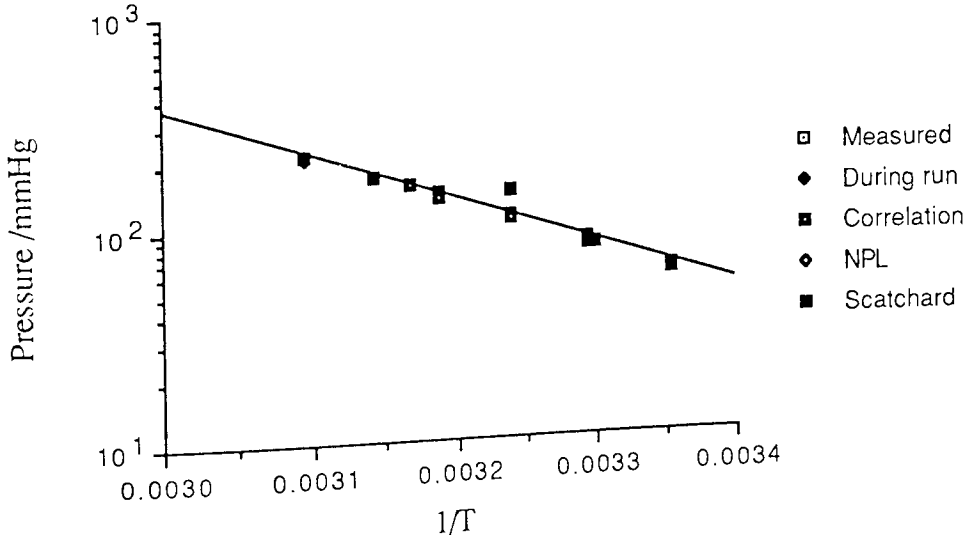


Figure 7.5: Plot of y against x for ethanol-water mixture at 30.47°

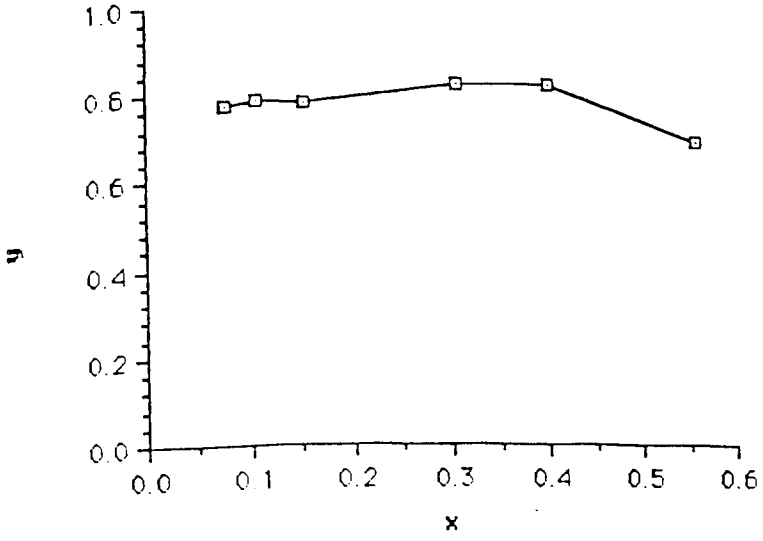


Figure 7.6: Plot of y against x for ethanol-water mixture at 40.57°C

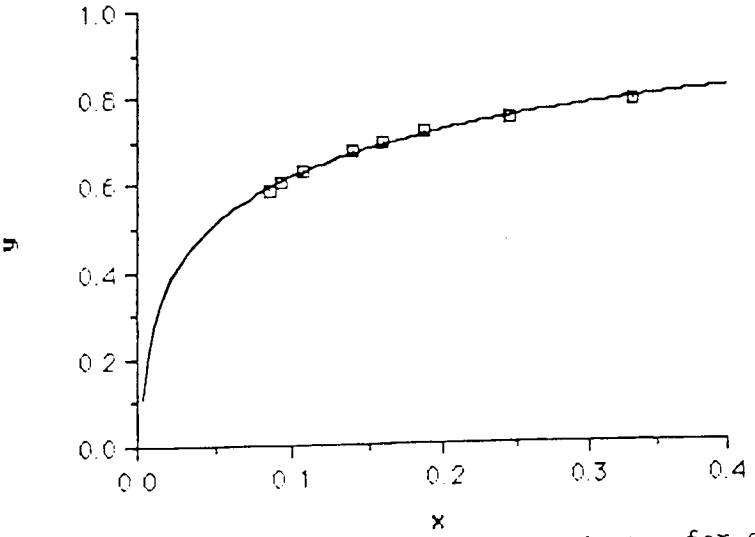
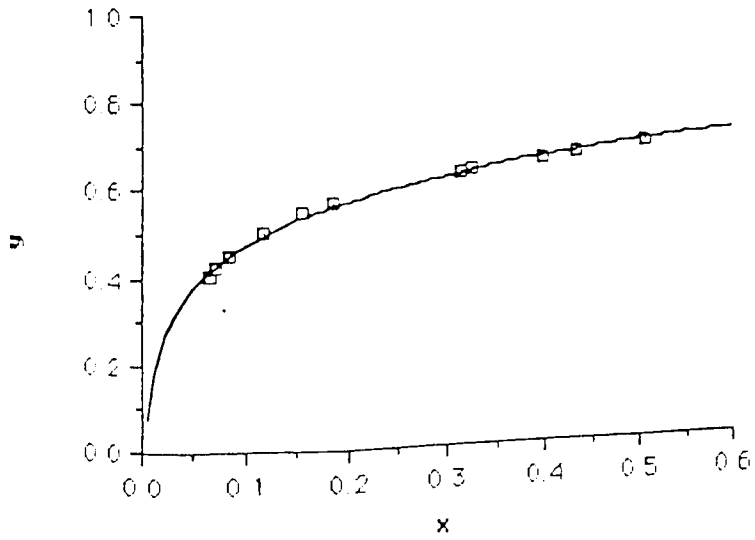


Figure 7.7: Plot of y against x for ethanol-water mixture at 50.60°C



close to the estimates of the experimental uncertainty in the measured data. For many of the fits this criterion is closely met, those where it was not are indicated at the appropriate place in the discussion.

For ethanol-water mixture the first isothermal vapour-liquid equilibrium data were measured at 30.47°C. Though valuable, these data appear to carry large errors (see Figure 7.5) and large differences were noted between the experimental and theoretical pressures, suggesting that some air had leaked into the system. Insufficient degassing of pure liquids was not responsible for the error since the saturated vapour pressures of both components were measured when they were introduced as single components during the run and were found to be consistent with the expected values.

The subsequent data for ethanol-water mixtures measured at 40.54°C and 50.00°C were found to be of good quality and gave a good fit as indicated by a small LSQ error function. For both temperatures the plots of y against x had similar features to those of the literature data. The vapour-liquid equilibrium data measured at 50.00°C were found to be in good agreement with the data of Larkin and Pemberton (1976) as shown in Figure 7.7. The data lie so closely together that they cannot be distinguished on this plot. Such a comparison was not possible for data measured at 40.54°C (see Figure 7.6).

7.2 Methanol-Water Mixtures.

As for the ethanol-water mixtures saturated vapour pressures of pure methanol and of pure water were measured at 35.00°C, 40.00°C, 50.00°C and 60.00°C. Where possible the values obtained were directly compared with those reported by McGlashan and Williamson (1976) and Srivastava et al. (1986) as well as with the P-T data deduced from the use of the Prausnitz derived Correlation. As shown in Figures 7.8 and 7.9 a good agreement exists between the experimentally measured P-T data and the data from other sources.

Table 7.3: *Showing data for pure methanol.*

Saturated Vapour Pressures in mmHg			
Temp /°C	**Measured**	**Correlation**	**McGlashan**
35	203.180	205.680	210.00
40	263.193	264.840	
50	412.231	409.220	417.400
60	625.720	623.160	
65	776.131	774.780	774.950

Once a satisfactory agreement of saturated vapour pressures for pure methanol between the experimental and literature values had been reached measurements of total vapour pressure as a function of composition were made at the above temperatures.

7.2.1 Methanol-Water Mixture at 35.00°C.

As shown in Figure 7.10 our experimentally measured vapour-liquid equilibrium data for methanol-water at 35.00°C shows good agreement with those of McGlashan and Williamson (1976).

7.2.2 Methanol-Water Mixture at 40.00°C.

The experimental vapour-liquid equilibrium data on methanol-water mixture at 40.00°C appears to carry large errors as indicated by the magnitude of the LSQ value even though the plot of y against x exhibits similar features to those found in the literature. A closer examination of the data reveals large pressure differences between the experimental and the theoretical pressure values thus suggesting that some air must have leaked into the system during the run. Despite the poor quality (see Figure 7.11) the data are still considered to be valuable from a developmental view point.

Figure 7.4: Plot of Pressure against Temperature for pure Methanol.

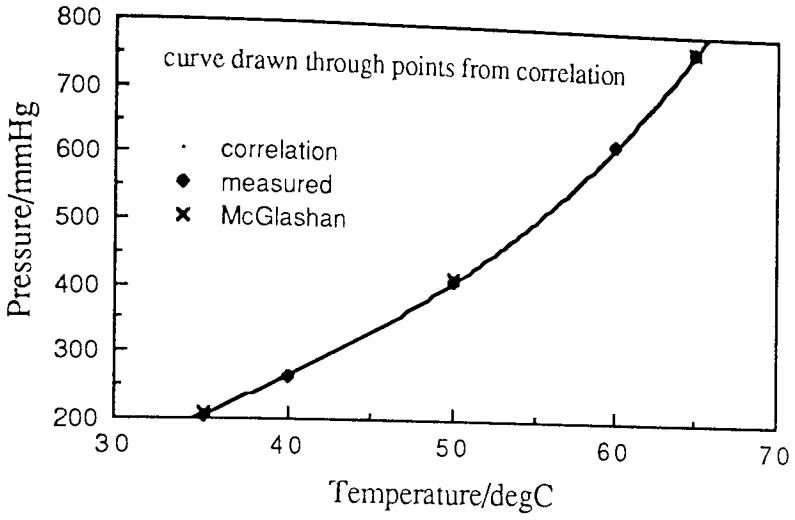
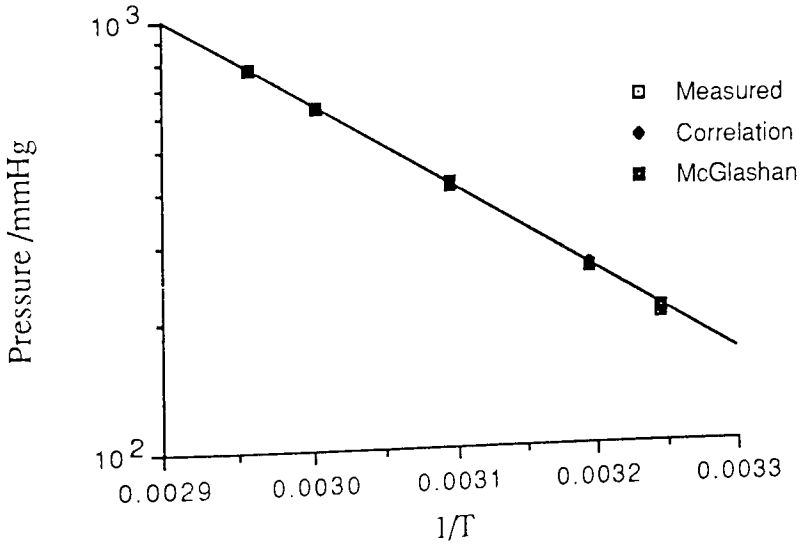


Figure 7.9: *Plot of ln P against 1/T for pure Methanol.*



7.2.3 Methanol-Water Mixture at 50.00°C.

The data measured on the methanol-water mixture at 50.00°C compare well with those of McGlashan and Williamson (1976) and as before during our initial screening there was a good agreement between the liquid phase composition values calculated manually and those

given by the Prausnitz correlation. A plot of y against x gave a good fit and when comparing with the literature data close agreement was noted (see Figure 7.12). However our experimental pressure values were found to be slightly higher than those of McGlashan and Williamson (1976) for a given composition. Due to the nature of phase equilibria studies small discrepancies are within the tolerance limits of the experimental apparatus.

7.2.4 Methanol-Water Mixture at 60.00°C.

The vapour-liquid equilibrium data for methanol-water mixture at 60.00°C appear to contain large errors as indicated by a very large LSQ error function. There are discrepancies between the measured pressure and theoretical pressure values suggesting that either the degassing was not sufficient or some air leakage had occurred. However the saturated vapour pressure for pure components measured at the beginning of the run agreed with the expected values thus the air leakage seems to be the cause of problem. The plot of y against x (see Figure 7.13) does exhibit features similar to those of literature data.

7.3 Cyclohexane-Ethanol Mixtures.

Pressure-temperature data on pure cyclohexane were measured and then compared with the data of Brown (1952), Mentzer et al. (1982), Younger et al. (1986), Scatchard et al. (1963) and those calculated from the Prausnitz derived correlation (1967). For ethanol see Section 7.1.2. For pure cyclohexane the P-T data were measured at 30.00°C, 35.00°C, 40.00°C, 50.00°C and 60.00°C.

As shown in Figures 7.14 and 7.15 the pure cyclohexane data agree well with the data from other sources and particularly with the data derived from the Prausnitz derived correlation.

Figure 7.10: Plot of y against x for methanol-water mixture at 35.00°C.

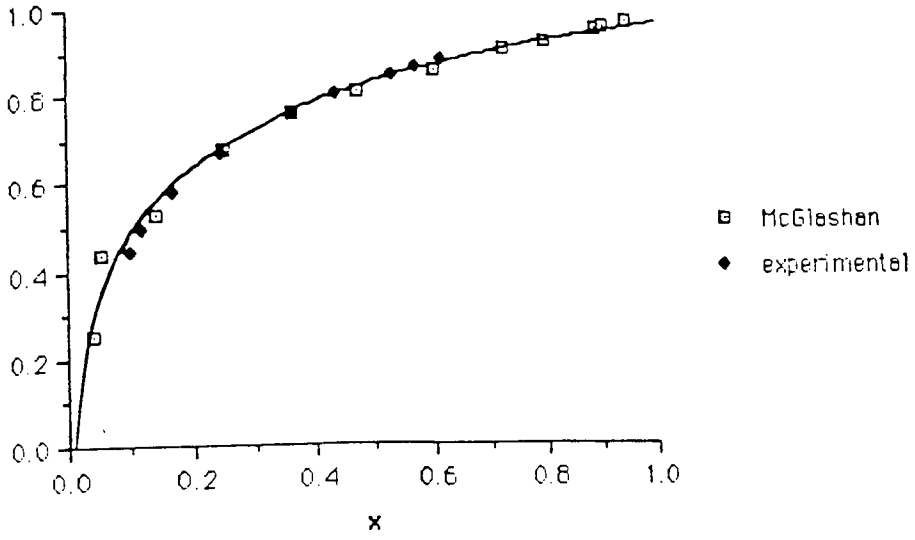


Figure 7.11: Plot of y against x for methanol-water mixture at 40.00°C.

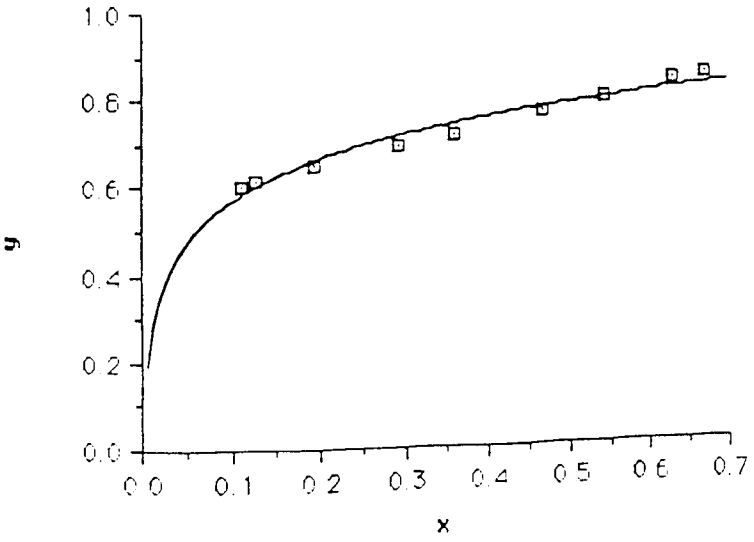


Figure 7.12: Plot of y against x for methanol-water mixture at 50.00°C.

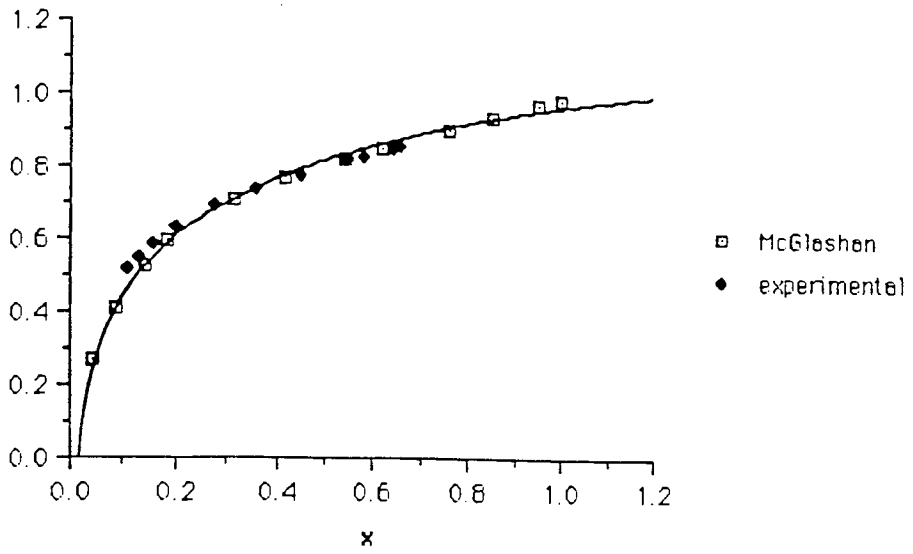
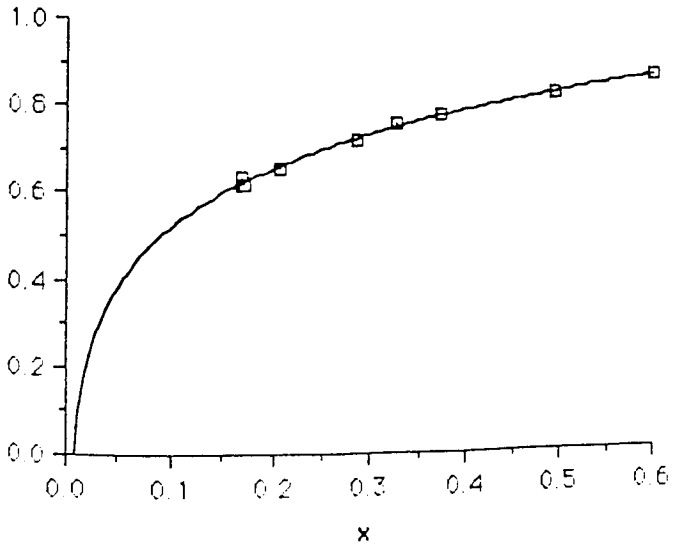


Figure 7.13: Plot of y against x for methanol-water mixture at 60.00°C.



7.3.1 Cyclohexane-Ethanol Mixture at 57.21°C.

The vapour-liquid equilibrium data for cyclohexane-ethanol mixtures at 57.21°C gave a good fit as indicated by moderately low value of LSQ error function. The data were found to be of reasonable quality as shown in Figure 7.16.

Table 7.4 : *Showing data for pure cyclohexane.*

Saturated Vapour Pressures in mmHg			
Temp /°C	Measured	Correlation	Scatchard
30	122.130	121.710	122.503
35	150.680	149.930	150.640
40	184.900	184.700	185.000
50	276.200	275.100	272.000
60	390.420	389.320	390.250
65	462.301	460.231	461.260
70	544.150	543.913	544.280

7.3.2 Cyclohexane-Ethanol Mixture at 70.00°C.

The vapour-liquid equilibrium data for cyclohexane-water mixture at 70.00°C gave a poor fit and large descrepancies were noted between the measured pressures and calculated pressure values, hence a large LSQ error value. Since the saturated vapour pressures for both components were measured at the beginning of the run and were found to be in line with the literature values (Scatchard et al. 1963), the pressure discrepancies for the actual mixture could be due to some leakage into the system. A plot of y against x is shown in Figure 7.17.

Figure 7.14: *Plot of Pressure against Temperature for Cyclohexane.*

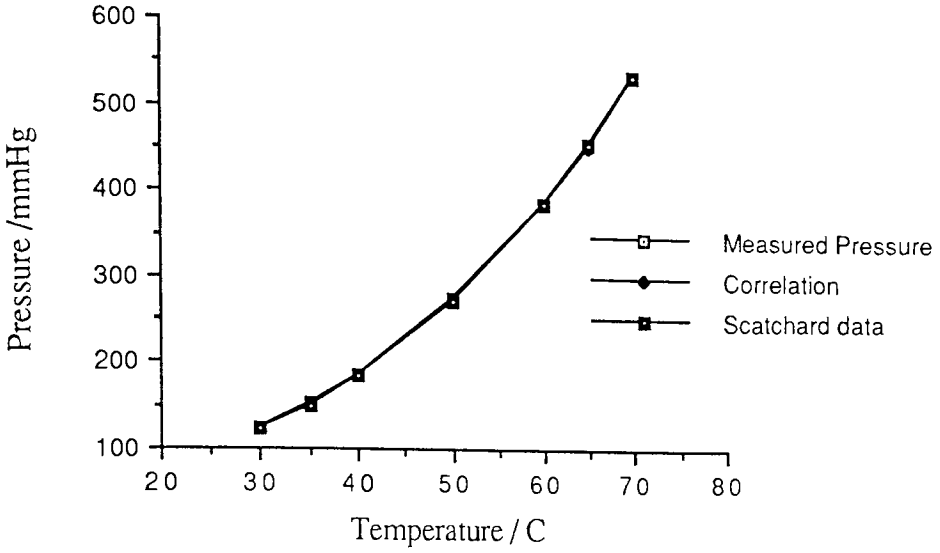


Figure 7.15: *Plot of ln P against 1/T for Cyclohexane.*

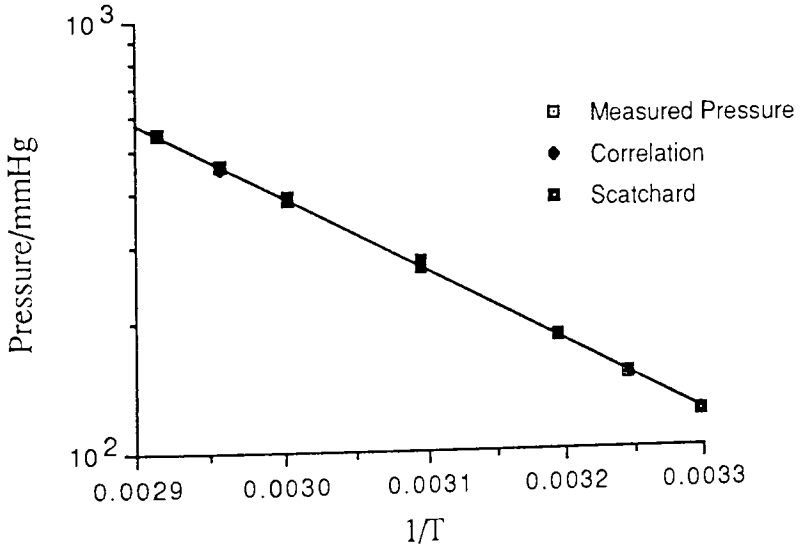


Figure 7.16: Plot of y against x for Cyclohexane-ethanol mixture at 57.20°C.

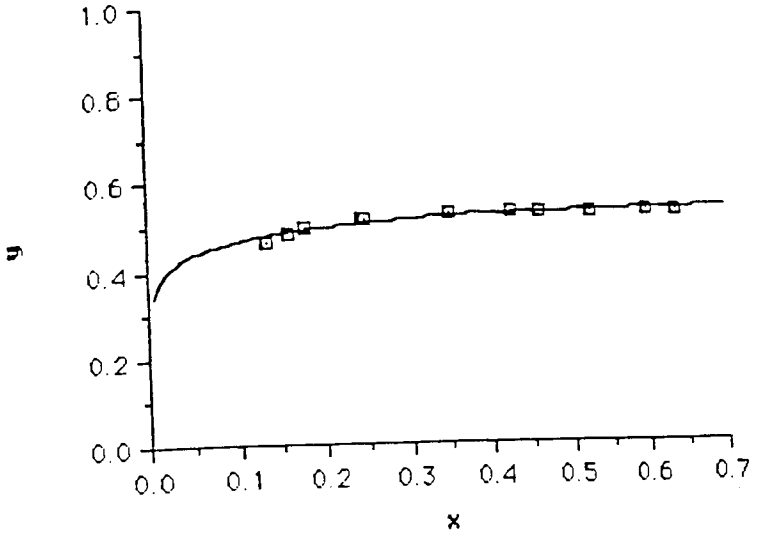
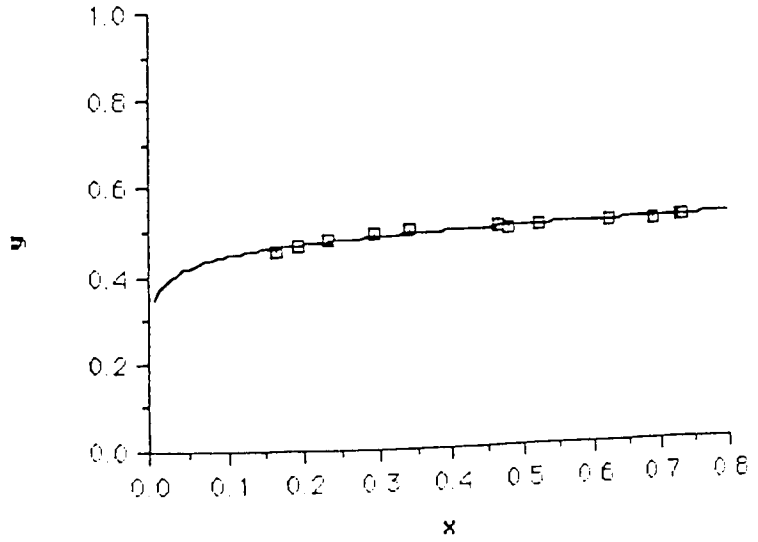


Figure 7.17: Plot of y against x for cyclohexane-ethanol mixture at 70.00°C.



Chapter 8: Conclusions and Recommendations.

As already noted for a total pressure approach to be valuable in the measurements of vapour-liquid equilibrium data it is essential to have a good degassing procedure, good measurement and control of temperature and pressure and the central apparatus must be leak-free.

Having achieved the above requirements the apparatus was commissioned on firstly the pure liquids and then liquid mixtures. Initial pressure against temperature measurements were taken for water, ethanol, methanol and cyclohexane. As discussed above the pure liquids data agreed well with the literature data. It should be noted that the initial pressure-temperature data for the pure liquids were compared with the pressure-temperature values measured when carrying out the actual run. A good agreement was noted once again. This suggested that the pressure-temperature measurements were consistent within themselves.

For liquid mixtures the vapour-liquid equilibrium measurements on ethanol-water mixture at 30.47 °C contained large pressure errors caused by the leakage of some air in to the system during the actual measurements. Despite of the poor quality the data could still be regarded to provide a useful guide. The subsequent data measured on ethanol-water mixtures was regarded to be within the precision of the experimental apparatus, this was particularly so with the data measured at 50.00°C.

The pressure-temperature data on pure methanol and pure water were found to be consistent within themselves and comparable to the literature data. For their mixtures the vapour-liquid equilibrium data were of good quality and gave good fits.

Similarly mixtures consisting of cyclohexane and ethanol were examined. For pure liquids P-T data were measured and compared with those from the literature and a good agreement was noted. The P-x data for cyclohexane -ethanol mixtures were measured isothermally at 57.21 °C and 70.00 °C. Direct comparison of our data with the literature data was not

possible for these particular temperatures but on plotting x against y familiar features were noted.

From the above it can be concluded that the method developed in this research programme has the potential to produce high quality vapour-liquid equilibrium data. Since an entire composition range could be covered in one working day, it would be unquestionably economical method. Two features which are important to this approach are the availability of a good and efficient degassing procedure and good leak-tight joints. Lack of either of these would certainly lead to large and false pressure values. The method almost entirely relies on the measurements of total pressure inside an equilibrium chamber as a function of liquid composition and any deviation in the shape of P-x curve would lead to large errors in the values of y. The method produces PTx data and a computational method must be available to deduce the y values. Several computational techniques exist to reduce PTx data to give x-y P-T data set. However, by the virtue of the method no consistency test could be applied to the y values.

Recommendations for Future Work.

There is still a considerable scope for the method of this work to be developed to its fullest potential. In this research programme several pieces of equipment used were available from the previous project. The following recommendations are made for future work using this method:

(1) A differential pressure transducer of high precision and sensitivity must be used capable of working at temperatures up to 140°C.

(2) Pressure fittings in the critical connections to the pressure transducer must be replaced by vacuum connections of either the Edwards or Cajon Ultra-torr fittings.

(3) A minimum number of joints should be involved because experience gained during this project showed that maintaining metal-metal and glass-metal joints leak tight was a cumbersome task. Long glass lines could be replaced by stainless steel 1/16 O.D lines, although their use would preclude visual checks of rig's performance.

(4) Extension of the method to work at higher pressures and temperatures would be of value in obtaining accurate data for studies in the extension of prediction methods such as UNIFAC to higher temperatures.

Nomenclature

a – Van der Waals constant

a_i – Activity of component i

a_{12} – Interaction parameters

a_{112} – Interaction parameters

$a_{n,m}$ – Unifac parameter

A_1 – Adjustable parameter in Van Laar equation

A – Virial coefficient

A_K – Van der Waals group surface area

b – Van der Waals constant

B – Virial coefficient

B_1 – Adjustable parameter in Van Laar equation

B_{ij} – Virial constant inVan Laar equation

C – Virial constant

D – Virial constant

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

G – Gibbs free energy

G^E – Excess Gibbs energy

g^E – Molar Gibbs excess energy

H – Enthalpy

H^E – Excess enthalpy

H^i – Henry's constant

$\overline{H}$ – Partial molar enthalpy

K_i – Equilibrium ratio

n_i – Number of moles of component i

n_T – Total number of moles

P – Pressure

P_{Ci} – Critical pressure of component i

P^S_i – Saturated vapour pressure of component i

p_i – Partial pressures of component i

q – Heat

q_1 – Effective volume, surface solubility parameter

q_2 – Effective volume, surface solubility parameter
q_k – Van der Waals group volume
r_k – Van der Waal group volume
S – Entropy
S^E – Excess entropy
T – Temperature
T_C – Critical temperature
T_r – Reduced temperature
U – Internal energy
v – Volume
V – Partial molar volume
v_k – Van der Waal group volume
w – Accentric factor
W – Work
x_i – Mole fraction of component i in liquid phase
x_{12} – Local mole fraction in liquid phase
y_i – Mole fraction of component i in vapour phase
Z – Compressibility factor

Greek letters

α_{ij} – Relative volatility
$\underline{\sigma_i}$ – Solubility parameter
$\bar{\sigma}$ – Average solubility parameter
φ – Interaction parameter
Γ_K – Residual activity coefficient of group k
Γ^i_K – Residual activity coefficient of group k in reference solution of type i only
Ω_a – Proportionality constant
Ω_b – Proportionality constant
γ^C_i – Combinational activity coefficient
γ^r_i – Residual activity coefficient
γ_i – Activity coefficient
ϕ – Fugacity coefficient
Φ –
λ_{ij} – Boltsman factor parameter
Λ – Adjustable parameter in Wilson equation
τ_{12} – NRTL parameter

α_{12} – Binary adjustable parameter

μ_i – Chemical potential of i component

μ_i^o – Standard state chemical potential

References

Abbott, M. M. and H. C. Van Ness, AIChE J., 21 (1), 62 (1975).

Abbott, M. M. and H. C. Van Ness, Fluid Phase Equilibria, 1, 3 (1977).

Abbott, M. M., Fluid Phase Equilibria, 29, 193 (1976).

Abrams, D. S. and J. M. Prausnitz, AIChE J., 21, 116 (1975).

Aim, K., Fluid Phase Equilibria, 29, 249 (1986).

Alessi, P., M. Fermeglia and I. Kikic, Fluid Phase Equilibria, 29, 249 (1986).

Ambrose, D. and C. H. S. Sparke, J. Chem. Thermodynamics, 2, 631 (1970).

Ashcroft, S. J., R. B. Shearn and G. J. J. Williams, Trans. IChemE (Chem. Engng Res. Dev.), 61,51 (1983).

Assilineau, L. and H. Renon, Chem. Engng Sci., 25, 124 (1970).

Barker, J. A., Austral. J. Chem., 6, 207 (1953).

Battino, R., M. Banzhof, M. Bogan, Part III Anal. Chem., 43(6), 806 (1971).

Beatie, J. A., Chem. Rev., 44, 141 (1949).

Bell, T. N., E. L. Cussler, and K. R. Harris, J. Phys. Chem., 72, 4693 (1968).

Benedict, M., G. B. Webb and L. C. Rubin, Chem. Engng Progr., 47, 419 (1951).

Benedict, M., G. B. Webb and L. C. Rubin, J. Chem. Phys., 8, 334 (1940).

Black, L., Ind. Engng Chem., 50, 403 (1958).

Bondi, A., Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York (1968).

Brewster, E. R. and M. L. McGlashan, J. Chem. Soc., Faraday Trans., 1, (69), 2046 (1973).

Brewster, E. R. and M. L. McGlashan, J. Chem. Thermodynamics, 9, 1095 (1977).

Brown, I., Austral. J. Sci. Res. Ser. A., A5, 530 (1952).

Brown, I. and F. Smith, Austral. J. Chem., 6, 207 (1953).

Brain, S. and J. M. Prausnitz, Ind. Engng Chem. Proc. Des. Dev., 10, 562 (1971).

Bukala, M. and J. Majewski, Przemysl. Chem., 31, 551 (1952).

Byer, S. M., R. E. Gibbs and H. C. Van Ness, AIChE J., 19, 245 (1973).

Carlson, H. C. and A. P. Colburn, Ind. Engng Chem., 34, 581 (1942).

Carnation, N. F. and K. E. Starling, AIChE J., 18 1184 (1972).

Cathala, J., D. Hardie and R. Leclerc, Bull. Soc. Chim. France, 17, 1129 (1950).

Cathala, J., D. Hardie and R. Leclerc, Ind. Eng. Chem., 27, 565 (1951).

Chao, K. C., Ind. Engng Chem., 51, 93 & 1318 (1959).

Coulson, E. A., J. L. Hall and E. F. G. Herington, Trans. Farad. Soc., 44, 636 (1948).

Christiansen, L. J. and A. Fredensland, AIChE J., 21, 49 (1975).

Christian, S. D., J. Phys. Chem., 64, 764 (1960).

Colburn, A. P., E. M. Schoenborn and D. Shilling, Ind. Engng Chem., 35, 1250 (1943).

Counsell, J. F. and C. P. Hicks, NPL Report, Chem. 56, National Physical Laboratory, November (1976).

Counsell, J. F. and C. P. Hicks, NPL Report, Chem. 61, National Physical Laboratory, November (1977).

Dale, G. H., J. Chem. Engng Data, 17 (2), 271 (1972).

Davies. B., PhD Thesis, University of Aston in Birmingham, UK, (1971).

d'Avila, S. G. and R. S. F. Silva, J. Chem. Engng Data, 15 (3), 421 (1970).

De Santis, R., F. Gironi and L. Marrelli, Ind. Engng Chem. Fundam., 15 (3), 183 (1976).

Dixon, D. T. and M. L. McGlashan, Nature, 206, 710 (1965).

Dobnal, V. and M. Novotna, Fluid Phase Equilibria, 23, 303 (1985).

Droplet, J. F. and R. S. Ramalho, J. Chem. Engng Data., 16, 1 (1971).

Dunlop, P. J., J. Phys. Chem., 72, 4693 (1968).

Dvorak, K. and T. Boublik, Coll. Czech. Chem. Commun., 28, 1249 (1963).

Eckert, C. A., B. A. Newman, G. L. Nicolaides and T. C. Tong, AIChE J., 27, 33 (1981).

Ellis, S. R. M., Trans. IChemE., 30, 58 (1952).

Erdos, E., Collect. Czech. Chem. Commun., 21, 1528 (1956).

Eubank, P. T., K. R. Hall and J. C. Holste, Second International Conference on Phase Equilibria and Fluid Properties in Chemical Industry, DECHEMA, Part II, Frankfurt, 675 (1980).

Everett, D. H., Trans. Far. Soc., 61, 1637 (1965).

Ewing, M. B., K. N. Marsh and R. H. Stokes, J. Chem. Thermodynamics, 21 (4), 735 (1975).

Feller, M. and H. J. McDonald, Anal. Chem., 22, 338 (1950).

Flory, P. J., J. Chem. Phys., 10, 51 (1942).

Fredenslund, A., Vapour-Liquid Equilibrium using UNIFAC, Elsevier, 1977.

Fredenslund, A., R. L. Jones and J. M. Prausnitz, AIChE J., 21, 1086 (1975).

Fredenslund, A. and P. Ramussen, Fluid Phase Equilibria, 27, 347 (1986).

French, H. I., A. Richards and R. H. Stokes, J. Chem. Thermodynamics, 11, 671 (1979).

Garner, F. H., S. R. M. Ellis and C. J. Pearce, Chem. Engng Sci., 3, 48 (1954).

Gibbs, R. E. and H. C. Van Ness, Ind. Engng Chem. Fundam., 11, 410 (1972).

Gibson-Robinson, M., PhD Thesis, University of Aston in Birmingham, UK (1977).

Gieryez, P., M. Rogalski and S. Malanowski, Fluid Phase Equilibria, 22, 107 (1985).

Gillespie, P. C., J. R. Cunningham and G. M. Wilson, Final Report, AIChE DIPPRA Project, 805A (1981).

Gillespie, P. C., J. R. Cunningham and G. M. Wilson, AIChE. Symp.Ser. No 244, 81, 57 (1985).

Gustin, J. L. and H. Renon, Bull. Soc. Chim. France, 2719, (1974).

Hala, E., J. Pick, V. Fried and O. Vilim, Vapour-Liquid Equilibria, Second English edition, Pergamon Press, (1967).

Hachenberg, H. and A. P. Schmidt, Gas Chromatographic Head Space Analysis, Heydon, N. Y. (1977).

Hall, K. R. and P. T. Eubank, AIChE J., 21 (6), 1111 (1975).

Hawkinson, R. W., B. D. Langfitt and D. P. Tassios, Can. J. Chem. Engng, 50, 511 (1972).

Hanson, R. S. and F. A. Miller, J. Phys. Chem., 58, 193 (1954).

Hayden, J. D. and J. P. O'Connell, Ind. Engng Chem. Process. Des. Dev., 32, 1250 (1975).

Heil, J. F. and J. M. Prausnitz, Ind. Engng Chem., 57 (5), 18 (1965).

Hermisen, R. W. and J. M. Prausnitz, Chem. Engng Sci., 18, 485 (1963).

Herskowitz, M. and M. Gottlieb, J. Chem. Engng Data, 29, 173 (1984).

Hildebrand, J. H. and R. L. Scott, Solubility of Non-electrolytes, Third Edition, Reinbold, New York, (1950).

Hipkin, H. and H. S. Myers, Ind. Engng Chem., 12, 2524 (1954).

Ho, J. C. K., O. Boshko and B. C. Y. Lu, Can. J. Chem. Engng, 39, 205 (1961).

Holtzlander, G. W. and J. W. Riggle, AIChE J., 1, 312 (1955).

Huggins, M. L., Ann. N. Y. Acad. Sci., 41, 1 (1942).

Hutchings, R. S. and W. A. Van Hook, J. Solution Chem., 14, 13 (1985a).

Imone, M., K. Azumi and N. Suzuki, Ind. Engng Chem. Fundam., 14, 312 (1975).

Jackowski, A., Rocz. Chem., 48 (3), 491 (1974).

Jakubrowski, G. and J. R. Norman, Austral. Chem. Engng, 11, 40 (1972).

Jakubrowski, G. and J. R. Norman, Austral. Chem. Engng, 10 (8), 9 (1969).

Janaszewski, B. and P. Oraez, Inter. Symp. on Vapour-liquid Equilibrium in Multicomponent Systems, Warsaw, Jablonna, November (1975).

Janaszewski, B., P. Oraez and S. Warycha, Fifth Int. Congress Chem. Eng., Chem. Equipment Design and Automation, Prague (1975).

Jenkins, J. D., PhD Thesis, University of Birmingham, UK (1963).

Jenkins, J. D. and B. D. Smith, Fifth Int. Congress Chem. Eng., Chem. Equipment Design and Automation, Prague, Volume F, F3.1, P6 (1975).

Jenkins, J. D. and M. Rafaquat, Vapour-Liquid Equilibrium Symp. IChemE, Aston University, UK (1990).

Jenkins, J. D. and M. Rafaquat, Unpublished Work, (1989).

Jenkins, J. D., Private Communication (1991).

Johnson, A. I. and T. W. Barry, Can. J. Tech., 32, 17 (1954).

Jones, C. A., E. M. Schoenborn and A. P. Colburn, Ind. Engng Chem., 35, 666 (1943).

Jose, J., R. Phillipe and P. Clechet, Bull. Soc. Chimie, France, 8, 2866 (1971).

Kassmann, K. D. and H. Knapp, Fluid Phase Equilibria, 29, 241 (1986).

Kato, M., H. Konishi and M. J. Hirata, J. Chem. Engng Data, 15, 4 (1970).

Kato, M., T. Sato and M. J. Hirata, J. Chem. Engng Japan, 4 (4), 311 (1971).

Kato, M., H. Konishi, M. J. Hirata and T. Kakayama, J. Chem. Engng Japan, 5 (1), 1 (1972).

Kay, W. B., Ind. Engng Chem, 28, 1014 (1936).

Kay, W. B., J. Chem. Engng Data, 15, 46 (1970).

Kemeny, S. and J. Manczinger, Chem. Engng Sci., 33, 71 (1978).

Kemeny, S., J. Manczinger and K. Toth, AIChE J., 28, 20 (1982).

Khurma, J. R., O. L. Mutha and S. Murijal, J. Chem. Engng Data, 28 (1), 113 (1983).

Kieglewski, A., A. C. Zawisza and J. Wecsile, Acad. Polon. Sci. Series Chim., 13, 195 (1965).

Klaus, R. L. and H. C. Van Ness, AIChE J., 13, 1132 (1967).

Kortum, G., H. J. Freier and F. Woerner, Chem. Ing. Tech., 3, 125 (1953).

Kolbe, B. and J. Gonehling, Fluid Phase Equilibria, 23, 213 (1985).

Kolodziej, E. J., Z. Jin, R. A. Greenkorn and K. C. Chao, AIChE Symp. Ser. No 244, 81, (1985).

Kretschmer, C. W. and R. Wiebe, J. Anal. Chem. Soc., 76, 2579 (1954).

Kunerth, W., Phys. Rev., Ser. 2, 19, 512 (1922).

Kunz, R. G. and R. S. Kapner, AIChE J., 17, 502 (1971).

Larkins, J. A. and R. C. Pemberton, NPL Report Chem. 43, National Physical Laboratory, January 1976,.

Lee, S. C., J. Phys. Chem., 35, 3558 (1931).

Legret, D., D. Richon and H. Renon, Ind. Engng Chem. Fundam., 19, 122 (1980).

Letcher, T. M., Chemical Thermodynamics, Volume 2, A, Specialist Periodical Report, The Chemical Society, London, (1978).

Lewis, G. N., Proc. Amer. Acad. Sci, 37, 49 (1901).

Lewis, G. N., Proc. Amer. Acad. Sci., 43, 259 (1907).

Ljunglin, J. J. and H. C. Van Ness, Chem. Engng Sci., 17, 531 (1962).

Ljunglin, J. J. and H. C. Van Ness, Chem. Engng Sci,. 18, 485 (1963).

Loblen, G. M. and J. M. Prausnitz, Ind. Engng Chem. Fundam., 21, 109 (1982).

Locke, D. C., Advances in Chromatography, Volume 14, Marcel Dekker, New York, Chapter 4. (1976).

Loche, J. R., H. C. Van Ness and M. M. Abbott, J. Chem. Engng Data, 28, 405 (1983).

Mackay, P. and R. J. Salvador, Ind. Engng Chem. Fundam., 10, 167 (1971).

Maher, P. J. and B. D. Smith, J. Amer. Chem. Data, 24 (1), 16 (1979a).

Maher, P. J. and B. D. Smith, Ind. Engng Chem. Fundam., 18 (4), 354 (1979b).

Malanowski, S., Fluid Phase Equilibria, 8, 197 (1982a).

Malanowski, S., Fluid Phase Equilibria, 9, 311 (1982b).

Mamers, H., PhD Thesis, University of Birmingham, UK, (1965).

Marek, J., Coll. Czech. Chem. Commun., 20, 1490 (1955).

Marek, J., Coll. Czech. Chem. Commun., 21, 269 (1956).

Marsh, K. N. and R. P. Tomlins, Trans. Faraday Soc., 66, 783 (1970).

Marsh, K. N., Trans. Faraday Soc., 64, 883 (1968).

Martin, W. R. and M. E. Panlantis, Ind. Engng Chem. Fundam., 19, 122 (1980).

Margules, M., Sitzer. Akad. Wiss. Wien. Maths. Nat. Klasse 11, 104, 1243 (1895).

McGlashan, M. L. and Williamson, A. G., J. Chem. Eng. Data, 21, (2), 1976.

Mentzer, R. A., R. A. Greenkorn and K. C. Chao, J. Chem. Thermodynamics, 14, 817 (1982).

Meskel-Lesavra, M., D. Richon and H. Renon, Ind. Engng Chem. Fundam., 20, 284 (1981).

Mihkelson, V., H. Kirss, L. Kudjavzeva and O. Eisen, Fluid Phase Equilibria, 1, 201 (1977/78).

Minh, D. C. and M. Ruel, Can. J. Chem. Engng, 49 (1), 159 (1971).

Mixon, F. O., B. Gumowski and B. H. Carpenter, Ind. Engng Chem. Fundam., 4, 455 (1965).

Monfort, J. P. and M. C. Rojas, Fluid Phase Equilibria, 2, 181 (1978).

Muthu, O., S. Munjal and B. D. Smith, J. Chem. Engng Data., 28 (2), 192 (1983).

Munjal, S., O. Mutu, J. R. Khurma and B. D. Smith, Fluid Phase Equilibria, 12 (1-2), 29 (1983).

Murthy, A. K. S. and Zudkevitch, D., Proc. 3rd Int. Symp. Distillation 1979, IChemE Symp. Ser. 56, 1.1/51 (1979).

Myers, D. B. and R. L. Scott, Ind. Engng Chem., 55, 43 (1963).

Nagata, I., J. Chem. Engng, Japan, 6, 13 (1973).

Nagata, I. and K. Gotoh, Ind. Engng Chem. Process Des. Dev., 14(1), 98 (1975).

Nagata, I. and O. Tatsuhiko, J. Chem. Engng Japan, 5(3), 232 (1972).

Nothnagel, K. H., D. S. Abrams and J. M. Prausnitz, Ind. Engng Chem. Proc. Des. Dev., 12, 25 (1973).

O'Connell, Y. P. and J. M. Prausnitz, Ind. Engng Chem. Proc. Des. Dev., 6, 265 (1967).

Ochi, K. and B. L. Y. Lu, Fluid Phase Equilibria, 1, 185 (1977/78).

O'Donnell, K. A., PhD Thesis, University of Aston in Birmingham, UK, 1980.

Othmer, D. F., Ind. Engng Chem., 20, 745 (1928).

Othmer, D. F., Ind. Engng Chem., Anal. Ed., 20, 763 (1948).

Orye, R. V. and J. M. Prausnitz, Ind. Engng Chem., 57 (5), 18 (1965).

Palmer, D. A. and B. D. Smith, Ind. Engng Chem. Proc. Des. Dev., 11, 114 (1972).

Paul, R. W., J. Chem. Engng Data, 21(2), 165 (1976).

Peng, D. Y. and D. B. Robinson, Ind. Engng Chem. Fundam., 15, 59 (1976).

Perrin, D. D., W. L. F. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon, 1966.

Perry, R. H. and C. H. Chilton, Chemical Engineering Handbook, 5th Edition, McGraw-Hill, New York, 1973.

Plank, C. A., J. D. Olson and H. R. Null, Fluid Phase Equilibria, 6(1-2), 39 (1981).

Prausnitz, J. M., Molecular Thermodynamics of Fluid Phase Equilibria, Prentice Hall, Englewood Cliffs, 1969.

Prausnitz, J. M., Phase Equilibria and Fluid Properties in the Chemical Industry, ACS Symp. Ser., 60, 20 (1977).

Prausnitz, J. M., C. A. Eckert, R. V. Orye and J. P. O'Connell, Computer Calculations for Multicomponent Vapor-Liquid Equilibrium, Prentice Hall, Englewood Cliffs, 1967.

Prengle, H. W. and C. F. Palm, Ind. Engng Chem., 49, 1769 (1957).

Raal, J. P., R. K. Code and D. A. Best, J. Chem. Engng Data, 17(2), 211 (1972).

Ramalho, R. S. and J. Delmas, J. Chem. Engng Data, 13(2), 161 (1961).

Ramsey, W. and S. Young, J. Chem. Soc., 47, 42 (1885).

Redlich, O. and A. T. Kister, Ind. Engng Chem., 40, 34 (1948).

Redlich, O. and A. T. Kister, Ind. Engng Chem., 40, 345 (1948).

Redlich, O. and A. T. Kister, J. Amer. Chem. Soc., 71, 505 (1949).

Redlich, O. and J. N. S. Kwong, Chem. Revs., 44, 233 (1949).

Reid, R. C., J. M. Prausnitz and T. K. Sherwood, The Properties of Gases and Liquids, 3rd edition, McGraw-Hill, New York, 1977.

Renon, H. and J. M. Prausnitz, AIChE J., 14, 135 (1968).

Richon, D. F., Ind. Engng Chem. Proc. Des. Dev., 24, 1160 (1985).

Rogalski, M. and S. Malanowski, Fluid Phase Equilibria, 5, 97 (1980).

Rogalski, M., K. Rybakiewicz and S. Malanowski, Ber. Bunsenges. Phys. Chem., 81 (1070) 1977.

Ronc, M. and G. R. Ratcliffe, Can. J. Chem. Engng, 54, 326 (1976).

Rose, A. and E. I. Williams, Ind. Engng Chem., 47, 1528 (1955).

Rosenbrock, H. H., The Computer Journal, 3, 175 (1960).

Rowlinson, J. S. and F. L. Swinton, Fluid and Liquid Mixtures, 3rd edition, Butterworths, London, 1968.

Rubens, T. B. T., S. Ramalho and S. Kaliagiure, Can. J. Chem. Engng, 771 (1972).

Ruis, A., J. L. Otero and A. Macarron, Chem. Engng Sci., 10, 105 (1959).

Samuels, M. R., D. L. Ulrichson and F. D. Stevenson, AIChE J., 18(5), 1004 (1972).

Scatchard, G., Chem. Rev., 44, 7 (1949).

Scatchard, G. and F. G. Satkiewicz, J.Amer.Chem.Soc. 1963.

Scatchard, G., C. L. Raymond and H. H. Gilman, J. Amer. Chem. Soc., 60, 1275 (1938).

Scatchard, G., G. M. Wilson and F. G. Satkiewicz, J. Amer. Chem. Soc., 86, 125 (1964).

Scheiber, L. B. and C. A. Eckert, Ind. Engng Chem. Proc.Res. Dev., 10, 572 (1971).

Sebastiani, E. and L. Laquanti, Chem. Engng Sci., 22, 1155 (1962).

Setty, A. and H. T. Cullianan, AIChE J., 18(4), 829 (1972).

Shaw, D. A. and T. F. Anderson, Ind. Engng Chem. Fundam., 22, 79 (1983).

Silverman, N. and D. Tassios, Ind. Engng Chem. Proc. Res. Dev., 16(1), 13 (1977).

Smith, D. B., PhD Thesis, University of Aston in Birmingham, UK, 1975.

Smith, J. M. and H. C. Van Ness, Introduction to Engineering Thermodynamics, 3rd edition, McGraw-Hill, New York, 1975.

Smith, B. D., M. S. Klis and T. J. Reynolds, AIChE Meeting, Salt Lake City, August 1974.

Srivastara, R. and B. D. Smith, J. Chem. Engng Data, 30(3), 313 (1985).

Stevenson, F. C. and V. E. Sater, AIChE J., 12, 586 (1966).

Stokes, R. H., K. N. Marsh and R. P. Tomlin, J. Chem. Thermodynamics, 1, 211 (1969).

Stokes, R. H., B. J. Levien and K. N. Marsh, J. Chem. Thermodynamics, 2, 43 (1970).

Saltan, T. L. and J. F. McGregor, Can. J. Chem. Engng, 55, 602 (1977).

Swietoslawski, W., Roczniki Chem, 9, 608, (1928).

Swietoslawski, W., Ebulliometric Measurements, Reinhold, New York, 1945.

Thomas, E. R., B. A. Newman and G. L. Nicolaides, J. Chem. Engng Data, 27, 333, (1982a).

Thomas, E. R., B. A. Newman and T. C. Long, J. Chem. Engng Data, 27, 399 (1982b).

Tomlins, R. P. and K. N. Marsh, J. Chem. Thermodynamics, 8, 1184 (1976).

Tsonopolous, C., AIChE J., 20, 263 (1974).

Tucker. E. E. and S. D. Christian, J. Amer. Chem. Soc., 94, 6109 (1976).

Tucker, E. E. and S. D. Christian, J. Chem. Thermodynamics, 11, 1137 (1979).

Turek, E. A., D. W. Arnold, R. A. Greenhorn and K. C. Chao, Ind. Engng Chem. Fundam. 18, 426 (1979).

Ulrichson, D. L. and F. D. Stevenson, Ind. Engng Chem. Fundam., 11, 287 (1972).

Van Laar, J. J., Z. Phyzik Chem., 72 , 723 (1910).

Van Ness, H. C. and R. V. Mrazek, AIChE J., 2, 209 (1959).

Van Ness, H. C., C. A. Soczek and G. L. Peloquin, J. Chem. Engng Data, 12, 217 (1967).

Van Ness, H. C. and M. M. Abbott, Ind. Engng Chem. Fundam., 17, 66 (1978).

Van Ness, H. C. and M. M. Abbott, Classical Thermodynamics of Non-electrolyte Solutions with Applications to Phase Equilibria, McGraw-Hill, New York, 1982.

Van Ness, H. C., S. M. Byer and R. E. Gibbs, AIChE J., 19(2), 238 (1973).

Vera, J. H., S. G. Sagegh and G. A. Ratcliffe, Fluid Phase Equilibria, 1, 113 (1977).

Wagner, M., A. Alexander and T. Abraham, 5th International Congress in Scandernavia on Chemical Engineering, Copenhagen, April 1980.

Wan, K. W. and J. M. Prausnitz, Ind. Engng Chem. Fundam., 12, 459 (1973).

Weihe, I. A., S. Dinai, C. G. Radar and A. Chandrasekhor, Chem. Engng Sci., 26, 901 (1971).

Wichterle, I., Fluid Phase Equilibria, 2, 143 (1978).

Wichterle, I. and E. Hala, Ind. Engng Chem. Fundam., 2, 155 (1963).

Wilkinson, S., Proc. 3rd Int. Symp. Distillation 1979, IChemE Symp. Ser. 56, 1.1/1 (1979).

Winterhalter, D. R. and H. C. Van Ness, J. Chem. Engng Data, 11, 189 (1966)

Wilson, G. M., J. Amer. Chem. Soc., 86, 127 (1964).

Wohl, K., Trans. AIChE, 42, 215 (1946).

Yasumori, I., S. Ohmo and E. Miyazuki, Bull. Chem. Soc., Japan, 40, 769 (1967).

Young, C. L., Chapter 3 in Chemical Thermodynamics, Volume 2, Ed. M. L. McGlashan, The Chemical Soc., London (1978).

Young, K. L., R. A. Greenkorn, R. A. Mentzer and K. C. Chao, J. Chem. Thermodynamics, 9, 979 (1977).

Zawidski, J., Z. Physik Chem., 35, 129 (1900).

Ziebovak, K. and W. Brosotowski, Bull. Acad. Pol. Ser. Sci., 5, 309 (1957).

Zhang, L. J., M. L. Ho and R. A. Greenkorn, AIChE Symp. Series, No 244, 81, 90 (1985a).

Zhang, L. J., M. L. Ho and R. A. Greenkorn, AIChE Symp. Series, No 244, 81, 151 (1985b).

Zudkevitch, D. and J. Joffe, AIChE J., 16, 112 (1970).

Appendix 1

Testing of capillary line between the equilibrium cell and the pressure transducer (5.2.3b,

Time (minutes)	Pressure (mm Hg)
0	0.01
5	0.01
10	0.01
15	0.01
20	0.01
25	0.01
30	0.01
35	0.012
40	0.012
45	0.013
50	0.013
55	0.013
60	0.013

Time (hours)	Pressure (mm Hg)
0	0.010
60	0.013
120	0.015
180	0.020
240	0.026
300	0.040
360	0.050
420	0.070
480	0.100

Appendix 2

Results from the experimental set up as shown in the Figure 5.7

Time (minutes)	Pressure (mm Hg)
0	0.01
60	0.01
120	0.02
180	0.04
240	0.06
300	0.07
360	0.10
420	0.15
480	0.20

Appendix 3.

The system was pumped down to 0.01 mm Hg and the vacuum pump was isolated. The balancing side of the pressure transducer was opened to the similar vacuum to obtain the null position which was then monitored as a function of time

Time (minutes)	Null Position (Arbitary scale)
0	0.50
60	0.50
120	0.51
180	0.51
240	0.51
300	0.52
360	0.52
420	0.53
480	0.53

Appendix 4

Equal and controlled amount of pressure was applied on both sides of the diaphragm and the null position was noted over a period of time. The procedure was repeated at different pressures.

Time (hours)	Null Position (Arbitrary Scale)				
	0.1 bar	0.2 bar	0.3 bar	0.4 bar	0.5 bar
0	0.50	0.50	0.50	0.50	0.50
1	0.50	0.50	0.50	0.50	0.50
2	0.50	0.50	0.50	0.50	0.50
3	0.50	0.50	0.50	0.50	0.50
4	0.51	0.50	0.50	0.50	0.50
5	0.51	0.51	0.51	0.50	0.50
6	0.52	0.52	0.51	0.50	0.50
7	0.52	0.52	0.51	0.51	0.51
8	0.53	0.52	0.51	0.51	0.51

Appendix 5

Saturated vapour pressure of water was measured at a fixed temperature as a function of its volume added to the cell. The experimental pressures are compared with those from National Physical Laboratory (NPL) and the steam table data.

Temperature 25.000 °C

Water Added (ml)	Expt. Pressure (bar)	NPL pressure (bar)	Steam Table Values (bar)
5	0.03180	0.03169	0.03170
10	0.03183	0.03169	0.03170
10	0.03183	0.03169	0.03170
10	0.03184	0.03169	0.03170

Temperature 30.000 °C

Water Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)	Steam table values (bar)
5	0.04169	0.04245	0.04240
10	0.04170	0.04245	0.04240
10	0.04169	0.04245	0.04240
10	0.04069	0.04245	0.04240

Temperature 35.000 °C

Water Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)	Steam Table values (bar)
5	0.05495	0.05430	0.05400
10	0.05497	0.05430	0.05400
10	0.05495	0.05430	0.05400
10	0.05496	0.05430	0.05400

Temperature 40.000 °C

Water Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)	Steam Table values (bar)
5	0.07244	0.07200	0.07380
10	0.07245	0.07200	0.07380
10	0.07245	0.07200	0.07380
10	0.07246	0.07200	0.07380

Temperature 44.000 °C

Water Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)	Steam Table values (bar)
5	0.08912	0.08900	0.0900
10	0.08914	0.08900	0.0900
10	0.08911	0.08900	0.0900
10	0.08912	0.08900	0.0900

Temperature 50.000 °C

Water Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)	Steam Table values (bar)
5	0.12256	0.12345	0.1230
10	0.12255	0.12345	0.1230
10	0.12255	0.12345	0.1230
10	0.12254	0.12345	0.1230

Appendix 6

Measurements of saturated vapour pressure of fixed volume of water as a function of temperature

Temperature (°C)	Pressure (bar)
23.000	0.02754
23.033	0.02810
25.000	0.03090
27.000	0.03460
27.300	0.03548
29.388	0.039810
30.000	0.041690
31.414	0.04466
32.000	0.04758
33.278	0.05011
35.000	0.05495
37.000	0.06067
40.000	0.07244
40.555	0.07973
42.000	0.08090
44.000	0.08912
48.000	0.10964

Appendix 7

Data for water

Temperature (°C)	Pressure (bar)	
	NPL Data	Steam Table Data
22.00		0.02640
25.00	0.03169	0.03170
26.00		0.03360
28.00		0.03700
30.00	0.04245	0.04240
34.00		0.05320
36.00		0.05940
40.00		0.07380
42.00		0.08200
46.00		0.10900
48.00		0.11160
50.00	0.12345	0.12340

Appendix 8

Varying volume of pure degassed ethanol was added to the cell and the vapour pressure was measured after each addition at different temperatures.

Temperature 25.000 °C

Ethanol Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)
5	0.07896	0.07893
10	0.07895	0.07893
10	0.07893	0.07893
10	0.07896	0.07893

Temperature 30.000 °C

Ethanol Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)
5	0.10470	0.10428
10	0.10470	0.10428
10	0.10470	0.10428
10	0.10470	0.10428

Temperature 35.551 °C

Ethanol Added (ml)	Expt. Pressure (bar)	NPL pressure (bar)
5	0.14705	0.14700
10	0.14707	0.14700
10	0.14707	0.14700
10	0.14707	0.14700

Temperature 40.544 °C

Ethanol Added (ml)	Expt. Pressure (bar)	NPL Pressure (bar)
5	0.18902	0.19200
10	0.18904	0.19200
10	0.18904	0.19200
10	0.18904	0.19200

Temperature 50.000 °C

Ethanol Added (ml)	Expet. Pressure (bar)	NPL Pressure (bar)
5	0.28756	0.29507
10	0.28755	0.29507
10	0.28755	0.29507
10	0.28754	0.29507

Appendix 9

Fixed volume of pure ethanol was taken and its vapour pressure was measured as a function of temperature, where possible a direct comparison with the data from NPL was made.

Temperature (°C)	Pressure (bar)	
	NPL Data	Expt. Data
25.000	0.07893	
30.000	0.10428	
30.488		0.1170
33.485		0.13234
35.551		0.14705
37.538		0.16238
40.544		0.18902
42.552		0.20850
43.576		0.21900
45.650		0.24195
47.665		0.26540
50.000	0.29507	

Appendix 10

To see whether the distilled water once degassed could be stored for one week

Storage Time (Days)	Day	Morning	Afternoon	Vapour Pressure (bar)
0	Monday	Degassing	Degassing	-
0	Tuesday	Degassing	Degassing	
1	Wednesday	Evacuation	P. reading	0.07973
2	Thursday	Evacuation	P. reading	0.07975
3	Friday	Evacuation	P. reading	0.07980
4	Saturday			
5	Sunday			
6	Monday	Evacuation	P. reading	0.07987
7	Tuesday	Evacuation	P. reading	0.08325
8	Wednesday	Evacuation	P. reading	0.09324

Appendix 11

To see whether pure ethanol once degassed could be stored for one week

Storage Time (Days)	Day	Morning	Afternoon	Vapour Pressure (bar)
0	Monday	Degassing	Degassing	-
1	Tuesday	Evacuation	P. reading	0.18902
2	Wednesday	Evacuation	P. reading	0.18906
3	Thursday	Evacuation	P. reading	0.18917
4	Friday	Evacuation	P. reading	0.18917
5	Saturday			
6	Sunday			
7	Monday	Evacuation	P. reading	0.18930
8	Tuesday	Evacuation	p. reading	0.19233

Appendix 12

Experimental data for water-ethanol mixture at different temperatures.

At 303.626K

V1 (ml)	V2 (ml)	Total Vapour Pressure (bars)
4.63	0.00	0.11174
"	1.14	0.10590
"	2.14	0.10364
"	3.29	0.10231
"	7.96	0.10144
"	11.92	0.09944
"	17.69	0.09920

At 308.735K

5.88	0.00	0.13700
"	2.44	0.12382
"	4.19	0.11876
"	5.81	0.11546
"	7.12	0.11260
"	9.00	0.10975
"	10.25	0.10830
"	11.75	0.10584
"	13.20	0.10490
"	15.04	0.10355
"	19.47	0.10222
"	23.00	0.97620
"	26.50	0.93512
"	30.00	0.82010

At 313.689K

6.80	0.00	0.20608
"	4.23	0.19012
"	6.50	0.18687
"	9.20	0.18454
"	11.10	0.18220
"	12.95	0.17930
"	17.65	0.17328
"	20.48	0.17024
"	22.60	0.16900

At 313.723K

5.62	0.00	0.17856
"	1.00	0.18157
"	2.00	0.18230
"	3.10	0.16134
"	4.20	0.16021
"	5.00	0.15801
"	6.25	0.15477
"	8.00	0.15233
"	9.63	0.14883
"	12.74	0.14436
"	15.00	0.14253
"	16.10	0.14250
"	19.25	0.13822
"	21.00	0.13601
"	23.55	0.13273
"	25.00	0.13000
"	27.50	0.12400
"	30.00	0.12030

At 323.154K

4.28	0.00	0.28756
"	2.76	0.25635
"	7.16	0.22737
"	10.07	0.22622
"	14.29	0.21096
"	17.19	0.20589
"	21.68	0.20345

Reversing the experimental measurements, thus

0.00	6.64	0.122256
4.88	"	0.24533
9.79	"	0.27008
14.12	"	0.28737
16.28	"	0.29498
21.98	"	0.30778

V1 is volume of ethanol present in the cell
V2 is volume of water present in the cell.

Appendix 13

Experimental data for methanol-water mixture.

At 308.153K

V1(ml)	V2(ml)	Total Vapour Pressure(bars)
6.06	0	0.26938
"	4.79	0.15456
"	8.42	0.13182
"	13.21	0.11492
"	19.88	0.10799
"	25.00	0.09321
Reversing the experiment,		
0.00	6.75	0.04732
4.86	"	0.13122
11.73	"	0.17500
17.18	"	0.19467
20.16	"	0.20430
24.28	"	0.22020

V1 is Total volume of Methanol present in the cell.
V2 is Total volume of Water present in the cell.

At 313.15K

V1(ml)	V2(ml)	Total Vapour Pressure(bars)
5.83	0	0.35540
"	4.65	0.23477
"	10.82	0.19998
"	17.84	0.19636
"	21.01	0.18426
Reversing the experiment,		
0.00	6.12	0.07247
5.65	"	0.19406
11.96	"	0.24258
16.30	"	0.26396
23.20	"	0.28880
27.75	"	0.30891

V1 is Total Volume of Methanol present in the cell.
V2 is Total Volume of Water present in the cell.

At 323.15K

V1(ml)	V2(ml)	Total Vapour Pressure(bar)
6.62	0	0.54920
"	5.04	0.34475
"	7.76	0.30835
"	11.56	0.27812
"	15.81	0.27812
"	20.07	0.24319

"	23.93	0.24044

Reversing the experiment,

0	6.26	0.12348
5.43	"	0.31427
11.47	"	0.37673
17.25	"	0.41192
19.51	"	0.42086
25.04	"	0.44404
27.25	"	0.44982

V1 is the Total Volume of Methanol present in the cell.
V2 is the Total Volume of Water present in the cell.

At 333.15K

V1(ml)	V2(ml)	Total Vapour Pressure(bar)
7.44	0.00	0.86964
"	5.56	0.57293
"	8.26	0.52720
"	12.66	0.48463
"	16.42	0.46680
"	21.76	0.46170

Reversing the experiment,

0	6.15	0.20010
6.69	"	0.54620
13.49	"	0.67765
20.67	"	0.80299
25.66	"	0.91544

V1 is the Total Volume of Methanol present in the cell.
V2 is the Total Volume of Water present in the cell.

Appendix 14

Experimental data for Cyclohexane-Ethanol mixtures at different temperatures.

At 330.358K

V1(ml)	V2(ml)	Totat Vapour Pressure(bar)
7.43	0.00	0.41866
"	4.55	0.73453
"	7.36	0.75549
"	11.76	0.76516
"	14.99	0.76879
"	20.23	0.77312
"	22.83	0.77632
Reversing the experiment,		
0	7.17	0.47057
5.22	"	0.75722
11.91	"	0.74568
18.03	"	0.73083
20.60	"	0.72814
25.47	"	0.71726

At 343.15K

V1(ml)	V2(ml)	Total Vapour Pressure(bar)
7.09	0.00	0.73083
"	6.72	1.16667
!	11.27	1.16498
"	14.30	1.21380
"	21.63	1.22935
"	28.92	1.30613
"	35.62	1.30256
"	41.54	1.30224
Reversing the experiment,		
0	8.37	0.78013
4.92	"	1.27393
10.82	"	1.27025
14.89	"	1.26088
18.88	"	1.24260
22.96	"	1.23444

V1 is the Total Volume of Ethanol present in the cell
V2 is the Total Volume of Cyclohexane present in the cell.

REDUCED DATA (x-y-P-T).

Appendix 15

x-y-P-T data for ethanol-water mixtures.

At 303.62K (30.47 C)

x	y	P (mmHg)
0.5563	0.7034	83.81
0.4004	0.8281	79.43
0.3029	0.8240	77.74
0.1522	0.7827	76.74
0.1071	0.7872	74.59
0.0748	0.7749	74.41

At 313.69K (40.540 C)

x	y	P (mmHg)
0.3317	0.7937	142.60
0.2441	0.7530	140.16
0.1858	0.7163	138.42
0.1590	0.6945	136.66
0.1395	0.6749	134.49
0.1063	0.6284	129.95
0.0930	0.6021	127.69
0.0850	0.5832	126.76

At 323.15K (50.000 C)

x	y	P (mmHg)
0.3237	0.6318	204.22
0.15558	0.5431	180.63
0.1160	0.4995	169.25
0.0846	0.4477	156.63
0.0714	0.4205	150.82
0.0653	0.4065	147.94
0.1849	0.5665	187.25
0.3128	0.6282	205.44
0.3969	0.6544	213.61
0.4308	0.6644	216.71
0.5054	0.6857	222.34

Appendix 16

x-y-P-T data for methanol-Water mixtures.

At 308.15K (35.00C)

x	y	P (mmHg)
0.3602	0.7587	119.64
0.2426	0.6661	99.19
0.1696	0.5790	84.90
0.1195	0.4945	74.42
0.0974	0.4418	68.75
0.2427	0.6661	99.17
0.4361	0.8025	132.49
0.5311	0.8477	147.59
0.5707	0.8641	153.91
0.6155	0.8815	161.58

At 313.15K (40.000 C)

x	y	P (mmHg)
0.3581	0.7208	173.45
0.1934	0.6454	150.15
0.1270	0.6122	140.44
0.1099	0.6030	137.60
0.2912	0.6909	163.48
0.4652	0.7672	187.95
0.5424	0.8003	198.83
0.6279	0.8369	211.02
0.6687	0.8544	217.17

At 323.15K (50.00 C)

x	y	P (mmHg)
0.3589	0.7375	259.86
0.2752	0.6889	235.31
0.2031	0.6326	211.57
0.1571	0.5823	193.23
0.1280	0.5429	181.23
0.1096	0.5156	174.08
0.2785	0.6915	273.23
0.4492	0.7798	282.82
0.5507	0.8217	307.41
0.5811	0.8337	314.28
0.6403	0.8568	329.19
0.6596	0.8643	333.59

At 333.15K (60.00C)

x	y	P (mmHg)
0.3733	0.7734	439.66
0.2862	0.7208	397.73
0.2073	0.6558	355.37
0.1678	0.6157	303.68
0.1697	0.6163	333.04
0.1696	0.6346	357.37
0.3262	0.7548	453.93
0.4940	0.8301	541.13
0.5993	0.8647	602.62

Appendix 17

x-y-P-T data for cyclohexane-water mixtures.

At 330.35K (57.200 C)

x	y	P (mmHg)
0.2485	0.5139	556.97
0.3485	0.5261	568.71
0.4608	0.5317	573.61
0.5214	0.5343	575.27
0.5952	0.5385	577.07
0.6329	0.5414	578.14
0.4258	0.5306	570.09
0.2453	0.5128	561.49
0.1768	0.4906	548.85
0.1582	0.4816	544.79
0.1319	0.4634	534.73

At 343.15K (70.00C C)

x	y	P (mmHg)
0.3385	0.4997	893.03
0.4619	0.5062	892.80
0.5213	0.5065	919.68
0.6222	0.5117	927.95
0.6877	0.5252	970.42
0.7306	0.5217	967.11
0.7363	0.5210	967.09
0.4788	0.5023	953.43
0.2946	0.4911	949.99
0.1931	0.4690	929.22
0.1646	0.4567	921.41

Densities used in calculating x values in the initial screening of data.

	Densities Kg/meter cube	Mol. Wt.
Water	1.00 ×1000	18.00
Methanol	0.7914 "	32.04
Ethanol	0.7893 "	46.07
Cyclohexane	0.7785 "	84.00

TABLE B-3
CONSTANTS FOR THE VAPOR PRESSURE EQUATION

$$\ln P(\text{atm.}) = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T$$

C_1	C_2	C_3	C_4	C_5	C_6	Temp. range, °K	
44.2059460	— 1058.6545	—	0.041087754	—	— 7.75000	63–112	Nitrogen
50.0429239	— 1201.1052	—	0.041779950	—	— 8.80000	68–119	Carbon monoxide
41.8128066	— 1170.9000	—	0.032032609	—	— 6.98000	84–135	Argon
41.8709559	—1224.0202	—	0.030413136	—	— 6.89500	54–135	Oxygen
38.3741899	— 1419.2160	—	0.021939158	—	— 5.96200	90–170	Methane
45.0344191	— 1634.8780	—	0.023946285	—	— 7.15693	116–209	Krypton
53.7102928	— 2284.3398	—	0.018916287	—	— 8.18081	128–189	Carbon tetrafluoride
65.8629494	— 2783.5525	—	0.023359992	—	— 10.40200	100–250	Ethylene
111.8988495	— 4341.5281	—	0.034886196	—	— 18.18100	217–274	Carbon dioxide
28.4951830	— 2437.7237	—	— 0.012916937	0.000025913	— 2.64100	90–275	Ethane
9.0693998	—1807.5300	—26.15000	—	—	—	161–242	Propylene
69.7179871	— 3854.5842	—	0.017343953	—	— 10.48090	160–331	Propane
45.1842532	— 3778.4598	—	0.008560725	—	— 6.00000	292–425	n–Butane
61.6057205	— 5260.1890	—	0.006170407	—	— 8.10000	227–353	Ethyl ether
95.3448400	— 6435.9872	—	0.015864708	—	— 14.00000	277–357	2–Methyl pentane
87.2105808	— 6477.3015	—	0.013061397	—	— 12.40000	253–493	Methyl acetate
113.2828617	— 7151.4899	—	0.019950338	—	— 17.00000	259–365	n–Hexane
3.2157274	— 3969.2218	—	— 0.008368738	—	2.00000	273–366	Acetone
49.9513216	— 5970.8229	—	0.004249923	—	— 5.79200	263–493	Methanol
123.9120350	— 8754.0896	—	0.020198435	—	— 18.10000	280–370	Ethanol
9.1689299	— 2731.0020	— 47.10800	—	—	—	250–379	Methylcyclopentane

C_1	C_2	C_3	C_4	C_5	C_6	Temp. range, °K	
129.7987595	— 7243.2153	—	0.026041523	—	— 20.00000	273–373	Chloroform
193.4523201	—471.2726	—	—0.065109104	—	37.00000	293–393	n–Propanol
122.7654028	— 8141.3862	—	0.019576170	—	— 18.27200	290–397	n–Heptane
105.5668631	— 7434.5352	—	0.016244866	—	— 15.48190	280–398	iso–Octane
-27.3364758	—3168.5819	—	—0.013622597	—	7.00000	293–377	Acetonitrile
98.5855598	— 6943.3635	—	0.015212700	—	— 14.37200	280–378	Cyclohexane
43.7312222	— 5270.9369	—	0.001759723	—	— 5.00000	273–393	Carbon tetrachloride
86.9184361	— 9933.2975	—	— 0.004680619	—	— 10.00000	295–413	n–Butanol
133.3127518	— 8026.2913	—	0.023929663	—	— 20.29000	280–377	Benzene
133.9437938	—6144.6379	—	—0.003676422	—	— 2.85000	293–433	n–Octane
114.3106956	— 7694.6047	—	0.018644080	—	— 17.00000	270–400	Methylcyclohexane
162.0804634	— 10040.5873	—	0.025114447	—	— 24.49000	286–415	Methyl isobutyl ketone
98.6363039	— 7559.9156	—	0.014741749	—	— 14.17000	294–383	Nitromethane
116.6243849	— 8457.0896	—	0.017309569	—	— 17.06100	298–403	2–Nitropropane
115.9658813	— 8111.7556	—	0.017867804	—	— 17.09000	279–409	Toluene
133.7920704	— 8921.0548	—	0.021761172	—	— 20.00000	298–397	Nitroethane
123.4715815	— 8970.7290	—	0.018043444	—	— 18.09000	298–415	1–Nitropropane
9.3780999	— 3456.7970	— 78.67000	—	—	—	331–476	n–Decane
70.4346943	— 7362.6981	—	0.006952085	—	—9.00000	273–398	Water
213.5877819	2887.9618	—	— 0.040982038	—	37.00000	313–443	Furfural