VAPOUR-LIQUID EQUILIBRIUM STUDIES AT ATMOSPHERIC TO MODERATE PRESSURES

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Doctor of Philosophy

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SUMMARY

A study of vapour-liquid equilibria is presented together with current developments. The theory of vapour-liquid equilibria is discussed. Both experimental and prediction methods for obtaining vapour-liquid equilibria data are critically reviewed.

The development of a new family of equilibrium stills to measure experimental VLE data from sub-atmosphere to 35 bar pressure is described. Existing experimental techniques are reviewed, to highlight the needs for these new apparati and their major attributes. Details are provided of how apparatus may be further improved and how computer control may be implemented.

To provide a rigorous test of the apparatus the stills have been commissioned using acetic acid-water mixture at one atmosphere pressure. A Barker-type consistency test computer program, which allows for association in both phases has been applied to the data generated and clearly shows that the stills produce data of a very high quality.

Two high quality data sets, for the mixture acetone-chloroform, have been generated at one atmosphere and 64.3°C. These data are used to investigate the ability of the new novel technique, based on molecular parameters, to predict VLE data for highly polar mixtures.

Eight vapour-liquid equilibrium data sets have been produced for the mixture cyclohexane-ethanol mixture at one atmosphere, 2, 4, 6, 8 and 11 bar, 90.9°C and 132.8°C. These data sets have been tested for thermodynamic consistency using a Barker-type fitting package and shown to be of high quality. The data have been used to investigate the dependence of UNIQUAC parameters with temperature. The data have in addition been used to compare directly the performance of the predictive methods, Original UNIFAC, a modified version of UNIFAC and the new novel technique, based on molecular parameters developed from generalised London's potential (GLP) theory.

Keywords: Equilibrium stills, Experimental, Vapour-liquid Equilibrium, Acetic Acid-Water, Cyclohexane-Ethanol, Chloroform-Acetone

Dedication

This thesis is dedicated to the memory of my late grandparents

Donald and Lucy Russell and Elsie Waldron.

Acknowledgements.

I wish to thank my supervisor Dr J. D. Jenkins for his advice and guidance throughout this project. I would like to thank the following people for their help and co-operation: Mr Ian Murkett, Mr Maurizio Santoro, Mrs L. Wright, Mr M. Lea, Mr P. Tack, Dr D. Walton, Dr Husni Zain and special thanks to Mr Alex Stewart the glass blower, without whom this project would have been very difficult.

Finally I would like to thank my family, especially my parents and two brothers, Mathew and Daniel, for supporting and encouraging me throughout my postgraduate studies.

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Chapter 1: Introduction.

Distillation is a mature technology which forms a massive proportion of the unit operations employed in the oil refining and chemicals businesses, indeed Fair (1987) suggested that "If the mixture is amenable to separation by distillation then that is the method most likely to be economically attractive". Exceptions to this rule exist but the widespread use of distillation confirms the truth of this statement. "Leaner and harder" designs (Rush, 1980) are required to meet the requirements of today's energy-conscious society. Even small incremental savings in energy requirements for distillation represent large cuts in energy requirements when applied across the full spectrum of distillation applications.

Design of any distillation equipment is dependent on the availability of vapour-liquid equilibrium (VLE) data. To achieve the tighter design criteria required for contemporary design data of a very high quality are required. Many data collections such as the vast selection held in the Dortmund Data Bank are available but a large proportion of the information is likely to be of dubious quality or not at the desired conditions.

Vapour-liquid equilibrium data may be obtained either experimentally or predicted using one of the many methods extant. In order to predict data many methods (see below) require some experimental data for determination of model parameters and to assess performance and limits of applicability of the individual prediction method. In final design it is still considered unwise to design solely on predicted data and essential to have available experimental data of high quality. Therefore a niche market still exists for the experimental determination of vapour-liquid equilibria to support predictive methods and provide final design data where none are available.

This project began with a review of existing experimental techniques from which a need was identified for a new family of equilibrium stills to measure experimentally VLE data from sub-atmosphere to 35 bar pressure, the practical limits of distillation apparatus outside the cryogenic region. The initial scope of the project was to design apparatus to accomplish this and commission the said apparatus to confirm its

performance. The commissioned apparati were then to be used to produce data for an investigation into the temperature dependence of UNIQUAC parameters.

It was decided to base the new equipment on the successful design of Raal et al. (1972) which has been shown to produce high accuracy VLE data. Two versions of the apparatus were required to meet the pressure specification, one for vacuum to one atmosphere pressure and one for moderate pressure work from one atmosphere to 35 bar. Design of these apparati was to proceed in parallel with any design improvements being incorporated in both versions of the equipment.

In commissioning the stills it was decided to use acetic acid-water at one atmosphere pressure as the test mixture. This mixture was chosen to provide a rigorous test of the apparatus to allow a comparative study of data produced using these stills with the best literature data. A Barker-type consistency test computer program developed by Jenkins and Gibson-Robinson (1977) which incorporates association in both phases and has been shown to model this mixture well was available and used to test the new data.

During the apparatus development phase of this project parallel research developing the AGAPE data prediction methods identified a need for data of a high accuracy for a polar mixture to test the AGAPE model. It was decided to use the new apparatus to measure this data. Two high quality data sets, for the mixture acetone-chloroform, were generated at 1 atmosphere and 64.3°C to meet this requirement. An investigation into the use of a fit on a single data point using the AGAPEFIT method to predict both isothermal and isobaric data sets was made using these data.

The investigation of the temperature dependence of UNIQUAC parameters require a series of data sets at a range of pressures/temperatures. The mixture cyclohexane/ethanol was chosen because the components of the mixture, when expressed as terms for group contribution prediction methods, are limited to only a few groups, thus the mixture is suitable for examining the temperature dependence of such models. In addition the mixture is strongly non-ideal exhibiting an azeotrope, accurate

VLE data exists below one atmosphere and there is an historic demand for data for flow boiling research.

A wide range of vapour-liquid equilibrium data sets were produced for the mixture cyclohexane-ethanol mixture over a range of pressures up to 11 bar and at two temperatures. These data sets were then to be subjected to an advanced test for thermodynamic consistency.

Such a set of data makes possible the further testing of data predictive methods. This has been done for a number of advanced predictive methods, the various UNIFAC methods, and a novel approach derived from molecular considerations, the AGAPEFIT technique. Now if this was successful it would validate using the vast literature collections of azeotrope data as the source for parameter fitting. In particular the single-point version of AGAPEFIT could be tested using the azeotropic point.

2.1 Introduction.

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

2.2 Criteria for equilibrium.

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

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

The definition of the Gibbs energy is:

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

Differentiation and substitution into equation 1 gives:

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

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

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

On partial differentiation we get:

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

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

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S \qquad : \qquad \left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V \qquad (2.6a \ \& \ 2.6b)$$

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

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_i} \qquad (2.7)$$

Therefore, for a system of variable composition we obtain:

$$dG = VdP - SdT + \Sigma \mu_i dn_i \qquad (2.8)$$

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

$$dG_A = \mu_i^A(-|\delta n_i|) \qquad (2.9)$$

$$dG_B = \mu_i^B(+|\delta n_i|) \qquad (2.10)$$

respectively. Overall we have:

$$dG = dG_A + dG_B = 0 \qquad (2.11)$$

$$\mu_i^A(-|\delta n_i|) + \mu_i^B(+|\delta n_i|) = 0 \qquad (2.12)$$

Rearranging, we have:

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

$|\delta n_i|$ has a finite value, hence the result:

$$\mu_i^A = \mu_i^B \qquad (2.14)$$

is obtained.

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

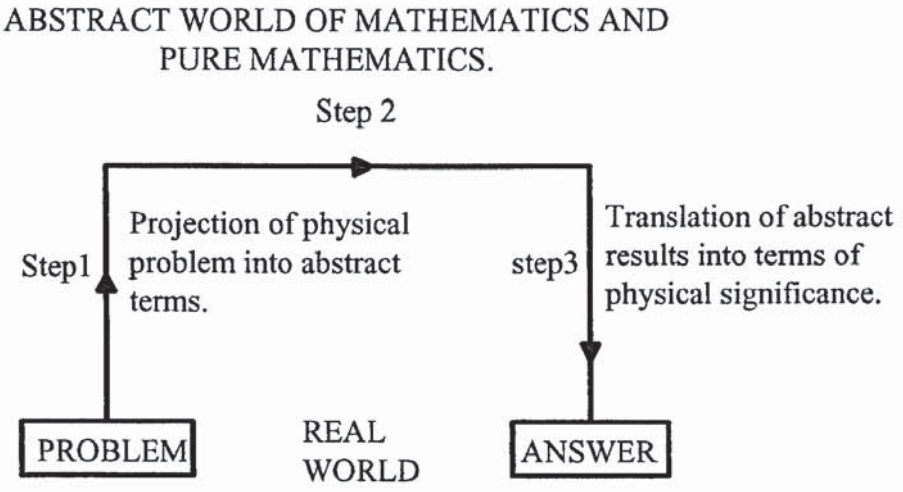


Figure 2.1 The problem to be solved.

Lewis (1901) defined fugacity as:

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

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

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

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

$$f_i^A = f_i^B \qquad (2.17)$$

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

2.3 The concept of Activity.

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

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

where a_i denotes the activity of the i^{th} constituent and f_i^0 the fugacity in the standard state at the same temperature.

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

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

The numerical value of the activity depends among other things on the choice of standard state, since if f_i^0 is changed, a_i^0 also changes according to equation (2.18). It is therefore necessary to consider which standard state is suitable for the solution of a given problem. For solutions of non-electrolytes, we choose as the standard state that of the pure constituent at the temperature and pressure of the system. Thus the activity of the pure substance is always equal to unity.

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

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

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

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

2.4 The Phase-Equilibrium relationship.

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

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

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

$$\ln\left(\frac{f_i}{P_i}\right)_{p=p'} = \int_0^{p'} \left(\frac{\bar{v}}{RT} - \frac{1}{P}\right) dP \tag{2.22}$$

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

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

can be used for both phases.

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

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

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

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

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

$$f_i = \gamma_i x_i f_i^{\circ} \qquad (2.26)$$

where f°_i is the standard state fugacity, hence from equations (2.17), (2.24) and (2.26) we have:

$$\gamma_i x_i f_i^{\circ} = \phi_i y_i P \qquad (2.27)$$

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

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

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

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

and $f_i^{l} = f_i^{V}$; (2.29)

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

and $f_i^{V} = \phi y_i P$; (2.31)

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

But the standard states for the two phases are not the same and so the value of f_i^{*L} has to be established with respect to the standard of the vapour phase. We choose the vapour standard state to be the one more commonly used, i.e. that at which the

fugacity of the pure component is one atmosphere. We can relate f_i^{*L} (pure i at T and P of mixture) to f_i^{oV} ($f_i^{oV} = 1.0$) in two steps.

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

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

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

Now

$$RT\ln f_i = \bar{v}dP \tag{2.35}$$

Hence,

$$RTd\ln f_i^L = v_i^L dP \tag{2.36}$$

$$\ln\frac{f_{i\,(T,P)}^{*L}}{f_{i\left(T,p_i^{sat}\right)}^{L}} = \frac{1}{RT}\int_{p_i^{sat}}^{P} v_i^L dP \tag{2.37}$$

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

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

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

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

This term is often neglected (but never by Prausnitz) since for pressures below about

ten atmospheres it is negligible.

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

$$\gamma_i x_i p_i^{sat} = y_i P \tag{2.39}$$

If we define the relative volatility ratio for two components, i j, in a mixture by,

$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} \tag{2.40}$$

then equation (2.39) for both i and j gives:

$$\alpha_{ij} = \frac{\gamma_i p_i^{sat}}{\gamma_j p_j^{sat}} \tag{2.41}$$

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

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

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

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

2.5 The Gibbs-Duhem Equation.

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

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

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

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

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

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

and on comparison with equation (2.44) we get:

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

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

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

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

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

and

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

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

2.6 Models for the Vapour-Phase.

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

2.6.1 The Indirect Model

The indirect model already encountered in the definition of fugacity:

$$d\mu_i = RTdlnf_i (dT = 0) \qquad (2.15)$$

is in its integrated form

$$\mu_i = RTlnf_i + \theta_i \qquad (2.16)$$

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

$$\mu_i - \mu_i^\circ = RTln\frac{f_i}{f_i^\circ} \qquad (2.19)$$

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

Further we have the limit $\frac{f_i}{P_i} \rightarrow 1.0$ as $P \rightarrow 0$ (2.51)

Equation (2.19) is usually written as:

$$\mu_i - \mu_i^\circ = RTlnf_i \qquad (2.52)$$

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

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

2.6.2 The Direct Models

The direct vapour phase models are the equations of state which are used in the calculation of vapour phase fugacity coefficients. The first of these is the ideal gas law ($PV = n\,RT$) whose only use is as a starting point. It is valid for most compounds upto one bar pressure and higher pressures for small non-associating molecules. At even low to moderate pressures of 1 to 10 bar vapour phase fugacity coefficients can deviate significantly from unity, especially if the substances involved are polar. The liquid phase nonideality normally dominates the equilibrium relationship but the vapour phase nonideality is not always insignificant and must be accounted for.

One approach for the representation of the vapour phase behaviour is the empirical cubic equation of state. This can be represented in the molar volume form by the general equation

$$P = \frac{RT}{v - b} - \frac{\Theta(V - \eta)}{(v - \delta v + \varepsilon)} \qquad (2.54)$$

where the quantities b, Θ, δ, and η are equation-of-state parameters, each of which may depend on temperature and composition.

The earliest of these cubic equations-of-state is due to Van der Waals who introduced two constants into the ideal gas law to allow for the attractive forces between molecules and the volume of the molecules themselves.

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \qquad (2.55)$$

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

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}v(v + b)} \qquad (2.56)$$

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

An alternative approach is that of the Virial equation which exists in two forms-

The volume form is:

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + ... \qquad (2.57)$$

The pressure form is:

$$Z = 1 + B'P + C'P^2 + D'P^3 + ... \qquad (2.58)$$

where Z is the compressibility factor. B, C and D are the second, third and fourth virial coefficients respectively and are, for pure components, each functions of temperature only.

The physical significance of second virial coefficient B is that it takes account of deviation from ideality resulting from interactions involving two molecules. The third virial coefficient C deals with three molecules effect and so on. Little information is available for the third and higher viral coefficients, thus the virial equation is often truncated after the second viral coefficient thus

$$Z = 1 + \frac{BP}{RT} \tag{2.59}$$

The virial coefficients are obtained by either fitting the equation to experimental data or by using a correlation of the corresponding-states type. It is better to use experimental data to give the virial coefficients and a compilation of second viral coefficients for some substances has been produced by Dymond and Smith (1969). Good volumetric data may not always be available and thus correlations employing corresponding states relationships are used.

One frequently used, for pure non-polar gases, is that of Pitzer and Curl (1955, 1957).

$$\frac{P_{ci}B_{ij}}{RT_{ci}} = f_B^{(0)} + \omega_i f_B^{(1)}(T_r) \tag{2.60}$$

where ω is the acentric factor of the i^{th} component defined as :

$$\omega_i = -\log_{10}\frac{P_i^s}{P_{ci}} - 1.000 \tag{2.61}$$

and $f^{0}_{B}(T_r)$, $f^{(1)}_{B}(T_r)$ are given by:

$$f_B^{o}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \tag{2.62}$$

$$f_B^{(1)}(T_r) = 0.073 + \frac{0.46}{T_r} - \frac{0.5}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8} \tag{2.63}$$

For polar compounds several other correlations have been proposed. The most used of these is the one proposed by Hayden and O'Connell (1975). This method uses only the critical properties and molecular parameters, all of which may be estimated from the molecular structure to calculate the second viral coefficients. The method is based on the assumption that the viral coefficient is based on the summation of several contributions due to different kinds of intermolecular forces

$$B_{total} = B_{free} + B_{metastable} + B_{bounds} + B_{chem} \tag{2.64}$$

B_{free} represents the molar volume; the contribution $B_{metastable} + B_{bounds}$ arises from the potential energy from more or less strongly bounded pairs of molecules and B_{chem} is due to associating substances. $B_{metastable} + B_{bounds}$ are common terms for all types of mixtures. B_{free} is comprised of two terms $B_{non\text{-}polar}$ and B_{polar}, B_{polar} is a correction term for the affects of polarity on the critical properties using the device of angle averaging, see Cook and Rowlinson (1953). B_{chem} accounts for association contributions as a separate term and is correlated as a equilibrium constant. This is likely to be the weakest link in the correlation and by fitting this parameter to experimental data is likely to yield the most significant improvements over the generalised equation.

Haydon and O'Connell (1975) concluded that this method is as good as any other for simple substances and is a signficant improvement for complex systems. This method appears to offer the most reliable framework for mixtures where no data are available. A summary of this method is given by Fredenslund et al. (1977) together with a computer program for its implementation.

Virial coefficients in a mixture are calculated using the relationship:

$$B_{MIX} = \sum_i \sum_j y_i y_j B_{ij} \tag{2.65}$$

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

$$\ln\phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_i} - \frac{RT}{v} \right] dv - \ln Z \tag{2.66}$$

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

$$\ln\phi_i = \frac{2}{RT} \sum_i y_i B_{ij} - \ln Z \tag{2.67}$$

It should be noted that the truncated viral equation of state is inappropriate for use with strongly interacting mixtures containing carboxylic acids and at high pressures

where large errors may occur.

2.7 The Liquid-Phase Models

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

$$f_i = \gamma_i x_i f_i^* \tag{2.68}$$

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

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

$$G_{MIXTURE} = \sum_i n_i \mu_i^{REAL} = \sum_i n_i \mu_i^* + \sum_i n_i RT \ln x_i + RT \sum_i n_i \ln \gamma_i \tag{2.69}$$

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

$$G^E = G_{MIXTURE} - G^{IDEAL}_{MIXTURE} = RT\sum_i n_i \ln\gamma_i \quad (2.70)$$

Dividing by the total number of moles we get:

$$g^E = RT\sum_i x_i \ln\gamma_i \quad (2.71)$$

For a binary mixture this becomes:

$$g^E = RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \quad (2.72)$$

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

$$RT\ln\gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_{i(i\neq j)}} \quad (2.73)$$

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,

$$g^E = h^E - Ts^E \quad (2.74)$$

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

$$g^E = h^E \quad (2.75)$$

The second approach is to assume that the non-ideality is due entirely to the entropy of

mixing, i.e. $h^E = 0$ and

$$g^E = -Ts^E \tag{2.76}$$

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

(a) it represents the experimental data well

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

2.7.1 Liquid-phase models based on the regular solution approach.

The Margules equation.

The classical approach to development of this type of model has been to express the Gibbs free energy of a binary mixture as a power series i.e.:

$$\frac{g^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2 - (B_{21}x_1 + B_{12}x_2)x_1^2x_2^2..... \tag{2.77}$$

This equation is the generalised form of the well known Margules equation. It can be used to give the following expressions for activity coefficients, here reduced to its most common form of 2 parameter, three suffix Margules equation :

$$\ln(\gamma_1) = x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] = x_2^2(2A_{21} - A_{12}) + 2x_1^3(A_{12} - A_{21}) \tag{2.78}$$

$$\ln(\gamma_2) = x_1^2[A_{21} + 2x_2(A_{12} - A_{21})] = x_2^2(2A_{12} - A_{21}) + 2x_2^3(A_{21} - A_{12}) \tag{2.79}$$

This equation can be extended to higher order equations to more accurately model less ideal systems.

The Van Laar equation.

The work of Van Laar also used this type of expansion and was a particular landmark, as it was the first non-ideal solution model. The non-ideality of the solution expressed

as the excess internal energy, U^E, is calculated by assuming a thermodynamic cycle in which two liquids are expanded isothermally at low pressure and then mixed ideally. The mixture is then cooled isobarically. Van Laar calculated the energy change during each step, assuming that the volumetric properties were given by the Van der Waals equation of state.

He obtained the well known Van Laar equations:

$$\log\gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12}}{A_{21}}\frac{x_1}{x_2}\right]^2} \tag{2.80}$$

$$\log\gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21}}{A_{12}}\frac{x_2}{x_1}\right]^2} \tag{2.81}$$

The constants A_{12} and A_{21} are functions of the Van der Waals constants, R the gas constant and absolute temperature.

Agreement between experimental activity coefficients and those calculated from equations (2.68) and (2.69) 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).

With symmetrical systems for which $A_{12} = A_{21} = A$, both the Margules and Van Laar equations further simplify to the common form:

$$\log\gamma_1 = Ax_2^2 \,,\ \log\gamma_2 = Ax_1^2 \tag{2.82}$$

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.

Their extension to ternary and higher order mixtures requires the evaluation of ternary

and higher order interaction parameters and so they become cumbersome and tedious. This disadvantage encountered in the regular solution approach was overcome by Scatchard in 1949 and Hildebrand in 1950.

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

$$RT\ln\gamma_1 = v_1 z_2^2[\delta_1 - \delta_2]^2 \tag{2.83}$$

$$RT\ln\gamma_2 = v_2 z_1^2[\delta_1 - \delta_2]^2 \tag{2.84}$$

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

$$\delta = \sqrt{\left(\frac{\Delta E_i}{v_i}\right)} \tag{2.85}$$

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

$$\Delta E_i = \Delta H_i^V - RT \tag{2.86}$$

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

The solubility parameters δ_1 and δ_2 are temperature dependent but the difference $(\delta_1 - \delta_2)$ is nearly independent of temperature and the equations hold good for moderate temperature ranges:

$$\delta_1 = \left(\frac{\Delta E_1}{v_1}\right)^{\frac{1}{2}}, \delta_2 = \left(\frac{\Delta E_2}{v_2}\right)^{\frac{1}{2}} \tag{2.87}$$

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

$$\bar{\delta} = \sum_i z_i \delta_i \tag{2.88}$$

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

$$z_i = \frac{x_i v_i}{\sum_i x_i v_i} \tag{2.89}$$

assuming that no volume change occur on mixing.

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

2.7.2 Liquid phase models using local composition expressions

The limited ability of the classical models to represent multicomponent mixtures has led to the development of molecular-based models. The most popular of these newer models are based on the concept of local composition.

The Wilson equation.

Wilson (1964) produced the first of these local composition models. He used the athermal theory for liquids, developed independently by Flory (1942) and Huggins (1942) and modified it with his local composition concept. The local composition concept arises due to the knowledge that molecules in a mixture do not arrange themselves randomly, but partially segregate due to the effect of intermolecular forces. Thus the composition at a point in the mixture will not be equal to the overall mole fraction. The local mole fraction x_{12} is related to the overall mole fraction by the relationship:

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp(-\lambda_{12}/RT)}{x_1 \exp(-\lambda_{11}/RT)} \tag{2.90}$$

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

$$\frac{x_{21}}{x_{22}} = \frac{x_2 \exp(\lambda_{12}/RT)}{x_1 \exp(\lambda_{11}/RT)} \qquad (2.91)$$

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

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

$$\ln\gamma_k = \ln\left(\sum_j x_j \Lambda_{kj}\right) + 1 - \sum_i \frac{x_i \Lambda_{ik}}{\sum_j x_i \Lambda_{ij}} \qquad (2.92)$$

and for a binary mixture

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(\frac{-(\lambda_{12} - \lambda_{11})}{RT}\right) \qquad (2.93)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(\frac{-(\lambda_{12} - \lambda_{22})}{RT}\right) \qquad (2.94)$$

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

Equation (2.92) has been proved to produce good representation for the behaviour of many mixtures and its extension to multi-component mixtures is relatively simple due to the fact that only binary parameters are needed. However, the Wilson equation does not produce a good representation of mixtures which produce internal extrema in the activity coefficients or which exhibit partial miscibility. Wilson (1964) tried to overcome the latter of these problems by the introduction of a third parameter but he encountered difficulties. One good feature of the Wilson equation is that the adjustable parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are only weakly temperature dependent and thus can be extrapolated over a wide temperature range.

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

The NRTL equation.

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. The Non-Random Two Liquid (NRTL) equation of Renon and Prausnitz (1968) was developed to address these considerations, by combining the local composition concept with Scott's two-liquid theory. This equation, besides two binary energy interaction parameters, contains a shape factor which expresses the non-randomness element.

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

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

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{2.95}$$

where

$$\tau_{12} = \frac{G_{12}}{RT} \, , \, \tau_{21} = \frac{G_{21}}{RT} \tag{2.96}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \, , \, G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{2.97}$$

with

$$G_{12} = \left(g_{12} - g_{22} \right) \tag{2.98}$$

$$G_{21} = \left(g_{21} - g_{11} \right) \tag{2.99}$$

and α_{12} is the binary adjustable parameter.

The activity coefficient forms are:

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \left(\frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right)\right] \qquad (2.100)$$

$$\ln\gamma_1 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \left(\frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right)\right] \qquad (2.101)$$

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

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

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) have assumed linear relationships for the parameters, arriving at a six-parameter NRTL equation:

$$g_{21} - g_{11} = C_1 + D_1(T\text{-}273.15) \qquad (2.102)$$

$$g_{12} - g_{22} = C_2 + D_2(T\text{-}273.15) \qquad (2.103)$$

$$\alpha_{12} = \alpha^0 + \alpha^T(T\text{-}273.15) \qquad (2.104)$$

The C-parameters represent the value of the NRTL parameters at 273 K and the D-parameters express their dependence upon temperature, where units of T are Kelvin.

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

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

The UNIQUAC equation.

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

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

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.105)$$

where is the combinatorial part and the residual part.

The combinatorial part is given by:

$$\ln_i^C = \ln\frac{\phi_k}{x_k} + \frac{z}{2}\ln\frac{\theta_k}{\phi_k} + l_k - \frac{\theta_k}{x_k}\sum_j x_j l_j \qquad (2.106)$$

where

$$l_k = \frac{z}{2}\left(r_k - q_k\right) - (r_k - 1),\ z = 10 \qquad (2.107)$$

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

the residual contribution is given by:

$$\ln \gamma_i^R = \left[1 - \ln\left(\sum_j \theta_j \tau_{ij} \right) \frac{\sum_j (\theta_j \tau_{ij})}{\sum_k (\theta_k \tau_{jk})} \right] \qquad (2.108)$$

where

$$\tau_{ij} = \exp\left[\frac{\mu_{ij} - \mu_{ii}}{RT} \right] \qquad (2.109)$$

The adjustable parameters are obtained by fitting to experimental data.

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

2.7.3 Other liquid-phase models.

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

$$g^E = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 ..... \right] \qquad (2.110)$$

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

$$\log\left(\frac{\gamma_1}{\gamma_2}\right) = a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + \ldots (2.111)$$

The determination of the constants is difficult due to an indeterminate condition. Ochi and Lu (1977) further modified the equation of Chao to facilitate the evaluation of these constants. Klaus and Van Ness (1967) proposed that G^E could be represented as a function of composition using orthogonal functions. Christiansen and Fredenslund (1975) reviewed this problem and used the method of orthogonal collocation largely as an aid in thermodynamic consistency testing.

2.7.4 Comparisons of the liquid phase activity coefficient models

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

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

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

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

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

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

Counsell and Hicks (1976) used the data on water and ethanol mixture 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 equations were also tested together using a fixed and variable α parameter in the NRTL equation. The NRTL equation with a variable α parameter was discovered to produce the best fits, although the UNIQUAC equation was found superior to models representing g^E instead of g^E/RT.

2.8 Associating systems.

It is well known that mixtures involving carboxylic acids cannot be modelled satisfactorily, using the conventional approaches already discussed. This is due to the association of the acid molecules in both phases. The most modelled systems of this type involve acetic acid and discussion here will be limited to this type of mixture.

It is known that acetic acid mixtures form not only dimers but higher order polymers in the vapour phase. It has been shown by Prausnitz et al. (1973) that considering only the dimerisation permits adequate modelling of the vapour phase. It is stated by Freedman (1953) that in the liquid phase only dimers are considered to exist.

The majority of workers have tended to only account for vapour phase association and have used the activity coefficients to account for the non-idealities from association in

the liquid phase. This approach has been adopted because the assumption can be made for the vapour phase that the association constant for dimerisation can be considered independent of composition and equal to the association constant for the pure associating substance. Prausnitz et al. (1980) discuss the use of "chemical" theory to represent the vapour phase association. In the liquid phase these assumptions are not valid, because Prigogine and Defay (1950) have shown by spectroscopic analysis that association is a function of composition .

The classical method for representing association in both phases is the analytic method which works in terms of the concentrations of the unreacted substances only, i.e. a mixture of acetic acid and water is regarded as just that, when in fact, there are at least three species present: acetic acid monomer, acetic acid dimer, and water. The earliest form of this approach is due to Marek and Standart (1954). They used an equilibrium constant defined by :

$$k = \frac{x_2}{x_1^2} \tag{2.112}$$

where x_2 and x_1 are the mole fractions of the dimer and monomer for the liquid phase. For the vapour phase they used :

$$k = \frac{p_2}{p_1^2} \tag{2.113}$$

where p_2 and p_1 are the partial pressures of the dimer and monomer respectively to make use of these equilibrium constants the relationship between the stoichiometric mole fractions and the true mole fractions are required. These are

$$y_A = \frac{y_1 + 2y_2}{1 + y_2}, \; x_A = \frac{x_1 + 2x_2}{1 + x_2} \tag{2.114}$$

obtained by writing down the definitions of the true mole fractions in terms of the moles present and rearranging. (similar relations exist for the non-associating substance)

Marek and Standart (1954) wrote down the phase equilibrium relationship for the monomer for the pure associating substance and so deduced values of x_1 and y_2 in the pure substance. These then gave expressions for the vapour pressure of the monomer in the pure substance. By now writing down the phase equilibrium for the monomer in the mixture, they deduced the final relationship in stoichiometric mole fractions. This is

$$Py_A Z_A \phi_A = p_A^{sat} x_A \Gamma_A \gamma_A \tag{2.115}$$

Here P is the total pressure, ϕ_A is the vapour phase fugacity coefficient (often assumed to be equal to 1) and Z_A is the vapour phase correction factor given by

$$Z_A = \frac{1 + \sqrt{\left(1 + 4K_A p_A^{sat}\right)}}{1 + \sqrt{[1 + 4kx_A(2 - x_A)]}} \tag{2.116}$$

When this method was applied to experimental data the then absence of information on k led Marek and Standart (1954) to set $\Gamma_A = 1$ and permit γ_A to represent all the non-ideality of the liquid phase. The success of this method was limited, even where values of k were available because it used an equilibrium constant based on mole fractions rather than a truly concentration-independent thermodynamic equilibrium constant.

This method was modified by Jenkins and Gibson-Robinson (1977) to relate the mole fraction equilibrium 'constant' to the thermodynamic equilibrium constant. The ratio of the correction factors required is concentration-dependent hence the mole fraction equilibrium 'constant' becomes concentration-dependent. To derive the required ratio, they obtained expressions for the true mole fractions for the dimer both in the pure acetic acid and in the mixture. That for the dimer in the vapour phase mixture is

$$y_2 = \frac{4KPy_A + 1 - 2KPy_A^2 - \sqrt{\left(1 + 8KPy_A - 4KPy_A^2\right)}}{2\left(KPy_A^2 + 4KP - 4KPy_A\right)} \tag{2.117}$$

with a similar one for the liquid phase. The parallel relationships for the pure substance give an expression for the vapour pressure of the dimer and this combined with the

vapour-liquid equilibrium relationship for the dimer, gives additional correction factors based on the dimer of

$$Z'_A = \frac{\left[\left(4KP + 1/y_A - 2KPy_A\right) - \sqrt{\left(1/y_A^2 + 8KP/y_A - 4KP\right)}\right]\left(2K_A p_A^{sat}\right)}{2\left(KPy_A^2 + 4KP - 4KPy_A\right)\left[2K_A p_A^{sat} + 1 - \sqrt{(4k_A + 1)}\right]} \quad (2.118)$$

and

$$\delta'_A = \frac{\left[(4k + 1/x_A - 2kx_A) - \sqrt{\left(1/x_A^2 + 8k/x_A - 4k\right)}\right](2k_A)}{2\left(kx_A^2 + 4k - 4kx_A\right)\left[2k_A + 1 - \sqrt{(4k_A + 1)}\right]} \quad (2.119)$$

The thermodynamic equilibrium constant is related to that based on mole fractions by

$$k = \frac{\gamma_A^2}{\gamma_2}.\frac{\gamma_{2A}}{\gamma_{1A}^2}.k_A \quad (2.120)$$

If the overall vapour-liquid equilibrium constant relationship based on the dimer is divided by that based on the monomer, the following relationship between the activity coefficients is obtained.

$$\gamma'_A = \frac{Z'_A \phi'_A \delta_A}{Z_A \phi_A \delta'_A} = \frac{\gamma_A}{\beta} \quad (2.121)$$

and this leads to

$$k = k_A.\beta.\gamma_A \quad (2.122)$$

β is a function of k through the definition of correction factors δ_A and δ'_A so successive approximation is used. While analytical in form, the values of K_A and k_A are known and given by Ritter and Simons(1945), Freedman (1953) and Barton and Hsu (1972).

This approach gives considerable improvement in the representation of the vapour-liquid equilibrium in acetic acid mixtures as can be seen in figure (2.2), which gives the data of Meehan (1963) at 50°C for the acetic acid - toluene mixture. The comparison is between the Marek and Standart model with only vapour phase correction, the same model with a liquid-phase association constant equal to that for the pure material (i.e. $k = k_A$) and this recent model. The Jenkins and Gibson-Robinson (1977) model is seen to be superior.

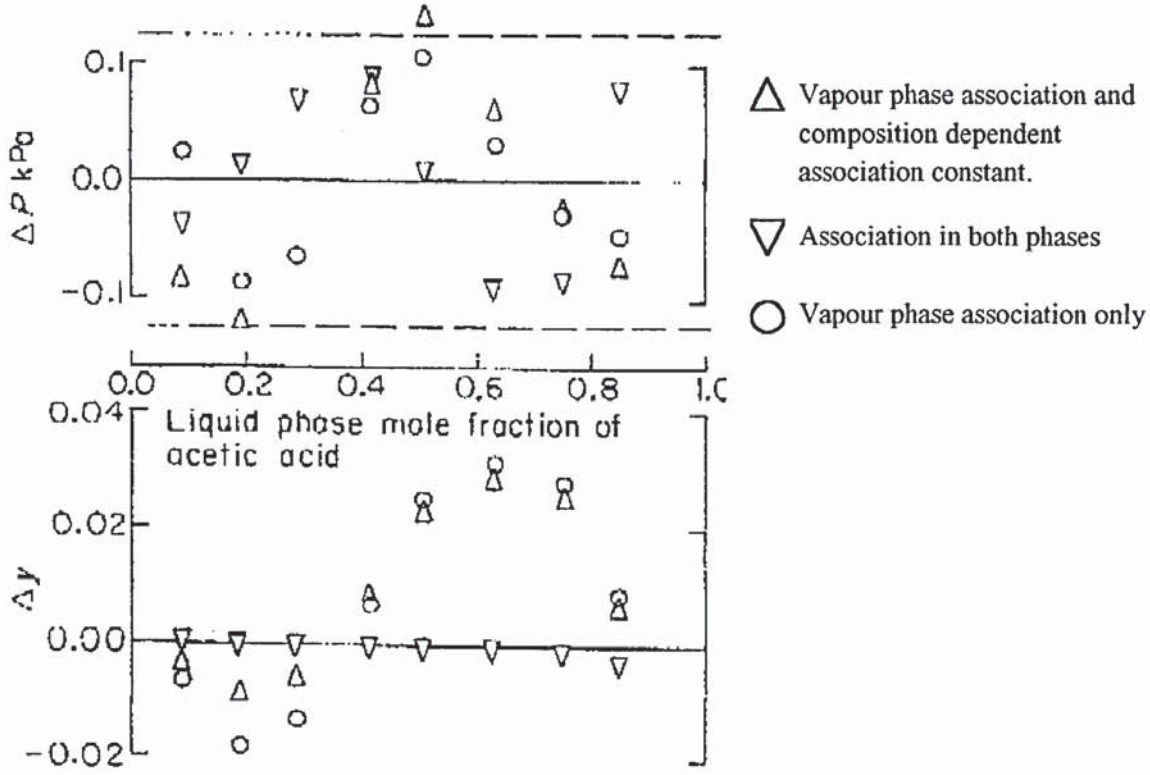


Figure 2.2 Deviation Plots for data of Meehan at 50°C for acetic acid/toluene system

2.9 Consistency tests.

2.91 Introduction.

All experimental VLE data of necessity contain errors, which can be categorised as either random or systematic. The extent of random errors can be assessed by the use of an initial screening using an y - x against x plot where all data should lie on a smooth curve. Systematic errors in the data can only be assessed through a thermodynamic consistency test normally based on the Gibbs - Duhem equation. If the data can be shown to obey the Gibbs - Duhem equation then it may be regarded as thermodynamically consistent. The Gibbs - Duhem equation as previously described is:

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \qquad (2.123)$$

For the general application of consistency tests, Van Ness (1959) expanded this to the form:

$$\sum_i x_i d\ln f_i + \left(\left(h - h^*\right)/RT^2\right)dT - (v/RT)dP = 0 \qquad (2.124)$$

and from this a general equation for the coexistence of liquid and vapour for binary mixtures was deduced by Ljunglin and Van Ness (1962):

$$AdP + BdT = \left(y_1 - x_1\right)d\ln\left(\frac{\gamma_1^V}{\gamma_2^V}\right) + \left(\frac{y_1 - x_1}{y_1 y_2}\right)dy_1 \qquad (2.125)$$

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

Consistency tests can be grouped into the following four types:

1. Area tests.

2. Slope tests.

3. Statistical tests.

4. Barker-type tests.

2.91 Area tests.

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

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2}.\, dx = 0 \qquad (2.126)$$

The curve of the line $\ln(\gamma_1 - \gamma_2)$ versus x crosses the line $\ln(\gamma_1 - \gamma_2) = 0$. For the data to be considered consistent the areas above and below this line must be equal. Many variations of this test have been proposed: Herington (1951), Broughton and Brearly (1955) and McDermot and Ellis (1965). The use of integration in all these methods leads to the main drawback of this method, i.e. errors may cancel out, thus area tests may only indicate gross error. In performing the area test on real data, the integral in equation (2.110) will not come out to be exactly equal to zero, thus a criterion must be stated so that the result of the integration can be compared with it and a judgement can then be made as to whether a set of data is consistent or not. It is usually agreed that a set of data is considered consistent if it obeys the relationship:

$$0.02 \rangle \left(\frac{\text{AREA ABOVE X-AXIS - AREA BELOW X-AXIS}}{\text{AREA ABOVE X-AXIS + AREA BELOW X-AXIS}}\right) \qquad (2.127)$$

although the value on the left hand side of equation (2.127) will depend on how non-ideal the mixture is. If it is very non-ideal, the value can be raised and vice versa.

2.92 Slope tests.

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

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

$$x_1 \frac{d\ln\gamma_1}{dx_1} = x_2 \frac{d\ln\gamma_2}{dx_2} \qquad (2.128)$$

Plots of $\ln\gamma_1$ versus x_1 and $\ln\gamma_2$ versus x_2 are prepared and the slopes measured at regular intervals and substituted into equation (2.128). If the relationship is obeyed the data are consistent. The problem here is that in practice, the slopes are hard to measure to any degree of accuracy and thus the method has not seen much use, although it provides a quick test to see if the data are consistent. Van Ness (1964) and Van Ness and Mrazek (1959) have developed a method which uses a value Q defined as:

$$Q = \frac{\Delta G^E}{RT} = \sum_i x_i \ln\gamma_i \qquad (2.129)$$

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

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

2.9.3 Statistical tests

As previously noted experimental data are associated with two types of error. The problem is distinguishing whether a particular error in the data is due to random or

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

$$f(x) = \sum_i x_i d\ln\gamma_i + \int_a^b \frac{\Delta h_m}{RT^2} dT - \int_a^b \frac{\Delta v_m}{RT} dP \qquad (2.130)$$

Ulrichson and Stevenson improved this method by considering that although for consistent data f (x) = 0, in reality, this will never happen and some means for determining acceptable bounds should be proposed. They did this by using the trapezoidal rule in the integration and then applying the propagation of error formulae.

Using the trapezoidal rule we have:

$$f(a,b) = \sum_i \frac{x_{ia} + x_{ib}}{2} d(\ln\gamma_{ib} - \ln\gamma_{ia}) + \int_a^b \frac{\Delta h_m}{RT^2} dT - \int_a^b \frac{\Delta v_m}{RT} dP \qquad (2.131)$$

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

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

1. It provides a quantitative meaning to the consistency test rather than just a comparison with the null value.

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

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

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

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

obtained from replicated experiments, but they may be estimated from experience associated with a particular type of experimental apparatus. It is customary to assume that the random errors in different experiments are uncorrelated.

For each experiment, the true values of the measured variables are related by one or more constraints. Because the number of data points exceeds the number of parameters to be estimated, all constraint equations are not exactly satisfied for all experimental measurements.

Exact agreement between theory and experiment is not achieved due to random and systematic errors in the data and to 'lack of fit' of the model used to the data. Optimum parameters and true values corresponding to the experimental measurements must be found by satisfaction of an appropriate statistical criterion.

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

The maximum-likelihood method is applicable to any type of data for which a model can be postulated and for which there are known random measurement errors in the variables. P-V-T data, enthalpy data, solid-liquid adsorption data, etc., can all be reduced by this method. The advantages indicated here for vapour-liquid equilibrium data apply also to other data.

In conclusion Jenkins and Gibson-Robinson (1978) used experimental data from a modified Cathala still to examine the consistency tests of Ulrichson and Stevenson (1972), of Samuels et al. (1972), of Van Ness et al. (1973), and of Wan and Prausnitz (1973) and Christiansen and Fredenslund (1975). They concluded that for consistency tests based on statistical analysis to be of use, forty to fifty data points per binary

mixture must be used if any reasonable assessment of the data was to be obtained. They also expressed the view that a small data set of high precision is preferable to a larger set of lower precision, parameters deduced from a larger set may not describe the true behaviour of the system.

2.9.4 Barker-type tests

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

The method of Barker (1953) is used to enable the value of the redundant fourth variable to be calculated from the reduced data. The most general approach was developed by Abbot and Van Ness (1975) who used Barker's method to reduce P, x, T data and used y in the consistency test. Calculated y (exp) - y (calc) and P (exp) - P (calc) data are plotted versus x and a consistent set of data is obtained when Δy and ΔP values are small and randomly distributed around the x axis. Abbot and Van Ness (1975) used a 5-parameter Margules equation and a modified version of the Margules equation to represent the liquid-phase behaviour and data could be erroneously declared as inconsistent due to misrepresentation of the liquid phase activity coefficients by the chosen model. This disadvantage has been overcome by Christiansen and Fredenslund (1975) who avoided the use of liquid phase activity coefficient models and used orthogonal collocation to solve for G^E, and hence obtained activity coefficients to predict y values. The resultant y (exp) - y (calc) versus x data were used as a screening test.

The original Barker method has been used to test the thermodynamic consistency of experimental VLE data for acetic acid mixtures where the occurrence of dimerisation introduces a specific interaction in both phases. This has been shown (see Jenkins and Gibson-Robinson, (1978)) to be unwise in mixtures where association occurs, unless a suitable association model was to be included.

2.9.5 Consistency tests. Some conclusions.

It is reasonable to say that no one consistency test method will give a definitive measure of the consistency of experimental data sets. It is therefore necessary for a detailed study of data consistency to adopt a systematic study of the data using a combination of the above consistency test methods. Gess, Danner and Nagvekar (1991) have recently suggested the following systematic approach to consistency tests:

1) A data set should consist of between 8 and 30 data points spanning the whole composition range.

2) Accurate vapour pressure data for both pure components must be available at the equilibrium conditions.

3) The data should be preliminarily scanned using a y versus y-x plot to identify and eliminate any obviously erroneous data points.

4) The tests used by the DECEMA group, i.e. an area test followed by a numerical method for calculation of the vapour-phase compositions using a Legendre polynomial to yield a value $\Delta y = y_{meas} - y_{calc}$ which for consistent data must be > 0.01 averaged across the full data set, are the first stage of the consistency test method.

5) As a second stage a Barker-type consistency test is applied using a 4-parameter Margules equation and the Hayden and O'Connell method to calculate the fugacity coefficients. Only the x-P-T data are used in the regression to calculate y composition values for each data point. Consistent data sets must meet the criteria $\Delta y = y_{meas} - y_{calc} < 0.01$ averaged across the full data set.

6) A graphical examination of the calculated Δy is made. Consistent data should show a random distribution about the x axis. If the deviations observed show a bias but are very small the data may also be considered consistent.

This method of Gess et al. (1991) represents a rigorous test for any experimental data. A similar approach is adopted throughout this study when assessing data for consistency.

Data for multicomponent mixtures are often not available particularly for mixtures used in new processes. Extensive data bases of mainly binary experimentally determined mixtures exist, e.g. the Dortmund data base, but it is unlikely that all data for binaries for a particular multicomponent mixture are available. Determination of the missing binary mixtures by experimentation at early stages in the design process would be very expensive and time consuming. To overcome these deficiencies a reliable, rational, accurate and flexible prediction method is required.

Prediction of experimental data are required for three main purposes:

1) Screening of possible extractive agents for extractive distillation. Infinite dilution activity coefficient models, either solubility parameter or group contribution methods, are used to rank prospective agents before further development of the more promising options.

2) Preliminary process design. A group-contribution method can be used to generate activity coefficients and K-values. The general distillation line may follow the correct trend but there may be significant errors in calculated tops and bottoms compositions. These are adequate for initial design but final design requires better VLE data or trial distillation studies. Care should be taken when using the above methods to determine data above atmospheric pressure as most model parameters are temperature dependent.

3) Final design. Prediction methods should only be used at this stage as a last resort and correlating equations should only be used to extrapolate to multicomponent data from all the available binaries composed from the separate components.

It is proposed to provide only a general overview of the prediction techniques available for vapour-liquid equilibrium estimation and to describe in detail only those methods which are used in this work. The prediction of vapour liquid equilibrium falls into three main categories which will be discussed in turn followed by a novel technique working from molecular properties developed at Aston University. The techniques discussed here are :

1) The solubility parameter approach.

2) Group Contribution approach (ASOG, UNIFAC).

3) Generalised equations-of-state approach.

4) AGAPE (A General Approach To Phase Equilibria).

3.1 The solubility parameter approach.

Many prediction methods using the solubility parameter are extant in the literature. The simplest method in this group was proposed by Hilderbrand (1959) to predict infinite dilution activity coefficients for regular solutions and has been widely used for hydrocarbon mixtures. Subsequent workers proposed alternative terms for predicting infinite dilution activity coefficients, i.e. Weimer and Prausnitz (1965), Helpinstill and Van Winkle (1967) and Weile and Bagley (1968). Null and Palmer (1969) combined the work of these previous authors by suggesting that the various contributions derived by these authors to $\ln\gamma^{\infty}$ were additive, i.e.

$$\ln\gamma_1^{\infty} = (\ln\gamma_1^{\infty})_I + (\ln\gamma_1^{\infty})_{II} + (\ln\gamma_1^{\infty})_{III}\cdots \qquad (3.1)$$

Null (1970) gives details of how the parameters I, II, III... etc can be determined and how additional parameters can be added as they are devised. Null also states that this method is only suitable for screening purposes and for calculating the distribution of minor components in a separation process.

3.2 Group contribution approach.

Any compound can be regarded as an aggregate of a small number of functional groups, CH_3, CH_2, OH etc. If the functional groups properties are known or can be derived, they can be used to calculate some of the physical properties of the parent molecule. A logical extension of this idea is to calculate the phase properties of mixtures from the functional groups of the constituent molecules in the test mixture. This has the significant advantage that a large number of mixtures can be handled from a small number of functional groups. Thus the group contribution approach has become a popular option for prediction of phase equilibrium.

Two principal methods, denoted here as ASOG and UNIFAC, have been developed using this methodology, both being similar in principle but differing in detail.

3.2.1 The ASOG method.

The analytical solution of groups (ASOG) method was developed by Wilson and Deal (1962) from earlier work by Redlich et al. (1959) and Derr et al. (1959). The basis of this method is to assume that the activity coefficient of component i consists of two components:

1) A configuration (entropic) contribution due to molecular size differences.
2) A group interaction contribution due to differences in intermolecular forces.

The configuration term is obtained from the athermal Flory-Huggins equation and the group interaction contribution from the Wilson equation, applied to functional groups. A detailed description of the ASOG method is presented by Kojima and Tochiga (1979). They also present listings of a substantial number of group parameters derived from experimental data. As this method is not used here no further details will be given.

3.2.2 The UNIFAC method.

UNIFAC in common with ASOG utilised the summation of two contribution terms, one due to size differences, the other due to molecular interactions, to obtain the activity coefficients of a mixture. The UNIFAC method is less arbitrary than the ASOG method. It uses the UNIQUAC equation which integrally uses a combinatorial term in part due to differences in molecular size and shape and a residual part due to molecular interactions. In addition functional group sizes and interaction surface areas are introduced from independently obtained pure component molecular structure data.

The UNIQUAC equations for activity coefficients of a molecular component i are:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.106)$$

(superscripts : C- combinatorial, R- Residual)
where

$$\ln\gamma_i^C = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \qquad (2.107)$$

and

$$\ln\gamma_i^R = q_i\,(1 - \ln\sum_j \theta_j\tau_{ij} - \sum_j \frac{\theta_j\tau_{ij}}{\sum_k \theta_k\tau_{kj}}) \qquad (2.109)$$

In the UNIQUAC equation, the two adjustable parameters τ_{ij} and τ_{ji} must be evaluated from experimental phase-equilibrium data. No ternary (or higher) parameters are required for systems containing three or more components. Pure component parameters r_i and q_i are, respectively, measures of molecular Van der Waals volumes and molecular surface areas.

In the UNIFAC method the combinatorial part of the UNIQUAC activity cocfficients is used directly. Only pure-component properties enter into this equation. Parameters r_i and q_i are calculated as the sum of the group volume and area parameters R_k and Q_k

$$r_i = \Sigma_k v_k^{(i)} R_k \text{ and } q_i = \Sigma_k v_k^{(i)} Q_k \qquad (3.2)$$

where $v_k^{(i)}$, always an integer, is the number of groups of type k in molecule i. Group parameters R_k and Q_k are obtained from the Van der Waals group volume and surface areas $v_k^{(i)}$ and A_{wk}, given by Bondi (1968);

$$R_k = V_{wk}/15.17 \text{ and } Q_k = A_{wk}/2.5 * 10^9 \qquad (3.3)$$

The normalisation factors 15.17 and $2.5 * 10^9$ are determined by the volume and external surface area of a CH_2 unit in polyethylene.

The residual part of the activity coefficient is replaced by the solution-of-groups concept. We write

$$\ln\gamma_i^R = \Sigma_k v_k \left(\ln\Gamma_k - \ln\Gamma_k^{(i)} \right) \qquad (3.4)$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i.

$$\ln\Gamma_k = Q_k \left[1 - \ln\left(\sum_k \Theta_m \Psi_{mk} \right) - \sum_m \left(\Theta_m \Psi_{mk} / \sum_n \Theta_n \Psi_{nm} \right) \right] \qquad (3.5)$$

$$\Psi_{nm} = \exp(-a_{nm} / T) \qquad (3.6)$$

$$\Theta_m = Q_m X_m / \sum_n Q_n X_n \qquad (3.7)$$

$$x_m = \frac{\sum_j v_{mj} x_j}{\sum_j \sum_n v_{nj} x_j} \qquad (3.8)$$

a_{mn} = group interaction parameter for the interaction between groups m and n. This parameter must be evaluated from experimental data.

The original UNIFAC model was proposed by Fredenslund et al. (1975) considering 18 functional groups and was revised by Fredenslund et al. (1977 a & b) by derivation

of new interaction parameters from the experimental data held in the Dortmund Data Base. The ready availability of computer programs has made this method the premier group contribution method with many updated lists of functional groups being published. The method has spawned a number of modified models aimed at addressing the limitations of the original model and increasing its range of applicability. A review and critical discussion of these developments is given by Zain (1992).

It is proposed to discuss only two of these modifications in detail, those by Larsen et al. (1987) and Gmehling and Weidlich (1987). Both of these methods aimed to overcome the temperature dependence limitation of the original model. They both addressed the problem in a similar way by making the group interaction parameters temperature dependent.

3.2.3. Modified UNIFAC equation of Larsen et al. (1987).

The Modified UNIFAC equation of Larsen et al. (1987) introduced two modifications intended in part to improve the temperature dependence of the model :

1) The combinatorial term has been slightly modified using the Kikic et al (1980) combinatorial term .

2) The group interactions have been made temperature dependent.

The change made to the combinatorial term involved dropping the Staverman-Guggenheim correction to the Flory-Huggins combinatorial. Donohue et al. (1975) modified the Flory-Huggins combinatorial term to the form:

$$\omega_i = \frac{x_i r_i^{p_i}}{\sum_j x_j r_j^{p_i}} \qquad (3.9)$$

where the exponent p_i varies with the type of molecule. Kikic et al. (1980) set $p_i = 2/3$ by comparison with experimental data for a large number of aliphatic hydrocarbon

mixtures. This was shown to describe the VLE mixtures of alkanes much better than the Staverman-Guggenheim combinatorial especially where the difference in molecular sizes is large. The combinatorial term used in Modified UNIFAC becomes:

$$\ln\gamma_i^C = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i} \qquad (3.10)$$

With the modified volume fractions following Kikic et al. (1980) we have

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad (3.11)$$

The residual term has been modified to use three coefficients to describe the temperature dependence of the interaction parameters

$$a_{ji} = a_{ji,1} + a_{ji,2} + a_{ji,3}\left(T \ln\frac{T_o}{T} + T - T_o\right) \qquad (3.12)$$

where T_o is a reference temperature (= 298.15 K)

$a_{ji,1}$, $a_{ji,2}$ and $a_{ji,3}$ are temperature coefficients.

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

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

2) The six adjustable parameters required for one binary group combination, can be based on vapour-liquid equilibrium and H^E data measured at different temperatures. The first second and third coefficients of the temperature function are related to G^E, H^E and Cp^E respectively. The term containing $a_{ji,3}$ can be dropped if H^E values are only known at one temperature.

The outcomes of this new model were:

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

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

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

3.2.4. Modified UNIFAC equation of Gmehling et al. (1987).

Gmehling et al. (1987) adopted a similar approach to Larsen et al. (1987) in their form of the modified UNIFAC method. The new modified (Oldenburg) UNIFAC method was established through the use of:

1) Modification of the temperature-independent combinatorial part similar to that of Kikic et al. (1980). The (Oldenburg) UNIFAC method uses $r^{3/4}$ derived empirically from experimental data, in place of Kikic's $r^{2/3}$.

2) The temperature-dependent interaction parameters to describe the residual part of the activity coefficient are given by the quadratic equation:

$$\Psi_{nm} = \exp\left(-\left(a_{nm} + b_{nm}T + c_{nm}T^2\right)/T\right) \qquad (3.13)$$

The parameters a_{nm}, b_{nm}, c_{nm} were fitted from experimental data

3) An extended database which included (VLE, H^E, γ^∞, LLE) for fitting the group parameters.

4) Slightly modified values for the Van der Waals volumes and surface areas were used. These were again derived empirically from experimental data.

This new version of the UNIFAC correlation was used for predicting the behaviour of systems including alkanes, alkenes, aromatics alcohols and ketones. They state very good VLE predictions and infinite-dilution activity coefficients were obtained for 16 different alkane-alcohol mixtures. The range of applicability of this method was increased by Gmehling et al. (1993) to 45 main groups using phase equilibrium data (VLE, H^E, γ^∞, LLE) stored in the Dortmund Data Bank. In conclusion to their review of this method Gmehling et al. (1993) concluded that their modified (Oldenburg) UNIFAC method allows better predictions of the real behaviour of non-electrolyte systems than do other group contribution techniques.

A note of caution should be made at this point, the values of the calculated temperature dependent interaction parameters are only as good as the experimental data from which they are derived. Therefore the predictions of the (Oldenburg) UNIFAC method are not always the best available for every system. This has been highlighted by Schmeltzer et al. (1996) who showed the (Oldenburg) UNIFAC method gave poor results for calculations involving Cyclohexane.

3.3 Generalised equations-of-state approach.

Multi-component forms of the generalised equations-of-state, e.g. Soave-Redlich-Kwong are of interest for the prediction of VLE data, as they contain only terms expressing binary interactions. Success with this approach depends on modelling the binary interaction parameters for each binary mixture involved in the general multi-component mixture of interest. A knowledge of a minimum of information regarding each binary is required to allow the interaction parameters to be deduced.

This predictive method is useful when for final design:

1) Data parameters are not available for all the binaries involved in a multicomponent mixture.

2) The two components of the mixture of interest to be separated are minor constituents but an exact specification has to be met as to their concentration level in any or all takeoff streams.

A review of calculating VLE data from equations of state is given by Reid et al. (1986). Generally speaking equations of state can be used to :

1) Represent the vapour phase though this is not predictive in nature.

2) Provide the principal method for modelling VLE data at high pressures.

3) Predict data for hydrocarbon mixtures by application of cubic equations-of-state and empirical quadratic mixing rules.

The prediction of VLE data for mixtures of polar compounds requires equations of state applied with specialist mixing rules (e.g.the Vidal (1978) Non Quadratic Mixing Rules).

3.4 AGAPE (A General Approach To Phase Equilibria).

This is a recent novel approach to predicting phase equilibria based on fundamental molecular considerations. The method uses a "whole molecule approach" in contrast to the Group contribution approach and uses only two dissimilar statistical thermodynamic parameters.

A full description of the AGAPE model exists elsewhere, e.g. Homer et al. (1991,1992). Only an over view of the main steps is given here. The AGAPE model is based on the same two fluid lattice theory employed by Prausnitz and Maurer (1978) and Prausnitz (1986) to derive the UNIQUAC model. The AGAPE model was initially developed for use with a generalised London's potential (GLP), an explicit form of intermolecular potential allowing for the first time proper utilisation of the concept of local composition (Wilson, 1964).

The Wilson concept of local composition assumes that the energetics of bulk liquids can be represented through a shell model. The model is based on the concept of a single molecule of type 1 surrounded by a spherical co-ordination shell of other molecules (see Figure 3.1). When a second molecule species is introduced a local composition is achieved (see Figure 3.1) which is not necessarily the same as the bulk mixture.

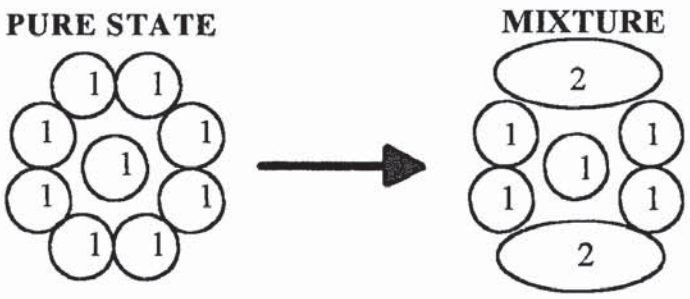


Figure 3.1 Representation of change in composition of the first solvation shell of molecule 1 when 1 molecule of type 2 is assumed to replace two molecules of 1.

The Wilson's concept is inadequate because the overall mass balance is not satisfied. Homer et al. (1991) introduced a model similar to that of Wilson but this time used a mass balance of the bulk system with the usual Boltzmann-type energy distributions based on the intermolecular pair potentials. From the summation of the radial molecular pair potentials in all solvation shells in the mixture an equation for the excess energy of mixing can be derived as:

$$U^e = \frac{1}{2}N_A[x_1\Delta U_{11}(t_1 - z) + x_2\Delta U_{22}(m_2 - z)] \tag{3.14}$$

where

$$\Delta U_{11} = \Phi_{11} - \Phi_{21}v_1/v_2 \tag{3.15}$$

$$\Delta U_{22} = \Phi_{22} - \Phi_{12}v_2/v_2 \tag{3.16}$$

$$\Phi_{21} - \Phi_{12} \tag{3.17}$$

$$t_1 = Z/\left\{1 + (v_2x_2/v_1x_1)\exp\left[-\left(\frac{\Phi_{21} - \Phi}{11}\right)/kT\right]\right\} \tag{3.18}$$

$$m_2 = z/\{1 + (v_1x_1/v_2x_2)\exp[-(\Phi_{12} - \Phi_{22})/kT]\} \qquad (3.19)$$

Φ_{11}, Φ_{22} and Φ_{12} are the relevant molecular pair potentials. v_1, v_2 are the volume parameters (molecular volumes or Van der Waals Volumes) which are normally expressed as ratios. z is the coordination number which for organic molecules of similar size is normally constant (see Homer and Mohammedi, 1987). The normal value of z is 11 though this can change, e.g. for water z has a value of 4. Here t_1 is the number of whole molecular contacts of a molecule of type 1 with other molecules of type 1, while m_2 is the number of whole molecular contacts of a molecule of type 2 with other molecules of type 2. Note that m_1 and t_2 are the number of 1-2 type contacts for each type of molecule.

Integration of equation 3.14 gives the Helmholtz energy at constant volume and temperature. The constant of integration can be determined by use of Gugginheim (1952) energy terms for athermal non-ideal monomer/r-mer lattice model. From Hildebrand and Scott (1977) for low to moderate pressures the Helmholtz energy can be substituted for the excess Gibbs free energy G^E . Homer et al. (1991) deduced, using standard thermodynamic procedures, expressions for the activity coefficients and by using the assumption of ideal vapour behaviour, for total pressure and composition. These equations are listed below:

$$\frac{G^E}{RT} = x_1 \ln\frac{z_1}{x_1} + x_2 \ln\frac{z_2}{x_2} - \frac{z}{2}qx_2\ln\frac{r}{q} + \frac{z}{2}(x_1 + x_2q)\ln\frac{x_1 + rx_2}{x_1 + qx_2} +$$

$$\frac{LZ}{RT}\left\{\frac{x_1\Delta U_{11}}{b_1}\ln[z_1 + z_2\exp(-b_1/T)] + \frac{x_2\Delta U_{22}}{b_2}\ln[z_2 + z_1\exp(-b_2/T)]\right\} \qquad (3.20)$$

$$\ln\gamma_1 = \ln\frac{z_1}{x_1} + z_2\left(1 - \frac{1}{r}\right) + \frac{z}{2}\left(\ln\frac{\theta_1}{z_1} + \frac{z_1}{\theta_1} - 1\right)$$

$$+ \frac{Lz}{RT}\{\frac{\Delta U_{22}}{b_2}\ln[z_2 + z_1\exp(-b_2/T)]$$

$$+ \frac{\Delta U_{22}}{b_2}z_2\left[\frac{1}{z_2 + z_1\exp(-b_2/T)} - 1\right]$$

$$+\frac{\Delta U_{11}}{b_1} z_1 r\left[\frac{\exp(-b_1/T)}{z_1 + z_2\exp(-b_1/T)} - 1\right]\} \qquad (3.21)$$

where $\theta_1 = \frac{x_1}{x_1 + qx_2}$ and $\theta_2 = \frac{x_2}{x_2 + qx_1}$

$$P = x_1\gamma_1 P_1^o \qquad y_1 = \frac{x_1\gamma_1 P_1^o}{P} \qquad (3.22 \& 3.23)$$

Here z_1, z_2 are the volume fractions of components 1 and 2, r is the molar volume ratio v_1 / v_2 and q the relative contact areas (surface areas of the two molecules). The pair potentials Φ_{11} and Φ_{22} can be calculated from the latent heat of vaporisation for the pure components (see Homer et al. 1991) leaving only two dissimilar statistical thermodynamic parameters, r and Φ_{12}, to be determined.

The two dissimilar statistical thermodynamic parameters, r and Φ_{12} can be determined by one of two procedures. The first is based on determining the value of r from a pure component data while the value of Φ_{12} is calculated using GLP theory (see 3.4.1) method. The second procedure involves a single point fitting process using appropriate experimental data (see 3.4.2).

Advantages of the AGAPE approach are:

1) In its pure predictive mode (with GLP) it requires only pure component atomic and molecular parameters.

2) It is applicable to species that do not contain any of the functional groups of the group contribution methods, i.e. inert atoms and small molecules.

3) It can distinguish between molecular isomers including those distinguished by cis/trans configurations

4) In the one point fitting mode it requires only estimates of two uncorrelated parameters that have a physical meaning. These parameters could be obtained from any appropriate source and allow application of this method to a wider range of compounds.

5) This model could be extended to other phenomena such as LLE, viscosity and solubility.

3.4.1 Implementation of AGAPE model using the generalised London potential.

A full description of the GLP theory is given by Mohammedi (1987). The GLP enables the calculation of dispersion forces between polyatomic molecules. It accounts for all electron centres whether they are bonded atoms, π-bonded electrons or single electrons. GLP implicitly accomodates the dependence of interaction energies on molecular size shape and motion and only pure component data are required to calculate both like and unlike potentials. The net GLP potential between two freely rotating molecules is given by:

$$\Phi_{ij} = -\tfrac{1}{4}R^{-6}\sum_i \sum_j w_i w_j F_{ij}\left(\alpha_i\langle m^2\rangle_j + \alpha_j\langle m^2\rangle_i\right) \qquad (3.24)$$

where w is the number of structurally equivalent atoms, i or j and α and $\langle m^2\rangle$ are, respectively the polarisability and mean-square electric dipole moment of the interacting bonded species that can be deduced from an inert gas approximation. F_{ij} are factors which depend on molecular structure and can be calculated from given analytical expressions. This equation is used to calculate the value of Φ_{12} directly. The parameter r determines the relative number of whole molecular contacts in the coordinate shell structure. This is taken to be the the ratio v_2/v_1 where v_1 and v_2 are taken to be the Van der Waals molecular volumes.

This method is subject to several limitations due to the means of determining Φ_{12}. These are:

1) Highly polar or hydrogen-bonded molecules cannot be represented because the dispersive forces cease to dominate the mixture.

2) It may not be used for pressures above 6 atmospheres due to the assumption of ideal gas phase behaviour. This limit has been adopted given that most of

the work performed using this method has employed small non-associating molecules.

3) The fundamental assumptions exclude long chain molecules greater than C_6.

3.4.1 Implimentation of the AGAPE model using a one point-fitting technique (AGAPEFIT.).

The one point-fitting method has been developed to overcome the limitations of the original GLP technique. A full discussion of this method is given together with sample results by McCoubrey et al. (1993). They used two techniques; the first uses the Gibbs free energy at the equimolar composition to calculate the value of Φ_{12}, the value of r being fixed by the ratio of Van der Waals volumes. The second technique simultaneously fits the values of Gibbs free energy and excess enthalpy at the equimolar composition to give both the values of r and Φ_{12}. The values of r and Φ_{12} were then used to correlate and predict VLE and enthalpy data.

Twenty five mixtures were initially examined at low to moderate pressures. Satisfactory results were obtained for small molecules, cryogenic mixtures, polar and large molecules (e.g. alcohols and methylethylketone).

While properties used in the fitting procedure were Gibbs free energy and excess enthalpy it is possible to substitute alternatives (i.e. vapour phase compositions, activity coefficients or pressures).

4.1 Introduction

Experimental methods to measure vapour-liquid equilibrium data were first developed in the early 1900s as a foundation for a theoretical treatment of non-ideality. More detailed extensive work was not conducted until reliable data became a necessity for industrial design. Much of this early work is limited to comparatively few mixtures and later workers by application of consistency tests have shown much of the data to be unreliable. As a result many improved techniques have evolved and the important ones are reviewed in this chapter.

In recent years many attempts have been made to predict vapour-liquid equilibrium data accurately using various proposed models of phase behaviour. It is still not possible to achieve this using pure component property data alone for all mixtures and conditions. An accurate prediction of phase equilibrium data must therefore, at some stage, use experimental data for the evaluation of parameters in the appropriate models. Data sets of high accuracy are required for performance evaluation of individual models for particular mixtures, since no individual model can claim to represent all mixtures well.

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

The design and construction of equilibrium stills can be a source of various errors. So far, it has not been possible to construct a still which would yield thermodynamically completely consistent data for all mixtures. Since the errors which arise are to a certain extent dependent on the nature of the mixture concerned (relative volatility, heat of vaporisation, etc.) they need not have the same importance in all mixtures. This has led to the design of different types of apparatus, suitable for different types of mixture, which can be classified into the following groups:

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

This discussion will include the most important and recent developments in determining vapour-liquid equilibrium data. More general reviews of the methods are available in Abbott (1986), Marsh (1978) and Malanowski (1982a&b). A review of older methods maybe found in Hala et al. (1967).

4.2 Differential Distillation Methods

Differential distillation methods are the oldest method of direct determination of vapour-liquid equilibrium data. Its main virtue was simplicity but marked disadvantages have now rendered it obsolete. This technique involved distillation of a large quantity of the mixture under consideration to produce a very small sample of condensate for analysis, since the composition of the liquid phase must remain constant. Large errors could also arise by condensation of vapour on the cold walls of the distillation flask at the beginning of the experiment.

4.3 Circulation Methods

The circulation method has been widely used for experimental data determination at medium and low pressures. Many different designs of circulation stills exist but all are based on the same principles of operation. A liquid mixture is charged to a boiling flask, boiled and the vapour produced is condensed into a separate receiver. Once the vapour condensate receiver is full the condensate is allowed to overflow back to the boiling flask. As circulation continues the vapour sample becomes enriched in the more volatile component until a steady state is attained. Either all the thermodynamic parameters (temperature, pressure, liquid and vapour compositions) are then measured simultaneously or only those sufficient for the determination of the equilibrium conditions.

Malanowski (1982a), proposed the following criteria which should be fulfilled by a properly designed recirculating still:

(1) The still should have a simple form.

(2) Small amounts of materials should be required.

(3) Facilities should be incorporated allowing accurate measurement of pressure and temperature.

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

(5) Neither partial condensation of vapour or overheating should occur on the surface of temperature-measuring sensor.

(6) No liquid drops should form in the vapour stream leaving the equilibrium chamber.

(7) Recirculated vapour or its condensate should be perfectly mixed with the liquid phase to prevent secondary evaporation.

(8) There should be no fluctuations in the recirculated stream's flow or composition.

(9) No pockets should allow accumulation of material outside the recirculation pathways.

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

The types of circulation apparatus can be segregated by number and thermodynamic condition of the recirculated streams, into the following groups:

(A) Vapour circulation methods;
(B) Condensation recirculation methods;
  (i) Liquid condensate recirculation;
  (ii) Revaporised condensate recirculation;
(C) Recirculation of liquid phase and vapour condensate.

4.3.1 Vapour circulation methods.

The vapour recirculation method, proposed initially by Inglis (1906) was an attempt to overcome uncertainty in attaining the steady state in flow methods. Figure 4.1 illustrates the mode of operation of this type of apparatus. A pump P_u recirculates vapour though the stationary liquid via a heat exchange system (thermostat) until steady state is reached. Then pressure temperature and phase compositions are measured.

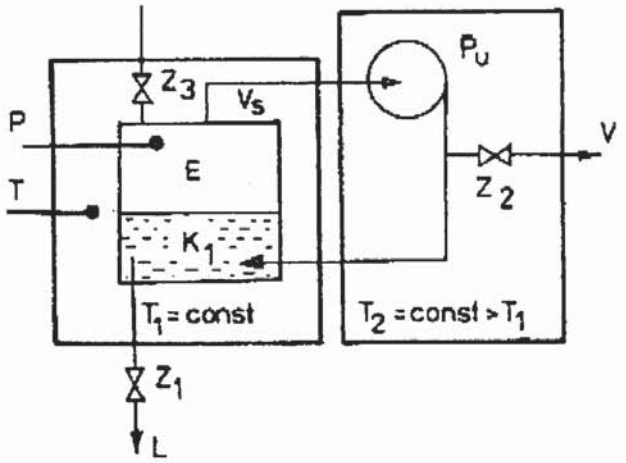


Figure 4.1 Principle of operation of vapour recirculation still. E equilibrium chamber chamber; K_1, liquid phase container, P, pressure gauge, P_U vapour pump, T thermometer, T_1, T_2, constant temperature baths, V_S vapour stream, Z_1 liquid phase (L) sampling valve; Z_2 vapour phase (V) sampling valve; sampling valve; Z_3 valve for still degassing.

This technique appears simple but numerous complications can be encountered in practical applications. In order to attain steady state operation the total volume of the system pressure and temperature must remain constant or the quantities and hence compositions of the phases will vary. However, pressure fluctuations are present in the system caused by pumping of the vapour stream through the liquid though these can be reduced by improved pump design. If the vapour velocity is reduced it has the dual benefit of decreasing pressure differences in the cell due to hydrostatic head and liquid entrainment in the vapour stream. The change of vapour phase composition due to this small pressure difference is generally not significant, although the error introduced may be large in the critical region when the vapour is very compressible. In order to minimise liquid entrainment, special separators can be placed in the vapour space of the still. Any condensation of vapour during recirculation must also be prevented. This may be accomplished by placing only the equilibrium chamber in the constant-temperature bath and maintaining the rest of the system at a temperature higher than the vapour dew-point. Isobaric conditions must be maintained during sampling, since vapour samples are removed without condensation, the quantity of sample removed may be too small for accurate analysis unless the operating pressure is high.

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

4.3.2 Condensate Recirculation Methods

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

After the steady state has been achieved, boiling is stopped at once, for example by increasing the pressure in the stabilising system M, to prevent non-equilibrium distillation in the container K_2. Samples of liquid and vapour condensate are withdrawn for analysis from vessels K_1 and K_2 through valves Z_1 and Z_2 respectively. After withdrawal of the samples, the still can be refilled and the process repeated.

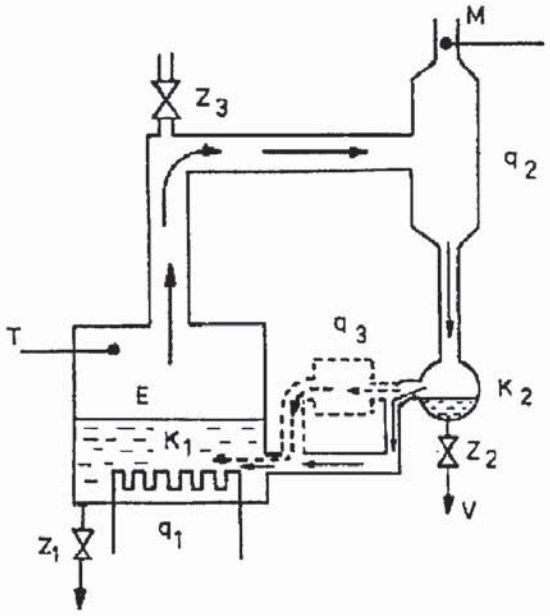


Figure 4.2 Principle of operation of the vapour condensate circulation method; dotted lines indicate the alternative pathway of the condensate when it enters the equilibrium chamber as vapour. K_2 vapour condensate receiver; M to pressure system; q_1 heater of boiling liquid; q_2 vapour condenser; q_3 heater to flash vapourise condensate.

The main drawbacks of this type of apparatus are:

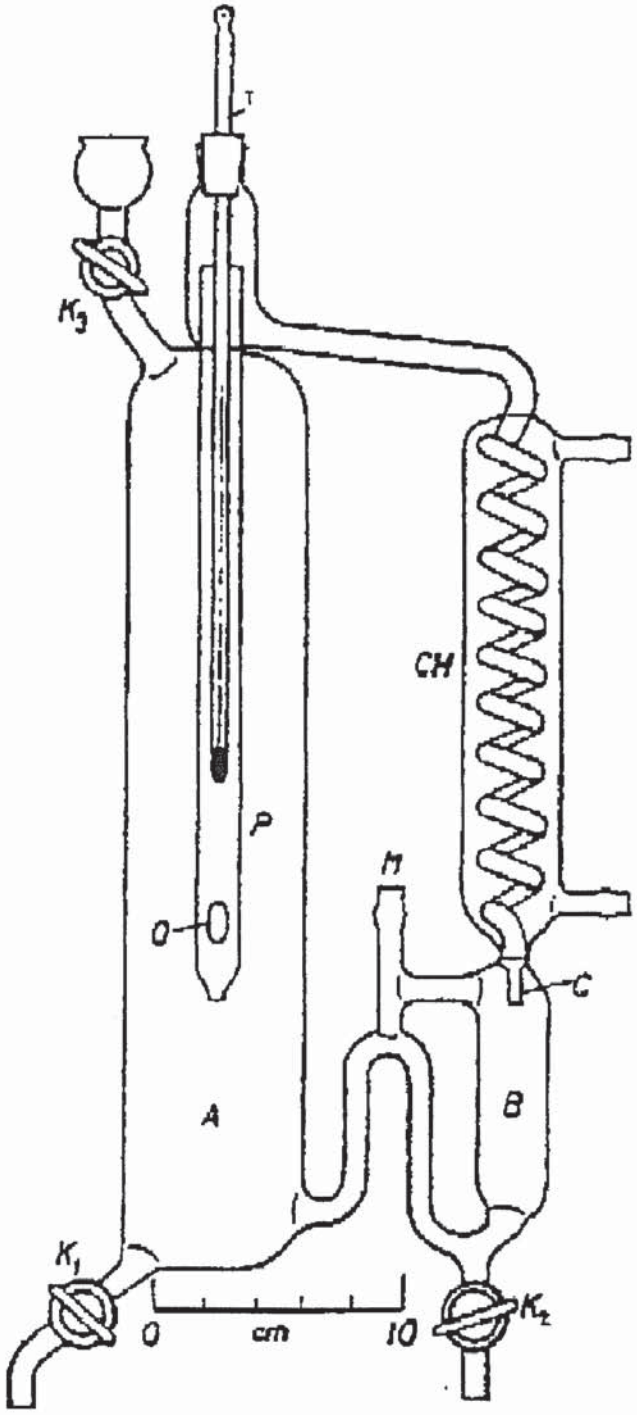
(1) There is partial condensation of vapour after stopping the apparatus;

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

(3) It is difficult to obtain uniform composition in vessel K_1.

4.3.2.1 Condensation recirculation methods; - Liquid condensate recirculation.

The first truly successful design using this mode of operation was proposed by Othmer (1928) (see figure 4.3). This still type was used extensively between 1930 and 1940 and was the subject of over 150 modifications. The aim of these many modifications was to remove the weaknesses of the original still (see the main drawbacks of condensate recirculation methods) but none of the attempts were truly successful. The chief factor which was never satisfactorily addressed was how to measure the boiling temperature accurately. A large amount of experimental data produced using a version of this still exists, mainly at atmospheric pressure, but has been shown to be of low reliability by the application of consistency tests.



.Figure 4.3 Othmer (1928) still; A = boiling vessel; B = receiver; K_1 K_2 sampling cocks; K_3 = vent cock; T = thermometer; CH = cooler; P = vapour tube; O = inlet; C = drop counter; M = to manostat.

Figure 4.4 Othmer (1946) moderate pressure still.

Othmer (1946) developed a moderate pressure version of the 1928 still (see figure 4.4) for use up to 14 bar in response to a demand for moderate pressure data but this again was subject to the same operational problems as the atmospheric still. In addition to which, natural circulation at higher pressures is less efficient and an "all" stainless steel apparatus would prevent observation of the still in operation.

4.3.2.2 Condensate recirculation stills; Revaporised condensate recirculation methods.

Jones et al. (1943) developed a still which vaporises the condensate before returning it to the still equilibrium chamber. This still produced data of very high accuracy and has been the subject of over 60 publications aimed at improving and simplifying its operation.

Figure 4.5 Jones, Shoenborn and Colburn (1943) Still: F, Tube for pressure equalisation for sample withdrawal; G, capillary for smoothing flow of condensate to vaporiser; q_3, q_4 heaters for overheating vapour streams; R, tube for bubbling vapour stream through residue chamber K_1; Z_3, valve for maintaining vacuum during withdrawal of samples.

The Jones Still (1943) is shown in figure 4.5. It consists of a heated residue-chamber K_1 and overhead condenser q_2 leading to a condensate chamber K_2 and a flash vaporiser q_3. The condensate flows under its own hydrostatic pressure through a three-way stopcock Z_3 and a capillary into the vaporiser q_3, which is a heated tube connecting K_1 and Z_3. The liquid level in K_2 remains constant. The capillary G is present to smooth the flow into K_2 and to prevent fluctuations in the vaporisation rate. The temperature in q_3 is maintained slightly above the equilibrium temperature. The vapour generated enters K_1 almost at its base via a tube R which directs the vapour stream upwards through the liquid and against the thermometer well. This ensures agitation of the residue liquid and allows measurement of temperature. The residue chamber K_1, is heated. The heater q_1 compensates for heat losses so that the quantity of vapour leaving K_1 is the same as that entering. The vapour flowing from K_1 to the condenser q_2 is slightly superheated in the heater q_4 in order to prevent condensation and refluxing of the condensate. The condensate flowing from q_2 to K_2 is recycled and when steady-state conditions have been obtained liquid and vapour samples are withdrawn from the residue (K_1) and condensate (K_2) chambers. The stopcock Z_3 allows vacuum to be maintained and the liquid to be sucked back during sample withdrawal.

Proper operation of this type of still is difficult to achieve. The chief difficulty encountered with this equipment is the balancing of the heat losses from the residue chamber K_1. Careful supervision is required in controlling the heat input into this still making it tedious to operate and requiring several hours to achieve equilibrium. Bubbling of the vapour through the liquid leads to pressure drop within the still which diminishes the accuracy of the pressure and temperature determinations. Thus these methods involving recirculation of the vaporised condensate have become less popular among experimental thermodynamicists.

4.3.3 Liquid-phase and vapour condensate recirculation methods.

The first stills using this principle were developed to measure boiling points. Cottrell (1919) developed a still, using an athermal lift pump (Cottrell pump) to throw a mixture of vapour and liquid on to a temperature sensor to allow very accurate

measurement of boiling points. This apparatus was further developed by Swietoslawski (1924), (see figure 4.6) and is considered to be the most accurate for the determination of boiling points in the pressure range 5-200 kPa (Leslie and Kuehner, 1968).

Figure 4.6 Swietoslawski ebulliometer (1924). A, heated bulb providing thermal lift of Cottrell pump; B, equilibrium chamber; C, tube preventing heat losses; D, condenser; I, Cottrell pump tube; II, condensate and liquid down stream tube; a-a liquid level.

The next natural progression from the Swietoslawski ebulliometer (1924) was development to allow simultaneous determination of pressure temperature and

composition of both phases. The first circulating still, which had the capability for withdrawal of liquid and condensate samples after temporary cessation of circulation by pressure increase, was proposed by Lee (1931), figure 4.7. Gillespie (1946) introduced two important modifications to the Lee still, i.e. the separator for the liquid and condensate streams and the facilities for withdrawing samples without interruption of boiling (figure 4.8). This still has the basic arrangement of the Swietoslawski ebulliometer, and gained high popularity after it was found by Coulson et al. (1948) to be greatly superior to stills with vapour condensate circulation (Othmer, 1943) and even to those modified with an additional Cottrell pump (Scatchard et al. 1938).

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

Brown (1952) modified the Gillespie still as show in figure 4.9. The electrically controlled valves are very useful as they permit the withdrawal of samples of liquid and condensate without causing interuption of the circulation. This arrangement also eliminates the error arising for the partial evaporation of the condensate after connecting the instrument with the external atmosphere and simultaneously prevents the contamination of the contents of the receivers with liquid flowing down the walls after stopping the still. The smaller cooler C_3 serves to cool the residual liquid returning from the droplet separator before its mixing with the condensate stream from the receiver. This completely eliminates the possibility of non-equilibrium vaporisation in the distilling chamber. This instrument gives very precise results even with mixtures having a high relative volatility.Its most important drawbacks are the very long time, up to four hours, necessary to achieve steady-state operation, and the large charge size required (200 cm^3).

Figure 4.7 Lee (1931) recirculation still; C condenser; E equilibrium chamber; H_1 Heater providing thermal lift to Cottrell pump; M to pressure system; S_2 liquid phase receiver; T temperature sensor; W Cottrell pump; Z_1 vapour condensate sampling valve.

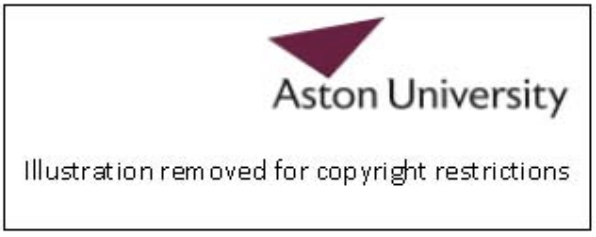


Figure 4.8 Gillespie still (1946); A, mixer for vapour and condensate streams; C_1, vapour condenser; C_2, cooler; K drop counter; R, separator for liquid and vapour phases E equilibrium chamber; H_1 Heater providing thermal lift to Cottrell pump; M to pressure system; S_2 liquid phase receiver; T temperature sensor; W Cottrell pump; Z_1 vapour condensate sampling valve.

Figure 4.9 Brown still (1952); C_1, vapour condenser; C_2, cooler;C_3 Liquid cooler; K drop counter; R, separator for liquid and vapour phases; H_1 Heater providing thermal lift to Cottrell pump; M to pressure system; S_2 liquid phase receiver; T temperature sensor; W Cottrell pump; Z_1 vapour condensate sampling valve.

Ellis (1952) derived another apparatus from the still of Lee (1931) which has provided good results, as a result mainly of its simplicity and is shown in figure 4.10. The heterogeneous mixture flows through the glass spiral of several turns which functions as the Cottrell pump and spurts on the thermometer well. The still is charged with about 250 ml of the mixture and equilibrium is reached after operating for one hour. The attainment of equilibrium was judged by the constancy of the thermometer readings and when the distillation rate is such that 40-70 drops per minute of condensate fell from the finger condenser.

Figure 4.10 Ellis still (1952): C_1, vapour condenser; C_2, cooler; R, separator for liquid and vapour phases; H_1 Heater providing thermal lift to Cottrell pump; M to pressure system; S_1 condensate receiver; T_2 temperature sensor; W Cottrell pump;Z_1 vapour condensate sampling valve; Z_1 liquid sampling valve;V_2 drain valve.

This still has the same disadvantages as the Brown still, but owing to its simplicity is much easier to operate. Ellis tested his still with four types of mixtures formed by close-boiling or wide-boiling components. In both cases, mixtures close to ideality and strongly non-ideal were tested. The resulting data were compared with those measured by Othmer (1943) and Fenske et al. (1947), and were found to correlate more favourably with the Gibbs-Duhem equation than was the case for the data from other stills.

An interesting apparatus suitable even for mixtures of very high relative volatility was proposed by Dvorak and Boublik (1963) and is shown in figure 4.11. They emphasised the importance of thorough stirring, in both the liquid and the condensate receivers.

Figure 4.11 Dvorak and Boublik (1963) still; C_1, vapour condenser; C_2, cooler; K drop counter; R, separator for liquid and vapour phases E equilibrium chamber; H_1 Heater providing thermal lift to Cottrell pump; M to pressure system; S_2 liquid phase receiver; T temperature sensor; W Cottrell pump; Z_1 vapour condensate sampling valve.

One of the most advanced stills in this group was proposed by Raal, Code and Best (1972) and is featured in figure 4.12. The still contains the excellent mixing characteristics of the Jones Colburn still (1943) and utilises a novel adaptation of the Cottrell pump to provide accurate temperature measurement and ensure adiabatic operation of the equilibrium chamber. As can be seen in figure 4.12, the Cottrell pump is the annulus between the inner equilibrium chamber and the outer chamber, where a mixture of liquid and vapour is propelled over the thermocouple well. The vapour-liquid mixture in the 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 to equilibrium with the vapour bubbling through it. The Raal et al. (1972) design had been shown capable of producing remarkably accurate vapour-liquid equilibrium data for highly non-ideal alcohol-hydrocarbon mixtures.

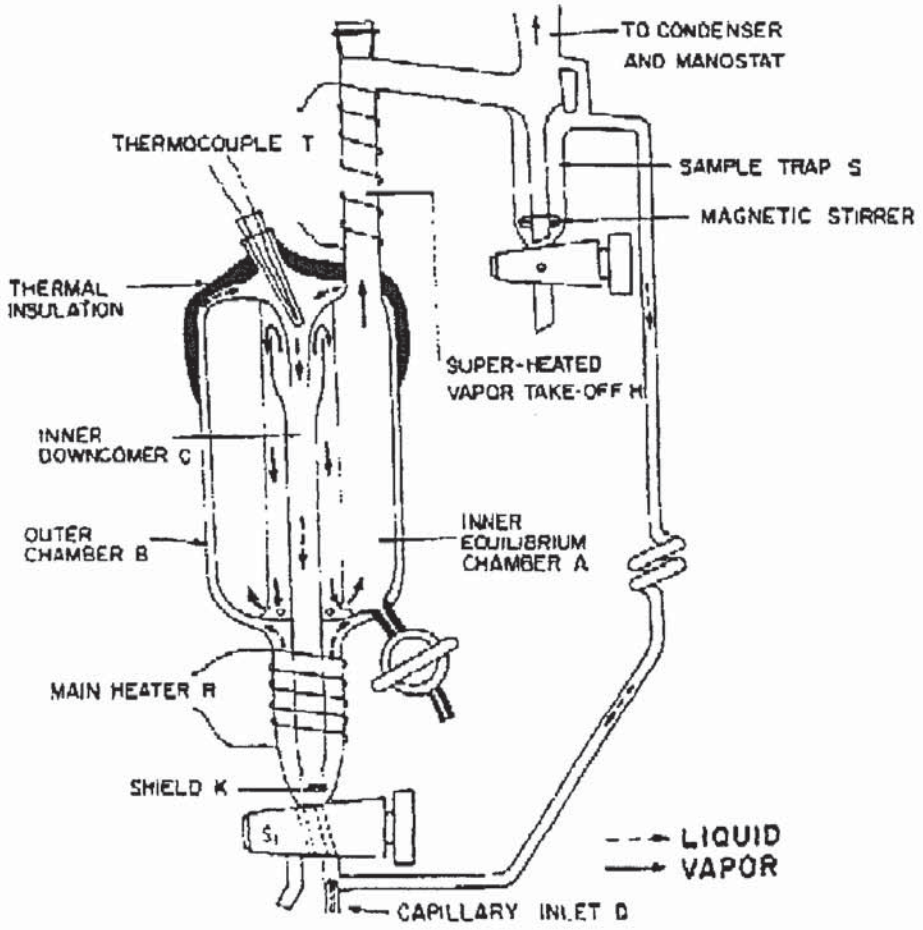


Figure 4.12 Raal, Code and Best still

Raal and Brouckaert (1992) proposed a recirculating equilibrium still for the determination of vapour-liquid equilibrium data for mixtures with partial liquid miscibility. The design shown in figure 4.13 differed only in detail from the Raal, Code and Best still. Capillary tubes were introduced in the condensate return line and in the liquid return line from the vapour-liquid disengagement chamber as shown. Rapid and effective stirring, particularly important in regions of partial liquid miscibility, was introduced in the condensate and boiling chambers. A split downcomer in the condensate receiver has subsequently been adopted for partially miscible mixtures.

Figure 4.13 Raal and Brouckaert (1992)

Jenkins and O'Donnell (1980) developed a modified version (Mark I) of the Raal et al (1972) still. This still was designed to run at pressures of 1 atmosphere or less. This still is described in full in chapter 5. The main differences between this still and the one proposed by Raal, Code and Best are:

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

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

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

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

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

Rogalski and coworkers (1977, 1980) returned to the Sweitoslawski ebulliometer as a starting point for their new equilibruim still apparatus shown in figure 4.14. The mixture boils in an electrically heated container H_1 . Powdered glass is sintered on the inside walls of this container, providing an activated surface to obtain steady boiling. The vapour generated provides gas lift via a Cottrell pump in the tube W, and the continuous stream, consisting of vapour and overheated liquid, is delivered into the equilibrium chamber E. This stream hits a thermometer well T. The expansion caused by the impact results in the equilibrium temperature being established on the outside wall of the thermometer well. In order to minimise heat losses, the equilibrium chamber is placed inside a vacuum jacket J. The liquid and vapour streams separate in the equilibrium chamber E. The vapour stream leaves E through a large-bore tube leading to a condenser, when it is totally condensed. This large-bore tube is heated using the

Figure 4.14 Rogalski (1977) Glass ebulliometer for atmospheric and sub-atmospheric use.

Figure 4.15 Malanowski (1993) moderate pressure ebulliometer. 1= equilibruim chamber; 2 = condenser; 3 = drop counter; 4 = vapour sampling valve; 5 = liquid sampling valve; 6 = mixing device; 7 = cottrell pump; 8 = feed valve; 9 = thermometer pocket; 10 pressure connection.

heater H_2 above the equilibrium temperature, to prevent partial condensation and refluxing, which may affect the composition of the condensate leaving the condenser C_2. The condensate then flows through a drop counter (flow meter) K and condensate container S_1 to the mixing chamber A, where it is mixed with the liquid flowing from the equilibrium chamber E via the liquid container S_2. Perfect mixing is very important for minimisation of boiling-temperature fluctuations. Each still is equipped with two mixing devices, A and B. The mixed stream of uniform composition re-enters the Cottrell pump H_1 where it is partly evaporated.

Malanowski et al. (1993) went on to develop a moderate pressure version of this apparatus for use at pressures upto 3 MPa. The still is shown in figure 4.15. The new still is of all stainless steel construction with the exception of the drop counter which is made from thick walled glass tube. The accuracy of measurements with this apparatus have been shown to be 0.01 K and 0.1 kPa for pure substances and for close boiling mixtures. For wide boiling mixtures, > 20 K the accuracy drops to 0.02 K and 0.3 kPa. The stability of the apparatus drops as the relative volatility of the mixture increases.

4.4 Static Methods

In static methods of direct experimental determination of vapour-liquid equilibrium data, the vapour and liquid phases of a mixture are maintained in contact within an evacuated chamber which is immersed in a thermostatically-controlled water bath. The two phases are vigorously agitated and sampled for analysis. Agitation is provided by either stirrers or shaking of the entire cell or use of pistons to move the cell or a combination of the above techniques. The method sounds simple but removing even a small sample for analysis affects the equilibrium. The problem of sampling has been reduced by only removing very small samples for analysis by chromatographic methods. Various approaches have been adopted to minimise the sample volumes, these are:

1) Capillary lines. See Wichterle and Wagner (1987).

2) Fast acting pneumatic or electromagnetic valves. See Figurier et al. (1980).

3) Detachable microcells. See Legret (1981).

Another disadvantage is the extensive and careful degassing of the components required.

Static methods can be segragated into two categories:

1) Constant volume cells.
2) Variable volume cells.

4.4.1 Constant volume static cells.

Variations of constant volume static cells have been proposed by Robinson (1978, 1979), Renon and Richon (1983), Melpolder (1986), Nakayama et al. (1987), Figurier et al. (1980) and Legret (1981)

An example of a static still is the apparatus of Wichterle and Hala (1963). They used a constant volume static method to carry out semimicro determination of vapour-liquid equilibrium data in multi-component mixtures at isothermal conditions. Their method was based on the sampling of very small volumes of the vapour phase which were then analysed by gas chromatography; the method makes possible the determination of equilibrium data on a small liquid mixture using only 2 ml per data 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 the components in the two phases. It is not necessary to reach the equilibrium partial pressures because it is sufficient to measure the concentration ratios of the components in order to determine the relative volatility. Very small vapour samples make it possible to obtain a large set of analytical data while leaving the concentrations in the liquid phase unchanged. A moderate pressure

version of this apparatus was proposed by Wichterle et al. (1974) which was capable of measuring two-phase mixtures up to 45 atmospheres.

4.4.2 Variable volume static cells.

Typically this type of apparatus uses movement of a piston to change the volume of the cell to increase or decrease the pressure. This type of apparatus is increasingly being designed with windows to allow observation of the cell contents which eliminates the possibility of missing the formation of multiple phases. Variations of this type of apparatus have been proposed by Robinson et al. (1985), Thodos et al. (1978), Huang et al. (1985), and Li et al. (1981).

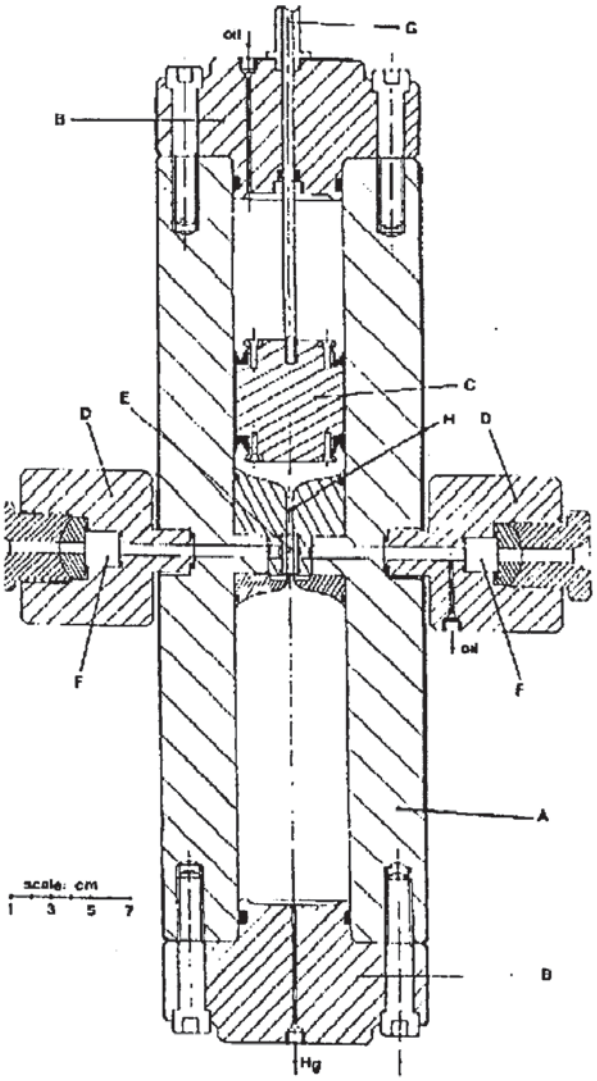


Figure 4.16 Ashcroft, Shearn and Williams high pressure equilibrium cell. B = End caps; C = pistons; D = window assemblies; E = Glass capillary; F = toughened glass windows; G = piston indicating rod; H = sampling valve

An example worthy of special consideration is the apparatus of Ashcroft, Shearn and Williams (1983) designed to operate up to 690 bar pressure. The static cell design for this apparatus is shown in figure 4.16. The static cell is mounted in a thermostat air bath with temperature control to $0.1^{o}C$. Pressure is applied to the cell by mercury in the lower section and by a steel piston actuated by hydraulic oil in the upper section. Dual action pumping of these two fluids allows the cell contents to be raised and lowered without pressure change. Visual observation of the phase boundaries, by means of a mirror and optical system, was made through the window assembly, D, and the glass capillary tube E, through which the system could be moved back and forth. A measuring rod, G, equipped with a vernier scale is used for the accurate location of the piston, thus allowing accurate determination of phase volumes simultaneously with VLE determinations. Sampling uses a micro sampling valve connected on line to a Pye 204 chromatograph. By manipulation of the position of the cell contents samples of each phase can be withdrawn for analysis. The cell is bought to equilibrium by mechanically rocking the still for 3 hours between each data point determination.

4.5 Total pressure methods.

The Total Pressure approach, sometimes abbreviated to P-T-x method, eliminates the need to separate the vapour and liquid phases and their analysis, in favour of the direct determination of the temperature, pressure and liquid-phase composition. The essential feature of this method is the measurement of the total pressure of the mixture as a function of composition at constant temperature. The vapour-phase composition is obtained by calculation from the observed saturated vapour pressure, as a function of liquid phase composition. The P-T-x method has earned its popularity for vapour-liquid equilibrium measurements as a fast and efficient method, although only suitable for binary systems.

Total pressure measurements can be performed in two types of apparatus ebulliometers discussed in section 4.3.3 and static cells. Static cells have proved particularly useful at low pressures, since no boiling takes place in static cells the method eliminates the bumping and unsteady state boiling frequently incurred at low pressures. The main draw back of this method is that a suitable theoretical model is required to obtain the

vapour phase compositions which limits its applicability in strongly associating systems.

Static equilibrium cells dedicated to determination of P-T-x data have been proposed by Ljunglin and Van Ness (1962), Gibbs and Van Ness (1972), Jenkins and Smith (1975), Ronc and Ratcliffe (1976), Young et al. (1977) and Mentzer, Greenkorn and Chao (1982).

Gmehling and Kolbe (1985) proposed the static apparatus shown in figure 4.17 for the determination of data in the pressure range 1- 10 bar to produce four isothermal data sets for the mixture ethanol-water. The cell works by precise metered feeds of the pure components to the cell via manually operated piston injectors. The cell (figure 4.18) is immersed in a thermostatted bath and pressure measurement is made by a differential pressure transducer. The cell itself comprises a glass body with stainless steel top, the valves are built directly in to the lid to keep the vapour volume small and to avoid dead spaces. A magnetically driven stirrer is mounted in the cell and secured to the cell lid. The cell is agitated and takes 10 to 30 minutes to reach temperature equilibrium per data point.

Gmehling and Rarey (1993) developed a differential version of this static still to work up to 72 bar with a maximum differential pressure of 1 bar. The apparatus uses two cells one, working on pure component, only to measure the differential pressure between the mixture and reference cells. The apparatus has been automated, reducing operator contact time to 3 hours for a typical 4-day run on one mixture to produce 60 data points. A key factor in automation of this apparatus has been the design of a high precision injection pump which can be remotely controlled. The apparatus has been specifically designed to measure activity coefficients at infinite dilution, gas solubilities and thermal compressibilities of liquids. The apparatus has further been developed as a commercial apparatus by the Mitsubishi Corporation of Japan.

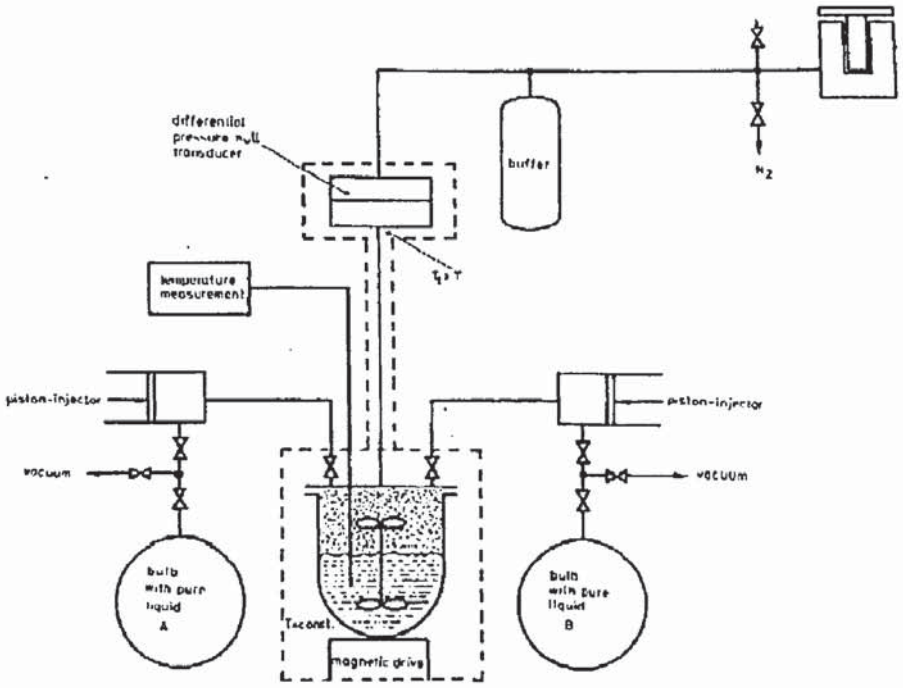


Figure 4.17 Layout of the Gmehling and Kolbe apparatus

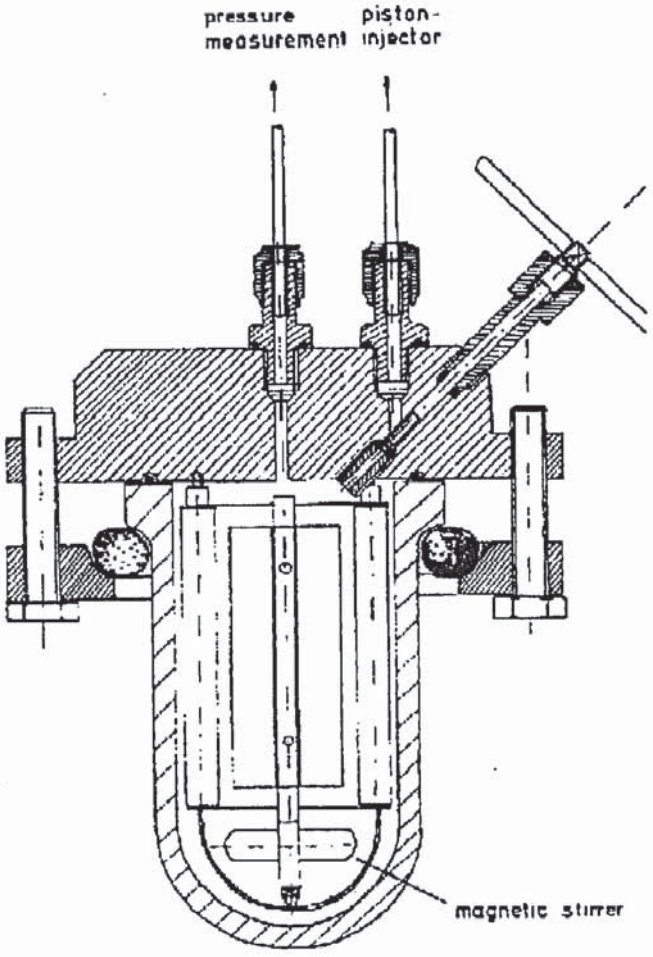


Figure 4.18 Section through Gmehling and Kolbe equilibrium cell.

4.6 Flow methods.

Dynamic flow stills have been specifically designed for use with systems of limited miscibility in the liquid phase, reacting mixtures or mixtures where prolonged exposure to the equilibrium conditions may cause degradation of the mixture components. These stills offer the option of rapid equilibrium determinations but consequently suffer a loss in accuracy.

These apparatus generally work by feeding a constant stream of vapour or liquid or both to the equilibrium chamber where the equilibrium temperature is measured, separation of the phases and sampling to determine the vapour and liquid compositions.

The first still using this method was developed by Colburn et al. (1943). A steady stream of mixed vapour, of known composition is bubbled continuously through the liquid sample contained in an adiabatic chamber. The liquid sample is formed from an initial heel and by partial condensation of the vapour. Equilibrium is judged to have been reached when the liquid sample volume and measured temperature remain constant.

One of the most successful flow stills was first proposed by Cathala (1950) and has been subject to modification by many people (see Marek (1955, 1956), Mamers (1965), Davies (1971) and Gibson-Robinson (1977)). The original Cathala still took vapour and preheated liquid, mixed them together in a contacting chamber and then passed the mixture up in to the adiabatic equilibrium chamber, where the equilibrium temperature was measured using a copper-constantan thermocouple. Equilibrium was achieved after 10 to 20 minutes when the recorded temperature changes were less than $\pm 0.05^{0}C$.

Cathala (1960) himself developed a modified version of the flow still (see figure 4.19). In this case the mixer-contactor, the equilibrium chamber, the de-entrainer and the vaporiser were constructed as a single unit. The liquid level in the vaporiser was

controlled and a magnetic stirrer was included to promote regular boiling whilst an air bleed was used to facilitate low pressure work.. Finally the mixer contacter and the equilibrium chamber were lagged and thermocouples used to measure temperatures to an accuracy of $\pm 0.05^{0}C$.

Alternative variations of dynamic flow cells have been proposed by Yesavage et al. (1986), Cruz and Renon (1979), Wang and Chao (1990), Hutchensen et al. (1990) and Thies and Paulaitis (1984).

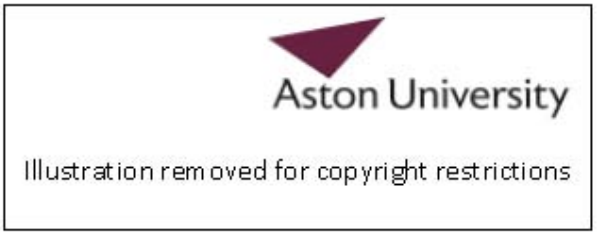


Figure 4.19 Cathala Flow Still (1960)

4.7 Other methods.

These methods are normally based on variations of variable volume equilibrium cells and are generally referred to as bubble point-dew point methods. The basic mode of operation is to hold the temperature and composition constant and develop a P-V isotherm. Breaks in the P-V isotherm correspond to the molar volumes of the coexisting phases, thus indicating the bubble and dew points. Construction of the bubble point-dew point curves across the composition range permit the x-y compositions to be determined at constant pressure, see figure 4.20.

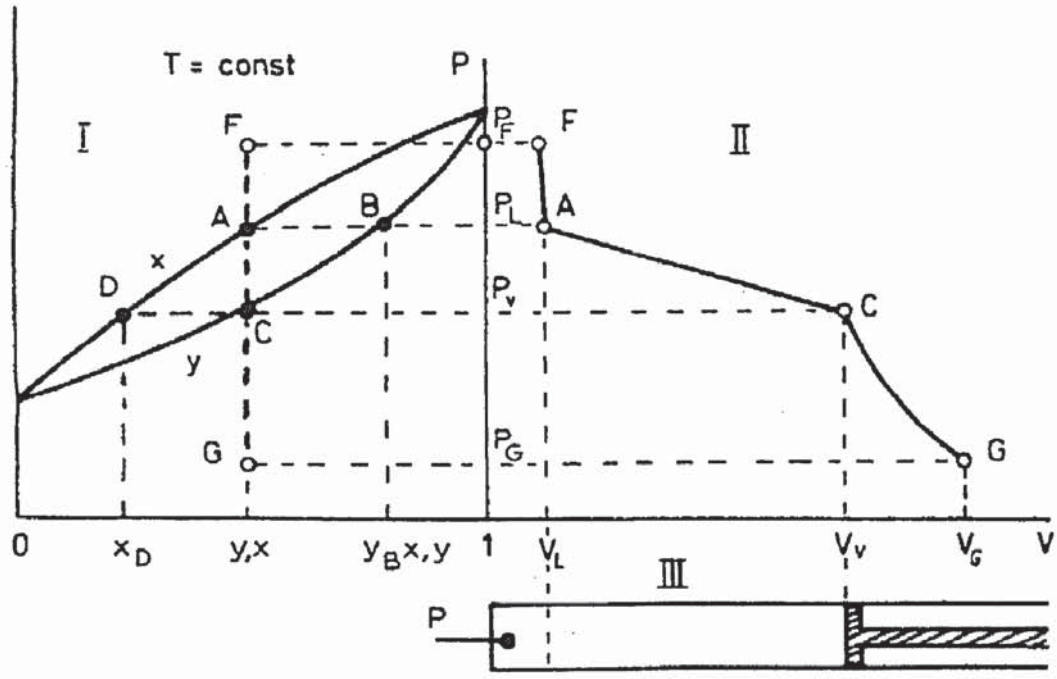


Figure 4.20 Principles of operation of dew point-bubble point method. I = Phase diagram showing change of state of sample in piston assembly, III. From the liquid composition x through the bubble point A and dew point C in to vapour of the same composition (y=x). II is the corresponding compression chart showing determination liquid volume V_L and vapour volume V_v at the bubble point A and dew point C.

This diagram clearly shows that the bubble point is easy to determine by virtue of the sharp transition but the dew point is much more difficult. This method is also unsuitable for multi-component mixtures. For these reasons this method has not been widely used recently but it does have the major advantage that analysis of phase compositions is not required.

The experimental methods using the bubble point-dew point technique are reviewed for low pressures by Feller and McDonald (1950) and Malanowski (1982b). For pressures above 10 MPa the methods have been reviewed by Schneider (1975), Young (1978) and Eubank et al. (1980). An example of apparatus used for this type of measurement is the variable volume cell of Ashcroft et al. (1983), see section 4.5.1. Its use for bubble point measurement is described in detail by Ashcroft et al. (1994).

Chapter 5: Development, design and operation of a family of equilibrium stills to work at low to moderate pressures up to 35 Bar.

5.1 Basic design of borosilicate glass equilibrium still.

All the stills are based on the still developed by O' Donnell (1980) from the earlier very successful still of Raal, Code and Best (1972) (see Chapter 4). The basic design of the borosilicate glass equilibrium chamber is common to all versions of the apparatus and is shown as a diagrammatic cross-section in Figure 5.1. A vapour-liquid mixture is fed into the outer annulus which is 3 mm wide and has a glass spiral wound onto the inner surface to act as a guide for the vapour-liquid mixture. The success of this design is due to the design of this annulus which fulfils two purposes :

1. The spiral wound jacket forms a Cottrell pump which is effectively 0.5 m long giving a long residence time for the mixture to reach equilibrium.

2. The outer annulus acts as a vapour jacket holding the contents of the equilibrium still within 0.1 ^{0}C of the equilibrium boiling point.

The vapour-liquid mixture is then forced down the central thermometer pocket which is also wound with a glass spiral which increases the liquid residence time in the thermometer pocket to enable better measurement of the boiling point. The liquid is separated in the vapour-disengaging cup from the vapour and returned to the reboiler for recirculation. The liquid level is controlled in the vapour disengaging cup to provide a liquid seal to prevent condensation of vapour in a region not at the equilibrium temperature. From the disengaging cup the vapour is forced though six 2 mm diameter radially spaced holes into the middle annulus. The liquid sample is produced by partial condensation of the vapour in this annulus as the vapour bubbles though the condensing liquid sample. By producing the liquid sample in this manner the formation of the liquid sample is independent of the recirculating fluid and hence more likely to form a representative sample. The vapour after passing though the

liquid sample leaves the equilibrium chamber, is condensed and returned to the reboiler.

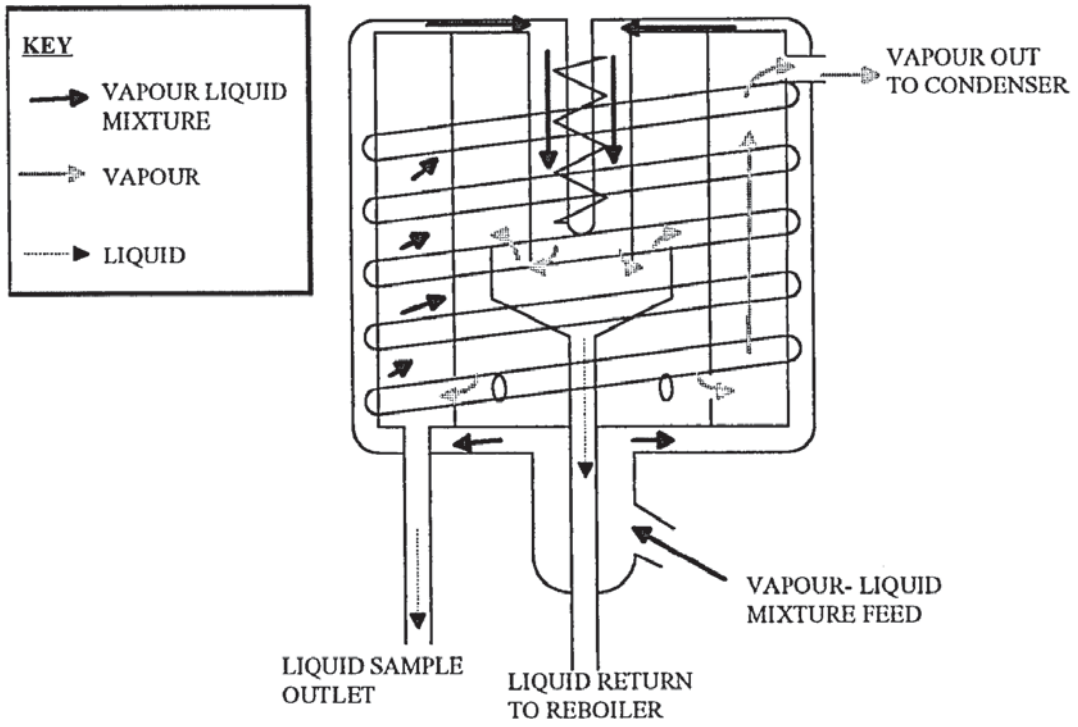


Figure 5.1 Basic design of borosilicate glass equilibrium still

5.2 Design of Russell, O'Donnell and Jenkins low pressure apparatus.

This still is a direct modification of the still developed by O' Donnell (1980) designed to incorporate improvements to overcome operational inadequacies noted from operation of the original apparatus. The O' Donnell apparatus is shown in figure 5.2. It is important to note at this point that the O'Donnell apparatus equilibrium chamber did not possess the glass spiral wound on the inside of the vapour jacket but the equilibrium chamber is otherwise identical to that shown in figure 5.1.

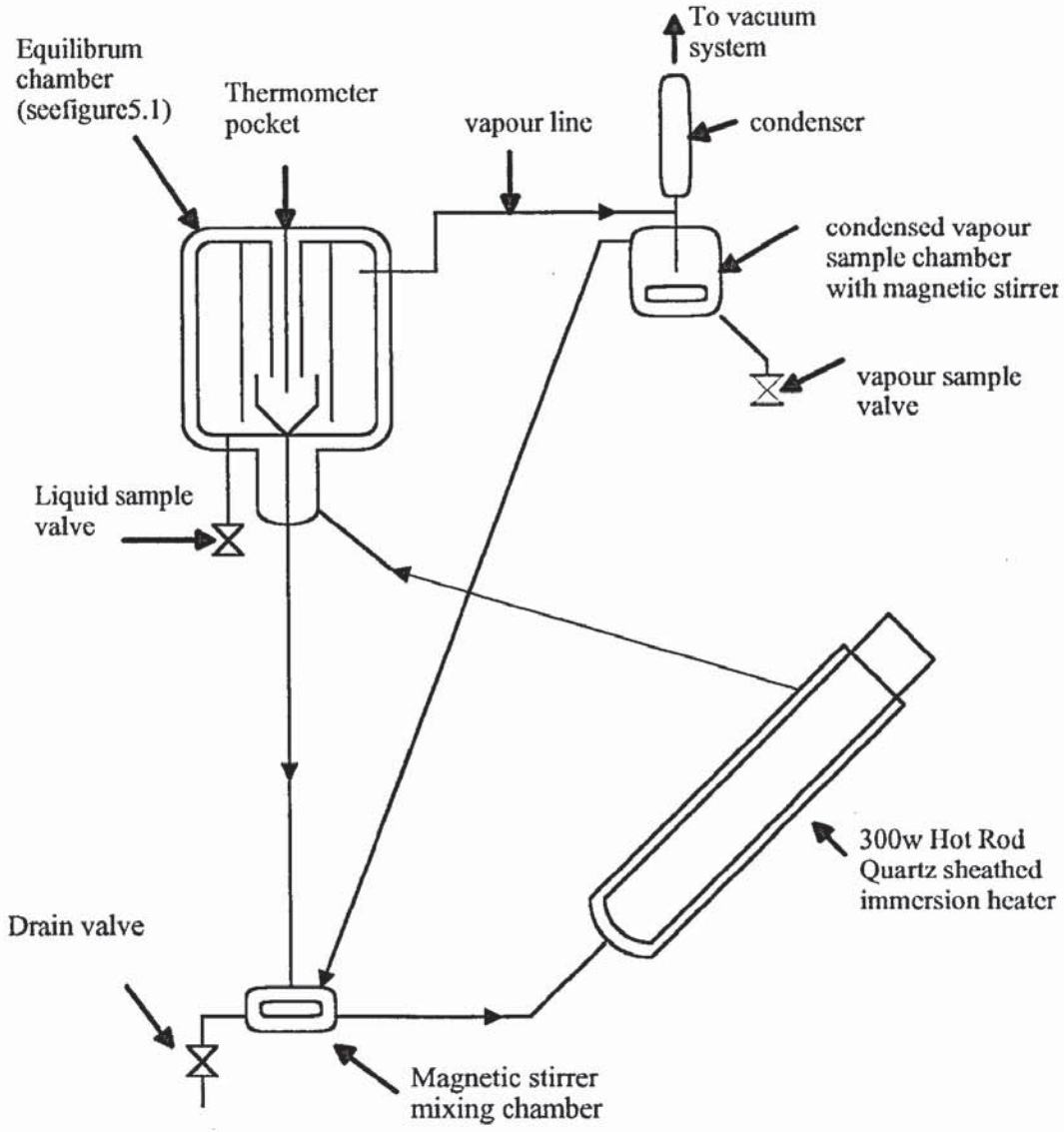


Figure 5.2 Diagrammatic arrangement of the O'Donnell and Jenkins low pressure still Mark 1

The Mark III version of the atmospheric still reboiler differs from the earlier version of the still in that the orientation of the reboiler has been changed to align the hot rod vertically. Mounting the reboiler vertically improves the performance of the thermosyphon which results in smoother boiling characteristics. The magnetic stirrer at the inlet to the reboiler fulfils two functions, it mixes the returning streams to give a homogeneous mixture to feed to the reboiler and imparts a minor pumping action to the liquid returning to the reboiler. Both of these actions help to smooth out the boiling pattern in the reboiler. The still can now be run satisfactorily under vacuum down to a pressure of 30 mmHg. Below this pressure the reboiler behaviour becomes erratic due to insufficient nucleation sites on the hot rod surface.

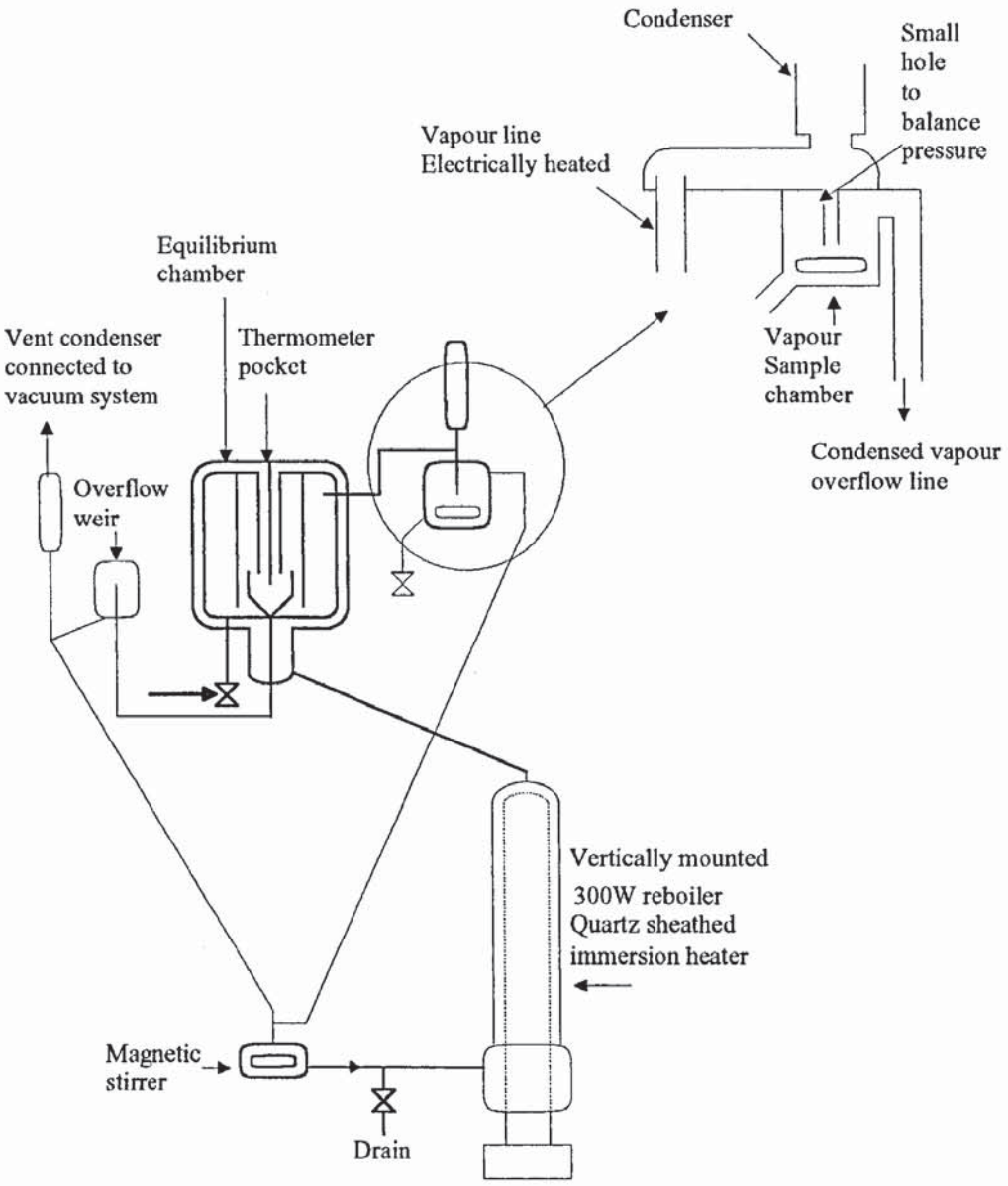


Figure 5.3 Diagrammatic arrangement of the Russell, O'Donnell and Jenkins low pressure still Mark III.

The vapour loop of the Mark III still has been modified as shown in figure 5.3. The vapour line leaving the equilibrium chamber is heated by electric tracing to 1^0C above the equilibrium boiling point of the mixture. The tracing prevents partial condensation of vapour before the condenser which may contaminate the liquid sample. In addition a weir has been placed in the vapour line as a physical barrier to prevent any condensed vapour returning to the equilibrium still. A 1 mm hole has been placed in the top of the down leg into the vapour sample chamber. This hole balances pressure in the vapour sample chamber with that in the condenser to allow the vapour sample to overflow.

The liquid line from the central cup of the still to the reboiler has been modified to incorporate a weir. The weir controls the liquid level in the central cup and prevents the still from flooding. The weir chamber is sealed with a PTFE/silicone rubber septum which allows a sample of the liquid stream to be taken whilst the still is running as a check on the final liquid sample.

The equilibrium chamber is lagged with 1 cm thick ceramic fibre rope above the central cup. This permits the observation of the critical portion of the still internals and prevents excessive heat loss from the top of the equilibrium chamber where heat losses may affect the equilibrium temperature measured. Operating instructions are given in Appendix 12

5.3 The Zain and Jenkins moderate pressure still.

The equilibrium cell is essentially the same as that shown in figure 5.1. As the equilibrium cell has to be contained in a steel pressure bomb (vessel), mounting the cell in the bomb would be made easier if all of the connections to and from the equilibrium cell passed through the bottom flange of the pressure vessel. Thus the still has been modified as shown in figure 5.4. The connection lines from the equilibrium chamber are different lengths to stagger the Rotolex joints to permit the clips securing the joints to fit inside the confined spaces of the pressure vessel without fouling the walls or each other.

Figure 5.5 shows a diagrammatic representation of the Zain and Jenkins still. The flange at the base of the pressure bomb is made of 316 stainless steel. This has four holes through which connection to the still is made. Each hole has a bored-through NPT to Swagelok connector in it. The appropriate line passes through each and then is connected (for the liquid/vapour feed, the vapour and liquid offtake lines) to Cajon glass-metal flexible connectors via standard Swagelok couplings. Each glass portion ends in a Rotolex cup which makes the connection with the appropriate ball joint on the equilibrium cell. Thus the glass cell is supported solely from the bottom flange.

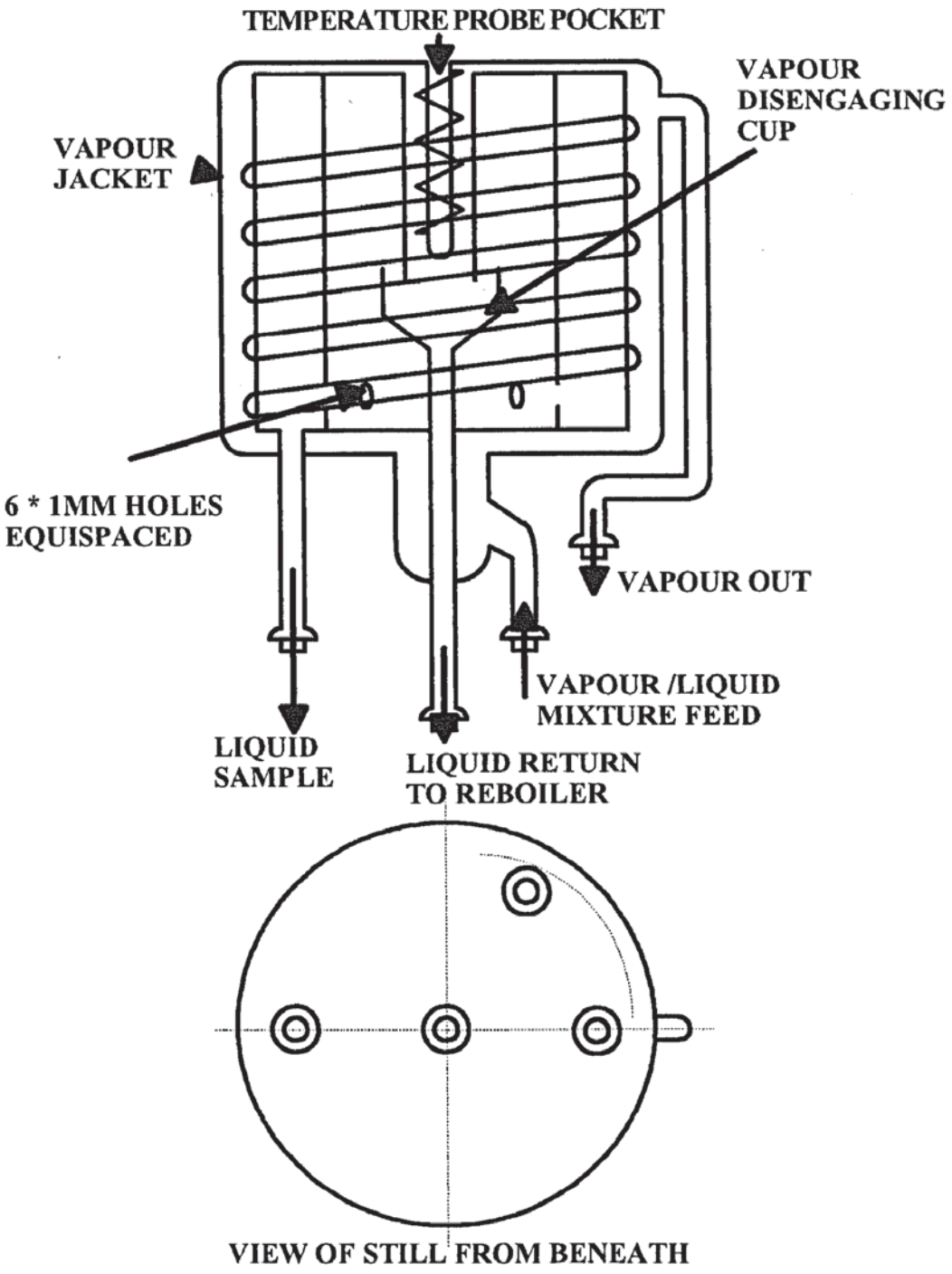


Figure 5.4 Zain-Jenkins borosilicate glass equilibrium still for moderate pressures

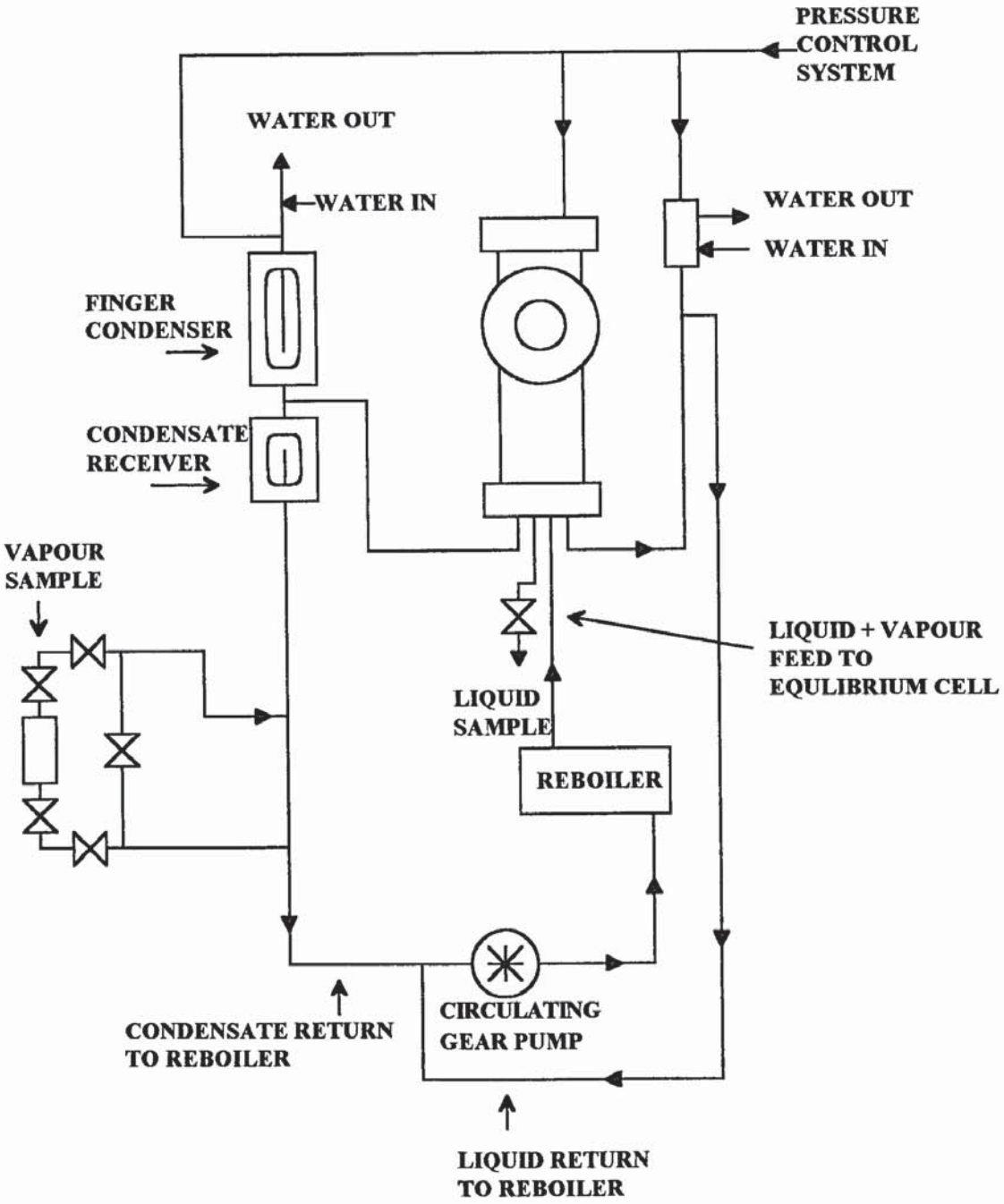


Figure 5.5 Diagrammatic representation of Zain-Jenkins moderate pressure apparatus .

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

It is essential to be able to observe the operation of the equilibrium still to ensure that it is operating correctly. To do this two windows are provided at the sides of the pressure bomb, but since these must not run at the temperature of the equilibrium cell itself, they are at the ends of the side arms, with further internal dividing glasses, close to the inner ends of the arms, reducing heat transfer by convection into the side arms. The bomb contents are viewed by placing a source of light in front of a window at one side of the pressure bomb, and looking at the equilibrium cell through the window at the other side of the pressure bomb.

Natural convection to provide circulation through the still is not used. Instead, a small graphite gear pump capable of working at pressures up to 35 bar is used to feed the reboiler. This pump is supplied with low voltage DC power from a constant current power source to give a steady flow. The reboiler is annular in construction and made of 316 stainless steel. The central tube contains a cartridge heater of a nominal 210 wattage. The reboiler is lagged using a mat heater, insulated and then sprayed with chrome aluminium spray paint.

If the only heat source were the reboiler, the still would never come to equilibrium because of the high thermal capacity of the pressure bomb. So three Hedin electrical mat heaters each of a nominal 310 wattage are provided along the vertical length of the pressure bomb. These electrical heaters are suitable for continuous operation at any surface temperature up to 200^{0}C. Their energy outputs are controlled separately through the use of three Variacs. The heaters are lagged using Contronic Corporation mouldable wet felts (mats) and then sprayed with chrome aluminium spray paint. This insulation material provides a lightweight resilient and highly efficient thermal insulation. As noted earlier, three chromel-alumel thermocouples measure the temperature profile up the pressure bomb; and the heaters outputs are adjusted to

maintain a nearly constant temperature profile, a degree or so above the equilibrium temperature measured in the equilibrium cell. The vapour line is also heated along its length to prevent condensation and the consequent high pressure drop in the line to the condenser. This is achieved by wrapping the vapour line around with a silicone-rubber encapsulated heating tape of a nominal 250 wattage. The heating tape is lagged using woven ceramic rope over-wrapped with woven ceramic self-adhesive tape.

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

(i) The sampling chamber which is made of 316 stainless steel,
(ii) five Whitey valves,
(iii) 1/8 " O.D 316 stainless steel tube from the condensate receiver to the circulating gear pump.

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

The guard condenser prevents any escape of vapour into the pressure system from the liquid overflow from the equilibrium cell. The level control device is a 316 stainless steel T-piece used to provide a simple weir-type overflow. It is arranged so that the free liquid surface in the vapour-liquid separating cup in the equilibrium cell is at a

suitable height, i.e. neither falling below the constant temperature zone in the equilibrium cell nor overflowing into the central volume of the equilibrium cell, where it could contaminate the liquid sample in the equilibrium cell.

5.4 The Russell-Jenkins moderate pressure equilibrium still.

The Russell-Jenkins moderate pressure equilibrium still is a direct descendant of the Zain-Jenkins apparatus modified to eliminate the short comings of this earlier design. The main modification has been to the vapour flow circuit which was found in the Zain-Jenkins apparatus to restrict vapour flow around the circuit preventing the still from reaching equilibrium. This has involved the modifications to the glass still shown in Figure 5.6 and the increase in diameter of the vapour transfer line from 1/4" O.D. to 3/8" O.D. It was thought that the measured temperature of the boiling mixture was being affected by excessive heat loss from the top of the glass still. This has been dealt with by lagging the top half of the glass still with ceramic tape 1/4" thick. To remove the temperature gradient causing the heat losses the top flange of the pressure vessel has also been lagged with ceramic wool blanket 1" thick.

The glass to metal Cajon flexible connectors used to support the glass still have shown to be too fragile for this duty when exposed to corrosive liquids, exhibiting a tendency to fail at the glass to metal interface. The glass Rotolex joints have been replaced with 316 stainless steel cups made to the same dimensions as the original glass cups and jointed to the flexible connectors by standard Swagelok straight connectors.

The liquid circulation loop has been modified as shown in figure 5.7 to permit mixing of the vapour sample in the vapour sample vessel and the vapour condensate reservoir. A second small graphite gear pump has been installed to circulate the vapour condensate from the vapour condensate reservoir through the vapour sample chamber and return it to the condensate reservoir. The pump is capable of recycling the reservoir contents 15 times a minute ensuring that the sample is well mixed. The vapour condensate takeoff from the vapour condensate reservoir has been designed to avoid any dead space and is shown in detail in Figure 5.8. Two additional Hoke 1/4"

ball valves have been added to the vapour condensate sample system to enable quick isolation of the sample. They also act as a safety measure providing double isolation of the equilibrium still from the sample vessel and give positive indication of when the sample bomb is isolated.

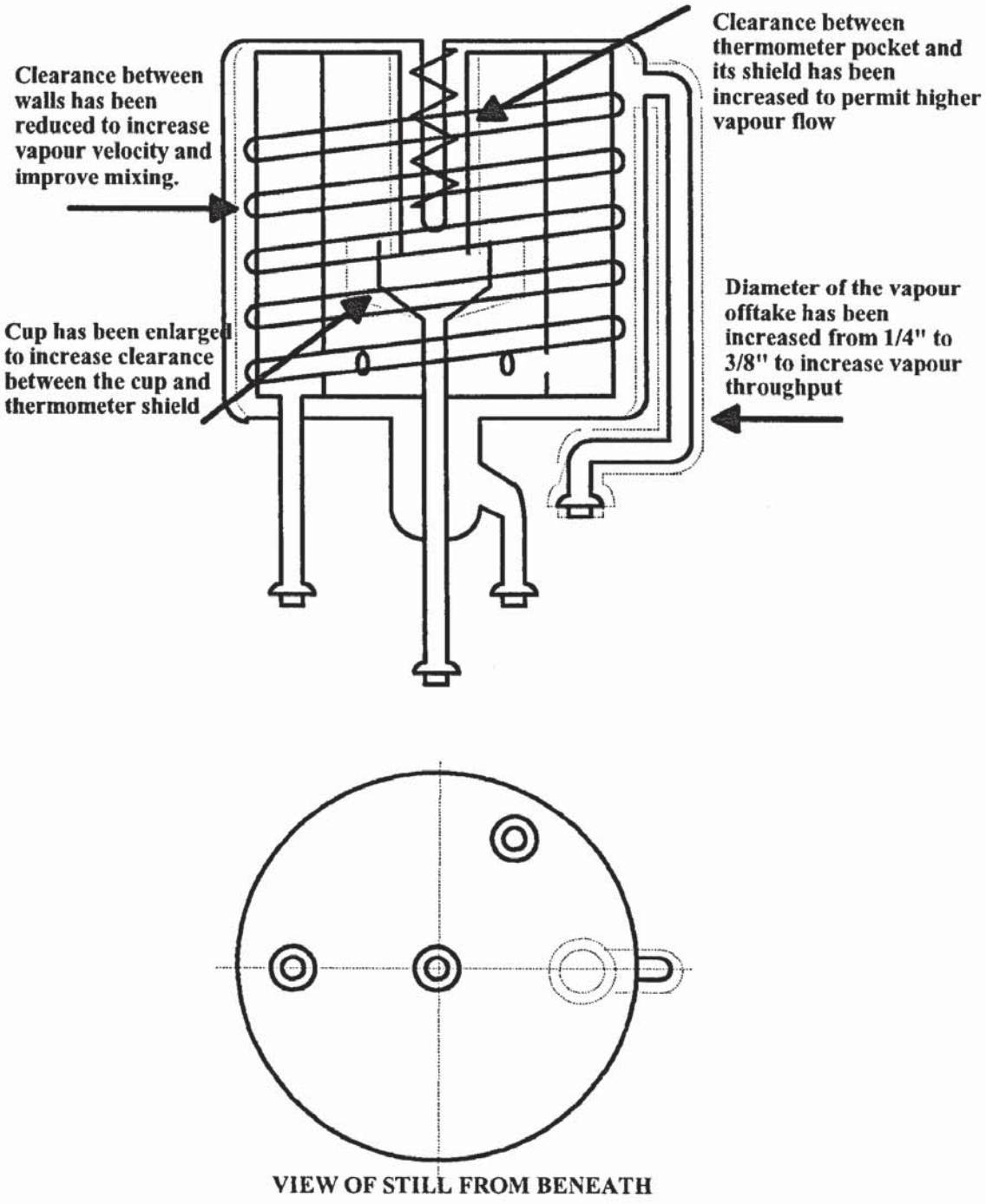


Figure 5.6 Russell-Jenkins borosilicate glass equilibrium still for moderate pressures .

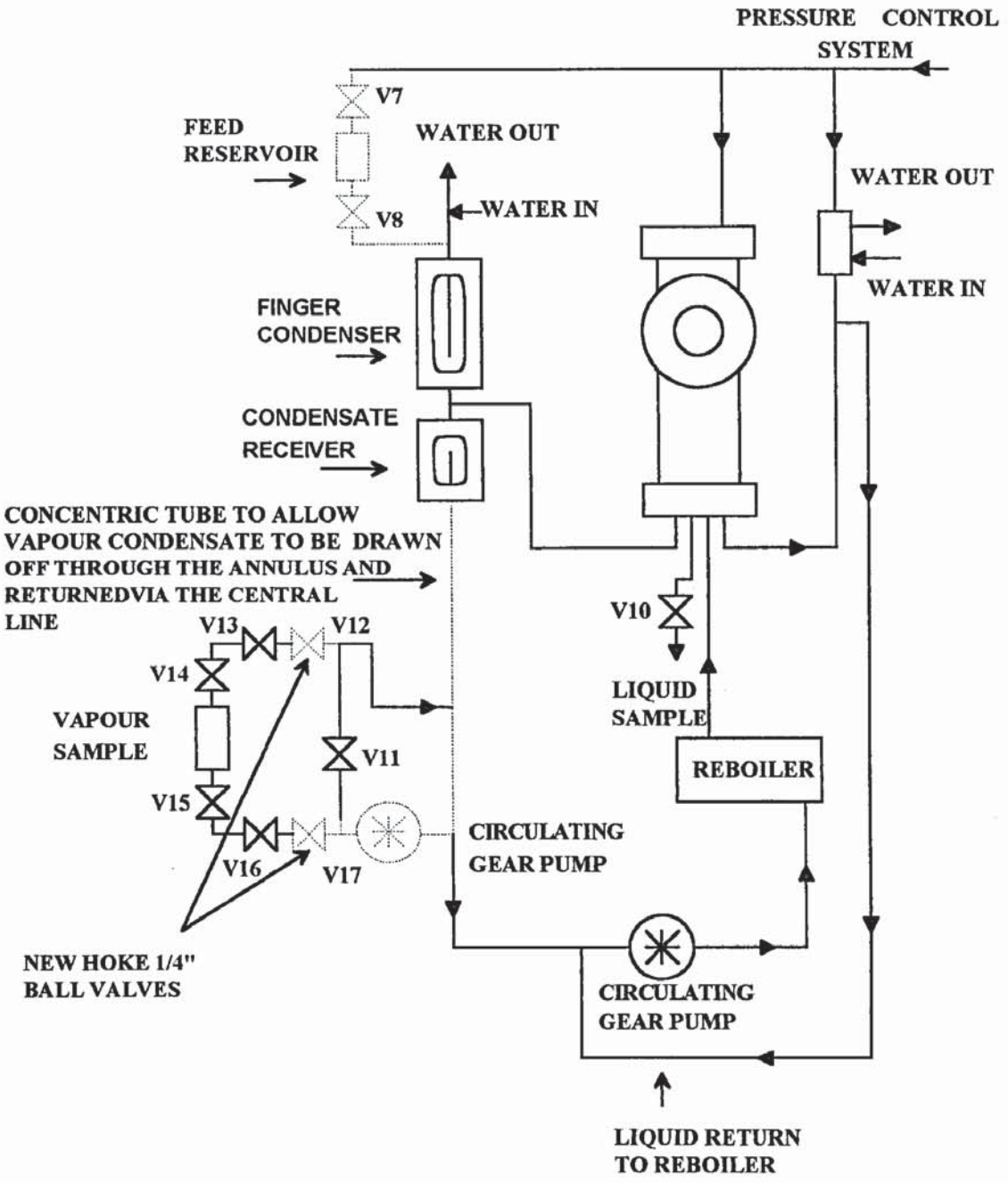


Figure 5.7 Diagrammatic representation of Russell-Jenkins moderate pressure apparatus .

A new charging system for the feed has been incorporated to allow charging of feed mixture to the apparatus during normal operation (see figure 5.7)

Operating instructions for the Russell-Jenkins moderate pressure still are given in Appendix 13.

5.4.1 Temperature measurement.

Temperature measurement on the Zain-Jenkins apparatus was achieved using a series of four chromel-alumel thermocouples, three thermocouples to measure the temperature profile up the pressure bomb and the remaining one to measure the boiling point of the liquid mixture. This mode of temperature measurement was found to be unstable when used over a prolonged time period.

The Russell Jenkins apparatus has replaced the thermocouples with 100Ω Platinum resistance thermometers (PRT). The temperature profile thermocouples have been replaced with three, three-wire PRT's which are connected to 1/4" Panel mounted Omega CN760000 temperature controllers with a control action precision of 0.2^{0}C. These controllers supply power directly to the three Hedin mat heaters, via solid state relays, maintaining the temperature along the pressure vessel within 0.2^{0}C of the boiling point. The boiling temperature in the equilibrium cell is measured by a central Four-wire PRT calibrated to 0.002 K against a Guildline 9540 platinum resistance thermometer with a discrimination of 0.001 K. This in turn has been calibrated against an NPL design type 5650F inductively coupled double ratio bridge, (with a precision of ±0.0001 K) using a platinum resistance thermometer No 221426 calibrated at the National Physical Laboratory to IPHS68. The calibration graph for the central PRT is given in Appendix 1 together with the temperature correction graph used for the Guildline 9540 platinum resistance thermometer.

The four-wire PRT is connected to two temperature measurement devices via a gold wafer switch. It is connected to a Omega DP41 RTD MDSS digital temperature indicator with a resolution of 0.01^{0} C which is used for constant monitoring of the boiling point as equilibrium is established. For very accurate measurement of the temperature once equilibrium is established it is connected to the NPL design type

5650F inductively coupled double ratio bridge, (with a precision of ±0.0001 K).

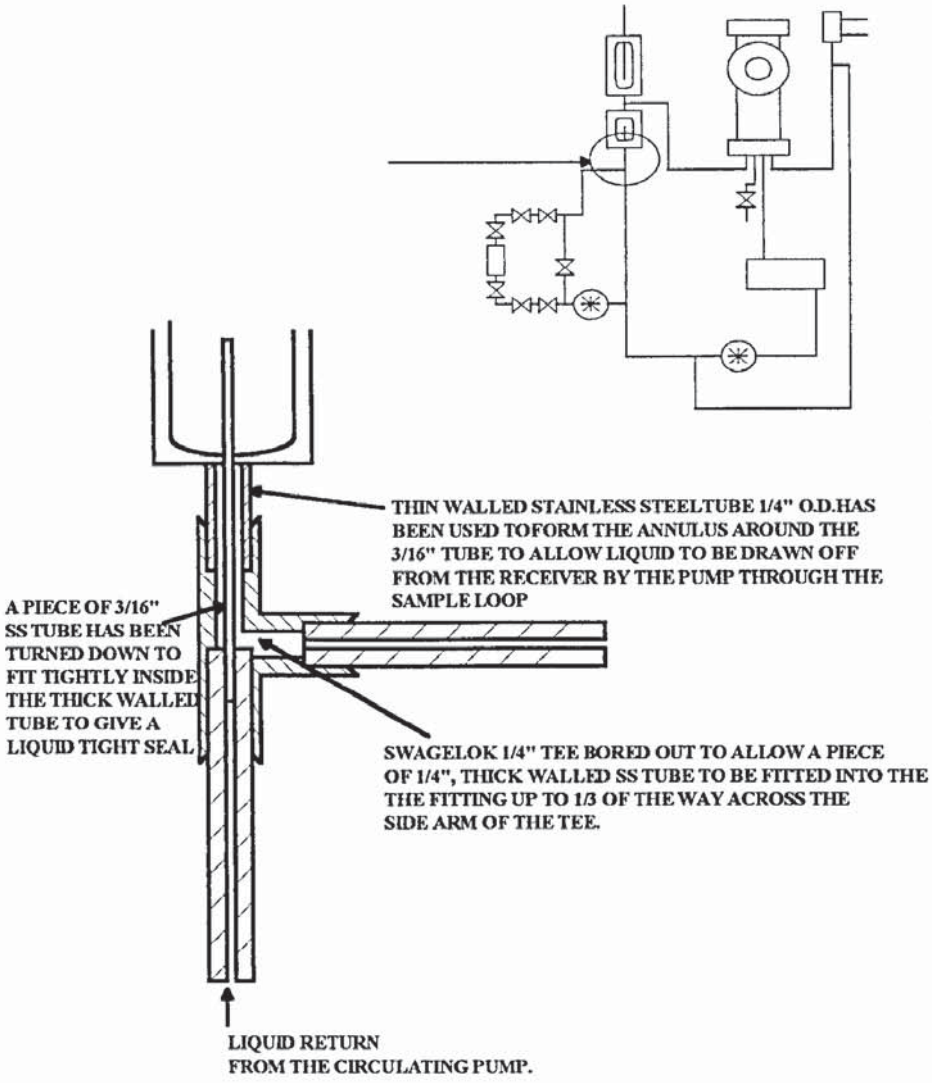


Figure 5.8 Detailed drawing of the design of the vapour condensate takeoff from the vapour condensate receiver.

Finally the vapour transfer line heating tape was observed to have over heated on the Zain-Jenkins still. This was replaced with a Cole Palmer insulated ceramic rope heater and lagged with ceramic tape to 1/4" thick. Three chromel-alumel thermocouples were equally spaced along the vapour transfer line on top of this layer of insulation. A further layer of ceramic wool, 1" thick was applied over this and covered with aluminium foil. The thermocouples were monitored using a Comark temperature indicator and power input was regulated to give an even temperature along the vapour line equal to the boiling point of the mixture.

5.4.2 Pressure control and measurement

The pressure control system is represented diagrammatically in figure 5.9. The pressure was controlled by a Druck digital pressure indicator/controller (DPI 500) accurate to 0.01 bar. For operating pressures below 3.5 bar, the pressure was measured by a Druck digital pressure indicator (DPI 140) to an accuracy of two parts in 10000 of a bar using a vibrating cylinder sensor with accuracy of 0.015% of full scale. For operating pressures above 3.5 and up to 35 bar (g), the pressure was controlled to match an on-line air-operated Budenburg dead weight tester also accurate to ±0.0l bar. This was used to check the pressure every 15 minutes as the Druck digital pressure indicator/controller (DPI 500) drifts slightly with prolonged use.

The pressure system was connected to four points on the equilibrium still, at the top flange of the pressure bomb, to the finger condenser, to the guard condenser and to the top of the feed vessel. The connections between the pressure bomb and the condenser were 3/8 " O.D tubing as against 1/8 " O.D. tubing to ensure that the bomb pressure and that supplied to the glass equilibrium cell were never appreciably different. 1/8 " O.D. was used for the rest of the pressure system to restrict the flowrate of the pressurising gas. A vapour trap of 3A molecular sieve in 1/2 "O.D. tube has been installed prior to the pressure indicators to prevent contamination of the pressure gauges. Two 1/4" pressure relief valves have been installed in the system, one prior to the DPI 500 pressure controller and one directly on to the top flange of the pressure bomb to protect the system from over pressure.

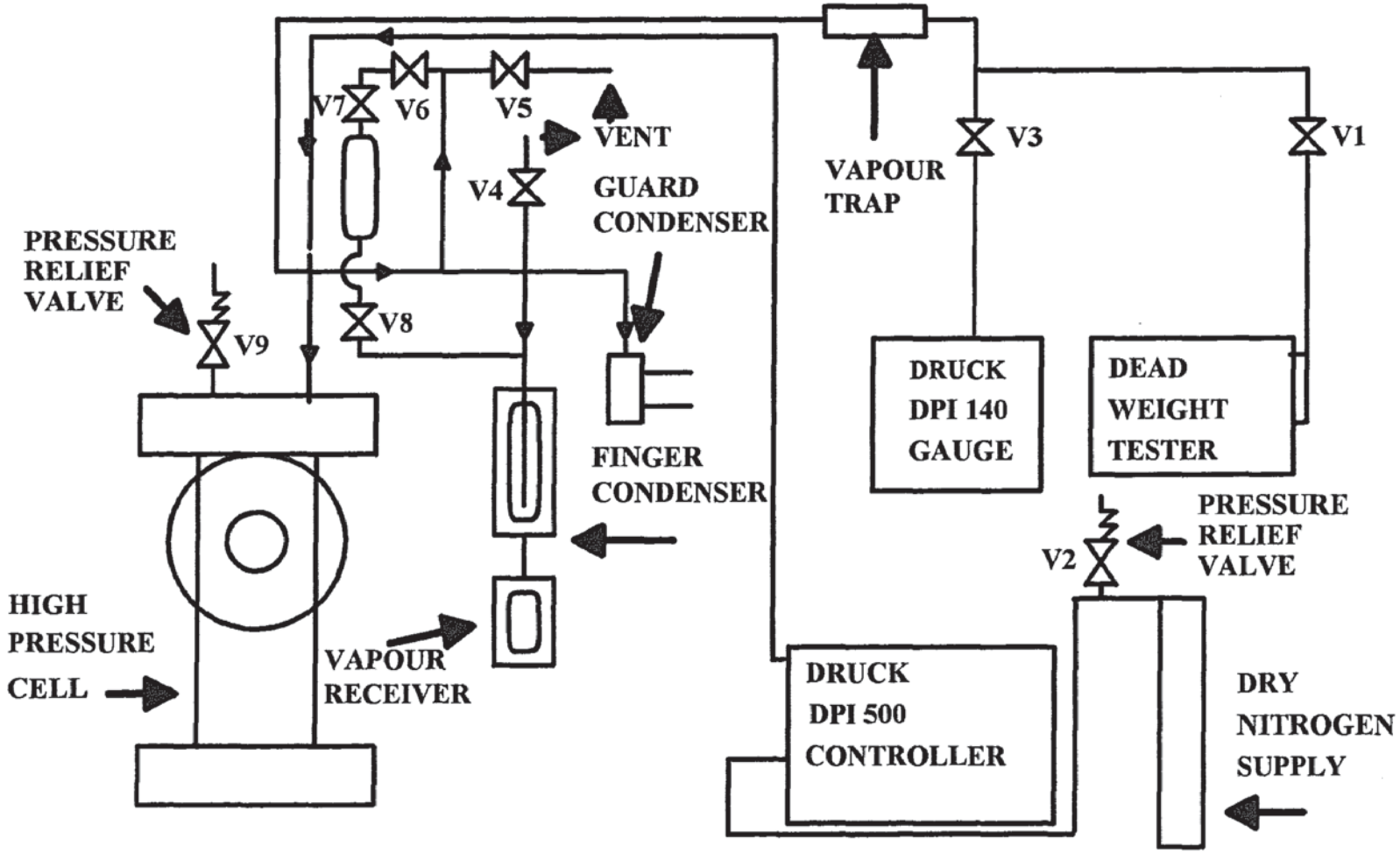


Figure 5.9 Pressure control system.

6.1 Introduction

Acetic acid-water mixtures have been used traditionally to test new designs of equilibrium stills. This is primarily due for two reasons; (i) the pure components are cheap, readily available and easily purified, (ii) analysis by titration can be made as sensitive as necessary to provide x and y values with very small errors arising from the analytical method. Over fifty sets of equilibrium data exist in the literature for this mixture at one atmosphere pressure but no two data sets agree.

Jenkins and Gibson-Robinson (1979) identified the best five data sets available in the literature from those listed by Sebastini and Laquanti (1967). In addition to these data sets O'Donnell (1980) produced using version 1 of the low pressure apparatus a number of isothermal and isobaric data sets at and below one atmosphere pressure. The data of O'Donnell (1980) were shown to be of good thermodynamic consistency using a Barker-type consistency test, developed for associating systems by Jenkins and Gibson-Robinson (1977). Thus determination of data at one atmosphere on both apparatus described here would demonstrate both their absolute and relative performances.

6.2 Materials.

Glacial acetic acid was purified by repeated thawing and freezing, the supernatant fluid being discarded in each cycle. The purified acetic acid was stored in 500 ml bottles over 3A molecular sieve to maintain dehydration. The water was deionised then double distilled freshly in 500 ml batches to prevent degradation with time

6.3 Analysis.

Density measurement is used as an analytical method for determination of the composition of the liquid and vapour phase samples. For this purpose calibration

mixtures of acetic acid and water were prepared by successive weighing. Their densities were determined at 25°C using an Anton Paar densimeter (DMA 60) with two DMA 602 cells (with a potential precision of better than 1 in 10^6). The temperature of the densimeter measuring cells was controlled to $\pm$ 0.01 K using a heater/controller (Heto Birkerod Denmark). The density measurements were made in comparative mode with a reference fluid of pure water in one densimeter cell. This method was adopted due to greater stability of measurement in comparison to absolute density measurements at a set temperature.

6.4 Results.

Fifteen data points were produced using the low pressure apparatus and thirteen data points were produced using the moderate pressure still. These data sets were initially screened using a (x-y) versus x plot and compared directly with the data set produced on the original low pressure still of O'Donnell (1980) (Figure 6.1). From this plot it can be seen all three data sets agree well. At low acetic acid concentrations there is some deviation between the new data sets and the O'Donnell data set, though the two new sets appear to agree with each other in this region.

This discrepancy is put into perspective when these data sets are compared with the other five data sets identified by Jenkins and Gibson Robinson (1979) (figure 6.2). It can be seen the new data sets show good agreement with the data of Brown and Ewald (1950) and Garner, Ellis and Pearce (1954). Jenkins and Gibson-Robinson (1979) had previously found the work of Brown and Ewald to be the most consistent. The discrepancy at low acetic acid concentrations is explained by a single high value data point in the O'Donnell data set.

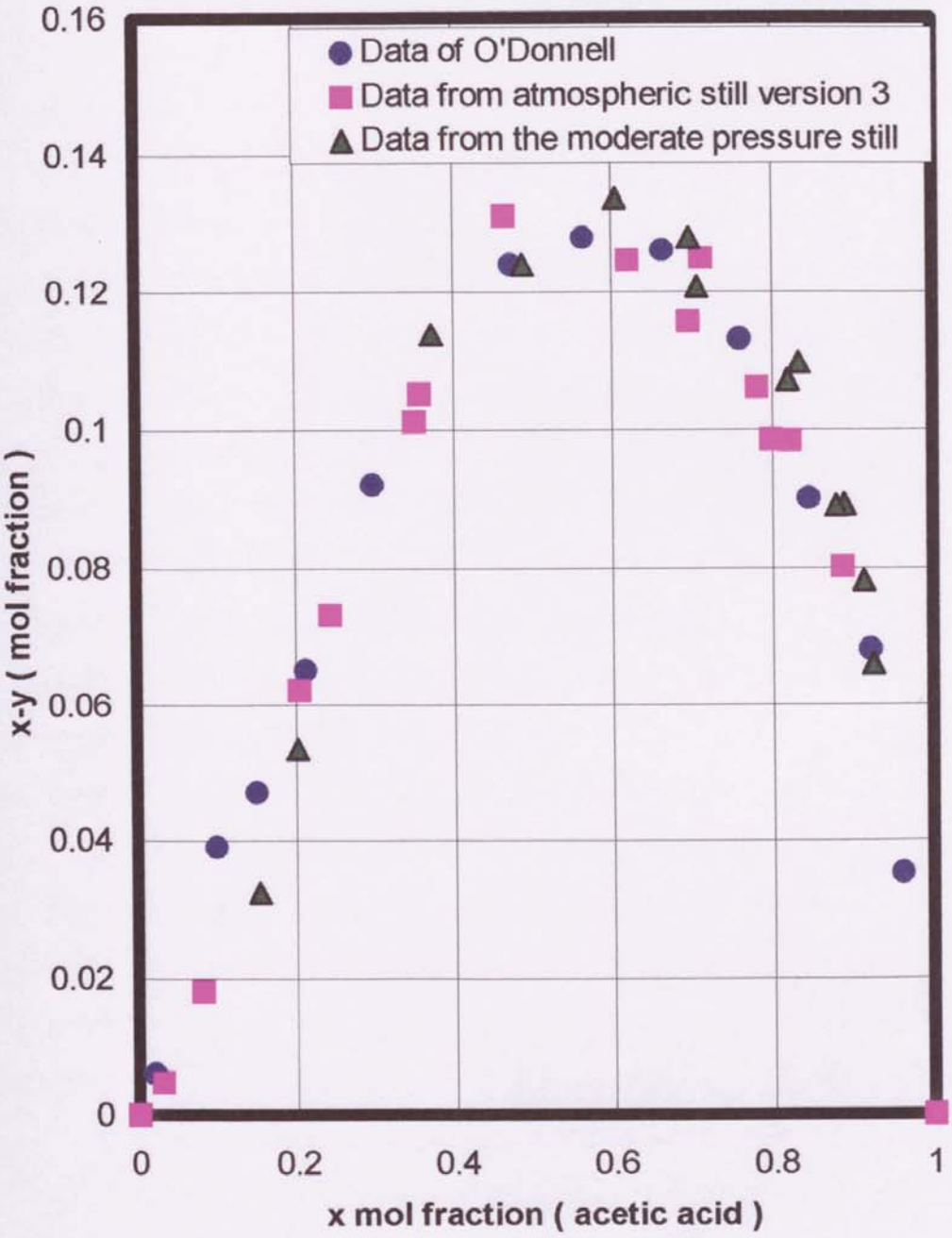


Figure 6.1 x-y against x plot for acetic acid-water at 1 atmosphere including work of O'Donnell

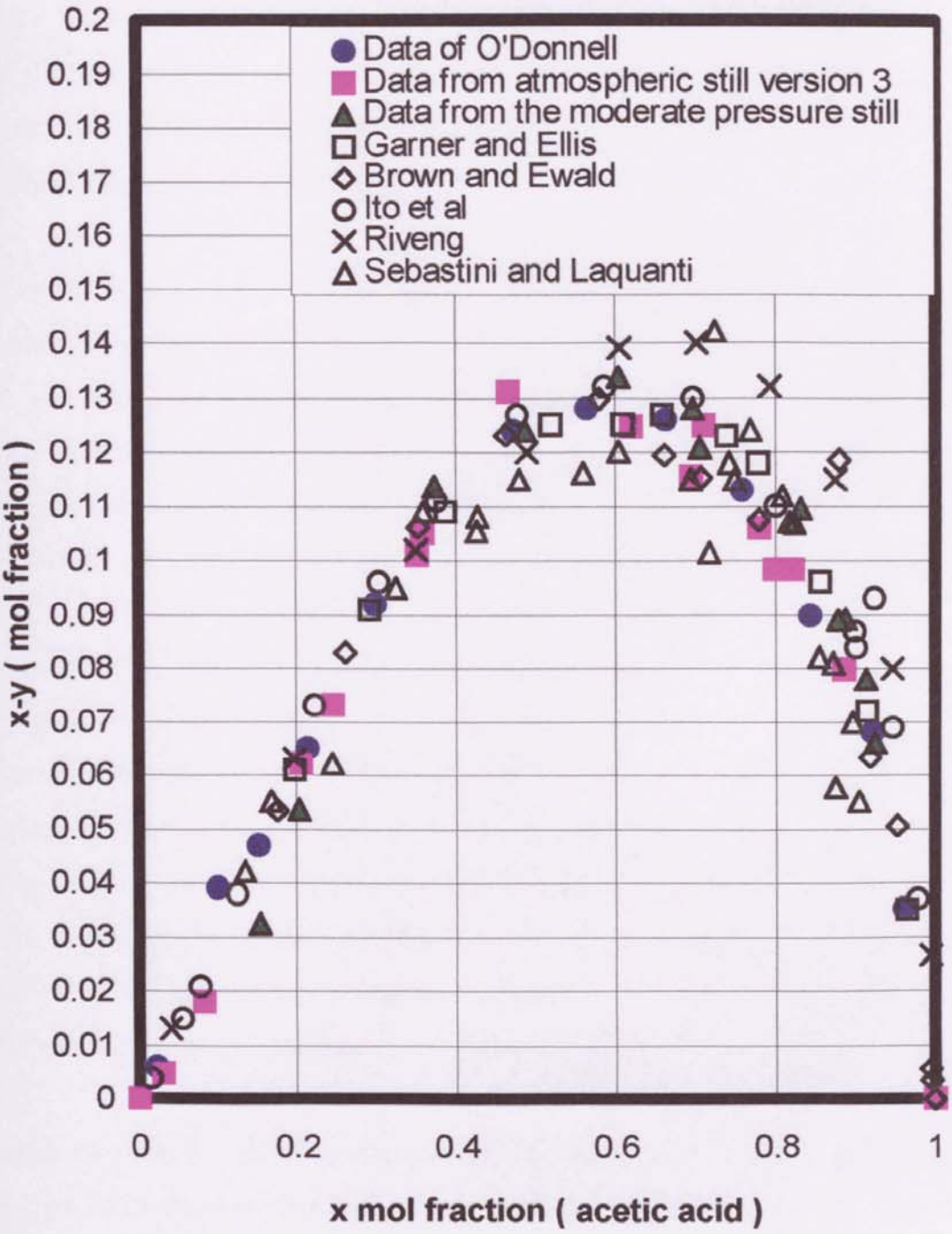


Figure 6.2 x-y against x plot for acetic acid-water at 1 atmosphere including work of earlier workers.

6.5 The application of consistency tests to the experimental vapour-liquid equilibrium data for acetic acid-water mixtures.

The experimental data sets have been tested using the Barker type consistency test developed by Jenkins and Gibson Robinson (1979). The programs used for performing the consistency tests are detailed by O'Donnell (1980).

The experimental y-values are the data usually most prone to errors and thus in this procedure they are not used in the data-fit. A comparison between the experimental and calculated y-values form the consistency test. For a completely consistent set of data, a simultaneous plot of $(P_{exp} - P_{calc})$ and $(y_{exp}-y_{calc})$ vs x should both show random distribution with about the expected error. Any systematic deviation indicates either a non-random source of error or failure of the liquid phase model to represent the data.

The saturated vapour pressures for the pure components were calculated using either the 3 parameter Antoine equation, the 6 parameter extended Antoine equation, or the 4 parameter Harlacher equation. No parameter values could be found for the extended Antoine equation for Acetic Acid. Combinations of these equations were tested to see which equation gave the best fit. No benefit was derived from using the Harlacher equation and the best results were obtained using the 3 parameter Antoine equation to represent acetic acid and the 6 parameter extended Antoine equation to represent the water saturated vapour pressures.

The vapour phase non-ideality was modelled by use of the fugacity coefficient derived from the correlation of Prausnitz et al. (1967). For acetic acid mixtures this is combined with correction factors accounting for the formation of dimers as developed by Marek and Standart (1954).

Liquid-phase association is accounted for by a model using a concentration-dependent K, as developed by Jenkins and Gibson-Robinson (1979). They state that it is insufficient to use liquid-phase activity coefficient models on acetic acid mixtures, without accounting for acetic acid association. The model they proposed has been

tested on many acetic acid systems by themselves and O'Donnell (1980). It has been shown to give better fitting than models which do not account for association in the liquid-phase.

The integrated forms of the Gibbs-Duhem Equation (activity coefficient models) used were the two-parameter Wilson equation, the three-parameter NRTL equation and a four-parameter version of the Redlich-Kister equation which has been found to correlate acetic acid mixtures well. Each activity coefficient model was run both with and without the acetic acid liquid-phase association model. This was done to ascertain what effect use of the association model has on the data fit.

The results for these consistency tests are recorded in Appendix 4 for the new data sets and that of the O'Donnell data at one atmosphere pressure. The best fits were achieved using the three-parameter NRTL equation with association in both phases. The use of the Redlich-Kister equation shows no significant differences for fit from the fit achieved using the 3-parameter NRTL equation. The results of the consistency tests without the use of the association model in both phases are very poor. These tests show an increase by a factor of 10 of the values of y_{EXP}-y_{CALC}. This confirms that it is essential to account for association in both phases and that the approach adopted by Jenkins and Gibson-Robinson (1979) works very well.

The data for the reduction procedure using the 3-parameter NRTL equation has been used to produce the deviation plots figures (6.3 and 6.4). These plots also contain data from the best two literature data sets i.e. Brown and Ewald (1950) and Garner Ellis and Pearce (1954) using the same consistency test parameters.

The dP sets show that all the data sets exhibit sinusoidal trends of similar magnitude. The O'Donnell and Garner and Ellis sets appear to give the smallest deviations. The new data set on the moderate pressure apparatus shows a single data point at the end of the composition range which is obviously in error.

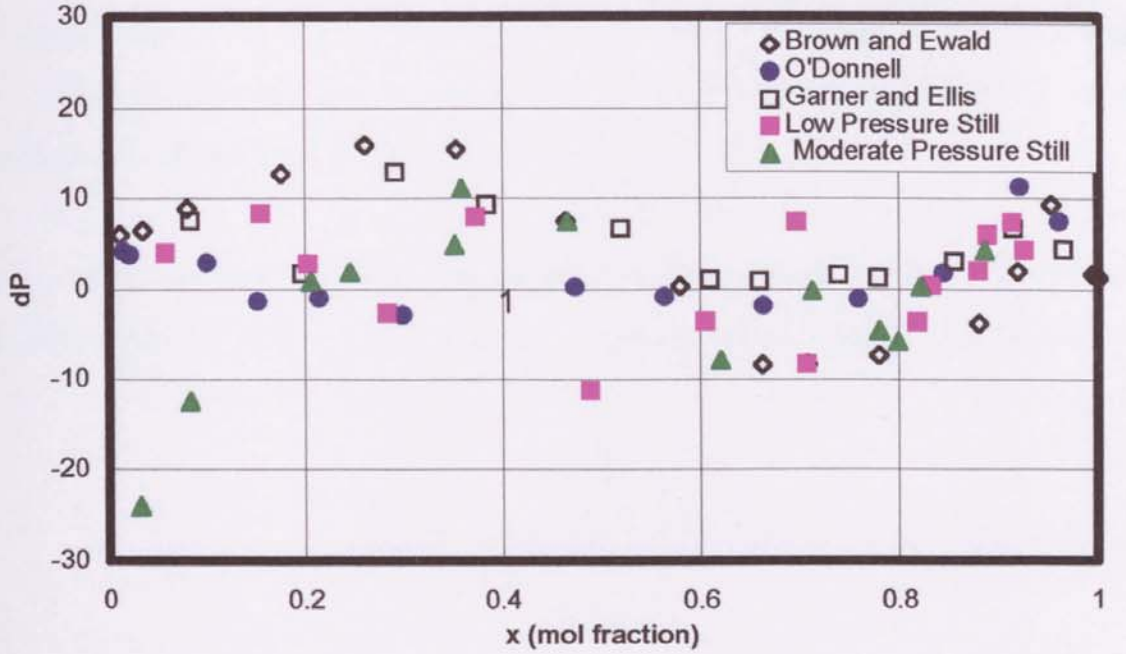


Figure 6.3 Deviation plot for pressure for acetic-acid water at atmospheric pressure

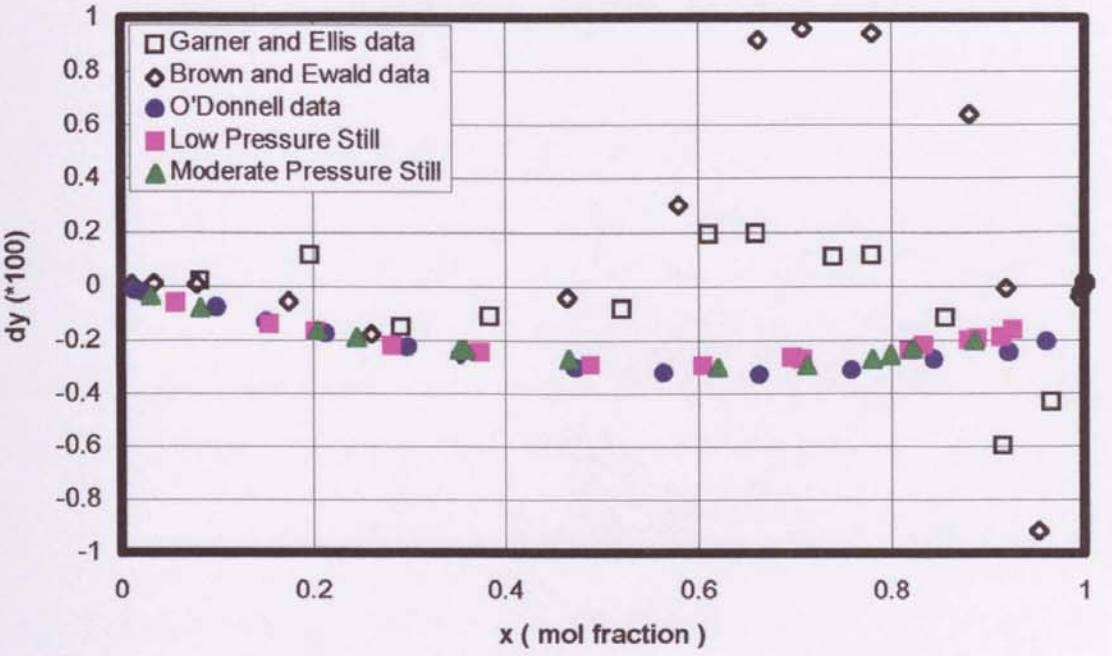


Figure 6.4 Deviation plot for vapour mol fraction for acetic-acid water at atmospheric pressure

The dy (100) deviation plots show very good agreement between the two new data sets and the data of O'Donnell. These data sets appear to give much better data fits on the y values than do the data of Garner and Ellis and Brown and Ewald which again exhibit sinusoidal patterns with much more scatter.

Thus it appears that the new data and the data of O'Donnell are the most consistent. It also demonstrates that all versions of the still produce data of a similar high quality.

7.1 Introduction

This mixture has been chosen for study because though well documented in literature sources very little of the reference material appears to agree or demonstrate high thermodynamic consistency. This inconsistency of experimental data is due in part to the presence of stabilisers in the chloroform used to determine the experimental data.

The mixture is a suitable choice for investigating the ability of the AGAPE phase equilibria prediction method to determine vapour-liquid equilibrium data for highly polar mixtures. The normal approach to the prediction of equilibrium values using the London potential to determine the molecular parameters is unsuitable because the London potential cannot predict the strong forces which exist between the molecules. The aim therefore is to test the prediction program using a single experimental data point as the source for the molecular parameters and fitting these parameters to the rest of the composition range.

For many mixtures good data are available for the azeotrope composition, from which it is possible to generate trend curves for the variation of azeotrope composition pressure and temperature. These curves can be used to provide single composition data points required from the AGAPEFIT method at any temperature and pressure. This therefore could be a valuable tool to predict vapour-liquid equilibria data given a minimum of experimental data.

In order to assess this technique for predicting vapour-liquid equilibrium data two experimental data sets are required for the mixture acetone-chloroform. These data sets are required to intersect at one point. This is so that the molecular properties of the intercept point can be used to predict the data for the two test conditions.

7.2 Materials and analysis.

The test materials used were Romil Super Purity acetone assaying at 99.9% minimum, with much of the remaining impurity being water and Fison Scientific's chloroform HPLC grade assaying at 99.98% chloroform with 100 ppm stabiliser. Both components were stored as 500 ml lots over 3A molecular sieve to complete dehydration.

The liquid and vapour samples were analysed using an automatic refractometer accurate to 4 decimal places when repeatedly standardised with HPLC grade water between measurements.

7.3 Acetone-chloroform Mixture at 1 atmosphere (absolute).

The one atmosphere pressure data set was obtained using the low pressure apparatus Mark III.

Twenty two data points were measured using the Mark III low pressure apparatus. The data were prescreened using the y-x vs x plot (figure 7.1) and t versus x plot (figure 7.2). No points were discarded since the screening plots did not indicate strongly that any should be.

Barker-type tests using the Principle of Maximum Likelihood (Prausnitz et al. 1980), were used to test both data sets. For this four different forms of the integrated Gibbs-Duhem equation were used, *viz.* Margules, Wilson, NRTL and UNIQUAC. The results of these consistency tests are given in tables Appendix 5. The best fit for the data was given by the two-parameter UNIQUAC equation which gave R.M.S. deviations of 1.41 mmHg for pressure, 0.09°C for temperature, 0.003 acetone liquid composition and 0.0027 acetone vapour composition. These R.M.S.deviations are better than the best of those given in the literature.

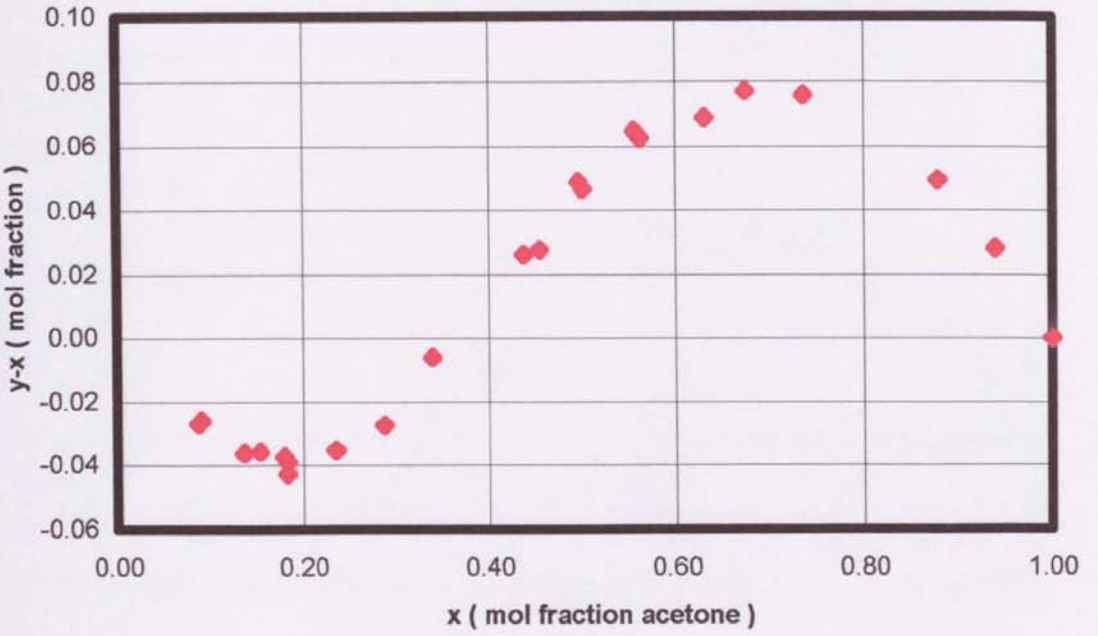


Figure 7.1 Plot of (y-x) against x for acetone-chloroform at 1 atmosphere.

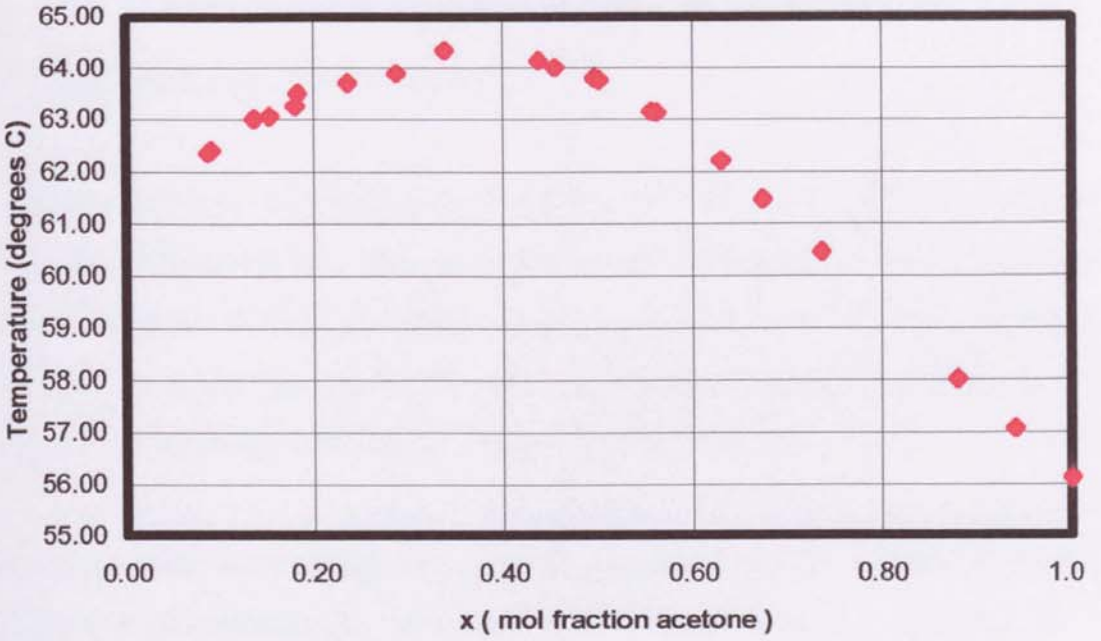


Figure 7.2 Plot of temperature against x for acetone-chloroform at 1 atmosphere.

While some twelve data sets for one atmosphere exist in the literature, no two agree. Figure 7.3 compares this data with the best of the literature data sets. The set of data for this work appears to represent a distinct improvement.

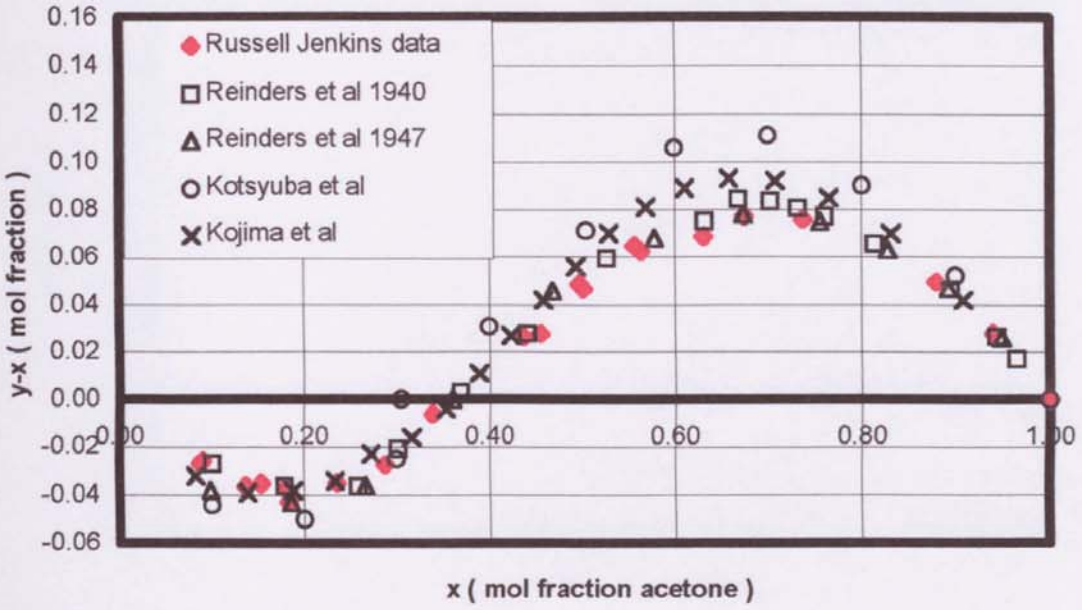


Figure 7.3 Plot of (y-x) against x for acetone-chloroform at 1 atmosphere, including data of earlier workers

7.4 Acetone - Chloroform Mixture at 64.3°C.

The isothermal data set at 64.3°C was obtained using the moderate pressure apparatus. A Churchill refrigeration unit was installed on the condenser circuit of the moderate pressure apparatus. A 10 % anti-freeze solution was used in the condenser circuit and the coolant circuit was run at 0°C. This was done to provide sufficient driving force to ensure total condensation of the vapour in the vapour condenser.

Twenty data points were measured using the moderate pressure apparatus. The data were prescreened using the y-x vs x plot (figure 7.4) and t versus x plot (figure 7.5). No points were discarded since the screening plots did not indicate strongly that any should be.

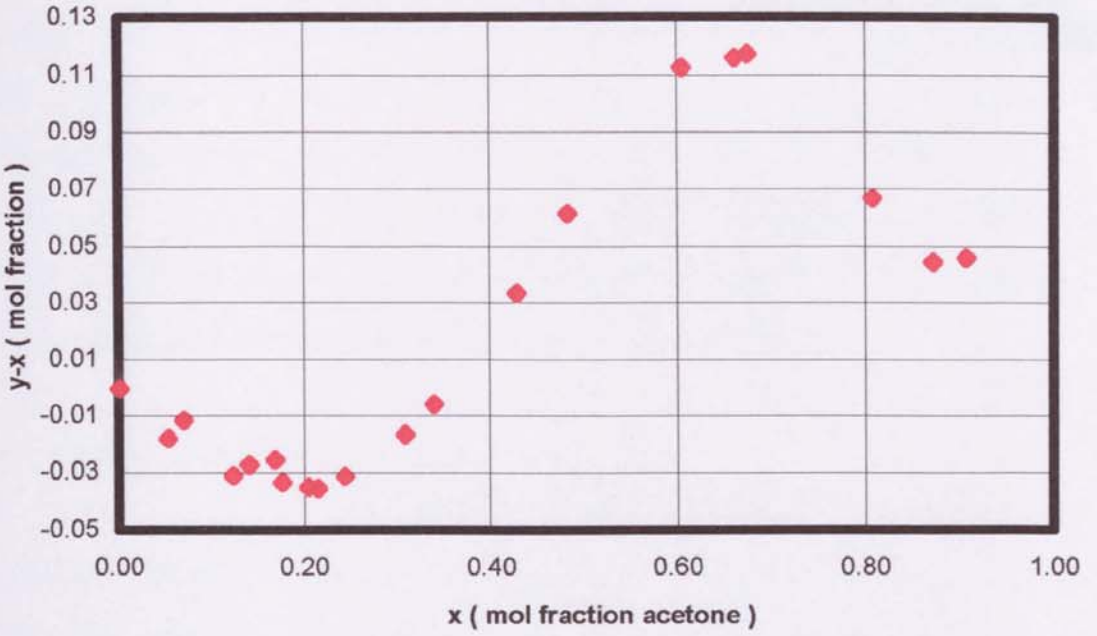


Figure 7.4 Plot of (y-x) against x for acetone-chloroform at 64.3^0 C.

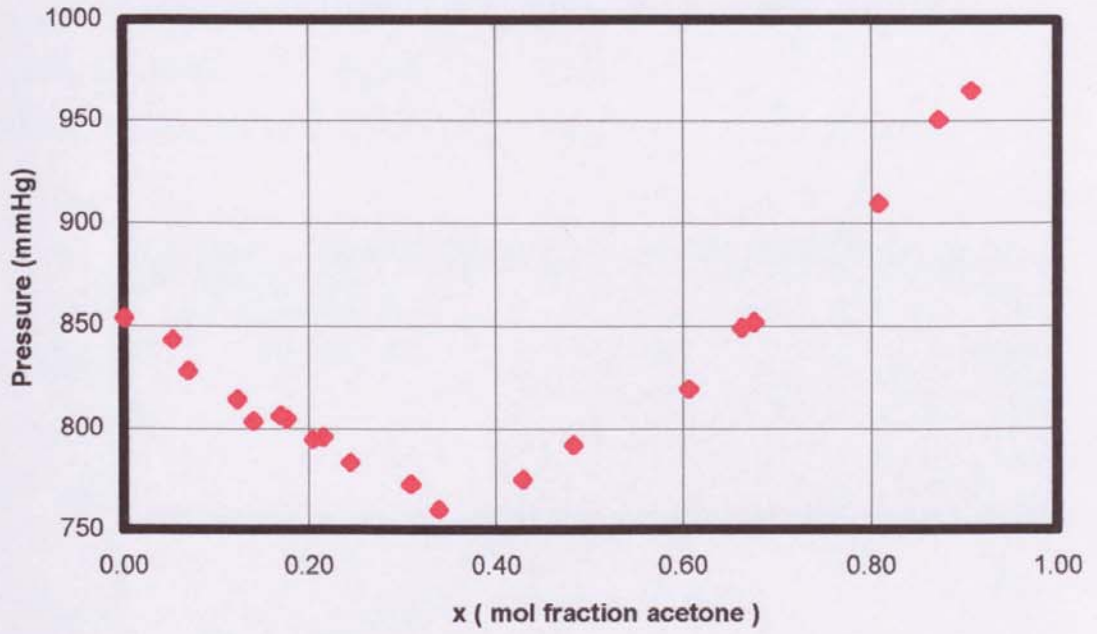


Figure 7.5 Plot of pressure against x for acetone-chloroform at 64.3^0 C.

The results of the Barker-type consistency tests are given in Appendix 5. The best fit for the data is given by the two-parameter UNIQUAC equation which gave R.M.S. deviations of 3.48 mmHg for pressure, 0.23°C for temperature, 0.0075 acetone liquid composition and 0.0074 acetone vapour composition. These R.M.S. deviations are

larger than the 1 atmosphere data set results but are still acceptable. It can be seen quite clearly from the results of the consistency tests that three of the data points at 0.6055, 0.6618 and 0.6755 acetone liquid mol fractions are erroneous. These points lie on the maxima turning point of the VLE curve where it is most difficult to obtain accurate VLE measurements. It is believed that these erroneous points have been produced in this case due to the greater difficulty of running at varying pressure to maintain a given boiling temperature to produce isothermal data.

7.5 AGAPE Predictions for both data sets

The AGAPE program VLEF, the fitting version of the AGAPE package, was used to determine the molecular parameters for the data point at 64.3°C which is common to both data sets. The values of Z and r were set to their normal values of 11 and 0.63 respectivily for this size and type of molecule. The value of Φ_{12} which represents the inter-molecular attractive forces was varied until a fit was achieved on the data point. This value of Φ_{12} was 1.03. This value of Φ_{12} together with the set values of Z and r was used to predict the vapour-liquid equilibrium data for the mixture isobaric conditions at 1 atmosphere and isothermal conditions at 64.3°C(see Appendix 9).

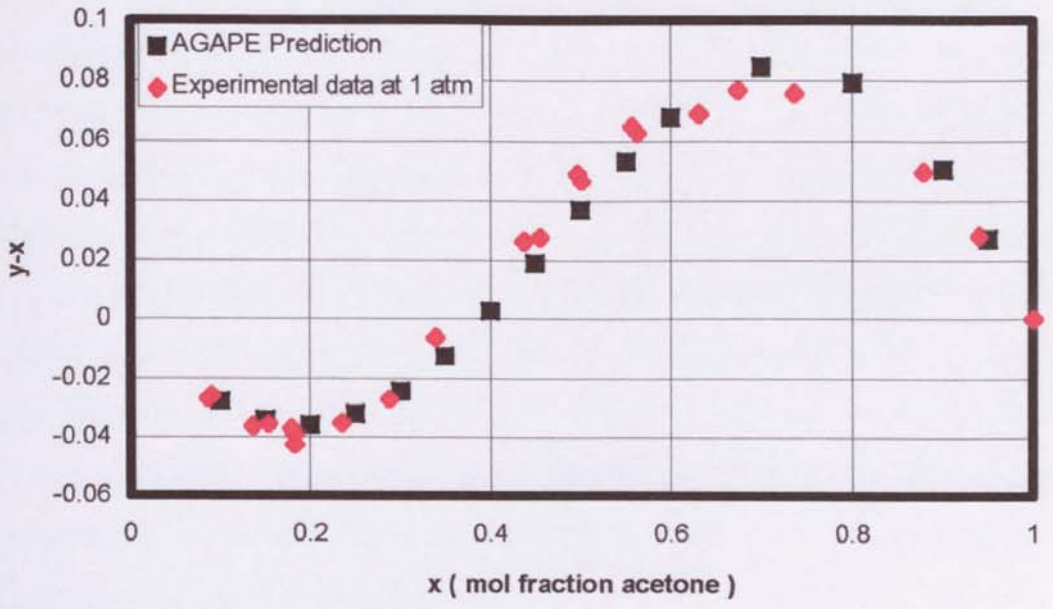


Figure 7.6 Plot of (y-x) against x for acetone-chloroform at 1 atmosphere, including AGAPE predicted data.

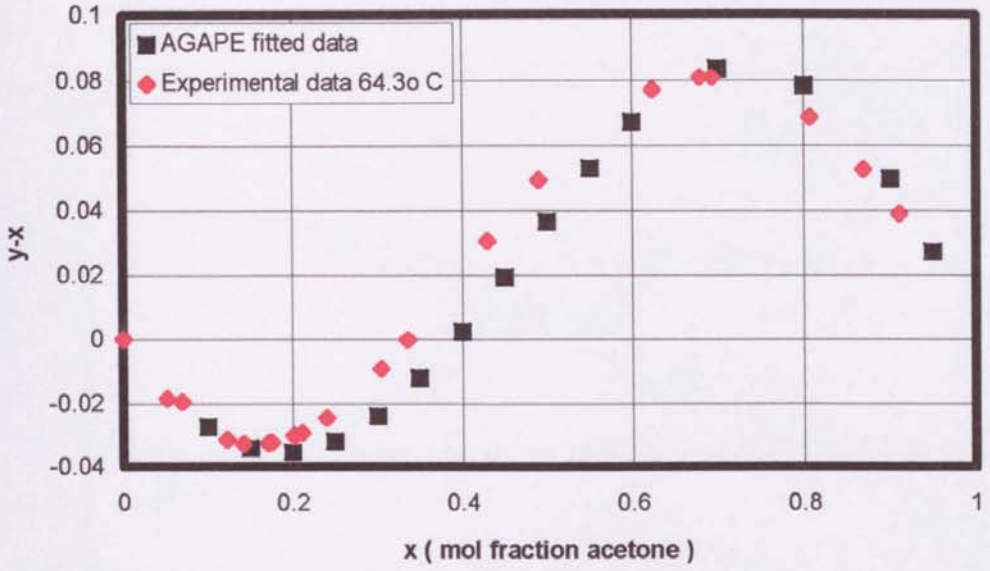


Figure 7.7 Plot of (y-x) against x for acetone-chloroform at 64.3^0 C, including AGAPE predicted data.

The predicted data set at one atmosphere is shown in figure 7.6 together with the experimental data at one atmosphere. It can be seen that very good agreement is achieved.

The predicted data set at 64.3°C is shown in figure 7.7 together with the smoothed data calculated from the consistency test using a two parameter UNIQUAC equation given in Appendix 7. The smoothed data was used because of the three erroneous data points in the experimental data which distort the results. It can be seen that agreement is achieved between the experimental and predicted data. Some deviation is noted but this is no greater than that observed between different experimental data sets. This deviation is probably due to the assumption of an ideal vapour phase in the AGAPE model. This explanation is supported by the activity coefficient graphs, figure 7.8 and 7.9. The very good agreement between the AGAPE activity coefficients and those obtained from the experimental data suggest that the errors in the predicted data lie in the calculated vapour phase compositions.

The activity coefficients have been calculated using the AGAPE fit model, the original UNIFAC model (see Fredenslund et al. 1977) and the modified UNIFAC model (see

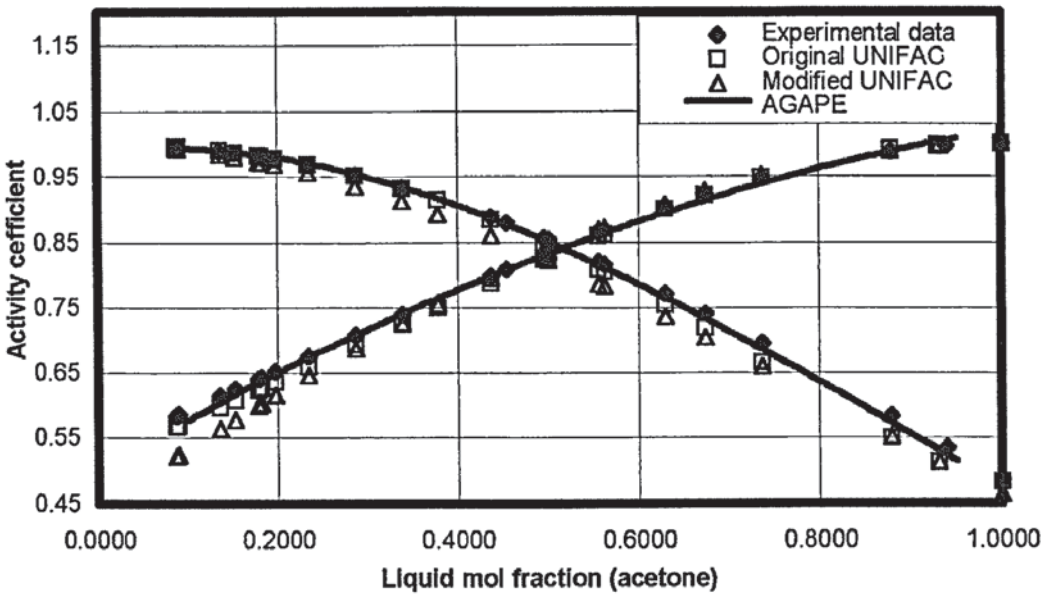


Figure 7.8 Plot of activity coefficients against x for acetone-chloroform at 1 atmosphere.

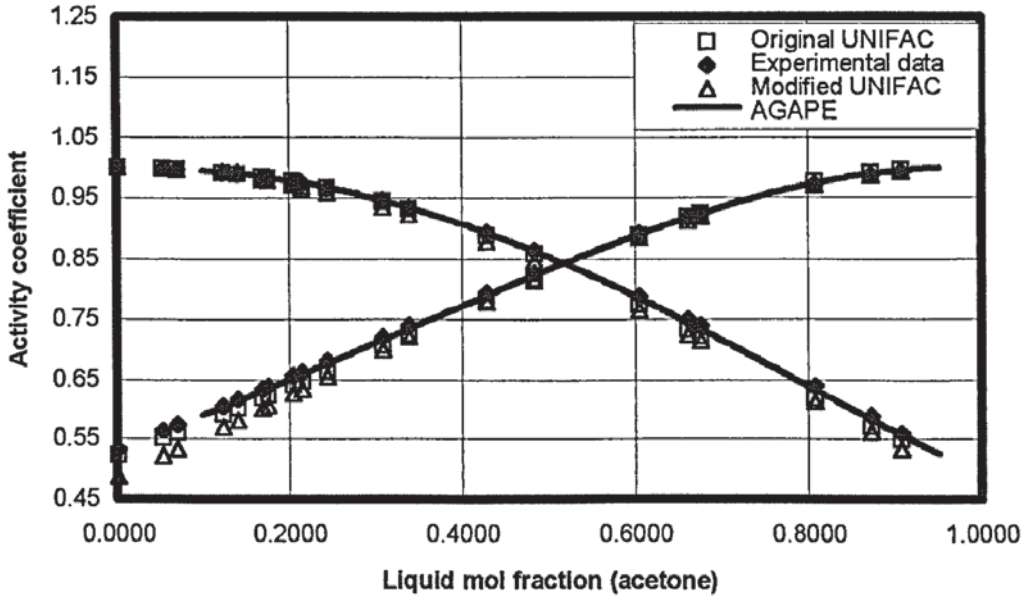


Figure 7.9 Plot of activity coefficients against x for acetone-chloroform at 64.3^0 C.

Larsen (1985). These activity coefficients have been plotted with those obtained for the experimetal data in figure 7.8 for the 1 atmosphere data set and for the 64.3^{0}C in figure 7.9. It can be seen that the activity coefficients obtained from AGAPEFIT program give the best agreement with the experimental data. Of the two UNIFAC

models used the best results are obtained with the original UNIFAC model. The modified model deviates more significantly from the experimental data which suggest that this model is less suitable for this mixture. This behaviour of this model has been observed before for highly polar mixtures see (Larsen 1985).

8.1 Introduction

Mixtures of cyclohexane and ethanol are of a complex nature, being strongly non-ideal and having an azeotrope have been selected to give a rigorous test of the performance of the moderate pressure apparatus above atmospheric pressure. Though some data exist for this mixture at and below one atmosphere pressure, for conditions above 1 atmosphere no data are extant.

The experimental work has involved the determination of saturated vapour pressure data for pure ethanol and pure cyclohexane at one bar intervals from one to 10 bar gauge. The equilibrium still was then used to investigate the binary mixture cyclohexane-ethanol isothermally at 90.9^{0}C and 138.2^{0}C and isobarically at 1 atmosphere and at 2, 4, 6, 8, 11 bar pressure respectively.

The data have been used to provide useful information on the temperature dependence of such integrated forms of the Gibbs-Duhem equation as the Margules, Wilson and UNIQUAC equations. They can also provide guidance on the robustness of UNIFAC predictions if extant literature values of the UNIFAC group parameters are used to predict VLE data over a wide range of temperatures and pressures.

The data provide a knowledge of the dependence of the azeotrope composition on pressure (and so also on temperature). This has been used to test the suitability of using azeotrope data to provide fit parameters for the AGAPE data prediction technique.

8.2 Materials

The ethanol used was obtained from James Burrough (F.A.D.) Ltd and was B.P. Absolute Alcohol (specified to be 99.86%v/v minimum ethanol with the remainder largely water). The cyclohexane was supplied by Aldrich chemicals as 99.9% HPLC

grade. It was further purified by batch distillation to remove water, using a 3-litre batch under a 30 plate Oldershaw column. The first litre of distillate was discarded and the next litre collected for use. Both components were stored as 500 ml lots over 3A molecular sieve to complete dehydration.

8.3 Saturated vapour pressure measurements for pure ethanol and pure cyclohexane.

Saturated vapour pressure measurements were made on the two pure components at one bar intervals from 1 bar to 10 bar gauge. The data are set out in table 8.1 and plotted in the form of log P against (1/T) in figures 8.1 and 8.2 where they are compared with those of other workers.

Table 8.1 Saturated vapour pressure data for ethanol and cyclohexane.

Saturated vapour pressure data Ethanol		Saturated vapour pressure data Cyclohexane	
Temperature °C	Pressure bar	Temperature °C	Pressure bar
77.51	1.01	79.12	0.99
95.65	2.01	104.09	2.01
116.44	4.00	120.70	3.01
124.11	5.00	133.00	3.98
130.27	6.00	143.50	4.98
136.48	7.00	152.43	5.98
141.27	8.00	166.49	7.98
145.44	9.00	184.64	11.00
149.27	10.00		

Figure 8.1 shows this experimental data for ethanol plotted with the sub-atmospheric results of Scatchard et al. (1964), Rafaquat and Jenkins (1982) and Larkins and Pemberton (1976), as well as a curve reported by Prausnitz et al. (1967). Good agreement is shown between this work and the previous results. These data confirm the reliability of the new still for the measurement of boiling points. The Prausnitz equation has a stated limit of applicability of 280 to 370 K. The new data confirm these limits and extends the upper limit to 423 K.

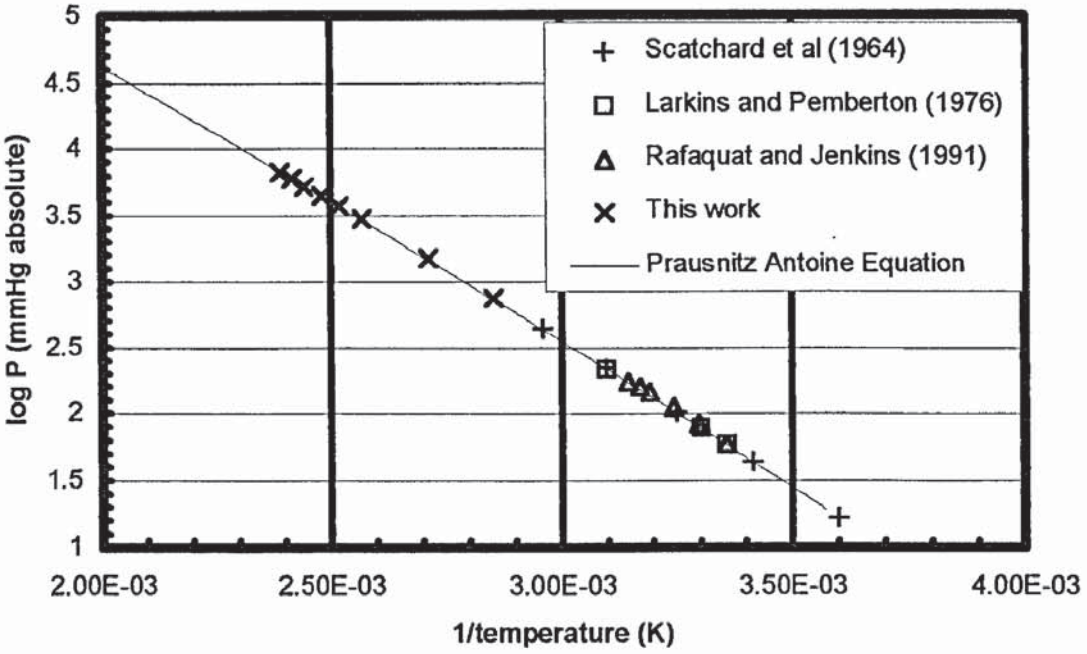


Figure 8.1 Plot of saturated vapour data for pure ethanol including data of other workers

Figure 8.2 gives a similar comparison for the cyclohexane data. Here the comparison is with the data of Scatchard et al. (1964). The 6-parameter Antoine equation of Prausnitz et al. (1967) agree well at the low pressures and up to the 2 bar limit of applicability but above this pressure deviate significantly from the new data. The data were found to be well represented by the simple 3-parameter Antoine equation whose constants are given in table 8.2.

Table 8.2 Constants for new Antoine equations for cyclohexane

Three-parameter equation					
$\ln P\ (mmHg\ (abs)) = c_1 + c_2 / (T(^0C)+c_3)$					
c_1	c_2	c_3			
756.56	-1661.2	273			
Six-parameter equation					
$\ln P\ (atm\ (abs)) = c_1 + c_2 / (T(K)+c_3) + c_4 T(K) + c_5 T(K) + c_6 \ln T(K)$					
c_1	c_2	c_3	c_4	c_5	c_6
98.585	-6943.3635	0	0.015303		

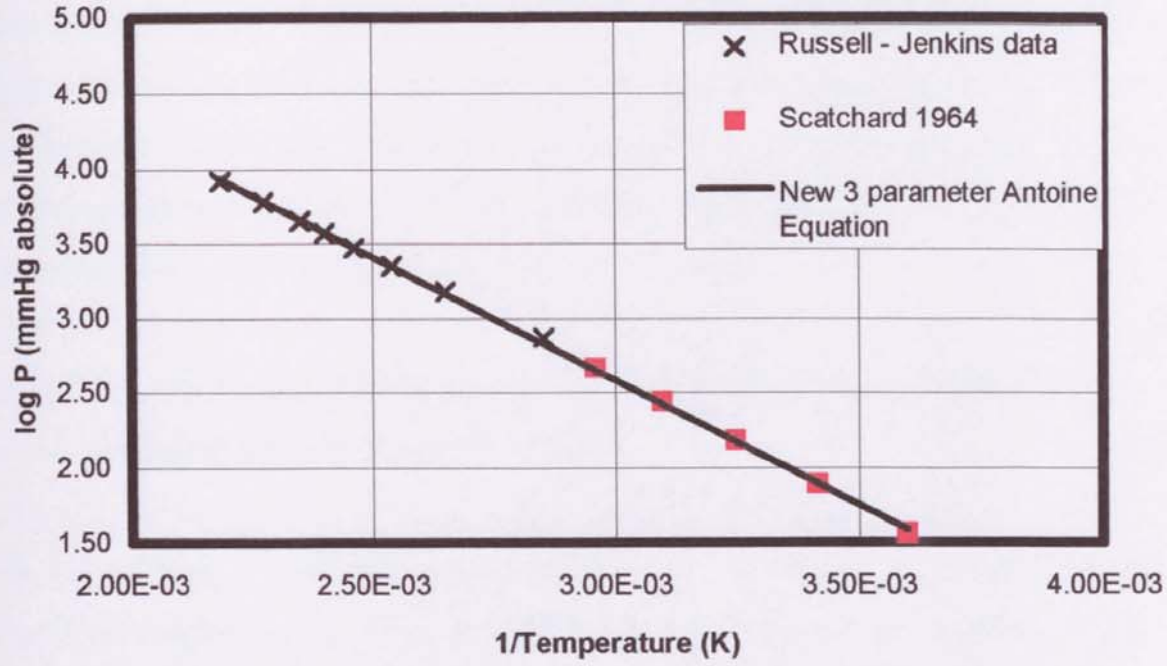


Figure 8.2 Plot of saturated vapour data for pure cyclohexane including data of other workers and three parameter Antoine equation.

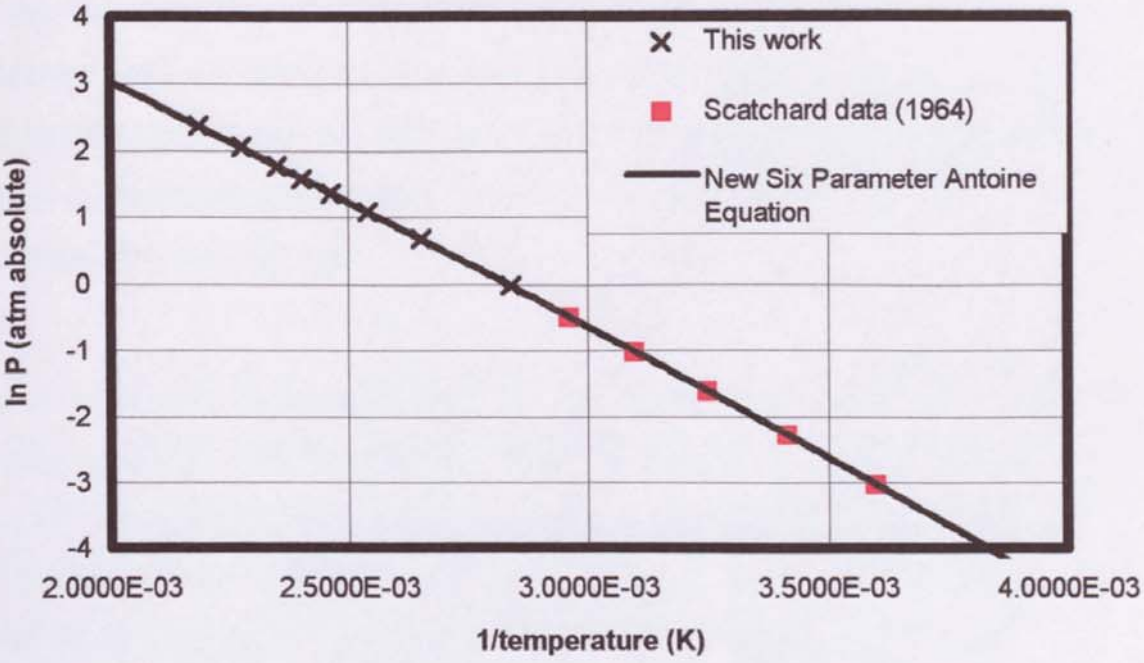


Figure 8.3 Plot of saturated vapour data for pure cyclohexane including data of other workers and six parameter Antoine equation.

The equation is valid over the pressure range 0 to 11atmospheres. The six-parameter Antoine equation of Prausnitz et al. (1967) was subsequently modified to account for the deviations experienced above 2 bar pressure. The new constants are given in table 8.2. Figure 8.3 shows the plot of the experimental data and the new six-parameter Antoine equation. It can be seen this six parameter equation gives a better fit for the data and is now valid over the temperature range 5 - 180^{0}C.

8.4 The application of consistency tests to the experimental vapour-liquid equilibrium data for cyclohexane ethanol.

Prior to application of the consistency test each data set has been initially screened using a (y-x) against x plot. The lack of alternative experimental data has precluded the use of these plots as comparative tests (apart from one atmosphere data set) but they have proved useful in identifying data points which appear to be erroneous. From these plots no data points have been identified as obviously erroneous and that the data appear to be of even consistency.

In the Barker method, the parameters in the integrated form of the Gibbs-Duhem equation used are adjusted by a non-linear least-squares fitting procedure until a minimum error between the experimental and calculated total pressures is obtained. In essence, the Barker method uses only the x-P-T data and assumes that the T and x measurements are error-free.

Since experimental uncertainty is likely to be greater for y (Van Ness et al. 1973), prudence suggests that the preferred procedure for data reduction is one based on just the x-P-T data. Values of y calculated from the correlation can then be compared with measured values as a check on the thermodynamic consistency of the vapour-liquid equilibrium data. Thus it was decided to correlate all the x-P-T data using this method but to vary the procedure slightly by minimising the differences between estimated and measured values for x, P and T, not just for the pressure after Prausnitz et al .(1980).

All the data sets have been tested for consistency using the Barker method (Barker 1953; Prausnitz et al, 1980). The basis of the Barker method is that an integrated form of the Gibbs-Duhem equation (e.g. the UNIQUAC equation) is used to relate the liquid-phase activity coefficients to the mole fractions in a binary mixture. It was decided to use a selection of liquid-phase activity coefficient models to represent the liquid-phase behaviour. The models chosen were Margules, Van Laar, NRTL, Wilson and UNIQUAC, representing a fair cross-section of the common models available. These models each have two adjustable binary parameters. The two adjustable binary parameters were estimated by a non-linear regression method based on the maximum-likelihood principle (Anderson et al. 1978) as set out in Prausnitz et al. (1980). The computer program used was VPLQFT which is capable of correlating binary vapour-liquid equilibrium data at low to moderate pressures. The most important feature of the maximum-likelihood principle is that it attempts properly to account for all measurement errors.

In the data reduction the default standard state liquid fugacity curve was not used. Instead for ethanol the extended Antoine equation was used. Parameters reported by Prausnitz (1967), for this equation, on comparison with the experimental data obtained here, have been shown to give good agreement across the full pressure range. This was not true for cyclohexane and so the new 3-parameter Antoine equation shown in table 8.2 has been used.

8.5 Cyclohexane-ethanol data at 1 atmosphere.

A P-T-x-y data set of 23 points was obtained for the mixture at 1 atmosphere. Figure 8.4 plots the data of Murachevsky and Zarkov (1963) and of Yuan et al. (1963) and of this work as a y-x against x plot. The data of Murachevsky and Zarkov (1963) show poor agreement with the other two and will be considered no further. The data of Yuan et al. (1963) agree with this work well, although an erroneous point close to the azeotrope led them to report an erroneous azeotrope composition. Our azeotrope composition at 1 atmosphere pressure is 0.446 mole fraction of ethanol, at 64.6^{0}C, in

good agreement with the reported value of 0.446 mole fraction of ethanol, at 64.9°C (Horsley 1977).

The results of the Barker type consistency tests are given in Appendix 6. The best fit was obtained using the Wilson equation. This returned values for the RMS deviations for the pressure of 1.48 mmHg, temperature 0.1 K, liquid mole fraction 0.0022 and vapour mole fraction 0.0093. The UNIQUAC returned similar values, whilst the other equations failed to represent the liquid phase as well. This was to be expected and similar patterns are observed with the data of Murachevsky and Zarkov (1963) and of Yuan et al. (1963). This data set represents a improvement in the consistency of data for this mixture at this pressure.

8.6 Cyclohexane-ethanol data at 2 bar.

A P-T-x-y data set of 15 points was obtained for the mixture at 2 bar. Figure 8.5 plots the data of this work as a y-x against x screening plot. By an oversight the atmospheric pressures were not measured for this data set. In order to correct for this a standard atmosphere was used to correct the gauge pressures. This will have reduced the accuracy of the pressure measurement and thus this data set is believed to be the least accurate of all those measured. The azeotrope has been determined from the experimental data at 2 bar pressure (absolute) is 0.488 mole fraction of ethanol, at 83.7°C.

The results of the Barker type consistency tests are given in Appendix 6. The best fit was obtained using the Wilson equation. This returned values for the RMS deviations for the pressure of 2.56 mmHg, temperature 0.14 K, liquid mole fraction 0.0026 and vapour mole fraction 0.0170. The UNIQUAC returned similar values, whilst the other equations failed to represent the liquid phase as well. These results indicate the RMS deviation for y is twice that obtained for the 1 atmosphere data set, this is as expected due to the error in pressure measurement. However the consistency of this data is still in line with the most reliable data for organic mixtures found in the literature.

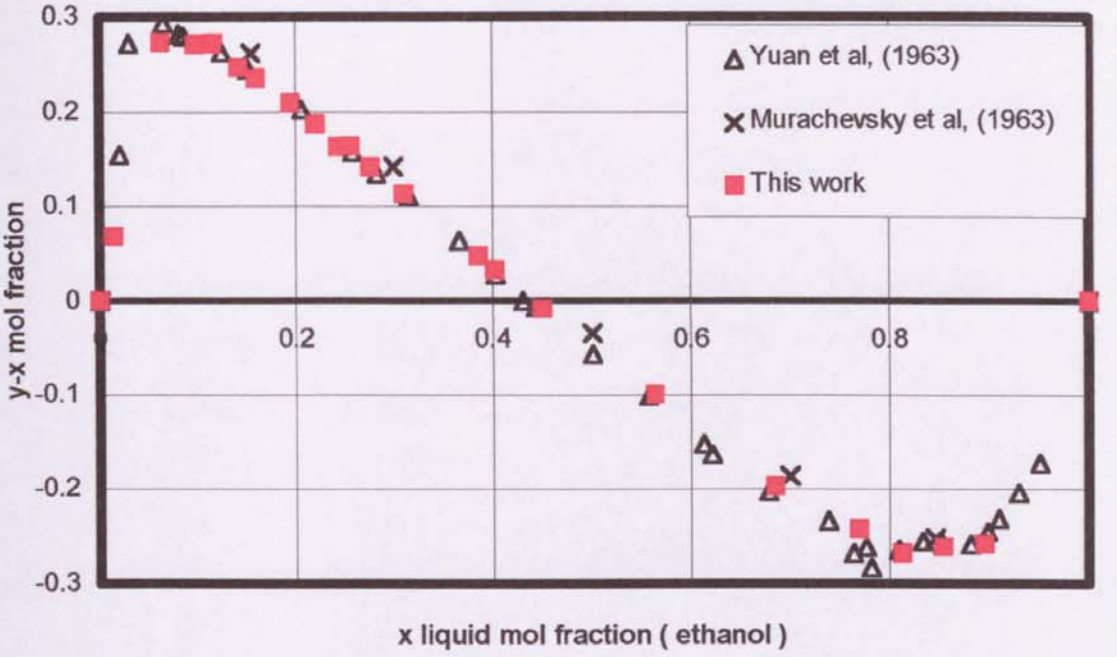


Figure 8.4 Plot of (y-x) against x for cyclohexane-ethanol at 1 atmosphere, including data of earlier workers.

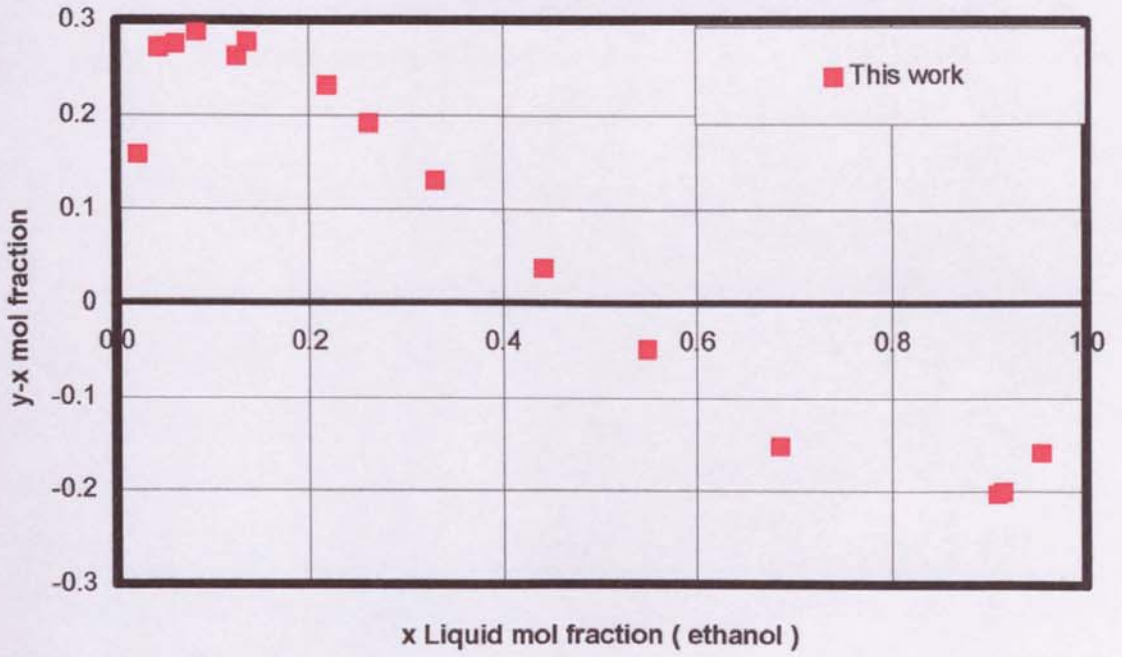


Figure 8.5 Plot of (y-x) against x for cyclohexane-ethanol at 2 bar.

8.7 Cyclohexane-ethanol data at 4 bar.

A P-T-x-y data set of 13 points was obtained for the mixture at 4 bar. Figure 8.7 plots of this work as a y-x against x screening plot. The atmospheric pressures were not measured for this data set. The gauge pressures measured experimentally were corrected using daily atmospheric pressure measurements obtained from The Birmingham Weather Centre, Birmingham University. The azeotrope has been determined from the experimental data at 4 bar pressure (absolute) as 0.549 mole fraction of ethanol, at 106.0^{0}C.

The results of the Barker-type consistency tests are given in Appendix 6. The best fit was obtained using the UNIQUAC equation. This returned values for the RMS deviations for the pressure of 9.71 mmHg, temperature 0.20 K, liquid mole fraction 0.0044 and vapour mole fraction 0.0085. The Wilson returned similar values, whilst the other equations failed to represent the liquid phase as well. For this pressure the minimisation of the pressure parameter was relaxed again. The RMS deviation for pressure is therefore much higher for this pressure. This is still acceptable because the deviation measured is still less than 0.5% of the actual pressure measured. Thus the consistency of this data is still in line with if not superior to the most reliable data for organic mixtures found in the literature.

8.8 Cyclohexane-ethanol data at 6 bar.

A P-T-x-y data set of 14 points was obtained for the mixture at 6 bar. Figure 8.7 plots the data of this work as a y-x against x screening plot. The atmospheric pressures were not measured for this data set. The gauge pressures measured experimentally were corrected using daily atmospheric pressure measurements obtained from The Birmingham Weather Centre, Birmingham University. The azeotrope has been determined from the experimental data at 6 bar pressure (absolute) as 0.59 mole fraction of ethanol, at 120.8^{0}C.

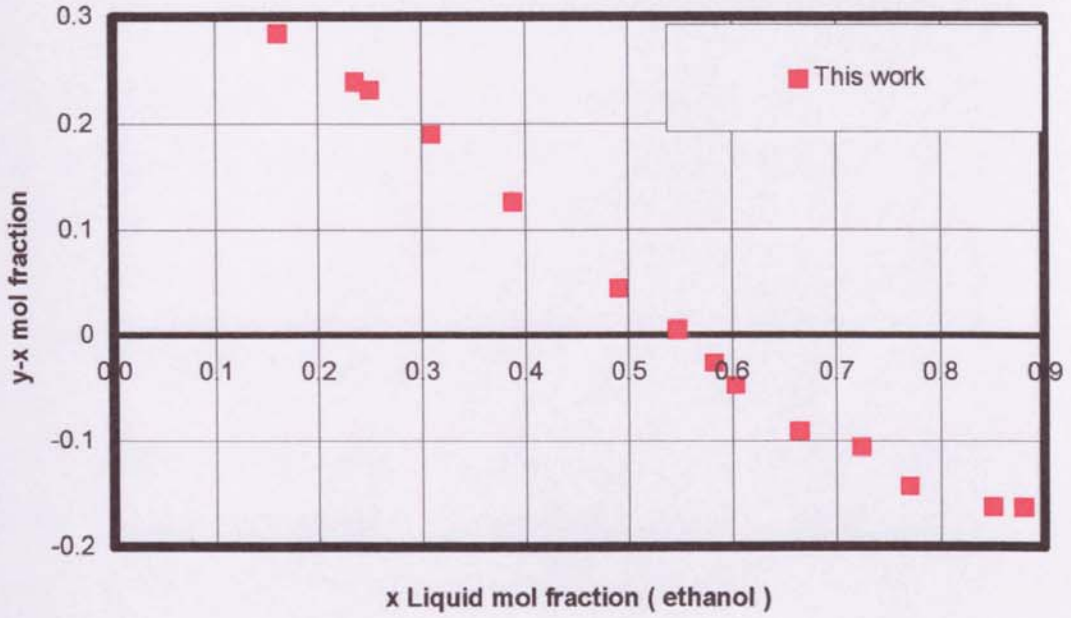


Figure 8.6 Plot of (y-x) against x for cyclohexane-ethanol at 4 bar.

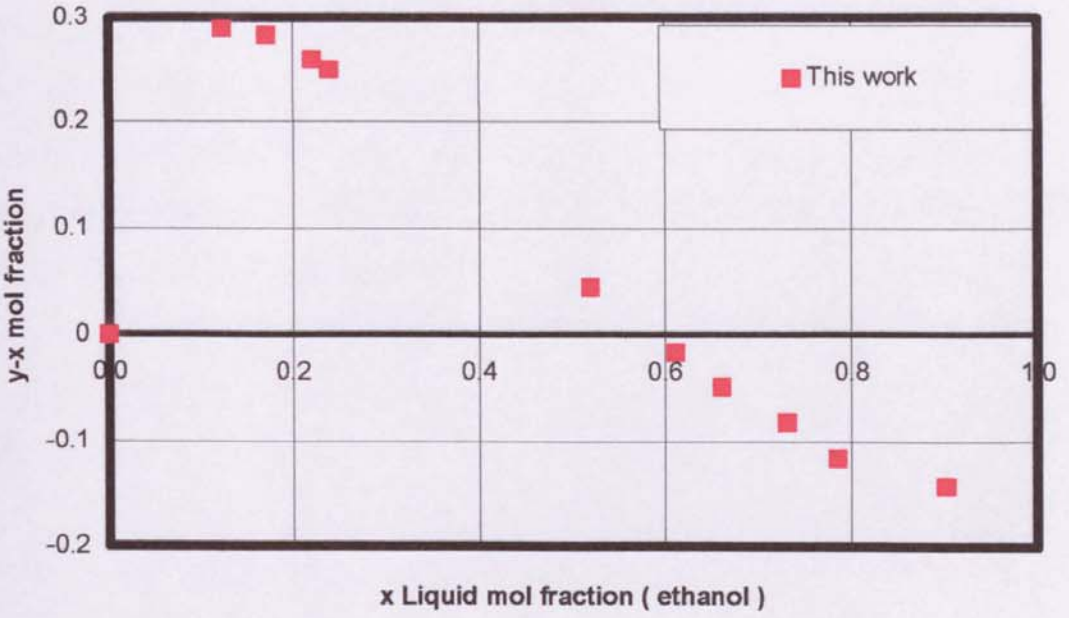


Figure 8.7 Plot of (y-x) against x for cyclohexane-ethanol at 6 bar.

The results of the Barker type consistency tests are given in Appendix 6. The best fit was obtained using the UNIQUAC equation. This returned values for the RMS deviations for the pressure of 19.04 mmHg, temperature 0.20 K, liquid mole fraction 0.0051 and vapour mole fraction 0.0089. The Wilson, NRTL and Margules equations

all returned similar values. For this pressure the minimisation of the pressure parameter was relaxed. The RMS deviation for pressure is therefore much higher for this pressure. This is still acceptable because the deviation measured is still less than 0.5% of the actual pressure measured. Thus the consistency of this data is the same as that at 4 bar.

8.9 Cyclohexane-ethanol data at 8 bar.

A P-T-x-y data set of 16 points was obtained for the mixture at 8 bar. Figure 8.8 is a plot as y-x against x screening plot. The atmospheric pressures were not measured for this data set. The gauge pressures measured experimentally were corrected using daily atmospheric pressure measurements obtained from The Birmingham Weather Centre, Birmingham University. The azeotrope determined from the experimental data at 8 bar pressure (absolute) as 0.616 mole fraction of ethanol, at 132.2^{0}C.

The results of the Barker type consistency tests are given in Appendix 6. The best fit was obtained using the Wilson equation. This returned values for the RMS deviations for the pressure of 6.54 mmHg, temperature 0.07 K, liquid mole fraction 0.0030 and vapour mole fraction 0.0127. The UNIQUAC and NRTL equations all returned similar values. For this pressure the minimisation of the pressure parameter was relaxed. This is acceptable because the deviation measured is still less than 0.5% of the actual pressure measured. Thus the consistency of this data is the same as for the data sets at 4 and 6 bar.

8.10 Cyclohexane-ethanol data at 11 bar.

A P-T-x-y data set of 14 points was obtained at 11 bar. Figure 8.9 is a plot this work as a y-x against x screening plot. The atmospheric pressures were not measured for this data set. The gauge pressures measured experimentally were corrected using daily atmospheric pressure measurements obtained from The Birmingham Weather Centre, Birmingham University. The azeotrope determined from the experimental data at 11 bar pressure (absolute) as 0.635 mole fraction of ethanol, at 145.3^{0}C.

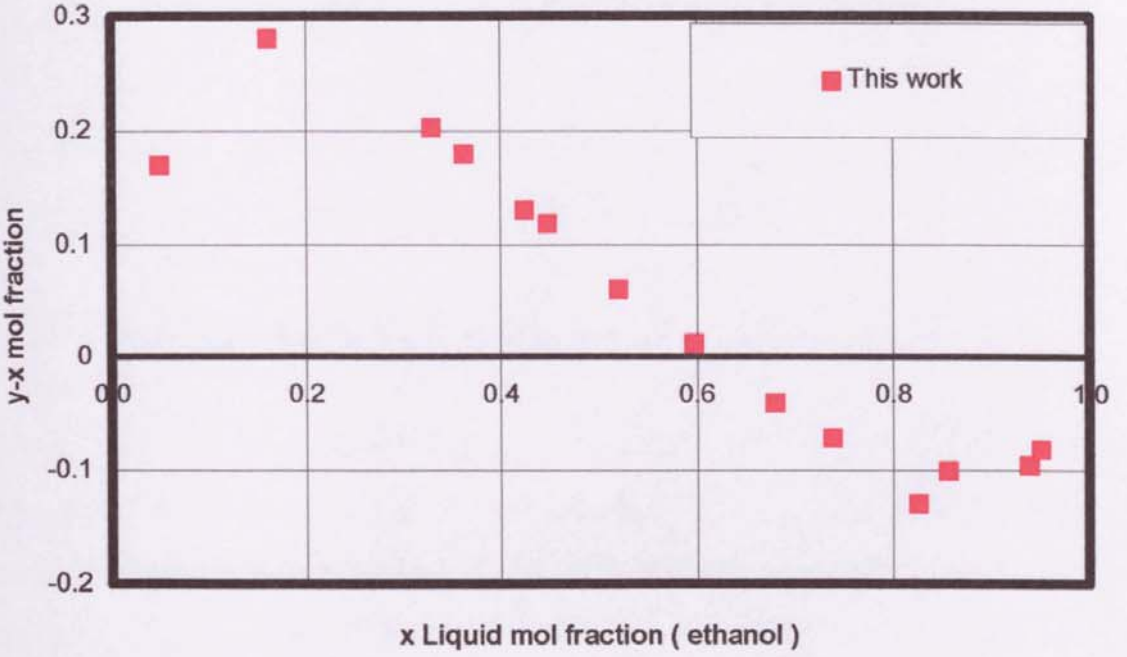


Figure 8.8 Plot of (y-x) against x for cyclohexane-ethanol at 8 bar.

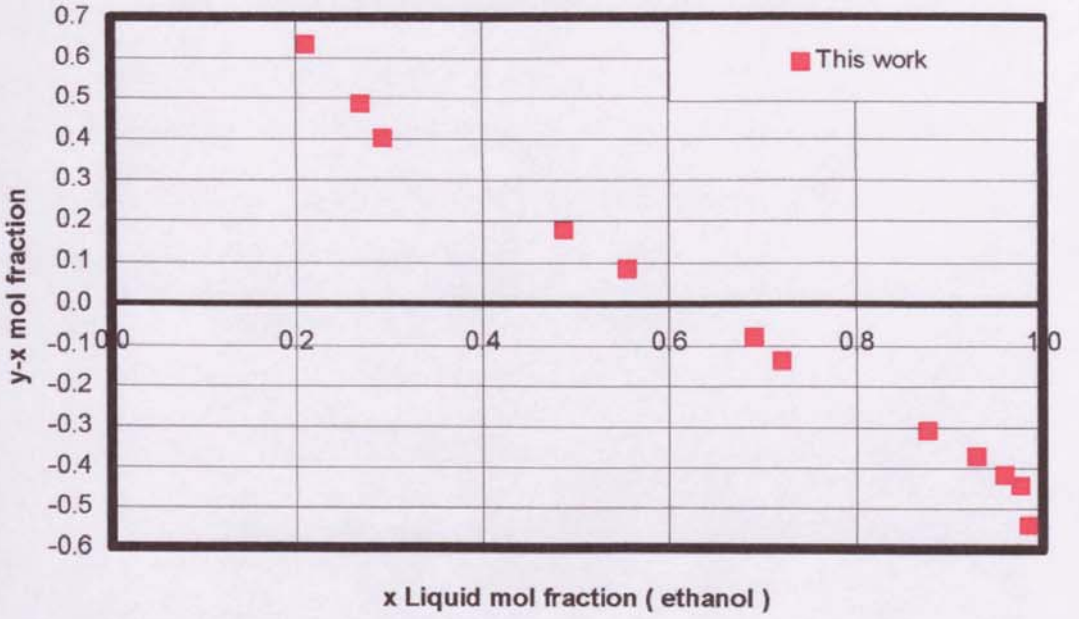


Figure 8.9 Plot of (y-x) against x for cyclohexane-ethanol at 11 bar.

The results of the Barker type consistency tests are given in Appendix 6. The best fit was obtained using the Wilson equation. This returned values for the RMS deviations for the Pressure of 12.42 mmHg, temperature 0.26 K, liquid mole fraction 0.0054 and

vapour mole fraction 0.0063. All the equations used returned similar RMS deviations. For this pressure the minimisation of the pressure parameter was relaxed. This is still acceptable because the deviation measured is still less than 0.5% of the actual pressure measured. Thus the consistency of this data is still in line with if not superior to the most reliable data for organic mixtures found in the literature.

8.11 Cyclohexane-ethanol data at 90.9°C.

A P-T-x-y data set of 24 points was obtained for the mixture at 90.9°C. Figure 8.10 is a plot as a y-x against x screening plot. The pressure measurement for this data set was produced using the Druck DPI 140 pressure gauge which measures absolute pressure and so for this data set no pressure correction was required. The azeotrope has been determined from the experimental data at 90.9°C as 0.507 mole fraction of ethanol, at 1895 mmHg (absolute).

The results of the Barker type consistency tests are given in tables in Appendix 6. The best fit was obtained using the UNIQUAC equation. This returned values for the RMS deviations for the pressure of 2.44 mmHg, temperature 0.14 K, liquid mole fraction 0.0025 and vapour mole fraction 0.0042. The Wilson returned similar values, whilst the other equations failed to represent the liquid phase as well. Thus the consistency of this data is in line with the new one atmosphere data and of a very high quality.

8.12 Cyclohexane-ethanol data at 138.2°C.

A P-T-x-y data set of 11 points was obtained for the mixture at 138.2° C. Figure 8.11 is a plot of this work as a y-x against x screening plot. The atmospheric pressure was measured daily for this data set using the Druck DPI 140 pressure gauge. This pressure measurement was used to correct the data gauge pressure readings. The azeotrope has been determined from the experimental data at 138.2°C as 0.630 mole fraction of ethanol, at 7195.5 mmHg pressure (absolute).

The results of the Barker type consistency tests are given in tables in Appendix 6. The best fit was obtained using the Wilson equation. This returned values for the RMS deviations for the pressure of 14.34 mmHg, temperature 0.26 K, liquid mole fraction 0.0081 and vapour mole fraction 0.0105. The Wilson and NRTL equations returned similar values. For this pressure the minimisation of the pressure parameter was relaxed. The RMS deviation for pressure is therefore much higher for this pressure. This is still acceptable because the deviation measured is still less than 0.5% of the actual pressure measured. The RMS deviation for the liquid composition is higher for this data set making this data set less reliable than the others. The still is more difficult to run isothermally because the pressure is continually adjusted to maintain a constant temperature. Since the temperature is dependent on the pressure it is more difficult to stabilise the still at the operating conditions. This may explain why this data set is not as reliable as the isobaric data sets.

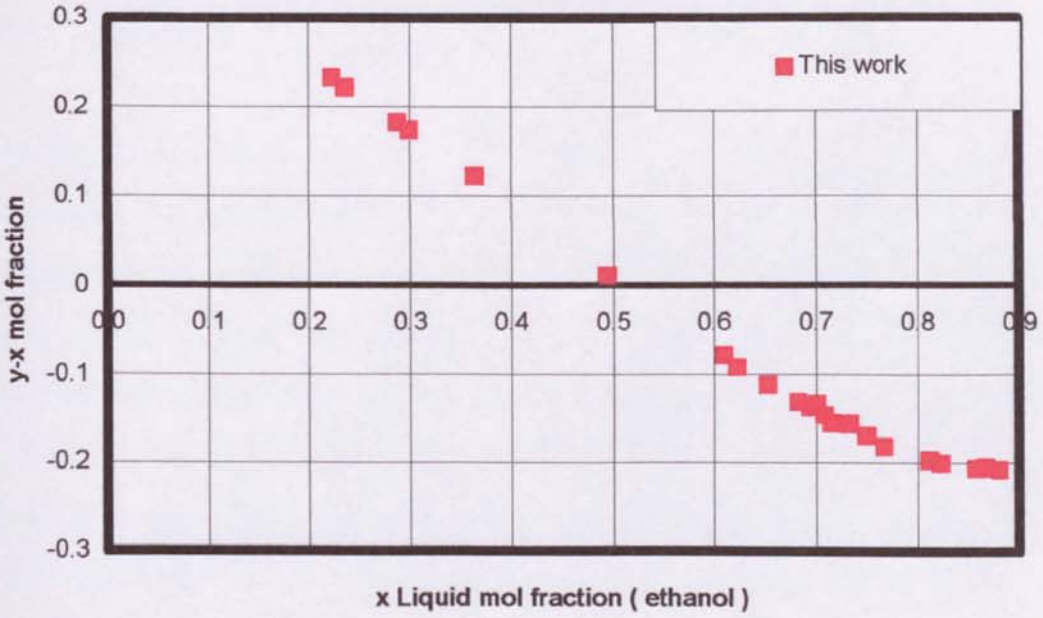


Figure 8.10 Plot of (y-x) against x for cyclohexane-ethanol at 90.9^{0}C.

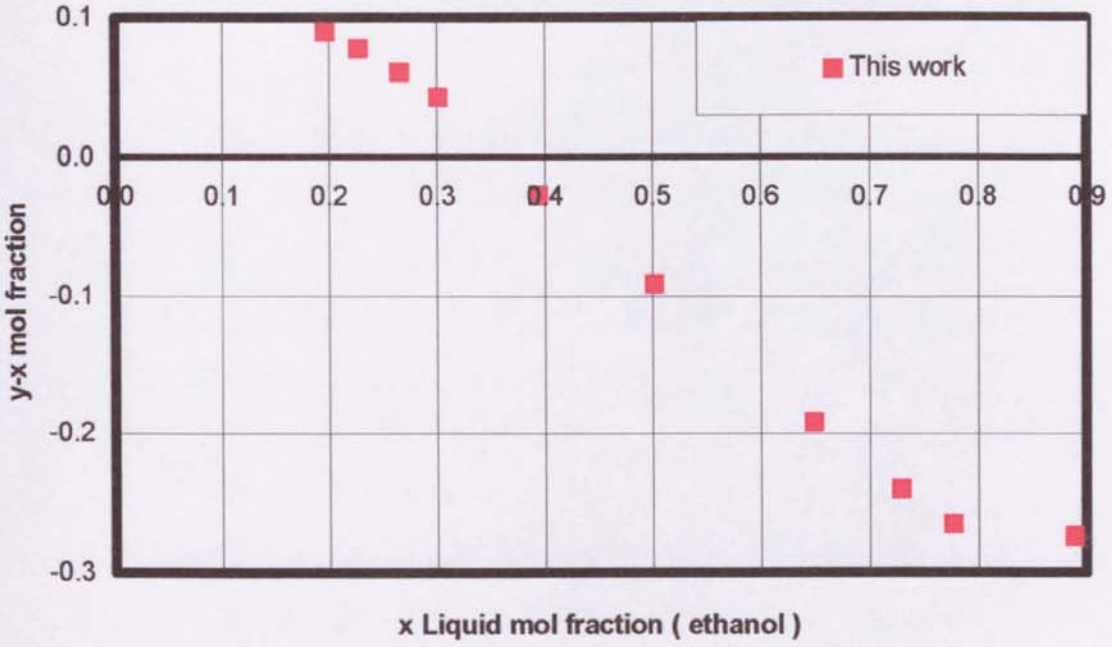


Figure 8.11 Plot of (y-x) against x for cyclohexane-ethanol at 138.2^{0}C.

8.13 Variation of UNIQUAC parameters with temperature.

One aspect of the performance of the UNIQUAC equation is the dependence of its parameters on temperature, a better knowledge of this relationship would give guidance on how reliable are predictions at conditions other than those for which data are available. Figure 8.12 gives plots of the values of the parameters for the two-parameter UNIQUAC equation as functions of temperature. The temperatures for the isobaric cases are those of the azeotropes. It can be seen that the variation is not linear with temperature, the curve shown is a simple quadratic. The observed spread is of the same order as the uncertainty in the fitted values of the parameters.

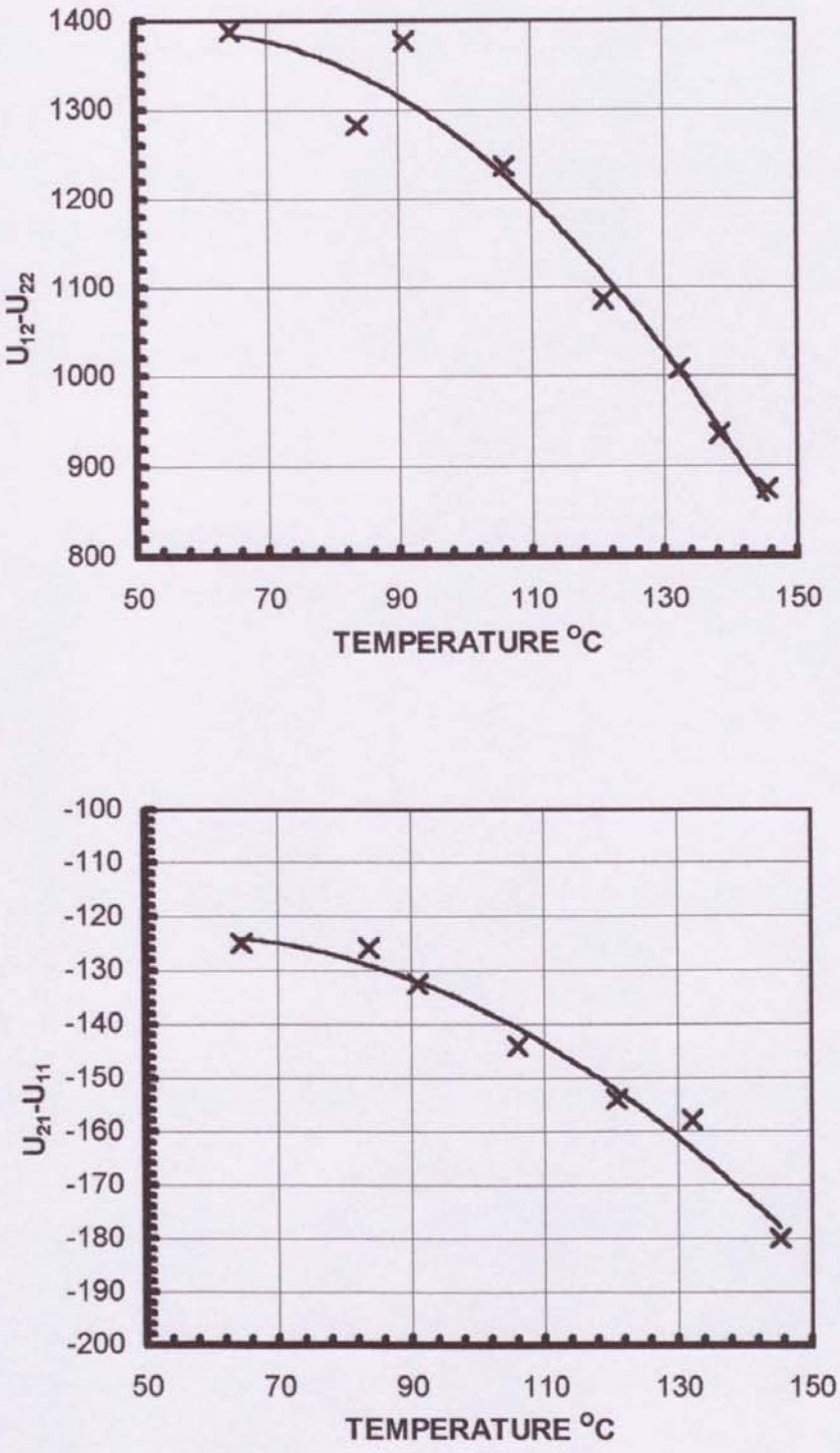


Figure 8.12 Dependence for the UNIQUAC parameters on temperature.

8.14 Prediction using literature UNIFAC group parameters.

For each data set measured activity coefficients were predicted using UNIFAC to determine the temperature dependence of these predicted activity coefficients. Two sets of group parameters were used, the original parameters proposed by Fredenslund et al. (1977) and the revised group parameters of Larson (1986). The revised UNIFAC model proposed by Gmehling et al. (1986) was also considered but rejected at this stage because work by Schmelzer et al. (1996), suggested that the Gmehling model represented alcohol- cyclohexane mixtures poorly.

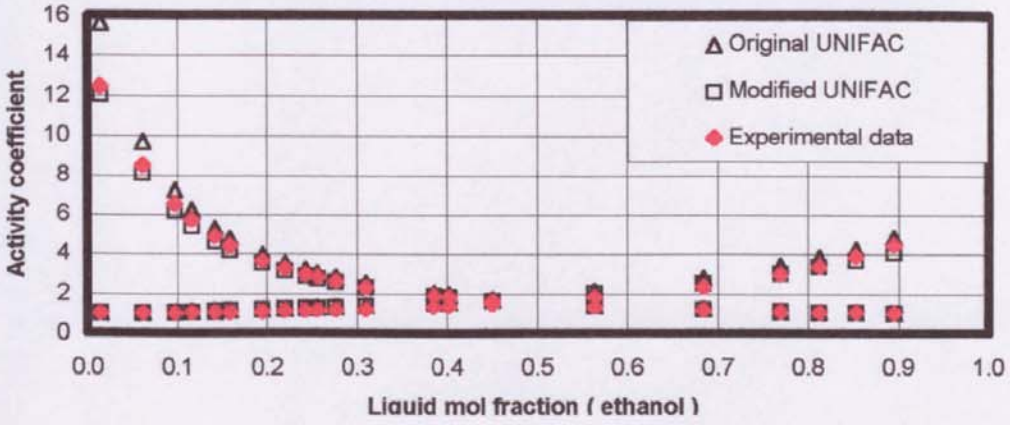


Figure 8.13 Activity coefficient against x plot for cyclohexane-ethanol at 1 atmosphere.

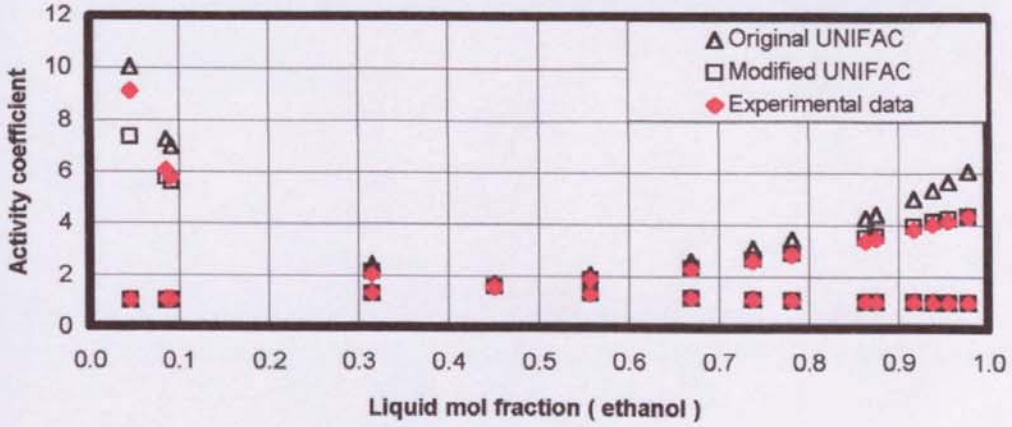


Figure 8.14 Activity coefficient against x plot for cyclohexane-ethanol at 2 bar.

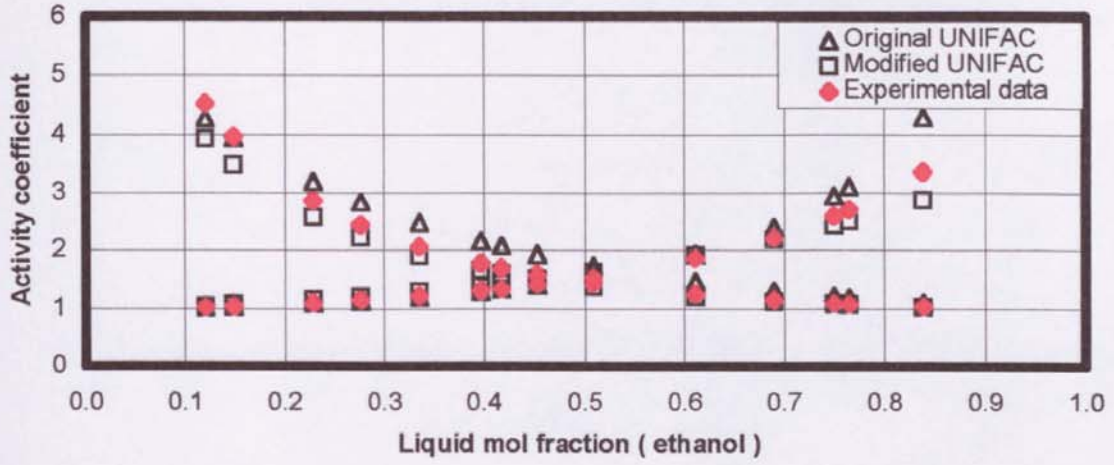


Figure 8.15 Activity coefficient against x plot for cyclohexane-ethanol at 4 bar.

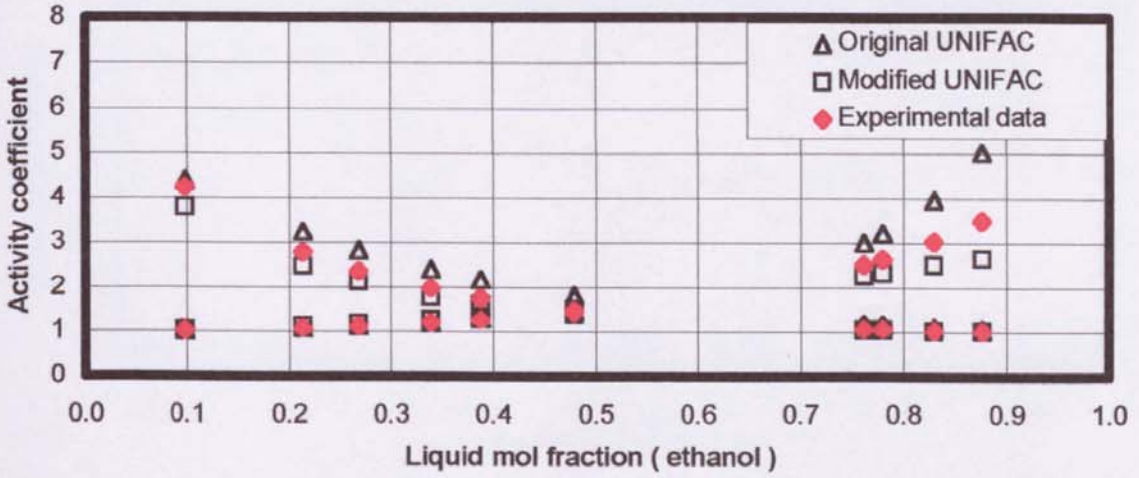


Figure 8.16 Activity coefficient against x plot for cyclohexane-ethanol at 6 bar.

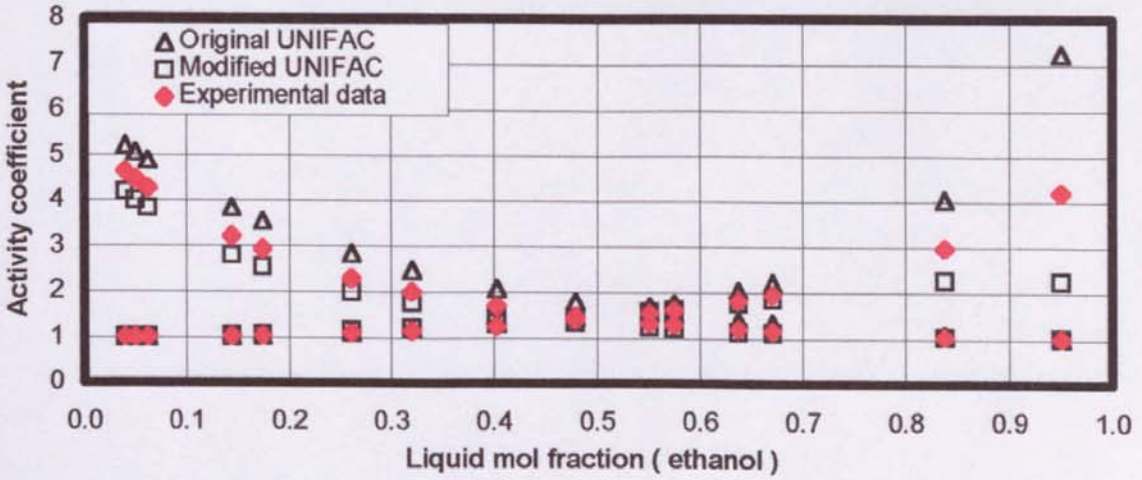


Figure 8.17 Activity coefficient against x plot for cyclohexane-ethanol at 8 bar.

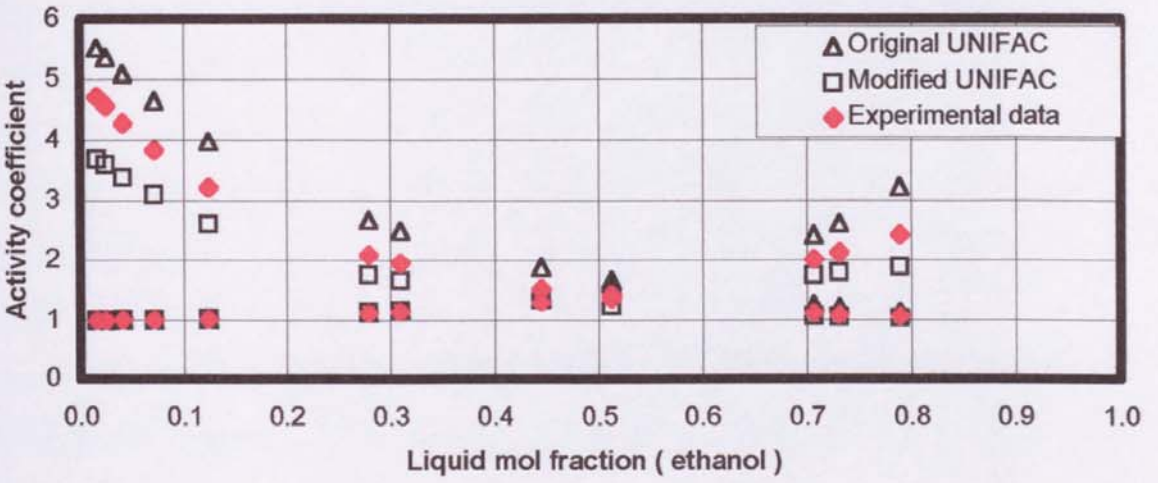


Figure 8.18 Activity coefficient against x plot for cyclohexane-ethanol at 11 bar.

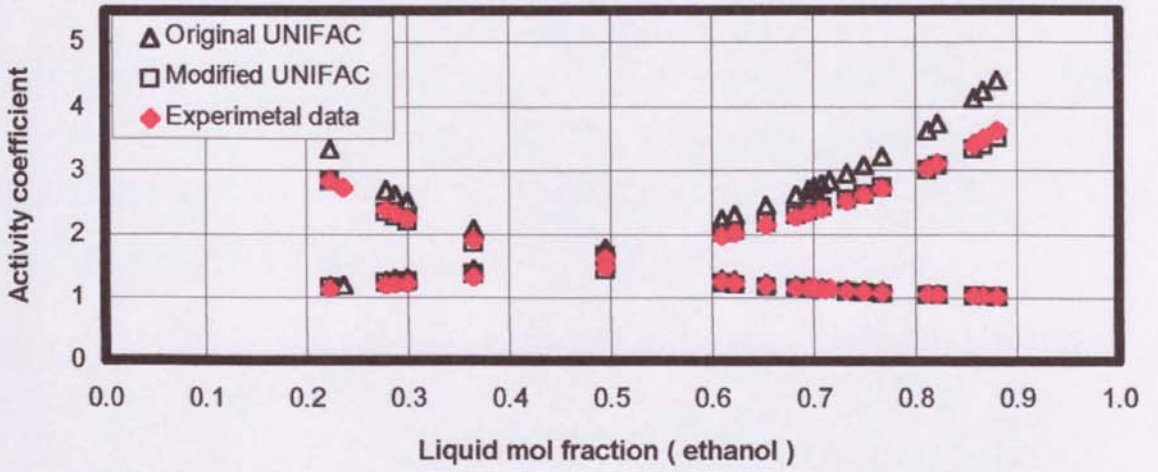


Figure 8.19 Activity coefficient against x plot for cyclohexane-ethanol at 90.9^{0}C.

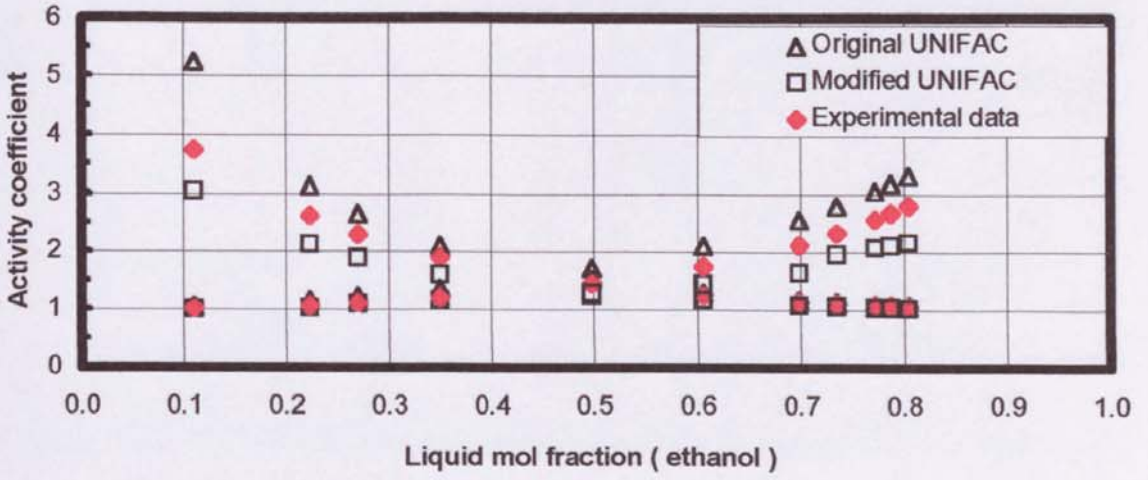


Figure 8.20 Activity coefficient against x plot for cyclohexane-ethanol at 138.2^{0}C.

Figures 8.13 to 8.20 show the activity coefficient against x plots for all the experimental data sets. Trials with the original parameters gave very poor predictions over-estimating the activity coefficients in all cases. It can be seen that for the modified parameters agreement is reasonable up to about 4 bar. Above these pressures the modified equation under-estimates the coefficients. Thus whilst revised group parameters of Larson (1986) are an improvement, further revision is necessary to account for, both the temperature dependence of the parameters (which ought to be in line with that observed above for UNIQUAC parameters) and the effects of the higher pressures .

8.15 Prediction of data cyclohexane ethanol using AGAPE prediction techniques.

The AGAPE direct prediction technique using the generalised London's potential has been used to predict VLE data for this mixture at and below one atmosphere pressure with some degree of success. This experimental data have been used to test this technique and find its limits of use above one atmosphere pressure.

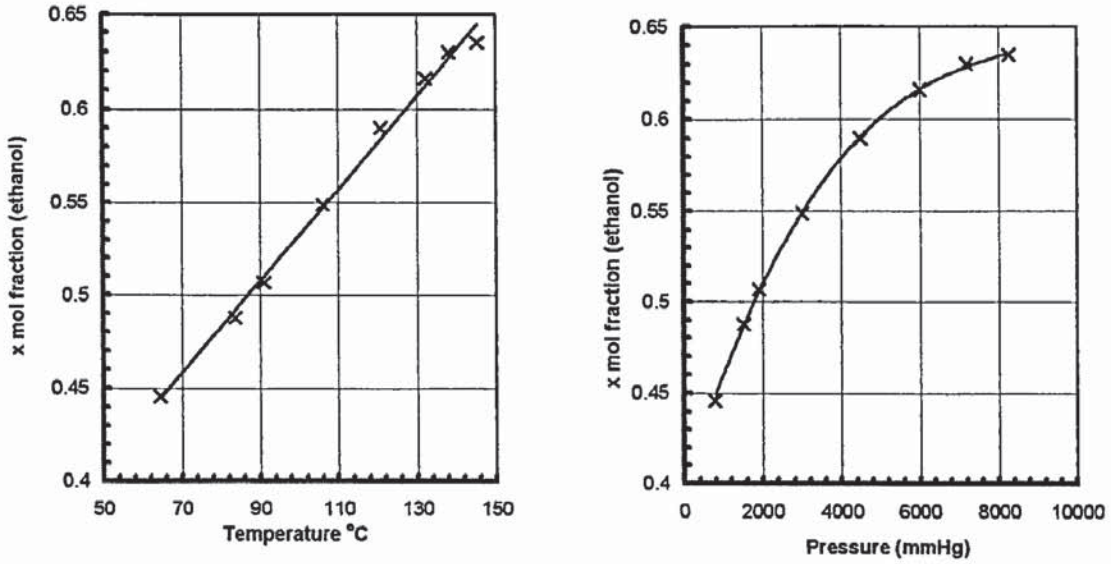


Figure 8.21 Dependence of azeotrope composition on temperature and pressure.

The use of the AGAPEFIT technique is discussed in chapters 4 and 7. It fits the variable parameters of the AGAPE model to a single experimental data point then uses

these fitted parameters to predict the VLE data for the rest of the composition range. A knowledge of the variation of azeotrope composition with pressure and temperature would permit the azeotrope values to be used as the fitting points for the model.

The experimental data determined for this mixture gives us a knowledge of the variation of azeotrope composition with pressure and temperature. The azeotrope obtained for each set are plotted in figure 8.21; a linear relationship is obtained between composition and temperature, while that for pressure is quadratic in form.

These two techniques have been used to predict data for the experimental data sets at 1 atmosphere, 2, 4, 6, 8, bar pressure and 90.9^{0}C. The data from the GLP predictions are given in tables Appendix 8 and the data from the AGAPEfit predictions are given in tables Appendix 8. The value of Z was set to its normal value of 11 for this size and type of molecule. The value of r was initially set at 0.7 the normal values of r for this mixture. The value of Φ_{12} which represents the inter-molecular attractive forces was varied until a fit was achieved on the data point activity activity coefficient values.

The activity coefficients predicted using r = 0.7 were plotted with those obtained from the experimental data. The fits obtained were poor. Homer (1996) suggested this was due to association between ethanol molecules to form dimers and advised that r be doubled to account for the association. The best results were obtained by taking a mean value of r of 1.1 which allows for some association at higher concentrations of ethanol band little association at low concentrations where single molecules are more likely to prevail.

Figures 8.22 to 8.27 show the screening plots of y-x against x for the experimental data replotted with the new data predicted using the AGAPE models. The data is represented well by both models for liquid mole fractions greater than 0.4 (ethanol). At lower concentrations the models both over estimate the vapour phase concentrations.

The observed differences in y values between experimental and predicted values do not appear to be temperature dependant. It is known from consistency tests performed on the experimental data that this mixture is not represented well by the assumption of

ideal vapour phase behaviour. Therefore the assumption of ideal vapour phase behaviour used by the AGAPE models may be responsible for the observed deviations.

In order to test this hypothesis the AGAPE predicted activity coefficients, from both methods, have been plotted with those obtained from the experimental data and the UNIFAC predictions (see figures 8.28 to 8.33). The experimental data activity coefficients have been deduced from the consistency tests performed on the data, using the best fit liquid activity coefficient model and allowing for vapour phase non-ideality.

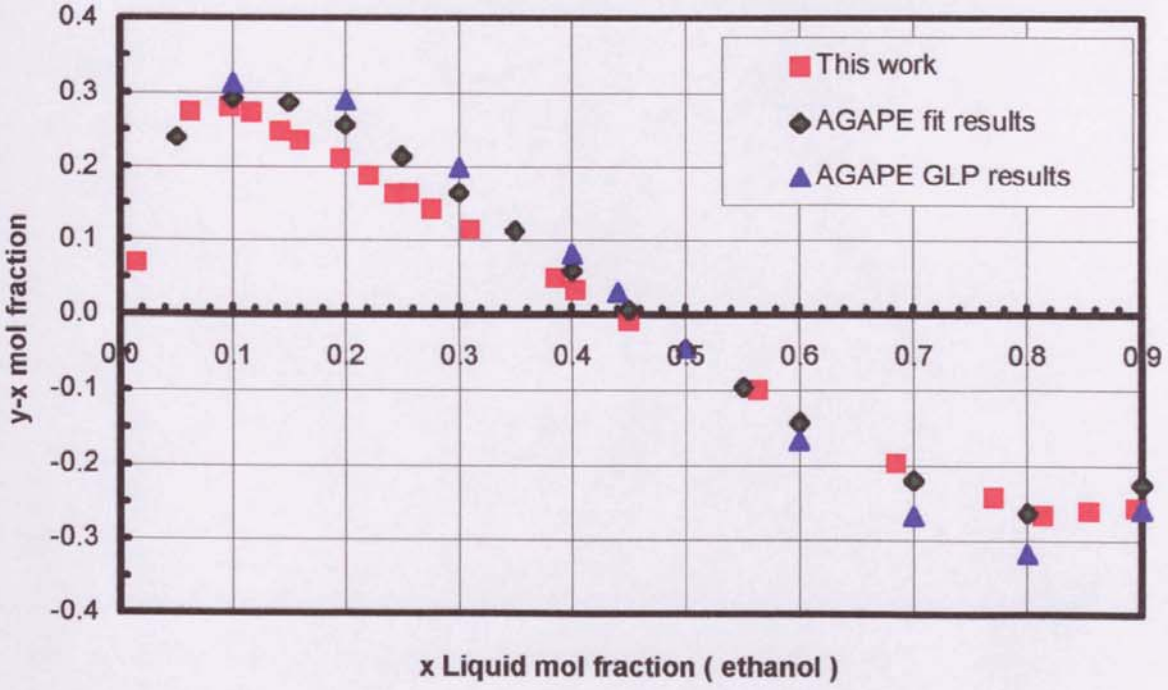


Figure 8.22 Plot of (y-x) against x for cyclohexane-ethanol at 1 atmosphere including data predicted using both AGAPE methods.

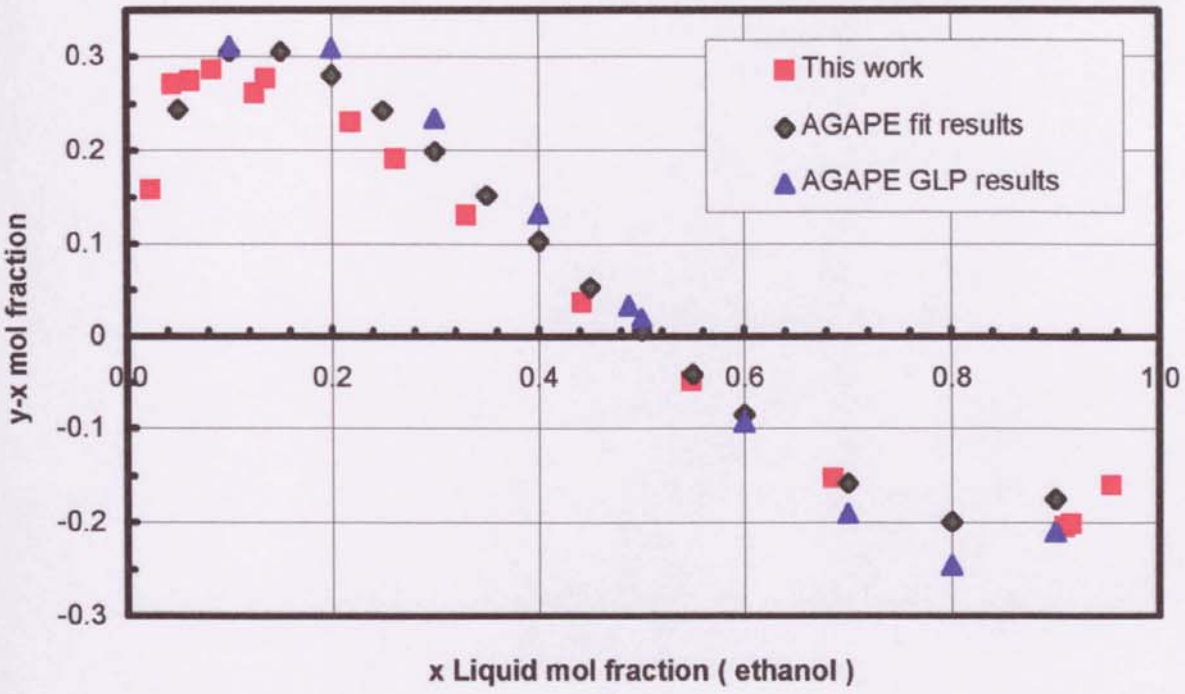


Figure 8.23 Plot of (y-x) against x for cyclohexane-ethanol at 2 bar including data predicted using both AGAPE methods.

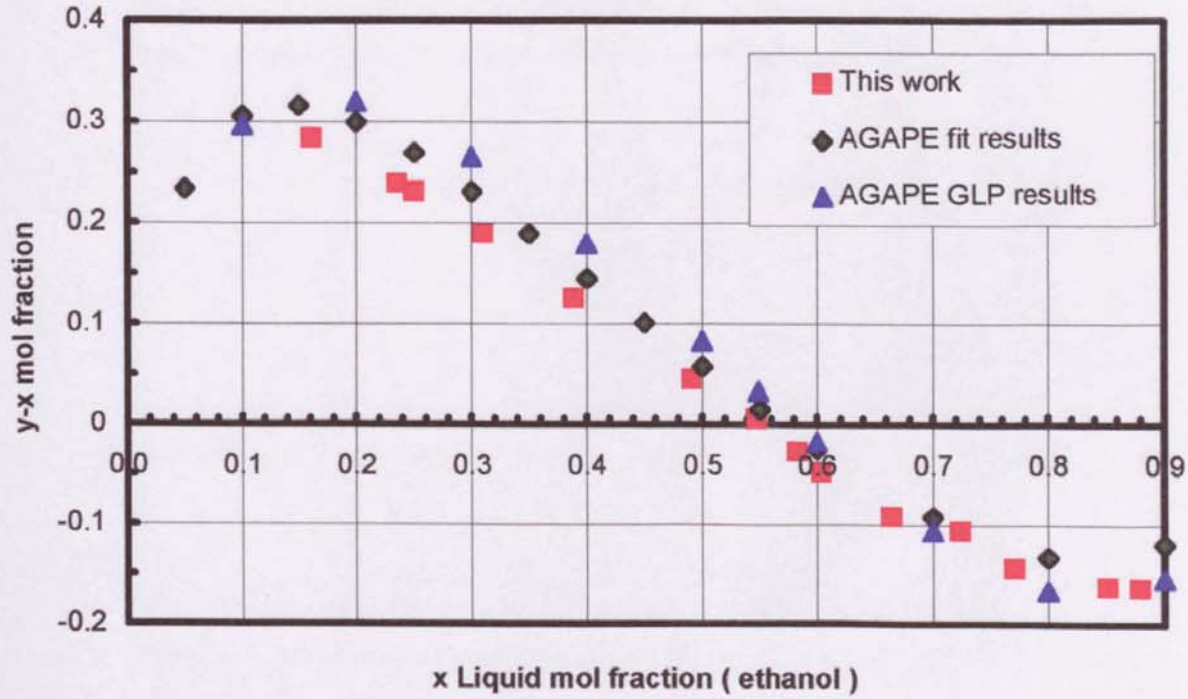


Figure 8.24 Plot of (y-x) against x for cyclohexane-ethanol at 4 bar including data predicted using both AGAPE methods.

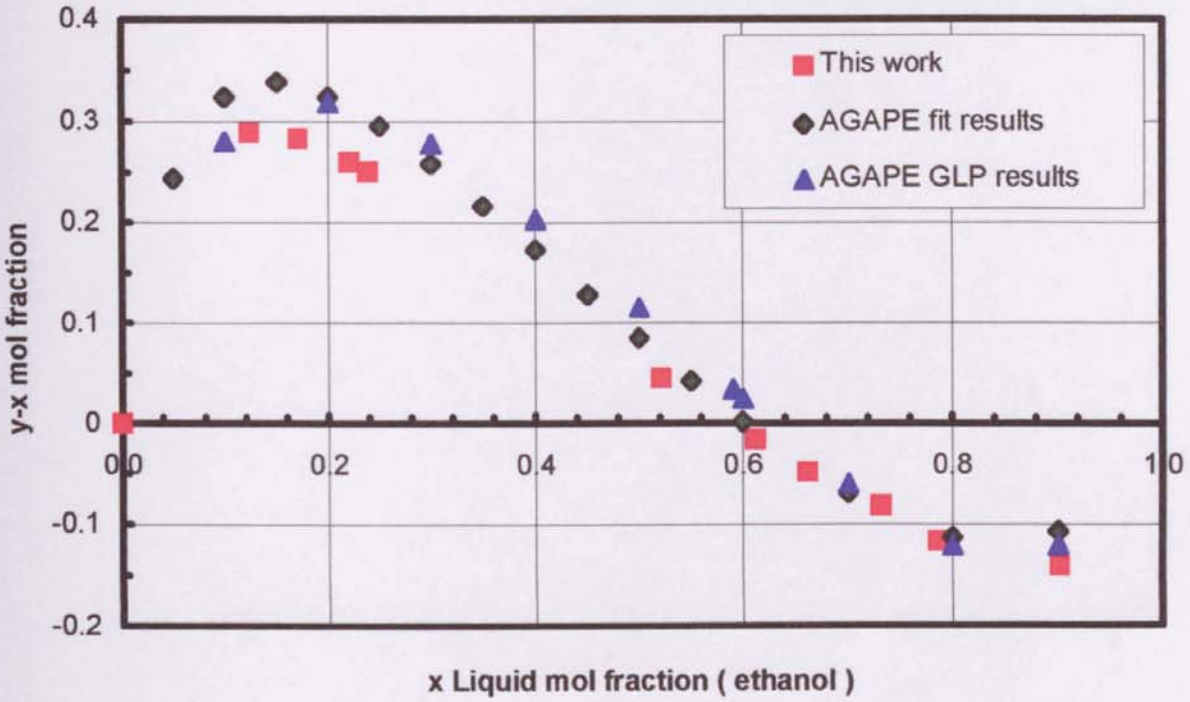


Figure 8.25 Plot of (y-x) against x for cyclohexane-ethanol at 6 bar including data predicted using both AGAPE methods.

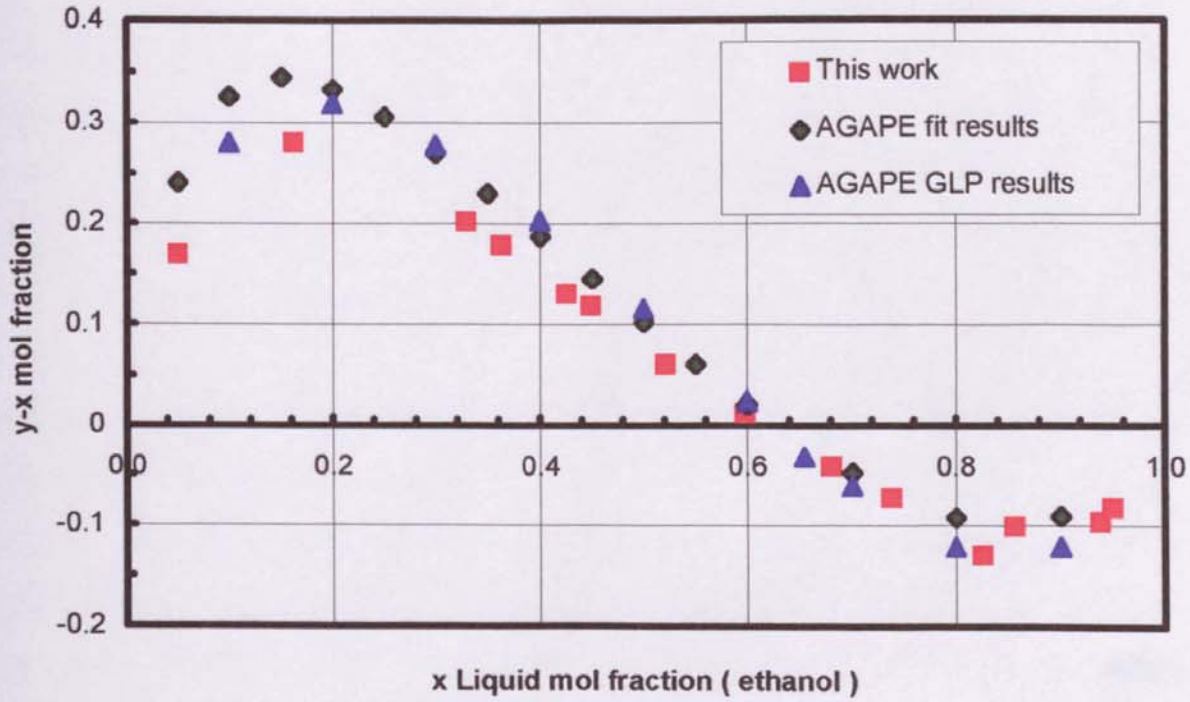


Figure 8.26 Plot of (y-x) against x for cyclohexane-ethanol at 8 bar including data predicted using both AGAPE methods.

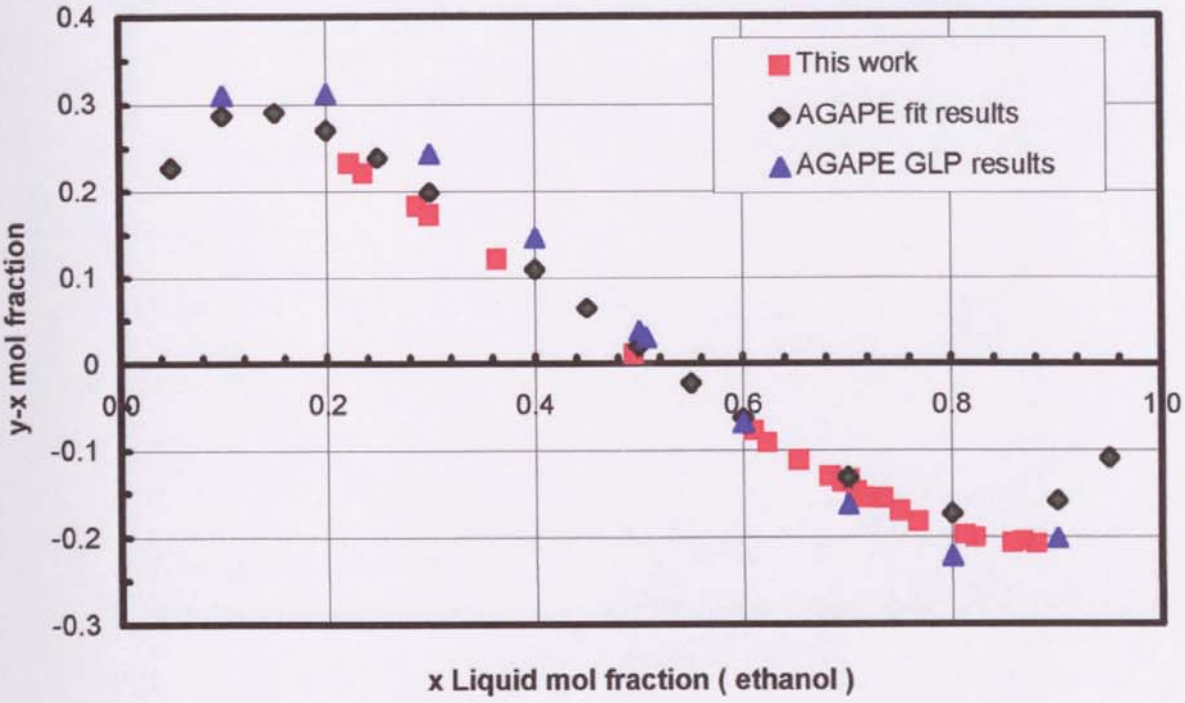


Figure 8.27 Plot of (y-x) against x for cyclohexane-ethanol at 90.9^{0}C including data predicted using both AGAPE methods.

The graphs indicate that both the AGAPE GLP model represent the activity coefficients surprisingly well. It overestimates the activity coefficients slightly, to about the same amount as the original UNIFAC model. For the higher pressures (see figures 8.31 and 8.32) the activity coefficients obtained from the AGAPE GLP model are better than those obtained from either of the UNIFAC models.

The data obtained from the AGAPEFIT predictions using the mean value of r = 1.1 indicate a strong improvement in the ability to predict activity coefficients for this mixture. The data fits obtained are not as perfect as those obtained for acetone chloroform mixture (see chapter 7) but are in themselves good data fits and validate the use of azeotrope data for parameter fitting. They also indicate that the errors found in the y data predictions using AGAPE are probably due to vapour phase non-ideality.

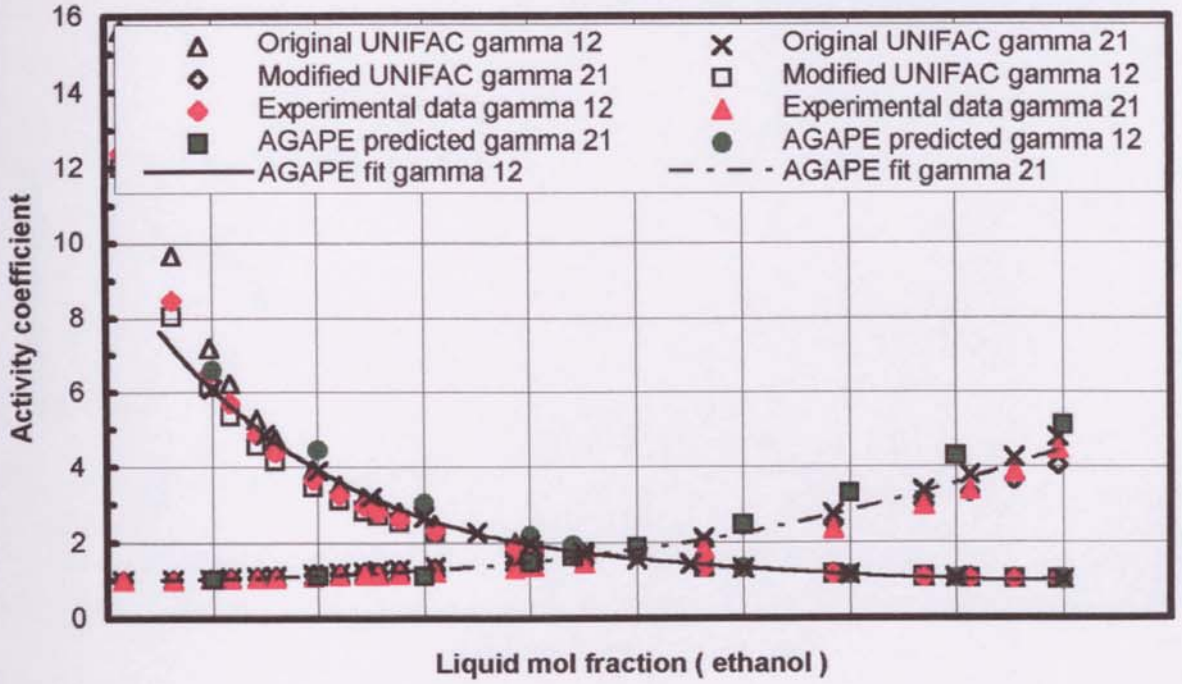


Figure 8.28 Activity coefficient against x plot for cyclohexane-ethanol at 1 atmosphere including data predicted using both AGAPE and UNIFAC methods.

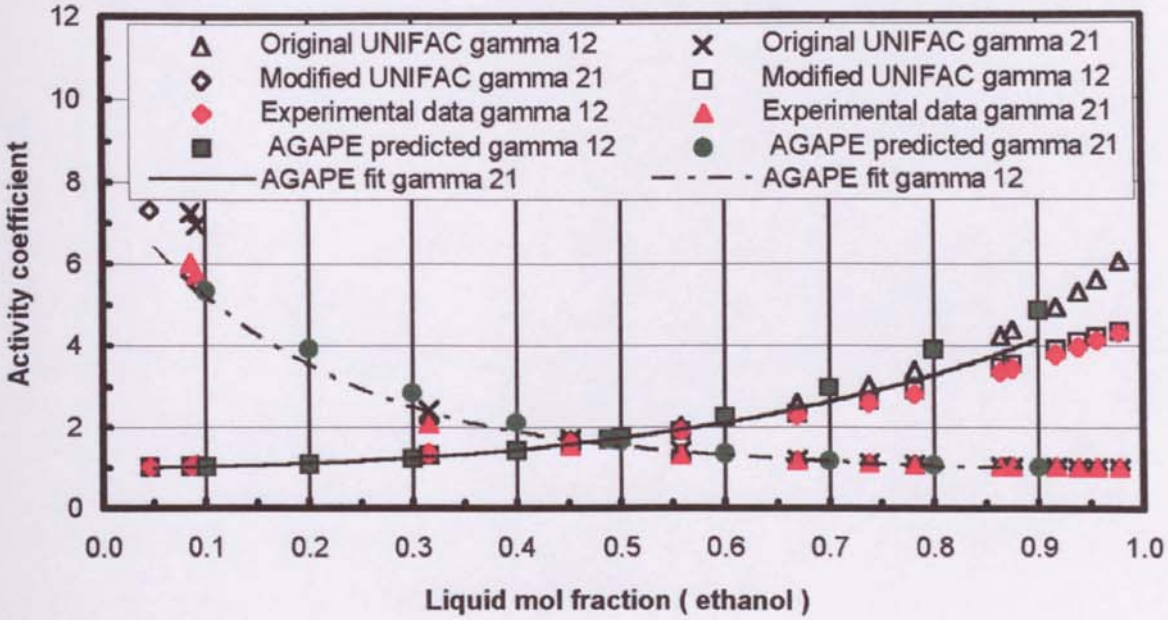


Figure 8.29 Activity coefficient against x plot for cyclohexane-ethanol at 2 bar including data predicted using both AGAPE and UNIFAC methods.

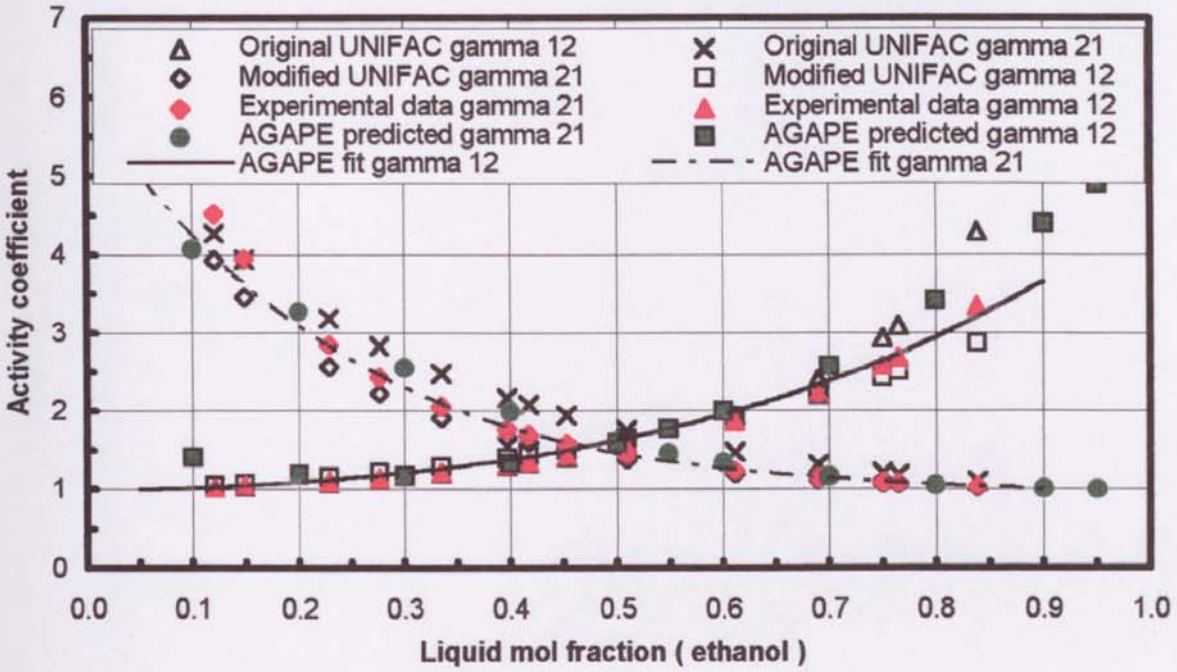


Figure 8.30 Activity coefficient against x plot for cyclohexane-ethanol at 4 bar including data predicted using both AGAPE and UNIFAC methods.

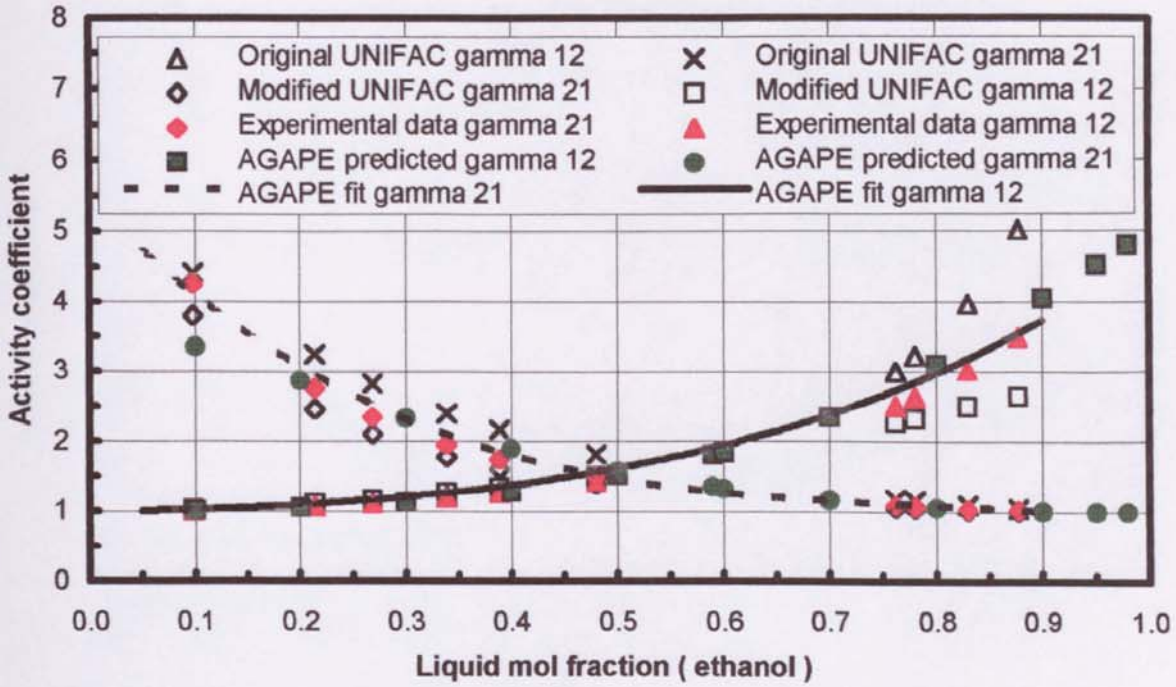


Figure 8.31 Activity coefficient against x plot for cyclohexane-ethanol at 6 bar including data predicted using both AGAPE and UNIFAC methods.

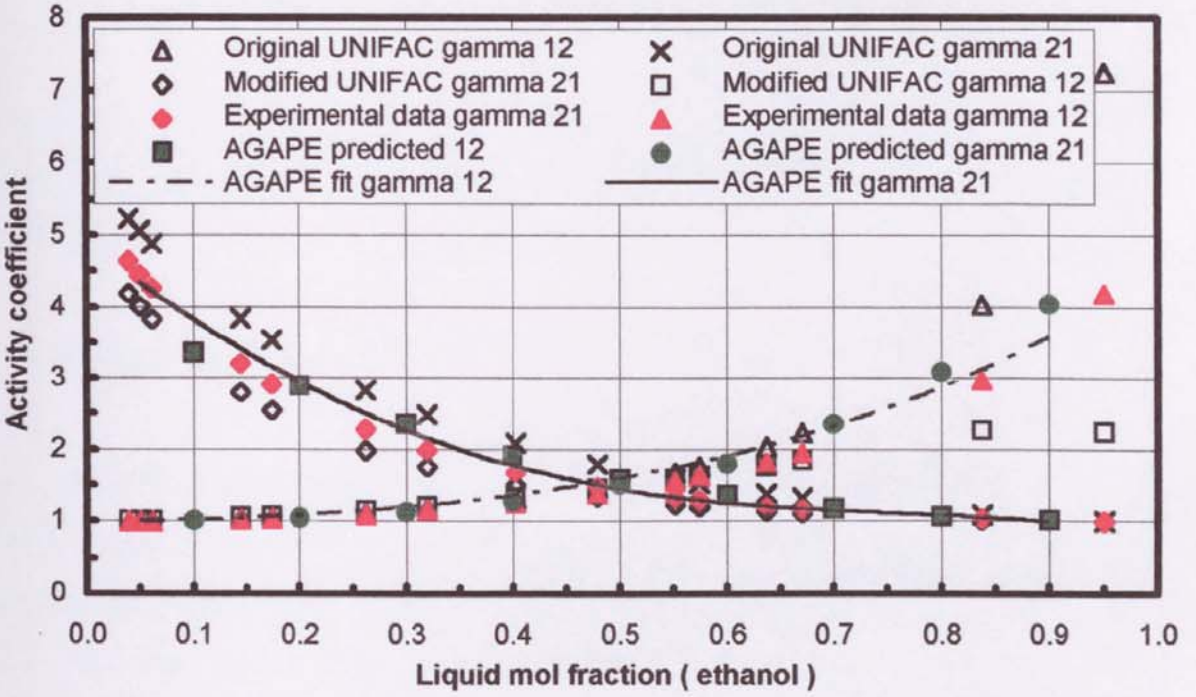


Figure 8.32 Activity coefficient against x plot for cyclohexane-ethanol at 8 bar including data predicted using both AGAPE and UNIFAC methods.

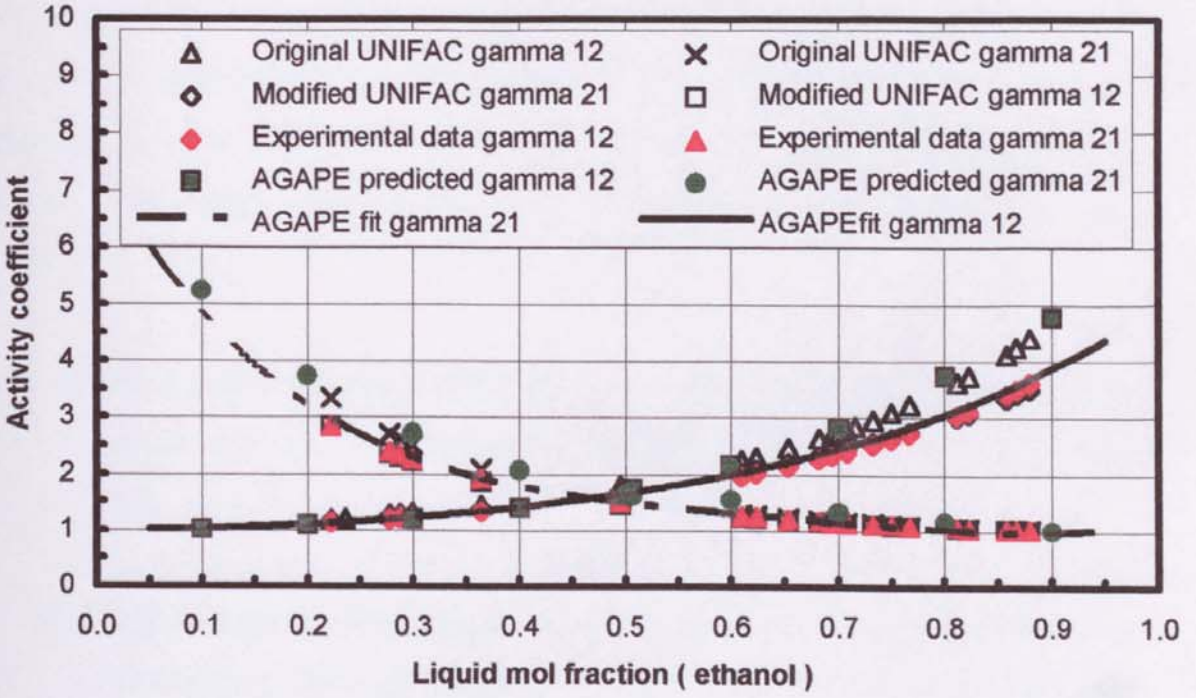


Figure 8.33 Activity coefficient against x plot for cyclohexane-ethanol at 90.9^{0}C including data predicted using both AGAPE and UNIFAC methods.

From the experience gained whilst running this apparatus several possible modifications were defined which would improve the performance, ease of operation and stability.

9.1 Reboiler redesign.

The acetic acid-water mixture highlighted some of the limitations of the present reboiler design. The reboiler is quite adequate for organic mixtures but the increased latent heat requirements for boiling an aqueous mixture mean that the reboiler must be run at maximum power input to barely achieve the minimum vapour flowrate required. Running at the maximum power input also leads to a higher wall temperature which with acid mixtures is undesirable. Severe corrosion was observed in the reboiler for the higher acid concentrations, a problem not noted elsewhere in the apparatus where the wall temperatures are considerably lower.

It is proposed that the reboiler be redesigned and constructed in nickel or monel metal which would give the high temperature surfaces greater resistance to corrosive mixtures. The single 250 W cartridge heater at present installed should be replaced with two 250W heaters inserted from either end of the reboiler. This will have two benefits :-

(i) The power input for the reboiler will no longer be restricted, thus aqueous mixtures will be handled better, by permitting finer control of the boilup rate.

(ii) The heat load will be spread over a greater surface area with a lower wall temperature. This will reduce the rate of corrosion at the wall surface and prevent degradation of the mixture due to thermal cracking from the very high wall temperatures.

9.2 The glass still.

The glass still, though significantly improved from the Zain-Jenkins version was prone to instability problems and flooding. These characteristics can be improved by further modifications to the Russell-Jenkins glass still.

The depth of the still needs to be increased. This would have several benefits. The residence time in the glass spiral would be increased allowing the vapour-liquid mixture greater time to reach equilibrium. The central thermometer pocket could be increased in length which would permit more of the central PRT to be immersed in the pocket improving the temperature measurement. The central cup could be deepened which would increase its ability to handle the fluctuations in liquid level reducing the still's tendency to flood.

The vapour pathways through the still need to be increased to the maximum permissible by the pressure vessel internal diameter and the limitations of standard glass sizes. The rate at which equilibrium is achieved and the stability of operation of the still are directly related to the vapour flowrate. The vapour pathways were enlarged in the present still but there is still room for further increases which would lead to better performance.

9.3 Modifications to the liquid circulation loop.

The liquid circulation loop requires two modifications. The recirculation pump on the vapour condensate circuit has been observed to intermittently interfere with the liquid feed to the main liquid circulation pump to the reboiler. This problem arises because the two pumps feed via a common line, of 1/8" O.D from the vapour condensate receiver. The capacity of this line is too small to meet the requirements of both pumps at the normal operating flowrates. It is proposed make the following modifications to the circuit:

i) The line forming the outer annulus from the liquid reservoir which forms the initial portion of the feed line to the pumps should be increased from 1/4"

O.D. to 3/8" O.D. and the 3/8" Swagelok tee should be replaced with a 3/8" Swagelok cross.

ii) The two outlets from the 3/8" cross should be reduced down to 1/4" O.D. and fed directly to each of the two pumps .

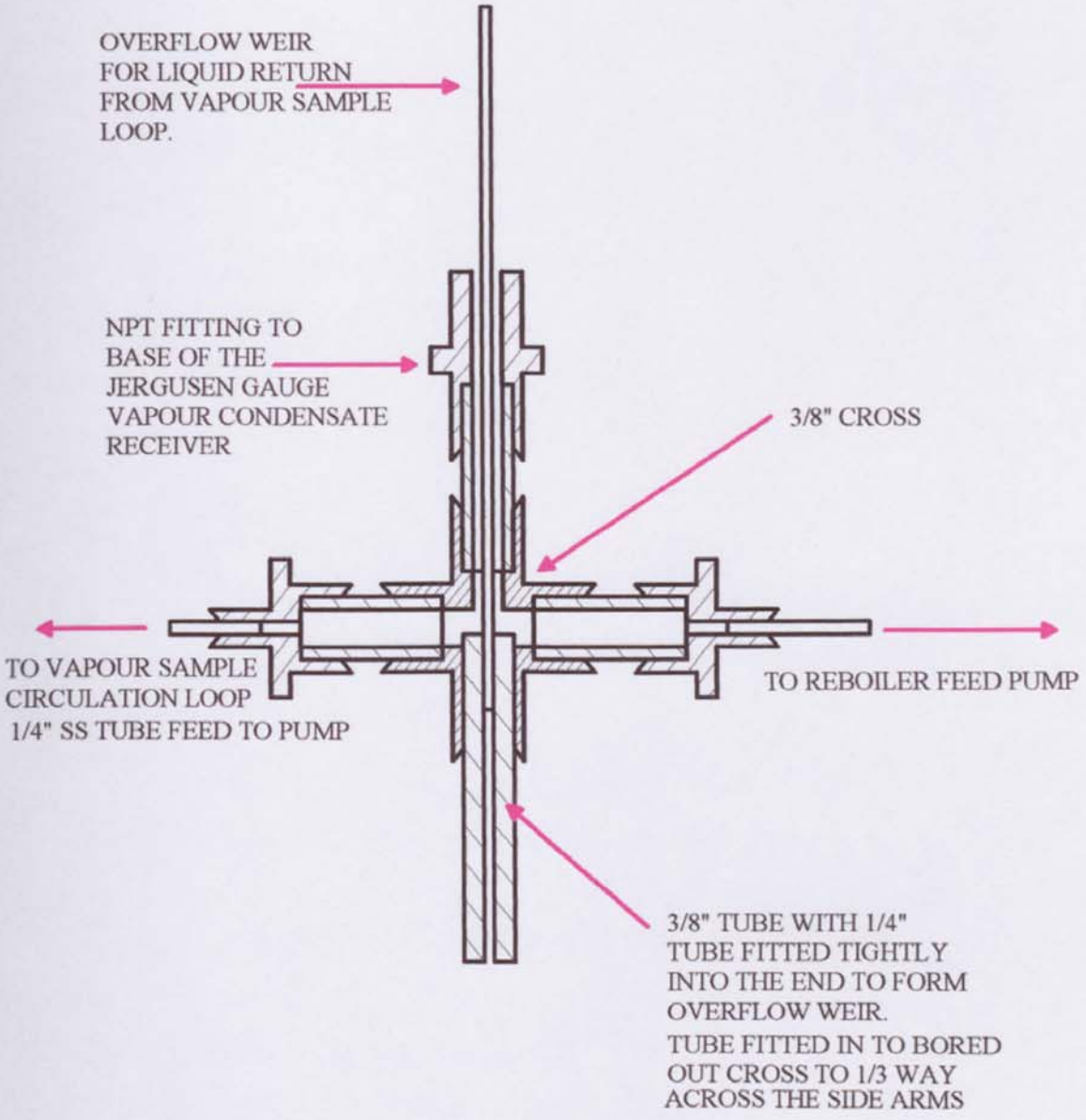


Figure 9.1 Modifications to liquid take off and returns from vapour condensate receiver.

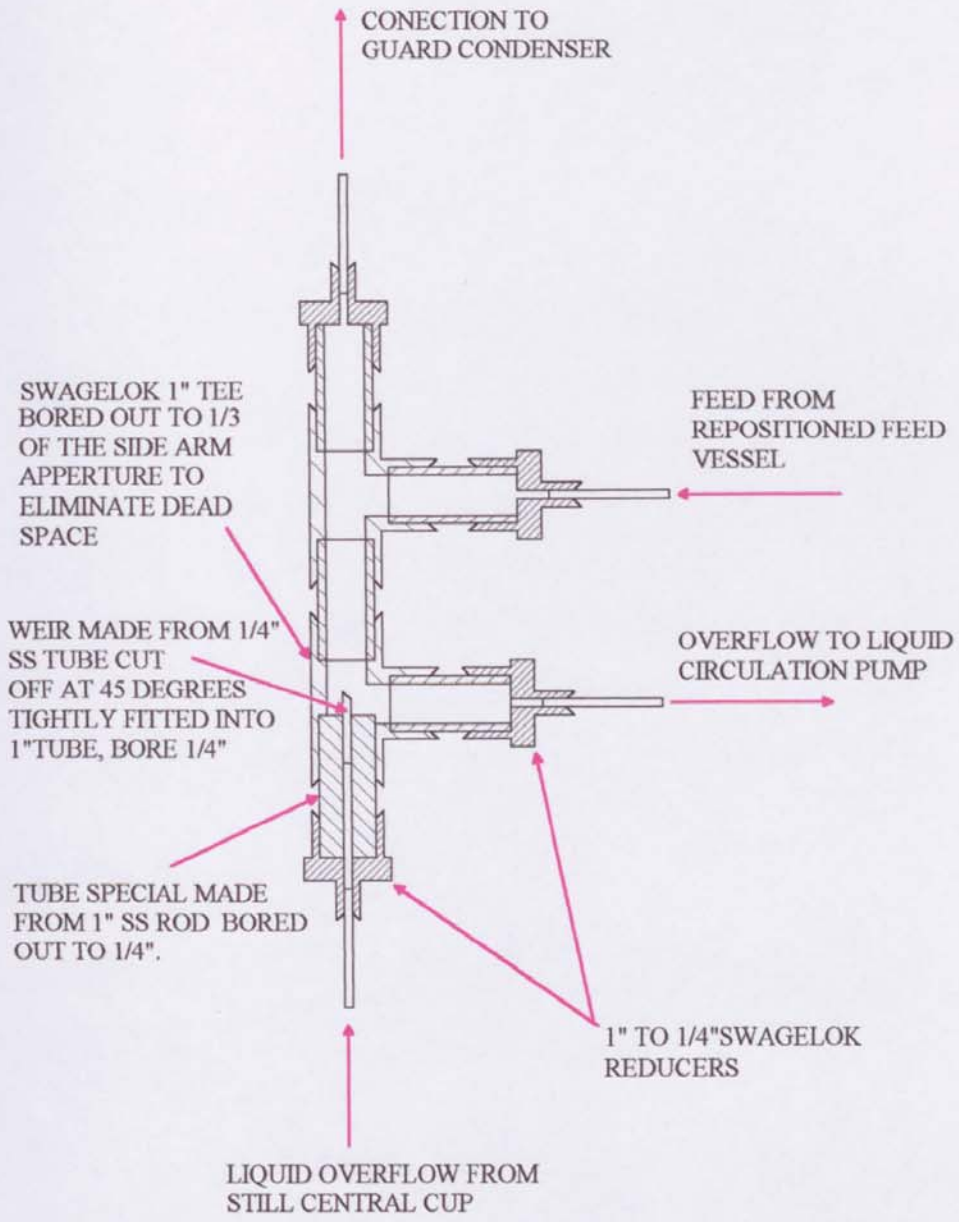


Figure 9.2 Modifications to liquid overflow weir

These modifications are shown in figure 9.1. The modifications made should increase the possible flowrates by a factor of four and guarantee that the pumps will no longer interfere with each other.

The liquid overflow weir which maintains the liquid level inside the still is prone to liquid backup in the line above the weir which causes intermittent flooding of the central cup of the still. This is believed to be due to the simple design of the weir which cannot handle surges of liquid. It is therefore proposed that the liquid weir be modified

to more closely resemble the weir design used in the atmospheric stills which do not exhibit this fault. Figure 9.2 shows how this modification could be achieved using standard stainless steel fittings.

9.4 Repositioning of the liquid feed vessel.

The position at which the liquid feed charging vessel is attached to the apparatus needs to be changed. In the present design the feed vessel is mounted above the pressure vessel and feed has been observed syphoning in to the pressure vessel rather than feeding directly in to the vapour condenser/vapour condensate receiver when charging at atmospheric pressure. This could be avoided by moving the feed vessel to feed into the liquid circulation line just above the liquid overflow weir as shown in Figure 9.2. This would move the feed vessel to a position below the top of the pressure vessel and prevent flow of the feed through the pressure lines to the pressure vessel.

9.5 On-line analysis.

Operation of the moderate pressure apparatus could be simplified and improved by the use of on-line analysis. On-line analysis has many benefits, i.e.

1) The possibilities of sample contamination and disruption of the sample composition by pressure reduction are eliminated.

2) The phase composition can be tracked accurately allowing easy determination of when equilibrium is achieved.

3) Operation of the still is rendered safer by removing the need to dismantle integral pipe work to allow vapour condensate samples to be removed. This effectively halves the operator exposure to the process materials.

4) Removal of the need to disconnect pipe work will reduce the turn round time between samples dramatically saving 0.5 hours per data point.

The Anton Paar densimeter could be installed directly into the vapour condensate loop in addition to the normal sample chamber. A filter would be required in the sample line feeding the densimeter to prevent any particulates entering the cell. The densimeter is fitted with high pressure adapter heads and can be operated up to 35 bar pressure.

For some mixtures refractive index measurements have proved more suitable for measuring composition. HPLC comparative refractive index instruments are available with operating pressure limits of about 100 psi, e.g. Varian Star 9040. Use of this type of instrument in comparative mode, using one of the pure components as reference fluid, should allow composition determinations to the same accuracy as presently measured by the Index Instruments refractive index instrument GPR 11-37 currently used for off-line measurements.

9.6 Computer control of moderate pressure apparatus.

Full automation of the apparatus, whilst desirable, is difficult to achieve due to the fine control of the apparatus being dependent on visual observation. A degree of automation can be achieved relatively easily, reducing the amount of manual supervision required and increasing the integral safety of the apparatus but retaining the fine control of the manual apparatus.

The critical operation characteristics of the apparatus are governed by a balance between the return pump rate and the reboiler heat input to give the optimum boilup rate. Control of the pump speed is insufficient to maintain this balance as gear wear reduces the flowrate with time. Therefore it is necessary to measure the feed rate to the reboiler and use this in a feed back loop to control the speed of the pump by controlling the power supply to the pump. A power cut-off to the reboiler and surface heaters should be installed for zero flow to prevent the apparatus boiling dry. The power control to the new boiler should be set from the computer via a Omega CN 76000 controller. A temperature sensor should be installed on the reboiler surface below the insulation and connected to a power cut off on the reboiler supply to guard against overheating.

The apparatus surface heaters are presently controlled by Omega CN 76000 controllers. These controllers can be connected to a computer via a RS 232 port for remote control. The controllers also have built in high/low temperature alarms/cutouts. These alarms should also have visual indicators on the control computer.

Pressure control has been improved and the provision of overpressure alleviated on the present apparatus by the provision of pressure relief valves. The inclusion of a pressure transducer in the control loop would permit remote pressure data logging by the computer and shut down of the apparatus if the pressure drops below 1 bar of the desired operating pressure. This is necessary to prevent the apparatus from boiling off the contents of the apparatus.

In addition to the control measures stated above the following alarms/cutouts are required:

1) No condenser coolant flow alarm. This must be crosslinked to cut power to all heaters and the reboiler.

2) Reboiler feed no flow alarm. This must be crosslinked to cut power to all heaters and the reboiler.

3) Alarms on both pumps to show when they are not working.

4) High temperature alarms for each heater on the pressure vessel body and vapour line set to 10 K above the boiling point of the test mixture with auto power shutoff to the associated heater.

10.1 Conclusions.

A family of recirculation stills of a common design have been developed to allow measurement of vapour-liquid equilibria from sub-atmospheric pressures to 35 bar pressure. By measurement of vapour-liquid equilibria data for the mixture acetic acid-water at one atmosphere, these stills have been shown to generate data of high quality and, more importantly, consistent with each other and the best data extant in literature sources.

Two high quality data sets for acetone-chloroform mixtures have been generated at 1 atmosphere pressure and isothermally at 64.3°C. These data have been used to test the limitations of the AGAPEFIT prediction method for polar compounds. It has been demonstrated that the AGAPE method predicts accurately the activity coefficients for this mixture and hence is suitable for use with other highly polar mixtures.

Eight vapour-liquid equilibrium data sets have been produced for the mixture cyclohexane-ethanol at 1 atmosphere, 2, 4, 6, 8, 11 bar, 90.9°C and 132.8°C. together with saturated vapour pressure curves for the pure components up to 11 bar. These data sets have been tested for thermodynamic consistency using a Barker-type fitting package and shown to be of high quality. The data have been used to investigate the dependence of UNIQUAC parameters on temperature. The data show the relationship to be non-linear but maybe represented by a simple quadratic equation with the same degree of uncertainty, as for the fitted parameters.

The data have been used to compare activity coefficients for this mixture, with those obtained from the data prediction methods, Original UNIFAC, Modified UNIFAC Larsen, (1986) and the AGAPEFIT technique. It can be seen that the Original UNIFAC predictions agree to 2 bar pressure. Above two bar this method overestimates the coefficients. The Modified UNIFAC method agrees up to 4 bar, above this pressure it underestimates the coefficients. The AGAPEFIT method can be

shown to best approximate the experimental coefficients up to 8 bar. This work has validated the use of azeotropic data to furnish the single experimental data point required by the AGAPEFIT method. This may open up the possibility of using this method to predict VLE data using the large data bases of azeotrope data for parameter fitting.

This study represents a significant contribution to the field of experimental vapour-liquid equilibrium data measurement. It has enabled through the provision of high quality experimental data the examination of existing data predictive techniques for temperature dependence. This study also makes a contribution to the development of the new novel predictive methods encompassed in the AGAPE suite of programs.

10.2 Recommendations.

Inter alia, this work has highlighted a severe limitation of the AGAPE prediction methods in their current form. Assumption of ideal behaviour at even atmospheric pressures for the type of mixtures encountered in this study has reduced calculated vapour compositions to very poor fits. It is imperative that this model should be modified to account for non-ideality in the vapour phase by implementation of the Hayden-O'Connell equation.

The AGAPEFIT model should be modified to allow the r constant to be made composition dependent for use with associating mixtures. As shown with the cyclohexane-ethanol activity coefficient predictions, a degree of success can be obtained by assuming a mean value for r. A better solution which would more realistically represent the true behaviour would be a weighted value of r dependent on composition. Kretschmer and Weibe (1954) and Renon and Prausnitz (1967) have shown that alcohol-saturated hydrocarbon mixtures could be modelled by assuming the alcohol is linear self-associated to form binaries and higher polymers and interacts with the hydrocarbon by physical forces alone. Both of these used a specific form of the Gibbs-Duhem equation based on the theory of polymer mixtures developed by Flory (1944). Nagata (1979) expanded on this approach to include mixtures with aromatic

hydrocarbons and chlorinated solvents by considering in addition the formation of complexes between solvent and alcohol. The equations presented by Nagata (1979) could be used as a basis to calculate r in the AGAPEFIT model from the overall concentrations and the equilibrium constants for the association and complex formation, thus making r truly composition dependent.

Accurate measurement of other mixtures at moderate pressures are now possible. In order to develop both AGAPE methods more data are required for a wider range of mixtures in the pressure range 1 to 10 bar.

Both AGAPE methods claim to be able to distinguish between isomers in a VLE mixture, a feature of which no other prediction method is capable. It is recommended that a study be made of isomeric binary mixtures of hydrocarbons, e.g. cis/trans isomers of ethyl pentene mixtures with a hexane solvent. The use of this mixture, though at the limits of GLP theory, makes experimental work easier and safer by avoiding the use of gaseous feeds. The complex problems of polar associating mixtures are avoided and this would permit a rigorous examination of the ability of AGAPE to discriminate between isomers at pressure.

Nomenclature

a	-	Van der Waals constant a
a_i	-	Activity of component i
a_{ii}	-	Energy size parameter
a_{12}	-	Interaction parameter
a_{112}	-	Interaction parameter
a_{mn}	-	UNIFAC group interaction parameter for groups m and n
A,B	-	Adjustable parameters in Van Larr and similar equations
A	-	First virial coefficient
A_K	-	Van der Waals group surface area
A_{mn}	-	Constant in temperautre dependence expression for UNIFAC
b	-	Van der Waals constant b
b_{ii}	-	Molecular size parameter
B	-	Second virial coefficient
B_{ij}	-	Mixture cross second virial coefficient for components i and j
B_{mn}	-	Constant in temperature dependence expression for UNIFAC
C	-	Third virial coefficient
C, D	-	Adjustable parameters in Margules and similar equations
D	-	Fourth virial coefficient
E_i	-	Energy required to vapourise one mole of component at infinite volume
f_i	-	Fugacity of component i
f^0_i	-	Standard state fugacity of component i
f_i^L	-	Fugacity of component i in the liquid phase
f_i^V	-	Fugacity of component i in the vapour phase
f_i^*	-	Standard state fugacity of component i in the liquid phase
$F_{i,j}$	-	Molecular structure-dependent factor in expression for net potential
g	-	Interaction energy in NRTL equation
g^E	-	Molar Gibbs free energy
G	-	Gibbs free energy
G	-	Parameter in the NRTL equation
G^E	-	Excess Gibbs free energy
h^E	-	Molar excess enthalpy
h_i	-	Molar enthalpy of component i
h^*	-	Standard state enthalpy
H	-	Enthalpy
H^E	-	Excess enthalpy
$\bar{H}_i$	-	Partial molar enthalpy of component i
K_i	-	Equilibrium ratio
l	-	Auxiliary relationship in UNIQUAC equation
m_1	-	Number off whole molecular contacts betweenacentral molecule of type 2 with molecules of type 2
m_2	-	Number off whole molecular contacts betweenacentral molecule of type 2 with molecules of type 1
n_i	-	Number of moles of component i
n_T	-	Total number of moles
P	-	Pressure
P_{Ci}	-	Critical pressure of component i

P_i	-	Partial pressure of component i
p_i^{sat}	-	Saturated vapour pressure of component i
q	-	Heat exchange
q_i	-	Pure component molecular surface area of component i in UNIQUAC equation
q_1	-	Effective volume, surface solubility parameter for component 1
q_2	-	Effective volume, surface solubility parameter for component 2
q_k	-	Van der Waals group surface area
Q_i	-	Group surface area parameter of group i in the UNIFAC equation
r	-	Relative molecular volumes of components 1 and 2
r_k	-	Van der Waals group volume
R	-	Universal gas constant
R_i	-	Group volume of group i in UNIFAC method
s^E	-	Molar excess entropy
S	-	Entropy
S^E	-	Excess entropy
T	-	Temperature
T_C	-	Critical temperature
T_R	-	Reduced temperature
U	-	Internal energy
U_{jj}	-	Interaction energy between two like segments in UNIFAC
v	-	Volume
v_i	-	Molar volume of i'th component
v^L_i	-	Specific volume of pure liquid i
V_{wk}	-	Van der Waals group volume for group k
$\bar{v}_i$	-	Partial molar volume of component i
x_i	-	Mole fraction of component i in liquid phase
x_{12}	-	Local mole fraction in liquid phase
X_i	-	Group fraction of group i in the liquid phase
y_i	-	Mole fraction of component i in vapour phase
z	-	Coordination number
z_1	-	Volume fraction of component 1 in the liquid phase
z_2	-	Volume fraction of component 2 in the liquid phase
Z	-	Compressibility factor
Z_C	-	Compressibility factor at critical point

Greek letters

α	-	Parameter in NRTL equation
α_{ij}	-	Relative volatility
α_{12}	-	Binary adjustable parameter
γ_i	-	Activity coefficient
γ_i^C	-	Combinatorial activity coefficient
γ_i^R	-	Residual activity coefficient
Γ	-	Group activity coefficient
Γ_A	-	Marek and Standart liquid phase correction factor (monomer)
Γ_k	-	Residual activity coefficient of group k
Γ_{ki}	-	Residual activity coefficient of group k in reference solution of type i only
δ_i	-	Solubility parameter

δ'_A	-	Jenkins and Gibson-Robinson vapour phase correction factor (dimer)
δ	-	Average solubility parameter
Δh_m	-	Enthalpy change on mixing
Δv_m	-	Volume change on mixing
θ	-	Surface area fraction for UNIQUAC equation
Θ	-	Group Surface area fraction for UNIFAC method
λ_{ij}	-	Boltzmann factor parameter
Λ	-	Adjustable parameter in Wilson equation
μ_i	-	Chemical potential of component i
μ_i^o	-	Standard state chemical potential in gaseous phase
μ_i*	-	standard state chemical potential in the liquid phase
ν_{ki}	-	Number of groups of type k in molecule i
Φ_{11}	-	Net potential between two molecules of type 1
Φ_{12}	-	Net potential between two molecules of type 1 and 2
ϕ	-	Fugacity coefficient
φ	-	Interaction parameter
φ	-	Volume fraction in the UNIFAC method
Ψ	-	Binary parameter for the Wilson equation in the UNIFAC method
τ	-	Parameter in NRTL and UNIFAC method
ω	-	Acentric factor
Ω_a	-	Proportionality constant in Redlich-Kwong equation of state
Ω_b	-	Proportionality constant in Redlich-Kwong equation of state

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Appendix 1 Temperature calibration of central PRT in the moderate pressure still.

The boiling temperature in the equilibrium cell, of the moderate pressure still, is measured by a central four-wire PRT. This has been calibrated to 0.002 K against a secondary standard, namely a Guildline 9540 platinum resistance thermometer with a discrimination of 0.001 K. The Guildline 9540 platinum resistance thermometer in turn has been calibrated against a primary standard which is an NPL design type 5650F inductively coupled double ratio bridge, (with a precision of ±0.0001 K) using a platinum resistance thermometer No 221426 calibrated at the National Physical Laboratory to IPTS68. The central PRT and the platinum resistance thermometer No 221426 use the same double ratio bridge as a readout device thus the central PRT had to be calibrated against a intermediate standard rather than directly against the platinum resistance thermometer No 221426.

Calibrations were carried out in a Pye Unicam 104 Chromatograph oven used as thermostated air bath with temperature control better than ± 0.1 K. The temperature sensors were immersed to the same depth, in a 1" diameter boiling tube filled with silicone oil and 1 mm balotini. This was done to ensure that both temperature sensors were measuring the same temperature and to damp out any minor temperature variations in the air bath.

The calibration graph for the central PRT resistance measurements versus the Guildline 9540 platinum resistance thermometer temperature readings is given in Figure A1.1. Figure A1.2 is the temperature correction graph used for the Guildline 9540 platinum resistance thermometer obtained from the calibration against the primary standard platinum resistance thermometer No 221426.

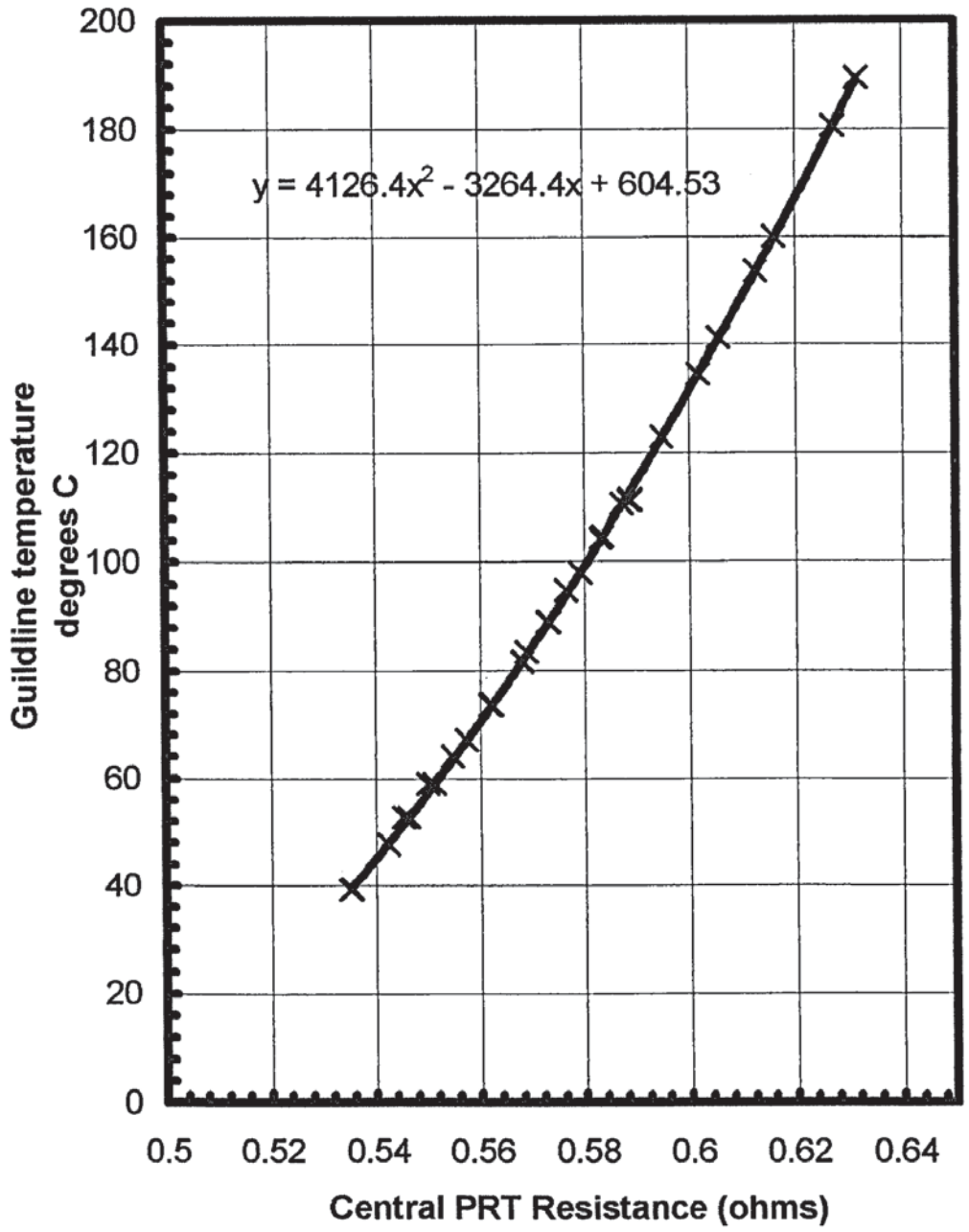

Figure A.1.1 The calibration graph for the central PRT resistance measurements versus the Guildline 9540 platinum resistance thermometer temperature readings

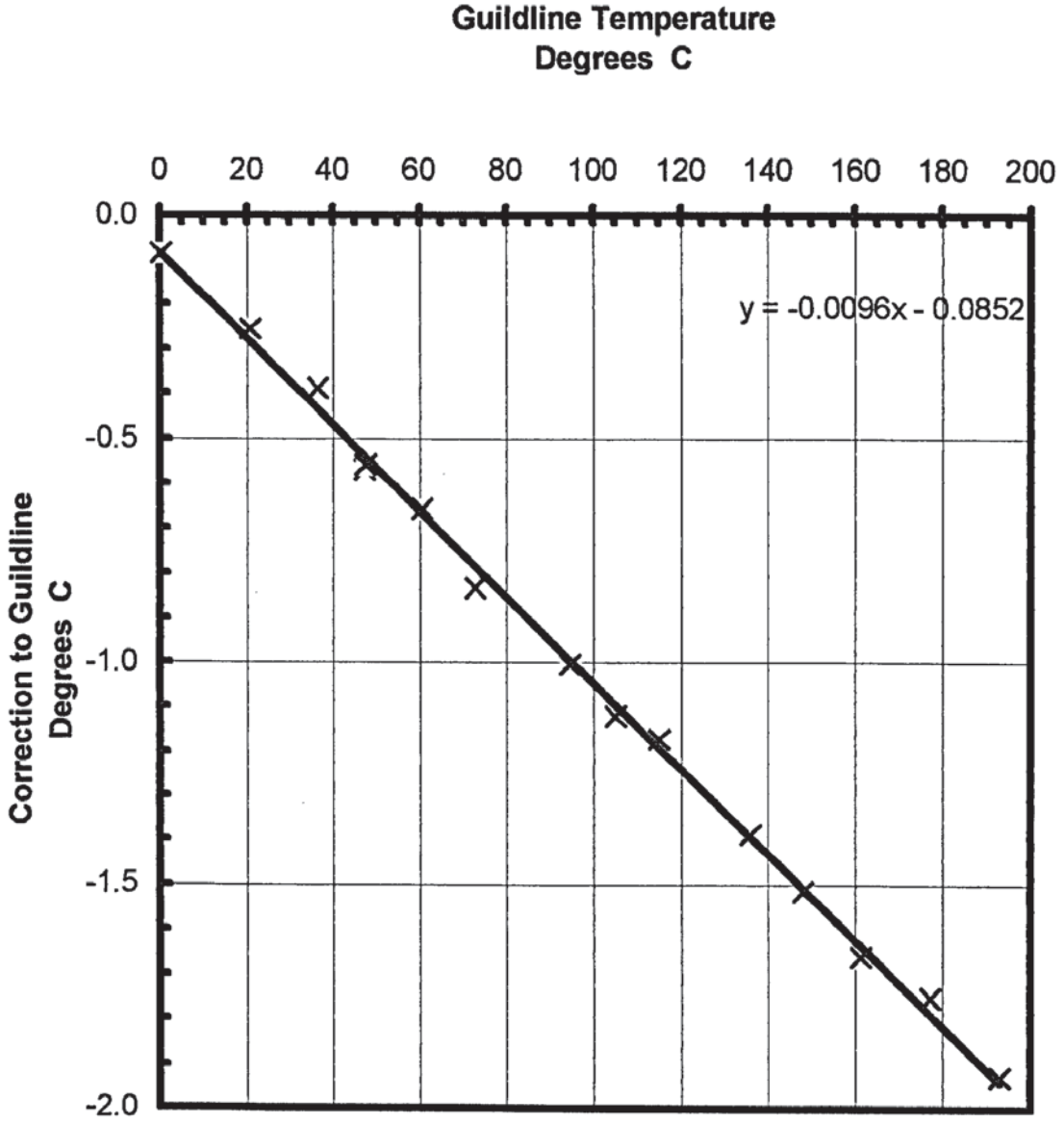

Figure A.1.2 Temperature correction graph used for the Guildline 9540 platinum resistance thermometer obtained from the calibration against the primary standard platinum resistance thermometer No 221426

Appendix 2 Calibration graphs used for analysis of test mixtures.

Two methods have been employed for the analysis of the vapour and liquid test samples obtained during this experimental program.

Density measurements have been used to determine compositions for mixtures of acetic acid and water. These measurements were made using an Anton Paar Densimeter (DMA 60) with two DMA 602 cells. The Anton Paar Densimeter was used in ratio mode measuring the density of a mixture sample in one cell against the density of pure water as a standard in the second cell. This method is known to be more stable than direct measurement of the mixture density. All density measurements were made at 25.00°C. Temperature control of the cells to ± 0.001 K was achieved using a heater controller (Heto Birkerod Demark)

Refractive Index was used to analyse test mixtures of acetone-chloroform and cyclohexane-ethanol. This method was preferred to density measurements as a minimum was detected in the density-composition curve for both of these mixtures which reduced the accuracy of composition determination to unacceptable levels. A Index Instruments automatic refractometer (GPR 11-37), accurate to 4 decimal places when repeatedly standardised with HPLC grade water, was used to obtain both refractive index calibration curves.

All calibrations were performed on a series of samples representing the full composition range, prepared by weight using a balance accurate to 0.001 g. The experimental data samples were analysed in batches over a period of time. It was therefore necessary to check that the calibration curve remained valid for all batches of samples. This was checked by measuring the density/refractive index of both pure components and the mid-point composition standard at the same time that each batch of samples were analysed .

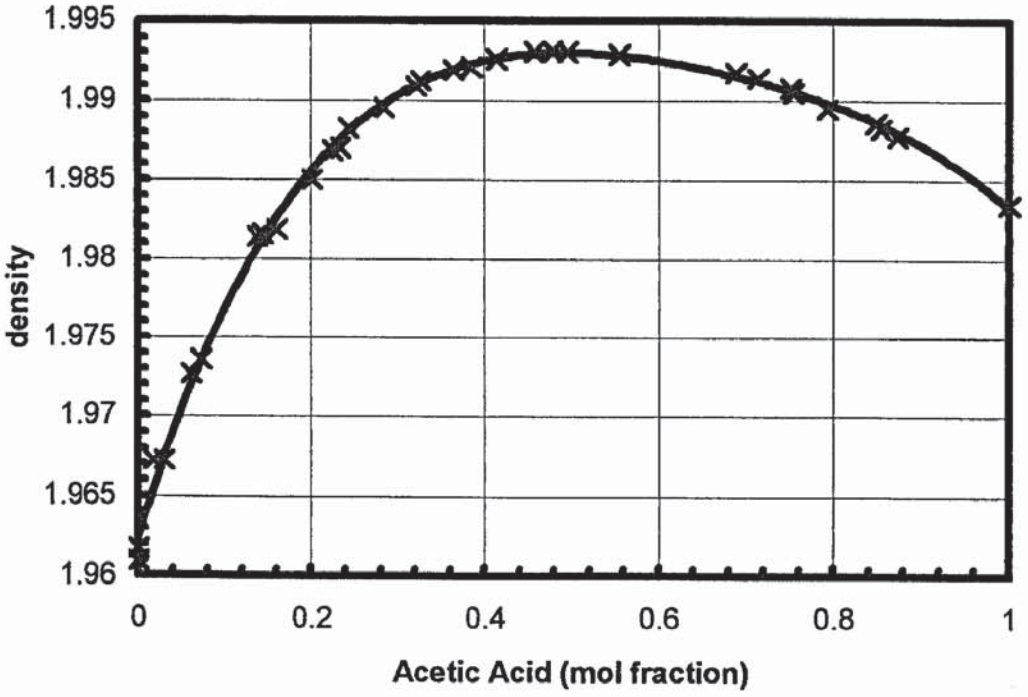

Figure A.2.1 Density-composition calibration for acetic acid-water mixture.

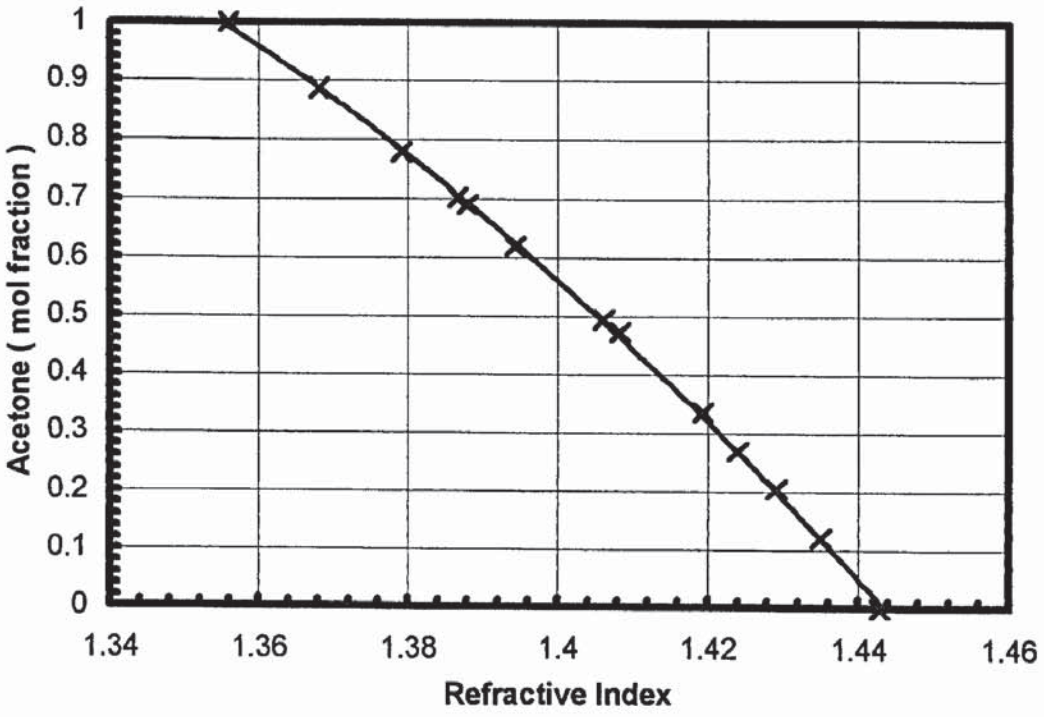

Figure A.2.2 Refractive index-composition calibration for acetone-chlorofrom mixture.

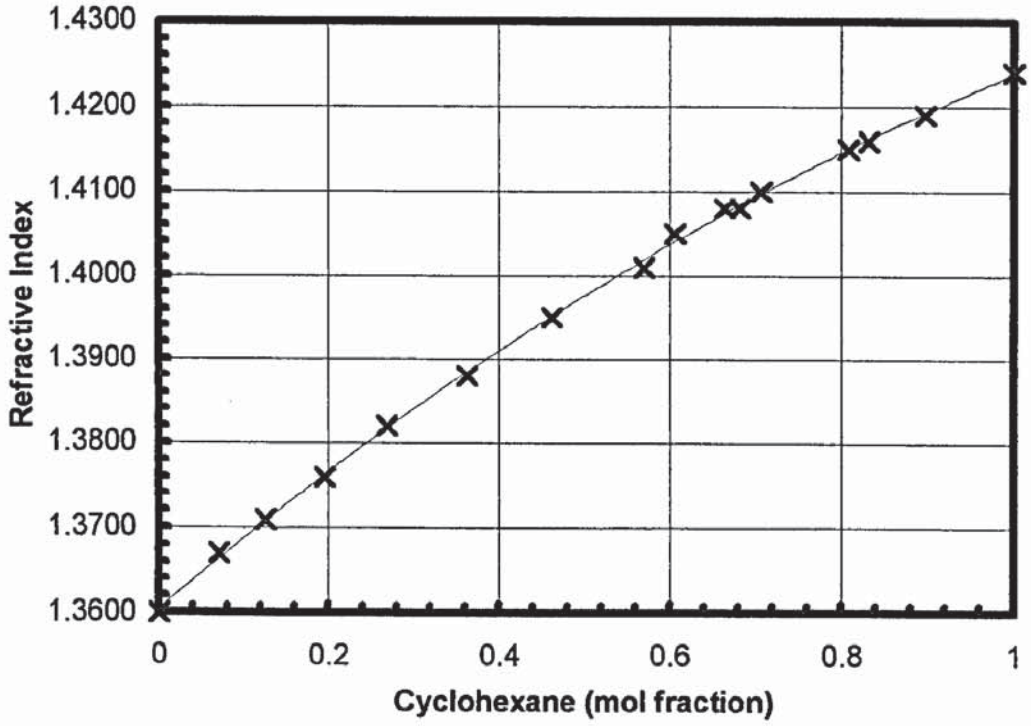

Figure A.2.3 Refractive index-composition calibration for cyclohexane-ethanol mixture.

Appendix 3 Raw experimental data for all test mixtures.

TABLE A.3.1

Vapour liquid equilibrium data for the mixture acetic acid-water at 760 mm Hg obtained using the low pressure still.

Mol fraction of Acetic Acid		Operating Pressure	Equilibrium Temperature	x-y
in liquid x	in vapour y	P/mmHg	t/°C	
0.0565	0.0470	758.89	100.4	0.0095
0.1543	0.1220	758.96	100.9	0.0323
0.2027	0.1492	758.13	101.6	0.0535
0.2830	0.2307	759.64	102.2	0.0523
0.3737	0.2600	757.72	103.15	0.1137
0.4885	0.3646	758.18	105.2	0.1239
0.6047	0.4710	759.30	106.3	0.1337
0.6970	0.5690	757.71	106.7	0.1280
0.7071	0.5864	758.93	108.0	0.1207
0.8183	0.7112	759.15	110.6	0.1071
0.8328	0.7232	760.91	110.8	0.1096
0.8792	0.7903	759.23	112.2	0.0889
0.8887	0.7993	760.80	112.5	0.0894
0.9135	0.8355	758.14	113.4	0.0780
0.9250	0.8591	760.60	113.9	0.0659

TABLE A.3.2

Vapour liquid equilibrium data for the mixture acetic acid-water at 760 mm Hg obtained using the moderate pressure still.

Mol fraction of Acetic Acid		Operating Pressure	Equilibrium Temperature	x-y
in liquid x	in vapour y	P/mmHg	t/°C	
0.0307	0.0260	759.285	100.31	0.0047
0.0820	0.0640	760.31	101.34	0.0180
0.2050	0.1430	755.56	101.66	0.0620
0.2450	0.1720	752.67	101.866	0.0730
0.3580	0.2530	762.98	102.97	0.1050
0.3520	0.2500	762.57	103.2	0.1020
0.4660	0.3350	767.26	104.66	0.1310
0.6200	0.4940	759.98	107.21	0.1260
0.7124	0.5878	756.51	108.42	0.1246
0.7804	0.6750	755.62	109.986	0.1054
0.7985	0.7001	757.14	110.46	0.0984
0.8216	0.7230	763.20	111.108	0.0986
0.8855	0.8060	760.68	112.87	0.0795

TABLE A.3.3

Vapour liquid equilibrium data for the mixture acetone-chloroform at 760 mm Hg obtained using the low pressure still.

Mol fraction Acetone of in liquid x	in vapour y	Operating Pressure P/mmHg	Equilibrium Temperature t/°C	y-x
1	1	759.9	56.1	0
0.9396	0.9676	759.8	57.05	0.028
0.8784	0.9278	759.9	58.00	0.0494
0.7361	0.8118	759.8	60.45	0.0757
0.6304	0.6992	760.0	62.2	0.0688
0.6741	0.7510	759.8	61.45	0.0769
0.5626	0.6251	759.8	63.13	0.0625
0.4966	0.5456	759.7	63.8	0.0490
0.5563	0.6211	760.3	63.14	0.0648
0.5012	0.5478	759.8	63.75	0.0466
0.4375	0.4637	759.8	64.15	0.0262
0.3389	0.3327	759.8	64.35	-0.0062
0.0901	0.0642	761.0	62.4	-0.0259
0.1827	0.1438	759.9	63.5	-0.0389
0.1532	0.1176	760.0	63.05	-0.0356
0.0870	0.0599	760.0	62.35	-0.0271
0.1361	0.0998	760.3	63.0	-0.0363
0.1827	0.1400	759.9	63.5	-0.0427
0.1795	0.1424	759.9	63.25	-0.0371
0.2352	0.2000	759.9	63.7	-0.0352
0.2876	0.2602	759.8	63.9	-0.0274
0.4551	0.4826	759.7	64.0	0.0275

TABLE A.3.4

Vapour liquid equilibrium data for the mixture acetone-chloroform at 64.3°C obtained using the moderate pressure still.

Mol fraction of Acetone		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.9072	0.9528	965.1	64.35	0.0456
0.8721	0.9165	950.7	64.64	0.0444
0.8076	0.8743	909.8	64.31	0.0667
0.6755	0.7926	851.49	64.32	0.1171
0.6618	0.7775	848.9	64.34	0.1157
0.6055	0.7178	818.85	64.28	0.1123
0.4833	0.5447	791.5	64.3	0.0614
0.4286	0.4620	774.6	64.36	0.0334
0.3389	0.3327	759.8	64.35	-0.0062
0.3086	0.2917	772.2	64.44	-0.0169
0.2440	0.2123	783.1	64.38	-0.0317
0.2149	0.1790	795.6	64.5	-0.0359
0.2040	0.1689	794.5	64.33	-0.0351
0.1759	0.1423	804.5	64.31	-0.0336
0.1686	0.1429	805.95	64.26	-0.0257
0.1398	0.1123	803.2	64.3	-0.0275
0.1227	0.0914	814.0	64.65	-0.0313
0.0699	0.0582	828.0	64.32	-0.0117
0.0532	0.0351	843.0	64.39	-0.0181
0.0011	0.0004	853.53	64.31	-0.0007

TABLE A.3.5

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 760 mm Hg obtained using the moderate pressure still.

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.9858	0.9179	754.8	76.5	-0.0679
0.9378	0.6648	759.8	67.6	-0.2730
0.8835	0.6117	762.6	65.93	-0.2718
0.8047	0.5954	760.1	65.00	-0.2093
0.6901	0.5765	763.5	64.66	-0.1136
0.5974	0.5647	762.0	64.53	-0.0327
0.5497	0.5583	761.7	64.52	0.0086
0.9029	0.6230	761.8	66.1	-0.2799
0.8582	0.6115	766.4	65.77	-0.2467
0.8406	0.6056	763.9	65.45	-0.2350
0.7798	0.5929	762.9	65.1	-0.1869
0.7564	0.5935	761.2	64.96	-0.1629
0.7438	0.5804	763.2	64.96	-0.1634
0.7238	0.5817	760.9	64.79	-0.1421
0.6146	0.5666	759.9	64.66	-0.0480
0.4364	0.5365	763.1	65.00	0.1001
0.3152	0.5136	763.2	65.04	0.1984
0.2301	0.4731	763.9	66.43	0.2430
0.1870	0.4546	765.6	67.05	0.2676
0.1462	0.4076	763.9	68.26	0.2614
0.1044	0.3617	763.6	69.55	0.2573

TABLE A.3.6

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 1500 mm Hg obtained using the moderate pressure still.

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.9544	0.7941	1500	91.3	-0.1603
0.9147	0.7134	1500	89.24	-0.2013
0.9089	0.7045	1500	88.96	-0.2044
0.6853	0.5320	1500	84.27	-0.1533
0.5490	0.4999	1500	83.74	-0.0491
0.4423	0.4795	1500	83.74	0.0372
0.3306	0.4614	1500	84.01	0.1308
0.2616	0.4524	1500	84.34	0.1908
0.2184	0.4489	1500	84.6	0.2305
0.1363	0.4128	1500	85.7	0.2765
0.1250	0.3858	1500	86.33	0.2608
0.0832	0.3698	1500	87.84	0.2866
0.0618	0.3356	1500	89.42	0.2738
0.0443	0.3150	1500	91.66	0.2707
0.0229	0.1813	1500	96.99	0.1584

TABLE A.3.7

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 4 bar obtained using the moderate pressure still.

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.8797	0.7160	3003.8	109.48	-0.1637
0.8512	0.6882	3005.6	108.83	-0.1630
0.7709	0.6273	3005.6	107.43	-0.1436
0.7238	0.6169	3005.6	107.06	-0.1069
0.6647	0.5730	3009.0	106.16	-0.0917
0.6034	0.5556	3009.0	106.15	-0.0478
0.5829	0.5560	3000.0	106.16	-0.0269
0.5473	0.5524	3009.0	106.05	0.0051
0.4908	0.5352	3007.1	106.05	0.0444
0.3888	0.5149	3007.1	106.45	0.1261
0.3104	0.5000	3007.1	107.1	0.1896
0.2502	0.4816	3003.8	107.83	0.2314
0.2354	0.4743	3003.8	107.96	0.2389
0.1612	0.4448	3003.8	109.36	0.2836
0.0229	0.1813	2996.99	1500	0.1584

TABLE A.3.8

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 6 bar obtained using the moderate pressure still

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.9022	0.7598	4500	124.00	-0.1424
0.7862	0.6693	4503.75	121.8	-0.1169
0.7314	0.6491	4503.75	121.34	-0.0823
0.6612	0.6124	4496.18	121.03	-0.0488
0.6117	0.5946	4496.18	120.94	-0.0171
0.5207	0.5650	4496.18	121.21	0.0443
0.2385	0.4882	4500.9	123.53	0.2497
0.2202	0.4792	4500.9	123.9	0.2590
0.1706	0.4530	4500.38	125.62	0.2824
0.1232	0.4120	4500.38	128.63	0.2888
0	0	4485	152.43	0

TABLE A.3.9

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 8 bar obtained using the moderate pressure still

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.9607	0.8907	6017.7	137.83	-0.0700
0.9501	0.8673	6017.7	137.34	-0.0828
0.9386	0.8420	6017.2	136.72	-0.0966
0.8560	0.7549	6017.2	133.94	-0.1011
0.8259	0.6957	6014.9	133.4	-0.1302
0.7384	0.6656	6014.2	132.82	-0.0728
0.6805	0.6392	6014.2	132.34	-0.0413
0.5979	0.6094	6018.5	132.44	0.0115
0.5211	0.5815	6012.4	132.43	0.0604
0.4490	0.5669	6012.4	132.84	0.1179
0.4255	0.5557	6012.4	133.25	0.1302
0.3630	0.5417	6011.2	133.59	0.1787
0.3630	0.5417	6011.2	133.59	0.1787
0.3297	0.5314	6011.2	133.99	0.2017
0.1620	0.4420	6020.8	138.68	0.2800

TABLE A.3.10

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 11 bar. obtained using the moderate pressure still

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.9845	0.4420	8267.3	151.1	-0.5425
0.9757	0.5314	8267.4	150.5	-0.4443
0.9592	0.5417	8274.3	149.95	-0.4175
0.9293	0.5557	8263.1	148.29	-0.3736
0.8762	0.5669	8252.3	147.18	-0.3093
0.7211	0.5815	8254.5	145.56	-0.1396
0.6915	0.6094	8254.5	145.46	-0.0821
0.5556	0.6392	8254.7	145.43	0.0836
0.4880	0.6656	8255.0	145.88	0.1776
0.2938	0.6957	8253.5	148.68	0.4019
0.2694	0.7549	8261.4	148.96	0.4855
0.2105	0.8420	8261.4	151.31	0.6315

TABLE A.3.11

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 90.9°C. obtained using the moderate pressure still

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.8801	0.6715	1691.6	90.93	-0.2086
0.8669	0.6613	1723.8	90.89	-0.2056
0.8572	0.6502	1728.9	90.92	-0.2070
0.8221	0.6205	1730.4	90.98	-0.2016
0.8117	0.6137	1779.2	90.9	-0.1980
0.7671	0.5846	1828.9	91.0	-0.1825
0.7495	0.5789	1838.8	90.94	-0.1706
0.7327	0.5761	1838.6	90.9	-0.1566
0.7156	0.5596	1851.6	90.88	-0.1560
0.7081	0.5608	1857.6	90.91	-0.1473
0.7007	0.5665	1856.7	90.84	-0.1342
0.6945	0.5563	1859.6	90.85	-0.1382
0.6824	0.5509	1864.7	90.9	-0.1315
0.6530	0.5404	1882.9	90.62	-0.1126
0.6225	0.5304	1876.8	90.85	-0.0921
0.6097	0.5314	1890.96	90.95	-0.0783
0.4951	0.5061	1894.1	90.94	0.0110
0.3644	0.4861	1886.7	90.95	0.1217
0.2993	0.4724	1865.7	90.85	0.1731
0.2991	0.4716	1863.1	90.86	0.1725
0.2871	0.4690	1860.9	90.87	0.1819
0.2777	0.4676	1850.8	90.85	0.1899
0.2358	0.4564	1831	90.87	0.2206
0.2225	0.4542	1836.6	90.97	0.2317

TABLE A.3.12

Vapour liquid equilibrium data for the mixture cyclohexane-ethanol at 138.2°C. obtained using the moderate pressure still

Mol fraction of Cyclohexane		Operating Pressure	Equilibrium Temperature	y-x
in liquid x	in vapour y	P/mmHg	t/°C	
0.8893	0.6146	5489.0	138.25	-0.2747
0.7772	0.5115	6389.0	138.22	-0.2657
0.7299	0.4894	6502.0	138.24	-0.2405
0.6500	0.4576	6866.3	138.14	-0.1924
0.5026	0.4107	7143.8	138.25	-0.0919
0.3947	0.3671	7167.3	138.16	-0.0276
0.3019	0.3446	7204.8	138.21	0.0427
0.2659	0.3264	7083.2	138.22	0.0605
0.2284	0.3066	7105.7	138.04	0.0782
0.2136	0.3975	7029.4	138.16	0.1839

Appendix 4 Consistency test results for acetic acid-water data.

The results of the consistency tests performed on the experimental data for the mixture acetic acid-water are reported here. The fitting package proposed by Gibson-Robinson (1977) has been used to perform the tests. Test results are given for each data set using three activity coefficient models, Wilson 2-parameter, NRTL 3-parameter and Redlich-Kister 4-parameter equations, to represent the liquid-phase.

The vapour pressure is represented by the 3-parameter Antoine equation for acetic acid and the 6-parameter Antoine equation for water. These equations were found to give the least deviations for pressure and vapour-phase compositions when used to represent the vapour phase behaviour in the consistency tests, irrespective of the liquid activity coefficient model used.

In order to demonstrate the benefit of including association in both phases when performing the tests, test results for each data set for each different liquid phase model are given with and without association being used.

Table A.4.19 and A.4.20 give the results of consistency tests for the data of Brown and Ewald (1950) and Garner and Ellis (1954) using the three parameter NRTL equation and association in both phases. The results of these consistency tests have been used in the deviation plots, figure 6.3 and 6.4.

TABLE A.4.1
Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

DataThis Work Low Pressure Still
Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0565	0.047	0.0464	0.064	758.9	755.059	3.841	2.6814	1.0059
0.1543	0.122	0.1206	0.14	759	751.115	7.885	1.9248	1.0361
0.2027	0.1492	0.1475	0.167	758.1	755.745	2.355	1.6549	1.058
0.283	0.2307	0.2285	0.223	759.6	762.173	-2.573	1.5777	1.0895
0.3737	0.26	0.2576	0.244	757.7	748.543	9.157	1.2689	1.1491
0.4885	0.3646	0.3617	0.292	758.2	767.046	-8.846	1.1776	1.2244
0.6047	0.471	0.4681	0.295	759.3	759.953	-0.653	1.1196	1.3206
0.697	0.569	0.5664	0.262	757.7	748	9.7	1.1087	1.4129
0.7071	0.5864	0.5837	0.275	758.9	765.749	-6.849	1.0918	1.4268
0.8183	0.7112	0.7088	0.238	759.2	764.415	-5.215	1.0475	1.5835
0.8328	0.7273	0.7251	0.222	760.9	762.36	-1.46	1.046	1.6068
0.8792	0.7903	0.7883	0.201	759.2	760.091	-0.891	1.0342	1.6901
0.8887	0.7993	0.7974	0.195	760.8	757.966	2.833	1.0288	1.7097
0.9135	0.8355	0.8336	0.19	758.1	754.114	3.986	1.021	1.7613
0.925	0.8591	0.8575	0.165	760.6	759.599	1.001	1.0264	1.7834
R.M.S.	Deviations							
			0.2198			6.074		

TABLE A.4.2

Mixture Acetic Acid - Water at 760 mm Hg

Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation

Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation

Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Low Pressure Still Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0565	0.047	0.0453	0.175	758.9	751.98	6.92	2.5932	1.0065
0.1543	0.122	0.1223	-0.025	759	752.311	6.689	1.9341	1.0409
0.2027	0.1492	0.1532	-0.401	758.1	763.153	-5.053	1.7301	1.0658
0.283	0.2307	0.2148	1.594	759.6	765.021	-5.421	1.4936	1.1164
0.3737	0.26	0.2629	-0.294	757.7	770.906	-13.206	1.318	1.1851
0.4885	0.3646	0.3474	1.725	758.2	789.015	-30.815	1.1769	1.2863
0.6047	0.471	0.4474	2.363	759.3	774.258	-14.958	1.0912	1.4051
0.697	0.569	0.5449	2.406	757.7	744.897	12.803	1.0487	1.5114
0.7071	0.5864	0.5537	3.268	758.9	765.337	-6.437	1.0446	1.5202
0.8183	0.7112	0.6901	2.107	759.2	755.795	3.405	1.0153	1.6529
0.8328	0.7273	0.7109	1.64	760.9	751.416	9.484	1.0128	1.6714
0.8792	0.7903	0.7806	0.97	759.2	746.047	13.153	1.0064	1.7282
0.8887	0.7993	0.7954	0.393	760.8	745.336	15.464	1.0054	1.7398
0.9135	0.8355	0.8364	-0.086	758.1	742.355	15.745	1.0032	1.7697
0.925	0.8591	0.857	0.209	760.6	743.17	17.43	1.0023	1.7832
R.M.S.	Deviations							
			1.552			13.58		

TABLE A.4.3

Mixture Acetic Acid - Water at 760 mm Hg

Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation

Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation

Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Low Pressure Still Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0565	0.047	0.0464	0.064	758.9	754.941	3.959	2.6815	1.0057
0.1543	0.122	0.1206	0.141	759	750.731	8.269	1.9248	1.0355
0.2027	0.1492	0.1475	0.167	758.1	755.327	2.773	1.655	1.0573
0.283	0.2307	0.2285	0.222	759.6	762.353	-2.753	1.5777	1.0899
0.3737	0.26	0.2576	0.245	757.7	749.766	7.934	1.2688	1.1516
0.4885	0.3646	0.3617	0.292	758.2	769.471	-11.271	1.1776	1.2304
0.6047	0.471	0.4681	0.295	759.3	762.91	-3.61	1.1196	1.3303
0.697	0.569	0.5664	0.263	757.7	750.333	7.367	1.1087	1.4232
0.7071	0.5864	0.5837	0.275	758.9	767.336	-8.436	1.0918	1.4339
0.8183	0.7112	0.7088	0.239	759.2	762.916	-3.716	1.0475	1.573
0.8328	0.7273	0.7251	0.223	760.9	760.538	0.362	1.046	1.5929
0.8792	0.7903	0.7883	0.201	759.2	757.147	2.053	1.0342	1.6594
0.8887	0.7993	0.7973	0.196	760.8	754.861	5.939	1.0288	1.6746
0.9135	0.8355	0.8336	0.19	758.1	750.781	7.319	1.021	1.7133
0.925	0.8591	0.8575	0.165	760.6	756.283	4.317	1.0264	1.7283
R.M.S.	Deviations							
			0.2201			6.074		

TABLE A.4.4

Mixture Acetic Acid - Water at 760 mm Hg

Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation

Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation

Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Low Pressure Still Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0565	0.047	0.0384	0.857	758.9	747.409	11.491	2.2227	1.0036
0.1543	0.122	0.1153	0.67	759	740.601	18.399	1.8403	1.0259
0.2027	0.1492	0.1512	-0.199	758.1	749.904	8.196	1.6959	1.0439
0.283	0.2307	0.2183	1.243	759.6	751.218	8.382	1.5072	1.0836
0.3737	0.26	0.2738	-1.377	757.7	757.916	-0.216	1.3487	1.143
0.4885	0.3646	0.3708	-0.621	758.2	780.294	-22.094	1.2073	1.2401
0.6047	0.471	0.4651	0.591	759.3	771.684	-12.384	1.1125	1.3662
0.697	0.569	0.5426	2.645	757.7	747.061	10.639	1.062	1.4887
0.7071	0.5864	0.5653	2.115	758.9	768.591	-9.691	1.0574	1.5011
0.8183	0.7112	0.6906	2.056	759.2	763.621	-4.421	1.0206	1.6745
0.8328	0.7273	0.7052	2.211	760.9	759.418	1.482	1.0173	1.6998
0.8792	0.7903	0.7689	2.136	759.2	754.235	4.965	1.0088	1.7825
0.8887	0.7993	0.7808	1.847	760.8	753.406	7.394	1.0074	1.8001
0.9135	0.8355	0.82	1.546	758.1	749.773	8.327	1.0044	1.8469
0.925	0.8591	0.8382	2.091	760.6	750.103	10.497	1.0033	1.8689
R.M.S.	Deviations							
			1.14			4.0495		

TABLE A.4.5

Mixture Acetic Acid - Water at 760 mm Hg

Liquid-phase Activity Coefficient Model :- Redlich-Kister 4 Parameter Equation

Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation

Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Low Pressure Still Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0565	0.047	0.0464	0.063	758.9	757.122	1.778	2.6836	1.0088
0.1543	0.122	0.1206	0.14	759	754.71	4.29	1.9261	1.0417
0.2027	0.1492	0.1475	0.167	758.1	759.531	-1.431	1.656	1.0642
0.283	0.2307	0.2285	0.223	759.6	765.435	-5.835	1.5786	1.0956
0.3737	0.26	0.2576	0.245	757.7	750.429	7.271	1.2695	1.153
0.4885	0.3646	0.3617	0.292	758.2	766.295	-8.095	1.178	1.2225
0.6047	0.471	0.468	0.296	759.3	757.801	1.499	1.1199	1.3136
0.697	0.569	0.5664	0.263	757.7	746.457	11.243	1.109	1.406
0.7071	0.5864	0.5837	0.275	758.9	763.828	-4.928	1.092	1.4184
0.8183	0.7112	0.7088	0.239	759.2	764.09	-4.89	1.0474	1.5812
0.8328	0.7273	0.7251	0.223	760.9	762.346	-1.446	1.0459	1.6067
0.8792	0.7903	0.7883	0.201	759.2	760.782	-1.582	1.034	1.6974
0.8887	0.7993	0.7974	0.195	760.8	758.775	2.025	1.0285	1.7188
0.9135	0.8355	0.8336	0.19	758.1	755.125	2.975	1.0207	1.7759
0.925	0.8591	0.8574	0.168	760.6	760.612	-0.012	1.0259	1.8006
R.M.S .	Deviations							
			0.2204			4.961		

TABLE A.4.6

Mixture Acetic Acid - Water at 760 mm Hg

Liquid-phase Activity Coefficient Model :- Redlich-Kister 4 Parameter Equation

Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation

Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Low Pressure Still Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0565	0.047	0.0351	1.195	758.9	748.833	10.067	2.0286	1.0092
0.1543	0.122	0.1035	1.85	759	748.001	10.999	1.6531	1.0516
0.2027	0.1492	0.1361	1.315	758.1	758.59	-0.49	1.5271	1.077
0.283	0.2307	0.1999	3.077	759.6	755.779	3.821	1.3814	1.1178
0.3737	0.26	0.26	0.003	757.7	754.263	3.437	1.2814	1.1572
0.4885	0.3646	0.3717	-0.714	758.2	765.194	-6.994	1.2108	1.2009
0.6047	0.471	0.4865	-1.553	759.3	756.139	3.161	1.1642	1.2624
0.697	0.569	0.5749	-0.589	757.7	740.226	17.474	1.1257	1.3498
0.7071	0.5864	0.5989	-1.251	758.9	762.494	-3.594	1.1206	1.3613
0.8183	0.7112	0.7202	-0.901	759.2	769.757	-10.557	1.0643	1.5603
0.8328	0.7273	0.7326	-0.529	760.9	766.749	-5.849	1.0568	1.5967
0.8792	0.7903	0.7882	0.213	759.2	763.964	-4.764	1.0338	1.7316
0.8887	0.7993	0.7981	0.119	760.8	763.295	-2.495	1.0295	1.7633
0.9135	0.8355	0.8323	0.321	758.1	759.49	-1.39	1.0191	1.8531
0.925	0.8591	0.8481	1.097	760.6	759.438	1.162	1.0148	1.8983
R.M.S. Deviations								
			1.247			7.3212		

TABLE A.4.7

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Moderate Pressure Still
Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0307	0.026	0.0256	0.036	759.29	785.396	-26.106	3.032	1.004
0.082	0.064	0.0632	0.082	760.31	777.714	-17.404	2.2711	1.0204
0.205	0.143	0.1414	0.165	755.56	764.48	-8.92	1.5822	1.0776
0.245	0.172	0.1701	0.19	752.67	761.148	-8.479	1.4922	1.0975
0.352	0.25	0.2476	0.237	762.57	766.963	-4.393	1.3152	1.1529
0.358	0.253	0.2506	0.237	762.98	760.956	2.024	1.3098	1.1564
0.466	0.335	0.3323	0.272	767.26	764.423	2.837	1.1837	1.2163
0.62	0.494	0.4909	0.306	759.98	763.761	-3.781	1.1119	1.3009
0.7124	0.5878	0.5849	0.293	756.51	748.309	8.201	1.0753	1.3585
0.7804	0.675	0.6723	0.271	755.62	749.955	5.665	1.0614	1.3997
0.7985	0.7001	0.6975	0.258	757.14	752.38	4.76	1.0599	1.4104
0.8216	0.723	0.7207	0.231	763.2	752.211	10.989	1.051	1.4263
0.8855	0.806	0.804	0.204	760.68	746.837	13.843	1.0322	1.471
R.M.S.	Deviations							
			0.2274			11.149		

TABLE A.4.8

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :-6 Parameter Antoine Equation

Data This Work Moderate Pressure Still Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0307	0.026	0.0207	0.531	759.29	776.935	-17.646	2.4458	1.0014
0.082	0.064	0.0593	0.47	760.31	764.45	-4.14	2.1317	1.0096
0.205	0.143	0.1475	-0.446	755.56	751.585	3.975	1.6505	1.0529
0.245	0.172	0.1762	-0.419	752.67	749.202	3.468	1.5457	1.0729
0.352	0.25	0.252	-0.203	762.57	760.761	1.809	1.3386	1.1389
0.358	0.253	0.2545	-0.151	762.98	754.966	8.014	1.33	1.1432
0.466	0.335	0.3362	-0.12	767.26	769.349	-2.089	1.1976	1.2272
0.62	0.494	0.4788	1.517	759.98	773.638	-13.658	1.0844	1.3733
0.7124	0.5878	0.5681	1.972	756.51	759.695	-3.185	1.0445	1.476
0.7804	0.675	0.6489	2.615	755.62	757.148	-1.528	1.0244	1.5564
0.7985	0.7001	0.6714	2.869	757.14	757.192	-0.052	1.0202	1.5783
0.8216	0.723	0.6963	2.667	763.2	757.224	5.976	1.0155	1.6069
0.8855	0.806	0.7836	2.239	760.68	749.77	10.91	1.0061	1.688
R.M.S.	Deviations							
			1.625			7.755		

TABLE A.4.9

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Moderate Pressure Still
Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0307	0.026	0.0256	0.036	759.29	783.37	-24.08	3.0311	1.0013
0.082	0.064	0.0632	0.082	760.31	772.883	-12.573	2.2711	1.0137
0.205	0.143	0.1414	0.165	755.56	754.712	0.848	1.5822	1.0616
0.245	0.172	0.1701	0.19	752.67	750.809	1.861	1.4923	1.0795
0.352	0.25	0.2476	0.237	762.57	757.693	4.878	1.3152	1.1344
0.358	0.253	0.2506	0.236	762.98	751.843	11.137	1.3098	1.1379
0.466	0.335	0.3323	0.271	767.26	759.769	7.491	1.1837	1.2052
0.62	0.494	0.491	0.304	759.98	767.974	-7.994	1.1119	1.3149
0.7124	0.5878	0.5849	0.295	756.51	756.661	-0.151	1.0753	1.3956
0.7804	0.675	0.6723	0.274	755.62	760.256	-4.636	1.0613	1.4594
0.7985	0.7001	0.6975	0.257	757.14	762.952	-5.812	1.0599	1.4769
0.8216	0.723	0.7207	0.233	763.2	762.909	0.291	1.051	1.5019
0.8855	0.806	0.804	0.204	760.68	756.387	4.293	1.0322	1.5748
R.M.S.	Deviations							
			0.2275			9.13		

TABLE A.4.10

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Moderate Pressure Still Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0307	0.026	0.0202	0.581	759.29	779.24	-19.95	2.389	1.0013
0.082	0.064	0.0583	0.57	760.31	765.926	-5.616	2.0972	1.0091
0.205	0.143	0.146	-0.3	755.56	751.887	3.673	1.6351	1.0512
0.245	0.172	0.1746	-0.26	752.67	749.253	3.417	1.5327	1.071
0.352	0.25	0.2502	-0.024	762.57	760.485	2.085	1.3298	1.136
0.358	0.253	0.2527	0.032	762.98	754.6	8.38	1.3212	1.1403
0.466	0.335	0.3344	0.057	767.26	768.914	-1.654	1.1918	1.2231
0.62	0.494	0.4775	1.646	759.98	773.323	-13.343	1.0818	1.3667
0.7124	0.5878	0.5672	2.06	756.51	759.436	-2.926	1.043	1.4673
0.7804	0.675	0.6484	2.661	755.62	757.295	-1.675	1.0236	1.5466
0.7985	0.7001	0.6711	2.904	757.14	757.48	-0.34	1.0196	1.5685
0.8216	0.723	0.6961	2.688	763.2	757.668	5.532	1.0151	1.5971
0.8855	0.806	0.7837	2.225	760.68	750.592	10.088	1.0059	1.679
R.M.S.	Deviations							
			0.4823			8.105		

TABLE A.4.11

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Redlich-Kister 4 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Moderate Pressure Still Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0307	0.026	0.0249	0.114	759.29	782.64	-23.35	3.0315	1.0004
0.082	0.064	0.0623	0.169	760.31	770.897	-10.587	2.2725	1.0109
0.205	0.143	0.1424	0.061	755.56	750.079	5.481	1.5832	1.054
0.245	0.172	0.1717	0.031	752.67	745.664	7.006	1.4931	1.0706
0.352	0.25	0.2511	-0.11	762.57	752.025	10.545	1.3159	1.1231
0.358	0.253	0.2563	-0.326	762.98	746.217	16.763	1.3105	1.1265
0.466	0.335	0.3379	-0.294	767.26	754.415	12.845	1.1842	1.1924
0.62	0.494	0.4891	0.495	759.98	762.931	-2.951	1.1122	1.2981
0.7124	0.5878	0.5887	-0.092	756.51	751.569	4.941	1.0755	1.3729
0.7804	0.675	0.6726	0.24	755.62	755.273	0.347	1.0614	1.4305
0.7985	0.7001	0.6967	0.341	757.14	758.047	-0.907	1.0598	1.4461
0.8216	0.723	0.7255	-0.246	763.2	758.188	5.012	1.0509	1.4685
0.8855	0.806	0.8126	-0.658	760.68	752.611	8.069	1.0319	1.5338
R.M.S .	Deviations							
			0.3002			10.4437		

TABLE A.4.12

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Redlich-Kister 4 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data This Work Moderate Pressure Still Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0307	0.026	0.026	-0.001	759.29	783.273	-23.983	3.1743	1
0.082	0.064	0.0635	0.05	760.31	765.257	-4.947	2.2991	1.0022
0.205	0.143	0.1404	0.261	755.56	733.172	22.388	1.5258	1.0326
0.245	0.172	0.1683	0.373	752.67	729.151	23.519	1.431	1.0512
0.352	0.25	0.2504	-0.037	762.57	746.434	16.136	1.3024	1.1159
0.358	0.253	0.2556	-0.257	762.98	741.207	21.773	1.2982	1.1199
0.466	0.335	0.3471	-1.209	767.26	764.033	3.227	1.2317	1.1909
0.62	0.494	0.4973	-0.33	759.98	764.5	-4.52	1.1332	1.2798
0.7124	0.5878	0.591	-0.318	756.51	747.463	9.047	1.0737	1.3579
0.7804	0.675	0.661	1.397	755.62	751.645	3.975	1.0381	1.4739
0.7985	0.7001	0.6798	2.029	757.14	755.35	1.79	1.0305	1.5211
0.8216	0.723	0.7027	2.03	763.2	761.179	2.021	1.022	1.5964
0.8855	0.806	0.7698	3.62	760.68	774.621	-13.941	1.0061	1.939
R.M.S.	Deviations							
			1.3935			14.461		

TABLE A.4.13

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data O'Donnell (1980)
Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.014	0.01	0.0099	0.014	760	755.854	4.146	3.0822	1.0031
0.021	0.015	0.0148	0.021	760	756.219	3.781	2.9184	1.0051
0.099	0.06	0.0592	0.08	760	759.008	0.992	1.8275	1.0411
0.151	0.104	0.1027	0.13	760	766.93	-6.93	1.7587	1.0674
0.213	0.148	0.1462	0.176	760	771.102	-11.102	1.5755	1.105
0.298	0.206	0.2037	0.226	760	778.673	-18.673	1.3839	1.162
0.473	0.349	0.346	0.304	760	781.211	-21.211	1.2062	1.2867
0.564	0.436	0.4328	0.325	760	781.61	-21.61	1.1544	1.3554
0.663	0.537	0.5337	0.329	760	779.501	-19.501	1.1055	1.4347
0.759	0.646	0.6429	0.312	760	774.096	-14.096	1.0708	1.5159
0.844	0.754	0.7513	0.274	760	766.207	-6.207	1.0514	1.5916
0.921	0.853	0.8506	0.245	760	752.348	7.652	1.0242	1.6669
0.96	0.922	0.9199	0.206	760	754.093	5.907	1.0272	1.7009
R.M.S.	Deviations							
			0.2295			12.95		

TABLE A.4.14

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :-6 Parameter Antoine Equation

Data O'Donnell (1980)
Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.014	0.01	0.0091	0.087	760	753.296	6.704	2.8558	1.0004
0.021	0.015	0.0141	0.09	760	752.567	7.433	2.7825	1.0008
0.099	0.06	0.0703	-1.028	760	750.486	9.514	2.1695	1.0164
0.151	0.104	0.111	-0.704	760	752.667	7.333	1.9014	1.0355
0.213	0.148	0.155	-0.697	760	754.128	5.872	1.6695	1.0655
0.298	0.206	0.2134	-0.735	760	761.996	-1.996	1.4492	1.1174
0.473	0.349	0.3421	0.691	760	766.284	-6.284	1.1927	1.257
0.564	0.436	0.419	1.704	760	767.562	-7.562	1.1176	1.3447
0.663	0.537	0.5131	2.389	760	767.893	-7.893	1.0628	1.4502
0.759	0.646	0.6178	2.816	760	763.601	-3.601	1.0291	1.5613
0.844	0.754	0.7226	3.144	760	753.46	6.54	1.0112	1.6655
0.921	0.853	0.8327	2.035	760	744.737	15.263	1.0027	1.7611
0.96	0.922	0.8962	2.585	760	739.516	20.484	1.0007	1.8092
R.M.S. Deviations								
			1.76			9.4		

TABLE A.4.15

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data O'Donnell (1980)
Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.014	0.01	0.0099	0.014	760	755.742	4.258	3.0822	1.0029
0.021	0.015	0.0148	0.021	760	756.076	3.924	2.9184	1.0049
0.099	0.06	0.0592	0.08	760	756.991	3.009	1.8276	1.0382
0.151	0.104	0.1027	0.132	760	761.363	-1.363	1.7584	1.0588
0.213	0.148	0.1462	0.176	760	761.011	-1.011	1.5755	1.0881
0.298	0.206	0.2037	0.226	760	762.871	-2.871	1.3839	1.1326
0.473	0.349	0.346	0.303	760	759.738	0.262	1.2063	1.2334
0.564	0.436	0.4328	0.323	760	760.821	-0.821	1.1544	1.2931
0.663	0.537	0.5337	0.329	760	761.77	-1.77	1.1055	1.3667
0.759	0.646	0.6429	0.312	760	761.117	-1.117	1.0708	1.447
0.844	0.754	0.7513	0.274	760	758.202	1.798	1.0514	1.5263
0.921	0.853	0.8506	0.245	760	748.744	11.256	1.0242	1.6101
0.96	0.922	0.9199	0.206	760	752.479	7.521	1.0272	1.6509
R.M.S.	Deviations							
			0.2297			4.344		

TABLE A.4.16

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data O'Donnell (1980)
Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.014	0.01	0.0127	-0.265	760	756.55	3.45	3.9543	1.0012
0.021	0.015	0.0186	-0.359	760	757.203	2.797	3.6693	1.0025
0.099	0.06	0.0692	-0.924	760	762.115	-2.115	2.1373	1.0345
0.151	0.104	0.1031	0.091	760	764.023	-4.023	1.7654	1.0624
0.213	0.148	0.1418	0.621	760	762.55	-2.55	1.5275	1.0964
0.298	0.206	0.1992	0.681	760	764.095	-4.095	1.353	1.1413
0.473	0.349	0.3404	0.857	760	755.658	4.342	1.187	1.2337
0.564	0.436	0.4264	0.965	760	754.758	5.242	1.1373	1.2896
0.663	0.537	0.5281	0.892	760	757.949	2.051	1.0938	1.3684
0.759	0.646	0.6349	1.112	760	761.712	-1.712	1.0575	1.4825
0.844	0.754	0.7356	1.841	760	761.095	-1.095	1.0295	1.6469
0.921	0.853	0.8382	1.476	760	757.957	2.043	1.0094	1.9023
0.96	0.922	0.898	2.399	760	750.477	9.523	1.0027	2.1049
R.M.S.	Deviations							
			1.14			4.0495		

TABLE A.4.17

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Redlich-Kister 4 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data O'Donnell (1980)
Using Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.014	0.01	0.0099	0.014	760	754.74	5.26	3.0823	1.0016
0.021	0.015	0.0148	0.021	760	754.605	5.395	2.9185	1.0029
0.099	0.06	0.0592	0.08	760	752.899	7.101	1.8276	1.0322
0.151	0.104	0.1027	0.132	760	757.858	2.142	1.7584	1.0534
0.213	0.148	0.1462	0.176	760	758.975	1.025	1.5755	1.0847
0.298	0.206	0.2037	0.226	760	762.253	-2.253	1.3839	1.1314
0.473	0.349	0.346	0.303	760	757.136	2.864	1.2062	1.2269
0.564	0.436	0.4328	0.323	760	756.801	3.199	1.1544	1.2811
0.663	0.537	0.5337	0.329	760	758.751	1.249	1.1055	1.3551
0.759	0.646	0.6429	0.312	760	762.753	-2.753	1.0708	1.4557
0.844	0.754	0.7513	0.275	760	765.549	-5.549	1.0514	1.5863
0.921	0.853	0.8506	0.244	760	758.532	1.468	1.0242	1.764
0.96	0.922	0.9199	0.206	760	759.807	0.193	1.0272	1.8777
R.M.S .	Deviations							
			0.2296			3.705		

TABLE A.4.18

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- Redlich-Kister 4 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data O'Donnell (1980)
Without Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.014	0.01	0.0089	0.111	760	753.395	6.605	2.7786	1.0008
0.021	0.015	0.0135	0.154	760	752.712	7.288	2.6568	1.0017
0.099	0.06	0.0585	0.155	760	751.809	8.191	1.8043	1.0314
0.151	0.104	0.0895	1.451	760	755.135	4.865	1.5325	1.0647
0.213	0.148	0.1259	2.208	760	758.608	1.392	1.3566	1.11
0.298	0.206	0.1845	2.149	760	767.514	-7.514	1.2533	1.1685
0.473	0.349	0.352	-0.299	760	761.57	-1.57	1.2272	1.2266
0.564	0.436	0.4579	-2.191	760	757.204	2.796	1.2215	1.2251
0.663	0.537	0.5733	-3.635	760	756.853	3.147	1.1876	1.2322
0.759	0.646	0.677	-3.099	760	759.834	0.166	1.1276	1.3026
0.844	0.754	0.7619	-0.79	760	762.664	-2.664	1.0663	1.4967
0.921	0.853	0.8472	0.578	760	765.411	-5.411	1.0202	1.9122
0.96	0.922	0.9006	2.139	760	758.615	1.385	1.0056	2.2956
R.M.S .	Deviations							
			1.858			4.839		

TABLE A.4.19 Consistency test for Brown and Ewald data

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data: Brown and Ewald
With Association Model

xLIQUID	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0109	0.0079	0.0078	0.01	760	753.96	6.05	3.1861	1.0000
0.0324	0.0239	0.0238	0.01	760	753.5	6.50	2.7738	1.0020
0.0790	0.0575	0.0574	0.01	760	751.09	8.91	2.2224	1.0118
0.1749	0.1217	0.1223	-0.06	760	747.25	12.75	1.6833	1.0441
0.2612	0.1783	0.1801	-0.18	760	744.06	15.94	1.4430	1.0831
0.3537	0.2426	0.2451	-0.25	760	744.57	15.43	1.2887	1.1345
0.4641	0.3409	0.3413	-0.04	760	752.48	7.58	1.2090	1.2056
0.5802	0.4504	0.4474	0.30	760	759.62	0.38	1.1401	1.2978
0.6622	0.5427	0.5336	0.92	760	768.43	-8.43	1.1135	1.3720
0.7083	0.5929	0.5833	0.96	760	768.35	-8.35	1.0969	1.4191
0.7802	0.6727	0.6633	0.94	760	767.34	-7.34	1.0657	1.5008
0.8503	0.7618	0.7554	0.64	760	763.77	-3.77	1.0504	1.5873
0.9188	0.8554	0.8555	-0.01	760	757.88	2.12	1.0305	1.6819

TABLE A.4.19 Consistency test for Brown and Ewald data Continued.

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.9526	0.9021	0.9112	-0.91	760	750.58	9.42	1.0201	1.7331
0.9945	0.9888	0.9892	-0.04	760	758.25	1.75	1.0190	1.7921
0.9966	0.9931	0.9933	-0.02	760	758.41	1.59	1.0188	1.7952
0.9998	0.9997	0.9996	0.01	760	758.63	1.37	1.0162	1.8003
0.9998	0.9998	0.9996	0.02	760	758.71	1.29	1.1843	1.2446
0.9998	0.9996	0.9996	0.00	760	758.56	1.44	1.1391	1.3165
R.M.S .	Deviations							
			0.46			7.89		

TABLE A.4.20 Consistency test for Garner and Ellis data

Mixture Acetic Acid - Water at 760 mm Hg
Liquid-phase Activity Coefficient Model :- NRTL 3 Parameter Equation
Acetic Acid Vapour Pressure Equation :- 3 Parameter Antoine Equation
Water Vapour Pressure Equation :- 6 Parameter Antoine Equation

Data: Garner and Ellis
With Association Model

LIQUID x	VAPOUR y_{EXP}	VAPOUR y_{CALC}	DELTA y *100	PRESSURE P_{EXP}	PRESSURE P_{CALC}	DELTA P	ACTIVITY COEFFICIENT	ACTIVITY COEFFICIENT
Mol Fraction	Mol Fraction	Mol Fraction	y*100	mmHg	mm Hg	mm Hg	12	21
0.0827	0.0663	0.0661	0.02	760	752.45	7.55	2.3582	1.0123
0.1970	0.1360	0.1348	0.12	760	758.33	1.67	1.5929	1.0570
0.2920	0.2010	0.2025	-0.15	760	747.06	12.94	1.3923	1.1021
0.3870	0.2780	0.2791	-0.11	760	750.59	9.42	1.2840	1.1547
0.5200	0.3950	0.3958	-0.08	760	753.35	6.66	1.1843	1.2446
0.6100	0.4850	0.4830	0.20	760	758.90	1.10	1.1391	1.3165
0.6600	0.5330	0.5310	0.20	760	759.12	0.88	1.1098	1.3624
0.7390	0.6160	0.6149	0.11	760	758.39	1.62	1.0741	1.4419
0.7790	0.6610	0.6599	0.12	760	758.69	1.31	1.0551	1.4862
0.8560	0.7600	0.7612	-0.12	760	756.97	3.03	1.0356	1.5768
0.9150	0.8430	0.8490	-0.60	760	753.33	6.68	1.0214	1.6536
0.9650	0.9300	0.9343	-0.43	760	755.61	4.39	1.0177	1.7205
R.M.S .	Deviations							
			0.25			6.05		

Appendix 5 consistency test results for acetone- chloroform mixture.

The results of the consistency tests performed on the experimental data for the mixture acetone-chloroform are reported here. The fitting package proposed by Prausnitz et al. (1980) was used to perform the tests, the vapour phase was represented by a 5 constant fugacity equation given in Appendix 10 for each pure component. Four different liquid phase activity coefficient models were used, i.e. Wilson, NRTL, Margules and UNIQUAC. Constants for each of these models at each condition are recorded in Appendix 11.

Tables A.5.1 to A.5.4 give the one atmosphere results for each liquid-phase model used Tables A.5.5 to A.5.8 give the 63.4°C results for each liquid-phase model used

TABLE A.5.1

Mixture Acetone - Chloroform at 1 atmosphere
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	760.62	-0.72	56.10	56.05	0.05	1.0000	0.9997	0.0003	1.0000	0.9999	0.0001
759.8	759.61	0.19	57.05	57.06	-0.01	0.9396	0.9388	0.0008	0.9676	0.9692	-0.0016
759.9	758.26	1.64	58.00	58.11	-0.11	0.8784	0.8768	0.0016	0.9278	0.9313	-0.0035
759.8	757.87	1.93	60.45	60.57	-0.12	0.7361	0.7335	0.0026	0.8118	0.8154	-0.0036
759.8	758.22	1.58	61.45	61.55	-0.10	0.6741	0.6722	0.0019	0.7510	0.7533	-0.0023
760.0	759.36	0.64	62.20	62.24	-0.04	0.6304	0.6267	0.0037	0.6992	0.7026	-0.0034
759.8	760.18	-0.38	63.13	63.11	0.02	0.5626	0.5574	0.0052	0.6151	0.6192	-0.0041
760.3	760.62	-0.32	63.14	63.12	0.02	0.5563	0.5579	-0.0016	0.6211	0.6198	0.0013
759.8	761.22	-1.42	63.75	63.66	0.09	0.5012	0.5019	-0.0007	0.5487	0.5479	0.0008
759.7	761.40	-1.70	63.80	63.69	0.11	0.4966	0.4987	-0.0021	0.5456	0.5437	0.0019
759.7	758.31	1.39	63.80	63.89	-0.09	0.4551	0.4488	0.0063	0.4726	0.4775	-0.0049
759.8	761.30	-1.50	64.15	64.06	0.09	0.4375	0.4381	-0.0006	0.4637	0.4632	0.0005
759.8	761.79	-1.99	64.35	64.23	0.12	0.3389	0.3394	-0.0005	0.3327	0.3324	0.0003
759.8	758.93	0.87	63.90	63.95	-0.05	0.2876	0.2844	0.0032	0.2602	0.2628	-0.0026
759.9	759.93	-0.03	63.70	63.70	0.00	0.2352	0.2330	0.0022	0.2000	0.2019	-0.0019

TABLE A5.1 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	763.22	-3.32	63.80	63.60	0.20	0.1979	0.2030	-0.0051	0.1727	0.1686	0.0041
759.9	761.48	-1.58	63.50	63.40	0.10	0.1827	0.1893	-0.0066	0.1600	0.1541	0.0059
759.9	759.96	-0.06	63.25	63.25	0.00	0.1795	0.1787	0.0008	0.1424	0.1432	-0.0008
760.0	760.57	-0.57	63.05	63.01	0.04	0.1532	0.1532	0.0000	0.1176	0.1178	-0.0002
760.3	762.13	-1.83	63.00	62.89	0.11	0.1361	0.1354	0.0007	0.0998	0.1011	-0.0013
761.0	761.77	-0.77	62.40	62.35	0.05	0.0901	0.0913	-0.0012	0.0642	0.0630	0.0012
760.0	761.15	-1.15	62.35	62.28	0.07	0.0870	0.0874	-0.0004	0.0599	0.0598	0.0001
R.M.S	Deviations										
		1.4			0.09			0.002			0.0027

TABLE A.5.2

Mixture Acetone - Chloroform at 1 atmosphere
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	760.62	-0.72	56.10	56.05	0.05	1.0000	0.9997	0.0003	1.0000	0.9999	0.0001
759.8	759.70	0.10	57.05	57.06	-0.01	0.9396	0.9388	0.0008	0.9676	0.9691	-0.0015
759.9	758.42	1.48	58.00	58.10	-0.10	0.8784	0.8768	0.0016	0.9278	0.9313	-0.0035
759.8	757.98	1.82	60.45	60.57	-0.12	0.7361	0.7331	0.003	0.8118	0.8158	-0.0040
759.8	758.22	1.58	61.45	61.55	-0.10	0.6741	0.6716	0.0025	0.7510	0.7539	-0.0029
760.0	759.26	0.74	62.20	62.25	-0.05	0.6304	0.6260	0.0044	0.6992	0.7033	-0.0041
759.8	760.41	-0.61	63.13	63.09	0.04	0.5626	0.5615	0.0011	0.6251	0.6259	-0.0008
760.3	760.35	-0.05	63.14	63.14	0.00	0.5563	0.5571	-0.0008	0.6211	0.6204	0.0007
759.8	760.82	-1.02	63.75	63.69	0.06	0.5012	0.5012	0.0000	0.5487	0.5485	0.0002
759.7	760.99	-1.29	63.80	63.72	0.08	0.4966	0.4980	-0.0014	0.5456	0.5443	0.0013
759.7	758.29	1.41	63.80	63.89	-0.09	0.4551	0.4488	0.0063	0.4726	0.4774	-0.0048
759.8	760.77	-0.97	64.15	64.09	0.06	0.4375	0.4375	0.0000	0.4637	0.4636	0.0001
759.8	761.13	-1.33	64.35	64.27	0.08	0.3389	0.3392	-0.0003	0.3327	0.3325	0.0002
759.8	758.26	1.54	63.90	63.99	-0.09	0.2876	0.2844	0.0032	0.2602	0.2627	-0.0025
759.9	759.30	0.60	63.70	63.74	-0.04	0.2352	0.2332	0.0020	0.2000	0.2017	-0.0017

TABLE A.5.2 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	763.29	-3.39	63.80	63.59	0.21	0.1979	0.2031	-0.0052	0.1727	0.1686	-0.0041
759.9	761.79	-1.89	63.50	63.38	0.12	0.1827	0.1797	0.0030	0.1400	0.1434	-0.0034
759.9	759.42	0.48	63.25	63.28	-0.03	0.1795	0.1790	0.0005	0.1424	0.1428	-0.0004
760.0	760.09	-0.09	63.05	63.04	0.01	0.1532	0.1535	-0.0003	0.1176	0.1173	0.0003
760.3	761.70	-1.40	63.00	62.91	0.09	0.1361	0.1357	0.0004	0.0998	0.1006	-0.0008
761.0	761.47	-0.47	62.40	62.37	0.03	0.0901	0.0916	-0.0015	0.0642	0.0626	0.0016
760.0	761.21	-1.21	62.35	62.27	0.08	0.0870	0.0874	-0.0004	0.0599	0.0599	0.0000
R.M.S	Deviations										
		1.17			0.07			0.001			0.002

TABLE A.5.3

Mixture Acetone - Chloroform at 1 atmosphere
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	760.66	-0.76	56.10	56.05	0.05	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000
759.8	759.75	-0.05	57.05	57.05	0.00	0.9396	0.9389	0.0007	0.9676	0.9689	-0.0013
759.9	758.42	1.48	58.00	58.09	-0.09	0.8784	0.8765	0.0019	0.9278	0.9307	-0.0029
759.8	757.97	1.83	60.45	60.57	-0.12	0.7361	0.7330	0.0031	0.8118	0.8150	-0.0032
759.8	758.22	1.58	61.45	61.55	-0.10	0.6741	0.6718	0.0023	0.7510	0.7531	-0.0021
760.0	759.30	0.70	62.20	62.25	-0.05	0.6304	0.6264	0.0040	0.6992	0.7026	-0.0034
759.8	760.44	-0.64	63.13	63.09	0.04	0.5626	0.5623	0.0003	0.6251	0.6253	-0.0002
760.3	760.34	-0.04	63.14	63.13	0.01	0.5563	0.5579	-0.0016	0.6211	0.6198	0.0013
759.8	760.87	-1.07	63.75	63.68	0.07	0.5012	0.5021	-0.0009	0.5487	0.5480	0.0007
759.7	761.03	-1.33	63.80	63.71	0.09	0.4966	0.4990	-0.0024	0.5456	0.5438	0.0018
759.7	758.19	1.51	63.80	63.89	-0.09	0.4551	0.4538	0.0013	0.4826	0.4836	0.0010
759.8	760.92	-1.12	64.15	64.08	0.07	0.4375	0.4384	-0.0009	0.4637	0.4630	0.0007
759.8	761.51	-1.71	64.35	64.24	0.11	0.3389	0.3399	-0.0010	0.3327	0.3319	0.0008
759.8	758.80	1.00	63.90	63.96	-0.06	0.2876	0.2849	0.0027	0.2602	0.2624	-0.0022
759.9	759.92	-0.02	63.70	63.70	0.00	0.2352	0.2334	0.0018	0.2000	0.2016	-0.0016

TABLE A.5.3 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	762.29	-2.39	63.50	63.35	0.15	0.1827	0.1812	0.0015	0.1438	0.1453	-0.0015
759.9	762.46	-2.56	63.50	63.34	0.16	0.1827	0.1793	0.0034	0.1400	0.1433	-0.0033
759.9	760.06	-0.16	63.25	63.24	0.01	0.1795	0.1789	0.0006	0.1424	0.1429	-0.0005
760.0	760.72	-0.72	63.05	63.01	0.04	0.1532	0.1532	0.0000	0.1176	0.1176	0.0000
760.3	762.32	-2.02	63.00	62.87	0.13	0.1361	0.1352	0.0009	0.0998	0.1008	-0.0010
761.0	761.96	-0.96	62.40	62.34	0.06	0.0901	0.0911	-0.0010	0.0642	0.0630	0.0012
760.0	761.34	-1.34	62.35	62.27	0.08	0.0870	0.0871	-0.0001	0.0599	0.0598	0.0001
R.M.S	Deviations										
		1.34			0.08			0.0018			0.0018

TABLE A.5.4
Mixture Acetone - Chloroform at 1 atmosphere
Liquid-phase Activity Coefficient Model :- NRTL 3, Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	760.66	-0.76	56.10	56.05	0.05	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000
759.8	764.79	-4.99	57.05	56.72	0.33	0.9396	0.9374	0.0022	0.9676	0.9689	-0.0013
759.9	763.55	-3.65	58.00	57.77	0.23	0.8784	0.8710	0.0074	0.9278	0.9376	-0.0098
759.8	757.40	2.40	60.45	60.61	-0.16	0.7361	0.7280	0.0081	0.8118	0.8206	-0.0088
759.8	756.52	3.28	61.45	61.66	-0.21	0.6741	0.6705	0.0036	0.7510	0.7552	-0.0042
760.0	757.43	2.57	62.20	62.36	-0.16	0.6304	0.6278	0.0026	0.6992	0.7019	-0.0027
759.8	758.85	0.95	63.13	63.19	-0.06	0.5626	0.5626	0.0000	0.6151	0.6152	-0.0001
759.7	759.35	0.95	63.80	63.20	-0.06	0.4966	0.4966	-0.0098	0.5456	0.5383	0.0073
760.3	761.02	-1.22	63.14	63.68	0.07	0.5563	0.5012	-0.0083	0.6211	0.5425	0.0062
759.8	761.28	-1.58	63.75	63.70	0.01	0.5012	0.5563	-0.0070	0.5487	0.6161	0.0050
759.8	759.36	0.34	64.15	63.82	-0.02	0.4375	0.4551	-0.0020	0.4637	0.4711	0.0015
759.8	762.67	-2.87	64.35	63.98	0.17	0.3389	0.4375	-0.0090	0.3327	0.4569	0.0068
761.0	765.49	-5.69	62.40	64.00	0.35	0.0901	0.3389	-0.0070	0.0642	0.3273	0.0054
759.9	763.52	-3.72	63.50	63.67	0.23	0.1827	0.2876	-0.0011	0.1438	0.2597	0.0005
760.0	759.36	0.34	63.05	63.82	-0.02	0.1532	0.2352	0.0003	0.1176	0.2011	-0.0011

TABLE A.5.4 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
759.9	768.17	-8.27	63.80	63.28	0.52	0.1979	0.2033	-0.0054	0.1727	0.1689	0.0038
759.9	766.37	-6.47	63.50	63.10	0.40	0.1827	0.1890	-0.0063	0.1600	0.1549	0.0051
759.9	764.71	-4.81	63.25	62.95	0.30	0.1795	0.1784	0.0011	0.1424	0.1446	-0.0022
760.0	765.00	-5.00	63.05	62.73	0.32	0.1532	0.1520	0.0012	0.1176	0.1201	-0.0025
760.3	766.24	-5.94	63.00	62.62	0.38	0.1361	0.1338	0.0023	0.0998	0.1039	-0.0041
761.0	764.85	-3.85	62.40	62.16	0.24	0.0901	0.0893	0.0008	0.0642	0.0664	-0.0022
760.0	764.12	-4.12	62.35	62.09	0.26	0.0870	0.0853	0.0017	0.0599	0.0632	-0.0033
R.M.S	Deviations										
		4.11			0.26			0.0051			0.0047

TABLE A.5.5

Mixture Acetone - Chloroform at 64.3°C
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
965.10	962.67	2.83	64.35	64.57	-0.22	0.9072	0.9108	-0.0036	0.9528	0.9494	0.0034
950.70	948.45	2.25	64.64	64.81	-0.17	0.8721	0.8695	0.0026	0.9165	0.9220	-0.0055
909.80	907.51	2.29	64.31	64.48	-0.17	0.8076	0.8075	0.0001	0.8743	0.8759	-0.0016
851.49	851.48	0.01	64.32	64.31	0.01	0.6755	0.6937	-0.0182	0.7926	0.7743	0.0183
848.90	848.01	0.89	64.34	64.39	-0.17	0.6618	0.6798	-0.0180	0.7775	0.7602	0.0173
818.85	820.51	-1.66	64.28	64.16	-0.17	0.6055	0.6239	-0.0184	0.7178	0.7008	0.0170
791.50	789.32	2.18	64.30	64.44	-0.13	0.4833	0.4903	-0.0070	0.5447	0.5396	0.0051
774.60	775.45	-0.85	64.36	64.30	-0.25	0.4286	0.4300	-0.0014	0.4620	0.4608	0.0012
759.80	763.83	-4.03	64.35	64.10	0.25	0.3389	0.3353	0.0036	0.3327	0.3354	-0.0027
772.20	772.52	-0.32	64.44	64.42	0.02	0.3086	0.3042	0.0044	0.2917	0.2951	-0.0034
783.10	780.93	2.17	64.38	64.51	-0.13	0.2440	0.2399	0.0041	0.2123	0.2155	-0.0032
795.60	791.63	3.97	64.50	64.75	-0.25	0.2149	0.2109	0.0040	0.1790	0.1819	-0.0029
794.50	790.00	4.50	64.33	64.62	-0.29	0.2040	0.2010	0.0030	0.1689	0.1708	-0.0019
804.50	798.20	6.30	64.31	64.71	-0.40	0.1759	0.1745	0.0014	0.1423	0.1422	0.0001
805.95	798.94	7.01	64.26	64.71	-0.45	0.1686	0.1712	0.0026	0.1429	0.1388	0.0041

TABLE A.5.5 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
803.20	800.40	2.80	64.30	64.48	-0.18	0.1398	0.1419	-0.0021	0.1123	0.1093	0.0030
814.00	812.61	1.39	64.65	64.74	-0.09	0.1227	0.1226	0.0001	0.0914	0.0911	0.0003
828.00	823.96	4.04	64.32	64.59	-0.27	0.0699	0.0747	-0.0048	0.0582	0.0503	0.0079
843.00	837.10	5.90	64.39	64.79	-0.40	0.0532	0.0522	0.0010	0.0351	0.0335	0.0016
853.50	850.10	3.43	64.31	64.54	-0.23	0.0011	0.0000	0.0011	0.0004	0.0000	0.0004
R.M.S	Deviations										
		3.51			0.23			0.0077			0.0075

TABLE A.5.6

Mixture Acetone - Chloroform at 64.3°C
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
965.10	962.27	2.83	64.35	64.57	-0.22	0.9072	0.9108	-0.0036	0.9528	0.9494	0.0034
950.70	948.45	2.25	64.64	64.81	-0.17	0.8721	0.8694	0.0027	0.9165	0.9220	-0.0055
909.80	907.50	2.30	64.31	64.48	-0.17	0.8076	0.8074	0.0002	0.8743	0.8759	-0.0016
851.49	851.43	0.06	64.32	64.32	0.00	0.6755	0.6937	-0.0182	0.7926	0.7743	0.0183
848.90	847.95	0.95	64.34	64.40	-0.06	0.6618	0.6797	-0.0179	0.7775	0.7603	0.0172
818.85	820.44	-1.59	64.28	64.17	0.11	0.6055	0.6238	-0.0183	0.7178	0.7008	0.0170
791.50	789.27	2.23	64.30	64.44	-0.14	0.4833	0.4904	-0.0071	0.5447	0.5396	0.0051
774.60	775.41	-0.81	64.36	64.31	0.05	0.4286	0.4302	-0.0016	0.4620	0.4607	0.0013
759.80	763.83	-4.03	64.35	64.10	0.25	0.3389	0.3355	0.0034	0.3327	0.3353	-0.0026
772.20	772.55	-0.35	64.44	64.42	0.02	0.3086	0.3044	0.0042	0.2917	0.2950	-0.0033
783.10	781.00	2.10	64.38	64.51	-0.13	0.2440	0.2400	0.0040	0.2123	0.2154	-0.0031
795.60	791.72	3.88	64.50	64.75	-0.25	0.2149	0.2110	0.0039	0.1790	0.1818	-0.0028
794.50	790.10	4.40	64.33	64.61	-0.28	0.2040	0.2011	0.0029	0.1689	0.1708	-0.0019
804.50	798.31	6.19	64.31	64.71	-0.40	0.1759	0.1746	0.0013	0.1423	0.1422	0.0001
805.95	799.04	6.91	64.26	64.71	-0.45	0.1686	0.1713	-0.0027	0.1429	0.1388	0.0041

TABLE A.5.6 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
803.20	800.50	2.70	64.30	64.48	-0.18	0.1398	0.1420	-0.0022	0.1123	0.1093	0.0030
814.00	812.72	1.28	64.65	64.73	-0.08	0.1227	0.1226	0.0001	0.0914	0.0911	0.0003
828.00	824.04	3.96	64.32	64.58	-0.26	0.0699	0.0746	-0.0047	0.0582	0.0504	0.0078
843.00	837.16	5.84	64.39	64.78	-0.39	0.0532	0.0522	0.0010	0.0351	0.0336	0.0015
853.53	850.10	3.43	64.31	64.54	-0.23	0.0011	0.0000	0.0011	0.0004	0.0000	0.0004
R.M.S	Deviations										
		3.46			0.23			0.0076			0.075

TABLE A.5.7

Mixture Acetone - Chloroform at 64.3° C
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
965.10	962.72	2.38	64.35	64.54	-0.19	0.9072	0.9093	-0.0021	0.9528	0.9472	0.0056
950.70	949.69	1.01	64.64	64.72	-0.08	0.8721	0.8716	0.0005	0.9165	0.9222	-0.0057
909.80	908.88	0.92	64.31	64.38	-0.07	0.8076	0.8079	-0.0003	0.8743	0.8752	-0.0009
851.49	851.71	-0.22	64.32	64.31	0.01	0.6755	0.6828	-0.0073	0.7926	0.7635	0.0291
848.90	848.32	0.58	64.34	64.39	-0.05	0.6618	0.6692	-0.0074	0.7775	0.7498	0.0277
818.85	820.94	-2.09	64.28	64.15	0.13	0.6055	0.6128	-0.0073	0.7178	0.6893	0.0285
791.50	790.51	0.99	64.30	64.37	-0.07	0.4833	0.4864	-0.0031	0.5447	0.5358	0.0089
774.60	776.80	-2.20	64.36	64.23	0.13	0.4286	0.4289	-0.0003	0.4620	0.4604	0.0016
759.80	765.12	-5.32	64.35	64.03	0.32	0.3389	0.3370	0.0019	0.3327	0.3384	-0.0057
772.20	773.67	-1.47	64.44	64.35	0.09	0.3086	0.3064	0.0022	0.2917	0.2987	-0.007
783.10	781.92	1.18	64.38	64.46	-0.08	0.2440	0.2420	0.0020	0.2123	0.2187	-0.0064
795.60	792.53	3.07	64.50	64.70	-0.20	0.2149	0.2128	0.0021	0.1790	0.1848	-0.0058
794.50	790.94	3.56	64.33	64.57	-0.24	0.2040	0.2022	0.0018	0.1689	0.1730	-0.0041
804.50	799.17	5.33	64.31	64.67	-0.36	0.1759	0.1746	0.0013	0.1423	0.1431	-0.0008
805.95	800.10	5.85	64.26	64.65	-0.39	0.1686	0.1688	-0.0002	0.1429	0.1372	0.0057

TABLE A.5.7 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
803.20	801.47	1.73	64.30	64.43	-0.13	0.1398	0.1402	-0.0004	0.1123	0.1086	0.0037
814.00	813.46	0.54	64.65	64.70	-0.05	0.1227	0.1224	0.0003	0.0914	0.0919	-0.0005
828.00	825.04	2.96	64.32	64.54	-0.22	0.0699	0.0709	-0.0010	0.0582	0.0483	0.0099
843.00	837.69	5.31	64.39	64.77	-0.38	0.0532	0.0517	0.0015	0.0351	0.0338	0.0013
853.53	850.13	3.40	64.31	64.54	-0.23	0.0011	0.0000	0.0011	0.0004	0.0000	0.0004
R.M.S	Deviations										
		3.05			0.21			0.0032			0.012

TABLE A.5.8
Mixture Acetone - Chloroform at 64.3°C
Liquid-phase Activity Coefficient Model :- NRTL 3, Parameter Equation
Acetone vapour phase :- 5 parameter Fugacity Equation.
Chloroform vapour phase :- 5 parameter Fugacity Equation.

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
965.10	962.38	2.72	64.35	64.56	-0.21	0.9072	0.9108	-0.0036	0.9528	0.9493	0.0035
950.70	948.59	2.11	64.64	64.80	-0.16	0.8721	0.8695	0.0026	0.9165	0.9219	-0.0054
909.80	907.69	2.11	64.31	64.47	-0.16	0.8076	0.8074	0.0002	0.8743	0.8759	-0.0016
851.49	851.63	-0.14	64.32	64.30	0.02	0.6755	0.6934	-0.0179	0.7926	0.7744	0.0182
848.90	848.15	0.75	64.34	64.38	-0.04	0.6618	0.6795	-0.0177	0.7775	0.7604	0.0171
818.85	820.60	-1.75	64.28	64.16	0.12	0.6055	0.6235	-0.0180	0.7178	0.7010	0.0168
791.50	789.31	2.19	64.30	64.44	-0.14	0.4833	0.4900	-0.0067	0.5447	0.5398	0.0049
774.60	775.40	-0.80	64.36	64.31	0.05	0.4286	0.4299	-0.0013	0.4620	0.4610	0.0010
759.80	763.74	-3.94	64.35	64.10	0.25	0.3389	0.3354	0.0035	0.3327	0.3354	-0.0027
772.20	772.45	-0.25	64.44	64.42	0.02	0.3086	0.3043	0.0043	0.2917	0.2951	-0.0034
783.10	780.89	2.21	64.38	64.52	-0.14	0.2440	0.2400	0.0040	0.2123	0.2154	-0.0031
795.60	791.61	3.99	64.50	64.75	-0.25	0.2149	0.2110	0.0039	0.1790	0.1818	-0.0028
794.50	789.99	4.51	64.33	64.62	-0.29	0.2040	0.2011	0.0029	0.1689	0.1707	-0.0018
804.50	798.94	7.01	64.26	64.71	-0.45	0.1686	0.1713	-0.0027	0.1429	0.1387	0.0042
805.95	798.21	6.29	64.31	64.72	-0.41	0.1759	0.1746	0.0013	0.1423	0.1421	0.0002

TABLE A.5.8 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
803.20	800.42	2.78	64.30	64.48	-0.18	0.1398	0.1420	-0.0022	0.1123	0.1092	0.0031
814.00	812.64	1.36	64.65	64.74	-0.09	0.1227	0.1226	0.0001	0.0914	0.0910	0.0004
828.00	824.00	4.00	64.32	64.59	-0.27	0.0699	0.0747	-0.0048	0.0582	0.0503	0.0079
843.00	837.13	5.87	64.39	64.78	-0.39	0.0532	0.0522	0.0010	0.0351	0.0335	0.0016
853.53	850.10	3.43	64.31	64.54	-0.23	0.0011	0.0000	0.0011	0.0004	0.0000	0.0004
R.M.S	Deviations										
		3.48			0.23			0.0075			0.0074

Appendix 6 Consistency test results for cyclohexane-ethanol mixture.

The results of the consistency tests performed on the experimental data for the mixture cyclohexane-ethanol are reported here. The fitting package proposed by Prausnitz et al. (1980) was used to perform the tests, the vapour phase was represented by a 5 constant vapour pressure equation given in Appendix 10 for ethanol. The vapour phase for cyclohexane was represented by the new 3-constant vapour pressure equation developed from the new vapour pressure measurements made as part of this work again given in Appendix 10. Five different liquid-phase activity coefficient models were used, i.e. Wilson, NRTL, Margules, Van Laar and UNIQUAC. Constants for each of these models at each condition are recorded in Appendix 11.

TABLE A.6.1

Mixture Cyclohexane - Ethanol at 1.01325 bar
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
754.80	752.68	2.12	76.53	76.65	-0.12	0.0142	0.0057	0.0085	0.0821	0.1997	0.0062
759.80	761.24	-1.44	67.60	67.50	0.10	0.0622	0.0574	0.0048	0.3352	0.2818	0.0048
761.80	761.42	0.38	66.10	66.12	-0.02	0.0971	0.0967	0.0004	0.3770	0.2920	0.0035
762.60	763.45	-0.85	65.93	65.87	0.06	0.1165	0.1153	0.0012	0.3883	0.4607	0.0073
766.40	767.08	-0.68	65.77	65.71	0.06	0.1418	0.1411	0.0007	0.3885	0.4903	0.0098
763.90	763.73	0.17	65.45	65.45	0.00	0.1594	0.1591	0.0003	0.3944	0.5051	0.0154
760.10	758.78	1.32	65.00	65.09	-0.09	0.1953	0.1953	0.0000	0.4046	0.5188	0.0198
762.90	762.41	0.49	65.10	65.13	-0.03	0.2202	0.2201	0.0001	0.4071	0.5289	0.0187
761.20	760.55	0.65	64.96	65.00	-0.04	0.2436	0.2435	0.0001	0.4065	0.5373	0.0138
763.20	762.22	0.98	64.96	65.03	-0.07	0.2562	0.2562	0.0000	0.4196	0.5652	0.0220
760.90	759.44	1.46	64.79	64.89	-0.10	0.2762	0.2762	0.0000	0.4183	0.5736	0.0406
763.50	760.45	3.05	64.66	64.87	-0.21	0.3099	0.3100	-0.0001	0.4235	0.6103	0.0199
759.90	758.73	1.17	64.66	64.74	-0.08	0.3854	0.3854	0.0000	0.4334	0.6454	0.0190
762.00	753.98	8.02	64.53	64.74	-0.21	0.4026	0.4026	0.0000	0.4353	0.6902	-0.0052
761.70	758.76	2.94	64.52	64.73	-0.21	0.4503	0.4503	0.0000	0.4417	0.8126	0.0061

TABLE A.6.1 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
763.20	762.66	0.54	65.40	65.44	-0.04	0.6848	0.6847	0.0001	0.4864	0.4866	-0.0002
763.10	763.28	-0.18	65.00	64.99	0.01	0.5636	0.5637	-0.0001	0.4635	0.4581	0.0054
763.90	765.01	-1.11	66.43	66.35	0.08	0.7699	0.7706	-0.0007	0.5269	0.5230	0.0039
765.60	765.33	0.27	67.05	67.07	-0.02	0.8130	0.8125	0.0005	0.5454	0.5502	-0.0048
763.90	765.57	-1.67	68.26	68.14	0.12	0.8538	0.8556	-0.0018	0.5924	0.5897	0.0027
763.60	763.77	-0.17	69.55	69.53	0.02	0.8956	0.8951	0.0005	0.6383	0.6425	-0.0042
R.M.S	Deviations										
		1.49			0.1			0.0022			0.0093

TABLE A.6.2

Mixture Cyclohexane - Ethanol at 1.01325 bar
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
754.80	752.75	2.05	76.53	76.65	-0.12	0.0142	0.0047	0.0095	0.0821	0.1023	-0.0202
759.80	762.43	-2.63	67.60	67.41	0.19	0.0622	0.0564	0.0058	0.3352	0.3508	-0.0156
761.80	761.19	0.61	66.10	66.14	-0.04	0.0971	0.0971	0.0000	0.3770	0.3824	-0.0054
762.60	762.93	-0.33	65.93	65.90	0.03	0.1165	0.1163	0.0002	0.3883	0.3909	-0.0026
766.40	766.45	-0.05	65.77	65.76	0.01	0.1418	0.1414	0.0004	0.3885	0.3993	-0.0108
763.90	763.10	0.80	65.45	65.50	-0.05	0.1594	0.1593	0.0001	0.3944	0.4035	-0.0091
760.10	758.28	1.82	65.00	65.13	-0.13	0.1953	0.1954	-0.0001	0.4046	0.4104	-0.0058
762.90	762.03	0.87	65.10	65.16	-0.06	0.2202	0.2201	0.0001	0.4071	0.4148	-0.0077
761.20	760.25	0.95	65.00	65.02	-0.06	0.2436	0.2435	0.0001	0.4065	0.4181	-0.0116
763.20	762.00	1.20	64.96	65.05	-0.09	0.2562	0.2562	0.0000	0.4196	0.4200	-0.0004
760.90	759.27	1.63	64.79	64.90	-0.11	0.2762	0.2762	0.0000	0.4183	0.4223	-0.0040
763.50	760.38	3.12	64.66	64.88	-0.22	0.3099	0.3100	-0.0001	0.4235	0.4265	-0.0030
759.90	758.71	1.19	64.66	64.74	-0.08	0.3854	0.3854	0.0000	0.4334	0.4347	-0.0013
762.00	758.99	3.01	64.53	64.75	-0.22	0.4026	0.4026	0.0000	0.4353	0.4366	-0.0013
761.70	758.78	2.92	64.52	64.73	-0.21	0.4503	0.4503	0.0000	0.4417	0.4421	-0.0004

TABLE A.6.2 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
763.10	763.33	-0.23	65.00	64.99	0.01	0.5636	0.5637	-0.0001	0.4635	0.4582	0.0053
763.20	762.99	0.21	65.40	65.42	-0.02	0.6848	0.6848	0.0000	0.4864	0.4894	-0.0030
763.90	765.61	-1.71	66.43	66.31	0.12	0.7699	0.7709	-0.0010	0.5269	0.5208	0.0061
765.60	766.05	-0.45	67.05	67.01	0.04	0.8130	0.8131	-0.0001	0.5454	0.5478	-0.0024
763.90	766.25	-2.35	68.26	68.09	0.17	0.8538	0.8565	-0.0027	0.5924	0.5874	0.0050
763.60	764.36	-0.76	69.55	69.49	0.06	0.8956	0.8962	-0.0006	0.6383	0.6408	-0.0025
R.M.S	Deviations										
		1.68			0.12			0.0022			0.0077

TABLE A.6.3

Mixture Cyclohexane - Ethanol at 1.01325 bar
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
754.80	752.35	2.45	76.53	76.67	-0.14	0.0142	0.0086	0.0056	0.0821	0.1048	-0.0227
759.80	757.36	2.44	67.60	67.75	-0.15	0.0622	0.0636	-0.0014	0.3352	0.3502	-0.0150
761.80	760.01	1.79	66.10	66.21	-0.11	0.0971	0.0971	0.0000	0.3770	0.3926	-0.0156
762.60	763.38	-0.78	65.93	65.87	0.06	0.1165	0.1149	0.0016	0.3883	0.4054	-0.0171
766.40	768.19	-1.79	65.77	65.63	0.14	0.1418	0.1400	0.0018	0.3885	0.4173	-0.0288
763.90	765.23	-1.33	65.45	65.34	0.11	0.1594	0.1583	0.0011	0.3944	0.4225	-0.0281
760.10	760.34	-0.24	65.00	64.97	0.03	0.1953	0.1949	0.0004	0.4046	0.4286	-0.0240
762.90	763.73	-0.83	65.10	65.03	0.07	0.2202	0.2199	0.0003	0.4071	0.4312	-0.0241
761.20	761.58	-0.38	64.90	64.92	0.04	0.2436	0.2435	0.0001	0.4065	0.4325	-0.0260
763.20	763.09	0.11	64.96	64.96	0.00	0.2562	0.2561	0.0001	0.4196	0.4331	-0.0135
760.90	760.07	0.83	64.79	64.84	-0.05	0.2762	0.2762	0.0000	0.4183	0.4223	-0.0040
763.50	760.73	2.77	64.66	64.85	-0.19	0.3099	0.3099	0.0000	0.4235	0.4345	-0.0110
759.90	758.59	1.31	64.66	64.75	-0.09	0.3854	0.3854	0.0000	0.4334	0.4365	-0.0031
762.00	758.80	3.20	64.53	64.75	-0.22	0.4026	0.4026	0.0000	0.4353	0.4373	-0.0020
761.70	758.56	3.14	64.52	64.74	-0.22	0.4503	0.4503	0.0000	0.4417	0.4421	0.0016

TABLE A.6.3 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
763.10	763.21	-0.11	65.00	64.99	0.01	0.5636	0.5637	-0.0001	0.4635	0.4532	0.0103
763.20	762.35	0.85	65.40	65.46	-0.06	0.6848	0.6848	0.0000	0.4864	0.4818	0.0046
763.90	763.96	-0.06	66.43	66.43	0.00	0.7699	0.7703	-0.0004	0.5269	0.5208	0.0061
765.60	763.77	1.83	67.05	67.18	-0.13	0.8130	0.8115	0.0015	0.5454	0.5497	-0.0043
763.90	763.56	0.34	68.26	68.29	-0.03	0.8538	0.8537	0.0001	0.5924	0.5911	0.0013
763.60	761.70	1.90	69.55	69.68	-0.13	0.8956	0.8920	0.0036	0.6383	0.6446	-0.0063
R.M.S	Deviations										
		1.69			0.12			0.0016			0.0162

TABLE A.6.4

Mixture Cyclohexane - Ethanol at 1.01325 bar
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
754.80	751.95	2.85	76.53	76.70	-0.17	0.0142	0.0100	0.0042	0.0821	0.1058	0.0237
759.80	753.00	6.80	67.60	68.06	-0.46	0.0622	0.0693	-0.0071	0.3352	0.3483	0.0131
761.80	755.67	6.13	66.10	66.52	-0.42	0.0971	0.0999	-0.0028	0.3770	0.3925	0.0155
762.60	759.74	2.86	65.93	66.12	-0.19	0.1165	0.1157	0.0008	0.3883	0.4078	0.0195
766.40	766.19	0.21	65.77	65.76	0.01	0.1418	0.1390	0.0028	0.3885	0.4249	0.0364
763.90	764.49	0.59	65.45	65.38	0.07	0.1594	0.1572	0.0022	0.3944	0.4342	0.0398
760.10	761.34	-1.24	65.00	64.88	0.12	0.1953	0.1943	0.0010	0.4046	0.4463	0.0417
762.90	762.90	-2.43	65.10	64.89	0.21	0.2202	0.2196	0.0006	0.4071	0.4510	0.0439
761.20	763.36	-2.16	64.96	64.77	0.19	0.2426	0.2434	-0.0008	0.4065	0.4530	0.0465
763.20	764.91	-1.71	64.96	64.81	0.15	0.2562	0.2562	0.0000	0.4196	0.4536	0.0340
760.90	761.77	0.87	64.79	64.70	0.09	0.2762	0.2763	-0.0001	0.4183	0.4534	0.0351
763.50	762.14	1.36	64.66	64.74	-0.08	0.3099	0.3100	-0.0001	0.4235	0.4522	0.0287
759.90	759.18	0.72	64.66	64.70	-0.04	0.3854	0.3854	0.0000	0.4334	0.4458	0.0124
762.00	759.31	2.69	64.53	64.72	-0.19	0.4026	0.4026	0.0000	0.4353	0.4442	0.0089
761.70	759.01	2.69	64.52	64.71	-0.19	0.4503	0.4503	0.0000	0.4417	0.4403	0.0014

TABLE A.6.4 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
763.10	764.57	-1.47	65.00	64.91	0.09	0.5636	0.5639	-0.0003	0.4635	0.4392	0.0243
763.20	764.08	0.88	65.40	65.35	0.05	0.6848	0.6855	-0.0007	0.4864	0.4627	0.0237
763.90	763.56	0.34	66.43	66.47	-0.04	0.7699	0.7703	-0.0004	0.5269	0.5080	0.0189
765.60	761.91	3.69	67.05	67.32	-0.27	0.8130	0.8098	0.0032	0.5454	0.5420	0.0034
763.90	760.20	3.70	68.26	68.53	-0.27	0.8538	0.8499	0.0039	0.5924	0.5891	0.0033
763.60	757.84	5.76	69.55	69.97	-0.42	0.8956	0.8862	0.0094	0.6383	0.6460	-0.0077
R.M.S	Deviations										
		3.06			0.22			0.0036			0.0268

TABLE A.6.5

Mixture Cyclohexane - Ethanol at 1.01325 bar
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
754.80	752.10	2.70	76.53	76.69	-0.16	0.0142	0.010	0.0042	0.0821	0.1054	-0.0233
759.80	754.54	5.26	67.60	67.95	-0.35	0.0622	0.0693	-0.0071	0.3352	0.3493	-0.0141
761.80	757.34	4.46	66.10	66.40	-0.30	0.0971	0.0999	-0.0028	0.3770	0.3933	-0.0163
762.60	761.30	1.30	65.93	66.01	-0.08	0.1165	0.1157	0.0008	0.3883	0.4082	-0.0199
766.40	767.37	-0.97	65.77	65.68	0.09	0.1418	0.1390	0.0028	0.3885	0.4241	-0.0356
763.90	765.26	-1.36	65.45	65.33	0.12	0.1594	0.1572	0.0022	0.3944	0.4321	-0.0377
760.10	761.41	-1.31	65.00	64.88	0.12	0.1953	0.1943	0.0010	0.4046	0.4418	-0.0372
762.90	765.08	-2.18	65.10	64.92	0.18	0.2202	0.2196	0.0006	0.4071	0.4454	-0.0383
761.20	762.93	-1.73	64.96	64.81	0.15	0.2436	0.2434	0.0002	0.4065	0.4466	-0.0401
763.20	764.41	-1.21	64.96	64.85	0.11	0.2562	0.2562	0.0000	0.4196	0.4469	-0.0273
760.90	761.22	-0.32	64.79	64.75	0.04	0.2762	0.2763	-0.0001	0.4183	0.4465	-0.0282
763.50	761.59	1.91	64.66	64.78	-0.12	0.3099	0.3100	-0.0001	0.4235	0.4451	-0.0216
759.90	758.76	1.14	64.66	64.74	-0.08	0.3854	0.3854	0.0000	0.4334	0.4399	-0.0065
762.00	758.93	3.07	64.53	64.75	-0.22	0.4026	0.4026	0.0000	0.4353	0.4389	-0.0036
761.70	758.65	3.05	64.52	64.74	-0.22	0.4503	0.4503	0.0000	0.4417	0.4365	0.0052

TABLE A.6.5 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
763.10	763.88	-0.78	65.00	64.96	0.04	0.5636	0.5639	-0.0003	0.4635	0.4398	0.0237
763.20	762.89	0.31	65.40	65.44	-0.04	0.6848	0.6855	-0.0007	0.4864	0.4666	0.0198
763.90	762.60	1.31	66.43	66.53	-0.10	0.7699	0.7703	-0.0004	0.5269	0.5119	0.0150
765.60	761.27	4.33	67.05	67.36	-0.31	0.8130	0.8098	0.0032	0.5454	0.5452	0.0002
763.90	759.98	3.92	68.26	68.55	-0.29	0.8538	0.8499	0.0039	0.5924	0.5911	0.0013
763.60	757.93	5.67	69.55	69.96	-0.41	0.8956	0.8862	0.0094	0.6383	0.6471	-0.0088
R.M.S	Deviations										
		2.78			0.2			0.0031			0.0238

TABLE A.6.6

Mixture Cyclohexane - Ethanol at 2 bar
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1500	1499.83	0.17	91.30	91.31	-0.01	0.0456	0.0478	-0.0022	0.2059	0.1997	0.0062
1500	1502.70	-2.70	89.24	89.08	0.16	0.0853	0.083	0.0023	0.2866	0.2818	0.0048
1500	1502.78	-2.78	88.96	88.80	0.16	0.0911	0.0886	0.0025	0.2955	0.2920	0.0035
1500	1497.80	2.20	84.27	84.39	-0.12	0.3147	0.3152	-0.0005	0.4680	0.4607	0.0073
1500	1495.38	4.62	83.74	83.99	-0.25	0.4510	0.4513	-0.0003	0.5001	0.4903	0.0098
1500	1495.21	4.79	83.74	84.00	-0.26	0.5577	0.5578	-0.0001	0.5205	0.5051	0.0154
1500	1496.37	3.63	84.01	84.20	-0.19	0.6694	0.6695	-0.0001	0.5386	0.5188	0.0198
1500	1497.55	2.45	84.34	84.47	-0.13	0.7384	0.7385	-0.0001	0.5476	0.5289	0.0187
1500	1497.65	2.35	84.60	84.72	-0.12	0.7816	0.7816	0.0000	0.5511	0.5373	0.0138
1500	1498.10	1.90	85.70	85.79	-0.09	0.8637	0.8642	-0.0005	0.5872	0.5652	0.0220
1500	1501.61	-1.61	86.33	86.23	0.10	0.8750	0.8790	-0.0040	0.6142	0.5736	0.0406
1500	1499.94	0.06	87.84	87.84	0.00	0.9168	0.9197	-0.0029	0.6302	0.6103	0.0199
1500	1499.34	0.66	89.42	89.45	-0.03	0.9382	0.9414	-0.0032	0.6644	0.6454	0.0190
1500	1501.70	-1.70	91.66	91.58	0.08	0.9557	0.9588	-0.0031	0.6850	0.6902	-0.0052
1500	1500.18	-0.18	96.99	96.98	0.01	0.9771	0.9833	-0.0062	0.8187	0.8126	0.0061
R.M.S Deviations											
		2.56			0.14			0.0026			0.017

TABLE A.6.7

Mixture Cyclohexane - Ethanol at 2 bar
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1500	1500.03	-0.03	91.30	91.30	0.00	0.0456	0.0474	-0.0018	0.2059	0.2002	0.0057
1500	1503.00	-3.00	89.24	89.06	0.18	0.0853	0.0823	0.0030	0.2866	0.2828	0.0038
1500	1503.11	-3.11	88.96	88.78	0.18	0.0911	0.0879	0.0032	0.2955	0.2931	0.0024
1500	1498.27	1.73	84.27	84.37	-0.10	0.3147	0.3151	-0.0004	0.4680	0.4623	0.0057
1500	1495.51	4.49	83.74	83.99	-0.25	0.4510	0.4512	-0.0002	0.5001	0.4900	0.0101
1500	1495.31	4.69	83.74	84.00	-0.26	0.5577	0.5578	-0.0001	0.5205	0.5040	0.0165
1500	1496.40	3.60	84.01	84.20	-0.19	0.6694	0.6695	-0.0001	0.5386	0.5180	0.0206
1500	1497.38	2.62	84.34	84.48	-0.14	0.7384	0.7385	-0.0001	0.5476	0.5289	0.5476
1500	1497.29	2.71	84.60	84.74	-0.14	0.7816	0.7815	0.0001	0.5511	0.5379	0.0132
1500	1497.51	2.49	85.70	85.83	-0.13	0.8637	0.8638	-0.0001	0.5872	0.5665	0.0207
1500	1501.06	-1.06	86.33	86.25	0.08	0.8750	0.8786	-0.0036	0.6142	0.5748	0.0394
1500	1499.98	0.02	87.84	87.83	0.01	0.9168	0.9196	-0.0028	0.6302	0.6108	0.0194
1500	1499.63	0.37	89.42	89.43	-0.01	0.9382	0.9419	-0.0037	0.6644	0.6457	0.0187
1500	1502.00	-2.00	91.66	91.56	0.10	0.9557	0.9596	-0.0039	0.6850	0.6905	-0.0055
1500	1500.29	-0.29	96.99	96.98	0.01	0.9771	0.9839	-0.0068	0.8187	0.8129	0.0058
R.M.S	Deviations										
		2.61			0.14			0.0028			0.0167

TABLE A.6.8

Mixture Cyclohexane - Ethanol at 2 bar
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1500	1498.39	1.61	91.30	91.39	-0.09	0.0456	0.0504	-0.0048	0.2059	0.1992	0.0067
1500	1500.71	-0.71	89.24	89.20	0.04	0.0853	0.0856	-0.0003	0.2866	0.2809	0.0057
1500	1500.74	0.74	88.96	88.92	0.04	0.0911	0.0911	0.0000	0.2955	0.2911	0.0044
1500	1498.11	1.89	84.27	84.37	-0.10	0.3147	0.3150	-0.0003	0.4680	0.4659	0.0021
1500	1495.82	4.18	83.74	83.97	-0.23	0.4510	0.4512	-0.0002	0.5001	0.4945	0.0056
1500	1495.75	4.25	83.74	83.97	-0.23	0.5577	0.5578	-0.0001	0.5205	0.5061	0.0144
1500	1497.76	2.24	84.01	84.12	-0.11	0.6694	0.6695	-0.0001	0.5386	0.5147	0.0239
1500	1499.93	0.07	84.34	84.33	0.01	0.7384	0.7388	-0.0004	0.5476	0.5213	0.0263
1500	1500.57	0.57	84.60	84.56	0.04	0.7816	0.7822	-0.0006	0.5511	0.5281	0.0230
1500	1499.65	0.35	85.70	85.71	-0.01	0.8637	0.8656	-0.0019	0.5872	0.5576	0.0296
1500	1502.03	-2.03	86.33	86.21	0.12	0.8750	0.8807	-0.0057	0.6142	0.5679	0.0463
1500	1498.02	1.98	87.84	87.94	-0.10	0.9168	0.9178	-0.0010	0.6302	0.6081	0.0221
1500	1497.12	2.88	89.42	89.56	-0.14	0.9382	0.9375	0.0007	0.6644	0.6438	0.0206
1500	1499.92	0.08	91.66	91.66	0.00	0.9557	0.9542	0.0015	0.6850	0.6885	-0.0035
1500	1499.51	0.49	96.99	97.01	-0.02	0.9771	0.9803	-0.0032	0.8187	0.8110	0.0077
R.M.S	Deviations										
		2.08			0.11			0.0022			0.202

TABLE A.6.9

Mixture Cyclohexane - Ethanol at 2 bar
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1500	1495.31	4.69	91.30	91.57	-0.27	0.0456	0.0555	-0.0099	0.2059	0.1980	0.0079
1500	1496.63	3.37	89.24	89.43	-0.19	0.0853	0.0908	-0.0055	0.2866	0.2802	0.0064
1500	1496.60	3.40	88.96	89.15	-0.19	0.0911	0.0961	-0.0050	0.2955	0.2905	0.0050
1500	1497.75	2.25	84.27	84.25	0.02	0.4510	0.4510	0.0000	0.5046	0.5046	-0.0045
1500	1497.71	2.29	83.74	83.87	-0.13	0.5577	0.5576	0.0001	0.5039	0.5039	-0.0166
1500	1496.60	3.40	83.74	83.86	-0.12	0.0911	0.0961	-0.0050	0.2955	0.2905	0.0050
1500	1501.62	-1.62	84.01	83.90	0.11	0.6694	0.6694	0.0000	0.5386	0.5004	0.0382
1500	1504.69	-4.69	84.34	84.05	0.29	0.7384	0.7393	-0.0009	0.5476	0.5036	0.0440
1500	1504.76	-4.76	84.60	84.31	0.29	0.7816	0.7837	-0.0021	0.5511	0.5113	0.0398
1500	1498.30	1.70	85.70	85.78	-0.08	0.8637	0.8659	-0.0022	0.5872	0.5512	0.0360
1500	1499.12	0.88	86.33	86.35	-0.02	0.8750	0.8802	-0.0052	0.6142	0.5641	0.0501
1500	1494.51	5.49	87.84	88.13	-0.29	0.9168	0.9128	0.0040	0.6302	0.6063	0.0239
1500	1494.06	5.94	89.42	89.72	-0.30	0.9382	0.9315	0.0067	0.6644	0.6423	0.0221
1500	1497.68	2.32	91.66	91.78	-0.12	0.9557	0.9485	0.0072	0.6850	0.6868	-0.0018
1500	1498.73	1.27	96.99	97.05	-0.06	0.9771	0.9773	-0.0002	0.8187	0.8096	0.0091
R.M.S	Deviations										
		3.45			0.19			0.0045			0.0266

TABLE A.6.10

Mixture Cyclohexane - Ethanol at 2 bar
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1500	1495.27	4.73	91.30	91.57	-0.27	0.0456	0.0556	-0.0100	0.2059	0.1978	0.0081
1500	1496.41	3.59	89.24	89.44	-0.20	0.0853	0.0911	-0.0058	0.2866	0.2796	0.007
1500	1496.34	3.66	88.96	89.17	-0.21	0.0911	0.0965	-0.0054	0.2955	0.2898	0.0057
1500	1499.24	0.76	84.27	84.32	-0.05	0.3147	0.3143	0.0004	0.4680	0.4815	-0.0135
1500	1496.83	3.17	83.74	83.92	-0.18	0.4510	0.4510	0.0000	0.5001	0.5052	-0.0051
1500	1496.82	3.18	83.74	83.91	-0.17	0.5577	0.5577	0.0000	0.5205	0.5067	0.0138
1500	1500.53	-0.53	84.01	83.96	0.05	0.6694	0.6694	0.0000	0.5386	0.5045	0.0341
1500	1503.70	-3.70	84.34	84.11	0.23	0.7384	0.7391	-0.0007	0.5476	0.5075	0.0401
1500	1504.14	-4.14	84.60	84.34	0.26	0.7816	0.7833	-0.0017	0.5511	0.5144	0.0367
1500	1499.02	0.98	85.70	85.74	-0.04	0.8637	0.8663	-0.0026	0.5872	0.5518	0.0354
1500	1500.05	-0.05	86.33	86.30	0.03	0.8750	0.8808	-0.0058	0.6142	0.5643	0.0499
1500	1495.44	4.56	87.84	88.07	-0.23	0.9168	0.9143	0.0025	0.6302	0.6064	0.0238
1500	1494.86	5.14	89.42	89.68	-0.26	0.9382	0.9331	0.0051	0.6644	0.6425	0.0219
1500	1498.29	1.71	91.66	91.75	-0.09	0.9557	0.9500	0.0057	0.6850	0.6871	-0.0021
1500	1498.97	1.03	96.99	97.04	-0.05	0.9771	0.9782	-0.0011	0.8187	0.8099	0.0088
R.M.S	Deviations										
		3.19			0.18			0.0043			0.0252

TABLE A.6.11

Mixture Cyclohexane - Ethanol at 4 bar
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
3003.8	2993.77	10.03	109.48	109.57	-0.09	0.1203	0.1222	-0.0019	0.2840	0.2852	0.0012
3005.6	2999.89	5.71	108.83	108.89	-0.06	0.1488	0.1481	0.0007	0.3118	0.3141	0.0023
3005.6	3002.48	3.12	107.43	107.46	-0.03	0.2291	0.2280	0.0011	0.3727	0.3753	0.0026
3005.6	3006.00	-0.40	107.06	107.08	-0.02	0.2762	0.2701	0.0061	0.3831	0.3969	0.0138
3009.0	2980.89	28.11	106.16	106.41	-0.25	0.3353	0.3376	-0.0023	0.4270	0.4232	0.0038
3009.0	2988.15	20.85	106.15	106.33	-0.18	0.3966	0.3980	-0.0014	0.4444	0.4402	0.0042
3000.0	2986.09	13.91	106.16	106.29	-0.13	0.4171	0.4170	0.0001	0.4440	0.4448	0.0008
3009.0	2985.71	23.29	106.05	106.27	-0.22	0.4527	0.4517	0.0010	0.4476	0.4524	0.0048
3007.1	2982.67	24.43	106.05	106.27	-0.22	0.5092	0.5092	0.0000	0.4648	0.4634	0.0014
3007.1	2991.56	15.54	106.45	106.58	-0.13	0.6112	0.6115	-0.0003	0.4851	0.4801	0.0050
3007.1	3007.55	-0.45	107.10	107.09	0.01	0.6896	0.6909	-0.0013	0.5000	0.4930	0.0070
3003.8	3020.08	-16.28	107.83	107.67	0.16	0.7498	0.7544	-0.0046	0.5184	0.5057	0.0127
3003.8	3018.61	-14.81	107.96	107.81	0.15	0.7646	0.7705	-0.0059	0.5257	0.5097	0.0160
3003.8	3020.21	-16.41	109.36	109.20	0.16	0.8388	0.8518	-0.0130	0.5552	0.5395	0.0157
R.M.S	Deviations										
		16.25			0.15			0.0044			0.0085

TABLE A.6.12

Mixture Cyclohexane - Ethanol at 4 bar
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
3003.8	2999.26	4.54	109.48	109.58	-0.10	0.1203	0.1210	-0.0007	0.2840	0.2863	0.0023
3005.6	3003.67	1.93	108.83	108.87	-0.04	0.1488	0.1467	0.0021	0.3118	0.3151	0.0033
3005.6	3005.33	0.27	107.43	107.44	-0.01	0.2291	0.2270	0.0021	0.3727	0.3766	0.0039
3005.6	3007.33	-1.73	107.06	107.04	0.02	0.2762	0.2694	0.0068	0.3831	0.3981	0.0150
3009.0	2992.48	16.92	106.16	106.50	-0.34	0.3353	0.3377	-0.0024	0.4270	0.4239	0.0031
3009.0	2996.79	12.21	106.15	106.40	-0.25	0.3966	0.3980	-0.0014	0.4444	0.4404	0.0040
3000.0	2992.08	7.92	106.16	106.33	-0.17	0.4171	0.4171	0.0000	0.4440	0.4449	0.0009
3009.0	2995.17	13.83	106.05	106.35	-0.30	0.4527	0.4518	0.0009	0.4476	0.4522	0.0046
3007.1	2992.52	14.58	106.05	106.35	-0.30	0.5092	0.5091	0.0001	0.4648	0.4630	0.0018
3007.1	2998.20	8.90	106.45	106.63	-0.18	0.6112	0.6115	-0.0003	0.4851	0.4798	0.0053
3007.1	3008.17	-1.07	107.10	107.07	0.03	0.6896	0.6910	-0.0014	0.5000	0.4933	0.0067
3003.8	3014.49	-10.69	107.83	107.59	0.24	0.7498	0.7551	-0.0053	0.5184	0.5067	0.0117
3003.8	3013.44	-9.64	107.96	107.74	0.22	0.7646	0.7712	-0.0066	0.5257	0.5109	0.0148
3003.8	3014.57	-10.77	109.36	109.13	0.23	0.8388	0.8531	-0.0143	0.5552	0.5410	0.0142
R.M.S	Deviations										
		9.71			0.20			0.0049			0.0082

TABLE A.6.13

Mixture Cyclohexane - Ethanol at 4 bar
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
3003.8	2996.34	7.46	109.48	109.64	-0.16	0.1203	0.1233	-0.0030	0.2840	0.2862	-0.0022
3005.6	3000.84	4.76	108.83	108.93	-0.10	0.1488	0.1486	0.0002	0.3118	0.3149	-0.0031
3005.6	3003.37	2.23	107.43	107.48	-0.05	0.2291	0.2275	0.0016	0.3727	0.3767	-0.0040
3005.6	3005.94	-0.34	107.06	107.08	-0.02	0.2762	0.2694	0.0068	0.3831	0.3983	-0.0152
3009.0	2991.18	17.82	106.16	106.52	-0.36	0.3353	0.3377	-0.0024	0.4270	0.4242	0.0028
3009.0	2995.54	13.46	106.15	106.42	-0.27	0.3966	0.3980	-0.0014	0.4444	0.4401	0.0043
3000.0	2990.91	9.09	106.16	106.34	-0.18	0.4171	0.4172	-0.0001	0.4440	0.4444	-0.0004
3009.0	2993.76	15.24	106.05	106.36	-0.31	0.4527	0.4521	0.0006	0.4476	0.4511	-0.0035
3007.1	2991.12	15.98	106.05	106.37	-0.32	0.5092	0.5095	-0.0003	0.4648	0.4604	0.0044
3007.1	2997.77	9.33	106.45	106.62	-0.17	0.6112	0.6121	-0.0009	0.4851	0.4737	0.0114
3007.1	3009.31	-2.21	107.10	107.04	0.06	0.6896	0.6924	-0.0028	0.5000	0.4844	0.0156
3003.8	3015.89	-12.09	107.S3	107.57	0.26	0.7498	0.7578	-0.0080	0.5184	0.4968	0.0216
3003.8	3014.27	-10.47	107.96	107.73	0.23	0.7646	0.7744	-0.0098	0.5257	0.5012	0.0245
3003.8	3006.42	-2.62	109.36	109.29	0.07	0.8388	0.8541	-0.0153	0.5552	0.536	0.0192
R.M.S	Deviations										
		10.37			0.21			0.0058			0.123

TABLE A.6.14

Mixture Cyclohexane - Ethanol at 4 bar
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
3003.8	2991.23	12.57	109.48	109.75	-0.27	0.1203	0.1255	-0.0052	0.2840	0.2879	-0.0039
3005.6	2995.85	9.75	108.83	109.04	-0.21	0.1488	0.1495	-0.0007	0.3118	0.3171	-0.0053
3005.6	3000.69	4.91	107.43	107.54	-0.11	0.2291	0.2253	0.0038	0.3727	0.3814	-0.0087
3005.6	3004.31	1.29	107.06	107.11	-0.05	0.2762	0.2668	0.0094	0.3831	0.4042	-0.0211
3009.0	2990.35	18.65	106.16	106.55	-0.39	0.3353	0.3361	-0.0008	0.4270	0.4297	-0.0027
3009.0	2994.04	14.96	106.15	106.46	-0.31	0.3966	0.3972	-0.0006	0.4444	0.4430	0.0014
3000.0	2989.08	10.92	106.16	106.39	-0.23	0.4171	0.4169	0.0002	0.4440	0.4461	-0.0021
3009.0	2991.81	17.19	106.05	106.41	-0.36	0.4527	0.4524	0.0003	0.4476	0.4504	-0.0028
3007.1	2989.46	17.64	106.05	106.40	-0.35	0.5092	0.5096	-0.0004	0.4648	0.4552	0.0096
3007.1	2998.54	8.56	106.45	106.60	-0.15	0.6112	0.6126	-0.0014	0.4851	0.4615	0.0236
3007.1	3010.97	-3.87	107.10	106.98	0.12	0.6896	0.6950	-0.0054	0.5000	0.4701	0.0299
3003.8	3012.75	-8.95	107.83	107.60	0.23	0.7498	0.7636	-0.0138	0.5184	0.4858	0.0326
3003.8	3008.82	-5.02	107.96	107.81	0.15	0.7646	0.7803	-0.0157	0.5257	0.4918	0.0339
3003.8	2993.42	10.38	109.36	109.54	-0.18	0.8388	0.8499	-0.0111	0.5552	0.5318	0.0234
R.M.S	Deviations										
		11.58			0.24			0.0072			0.0187

TABLE A.6.15

Mixture Cyclohexane - Ethanol at 4 bar
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
3003.8	2976.89	26.91	109.48	109.73	-0.25	0.1203	0.1269	-0.0066	0.2840	0.2862	-0.0022
3005.6	2982.79	22.81	108.83	109.05	-0.22	0.1488	0.1513	-0.0025	0.3118	0.3156	-0.0038
3005.6	2989.56	16.04	107.43	107.59	-0.16	0.2291	0.2267	0.0024	0.3727	0.3802	-0.0075
3005.6	2995.39	10.21	107.06	107.18	-0.12	0.2762	0.2675	0.0087	0.3831	0.4033	-0.0202
3009.0	2972.39	36.61	106.16	106.50	-0.34	0.3353	0.3358	-0.0005	0.4270	0.4303	-0.0033
3009.0	2979.17	29.83	106.15	106.42	-0.27	0.3966	0.3969	-0.0003	0.4444	0.4450	-0.0006
3000.0	2976.76	23.24	106.16	106.38	-0.22	0.4171	0.4165	0.0006	0.4440	0.4485	-0.0045
3009.0	2976.09	32.91	106.05	106.36	-0.31	0.4527	0.4520	0.0007	0.4476	0.4536	-0.0060
3007.1	2973.54	33.56	106.05	106.35	-0.30	0.5092	0.5095	-0.0003	0.4648	0.4594	0.0054
3007.1	2987.59	19.51	106.45	106.60	-0.15	0.6112	0.6123	-0.0011	0.4851	0.4664	0.0187
3007.1	3008.23	-1.13	107.10	107.06	0.04	0.6896	0.6935	-0.0039	0.5000	0.4743	0.0257
3003.8	3016.90	-13.1	107.83	107.67	0.16	0.7498	0.7606	-0.0108	0.5184	0.4881	0.0303
3003.8	3011.95	-8.15	107.96	107.84	0.12	0.7646	0.7776	-0.0130	0.5257	0.4936	0.0321
3003.8	2989.01	14.79	109.36	109.46	-0.10	0.8388	0.8514	-0.0126	0.5552	0.5335	0.0217
R.M.S	Deviations										
		23.03			0.22			0.0065			0.0169

TABLE A.6.16

Mixture Cyclohexane - Ethanol at 6 bar
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
4500.00	4478.79	21.21	124.00	124.25	-0.25	0.0978	0.1082	-0.0104	0.2402	0.2347	0.0055
4503.75	4481.94	21.81	121.80	122.07	-0.27	0.2138	0.2156	-0.0018	0.3307	0.3298	0.0009
4503.75	4483.05	20.70	121.34	121.62	-0.28	0.2686	0.2667	0.0019	0.3509	0.3568	-0.0059
4496.18	4477.37	18.81	121.03	121.26	-0.23	0.3388	0.3398	-0.0010	0.3876	0.3854	0.0022
4496.18	4475.89	20.29	120.94	121.18	-0.24	0.3883	0.3897	-0.0014	0.4054	0.4005	0.0049
4496.18	4483.94	12.24	121.21	121.32	-0.11	0.4793	0.4819	-0.0026	0.4350	0.4231	0.0119
4500.90	4492.44	8.46	123.53	123.60	-0.07	0.7615	0.7674	-0.0059	0.5118	0.4964	0.0154
4500.90	4490.89	10.01	123.90	123.99	-0.09	0.7798	0.7865	-0.0067	0.5208	0.5049	0.0159
4500.38	4499.50	0.88	125.62	125.61	0.01	0.8294	0.8383	-0.0089	0.5470	0.5350	0.0120
4500.38	4516.55	-16.17	128.63	128.44	0.19	0.8768	0.8887	-0.0119	0.5880	0.5829	0.0051
4485.00	4533.19	-48.19	152.43	151.97	0.46	1.0000	1.0009	-0.0009	1.0000	1.0091	-0.0091
R.M.S	Deviations										
		21.38			0.23			0.0062			0.0094

TABLE A.17

Mixture Cyclohexane - Ethanol at 8 bar
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
4500.00	4477.98	22.02	124.00	124.28	-0.28	0.0978	0.1081	-0.0103	0.2402	0.2350	0.0052
4503.75	4480.63	23.12	121.80	122.10	-0.30	0.2138	0.2152	-0.0014	0.3307	0.3306	0.0001
4503.75	4481.48	22.27	121.34	121.65	-0.31	0.2686	0.2663	0.0023	0.3509	0.3577	-0.0068
4496.18	4475.69	20.49	121.03	121.29	-0.26	0.3388	0.3395	-0.0007	0.3876	0.3862	0.0014
4496.18	4474.14	22.04	120.94	121.21	-0.27	0.3883	0.3895	-0.0012	0.4054	0.4011	0.0043
4496.18	4482.15	14.03	121.21	121.35	-0.14	0.4793	0.4818	-0.0025	0.4350	0.4233	0.0117
4500.90	4491.83	9.07	123.53	123.59	-0.06	0.7615	0.7673	-0.0058	0.5118	0.4966	0.0152
4500.90	4490.53	10.37	123.90	123.98	-0.08	0.7798	0.7865	-0.0067	0.5208	0.5050	0.0158
4500.38	4500.26	0.12	125.62	125.59	0.03	0.8294	0.8384	-0.0090	0.5470	0.5350	0.0120
4500.38	4518.33	-17.95	128.63	128.41	0.22	0.8768	0.8894	-0.0126	0.5880	0.5828	0.0052
4485.00	4533.06	-48.06	152.43	151.98	0.45	1.0000	1.0008	-0.0008	1.0000	1.0091	-0.0091
R.M.S	Deviations										
		19.04			0.2			0.0051			0.0089

TABLE A.6.18

Mixture Cyclohexane - Ethanol at 6 bar
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
4500.00	4474.35	25.65	124.00	124.31	-0.31	0.0978	0.1090	-0.0112	0.2402	0.2348	0.0054
4503.75	4480.02	23.73	121.80	122.10	-0.30	0.2138	0.2150	-0.0012	0.3307	0.3311	0.0004
4503.75	4482.05	21.70	121.34	121.64	-0.30	0.2686	0.2660	0.0026	0.3509	0.3584	-0.0075
4496.18	4476.72	19.46	121.03	121.27	-0.24	0.3388	0.3393	-0.0005	0.3876	0.3867	0.0009
4496.18	4475.16	21.02	120.94	121.19	-0.25	0.3883	0.3895	-0.0012	0.4054	0.4011	0.0043
4496.18	4483.35	12.83	121.21	121.33	-0.12	0.4793	0.4818	-0.0025	0.4350	0.4219	0.0131
4500.90	4490.70	10.20	123.53	123.61	-0.08	0.7615	0.7694	-0.0079	0.5118	0.4922	0.0196
4500.90	4487.45	13.45	123.90	124.02	-0.12	0.7798	0.7885	-0.0087	0.5208	0.5012	0.0196
4500.38	4490.47	9.91	125.62	125.71	-0.09	0.8294	0.8388	-0.0094	0.5470	0.5331	0.0139
4500.38	4504.74	-4.36	128.63	128.57	0.06	0.8768	0.8863	-0.0095	0.5880	0.5821	0.0059
4485.00	4533.49	-48.49	152.43	151.97	0.46	1.0 000	1.0009	-0.0009	1.0000	1.0090	-0.0090
R.M.S	Deviations										
		22.22			0.24			0.0065			0.0111

TABLE A.6.19

Mixture Cyclohexane - Ethanol at 6 bar
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
4500.00	4475.51	24.49	124.00	124.31	-0.31	0.0978	0.1100	-0.0122	0.2402	0.2343	0.0059
4503.75	4487.54	16.21	121.80	122.02	-0.22	0.2138	0.2138	0.0000	0.3307	0.3324	-0.0017
4503.75	4492.06	11.69	121.34	121.52	-0.18	0.2686	0.2643	0.0043	0.3509	0.3609	-0.0100
4496.18	4489.35	6.83	121.03	121.13	-0.10	0.3388	0.3382	0.0006	0.3876	0.3899	-0.0023
4496.18	4488.47	7.71	120.94	121.04	-0.10	0.3883	0.3887	-0.0004	0.4054	0.4040	0.0014
4496.18	4497.16	-0.98	121.21	121.17	0.04	0.4793	0.4815	-0.0022	0.4350	0.4233	0.0117
4500.90	4491.89	9.01	123.53	123.60	-0.07	0.7615	0.7684	-0.0069	0.5118	0.4965	0.0153
4500.90	4486.39	14.51	123.90	124.04	-0.14	0.7798	0.7865	-0.0067	0.5208	0.5062	0.0146
4500.38	4485.82	14.56	125.62	125.78	-0.16	0.8294	0.8333	-0.0039	0.5470	0.5388	0.0082
4500.38	4501.14	-0.76	128.63	128.62	0.01	0.8768	0.8789	-0.0021	0.5880	0.5867	0.0013
4485.00	4533.76	-48.76	152.43	151.97	0.46	1.0000	1.0010	-0.0010	1.0000	1.0090	-0.0090
R.M.S	Deviations										
		19.04			0.2			0.0051			0.0089

TABLE A.6.20

Mixture Cyclohexane - Ethanol at 6 bar
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
4500	4465.69	34.31	124.00	124.43	-0.43	0.0973	0.1110	-0.0132	0.2402	0.2347	0.0055
4503.75	4472.39	31.36	121.80	122.21	-0.41	0.2138	0.2141	-0.0003	0.3307	0.3334	-0.0027
4503.75	4475.57	28.18	121.34	121.74	-0.40	0.2686	0.2645	0.0041	0.3909	0.3619	-0.0110
4496.18	4471.19	24.99	121.03	121.36	-0.33	0.3388	0.3333	0.0005	0.3876	0.3902	-0.0026
4496.18	4469.58	26.6	120.94	121.28	-0.34	0.3883	0.3888	-0.0005	0.4054	0.4034	0.0020
4496.18	4478.22	17.96	121.21	121.40	-0.19	0.4793	0.4814	-0.0021	0.4350	0.4204	0.0146
4300.90	4483.56	17.34	123.33	123.67	-0.14	0.7613	0.7723	-0.0108	0.5118	0.4870	0.0248
4500.90	4478.07	22.83	123.90	124.11	-0.21	0.7798	0.7910	-0.0112	0.5208	0.4970	0.0238
4500.38	4476.52	23.86	125.62	125.87	-0.25	0.3294	0.8387	-0.0093	0.5470	0.5311	0.0159
4500.38	4491.00	9.32	128.63	128.72	-0.09	0.8768	0.8837	-0.0069	0.5880	0.5810	0.0070
4485.00	4532.62	-48.62	152.43	151.97	0.46	1.0000	1.0010	-0.0010	1.0000	1.0090	-0.0090
R.M.S	Deviations										
		27.72			0.32			0.0072			0.0133

TABLE A.6.21

Mixture Cyclohexane - Ethanol at 8 bar
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
6017.7	6008.66	9.04	137.83	137.93	-0.10	0.0393	0.0406	-0.0013	0.1044	0.1095	0.0051
6017.7	6015.05	2.65	137.34	137.37	-0.03	0.0499	0.0510	-0.0011	0.1327	0.1308	0.0019
6017.2	6014.66	2.54	136.72	136.75	-0.03	0.0614	0.0629	-0.0015	0.1580	0.1529	0.0051
6015.5	6009.36	6.14	136.28	136.35	-0.07	0.0693	0.0708	-0.0015	0.1674	0.1661	0.0013
6017.2	6008.40	8.80	133.94	134.04	-0.10	0.1440	0.1438	0.0002	0.2451	0.2554	-0.0103
6014.9	6008.94	5.96	133.40	133.46	-0.06	0.1741	0.1763	-0.0022	0.3043	0.2819	0.0224
6014.2	6024.08	-9.88	132.82	132.71	0.11	0.2616	0.2615	0.0001	0.3344	0.3310	0.0034
6014.2	6009.46	4.74	132.34	132.39	-0.05	0.3195	0.3198	-0.0003	0.3608	0.3546	0.0062
6018.5	6020.03	-1.53	132.44	132.42	0.02	0.4021	0.4024	-0.0003	0.3906	0.3803	0.0103
6012.4	6005.20	7.20	132.43	132.50	-0.07	0.4789	0.4793	-0.0004	0.4185	0.4005	0.0180
6012.4	6009.39	3.01	132.84	132.87	-0.03	0.5510	0.5513	-0.0003	0.4331	0.4183	0.0148
6012.4	6023.90	-11.5	133.25	133.12	0.13	0.5745	0.5754	-0.0009	0.4443	0.4244	0.0199
6011.2	6011.66	-0.46	133.59	133.58	0.01	0.6370	0.6376	-0.0006	0.4583	0.4416	0.0167
6011.2	6011.86	-0.66	133.99	133.98	0.01	0.6703	0.6710	-0.0007	0.4686	0.4521	0.0165
6020.8	6019.65	1.15	138.68	138.69	-0.01	0.8380	0.8394	-0.0014	0.5580	0.5423	0.0157
6017.7	6028.71	-11.01	153.00	152.90	0.10	0.9501	0.9613	-0.0112	0.7810	0.7764	0.0046
R.M.S	Deviations										
		6.54			0.07			0.003			0.0127

TABLE A.6.22

Mixture Cyclohexane - Ethanol at 8 bar
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
6017.7	6008.19	9.51	137.83	137.94	-0.11	0.0393	0.0408	-0.0015	0.1044	0.1096	0.0052
6017.7	6014.51	3.19	137.34	137.38	-0.04	0.0499	0.0511	-0.0012	0.1327	0.1310	0.0017
6017.2	6014.08	3.12	136.72	136.76	-0.04	0.0614	0.0630	-0.0016	0.1580	0.1532	0.0048
6015.5	6008.76	6.74	136.28	136.36	-0.08	0.0693	0.0709	-0.0016	0.1674	0.1665	0.0009
6017.2	6007.97	9.23	133.94	134.05	-0.11	0.144	0.1438	0.0002	0.2451	0.2565	-0.0114
6014.9	6008.69	6.21	133.40	133.47	-0.07	0.1741	0.1762	-0.0021	0.3043	0.2832	0.0211
6014.2	6023.32	-9.12	132.82	132.71	0.11	0.2616	0.2615	0.0001	0.3344	0.3322	0.0022
6014.2	6008.51	5.69	132.34	132.40	-0.06	0.3195	0.3198	-0.0003	0.3608	0.3553	0.0055
6018.5	6019.02	-0.52	132.44	132.43	0.01	0.4021	0.4024	-0.0003	0.3906	0.3802	0.0104
6012.4	6004.62	7.78	132.43	132.51	-0.08	0.4789	0.4793	-0.0004	0.4185	0.3996	0.0189
6012.4	6009.41	2.99	132.84	132.87	-0.03	0.5510	0.5514	-0.0004	0.4331	0.4170	0.0161
6012.4	6024.04	-11.64	133.25	133.11	0.14	0.5745	0.5755	-0.0010	0.4443	0.4230	0.0213
6011.2	6012.30	-1.10	133.59	133.57	0.02	0.6370	0.6377	-0.0007	0.4583	0.4401	0.0182
6011.2	6012.62	-1.42	133.99	133.97	0.02	0.6703	0.6711	-0.0008	0.4686	0.4506	0.0180
6020.8	6020.11	0.69	138.68	138.68	0.00	0.8380	0.8396	-0.0016	0.5580	0.5416	0.0164
6017.7	6028.96	-11.26	153.00	152.90	0.10	0.9501	0.9616	-0.0115	0.7810	0.7765	0.0045
R.M.S	Deviations										
		6.76			0.08			0.0031			0.0132

TABLE A.6.23

Mixture Cyclohexane - Ethanol at 8 bar
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
6017.7	6004.80	12.90	137.83	137.98	-0.15	0.0393	0.0417	-0.0024	0.1044	0.1093	-0.0049
6017.7	6010.75	6.95	137.34	137.42	-0.08	0.0499	0.0521	-0.0022	0.1327	0.1305	0.0022
6017.2	600.99	7.21	136.72	136.80	-0.08	0.0614	0.0640	-0.0026	0.1580	0.1527	0.0053
6015.5	6004.56	10.94	136.28	136.40	-0.12	0.0693	0.0718	-0.0025	0.1674	0.1660	0.0014
6017.2	6005.40	11.80	133.94	134.08	-0.14	0.1440	0.1440	0.0000	0.2451	0.2564	0.0113
6014.9	6007.24	7.66	133.40	133.48	-0.08	0.1741	0.1763	-0.0022	0.3043	0.2836	0.0207
6014.2	6024.29	-10.09	132.82	132.11	0.11	0.2616	0.2614	0.0002	0.3344	0.3332	0.0012
6014.2	6009.97	4.23	132.34	132.39	-0.05	0.3195	0.3197	-0.0002	0.3608	0.3564	0.0044
6018.5	6020.79	-2.29	132.44	132.41	0.03	0.4021	0.4024	-0.0003	0.3906	0.3808	0.0098
6012.4	6006.66	5.74	132.43	132.49	-0.06	0.4789	0.4793	-0.0004	0.4185	0.3994	0.0191
6012.4	6011.94	0.46	132.84	132.84	0.00	0.5510	0.5514	-0.0004	0.4331	0.4159	0.0172
6012.4	6026.89	-14.49	133.25	133.08	0.17	0.5745	0.5756	-0.0011	0.4443	0.4216	0.0227
6011.2	6015.40	-4.20	133.59	133.54	0.05	0.6370	0.6379	-0.0009	0.4583	0.4380	0.0203
6011.2	6015.63	-4.43	133.99	133.94	0.05	0.6703	0.6713	-0.0010	0.4686	0.4483	0.0203
6020.3	6015.41	5.39	138.68	138.73	-0.05	0.8380	0.8387	-0.0007	0.5580	0.5404	0.0176
6017.7	6027.03	-9.33	153.00	152.92	0.08	0.9501	0.9600	-0.0099	0.7810	0.7756	0.0054
R.M.S	Deviations										
		8.31			0.09			0.0029			0.0139

TABLE

TABLE A.6.24

Mixture Cyclohexane - Ethanol at 8 bar
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
6017.7	6001.93	15.77	137.83	138.01	-0.18	0.0393	0.0425	-0.0032	0.1044	0.1091	0.0047
6017.7	6007.42	10.28	137.34	137.46	-0.12	0.0499	0.0529	-0.0030	0.1327	0.1305	0.0022
6017.2	6006.25	10.95	136.72	136.85	-0.13	0.0614	0.0649	-0.0035	0.1580	0.1527	0.0053
6015.5	6000.60	14.90	136.28	136.45	-0.17	0.0693	0.0726	-0.0033	0.1674	0.1661	0.0013
6017.2	6001.85	15.35	133.94	134.12	-0.18	0.1440	0.1442	-0.0002	0.2451	0.2580	0.0129
6014.9	6004.79	10.11	133.40	133.51	-0.11	0.1741	0.1764	-0.0023	0.3043	0.2861	0.0182
6014.2	6022.73	-8.53	132.82	132.72	0.10	0.2616	0.2613	0.0003	0.3344	0.3365	0.0021
6014.2	6008.42	5.78	132.34	132.41	-0.07	0.3195	0.3196	-0.0001	0.3608	0.3588	0.0020
6018.5	6019.29	-0.79	132.44	132.43	0.01	0.4021	0.4023	-0.0002	0.3906	0.3807	0.0099
6012.4	6006.67	5.73	132.43	132.49	-0.06	0.4789	0.4793	-0.0004	0.4185	0.3963	0.0222
6012.4	6014.53	-2.13	132.84	132.81	0.03	0.5510	0.5516	-0.0006	0.4331	0.4101	0.0230
6012.4	6030.26	-17.86	133.25	133.04	0.21	0.5745	0.5757	-0.0012	0.4443	0.4151	0.0292
6011.2	6020.58	-9.38	133.59	133.48	0.11	0.6370	0.6383	-0.0013	0.4583	0.4303	0.0280
6011.2	6020.83	-9.63	133.99	133.89	0.12	0.6703	0.6720	-0.0017	0.4686	0.4404	0.0282
6020.8	6008.94	11.86	138.68	138.80	-0.12	0.8380	0.8375	0.0005	0.5580	0.5370	0.0210
6017.7	6024.95	-7.25	153.00	152.93	0.07	0.9501	0.9587	-0.0086	0.7810	0.7746	0.0064
R.M.S Deviations											
		10.82			0.12			0.0028			0.0170

TABLE A.6.25

Mixture Cyclohexane - Ethanol at 8 bar
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
6017.7	6002.16	15.54	137.83	138.01	-0.18	0.0393	0.0424	-0.0031	0.1044	0.1092	-0.0048
6017.7	6007.69	10.01	137.34	137.45	-0.11	0.0499	0.0528	-0.0029	0.1327	0.1305	0.0022
6017.2	6006.57	10.63	136.72	136.84	-0.12	0.0614	0.0648	-0.0034	0.1580	0.1527	0.0053
6015.5	6000.95	14.55	136.28	136.45	-0.17	0.0693	0.0725	-0.0032	0.1674	0.1661	0.0013
6017.2	6002.21	14.99	133.94	134.12	-0.18	0.1440	0.1442	-0.0002	0.2451	0.2580	0.0129
6014.9	6005.05	9.85	133.40	133.51	-0.11	0.1741	0.1764	-0.0023	0.3043	0.2860	0.0183
6014.2	6022.70	-8.50	132.82	132.72	0.10	0.2616	0.2613	0.0003	0.3344	0.3362	0.0018
6014.2	6008.23	5.97	132.34	132.41	-0.07	0.3195	0.3196	-0.0001	0.3608	0.3584	0.0024
6018.5	6018.98	-0.48	132.44	132.43	0.01	0.4021	0.4024	-0.0003	0.3906	0.3802	0.0104
6012.4	6006.28	6.12	132.43	132.49	-0.06	0.4789	0.4793	-0.0004	0.4185	0.3958	0.0227
6012.4	6013.99	-1.59	132.84	132.82	0.02	0.5510	0.5516	-0.0006	0.4331	0.4097	0.0234
6012.4	6029.65	-17.25	133.25	133.05	0.20	0.5745	0.5757	-0.0012	0.4443	0.4147	0.0296
6011.2	6019.70	-8.50	133.59	133.49	0.10	0.6370	0.6383	-0.0013	0.4583	0.4300	0.0283
6011.2	6019.77	-8.57	133.99	133.89	0.10	0.6703	0.6719	-0.0016	0.4686	0.4402	0.0284
6020.8	6007.44	13.36	138.68	138.82	-0.14	0.8380	0.8372	0.0008	0.5580	0.5370	0.0210
6017.7	6024.67	-6.97	153.00	152.93	0.07	0.9501	0.9585	-0.0084	0.7810	0.7745	0.0065
R.M.S	Deviations										
		10.63			0.12			0.0028			0.0171

TABLE A.6.26

Mixture Cyclohexane - Ethanol at 11 bar
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
8267.3	8251.12	16.18	151.10	151.45	-0.35	0.0155	0.0226	-0.0071	0.0537	0.0543	-0.0006
8267.4	8243.63	23.77	150.50	151.01	-0.51	0.0243	0.0294	-0.0051	0.0657	0.0689	-0.0032
8274.3	8262.76	11.54	149.95	150.20	-0.25	0.0408	0.0465	-0.0057	0.1026	0.1021	0.0005
8263.1	6240.37	22.73	148.29	148.77	-0.48	0.0707	0.0777	-0.0070	0.1524	0.1524	0.0000
8252.3	8241.56	10.74	147.18	147.41	-0.23	0.1238	0.1235	0.0003	0.2068	0.2092	-0.0024
8254.5	8253.13	1.37	145.56	145.58	-0.02	0.2789	0.2803	-0.0014	0.3236	0.3208	0.0028
8254.5	8252.61	1.89	145.46	145.49	-0.03	0.3085	0.3103	-0.0018	0.3387	0.3345	0.0042
8254.7	8246.45	8.25	145.43	145.60	-0.17	0.4444	0.4442	0.0002	0.3825	0.3822	0.0003
8255.0	8249.85	5.15	145.88	145.97	-0.09	0.5120	0.5142	-0.0022	0.4112	0.4029	0.0084
8253.5	8263.44	-9.94	148.68	148.47	0.21	0.7062	0.7128	-0.0066	0.4796	0.4687	0.0109
8261.4	8259.78	1.62	148.96	148.98	-0.02	0.7306	0.7355	-0.0049	0.4896	0.4790	0.0106
8261 .4	8269.05	-7.65	151.31	151.15	0.16	0.7895	0.8001	-0.0106	0.5278	0.5165	0.0113
R.M.S	Deviations										
		12.42			0.26			0.0054			0.0063

TABLE A.6.27

Mixture Cyclohexane - Ethanol at 11 bar
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
8267.3	8250.93	16.37	151.10	151.45	-0.35	0.0155	0.0226	-0.0071	0.0537	0.0543	0.0006
8267.4	8243.39	24.01	150.50	151.02	-0.52	0.0243	0.0295	-0.0052	0.0657	0.0689	0.0032
8274.3	8262.33	11.96	149.95	150.21	-0.26	0.0408	0.0467	-0.0059	0.1026	0.1021	0.0005
8263.1	8239.71	23.39	148.29	148.80	-0.51	0.0707	0.0778	-0.0071	0.1524	0.1526	-0.0002
8252.3	8240.33	11.97	147.18	147.44	-0.26	0.1238	0.1235	0.0003	0.2068	0.2094	-0.0026
8254.5	8251.51	2.99	145.56	145.62	-0.06	0.2789	0.2801	-0.0012	0.3236	0.3214	0.0022
8254.5	8250.98	3.52	145.46	145.53	-0.07	0.3085	0.3101	-0.0016	0.3387	0.335	0.0037
8254.7	8245.18	9.52	145.43	145.63	-0.20	0.4444	0.4442	0.0002	0.3825	0.3823	0.0002
8255.0	8248.89	6.11	145.88	145.99	-0.11	0.5120	0.5142	-0.0022	0.4113	0.4027	0.0086
8253.5	8263.88	-10.38	148.68	148.44	0.24	0.7062	0.7131	-0.0069	0.4796	0.4683	0.0113
8261.4	8260.70	0.70	148.96	148.95	0.01	0.7306	0.7359	-0.0053	0.4896	0.4787	0.0109
8261.4	8270.52	-9.12	151.31	151.11	0.20	0.7895	0.8010	-0.0115	0.5278	0.5162	0.0116
R.M.S	Deviations										
		12.97			0.28			0.0056			0.0064

TABLE A.6.28

Mixture Cyclohexane - Ethanol at 11 bar
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
8267.3	824,979	17.50	151.10	151.47	-0.37	0.0155	0.0231	-0.0076	0.0537	0.0542	-0.0005
8267.4	8242.02	25.38	150.50	151.04	-0.54	0.0243	0.0301	-0.0058	0.0657	0.0687	-0.0030
8274.3	8260.64	13.66	149.95	150.24	-0.29	0.0408	0.0474	-0.0066	0.1026	0.1020	0.0006
8263.1	8237.67	25.43	148.29	148.83	-0.54	0.0707	0.0786	-0.0079	0.1524	0.1524	0.0000
8252.3	8238.98	13.32	147.18	147.47	-0.29	0.1238	0.1239	-0.0001	0.2068	0.2093	-0.0025
8254.5	8252.48	2.02	145.56	145.60	-0.04	0.2789	0.2798	-0.0009	0.3236	0.3218	0.0018
8254.5	8252.10	2.40	145.46	145.50	-0.04	0.3085	0.3099	-0.0014	0.3287	0.3354	0.0033
8254.7	8246.20	8.50	145.43	145.60	-0.17	0.4444	0.4444	0.0000	0.3825	0.3818	0.0007
8255.0	8250.09	4.91	145.88	145.96	-0.08	0.5120	0.5145	-0.0025	0.4113	0.4014	0.0099
8253.5	8263.22	-9.72	148.68	148.47	0.21	0.7062	0.7140	-0.0078	0.4796	0.4660	0.0136
8261.4	8258.87	2.53	148.96	149.00	-0.04	0.7306	0.7367	-0.0061	0.4896	0.4765	0.0131
8261.4	8265.42	-4.02	151.31	151.22	0.09	0.7895	0.8005	-0.0110	0.5278	0.5149	0.0129
		13.49			0.29			0.006			0.0074

TABLE A.6.29

Mixture Cyclohexane - Ethanol at 11 bar
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
8267.3	8248.93	18.37	151.10	151.49	-0.39	0.0155	0.0235	-0.0080	0.0537	0.0541	-0.0004
8267.4	8240.92	26.48	150.50	151.07	-0.57	0.0243	0.0305	-0.0062	0.0657	0.0687	-0.0030
8274.3	8259.09	15.21	149.95	150.27	-0.32	0.0408	0.0480	-0.0072	0.1026	0.1020	0.0006
8263.1	8235.58	27.52	148.29	148.88	-0.59	0.0707	0.0791	-0.0084	0.1524	0.1525	-0.0001
8252.3	8236.26	16.04	147.18	147.53	-0.35	0.1238	0.1241	-0.0003	0.2068	0.2097	-0.0029
8254.5	8250.45	4.05	145.56	145.65	-0.09	0.2789	0.2792	-0.0003	0.3236	0.3232	0.0004
8254.5	8250.12	4.38	145.46	145.55	-0.09	0.3085	0.3095	-0.0010	0.3387	0.3365	0.0022
8254.7	8244.70	10.00	145.43	145.64	-0.21	0.4444	0.4448	-0.0004	0.3825	0.3799	0.0026
8255.0	8249.65	5.35	145.88	145.97	-0.09	0.5120	0.5152	-0.0032	0.4113	0.3975	0.0138
8253.5	8262.13	-8.63	148.68	148.47	0.21	0.7062	0.7168	-0.0106	0.4796	0.4608	0.0188
8261.4	8257.17	4.23	148.96	149.02	-0.06	0.7306	0.7393	-0.0087	0.4896	0.4718	0.0178
8261.4	8260.05	1.35	151.31	151.31	0.00	0.7895	0.8019	-0.0124	0.5278	0.5119	0.0159
R.M.S	Deviations										
		14.56			0.31			0.0069			0.0098

TABLE A.6.30

Mixture Cyclohexane - Ethanol at 11 bar
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
8267.3	8250.59	16.71	151.10	151.46	-0.36	0.0155	0.0230	-0.0075	0.0537	0.0542	0.0005
8267.4	8243.14	24.26	150.50	151.02	-0.52	0.0243	0.0299	-0.0056	0.0657	0.0687	0.0030
8274.3	8262.48	11.82	149.95	150.21	-0.26	0.0408	0.0472	-0.0064	0.1026	0.1018	0.0008
8263.1	8241.23	21.87	148.29	148.77	-0.48	0.0707	0.0784	-0.0077	0.1524	0.1521	0.0003
8252.3	8244.12	8.18	147.18	147.36	-0.18	0.1238	0.1236	0.0002	0.2068	0.2087	0.0019
8254.5	8261.86	-7.36	145.56	145.40	0.16	0.2789	0.2795	-0.0006	0.3236	0.3218	0.0018
8254.5	8261.84	-7.34	145.46	145.30	0.16	0.3085	0.3097	-0.0012	0.3387	0.3355	0.0032
8254.7	8255.84	-1.14	145.43	145.41	0.02	0.4444	0.4444	0.0000	0.3825	0.3825	0.0000
8255.0	8258.58	-3.58	145.88	145.79	0.09	0.5120	0.5147	-0.0027	0.4113	0.4029	0.0084
8253.5	8259.23	-5.73	148.68	148.55	0.13	0.7062	0.7110	-0.0048	0.4796	0.4725	0.0071
8261.4	8233.94	7.46	148.96	149.10	-0.14	0.7306	0.7322	-0.0016	0.4896	0.4834	0.0062
8261.4	8257.42	3.98	151.31	151.38	-0.07	0.7895	0.7925	-0.003	0.5278	0.5222	0.0056
R.M.S	Deviations										
		12.18			0.26			0.0044			0.0043

TABLE A 6.31

Mixture Cyclohexane - Ethanol at 90.9 °C
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1691.60	1689.51	2.09	90.93	91.23	-0.30	0.1199	0.1234	-0.0035	0.3285	0.3290	-0.0005
1723.80	1720.50	3.30	90.89	91.38	-0.49	0.1331	0.1351	-0.0020	0.3387	0.3423	-0.0036
1728.90	1726.86	2.04	90.92	91.23	-0.31	0.1428	0.1439	-0.0011	0.3498	0.3520	-0.0022
1730.40	1733.18	-2.78	90.98	90.58	0.40	0.1779	0.1736	0.0043	0.3795	0.3804	-0.0009
1779.20	1778.13	1.07	90.90	91.08	-0.18	0.1883	0.1870	0.0013	0.3863	0.3897	-0.0034
1828.90	1827.77	1.13	91.00	91.18	-0.18	0.2329	0.2324	0.0005	0.4154	0.4179	-0.0025
1838.80	1837.59	1.21	90.94	91.15	-0.21	0.2505	0.2488	0.0017	0.4211	0.4263	-0.0052
1838.60	1838.19	0.41	90.90	91.01	-0.11	0.2673	0.2633	0.0040	0.4239	0.4334	-0.0095
1851.60	1850.66	0.94	90.88	91.03	-0.15	0.2844	0.2842	0.0002	0.4404	0.4421	-0.0017
1857.00	1856.10	0.90	90.91	91.07	-0.16	0.2919	0.2903	0.0016	0.4392	0.4444	-0.0052
1856.70	1855.84	0.86	90.84	91.04	-0.20	0.2993	0.2950	0.0043	0.4335	0.4462	-0.0127
1859.60	1858.67	0.93	90.85	91.02	-0.17	0.3055	0.3038	0.0017	0.4437	0.4494	-0.0057
1864.70	1864.00	0.70	90.90	91.03	-0.13	0.3176	0.3163	0.0013	0.4491	0.4537	-0.0046
1882.90	1879.67	3.23	90.62	91.13	-0.51	0.3470	0.3469	0.0001	0.4596	0.4629	-0.0033
1876.80	1876.10	0.70	90.85	90.97	-0.12	0.3775	0.3772	0.0003	0.4696	0.4713	-0.0017

TABLE A.6.31 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1890.96	1889.79	1.17	90.95	91.16	-0.21	0.3903	0.3893	0.0010	0.4686	0.4738	-0.0052
1894.10	1893.17	0.93	90.94	91.09	-0.15	0.5049	0.5046	0.0003	0.4939	0.4958	-0.0019
1886.70	1885.62	1.08	90.95	91.11	-0.16	0.6356	0.6355	0.0001	0.5139	0.5134	0.0005
1865.70	1864.98	0.72	90.85	90.93	-0.08	0.7007	0.7013	-0.0006	0.5276	0.5220	0.0056
1863.10	1862.67	0.43	90.86	90.90	-0.04	0.7009	0.7016	-0.0007	0.5284	0.5221	0.0063
1860.90	1860.50	0.40	90.87	90.90	-0.03	0.7129	0.7138	-0.0009	0.5310	0.5237	0.0073
1850.80	1851.10	-0.30	90.85	90.77	0.08	0.7223	0.7234	-0.0011	0.5324	0.5252	0.0072
1831.00	1832.22	-1.22	90.87	90.64	0.23	0.7642	0.7665	-0.0023	0.5436	0.5319	0.0117
1836.60	1837.41	-0.81	90.97	90.80	0.17	0.7775	0.7799	-0.0024	0.5458	0.5339	0.0119
R.M.S	Deviations										
		1.48			0.23			0.002			0.0061

TABLE A.6.32

Mixture Cyclohexane - Ethanol at 90.9° C
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1691.6	1688.31	3.29	90.93	91.11	-0.18	0.1199	0.1254	-0.0055	0.3285	0.3295	-0.001
1723.8	1718.16	5.64	90.89	91.2	-0.31	0.1331	0.138	-0.0049	0.3387	0.3437	-0.005
1728.9	1725.74	3.16	90.92	91.09	-0.17	0.1428	0.1459	-0.0031	0.3498	0.3521	-0.0023
1730.4	1736.89	-6.49	90.98	90.62	0.36	0.1779	0.1717	0.0062	0.3795	0.3763	0.0032
1779.2	1778.12	1.08	90.9	90.96	-0.06	0.1883	0.1881	0.0002	0.3863	0.3884	-0.0021
1828.9	1827.98	0.92	91	91.05	-0.05	0.2329	0.2332	-0.0003	0.4154	0.4162	-0.0008
1838.8	1837.62	1.18	90.94	91.11	-0.17	0.2505	0.2497	0.0008	0.4211	0.4246	-0.0035
1838.6	1839.01	-0.41	90.9	90.89	0.01	0.2673	0.2638	0.0035	0.4239	0.4313	-0.0074
1851.6	1851.23	0.37	90.88	90.9	-0.02	0.2844	0.2848	-0.0004	0.4404	0.4399	0.0005
1857	1856.6	0.4	90.91	90.95	-0.04	0.2919	0.291	0.0009	0.4392	0.4422	-0.003
1856.7	1856.04	0.66	90.84	90.89	-0.05	0.2993	0.2958	0.0035	0.4335	0.444	-0.0105
1859.6	1859.11	0.49	90.85	90.62	0.23	0.3055	0.3045	0.001	0.4437	0.4472	-0.0035
1864.7	1864.81	-0.11	90.9	90.9	0	0.3176	0.3168	0.0008	0.4491	0.4513	-0.0022
1882.9	1877.33	5.57	90.62	90.94	-0.32	0.347	0.3482	-0.0012	0.5696	0.4607	0.1089
1876.8	1877.06	-0.26	90.85	90.83	0.02	0.3775	0.3777	-0.0002	0.4696	0.4686	0.001

TABLE A.6.32 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1890.96	1890.08	0.88	90.95	91.01	-0.06	0.3903	0.3898	0.0005	0.4686	0.4712	-0.0026
1894.10	1893.87	0.23	90.94	90.95	-0.01	0.5049	0.5050	-0.0001	0.4939	0.4935	0.0004
1886.70	1885.81	0.89	90.95	91.00	-0.05	0.6356	0.6356	0.0000	0.5139	0.5132	0.0007
1865.70	1865.10	0.60	90.85	90.88	-0.03	0.7007	0.7012	-0.0005	0.5276	0.5237	0.0039
1863.10	1863.17	-0.07	90.86	90.85	0.01	0.7009	0.7017	-0.0008	0.5284	0.5239	0.0045
1860.90	1860.87	0.03	90.87	90.86	0.01	0.7129	0.7138	-0.0009	0.5310	0.5259	0.0051
1850.80	1852.16	-1.36	90.85	90.77	0.08	0.7223	0.7235	-0.0012	0.5324	0.5279	0.0045
1831.00	1833.63	-2.63	90.87	90.71	0.16	0.7642	0.7668	-0.0026	0.5436	0.5366	0.007
1836.60	1838.02	-1.42	90.97	90.88	0.09	0.7775	0.7797	-0.0022	0.5458	0.5392	0.0066
R.M.S	Deviations										
		2.44			0.14			0.0025			0.0042

TABLE A.6.33

Mixture Cyclohexane - Ethanol at 90.9°C
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1691.60	1686.78	4.82	90.93	91.18	-0.25	0.1199	0.1258	-0.0059	0.3285	0.3315	-0.0030
1723.80	1716.43	7.37	90.89	91.28	-0.39	0.1331	0.1384	-0.0053	0.3387	0.3460	-0.0073
1728.90	1724.05	4.85	90.92	91.18	-0.26	0.1428	0.1461	-0.0033	0.3498	0.3545	-0.0047
1730.40	1735.50	-5.10	90.98	90.72	0.26	0.1779	0.1714	0.0650	0.3795	0.3791	0.0004
1779.20	1776.31	2.89	90.90	91.06	-0.16	0.1883	0.1879	0.0004	0.3863	0.3914	-0.0051
1828.90	1826.00	2.90	91.00	91.16	-0.16	0.2329	0.2327	0.0002	0.4154	0.4199	-0.0045
1838.80	1335.65	3.15	90.94	91.12	-0.18	0.2505	0.2491	0.0014	0.4211	0.4284	-0.0073
1838.60	1837.15	1.45	90.90	91.00	-0.10	0.2673	0.2631	0.0042	0.4239	0.4353	-0.0114
1851.60	1849.30	2.30	90.88	91.01	-0.13	0.2844	0.2841	0.0003	0.4404	0.4441	-0.0037
1857.00	1854.65	2.35	90.91	91.05	-0.14	0.2919	0.2902	0.0017	0.4392	0.4464	-0.0072
1856.70	1854.13	2.57	90.84	91.01	-0.17	0.2993	0.2950	0.0043	0.4335	0.4483	-0.0148
1859.60	1857.17	2.43	90.85	91.00	-0.15	0.3055	0.3037	0.0016	0.4437	0.4515	-0.0078
1864.70	1862.86	1.84	90.90	91.01	-0.11	0.3176	0.3161	0.0019	0.4491	0.4556	-0.0065
1882.90	1875.10	7.80	90.62	91.06	-0.44	0.3470	0.3475	-0.0005	0.4596	0.4650	-0.0054
1876.80	1875.02	1.78	90.85	90.95	-0.10	0.3775	0.3771	0.0004	0.4696	0.4727	-0.0031

TABLE A.6.33 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1890.96	1887.86	3.08	90.95	91.13	-0.18	0.3903	0.3893	0.0010	0.4686	0.4751	-0.0065
1894.10	1891.50	2.60	90.94	91.08	-0.14	0.5049	0.5048	0.0001	0.4939	0.4944	-0.0005
1886.70	1884.34	2.36	90.95	91.07	-0.12	0.6356	0.6360	-0.0004	0.5139	0.5065	0.0074
1865.70	1865.23	0.47	90.85	90.85	0.00	0.7007	0.7019	-0.0012	0.5276	0.5117	0.0159
1863.10	1863.36	-0.26	90.84	90.82	0.04	0.7009	0.7023	-0.0014	0.5284	0.5118	0.0166
1860.90	1861.43	-0.53	90.87	90.81	0.06	0.7129	0.7146	-0.0017	0.5310	0.5123	0.0182
1850.80	1853.12	-2.32	90.85	90.70	0.15	0.7223	0.7244	-0.0021	0.5324	0.5139	0.0185
1831.00	1836.11	-5.11	90.87	90.57	0.30	0.7642	0.7692	-0.0050	0.5436	0.5192	0.0244
1836.60	1840.72	-4.12	90.97	90.72	0.25	0.7775	0.7832	-0.0057	0.5458	0.5211	0.0247
R.M.S	Deviations										
		3.64			0.2			0.0031			0.0116

TABLE A.6.34

Mixture Cyclohexane - Ethanol at 90.9°C
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1691.60	1686.78	4.82	90.93	91.62	-0.69	0.1199	0.1300	-0.0101	0.3285	0.3284	0.0001
1723.80	1717.77	6.03	90.89	91.78	-0.89	0.1331	0.1408	-0.0077	0.3387	0.3419	-0.0032
1728.90	1724.13	4.77	90.92	91.62	-0.70	0.1428	0.1491	-0.0063	0.3498	0.3519	-0.0021
1730.40	1730.45	-0.05	90.98	90.98	0.00	0.1779	0.1764	0.0015	0.3795	0.3810	-0.0015
1779.20	1775.64	3.56	90.90	91.45	-0.55	0.1883	0.1889	-0.0006	0.3863	0.3912	-0.0049
1828.90	1825.76	3.14	91.00	91.51	-0.51	0.2329	0.2319	0.0010	0.4154	0.4217	-0.0063
1838.80	1835.71	3.09	90.94	91.46	-0.52	0.2505	0.2477	0.0028	0.4211	0.4308	-0.0097
1838.60	1836.38	2.22	90.90	91.31	-0.41	0.2673	0.2619	0.0054	0.4239	0.4382	-0.0143
1851.60	1849.01	2.59	91.03	91.31	-0.28	0.2844	0.2829	0.0015	0.4404	0.4475	-0.0071
1857.00	1854.47	2.53	90.91	91.35	-0.44	0.2919	0.2890	0.0029	0.4392	0.4499	-0.0107
1856.70	1854.19	2.51	91.04	91.31	-0.27	0.2993	0.2937	0.0056	0.4335	0.4517	-0.0182
1859.60	1857.06	2.54	90.85	91.29	-0.44	0.3055	0.3026	0.0029	0.4437	0.4549	-0.0112
1864.70	1862.40	2.30	90.90	91.30	-0.40	0.3176	0.3153	0.0023	0.4491	0.4591	-0.0100
1882.90	1878.04	4.86	90.62	91.41	-0.79	0.3470	0.3463	0.0007	0.4596	0.4673	-0.0077
1876.80	1874.27	2.53	90.97	91.26	-0.29	0.3775	0.3771	0.0004	0.4696	0.4740	-0.0044

TABLE A.6.34 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1 890.96	1887.91	3.05	90.95	91.46	-0.51	0.3903	0.3895	0.0008	0.4686	0.4757	-0.0071
1894.10	1890.63	3.47	91.09	91.44	-0.35	0.5049	0.5052	-0.0003	0.4939	0.4855	0.0084
1886.70	1883.35	3.35	90.95	91.36	-0.41	0.6356	0.6363	-0.0007	0.5139	0.4883	0.0256
1865.70	1862.85	2.85	90.85	91.13	-0.28	0.7007	0.7041	-0.0034	0.5276	0.4933	0.0343
1863.10	1860.53	2.57	90.86	91.10	-0.24	0.7009	0.7044	-0.0035	0.5284	0.4934	0.0350
1860.90	1858.30	2.60	90.87	91.11	-0.24	0.7129	0.7173	-0.0044	0.5310	0.4951	0.0359
1850.80	1848.79	2.01	90.85	90.99	-0.14	0.7223	0.7275	-0.0052	0.5324	0.4968	0.0356
1831.00	1829.00	2.00	90.64	91.01	-0.37	0.7642	0.7739	-0.0097	0.5436	0.5073	0.0363
1836.60	1833.75	2.85	90.97	91.24	-0.27	0.7775	0.7877	-0.0102	0.5458	0.5115	0.0343
R.M.S	Deviations										
		3.23			0.48			0.0049			0.198

TABLE A.6.35

Mixture Cyclohexane - Ethanol at 90.9°C
Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1691.60	1686.14	5.46	90.93	91.71	-0.78	0.1199	0.1322	-0.0123	0.3285	0.3277	0.1409
1723.80	1717.10	6.70	90.89	91.88	-0.99	0.1331	0.1430	-0.0099	0.3387	0.3412	-0.0127
1728.90	1723.43	5.47	90.92	91.73	-0.81	0.1428	0.1512	-0.0084	0.3498	0.3511	0.0956
1730.40	1729.71	0.69	90.98	91.09	-0.11	0.1779	0.1782	-0.0003	0.3795	0.3803	0.0793
1779.20	1774.90	4.30	90.90	91.57	-0.67	0.1883	0.1905	-0.0022	0.3863	0.3904	0.0307
1828.90	1825.07	3.83	91.00	91.62	-0.62	0.2329	0.2326	0.0003	0.4154	0.4215	-0.4215
1838.80	1835.06	3.74	90.94	91.56	-0.62	0.2505	0.2480	0.0025	0.4211	0.4308	0.0183
1838.60	1835.76	2.84	90.90	91.41	-0.51	0.2673	0.2618	0.0055	0.4239	0.4385	-0.4385
1851.60	1848.50	3.10	90.88	91.40	-0.52	0.2844	0.2826	0.0018	0.4404	0.4485	-0.0081
1857.00	1853.98	3.02	90.91	91.43	-0.52	0.2919	0.2885	0.0034	0.4392	0.4510	-0.451
1856.70	1853.71	2.99	90.84	91.39	-0.55	0.2993	0.2929	0.0064	0.4335	0.4529	-0.0194
1859.60	1856.64	2.96	90.85	91.37	-0.52	0.3055	0.3019	0.0036	0.4467	0.4565	-0.0128
1864.70	1862.04	2.66	90.90	94.37	-3.47	0.3176	0.3145	0.0031	0.4491	0.4611	-0.0748
1882.90	1877.84	5.06	90.62	91.46	-0.84	0.3470	0.3454	0.0016	0.4596	0.4705	-0.0109
1876.8	1874.20	2.60	90.85	91.29	-0.44	0.3775	0.3761	0.0014	0.4696	0.4783	-0.0087

TABLE A.6.35 CONTINUED

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
1890.96	1887.89	3.07	90.95	91.48	-0.53	0.3903	0.3885	0.0018	0.4686	0.4804	-0.0118
1894.10	1890.85	3.25	90.94	91.45	-0.51	0.5049	0.5049	0.0000	0.4939	0.4933	0.0006
1886.70	1883.63	3.07	90.95	91.35	-0.40	0.6356	0.6359	-0.0003	0.5139	0.4964	0.0175
1865.70	1863.35	2.35	90.85	90.92	-0.07	0.7007	0.7025	-0.0018	0.5276	0.4997	0.0279
1863.10	1861.03	2.07	90.86	91.05	-0.19	0.7009	0.7028	-0.0019	0.5284	0.4998	0.0286
1860.90	1858.89	2.01	90.87	91.04	-0.17	0.7129	0.7154	-0.0025	0.5310	0.5009	0.0301
1850.80	1849.46	1.34	90.85	90.92	-0.07	0.7223	0.7254	-0.0031	0.5324	0.5021	0.0303
1831.00	1830.17	0.83	90.87	90.84	0.03	0.7642	0.7715	-0.0073	0.5436	0.5099	0.0337
1836.60	1835.09	1.51	90.97	91.05	-0.08	0.7775	0.7858	-0.0083	0.5458	0.5132	0.0326
R.M.S	Deviations										
		3.44			0.53			0.005			0.0177

TABLE A6.36

Mixture Cyclohexane - Ethanol at 138.2°C
Liquid-phase Activity Coefficient Model :- Wilson 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
5489.0	5485.30	3.70	138.25	138.30	-0.05	0.8893	0.8968	-0.0075	0.6146	0.6054	0.0092
6389.0	6389.34	-0.34	138.22	138.21	0.01	0.7772	0.7872	-0.0100	0.5115	0.4956	0.0159
6502.0	6520.94	-18.94	138.24	137.92	0.32	0.7299	0.7492	-0.0193	0.4894	0.4752	0.0142
6866.3	6860.63	5.67	138.14	138.23	-0.09	0.6500	0.6542	-0.0042	0.4576	0.4379	0.0197
7143.8	7129.11	14.69	138.25	138.51	-0.26	0.5026	0.5036	-0.0010	0.4107	0.3979	0.0128
7167.3	7157.27	10.03	138.16	138.35	-0.19	0.3947	0.3933	0.0014	0.3671	0.3710	-0.0039
7204.8	7186.25	18.55	138.21	138.56	-0.35	0.3019	0.3036	-0.0017	0.3446	0.3439	0.0007
7083.2	7085.56	-2.36	138.22	138.18	0.04	0.2659	0.2643	0.0016	0.3264	0.3295	-0.0031
7105.7	7086.29	19.41	138.04	138.41	-0.37	0.2284	0.2297	-0.0013	0.3066	0.3137	-0.0071
7029.4	7024.57	4.83	138.16	138.25	-0.09	0.2126	0.2105	0.0021	0.2975	0.3040	-0.0065
6971.6	6999.73	-28.13	138.96	138.44	0.52	0.1965	0.1840	0.0125	0.2866	0.2881	-0.0015
R.M.S	Deviations										
		14.34			0.26			0.0081			0.0105

TABLE A6.37

Mixture Cyclohexane - Ethanol at 138.2° C
Liquid-phase Activity Coefficient Model :- UNIQUAC 2 Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
5489.0	5484.84	4.16	138.25	138.30	-0.05	0.8893	0.8963	-0.0070	0.6146	0.6051	0.0095
6389.0	6389.08	-0.08	138.22	138.21	0.01	0.7772	0.7873	-0.0101	0.5115	0.4955	0.0160
6502.0	6520.59	-18.59	138.24	137.92	0.32	0.7299	0.7494	-0.0195	0.4894	0.4747	0.0147
6866.3	6861.56	4.74	138.14	138.21	-0.07	0.6500	0.6547	-0.0047	0.4576	0.4373	0.0203
7143.8	7129.92	13.88	138.25	138.50	-0.25	0.5026	0.5037	-0.0011	0.4107	0.3979	0.0128
7167.3	7157.24	10.06	138.16	138.36	-0.20	0.3947	0.3931	0.0016	0.3671	0.3722	-0.0051
7204.8	7186.19	18.61	138.21	138.57	-0.36	0.3019	0.3031	-0.0012	0.3446	0.3458	-0.0012
7083.2	7084.59	-1.39	138.22	138.20	0.02	0.2659	0.2636	0.0023	0.3264	0.3314	-0.0050
7105.7	7085.50	20.20	138.04	138.43	-0.39	0.2284	0.2290	-0.0006	0.3066	0.3156	-0.0090
7029.4	7023.18	6.22	138.16	138.28	-0.12	0.2126	0.2100	0.0026	0.2975	0.3057	-0.0082
6971.6	6997.47	-25.87	138.96	138.47	0.49	0.1965	0.1835	0.0130	0.2866	0.2895	-0.0029
R.M.S Deviations											
		13.96			0.26			0.0082			0.0111

TABLE A6.38

Mixture Cyclohexane - Ethanol at 138.2°C
Liquid-phase Activity Coefficient Model :-NRTL 3, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
5489.0	5481.87	7.13	138.25	138.30	-0.05	0.8893	0.8937	-0.0044	0.6146	0.6031	0.0115
6389.0	6387.37	1.63	138.22	138.21	0.01	0.7772	0.7876	-0.0104	0.5115	0.0493	0.4622
6502.0	6520.00	-18.00	138.24	137.92	0.32	0.7299	0.7509	-0.021	0.4894	0.4723	0.0171
6866.3	6862.56	3.74	138.14	138.21	-0.07	0.6500	0.6558	-0.0058	0.4576	0.4346	0.0230
7143.8	7129.94	13.86	138.25	138.50	-0.25	0.5026	0.5039	-0.0013	0.4107	0.3964	0.0143
7167.3	7157.15	10.15	138.16	138.36	-0.20	0.3947	0.3933	0.0014	0.3671	0.3716	-0.0045
7204.8	7185.81	18.99	138.21	138.57	-0.36	0.3019	0.3031	-0.0012	0.3446	0.3458	-0.0012
7083.2	7085.09	-1.89	138.22	138.20	0.02	0.2659	0.2635	0.0024	0.3264	0.3316	-0.0052
7105.7	7085.33	20.37	138.04	138.43	-0.39	0.2284	0.2290	-0.0006	0.3066	0.3158	-0.0092
7029.4	7023.41	5.99	138.16	138.28	-0.12	0.2126	0.2038	0.0088	0.2975	0.3059	-0.0084
6971.6	6998.01	-26.41	138.96	138.47	0.49	0.1965	0.1832	0.0133	0.2866	0.2895	-0.0029
R.M.S Deviations											
		14.14			0.26			0.0085			0.124

TABLE A6.39

Mixture Cyclohexane - Ethanol at 138.2°C
Liquid-phase Activity Coefficient Model :-Margules 2 , Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
5489.0	5476.48	12.52	138.25	138.41	-0.16	0.8893	0.8888	0.0005	0.6146	0.5996	0.0150
6389.0	6384.28	4.72	138.22	138.29	-0.07	0.7772	0.7884	-0.0112	0.5115	0.4889	0.0226
6502.0	6517.93	-15.93	138.24	137.96	0.28	0.7299	0.7541	-0.0242	0.4894	0.4677	0.0217
6866.3	6867.21	-0.91	138.14	138.11	0.03	0.6500	0.6591	-0.0091	0.4576	0.4286	0.0290
7143.8	7132.35	11.45	138.25	138.46	-0.21	0.5026	0.5042	-0.0016	0.4107	0.3946	0.0161
7167.3	7156.95	10.35	138.16	138.36	-0.20	0.3947	0.3929	0.0018	0.3671	0.3745	-0.0074
7204.8	7185.30	19.50	138.21	138.59	-0.38	0.3019	0.3017	0.0002	0.3446	0.3506	-0.0060
7083.2	7082.90	0.30	138.22	138.23	-0.01	0.2659	0.3619	-0.0960	0.3264	0.3361	-0.0097
7105.7	7082.92	22.78	138.04	138.48	-0.44	0.2284	0.2278	0.0006	0.3066	0.3200	-0.0134
7029.4	7019.76	9.64	138.16	138.35	-0.19	0.2126	0.2089	0.0037	0.2975	0.3095	-0.0120
6971.6	6992.63	-21.03	138.96	138.56	0.40	0.1965	0.1825	0.0140	0.2866	0.2922	-0.0056
R.M.S	Deviations										
	13.84				0.26			0.0097			0.0161

TABLE A6.40

Mixture Cyclohexane - Ethanol at 138.2°C

Liquid-phase Activity Coefficient Model :-Van Larr 2, Parameter Equation
Cyclohexane Vapour Pressure Equation :- New 3 Parameter Antione Equation
Ethanol Vapour Pressure Equation :- 6 Parameter Antione Equation

Pressure mmHg			Temperature °C			Liquid mol fraction			Vapour mol fraction		
P_{EXP}	P_{CALC}	P_{DIFF}	T_{EXP}	T_{CALC}	T_{DIFF}	x_{EXP}	x_{CALC}	x_{DIFF}	y_{EXP}	y_{CALC}	y_{DIFF}
5489.0	5475.99	13.01	138.25	138.42	-0.17	0.8893	0.8883	0.0010	0.6146	0.5994	0.6146
6389.0	6383.42	5.58	138.22	138.30	-0.08	0.7772	0.7878	-0.0106	0.5115	0.4887	0.5115
6502.0	6516.96	-14.96	138.24	137.97	0.27	0.7299	0.7535	-0.0236	0.4894	0.4675	0.4894
6866.3	6866.32	-0.02	138.14	138.12	0.02	0.6500	0.6589	-0.0089	0.4576	0.4283	0.4576
7143.8	7131.91	11.89	138.25	138.47	-0.22	0.5026	0.5042	-0.0016	0.4107	0.3941	0.4107
7167.3	7156.62	10.68	138.16	138.37	-0.21	0.3947	0.3930	0.0017	0.3671	0.3740	0.3671
7204.8	7185.09	19.71	138.21	138.59	-0.38	0.3019	0.3018	0.0001	0.3446	0.3502	0.3446
7083.2	7082.80	0.40	138.22	138.23	-0.01	0.2659	0.2621	0.0038	0.3264	0.3358	0.3264
7105.7	7082.92	22.78	138.04	138.48	-0.44	0.2284	0.2280	0.0004	0.3066	0.3197	0.3066
7029.4	7019.83	9.57	138.16	138.35	-0.19	0.2126	0.2090	0.0036	0.2975	0.3093	0.2975
6971.6	6992.80	-21.2	138.96	138.56	0.40	0.1965	0.1826	0.0139	0.2866	0.2921	0.2866
R.M.S	Deviations										
		13.91			0.26			0.0094			0.0161

Appendix 7 Tabulated activity coefficients deduced for cyclohexane-ethanol and acetone-chloroform.

This appendix contains the activity coefficients deduced for each experimertal data set. The activity coefficients have been deduced from the reduced experimental data from the Prausnitz type consistancy tests. Data are presented only for the liquid activity coefficient model which best described the individual data set. Table A.7.1 to A.7.8 list data for cyclohexane-ethanol mixture at 1 atmosphere, 2, 4, 6, 8, 11 bar and at 90.9°C and 138.2°C. Table A.7.1 to A.7.8 list data for Acetone Chloroform. mixture at 1 atmosphere and 63.4°C.

The tables also present the activity coefficient calculated for the data sets using the original UNIFAC method of Fredenslund et al. (1977) and the Modified UNIFAC method of Larsen et al. (1987).

TABLE A.7.1 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 1 atmosphere.

Liquid mol Frac (Ethanol)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0142	12.4183	1.0005	15.6356	1.0014	12.0335	1.0012
0.0622	8.4431	1.0090	9.6626	1.0230	8.0526	1.0212
0.0971	5.6937	1.0307	7.1813	1.0502	6.1302	1.0467
0.1165	6.4999	1.0216	6.2221	1.0685	5.3621	1.0637
0.1418	4.8620	1.0450	5.2657	1.0953	4.5859	1.0888
0.1594	4.3976	1.0564	4.7449	1.1160	4.1611	1.1081
0.1953	3.6536	1.0838	3.9272	1.1629	3.4872	1.1518
0.2202	3.2558	1.1059	3.4957	1.1987	3.1238	1.1850
0.2436	2.9496	1.1292	3.1648	1.2354	2.8490	1.2189
0.2562	2.8059	1.1428	3.0098	1.2562	2.7185	1.2381
0.2762	2.6041	1.1659	2.7921	1.2912	2.5353	1.2703
0.3099	2.3216	1.2093	2.4866	1.3548	2.2765	1.3285
0.3854	1.8731	1.3293	1.9970	1.5222	1.8589	1.4794
0.4026	1.7936	1.3617	1.9123	1.5661	1.7866	1.5187
0.4503	1.6173	1.4630	1.7132	1.6994	1.6156	1.6366
0.5636	1.3317	1.7894	1.3896	2.1046	1.3364	1.9851
0.6848	1.1551	2.3466	1.1845	2.7406	1.1592	2.5096
0.7699	1.0787	2.9524	1.0944	3.3785	1.0812	3.0110
0.8130	1.0511	3.3668	1.0616	3.7883	1.0528	3.3221
0.8538	1.0309	3.8476	1.0374	4.2434	1.0319	3.6552
0.8956	1.0156	4.4601	1.0190	4.7962	1.0161	4.0473

TABLE A.7.2 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 2 bar.

Liquid mol Frac (Ethanol)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0456	9.1049	1.0017	10.0342	1.0114	7.3242	1.0108
0.0853	6.0292	1.0467	7.2531	1.0353	5.7620	1.0297
0.0911	5.7406	1.0518	6.9513	1.0397	5.5600	1.0334
0.3147	2.0452	1.3379	2.4126	1.3430	2.1531	1.3052
0.4510	1.5234	1.6038	1.6988	1.6678	1.5747	1.5847
0.5577	1.3006	1.8827	1.3972	2.0336	1.3265	1.8857
0.6694	1.1547	2.2723	1.2025	2.5781	1.1656	2.3104
0.7384	1.0939	2.5830	1.1223	3.0370	1.0995	2.6515
0.7816	1.0646	2.8138	1.0839	3.3893	1.0680	2.9031
0.8637	1.0248	3.3508	1.0321	4.2448	1.0257	3.4796
0.8750	1.0208	3.4347	1.0270	4.3834	1.0215	3.5635
0.9168	1.0092	3.7798	1.0119	4.9637	1.0094	3.9127
0.9382	1.0051	3.9719	1.0061	5.3357	1.0048	4.1119
0.9557	1.0026	4.1327	1.0030	5.6325	1.0023	4.2384
0.9771	1.0007	4.3207	1.0005	6.0645	1.0004	4.3444

TABLE A.7.3 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 4 bar.

Liquid mol Frac (Ethanol)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.1203	4.5278	1.0276	4.2770	1.0247	3.9340	1.0472
0.1488	3.9534	1.0420	3.9445	1.0378	3.4646	1.0694
0.2291	2.8563	1.0990	3.1860	1.0914	2.5669	1.1499
0.2762	2.4390	1.1445	2.8360	1.1353	2.2211	1.2085
0.3353	2.0590	1.2161	2.4765	1.2060	1.9079	1.2957
0.3966	1.7747	1.3096	2.1709	1.3013	1.6673	1.4004
0.4171	1.6980	1.3459	2.0819	1.3392	1.6021	1.4392
0.4527	1.5819	1.4160	1.9411	1.4135	1.5033	1.5121
0.5092	1.4333	1.5481	1.7477	1.5580	1.3756	1.6415
0.6112	1.2441	1.8710	1.4728	1.9375	1.2114	1.9251
0.6896	1.1466	2.2251	1.3121	2.4007	1.1263	2.1962
0.7498	1.0921	2.5890	1.2124	2.9363	1.0787	2.4418
0.7646	1.0809	2.6947	1.1908	3.1042	1.0690	2.5078
0.8388	1.0369	3.3483	1.0982	4.2946	1.0310	2.8719

TABLE A.7.4 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 6 bar.

Liquid mol Frac	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0978	2.5977	1.0077	4.4034	1.0162	3.7988	1.0279
0.2138	2.2007	1.0402	3.2436	1.0785	2.4714	1.1167
0.2686	2.0372	1.0664	2.8317	1.1264	2.1118	1.1756
0.3388	1.8493	1.1127	2.4102	1.2087	1.7844	1.2664
0.3883	1.7304	1.1558	2.1690	1.2839	1.6148	1.3413
0.4793	1.5384	1.2648	1.8156	1.4711	1.3882	1.5031
0.7615	1.1307	2.1318	1.1851	3.0078	1.0617	2.2684
0.7798	1.1132	2.2457	1.1605	3.2236	1.0519	2.3325
0.8294	1.0712	2.6254	1.1017	3.9731	1.0298	2.5053
0.8768	1.0392	3.1213	1.0564	5.0149	1.0147	2.6484

TABLE A.7.5 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 8 bar.

Liquid mol Frac (Ethanol)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0393	3.8482	1.0028	5.0583	1.0042	4.1864	1.0042
0.0499	3.7169	1.0045	5.2280	1.0026	4.0056	1.0067
0.0614	3.5833	1.0067	4.8833	1.0063	3.8271	1.0100
0.1440	2.8123	1.0356	3.8354	1.0349	2.7954	1.0497
0.1741	2.5985	1.0514	3.5337	1.0512	2.5367	1.0705
0.2616	2.1179	1.1131	2.8299	1.1186	1.9897	1.1472
0.3195	1.8841	1.1679	2.4757	1.1820	1.7497	1.2116
0.4021	1.6291	1.2677	2.0774	1.3050	1.5008	1.3202
0.4789	1.4511	1.3886	1.7934	1.4652	1.3412	1.4421
0.5510	1.3219	1.5329	1.5822	1.6730	1.2315	1.5742
0.5745	1.2863	1.5877	1.5225	1.7566	1.2017	1.6188
0.6370	1.2041	1.7573	1.3843	2.0323	1.1379	1.7559
0.6703	1.1671	1.8638	1.3216	2.2211	1.1114	1.8449
0.8380	1.0405	2.6599	1.0882	4.0285	1.0226	2.2660
0.9501	1.0041	3.6404	1.0095	7.2456	1.0016	2.2422

TABLE A.7.6 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 11 bar.

Liquid mol Frac (Ethanol)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0155	5.5191	1.0004	9.4375	1.0010	3.7013	1.0005
0.0243	5.3677	1.0010	8.8302	1.0024	3.6011	1.0014
0.0408	5.0938	1.0028	7.8242	1.0066	3.3872	1.0037
0.0707	4.6524	1.0083	6.4354	1.0187	3.0909	1.0110
0.1238	3.9827	1.0256	4.7624	1.0526	2.6000	1.0320
0.2789	2.6725	1.1348	2.5549	1.2285	1.7605	1.1425
0.3085	2.4975	1.1673	2.3367	1.2750	1.6614	1.1709
0.4444	1.8873	1.3830	1.6806	1.5538	1.3439	1.3301
0.5120	1.6702	1.5461	1.4826	1.7417	1.2416	1.4249
0.7062	1.2490	2.4332	1.1503	2.5714	1.0692	1.7472
0.7306	1.2122	2.6239	1.1250	2.7203	1.0568	1.7944
0.7895	1.1348	3.2154	1.0747	3.1326	1.0319	1.8857

TABLE A.7.7 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 90.9°C

Liquid mol Frac (Ethanol)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.1199	3.6241	1.0228	4.4162	1.0248	3.5191	1.0193
0.1331	3.4982	1.0281	4.2481	1.0305	3.4127	1.0238
0.1428	3.4096	1.0323	4.1304	1.0352	3.3374	1.0275
0.1779	3.1171	1.0562	3.7420	1.0549	3.0845	1.0431
0.1883	3.0385	1.0562	3.6372	1.0616	3.0150	1.0484
0.2329	2.7327	1.0864	3.2335	1.0955	2.7416	1.0754
0.2673	2.6257	1.0323	2.9662	1.1275	2.5552	1.1009
0.2505	2.5296	1.1149	3.0924	1.1112	2.6438	1.0879
0.2844	2.4374	1.1308	2.8494	1.1448	2.4724	1.1148
0.2919	2.3985	1.1381	2.7949	1.1538	2.4334	1.1220
0.2993	2.3614	1.1457	2.7464	1.1623	2.3985	1.1288
0.3055	2.3309	1.1521	2.7066	1.1697	2.3698	1.1347
0.3176	2.2730	1.1653	2.6316	1.1846	2.3153	1.1467
0.3470	2.1425	1.2004	2.4622	1.2245	2.1906	1.1788
0.3775	2.0190	1.2413	2.3037	1.2717	2.0719	1.2167
0.3903	1.9707	1.2600	2.2420	1.2934	2.0250	1.2342
0.5049	1.6144	1.4816	1.7903	1.5527	1.6714	1.4425
0.6356	1.3321	1.9143	1.4378	2.0806	1.3802	1.8630
0.7007	1.2280	2.2563	1.3075	2.5202	1.2688	2.2081
0.7009	1.2277	2.2575	1.3072	2.5219	1.2685	2.2093
0.7129	1.2107	2.3344	1.2859	2.6240	1.2500	2.2888
0.7223	1.1979	2.3984	1.2697	2.7097	1.2360	2.3553
0.7642	1.1457	2.7290	1.2032	3.1672	1.1781	2.7072
0.7775	1.1308	2.8519	1.1839	3.3441	1.1612	2.8419

TABLE A.7.8 Liquid-phase activity coefficients for Cyclohexane-Ethanol mixture at 132.8°C.

Liquid mol Frac	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.1107	3.8966	1.0293	5.2390	1.0447	3.0529	1.0039
0.2228	2.6906	1.1075	3.1285	1.1561	2.1306	1.0295
0.2701	2.3703	1.1543	2.6490	1.2207	1.8944	1.1052
0.3500	1.9699	1.2543	2.0967	1.3554	1.6073	1.1484
0.4974	1.5060	1.5272	1.5242	1.7109	1.2925	1.2360
0.6053	1.2959	1.8370	1.2911	2.0972	1.1605	1.4488
0.6981	1.1699	2.2250	1.1604	2.5602	1.0868	1.6530
0.7341	1.1316	2.4197	1.1224	2.7846	1.0656	1.9636
0.7716	1.0793	2.6577	1.0891	3.0521	1.0472	2.0704
0.7864	1.0853	2.7631	1.0769	3.1767	1.0405	2.1179
0.8035	1.0725	2.8937	1.0654	3.3117	1.0343	2.1680

TABLE A.7.9 Liquid-phase activity coefficients for Acetone-Chloroform mixture at 1 atmosphere.

Liquid mol Frac (Acetone)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0870	0.5863	0.9948	0.5659	0.9959	0.5214	0.9935
0.0901	0.5844	0.9952	0.5678	0.9956	0.5241	0.9930
0.1361	0.6138	0.9561	0.5960	0.9898	0.5635	0.9844
0.1532	0.6149	0.9882	0.6063	0.9869	0.5776	0.9804
0.1795	0.6254	0.9850	0.6226	0.9819	0.5994	0.9734
0.1827	0.6418	0.9794	0.6251	0.9812	0.6027	0.9725
0.1827	0.6418	0.9794	0.6251	0.9812	0.6027	0.9725
0.2352	0.6439	0.9787	0.6578	0.9682	0.6451	0.9555
0.2876	0.6766	0.9648	0.6911	0.9517	0.6864	0.9351
0.3389	0.7091	0.9474	0.7246	0.9320	0.7266	0.9124
0.4375	0.7409	0.9274	0.7871	0.8839	0.7956	0.8606
0.4966	0.8098	0.8708	0.8236	0.8487	0.8335	0.8252
0.5012	0.8335	0.8474	0.8263	0.8458	0.8363	0.8223
0.5563	0.8360	0.8446	0.8588	0.8085	0.8685	0.7866
0.5626	0.8656	0.8105	0.8625	0.8040	0.8721	0.7825
0.6304	0.8689	0.8065	0.8997	0.7529	0.9071	0.7357
0.6741	0.9221	0.7295	0.9215	0.7175	0.9271	0.7041
0.7361	0.9470	0.6833	0.9492	0.6656	0.9516	0.6585
0.8784	0.9879	0.5721	0.9912	0.5487	0.9895	0.5525
0.9396	0.9969	0.5236	0.9977	0.5131	0.9966	0.5142
1.0000	1.0000	0.4760	1.0000	0.4831	1.0000	0.4647

TABLE A.7.10 Liquid-phase activity coefficients for Acetone-Chloroform mixture at 64.3°C.

Liquid mol Frac (Acetone)	Experimental		Original UNIFAC		Modified UNIFAC	
x	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
0.0011	0.5605	0.9916	0.5557	1.0000	0.4872	1.0000
0.0532	0.5941	0.9846	0.5512	0.9985	0.5221	0.9981
0.0699	0.6528	0.9670	0.5606	0.9974	0.5335	0.9967
0.1227	0.7619	0.9166	0.5911	0.9918	0.5697	0.9937
0.1398	0.7721	0.9106	0.6012	0.9892	0.5816	0.9918
0.1686	0.8118	0.8846	0.6184	0.9842	0.6016	0.9806
0.1759	0.8845	0.8236	0.6228	0.9827	0.6067	0.9789
0.2040	0.9110	0.7952	0.6399	0.9765	0.6262	0.9716
0.2149	0.9463	0.7482	0.6466	0.9621	0.6338	0.9685
0.2440	0.9561	0.7324	0.6646	0.9658	0.6541	0.9595
0.3086	0.9734	0.6989	0.7053	0.9442	0.6987	0.9356
0.3389	0.9796	0.6841	0.7246	0.9320	0.7194	0.9226
0.4286	0.9817	0.6784	0.7818	0.8889	0.7791	0.8779
0.4833	0.9866	0.6642	0.8161	0.8574	0.8138	0.8464
0.6055	0.9877	0.6605	0.8883	0.7746	0.8844	0.7662
0.6618	0.9917	0.6463	0.9178	0.7320	0.9127	0.7255
0.6755	0.9937	0.6382	0.9245	0.7213	0.9192	0.7153
0.8076	0.9980	0.6123	0.9761	0.6175	0.9700	0.6128
0.8721	0.9988	0.6044	0.9910	0.5708	0.9864	0.5610
0.9072	1.0000	0.5801	0.9958	0.5485	0.9928	0.5327

Appendix 8 Predicted data using AGAPE GLP method.

Data are presented in tables A.8.1 to A.8.6 for cyclohexane-ethanol mixture at 1 atmosphere, 2, 4, 6, 8, bar and 90.9°C predicted using the AGAPE method with GLP theory.

TABLE A.8.1

Data predicted for Ethanol-Cyclohexane mixture at 1.01325 bar using AGAPE GLP prediction program.

x Mol Fraction	y Mol Fraction	T °C	P mmHg	A_{12}	A_{21}
0.1	0.4121	66.8	760	6.5965	1.0236
0.2	0.4898	63.81	760	4.4601	1.1028
0.3	0.4977	63.56	760	3.054	1.1165
0.4	0.4805	63.81	760	2.1873	1.4976
0.44	0.4705	63.88	760	1.9419	1.6322
0.5	0.4549	63.88	760	1.6521	1.8836
0.6	0.4327	63.63	760	1.3241	2.4685
0.7	0.4316	63.63	760	1.132	3.2975
0.8	0.4813	65.13	760	1.0348	4.298
0.9	0.6403	69.81	760	1.0022	5.1118

TABLE A.8.2

Data predicted for Ethanol-Cyclohexane mixture at 2 bar using the AGAPE GLP prediction program.

x Mol Fraction	y Mol Fraction	T °C	P Bar	A_{12}	A_{21}
0.1	0.4108	89.19	2	5.3403	1.0192
0.2	0.5098	84.66	2	3.9232	1.0856
0.3	0.5349	83.72	2	2.8438	1.2113
0.4	0.5329	83.75	2	2.1224	1.4181
0.488	0.5214	83.84	2	1.6961	1.6960
0.5	0.5201	83.88	2	1.6494	1.7427
0.6	0.5073	83.81	2	1.3438	2.2385
0.7	0.5097	83.88	2	1.1546	2.9647
0.8	0.5547	85.08	2	1.0504	3.8997
0.9	0.6895	88.88	2	1.0074	4.876

TABLE A.8.3

Data predicted for Ethanol-Cyclohexane mixture at 4 bar using the AGAPE GLP prediction program.

x Mol Fraction	y Mol Fraction	T °C	P Bar	A_{12}	A_{21}
0.1	0.3966	116.78	4	4.0779	1.4056
0.2	0.5198	110.20	4	3.2845	1.1892
0.3	0.5648	107.98	4	2.5560	1.1682
0.4	0.5798	107.48	4	2.0003	1.3326
0.5	0.5823	107.34	4	1.6144	1.5959
0.549	0.5819	107.34	4	1.4693	1.7708
0.6	0.5821	107.34	4	1.3450	1.9951
0.7	0.5931	107.53	4	1.1674	2.5791
0.8	0.6333	108.36	4	1.0618	3.4149
0.9	0.7457	111.28	4	1.0117	4.4049
0.95	0.8489	113.97	4	1.0024	4.9010

TABLE A.8.4

Data predicted for Ethanol-Cyclohexane mixture at 6 bar using the AGAPE GLP prediction program.

x Mol Fraction	y Mol Fraction	T °C	P Bar	A_{12}	A_{21}
0.1	0.3795	135.94	6	3.3582	1.0118
0.2	0.5191	127.87	6	2.8796	1.0556
0.3	0.5772	124.58	6	2.3481	1.1416
0.4	0.6033	123.39	6	1.9063	1.2838
0.5	0.6156	122.97	6	1.5755	1.5085
0.59	0.6231	122.91	6	1.3589	1.8058
0.6	0.6241	122.91	6	1.3336	1.8465
0.7	0.6391	122.95	6	1.1691	2.3632
0.8	0.6790	123.61	6	1.0657	3.1016
0.9	0.7791	126.00	6	1.0136	4.0425
0.95	0.8699	128.31	6	1.0030	4.5168
0.98	0.9925	130.13	6	1.0002	4.7951

TABLE A.8.5

Data predicted for Ethanol-Cyclohexane mixture at 8 bar using AGAPE GLP prediction program.

x Mol Fraction	y Mol Fraction	T °C	P bar	A_{12}	A_{21}
0.1	0.3795	135.94	8	3.3539	1.0118
0.2	0.5191	127.87	8	2.8796	1.0556
0.3	0.5772	124.58	8	2.3481	1.1416
0.4	0.6033	123.39	8	1.9063	1.2838
0.5	0.6156	122.97	8	1.5755	1.5085
0.6	0.6241	122.91	8	1.3336	1.8465
0.6546	*0.6231*	*122.91*	8	1.3539	1.8058
0.7	0.6391	122.95	8	*1.1691*	*2.3632*
0.8	0.6790	123.61	8	1.0657	3.1016
0.9	0.7791	126.00	8	1.0136	4.0425

TABLE A.8.6

Data predicted for Ethanol-Cyclohexane mixture at 90.9°C using the AGAPE GLP prediction program.

x Mol Fraction	y Mol Fraction	T °C	P bar	A_{12}	A_{2}
0.1	0.4101	90.9	2.0982	5.2529	1.0194
0.2	0.5118	90.9	2.3936	3.7397	1.0826
0.3	0.5424	90.9	2.4798	2.7374	1.2015
0.4	0.5456	90.9	2.4874	2.0712	1.3963
0.5	0.5379	90.9	2.4807	1.6293	1.6293
0.507	0.5373	90.9	2.4805	1.6048	1.7257
0.6	0.5308	90.9	2.4813	1.545	2.1574
0.7	0.5372	90.9	2.4721	1.3401	2.8269
0.8	0.5780	90.9	2.3905	1.1582	3.7383
0.9	0.6976	90.9	2.1317	1.0087	4.7787

Appendix 9 VLE data predicted for mixtures acetone-chloroform and cyclohexane-ethanol using the AGAPE fitting program.

Data are presented here for the mixtures acetone-chloroform and cyclohexane-ethanol predicted using the AGAPE fitting program. The value of Z the coordination number is set to 11 for all predictions. The values of r have been set using molar volume ratios for the molecules concerned. For the cyclohexane mixture an average value of r to account for association of ethanol molecules has been used. Values of ϕ_{12} have been determined using an iterative fitting procedure.

TABLE A.9.1

Data predicted for Ethanol-Cyclohexane mixture at 1.01325 atm using the AGAPE fitting program.

Constants used :- Z = 11 R = 1.3 Ratio = 0.9025

x Mol Fraction (Ethanol)	y Mol Fraction (Ethanol)	T °C	P bar	A_{12}	A_{21}
0.05	0.2897	71.38	1.0133	7.6473	1.0074
0.1	0.3931	67.56	1.0133	6.0903	1.0297
0.15	0.4373	65.88	1.0133	4.8545	1.0669
0.2	0.4571	65.25	1.0133	3.9097	1.1189
0.25	0.4641	65.06	1.0133	3.2014	1.1860
0.3	0.4647	65.03	1.0133	2.6752	1.2696
0.35	0.4625	65.06	1.0133	2.2792	1.3712
0.4	0.4592	65.09	1.0133	1.9774	1.4930
0.45	0.4565	65.13	1.0133	1.7447	1.6375
0.5	0.4546	65.13	1.0133	1.5638	1.8079
0.55	0.4547	65.13	1.0133	1.4221	2.0078
0.6	0.4573	65.13	1.0133	1.3108	2.2418
0.7	0.4802	65.63	1.0133	1.1546	2.8224
0.8	0.5376	67.09	1.0133	1.062	3.5835
0.9	0.6738	70.75	1.0133	1.0141	4.5021

TABLE A.9.2

Data predicted for Ethanol-Cyclohexane mixture at 2.bar using the AGAPE fitting program.

Constants used :- Z = 11 R = 1.1 Ratio = 0.895

x Mol Fraction (Ethanol)	y Mol Fraction (Ethanol)	T °C	P Bar	A_{12}	A_{21}
0.05	0.2945	94.13	2	6.4057	1.0067
0.1	0.4062	89.19	2	5.2800	1.0273
0.15	0.4561	86.94	2	4.2958	1.0612
0.2	0.481	85.94	2	3.5275	1.1084
0.25	0.4935	85.47	2	2.9467	1.1697
0.3	0.499	85.28	2	2.5005	1.2452
0.35	0.502	85.25	2	2.1588	1.3365
0.4	0.5034	85.22	2	1.8962	1.4453
0.45	0.5039	85.19	2	1.6894	1.5742
0.5	0.5059	85.19	2	1.5263	1.7255
0.55	0.5094	85.19	2	1.3971	1.9026
0.6	0.5158	85.25	2	1.2938	2.1083
0.7	0.5423	85.66	2	1.1483	2.6263
0.8	0.6012	86.97	2	1.0604	3.3042
0.9	0.7258	90.09	2	1.0140	4.1607

TABLE A.9.3

Data predicted for Ethanol-Cyclohexane mixture at 4 bar using the AGAPE fitting program.

Constants used :- Z = 11 R = 1.1 Ratio = 0.898

x Mol Fraction (Ethanol)	y Mol Fraction (Ethanol)	T °C	P Bar	A_{12}	A_{21}
0.05	0.2844	122.09	4	4.9797	1.0056
0.1	0.4059	115.8	4	4.3012	1.0230
0.15	0.4665	112.56	4	3.6466	1.0523
0.2	0.4996	110.89	4	3.0883	1.0933
0.25	0.5191	109.98	4	2.6425	1.1463
0.3	0.5313	109.48	4	2.2908	1.2121
0.35	0.5395	109.22	4	2.0107	1.2911
0.4	0.5460	109.05	4	1.7905	1.3850
0.45	0.5515	108.92	4	1.6142	1.4972
0.5	0.5577	108.84	4	1.4727	1.6269
0.55	0.5656	108.81	4	1.3591	1.7779
0.6	0.5756	108.81	4	1.2679	1.9531
0.7	0.6081	109.13	4	1.1367	2.3869
0.8	0.6677	110.17	4	1.0560	2.9562
0.9	0.7807	112.69	4	1.0131	3.6680

TABLE A.9.4

Data predicted for Ethanol-Cyclohexane mixture at 6 bar using the AGAPE fitting program.

Constants used :- Z = 11 R =1.05 Ratio = 0.890

x Mol Fraction (Ethanol)	y Mol Fraction (Ethanol)	T °C	P Bar	A_{12}	A_{21}
0.05	0.2942	139.75	6	4.6973	1.0052
0.1	0.4241	132.09	6	4.1735	1.0217
0.15	0.4889	128.06	6	3.5957	1.0499
0.2	0.5241	125.94	6	3.0737	1.0897
0.25	0.5451	124.76	6	2.6470	1.1416
0.3	0.5580	124.12	6	2.3011	1.2061
0.35	0.5668	123.76	6	2.0245	1.2837
0.4	0.5731	123.52	6	1.8037	1.3777
0.45	0.5789	123.37	6	1.6270	1.4878
0.5	0.5849	123.27	6	1.4840	1.6172
0.55	0.5921	123.19	6	1.3687	1.7686
0.6	0.6015	123.16	6	1.2757	1.9453
0.7	0.6312	123.34	6	1.1412	2.3903
0.8	0.6869	124.25	6	1.0581	2.9801
0.9	0.7932	126.62	6	1.0136	3.7317

TABLE A.9.5

Data predicted for Ethanol-Cyclohexane mixture at 8 bar using the AGAPE fitting program.

Constants used :- Z = 11 R = 1.1 Ratio = 0.885

x Mol Fraction (Ethanol)	y Mol Fraction (Ethanol)	T °C	P bar	A_{12}	A_{21}
0.05	0.2913	154.12	8	4.2890	1.0048
0.1	0.4258	145.55	8	3.8905	1.0205
0.15	0.4944	140.91	8	3.4016	1.0476
0.2	0.5324	138.38	8	2.9397	1.0857
0.25	0.5555	136.92	8	2.5523	1.1356
0.3	*0.5702*	*136.09*	*8*	*2.2330*	*1.1972*
0.35	0.5806	135.59	8	1.9757	1.2722
0.4	0.5885	135.25	8	1.7688	1.3621
0.45	0.5956	135.05	8	1.6003	1.4671
0.5	0.6027	134.85	8	1.4652	1.5920
0.55	0.6111	134.73	8	1.3549	1.7362
0.6	0.6214	134.66	8	1.2658	1.9039
0.7	0.6526	134.75	8	1.1364	2.3245
0.8	0.7085	135.55	8	1.0562	2.8750
0.9	0.8102	137.67	8	1.0132	3.5792

TABLE A.9.6

Data predicted for Ethanol-Cyclohexane mixture at 90.9°C using the AGAPE fitting program.

Constants used :- Z = 11 R = 1.1 Ratio =0.905

x Mol Fraction (Ethanol)	y Mol Fraction (Ethanol)	T °C	P bar	A_{12}	A_{21}
0.05	0.2779	90.9	1.7867	6.0636	1.0066
0.1	0.3874	90.9	2.0329	4.8079	1.0256
0.15	0.4415	90.9	2.1699	3.8994	1.0567
0.2	0.4712	90.9	2.2448	3.2288	1.0998
0.25	0.4884	90.9	2.2848	2.7250	1.1553
0.3	0.4988	90.9	2.3059	2.3405	1.2238
0.4	0.5106	90.9	2.3233	1.8104	1.4047
0.45	0.5153	90.9	2.3271	1.6268	1.5202
0.5	0.5207	90.9	2.3293	1.4808	1.6551
0.55	0.5277	90.9	2.3291	1.3642	1.8121
0.6	0.5372	90.9	2.3252	1.2710	1.9941
0.7	0.5683	90.9	2.2954	1.1376	2.4484
0.8	0.6267	90.9	2.2088	1.0564	3.0557
0.9	0.7411	90.9	2.0155	1.0133	3.8672
0.95	0.8411	90.9	1.8559	1.0032	4.3706

TABLE A.9.7

Data predicted for Acetone-Chloroform mixture at 1 atmosphere using the AGAPE fitting program.

Constants used :- Z = 11 R = 0.7 Ratio = 1.03

x Mol Fraction	y Mol Fraction	T °C	P bar	A_{12}	A_{21}
0.1000	0.0722	62.28	1.0133	0.5867	0.9946
0.1500	0.1157	62.78	1.0133	0.6168	0.9877
0.2000	0.1643	63.21	1.0133	0.6476	0.9779
0.2500	0.2178	63.59	1.0133	0.6787	0.9649
0.3000	0.2756	63.84	1.0133	0.7098	0.9489
0.3500	0.3376	64.03	1.0133	0.7408	0.9296
0.4000	0.4027	64.09	1.0133	0.7716	0.9072
0.4500	0.4689	63.96	1.0133	0.8019	0.8816
0.5000	0.537	63.78	1.0133	0.8316	0.8529
0.5500	0.6033	63.4	1.0133	0.8598	0.8215
0.6000	0.6679	62.9	1.0133	0.8868	0.7874
0.7000	0.7847	61.53	1.0133	0.9341	0.7126
0.8000	0.8794	59.78	1.0133	0.9706	0.6332
0.9000	0.9505	57.9	1.0133	0.9929	0.5544
0.9500	0.9773	56.96	1.0133	0.9983	0.5174

TABLE A.9.8

Data predicted for Acetone-Chloroform mixture at 64.3°C using the AGAPE fitting program.

Constants used :- Z = 11 R = 0.7 Ratio = 1.03

x Mol Fraction	y Mol Fraction	T °C	P bar	A_{12}	A_{21}
0.1000	0.0726	64.3	1.0815	0.5899	0.9947
0.1500	0.1161	64.3	1.0643	0.6192	0.9878
0.2000	0.1647	64.3	1.0493	0.6491	0.9780
0.2500	0.2181	64.3	1.0370	0.6796	0.9650
0.3000	0.2760	64.3	1.0279	0.7104	0.9490
0.3500	0.3378	64.3	1.0223	0.7413	0.9297
0.4000	0.4026	64.3	1.0209	0.7720	0.9073
0.4500	0.4693	64.3	1.0239	0.8024	0.8818
0.5000	0.5366	64.3	1.0317	0.8319	0.8534
0.5500	0.6030	64.3	1.0443	0.8603	0.8223
0.6000	0.6671	64.3	1.0620	0.8872	0.7888
0.7000	0.7835	64.3	1.1114	0.9345	0.7160
0.8000	0.8783	64.3	1.1768	0.9707	0.6390
0.9000	0.9497	64.3	1.2523	0.9929	0.5623
0.9500	0.9772	64.3	1.2917	0.9983	0.5260

Appendix 10 Vapour pressure equations.

The vapour pressure equations and fugacity equations used in this work are reported together with the relevant constants used for each pure component. All temperatures are given in K. Pressures for three parameter Antoine equation and Harlacher equation given in mmHg. Pressures for six parameter Antoine equation and Fugacity equation given in bar

Three parameter Antoine Equation

$$\ln P^{sat} = C_1 + C_2 / (T+C_3)$$

Table A.10.1 constants for three parameter Antoine equation.

Component	C_1	C_2	C_3
Water	18.3036	3,816.44	-46.13
Acetic Acid	16.808	3,405.57	-56.34
Cyclohexane	756.56	-1,661.2	0

Six parameter Antoine Equation

$$\ln P^{sat} = C_1 + C_2 / (T+C_6) + C_3T + C_4\ln T + C_5T^2$$

Table A.10.2 constants for six parameter Antoine equation.

Component	C_1	C_2	C_3	C_4	C_5	C_6
Water	70.4347	-7,362.6981		0.007		-9
Cyclohexane	98.585	-6,943.3635		0.0153		-14.372
Ethanol	123.912	-8,754.0896		0.0202		-18.1

Five parameter fugacity Equation

$$\ln f_i^{OL} = C_1 + C_2 / T + C_3T + C_4\ln T + C_5T^2$$

Table A.10.3 constants for five parameter fugacity equation.

Component	C_1	C_2	C_3	C_4	C_5
Acetone	$-2.3066*10^{2}$	$6.8603*10^{2}$	$-1.4358*10^{-1}$	$4.6384*10^{1}$	$6.3961*10^{-5}$
Chloroform	$1.7424*10^{2}$	$-8.14*10^{3}$	$6.5975*10^{-2}$	$-2.9011*10^{1}$	$-3.0001*10^{-5}$

Four parameter Harlacher Equation

$$\ln P^{sat} = C_1 + C_2 / T + C_3 \ln T + C_4 * P^{sat} / T^2$$

Table A.10.4 constants for four parameter Harlacher equation.

Component	C_1	C_2	C_3	C_4
Acetic Acid	57.834	-6,841.98	-5.647	3.44
Water	55.336	-6,869.5	-5.115	1.05

Appendix 11 Parameters for liquid phase activity coefficients deduced from consistency test data.

Table A.11.1 gives the parameters derived as part of the consistency test for the cyclohexane-ethanol data sets. Parameters are provided for Wilson two parameter equation, UNIQUAC two parameter equation, Van Laar two parameter equation, Margules two parameter equation and NRTL three parameter equation.

Table A.11.2 gives the parameters derived as part of the consistency test for the acetone-chloroform data sets. Parameters are provided for Wilson two parameter equation, UNIQUAC two parameter equation, Margules two parameter equation and NRTL three parameter equation. Values are not provided for Van Laar two parameter equation as problems were encountered with this fit which would not converge.

Table A.11.3 gives the parameters derived as part of the consistency test, using the Lshark program for the Acetic acid water data sets. Parameters are provided for Wilson two parameter equation, Redlich-Kister four parameter equation and NRTL three parameter equation. The values quoted are those obtained form the best fit consistency test for each activity coefficient model.

TABLE A .11.1

Calculated constants for activity coefficient models for Cyclohexane-Ethanol data sets

Data Set	Wilson (2-para)		Van Laar (2-para)		Margules (2-para)		UNIQUAC (2-para)		NRTL (3-para)		
	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_3
1 atm	2,112.8	333.3	2.5	1.73	2.41	1.7	-125.0	1,388	736.54	1,382.87	0.44
2 bar	1,877.7	407.6	2.3	1.78	2.26	1.77	-125.8	1,283	823.3	1,281.45	0.44
4 bar	1,892.1	298.73	2.05	1.68	2.01	1.71	-144.0	1,237	773.52	1,220.64	0.44
6 bar	1,597.2	318.91	1.79	1.64	1.69	1.57	-154.0	1,085	781.39	1,017.3	0.44
8 bar	1,413.5	357.59	1.59	1.64	1.6	1.64	-158.0	1,008	826.88	859.79	0.44
11 bar	1,447.6	209.33	1.37	1.37	1.52	1.48	-180.0	875	714.95	867.59	0.44
90.9 C	2,129.1	306.8	2.23	1.7	2.13	1.73	-132.6	1,377	778.41	1,369.64	0.44
138.2 C	1,448.7	431.94	1.69	1.62	1.68	1.63	-170.1	935.9	859.45	903.56	0.4291

TABLE A.11.2

Calculated constants for activity coefficient models for Acetone-Chloroform data sets

Data Set	Wilson (2-para)		Margules (2-para)		UNIQUAC (2-para)		NRTL (3-para)		
	c_1	c_2	c_1	c_2	c_1	c_2	c_1	c_2	c_3
1 atm	-68.16	-343.5	-0.72	-0.63	-194.85	11.77	-363.05	-55.38	0.3066
63.4 C	85.19	-443.47	-0.72	-0.63	-295.88	151.74	-569.13	239.13	0.3066

TABLE A.11.3

Calculated constants for activity coefficient models for Acetic Acid-water data sets

Data Set	Wilson (2-para)		Redlich-Kister (4-para)				NRTL (3-para)		
	c_1	c_2	c_1	c_2	c_3	c_4	c_1	c_2	c_3
O'Donnell data	200	400	257.85	-27.29	135.58	-0.325	51.14	1,416.3	2.249
New atmospheric still data	355.145	299.3	-16.018	21.175	51.194	0.07	207.35	-44.1	1.764
Moderate pressure still data	182.89	324.32	38.59	0.0033	-0.0352	0.0352	242.96	1.764	-0.0836

Appendix 12 Operating instructions for the Atmospheric pressure still.

The equilibrium still is operated using the pressure control system shown in figure A.12.1.

1) 125ml of one of the lower boiling pure component is charged to the still. It is fed into the still via the rotolex joint above the liquid return guard condenser.

2) The vacuum is applied to the still via the vacuum system figure A.12.1 and controlled to give the required pressure via the Fairchild valve V1. A nitrogen balance of 5psi is applied to the Fairchild valve so that any balance gas admitted to the still is inert nitrogen.

3) The magnetic stirrer in the liquid return line is switched on and run continuously .

4) *The main reboiler is switched on and the controlling* variac set to 50% full scale to warm up the still contents. Fine adjustment of the reboiler settings is made as the still reaches the boiling point of the mixture to give a constant vapour overflow from the vapour receiver whilst maintaining the liquid level in the heated portion of the liquid disengaging cup.

5) The vapour line tracing wire is supplied with 15 volts DC to maintain the vapour line at 1°C above the mixture boiling point.

6) The vapour receiver is agitated every fifteen minutes to mix the sample and readings are taken at this interval.

7) The still is maintained at constant temperature for at least 1.5 hours before it is deemed to have reached equilibrium.

8) If the apparatus is run under vacuum, the vacuum is released rapidly via the Fairchild valve V1 quenching the boiling action of the still and preserving the vapour and liquid samples.

9) The vapour and liquid samples are drawn off through valves V2 and V3 in to ice cooled vials. The first 2 mls of each sample are discarded to account for dead space in the sample line.

10) The still mixture composition is changed by with drawing a known amount from the still via drain valve V3 and adding a corresponding amount of the higher boiling component to the still .The procedure is then repeated from step 2

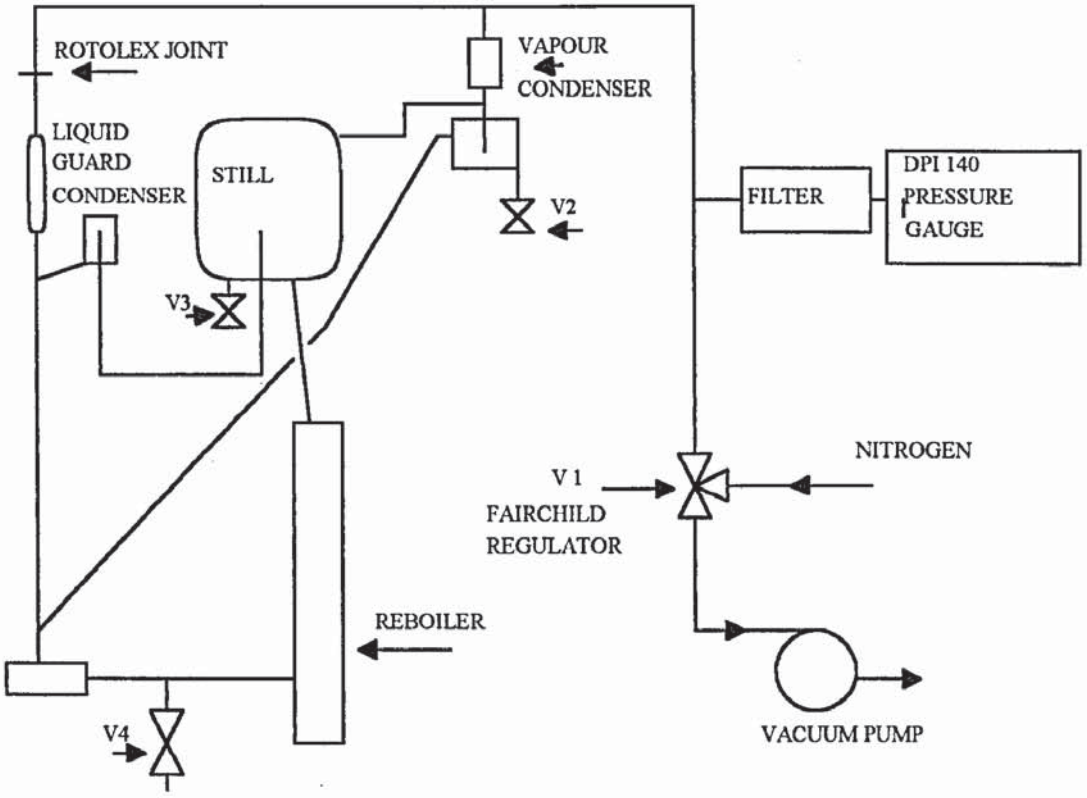

Figure A12.1 Flow diagram low pressure apparatus with pressure control system

Appendix 13 Operating instructions for the moderate pressure still.

The equilibrium still is operated using the pressure control system shown in figure 5.7 All valves referred to in these operating instructions are detailed in figures 5.6 and 5.7

1) Pressure vessel heaters at the top and middle of the pressure bomb are switched on and set to 10°C below the boiling point of the lower boiling component of the test mixture at the desired pressure to preheat the pressure vessel. The tape heater on the vapour line is set to 10% which is sufficient to maintain it at 1°C above the mixture boiling point

2) Close ALL valves before commencing operations.

3) Pressurising the apparatus. If the apparatus is to be run below three bar pressure open valves V3 and V1. If the apparatus is to be run above 3 bar open valve V1 only and disconnect the Druck DPI 140 gauge from the pressure system. The pressure system should be blanked off behind valve V3. Use the DPI500 Pressure controller to raise the apparatus pressure to the desired pressure, and match it to the balance pressure of the dead weight tester.

4) Cooling water to condensers is switched on.

5) Filling the apparatus. 225ml of feed is charged to the apparatus via the 50 ml feed vessel above the condenser as four aliquots of 50ml and one of 25ml. Break Swagelok joint above V7 CAREFULLY. Open V7 and fill feed vessel. Close V7 and reconnect Swagelok joint. Open in sequence V6, V7 and V8, allow contents of feed vessel to drain in to the liquid receiver. When no more liquid is seen to drain into the receiver close valves, V6, V7 and V8. Slowly break open the Swagelok joint above V7 and allow line to vent between valves V6 and V7. Open V7 SLOWLY and vent feed vessel. Repeat filling operation until total charge has been transferred to still

6) Open valves V12, V13, V14, V15, V16 and V17

7) Switch on the two recirculation pumps. Set main recirculation pump to 5 volts and the liquid sample circulation pump to 15 volts

8) Set reboiler to 50% and allow vapour flowrate to bring the apparatus up to the boiling point. Refine reboiler setting to give steady vapour flowrate to allow 1" of condensing liquid on the cold finger condenser. Increase the pressure vessel heaters, setpoints to match the measured boiling point of the mixture.

9) The boiling point is monitored for the next 2.5 hours using the Omega Digital temperature reader. The NPL resistance bridge is used to take definitive temperature measurements every fifteen minutes for this 2.5 hour period.

10) If an isothermal run is required the pressure has to be adjusted FINELY to maintain a constant temperature. Equilibrium is assumed to have been reached when the temperature remains constant for a period of two hours during which the pressure is not adjusted.

11) Taking a liquid sample. Valve V10 is opened and the first 5mls of liquid are discarded. A sample of 5 to 10 ml is then taken in to a vial cooled in dry ice. Valve 10 is then closed.

12) Taking a vapour sample. Ball Valves V12 and V13 are closed simultaneously. Valve V11 is opened to allow circulation through the still to be maintained. Valves V13, V14, V15 and V16 are then closed. The vapour sample vessel can then be removed and the sample drained in to a vial cooled with dry ice.

13) Changing the still composition, with the vapour sample vessel removed a known volume of mixture can be removed from the still by carefully opening valves V12 and V13 and draining liquid into a receiver. Extra feed of a pure component can be charged from the feed vessel using procedure described in 4.

14) Shut down. ALL heaters are shut off. The Pressure vessel is allowed to cool naturally to under 100°C. The pressure is then released. Pressurising nitrogen is shut off from the Druck DPI500 pressure controller. The pressure is vented slowly by opening Valve V5. The apparatus is then left to cool to ambient temperature. ALL pumps are shut down. Cooling water to condensers is shutoff.