Prediction of Finite Concentration Behavior from Infinite Dilution Equilibrium Data

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CERTIFICATE

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Abstract

The principle aim of this project is to show if it is possible to use the activities coefficients at infinite dilution to find the parameters of different models.

It was suggested two modern methods for calculating the activities coefficients at infinite dilution (γ^{∞}), MOSCED method (modified separation of cohesive energy density) and SPACE method (Solvatochromic Parameters for Activity Coefficient Estimation). The two equations are applied to 18 systems and SPACE equation gives better results than MOSCED equation.

This project presents the evaluation of the uses of activities coefficients at infinite dilution, γ^{∞}, to calculate the parameters of different equations: Wilson, NRTL and UNIQUAC. One of the uses is azeotropic calculation where it is applied for 10 different binary systems from the experimental γ^{∞} and the results when compared with the experimental data for azeotrope at the same temperature show as nearly as good if using the actual parameters of the equations. The other use is the calculation of Vapor Liquid Equilibrium data where it applied for 13 different binary systems (194 points) from the experimental γ^{∞} and the results also show as high accuracy as if using the actual parameters of the equations. From these calculations UNIQUAC equation gives the highest accuracy than the other equations.

In the system that only one γ^{∞} is available one parameter equation is used for Wilson, NRTL and UNIQUAC equation which it gives result closer accuracy to the two parameters equation.

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Nomenclature

$\hat{a}_i$	Activity of component *i*	
γ_i	Activity coefficient	
$\gamma^{\infty}{}_{i}$	Activity coefficient at infinite dilution component *i*	
γ_i^{az}	Activity coefficient at azeotrope of component i	
ΔH_v	Enthalpy of vaporization	J/mol
$\varepsilon_{11}, \varepsilon_{21}$	Energies of interaction	J/mol
$\hat{f}_i$	Partial molar fugacity of component *i*	
f_i^o	Fugacity of pure component *i*	
$\hat{\Phi}_i^V$	Partial molar fugacity coefficient	m^2 / N
$\overline{G}_i$	Partial molar excess Gibbs free energy	J/mol
G_m^c	Configurational term	J/mol
G_m^r	Residual term	J/mol
μ_i^*	Chemical potential of pure *i*	J/mol
n_i	Numbers of moles of component *i*	mole
P	Pressure	bar
P^{sat}	Saturated Pressure	bar
P^{az}	Azeotropic Pressure	bar
R	Gas constant (8.314)	J/mol K
T	Temperature	K

V_i	partial molar volume of species i	cm^3/ mole
λ_{ij}	Wilson parameter, energy parameter	KJ/mol
g_{ij}	NRTL parameter, energy parameter	KJ/mol
α_{12}	NRTL parameter, non randomness	
u_{ij}	UNIQUAC parameter, energy parameter	KJ/mol
z	UNIQUAC parameter	
x_i	Mole fraction in the liquid phase	
x_{11}, x_{12}	local compositions	
x_i^{az}	Azeotropic composition of component i	
y_i	Mole fraction in the gas phase	
z_i	Local volume fraction of species i	

Chapter One

Introduction

Activities coefficients at infinite dilution γ^{∞} have many uses, some of them: calculating the Vapor Liquid Equilibrium for any mixture, finding the azeotrope composition and pressure and the estimation of mutual solubilities. These calculations are carried out by finding the two adjustable constants of any desired expression for G^E (Wilson, NRTL and UNIQUAC equations).

Wilson equation has two adjustable constants λ_{12} and λ_{21} (energy parameters) where they can be found from the γ^{∞} by solving the equations for the two component simultaneously. But NRTL or UNIQUAC equations have three parameters. The parameters of NRTL equation are τ_{12}, τ_{21} and α_{12} where α_{12} is related to the non randomness in the mixture and the other are energy parameters. The UNIQUAC equation contains three parameters, u_{12} and u_{21} are adjustable binary energy parameters and the third parameter is co-ordination number z.

There are many methods for calculating the constants of the above equations some of them from Vapor Liquid Equilibrium or from Liquid - Liquid Equilibrium or from solubility. These methods are tedious and long methods. The parameters for activity coefficient equations (Wilson, NRTL and UNIQUAC) for most binary mixtures are not available in the literature.

However there is another method to calculate these constants and this is from the activity coefficient at infinite dilution γ^{∞}.

Several methods were developed for the measurement of activities coefficients at infinite dilution (γ^{∞}). The most important methods are: gas-liquid chromatography (GLC), non-steady-state gas-liquid chromatography, differential ebulliometry, static methods and the dilutor method. The simple experimental method for rapid determination of activity coefficients at infinite dilution is based on gas-liquid chromatography.

The principle aim of this project is to show if it is possible to use the activities coefficients at infinite dilution to find the parameters of different models which is not easy to find these parameters from other way but by using activities coefficients at infinite dilution it is easy, because these can be find from simple experimental methods. The other aim is to evaluate the uses of the activities coefficients at infinite dilution (γ^{∞}) and the methods that can be used and compare between them.

Chapter Two

Theory and Literature Review

(2-1) Activity and Activity Coefficients [1]

The activity of component *i* at some temperature, pressure, and composition is the ratio of the partial molar fugacity of component *i* at these conditions to the fugacity of pure component *i* at the same condition of temperature and pressure:

$$\widehat{a}_i(T,P,x) = \frac{\widehat{f}_i(T,P,x)}{f_i^o(T,P)} \qquad (2\text{-}1.1)$$

The activity coefficient γ_i is the ratio of the activity of *i* to some convenient measure of the concentration of *i* which is usually taken to be the mole fraction:

$$\gamma_i \equiv \frac{\widehat{a}_i}{x_i} \qquad (2\text{-}1.2)$$

The relation between partial molar excess Gibbs free energy and activity coefficient is obtained by first recalling the definition of fugacity. At constant temperature and pressure, for a component *i* in solution,

$$\overline{G}_{i(real)} - \overline{G}_{i(ideal)\,i} = \text{RT}\ [\ln\ \hat{f}_{i\,(\text{real})} - \ln f_{i(\text{ideal})}] \qquad (2\text{-}1.3)$$

If the partial molar excess function $\overline{G}_i^{\,E}$ at a constant T, P and n_i is introduced as:

$$\overline{G}_i^{\,E} = \overline{G}_{i(real)} - \overline{G}_{i(ideal)} \qquad (2\text{-}1.4)$$

Substitution then gives

$$\overline{G}_i^{\,E} = \text{RT}\ \ln\ \frac{\hat{f}_{i(real)}}{f_{i(ideal)}} \qquad (2\text{-}1.5)$$

From eq (2-1.1) and (2-1.2)

$$\hat{f}_i = \gamma_i\, x_i f_i^o \qquad (2\text{-}1.6)$$

Since

$$\hat{f}_{i\,(\text{ideal})} = x_i f_i^o \qquad (2\text{-}1.7)$$

Where $\hat{f}_i$ is partial molar of fugacity of component *i*.

Substitution of Eq. (2-1.6) and Eq. (2-1.7) into Eq. (2-1.5) gives the important and useful result:

$$\overline{G}_i^{\,E} = \text{RT}\ \ln \gamma_i \qquad (2\text{-}1.8)$$

And for multi component system:

$$\overline{G}_i^{\,E} = RT\sum_i x_i \ln \gamma_i \qquad (2\text{-}1.9)$$

(2-2) Activity Coefficients; Gibbs-Duhem Equation and Excess Gibbs Free Energy [2]

The utility of the Gibbs-Duhem equation is best realized through the concept of excess Gibbs free energy, i.e., the observed Gibbs energy of a mixture above and beyond what it would be for an ideal solution at the same temperature, pressure, and composition. By definition, an ideal solution is one where all $\gamma_i = 1$. The *total* excess Gibbs free energy G^E for a binary solution, containing $n1$ moles of component 1 and n_2 moles of component 2, is defined by

$$G^E = \mathrm{RT}\,(n_1 \ln \gamma_1 + n_2 \ln \gamma_2) \qquad (2\text{-}2.1)$$

Equation (2-2.1) gives G^E as a function of both γ_1 and γ_2. Upon applying the Gibbs-Duhem equation, the *individual* activity coefficients γ_1 or γ_2 can be related to G^E by differentiation

$$\mathrm{RT1n}\,\gamma_1 = \left(\frac{\partial G^E}{\partial n_1}\right)_{T,P,n_2} \qquad (2\text{-}2.2)$$

$$\mathrm{RT1n}\,\gamma_2 = \left(\frac{\partial G^E}{\partial n_2}\right)_{T,P,n_1} \qquad (2\text{-}2.3)$$

Equations (2-2.1) to (2-2.3) are useful because they enable us to interpolate and extrapolate limited data with respect to composition. To do so, first some mathematical expression for G^E as a function of composition must be adopted. Second, the numerical values of the constants in that expression from the limited data be fixed; these constants are independent of x, but they usually depend on temperature. Third, activity coefficients at any desired composition are calculated by differentiation, as indicated by Eqs. (2-2.2) and (2-2.3).

To illustrate, consider a simple binary mixture. Suppose that activity coefficients for a binary mixture over the entire composition range are needed at a fixed temperature T. If experimental data are available for only one composition, say $x_1=x_2=\frac{1}{2}$. From that one datum $\gamma_1(x_1 = \frac{1}{2})$ and $\gamma_2\ (x_2 = \frac{1}{2})$ are calculated; for simplicity, it is assume symmetrical behavior $\gamma_1\ (x_1 = \frac{1}{2}) = \gamma_2\ (x_2 = \frac{1}{2})$.

An expression relating G^E to the composition must be adopted which is subject to the conditions that at fixed composition G^E is proportional to $n_1 + n_2$ and that $G^E = 0$ when $x_1 = 0$ or $x_2 = 0$. The simplest expression that can be constructed is

$$G^E = (n_1 + n_2)\, g^E = (n_1 + n_2)\, A\, x_1\, x_2 \qquad (2\text{-}2.4)$$

Where g^E is the excess Gibbs free energy per mole of mixture and A is a constant depending on temperature. The mole fraction x is simply related to mole number n by

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad (2\text{-}2.5)$$

$$x_2 = \frac{n_2}{n_1 + n_2} \qquad (2\text{-}2.6)$$

The constant A is found from substituting Eq. (2-2.4) into Eq. (2-2.1) and using the experimentally determined γ_1 and γ_2 at the composition midpoint:

$$A = \frac{RT}{(\frac{1}{2})(\frac{1}{2})}[\tfrac{1}{2} \ln \gamma_1 (x_1 = \tfrac{1}{2}) + \tfrac{1}{2} \ln \gamma_2 (x_2 = \tfrac{1}{2})] \qquad (2\text{-}2.7)$$

Upon differentiating Eq. (2-2.4) as indicated by Eqs. (2-2.2) and (2-2.3):

$$RT \ln \gamma_1 = A\, x_2^2 \qquad (2\text{-}2.8)$$

$$RT \ln \gamma_2 = A\, x_1^2 \qquad (2\text{-}2.9)$$

With these relations activity coefficients γ_1 and γ_2 can be calculated at any desired x even though experimental data were obtained only at one point, namely, $x_1 = x_2 = \frac{1}{2}$

This simplified example explains how the concept of excess function, coupled with the Gibbs-Duhem equation, can be used to interpolate or extrapolate experimental data with respect to composition. Unfortunately, the Gibbs-Duhem equation tells nothing about interpolating or extrapolating such data with respect to temperature or pressure.

Equations (2-2.1) to (2-2.3) indicate the intimate relation between activity coefficients and excess Gibbs free energy G^E. Many expressions relating g^E (per mole of mixture) to composition have been proposed, and a few are given below. All these expressions contain adjustable parameters which, at least in principle, depend on temperature. That dependence may in some cases be neglected, especially if the temperature interval is not large. In practice, the number of adjustable constants per binary is typically two or three; the larger the number of constants, the better the representation of the data but, at the same time, the larger the number of reliable experimental data points required to determine the constants. Extensive and highly accurate experimental data are required to justify more than three empirical constants for a binary mixture at a fixed temperature.

For many moderately nonideal binary mixtures, all equations for g^E containing two (or more) binary parameters give good results; there is little reason to choose one over another except that the older ones (van Laar) are mathematically easier to handle than the newer ones (Wilson, NRTL, UNIQUAC). For strongly nonideal binary mixtures, e.g., solutions of alcohols with hydrocarbons, the equation of Wilson is probably the most useful because, unlike the NRTL equation, it contains only two adjustable parameters and it is mathematically simpler than the UNIQUAC equation. For such mixtures, the van Laar equation is likely to represent the data with significantly less success, especially in the region dilute with respect to alcohol, where the Wilson equation is particularly suitable.

The Wilson equation is not applicable to a mixture which exhibits a miscibility gap; it is inherently unable, even qualitatively, to account for phase splitting. Nevertheless, Wilson's equation may be useful even for those mixtures where miscibility is incomplete provided attention is confined to the one-phase region.

Unlike Wilson's equation, the NRTL and UNIQUAC equations are applicable to *both* vapor-liquid and liquid-liquid equilibria. Therefore, mutual solubility data can be used to determine NRTL or UNIQUAC parameters but not Wilson parameters. While UNIQUAC is mathematically more complex than NRTL, it has three advantages: (1) it has only two (rather than three) adjustable parameters, (2) UNIQUAC's parameters often have a smaller dependence on temperature, and (3) because the primary concentration variable is a surface fraction (rather than mole fraction), UNIQUAC is applicable to solutions containing small or large molecules, including polymers.

(2-3) The Uses of Activity Coefficient at Infinite Dilution

Activity coefficients at infinite dilution γ^{∞} are useful for calculating the parameters needed in an expression for the excess Gibbs energy G^E. In a binary mixture, experimental data are available for infinite-dilution activity coefficients $\gamma^{\infty}{}_1$and $\gamma^{\infty}{}_2$. These can be used to evaluate two adjustable constants in any desired expression for G^E. For example: Wilson equation, NRTL equation and UNIQUAC equation.

Relatively simple experimental methods have been developed for rapid determination of activity coefficients at infinite dilution. These are based on gas-liquid chromatography. The activity coefficients at infinite dilution γ^{∞} are important for:

- characterizing the behavior of liquid mixtures
- fitting g^E-model parameters (e.g. Margules, van Laar, Wilson, NRTL, UNIQUAC)
- predicting the existence of an azeotrope
- the estimation of mutual solubilities
- providing incisive information for the statistical thermodynamicist (no solute-solute interactions)
- analytical chromatographers
- screening solvents for extraction and extractive distillation processes
- the calculation of limiting separation factors necessary for the reliable design of distillation processes
- the calculation of Henry constants and partition coefficients
- the development of predictive methods (mod. UNIFAC)

2-4 Activity Coefficient Models

In order to represent activity coefficients as a function of temperature and composition at constant pressure, some kind of thermodynamic model is required. Typical activity-coefficient models contain parameters that are fitted to experimental data on binary mixtures. The most useful models contain semi-theoretical expressions which permit the prediction of activity coefficients for both binary and multi-component systems over a range of temperatures while requiring only experimental input from the binary sub-systems at one temperature [3].

The modern development of activity-coefficient models began with the work of Wilson, published in 1964 [4], in which he introduced the "local composition" model. Later developments include the Non-Random Two-Liquid model (NRTL) of Renon [5, 6], and the UNIQUAC equations.

2-4-1 Wilson Model

The model proposed by Wilson [4] in 1964 is based on the concept of *local composition* and leads to an expression for the Gibbs free energy from which the activity coefficients can be obtained. Wilson recognized that, in a mixture with specific interactions, the distribution of molecules is not purely random and that non-ideal mixing is associated with this fact. Consider a binary mixture of components 1 and 2 with bulk mole fractions x_1 and x_2. The composition in the immediate vicinity of a molecule of species 1 will not usually be the same as the mean bulk composition. Instead, Wilson suggested that the *local* compositions x_{11} and x_{21} of components 1 and 2 around a molecule of species 1 are given by Boltzmann-weighted averages of the bulk mole fractions. Thus

$$\frac{x_{11}}{x_{21}} = \frac{x_1 \exp(-\varepsilon_{11}/RT)}{x_2 \exp(-\varepsilon_{21}/RT)} = \frac{x_1}{x_2}\exp(\lambda_{12}/RT) \qquad (2\text{-}4.1)$$

where ε_{11} and ε_{21} are energies of interaction defined in a manner similar to the attractive part of the van der Waals potential and $\lambda_{12} = \varepsilon_{21} - \varepsilon_{11}$. As one might expect, the compositional ordering of the fluid is determined not by the absolute magnitude of the molecular interactions but by the difference between the like and unlike interactions.

Eq.(2-4.1) is next used to evaluate the local volume fraction, z_1, of species 1 around itself, with the result

$$z_1 = \frac{x_{11}V_1}{x_{11}V_1 + x_{21}V_2} = \frac{x_1}{x_1 + \Lambda_{12}x_2} \qquad (2\text{-}4.2)$$

where:

$$\Lambda_{12} = V_{12}\exp\left(-\frac{\lambda_{12}}{RT}\right) \quad \text{and} \quad V_{12} = \left(\frac{V_2}{V_1}\right) \qquad (2\text{-}4.3)$$

Here, V_1 and V_2 are respectively the partial molar volumes of species 1 and 2 in the liquid mixture.

In a similar manner, the local volume fraction z_2 occupied by molecules of type 2 around a molecule of the same species is found to be

$$z_2 = \frac{x_{22}V_2}{x_{22}V_2 + x_{12}V_1} = \frac{x_2}{x_{12} + \Lambda_{21}x_1} \qquad (2\text{-}4.4)$$

where:

$$\Lambda_{21} = V_{21}\exp\left(-\frac{\lambda_{21}}{RT}\right) \qquad \text{and} \qquad V_{21} = \left(\frac{V_1}{V_2}\right) \tag{2-4.5}$$

It should be noted that Λ_{ij} cannot be negative, that $\Lambda_{11} = \Lambda_{22} = 1$, and that, in general, $\Lambda_{12} \neq \Lambda_{21}$.

In order to obtain an expression for the Gibbs free energy G_m of the mixture, Wilson employed the Flory-Huggins theory [7] according to which

$$G_m = \sum_{i=1}^{n} x_i(\mu_i^* + RT\ln z_i) \tag{2-4.6}$$

Where μ_i^* is the chemical potential of pure *i*. Since the molar Gibbs free energy of an ideal mixture is given by

$$G_m^{id} = \sum_{i=1}^{n} x_i(\mu_i^* + RT\ln x_i) \tag{2-4.7}$$

it follows that the excess molar Gibbs free energy of the mixture $G_m^E = G_m - G_m^{id}$,is given by

$$G_m^E / RT = \sum_{i=1}^{n} x_i \ln(z_i / x_i) \tag{2-4.8}$$

Combining Eqs.(2-4.2) and (2-4.4) with Eq.(2-4.8) for a binary mixture, one obtains

$$G_m^E / RT = -x_1\ln(x_1 + x_2\Lambda_{12}) - x_2\ln(x_1\Lambda_{21} + x_2) \tag{2-4.9}$$

and, applying the thermodynamic identity

$$\mu_i^E = \mathrm{RT} \ln \gamma_i = G_m^E + (1 - x_i)\left(\frac{\partial G_m^E}{\partial x_i}\right)_{T,P} \qquad (2\text{-}4.10)$$

the activity coefficients are found to be:

$$\left.\begin{aligned} \mathrm{Ln}\,\gamma_1 &= 1 - \ln (x_1 + x_2 \Lambda_{12}) - \frac{x_1}{x_1 + x_2\Lambda_{12}} - \frac{x_2\Lambda_{21}}{x_1\Lambda_{21} + x_2} \\ \mathrm{Ln}\,\gamma_2 &= 1 - \ln (x_1 \Lambda_{21} + x_2) - \frac{x_1\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{x_2}{x_1\Lambda_{21} + x_2} \end{aligned}\right\} \qquad (2\text{-}4.11)$$

Generalized expressions for multi-component mixtures are given in Table 2-1 and may be used to obtain the activity coefficient of each component *i* in a mixture of *n* components provided that all the binary parameters λ_{ij} and the partial molar volumes are known. No additional parameters are required. Typically, partial molar volumes are approximated by the molar volume of the pure liquids and, provided that this is done consistently in both parameter determination and application, the results are generally satisfactory.

The binary parameters λ_{12} and λ_{21} are usually determined by fitting either experimentally determined excess Gibbs free energies to Eq.(2-4.9) or experimentally determined activity coefficients to Eqs.(2-4.11). In either case Eq.(2-4.13) is used to relate Λ_{ij} and Λ_{ji}. Usually, results over a range of liquid compositions are employed and the optimum parameters found by a non-linear regression analysis. However, it is possible, though probably less reliable, to determine the parameters from a single pair of activity coefficients, for example those determined at an azeotrope, or from the values of γ_1 and γ_2, in the limits of infinite dilution.

Table 2-1 The Wilson Model, 1964 [4]

$$\text{Ln}\gamma_i = 1\text{-ln}\left(\sum_{j=1}^{n} x_j \Lambda_{ij}\right) - \sum_{k=1}^{n} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{n} x_j \Lambda_{kj}} \qquad (2\text{-}4.12)$$

Where $\Lambda_{ij} = V_{ij} \exp\left(-\frac{\lambda_{ij}}{RT}\right)$ $\qquad V_{ij} = \left(\frac{V_j}{V_i}\right)$ (2-4.13)

and $\Lambda_{ii} = \Lambda_{jj} = 1$ $\qquad \Lambda_{ij} \neq \Lambda_{ji}$

2-4-2 Non-Random Two-Liquid (NRTL) Model

The NRTL model was developed by Renon and Prausnitz [22, 23] in an attempt to overcome the inadequacy of the Wilson equations in describing liquid-liquid equilibria. The NRTL model contains three parameters per binary interaction, compared with the two parameters of the Wilson model, but is based on a similar local composition treatment. According to the NRTL model, the excess Gibbs free energy is correlated by

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right) \qquad (2\text{-}4.14)$$

where $\tau_{12} = \frac{g_{12}}{RT}$ $\qquad \tau_{21} = \frac{g_{21}}{RT}$ (2-4.15)

and $\ln G_{12} = -\alpha_{12}\tau_{12}$ $\qquad \ln G_{21} = -\alpha_{12}\tau_{21}$ (2-4.16)

Here g_{ij} and g_{ji} denote energy parameters, while α_{12} is best viewed as a purely empirical parameter and α_{12} is related to the nonrandom ness in the mixture; when α_{12} is zero, the mixture is completely random; all three are supposed independent of temperature. The NRTL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from about 0.20 to 0.47; when experimental data are scarce, the value of α_{12} can often be set arbitrarily; a typical choice is $\alpha_{12} = 0.3$ The activity coefficients determined for a binary system from Eq.(2-4.14) are:

$$\left.\begin{aligned} \mathrm{Ln}\,\gamma_1 &= x_2^2\left(\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{\left(x_2 + x_1 G_{12}\right)^2}\right) \\ \mathrm{Ln}\,\gamma_2 &= x_1^2\left(\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{\left(x_1 + x_2 G_{21}\right)^2}\right) \end{aligned}\right\} \qquad (2\text{-}4.17)$$

In Table (2-2) the corresponding expressions for multi-component systems are given.

Table 2-2 The NRTL Model [5]

$$\mathrm{Ln}\,\gamma_i = \frac{\sum_{k=1}^{n}\tau_{ki}x_i G_{ki}}{\sum_{k=1}^{n}x_k G_{ki}} + \sum_{j=1}^{n}\frac{x_j G_{ij}}{\sum_{k=1}^{n}x_k G_{kj}}\left[\tau_{ij} - \frac{\sum_{k=1}^{n}x_k \tau_{ji} G_{kj}}{\sum_{k=1}^{n}x_k G_{kj}}\right] \qquad (2\text{-}4.18)$$

where $G_{ij} = \exp(\alpha_{ij}\,\tau_{ij})$ (2-4.19)

$\tau_{ii} = \tau_{jj} = 0$ and $G_{ii} = G_{jj} = 1$ (2-4.20)

and $\tau_{ij} = g_{ij}/RT$ (2-4.21)

2-4-3 The UNIQUAC Equations

The UNIQUAC (Universal Quasi-Chemical) equations were developed by Abrams and Prausnitz [8] and are based on a semi-theoretical approach to the mixture problem that includes a local composition model. It was also recognized that the non-ideality of liquid mixtures has contributions not only from specific interactions but also from the differences in the size and shape of the molecules. Consequently, in the UNIQUAC model, the Gibbs free energy of the mixture is correlated by the sum of two separate terms,

$$G_m^E / RT = (\Delta G_m^c + \Delta G_m^r)/RT \qquad (2\text{-}4.22)$$

which comprise:

- a contribution G_m^c, known as the *configurational term,* due to differences in sizes and shapes; and
- a contribution G_m^r known as the *residual term,* due to energetic interactions between the molecules.

Consequently, the logarithm of the activity coefficient for each component also has configurational and residual contributions:

$$\mathrm{Ln}\gamma_i = \ln\gamma_i^c + \ln\gamma_i^r \qquad (2\text{-}4.23)$$

The original formulation of the free energy terms was modified by Andcrsen *et aI.* [9] who arrived at the following expressions for a binary mixture:

$$\Delta G_m^c / RT = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \right) \qquad (2\text{-}4.24)$$

$$\Delta G_m^r / RT = -q_1' x_1 \ln\left[\theta_1' + \theta_2' \tau_{21}\right] - q_2' x_2 \ln(\theta_1' \tau_{12} + \theta_2') \qquad (2\text{-}4.25)$$

The quantities φ_i, θ_i and θ_i' which appear here are pure-substance parameters given by:

$$\varphi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2} \qquad (2\text{-}4.26)$$

$$\theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2} \qquad (2\text{-}4.27)$$

and

$$\theta_i' = \frac{x_i q_i'}{x_1 q_1' + x_2 q_2'} \qquad (2\text{-}4.28)$$

where r_1 is determined by the volume and q_i by the surface area of the molecule both of which may be deduced in principle from crystallographic measurements on the pure solid. These area and volume parameters are however usually obtained by a group contribution method and tables exist [11, 12] which permit values to be determined for a very large selection of molecules. Usually, $q'_i = q_i$ so that $\theta_i' = \theta_i$ but for water and alcohols modifications to q_i' have been made to improve agreement with experimental results. z is a co-ordination number to which the value 10 is usually, but not necessarily[13], assigned. Finally, the model contains two adjustable binary energy parameters u_{12} and u_{21} that enter the residual part of the excess Gibbs free energy through the quantities τ_{12} and τ_{21} which is defined by

$$\tau_{ij} = \exp(-u_{ij}/RT) \tag{2-4.29}$$

The contributions to the activity coefficient of component i which result from this formulation are:

$$\left.\begin{aligned} \ln \gamma_i^c &= \ln\left(\frac{\varphi_i}{x_i}\right) + \frac{z}{2}\ln\left(\frac{\theta i}{\varphi_i}\right) + \varphi_j(l_i - r_i l_j / r_j) \\ \ln \gamma_i^r &= -q_i' \ln(\theta_i' + \theta_j'\tau_{ji}) + \theta_j' q_i'\left(\frac{\tau_{ji}}{\theta_i' + \theta_j'\tau_{ji}} - \frac{\tau_{ij}}{\theta_i'\tau_{ij} + \theta_j'}\right) \end{aligned}\right\} \tag{2-4.30}$$

where

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \tag{2-4.31}$$

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1) \tag{2-4.32}$$

The corresponding results for a multi-component system are given in Table (2-3).The UNIQUAC model is one of the most successful two-parameter models in use today and extensive tabulations of the pure-component and binary parameters are available [14]. Only pure-component and binary parameters are required for application to multi-component systems and the model is useful in VLE problems.

Table 2-3 UNIQUAC Equations [8]

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^r \tag{2-4.33}$$

where $$\ln\gamma_i^c = \ln\left(\frac{\varphi_i}{x_i}\right) + \frac{z}{2}\ln\left(\frac{\theta_i}{\varphi_i}\right) + l_i - \frac{\varphi_i}{x_i}\sum_{j=1}^{n} x_j l_j \tag{2-4.34}$$

$$\ln\gamma_i^r = q'_i\left[1 - \ln\left(\sum_{k=1}^{n}\theta'_k\tau_{ki}\right) - \sum_{j=1}^{n}\frac{\theta'_j\tau_{ij}}{\sum_{k=1}^{n}\theta'_k\tau_{kj}}\right] \tag{2-4.35}$$

and $$\tau_{ij} = \exp\left(-\frac{u_{ij}}{RT}\right), \qquad \tau_{ii} = \tau_{jj} = 1 \tag{2-4.36}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1), \qquad \text{and} \qquad z=10 \tag{2-4.37}$$

$$\varphi_i = \frac{x_i r_i}{\sum_{j=1}^{n} x_j r_j} \qquad \theta_i = \frac{x_i q_i}{\sum_{j=1}^{n} x_j q_j} \qquad \theta'_i = \frac{x_i q'_i}{\sum_{j=1}^{n} x_j q'_j} \tag{2-4.38}$$

2-5 Determination of Model Parameters from Infinite-Dilution Activity Coefficients

When there is insufficient experimental data for the evaluation of model parameters, and new experimental studies are not feasible, one method of estimating the parameters is by analysis of infinite-dilution activity coefficients. These may have been measured for the binary systems of interest and, if they have not, group-contribution estimation schemes are available as a last resort.

The activity coefficient of component i in the limit of infinite dilution ($x_1 \rightarrow 0$) is denoted γ^{∞} and is a function of temperature only at constant pressure. The expressions for the activity coefficients in terms of model parameters become rather simple in the limit of infinite dilution, allowing solutions for the parameters to be obtained easily. Those for the models considered previously are given in table (2-4) [3].

Both parameters of a two-parameter model may be evaluated from the two infinite-dilution activity coefficients. In the case of a three-parameter model, one of the parameters must be constrained to a 'typical' value unless activity coefficients are available over a range of compositions. For example, in the NRTL model one might constrain α_{12} to be 0.2.

Table 2-4 Binary Activity Coefficient Correlations at Infinite Dilution

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Wilson model

$$\left.\begin{aligned} 1 - \ln\gamma_1^{\infty} &= \ln\Lambda_{12} + \Lambda_{21} \\ 1 - \ln\gamma_2^{\infty} &= \ln\Lambda_{21} + \Lambda_{12} \end{aligned}\right\} \qquad (2\text{-}5.1)$$

NRTL model

$$\left.\begin{aligned} \ln\gamma_1^{\infty} &= \tau_{21} + \tau_{12}\exp(-\alpha_{12}\tau_{12}) \\ \ln\gamma_2^{\infty} &= \tau_{12} + \tau_{21}\exp(-\alpha_{12}\tau_{21}) \end{aligned}\right\} \qquad (2\text{-}5.2)$$

UNIQAC model

$$\left.\begin{aligned} \ln\gamma_1^{\infty} &= \ln\left(\frac{r_1}{r_2}\right) + \frac{z}{2}\ln\left(\frac{q_1 r_1}{q_2 r_2}\right) + l_1 - \frac{r_1}{r_2} l_2 - q_1' \ln\tau_{21} + q_1'\left(1 - \tau_{12}\right) \\ \ln\gamma_2^{\infty} &= \ln\left(\frac{r_2}{r_1}\right) + \frac{z}{2}\ln\left(\frac{q_2 r_2}{q_1 r_1}\right) + l_2 - \frac{r_2}{r_1} l_1 - q_2' \ln\tau_{12} + q_2'\left(1 - \tau_{21}\right) \end{aligned}\right\} \qquad (2\text{-}5.3)$$

2-6 One-Parameter Equations

It frequently happens that experimental data for a given binary mixture are so fragmentary that it is impossible to determine two (or three) meaningful binary parameters; limited data can often yield only one significant binary parameter. In that event, it is tempting to use the two-suffix (one-parameter) Margules equation, but this is usually an unsatisfactory procedure because activity coefficients in a real binary mixture are rarely symmetric with respect to mole fraction. In most cases better results are obtained by choosing Wilson, NRTL, or UNIQUAC equation and reducing the number of adjustable parameters through reasonable physical approximations.

To simplify the Wilson equation, first note that

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left(- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \qquad (2\text{-}6.1)$$

where V_i^L is the molar volume of pure liquid *i* and λ_{ij} is an energy parameter characterizing the interaction of molecule *i* with molecule *j*.

The Wilson equation can be reduced to a one-parameter form by assuming that $\lambda_{ij} = \lambda_{ji}$ and that

$$\lambda_{ii} = - \beta \, (\Delta H_{vi} - RT) \qquad (2\text{-}6.2)$$

where β is a proportionality factor and ΔH_{vi} is the enthalpy of vaporization of pure component *i* at *T*. A similar equation is written for λ_{jj}. When β is fixed, the only adjustable binary parameter is λ_{ij}.

Theoretical considerations suggest that $\beta = 2/z$, where z is the coordination number (typically, $z = 10$) this assumption, was used by Wong and Eckert [15] and Schreiber and Eckert [16].

Ladurelh et al. (1975) [17] have suggested $\beta = 2/z$ for component 2, having the smaller molar volume, while for component 1, having the larger molar volume,

$$\beta = \frac{2}{z}\left(\frac{V_2^L}{V_1^L}\right) \tag{2-6.3}$$

This suggestion follows from the notion that a larger molecule has a larger area of interaction; parameters λ_{ii}, λ_{jj}, and λ_{ij} are considered as interaction energies per segment rather than per molecule. In this particular case the unit segment is that corresponding to one molecule of component 2.

Using similar arguments, Bruin and Prausnitz (1971) [18] have shown that it is possible to reduce the number of adjustable binary parameters in the NRTL equation by making a reasonable assumption for α_{12} and by substituting NRTL parameter G_{ii} for Wilson parameter λ_{ii} in Eq. (2-6.2). Bruin gives some correlations for g_{ij}, especially for aqueous systems.

The UNIQUAC equation can be simplified by assuming that

$$u_{11} = \frac{-\Delta U_1}{q_1} \quad \text{and} \quad u_{22} = \frac{-\Delta U_2}{q_2} \tag{2-6.4}$$

and that

$$u_{12} = u_{21} = (u_{11}u_{22})^{1/2}(1-c_{12}) \tag{2-6.5}$$

where, remote from the critical temperature, energy ΔU_i is given very nearly by $\Delta U_i \approx \Delta H_{vi} - RT$. The only adjustable binary parameter is c_{12}, which, for mixtures of nonpolar liquids, is positive and small compared with unity. For some mixtures containing polar components, however, c_{12} is of the order of 0.5; and when the unlike molecules in a mixture are attracted more strongly than like molecules, c_{12} may be negative, e.g., in acetone-chloroform.

Enthalpy of Vaporization of Pure Component

The enthalpy of vaporization ΔH_{vi} is sometimes referred to as the latent heat of vaporization. It is the difference between the enthalpy of the saturated vapor and that of the saturated liquid at the same temperature.

Because molecules in the vapor do not have the energy of attraction than those in the liquid have, energy must be supplied for vaporization to occur. This is the internal energy of vaporization ΔU_v. A widely used correlation between ΔH_i and T_r is the Watson relation [19]:

$$\Delta H_{v2} = \Delta H_{v1}\left(\frac{1-T_{r2}}{1-T_{r1}}\right)^{n} \qquad (2\text{-}6.6)$$

where subscripts 1 and 2 refer to reduced temperatures T_{r1} and T_{r2}. A common choice for n is 0.375.

ΔH_{v1} is for boiling ($\Delta H_{boiling}$) and T_{r1} is T_r boiling and the data are taken from reference [20].

2-7 Application of the Uses of Activity Coefficient at Infinite Dilution

If reliable values of $\gamma^{\infty}{}_{1}$ and $\gamma^{\infty}{}_{2}$ are available, either from direct experiment or from a correlation, it is possible to predict the composition of the azeotrope and vapor-liquid equilibrium and solubility over the entire range of composition.

2-7-1 Azeotrope Calculation

Many binary systems exhibit azeotrope, i.e., a condition in which the composition of a liquid mixture is equal to that of its equilibrium vapor. When the activities coefficients at infinite dilution of a system having azeotrope are known, azeotrope composition and pressure at that temperature can be found. Extensive compilations of azeotrope data are available [21] (Horsley, 1962).

To calculate the azeotrope for any system, first to determine whether or not azeotropic exists at the system temperature. This calculation is facilitated by the definition of a quantity called the relative volatility α_{12} [22]:

$$\alpha_{12} \equiv \frac{y_1/x_1}{y_2/x_2} \tag{2-7.1}$$

this quantity becomes unity at an azeotrope and applying *modified Raoult's law* [22]:

$$y_i\, P = x_i\, \gamma_i\, P_i^{sat} \qquad (2\text{-}7.2)$$

$$\frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \qquad (2\text{-}7.3)$$

Therefore

$$\alpha_{12} = \frac{\gamma_1 p_1^{sat}}{\gamma_2 P_2^{sat}} \qquad (2\text{-}7.4)$$

at the limits $x_1 = 0$ ($\gamma^{\infty}{}_2=1$) and $x_1 = 1$($\gamma^{\infty}{}_1=1$), this quantity is given by:

$$(\alpha_{12})_{x1=0} = \frac{\gamma_1^{\infty} p_1^{sat}}{P_2^{sat}} \qquad (2\text{-}7.5)$$

and

$$(\alpha_{12})_{x1=1} = \frac{p_1^{sat}}{\gamma_2^{\infty} P_2^{sat}} \qquad (2\text{-}7.6)$$

these values are readily calculated from the given information. If one of them is less than 1 and the other is greater than 1, then an azeotrope exists, because α_{12} is a continuous function of x_1 and must then pass through the value of 1.0 at some intermediate composition.

For a binary azeotrope, $x_1 = y_1$ and $x_2 = y_2$ then eq. (2-7.1) is equal to $\alpha_{12} = 1$.

Eq. (2-7.4) at azeotrope becomes:

$$\frac{\gamma_1^{az}}{\gamma_2^{az}} = \frac{P_2^{sat}}{P_1^{sat}} \qquad (2\text{-}7.7)$$

The difference between any equations of activity coefficients γ_1, γ_2

$$\ln \gamma_1 = f_1(x_1, A, B) \tag{2-7.8}$$

$$\ln \gamma_2 = f_2(x_2, A, B) \tag{2-7.9}$$

Gives the general expression:

$$\ln \frac{\gamma_1}{\gamma_2} = f_1(x_1, A, B) - f_2(x_2, A, B) \tag{2-7.10}$$

Thus the azeotropic composition is the value of x_1 (with $x_2 = 1 - x_1$) for which this equation is satisfied when

$$\ln \frac{\gamma_1^{az}}{\gamma_2^{az}} = \ln \frac{P_2^{sat}}{P_1^{sat}} \tag{2-7.11}$$

where P_1^{sat}, P_2^{sat} are known and by trial and error for x_1 using eq. (2-7.10) for any models the azeotrope composition can be found.

For *Wilson models* equation (2-7.10) is equal to

$$\ln \frac{\gamma_1}{\gamma_2} = \ln \frac{x_2 + x_1\Lambda_{21}}{x_1 + x_2\Lambda_{12}} + \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \tag{2-7.12}$$

, for *NRTL models*

$$\ln\frac{\gamma_1}{\gamma_2}=x_2^2\left(\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2+\frac{\tau_{12}G_{12}}{\left(x_2+x_1G_{12}\right)^2}\right)-$$

$$x_1^2\left(\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2+\frac{\tau_{21}G_{21}}{\left(x_1+x_2G_{21}\right)^2}\right) \qquad (2\text{-}7.13)$$

and for *UNIQUAC models*

$$\ln\frac{\gamma_1}{\gamma_2}=\ln\frac{\Phi_1}{x_1}+\frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1}+\Phi_2\left(l_1-\frac{r_1}{r_2}l_2\right)-q_1\ln\left(\theta_1+\theta_2\tau_{21}\right)$$

$$+\theta_{12}q_1\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}}-\frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right)-\ln\frac{\Phi_2}{x_2}-\frac{z}{2}q_2\ln\frac{\theta_2}{\Phi_2}-\Phi_1\left(l_2-\frac{r_2}{r_1}l_1\right)$$

$$+q_2\ln\left(\theta_2+\theta_1\tau_{12}\right)-\theta_{21}q_2\left(\frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}-\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}}\right) \qquad (2\text{-}7.14)$$

From the calculated x_1^{az} with $x_1^{az} = y_1^{az}$ activity coefficient at the azeotrope can be calculated by using any of Wilson, NRTL or UNIQUAC equations at x_1^{az} then the pressure of azeotrope P^{az} can be calculated from this equation:

$$P^{az}=\gamma_1^{az}P_1^{sat} \qquad (2\text{-}7.15)$$

2-7-2 Vapor Liquid Equilibrium

The liquid mixture, at temperature T and pressure P, is in equilibrium with a vapor mixture at the same temperature and pressure. The quantities of interest are the temperature, the pressure, and the compositions of both phases. Given some of these quantities, our task is to calculate the others.

For every component i in the mixture, the condition of thermodynamic equilibrium is given by

$$\hat{f}_i^V = \hat{f}_i^L \qquad (2\text{-}7.16)$$

where $\hat{f}$ = partial molar fugacity

V = vapor

L = liquid

The partial molar fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. In principle any measurement of composition can be used. For the vapor phase, the composition is nearly always expressed by the mole fraction y. To relate $\hat{f}_i^V$ to temperature, pressure, and mole fraction, it is useful to introduce the vapor-phase partial molar fugacity coefficient $\hat{\Phi}_i^V$

$$\hat{\Phi}_i^V = \frac{\hat{f}_i^V}{y_i P} \qquad (2\text{-}7.17)$$

The partial molar fugacity coefficient $\widehat{\Phi}_i^V$ depends on temperature and pressure and, in a multi component mixture, on *all* mole fractions in the vapor phase, not just y_1. The partial molar fugacity of component *i* in the liquid phase is generally calculated by one of two approaches: the equation of state approach or the activity coefficient approach. In the former, the liquid-phase partial molar fugacity coefficient, $\widehat{\Phi}_i^L$ is introduced

$$\widehat{\Phi}_i^L = \frac{\widehat{f}_i^L}{x_i P} \tag{2-7.18}$$

where x_l is the liquid phase mole fraction. Certain equations of state are capable of representing liquid-phase, as well as vapor-phase behavior. In the activity coefficient approach, the partial molar fugacity of component *i* in the liquid phase is related to the composition of that phase through the activity coefficient γ_i. Activity coefficient γ_i is related to x_i and to standard-state partial molar fugacity f_i^o by

$$\gamma_i \equiv \frac{a_i}{x_i} = \frac{\widehat{f}_i^L}{x_i f_i^o} \tag{2-7.19}$$

where a_i is the activity of component i. The standard-state partial molar fugacity f_i^o is the partial molar fugacity of component i at the temperature of the system, i.e., the mixture, and at some arbitrarily chosen pressure and composition. The choice of standard-state pressure and composition is dictated only by convenience, but it is important to bear in mind that the numerical values of γ_i, and a_i, have no meaning unless f_i^o is clearly specified.

The partial molar fugacity of pure liquid *i* at temperature *T* and pressure *P* is given by

$$\hat{f}_i^L(T,P,x_i=1) = P_{vpi}(T)\phi_i^s(T)\exp\int_{P_{vpi}}^{P}\frac{V_i^L(T,P)}{RT}dP \qquad (2\text{-}7.20)$$

where P_{vp} is the vapor pressure and superscript *s* stands for saturation [22]. The partial molar fugacity coefficient ϕ_i^s is calculated from vapor-phase volumetric data for typical non associated fluids at temperatures well below the critical, ϕ_i^s is close to unity.

The molar liquid volume V_i^L is the ratio of the molecular weight to the density, where the latter is expressed in units of mass per unit volume. At a temperature well below the critical, a liquid is nearly incompressible. In that case the effect of pressure on liquid-phase partial molar fugacity is not large unless the pressure is very high or the temperature is very low. The exponential term in Eq. (2-7.20) is called the *Poynting factor*.

Equation (2-7.16) gives the rigorous, fundamental relation for vapor-liquid equilibrium. Substitution of Eqs. (2-7.17), (2-7.18), (2-7.19), and (2-7.20) into Eq. (2-7.16) gives

$$y_i P = x_i \gamma_i P_i^{sat} \mathcal{F}_i \qquad (2\text{-}7.21)$$

where

$$\mathcal{F}_i = \frac{\phi_i^s}{\hat{\phi}_i^V}\exp\int_{P_{vpi}}^{P}\frac{V_i^L(T,P)}{RT}dP \qquad (2\text{-}7.22)$$

In Eq. (2-7.21), both $\widehat{\phi}_i^V$ and γ_i depend on temperature, composition, and pressure. However, remote from critical conditions, and unless the pressure is large, the effect of pressure on γ_i is usually small.

Equation (2-7.21) can be written in this form:

$$y_i P \widehat{\phi}_i^V = x_i \gamma_i P_i^{sat} \phi_i^{sat} \exp \frac{V_i^L (P - P_i^{sat})}{RT} \tag{2-7.23}$$

The molar liquid volume V_i^L is very near to the molar liquid volume at saturation therefore V_i^L can be calculated by using Rackett equation:

$$V_i^{sat} = V_C Z_C^{(1-T_r)^{0.2857}} \tag{2-7.24}$$

By using Peng – Robinson equation of state the partial molar fugacity coefficient at saturated ϕ_i^{sat} and the partial molar fugacity coefficient at vapor phase ϕ_i^V can be calculated.

Peng – Robinson Equation of State

Peng – Robinson equation of state [23] is summarized in the equations below where expressions for the partial molar fugacity coefficients are also given.

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b) + b(V_m - b)} \tag{2-7.25}$$

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)z - \left(AB - B^2 - B^3\right) = 0 \qquad (2\text{-}7.26)$$

where

$$A = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (1-k_{ij})\sqrt{A_i A_j} \qquad (2\text{-}7.27)$$

$$B = \sum_{i=1}^{n} x_i B_i \qquad (2\text{-}7.28)$$

$$a\alpha = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (1-k_{ij})\sqrt{(a_i\alpha_i)(a_j\alpha_j)} \qquad (2\text{-}7.29)$$

$$b = \sum_{i=1}^{n} x_i b_i \qquad (2\text{-}7.30)$$

and $A_i = 0.45724\alpha_i \dfrac{P_{r,i}}{T_{r,i}^2}$ $\qquad B_i = 0.07780\dfrac{P_{r,i}}{T_{r,i}}$ (2-7.31)

$$a_i = 0.45724\frac{(RT_i^c)^2}{P_i^c} \qquad b_i = 0.07780\frac{RT_i^c}{P_i^c} \qquad (2\text{-}7.32)$$

$$\alpha_i = \left[1 + n_i\left(1 - \sqrt{T_{r,i}}\right)\right]^2 \qquad (2\text{-}7.33)$$

$$n_i = 0.37464 + 1.54223\omega_i - 0.26992\omega_i^2 \qquad (2\text{-}7.34)$$

For partial molar fugacity Coefficient

$$\ln\hat{\phi}_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) \qquad (2\text{-}7.35)$$

$$+\frac{A}{2.828B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_{j=1}^{N} x_j (1-k_{ij})\sqrt{(a_i\alpha_i)(a_j\alpha_j)}\right]\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right)$$

Where $k_{ii} = 0$

2-7-3 Calculation of Mutual Solubitities of Liquids from Activity Coefficient at Infinite Dilution

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At a fixed temperature and pressure, by considering a binary system containing two liquid phases at equilibrium. Let ′ (prime) designate one phase and let ″ (double prime) designate the other phase. For component 1 the equation of equilibrium is

$$\hat{f}_1' = \hat{f}_1'' \tag{2-7.36}$$

Since both phases are liquids, it is convenient to use the same standard-state partial molar fugacity for both phases. Equation (2-7.36) can then be rewritten

$$\gamma'_1 x'_1 = \gamma_1'' x_1'' , \tag{2-7.37}$$

where x'_1 and x_1'' are equilibrium mole fractions of component 1 in the two phases. Similarly, for component 2,

$$\gamma'_2 x'_2 = \gamma_2'' x_2'' , \tag{2-7.38}$$

Where x'_2 and x_2'' are equilibrium mole fractions of component 2 in the two phases. For a given binary system at a fixed temperature and pressure, mutual solubilities can be calculated if information concerning activity coefficients is available. Supposing that informations in such form are available

$$G^E = \mathcal{F}(x_1, A, B, \ldots.) \tag{2-7.39}$$

Where G^E**,** the molar excess Gibbs energy, is a function of composition, with parameters *A, B,...* depending only on temperature (and to a lesser extent, on pressure). From Eq. (2-1.8) activity coefficients of both components can be readily obtained. Upon substitution, Eqs. (2-7.37) and (2-7.38) are of the form

$$\mathcal{F}_1(x_1')\, x_1' = \mathcal{F}_1(x_1'')\, x_1'' \qquad (2\text{-}7.40)$$

$$\mathcal{F}_2(x_2')\, x_2' = \mathcal{F}_2(x_2'')\, x_2'' \qquad (2\text{-}7.41)$$

Where the functions $\mathcal{F}_1$ and $\mathcal{F}_2$ are obtain upon differentiating Eq. (2-7.39) as indicated by Eq. (2-1.8). There are two unknowns: x_1' and x_2''.where $x_1' + x_2' = 1$ and $x_1'' + x_2'' = 1$. If phase $'$ is rich in component 1 and phase $''$ is rich in component 2, then x_1' and x_2'' are the two mutual solubilities. These can be found from the two equations of equilibrium, Eqs. (2-7.40) and (2-7.41). For example, suppose using two-suffix Margules equation for the excess Gibbs energy in Eq. (2-7.39).

$$G^E = A\, x_1\, x_2 \qquad (2\text{-}7.42)$$

then there are two equations of equilibrium:

$$\left[\exp\left(\frac{A(1-x_1')^2}{RT}\right)\right]x_1' = \left[\exp\left(\frac{A(1-x_1'')^2}{RT}\right)\right]x_1'' \qquad (2\text{-}7.43)$$

$$\left[\exp\left(\frac{A(x_1')^2}{RT}\right)\right][1-x_1'] = \left[\exp\left(\frac{A(x_1'')^2}{RT}\right)\right][1-x_1''] \qquad (2\text{-}7.44)$$

For a given value of *A/RT,* Eqs. (2-7.43) and (2-7.44) give a solution for x_1' and x_2''. In principle the calculation is simple although the algebra may be tedious, depending on the complexity of the functions $\mathcal{F}_1$ and $\mathcal{F}_2$.

2-8 Activity Coefficients at Infinite Dilution Calculation Theory

There are two methods to calculate the activity coefficients at infinite dilution: MOSCED, stands for Modified Separation of Cohesive Energy Density, and SPACE, stands for Solvatochromic Parameters for Activity Coefficient Estimation.

2-8-1 MOSCED model

A method for estimating activity coefficients at infinite dilution is provided by a modified regular solution theory. MOSCED (modified separation of cohesive energy density) is a model proposed by Thomas and Eckert [24] for predicting limiting activity coefficients (γ^{∞}`s) from pure component parameters only. It is essentially an extension of regular solution theory to polar and associating systems. The extension is based on the assumption that forces contributing to the cohesive energy density are additive. Forces included are dispersion, orientation, induction, and hydrogen bonding. The five parameters associated with these forces are the dispersion parameter λ, the induction parameter q, the polar parameter τ, and the acidity α and basicity β parameters. These modifications affect the magnitudes of the activity coefficients, but they do so in a symmetric way; i.e. both γ_1^{∞} and γ_2^{∞} are affected the same way, contrary to experiment. To account for asymmetry, Thomas and Eckert introduce two more parameters, ψ and ξ, to account for asymmetry effects resulting from differences in polarity and degree of hydrogen bonding, respectively. These two parameters are functions of the other parameters.

A list of the parameters for 15 substances at 20 ^{0}C is given in Table 2-5[25]. In a binary mixture, the activity coefficient for component 2 at infinite dilution is

$$\ln\gamma_2^\infty = \frac{v_2}{RT}\left[[(\lambda_1-\lambda_2)^2 + \frac{q_1^2 q_2^2(\tau_1-\tau_2)^2}{\psi_1} + \frac{(\alpha_1-\alpha_2)(\beta_1-\beta_2)}{\xi_1}\right] + d_{12} \tag{2-8.1}$$

There is a corresponding expression for ln γ_1^∞. Here, v_2 is liquid molar volume at 20^{0}C in cm^3 mol^{-1} and d_{12} is a Flory-Huggins combinatorial term to account for differences in molecular size:

$$d_{12} = \ln\left(\frac{v_2}{v_1}\right)^{aa} + 1 - \left(\frac{v_2}{v_1}\right)^{aa} \tag{2-8.2}$$

Parameters τ, α, β, ψ, ξ, and *aa* are temperature-dependent. The temperature dependence is given by

$$\tau_{\mathrm{T}} = \tau_{293}\left(\frac{293}{T}\right)^{0.4} \tag{2-8.3}$$

$$\alpha_{\mathrm{T}} = \alpha_{293}\left(\frac{293}{T}\right)^{0.8} \tag{2-8.4}$$

$$\beta_{\mathrm{T}} = \beta_{293}\left(\frac{293}{T}\right)^{0..8} \tag{2-8.5}$$

$$\psi = \mathrm{POL} + 0.011\,\alpha_T \beta_T \qquad (2\text{-}8.6)$$

$$\xi = 0.68(\mathrm{POL} - 1) + \left\{3.4 - 2.4\exp\left[(-0.023)(\alpha_o\beta_o)^{1.5}\right]\right\}^{t^2} \qquad (2\text{-}8.7)$$

where

$$\mathrm{POL} = q^4[1.15 - 1.15\exp(-0.020\,\tau^3{}_T)] + 1 \qquad (2\text{-}8.8)$$

and where $t = 293/T$ (T in Kelvin). Subscript 0 refers to 20^0C (293 K), and subscript T refers to system temperature.

$$\mathrm{aa} = 0.953 - (0.00968)(\tau_2^2 + \alpha_2\,\beta_2) \qquad (2\text{-}8.9)$$

where τ, α, and β are at system temperature T.

In Eq. (2-8.1), when subscripts 1 and 2 are interchanged, there is no effect in the terms $(\lambda_1 - \lambda_2)^2$, $q_1^2\, q_2^2\, (\tau_1 - \tau_2)^2$, and $(\alpha_1 - \alpha_2)\, (\beta_1 - \beta_2)$. Asymmetry is introduced through parameters ψ and ξ because $\psi_1 \neq \psi_2$ and $\xi_1 \neq \xi_2$.

In Table 2-5, RI refers to refractive index and ID refers to identification number. ID = 1 for alkane, 2 for naphthene, and 3 for aromatic.

The units of the parameters in Table 2-5 are such that, in the equation for ln γ_2^∞, gas constant R has the value 1.987 cal/mol·K.

Table 2-5 Parameters for MOSCED Model at 20 °C [25]

	compound	RI	*v*	λ	τ	*q*	α	β	ψ	ξ	*aa*	ID
1	Acetone	1.359	74.4	7.49	4.10	1.00	0.00	4.87	1.86	1.58	0.790	1
2	Acetonitrile	1.344	52.2	7.43	5.99	1.00	0.86	3.98	2.17	2.10	0.573	1
3	Benzene	1.501	89.1	8.49	1.95	0.90	0.22	0.56	1.11	1.07	0.915	3
4	Carbontetrachloride	1.460	96.5	8.58	0.87	1.00	0.58	0.15	1.02	1.01	0.945	1
5	Chloroform	1.446	80.7	8.43	1.95	1.00	3.05	0.06	1.16	1.11	0.914	1
6	Methanol	1.328	40.5	7.14	2.55	1.00	7.45	7.45	1.94	3.62	0.353	1
7	Methyl acetate	1.361	79.3	7.52	3.32	1.00	0.00	3.83	1.60	1.41	0.846	1
8	Nitromethane	1.381	53.7	7.73	6.24	1.00	1.30	2.40	2.18	2.06	0.546	1
9	Heptane	1.388	146.6	7.81	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1
10	Hexane	1.375	130.8	7.67	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1
11	Ethanol	1.361	58.4	7.51	1.36	1.00	6.19	6.19	1.48	3.43	0.564	1
12	Methylcyclopentane	1.410	112.4	8.05	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1
13	2-Methylpentane	1.372	131.9	7.63	0.00	1.00	0.00	0.00	1.00	1.00	0.953	1
14	Nitroethane	1.392	72.0	7.85	4.85	1.00	0.29	2.20	2.04	1.73	0.719	1
15	2-Nitropropane	1.394	90.1	7.88	4.13	1.00	0.23	1.85	1.87	1.61	0.784	1

2-8-2 SPACE model

A predictive method for estimating γ^{∞} is provided by the solvatochromic correlation of Bush and Eckert (2000) [2] through the SPACE equation. SPACE stands for Solvatochromic Parameters for Activity Coefficient Estimation. The SPACE formulation for γ_2^{∞} in solvent 1 is

$$\ln\gamma_2^{\infty} = \frac{V_2}{RT}[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_{2\mathrm{eff}})^2 + (\alpha_1 - \alpha_{2\mathrm{eff}})(\beta_1 - \beta_{2\mathrm{eff}})]$$

$$+\ln\left(\frac{V_2}{V_1}\right)^{0.936} + 1 - \left(\frac{V_2}{V_1}\right)^{0.936} \qquad (2\text{-}8.10)$$

The dispersion terms are calculated as functions of the molar refractivity n_D:

$$\lambda = k\left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \tag{2-8.11}$$

where constant k is 15.418 for aliphatic compounds, 15.314 for aromatics, and 17.478 for halogen compounds[2]. In equation (2-8.11), R is 1.987, T is in Kelvin, and V is in cm^3/mol.

The polarity and hydrogen-bond parameters for the solvent are

$$\tau_1 = \left|\frac{A_1\pi_1^{*KT} + B}{\sqrt{V_1}}\right| \tag{2-8.12}$$

$$\alpha_1 = \left|\frac{C_1\alpha_1^{KT} + D_1}{\sqrt{V_1}}\right| \tag{2-8.13}$$

$$\beta_1 = \left|\frac{E_1\beta_1^{KT} + F_1}{\sqrt{V_1}}\right| \tag{2-8.14}$$

Parameters $\tau_{2\mathrm{eff}}$, $\alpha_{2\mathrm{eff}}$, and $\beta_{2\mathrm{eff}}$ are for the solute. Subscript eff means they are normalized such that limiting activity coefficients for a solute in itself (solvent) will be unity. Calculation of these quantities requires both solvent and solute parameters for the solute.

$$\tau_{2\mathrm{eff}} = \tau_2^{\circ} + (\tau_2 - \tau_2^{\circ})\frac{\left|\pi_1^{*KT} - \pi_2^{*KT}\right|}{1.33} \tag{2-8.15}$$

$$\alpha_{2\mathrm{eff}} = \alpha_2^{\mathrm{o}} + (\alpha_2 - \alpha_2^{\mathrm{o}})\frac{\left|\alpha_1^{KT} - \alpha_2^{KT}\right|}{1.20} \tag{2-8.16}$$

$$\beta_{2\mathrm{eff}} = \beta_2^{\mathrm{o}} + (\beta_2 - \beta_2^{\mathrm{o}})\frac{\left|\beta_1^{KT} - \beta_2^{KT}\right|}{0.95} \tag{2-8.17}$$

where

$$\tau_2 = \left|\frac{A_2\pi_2^{*H} + B}{\sqrt{\mathrm{V}_2}}\right| \tag{2-8.18}$$

$$\alpha_2 = \left|\frac{C_2\alpha_2^{H} + D_2}{\sqrt{\mathrm{V}_2}}\right| \tag{2-8.19}$$

$$\beta_2 = \left|\frac{E_2\beta_2^{H} + F_2}{\sqrt{\mathrm{V}_2}}\right| \tag{2-8.20}$$

and

$$\tau_2^{\mathrm{o}} = \left|\frac{A_1\pi_2^{*KT} + B}{\sqrt{\mathrm{V}_2}}\right| \tag{2-8.21}$$

$$\alpha_2^{o} = \left|\frac{C_1\alpha_2^{KT} + D_1}{\sqrt{\mathrm{V}_2}}\right| \tag{2-8.22}$$

$$\beta_2^{o} = \left|\frac{E_1\beta_2^{KT} + F_1}{\sqrt{\mathrm{V}_2}}\right| \tag{2-8.23}$$

Parameters π^{*KT}, α^{KT}, and β^{KT} for the solvent - like state and parameters π^{*H}, α^{H}, and β^{H} for the solute are given in table (2-6) [2] for 15 components. Subscription $^{\mathrm{o}}$ means that properties for the solute in its solvent - like state.

There are 19 families or classes of compounds based on functional group as well as methanol and carbon tetrachloride. Each constitutes is an independent family. Parameters A_1, A_2, B, D_1, D_2, F_1 and F_2 are class-dependent. Parameters C_1, C_2, E_1 and E_2 are class-independent. Of these, A_1, D_1, F_1 and E_1 are for solvent state while A_2, D_2, F_2 and E_2 are for solute state. B is the same in both solvent and solute states. These parameters are given in table (2-7) [2].

Table 2-6 Solvatochromic Parameters

	Component	n_D	**V**	π^{*KT}	π^{*H}	α^{KT}	α^{H}	β^{KT}	β^{H}
1	Acetone	1.35596	74.1	0.71	0.7	0.08	0.04	0.43	0.51
2	Acetonitrile	1.34163	52.9	0.75	0.9	0.19	0.04	0.4	0.33
3	Benzene	1.49792	89.4	0.59	0.52	0	0	0.1	0.14
4	Carbon tetrachloride	1.45739	97.1	0.28	0.38	0	0	0.1	0
5	Chloroform	1.44293	80.7	0.58	0.49	0.2	0.15	0.1	0.02
6	Methanol	1.32652	40.8	0.6	0.44	0.98	0.43	0.66	0.47
7	Methyl acetate	1.3589	79.8	0.6	0.64	0	0	0.42	0.45
8	Nitro methane	1.37964	54.0	0.85	0.95	0.22	0.06	0.06	0.32
9	n-heptane	1.38511	147.5	-0.01	0	0	0	0	0
10	n-hexane	1.37226	131.6	-0.04	0	0	0	0	0
11	Ethanol	1.35941	58.7	0.54	0.42	0.86	0.37	0.75	0.48
12	Methylcyclopentane	1.407	113.2	0.01	0.1	0	0	0	0
13	2-Methylpentane	1.36873	132.9	-0.02	0	0	0	0	0
14	Nitro ethane	1.38973	71.9	0.8	0.95	0.22	0.02	0.25	0.33
15	2-Nitropropane	1.39235	90.6	0.75	0.92	0.22	0	0.27	0.32

TABLE 2-7 SPACE Equation Parameters, Eqs. (2-8.12) to (2-8.23)[2]

	A_1	A_2	B	D_1	D_2	F_1	F_2
Alkanes	18.522	12.802	-4.055	0	0	0	0
Alkenes	65.738	-85.606	-0.245	0	0	-4.095	-0.15
Amides	19.929	—	17. 142	0	—	14.944	—
Amnes	-66.112	-173.878	19.903	0	0	11.346	-22.023
Aromatics	30.949	31.114	1.081	0	0	-0.273	-0.306
Aromatics with N	-4.569	—	-23.106	-25.226	—	-0.685	—
Aromatics with 0	17.295	—	11.889	-10.671	—	0.877	—
Naphthenes	-113.528	56.428	-2.632	0	0	0	0
1,4-Dioxane	-10.866	-22.769	-19.37	0	0	15.902	-1.375
Ethers/Esters	32.795	42.132	8.889	0	0	5.147	-0.941
Halog. Aliphatics	-12.186	-18.479	-12.359	-9.141	-1.737	-2.756	-0.103
Halog. Arom.	12.576	—	11.083	0	—	-9.124	—
Heterocycles	-50.622	—	16.334	0	—	-48.53 1	—
Ketones	8.067	27.477	22.021	0.336	5.3	10.617	-1.095
Nitriles	11.419	38.912	22.092	-2.269	-50.619	-25.227	-65.782
Nitroalkanes	-14.439	-31.992	-20.876	17.172	-162.981	-10.864	9.39
Methanol	-30.494	59.387	29.223	2.659	-5.007	9.377	40.347
Alcohols	10.132	-83.652	-16.27	-4.851	73.597	-45.278	-31.23
Sec. Alcohols	- 10.079	—	- 12.643	-2.86	—	0.054	—
Sulfoxides	18.402	—	21.287	0	—	0	—
Carbon Tet.	-12.227	-76.165	13.971	0	0	-1.63	7.374
THF	15.102	-12.603	7.983	0	0	28.447	61.373

C_1 = -26.92 C_2 = -132.494 C_2 (alcoho1s) = 3.702

E_1 = 27.561 E_2 = 2.147

Chapter Three

Investigation and Calculation

3-1 Experimental Data

The experimental data of activities coefficients at infinite dilution obtained from literature [32] for 23 systems as shown in table 3-1.and the other experimental data can be found in literatures [33, 34]

Table 3-1 Experimental Data of Activity Coefficient at Infinite Dilution

	System,1-2	T ^oC	Experimental γ^{∞}_1	γ^{∞}_2
1	Acetone – Acetonitrile	45	1.05	1.04
2	Acetone – Benzene	45	1.65	1.52
3	Acetone –carbon tetrachloride	45	3.00	2.15
4	Acetone –Chloroform	50	0.44	0.54
5	Acetone –nitro methane	50	0.94	0.96
6	Acetone – Methyl acetate	50	1.32	1.18
7	Acetonitrile – Nitro methane	40	0.96	1.00
8	Acetone –Water	45	8.75	3.60
9	Acetonitrile – Benzene	100	3.20	3.00
10	Benzene – n-heptane	30	1.35	1.82
11	Carbon tetrachloride - Acetonitrile	60	5.66	9.30
12	Chloroform – Methanol	50	2.00	9.40
13	Ethanol – Benzene	45	10.6	4.45
14	Ethanol – Methylcyclopentane	72-79	20.0	5.75
15	n-Hexane – Benzene	69-80	1.68	1.49
16	n-Hexane – Methylcyclopentane	69-72	1.17	1.03
17	Methanol – Water	100	2.74	1.39
18	Methylcyclopentane – Benzene	72-80	1.47	1.34
19	Nitroethane – Benzene	25	2.78	1.91
20	Nitro methane – Benzene	25	3.20	3.72
21	Nitro methane – Benzene	45	3.20	3.40
22	Nitro methane - Carbon tetrachloride	45	10.6	7.45
23	2-Nitropropane - carbon tetrachloride	25	3.24	1.92

3-2 Calculation of Activity Coefficients at Infinite Dilution

3-2-1 MOSCED model

The calculation that cared out by using MOSCED model is shown in table 3-2 which is gives some different systems and their infinite dilution activity coefficients achieved experimentally and calculated by MOSCED equation and the deviation between them where:

Table 3-2 Activity Coefficients at Infinite Dilution Calculated by MOSCED equation.

	System,1-2	T ^{o}C	Experimental		Calculated		Deviation	
			γ^{∞}_1	γ^{∞}_2	γ^{∞}_1	γ^{∞}_2	γ^{∞}_1	γ^{∞}_2
1	Acetone – Acetonitrile	45	1.05	1.04	1.105	1.1	0.055	0.06
2	Acetone – Benzene	45	1.65	1.52	1.48061	1.3809	0.16939	0.1391
3	Acetone –Carbon tetrachloride	45	3.00	2.15	2.64655	2.0804	0.35345	0.0696
4	Acetone – Methyl acetate	50	1.32	1.18	1.0417	1.0376	0.2783	0.1424
5	Acetone –nitro methane	50	0.94	0.96	1.0377	1.0362	0.0977	0.0762
6	Acetonitrile – Benzene	100	3.20	3.00	2.3056	2.0093	0.8944	0.9907
7	Acetonitrile – nitro methane	40	0.96	1.00	0.9839	0.9838	**0.0239**	0.0162
8	Benzene – n-heptane	30	1.35	1.82	1.55136	1.95156	0.20136	0.1316
9	Carbon tetrachloride - Acetonitrile	60	5.66	9.30	5.2169	7.0278	0.4431	2.2722
10	Chloroform – Methanol	50	2.00	9.40	3.23174	5.34556	1.23174	**4.0544**
11	Ethanol – Benzene	45	10.6	4.45	13.9057	4.6284	**3.3057**	0.1784
12	n-Hexane – Benzene	69	1.68	1.49	1.73638	1.4944	0.0564	**0.0044**
13	n-Hexane – Methylcyclopentane	69	1.17	1.03	1.01697	1.01402	0.15303	0.016
14	Methylcyclopentane – Benzene	72	1.47	1.34	1.5328	1.44367	0.0628	0.1037
15	Nitroethane – Benzene	25	2.78	1.91	2.20598	1.72945	0.57402	0.1806
16	Nitromethane – Benzene	25	3.20	3.72	4.00663	3.064	0.80663	0.656
17	Nitro methane – Benzene	45	3.20	3.40	3.42507	2.67778	0.22507	0.7222
18	2-Nitropropane - carbon tetrachloride	25	3.24	1.92	4.73716	2.54479	1.4972	0.6248
	Average Deviation						0.5794	0.5799

$$\text{Deviation} = \left|\gamma_{i\ \text{Experimental}}^{\infty} - \gamma_{i\ \text{Calculated}}^{\infty}\right| \qquad (3\text{-}2.1)$$

The average deviation for 18 systems is 0.5794 for γ^{∞}_1 and 0.5799 for γ^{∞}_2. Where the maximum deviation in system Ethanol – Benzene for γ^{∞}_1 and in system Chloroform – Methanol for γ^{∞}_2 and the minimum deviation in system Acetonitrile – nitro methane for γ^{∞}_1 and in system n-Hexane – Benzene for γ^{∞}_2.

3-2-2 SPACE model

The calculation that cared out by using SPACE model is shown in table 3-3 which is gives the same systems that used in MOSCED model and their infinite dilution activity coefficients achieved experimentally and calculated by SPACE model and the deviation between them where the deviation are calculated from equation (3-2.1)

SPACE equation gives average deviation of 0.4526 for γ^{∞}_1 and 0.3042 for γ^{∞}_2 for 18 different systems. Where the maximum deviation in system Ethanol – Benzene for γ^{∞}_1 and in system Chloroform – Methanol for γ^{∞}_2 and the minimum deviation in system Benzene – n-heptane for γ^{∞}_1 and in system Acetone –Carbon tetrachloride for γ^{∞}_2.

Table 3-3 Activity Coefficients at Infinite Dilution Calculated by SPACE equation.

	System,1-2	**T °C**	**Experimental**		**Calculated**		**Deviation**	
			γ^{∞}_{1}	γ^{∞}_{2}	γ^{∞}_{1}	γ^{∞}_{2}	γ^{∞}_{1}	γ^{∞}_{2}
1	Acetone – Acetonitrile	45	1.05	1.04	0.9954	1.0061	0.0546	0.0339
2	Acetone – Benzene	45	1.65	1.52	1.4475	1.5476	0.2025	0.0276
3	Acetone –Carbon tetrachloride	45	3.00	2.15	2.5052	2.1490	0.4948	**0.001**
4	Acetone – Methyl acetate	50	1.32	1.18	1.044	1.0472	0.276	0.1328
5	Acetone –Nitro methane	50	0.94	0.96	1.0499	0.7709	0.1099	0.1891
6	Acetonitrile – Benzene	100	3.20	3.00	2.9103	2.3198	0.2897	0.6802
7	Acetonitrile – Nitro methane	40	0.96	1.00	0.9173	0.9691	0.0427	0.0309
8	Benzene – n-heptane	30	1.35	1.82	1.3591	1.8565	**0.0091**	0.0365
9	Carbon tetrachloride - acetonitrile	60	5.66	9.30	4.4317	8.816	1.2283	0.484
10	Chloroform – Methanol	50	2.00	9.40	2.1859	7.7311	0.1859	**1.6689**
11	Ethanol – Benzene	45	10.6	4.45	12.9898	5.1616	**2.3898**	0.7116
12	n-Hexane – Benzene	69	1.68	1.49	1.6637	1.3251	0.0163	0.1649
13	n-Hexane – Methylcyclopentane	69	1.17	1.03	1.0795	1.0668	0.0905	0.0368
14	Methylcyclopentane – Benzene	72	1.47	1.34	1.2499	1.161	0.2201	0.1790
15	Nitroethane – Benzene	25	2.78	1.91	2.2299	1.8874	0.5501	0.0226
16	Nitro methane – Benzene	25	3.20	3.72	3.5746	3.2465	0.3746	0.4735
17	Nitro methane – Benzene	45	3.20	3.40	3.2797	2.9901	0.0797	0.4099
18	2-Nitropropane - carbontetrachloride	25	3.24	1.92	4.7714	2.1122	1.5314	0.1922
	Average Deveation						**0.4526**	**0.3042**

3-3 Calculation of the Uses of Activity Coefficient at Infinite Dilution

3-3-1 Azeotrope Calculation

From the activities coefficients at infinite dilution azeotrope composition and pressure can be calculated for any system having azeotrope. The equation of Azeotrope is presented in Chapter two (2-7.7). The azeotrope composition for 10 systems has been calculated by using Wilson, NRTL and UNIQUAC equations for one parameter and two parameters. These systems were chosen because, in all cases, reliable activities coefficients at infinite dilution were available in the literatures where the experimental azeotrope compositions are taken from Lee H. Horsley [24]. The results are presented in table 3-4 to table 3-15 for calculated and experimental azeotrope composition and azeotrope pressure.

Steps of Calculation of Azeotrope

1. Calculating the parameters of the activity coefficient equations (Wilson, NRTL and UNIQUAC equations) from experimental γ^{∞}.
2. Calculating the composition of azeotrope using activity coefficient equations.
3. Calculating the activity coefficient of the azeotrope $\gamma^{az}{}_{1}$.
4. Calculating the azeotropic pressure from eq. (3-4.15) $P^{az} = \gamma_1^{az} P_1^{sat}$.

Steps of Investigation

The following steps of investigation were carried out:

1- Wilson Equation was used for calculating the azeotrope composition (x_1^{az}) and pressure (P^{az}) for all the experimental data available. It was found that the Average Absolute Percent Deviation (Average X_1^{az} %Deviation) is 2.491708 for azeotrope composition and the Average Absolute Deviation (Average P^{az} Deviation) is 0.062142 bar for azeotrope pressure by using two parameters. For one parameter the Average Absolute Percent Deviation (Average X_1^{az} %Deviation) is 3.06318 for azeotrope composition and the Average Absolute Deviation (Average P^{az} Deviation) is 0.077835 bar for azeotrope pressure.

2- The Non-Random Two-Liquid (NRTL) Equation was also used to calculate the azeotrope composition (x_1^{az}) and pressure (P^{az}) for all the experimental data. It was found that the Average Absolute Percent Deviation (Average X_1^{az} %Deviation) is 1.129017 for azeotrope composition and the Average Absolute Deviation (Average P^{az} Deviation) is 0.061449 bar for azeotrope pressure by using two parameters. For one parameter the Average Absolute Percent Deviation (Average X_1^{az} %Deviation) is 2.491708 for azeotrope composition and the Average Absolute Deviation (Average P^{az} Deviation) is 0.083049 bar for azeotrope pressure.

3- The UNIQUAC (Universal Quasi-Chemical) equations were also used to calculate the azeotrope composition (x_1^{az}) and pressure (P^{az}) for all the experimental data available. It was found that the Average Absolute Percent Deviation (Average X_1^{az} %Deviation) is 0.686426 for azeotrope composition and the Average Absolute Deviation (Average P^{az} Deviation) is 0.060575 bar for azeotrope pressure by using two parameters. For one parameter the Average Absolute Percent Deviation (Average X_1^{az} %Deviation) is 1.632101 for azeotrope composition and the Average Absolute Deviation (Average P^{az} Deviation) is 0.133212 bar for azeotrope pressure.

In overall view for the results, a one parameter form (Wilson, NRTL, UNIQUAC) often gives results nearly as good as those obtained by using two parameters.

Table 3-4 gives the azeotropic composition calculated from experimental activities coefficients at infinite dilution, by using Wilson equation, and the deviation between the experimental and calculated

Where:

$$X_1^{az}\ \%\text{Deviation} = \left| X_1^{az}{}_{\text{Experimental}} - X_1^{az}{}_{\text{Calculated}} \right| * 100 \qquad (3\text{-}3.1)$$

Where the Average %Deviation of X_1^{az} for 10 systems is 2.4917

Table 3-5 gives the azeotropic Pressure calculated from experimental activities coefficients at infinite dilution, by using Wilson equation of two parameters, and the deviation between the experimental and calculated

Where:

$$P^{az}\ \text{Deviation} = \left| P^{az}{}_{\text{Experimental}} - P^{az}{}_{\text{Calculated}} \right| \qquad (3\text{-}3.2)$$

The average Deviation for P^{az} is 0.062042 bar for 10 systems.

Table 3-4 Calculated and Experimental Azeotrope Composition by Using Wilson Equation of Two Parameters $\gamma^{\infty}{}_1$ and $\gamma^{\infty}{}_2$

	Component	T °C	X_1 wt% at Azeotrope Experimental	X_1wt % at Azeotrope Calculated	X_1^{az} %Deviation
1	Acetone –Carbon tetrachloride	45	91	83.0338	7.9662
2	Acetone – chloroform	50	22.9	19.2754	3.6246
3	Acetonitrile – Benzen	45	30.7	31.9997	1.2997
4	Carbontetrachloride -Acetonitrile	45	84.5	84.1988	0.3012
5	Chloroform - Methanol	50	87.8	90.8768	3.0768
6	Methyl cyclopentane – Benzene	72	91	93.8899	2.8899
7	Nitromethane – Benzene	25	6.4	6.326	0.074
8	Nitromethane – Benzene	45	9.6	9.8254	0.2254
9	Nitromethane - carbontetrachloride	45	10.6	9.7866	0.8134
10	n-hexane –Benzene	69	99.8	95.1542	4.6458
	Average %deviation				**2.4917**

Table 3-5 Calculated and Experimental Ezeotrope Pressure (bar) by Using Wilson Equation of Two Parameters $\gamma^{\infty}{}_1$ and $\gamma^{\infty}{}_2$

	Component	T °C	P^{az} Experimental	P^{az} Calculated	P^{az} Deviation
1	Acetone –Carbon tetrachloride	45	0.68421	0.68578	0.00157
2	Acetone – chloroform	50	0.60662	0.59379	0.01283
3	Acetonitrile – Benzene	45	0.37064	0.38272	0.01208
4	Carbontetrachloride - Acetonitrile	45	0.49489	0.49205	0.00284
5	Chloroform - Methanol	50	0.83598	0.83946	0.00348
6	Methyl cyclopentane – Benzene	72	0.69861	1.01761	0.319
7	Nitromethane – Benzene	25	0.13026	0.12777	0.00249
8	Nitromethane – Benzene	45	0.30398	0.30282	0.00116
9	Nitromethane - carbon tetrachloride	45	0.40397	0.39316	0.01081
10	n-hexane –Benzene	69	0.76660	1.02179	0.25519
	Average deviation				**0.062145**

Table 3-6 gives the azeotropic composition calculated from experimental activities coefficients at infinite dilution, by using Wilson equation of one parameter, and the deviation between the experimental and the calculated.

The Average %Deviation is calculated from equation (3-3.1) for 10 systems where the Average %Deviation is 3.053157.

Table 3-7 give the azeotropic Pressure calculated from experimental activities coefficients at infinite dilution, by using Wilson equation of *one parameter*, and the deviation between the experimental and calculated.

The Average Deviation for P^{az} is 0.077836 bar for 10 systems calculated from equation (3-3.2).

Similar calculation for the NRTL and UNIQUAC equations and the results of these calculations are present in tables (3-8), (3-9) for NRTL equation *two parameters* where the Average %Deviation is 0.97596 for X^{az} and the Average Deviation for P^{az} is 0.061452 bar for 10 systems.

Tables (3-10), (3-11) for NRTL equation *one parameter* where the Average %Deviation is 2.4917 for X^{az} and the Average Deviation for P^{az} is 0.08303 bar for 10 systems.

Tables (3-12), (3-13) for UNIQUAC equation *two parameters* where the Average %Deviation is 0.52713 for X^{az} and the Average Deviation for P^{az} is 0.060574 bar for 10 systems.

Table (3-14), (3-15) for UNIQUAC equation *one parameter* where the Average %Deviation is 1.504362 for X^{az} and the Average Deviation for P^{az} is 0.133212 bar for 10 systems.

Table 3-6 Calculated and Experimental Azeotrope Composition by Using Wilson Equation of *One* Parameters γ^{∞}_1 or γ^{∞}_2

	Component	T °C	X_1 wt% at Azeotrope Experimental	X_1wt % at Azeotrope Calculated	X_1^{az} %Deviation
1	Acetone –Carbontetrachloride	45	91	92.6200	1.6200
2	Acetone – Chloroform	50	22.9	23.6269	0.7269
3	Acetonitrile – Benzen	45	30.7	30.2309	0.4691
4	Carbontetrachloride - Acetonitrile	45	84.5	82.1122	2.3878
5	Chloroform - Methanol	50	87.8	87.9172	0.1172
6	Methyl cyclopentane – Benzene	72	91	84.9816	6.0184
7	Nitromethane – Benzene	25	6.4	4.44970	1.9503
8	Nitromethane – Benzene	45	9.6	6.89904	2.70096
9	Nitromethane - Carbontetrachloride	45	10.6	8.44299	2.15701
10	n-hexane –Benzene	69	99.8	87.4161	12.3839
	Average %deviation				**3.053157**

Table 3-7 Calculated and Experimental Azeotrope Pressure (bar) by Using Wilson Equation of *One* Parameters γ^{∞}_1 or γ^{∞}_2

	Component	T °C	P^{az} Experimental	P^{az} Calculated	P^{az} Deviation
1	Acetone – Carbontetrachloride	45	0.68421	0.7045251	0.020315
2	Acetone – Chloroform	50	0.60662	0.6117064	0.005086
3	Acetonitrile – Benzene	45	0.37064	0.3752523	0.004612
4	Carbontetrachloride - Acetonitrile	45	0.49489	0.4544587	0.040431
5	Chloroform - Methanol	50	0.83598	0.7432916	0.092688
6	Methyl cyclopentane – Benzene	72	0.69861	1.026725	0.328115
7	Nitromethane – Benzene	25	0.13026	0.1273378	0.002922
8	Nitromethane – Benzene	45	0.30398	0.3011422	0.002838
9	Nitromethane - Carbon tetrachloride	45	0.40397	0.3863205	0.01765
10	n-hexane –Benzene	69	0.76660	1.030297	0.263697
	Average deviation				**0.077836**

Table 3-8 Calculated and Experimental Azeotrope Composition by Using NRTL Equation of *two* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T °C	α_{12}	X_1 wt% at Azeotrope Experimental	X_1wt % at Azeotrope calculated	X_1^{az} %Deviation
1	Acetone –Carbon tetrachloride	45	0.47	91	90.8107	0.1893
2	Acetone – chloroform	50	0.3	22.9	25.7412	2.8412
3	Acetonitrile – Benzen	45	0.47	30.7	30.0615	0.6385
4	Carbontetrachloride - Acetonitrile	45	0.47	84.5	84.3994	0.1006
5	Chloroform - Methanol	50	0.47	87.8	90.3624	2.5624
6	Methyl cyclopentane – Benzene	72	0.47	91	93.7580	2.758
7	Nitromethane – Benzene	25	0.47	6.4	6.7034	0.3034
8	Nitromethane – Benzene	45	0.47	9.6	9.5541	0.0459
9	Nitromethane- carbontetrachloride	45	0.4	10.6	10.7995	0.1995
10	n-hexane –Benzene	69	0.47	99.8	99.9208	0.1208
	Average %deviation					**0.97596**

Table 3-9 Calculated and Experimental Azeotrope Pressure (bar) by Using NRTL Equation of *Two* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T °C	α_{12}	P^{az} Experimental	P^{az} Calculated	P^{az} Deviation
1	Acetone –Carbon tetrachloride	45	0.47	0.68421	0.68472	0.00051
2	Acetone – chloroform	50	0.3	0.60662	0.59934	0.00728
3	Acetonitrile – Benzene	45	0.47	0.37064	0.35051	0.02013
4	Carbontetrachloride-Acetonitrile	45	0.47	0.49489	0.49401	0.00088
5	Chloroform - Methanol	50	0.47	0.83598	0.86534	0.02936
6	Methyl cyclopentane – Benzene	72	0.47	0.69861	1.00203	0.30342
7	Nitromethane – Benzene	25	0.47	0.13026	0.12773	0.00253
8	Nitromethane – Benzene	45	0.47	0.30398	0.30265	0.00133
9	Nitromethane - carbontetrachloride	45	0.4	0.40397	0.40086	0.00311
10	n-hexane –Benzene	69	0.47	0.76660	1.01257	0.24597
	Average deviation					**0.061452**

Table 3-10 Calculated and Experimental Azeotrope Composition by Using NRTL Equation of *One* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T °C	α_{12}	X_1 wt% at azeotrope Experimental	X_1wt % at azeotrope calculated	X_1^{az} %Deviation
1	Acetone –Carbon tetrachloride	45	0.47	91	88.2587	4.7413
2	Acetone – chloroform	50	0.3	22.9	26.7476	3.8476
3	Acetonitrile – Benzen	45	0.47	30.7	17.5476	13.1524
4	Carbontetrachloride - Acetonitrile	45	0.47	84.5	80.4428	4.0572
5	Chloroform - Methanol	50	0.47	87.8	91.3657	3.5657
6	Methyl cyclopentane – Benzene	72	0.47	91	91.7786	0.7786
7	Nitromethane – Benzene	25	0.47	6.4	8.1236	1.7236
8	Nitromethane – Benzene	45	0.47	9.6	12.5794	2.9794
9	Nitromethane-carbontetrachloride	45	0.4	10.6	13.8429	3.2429
10	n-hexane –Benzene	69	0.47	99.8	99.9238	0.1238
	Average %deviation					**2.4917**

Table 3-11 Calculated and Experimental Azeotrope Pressure (bar) by Using NRTL Equation of *One* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T °C	α_{12}	P^{az} Experimental	P^{az} calculated	P^{az} Deviation
1	Acetone –Carbon tetrachloride	45	0.47	0.68421	0.70284	0.01863
2	Acetone – chloroform	50	0.3	0.60662	0.59908	0.00754
3	Acetonitrile – Benzene	45	0.47	0.37064	0.32809	0.04255
4	Carbontetrachloride-Acetonitrile	45	0.47	0.49489	0.43264	0.06225
5	Chloroform - Methanol	50	0.47	0.83598	0.69886	0.13712
6	Methyl cyclopentane – Benzene	72	0.47	0.69861	1.00296	0.30435
7	Nitromethane – Benzene	25	0.47	0.13026	0.12795	0.00231
8	Nitromethane – Benzene	45	0.47	0.30398	0.30424	0.00026
9	Nitromethane - carbon tetrachloride	45	0.4	0.40397	0.41330	0.00933
10	n-hexane –Benzene	69	0.47	0.76660	1.01256	0.24596
	Average deviation					**0.08303**

Table 3-12 Calculated and Experimental Azeotrope Composition by Using UNIQUAC Equation of *Two* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T °C	z	X_1 wt% at azeotrope Experimental	X_1wt % at azeotrope calculated	X_1^{az} %Deviation
1	Acetone –Carbon tetrachloride	45	0.8	91	90.8730	0.127
2	Acetone – chloroform	50	3.9	22.9	22.9058	0.0058
3	Acetonitrile – Benzen	45	0.65	30.7	30.7092	0.0092
4	Carbontetrachloride - Acetonitrile	45	1.4	84.5	84.5021	0.0021
5	Chloroform - Methanol	50	0.01	87.8	89.8536	2.0536
6	Methyl cyclopentane – Benzene	72	0.01	91	93.8282	2.8282
7	Nitromethane – Benzene	25	6	6.4	6.3678	0.0322
8	Nitromethane – Benzene	45	3.5	9.6	9.5828	0.0172
9	Nitromethane-carbontetrachloride	45	2.5	10.6	10.7628	0.1628
10	n-hexane –Benzene	69	0.36	99.8	99.8332	0.0332
	Average %deviation					**0.52713**

Table 3-13 Calculated and Experimental Azeotrope Pressure (bar) by Using UNIQUAC Equation of *Two* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T °C	z	P^{az} Experimental	P^{az} calculated	P^{az} Deviation
1	Acetone –Carbon tetrachloride	45	0.8	0.68421	0.68408	0.00013
2	Acetone – chloroform	50	3.9	0.60662	0.59263	0.01399
3	Acetonitrile – Benzene	45	0.65	0.37064	0.38309	0.01245
4	Carbontetrachloride-Acetonitrile	45	1.4	0.49489	0.50512	0.01023
5	Chloroform - Methanol	50	0.01	0.83598	0.85041	0.01443
6	Methyl cyclopentane – Benzene	72	0.01	0.69861	1.00202	0.30341
7	Nitromethane – Benzene	25	6	0.13026	0.13016	0.000101
8	Nitromethane – Benzene	45	3.5	0.30398	0.30789	0.00391
9	Nitromethane - carbon tetrachloride	45	2.5	0.40397	0.40511	0.00114
10	n-hexane –Benzene	69	0.36	0.76660	1.01255	0.24595
	Average deviation					**0.060574**

Table 3-14 Calculated and Experimental Azeotrope Composition by Using UNIQUAC Equation of *One* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T ^{o}C	z	X_1 wt% at azeotrope Experimental	X_1wt % at azeotrope calculated	X_1^{az} %Deviation
1	Acetone –Carbon tetrachloride	45	0.25	91	90.5575	0.4425
2	Acetone – chloroform	50	0.01	22.9	24.2491	1.3491
3	Acetonitrile – Benzen	45	7.9	30.7	30.7088	0.0088
4	Carbontetrachloride - Acetonitrile	45	8.4	84.5	84.4917	0.0083
5	Chloroform - Methanol	50	5.9	87.8	87.8072	0.0072
6	Methyl cyclopentane – Benzene	72	0.1	91	89.2809	1.7191
7	Nitromethane – Benzene	25	0.01	6.4	3.37393	3.02607
8	Nitromethane – Benzene	45	0.01	9.6	5.28095	4.31905
9	Nitromethane-carbontetrachloride	45	0.01	10.6	6.60830	3.9917
10	n-hexane –Benzene	69	0.37	99.8	99.6282	0.1718
	Average %deviation					**1.504362**

Table 3-15 Calculated and Experimental Azeotrope Pressure (bar) by Using UNIQUAC Equation of *One* Parameters γ^{∞}_1 and γ^{∞}_2

	Component	T ^{o}C	z	P^{az} Experimental	P^{az} calculated	P^{az} Deviation
1	Acetone –Carbon tetrachloride	45	0.25	0.68421	0.68427	0.000056
2	Acetone – chloroform	50	0.01	0.60662	0.60871	0.00209
3	Acetonitrile – Benzene	45	7.9	0.37064	0.15446	0.21618
4	Carbontetrachloride-Acetonitrile	45	8.4	0.49489	0.01852	0.47637
5	Chloroform - Methanol	50	5.9	0.83598	0.88632	0.05034
6	Methyl cyclopentane – Benzene	72	0.1	0.69861	1.00765	0.30904
7	Nitromethane – Benzene	25	0.01	0.13026	0.12714	0.00312
8	Nitromethane – Benzene	45	0.01	0.30398	0.30020	0.00378
9	Nitromethane - carbon tetrachloride	45	0.01	0.40397	0.37879	0.02518
10	n-hexane –Benzene	69	0.37	0.76660	1.01256	0.24596
	Average deviation					**0.133212**

3-3-2 Vapor Liquid Equilibrium Calculation

The Vapor Liquid Equilibrium (VLE) data can be calculated from the activities coefficients at infinite dilution (γ^{∞}_1, γ^{∞}_2) for any binary system. The equations of Vapor Liquid Equilibrium are presented in chapter two (2-7-2). The VLE data for 13 systems has been calculated by using Wilson, NRTL and UNIQUAC equations for one parameter and two parameters.

Experimental Data

From the experimental data can be determined the accuracy of any calculation and this can be done by calculating the deviation between the experimental data and the calculated results. The experimental data for Vapor Liquid Equilibrium obtained from literature for 13 systems are shown in table 3-16

Table 3-16 Vapor Liquid Equilibrium Systems Data

	Systems	P (mmHg) or T (C^o)	Number of Point	Data Reference
1	Benzene (1) – Acetonitrile (2)	T = 70.00	21	35
2	Methanol (1) –Water (2)	P = 760.00	26	36
3	Acetone (1) – Carbon tetrachloride (2)	P = 450.00	24	37
4	Hexane (1) – Benzene (2)	P = 735.00	11	38
5	Acetone (1) - Benzene (2)	P= 738.00	10	39
6	Acetone (1)-Water (2)	P = 760.00	13	40
7	Methelcyclopentane (1) – Benzene (2)	P = 760.00	15	41
8	Benzene (1) – Heptane (2)	P = 760.00	18	42
9	Acetone (1) - Benzene (2)	T= 45.00	11	43
10	Acetone (1) – Acetonitrile (2)	T= 45.00	10	44
11	Acetonitrile (1) – Nitro methane (2)	T= 60.00	10	45
12	Nitro methane (1)- Carbon tetrachloride (2)	T= 45.00	12	46
13	Carbon tetrachloride (1) – Acetonitrile (2)	T= 45.00	13	47

Steps of Calculation of VLE Data

1. Calculating the parameters of the activity coefficient equations (Wilson, NRTL and UNIQUAC) from experimental γ^{∞}.
2. for each point of the VLE data (x_1) the following steps were taken
   a. Finding the pure-component saturated vapor pressure P^{sat}_1, P^{sat}_2 at temperature of that point using Wagner equation appendix A.
   b. Calculating the constants of the equation at that temperature corresponding to that point
   c. Calculating the activities coefficients (γ_1, γ_2) at that point from the employed equation (Wilson, NRTL or UNIQUAC)
   d. Calculating V_i^L from Rackett equation (3-4.24)
   e. Solving equation (3-4.23) where ϕ_i^{sat} and ϕ_i^V must be calculated using Peng – Robinson equation of state.
   f. Calculating y_1 from the following equation:

$$y_1 = \left(\frac{x_1 \gamma_1 P_1^{sat} \phi_1^{sat}}{P \phi_1^V} \right) \exp \frac{V_1^L (P - P_1^{sat})}{RT}$$

These steps are repeated for each point of VLE data (for each x_1).

Steps of Investigation for VLE Calculation

The following steps of investigation were carried out on 13 different systems some of them are Isothermal and the others are Isobaric:

1- Wilson Equation was used for calculating the VLE composition (y_1) for all the experimental data. It was found that the Average Absolute

Percent Deviation (Average y_1 %Deviation) is 0.8186 for two parameters. For one parameter the Average Absolute Percent Deviation (Average y_1 %Deviation) is 2.3627.

2- The Non-Random Two-Liquid (NRTL) Equation was also used to calculate the VLE composition (y_1) for all the experimental data. It was found that the Average Absolute Percent Deviation (Average y_1 %Deviation) is 2.491708 for two parameters. For one parameter the Average Absolute Percent Deviation (Average y_1 %Deviation) is 3.06318.

3- The UNIQUAC (Universal Quasi-Chemical) equations were also used to calculate the VLE composition (y_1) for all the experimental data. It was found that the Average Absolute Percent Deviation (Average y_1 %Deviation) is 2.491708 for two parameters. For one parameter the Average Absolute Percent Deviation (Average y_1 %Deviation) is 3.06318.

Table 3-17 shows the Average Absolute % Deviation for 13 systems where UNIQUAC gives better result for all systems. And similar to the azeotrope using one parameter form (Wilson, NRTL, UNIQUAC) often gives results nearly as good as those obtained by using two parameters.

$$\text{Average Absolute \% Deviation} = \frac{\sum_{i=1}^{n} \left| y_{1Experimental} - y_{1Calculated} \right|}{n} * 100$$

Where n is number of points for VLE data (for each point there is x_1 verses Temperature).

Table 3-17 Average Absolute % Deviation for y_1 for All Systems

	Systems	P in mmHg T in C^o	No. of point	Wilson		NRTL		UNIQUAC	
				Parameters One	Parameters Two	Parameters One	Parameters Two	Parameters One	Parameters Two
1	**Benzene – Acetonitrile**	Isothermal T =70	21	1.9294	1.9044	2.7988	1.7167	1.6661	1.6163
2	**Methanol –Water**	Isobaric P = 760	26	3.2758	2.1413	2.4775	2.0513	1.9821	1.5083
3	**Acetone (1)-Carbontetrachloride (2)**	Isobaric P = 450	24	0.7259	0.3249	3.8627	2.0761	0.3735	0.2005
4	**Hexane (1) - Benzene (2)**	Isobaric P=735	11	2.3379	0.6727	1.8786	0.7361	5.3490	0.6812
5	**Acetone (1) - Benzene (2)**	Isobaric P= 738	10	1.8799	0.8494	1.1519	2.0163	0.8019	0.7854
6	**Acetone (1)- Water (2)**	Isobaric P= 760	13	1.2764	1.0586	2.0921	1.2743	1.1605	0.7809
7	**Methelcyclopentane (1) – Benzene (2)**	Isobaric P= 760	15	0.4823	0.3538	1.1235	0.6554	0.3601	0.4110
8	**Benzene (1) – Heptane (2)**	Isobaric P= 760	18	9.8944	0.4573	1.4158	0.6411	0.5809	0.4804
9	**Acetone (1) - Benzene (2)**	Isothermal T = 45	11	0.48319	0.3964	3.1053	0.7277	0.4547	0.3527
10	**Acetone (1) – Acetonitrile (2)**	Isothermal T = 45	10	0.76065	0.7518	0.7776	0.7738	0.7467	0.7153
11	**Acetonitrile (1) – Nitro methane (2)**	Isothermal T = 60	10	2.50597	0.3938	0.7455	0.5826	0.4469	0.391
12	**Nitro methane (1) – carbon tetrachloride (2)**	Isothermal T = 45	12	0.95157	0.7698	3.4571	0.6849	1.2256	0.5957
13	**Carbon tetrachloride (1) – Acetonitrile (2)**	Isothermal T = 45	13	4.21182	0.5674	4.8732	1.8375	1.9538	1.7218
	Average Absolute % Deviation for 13 systems		**194**	**2.3627**	**0.8186**	**2.2892**	**1.2134**	**1.3155**	**0.7877**

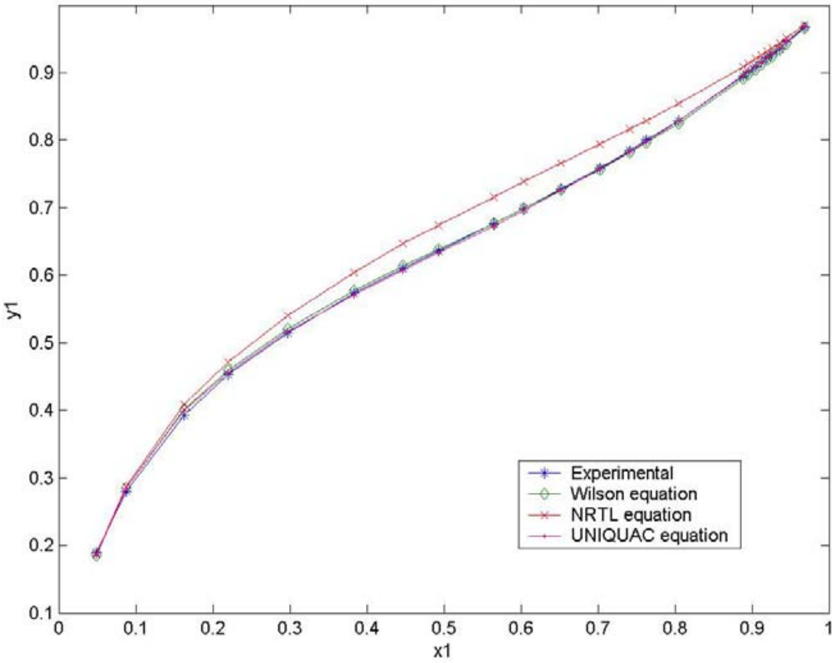

Figure 3-1 VLE for Acetone (1) –Carbon tetrachloride (2) P = 450 mmHg by Using Different Equations of Two Parameters

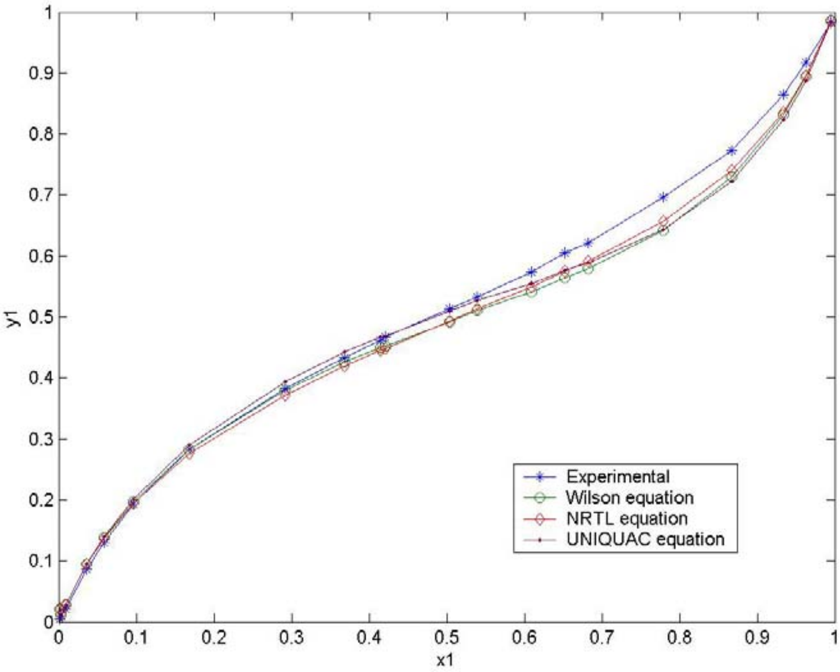

Figure 3-2 VLE for Benzene (1) – Acetonitrile (2) T = 70 C^o by Using Different Equations of Two Parameters

In figure 3-1 VLE is plotted for the system Acetone (1) – Carbon tetrachloride (2) Isobaric P = 450 mmHg for 24 points where x_1 is plotted vices y_1 for experimental and calculated by using Wilson, NRTL, UNIQUAC equation of two parameters.

Figure 3-2 is similar to figure 3-1 but for the system Benzene (1) – Acetonitrile (2) Isothermal at T =70 °C.

Figures 3-3, 3-4 and 3-5 show the difference between using one parameter and two parameters for each equation (Wilson, NRTL, UNIQUAC) for the system Acetone (1) – Carbon tetrachloride (2) at P=450 mmHg

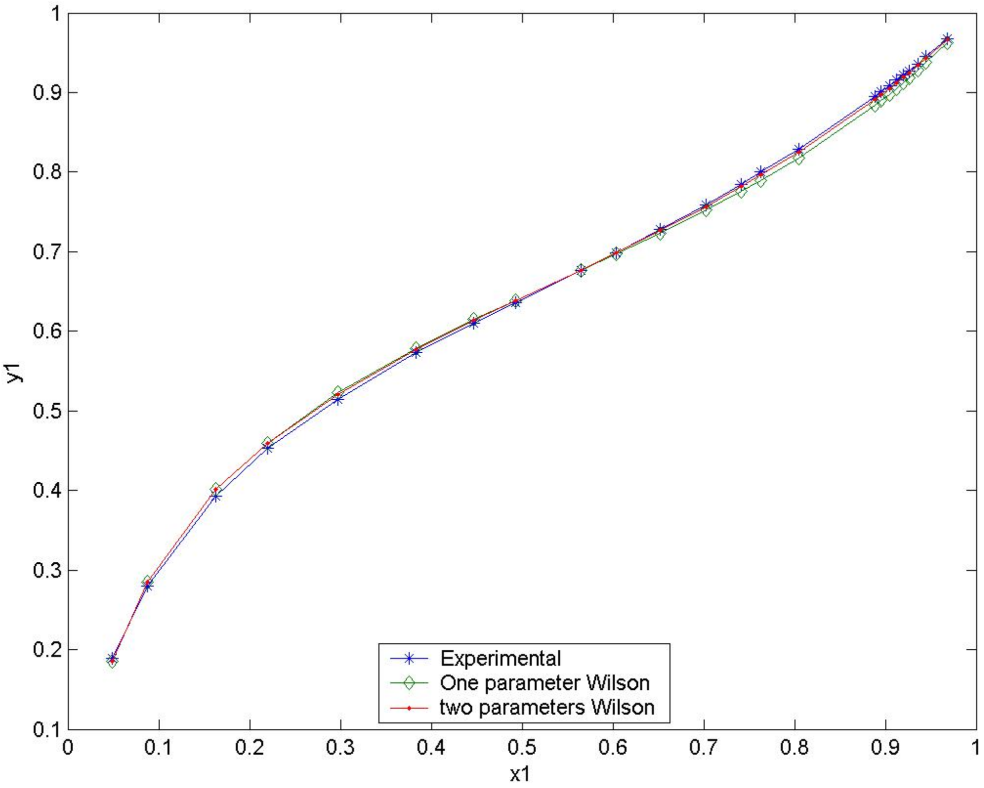

Figure 3-3 VLE for Acetone (1) – Carbon tetrachloride (2) P=450 mmHg by Using Wilson Equation for One Parameter and Two Parameters

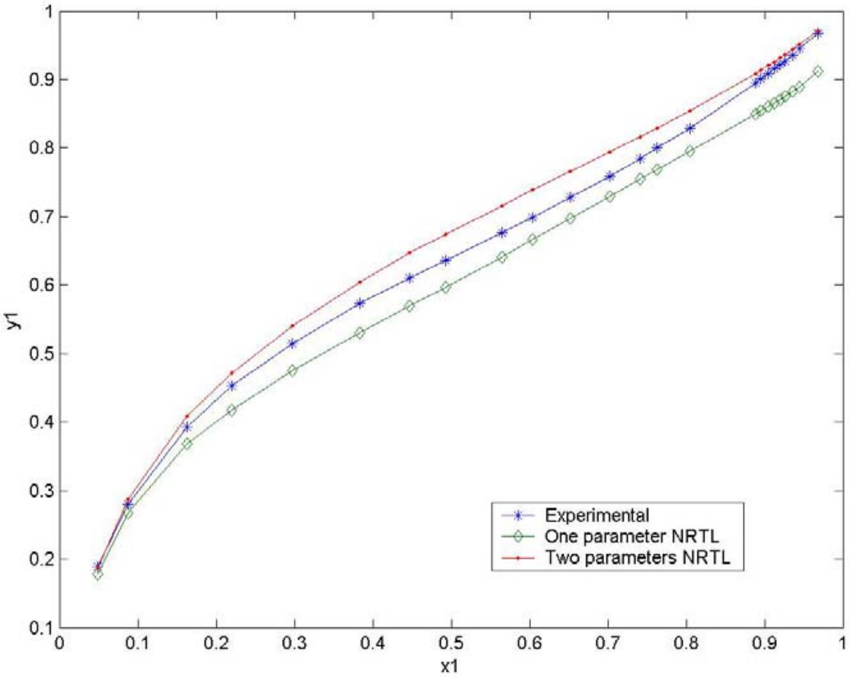

Figure 3-4 VLE for Acetone (1) – Carbon tetrachloride (2) P=450 mmHg by Using NRTL Equation for One Parameter and Two Parameters

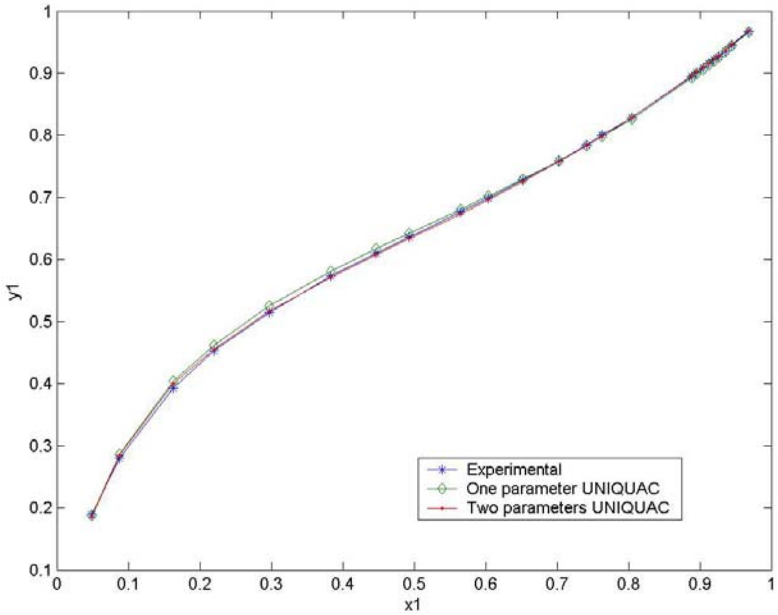

Figure 3-5 VLE for Acetone (1) – Carbon tetrachloride (2) P=450 mmHg by Using UNIQUAC equation for One Parameter and Two Parameters

Chapter Four

Discussion and Conclusions

4-1 Discussion

Experimental activity coefficients at infinite dilution are particularly useful for calculating the parameters needed in an expression for the excess Gibbs energy. In a binary mixture, suppose that experimental data are available for infinite-dilution activity coefficients γ^{∞}_1 and γ^{∞}_2. These can be used to evaluate two adjustable constants in any desired expression for G^E.

If reliable values of γ^{∞}_1 and γ^{∞}_2 are available, either from direct experiment or from a correlation, it is possible to predict the composition of the azeotrope and vapor-liquid equilibrium over the entire range of composition.

MOSCED equation and SPACE equation are two deferent methods used to calculate γ^{∞}_1 and γ^{∞}_2. Table (4-1) show the absolute deviation between the experimental and calculated γ^{∞}_1 and γ^{∞}_2 from MOSCED equation and SPACE equation for 18 systems.

Table 4-1 Absolute Deviation Between The Experimental and Calculated for MOSCED Equation and SPACE Equation.

	System,1-2	T °C	MOSCED eq. Absolute Deviation		SPACE eq. Absolute Deviation	
			γ^{∞}_1	γ^{∞}_2	γ^{∞}_1	γ^{∞}_2
1	Acetone – Acetonitrile	45	0.055	0.06	0.0546	0.0339
2	Acetone – Benzene	45	0.16939	0.1391	0.2025	0.0276
3	Acetone –Carbon tetrachloride	45	0.35345	0.0696	0.4948	0.001
4	Acetone – Methyl acetate	50	0.2783	0.1424	0.276	0.1328
5	Acetone –nitro methane	50	0.0977	0.0762	0.1099	0.1891
6	Acetonitrile – Benzene	100	0.8944	0.9907	0.2897	0.6802
7	Acetonitrile – nitro methane	40	0.0239	0.0162	0.0427	0.0309
8	Benzene – n-heptane	30	0.20136	0.1316	0.0091	0.0365
9	Carbon tetrachloride - Acetonitrile	60	0.4431	2.2722	1.2283	0.484
10	Chloroform – Methanol	50	1.23174	4.0544	0.1859	1.6689
11	Ethanol – Benzene	45	3.3057	0.1784	2.3898	0.7116
12	n-Hexane – Benzene	69	0.0564	0.0044	0.0163	0.1649
13	n-Hexane – Methylcyclopentane	69	0.15303	0.016	0.0905	0.0368
14	Methylcyclopentane – Benzene	72	0.0628	0.1037	0.2201	0.1790
15	Nitroethane – Benzene	25	0.57402	0.1806	0.5501	0.0226
16	Nitromethane – Benzene	25	0.80663	0.656	0.3746	0.4735
17	Nitro methane – Benzene	45	0.22507	0.7222	0.0797	0.4099
18	2-Nitropropane - carbon tetrachloride	25	1.4972	0.6248	1.5314	0.1922
	Average Absolute Deviation		**0.5794**	**0.5799**	**0.4526**	**0.3042**

In table 4-1 SPACE equation gives better results thane MOSCED equation where Average Absolute Deviation for SPACE equation = 0.4526, 0.3042 for γ^{∞}_1 and γ^{∞}_2 respectively and Average Absolute Deviation for MOSCED equation = 0.5794, 0.5799 for γ^{∞}_1 and γ^{∞}_2 respectively. SPACE is similar to MOSCED, but reduces the three adjustable parameters for each component to

0 and adds 7 adjustable parameters per functionality of compound. Thus, for a database containing 100 different solvents, MOSCED will have 300 parameters (3 per solvent) and SPACE about 100 parameters. The main advantage of SPACE over MOSCED is the prediction of activities coefficients of compounds that were not in the original database provided they have the same functionality as others in the database as well as the required solvent and solute parameters. The SPACE method is probably the best general method now available for estimating activities coefficients at infinite dilution.

For azeotropic calculation table (4-2) gives summarized results of percent deviation of azeotrope *Composition* obtained from Wilson, NRTL and UNIQUAC equations for *two* parameters calculated from experimental activities coefficients at infinite dilution. UNIQUAC equation gives best results than NRTL and Wilson equations and NRTL gives better results than Wilson equation.

For ten binary mixtures using two activities coefficients at infinite dilution

Average %deviation X^{az}_1 Wilson = 2.4917
Average %deviation X^{az}_1 NRTL = 0.97596
Average %deviation X^{az}_1 UNIQUAC = 0.52713

Similar to table (4-2) table (4-3) gives results of percent deviation of azeotrope *Pressure* obtained from Wilson, NRTL and UNIQUAC equations for *two* parameters. UNIQUAC equation gives best results than NRTL and Wilson eqs. And NRTL gives better results than Wilson equation

For ten binary mixtures using two activities coefficients at infinite dilution

Average deviation for P^{az} Wilson = 0.062145
Average deviation for P^{az} NRTL = 0.061452
Average deviation for P^{az} UNIQUAC = 0.060574

When only one γ^{∞} is available, we used one parameter Wilson, NRTL and UNIQUAC equations. Table 4-4 shows the percent deviation of azeotrope *Composition* obtained from Wilson, NRTL and UNIQUAC equations for *one* parameter calculated from experimental activities coefficients at infinite dilution. UNIQUAC equation gives best results than NRTL and Wilson eqs. And NRTL equation gives better results than Wilson equation.

For ten binary mixtures using one activity coefficient at infinite dilution

Average %deviation X^{az}_1Wilson = 3.0532
Average %deviation X^{az}_1 NRTL = 2.4917
Average %deviation X^{az}_1 UNIQUAC = 1.5044

Table 4-5 gives results of percent deviation of azeotrope *Pressure* obtained from Wilson, NRTL and UNIQUAC equations for *one* parameter. Wilson equation gives best results than NRTL and UNIQUAC eqs. And NRTL gives better results than UNIQUAC equation

For ten binary mixtures using one activity coefficient at infinite dilution
Average deviation Wilson = 0.077836
Average deviation NRTL = 0.08303
Average deviation UNIQUAC = 0.133212

Table 4-2 Percent Deviation of Azeotrope Composition from Two Parameters Equation γ^{∞}_1 and γ^{∞}_2

	Component	T °C	Wilson X_1^{az}%Deviation	NRTL X_1^{az}%Deviation	UNIQUAC X_1^{az}%Deviation
1	Acetone – Carbontetrachloriede	45	7.9662	0.1893	0.127
2	Acetone – chloroform	50	3.6246	2.8412	0.0058
3	Acetonitrile – Benzen	45	1.2997	0.6385	0.0092
4	Carbontetrachloride - Acetonitrile	45	0.3012	0.1006	0.0021
5	Chloroform - Methanol	50	3.0768	2.5624	2.0536
6	Methyl cyclopentane – Benzene	72	2.88998	2.758	2.8282
7	Nitromethane – Benzene	25	0.074	0.3034	0.0322
8	Nitromethane – Benzene	45	0.2254	0.0459	0.0172
9	Nitromethane - carbon tetrachloride	45	0.8133	0.1995	0.1628
10	n-hexane –Benzene	69	4.6458	0.1208	0.0332
	Average %deviation		**2.4917**	**0.97596**	**0.52713**

Table 4-3 Percent Deviation of Azeotrope Pressure (bar) from Two Parameters Equation γ^{∞}_1 and γ^{∞}_2

	Component	T °C	Wilson P^{az} Deviation	NRTL P^{az} Deviation	UNIQUAC P^{az} Deviation
1	Acetone – Carbontetrachloriede	45	0.00157	0.00051	0.00013
2	Acetone – chloroform	50	0.01283	0.00728	0.01399
3	Acetonitrile – Benzen	45	0.01208	0.02013	0.01245
4	Carbontetrachloride - Acetonitrile	45	0.00284	0.00088	0.01023
5	Chloroform - Methanol	50	0.00348	0.02936	0.01443
6	Methyl cyclopentane – Benzene	72	0.319	0.30342	0.30341
7	Nitromethane – Benzene	25	0.00249	0.00253	0.000101
8	Nitromethane – Benzene	45	0.00116	0.00133	0.00391
9	Nitromethane - carbon tetrachloride	45	0.01081	0.00311	0.00114
10	n-hexane –Benzene	69	0.25519	0.24597	0.24595
	Average deviation		**0.062145**	**0.061452**	**0.060574**

Table 4-4 Percent Deviation of Azeotrope Composition from One Parameter Equation

	Component	T °C	Wilson X_1^{az}%Deviation	NRTL X_1^{az}%Deviation	UNIQUAC X_1^{az}%Deviation
1	Acetone – Carbontetrachloriede	45	1.6200	4.7413	0.4425
2	Acetone – chloroform	50	0.7269	3.8476	1.3491
3	Acetonitrile – Benzen	45	0.4691	13.1524	0.0088
4	Carbontetrachloride - Acetonitrile	45	2.3878	4.0572	0.0083
5	Chloroform - Methanol	50	0.1172	3.5657	0.0072
6	Methyl cyclopentane – Benzene	72	6.0184	0.7786	1.7191
7	Nitromethane – Benzene	25	1.9503	1.7236	3.02607
8	Nitromethane – Benzene	45	2.70096	2.9794	4.31905
9	Nitromethane - carbon tetrachloride	45	2.15701	3.2429	3.9917
10	n-hexane –Benzene	69	12.3839	0.1238	0.1718
	Average %deviation		**3.053157**	**2.4917**	**1.504362**

Table 4-5 Percent Deviation of Azeotrope Pressure (bar) from One Parameter Equation

	Component	T °C	Wilson P^{az}Deviation	NRTL P^{az} Deviation	UNIQUAC P^{az} Deviation
1	Acetone – Carbontetrachloriede	45	0.020315	0.01863	0.000056
2	Acetone – chloroform	50	0.005086	0.00754	0.00209
3	Acetonitrile – Benzen	45	0.004612	0.04255	0.21618
4	Carbontetrachloride - Acetonitrile	45	0.040431	0.06225	0.47637
5	Chloroform - Methanol	50	0.092688	0.13712	0.05034
6	Methyl cyclopentane – Benzene	72	0.328115	0.30435	0.30904
7	Nitromethane – Benzene	25	0.002922	0.00231	0.00312
8	Nitromethane – Benzene	45	0.002838	0.00026	0.00378
9	Nitromethane - carbon tetrachloride	45	0.01765	0.00933	0.02518
10	n-hexane –Benzene	69	0.263697	0.24596	0.24596
	Average deviation		**0.077836**	**0.08303**	**0.133212**

To compare between one parameter equation and two parameters equation table 4-6 shows the deference between them for Wilson equation, table 4-7 for NRTL equation and table 4-8 for UNIQUAC equation. In all equations the two parameters give better results than one parameter but the deference between them are not so high and therefore using one parameter gives rather good and accepted results compared with two parameters in the systems that have only one γ^{∞} available.

Table 4-6 Two parameters and one parameter Wilson equation for percent deviation of azeotrope composition and pressure (bar).

	Component	**T °C**	**X_1^{az} %Deviation**		**P^{az}Deviation**	
			One	**Two**	**One**	**Two**
1	Acetone – Carbontetrachloriede	45	1.6200	7.9662	0.020315	0.00157
2	Acetone – chloroform	50	0.7269	3.6246	0.005086	0.01283
3	Acetonitrile – Benzen	45	0.4691	1.2997	0.004612	0.01208
4	Carbontetrachloride - Acetonitrile	45	2.3878	0.3012	0.040431	0.00284
5	Chloroform - Methanol	50	0.1172	3.0768	0.092688	0.00348
6	Methyl cyclopentane – Benzene	72	6.0184	2.88998	0.328115	0.319
7	Nitromethane – Benzene	25	1.9503	0.074	0.002922	0.00249
8	Nitromethane – Benzene	45	2.70096	0.2254	0.002838	0.00116
9	Nitromethane - carbon tetrachloride	45	2.15701	0.8133	0.01765	0.01081
10	n-hexane –Benzene	69	12.3839	4.6458	0.263697	0.25519
	Average deviation		**3.053157**	**2.4917**	**0.077836**	**0.062145**

Table 4-7 Two Parameters and One Parameter NRTL Equation for Percent Deviation of Azeotrope Composition and Pressure (bar).

	Component	T °C	X_1^{az} %Deviation		P^{az} Deviation	
			One	Two	One	Two
1	Acetone – Carbontetrachloriede	45	4.7413	0.1893	0.01863	0.00051
2	Acetone – chloroform	50	3.8476	2.8412	0.00754	0.00728
3	Acetonitrile – Benzen	45	13.1524	0.6385	0.04255	0.02013
4	Carbontetrachloride - Acetonitrile	45	4.0572	0.1006	0.06225	0.00088
5	Chloroform - Methanol	50	3.5657	2.5624	0.13712	0.02936
6	Methyl cyclopentane – Benzene	72	0.7786	2.758	0.30435	0.30342
7	Nitromethane – Benzene	25	1.7236	0.3034	0.00231	0.00253
8	Nitromethane – Benzene	45	2.9794	0.0459	0.00026	0.00133
9	Nitromethane - carbon tetrachloride	45	3.2429	0.1995	0.00933	0.00311
10	n-hexane –Benzene	69	0.1238	0.1208	0.24596	0.24597
	Average deviation		**2.4917**	**0.97596**	**0.08303**	**0.061452**

Table 4-8 Two Parameters and One Parameter UNIQUAC Equation for Percent Deviation of Azeotrope Composition and Pressure (bar).

	Component	T °C	X_1^{az} %Deviation		P^{az} Deviation	
			One	Two	One	Two
1	Acetone – Carbontetrachloriede	45	0.4425	0.127	0.000056	0.00013
2	Acetone – chloroform	50	1.3491	0.0058	0.00209	0.01399
3	Acetonitrile – Benzen	45	0.0088	0.0092	0.21618	0.01245
4	Carbontetrachloride - Acetonitrile	45	0.0083	0.0021	0.47637	0.01023
5	Chloroform - Methanol	50	0.0072	2.0536	0.05034	0.01443
6	Methyl cyclopentane – Benzene	72	1.7191	2.8282	0.30904	0.30341
7	Nitromethane – Benzene	25	3.02607	0.0322	0.00312	0.000101
8	Nitromethane – Benzene	45	4.31905	0.0172	0.00378	0.00391
9	Nitromethane - carbon tetrachloride	45	3.9917	0.1628	0.02518	0.00114
10	n-hexane –Benzene	69	0.1718	0.0332	0.24596	0.24595
	Average deviation		**1.504362**	**0.52713**	**0.133212**	**0.060574**

From tables (4-6), (4-7) and (4-8) the Average % deviation of azeotrope composition for Wilson one parameter = 3.053157, two parameters = 2.4917, for NRTL one parameter = 2.4917, two parameters = 0.97596 and for UNIQUAC one parameter = 1.504362, two parameters = 0.52713.

And for the Average deviation of azeotrope Pressure (bar):
Wilson one parameter = 0.077836, two parameters = 0.062145
NRTL one parameter = 0.08303, two parameters = 0.061452
UNIQUAC one parameter = 0.133212, two parameters = 0.060574.

Therefore UNIQUAC is the best equation between the others for one parameter and two parameters for azeotrope calculation.

The other calculation that used is Vapor Liquid Equilibrium calculated from Experimental γ^{∞} for 13 systems of 194 points, some of them are isobaric and the other is isothermal.

Table 4-9 shows the average absolute % deviation for these systems where:

Wilson equation one parameter = 2.3627, two parameters = 0.8186
NRTL equation one parameter = 2.2892, two parameters = 1.2134
UNIQUAC equation one parameter = 1.3155, two parameters = 0.7877

In VLE calculation UNIQUAC is the best between the other equations and then Wilson equation and then NRTL equation. For strongly nonideal binary mixtures, e.g., solutions of alcohols with hydrocarbons, the equation of Wilson is probably better than NRTL because it contains only two adjustable parameters while NRTL equation contain three parameters g_{ij} and g_{ji} denote energy parameters, and α_{12} that related to the nonrandom ness in the mixture NRTL equation gives less than the others because the third parameter α_{12} where it is found by fitting.

Table 4-9 Average Absolute % Deviation for y_1 for all systems

	Systems	**P in mmHg T in C^o**	**No. of point**	**Wilson**		**NRTL**		**UNIQUAC**	
				Parameters One	**Two**	**Parameters One**	**Two**	**Parameters One**	**Two**
1	Benzene – Acetonitrile	Isothermal T =70	21	1.9294	1.9044	2.7988	1.7167	1.6661	1.6163
2	Methanol –Water	Isobaric P = 760	26	3.2758	2.1413	2.4775	2.0513	1.9821	1.5083
3	Acetone (1)- Carbontetrachloride (2)	Isobaric P = 450	24	0.7259	0.3249	3.8627	2.0761	0.3735	0.2005
4	Hexane (1) - Benzene (2)	Isobaric P=735	11	2.3379	0.6727	1.8786	0.7361	5.3490	0.6812
5	Acetone (1) - Benzene (2)	Isobaric P= 738	10	1.8799	0.8494	1.1519	2.0163	0.8019	0.7854
6	Acetone (1)-Water (2)	Isobaric P= 760	13	1.2764	1.0586	2.0921	1.2743	1.1605	0.7809
7	Methelcyclopentane (1) – Benzene (2)	Isobaric P= 760	15	0.4823	0.3538	1.1235	0.6554	0.3601	0.4110
8	Benzene (1) – Heptane (2)	Isobaric P= 760	18	9.8944	0.4573	1.4158	0.6411	0.5809	0.4804
9	Acetone (1) - Benzene (2)	Isothermal T = 45	11	0.48319	0.3964	3.1053	0.7277	0.4547	0.3527
10	Acetone (1) – Acetonitrile (2)	Isothermal T = 45	10	0.76065	0.7518	0.7776	0.7738	0.7467	0.7153
11	Acetonitrile (1) – Nitro methane (2)	Isothermal T = 60	10	2.50597	0.3938	0.7455	0.5826	0.4469	0.391
12	Nitro methane (1) – carbon tetrachloride (2)	Isothermal T = 45	12	0.95157	0.7698	3.4571	0.6849	1.2256	0.5957
13	Carbon tetrachloride (1) – Acetonitrile (2)	Isothermal T = 45	13	4.21182	0.5674	4.8732	1.8375	1.9538	1.7218
	Average Absolute % Deviation for 13 systems		**194**	**2.3627**	**0.8186**	**2.2892**	**1.2134**	**1.3155**	**0.7877**

4-2 Conclusions

1. The most important two methods for calculating the activities coefficients at infinite dilution are SPACE method and MOSCED method. And it was found that SPACE method is better than MOSCED where SPACE gives Average Absolute Deviation = 0.4526, 0.3042 for γ^{∞}_1 and γ^{∞}_2 respectively and MOSCED equation give Average Absolute Deviation = 0.5794, 0.5799 for γ^{∞}_1 and γ^{∞}_2 respectively

2. One of the uses of activities coefficients at infinite dilution is the calculation of azeotropic properties (azeotropic composition and pressure). The equations used are Wilson, NRTL and UNIQUAC where UNIQUAC equation gives better results than NRTL and Wilson equations.

3. The other uses of activities coefficients at infinite dilution is the calculation of VLE and the same equation are used (Wilson, NRTL and UNIQUAC).UNIQUAC equation also gives the best results than the others.

4. In the system that has only one γ^{∞} available, the use of one parameter equation gives result with accuracy near to the two parameters equation which is accepted.

4-3 Recommendations

For those who would carry future studies on related subject, the following recommendations may be considered:

1. Studying the possibility of applying these methods to ternary systems.
2. Finding other equations to calculate the activity coefficient at infinite dilution
3. Studying the other uses of the activity coefficient at infinite dilution.

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Appendix A

Pure Component Critical Parameters and Thermodynamic parameters

Table A-1 Pure Component Critical Parameters

	Component	Formula	MW	Tc (K)	Pc bar	Vc cm^3/ mol	Zc	w
1	**Acetone**	C_3H_6O	58.080	508.1	47	209	0.232	0.304
2	**Acetonitrile**	C_2H_3N	41.053	545.5	48.3	173	0.184	0.327
3	**Benzene**	C_6H_6	78.114	562.2	48.9	259	0.271	0.212
4	**Carbon tetrachloride**	CCl_4	153.823	556.4	45.6	275.9	0.272	0.193
5	**Chloroform**	$CHCl_3$	119.378	536.4	53.7	238.9	0.293	0.218
6	**Water**	H_2O	18.015	647.3	221.2	57.1	0.235	0.344
7	**Methanol**	CH_4O	32.042	512.6	80.9	118.0	0.224	0.556
8	**Methylcyclopentane**	C_6H_{12}	84.162	532.7	37.8	319	0.272	0.231
9	**n-Heptane**	C_7H_{16}	100.205	540.3	27.4	432	0.263	0.349
10	**n-Hexane**	C_6H_{14}	86.178	507.5	30.1	370	0.264	0.299
11	**Nitromethane**	CH_3NO_2	61.041	588	63.1	173	0.208	0.310

Table A-2 Enthalpy of Vaporization of Pure Component

	Component	Boiling Temperature ^{o}C	ΔH_v at T_b KJ/mol
1	**Acetone**	56.05	29.10
2	**Acetonitrile**	81.65	29.75
3	**Benzene**	80.09	30.72
4	**Carbon tetrachloride**	76.8	29.82
5	**Chloroform**	61.17	29.24
6	**Water**	100.0	40.65
7	**Methanol**	64.6	35.21
8	**Methylcyclopentane**	71.8	29.08
9	**n-Heptane**	98.5	31.77
10	**n-Hexane**	68.73	28.85
11	**Nitromethane**	101.19	33.99

Table A-3 Pure Component Vapor Pressure Correlations Parameters

	Component	A	B	C	D	eq.
1	**Acetone**	-7.45514	1.202	-2.43926	-3.3559	1
2	**Acetonitrile**	40.774	5392.43	-4.357	2615	2
3	**Benzene**	-6.98273	1.33213	-2.62863	-3.33399	1
4	**Carbon tetrachloride**	-7.07139	1.71497	-2.8993	-2.49466	1
5	**Chloroform**	-6.95546	1.16625	-2.1397	-3.44421	1
6	**Water**	-7.76451	1.45838	-2.7758	-1.23303	1
7	**Methanol**	-8.54796	0.76982	-3.10850	1.54481	1
8	**Methylcyclopentane**	-7.15937	1.48017	-2.92482	-1.98377	1
9	**n-Heptane**	-7.67468	1.37068	-3.53620	-3.20243	1
10	**n-Hexane**	-7.46765	1.44211	-3.28222	-2.50941	1
11	**Nitromethane**	-8.41688	2.76466	-3.65341	-1.01376	1

Eq1 (Wagner equation)

$\ln (P/Pc) = (1-x)^{-1} [A * x + B * x^{1.5} + C * x^3 + D * x^6]$

$x = 1- (T / Tc)$

Eq2

$\text{Ln } P = A - (B/ T) + C* \ln T + D* P / T^2$

Table A-4 UNIQUAC Parameters r, q and q`

	Component	*r*	*q*	*q`*
1	**Acetone**	2.57	2.34	2.34
2	**Acetonitrile**	1.87	1.72	1.72
3	**Benzene**	3.19	2.40	2.40
4	**Carbon tetrachloride**	3.33	2.82	2.82
5	**Chloroform**	2.70	2.34	2.34
6	**Water**	0.92	1.40	1.00
7	**Methanol**	1.43	1.43	0.96
8	**Methylcyclopentane**	3.97	3.01	3.01
9	**n-Heptane**	5.17	4.40	4.40
10	**n-Hexane**	4.50	3.86	3.86
11	**Nitromethane**	2.0086	1.868	1.868

Appendix B

Azeotropic Calculation Results

Table B-1 Wilson Equation Two Parameters

	Component	**T °C**	**X_1^{az} wt% Exp.**	**X_1^{az}wt % Calculated**	**X_1^{az} %Deviation**	**P^{az} (bar) Exp.**	**P^{az} (bar) calculated**	**P^{az} Deviation**
1	Acetone – carbontetrachloriede	45	91	83.0338	7.9662	0.68421	0.6857756	0.0005656
2	Acetone – chloroform	50	22.9	19.2754	3.6246	0.6066168	0.5937878	0.012829
3	Acetonitrile – benzene	45	30.7	31.9997	1.2997	0.3706362	0.3827165	0.012083
4	Carbontetrachloride - Acetonitrile	45	84.5	84.1988	0.3012	0.494893	0.4920531	0.00284
5	Chloroform - Methanol	50	87.8	90.8768	3.0768	0.835981	0.8394568	0.0034758
6	Methyl cyclopentane – benzene	72	91	93.88997	2.88998	0.69861	1.017614	0.319004
7	Nitromethane – benzene	25	6.4	6.326	0.074	0.1302559	0.1277741	0.0024818
8	Nitromethane – benzene	45	9.6	9.82538	0.22538	0.303975	0.3028223	0.0011527
9	Nitromethane- carbon tetrachloride	45	10.6	9.7867	0.81334	0.40396678	0.3931637	0.010803
10	n-hexane- Benzene	69	99.8	95.1542	4.6458	0.76660362	1.02179	0.2551862
	Average deviation				**2.491708**			**0.062042**

Table B-2 Wilson Equation One Parameter

	Component	**T °C**	**X_1^{az} wt% Exp.**	**X_1^{az}wt % Calculated**	**X_1^{az} %Deviation**	**P^{az} (bar) Exp.**	**P^{az} (bar) calculated**	**P^{az} Deviation**
1	Acetone – carbontetrachloriede	45	92.62	91	26.05313	0.7045251	0.68421	0.020315
2	Acetone – chloroform	50	23.62689	22.9	0.7268944	0.6117064	0.6066168	0.00509
3	Acetonitrile – benzene	45	30.23095	30.7	0.4690552	0.3752523	0.3706362	0.004616
4	Carbontetrachloride - Acetonitrile	45	82.11217	84.5	2.387825	0.4544587	0.494893	0.040434
5	Chloroform - Methanol	50	87.91739	87.8	0.1173859	0.7432916	0.835981	0.092689
6	Methyl cyclopentane – benzene	72	84.98158	91	6.018425	1.026725	0.69861	0.328115
7	Nitromethane – benzene	25	4.449703	6.4	1.950297	0.1273378	0.1302559	0.002918
8	Nitromethane – benzene	45	6.899038	9.6	2.700963	0.3011422	0.303975	0.002833
9	Nitromethane- carbon tetrachloride	45	8.442991	10.6	2.157009	0.3863205	0.40396678	0.017646
10	n-hexane- Benzene	69	87.41606	99.8	12.38394	1.030297	0.76660362	0.263693
	Average deviation				**3.06318**			**0.077835**

Table B-3 NRTL Equation Two Parameters

	Component	**T °C**	**X_1^{az} wt% Exp.**	**X_1^{az}wt % Calculated**	**X_1^{az} %Deviation**	**P^{az} (bar) Exp.**	**P^{az} (bar) calculated**	**P^{az} Deviation**
1	Acetone – carbontetrachloriede	45	91	90.8107	0.1893	0.68421	0.6847202	0.00051
2	Acetone – chloroform	50	22.9	25.7412	2.8412	0.6066168	0.5993353	0.007281
3	Acetonitrile – benzene	45	30.7	30.0615	0.6386	0.3706362	0.3505138	0.020122
4	Carbontetrachloride - Acetonitrile	45	84.5	84.3994	0.1006	0.494893	0.4940087	0.000884
5	Chloroform - Methanol	50	87.8	90.3624	2.5624	0.835981	0.8653398	0.029359
6	Methyl cyclopentane – benzene	72	91	93.758	2.758	0.69861	1.00203	0.30342
7	Nitromethane – benzene	25	6.4	6.70343	0.3034	0.1302559	0.1277272	0.002529
8	Nitromethane – benzene	45	9.6	9.55408	0.0459	0.303975	0.3026555	0.001319
9	Nitromethane-carbon tetrachloride	45	10.6	10.7995	0.1995	0.4039668	0.400862	0.003105
10	n-hexane-Benzene	69	99.8	99.9208	0.1208	0.7666036	1.012566	0.245962
	Average deviation				**1.129017**			**0.061449**

Table B-4 NRTL Equation One Parameter

	Component	**T °C**	**X_1^{az} wt% Exp.**	**X_1^{az}wt % Calculated**	**X_1^{az} %Deviation**	**P^{az} (bar) Exp.**	**P^{az} (bar) calculated**	**P^{az} Deviation**
1	Acetone – carbontetrachloriede	45	86.2587	91	4.741302	0.7028383	0.68421	0.018628
2	Acetone – chloroform	50	26.74765	22.9	3.847649	0.5990843	0.6066168	0.007532
3	Acetonitrile – benzene	45	17.54763	30.7	13.15237	0.3280944	0.3706362	0.042542
4	Carbontetrachloride - Acetonitrile	45	80.44278	84.5	4.05722	0.4326412	0.494893	0.062252
5	Chloroform - Methanol	50	91.36569	87.8	3.565689	0.6988636	0.835981	0.137117
6	Methyl cyclopentane – benzene	72	91.77856	91	.7785645	1.002964	0.69861	0.304354
7	Nitromethane – benzene	25	8.123585	6.4	1.723585	0.1279538	0.1302559	0.002302
8	Nitromethane – benzene	45	12.57942	9.6	2.979422	0.304242	0.303975	0.000267
9	Nitromethane- carbon tetrachloride	45	13.84286	10.6	3.242859	0.4134979	0.40396678	0.009531
10	n-hexane- Benzene	69	99.92377	99.8	.1237717	1.012565	0.76660362	0.245961
	Average deviation				**2.491708**			**0.083049**

Table B-5 UNIQUAC Equation Two Parameters

	Component	**T °C**	**z**	**X_1^{az} wt% Exp.**	**X_1^{az}wt % Calculated**	**X_1^{az} %Deviation**	**P^{az} (bar) Exp.**	**P^{az} (bar) calculated**	**P^{az} Deviation**
1	Acetone – carbontetrachloriede	45	0.8	91	90.87299	0.12701	0.68421	.6840771	0.000133
2	Acetone – chloroform	50	3.9	22.9	22.90575	0.0057526	0.60662	.5926337	0.013983
3	Acetonitrile – benzene	45	0.65	30.7	30.70921	0.0092077	0.37064	.38309	0.012454
4	Carbontetrachloride - Acetonitrile	45	1.4	84.5	84.50208	0.0020752	0.49489	.5051199	0.010227
5	Chloroform - Methanol	50	0.01	87.8	89.85361	2.053612	0.83598	.8704141	0.034433
6	Methyl cyclopentane – benzene	72	0.01	91	93.82825	2.828247	0.69861	1.002017	0.303407
7	Nitromethane – benzene	25	6	6.4	6.367856	0.032145	0.13026	.1301554	0.000101
8	Nitromethane – benzene	45	3.5	9.6	9.582777	0.01722	0.30398	.3078898	0.003915
9	Nitromethane- carbon tetrachloride	45	2.5	10.6	10.7628	0.16280	0.403967	.4051147	0.001148
10	n-hexane- Benzene	69	0.36	99.8	99.83319	0.03319	0.766604	1.012552	0.245948
	Average deviation					**0.686426**			**0.062575**

Table B-6 UNIQUAC Equation One Parameter

	Component	T °C	z	X_1^{az} wt% Exp.	X_1^{az}wt % Calculated	X_1^{az} %Deviation	P^{az} (bar) Exp.	P^{az} (bar) calculated	P^{az} Deviation
1	Acetone – carbontetrachloriede	45	0.25	91	90.55747	0.4425	0.68421	0.68427	5.64E-05
2	Acetone – chloroform	50	0.01	22.9	24.24907	1.3491	0.60662	0.60871	0.002095
3	Acetonitrile – benzene	45	7.9	30.7	30.70876	0.00876	0.37064	0.15446	0.21618
4	Carbontetrachloride - Acetonitrile	45	8.4	84.5	84.49172	0.00828	0.49489	0.01852	0.476378
5	Chloroform - Methanol	50	5.9	87.8	87.80721	0.007218	0.83598	0.05863	0.777348
6	Methyl cyclopentane – benzene	72	0.1	91	89.28091	1.719093	0.69861	1.00765	0.30904
7	Nitromethane – benzene	25	0.01	6.4	3.373932	3.026068	0.13026	0.12714	0.003115
8	Nitromethane – benzene	45	0.01	9.6	5.280945	4.319055	0.30398	0.30020	0.003772
9	Nitromethane- carbon tetrachloride	45	0.01	10.6	6.608303	3.991698	0.403967	0.37879	0.025173
10	n-hexane- Benzene	69	0.37	99.8	99.62823	0.1717682	0.766604	1.0126	0.245961
	Average deviation					**1.632101**			**0.205912**

Appendix C

VLE Calculation Results

Table C-1 Benzene – Acetonitrile At T = 70 for Two Parameters equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	P torr.	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	526.60	0.0014	0.0049	0.0218	0.01688	0.0218	0.01688	0.0218	0.01688
2	527.36	0.0027	0.0100	0.0121	0.00206	0.0121	0.00206	0.0121	0.00207
3	533.14	0.0088	0.0212	0.0284	0.00722	0.0284	0.00718	0.0285	0.00726
4	558.22	0.0356	0.0862	0.0949	0.00868	0.0942	0.00804	0.0954	0.00918
5	574.41	0.0589	0.1300	0.1388	0.00879	0.1373	0.00726	0.14	0.01004
6	596.75	0.0963	0.1927	0.1978	0.00507	0.1945	0.00182	0.2007	0.00796
7	628.29	0.1688	0.2830	0.2826	0.00039	0.2762	0.00682	0.2894	0.00642
8	661.27	0.2918	0.3825	0.3805	0.00202	0.3721	0.01037	0.3937	0.01123
9	673.44	0.3685	0.4337	0.4261	0.00762	0.4194	0.01433	0.4421	0.00839
10	677.92	0.4143	0.4615	0.4498	0.01175	0.445	0.01653	0.4667	0.00524
11	677.01	0.4213	0.4669	0.4521	0.01482	0.4476	0.01926	0.4692	0.00231
12	681.87	0.5040	0.5134	0.4921	0.02129	0.4926	0.02077	0.5093	0.00413
13	685.67	0.5391	0.5325	0.5108	0.02173	0.5137	0.01879	0.5272	0.00528
14	679.97	0.6088	0.5740	0.5411	0.03294	0.5489	0.02511	0.5551	0.01887
15	678.98	0.6524	0.6049	0.5643	0.04057	0.5749	0.03001	0.576	0.02889
16	673.66	0.6825	0.6219	0.5792	0.04268	0.5914	0.03048	0.5889	0.03295
17	656.26	0.7794	0.6958	0.6421	0.05366	0.6566	0.03916	0.6439	0.0519
18	631.94	0.8672	0.7725	0.7287	0.04377	0.7395	0.03304	0.723	0.04948
19	602.22	0.9338	0.8640	0.8315	0.03252	0.8355	0.02845	0.8234	0.04055
20	582.01	0.9630	0.9168	0.894	0.02275	0.8952	0.02158	0.8876	0.02925
21	556.24	0.9955	0.9824	0.9851	0.0027	0.985	0.00255	0.9839	0.00154
	Average Deviation			**0.019044**		**0.0171674**		**0.0166577**	

Table C-2 Benzene – Acetonitrile At T = 70 for One Parameter equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	P torr.	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	526.60	0.0014	0.0049	0.0218	0.01688	0.0218	0.01688	0.0218	0.01689
2	527.36	0.0027	0.0100	0.0121	0.00206	0.0121	0.00206	0.0121	0.00206
3	533.14	0.0088	0.0212	0.0284	0.00724	0.0284	0.00725	0.0284	0.00722
4	558.22	0.0356	0.0862	0.0951	0.00893	0.0953	0.00906	0.0953	0.00913
5	574.41	0.0589	0.1300	0.1394	0.0094	0.1398	0.0098	0.1401	0.01005
6	596.75	0.0963	0.1927	0.1992	0.00649	0.2004	0.00772	0.2009	0.00823
7	628.29	0.1688	0.2830	0.286	0.00298	0.2904	0.00741	0.2905	0.00752
8	661.27	0.2918	0.3825	0.3872	0.00467	0.4025	0.01998	0.3966	0.01415
9	673.44	0.3685	0.4337	0.4342	0.00053	0.4599	0.02625	0.4461	0.0124
10	677.92	0.4143	0.4615	0.4584	0.0031	0.4917	0.03016	0.4713	0.00981
11	677.01	0.4213	0.4669	0.4608	0.0061	0.4954	0.02847	0.4739	0.00696
12	681.87	0.5040	0.5134	0.5006	0.01279	0.5514	0.03797	0.5146	0.00117
13	685.67	0.5391	0.5325	0.5187	0.01382	0.5769	0.04435	0.5326	0.00011
14	679.97	0.6088	0.5740	0.5469	0.0271	0.6218	0.04779	0.5604	0.01362
15	678.98	0.6524	0.6049	0.5681	0.03683	0.6534	0.04848	0.5808	0.02408
16	673.66	0.6825	0.6219	0.5811	0.04077	0.6741	0.05215	0.5933	0.02858
17	656.26	0.7794	0.6958	0.6359	0.05987	0.7496	0.05379	0.6458	0.05
18	631.94	0.8672	0.7725	0.7138	0.05873	0.8312	0.05869	0.7216	0.05091
19	602.22	0.9338	0.8640	0.814	0.04995	0.906	0.042	0.8202	0.04383
20	582.01	0.9630	0.9168	0.88	0.03682	0.9441	0.02725	0.8846	0.03223
21	556.24	0.9955	0.9824	0.9825	0.00011	0.9926	0.01024	0.9833	0.00094
	Average Deviation			**0.019294**		**0.027988**		**0.01666099**	

Table C-3 Methanol –Water At P = 760 mmHg for Two Parameters equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	100.00	0.000006	0.000045	0.00001	0.000032	0.000202	0.00016	0.00004	0.000005
2	100.00	0.000004	0.000044	0.00001	0.000036	0.00013	0.00009	0.00003	0.00002
3	100.00	0.000004	0.000037	0.00001	0.000029	0.00013	0.00009	0.00003	0.00001
4	100.00	0.000054	0.000516	0.00011	0.000401	0.001752	0.00124	0.00038	0.00014
5	100.00	0.000053	0.000458	0.00011	0.000346	0.001719	0.00126	0.00037	0.00009
6	100.00	0.000047	0.000428	0.0001	0.000328	0.001525	0.0011	0.00033	0.0001
7	100.00	0.000048	0.000423	0.0001	0.000321	0.001557	0.00113	0.00034	0.00009
8	99.95	0.000450	0.003849	0.00095	0.002895	0.014531	0.01068	0.00315	0.0007
9	99.95	0.000394	0.003296	0.00084	0.002461	0.012729	0.00943	0.00276	0.00053
10	99.25	0.005719	0.045222	0.03133	0.013893	0.031313	0.01391	0.03127	0.01395
11	99.25	0.005840	0.045705	0.03145	0.014257	0.031431	0.01427	0.03139	0.01432
12	95.10	0.0342	0.2222	0.1904	0.03179	0.19	0.03225	0.1888	0.03343
13	95.00	0.0335	0.2195	0.1927	0.02675	0.1923	0.02719	0.1912	0.02832
14	94.95	0.0329	0.2179	0.1937	0.0242	0.1933	0.02463	0.1922	0.02572
15	90.35	0.0761	0.3674	0.3526	0.01477	0.351	0.01643	0.3464	0.021
16	90.15	0.0738	0.3665	0.3557	0.01076	0.3542	0.01232	0.3499	0.01661
17	86.50	0.1176	0.4855	0.4688	0.01675	0.4657	0.01976	0.457	0.02854
18	86.45	0.1207	0.4694	0.4719	0.00248	0.4687	0.00067	0.4596	0.00984
19	79.15	0.2646	0.6184	0.678	0.05963	0.6706	0.05217	0.6451	0.0267
20	75.20	0.4092	0.7305	0.788	0.05749	0.7782	0.04771	0.739	0.00854
21	71.80	0.5810	0.8079	0.8759	0.06804	0.8665	0.05863	0.8201	0.01223
22	71.80	0.5816	0.8313	0.8761	0.04484	0.8667	0.03543	0.8203	0.011
23	69.10	0.7218	0.8542	0.9297	0.07547	0.9227	0.06846	0.881	0.02684
24	66.50	0.8808	0.9417	0.9744	0.03266	0.9712	0.02948	0.9475	0.00584
25	64.95	0.9657	0.9569	0.9933	0.03638	0.9924	0.03547	0.9847	0.02779
26	64.70	0.9871	0.9778	0.9975	0.01972	0.9972	0.01937	0.9942	0.01639
	Average Deviation			**0.02141256**		**0.02051305**		**0.01264267**	

Table C-4 Methanol –Water At P = 760 mmHg for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C°	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	100.00	0.000006	0.000045	0.00032	0.000279	0.0485	0.04842	0.0485	0.04842
2	100.00	0.000004	0.000044	0.00021	0.000165	0.0005	0.00056	0.0005	0.00056
3	100.00	0.000004	0.000037	0.00021	0.000172	0.0005	0.00055	0.0005	0.00055
4	100.00	0.000054	0.000516	0.00282	0.002299	0.0005	0.00098	0.0005	0.00098
5	100.00	0.000053	0.000458	0.00276	0.002305	0.0005	0.00093	0.0005	0.00093
6	100.00	0.000047	0.000428	0.00245	0.002022	0.0005	0.0009	0.0005	0.0009
7	100.00	0.000048	0.000423	0.0025	0.002079	0.0005	0.0009	0.0005	0.0009
8	99.95	0.000450	0.003849	0.0233	0.019454	0.0017	0.00215	0.0017	0.00215
9	99.95	0.000394	0.003296	0.02042	0.017122	0.0016	0.00165	0.0016	0.00165
10	99.25	0.005719	0.045222	0.03111	0.014116	0.0313	0.0139	0.0313	0.01391
11	99.25	0.005840	0.045705	0.03122	0.01449	0.0314	0.01426	0.0314	0.01427
12	95.10	0.0342	0.2222	0.1845	0.03767	0.1903	0.0319	0.1896	0.03256
13	95.00	0.0335	0.2195	0.1871	0.03239	0.1926	0.02685	0.192	0.02749
14	94.95	0.0329	0.2179	0.1883	0.02965	0.1936	0.0243	0.193	0.02491
15	90.35	0.0761	0.3674	0.3326	0.03484	0.3525	0.01493	0.3496	0.01779
16	90.15	0.0738	0.3665	0.3368	0.02967	0.3556	0.01089	0.3529	0.01359
17	86.50	0.1176	0.4855	0.4336	0.05192	0.4689	0.01663	0.4631	0.02239
18	86.45	0.1207	0.4694	0.4353	0.0341	0.472	0.0026	0.466	0.00342
19	79.15	0.2646	0.6184	0.592	0.02636	0.6806	0.06222	0.6633	0.04489
20	75.20	0.4092	0.7305	0.6615	0.06899	0.7936	0.06308	0.7676	0.03713
21	71.80	0.5810	0.8079	0.7169	0.09098	0.8836	0.07572	0.8548	0.0469
22	71.80	0.5816	0.8313	0.717	0.11433	0.8838	0.05252	0.855	0.02371
23	69.10	0.7218	0.8542	0.7636	0.09063	0.9369	0.08272	0.9127	0.05854
24	66.50	0.8808	0.9417	0.839	0.10266	0.9784	0.0367	0.9659	0.02422
25	64.95	0.9657	0.9569	0.9313	0.02562	0.9946	0.03767	0.9907	0.03383
26	64.70	0.9871	0.9778	0.9704	0.0074	0.998	0.02021	0.9965	0.01874
	Average Deviation			**0.03275814**		**0.02477507**		**0.01982079**	

Table C-5 Acetone – Carbon tetrachloride At P = 450 mmHg for Two Parameters equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	55.29	0.0490	0.1890	0.1856	0.00344	0.1862	0.00275	0.1852	0.00376
2	52.80	0.0875	0.2795	0.2853	0.00581	0.2875	0.00797	0.2844	0.00494
3	49.50	0.1625	0.3930	0.4019	0.00889	0.4089	0.01591	0.3996	0.00657
4	47.96	0.2200	0.4530	0.4589	0.00591	0.471	0.01796	0.4554	0.00242
5	46.26	0.2970	0.5150	0.5211	0.00612	0.5406	0.02564	0.5164	0.00136
6	44.88	0.3830	0.5735	0.5766	0.00309	0.6043	0.03082	0.5712	0.00234
7	44.06	0.4470	0.6100	0.6135	0.00353	0.6465	0.03648	0.6082	0.00176
8	43.65	0.4930	0.6355	0.6378	0.00225	0.6738	0.03829	0.6329	0.00258
9	43.05	0.5650	0.6770	0.6766	0.00044	0.7157	0.03867	0.6731	0.00393
10	42.68	0.6040	0.6990	0.6991	0.00012	0.7387	0.03972	0.6966	0.00236
11	42.42	0.6525	0.7280	0.7263	0.00169	0.7656	0.03758	0.7253	0.00275
12	42.11	0.7025	0.7590	0.7568	0.0022	0.7942	0.03517	0.7573	0.00165
13	41.92	0.7410	0.7840	0.7815	0.00253	0.8164	0.03235	0.7832	0.00077
14	41.82	0.7630	0.8000	0.7962	0.00377	0.8293	0.02927	0.7986	0.00136
15	41.73	0.8045	0.8290	0.825	0.00395	0.8539	0.02489	0.8285	0.00049
16	41.58	0.8890	0.8945	0.8917	0.000276	0.9091	0.01459	0.8961	0.00155
17	41.54	0.8955	0.9015	0.8975	0.004	0.9138	0.01231	0.9018	0.00026
18	41.56	0.9045	0.9090	0.9053	0.00369	0.9202	0.01123	0.9095	0.00048
19	41.57	0.9125	0.9165	0.9124	0.00407	0.9261	0.00958	0.9165	0.00002
20	41.53	0.9200	0.9225	0.9194	0.00313	0.9318	0.0093	0.9233	0.00078
21	41.53	0.9260	0.9270	0.9249	0.00209	0.9364	0.00938	0.9287	0.00168
22	41.49	0.9360	0.9360	0.9344	0.00158	0.9443	0.00825	0.9379	0.0019
23	41.46	0.9450	0.9450	0.9431	0.00188	0.9515	0.00649	0.9463	0.0013
24	41.50	0.9685	0.9675	0.9665	0.00102	0.9711	0.00363	0.9686	0.0011
	Average Deviation			**0.003248604**		**0.02076054**		**0.002005097**	

Table C-6 Acetone – Carbon tetrachloride At P = 450 mmHg for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	55.29	0.0490	0.1890	0.1852	0.0038	0.1775	0.01153	0.1878	0.00123
2	52.80	0.0875	0.2795	0.2848	0.00533	0.2678	0.01174	0.2863	0.00685
3	49.50	0.1625	0.3930	0.4019	0.00892	0.3687	0.02427	0.4041	0.01112
4	47.96	0.2200	0.4530	0.4595	0.0065	0.4175	0.03546	0.4619	0.00891
5	46.26	0.2970	0.5150	0.5226	0.00757	0.4746	0.04041	0.5249	0.00990
6	44.88	0.3830	0.5735	0.5785	0.00496	0.5301	0.04345	0.5808	0.00726
7	44.06	0.4470	0.6100	0.6152	0.00519	0.5699	0.04014	0.6177	0.00768
8	43.65	0.4930	0.6355	0.6387	0.0032	0.5969	0.03857	0.6417	0.0062
9	43.05	0.5650	0.6770	0.676	0.001	0.6411	0.03587	0.6801	0.00309
10	42.68	0.6040	0.6990	0.6978	0.0012	0.6667	0.03231	0.7024	0.00342
11	42.42	0.6525	0.7280	0.7234	0.00464	0.6969	0.03107	0.7292	0.00119
12	42.11	0.7025	0.7590	0.7523	0.00665	0.7296	0.02945	0.7593	0.00029
13	41.92	0.7410	0.7840	0.7758	0.00818	0.7547	0.02933	0.7836	0.00036
14	41.82	0.7630	0.8000	0.79	0.01005	0.7691	0.03093	0.7982	0.00177
15	41.73	0.8045	0.8290	0.8175	0.01149	0.7957	0.03329	0.8267	0.00233
16	41.58	0.8890	0.8945	0.8836	0.01086	0.8502	0.04435	0.8927	0.00182
17	41.54	0.8955	0.9015	0.8896	0.0119	0.8545	0.04699	0.8984	0.0031
18	41.56	0.9045	0.9090	0.8976	0.01145	0.8603	0.04874	0.9061	0.00287
19	41.57	0.9125	0.9165	0.9049	0.01162	0.8655	0.051	0.9132	0.00332
20	41.53	0.9200	0.9225	0.9122	0.0103	0.8707	0.0518	0.9201	0.00242
21	41.53	0.9260	0.9270	0.918	0.00901	0.8748	0.05216	0.9256	0.00143
22	41.49	0.9360	0.9360	0.9281	0.00791	0.8822	0.05381	0.935	0.001
23	41.46	0.9450	0.9450	0.9374	0.0076	0.8893	0.0557	0.9436	0.00137
24	41.50	0.9685	0.9675	0.9626	0.00489	0.9128	0.0547	0.9668	0.00072
	Average Deviation			**0.007258996**		**0.03862729**		**0.003735822**	

Table C-7 Hexane - Benzene At P = 735 mmHg for Two Parameters equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	Temp. C^{o}	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	78.40	0.0040	0.0090	0.0085	0.000529	0.0085	0.000522	0.0085	0.00053
2	77.70	0.0250	0.0600	0.0518	0.008204	0.052	0.007976	0.0518	0.00820
3	77.30	0.0430	0.0830	0.0798	0.0032	0.0804	0.002554	0.0798	0.00319
4	76.00	0.0750	0.1530	0.1431	0.009857	0.1449	0.008072	0.1432	0.00983
5	72.80	0.2150	0.3330	0.3259	0.00715	0.3362	0.003158	0.3259	0.00714
6	69.80	0.4300	0.5450	0.5229	0.022087	0.5474	0.002415	0.5226	0.02236
7	67.80	0.7130	0.7530	0.7424	0.010617	0.7711	0.01811	0.7421	0.01094
8	67.70	0.7630	0.7900	0.7821	0.007945	0.8087	0.018712	0.7818	0.00821
9	67.50	0.8890	0.8930	0.8909	0.0021	0.9071	0.014126	0.8908	0.00217
10	67.40	0.9650	0.9660	0.9641	0.00192	0.97	0.003964	0.9641	0.00191
11	67.30	0.9900	0.9900	0.9896	0.000392	0.9914	0.001361	0.9896	0.00039
	Average Deviation			**0.006727158**		**0.007360885**		**0.00680608**	

Table C-8 Hexane - Benzene At P = 735 mmHg for One Parameter equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	Temp. C^{o}	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	78.40	0.0040	0.0090	0.0085	0.00054	0.0085	0.00052	0.0085	0.00051
2	77.70	0.0250	0.0600	0.0516	0.00845	0.0522	0.00784	0.0507	0.00925
3	77.30	0.0430	0.0830	0.0791	0.00388	0.0809	0.00215	0.0768	0.00625
4	76.00	0.0750	0.1530	0.1413	0.0117	0.1462	0.00683	0.1348	0.01819
5	72.80	0.2150	0.3330	0.3152	0.01783	0.345	0.01205	0.28	0.05303
6	69.80	0.4300	0.5450	0.4943	0.05074	0.5726	0.02758	0.4177	0.12734
7	67.80	0.7130	0.7530	0.6972	0.05584	0.8043	0.05134	0.6172	0.13579
8	67.70	0.7630	0.7900	0.737	0.05296	0.8399	0.04991	0.6648	0.12521
9	67.50	0.8890	0.8930	0.8578	0.03519	0.9267	0.0337	0.8176	0.07536
10	67.40	0.9650	0.9660	0.9505	0.01547	0.9772	0.0112	0.937	0.02897
11	67.30	0.9900	0.9900	0.9854	0.00458	0.9935	0.00354	0.9815	0.00849
	Average Deviation			**0.02337906**		**0.01878623**		**0.05349025**	

Table C-9 Acetone - Benzene P=738 mmHg for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	78.02	0.0148	0.0465	0.0467	0.00017	0.0467	0.00016	0.0465	0.000049
2	75.85	0.0535	0.1468	0.1439	0.00287	0.1439	0.00288	0.1427	0.004136
3	73.45	0.1040	0.2468	0.2446	0.00223	0.2448	0.002	0.2409	0.005872
4	70.85	0.1791	0.3510	0.3555	0.00452	0.3568	0.00581	0.3482	0.002789
5	66.31	0.2374	0.4438	0.4769	0.03306	0.4794	0.03556	0.4683	0.02448
6	62.89	0.3403	0.5481	0.5846	0.03645	0.5899	0.04177	0.5752	0.027137
7	62.89	0.4620	0.6461	0.646	0.0001	0.6553	0.00915	0.6382	0.007883
8	60.31	0.6014	0.7446	0.7441	0.00053	0.7553	0.01075	0.742	0.002551
9	58.22	0.7590	0.8475	0.8431	0.00437	0.8525	0.00501	0.8472	0.000259
10	56.25	0.9276	0.9517	0.9511	0.00064	0.9538	0.00209	0.9551	0.003379
	Average Deviation			**0.008493556**		**0.01151911**		**0.007853623**	

Table C-10 Acetone - Benzene P=738 mmHg for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	78.02	0.0148	0.0465	0.0465	0.00004	0.0451	0.00138	0.0468	0.00033
2	75.85	0.0535	0.1468	0.1417	0.00514	0.1314	0.01541	0.1434	0.00337
3	73.45	0.1040	0.2468	0.2378	0.009	0.2164	0.03042	0.2427	0.00405
4	70.85	0.1791	0.3510	0.3404	0.01055	0.3112	0.03976	0.3515	0.00047
5	66.31	0.2374	0.4438	0.459	0.01523	0.4317	0.01213	0.4724	0.02856
6	62.89	0.3403	0.5481	0.5602	0.0121	0.5396	0.00851	0.5795	0.03141
7	62.89	0.4620	0.6461	0.6084	0.03771	0.6055	0.04061	0.6409	0.00519
8	60.31	0.6014	0.7446	0.7034	0.04125	0.7178	0.02683	0.742	0 .00255
9	58.22	0.7590	0.8475	0.8068	0.04066	0.8308	0.01666	0.8447	0.00279
10	56.25	0.9276	0.9517	0.9354	0.0163	0.9418	0.00992	0.9532	0.00146
	Average Deviation			**0.01879854**		**0.02016328**		**0.008018757**	

Table C-11 Acetone – Water At P = 760mmHg for Two Parameters equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	100.00	0.0030	0.0440	0.037	0.00702	0.037	0.007	0.037	0.00699
2	94.00	0.0110	0.2040	0.2024	0.00161	0.2026	0.00136	0.2027	0.00131
3	84.70	0.0250	0.4220	0.4461	0.02414	0.4469	0.02493	0.4471	0.02514
4	75.00	0.0540	0.6150	0.6334	0.01841	0.6355	0.02049	0.636	0.02102
5	72.10	0.0820	0.6780	0.6809	0.00295	0.6847	0.00667	0.6854	0.00743
6	68.30	0.1040	0.7300	0.7322	0.00218	0.7368	0.00683	0.7376	0.0076
7	64.60	0.1560	0.7910	0.7778	0.0132	0.7853	0.00571	0.7856	0.00535
8	64.00	0.1940	0.7950	0.787	0.00801	0.7971	0.00214	0.7967	0.00175
9	63.80	0.3300	0.8250	0.8003	0.02473	0.8213	0.00375	0.815	0.00996
10	62.40	0.4450	0.8330	0.8235	0.00955	0.851	0.01797	0.8382	0.00519
11	63.30	0.6220	0.8550	0.8438	0.01124	0.878	0.023	0.8537	0.00133
12	60.40	0.7950	0.8960	0.9041	0.00807	0.928	0.03195	0.9032	0.0072
13	60.00	0.9410	0.9590	0.9655	0.00652	0.9729	0.01385	0.9603	0.00126
	Average Deviation			**0.01058574**		**0.01274337**		**0.007809366**	

Table C-12 Acetone – Water At P = 760mmHg for One Parameter equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	100.00	0.0030	0.0440	0.037	0.00703	0.0022	0.04178	0.0023	0.04174
2	94.00	0.0110	0.2040	0.2023	0.00166	0.2027	0.00135	0.2027	0.00125
3	84.70	0.0250	0.4220	0.446	0.024	0.4471	0.02508	0.4471	0.02513
4	75.00	0.0540	0.6150	0.6331	0.01813	0.6362	0.02124	0.6357	0.02067
5	72.10	0.0820	0.6780	0.6805	0.00247	0.6863	0.00829	0.6845	0.00655
6	68.30	0.1040	0.7300	0.7317	0.00166	0.7391	0.0091	0.7364	0.00641
7	64.60	0.1560	0.7910	0.777	0.01401	0.7893	0.00171	0.7836	0.00737
8	64.00	0.1940	0.7950	0.7858	0.00924	0.8026	0.00758	0.7939	0.00107
9	63.80	0.3300	0.8250	0.7963	0.02873	0.832	0.00701	0.81	0.01505
10	62.40	0.4450	0.8330	0.8165	0.01654	0.8649	0.03191	0.8331	0.00014
11	63.30	0.6220	0.8550	0.8279	0.02706	0.8973	0.04228	0.8516	0.00337
12	60.40	0.7950	0.8960	0.8858	0.01021	0.9465	0.05045	0.9095	0.01353
13	60.00	0.9410	0.9590	0.9538	0.00519	0.9832	0.02417	0.9676	0.00858
	Average Deviation			**0.0127643**		**0.0209212**		**0.01160525**	

Table C-13 Methelcyclopentane – Benzene At P = 760 mmHg for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	79.64	0.0297	0.0526	0.0423	0.0103	0.0424	0.01024	0.0423	0.01029
2	77.62	0.1080	0.1668	0.1689	0.0021	0.1699	0.00311	0.1689	0.00211
3	76.62	0.1751	0.2533	0.2481	0.00524	0.2509	0.00239	0.2481	0.00524
4	74.85	0.3017	0.3870	0.382	0.00501	0.39	0.00296	0.3819	0.00508
5	74.00	0.3806	0.4598	0.4551	0.00471	0.4665	0.00668	0.455	0.00484
6	73.43	0.4450	0.5179	0.5111	0.00675	0.525	0.00707	0.511	0.00692
7	72.84	0.5737	0.6255	0.6151	0.0104	0.6319	0.00637	0.6149	0.01059
8	72.06	0.6434	0.6795	0.6775	0.00199	0.6941	0.01456	0.6774	0.00215
9	71.97	0.7206	0.7442	0.7403	0.00394	0.7553	0.01114	0.7401	0.00405
10	71.54	0.8224	0.8299	0.83	0.00011	0.8407	0.01079	0.83	0.00009
11	71.47	0.9030	0.9034	0.904	0.00063	0.9099	0.0065	0.9041	0.00066
12	71.53	0.9180	0.9174	0.9182	0.00077	0.9231	0.00569	0.9182	0.00081
13	71.65	0.9373	0.9360	0.9367	0.00065	0.9404	0.00435	0.9367	0.00069
14	71.68	0.9450	0.9442	0.9442	0.00001	0.9474	0.0032	0.9442	0.00002
15	71.80	0.9518	0.9503	0.9508	0.00045	0.9536	0.00325	0.9508	0.00049
	Average Deviation			**0.003538205**		**0.006553726**		**0.003600932**	

Table C-14 Methelcyclopentane – Benzene At P = 760 mmHg for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	79.64	0.0297	0.0526	0.0424	0.0102	0.0417	0.0109	0.0428	0.00976
2	77.62	0.1080	0.1668	0.1701	0.00326	0.168	0.0012	0.1704	0.0036
3	76.62	0.1751	0.2533	0.2508	0.00253	0.2499	0.00336	0.2512	0.00214
4	74.85	0.3017	0.3870	0.3885	0.00146	0.393	0.00596	0.3883	0.00132
5	74.00	0.3806	0.4598	0.4639	0.00408	0.472	0.01216	0.4631	0.00332
6	73.43	0.4450	0.5179	0.5215	0.00363	0.5321	0.01422	0.5203	0.00236
7	72.84	0.5737	0.6255	0.6268	0.00129	0.6411	0.01557	0.6253	0.00021
8	72.06	0.6434	0.6795	0.6899	0.01042	0.7037	0.02417	0.6875	0.00803
9	71.97	0.7206	0.7442	0.7513	0.00709	0.7646	0.02043	0.7495	0.00526
10	71.54	0.8224	0.8299	0.8385	0.00857	0.8484	0.01848	0.837	0.00714
11	71.47	0.9030	0.9034	0.909	0.00561	0.915	0.01161	0.9084	0.00498
12	71.53	0.9180	0.9174	0.9224	0.00495	0.9276	0.01016	0.9219	0.00453
13	71.65	0.9373	0.9360	0.9398	0.00378	0.9439	0.0079	0.9396	0.00361
14	71.68	0.9450	0.9442	0.9469	0.00271	0.9506	0.00636	0.9468	0.00261
15	71.80	0.9518	0.9503	0.9531	0.00277	0.9563	0.00604	0.9531	0.00277
	Average Deviation			**0.004822955**		**0.01123451**		**0.004110143**	

Table C-15 Benzene–Heptane At P = 760 mmHg for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	97.63	0.0150	0.0320	0.0369	0.00488	0.0367	0.0047	0.0369	0.00488
2	96.11	0.0540	0.1060	0.1137	0.00771	0.1118	0.0058	0.1138	0.00775
3	95.11	0.0850	0.1600	0.1664	0.00641	0.1623	0.00232	0.1665	0.0065
4	93.64	0.1310	0.2340	0.2401	0.0061	0.2323	0.00173	0.2403	0.00629
5	93.02	0.1500	0.2630	0.2694	0.00641	0.26	0.00296	0.2696	0.00665
6	90.75	0.2260	0.3670	0.3748	0.0078	0.36	0.00701	0.3752	00.00824
7	87.80	0.3480	0.5060	0.5114	0.00537	0.4922	0.01383	0.5121	0.0061
8	86.44	0.4150	0.5700	0.5744	0.00443	0.5554	0.01462	0.5752	0.00525
9	85.21	0.4800	0.6280	0.6302	0.0022	0.6129	0.01513	0.631	0.00302
10	84.71	0.5100	0.6520	0.654	0.00196	0.6378	0.01415	0.6548	0.00276
11	84.15	0.5470	0.6790	0.6818	0.00282	0.6675	0.01149	0.6826	0.00356
12	83.52	0.5940	0.7110	0.7153	0.00432	0.7037	0.00733	0.7159	0.00493
13	82.99	0.6330	0.7370	0.7424	0.00541	0.7332	0.0038	0.7429	0.00588
14	82.29	0.6930	0.7770	0.7822	0.00521	0.7768	0.00017	0.7824	0.0054
15	81.70	0.7480	0.8140	0.8179	0.00387	0.8157	0.00169	0.8178	0.00376
16	81.12	0.8100	0.8540	0.8579	0.00394	0.8584	0.00437	0.8575	0.00348
17	80.66	0.8710	0.8960	0.8986	0.00257	0.8998	0.00377	0.8978	0.00185
18	80.31	0.9350	0.9440	0.9449	0.00088	0.9445	0.00053	0.9442	0.00018
	Average Deviation			**0.004572639**		**0.00641136**		**0.004803574**	

Table C-16 Benzene–Heptane At P = 760 mmHg for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	Temp. C^o	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	97.63	0.0150	0.0320	0.0363	0.00425	0.0283	0.00368	0.037	0.00497
2	96.11	0.0540	0.1060	0.1069	0.00095	0.0917	0.01432	0.1138	0.00776
3	95.11	0.0850	0.1600	0.1516	0.0084	0.1411	0.01889	0.1662	0.00619
4	93.64	0.1310	0.2340	0.2105	0.02346	0.214	0.01998	0.2392	0.00523
5	93.02	0.1500	0.2630	0.2332	0.02976	0.2437	0.01928	0.2682	0.0052
6	90.75	0.2260	0.3670	0.3112	0.05583	0.3527	0.01435	0.3719	0.00493
7	87.80	0.3480	0.5060	0.4055	0.10047	0.4982	0.00778	0.5053	0.00071
8	86.44	0.4150	0.5700	0.4484	0.12159	0.5671	0.00291	0.5666	0.00344
9	85.21	0.4800	0.6280	0.4878	0.14023	0.6288	0.00075	0.6208	0.00722
10	84.71	0.5100	0.6520	0.5049	0.14705	0.6553	0.00327	0.6439	0.00811
11	84.15	0.5470	0.6790	0.5257	0.15334	0.6865	0.00751	0.6711	0.00794
12	83.52	0.5940	0.7110	0.5519	0.15912	0.7242	0.01323	0.7039	0.00715
13	82.99	0.6330	0.7370	0.5752	0.16179	0.7546	0.01762	0.7306	0.00641
14	82.29	0.6930	0.7770	0.6132	0.16384	0.799	0.02198	0.7703	0.00674
15	81.70	0.7480	0.8140	0.6529	0.16105	0.8379	0.0239	0.8064	0.0076
16	81.12	0.8100	0.8540	0.7064	0.14764	0.8799	0.0259	0.8478	0.00619
17	80.66	0.8710	0.8960	0.7725	0.12348	0.9196	0.02359	0.8907	0.00528
18	80.31	0.9350	0.9440	0.8653	0.07874	0.9599	0.01591	0.9405	0.00349
	Average Deviation			**0.09894437**		**0.0141576**		**0.005809283**	

Table C-17 Acetone - Benzene At T= $45C^o$ for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	250.73	0.0470	0.1444	0.1253	0.01911	0.1253	0.01905	0.125	0.01939
2	275.02	0.0963	0.2574	0.261	0.00358	0.2614	0.00399	0.2601	0.00271
3	324.25	0.2207	0.4417	0.4462	0.00454	0.4491	0.0074	0.4438	0.00206
4	348.40	0.2936	0.5204	0.5231	0.00273	0.5281	0.00771	0.5201	0.00032
5	379.88	0.4011	0.6139	0.6148	0.00092	0.623	0.00915	0.6117	0.00219
6	399.73	0.4759	0.6697	0.6694	0.00026	0.6795	0.00981	0.6668	0.00291
7	432.95	0.6125	0.7614	0.7588	0.00265	0.7703	0.00887	0.7578	0.00365
8	453.99	0.7045	0.8201	0.8153	0.00477	0.826	0.00587	0.8156	0.00447
9	475.39	0.8081	0.8805	0.878	0.00249	0.8858	0.00531	0.8794	0.00107
10	495.32	0.9084	0.9418	0.9403	0.00152	0.944	0.00216	0.9418	0.00002
11	503.96	0.9529	0.9699	0.9689	0.00103	0.9706	0.00073	0.9699	0.00002
	Average Deviation			**0.003963969**		**0.007277213**		**0.003527349**	

Table C-18 Acetone - Benzene At T= $45C^o$ for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	250.73	0.0470	0.1444	0.1252	0.01924	0.1216	0.02284	0.1254	0.01903
2	275.02	0.0963	0.2574	0.2611	0.00367	0.25	0.00738	0.2608	0.00343
3	324.25	0.2207	0.4417	0.4468	0.00506	0.416	0.02574	0.4473	0.00562
4	348.40	0.2936	0.5204	0.5237	0.00328	0.485	0.03542	0.5251	0.00473
5	379.88	0.4011	0.6139	0.6151	0.00118	0.571	0.04294	0.6182	0.00434
6	399.73	0.4759	0.6697	0.6693	0.00042	0.6253	0.04442	0.6737	0.00405
7	432.95	0.6125	0.7614	0.7576	0.00382	0.7196	0.0418	0.7642	0.00283
8	453.99	0.7045	0.8201	0.8135	0.00659	0.7816	0.03849	0.821	0.00091
9	475.39	0.8081	0.8805	0.8758	0.00465	0.8498	0.03065	0.8831	0.00257
10	495.32	0.9084	0.9418	0.9386	0.00319	0.9148	0.02701	0.9435	0.00168
11	503.96	0.9529	0.9699	0.9678	0.00207	0.1216	0.02488	0.9707	0.00083
	Average Deviation			**0.004831921**		**0.03105299**		**0.004547114**	

Table C-19 Acetone – Acetonitrile At T= $45C^o$ for Two Parameters equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	P mmHg	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	225.30	0.0520	0.1200	0.122	0.002	0.1171	0.00287	0.1217	0.00172
2	239.90	0.0950	0.2060	0.2083	0.0023	0.2008	0.00522	0.2079	0.00192
3	268.50	0.1920	0.3670	0.3732	0.0062	0.363	0.00404	0.3729	0.00589
4	302.70	0.3050	0.5100	0.5221	0.0121	0.5122	0.00222	0.5221	0.01207
5	331.70	0.4030	0.6110	0.6267	0.0157	0.6184	0.00744	0.6268	0.01577
6	355.20	0.4810	0.6820	0.6965	0.0145	0.69	0.00804	0.6967	0.01472
7	393.20	0.6060	0.7810	0.7904	0.0094	0.7867	0.0057	0.7906	0.0096
8	423.60	0.7060	0.8490	0.8537	0.0047	0.8519	0.00291	0.8538	0.00485
9	454.10	0.8070	0.9040	0.91	0.006	0.9096	0.0056	0.91	0.00604
10	481.40	0.8960	0.9510	0.9534	0.0024	0.9537	0.00272	0.9534	0.0024
	Average Deviation			**0.007518143**		**0.004677154**		**0.007497153**	

Table C-20 Acetone – Acetonitrile At T= $45C^o$ for One Parameter equations

	Experimental			**Wilson**		**NRTL**		**UNIQUAC**	
	P mmHg	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	225.30	0.0520	0.1200	0.122	0.002	0.1618	0.0418	0.1622	0.04218
2	239.90	0.0950	0.2060	0.2083	0.0023	0.2078	0.0018	0.208	0.00195
3	268.50	0.1920	0.3670	0.3732	0.0062	0.3667	0.0003	0.3669	0.00008
4	302.70	0.3050	0.5100	0.5221	0.0121	0.5154	0.0054	0.5155	0.00554
5	331.70	0.4030	0.6110	0.6267	0.0157	0.6189	0.0079	0.6189	0.00789
6	355.20	0.4810	0.6820	0.6966	0.0146	0.6897	0.0077	0.6894	0.00744
7	393.20	0.6060	0.7810	0.7905	0.0095	0.786	0.005	0.7853	0.00429
8	423.60	0.7060	0.8490	0.8538	0.0048	0.8509	0.0019	0.85	0.00099
9	454.10	0.8070	0.9040	0.9101	0.0061	0.9081	0.0041	0.9071	0.00311
10	481.40	0.8960	0.9510	0.9536	0.0026	0.9529	0.0019	0.9522	0.00121
	Average Deviation			**0.007606524**		**0.00777576**		**0.007467044**	

Table C-21 Acetonitrile–Nitro methane At T= $60C^{o}$ for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	195.50	0.0951	0.1741	0.12	0.00412	0.1193	0.00484	0.12	0.00411
2	213.70	0.1940	0.3255	0.3286	0.00311	0.3261	0.00062	0.3286	0.00313
3	232.24	0.2930	0.4539	0.4586	0.00468	0.4536	0.00033	0.4586	0.00469
4	251.20	0.3939	0.5658	0.5715	0.00568	0.5635	0.00227	0.5715	0.00569
5	264.24	0.4614	0.6325	0.6384	0.00589	0.6284	0.00407	0.6384	0.00588
6	271.45	0.5001	0.6674	0.6735	0.00609	0.6624	0.00499	0.6735	0.00607
7	291.64	0.6051	0.7548	0.7602	0.00543	0.7464	0.00839	0.7602	0.00538
8	329.97	0.8055	0.8925	0.8953	0.00279	0.8795	0.01296	0.8952	0.00269
9	349.17	0.9025	0.9488	0.95	0.00118	0.9374	0.01141	0.9499	0.0011
10	358.27	0.9486	0.9737	0.9741	0.00042	0.9653	0.00838	0.9741	0.00037
	Average Deviation			**0.003937834**		**0.005826259**		**0.003909826**	

Table C-22 Acetonitrile–Nitro methane At T= $60C^{o}$ for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	195.50	0.0951	0.1741	0.1159	0.0082	0.1188	0.05526	0.1693	0.00481
2	213.70	0.1940	0.3255	0.316	0.0095	0.327	0.00152	0.3269	0.00143
3	232.24	0.2930	0.4539	0.4352	0.0187	0.4564	0.00247	0.4567	0.0028
4	251.20	0.3939	0.5658	0.5374	0.0284	0.5688	0.00297	0.5703	0.00449
5	264.24	0.4614	0.6325	0.5983	0.0342	0.6355	0.003	0.6368	0.00434
6	271.45	0.5001	0.6674	0.6306	0.0368	0.6706	0.00317	0.6729	0.00552
7	291.64	0.6051	0.7548	0.7128	0.042	0.7576	0.00277	0.7606	0.00576
8	329.97	0.8055	0.8925	0.8562	0.0363	0.8943	0.00179	0.8993	0.00683
9	349.17	0.9025	0.9488	0.9259	0.0229	0.9499	0.00107	0.9537	0.00491
10	358.27	0.9486	0.9737	0.9602	0.0135	0.9742	0.00052	0.9775	0.00379
	Average Deviation			**0.02505971**		**0.007455264**		**0.004469052**	

Table C-23 Nitro methane – carbon tetrachloride At T= 45C^{o} for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	287.42	0.0459	0.1296	0.1171	0.0125	0.1379	0.00835	0.132	0.00237
2	297.19	0.0918	0.1780	0.1592	0.01875	0.1832	0.0052	0.1854	0.00743
3	302.91	0.1954	0.2217	0.2062	0.0155	0.2275	0.00583	0.2384	0.01666
4	302.56	0.2829	0.2368	0.2241	0.01267	0.2429	0.00608	0.2497	0.01286
5	301.42	0.3656	0.2458	0.235	0.01081	0.2525	0.00674	0.2519	0.00612
6	298.86	0.4659	0.2532	0.2459	0.00731	0.2627	0.00947	0.2533	0.00009
7	296.88	0.5366	0.2598	0.2531	0.00667	0.2691	0.00932	0.2553	0.00449
8	293.27	0.6065	0.2657	0.2619	0.00377	0.2766	0.01094	0.2604	0.00529
9	287.10	0.6835	0.2773	0.2746	0.00269	0.2871	0.00984	0.2707	0.00659
10	264.65	0.8043	0.3138	0.313	0.00082	0.3207	0.00686	0.3086	0.0052
11	214.63	0.9039	0.4078	0.4075	0.00028	0.4107	0.00286	0.4051	0.00267
12	170.95	0.9488	0.5283	0.5277	0.00061	0.529	0.00068	0.5266	0.00172
	Average Deviation			**0.007697881**		**0.006849119**		**0.005957237**	

Table C-24 Nitro methane – carbon tetrachloride At T= 45C^{o} for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	X1	Y1	Y_1 calculate	Deviation	Y_1 calculate	Deviation	Y_1 calculate	Deviation
1	287.42	0.0459	0.1296	0.1164	0.01324	0.0884	0.0412	0.1231	0.00649
2	297.19	0.0918	0.1780	0.1577	0.02033	0.1171	0.0609	0.1694	0.00862
3	302.91	0.1954	0.2217	0.2035	0.01816	0.1511	0.0706	0.2134	0.00829
4	302.56	0.2829	0.2368	0.2212	0.01563	0.1706	0.0662	0.2238	0.013
5	301.42	0.3656	0.2458	0.232	0.01377	0.1888	0.057	0.228	0.01778
6	298.86	0.4659	0.2532	0.2431	0.01007	0.2127	0.0405	0.2334	0.01981
7	296.88	0.5366	0.2598	0.2506	0.00918	0.2305	0.0293	0.2387	0.02112
8	293.27	0.6065	0.2657	0.2597	0.00598	0.2499	0.0158	0.247	0.01865
9	287.10	0.6835	0.2773	0.2728	0.00451	0.2734	0.0039	0.2609	0.01645
10	264.65	0.8043	0.3138	0.3119	0.00191	0.324	0.0102	0.3037	0.01012
11	214.63	0.9039	0.4078	0.4071	0.00069	0.4197	0.0119	0.4034	0.0044
12	170.95	0.9488	0.5283	0.5276	0.00071	0.5355	0.0072	0.526	0.00235
	Average Deviation			**0.009515667**		**0.03457057**		**0.01225623**	

Table C-25 Carbon tetrachloride – Acetonitrile T= 45C^o for Two Parameters equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	247.96	0.0347	0.1801	0.2222	0.04211	0.2202	0.04011	0.2228	0.04269
2	291.58	0.0892	0.3309	0.3328	0.00188	0.3237	0.00724	0.3354	0.00454
3	335.99	0.1914	0.4603	0.4586	0.00169	0.4359	0.02438	0.4651	0.00481
4	355.85	0.2887	0.5129	0.5147	0.00178	0.484	0.0289	0.5227	0.00981
5	364.67	0.3752	0.5429	0.5448	0.00187	0.5126	0.03029	0.5515	0.0086
6	368.82	0.4567	0.5633	0.5649	0.00158	0.5363	0.02705	0.5676	0.00434
7	369.62	0.4790	0.5684	0.5697	0.0013	0.5428	0.02558	0.5709	0.00248
8	370.23	0.5060	0.5740	0.5751	0.00106	0.5507	0.02335	0.574	0.00001
9	371.09	0.6049	0.5936	0.5933	0.00027	0.5808	0.01284	0.5814	0.01222
10	368.95	0.7164	0.6181	0.6152	0.0029	0.617	0.00106	0.5868	0.03126
11	362.78	0.8069	0.6470	0.6413	0.00569	0.6489	0.0019	0.6005	0.04655
12	346.97	0.8959	0.7004	0.6962	0.00416	0.6946	0.00585	0.6555	0.0449
13	314.43	0.9609	0.8001	0.8076	0.00748	0.7898	0.01033	0.7885	0.01164
	Average Deviation			**0.00567394**		**0.01837497**		**0.01721788**	

Table C-26 Carbon tetrachloride – Acetonitrile T= 45C^o for One Parameter equations

	Experimental			Wilson		NRTL		UNIQUAC	
	P mmHg	**X1**	**Y1**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**	**Y_1 calculate**	**Deviation**
1	247.96	0.0347	0.1801	0.2216	0.0415	0.2161	0.03598	0.2231	0.04295
2	291.58	0.0892	0.3309	0.3308	0.0001	0.3136	0.01729	0.3329	0.002
3	335.99	0.1914	0.4603	0.4551	0.0052	0.4334	0.02691	0.4648	0.00446
4	355.85	0.2887	0.5129	0.5123	0.0006	0.5011	0.01177	0.5268	0.01392
5	364.67	0.3752	0.5429	0.5468	0.0039	0.5503	0.00742	0.5611	0.01818
6	368.82	0.4567	0.5633	0.5746	0.0113	0.5927	0.02941	0.5836	0.02031
7	369.62	0.4790	0.5684	0.5823	0.0139	0.604	0.03563	0.5888	0.02042
8	370.23	0.5060	0.5740	0.5916	0.0176	0.6174	0.04337	0.5945	0.02048
9	371.09	0.6049	0.5936	0.6294	0.0358	0.6646	0.07101	0.6125	0.01893
10	368.95	0.7164	0.6181	0.6846	0.0665	0.7139	0.09584	0.633	0.01495
11	362.78	0.8069	0.6470	0.7463	0.0993	0.7512	0.10417	0.6605	0.01355
12	346.97	0.8959	0.7004	0.8317	0.1313	0.7934	0.09303	0.7241	0.0237
13	314.43	0.9609	0.8001	0.9207	0.1206	0.8618	0.0617	0.8402	0.04013
	Average Deviation			**0.04211817**		**0.04873185**		**0.01953774**	

Appendix D

Sample of Calculations

D-1 Sample of Calculation for MOSCED Model:

Calculation of Activity coefficients at infinite dilution of Acetone – Acetonitrile at 45 C^o

MOSCED parameters at 20 C^o are taken from table 2-5

	Acetone (1)	Acetonitrile (2)		Acetone (1)	Acetonitrile (2)
v	74.4	52.2	**β**	4.87	3.98
λ	7.49	7.43	**ψ**	1.86	2.17
τ	4.10	5.99	**ξ**	1.58	2.10
q	1.00	1.00	***aa***	0.790	0.573
α	0.00	0.86			

τ, α, β, ψ, ξ and *aa* are temperature- dependent. For Acetonitrile, these parameters at 45 C^o (318.15K) are obtained from:

$$\tau_{318.15} = (5.99)\left(\frac{293.15}{318.15}\right)^{0.4} = 5.7971$$

$$\alpha_{318.15} = (0.86)\left(\frac{293.15}{318.15}\right)^{0.8} = 0.8055$$

$$\beta_{318.15} = (3.98)\left(\frac{293.15}{318.15}\right)^{0..8} = 3.7278$$

$$\mathrm{POL} = 1^4\{1.15 - 1.15 \exp[(-0.020)\ (5.7971)^3]\} + 1 = 2.1266$$

$$\Psi_{318.15} = 2.1266 + (0.011)\ (0.8055)\ (3.7278) = 2.1597$$

$$\xi_{318.15} = (0.68)(2.1266 - 1) + \left\{3.4 - 2.4\exp\left[(-0.023)[(0.86)(3.98)]^{1.5}\right]\right\}^{(293.15/318.15)^2}$$

$$= 2.0362$$

$$aa_{318.15} = 0.953 - (0.00968)\ [(5.7971)^2 + (0.8055)\ (3.7278)] = 0.5986$$

The temperature - dependent parameters are obtained similarly for Acetone at 45 °C. Summarizing,

	Acetone (1)	Acetonitrile (2)		Acetone (1)	Acetonitrile (2)
v	74.4	52.2	**β**	4.5614	3.7278
λ	7.49	7.43	**ψ**	1.8204	2.1597
τ	3.968	5.7971	**ξ**	1.5578	2.0362
q	1.00	1.00	***aa***	0.8006	0.5986
α	0.00	0.8055			

Next, calculating the combinatorial term:

$$d_{12}(1) = \ln\left(\frac{52.2}{74.4}\right)^{0.5986} + 1 - \left(\frac{52.2}{74.4}\right)^{0.5986} = -0.02099$$

$$d_{12}(2) = \ln\left(\frac{74.4}{52.2}\right)^{0.8006} + 1 - \left(\frac{74.4}{52.2}\right)^{0.8006} = -0.04434$$

Finally, calculating the infinite dilution activity coefficients:

$$\ln\gamma_1^\infty = \frac{74.4}{(1.987)(318.15)}\left[(7.43 - 7.49)^2 + \frac{(1.8291)^2}{2.1597} + \frac{(0.8055)(-0.8336)}{2.0362}\right] - 0.04434 = 0.0996$$

$$\ln\gamma_2^\infty = \frac{52.2}{(1.987)(318.15)}\left[(7.49 - 7.43)^2 + \frac{(-1.8291)^2}{1.8204} + \frac{(-0.8055)(0.8336)}{1.5578}\right] - 0.02099 = 0.09548$$

$\gamma^\infty{}_1 = 1.015$, $\gamma^\infty{}_2 = 1.1$

Where the experimental values of the system Acetone – Acetonitrile at 45C^o are $\gamma^\infty{}_1 = 1.05$, $\gamma^\infty{}_2 = 1.04$.

D-2 Sample of Calculation for SPACE Model:

Calculation of Activity coefficients at infinite dilution of Acetone – Acetonitrile at 45 C^o

SPACE parameters are taken from tables 2-6 and 2-7

	Acetone (1)	Acetonitrile (2)		Acetone (1)	Acetonitrile (2)
n_D	1.35596	1.34163	B	22.021	22.092
V	74.1	52.9	C_1	-26.92	-26.92
π^{*KT}	0.71	0.75	C_2	-132.494	-132.494
π^{*H}	0.7	0.9	D_1	0.336	-2.269
α^{KT}	0.08	0.19	D_2	5.3	-50.619
α^{H}	0.04	0.04	E_1	27.561	27.561
β^{KT}	0.43	0.4	E_2	2.147	2.147
β^{H}	0.51	0.33	F_1	10.617	-25.227
A_1	8.067	11.419	F_2	-1.095	-65.782
A_2	27.477	38.912			

Using equation (2-8.10) to (2-8.23) to determine γ^{∞}_2 for Acetonitrile

Acetonitrile is aliphatic compounds there for *k* for Acetonitrile is 15.418

$$\lambda_1 = 15.418\left(\frac{1.35596^2 - 1}{1.35596^2 + 2}\right) = 3.3684$$

$$\lambda_1 = 15.418\left(\frac{1.34163^2 - 1}{1.34163^2 + 2}\right) = 3.2458$$

$$\tau_1 = \left|\frac{8.067 \cdot 0.71 + 22.021}{\sqrt{74.1}}\right| = 3.2235$$

$$\tau_{2\mathrm{eff}} = \left|\frac{11.419\cdot 0.75 + 22.092}{\sqrt{52.9}}\right| + \left(\left|\frac{38.912\cdot 0.9 + 22.092}{\sqrt{52.9}}\right| - \left|\frac{11.419\cdot 0.75 + 22.092}{\sqrt{52.9}}\right|\right)\frac{|0.71 - 0.75|}{1.33} = 4.3243$$

$$\alpha_1 = \left|\frac{-26.92\cdot 0.08 + 0.336}{\sqrt{74.1}}\right| = 0.2112$$

$$\alpha_{2\mathrm{eff}} = \left|\frac{-26.92\cdot 0.19 - 2.269}{\sqrt{52.9}}\right| + \left(\left|\frac{-132.494\cdot 0.04 - 50.619}{\sqrt{52.9}}\right| - \left|\frac{-26.92\cdot 0.19 - 2.269}{\sqrt{52.9}}\right|\right)\frac{|0.08 - 0.19|}{1.20} = 1.6269$$

$$\beta_1 = \left|\frac{27.561\cdot 0.43 + 10.617}{\sqrt{74.1}}\right| = 2.6101$$

$$\beta_{2\mathrm{eff}} = \left|\frac{27.561\cdot 0.4 - 25.227}{\sqrt{52.9}}\right| + \left(\left|\frac{2.147\cdot 0.33 - 65.782}{\sqrt{52.9}}\right| - \left|\frac{27.561\cdot 0.4 - 25.227}{\sqrt{52.9}}\right|\right)\frac{|0.43 - 0.4|}{0.95} = 2.1736$$

$$\ln\gamma_2^{\infty} = \frac{52.9}{1.987\cdot 318.15}[(3.3684 - 3.2458)^2 + (3.2235 - 4.3243)^2 + (0.2112 - 1.6269)(2.6101 - 2.1736)] + \ln\left(\frac{52.9}{74.1}\right)^{0.936} + 1 - \left(\frac{52.9}{74.1}\right)^{0.936} = 0.00604$$

$\gamma^{\infty}{}_2 = 1.0061$

And by similar equations $\gamma^{\infty}{}_1 = 0.9954$

D-3 Sample of Calculation for Azeotrope Composition by Using Wilson Equation of TWO Parameters

Calculation of azeotrope composition for the system Acetone (1) – chloroform (2) at 50 C^o where the experimental activity coefficients at infinite dilution is $\gamma^{\infty}{}_1 = 0.44$ and $\gamma^{\infty}{}_2 = 0.54$ at 50 C^O.

At temperature 50 C^o Acetone vapor pressure is $P_1^{sat} = 0.\ 8196449$ bar and for Chloroform vapor pressure is $P_2^{sat} = 0.\ 6927763$ bar.

First determines whether or not azeotrope exists at the system temperature. This can be determined by calculating the relative volatility α_{12}. From equation (2-7.5) and (2-7.6)

$$(\alpha_{12})_{x1=0} = \frac{0.44 \cdot 0.8196449}{0.6927763} = 0.5208$$

$$(\alpha_{12})_{x1=1} = \frac{0.8196449}{0.54 \cdot 0.6927763} = 2.19098$$

Because of $(\alpha_{12})_{x1=0}$ is less than 1 and $(\alpha_{12})_{x1=1}$ is greater than 1 an azeotrope is indeed exist.

Calculating the parameters of Wilson, Λ_{12} and Λ_{21}, from Wilson equation of γ^{∞}s equation (2-5.1):

$$1 - \ln 0.44 = \ln \Lambda_{12} + \Lambda_{21}$$

$$1 - \ln 0.54 = \ln \Lambda_{21} + \Lambda_{12}$$

by solving the two equations spontaneously or by trial and error,

$$\Lambda_{12} = 0.051911$$

$$\Lambda_{21} = 4.779211$$

From equation (2-7.7)

$$\frac{\gamma_1^{az}}{\gamma_2^{az}} = \frac{P_2^{sat}}{P_1^{sat}} = \frac{0.6927763}{0.8196449} = 0.845215$$

Equation (2-7.12) is the difference between the Wilson equations for γ_2 and γ_1

$$\ln\frac{\gamma_1}{\gamma_2} = \ln\frac{x_2 + x_1\Lambda_{21}}{x_1 + x_2\Lambda_{12}} + \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}$$

Thus the azeotropic composition is the value of x_1 (with x_2=1- x_1) for which this equation is satisfied when

$$\ln\frac{\gamma_1}{\gamma_2} = \ln 0.845215 = -0.168164$$

and

$$\Lambda_{12} = 0.051911 \qquad \Lambda_{21} = 4.779211$$

Solution by trial and error for x_1 gives x_1^{az}= 0.1927538 weight percent. x_1^{az} mole percent is equal to 0.3292185, for this value of x_1 and from equation (2-4.11) γ_1^{az} is equal to 0.72442

$$\gamma_1^{az} = \exp\left(1 - \ln(0.32922 + 0.6708 \cdot 0.051911) - \frac{0.32922}{0.32922 + 0.6708 \cdot 0.051911}\right.$$
$$\left. - \frac{0.6708 \cdot 4.779211}{0.32922 \cdot 4.779211 + 0.6707815}\right) = 0.72442$$

with $x_1^{az} = y_1^{az}$

$$P^{az} = \gamma_1^{az} P_1^{sat} = (0.72442)(0.8196449) = 0.59376\,\text{bar}.$$

Thus

P^{az}=0.59376 bar

$x_1^{az} = y_1^{az}$ = 0.19275 by weight

D-4 Sample of Calculation for Azeotrope Composition by Using Wilson Equation of ONE Parameter

The first steppes of calculation is similar to the two parameters but in calculating the parameters of Wilson is different because two parameters $\gamma^{\infty}{}_1$ and $\gamma^{\infty}{}_2$ are used while for one parameter only $\gamma^{\infty}{}_1$ or $\gamma^{\infty}{}_2$ is used .

For calculating the parameters of Wilson for the same system used in the above calculation Acetone (1) –chloroform (2) at 50 C^o is followed by using $\gamma^{\infty}{}_1 = 0.44$.

For Acetone (1): [from appendix A]

Tc = 508.1K	Pc = 47 bar
Vc =209 cm^3/mol	Zc = 0.232
$\Delta H_{v\ \text{boiling}}$ = 29.1 KJ/mol	T_{boiling} = 56.05 C^o

$$T_r = \frac{T}{Tc} = \frac{323.15}{508.1} = 0.636$$

$$T_{rb} = \frac{T_b}{Tc} = \frac{329.2}{508.1} = 0.6479$$

From Equation (2-6.6) Watson eq.:

$$\Delta H_{v1} = 29.1\left(\frac{1-0.636}{1-0.6479}\right)^{0.375} = 29.46499\,\text{kJ/mol}$$

Calculating molar liquid volume from equation (2-7.24)

$$V_1^L = (209)(0.232)^{(1-0.636)^{0.2857}} = 69.9456\,\text{cm}^3/\text{mol}$$

For Chloroform (2): Tc = 536.4 K Pc = 53.7 bar

Vc =238.9 cm^3/mol Zc = 0.293

ΔH_{vb} = 29.24 KJ/mol T_b = 61.17 C^o

$$T_r = \frac{T}{Tc} = \frac{323.15}{536.4} = 0.60244$$

$$T_{rb} = \frac{T_b}{Tc} = \frac{334.32}{536.4} = 0.623266$$

$$\Delta H_{v2} = 29.24\left(\frac{1-0.60244}{1-0.623266}\right)^{0.375} = 29.83599\,\text{kJ/mol}$$

$$V_2^L = (238.9)(0.293)^{(1-0.60244)^{0.2857}} = 93.0236\,\text{cm}^3/\text{mol}$$

From equation (2-6.2) and (2-6.3) where z = 10

$$\lambda_{11} = -\frac{2}{z}\left(\frac{V_2^L}{V_1^L}\right)\left(\Delta H_{v1} - RT\right)$$

$$\lambda_{11} = -\frac{2}{10}\left(\frac{93.0236}{69.9456}\right)\left(29464.99 - (8.314)(323.15)\right) = -7122.72341 \text{ kJ/mol}$$

$$\lambda_{22} = -\frac{2}{z}\left(\Delta H_{v2} - RT\right)$$

$$\lambda_{22} = -\frac{2}{10}\left(29835.99 - (8.314)(323.15)\right) = -5429.8642 \text{ kJ/mol}$$

By trial and error calculating Λ_{12} and Λ_{21} from equation (2-6.1)

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right)$$

and equation (2-5.1)

$$1 - \ln\gamma_1^\infty = \ln\Lambda_{12} + \Lambda_{21}$$

where $\lambda_{12} = \lambda_{21}$

$\Lambda_{12} = 1.3858$ $\Lambda_{21} = 1.4947$

Similar to the calculation of two parameters given above the trial and error for x_1 gives x_1^{az}= 0.236269 weight percent. x_1^{az} mole percent is equal to 0.3887, for this value of x_1 and from equation (2-4.11) γ_1^{az} is equal to 0.7463

$$\text{Ln}\,\gamma_1^{\text{az}} = 1 - \ln(0.3887 + 0.6113\cdot 1.3858) - \frac{0.3887}{0.3887 + 0.6113\cdot 1.3858}$$

$$- \frac{0.6113\cdot 1.4947}{0.3887\cdot 1.4947 + 0.6113} = 0.7463$$

with $x_1^{az} = y_1^{az}$

$$P^{az} = \gamma_1^{az} P_1^{sat} = (0.7463)(0.8196449) = 0.6117\,\text{bar.}$$

Thus

P^{az}=0.6117 bar

$x_1^{az} = y_1^{az}$ = 0.23627 by weight

D-5 Sample of Calculation for VLE by Using UNIQUAC Equation of TWO Parameters

For Acetone (1) – Carbon tetrachloride (2) experimental activities coefficients at infinite dilution $\gamma^{\infty}{}_1 = 3$ and $\gamma^{\infty}{}_2 = 2.15$ at T = 318.15

The system is Isobaric P = 450 mmHg (0.5998026bar). From appendix A:

For Acetone (1):

$Tc_1 = 508.1K$

$Pc_1 = 47$ bar

$Vc_1 = 209$ cm^3/mol

$Zc_1 = 0.232$

$w_1 = 0.304$

UNIQUAC parameters

$r_1 = 2.57$

$q_1 = 2.34$

$q`_1 = 2.34$

For Carbon tetrachloride (2):

$Tc_2 = 556.4$ K

$Pc_2 = 45.6$ bar

$Vc_2 = 275.9$ cm^3/mol

$Zc_2 = 0.272$

$w_2 = 0.193$

UNIQUAC parameters

$r_2 = 3.33$

$q_2 = 2.82$

$q`_2 = 2.82$

For calculating the constants of UNIQUAC (u_{12}, u_{21}) from $\gamma^{\infty}{}_1$ and $\gamma^{\infty}{}_2$ equation (2-5.3) must be solved at Z = 1.11

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1) = \frac{1.11}{2}(2.57 - 2.34) - (2.57 - 1) = -1.44235$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) = \frac{1.11}{2}(3.33 - 2.82) - (3.33 - 1) = -2.04695$$

$$\ln\gamma_1^{\infty} = \ln\left(\frac{2.57}{3.33}\right) + \frac{1.11}{2}\ln\left(\frac{2.34 \cdot 2.57}{2.82 \cdot 3.33}\right) - 1.44235 - \frac{2.57}{3.33}(-2.04695)$$
$$- (2.34)\ln\tau_{21} + (2.34)(1 - \tau_{12})$$

$$\ln\gamma_2^{\infty} = \ln\left(\frac{3.33}{2.57}\right) + \frac{1.11}{2}\ln\left(\frac{2.82 \cdot 3.33}{2.34 \cdot 2.57}\right) - 2.04695 - \frac{3.33}{2.57}(-2.04695)$$
$$- (2.82)\ln\tau_{12} + (2.82)(1 - \tau_{21})$$

From these two above equations and by trial and error at T = 318.15:

$\tau_{12} = 1.405535$ $\tau_{21} = 0.402597$

To calculate the constants of UNIQUAC using equation (2-4.29)

$u_{12} = -(318.15)(8.314)\ln(1.405535) = -900.4394$

$u_{21} = -(318.15)(8.314)\ln(0.402597) = 2406.562$

From these constants, VLE at isobaric (x1 versus y1) can be calculated.

For the first point $x_1 = 0.0490$ T = 55.29 C^o the following steps were taken:

1- Finding the pure-component saturated vapor pressure $P^{sat}{}_1$, $P^{sat}{}_2$ at T = 55.29 C^o (328.44 K) and T_r and P_r

$P^{sat}{}_1 = 0.986213$ bar

$P^{sat}{}_2 = 0.504593$ bar

$T_{r1} = 328.44/508.1 = 0.6464$

$T_{r2} = 328.44/556.4 = 0.590295$

where

$P_{r1} = 0.5998026 / 47 = 0.01276176$

$P_{r2} = 0.5998026 / 45.6 = 0.0131536$

2- Calculating the UNIQUAC constants

$\tau_{12} = \exp(-u_{12}/RT) = \exp(900.4394/(8.314 \cdot 328.44)) = 1.39062$

$\tau_{21} = \exp(-u_{21}/RT) = \exp(-2406.562/(8.314 \cdot 328.44)) = 0.414238$

3- Calculating the activities coefficients (γ_1, γ_2) at x1= 0.189 from equation (2-4.30)

$$\ln \gamma_1 = \ln\left(\frac{\varphi_1}{x_1}\right) + \frac{z}{2}\ln\left(\frac{\theta_1}{\varphi_1}\right) + \varphi_2(l_1 - r_1 l_2 / r_2)$$

$$- q_1' \ln(\theta_1' + \theta_2'\tau_{21}) + \theta_2' q_1' \left(\frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_1'\tau_{12} + \theta_2'}\right)$$

$$\ln \gamma_1 = \ln\left(\frac{\varphi_2}{x_2}\right) + \frac{z}{2}\ln\left(\frac{\theta_2}{\varphi_2}\right) + \varphi_1(l_2 - r_2 l_1 / r_1)$$

$$- q_2' \ln(\theta_2' + \theta_1'\tau_{12}) + \theta_1' q_2' \left(\frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}} - \frac{\tau_{21}}{\theta_2'\tau_{21} + \theta_1'}\right)$$

$$\varphi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} = \frac{(0.049)(2.57)}{(0.049)(2.57) + (0.951)(3.33)} = 0.0382$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_2 + x_2 q_2} = \frac{(0.049)(2.34)}{(0.049)(2.34) + (0.951)(2.82)} = 0.041$$

$$\theta_1' = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'} = \frac{(0.049)(2.34)}{(0.049)(2.34) + (0.951)(2.82)} = 0.041$$

$$\varphi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} = \frac{(0.951)(3.33)}{(0.049)(2.57) + (0.951)(3.33)} = 0.9618$$

$$\theta_2 = \frac{x_2 q_2}{x_1 q_2 + x_2 q_2} = \frac{(0.951)(2.82)}{(0.049)(2.34) + (0.951)(2.82)} = 0.959$$

$$\theta_2' = \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'} = \frac{(0.951)(2.82)}{(0.049)(2.34) + (0.951)(2.82)} = 0.959$$

$$\ln \gamma_1 = \ln\left(\frac{0.0382}{0.049}\right) + \frac{1.11}{2}\ln\left(\frac{0.041}{0.0382}\right) + 0.9618\left((-1.44235) + 2.04695\frac{2.57}{3.33}\right)$$
$$- (2.34)\ln(0.041 + 0.959 \cdot 0.414238)$$

$$+ (0.959 \cdot 2.34)\left(\frac{0.414238}{0.041 + (0.959 \cdot 0.414238)} - \frac{1.390625}{(0.041 \cdot 1.390625) + 0.959}\right) = 0.954778$$

$$\ln \gamma_2 = \ln\left(\frac{0.9618}{0.951}\right) + \frac{1.11}{2}\ln\left(\frac{0.959}{0.9618}\right) + 0.0382\left((-2.04695) + 1.44235\frac{3.33}{2.57}\right)$$
$$- (2.82)\ln(0.959 + 0.041 \cdot 1.390625)$$

$$+ (0.041 \cdot 2.82)\left(\frac{1.390625}{0.959 + (0.041 \cdot 1.390625)} - \frac{0.414238}{(0.959 \cdot 0.414238) + 0.041}\right) = 0.0041$$

$$\gamma_1 = 2.5981, \qquad \gamma_2 = 1.00411$$

4- Calculating V_i^L from Rackett equation (2-7.24):

$$V_1^L = (209)(0.232)^{(1-(0.56618)^{0.2857}} = 70.5804 \quad \text{cm}^3/\text{mol}$$

$$V_2^L = (275.9)(0.272)^{(1-0.590295)^{0.2857}} = 100.5915 \quad \text{cm}^3/\text{mol}$$

5- For solving equation (2-7.23)

$$y_i P \phi_i^V = x_i \gamma_i P_i^{sat} \phi_i^{sat} \exp \frac{V_i^L (P - P_i^{sat})}{RT}$$

ϕ_i^{sat} and ϕ_i^V must be calculated and they are calculated from Peng – Robinson equation of state.

The following steps were used for solving the above equation for y_1:

a- Calculating ϕ_1^{sat} ϕ_2^{sat} at saturation for pure component ($x_i = 1$) Peng - Robinson equation become

$$A = A_i \qquad B = B_i \qquad a\alpha = a_i \alpha_i \qquad b = b_i$$

Where

$$A_i = 0.45724 \alpha_i \frac{P_{r,i}}{T_{r,i}^2} \qquad B_i = 0.07780 \frac{P_{r,i}}{T_{r,i}}$$

$$a_i = 0.45724 \frac{(RT_i^c)^2}{P_i^c} \qquad b_i = 0.07780 \frac{RT_i^c}{P_i^c}$$

$$\alpha_i = \left[1 + n_i \left(1 - \sqrt{T_{r,i}}\right)\right]^2$$

$$n_i = 0.37464 + 1.54223 \omega_i - 0.26992 \omega_i^2$$

Then

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)z - \left(AB - B^2 - B^3\right) = 0$$

Fugacity Coefficient

$$\ln\phi_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) + \frac{A}{2.828B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}(a_i\alpha_i)\right]\ln\left(\frac{Z+2.414B}{Z-0.414B}\right)$$

for calculating ϕ_1^{sat}:

$P_{r1}^{sat} = P_1^{sat} / P_c = 0.986213 / 47 = 0.020983$

$$n_1 = 0.37464 + 1.54223 \cdot 0.304 - 0.26992 \cdot 0.304^2 = 0.8185$$

$$\alpha_1 = \left[1 + 0.8185\left(1 - \sqrt{0.6464}\right)\right]^2 = 1.34661$$

$$A = A_1 = 0.45724 \cdot 1.34661 \frac{0.020983}{0.6464^2} = 0.03092$$

$$B = B_1 = 0.07780 \frac{0.020983}{0.6464} = 0.0025255$$

$$a_1 = 0.45724 \frac{(8.314 \cdot 508.1)^2}{47 \cdot 10^5} = 1.73606$$

$$b_1 = 0.07780 \frac{8.314 \cdot 508.1}{47 \cdot 10^5} = 6.99264 \cdot 10^{-5}$$

$$a\alpha = a_1\alpha_1 = 1.34661 \cdot 1.73606 = 2.337796$$

$$Z^3 - (1 - 0.0025255)Z^2 + (0.03092 - 3(0.0025255)^2 - 2 \cdot 0.0025255)Z$$
$$-\left((0.03092)(0.0025255) - (0.0025255)^2 - (0.0025255)^3\right) = 0$$

The above equation is solved by trial and error by using Newton – Raphson method of third order polynomial.

$Z^{sat}{}_1 = 0.003150644$

Fugacity Coefficient

$$\ln \phi_1^{sat} = (0.00315-1)-\ln(0.00315-0.0025255)$$
$$-\frac{0.03092}{2.828\cdot 0.0025255}\ln\left(\frac{0.00315+(2.414\cdot 0.0025255)}{0.00315-(0.414\cdot 0.0025255)}\right)=-0.02645$$

$\phi_1^{sat} = 0.9738$

Similar calculation is taken for component 2

$Z^{\mathrm{sat}}{}_2 = 0.00177968$

$\phi_2^{sat} = 0.9923965$

b- To calculate Fugacity Coefficient of vapor phase for component 1 ϕ_1^V first the following must be calculated:

$$n_1 = 0.37464+1.54223\cdot 0.304-0.26992\cdot 0.304^2 = 0.8185$$

$$n_2 = 0.37464+1.54223\cdot 0.193-0.26992\cdot 0.193^2 = 0.66224$$

$$\alpha_1 = \left[1+0.8185\left(1-\sqrt{0.6464}\right)\right]^2 = 1.34661$$

$$\alpha_2 = \left[1+0.66224\left(1-\sqrt{0.5903}\right)\right]^2 = 1.33041$$

$$A_1 = 0.45724\cdot 1.34661\frac{0.01276176}{0.6464^2} = 0.018806$$

$$A_2 = 0.45724\cdot 1.3304\frac{0.0131536}{0.5903^2} = 0.0022963$$

$$B_1 = 0.07780\frac{0.01276}{0.6464} = 0.001536$$

$$B_2 = 0.07780\frac{0.0131536}{0.5903} = 0.001734$$

$$a_1 = 0.45724\frac{(8.314 \cdot 508.1)^2}{47 \cdot 10^5} = 1.73606$$

$$a_1 = 0.45724\frac{(8.314 \cdot 556.4)^2}{45.6 \cdot 10^5} = 2.145723$$

$$b_1 = 0.07780\frac{8.314 \cdot 508.1}{47 \cdot 10^5} = 6.99264 \cdot 10^{-5}$$

$$b_2 = 0.07780\frac{8.314 \cdot 556.4}{45.6 \cdot 10^5} = 7.89245 \cdot 10^{-5}$$

c- For calculating the Fugacity Coefficient of vapor phase for component 1 (ϕ_1^V), x_1 refer to vapor composition y_1. and y_1 is calculated by trial and error and for _each trial_ the following steps must be used, were for the first trial assume y_1 and calculate the following:

$$A = (y_1 y_1 \sqrt{A_1 A_1}) + 2(y_1 y_2 \sqrt{A_1 A_2}) + (y_2 y_2 \sqrt{A_2 A_2})$$

$$B = (y_1 B_1 + y_2 B_2)$$

$$a\alpha = (y_1 y_1 \sqrt{(a_1\alpha_1)(a_1\alpha_1)} + 2y_1 y_2 \sqrt{(a_1\alpha_1)(a_2\alpha_2)} + y_2 y_2 \sqrt{(a_2\alpha_2)(a_2\alpha_2)}$$

$$b = y_1 b_1 + y_2 b_2$$

The equation of Z is solved by trial and error by using Newton – Raphson method of third order polynomial.

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)z - \left(AB - B^2 - B^3\right) = 0$$

After calculating Z and the other parameters Fugacity Coefficients for component 1 and 2 are found from:

$$\ln\phi_1 = \frac{B_1}{B}(Z-1) - \ln(Z-B)$$
$$+\frac{A}{2.828B}\left[\frac{B_1}{B} - \frac{2}{a\alpha}\left(y_1\sqrt{(a_1\alpha_1)(a_1\alpha_1)} + y_2\sqrt{(a_1\alpha_1)(a_2\alpha_2)}\right)\right]\ln\left(\frac{Z+2.414B}{Z-0.414B}\right)$$

$$\ln\phi_2 = \frac{B_2}{B}(Z-1) - \ln(Z-B)$$
$$+\frac{A}{2.828B}\left[\frac{B_2}{B} - \frac{2}{a\alpha}\left(y_2\sqrt{(a_2\alpha_2)(a_2\alpha_2)} + y_1\sqrt{(a_1\alpha_1)(a_2\alpha_2)}\right)\right]\ln\left(\frac{Z+2.414B}{Z-0.414B}\right)$$

Then y_1 is calculated from:

$$y_1 = \left(\frac{x_1\gamma_1 P_1^{sat}\phi_1^{sat}}{P\phi_1^{V}}\right)\exp\frac{V_1^{L}(P-P_1^{sat})}{RT}$$

After calculating y_1 the above steps were repeated until the last calculated y1 is equal to the calculated y_1 from the last above equation where

$$y_1 = 0.1852$$

And the experimental y_1 at this point is 0.189. The deviation between the experimental and calculated is

$$\text{Absolute Deviation} = \left|\, y_{1\text{Experimental}} - y_{1\text{ Calculated}} \,\right|$$
$$= \left|\, 0.189 - 0.1852 \,\right| = 0.0038$$

Steps 3, 4 and 5 are repeated for every point of VLE data (x_1, T). For the system Acetone (1) – Carbon tetrachloride (2) the VLE data have 24 point of x_1 versus T. And the Average Absolute Deviation is 0.0020051 for UNIQUAC model

$$\text{Average Absolute \% Deviation} = \frac{\sum_{i=1}^{n} \left| y_{1Experimental} - y_{1Calculated} \right|}{n} * 100$$

Where *n* is number of pints for VLE data (for each point there is x_1 versus T).

Table D-1 show the Average Absolute % Deviation for the system Acetone (1) – Carbon tetrachloride (2) calculated by using different equations, one parameter and two parameters.

Table D-1 Acetone (1) – Carbon tetrachloride (2) Isobaric P = 450 mmHg 24 point

	Equations	Average Absolute % Deviation
1	Wilson eq. One Parameter	0.7259
2	Wilson eq. Two Parameters	0.32486
3	NRTL eq. One Parameters	3.862729
4	NRTL eq. Two Parameters	2.076054
5	UNIQUAC eq. One Parameters	0.373582
6	UNIQUAC eq. Two Parameters	0.20051

الخُلاصة

الهدف الاساسي من هذا المشروع هو توضيح هل من الممكن ان نستخدم ال γ^{∞} (activity coefficient infinite dilution) لايجاد الثوابت لِعدت معادلات.

لِحساب الγ^{∞} اقترح طريقتين حديثتين هما MOSCED و SPACE. المعادلتين طُبِّقت لِـ 18 منظومة ثنائية مختلفة و معادلة الـSPACE اعطت نتائج افضل من معادلة الـMOSCED.

في هذا المشروع تُبين الفوائد لِـ γ^{∞} (activity coefficient infinite dilution) و الطرق لحساب هذه الفوائد باستخدام عدة معادلات (Wilson, NRTL, UNIQUAC). واحد هذهِ الفوائد هي الـ(azeotropic calculation) حيث انها طبقت لـ10 انظمة ثنائية مختلفة من النتائج العملية لـγ^{∞} و النتائج عندما قورنت مع النتائج العملية لـ (azeotrope) في نفس درجة الحرارة بينت نتائج جيدة و قريبة من النتائج التي تحسب باستخدام الثوابت الحقيقية للمعادلات. الفائدة الاخرى هي حساب الـ (Vapor Liquid Equilibrium data) حيث انها طبقت على 13 منضومة ثنائية (194 نقطة) من الـγ^{∞} العملية حيث ان النتائج ايضاً اعطت دقة عالية كمالو استخدمت الثوابت الحقيقية للمعادلات. من هذه الحسابات معادلة ال UNIQUAC اعطت افضل دقة من باقي المعادلات لكل الاستخدامات.

في الانظمة التي يتوفر لها γ^{∞} واحدة استخدم المعادلات ذات المتغير الواحد لكل من (Wilson, NRTL, UNIQUAC) حيث انها اعطت نتائج ذات دقة قريبة من المعادلات ذات المتغيرين.

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رسالة
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في الهندسة الكيمياوية

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