THE STUDY OF AZEOTROPES IN THE REPLACEMENT OF INDUSTRIALLY IMPORTANT SOLVENTS

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by

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ABSTRACT

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The determination of the existence and composition of azeotropes is important both from theoretical and practical aspects. Finding azeotropy by experiment is usually expensive and time consuming but a reliable theoretical method will narrow the experimental search and reduce the cost. This research has evaluated three inexpensive methods for finding azeotropes. The first method is the absolute vapor pressure method using vacuum-assisted simple distillation. Several vapor-liquid equilibrium (VLE) data points are needed, and linear interpolation is used to find the azeotropic composition (x_1^{az}). The second method is an estimate of x_1^{az} using a single VLE data point. In this process, the Wilson equation is used to find the activity coefficients of a binary vapor-liquid equilibrium system. The Antoine equation is used to determine the saturated vapor pressure of the individual components. The total vapor pressure, molar fractions in liquid phase and molar fractions in the vapor phase are used to calculate the Wilson parameters, the excess Gibbs energy of mixing, and eventually x_1^{as} using the solver tool in Microsoft Excel. The third method explores the relationships of the Wilson parameters to the Hansen solubility parameters as an effort to find a purely theoretical method for predicting x_1^{az}. The first two methods are evaluated for accuracy using three VLE data sets from the literature and two VLE data sets that were obtained using a newly-constructed apparatus in the Williams lab.

KEY WORDS: Azeotropes, vapor-liquid equilibrium, Wilson equation, Antoine equation, excess Gibbs energy of mixing, Hansen solubility parameters, Microsoft Excel

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CHAPTER I

INTRODUCTION

The purpose of this research was to develop vapor-liquid equilibrium (VLE) measurement capabilities at SHSU and to improve the data analysis techniques by incorporating Microsoft Excel. A secondary goal was to explore the ability to predict azeotropy in binary mixtures from a single VLE data point and the Hansen solubility parameters.

The intended audience of this thesis is the researcher who is needing to explore azeotropes with minimal equipment and chemists and engineers looking for excel implementation of more expensive azeotropy models.

This thesis begins with the derivation and outline of the basic requirements for finding azeotropes. These equations (Eqs 1, 2, 3, 18, 19, 20, 21 and 25) will be used to demonstrate a mathematical model for determining the existence of azeotropes. A known set of VLE data from the literature is used to investigate the accuracy of the Excel implementation of the azeotropy models. These models are then extended to explore the possibility of connecting the binary interaction parameters to the Hansen solubility parameters. An experimental setup was devised and described for finding the VLE data for binary systems. The VLE data of a known binary system was evaluated to find the reliability of the instrumental setup. The ultimate future goal is to use this work to find azeotropes of interesting solvent blends such as a nonflammable (acetone-flame retardant) azeotrope for use in industrial cleaning applications.

Azeotropy

An azeotrope is a mixture of two or more liquids whose proportions are not altered by simple distillation. This is due to the fact that when an azeotrope is boiled, the vapor phase has the same molar ratio of the constituents as the liquid. Thus, azeotropes are called "constant boiling mixtures."

Two component mixtures are known as binary systems and three component mixtures are ternary systems. The azeotropes obtained from these systems are known as binary azeotropes and ternary azeotropes, respectively. There are two types of azeotropes: minimum boiling azeotropes and maximum boiling azeotropes. Azeotropes have specific boiling points and the boiling point of an azeotrope is either less than the boiling temperatures of any of its constituents (a positive azeotrope), or greater than the boiling temperatures of any of its constituents (a negative azeotrope) (Figure 1).

A solution that shows a positive deviation from Raoult's law forms a minimum boiling azeotrope at a specific composition.[1] Ethanol (95% by volume) and water is an example of this class of azeotrope. An example for positive azeotrope is 95.63% ethanol (by Weight) and water. Ethanol boils at 78.4 °C and water boils at 100 °C, but the azeotrope boils at 78.2 °C, which is lower than either of its constituents. In general, a positive azeotrope boils at a lower temperature than any other ratio of its constituents. They are also known as minimum boiling mixtures or pressure maximum azeotropes.

A solution that shows a negative deviation from Raoult's law forms a maximum boiling azeotrope at a specific composition. Nitric acid (68% by volume) and water is an example of this class of azeotrope. Once azeotropic composition is achieved, no further separation can be done. An example of a negative azeotrope is hydrochloric acid at a concentration of 20.2% (by weight) in water. Hydrogen chloride boils at −84 °C and water at 100 °C, but the azeotrope boils at 110 °C, which is higher than either of its constituents. In general, a negative azeotrope boils at a higher temperature than any other ratio of its constituents. Negative azeotropes are also called maximum boiling mixtures or pressure minimum azeotropes.

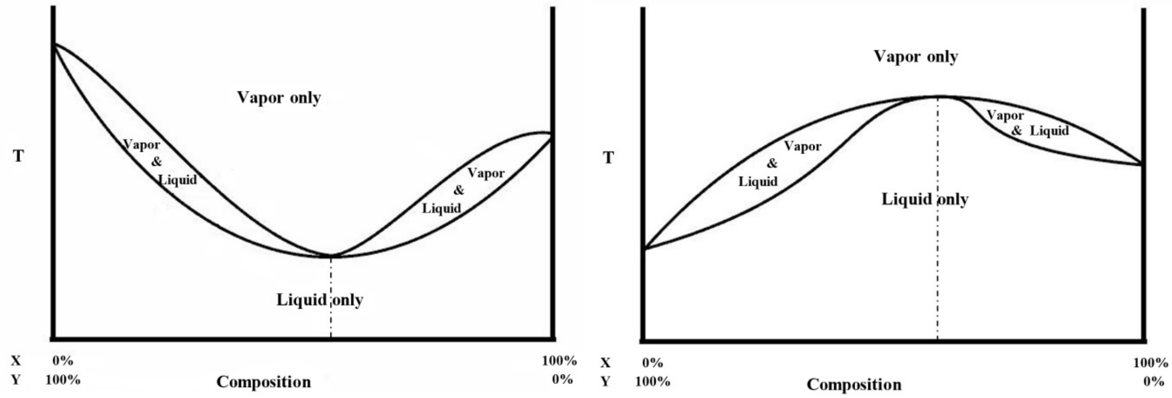


Figure 1. Phase diagram of a positive (min) azeotrope (left) and negative (max) azeotrope (right).

Wilson Equation

Many equations have been proposed to explain the (VLE) relationships. For two-component systems the two-parameter Wilson equation[2] is very useful. For a multicomponent system it reads as

$$g^E = \frac{\Delta G_{mix}^{excess}}{RT} = -\sum_i x_i \ln(\sum_j x_j A_{ij}) \tag{1}$$

Where, x_i and x_j are the mole fractions of component i and j in the liquid phase and A_{ij} are the Wilson interaction parameters ($i \neq j$) between i and j. The Wilson parameters model the interaction energy of the two molecules upon mixing. The Wilson equation is very useful due to the fact that it has a built-in effect of temperature. Here, g^E is the ratio between excess Gibbs energy of mixing and the product of universal gas constant and temperature. For a binary system the activity coefficients (γ) which are discussed in detail in Chapter II are given by the following equations:[2]

$$\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2\left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1}\right) \tag{2}$$

$$\ln \gamma_2 = -\ln(x_2 + A_{21}x_1) - x_1\left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1}\right) \tag{3}$$

Where, A_{12} & A_{21} are the Binary interaction parameters which depend on the molecular properties, and x_1 and x_2 are the molar fractions of component one and two in the liquid phase.

Antoine Equation

The saturated vapor pressure data are very important in the calculation of phase equilibrium. In this work, the Antoine equation (Eq 4) is used to calculate the saturated vapor pressure.

$$\log_{10}\frac{P_i^{sat}}{10^5} = A_i - \left(\frac{B_i}{T + C_i - 273.15}\right) \tag{4}$$

Where, P_i^{sat} is in Pa and T is in K, A_i, B_i, and C_i are "Antoine coefficients" that vary from substance to substance (see Appendix A). Sublimations and vaporizations of the same substance have separate sets of Antoine coefficients, as do components in mixtures. The Antoine equation is accurate to a few percent for most volatile substances (with vapor pressures over 10 Torr). Antoine coefficients for many substances are tabulated in *Lange's Handbook of Chemistry* [3] and they are available online from the NIST Chemistry Web Book[4].

Other Available Methods for Calculation of Azeotropes

The Nonrandom Two Liquid (NRTL) Equation

The basic idea used in the Wilson equation (eq 1) and the concept of local composition was used by Renon (1968) to derive the NRTL equation.[5] This equation is applicable to partially and completely miscible systems. The NRTL equation for the excess Gibbs energy is,

$$g^E = x_i x_j \left(\frac{\tau_{ji} G_{ji}}{x_i + x_j G_{ji}} + \frac{\tau_{ij} G_{ij}}{x_j + x_i G_{ij}} \right) \tag{5}$$

Where,

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{6}$$

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \tag{7}$$

The significance of g_{ij} is an energy parameter characteristic of the *i-j* interactions and it is similar to λ_{ij} in Wilson's equation (eqs 35 and 36). The term α_{12} is related to the non-randomness of the mixture.[6] When α_{12} is zero, the mixture is completely random but experimental studies show a range of α_{12} varying from 0.2 to 0.47 for binary mixtures. The value of α_{12} is often set arbitrarily to 0.3. The NRTL parameters are fitted to activity coefficients that have been derived from experimentally determined phase equilibrium data as well as from heats of mixing. The source of the data is often experimental data banks like the Dortmund Data Bank[7].

The activity coefficients derived from the NRTL equations are,

$$\ln\gamma_i = x_j^2\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + x_j G_{ji}}\right)^2 + \frac{\tau_{ij}G_{ij}}{\left(x_j + x_i G_{ij}\right)^2}\right] \tag{8}$$

The UNIversal QUAsi Chemical (UNIQUAC) Equation

The UNIQUAC equation for g^E consists of two parts: a combinatorial part that attempts to describe the dominant entropic contribution, and a residual part that is due primarily to the intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined only by the composition mixture and by the size and the shape of the molecules.[6]

The UNIQUAC equation is:

$$g^E = g^E_{combinatorial} + g^E_{residual} \tag{9}$$

For a binary mixture:

$$g^E_{combinatorial} = x_i \ln\frac{\phi_i^*}{x_i} + x_j \ln\frac{\phi_j^*}{x_j} + \frac{z}{2}\left[x_i q_i \ln\frac{\theta_i}{\phi_i^*} + x_j q_j \ln\frac{\theta_j}{\phi_j^*}\right] \tag{10}$$

$$g^E_{residual} = -x_i q_i' \ln\left(\theta_i' + \theta_j' \tau_{ji}\right) - x_j q_j' \ln\left(\theta_j' + \theta_i' \tau_{ij}\right) \tag{11}$$

Where, the coordination number z is equal to 10. The segment fraction, ϕ_i^* and area fractions, θ_i and θ_i', are given by:

$$\phi_i^* = \frac{x_i r_i}{x_i r_i + x_j r_j} \;;\; \theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j} \;;\; \theta_i' = \frac{x_i q_i'}{x_i q_i' + x_j q_j'} \tag{12}$$

$$l_i = \frac{z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right); \tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right) \tag{13}$$

Here, r, q, and q' are pure component molecular-structure constants depending on the molecular size and external surface areas. The Δu_{ij} is the characteristic energy associated with the two component system, and a_{ij} is the binary parameter.

By using the above equations (Eqs 9, 10, 11, 12, and 13) the activity coefficients for the UNIQUAC equation are given by,

$$\ln \gamma_i = \ln \frac{\phi_i^*}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i^*} + \phi_i^* \left(l_i - \frac{r_i}{r_j} l_j \right) - q_i^{'} \ln\left(\theta_i^{'} + \theta_j^{'} \tau_{ji}\right) + \theta_j^{'} q_i^{'} \left(\frac{\tau_{ji}}{\theta_i^{'} + \theta_j^{'} \tau_{ji}} - \frac{\tau_{ij}}{\theta_j^{'} + \theta_i^{'} \tau_{ij}} \right) \quad (14)$$

These NRTL and UNIQUAC activity coefficient equations can be used to model the azeotropic point seperately.

Several other models have been proposed for predicting homogeneous azeotropes. Fidkowski et al.[8] described a method to compute all the homogeneous azeotropes using the homotopy continuation technique in a multi-component mixture. The homotopy continuation technique is a mathematical technique to find roots of a non-linear system using a similar known system. Tolsma and Barton[9,10] developed the work done by Fidkowski to compute homogeneous and heterogeneous azeotropes. To predict azeotropes of refrigerant mixtures the above approaches are combined by Maranas et al.[11] Harding et al.[12] found a method to locate all the azeotropes in a refrigerants mixture using global optimization (a method of locating global minimum or maximum using numerical, deterministic, stochastic approaches). Maier et al.[13,14] used an interval analysis and Newton algorithm to find the existence of homogeneous azeotropes and to locate all homogeneous azeotropes in a mixture.

Most of the above methods are very involved and have specific mathematical calculations. Sometimes one just wants to know whether a binary mixture is going to form an azeotrope without consuming time and chemicals. Liu et al.[15] described a method to predict azeotropy using the relative volatility test and UNIQUAC equations. No complicated numerical calculations are used in their method, so their approach is very simple and easily implemented. In their method, all the interaction parameters must be known at first, but they are unavailable in most of the cases that are of interest to the Williams lab.

In this research, the Wilson activity coefficient equations (Eqs 2 and 3) and Antoine equation (Eq 4) are used to derive a new equation to find the existence of the azeotrope point. The method presented by Apelblat et al.[16] was used to find the binary interaction parameters if they were unavailable.

Solubility Parameters

There is a relationship between binary interaction parameters and the solubility parameters. Solubility parameters are derived from the Gibbs energy of mixing equation.

$$\Delta G_{mix}^{excess} = \Delta H_{mix} - T\Delta S \tag{15}$$

The enthalpy of mixing can be related to the cohesive energy density of the individual components.[17]

$$\Delta H_{mix} = \phi_1 \phi_2 v_{total} \left(\delta_{T,1} - \delta_{T,2}\right)^2 \text{ Where } \delta_{T,1} = \sqrt{\frac{\Delta H_{vap}}{v_1}} \tag{16}$$

The Hildebrand solubility parameter ($\delta_{T,1}$) is the square root of the energy of vaporization (ΔH_{vap}) divided by the molar volume (v_1). The ϕ_1 and ϕ_2 in eq 16 are the volume ratios of the individual components. Hildebrand's work involved only hydrocarbons, so problems developed when predicting the mixing behavior of polar molecules. Hansen separated

Hildebrand's solubility parameter into three individual parts to account for dispersion (δ_D), polarity (δ_P), and hydrogen bonding ability (δ_H).[18]

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{17}$$

These (δ_D, δ_P, and δ_H) are known as the Hansen solubility parameters (HSPs). In the 1960's, Hansen carried out swelling experiments to compile a table of HSP values, which has grown to over 10,000 substances. Since then, Hansen and others have explored other ways to determine the various HSP values.[19,20] A literature search revealed that the Wilson binary interaction parameters have molar volume and a Hildebrand solubility parameter portion which can be connected to the HSP easily.

Algorithm and Methods Used by Excel Solver 2013

Solver is part of a suite of commands sometimes called what-if analysis tools. With Solver, one can find an optimal value for a formula in one cell, called the target cell on a worksheet. Solver works with a group of cells that are related, either directly or indirectly, to the formula in the target cell. Solver adjusts the values in the cells you specify as adjustable cells. By applying constraints to restrict the values Solver can use in the model we can adjust the value of the objective cell very rapidly. The Microsoft Excel Solver tool uses the Generalized Reduced Gradient (GRG2) nonlinear optimization code developed by Leon Lasdon, University of Texas at Austin, and Allan Waren, Cleveland State University.[21]

Although, many methods have been mentioned in this introduction, the materials and methods chapter outlines specifically the combination of theoretical tools found useful for predicting binary azeotropes. The experimental verification of these methods is also developed using literature data and experimental data obtained in-house.

Throughout this research project three approaches were used to predict the azeotropic point (Figure 2).

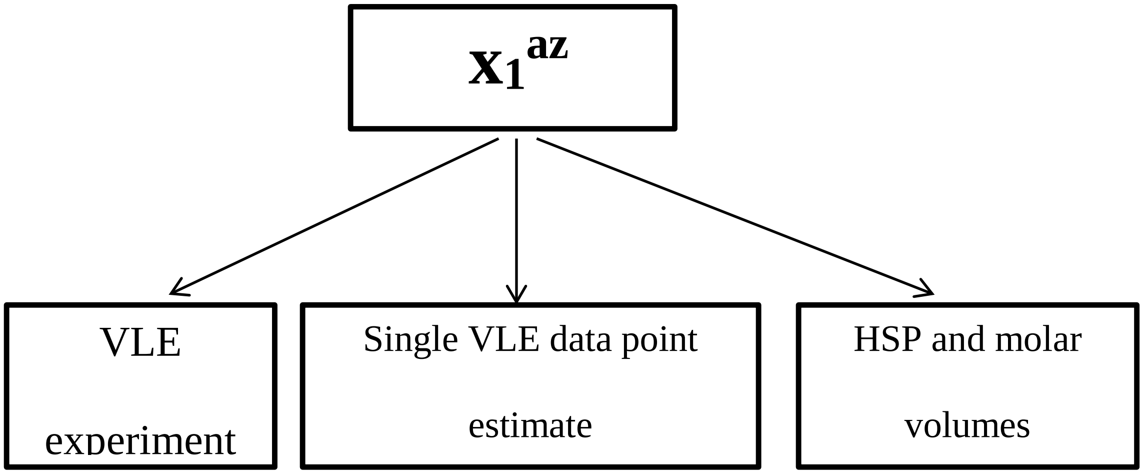


Figure 2. The three approaches used to calculated the azeotropic point

CHAPTER II

MATERIALS AND METHODS

Reagents

Reagents used in these experiments include: DI water from a RiOs 3 water purification system, Isopropyl alcohol: C_3H_8O (99.5 %) (Mallinckrodt chemicals, Phillipsburg, NJ, USA), Apiezon High Vacuum Grease (M & I materials LTD, Manchester, UK)

Other Equipment and Instruments

Other equipment used in these experiments include: RiOs 3 water purification system from Millipore (Billerica, MA, USA) for water deionization, semi-micro organic chemistry kit from Kimble and Chase (USA), traceable manometer and data acquisition software from Control Company (Friendswood, TX, USA), data logger multimeter (383274) from Extech (Taiwan), Microsoft Excel 2013 licensed to Sam Houston State University, 60 MHz (Varian EM360L) NMR spectrophotometer.

Part 1. Derivation of Mathematical Formulae to Find the Azeotrope Point for Binary Mixtures from a Single VLE Data Point

Starting from the Gibbs energy of mixing, an equation was derived (see appendix B) to find the excess Gibbs free energy of mixing which was combined with the Wilson's equation (eq 1) to give an equation (see appendix B) to find the existence of azeotropes for binary systems. Maranas et al. showed that there are three thermodynamic conditions that must be satisfied for a homogeneous azeotrope system;[11] They are, 1) phase equilibrium, 2) The composition of the vapor phase should be identical to the composition of the liquid phase, and 3) the mole fractions in each phase must sum to one and must be positive. Starting from these three conditions and the activity coefficient models an equation to find the existence of azeotropes can be derived. The Antoine equation was used to find the saturated vapor pressure for the pure component as a function of Temperature.

The Gibbs energy of mixing was calculated by forming the difference of the Gibbs energies before and after mixing. The excess function is defined as the difference between the actual value of the mixture and the value for an ideal mixture.

1. Phase equilibrium

For binary systems, the phase equilibrium condition can be written in terms of the equality of fugacity. The fugacity of a real gas is an effective pressure which replaces the true pressure in accurate chemical equilibrium calculations. It is equal to the pressure of an ideal gas, which has the same chemical potential as the real gas (a thermodynamic property of a real gas that, if substituted for the pressure or partial pressure in the equations for an ideal gas, gives equations applicable to the real gas).

$$f_i^V = f_i^L \tag{18}$$

Where, i = 1, 2, f_i^V is fugacity of component i in vapor, and f_i^L is fugacity of component *i* in liquid.

2. Composition of the vapor phase is identical to the composition of the liquid phase.

For the refrigerant mixtures pressure is not high so the vapor phase may be treated as an ideal gas.

$$y_i P^{total} = x_i \gamma_i P_i^{sat} \tag{19}$$

In eq 19, y_i is the mole fraction is in the vapor phase, P^{total} is the total vapor pressure, x_i is the mole fraction in liquid phase, γ_i is the activity coefficient of component *i*, and P_i^{sat} is the saturated vapor pressure of component *i*.

3. The mole fractions in each phase must sum to one and must be positive.

$$x_1 + x_2 = y_1 + y_2 = 1 \tag{20}$$

From eq 19 and 20, eq 21 can be obtained.

$$P^{total} = x_1 \gamma_1 p_1^{sat} + x_2 \gamma_2 p_2^{sat} \tag{21}$$

By using VLE data and the saturated vapor pressure, the activity coefficient can be calculated.[22]

$$\gamma_i = \frac{y_i P^{total}}{x_i P_i^{sat}} \tag{22}$$

The excess Gibbs energy of mixing is the difference between the non-ideal and ideal Gibbs energy of mixing. Eq 24 can be obtained by using eq 23 (see appendix B).

$$\Delta G_{mix}^{excess} = \Delta G_{mix}^{actual} - \Delta G_{mix}^{ideal} \tag{23}$$

$$\Delta G_{mix}^{excess} = RT\left(x_1 \ln \gamma_1 + x_2 \ln \gamma_2\right) \tag{24}$$

Rearranging equation 24 will give,

$$g^E = \frac{\Delta G_{mix}^{excess}}{RT} = \left(x_1 \ln \gamma_1 + x_2 \ln \gamma_2\right) \tag{25}$$

Calculation of binary interaction parameters.

The most difficult part of the Wilson equation is to find the binary interaction parameters. The following equations were used in the method derived by Apelblat et al.[16] In their work they used a set of vapor liquid equilibrium data (VLE) to calculate activity coefficients (eq 5). For binary mixtures, the Wilson model expresses the excess Gibbs energy of mixing ΔG_{mix}^{excess} as follows:

$$g^E = -x_1 \ln\left(x_1 + A_{12} x_2\right) - x_2 \ln\left(x_2 + A_{21} x_1\right) \tag{26}$$

Wilson's binary interaction parameters were replaced by Z_1 and Z_2 in order to simplify eq 26.

$$Z_1 = \frac{1 - A_{12}}{x_1 + A_{12}x_2} \tag{27}$$

$$Z_2 = \frac{1 - A_{21}}{x_2 + A_{21}x_1} \tag{28}$$

From eqs 26, 27 and 28 following equation can be obtained (see appendix B).

$$g^E = x_1 \ln(1 + Z_1x_2) + x_2 \ln(1 + Z_2x_1) \tag{29}$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1 + Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = Z_1 \tag{30}$$

$$0 = x_1 \ln\left(1 + \left\{\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1 + Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right]\right\}x_2\right) + x_2 \ln(1 + Z_2x_1) - g^E \tag{31}$$

Excel solver can be used to find Z_2 by changing Z_2 until eq 31 is zero. This Z_2 value can be used to find Z_1 via eq 30. By using Z_2 and Z_1, A_{12} and A_{21} can be calculated.

Calculation of azeotropic point.

To find the azeotropic point in the phase diagram we have to find the point of zero slope in the pressure vs x_1 curve. Mathematically, the place at which $\frac{dP}{dx_1} = 0$ is the point where the azeotrope is located.

From eq 21,

$$\frac{dP}{dx_1} = \frac{\partial\left(x_1\gamma_1P_1^{sat}\right)}{\partial x_1} + \frac{\partial\left(x_2\gamma_2P_2^{sat}\right)}{\partial x_1} = 0 \tag{32}$$

The molar fraction of the second component can be written in terms of molar fraction of component one by the definition in eq 20.

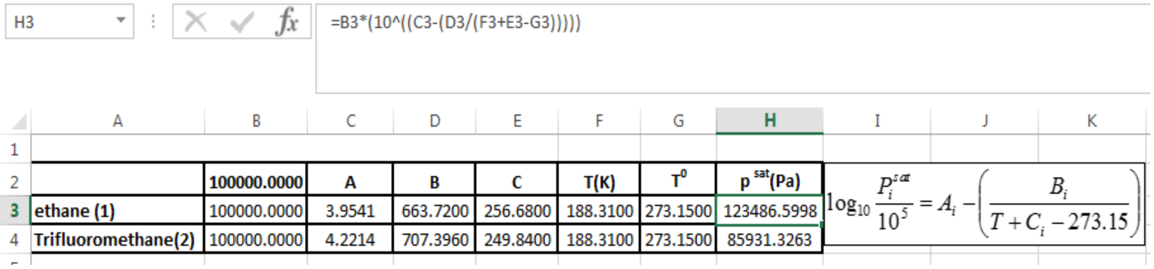
$$\frac{dP}{dx_1} = \frac{\partial\left(x_1\gamma_1P_1^{sat}\right)}{\partial x_1} + \frac{\partial\left[\left(1-x_1\right)\gamma_2P_2^{sat}\right]}{\partial x_1} \tag{33}$$

Breaking the total derivative in to its components gives eq 34.

$$\frac{dP}{dx_1} = \gamma_1P_1^{sat} + x_1P_1^{sat}\frac{\partial\gamma_1}{\partial x_1} + P_2^{sat}\frac{\partial\gamma_2}{\partial x_1} - \gamma_2P_2^{sat} - x_1P_2^{sat}\frac{\partial\gamma_2}{\partial x_1} = 0 \tag{34}$$

Part 2. Microsoft Excel Calculations

An example is given using the VLE literature values for ethane (1) – trifluoromethane (2) from Zhang et al.[23] Microsoft Excel 2013 was used for all the calculations and the steps are explained below. First, saturated vapor pressures were calculated using the Antione equation (eq 4). The values (units of Pascal) for the relevant compounds are located in cells H3 and H4 in Figure 3.



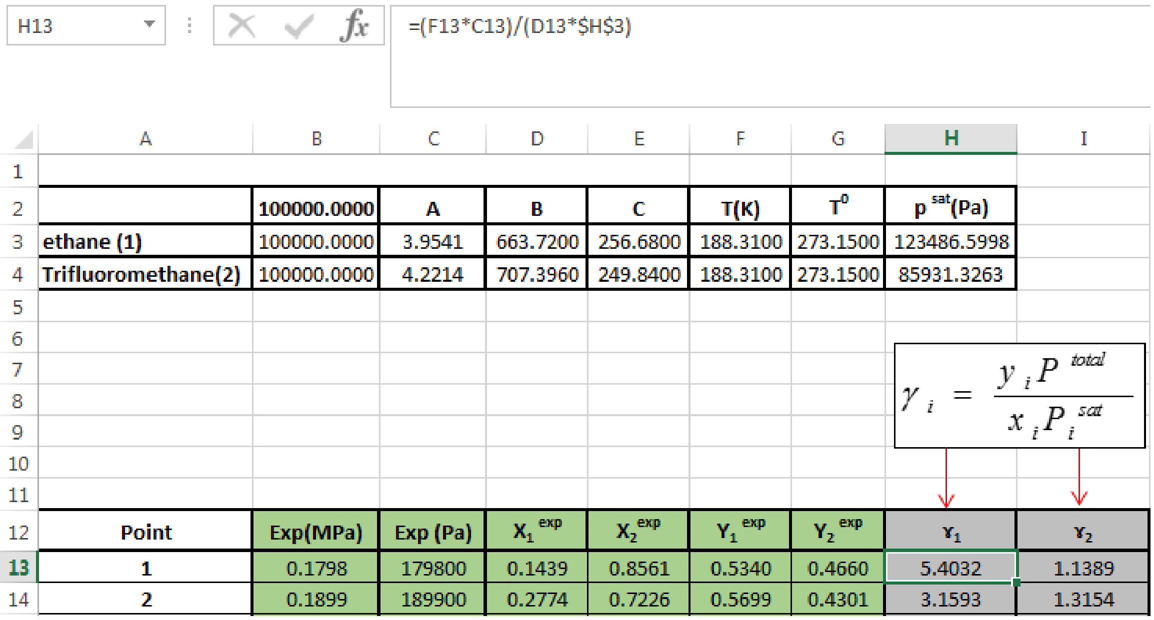
```
=B3*(10^((C3-(D3/(F3+E3-G3)))))
```

	100000.0000	A	B	C	T(K)	T^0	p^{sat}(Pa)
ethane (1)	100000.0000	3.9541	663.7200	256.6800	188.3100	273.1500	123486.5998
Trifluoromethane(2)	100000.0000	4.2214	707.3960	249.8400	188.3100	273.1500	85931.3263

$$\log_{10}\frac{P_i^{sat}}{10^5} = A_i - \left(\frac{B_i}{T+C_i-273.15}\right)$$

Figure 3. Microsoft Excel equations and numerical values for the saturated vapor pressure.

Second, the calculated saturated vapor pressure for each component at the relevant temperature was used along with the VLE data to calculate the activity coefficients (eq 22). The calculated activity coefficients are located in cells H13 and I13 in Figure 4.



H13 =(F13*C13)/(D13*H3)

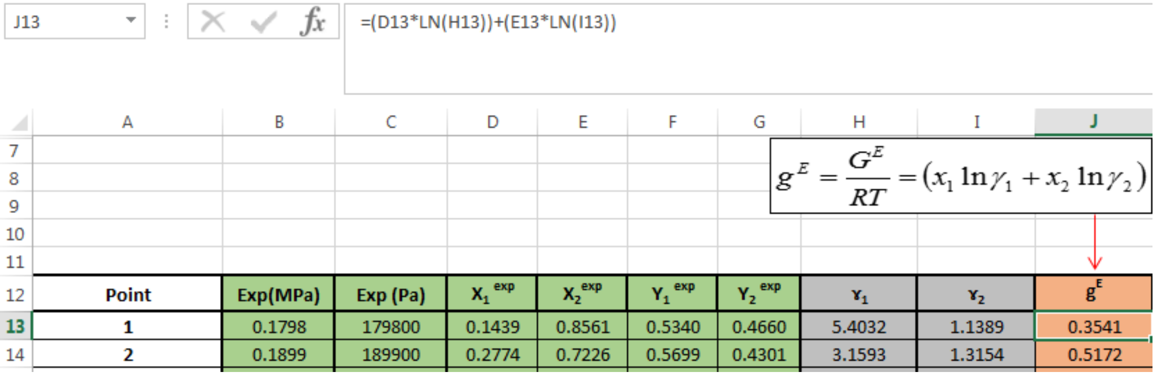
	100000.0000	A	B	C	T(K)	T^0	p^{sat}(Pa)
ethane (1)	100000.0000	3.9541	663.7200	256.6800	188.3100	273.1500	123486.5998
Trifluoromethane(2)	100000.0000	4.2214	707.3960	249.8400	188.3100	273.1500	85931.3263

$$\gamma_i = \frac{y_i P^{total}}{x_i P_i^{sat}}$$

Point	Exp(MPa)	Exp (Pa)	X_1^{exp}	X_2^{exp}	Y_1^{exp}	Y_2^{exp}	γ_1	γ_2
1	0.1798	179800	0.1439	0.8561	0.5340	0.4660	5.4032	1.1389
2	0.1899	189900	0.2774	0.7226	0.5699	0.4301	3.1593	1.3154

Figure 4. Microsoft Excel equations that were used to calculate the activity coefficients.

The excess Gibbs free energy of mixing (eq 17) was calculated using the activity coefficients above and mole fractions of components one and two in the liquid. The results are located in column J of Figure 5.



J13 =(D13*LN(H13))+(E13*LN(I13))

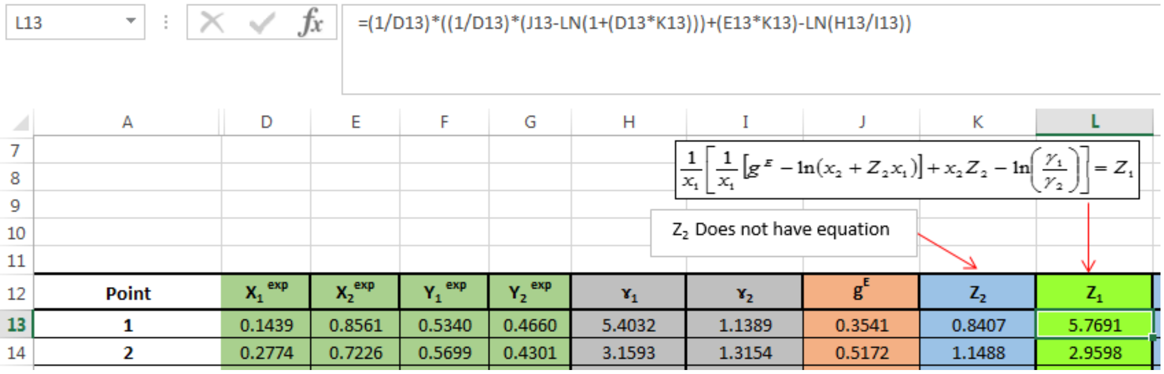
$$g^E = \frac{G^E}{RT} = (x_1 \ln\gamma_1 + x_2 \ln\gamma_2)$$

Point	Exp(MPa)	Exp (Pa)	X_1^{exp}	X_2^{exp}	Y_1^{exp}	Y_2^{exp}	γ_1	γ_2	g^E
1	0.1798	179800	0.1439	0.8561	0.5340	0.4660	5.4032	1.1389	0.3541
2	0.1899	189900	0.2774	0.7226	0.5699	0.4301	3.1593	1.3154	0.5172

Figure 5. Microsoft Excel equations that were used to calculate the excess Gibbs free energy of mixing.

A new column K was introduced to hold the solver-controlled values for Z_2 (see Figure 6). Column L contains the equation (eq 30) that was derived to find the values for Z_1.

Since we do not know the values for Z_1 and Z_2 Excel Solver was used to find an acceptable value for Z_2.



```
=(1/D13)*((1/D13)*(J13-LN(1+(D13*K13)))+(E13*K13)-LN(H13/I13))
```

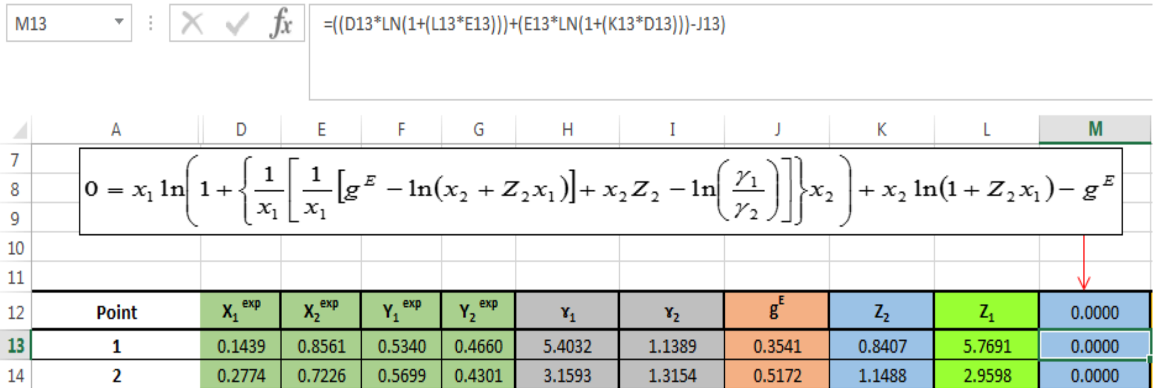
$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(x_2 + Z_2 x_1)\right] + x_2 Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = Z_1$$

Z_2 Does not have equation

Point	X_1^{exp}	X_2^{exp}	Y_1^{exp}	Y_2^{exp}	γ_1	γ_2	g^E	Z_2	Z_1
1	0.1439	0.8561	0.5340	0.4660	5.4032	1.1389	0.3541	0.8407	5.7691
2	0.2774	0.7226	0.5699	0.4301	3.1593	1.3154	0.5172	1.1488	2.9598

Figure 6. Microsoft Excel equations that were used to calculate the Z_1 & Z_2.

Next, eq 31 which includes Z_1, Z_2 and g^E was used to find a value of zero. The equation was included in the column M in the excel spreadsheet (Figure 7).



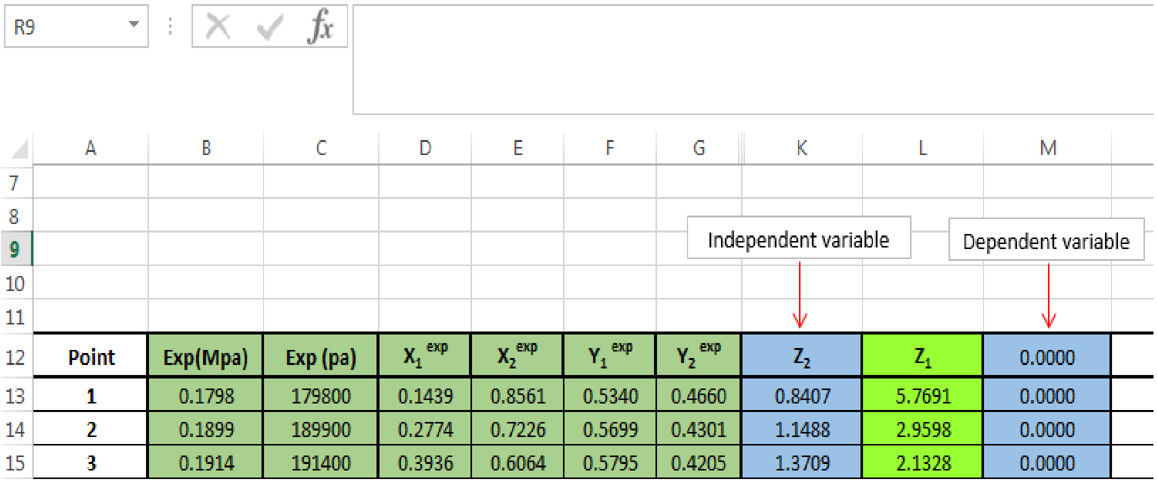
```
=((D13*LN(1+(L13*E13)))+(E13*LN(1+(K13*D13)))-J13)
```

$$0 = x_1 \ln\left(1 + \left\{\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(x_2 + Z_2 x_1)\right] + x_2 Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right]\right\} x_2\right) + x_2 \ln(1 + Z_2 x_1) - g^E$$

Point	X_1^{exp}	X_2^{exp}	Y_1^{exp}	Y_2^{exp}	γ_1	γ_2	g^E	Z_2	Z_1	0.0000
1	0.1439	0.8561	0.5340	0.4660	5.4032	1.1389	0.3541	0.8407	5.7691	0.0000
2	0.2774	0.7226	0.5699	0.4301	3.1593	1.3154	0.5172	1.1488	2.9598	0.0000

Figure 7. Microsoft Excel equation that was used to calculate the column M.

The Microsoft Excel Solver tool was used to calculate the value of the dependent variable cell (value of zero), that is column M (repeated for each row of experimental data) changing the values of the independent variable, that is column K (Z_2) (Figure 8). Since the value of the Z_2 (column K) referred in the calculation of Z_1 (eq 30), the value for the Z_1 shows in column L automatically.



R9

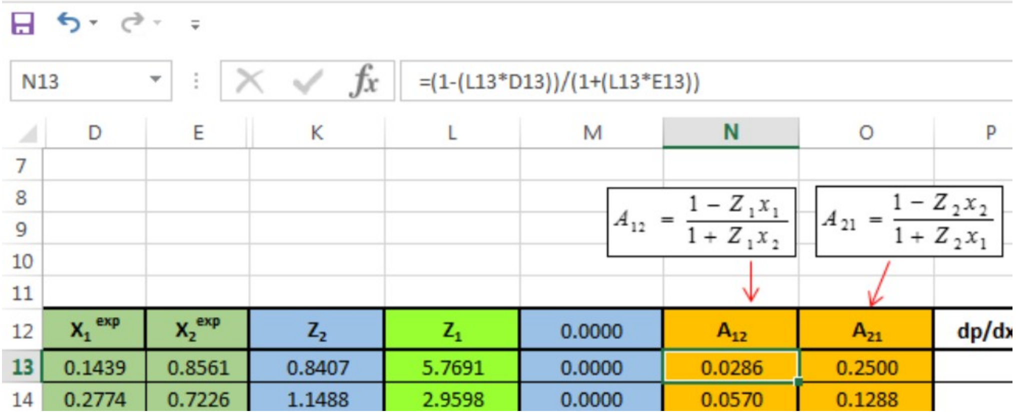
Independent variable

Dependent variable

Point	Exp(Mpa)	Exp (pa)	X_1^{exp}	X_2^{exp}	Y_1^{exp}	Y_2^{exp}	Z_2	Z_1	0.0000
1	0.1798	179800	0.1439	0.8561	0.5340	0.4660	0.8407	5.7691	0.0000
2	0.1899	189900	0.2774	0.7226	0.5699	0.4301	1.1488	2.9598	0.0000
3	0.1914	191400	0.3936	0.6064	0.5795	0.4205	1.3709	2.1328	0.0000

Figure 8. Target cells for Microsoft Excel Solver calculation.

The above calculated Z_1 and Z_2 values were used to determine the values for A_{12} and A_{21} as shown below in Figure 9 (eqs 27 and 28). The values for A_{12} and A_{21} are shown in columns N and O, respectively.



N13

=(1-(L13*D13))/(1+(L13*E13))

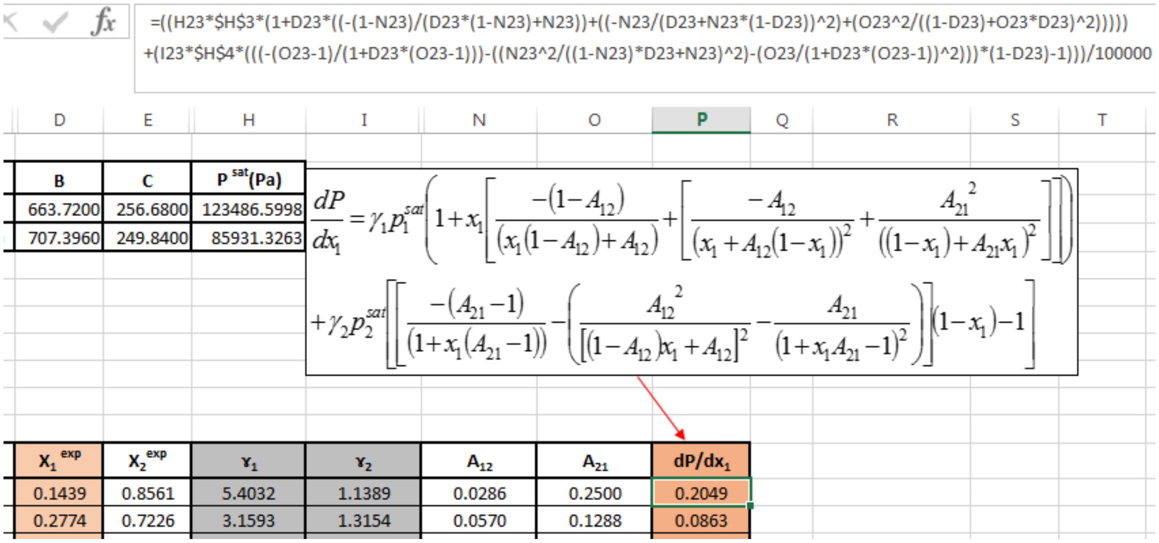
$$A_{12} = \frac{1 - Z_1 x_1}{1 + Z_1 x_2}$$

$$A_{21} = \frac{1 - Z_2 x_2}{1 + Z_2 x_1}$$

X_1^{exp}	X_2^{exp}	Z_2	Z_1	0.0000	A_{12}	A_{21}	dp/dx
0.1439	0.8561	0.8407	5.7691	0.0000	0.0286	0.2500	
0.2774	0.7226	1.1488	2.9598	0.0000	0.0570	0.1288	

Figure 9. Microsoft Excel equations that were used to calculate the values of A_{12} and A_{21}.

Finally, dP/dx1 was calculated using equation 44 and the results are shown in Figure 10.



```
=((H23*$H$3*(1+D23*((-(1-N23)/(D23*(1-N23)+N23))+((-N23/(D23+N23*(1-D23))^2)+(O23^2/((1-D23)+O23*D23)^2)))))
+(I23*$H$4*(((-(O23-1)/(1+D23*(O23-1)))-((N23^2/((1-N23)*D23+N23)^2)-(O23/(1+D23*(O23-1))^2)))*(1-D23)-1)))/100000
```

B	C	P^{sat}(Pa)
663.7200	256.6800	123486.5998
707.3960	249.8400	85931.3263

$$\frac{dP}{dx_1}=\gamma_1 p_1^{sat}\left(1+x_1\left[\frac{-(1-A_{12})}{(x_1(1-A_{12})+A_{12})}+\left[\frac{-A_{12}}{(x_1+A_{12}(1-x_1))^2}+\frac{A_{21}{}^2}{((1-x_1)+A_{21}x_1)^2}\right]\right]\right)$$
$$+\gamma_2 p_2^{sat}\left[\left[\frac{-(A_{21}-1)}{(1+x_1(A_{21}-1))}-\left(\frac{A_{12}{}^2}{[(1-A_{12})x_1+A_{12}]^2}-\frac{A_{21}}{(1+x_1A_{21}-1)^2}\right)\right](1-x_1)-1\right]$$

X_1^{exp}	X_2^{exp}	γ_1	γ_2	A_{12}	A_{21}	dP/dx_1
0.1439	0.8561	5.4032	1.1389	0.0286	0.2500	0.2049
0.2774	0.7226	3.1593	1.3154	0.0570	0.1288	0.0863

Figure 10. Microsoft Excel equation that was used to calculate the values of dp/dx1.

The Microsoft Excel Solver add-in was used again to calculate the value of zero in objective cell, that is column P (individual cells should be introduced) by changing the values of x_1^{exp}, that is column D. By performing this calculation to each and every row azeotropic points were calculated and the results are shown in the results section.

To check the accuracy of the Microsoft Excel method, calculations were carried out using the following literature data (Tables 1, 2, and 3).

Table 1. Literature vapor liquid equilibrium data for the ethane (1) - trifluoromethane (2) binary system from Zhang et al.[23]

Data point	P^{vap}/MPa	x_1	x_2	y_1	y_2
1	0.1798	0.1439	0.8561	0.5340	0.4660
2	0.1899	0.2774	0.7226	0.5699	0.4301
3	0.1914	0.3936	0.6064	0.5795	0.4205
4	0.1915	0.5023	0.4977	0.5829	0.4171
5	0.1916	0.5755	0.4245	0.5844	0.4156
6	0.1916	0.5919	0.4081	0.5862	0.4138
7	0.1914	0.6221	0.3779	0.5872	0.4128
8	0.1892	0.7968	0.2032	0.6069	0.3931

Table 2. Literature vapor liquid equilibrium data for the difluoromethane (1) - propane (2) binary system from Bobbo et al.[24]

Data point	P^{vap}/MPa	x_1	x_2	y_1	y_2
1	0.4486	0.0993	0.9007	0.4522	0.5478
2	0.5015	0.1589	0.8411	0.5227	0.4773
3	0.5393	0.2358	0.7642	0.5705	0.4295
4	0.5527	0.2872	0.7128	0.5872	0.4128
5	0.5648	0.3763	0.6237	0.6064	0.3936
6	0.5743	0.5354	0.4646	0.6287	0.3713
7	0.5751	0.5668	0.4332	0.6329	0.3671
8	0.5752	0.6407	0.3593	0.6410	0.3590

(continued)

Data point	P^{vap}/MPa	x_1	x_2	y_1	y_2
9	0.5746	0.7184	0.2816	0.6539	0.3461
10	0.5735	0.7485	0.2515	0.6602	0.3398
11	0.5556	0.8616	0.1384	0.7084	0.2916
12	0.5434	0.8921	0.1079	0.7348	0.2652

Table 3. Literature vapor liquid equilibrium data for the pentafluoroethane (1) - propane (2) binary system from Kim et al.[25]

Data point	P^{vap}/MPa	x_1	x_2	y_1	y_2
1	0.8828	0.1300	0.8700	0.3150	0.6850
2	0.9244	0.1710	0.8290	0.3670	0.6330
3	0.9857	0.2470	0.7530	0.4300	0.5700
4	1.0482	0.3830	0.6170	0.5090	0.4910
5	1.0802	0.4760	0.5240	0.5530	0.4470
6	1.0870	0.5090	0.4910	0.5670	0.4330
7	1.0953	0.5710	0.4290	0.6020	0.3980
8	1.0923	0.6970	0.3030	0.6660	0.3340
9	1.0779	0.7660	0.2340	0.7210	0.2790
10	1.0606	0.8190	0.1810	0.7550	0.2450

Part 3. Design and Implementation of an Instrumental Setup to Measure the Vapor Liquid Equilibrium (VLE) Data

The following experimental setup (Figure 11) was designed to measure VLE data.

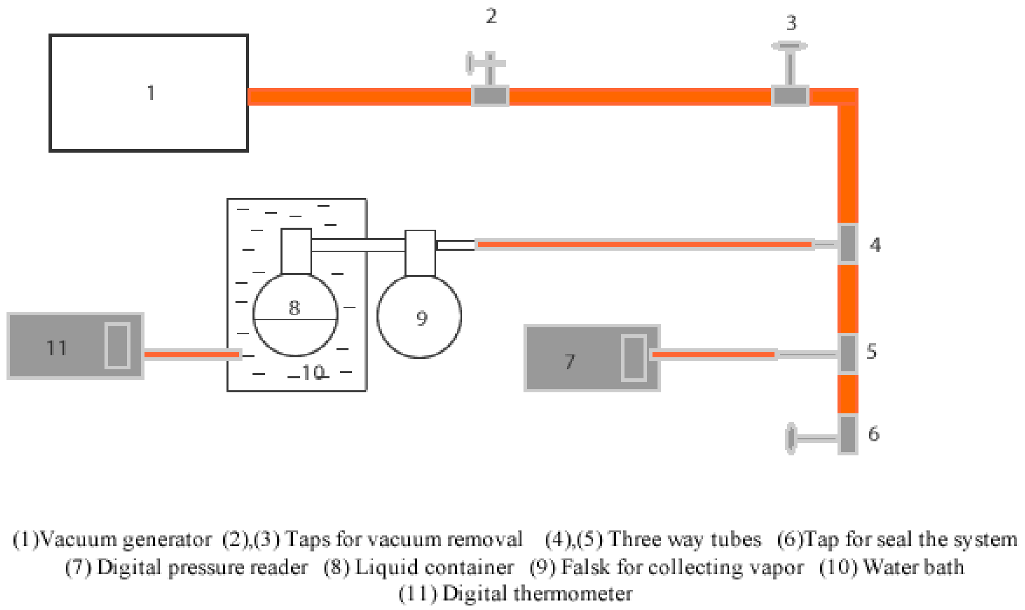


Figure 11. Instrumental setup prepared for the measurement of VLE data.

Steel valves 2, 3 and 6 were used to maintain the vacuum. Valve 2 was used to break the vacuum (preventing excessive usage of the vacuum pump). Valves 3 and 6 were used to maintain the vacuum of the system. Three-way unions (4, 5 in fig 11) were used to connect the glassware and pressure gauge to the vacuum system. Round bottom flask 8 was maintained in a water bath and it contained the solvent mixture. A magnetic stir bar was used to stir the mixture. Flask 9 was connected to flask 8 and to the vacuum system. A digital thermometer (11) monitored the water bath (10) temperature. To measure the internal pressure a digital manometer (7) was used. To measure the external pressure to 0.1 mmHg a Hg barometer fitted with a Vernier scale was used.

After preparing the above instrumental setup tap (3) and (6) were closed to isolate the system and to let it reach equilibrium. The vacuum pump (1) was switched on and tap (2) was closed. The computer-controlled pressure gauge recorded the pressure in one second intervals. Tap (3) was opened slowly so that the air above the liquid was slowly removed. The solution started boiling and was allowed to boil for 30 seconds before tap (3) was closed and tap (2) was opened. The vacuum pump was switched off. During the entire process the temperature of the water bath was maintained at 25.0 ± 0.2 ºC. The system equilibrated for another 30 minutes as the pressure readings stabilized. At that point the atmospheric pressure was measured. An ice water bath was placed around flask (9) to condense the vapor. After 5 minutes, the cooled flask was warmed to 25.0 ºC using a water bath to reestablish thermal equilibrium conditions. Finally, 1 ml portions of the liquid phase and condensed-vapor phase were transferred to NMR tubes. Molar ratios were determined by integrating the respective ^{1}H NMR signals using the 60 MHz (Varian EM360L) NMR spectrophotometer.

Part 4. Investigation of the Relationship between Wilson Parameters and the Hansen Solubility Parameters

The Wilson equation has two adjustable parameters A_{12} and A_{21}. In Wilson's derivation, these are related to the pure-component molar volumes and the characteristic energy differences by,[26]

$$A_{12} = \frac{v_2}{v_1} \exp\left(- \frac{\lambda_{12} - \lambda_{11}}{RT} \right) \qquad (35)$$

$$A_{21} = \frac{v_1}{v_2}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right) \tag{36}$$

Where v_1 is the liquid molar volume of pure compound 1, v_2 is the liquid molar volume of the pure compound 2, λ is interaction energy due to attractive forces (J/mol). The energy interaction parameters for pure components can be estimated as follows[26].

$$\lambda_{11} = -\left(\frac{2}{z}\right)v_1\delta_{T,1}^2 \tag{37}$$

$$\lambda_{22} = -\left(\frac{2}{z}\right)v_2\delta_{T,2}^2 \tag{38}$$

Where z is the coordination number and it is approximated to 2, $\delta_{i,T}$ is the solubility parameter (J/cm^3).$^{1/2}$

The interaction energy due to attractive forces between unlike molecules are approximated as follows,

$$\lambda_{12} = -(1-\varepsilon_{12})\left(\frac{2}{z}\right)(v_1v_2)^{0.5}\delta_{T,1}\delta_{T,2} \tag{39}$$

$$\lambda_{21} = -(1-\varepsilon_{21})\left(\frac{2}{z}\right)(v_2v_1)^{0.5}\delta_{T,2}\delta_{T,1} \tag{40}$$

Where ε_{12} and ε_{21} are the interaction parameters between unlike molecules and should be evaluated by VLE data fitting. Moreover, an alternative method will be discussed in discussion section.

To find the molar volume of an unknown compound HSPIP software or the following method can be used.

$$v_t = v_{25} + \beta(t-25) \tag{41}$$

$$\beta = \frac{(v_b - v_{25})}{(t_b - 25)} \tag{42}$$

$$\delta_t = \left(\frac{v_{25}}{v_t}\right)\delta_{25} \tag{43}$$

Where, t_b is normal boiling point, v_b molar volume at boiling point (which can be estimated using the additive method of Le Bas),[27] v_{25} is the molar volume at 25 °C, and δ_{25} is the Hildebrand solubility parameter at 25 °C. Both v_{25} and δ_{25} can be predicted by the method developed by Robert D. Fedors (group-contribution treatment)[28] or HSPIP[18]. Substitution of the above equations into the dP/dx_1 equation (eq 44) will give the relationship for the azeotropes. After relating the azeotropes to the Hildebrand solubility parameters, the solubility parameter can be expanded to include the Hansen solubility parameters.

CHAPTER III

RESULTS AND DISCUSSION

Derived Equation for Finding an Azeotropic Point

Starting from equations 1, 2, and 3, eq 44 was derived. This equation was derived using the method of Dong et al.[22] and its derivation can be found in Appendix B.

This equation contains the activity coefficients of components 1 and 2, Saturated vapor pressure of the components 1 and 2, molar fraction of component 1 in liquid phase, and the binary interaction parameters. This equation looks like a long unfriendly equation but our research work shows that this equation is easy to handle in Microsoft Excel 2013. Eq 44 is very useful for calculating the azeotropic point for binary systems. This equation relates the derivative of P with respect to the mole fraction of component 1 to the activity coefficients, saturated vapor pressures, binary interaction parameters and the molar fractions.

$$\begin{aligned}\frac{dP}{dx_1} &= \gamma_1 p_1^{sat}\left(1 + x_1\left[\frac{-(1-A_{12})}{(x_1(1-A_{12})+A_{12})} + \left[\frac{-A_{12}}{(x_1+A_{12}(1-x_1))^2} + \frac{{A_{21}}^2}{((1-x_1)+A_{21}x_1)^2}\right]\right]\right) \\ &+ \gamma_2 P_2^{sat}\left[\left[\frac{-(A_{21}-1)}{(1+x_1(A_{21}-1))} - \left(\frac{{A_{12}}^2}{[(1-A_{12})x_1+A_{12}]^2} - \frac{A_{21}}{(1+x_1A_{21}-1)^2}\right)\right](1-x_1)-1\right]\end{aligned} \tag{44}$$

Microsoft Excel Calculations and the Results Obtained

In this research, the azeotropic points were calculated using two distinct methods. In the first method, a complete set of VLE data was applied and linear interpolation was used to locate the azeotrope point. Locating the point $dP/dx_1=0$ through linear interpolation allows the azeotropic composition to be located between experimental data points as seen in the analysis of the literature data sets in Tables 4, 7, and 10 as well as the experimental data in Tables 13 and 14.

In the second method, a single VLE data point was used for azeotrope estimation. Here, in these calculations eq 30 contains two unknown values (Z_1 and Z_2) so it cannot be solved directly. Substitution of eq 30 into eq 29 will give eq 31 which contains only one variable. But a problem arises, due to the complexity of eq 31, it is not directly solvable. Excel Solver was used to find the value of Z_2 in eq 31. When doing the single data point calculation Excel Solver was used again to find the individual azeotrope point. Here all cells should be connected to each other to get accurate results for the azeotrope point. Eq 44 was inserted to the cell and solver is used to find the value of x_1 while dP/dx_1 goes to zero. This shows that Excel Solver is very useful to find the azeotrope estimate from a single VLE datapoint.

Three sets of VLE data from the literature were used to test the Microsoft Excel calculations. Activity coefficients (γ_1 and γ_2) were calculated by using eq 22, the excess Gibbs energy of mixing was calculated by using eq 25 and the binary interaction parameters were calculated by using the equations 27, 28, 29, 30, and 31. By using eq 44 the azeotropic point was calculated. And the dP/dx_1 column shows one point where the positive and negative sign changes (Figures 12, 13, and 14). The azeotrope is located in between these two values.

Tables 4, 5, and 6 contain the calculated values for the ethane (1) - trifluoromethane (2) binary system.

Table 4. Calculated activity coefficient, excess free energy of mixing, binary interaction parameters and dp/dx_1 for ethane (1) - trifluoromethane (2) binary system.

Point	P^{vap}/MPa	x_1	x_2	y_1	y_2	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.1798	0.1439	0.8561	0.5340	0.4660	5.4032	1.1389	0.3541	0.0286	0.2500	0.2049
2	0.1899	0.2774	0.7226	0.5699	0.4301	3.1593	1.3154	0.5172	0.0570	0.1288	0.0863
3	0.1914	0.3936	0.6064	0.5795	0.4205	2.2820	1.5445	0.5884	0.0700	0.1096	0.0400
4	0.1915	0.5023	0.4977	0.5829	0.4171	1.7996	1.8676	0.6060	0.0727	0.1095	0.0178
5	0.1916	0.5755	0.4245	0.5844	0.4156	1.5756	2.1829	0.5930	0.0702	0.1112	0.0025
6	0.1916	0.5919	0.4081	0.5862	0.4138	1.5366	2.2608	0.5872	0.0740	0.1083	-0.0017
7	0.1914	0.6221	0.3779	0.5872	0.4128	1.4630	2.4331	0.5727	0.0740	0.1101	-0.0121
8	0.1982	0.7968	0.2032	0.6069	0.3931	1.2225	4.4620	0.4640	0.0946	0.0289	-0.0366

As can be seen from Table 4, there is an azeotrope point located between data point 5 and 6 for the ethane (1) - trifluoromethane (2) binary system. This is clearly shown in Figure 12. The value of the x-intercept is between 0.5755 and 0.5919. To find the azeotropic point in a graphical method linear interpolation was used between points 5 and 6 and the mole fraction obtained for component one is 0.5853, and the literature value is 0.5874.[23]

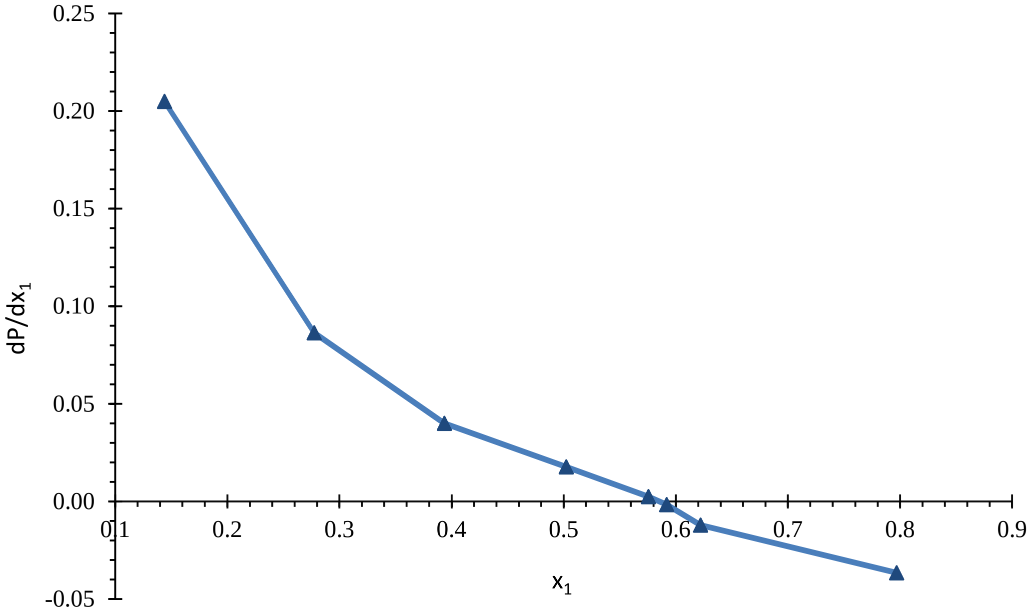


Figure 12. The Plot of dP/dx$_1$ vs x$_1$ for ethane (1) - trifluoromethane (2) binary system.

By using the single VLE data point method part 2 in Chapter II the azeotropic point calculation was carried out for ethane (1) - trifluoromethane (2) binary system and the results are shown in Table 5. The values corresponding to the azeotrope and range 0.5340 to 0.5897, which encompasses the literature value of 0.5874.

Table 5. Results for the single VLE data point azeotropic point estimation for the ethane (1) -trifluoromethane (2) binary system.

Point	P^{vap}/MPa	x_1^{az}	x_2^{az}	y_1^{az}	y_2^{az}	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.1798	0.5340	0.4660	0.5340	0.4660	1.4560	2.0924	0.5447	-0.0411	0.4198	0.0172
2	0.1899	0.5699	0.4301	0.5699	0.4301	1.5378	2.2099	0.5863	-0.0010	0.3057	-0.0076
3	0.1914	0.5795	0.4205	0.5795	0.4205	1.5500	2.2274	0.5907	0.0300	0.2360	0.0034
4	0.1915	0.5829	0.4171	0.5829	0.4171	1.5508	2.2285	0.5900	0.0541	0.1692	0.0004
5	0.1916	0.5844	0.4156	0.5844	0.4156	1.5516	2.2297	0.5900	0.0681	0.1182	-0.0001
6	0.1916	0.5862	0.4138	0.5862	0.4138	1.5516	2.2297	0.5893	0.0753	0.1037	0.0001
7	0.1914	0.5872	0.4128	0.5872	0.4128	1.5500	2.2274	0.5879	0.0827	0.0816	0.0007
8	0.1982	0.5897	0.4103	0.6069	0.3931	1.6518	2.2098	0.6213	0.0202	-0.2156	0.0009

Table 6. Final data comparison between the single VLE data point estimates and the literature values for the ethane (1) -trifluoromethane (2) binary system.

Point	x_1^{exp}	x_{az}^{cal}	x_{az}^{lit}	% error
1	0.1439	0.5584	0.5874	9
2	0.2774	0.5793	0.5874	3
3	0.3936	0.5849	0.5874	1
4	0.5023	0.5855	0.5874	0.8
5	0.5755	0.5847	0.5874	0.5
6	0.5919	0.5860	0.5874	0.2
7	0.6221	0.5857	0.5874	0.03
8	0.7968	0.5919	0.5874	-0.4

For difluoromethane (1) - propane (2) binary system also there is one azeotrope point located between data point 8 and 9 (Table 7). The value of the x-intercept (Figure 13) is in between 0.6407 and 0.7184 of mole fraction of component one. By using the single VLE data point method part 2 in Chapter II the azeotropic point calculation was carried out for difluoromethane (1) - propane (2) binary system and the results are shown in Table 8. The values correspond to the azeotrope is vary from 0.4522 to 0.7348. Table 9 contains the calculated relative percent errors for difluoromethane (1) - propane (2) binary system.

Table 7. Calculated activity coefficient, excess free energy of mixing, binary interaction parameters and dP/dx_1 for difluoromethane (1) - propane (2) binary system.

Point	P^{vap}/MPa	x_1	x_2	y_1	y_2	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.4486	0.0993	0.9007	0.4522	0.5478	4.8483	1.0797	0.2258	0.0319	0.7600	2.0553
2	0.5015	0.1589	0.8411	0.5227	0.4773	3.9152	1.1262	0.3168	0.0693	0.4686	1.7367
3	0.5393	0.2358	0.7642	0.5705	0.4295	3.0967	1.1995	0.4055	0.1142	0.2941	1.2512
4	0.5527	0.2872	0.7128	0.5872	0.4128	2.6819	1.2667	0.4518	0.1291	0.2484	0.9022
5	0.5648	0.3763	0.6237	0.6064	0.3936	2.1601	1.4105	0.5043	0.1521	0.2066	0.5408
6	0.5743	0.5354	0.4646	0.6287	0.3713	1.6005	1.8163	0.5291	0.1779	0.1735	0.1946
7	0.5751	0.5668	0.4332	0.6329	0.3671	1.5241	1.9286	0.5234	0.1838	0.1686	0.1434
8	0.5752	0.6407	0.3593	0.6410	0.3590	1.3658	2.2744	0.4950	0.1888	0.1668	0.0008
9	0.5746	0.7184	0.2816	0.6539	0.3461	1.2413	2.7947	0.4447	0.2042	0.1562	-0.2429
10	0.5735	0.7485	0.2515	0.6602	0.3398	1.2005	3.0664	0.4186	0.2123	0.1519	-0.3958
11	0.5556	0.8616	0.1384	0.7084	0.2916	1.0841	4.6325	0.2818	0.3405	0.1143	-1.5706
12	0.5434	0.8921	0.1079	0.7348	0.2652	1.0623	5.2854	0.2335	0.4503	0.0925	-2.0882

Linear interpolation gives the value of x_{az}, 0.6410 for the azeotropic point, and the literature value is 0.6250.[24]

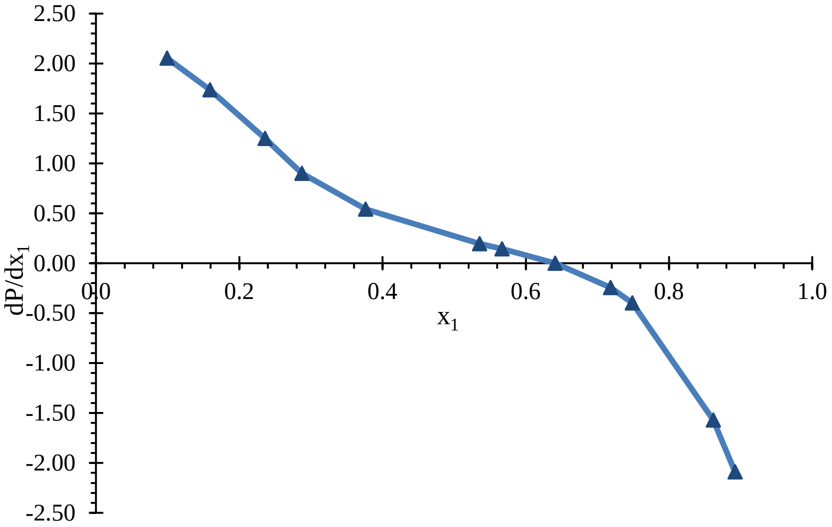


Figure 13. The Plot of dP/dx_1 vs x_1 for difluoromethane (1) - propane (2) binary system.

Table 8. Results for the single VLE data point azeotropic point estimation for the difluoromethane (1) - propane (2) binary system.

Point	P^{vap}/MPa	x_1^{az}	x_2^{az}	y_1^{az}	y_2^{az}	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.4486	0.4522	0.5478	0.4522	0.5478	1.0647	1.7753	0.3427	-0.0706	0.7788	-0.0650
2	0.5015	0.5227	0.4773	0.5227	0.4773	1.1902	1.9846	0.4182	-0.0410	0.5547	0.1222
3	0.5393	0.5705	0.4295	0.5705	0.4295	1.2799	2.1342	0.4664	-0.0009	0.4290	-0.1243
4	0.5527	0.5872	0.4128	0.5872	0.4128	1.3117	2.1872	0.4824	0.0190	0.3867	0.0860
5	0.5648	0.6064	0.3936	0.6064	0.3936	1.3404	2.2351	0.4942	0.0564	0.3291	-0.0118
6	0.5743	0.6287	0.3713	0.6287	0.3713	1.3630	2.2727	0.4995	0.1294	0.2327	0.0066
7	0.5751	0.6329	0.3671	0.6329	0.3671	1.3649	2.2759	0.4988	0.1476	0.2119	0.0038
8	0.5752	0.6410	0.3590	0.6410	0.3590	1.3651	2.2763	0.4948	0.1886	0.1670	0.0000
9	0.5746	0.6539	0.3461	0.6539	0.3461	1.3637	2.2739	0.4872	0.2534	0.1077	0.0229
10	0.5735	0.6602	0.3398	0.6602	0.3398	1.3611	2.2695	0.4820	0.2858	0.0832	0.0131
11	0.5556	0.7084	0.2916	0.7084	0.2916	1.3186	2.1987	0.4257	0.5411	-0.0248	-0.0495
12	0.5434	0.7348	0.2652	0.7348	0.2652	1.2896	2.1504	0.3900	0.6783	-0.0587	-0.1197

Table 9. Final data comparison between the single VLE datapoint estimates and the literature values for the difluoromethane (1) - propane (2) binary system.

Point	x_1^{exp}	x_{az}^{cal}	x_{az}^{lit}	% error
1	0.0993	0.4522	0.6416	29
2	0.1589	0.5227	0.6416	18
3	0.2358	0.5705	0.6416	11
4	0.2872	0.5872	0.6416	8
5	0.3763	0.6064	0.6416	5
6	0.5354	0.6287	0.6416	2
7	0.5668	0.6329	0.6416	1
8	0.6407	0.6410	0.6416	0.09
9	0.7184	0.6539	0.6416	-2
10	0.7485	0.6602	0.6416	-3
11	0.8616	0.7084	0.6416	-10
12	0.8921	0.7348	0.6416	-14

For pentafluoroethane (1) - propane (2) binary system there is one azeotrope point located in-between data point 7 and 8 (Table 10). The value of the x-intercept (Figure 14) is in between 0.5710 and 0.6970 of mole fraction of component one. By using the single VLE data point method part 2 in Chapter II the azeotropic point calculation was carried out for pentafluoroethane (1) - propane (2) binary system and the results are shown in Table 11. The values corresponding to the azeotrope range from 0.5710 and 0.6970, which encompasses the literature value 0.6250.[24] Table 12 contains the calculated relative percent errors for pentafluoroethane (1) - propane (2) binary system.

Table 10. Calculated activity coefficient, excess free energy of mixing, binary interaction parameters and dP/dx_1 for pentafluoroethane (1) - propane (2) binary system.

Point	P^{vap}/MPa	x_1	x_2	y_1	y_2	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.8828	0.1300	0.8700	0.3150	0.6850	2.3617	1.1007	0.1952	0.0318	1.4082	386740
2	0.9244	0.1710	0.8290	0.3670	0.6330	2.1904	1.1177	0.2263	0.0743	1.1648	388660
3	0.9857	0.2470	0.7530	0.4300	0.5700	1.8946	1.1815	0.2835	0.1122	0.9427	302730
4	1.0482	0.3830	0.6170	0.5090	0.4910	1.5380	1.3209	0.3366	0.1877	0.7192	187840
5	1.0802	0.4760	0.5240	0.5530	0.4470	1.3855	1.4592	0.3532	0.2308	0.6098	115160
6	1.0870	0.5090	0.4910	0.5670	0.4330	1.3369	1.5180	0.3527	0.2439	0.5850	892600
7	1.0953	0.5710	0.4290	0.6020	0.3980	1.2749	1.6091	0.3428	0.3309	0.4845	501190
8	1.0923	0.6970	0.3030	0.6660	0.3340	1.1523	1.9067	0.2944	0.4636	0.3819	-652010
9	1.0779	0.7660	0.2340	0.7210	0.2790	1.1202	2.0351	0.2532	0.7407	0.2376	-106980
10	1.0606	0.8190	0.1810	0.7550	0.2450	1.0795	2.2733	0.2113	0.8244	0.2188	-198450

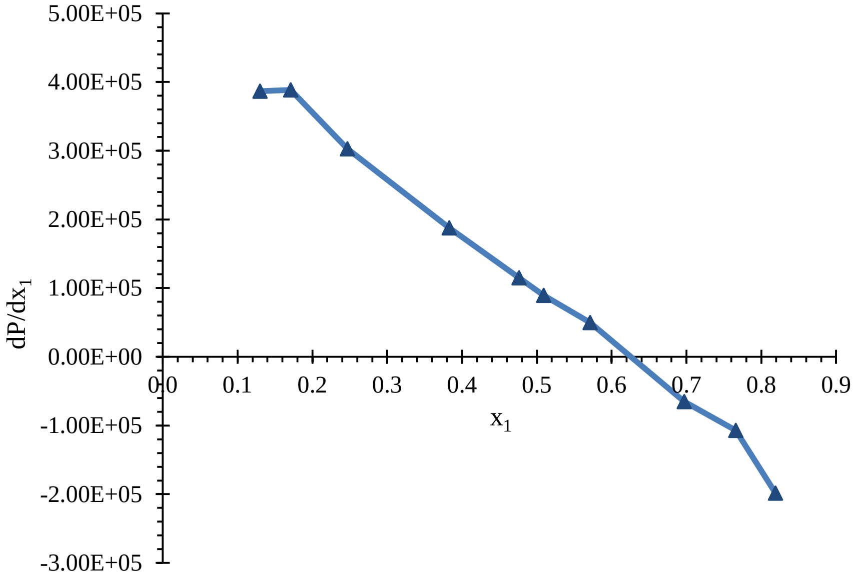


Figure 14. The plot of dP/dx_1 vs x_1 for pentafluoroethane (1) - propane (2) binary system.

Linear interpolation gives the value of x_{az}, 0.6258 for the azeotropic point.

Table 11. Results for the single VLE data point azeotropic point estimation for the pentafluoroethane (1) - propane (2) binary system.

Point	P^{vap}/MPa	x_1^{az}	x_2^{az}	y_1^{az}	y_2^{az}	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.8828	0.3150	0.6850	0.3150	0.6850	0.9747	1.3979	0.2214	-0.0582	1.4415	0.2516
2	0.9244	0.3670	0.6330	0.3670	0.6330	1.0206	1.4638	0.2487	-0.0352	1.1703	0.1710
3	0.9857	0.4300	0.5700	0.4300	0.5700	1.0883	1.5609	0.2902	-0.0048	0.9433	0.0774
4	1.0482	0.5090	0.4910	0.5090	0.4910	1.1573	1.6599	0.3232	0.0776	0.7288	0.0275
5	1.0802	0.5530	0.4470	0.5530	0.4470	1.1926	1.7105	0.3374	0.1488	0.6212	0.0087
6	1.0870	0.5670	0.4330	0.5670	0.4330	1.2001	1.7213	0.3386	0.1769	0.5947	0.0462
7	1.0953	0.6020	0.3980	0.6020	0.3980	1.2093	1.7344	0.3336	0.2864	0.4926	-0.0376

(continued)

Point	P^{vap}/MPa	x_1^{az}	x_2^{az}	y_1^{az}	y_2^{az}	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
8	1.0923	0.6660	0.3340	0.6660	0.3340	1.2060	1.7297	0.3077	0.5332	0.3698	0.0139
9	1.0779	0.7210	0.2790	0.7210	0.2790	1.1901	1.7069	0.2746	0.8861	0.2105	-0.0837
10	1.0606	0.7550	0.2450	0.7550	0.2450	1.1710	1.6795	0.2462	1.0900	0.1777	0.0568

Table 12. Final data comparison between the single VLE data point estimates and the literature values for the pentafluoroethane (1) - propane (2) binary system.

Point	x_1^{exp}	x_{az}^{cal}	x_{az}^{lit}	% error
1	0.1300	0.3150	0.6250	50
2	0.1710	0.3670	0.6250	41
3	0.2470	0.4300	0.6250	31
4	0.3830	0.5090	0.6250	18
5	0.4760	0.5530	0.6250	11
6	0.5090	0.5670	0.6250	9
7	0.5710	0.6020	0.6250	4
8	0.6970	0.6660	0.6250	-6
9	0.7660	0.7210	0.6250	-15
10	0.8190	0.7550	0.6250	-21

Experimental Data and Errors

To check the accuracy and the acceptance of results the isopropyl alcohol and water binary system was studied by using the above mentioned experimental method. The experimental data is shown below (Tables 13 and 14). The atmospheric pressure was measured by a mercury (Hg) manometer located in the CFS 235 in the units of millimeters of mercury (Torr). For trial I, the range of values was 750.4 to 751.9 Torr and the average of 750.9 Torr. For trial II, the range of values was 750.3 to 752.2 Torr and the average of 751.3 Torr. To read the system pressure a digital manometer was used to record the pressure in Torr. The difference between atmospheric pressure and the reading shown in the digital manometer gives the absolute vapor pressure inside. For molar ratio calculation, 1.00 ml portions were taken of the condensed vapor phase and the liquid phase. The H-NMR was obtained on the 60 MHz spectrophotometer. The molar ratios of water and IPA were calculated by the integration of the peak areas in the NMR spectra. The values obtained are shown in Tables 13 and 14.

In the process of running VLE data experiments problems arise when using rubber tubing and grease. The solvents attack grease and rubber tubing to dissolve it and this affects the instrumental setup. In the future, stainless steel tubing will be used to avoid this problem.

The data (molar fractions of liquid phase, molar fractions of vapor phase and the total vapor pressure) collected from the experimental setup was used to calculate the azeotrope point and it shows agreement to the literature data only when molar fractions are close to the azeotropic point (Table 15). It is observed that 1:1 mole ratio of components leads to an accurate acceptably estimate for the azeotrope point with low percent error. For example, the percent error results (Tables 19 and 20) show that when the starting molar fraction is in the 0.2012 percent error is high and when come to the middle concentration region percent error is getting low.

NMR Analysis

The NMR spectra obtained at 60 MHz on an (Varian EM360L) NMR spectrophotometer, were analyzed to obtain the molar ratios of the water and IPA. An example of an NMR spectrum is shown below (Figure 15).

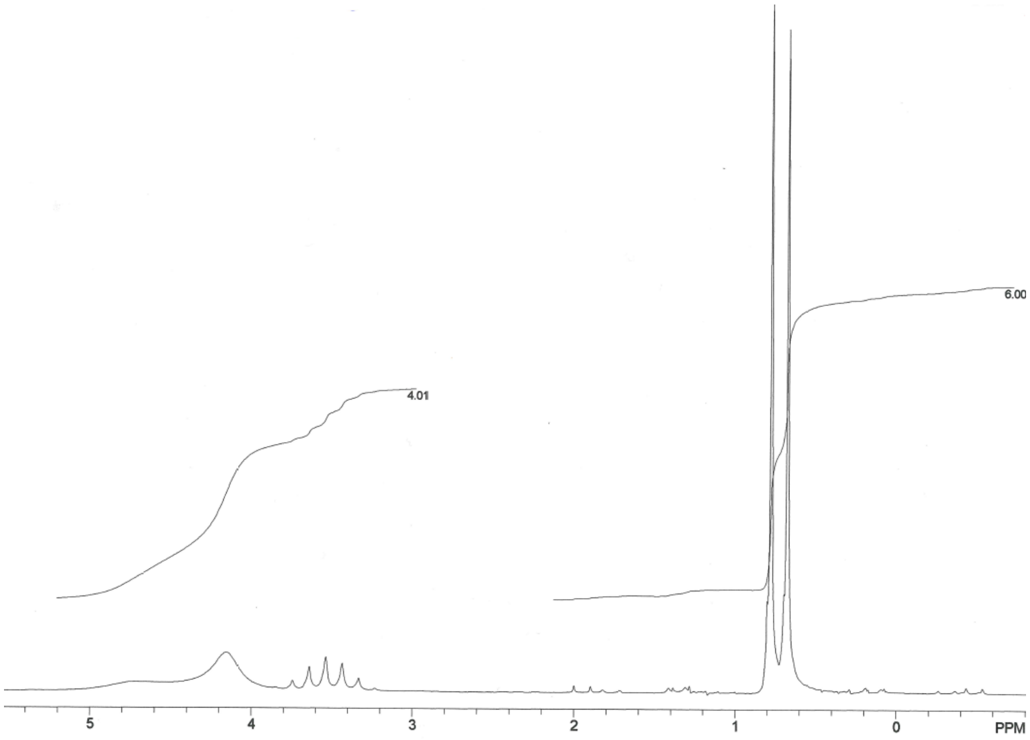


Figure 15. The NMR spectrum of IPA-H_2O binary system

The doublet signal at δ 0.8 ppm belongs to the two methyl groups (6H) of IPA. The value of the integral divided by the number of hydrogen atoms (6 H) relative to the signal will give the relative molar integral units for IPA. Signals from δ 3-5 ppm belong to water and the hydroxyl and methine H's of IPA. Subtract two from the molar integral units from the region over δ 3-5 ppm then dividing by two (due to having 2H in H_2O) will give the relative molar integral units H_2O. Since the molar ratios are known, molar fractions of H_2O and IPA can be determined. To determine the relative percent error due to integration by NMR, a known sample of Water (1) – IPA (2) was tested by using NMR and the percent error due to integration by NMR was calculated by taking the difference between the known mole fraction and the mole fraction obtained by integration divided by the mole fraction to get a percent value.

$$\frac{x_{act} - x_{NMR}}{x_{act}} \times 100 = \% \tag{45}$$

Table 13. VLE data obtained from the experiment for the IPA (1) -H_2O (2) binary system trial I.

Point	x_1	x_2	y_1	y_2	P_{Vap}/Mpa
1	0.2012	0.7988	0.5333	0.4667	0.0106
2	0.3591	0.6409	0.5952	0.4048	0.0086
3	0.4988	0.5012	0.6192	0.3808	0.0063
4	0.6734	0.3266	0.6734	0.3266	0.0067

Table 14. VLE data obtained from the experiment for the IPA (1) -H_2O (2) binary system trial II.

Point	x_1	x_2	y_1	y_2	P_{Vap}/Mpa
1	0.2030	0.7970	0.5348	0.4652	0.0058
2	0.3663	0.6337	0.5236	0.4764	0.0081
3	0.5076	0.4924	0.6006	0.3994	0.0096
4	0.6897	0.3103	0.6780	0.3220	0.0102

After collecting the VLE data, calculations were carried out in Microsoft Excel and the results are shown in the Tables 15 and 16. In IPA (1) -H_2O (2) system two trials were performed for the same volume ratios of two components added and Figures 16 and 17 show the x-intercept of the two trials.

Table 15. Calculated activity coefficient, excess free energy of mixing, binary interaction parameters and dP/dx_1 for IPA (1) – H_2O (2) binary system trial I.

Point	P_{vap}/MPa	x_1	x_2	y_1	y_2	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.0106	0.2012	0.7988	0.5333	0.4667	0.0491	0.0026	-5.3596	1.1231E+13	-3.5354	72.0490
2	0.0086	0.3591	0.6409	0.5952	0.4048	0.0251	0.0023	-5.2168	3.6498E+08	-1.5905	16.6185
3	0.0063	0.4988	0.5012	0.6192	0.3808	0.0138	0.0020	-5.2457	1.3484E+06	-0.8946	4.0715
4	0.0067	0.6734	0.3266	0.6734	0.3266	0.0118	0.0028	-4.9057	1.5103E+04	-0.4244	0.0000

Table 16. Calculated activity coefficient, excess free energy of mixing, binary interaction parameters and dP/dx_1 for IPA (1) – H_2O (2) binary system trial II.

Point	P_{vap}/MPa	x_1	x_2	y_1	y_2	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.0058	0.2030	0.7970	0.5348	0.4652	0.0266	0.0014	-5.9623	1.7968E+13	-3.5250	45.3145
2	0.0081	0.3663	0.6337	0.5236	0.4764	0.0204	0.0026	-5.2039	3.8858E+06	-1.5386	9.7963
3	0.0096	0.5076	0.4924	0.6006	0.3994	0.0198	0.0033	-4.8070	4.1536E+05	-0.8565	4.0603
4	0.0102	0.6897	0.3103	0.6780	0.3220	0.0175	0.0045	-4.4682	8.5165E+03	-0.3888	-0.3435

For trial I, no linear interpolation is needed since dP/dx is zero (Table 15) and the x_{az} is 0.6734 (Figure 16). For trial II, x_{az} obtained is 6755 (Figure 17), and the literature value is 0.6853.[4]

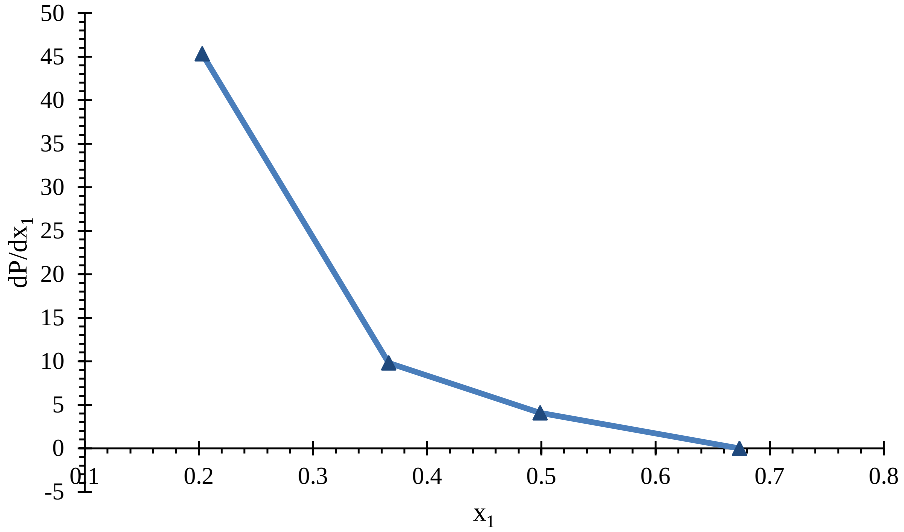


Figure 16. The Plot of dP/dx_1 vs x_1 for IPA (1) – H_2O (2) binary system trial I.

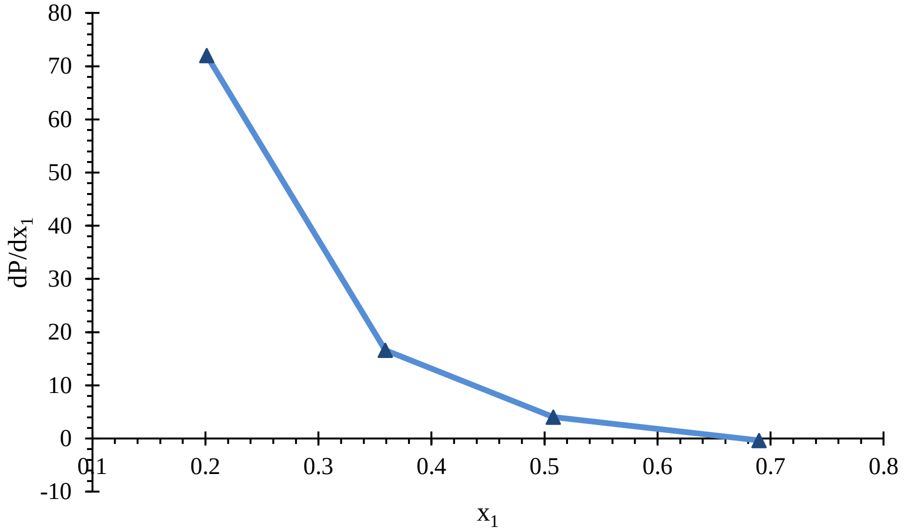


Figure 17. The Plot of dP/dx_1 vs x1 for IPA (1) – H_2O (2) binary system trial II.

Tables 17 and 18 shows the single data point azeotrope point calculations for IPA (1) – H_2O (2) binary system. Tables 19 and 20 contains the calculated relative percent errors for IPA (1) – H_2O (2) binary system.

Table 17. Results for the single VLE data point azeotropic point estimation for the IPA (1) – H_2O (2) binary system trial I.

Point	P^{vap}/MPa	x_1^{az}	x_2^{az}	y_1^{az}	y_2^{az}	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.0106	0.5333	0.4667	0.5333	0.4667	0.0185	0.0045	-4.6532	-0.8679	-0.8096	0.0000
2	0.0086	0.5952	0.4048	0.5952	0.4048	0.0151	0.0036	-4.7673	0.5760	-0.6072	0.0000
3	0.0063	0.6192	0.3808	0.6192	0.3808	0.0111	0.0027	-5.0443	27.4686	-0.5426	0.0000
3	0.0067	0.6734	0.3266	0.6734	0.3266	0.0118	0.0028	-4.9057	1.5103E+4	-0.4244	0.0000

Table 18. Results for the single VLE data point azeotropic point estimation for the IPA (1) – H_2O (2) binary system trial II.

Point	P^{vap}/MPa	x_1^{az}	x_2^{az}	y_1^{az}	y_2^{az}	γ_1	γ_2	g^E	A_{12}	A_{21}	dP/dx_1
1	0.0058	0.5348	0.4652	0.5348	0.4652	0.0101	0.0024	-5.2573	-0.8868	-0.8093	0.0000
2	0.0081	0.5236	0.4764	0.5236	0.4764	0.0142	0.0034	-4.9299	0.1854	-0.8143	0.0000
3	0.0096	0.6006	0.3994	0.6006	0.3994	0.0168	0.0040	-4.6569	19.8860	-0.5832	0.0000
4	0.0102	0.6780	0.3220	0.6780	0.3220	0.0179	0.0043	-4.4845	2.7160E+2	-0.4118	0.0000

Table 19. Final data comparison between the single VLE data point estimates and the literature values for the IPA (1) – H_2O (2) binary system trial I.

Point	$\mathbf{X_1}^{\mathbf{exp}}$	$\mathbf{X_{az}}^{\mathbf{cal}}$	X_{az}^{Lit}	% error
1	0.2012	0.5333	0.6853	22%
2	0.3591	0.5952	0.6853	13%
3	0.4988	0.6192	0.6853	10%
4	0.6734	0.6734	0.6853	2%

Table 20. Final data comparison between the single VLE data point estimates and the literature values for the IPA (1) – H_2O (2) binary system trial II.

Point	$\mathbf{X_1^{exp}}$	$\mathbf{X_{az}^{cal}}$	X_{az}^{Lit}	% error
1	0.2030	0.5348	0.6853	22%
2	0.3663	0.5236	0.6853	24%
3	0.5076	0.6006	0.6853	12%
4	0.6897	0.6780	0.6853	1%

The interpolation method had an relative error (based on literature value) of 0.36 % for ethane (1) -trifluoromethane (2) system, 0.09% for difluoromethane (1) – propane (2) system, 0.13 % for pentafluoroethane (1) - propane (2) and 1.74 % for IPA (1) – H_2O (2) system. The single data point method had an error range of 9 % to 0.03 % for ethane (1) – trifluoromethane (2) system (Table 6), 29 % to 0.09 % for difluoromethane (1) – propane (2) system (Table 9), 50 % to 4 % for pentafluoroethane (1) - propane (2) system (Table 12) and 22 % to 1 % for IPA (1) – H_2O (2) system (Tables 19 and 20). When the starting molar fraction is far away from the x_1^{az}, the percent error is very high (Tables 6, 9, 12, 19 and 20).

The single VLE data point method can still give a good x_{az} estimate. For single VLE data point method IPA (1) – H_2O (2) system shows lowest percent error (1 %) around x_1^{exp} 0.6887 mole fraction of component one. When the starting molar fraction is 0.5, the percent errors are, 0.8 % for ethane (1) -trifluoromethane (2) system, 2 % for difluoromethane (1) – propane (2) system 9 % for pentafluoroethane (1) - propane (2) 10 % for (trial I) IPA (1) – H_2O (2) system and 12 % for (trial II) IPA (1) – H_2O (2) system. These five data sets have 9% of median relative error and 6.7 % average error.

In industry there are several software packages available to find the azeotropes directly. But this excel method is very useful to find an azeotropic point without spending annual license fees for expensive software. Our calculations show that the existence of an azeotrope point can be determined by finding the point at which the sign of dP/dx_1 changes from positive to negative (Tables 4, 7, 10 and Figures 5, 6, 7). If two sign changes occur, that indicates the presence of two azeotropic points.

When the calculations use a single VLE data point, the percentile errors show higher value in the two extremes of molar fractions. In the middle region the error is comparatively low (Tables 5, 8, and 11). This suggests that if a scientist wants to check whether is there are any azeotrope points in a new binary system VLE data in the middle concentration region (1:1 ratio of component one and two) will be the most reasonable starting point.

Connectivity in between HSP and the Azeotropes

To find a relationship between HSP and azeotropy eq 44 was studied further. The only possible way of connecting HSP to azeotropy was to explore the binary interaction parameters. Eq 35 and eq 36 give the relationship between binary interaction parameters and the molar volume. In this equation a term is defined as the interaction energy due to attractive forces. Further study of this term gives a relationship between solubility parameters and the attractive forces (eqs 37 and 38). By combining eqs 35, 36, 37, 38, 39 and 40 the following eqs 46 and 47 were obtained.

$$A_{12} = \frac{v_2}{v_1} \exp\left(\frac{\left((1-\varepsilon_{12})\left(\frac{2}{z}\right)(v_1 v_2)^{0.5} \delta_{T,1}\delta_{T,2} \right) - \left(\left(\frac{2}{z}\right) v_1 \delta_{T,1}^2 \right)}{RT} \right) \tag{45}$$

$$A_{21} = \frac{v_1}{v_2} \exp\left(\frac{\left((1 - \varepsilon_{21}) \left(\frac{2}{z} \right) (v_2 v_1)^{0.5} \delta_{T,2} \delta_{T,1} \right) - \left(\left(\frac{2}{z} \right) v_2 \delta_{T,2}^{2} \right)}{RT} \right) \tag{46}$$

Here in above, eq 46 and 47 the terms ε_{12} and ε_{21} are the interaction energy parameters between unlike molecules. Kobuchi et al. have found common formulae to predict values for ε_{12} and ε_{21} in binary systems.[29] The VLE data of several binary systems (hydrocarbon binary systems, binary systems containing ethers, binary systems containing ketones, ethanol + hydrocarbon systems and water + polar molecule systems) were used to obtain values for ε_{12} and ε_{21}. Eqs 46 and 47 can be substituted into eq 44 so that the azeotropic point can be calculated using only the molar volumes and the solubility parameters.

CHAPTER IV

CONCLUSIONS

Derived Equation for Finding an Azeotropic Point

Eq 44 was derived to calculate the azeotrope point for homogeneous binary systems, and this equation has binary interaction parameters which were investigated. The interpolation method had an average error of 0.58%.

Microsoft Excel Calculation

Microsoft Excel calculations revealed that the derived model used for calculation of an azeotrope point gives correct results for binary homogeneous systems found in the literature. The Excel solver tool can be used to solve for the azeotrope composition and the results obtained show a good agreement with literature data. The best results obtained are, ethane (1) -trifluoromethane (2) system, x_{az}^{Cal} 0.5857, x_{az}^{Lit} 0.5874, difluoromethane (1) – propane (2) system, x_{az}^{Cal} 0.6410, x_{az}^{Lit} 0.6416, and pentafluoroethane (1) - propane (2), x_{az}^{Cal} 0.6020, x_{az}^{Lit} 0.6250. This shows our method can be used to calculate the azeotrope point successfully from VLE data. Eventhough, this method has high error range the percent error decreases when the starting molar fraction is close to the x_{az}. These five data sets (three literature data sets and two experimental data sets) have 9% of median relative error and 6.7 % average error.

Experimental Setup and Errors

Data obtained from the experimental setup shows that, our instrument is capable of gathering VLE data. The experiments carried out for the IPA (1) – H_2O (2) binary system showed that, for trial I x_{az}^{Cal} 0.6734, x_{az}^{Lit} 0.6853 with percentile error of 2% and for trial II x_{az}^{Cal} 0.6780, x_{az}^{Lit} 0.6853 with percentile error of 1%. Modification to a stainless steel system should be done to improve the data quality. Rubber tubing need grease and the tubing have short lifetime. Also, grease is dissolved by the solvents that we used in the system. Replacement of rubber tubing with stainless steel will reduce the errors associated with this setup.

NMR Analysis

The average relative percentile error due to NMR analysis is 2.25 %. This gave errors to the molar fraction calculations as well as to the calculation of azeotrope point.

Connectivity in-between HSP and the Azeotropes

HSP and azeotropes can be connected via the binary interaction energy parameters. The molar volumes and the solubility parameters are readily available in tabulated form in HSPiP. The problem is to find the values for ε_{12} and ε_{21}, Kobuchi et al. have found common formulae to predict values for ε_{12} and ε_{21} in binary systems. This gives a purely theoretical way to predict azeotropic tendencies in binary mixtures.

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APPENDIX A

Antoine coefficients that used to calculate saturated vapor pressure.

Compound	A_i	B_i	C_i
ethane	3.9541	663.7200	256.6800
trifluoromethane	4.2214	707.3960	249.8400
difluoromethane	4.2971	833.1370	245.8600
Propane	3.9283	803.9970	247.0400
pentafluoroethane	4.1339	800.8690	242.0900
Propane	3.9283	803.9970	247.0400
isopropyl alcohol	6.86618	1360.130	197.5920
water	8.07131	1730.630	233.4260

APPENDIX B

Derivation of Excess Free Energy of Mixing Equation

Gibbs obtained a thermodynamic solution to the phase equilibrium problem and he introduced an abstract concept called chemical potential. We cannot measure the absolute value of chemical potential, but we can measure changes in chemical potential. For a pure substance I, the change in chemical potential is related to the temperature (T) and pressure (P) by the differential equation,

$$d\mu_i = -S_i dT + v_i dP \tag{1.1}$$

Where S_i is the molar entropy and the v_i is the molar volume. Integration of above eq 1.1 will give eq 1.2.

$$\mu_i(T,P) = \mu_i(T^r, P^r) - \int_{T^r}^{T} S_i dT + \int_{P^r}^{P} v_i dP \tag{1.2}$$

Where, superscript r refers to arbitrary reference state. Since chemical potential does not have an immediate equivalent in the physical world, the concept of fugacity (*f*) has been introduced by Lewis. He generalized the chemical potential eq 1.1 as follows

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = vi \,, \left(\frac{\partial u_i}{\partial T}\right)_P = S_i \tag{1.3}$$

From the ideal gas equation,

$$v_i = \frac{RT}{P} \tag{1.4}$$

Integration of eq 1.3 at constant temperature yields,

$$\mu_i - \mu_i^\circ = RT \ln \frac{P}{P^\circ} \tag{1.5}$$

where, P^o is the pressure of reference state. Eq 1.5 is valid only for pure ideal gases. For generalization, Lewis defined the state function fugacity. For solid, liquid, or gases, pure or mixed, ideal or not,

$$\mu_i - \mu_i^\circ = RT \ln \frac{f_i}{f_i^\circ} \tag{1.6}$$

Where, either μ_i° or f_i° is arbitrary, but the two cannot be independent; when one is chosen, the other is fixed, Fugacity for an ideal gas is equal to the pressure. In an ideal gas mixture, the fugacity of component *i* is its partial pressure, that is y_iP, where y_i is the mole fraction of component *i*. According to the Lewis definition, the ratio f/f^o is the activity. For component *i* in different phases 1, and 2,

$$\mu_i^1 - \mu_i^{\circ,1} = RT \ln \frac{f_i^1}{f_i^{\circ,1}} \tag{1.7}$$

$$\mu_i^2 - \mu_i^{\circ,2} = RT \ln \frac{f_i^2}{f_i^{\circ,2}} \tag{1.8}$$

At the equilibrium between the two phases,

$$\mu_i^1 = \mu_i^2 \tag{1.9}$$

So, from eq 1.7, 1.8, and 1.9, were obtain

$$\mu_i^{\circ,1} + RT \ln \frac{f_i^1}{f_i^{\circ,1}} = \mu_i^{\circ,2} + RT \ln \frac{f_i^2}{f_i^{\circ,2}} \tag{1.10}$$

If the standard states of two systems are same; $\mu_i^{\circ,1}$ is equal to $\mu_i^{\circ,2}$ which gives, $f_i^1 = f_i^2$ The other way is the standard states for the two phases are at the same temperature but not at the same pressure then, $\mu_i^{\circ,1} - \mu_i^{\circ,2} = RT \ln \frac{f_i^{\circ,1}}{f_i^{\circ,2}}$. This will lead to $f_i^1 = f_i^2$ again. So that for two different phases (liquid and vapor) it can be written as,

$$f_i^L = f_i^V \tag{1.11}$$

The activity of component i at some temperature, pressure, and composition is defined as the ratio of the fugacity of i at these conditions to the fugacity of I in the standard state, that is a state at the same temperature as that of the mixture and at some specified condition of pressure and composition.

$$a_i(T, P, x) = \frac{f_i(T, P, x)}{f_i(T, P^\circ, x^\circ)} \tag{1.12}$$

Where, P^o and x^o are, respectively, an arbitrary but specified pressure and composition. The activity coefficient γ_i is the ratio of the activity of i to the mole fraction of i.

$$\gamma_i = \frac{a_i}{x_i} \tag{1.13}$$

The relation between partial molar excess Gibbs energy and the activity coefficient is obtained any first recalling the definition of fugacity. For constant T and P, for a component i in solution,

$$G^{excess} = G_{real} - G_{ideal} = RT(\ln f_{i(real)} - \ln f_{i(ideal)}) \tag{1.14}$$

Substitution of the concept of fugacity of an ideal liquid ($f_i^L = \Re_i x_i$, where $\Re_i$ is a proportionality constant depends on temperature and pressure but independent of *xi*) in constant temperature and pressure to the equation 1.14 will give eq 1.15.

$$G^{excess} = RT \frac{\ln f_{i(real)}}{\ln \Re_i x_i} \tag{1.15}$$

For an ideal solution activity coefficient is equal to one and the molar fraction is equal to activity. If we set the standard-state fugacity f_i° equal to $\Re_i$ we then have,

$$a_i = \gamma_i x_i = \frac{f_i}{\Re_i} \tag{1.16}$$

So that for an ideal solution, $f_i^L = \Re_i x_i$, therefore, for and ideal solution activity coefficient is equal to one and activity equal to mole fraction of i. So the substitution of eq. 1.16 to 1.15 will give following equation.

$$G^{excess} = RT \ln \gamma_i \tag{1.18}$$

For a mixture eq 1.18 read as,

$$G_{Mix}^{excess} = RT \sum_i x_i \ln \gamma_i \tag{1.19}$$

Calculation of Binary Interaction Parameters

To find the change in activity coefficient two parameter activity coefficient equation by Wilson,

$$\ln \gamma_1 = -\ln(x_1 + A_{12} x_2) + x_2 \left(\frac{A_{12}}{x_1 + A_{12} X_2} - \frac{A_{21}}{x_2 + A_{21} x_1} \right) \tag{2.0}$$

$$\ln \gamma_2 = -\ln(x_2 + A_{21} x_1) - x_1 \left(\frac{A_{12}}{x_1 + A_{12} X_2} - \frac{A_{21}}{x_2 + A_{21} x_1} \right) \tag{2.1}$$

Here,A_{12} and A_{21} are the Binary interaction parameters which depend on molecular properties.

For binary mixture, the Wilson model expresses the excess Gibbs energy of mixing G^E, as follows:

$$g^E = \frac{\Delta_{Mix} G^{excess}}{RT} = -x_1 \ln\left(x_1 + A_{12} x_2\right) - x_2 \ln\left(x_2 + A_{21} x_1\right) \tag{2.2}$$

Two parameters are defined (Z_1 and Z_2) to simplify the equation

$$Z_1 = \frac{1 - A_{12}}{x_1 + A_{12} x_2} \tag{2.3}$$

$$Z_2 = \frac{1 - A_{21}}{x_2 + A_{21} x_1} \tag{2.4}$$

From eqs 1.20, 2.3 and 2.4,

$$g^E = x_1 \ln\left(1 + Z_1 x_2\right) + x_2 \ln\left(1 + Z_2 x_1\right) \tag{2.5}$$

By applying x_2 in terms of x_1 eq 2.6 obtained

$$g^E = x_1 \ln\left(1 + Z_1 x_2\right) + \left(1 - x_1\right) \ln\left(1 + Z_2 x_1\right) \tag{2.6}$$

Distribution of 1-x_1 to eq 2.6 will give following eq 2.7 and further simplification gives eq 2.8.

$$g^E = x_1 \ln\left(1 + Z_1 x_2\right) + \ln\left(1 + Z_2 x_1\right) - x_1 \ln\left(1 + Z_2 x_1\right) \tag{2.7}$$

$$g^E - \ln\left(1 + Z_2 x_1\right) = x_1 \ln\left(1 + Z_1 x_2\right) - x_1 \ln\left(1 + Z_2 x_1\right) \tag{2.8}$$

Multiplication of the eq 2.8 by $1/x_1$ will give eq 2.9 and simplification will give eq 2.10

$$\frac{1}{x_1}\left[g^E - \ln\left(1 + Z_2 x_1\right)\right] = \frac{1}{x_1}\left[x_1 \ln\left(1 + Z_1 x_2\right) - x_1 \ln\left(1 + Z_2 x_1\right)\right] \tag{2.9}$$

$$\frac{1}{x_1}\left[g^E - \ln\left(1 + Z_2 x_1\right)\right] = \left[\ln\left(1 + Z_1 x_2\right) - \ln\left(1 + Z_2 x_1\right)\right] \tag{2.10}$$

By adding, $x_2 Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)$ to eq 2.10 will give eq 2.11

$$\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right) = \left[\ln(1+Z_1x_2) - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right) \quad (2.11)$$

Subtracting eq 2.1 from eq 2.0 will give the following eq 2.12.

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right) = \ln(1+Z_1x_2) - \ln(1+Z_2x_1) + (x_1+x_2)\left(\frac{A_{12}}{x_1+A_{12}x_2} - \frac{A_{21}}{x_2+A_{21}x_1}\right) \quad (2.12)$$

Applying the principle $x_1 + x_2 = 1$, to eq 2.12 will give the following equation (eq 2.13). Then the rearrangement of eq 2.13 will give eq 2.14

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right) = \ln(1+Z_1x_2) - \ln(1+Z_2x_1) + 1\left(\frac{A_{12}}{x_1+A_{12}x_2} - \frac{A_{21}}{x_2+A_{21}x_1}\right) \quad (2.13)$$

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right) - \frac{A_{12}}{x_1+A_{12}x_2} + \frac{A_{21}}{x_2+A_{21}x_1} = \ln(1+Z_1x_2) - \ln(1+Z_2x_1) \quad (2.14)$$

Substitution of eq 2.14 to eq 2.11 will give the following eq 2.15. Further simplification of equation 2.15 will give equation 2.16.

$$\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right) = \ln\left(\frac{\gamma_1}{\gamma_2}\right) - \frac{A_{12}}{x_1+A_{12}x_2} + \frac{A_{21}}{x_2+A_{21}x_1} + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right) \quad (2.15)$$

$$\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right) = x_2Z_2 - \frac{A_{12}}{x_1+A_{12}x_2} + \frac{A_{21}}{x_2+A_{21}x_1} \quad (2.16)$$

Multiplication of the eq 2.16 by $\left(\frac{1}{x_1}\right)$ will give the following eq 2.17

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}\left[x_2Z_2 - \frac{A_{12}}{x_1+A_{12}x_2} + \frac{A_{21}}{x_2+A_{21}x_1}\right] \quad (2.17)$$

The term, $1+Z_2x_1$ in eq 2.17 can be substituted for the term, $\frac{1}{x_2+A_{21}x_1}$ according to the method shown below. Starting from the replacement of *Z2* by eq 2.4, following eq 2.18 was obtained. Distribution of x1 in to the parenthesis in eq 2.18 yield eq 2.19.

$$1+Z_2x_1=1+x_1\left(\frac{1-A_{21}}{x_2+A_{21}x_1}\right) \tag{2.18}$$

$$1+Z_2x_1=1+\frac{x_1-x_1A_{21}}{x_2+x_1A_{21}} \tag{2.19}$$

Further simplification of eq 2.19 and applying $x_1+x_2=1$ to the equation will give eq 2.20

$$1+Z_2x_1=\frac{x_2+A_{21}x_1+x_1-x_1A_{21}}{x_2+A_{21}x_1}$$

$$1+Z_2x_1=\frac{1}{x_2+A_{21}x_1} \tag{2.20}$$

From the same criteria, it can be show that $1+x_2Z_1$is going to be substituted for $\frac{1}{x_1+A_{12}x_2}$

$$1+x_2Z_1=\frac{1}{x_1+A_{12}x_2} \tag{2.21}$$

Substitution of eq 2.20 and 2.21 to eqs 2.17 will give following eq 2.22.

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E-\ln(1+Z_2x_1)\right]+x_2Z_2-\ln\left(\frac{\gamma_1}{\gamma_2}\right)\right]=\frac{1}{x_1}\left[x_2Z_2-(1+x_2Z_1-Z_1)+(1+x_1Z_2-Z_2)\right] \tag{2.22}$$

Stepwise rearrangement of eq 2.22 will give eq 2.23

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}\left[x_2Z_2 - 1 - x_2Z_1 + Z_1 + 1 + x_1Z_2 - Z_2\right]$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}\left[x_2Z_2 + x_1Z_2 - Z_2 - x_2Z_1 + Z_1\right]$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}\left[Z_2(x_2 + x_1 - 1) - Z_1(x_2 - 1)\right]$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}\left[Z_2(0) + Z_1(x_1)\right]$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln 1(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}\left[Z_2(0) + Z_1(x_1)\right]$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = \frac{1}{x_1}(Z_1x_1)$$

$$\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right] = Z_1 \tag{2.23}$$

By combining eqs 2.5 & 2.23, eq 2.24 was obtained and it was rearranged to obtain eq 2.25.

$$g^E = x_1 \ln\left(1 + \left\{\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right]\right\}x_2\right) + x_2 \ln(1+Z_2x_1) \tag{2.24}$$

$$0 = x_1 \ln\left(1 + \left\{\frac{1}{x_1}\left[\frac{1}{x_1}\left[g^E - \ln(1+Z_2x_1)\right] + x_2Z_2 - \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right]\right\}x_2\right) + x_2 \ln(1+Z_2x_1) - g^E \tag{2.25}$$

Calculation of Azeotropic Point

$$\frac{dP}{dx_1} = \frac{\partial\left(x_1\gamma_1P_1^{sat}\right)}{\partial x_1} + \frac{\partial\left(x_2\gamma_2P_2^{sat}\right)}{\partial x_1} \tag{3.0}$$

$$f(x_1) = \frac{\partial\left(x_1\gamma_1P_1^{sat}\right)}{\partial x_1} + \frac{\partial\left(x_2\gamma_2P_2^{sat}\right)}{\partial x_1} = 0 \tag{3.1}$$

The point at which $\frac{dP}{dx_1} = 0$ is the point where the azeotropic point locate. By writing the x_2 in terms of x_1 following eq 3.2 was obtained. Rearrangment of eq 3.2 will give the eq 3.3.

$$\frac{dP}{dx_1} = \frac{\partial\left(x_1\gamma_1P_1^{sat}\right)}{\partial x_1} + \frac{\partial\left[(1-x_1)\gamma_2P_2^{sat}\right]}{\partial x_1} \tag{3.2}$$

$$\frac{dP}{dx_1} = \gamma_1P_1^{sat} + x_1P_1^{sat}\frac{\partial\gamma_1}{\partial x_1} + P_2^{sat}\frac{\partial\gamma_2}{\partial x_1} - \gamma_2P_2^{sat} - x_1P_2^{sat}\frac{\partial\gamma_2}{\partial x_1}$$

$$\frac{dP}{dx_1} = P_1^{sat}\left(\gamma_1 + x_1\frac{\partial\gamma_1}{\partial x_1}\right) + P_2^{sat}\left(\frac{\partial\gamma_2}{\partial x_1} - \gamma_2 - x_1\frac{\partial\gamma_2}{\partial x_1}\right)$$

$$\frac{dP}{dx_1} = P_1^{sat}\left(\gamma_1 + x_1\frac{\partial\gamma_1}{\partial x_1}\right) + P_2^{sat}\left(\frac{\partial\gamma_2}{\partial x_1}(1-x_1) - \gamma_2\right) \tag{3.3}$$

Writing x_2 in terms of x_1 in eq 2.0 will give following eq 3.4 eq 3.5 was obtained by rearranging eq 3.4.

$$\ln\gamma_1 = -\ln\left(x_1 + A_{12}(1-x_1)\right) + (1-x_1)\left(\frac{A_{12}}{x_1 + A_{12}(1-x_1)} - \frac{A_{21}}{(1-x_1) + A_{21}x_1}\right) \tag{3.4}$$

$$\ln\gamma_1 = -\ln\left(x_1 + A_{12} - A_{12}x_1\right) + \left(\frac{(1-x_1)A_{12}}{x_1 + A_{12}(1-x_1)} - \frac{(1-x_1)A_{21}}{(1-x_1) + A_{21}x_1}\right)$$

$$\ln\gamma_1 = -\ln\left(x_1 + A_{12} - A_{12}x_1\right) + \left(\frac{A_{12}}{\frac{x_1 + A_{12}(1-x_1)}{(1-x_1)}} - \frac{A_{21}}{\frac{(1-x_1) + A_{21}x_1}{(1-x_1)}}\right)$$

$$\ln\gamma_1 = -\ln\left(x_1 + A_{12} - A_{12}x_1\right) + \left(\frac{A_{12}}{\left(\frac{x_1}{1-x_1}\right) + A_{12}} - \frac{A_{21}}{1 + A_{21}\left(\frac{x_1}{(1-x_1)}\right)}\right) \tag{3.5}$$

To find the activity coefficient change with respect to molar fraction of component one the following derivative is necessary (eq 3.6).

$$\frac{\partial \ln \gamma_1}{\partial x_1} = \frac{\partial}{\partial x_1}\left[-\ln\left(x_1 + A_{12} - A_{12}x_1\right) + \left(\frac{A_{12}}{\left(\frac{x_1}{1-x_1}\right) + A_{12}} - \frac{A_{21}}{1 + A_{21}\left(\frac{x_1}{(1-x_1)}\right)}\right)\right] \tag{3.6}$$

$$\frac{1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_1} = \frac{-(1-A_{12})}{\left(x_1(1-A_{12}) + A_{12}\right)} + \frac{-A_{12}}{\left[\left(\frac{x_1}{1-x_1}\right) + A_{12}\right]^2}\frac{-x_1(-1) + (1-x_1)}{(1-x_1)^2} - \frac{-A_{21}}{1 + A_{21}\left(\frac{x_1}{(1-x_1)}\right)^2}\left(A_{21}\frac{-x_1(-1) + (1-x_1)}{(1-x_1)^2}\right)$$

In above equation the term, $-x_1(-1) + (1-x_1)$ can be solved to get value of 1 as follows to obtain equation (3.7). Rearrangement of eq 3.7 will give following eq 3.8.

$$= \left[-x_1(-1) + (1-x_1)\right]$$

$$= \left[-x_1(-1) + (x_2)\right]$$

$$x_1 + x_2 = 1$$

$$\frac{1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_1} = \frac{-(1-A_{12})}{\left(x_1(1-A_{12}) + A_{12}\right)} + \frac{-A_{12}}{\left[\left(\frac{x_1}{1-x_1}\right) + A_{12}\right]^2}\frac{1}{(1-x_1)^2} + \frac{A_{21}}{1 + A_{21}\left(\frac{x_1}{(1-x_1)}\right)^2}\left(A_{21}\frac{1}{(1-x_1)^2}\right) \tag{3.7}$$

$$\frac{1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_1} = \frac{-(1-A_{12})}{\left(x_1(1-A_{12}) + A_{12}\right)} + \left[\frac{-A_{12}}{\left(x_1 + A_{12}(1-x_1)\right)^2} + \frac{{A_{21}}^2}{\left((1-x_1) + A_{21}x_1\right)^2}\right]$$

$$\frac{\partial \gamma_1}{\partial x_1} = \gamma_1\left[\frac{-(1-A_{12})}{\left(x_1(1-A_{12}) + A_{12}\right)} + \left[\frac{-A_{12}}{\left(x_1 + A_{12}(1-x_1)\right)^2} + \frac{{A_{21}}^2}{\left((1-x_1) + A_{21}x_1\right)^2}\right]\right] \tag{3.8}$$

Eq 3.9 was obtained by repeating the steps followed by eq 3.4 to eq 3.8.

$$\frac{\partial \gamma_2}{\partial x_1} = \gamma_2 \left[\frac{-(A_{21}-1)}{(1+x_1(A_{21}-1))} - \left(\frac{{A_{12}}^2}{[(1-A_{12})x_1 + A_{12}]^2} - \frac{A_{21}}{(1+x_1 A_{21}-1)^2} \right) \right] \tag{3.9}$$

From the eq 3.3, 3.8 and 3.9 following eq 3.10 was obtained.

$$\begin{aligned} \frac{dP}{dx_1} = {} & P_1^{sat} \Bigg(\gamma_1 + x_1 \Bigg(\gamma_1 \Bigg[\frac{-(1-A_{12})}{(x_1(1-A_{12})+A_{12})} + \Bigg[\frac{-A_{12}}{(x_1 + A_{12}(1-x_1))^2} + \frac{{A_{21}}^2}{((1-x_1)+A_{21}x_1)^2} \Bigg]\Bigg]\Bigg]\Bigg)\Bigg) \\ & + P_2^{sat} \Bigg[\Bigg(\gamma_2 \Bigg[\frac{-(A_{21}-1)}{(1+x_1(A_{21}-1))} - \Bigg(\frac{{A_{12}}^2}{[(1-A_{12})x_1 + A_{12}]^2} - \frac{A_{21}}{(1+x_1 A_{21}-1)^2} \Bigg) \Bigg]\Bigg]\Bigg) (1-x_1) - \gamma_2 \Bigg] \end{aligned} \tag{3.10}$$

Eq 3.10 was rearranged to obtain eq 3.11

$$\begin{aligned} \frac{dP}{dx_1} = {} & \gamma_1 P_1^{sat} \Bigg(1 + x_1 \Bigg[\frac{-(1-A_{12})}{(x_1(1-A_{12})+A_{12})} + \Bigg[\frac{-A_{12}}{(x_1 + A_{12}(1-x_1))^2} + \frac{{A_{21}}^2}{((1-x_1)+A_{21}x_1)^2} \Bigg]\Bigg]\Bigg) \\ & + \gamma_2 P_2^{sat} \Bigg[\Bigg[\frac{-(A_{21}-1)}{(1+x_1(A_{21}-1))} - \Bigg(\frac{{A_{12}}^2}{[(1-A_{12})x_1 + A_{12}]^2} - \frac{A_{21}}{(1+x_1 A_{21}-1)^2} \Bigg) \Bigg] (1-x_1) - 1 \Bigg] \end{aligned} \tag{3.11}$$

VITA

Nilan Jayabahu Bandara Kamathewatta was born on September 19, 1985 in Kandy, Sri Lanka, to Lionel Kamathewatta and Lakshmi Udalagama. He is the third of three children and second in his family to pursue a degree beyond that of a Bachelor's degree. In August of 2006, he began working towards his undergraduate degree at University of Peradeniya, Peradeniya. He also worked two years as a teaching assistant in Sri Lanka. He was offered a scholarship as a graduate teaching assistant at Sam Houston State University, USA in October 2012. There, he began working on his Master's degree in Chemistry in January 2013. He carried out research with Dr. Darren L. Williams in physical chemistry. During his graduate studies he was able to win the graduate school scholarship in 2013 and 2014.