AN INVESTIGATION OF VARIOUS METHODS AND CORRELATIONS OF VLE OF HYDROCARBON MIXTURES (THAT CAN BE USED AS SUBSTITUTE FOR FREON-12 IN REFRIGERATION)

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CERTIFICATION

I certify that the preparation of this thesis titled "An Investigation of Various Methods and Correlations of VLE of Hydrocarbon Mixtures (That Can Be Used As Substitute For Freon-12 in Refrigeration)" ***was prepared under my supervision at Al-Nahrain University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.***

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CERTIFICATION

*We certify, as an examining committee, that we have read the thesis titled "*An Investigation of Various Methods and Correlations of VLE of Hydrocarbon Mixtures (That Can Be Used As Substitute For Freon-12 in Refrigeration)*", and examined the student Venus Majied Hameed Al-Timmeeme at Al-Nahrain University and found that the thesis meets the standerd of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.*

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Abstract

Various paths and models have been tested for more accurate VLE predictions for 36 binary systems with 376 data points and 14 ternary mixtures with 368 data points, especially for mixtures of industrial interest in refrigeration units. This lead to select a model for calculation VLE data of hydrocarbon systems with no adjustable parameter and other with one adjustable parameter depending on the accuracy requirement of industrial design .

The ***first path*** deals with the calculation of VLE of hydrocarbon systems by applying PR-EOS and PRSV-EOS with different mixing rules in vapor and liquid phases. These mixing rules have different forms with a different number of adjustable parameter. The results of this path shows AS mixing rules gives approximately the best VLE calculated data for both binary and ternary systems when it is compared with other used mixing rules types in these equations of state (PR and PRSV). The overall AAD% by applying AS-mixing rules with PRSV-EOS for 36 binary systems is 1.70525. While for 14 ternary system the overall AAD% is 2.86145.

The ***second path*** deals with the calculation of VLE data of hydrocarbon systems by applying PRSV-EOS with AS-mixing rules for the vapor phase (since AS-mixing rules with PRSV-EOS gives the better VLE data calculation for both phases) and activity coefficient model for the liquid phase. Where UNIFAC and Wilson models are used to represent the liquid phase activity coefficient. The calculated VLE data of hydrocarbon systems have some limitation during its application, near the critical region with supercritical condition and with systems under high pressure, and then this path will be no more applicable. So, that the number of systems which adapted by this path are reduced to 23 binary systems and only to 5 ternary systems. In this path the overall AAD% for binary systems by applying UNIFAC and Wilson activity coefficient models are 9.31151 and 3.07893 respectively. While for the ternary systems the overall AAD% when UNIFAC model applied is 16.36047 and when Wilson model is used the overall AAD% are 3.6366. Also, the UNIFAC activity coefficient model has an additional limitation through its application, when methane component is present in the system mixture where VLE calculated data will be poor. While the overall ADD% for systems which do not contain methane in binary and ternary systems are 2.91742 and 2.78714 respectively.

Third path: In this path PRSV-EOS with new mixing rules are applied for both system phases (vapor and liquid phase). This mixing rule is derived from Gibbs free energy equation at infinite dilution which in turn is derived from the activity coefficient at infinite dilution condition. The third path links between PRSV-EOS and Gibbs free energy at infinite dilution which adopts UNIFAC and Wilson models. This linking in EOS mixing rules with Gibbs free energy at infinite dilution makes it possible to take advantageous of an EOS route over the activity coefficient route which has the possibility of treating systems containing supercritical compounds. The overall AAD% for 36 binary systems by applying UNIFAC and Wilson models are 2.60706 and 2.01276 respectively. While, for 14 ternary systems by using UNIFAC and Wilson models AAD% are 6.08109 and 5.20716 respectively. These results are obtained without using any adjustable parameter (k_{ij}=0). The results of the first path with AS-mixing rules gives approximately the same accuracy when it is compared with the results of the third path without using any adjustable parameter for binary systems. While, for ternary systems AS-mixing rules in PRSV-EOS gives a higher accuracy in VLE data calculation. So, the third path is modified in order to give a higher accuracy for ternary systems.

Different modifications in mixing rules are tried. The best results are obtained when the mixing rules is modifying to a quadratic form with one adjustable parameter (k_{ij}). This modification allows accurately calculate phase equilibrium of hydrocarbon components even in the presence of polar components which is existed in the system as traces. The over all AAD% for binary systems by applying UNIFAC and Wilson models are 2.22391 and 1.97773 respectively. While, for the ternary systems they are 3.63341 for UNIFAC model and 3.55501 for Wilson model. This path is found to be superior when it compared with the other two paths which are adopted in this work for VLE calculation of hydrocarbon systems especially for ternary systems where high accuracy without or with minimum number of adjustable parameters are rare.

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Nomenclature

A	*Constant for vapor pressure estimation depend on type of the equation used*	-
a	*Equation of state attraction term parameter*	-
A_m	*Helmholtz constant*	-
b	*Equation of state covolume term parameter*	
B, C	*Constant for vapor pressure estimation depend on type of the equation used*	-
c, d	*Empirical constant that depend on composition*	-
f	*fugacity*	*Pa*
G	*Gibbs energy*	J or $J\ mol^{-1}$
H	*Enthalpy*	J or $J\ mol^{-1}$
h_{ij}	*Covolume term adjustable parameter*	-
K_B	*Boltzmann constant*	-
ki	*Vapor/liquid equilibrium constant for species i*	-
k_{ij}	*Equation-of-state interaction parameter*	-
L_{ij}	*Binary Adachi-Sugie interaction parameter*	-
m_{ij}	*Binary Adachi-Sugie interaction parameter*	-
Mw	*Molecular weight*	$kg\ mol^{-1}$
n_i	*Number of moles of component i*	-
P	*Pressure*	*Pa*
q	*Parameter proportional to the molecule's external surface area*	-
R	*Gas constant*	$J\ K^{-1}\ mol^{-1}$
r	*Number of segments per molecule*	-
S	*Entropy*	$J\ K^{-1}$
T	*Temperature*	K or ^{o}C
U	*Internal energy*	J or $J\ mol^{-1}$
u	*Energy of interaction between groups*	$J\ mol^{-1}$
V	*volume*	m^3 or $m^3\ mol^{-1}$
x	*Mole fraction in liquid phase*	-
y	*Mole fraction in gas phase*	-
Z	*Compressibility factor*	-
Z_c	*Critical compressibility factor*	-
Ω_c	*Parameter characterized on type of EOS*	-
ω	*Acentric factor*	-
γ	*Activity coefficient*	-
ϕ_i	*Fugacity coefficient of pure species i*	-
$\hat{\phi}_i$	*Fugacity coefficient of species I in solution*	-
θ_{ij}	*Fraction of external sites around molecule j which are occupied by segments of molecule I*	-
n_{20}^{D}	*Refractive index at 20* ^{o}C	-
α	*Activity*	-
ε	*Energy of a molecule*	*J*
σ	*Distance between molecules in the Lennard-Jones*	*m*

Superscripts

E	*Denotes excess thermodynamic property*
id	*Denotes value for an ideal solution*
g	*Denotes value for gas*
L	*Denotes liquid phase*
V	*Denotes vapor phase*
sat	*Denotes saturation*
o	*Denotes Pure component*
R	*Denotes Residual thermodynamic property*
∧	*Denotes a property in solution*
***	*Denotes a pseudo property*

Subscripts

C	*Denotes a value for the critical state*
r	*Denotes a reduced value*
∞	*Denotes a value at infinite dilution*

Glossary

AAO	*Average absolute deviation*
AS	*Adchi-Sugie*
BWR	*Bendich Webb Robin*
CEOS	*Cubic Equation Of State*
CFC	*Chlorofluorocarbon*
EOS	*Equation Of State*
HCFC	*Hydro chlorofluorocarbon*
HFC	*Hydro fluorocarbon*
HV	*Huron and Vidal*
LJ	*Lennard-Jones*
ODP	*Ozone Depletion Potential factor*
OF	*Objective Function*
PR	*Peng Robinson*
PR-EOS	*Peng-Robinson*
PRSV	*Peng-Robinson-Stryjek-Vera*
RK	*Radlich Kwong*
RK	*Redlich Kwong*
SRK	*Soave Radlich Kwong*
SRK	*Soave Redlich Kwong*
UNIQUAC	*Functional Group Activity Coefficient*
vdW	*van der Waals*
VLE	*Vapor Liquid Equilibrium*
VLLE	*Vapor liquid liquid equilibrium*

1

Introduction

Equilibrium is a dynamic condition in which no changes occur in the microscopic properties of a system with time. This implies a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory accuracy.

Vapor Liquid Equilibrium (VLE) refers to a system in which a single liquid phase is in equilibrium with its vapors [84]. The selections of a method which predict accurate values of VLE data are very important in process design calculations and any other industrial applications.

Experimental measurements of VLE data are essential and form the basis of desired information. These measurements are both laborious and expensive, so prediction methods are desirable and thus various methods of prediction have been developed. [85]

Hydrocarbon mixtures of highly similar components may show only slight deviations from an ideal solution, which are insignificant for ordinary purposes, but must be considered in connection with accurate design practice. Considerable deviations are however, observed in almost all other mixtures, where the components are more different in size, shape and chemical nature. [12]

Because of the compression and expansion of vapors and liquids through the refrigeration operation cycle, VLE-data are needed, and techniques for calculation and experimental determination of this particular type of phase equilibrium are more highly developed than for any other applications. [38]

1.1 Why, Substitute Refrigerants?

Recent theories and experimental observations have indicated that CFC refrigerants are a major contributor to the depletion of the upper atmosphere ozone layer, which shields the earth from harmful radiation [50]. Therefore, it is urgently required to replace CFCs with new stratospherically safe chemicals.

As a result, these refrigerants are in process of being phased out and there is an urgent need to look for alternative refrigerants [5]. There are three main families of refrigerants which are CFCs, HCFCs and HFCs. CFCs in use in refrigeration application since 1928. They are a combination of chlorine, fluorine and carbon and because they contain chlorine and no hydrogen. They are stable and do not readily break down when released to atmosphere. [106]

In 1974, scientists presented the theory that CFCs slowly migrate into stratosphere where they decompose by the action of sunlight and split off chlorine molecules that react with ozone, thus reducing the concentration of ozone in the upper atmosphere [62]. They may also be responsible for a rise in the temperature of earth, or so-called global warming [16]. This theory with other findings, led many countries in 1987 to sign a land mark agreement (Montreal Protocol) to protect the stratospheric ozone layer from emissions of chlorinated and brominated compounds (UNEP 1987) [98]. To quantify the ozone damaging-effect, each CFC has an assigned Ozone Depletion Potential factor (ODP) between 0.6 and 1.0. The most common CFCs in use are: CFC-11, CFC-12, CFC-113, CFC-114 and CFC-502.

HCFCs have hydrogen to their chemical structure, which makes them less stable when released to atmosphere. Although still considered damaging, the ODP of HCFCs is significantly lower than CFC and range between 0.01 and 0.05 while, HFCs not contain chlorine and have an ODP equal to zero. The multi- nationality ratified Montreal Protocol mandated a decrease and eventual stoppage of CFC production in 31 December 1995 in the industrialized countries. An extra 15 years period is allowed for developing countries [56]. However, even HCFCs may do some damage to the environment and they also are to be phased out by the year 2030.

1.2 Refrigerants Substitute

Refrigerants are the working fluids used in refrigeration cycle. At certain times, during a cycle, they evaporate and so absorb heat and at other times they condense and reject heat. Most refrigerants boil at low temperatures so that they are gases at normal atmospheric pressure.

An internationally recognized system of numbering has been developed for refrigerants. Each number begins with R, for refrigerants [59]. Probably one of the most commonly used refrigerants is Freon-12 (R-12), which is a compound made entirely of chlorine, fluorine and carbon, known as a *chlorofluorocarbon* or CFC, which is mainly used in refrigeration cycle of refrigerators and deep freezers.

1.3 Hydrocarbons as a Refrigerant Alternative

Until now, CFCs have been among the most commonly used refrigerants for refrigeration units in developing countries including Iraq. Since it believed that CFC refrigerants damage the earth's protective ozone layer [91].There is an urgency to replace the traditional refrigerants (CFCs and HCFCs) as the import of CFCs is already banned in industrial countries since 1996. [70]

Throughout the world, scientists and engineers are working to find replacement refrigerants, which do not damage the atmosphere at all [16]. The major requirements of residential alternative refrigerant are that it must be ozone friendly, non-toxic, stable, non-flammable, compatible with lubricant oils, similar in thermodynamic performance to the original CFC refrigerant and available at low cost. [56]

New refrigerant mixtures have been of interest for many years since they offer properties different from those of the limited number of pure candidates and which are compatible to the properties of CFC refrigerants. Refrigerant mixtures are of two types:

- ***a.*** Isotropic mixtures.
- ***b.*** Non-isotropic mixtures**.**

Isotropic mixture is constant boiling mixture and its temperature as well as composition stays constant during evaporation and condensation. Non-isotropic mixture behaves differently from pure fluids or isotropic mixtures in two significance ways [5, 9]:

1. During phase changing process, the composition of the liquid and vapor phases change also.

2. The phase changing processes during constant pressure evaporation and condensation do not occur isothermally as in conventional systems but instead occur over temperature ranges. Evaporation (at constant pressure) is accompanied by a temperature rise and condensation (at constant pressure) is accompanied by a temperature drop.

In Iraq research had been started since 1993 to find the most suitable substitutes for refrigerants R-12 and R-22 [3, 57]. Hydrocarbons as pure compound or mixture proved to be good substitutes. Propane is suitable substitute for R-22 in air conditioning cycles. Mixtures of Propane, n-Butane and iso-Butane or mixture of Propane and iso-Butane are suitable substitute for R-12 in refrigerators and deep freezers. Thus much accurate thermodynamic data are needed for these candidate refrigerants and accurate VLE-data are the most important data needed for refrigeration cycles. [66]

1.4 Aim of the Present Study

The main goal of this study is to find the most suitable method to predict VLE-data accurately for hydrocarbon compounds and their mixtures, which may be used as refrigerants substitute for Freon-12 in refrigeration unit. This study also includes more than one selected path to calculate the VLE-data for the refrigerant replacement derivative from Iraqi natural gas.

- The first path is the examining of cubic equation of state with different selected mixing rules to find their abilities to calculate VLE-data.
- The second path is the determination of activity coefficient values for the liquid phase from the group contribution equation UNIFAC and also from Wilson equation. Fugacity coefficient for the vapor phase was calculated from the best-selected equation with best mixing rules in the first path with the shear of Wagner equation to calculate the saturation pressure.
- The third path investigates the use of infinite dilution activity coefficients in cubic equation of state mixing rules with no adjustable parameter for the prediction of phase behavior of hydrocarbon systems. Trying to modify the obtained VLE calculated results by modifying the used mixing rules in this path.

2

Litrature Survey

It is believed now that R-12 had caused damage to the environment. Therefore, scientists and engineers had found substitute refrigerants, which are mainly hydrocarbons and hydrocarbon mixtures. Thus, it is very important to study the properties and behavior of the new refrigerants and to find the range of its suitability to replacement. There are some important theories and definitions require to be known to pare the way of this investigation. These are described in the following sections:

2.1 Saturated Vapors and Liquids

The temperature at which a liquid changes into a vapor or vapor changes into liquid is called the *saturation temperature.*

The vapor, which is above the surface of the liquid, is called a *saturated vapor.* Molecules from the liquid are passing through the surface and entering the vapor the whole time, while molecules from the vapor re-enter the liquid. The liquid is called *saturated liquid.*

The saturation temperature depends upon the atmospheric pressure or at least upon the pressure above the surface of the liquid and the saturation temperature is equal to the boiling point of a liquid. [16]

2.2 Superheated Vapor

A vapor heated to a temperature above saturation temperature is said to be *superheated.* The temperature can only be raised by the addition of heat energy is known as *superheat.* Superheating can only occur once a liquid has been completely vaporized or the vapor is removed completely from the presence of the liquid. [16]

2.3 Subcooled Liquids

A liquid at any temperature below its saturation temperature is called a *subcooled liquid*. [16]

2.4 Critical Properties

Critical temperature, pressure and volume represent three widely used pure component constants. In appendix 'A', the critical properties of some pure hydrocarbons are tabulated.

The properties (*T, P* and *V*), measured at the critical point, are called *critical properties* [30]. The coordinates of this point are the critical pressure P_C and the critical temperature T_C. The highest temperature and pressure at which a pure chemical species can exist in vapor liquid equilibrium.

The temperature of a vapor can be raised to a point at which it cannot be liquefied (or saturated) regardless how much pressure is applied on it. The temperature at which this occurs is the *critical temperature*.

2.5 Acentric Factor

Pitzer introduced acentric factor in 1955 in order to apply the theorem of corresponding state to normal fluids.

The acentric factor is defined as:

$$\omega = -log\left(P_r^{sat}\right)_{T_r=0.7} - 1.0 \qquad ...(2\text{-}1)$$

where P_r^{sat} is the reduced saturated vapor pressure at reduced temperature (T_r=0.7). This form is chosen to make ω=0 for simple fluids like *Ar, Kr*, and *Xe* with simple spherical molecules. Hence *acentric factor* is a factor that measures deviation of the simple intermolecular potential function from those values of some substances as shown in Figure 2-1 [15, 68]. However, it should be noted that T_r=0.7 is close to the normal boiling point of most substances. Thus, the particular choice of T_r=0.7 adopted by Pitzer not only provides numerical simplicity because $log(P_r^{sat})=1.0$ for simple fluids but also convenience because vapor-pressure data are most commonly available at pressure near atmospheric. [85]

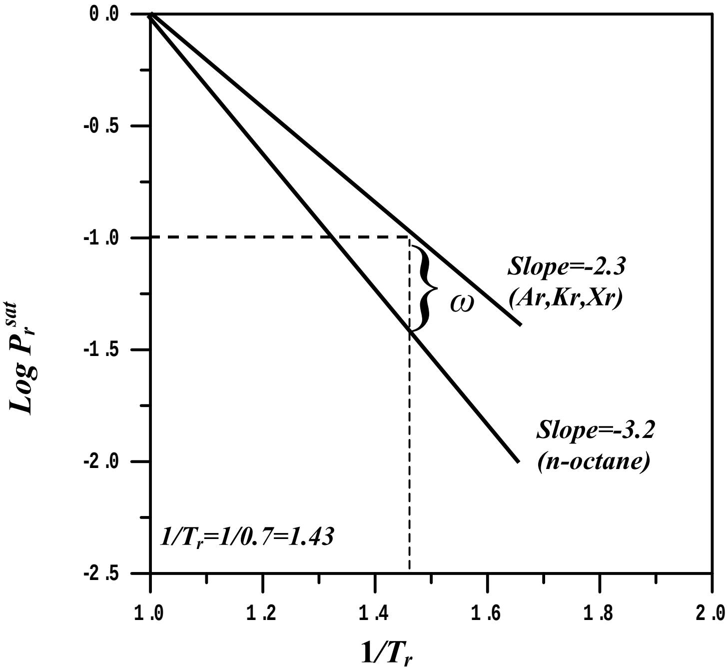


Figure 2-1: Approximate temperature dependence of reduced vapor pressure

2.6 Rackett Equation

Rackett equation is the generalized equation available for estimation of molar volumes of saturated liquids. The equation proposes by Rackett [90, 4] has the following form:

$$V^{sat} = V_C Z_C^{(1-Tr)^{0.2857}} \qquad \ldots(2\text{-}2)$$

The only data required are the critical constants of the pure component. Rackett equation results are usually accurate from 1 to 2 percent. [84]

2.7 Vapor Pressure Estimation

Most vapor pressure estimation correlation equations stem from an integration of clausius-clapeyron equation which has the form:

$$\frac{d\left(ln\left(P_{vap}\right)\right)}{d\left(1/T\right)} = -\frac{\Delta H^V}{R\,\Delta Z^V} \qquad \ldots(2\text{-}3)$$

where ΔH^V and ΔZ^V refer to differences in the enthalpies and compressibility factors of saturated vapor and saturated liquid.

The simplest approach is to assume that the group ($\Delta H^V/R\ \Delta Z^V$) is constant and independent of temperature then the constant of integration denoted as *A*, so Clapeyron equation will be:

$$ln\ (P_{vap}) = A - (B/T) \qquad \ldots(2\text{-}4)$$

Where *A* and *B* are constants for a given species. This equation gives a rough approximation of the vapor-pressure relation for the entire temperature range from the triple point to the critical point. Moreover, it provides excellent bases for interpolation between values that are reasonably spaced.

Extending our consideration of Eq.*(2-4)* one step further, a common practice is to use both the normal boiling point and the critical point to obtain generalized constant, Eq.*(2-4)* as:

$$ln\left(P_{vap}\right) = h\left(1 - \frac{1}{T_r}\right) \qquad \ldots(2\text{-}5)$$

where

$$h = T_{br}\,\frac{ln\left(P_C\ /\ 1.01325\right)}{1 - T_{br}} \qquad \ldots(2\text{-}6)$$

This equation generally predicts vapor-pressure within 1 to 2 percent between T_b and T_C. Below T_b, it may under predict P_{vap} by several percent.

Antoine [90] proposed a simple modification of Eq.*(2-4)* which has been widely used over a limited temperature ranges.

$$ln\left(P_{vap}\right) = A - \frac{B}{T + C} \qquad \ldots(2\text{-}7)$$

when $C=0$, Eq.*(2-7)* reverts to Clapeyron equation Eq.*(2-4)*.

Values of *A, B* and *C* are tabulated for a number of materials with P_{vap} in certain units of pressure and temperature. The applicable temperature is not large and in most instances corresponds to a pressure interval of about 0.01 to 2 bars. The Antoine equation should never be used outside the stated temperature limits. Extrapolation beyond these limits may lead to an absurd result. The constants *A*, *B* and *C* from a table where one should never use one constant from one tabulation and the other constants from a different tabulation.

The accurate representation of vapor-pressure data over a wide temperature range required an equation of greater complexity. The Wagner equation is one of the best available equations; it expresses the reduced vapor-pressure as a function of reduced temperature:

$$\ln P_r^{sat} = \frac{A\lambda + B\lambda^{1.5} + C\lambda^3 + D\lambda^6}{T_r} \qquad \ldots(2\text{-}8)$$

where $\lambda = 1 - T_r$ and A, B, C, and D are constants appear in appendix "*B*".

Wagner equation is more applicable to hydrocarbon systems. Ambrose and Patel [4] have examined this application and report average errors in P_C of about 2 percent for 65 compounds. [84, 76]

2.8 Bubble and Dew Points

The basic fact of most phase equilibrium calculations is to calculate the dew or bubble point for a mixture of a specified composition [59]. *Bubble point* is defined as the temperature or pressure at which a liquid of known composition first begins to boil. While *dew point* is defined temperature or pressure at which a vapor of known composition first begins to condense [92]. The bubble and dew point curves are shown in the Figures 2- 2, and 3.

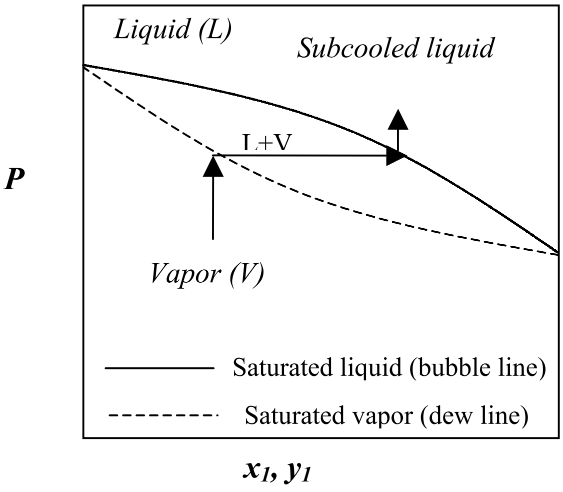


Figure 2-2: Pressure vs. x_1, y_1 diagram

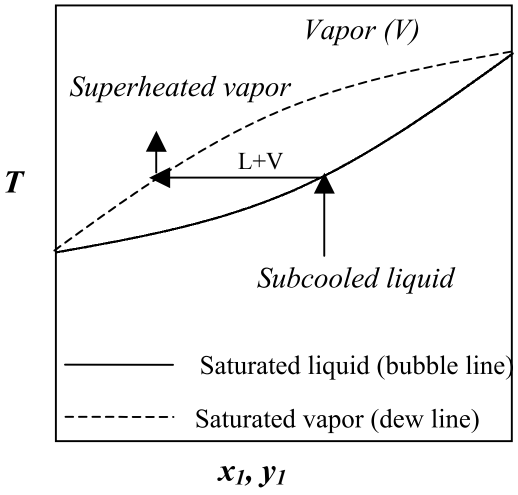


Figure 2-3: Temperature vs x_1, y_1 diagram

2.9 Phase and Phase Equilibrium

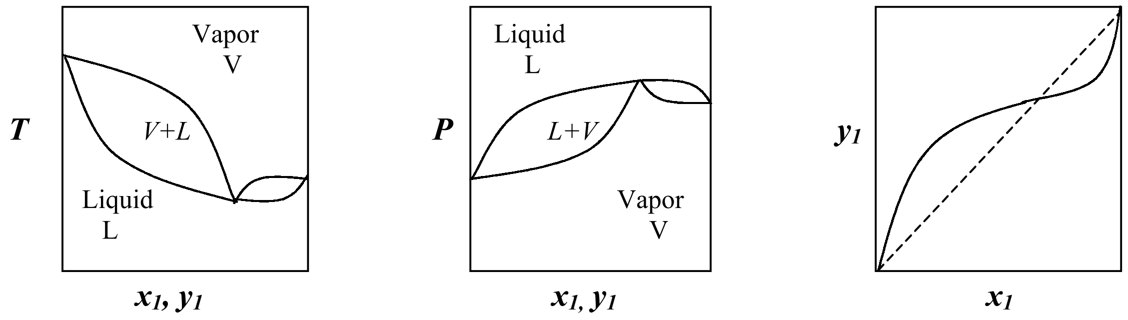
When mixtures are separated using thermal processes, heat and matter are usually exchanged between phases in contact with one other. This exchange is completed when these phases have reached equilibrium.

In refrigeration system the working fluid, the refrigerant, repeatedly changes phase from liquid to vapor and from vapor back to liquid. A *phase* is defined as a part of a system with homogeneous microscopic properties, which is separated from other parts by its phase boundary. A system is in equilibrium when no further microscopic changes take place under specified external conditions. All transfer of matter and energy through the phase boundaries is reversible. Phases of a heterogeneous mixture are said to be in equilibrium when there is neither a pressure difference (mechanical equilibrium) nor a temperature difference (thermal equilibrium).

When the system single liquid phase is in equilibrium with its vapor the system is reached vapor liquid equilibrium state. Equality of temperature of phases in contact is required for thermal equilibrium and equality of pressure for hydrostatics equilibrium. The uniformity of chemical potentials for diffusive equilibrium can be shown readily. [92]

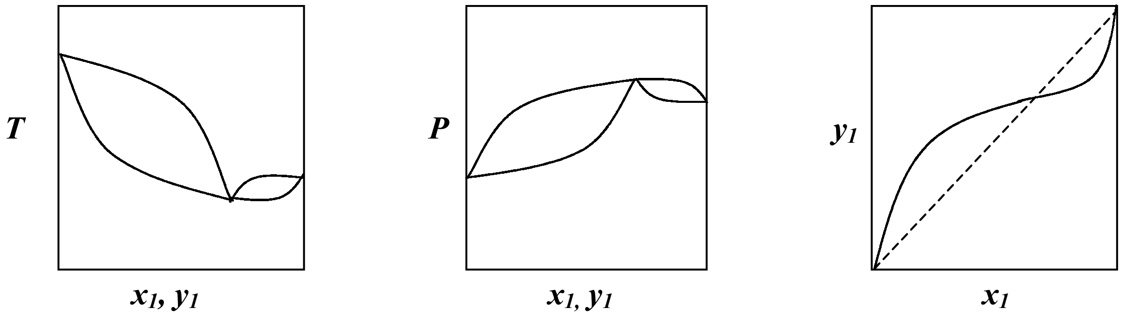
2.10 Vapor-Liquid Equilibrium

The main type of vapor-liquid behaviors is summarized in the following Figures. The popular kinds of diagrams are *T-x, P-x,* and *x-y*. In this classification type I is that for which all compositions have boiling points between those of the pure substances, which includes systems conforming to Raoult's law. An azeotropic condition is one for which the composition of the liquid and vapor phases are the same, or for which the boiling temperature and vapor composition are constant over a range of liquid composition. On the *x-y* diagram, the curve of an azeotropic system crosses the 45° line.

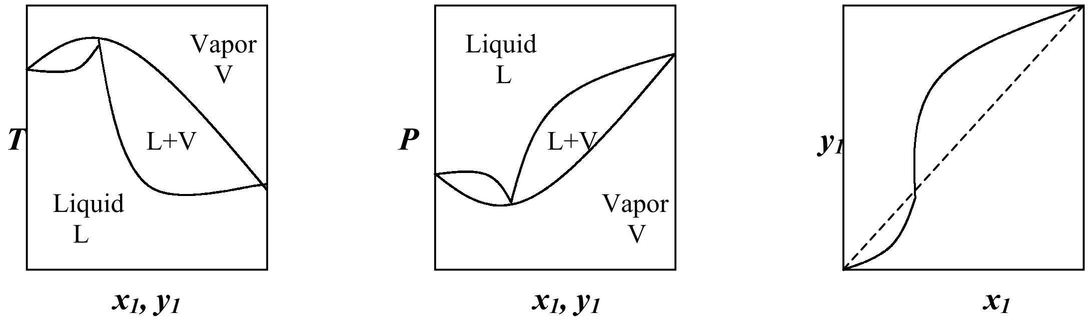


I. Intermediate-boiling systems*, *including Raoult's law behavior

Type II and III are of homogeneous azeotrope. Minimum boiling azeotrope is quite common, the maximum boiling one less so.

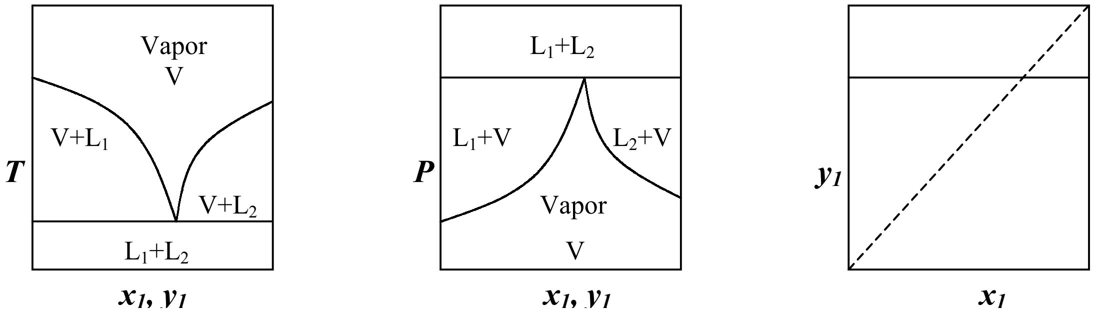


II. Systems having a minimum boiling azeotope

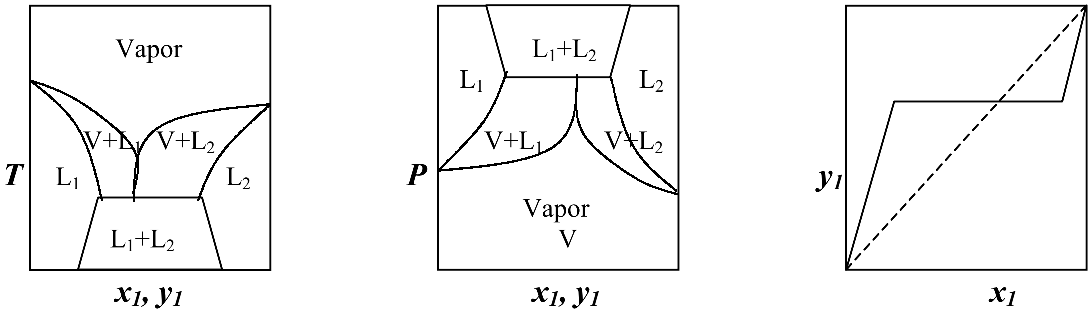


III. Systems having a maximum boiling azeotrope

Type IV and V involve liquid phase that are partially miscible or immiscible, respectively, and exhibit heterogeneous azeotropy.

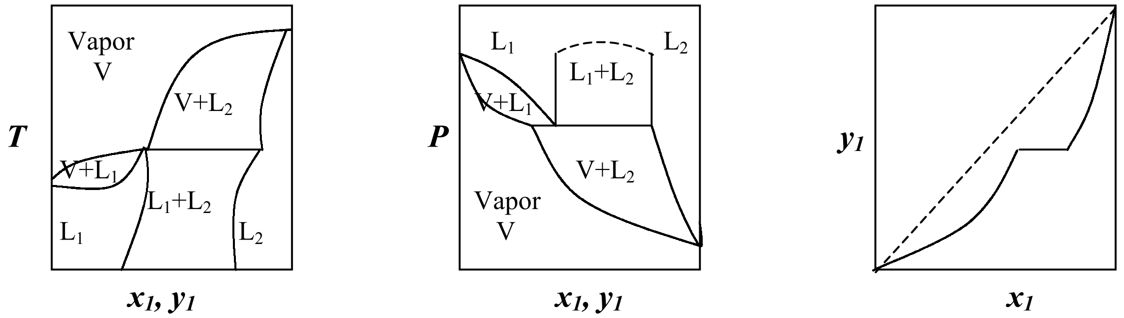


IV. Systems having immiscible liquid phases



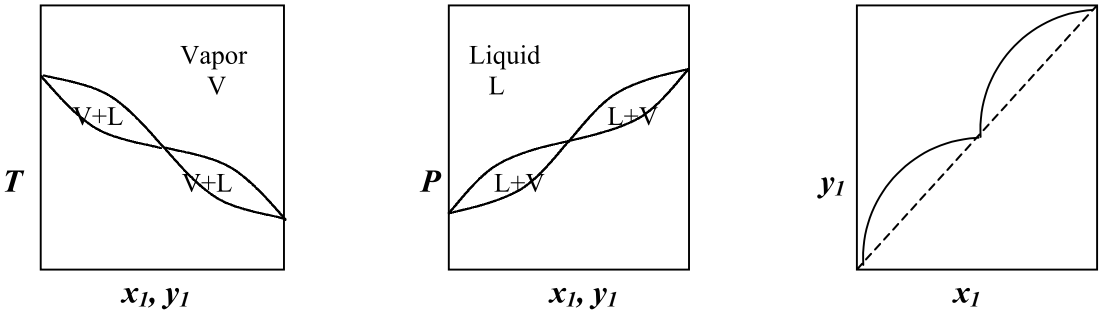
V. Systems having partially miscible liquid phases

In the less common systems of type *VI*, immiscible liquid phases exist at temperatures intermediate to the condensation temperatures of the pure substances; here the two liquid-phase compositions remain constant over a wide range of vapor compositions.



VI. Systems with immiscible liquid phases at temperatures between the condensations temperatures of the pure substances

If a system forms intermolecular compounds that are stable at their boiling points, the phase diagrams will look like type VII. And similar diagrams of liquid-solid systems. [18]



VII. System forming an intermolecular compound with boiling point between those of the pure components.

2.11 Intermolecular Forces

Thermodynamic properties of any pure substance are determined by intermolecular forces, which operate between the molecules of that substance. Similarly, thermodynamic properties of a mixture depend on intermolecular forces, which operate between the molecules of the mixture. The case of a mixture, however, it is usually more complicated because consideration must be given not only to interaction between molecules belonging to the same component, but also to interaction between dissimilar molecules. In order to interpret and correlate thermodynamic properties of solution, it is therefore necessary to have some understanding of the nature of intermolecular forces.

The understanding of intermolecular forces is far from complete and that quantitative results have been obtained for only simple and idealized models of real matter so, we can use our knowledge of intermolecular forces only in an approximation manner to interpret and generalized phase-equilibrium data.

When a molecule is in the approximate of another, forces of attraction and repulsion strongly influence its behavior. If there are no forces of attraction, gases will not condense to form liquids and solids, and in the absence of repulsive forces, vapor condense to liquid matter would not show resistance to compression.

There are many different types of intermolecular forces. These are:

1. Electrostatic forces between particles (ions) and between permanent dipoles, quadrupoles and multipoles.

2. Induction forces between a permanent dipole or quadrpole and induced dipole.

3. Forces of attraction (dispersion forces) and repulsion between non-polar molecules.

4. Specific (chemical) forces leading to association and complex formation, i.e., to the formation of loose chemical bonds of which hydrogen bonds are perhaps the best example.

These intermolecular forces acting between non-polar molecules and the molecules of theory of corresponding states. [69].

Real gases show deviations from perfect gas low because molecules interact with each other: repulsive forces between molecules assist expansion and attraction forces assist compression. Repulsive forces between neutral molecules are significant only when the molecules are almost in contact (they are short-range interaction), so repulsion forces can be expected to be important only when the molecules are close together. This is a case at high pressure when a large number of molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long-range interaction. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separation). Attractive forces are ineffective when the molecules are far apart. [8]

2.12 Ideal Solution

It is a solution for which mutual solubility results when the components are mixed. No chemical interaction occurs upon mixing. The molecular diameters of the components are the same. And the intermolecular forces of attraction and repulsion are the same between unlike as between like molecules.

These properties of ideal solutions lead to two practical results. ***First***, there is no heating effect when the components of an ideal solution are mixed. ***Second***, the volume of the ideal solution equals the sum of the volumes of components that would occupy as pure liquids at the same temperature and pressure. Also it can be defined as a solution in which all activity coefficients are unity (i.e. $\gamma_i = 1.0$ for all i). Ideal gas mixture is an ideal solution, and any equation applying to an ideal solution can also be applied to an ideal gas mixture. The converse, however, is not true; there are many ideal solutions that are not ideal gases [69].

At pressure sufficiently low for the partial pressures to approximate to the fugacity, an ideal solution may be defined as one for which Raoult's law, expressed in partial pressures, is obeyed by all components over the entire composition range, so that

$$P_i = x_i P_i^o \qquad \text{...(2-9)}$$

where P_i is the partial pressures of component 'i' where it is in equilibrium with a liquid phase containing a mole fraction x_i, P_i^o is the vapor pressure of pure component 'i'

Such a solution (ideal solution) must have the following additional characteristics:

1. No volume change on mixing.

2. No heat absorbed or evolved on mixing. [18]

When all molecules are of the same size and all forces between molecules (like and unlike) are equal, then the equation based on these characteristics provides a model of behavior known as ideal solution. Since the formation of ideal solution results in no change in molecular energies or volumes, then any equation of an ideal solution may be written as:

For vapor phase: $$M^{id} = \sum_i y_i M_i^o \qquad \text{...(2-10)}$$

For liquid phase $$M^{id} = \sum_i x_i M_i^o \qquad \text{...(2-11)}$$

where M^{id} is any property of an ideal solution

M^o is any property of pure species 'i' in a mixture at specified temperature and pressure.

y_i, x_i are the mole fractions of component '*i*' in the vapor and liquid phase respectively.[85]

No known solution is exactly ideal. Only very limited classes of solution are even approximately ideal. For approximately ideal solutions are mixtures of the alkanes. This latter class of solution is of considerable importance in petroleum industry. n-Alkanes at atmospheric and sub-atmospheric pressures usually show very small negative deviations from Raoult's law. [18]

The ideal solution behavior is represented in the following Figures:

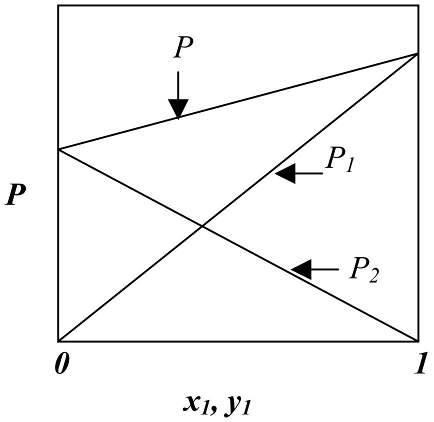


Figure 2-4: Vapor Pressure diagram at constant temperature

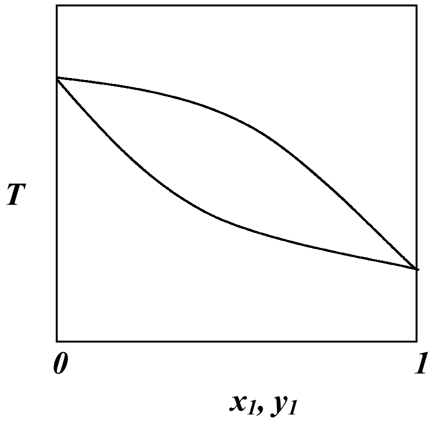


Figure 2-5: Boiling point diagram at constant pressure

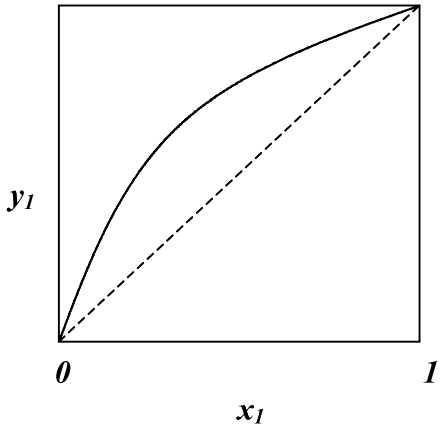


Figure 2-6: Equilibrium diagram at constant pressure

As in the case of ideal gases, ideal liquid solutions do not exist. Actually, the only solutions which approach ideal solution behavior are gas mixtures at low pressures. Liquid mixtures of components of the same homologous series approach ideal solution behavior. The theory of ideal solutions helps us to understand the behavior of real solution. [104]

2.13 Regular Solutions

Another concept frequently used in solution theory is that of the "*regular*" solution. Regular solution can be defined as one in which the components mix with no excess entropy provided there is no volume change upon mixing. Another way of saying this is to define regular solution as one which has vanishing excess entropy of mixing at constant temperature and volume.

Regular solution theory like most theories of solution is more reliable for excess Gibbs free energy than it is for excess enthalpy and excess volume. All simple theories of solution neglect changes in molecular vibration and rotation which results from the changes in molecular environment that inevitably produced by mixing; these changes, in many cases, affect the excess enthalpy end excess entropy in such away that they tend to cancel in the excess Gibbs free energy. [69]

Regular solutions are those without molecular interactions such as dipole interactions, association, or chemical effects generally. Thermodynamically they are characterized by having excess entropy equal to zero. If, moreover, the excess volume likewise is zero, these relations follow:

$$G^E = H^E = U^E = RT \Sigma x_i \ln(\gamma_i) \qquad ...(2\text{-}12)$$

In this theory the volatility and miscibility behavior of liquid mixtures is visualized to depend on the relative ease with which molecules are separable from each other. Plausibly, this effect is measured by the energy of vaporization per unit volume. [92]

Regular solution theory is useful only for estimating values of γ_i^L for mixtures of non-polar species. However, many empirical and semi-theoretical equations exist for estimating activity coefficients of binary mixtures containing polar and/or non-polar species. These equations contain binary interaction parameters, which are back-calculated from experimental data. Some of the more useful equations are Margules, Margules (Two-constants), van Laar (two-constants), and UNIQUAC (two-constants). [83]

2.14 Fugacity and Fugacity Coefficients

For real fluid the fugacity (f) is introduced which has the dimensions of pressure. Fugacity of an ideal gas is equals to its pressure, i.e.

$$f^{id} = P \qquad ...(2\text{-}13)$$

where f^{id} is the fugacity of an ideal gas [85]. For vapor liquid equilibrium the fugacity of component '*i*' in the mixture of vapor phase is equal to fugacity of component '*i*' in the mixture of liquid phase where the calculation of the fugacity of a component in a mixture under conditions of specified composition, temperature and pressure is of fundamental importance. *Fugacity coefficient* of pure component is defined as the ratio of fugacity to pressure and it is a dimensionless ratio.

$$\phi_i = \frac{f_i}{P} \qquad ...(2\text{-}14)$$

The fugacity coefficient for species '*i*' in a solution $\hat{\phi}_i$ can be expressed in the following form:

$$\hat{\phi}_i^L = \frac{\hat{f}^L{}_i}{x_i P} \qquad ...(2\text{-}15)$$

where x_i is the liquid phase mole fraction of component '*i*' in the solution. The fugacity coefficient for species *'i'* in gas mixture

$$\hat{\phi}_i^V = \frac{\hat{f}_i^V}{y_i P} \qquad ...(2\text{-}16)$$

where y_i is the mole fraction of component '*i*' in the vapor phase. The identification of $ln(\phi_i)$ from cubic EOS can be written as follows

$$ln(\phi_i) = \int_0^P (Z_i - 1)\frac{dP}{P} \qquad ...(2\text{-}17)$$

Z_i is the compressibility factor of component '*i*' which is calculated from selected cubic EOS. To calculate $\ln(\hat{\phi}_i)$ values from a general cubic EOS

$$ln(\hat{\phi}_i) = \int_0^P \frac{\partial(nZ - n)}{\partial n_i}\frac{dP}{P} \qquad ...(2\text{-}18)$$

Since $\partial(nZ)/\partial n_i = \bar{Z}_i$ and $\partial n/\partial n_i = 1$, this reduces to

$$ln(\hat{\phi}_i) = \int_0^P (\bar{Z}_i - 1)\frac{dP}{P} \qquad ...(2\text{-}19)$$

where integration is at constant temperature and composition. This equation is the partial-property analog. It allows the calculation of $\hat{\phi}_i$ values from *PVT* data. [16, 84]

2.15 Activity and Activity Coefficients

The *activity* (α_ι) a of substance '*i*' in a mixture of *n* components is defined by the relation

$$\alpha_\iota\ (T, P, x_1, x_2 ... x_n) = \hat{f}_i\ (T, P, x_1, x_2 ... x_n)\ / f_i^o(T) \qquad ...(2\text{-}20)$$

in which $f_i\ (T, P, x_1, x_2 ... x_n)$ is the fugacity of component '*i*' under the specified conditions of temperature, pressure and composition, and $f_i^o(T)$ is the standard-state fugacity at a given temperature [59].

Activity coefficient is a dimensionless ratio of fugacity of pure component '*i*' in the solution to the fugacity of component '*i*' in an ideal solution and it has the symbol (γ_i). Thus by definition,

$$\gamma_i = \frac{\hat{f}_i^{\,L}}{\hat{f}_i^{\,id}} \qquad ...(2\text{-}21)$$

and $$\overline{G}_i^E = RT\ ln(\gamma_i) \qquad ...(2\text{-}22)$$

$$\ln(\gamma_i) = \left[\frac{\partial\left(nG_i^E / RT\right)}{\partial n_i}\right]_{T,P,nj} \qquad ...(2\text{-}23)$$

where $\overline{G}_i^E$ is the excess Gibbs free energy, for an ideal solution, $\overline{G}_i^E = 0;$ and therefore γ_i=1.0 ,

$$\hat{f}_i^{\,id} = x_i f_i^o \qquad ...(2\text{-}24)$$

where f_i^o is the fugacity of pure component '*i*' and this equation is known as Lewis Randel rule [84, 85]

so, $$\gamma_i = \frac{\hat{f}_i^{\,L}}{x_i f_i^o} \qquad ...(2\text{-}25)$$

where the standard state for a component in the liquid phase is defined as that of the pure liquid at the conditions of the system at equilibrium [59]

2.16 Raoult's Law

Raoult's law is applied to VLE for which the ideal-gas model is applied to vapor phase and the ideal- solution model applied to liquid phase. By the definition it has the form

$$y_i P = x_i P_i^{sat} \qquad ...(2\text{-}26)$$

Raoult's law equation expresses the simplest possible equation for VLE, and as such fails to provide a realistic representation of real behavior for most systems. Nevertheless, it is useful for displaying VLE calculations in their least complex form. [84]

Positive or negative deviation from the ideal state are the terms used if the experimental values for the mole fraction y, or partial pressure P_i are greater or less those than calculated using Raoult's law.

2.16.1 Negative Deviation from Raoult's Law

Here, the forces of attraction between the molecules of both components are greater than those between the molecules of one and the same component.

The mixing process is exothermal and the total volume is less than the sum of the individual volumes. The enthalpy of vaporization increases. The total pressure curve exhibits a minimum and the corresponding boiling-point diagrams a maximum. A mixture boils at a constant pressure and the azeotropic composition remains unchanged.

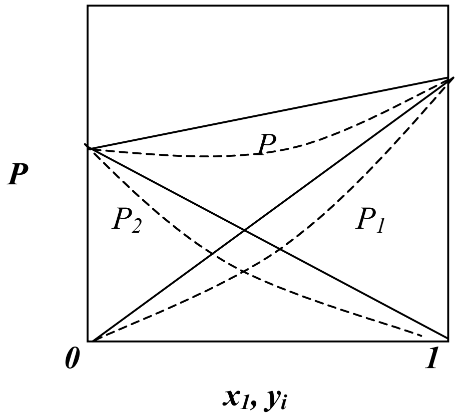


Figure 2-7: Pressure diagram at constant temperature

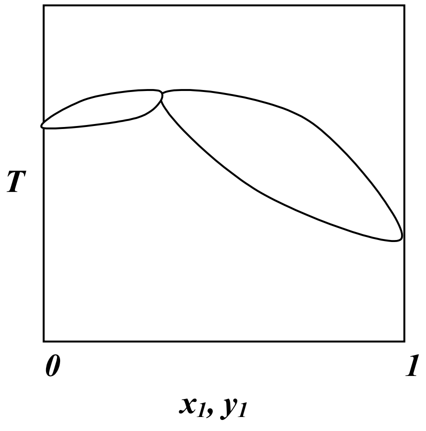


Figure 2-8: Boiling-point diagram at constant pressure

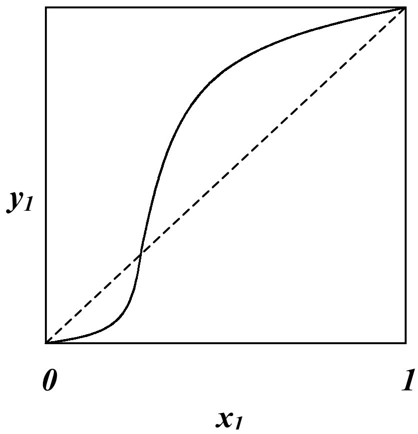


Figure 2-9: Equilibrium diagram at constant pressure

2.16.2 Positive Deviation from Raoult's Law

Here, the forces of attraction between the molecules of both components are weaker than those between molecules of one and the same component. The mixing process is endothermal and the total volume is greater than the sum of the individual volumes. The enthalpy of vaporization decreases. The boiling-diagram exhibits a minimum and possesses an azeotropic point.

The following Figures show the deviation in behavior of binary mixtures at equilibrium.

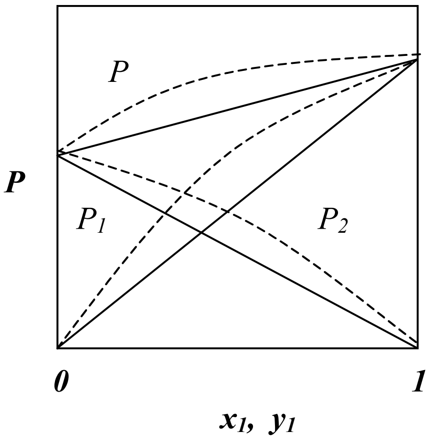


Figure 2-10: Pressure diagram at constant temperature

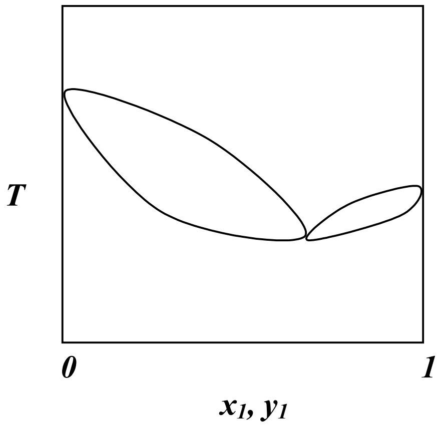


Figure 2-11: Boiling-point diagram at constant pressure

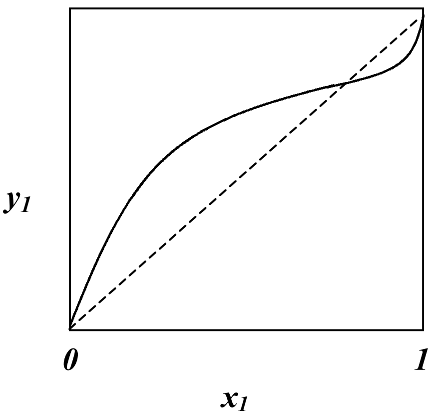


Figure 2-12: Equilibrium diagram at constant pressure

2.16.3 Modified Raoult's Law and Its Effect on Equilibrium Constant

Equilibrium ratio (k) is not constant; it changes with pressure, temperature, and type of mixture. In VLE, the ratio or equilibrium constant is defined as;

$$k_i = \frac{y_i}{x_i} \qquad \text{...(2-27)}$$

If Raoult's law is applied the equilibrium constant k_i will be

$$k_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \qquad \text{...(2-28)}$$

For real systems the fugacity coefficient is introduced in the vapor phase part. If the system composes components which are greatly different in their chemical structure then activity coefficient is introduced in the liquid phase part.

At equilibrium the fugacity of component '*i*' in the liquid phase is equal to the fugacity of the same component in the vapor phase at the same condition of the mixture i.e.

$$\hat{f}_i^L = \hat{f}_i^V \qquad \text{...(2-29)}$$

For non-ideal gas phase and non-ideal liquid solution the following schemes of calculations are usually used:

1- Using an equation of state model to calculate partial molal fugacity coefficient for every component in vapor phase and also for liquid phase

$$k_i = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V} \qquad \text{...(2-30)}$$

which is derived from $$\hat{\phi}_i^L = \frac{\hat{f}^L{}_i}{x_i P} \qquad ...(2\text{-}31)$$

$$\hat{\phi}_i^V = \frac{\hat{f}_i^V}{y_i P} \qquad ...(2\text{-}16)$$

and since fugacity of vapor phase is equal to the fugacity of the liquid phase Eq.*(2-27)* then

$$\therefore \qquad \hat{\phi}_i^V y_i P = \hat{\phi}_i^L x_i P \qquad ...(2\text{-}32)$$

since $k_i = y_i/x_i$ from Eq.*(2-27)* $\quad \therefore \quad k_i = \dfrac{\hat{\phi}_i^L}{\hat{\phi}_i^V}$

2- Using an equation of state to calculate partial molar fugacity coefficient of a component in vapor phase and using the activity coefficient model to calculate the partial molal fugacity coefficient in the liquid phase.

$$k_i = \frac{\gamma_i \phi_i^{o\,sat} P_i^{sat}}{\hat{\phi}_i^V P} exp\left(\frac{V^L\left(P - P_i^{sat}\right)}{RT}\right) \qquad ...(2\text{-}33)$$

This equation is derived as follows

From Eq.*(2-16)* and Eq.*(2-31)* which they have the following form respectively;

$$\hat{\phi}_i^V = \frac{\hat{f}_i^V}{y_i P} \quad ; \quad \gamma_i = \frac{\hat{f}_i^L}{x_i f_i^o}$$

based on the main definition of equilibrium condition Eq.*(2-29)*

$$\hat{\phi}_i^V y_i P = \gamma_i x_i f_i^{o\,L} \qquad ...(2\text{-}34)$$

the effect of pressure on fugacity in the liquid phase is:

$$ln(\frac{f_i^o}{f^{o\,sat.}{}_i}) = \frac{V_i^{sat}}{RT}(P - P_i^{sat.}) \qquad ...(2\text{-}35)$$

$$f_i^o = f_i^{o\,sat.} exp\left(\frac{V_i^{sat}}{RT}(P - P_i^{sat})\right) \qquad ...(2\text{-}36)$$

From Eq.*(2-34)* and Eq.*(2-36)*

$$\hat{\phi}_i^V y_i P = \gamma_i x_i f_i^{o\,sat.} exp\left(\frac{V_i^{sat}}{RT}(P - P_i^{sat})\right) \qquad ...(2\text{-}37)$$

$$\phi_i^{sat.} = \frac{f_i^{o\,sat.}}{P_i^{sat}} \qquad ...(2\text{-}38a)$$

From Eq.*(2-38)* $f_i^{o\,sat.} = P_i^{sat.}\phi_i^{sat.}$ *...(2-38b)*

Substituting Eq.*(2-38b)* in Eq.*(2-37)*

$$\hat{\phi}_i^{V}\, y_i P = \gamma_i x_i \phi_i^{sat.} P_i^{sat.}\, exp\left(\frac{V_i^{sat}}{RT}(P - P_i^{sat})\right) \qquad ...(2\text{-}39)$$

the fugacity coefficient term is terminated from the two equation sides since at equilibrium condition they are equal.

From the same relation $k_i = y_i/x_i$ from Eq.*(2-27)* the equilibrium constant k_i will be

$$k_i = \frac{\gamma_i \phi_i^{o\,sat} P_i^{sat}}{\hat{\phi}_i^{V} P}\, exp\left(\frac{V^L\left(P - P_i^{sat}\right)}{RT}\right) \qquad ...(2\text{-}33)$$

2.17 Three - Components System

For a three components system, the phase rule has the form

$$F = C - P + 2 \qquad ...(2\text{-}40)$$

where F= numbers of degree of freedom

C = number of components in the mixture.

P = number of phases which are formed.

will be, $F = 5-P$, and hence the variance may reach 4. Holding the temperature and pressure constant leaves two degrees of freedom (the mole fractions of two of components). One of the best ways of showing how phase equilibria vary with the composition of the system is to use a triangular phase diagram. This section explains how these are constructed and interpreted.[8]

2.17.1 Triangular Phase Diagrams

The mole fractions of the three components of a ternary system *(C=3)* satisfy

$$x_A + x_B + x_C = 1.0$$

A phase diagram drawn as an equilateral triangle ensures that this property is satisfied automatically because the sum of the distances to a point inside an equilateral triangle measured parallel to the edge is equal to the length of the side of the triangle *Figure 2-13*, which may be taken to have unit length.

Figure 2-13 Shows how this works in practice. The edge *AB* corresponds to x_C =0, and likewise for the other tow edges. Hence, each of the three edges corresponds to one of the three binary systems (*A, B*), (*B, C*), and (*C, A*). An interior point corresponds to a system in which all three substances are present. The point *P*, for instance, represents x_A=0.5, x_B =0.40, and x_C=0.10.

Any point of a straight line joining an apex to a point on the opposite edge (the broken line in *Figure 2-13* represents a composition that is progressively richer in A the closer the point is to the *A* apex but which has the same properties of *B* and *C*. Therefore, if we wish to represent the changing composition of a system as *A* is added, we draw a line from the *A* apex to the point on *BC* representing the initial binary system. Any ternary system formed by adding *A* then lies at some point on this line [8].

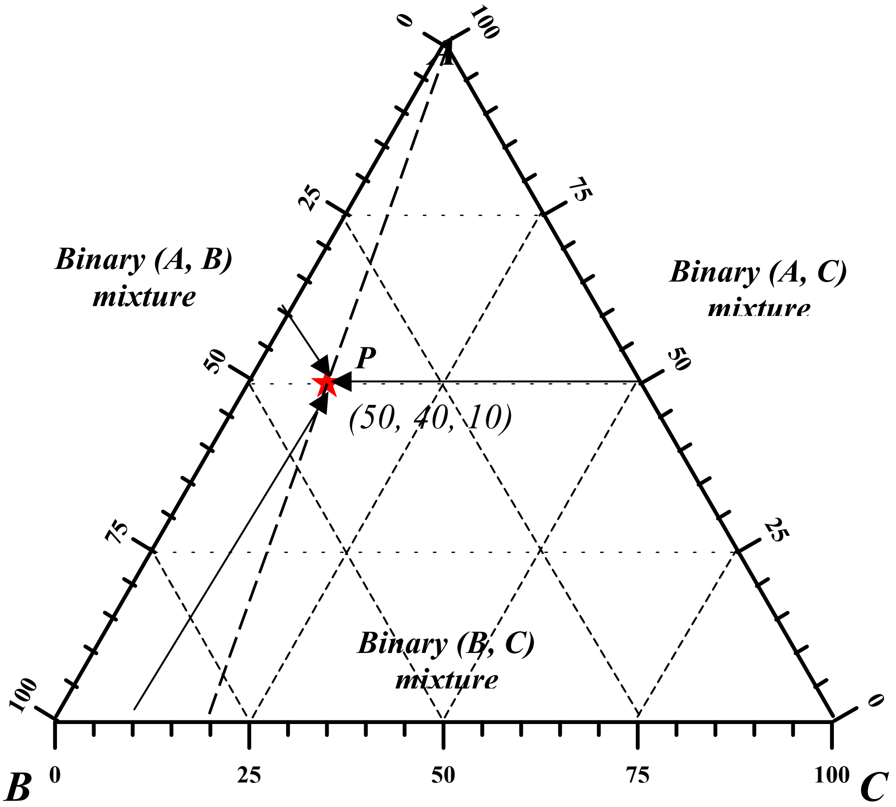


Figure 2-13: Ternary system diagram representation

2.18 Effect of Temperature on VLE

A particularly troublesome question is the effect of temperature on the molar excess Gibbs free energy G^E. This question is directly related to molar excess entropy S^E. The molar excess entropy of mixing about which little is known,

$$S^E = -\left[\frac{\partial(G^E)}{\partial T}\right] \qquad and \qquad G^E = H^E - TS^E \qquad ...(2\text{-}41)$$

In practice, either one of two approximations is frequently used.

(a) A thermal solution: This approximation sets $G^E=-TS^E$, which assumes that the components mix at constant temperature, without change of enthalpy ($H^E=0$). This assumption leads to the conclusion that, at constant composition, $ln(\gamma_i)$ is independent of T or, its equivalent, that G^E/RT is independent of temperature.

(b) Regular Solution: This approximation sets $G^E=H^E$, which is the same as assuming that $S^E=0$. This assumption leads to the conclusion that, at constant composition, $ln\ (\gamma_i)$ varies as $(1/T)$ or, its equivalent, that G^E is independent of temperature.

Neither one of these extreme approximations is valid, although the second one is often better than the first. Good experimental data for the effect of temperature on activity coefficients are rare, but when such data are available, they suggest that, for a moderate temperature range, they can be expressed by an empirical equation of the form:

$$ln(\gamma_i)_{\substack{constant\\composition}} = c + \frac{d}{T} \qquad ...(2\text{-}42)$$

where c and d are empirical constants that depend on composition. In most cases constant d is positive. It is evident that, when $d=0$, Eq.*(2-42)* reduces to assumption (*a*) and, when $c=0$, it reduces to assumption *(b)*. Unfortunately, in typical cases c and (d/T) are of comparable magnitude. [76]

2.19 VLE Apparatus

There are so many applications of VLE; therefore, techniques for calculation and experimental determination of this particular type of phase equilibrium are more highly developed than for any other type. It is therefore, fitting that this subject should be the first of the applications to be mastered.

2.19.1 Single-Stage VLE Apparatus

2.19.1.1 Recirculating Stills

The typical recirculating still is shown schematically in *Figure 2-14*. The equilibrium between phases is established in the reboiler, which must be thoroughly agitated to give a uniform liquid composition. This agitation may be accomplished either by the boiling action of the vapor bubbles or by mechanical agitation. The vapor passes through a condenser, and the condensate is collected in a receiver. The condensate, which at steady state must have the same composition as the vapor, is returned through a condensate return line, which must be small enough to prevent back mixing between the reboiler and receiver. The return is usually accomplished by gravity flow, although pumping may be utilized.

The measurements consist of liquid composition (via a liquid sample from the reboiler), vapor composition (via a sample of the liquid condensate), reboiler temperature, and system pressure. If it is convenient to measure vapor composition directly from a vapor sample, the condenser and receiver may be replaced by a vapor pump.

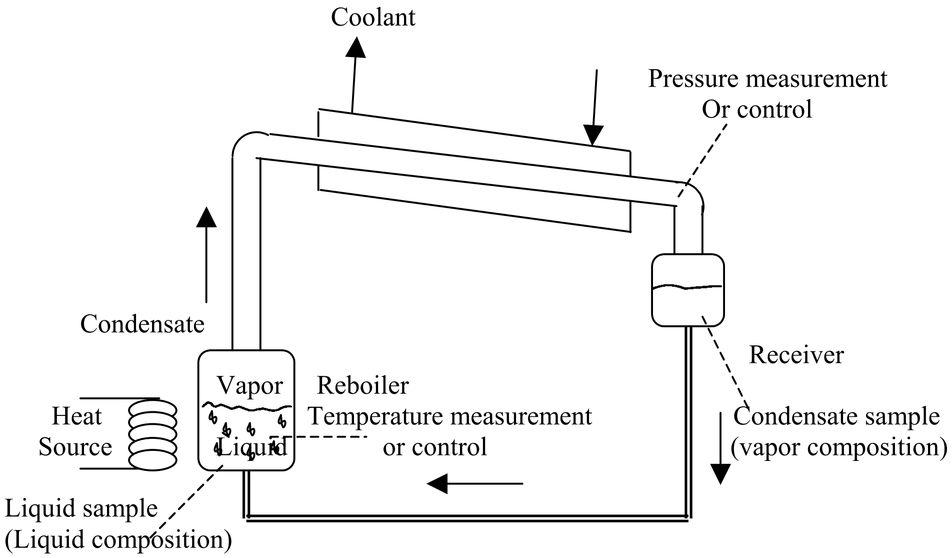


Figure 2-14: Typical schematic arrangement of a recirculating still

The problems encountered are associated with ensuring that the measurements represent truly equilibrium conditions. In measuring temperature care must be taken that the temperature is that of vapor and liquid in equilibrium not superheated and liquid. The pressure drop between the reboiler and point of pressure measurement must be minimal. The most severe problems, however, are associated with the composition measurements. Within the apparatus itself, there must be absolutely no partial condensation of the vapor in the line between the liquid in the reboiler and the condenser. Such condensation would result in liquid reflux to the reboiler and a change in the vapor composition. Further care must be taken in the handling of the samples to ensure that none is lost through partial vaporization or condensation as the samples are removed from the pressure-and temperature environment of the apparatus to that of the analysis. Any entrainment of liquid droplets into the condenser must also be avoided.

Measurements are generally made either isobarically, in which case pressure is controlled at a constant level and temperature measured, or isothermally, in which case temperature is controlled and pressure is measured. In making isothermal measurements the apparatus must be completely freed of inert gases, which would affect pressure measurements, and mechanical agitation is generally necessary since the rate of boiling (heat input) must be a part of the temperature-control loop. Data from recirculating stills are most frequently isobaric. [38]

2.19.1.2 Static Apparatus

In a static apparatus a solution is charged into an evacuated chamber, which is immersed in a constant-temperature bath. After equilibrium is attained the pressure is measured and samples of vapor and liquid are withdrawn for analysis. This type of apparatus is shown schematically in *Figure 2-15*.

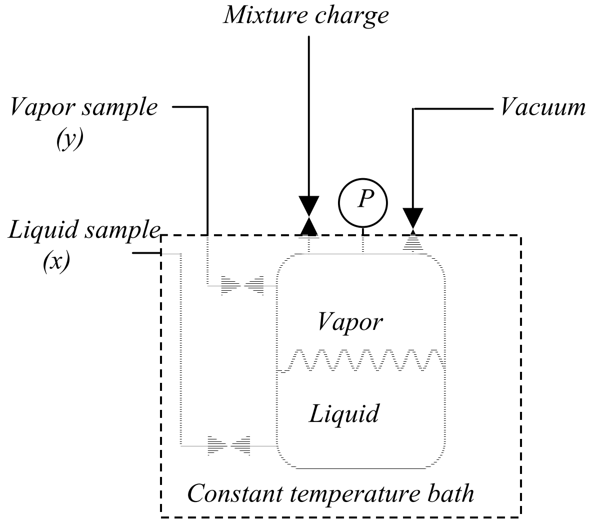


Figure 2-15: Static VLE apparatus

This method is deceptively simple in principle, but quite difficult to use in practice. Complete degassing is essential with each charge to ensure the accuracy of the pressure measurement. This degassing refers to dissolved gases in the liquid as well as evacuation of the apparatus before charging. Equilibration times are long, although they can be shortened by mechanical agitation or by pumping either liquid or vapor through the other phase i.e., allowing the liquid to spray in droplets through the vapor or the vapor to bubble through the liquid. Sampling in such a system can cause the equilibrium to change as the sample is withdrawn, although with modern instrumental analyses (particularly chromatography) large samples are not needed as frequently as they once were. [38]

2.19.1.3 Flow Apparatus

The typical flow apparatus, of which there are many varieties, is shown schematically in *Figure 2-16*. One or more feed streams, which may be either vapor or liquid, are metered continuously into an equilibrium chamber where the total feed mixture is partially flashed.

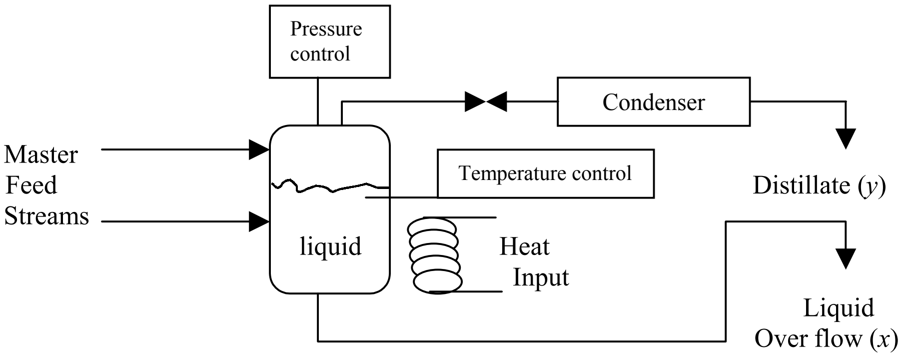


Figure 2-16: Flow VLE apparatus

The liquid effluent is withdrawn continuously by overflow and the vapor effluent by pressure control. Heat-input rate is controlled to give a set temperature in the reboiler. A change in either pressure or temperature changes the relative fraction of liquid and vapor output, and these pressure-temperature values must lie in a range between the bubble point and dew point of a mixture having the overall feed composition. The primary disadvantages are that the apparatus is inherently more complex and uses more material than other methods; its advantages are more rapid approach to equilibrium, relatively easier change of feed composition, and low residence time in the reboiler. This last advantage can be quite significant with heat-sensitive materials. [38]

2.19.2 Multistage Apparatus

The multistage apparatus is usually a calibrated distillation column operating adiabatically at total reflux, as shown schematically in *Figure 2-17*. In practice a charge is placed in the reboiler, which is heated at a constant rate. Ultimately the vapors reach the condenser, where they are totally condensed, and all the condensate is returned to the top of the column.

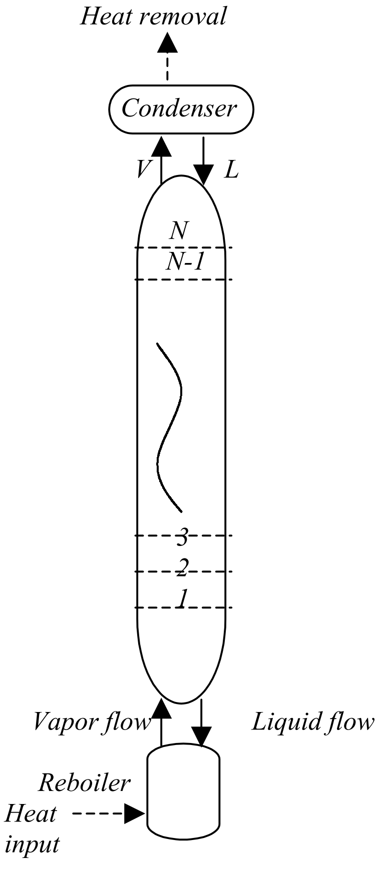


Figure 2-17: Total reflux multi-stage distillation apparatus

As liquid builds up in the top stage, it ultimately overflows and drops to the next lower stage. Ultimately all stages are filled and overflowing, and at steady state the liquid down flow at each stage is equal to the vapor flowing upward, and the heat removed through the condenser is equal to that added at the reboiler.

At steady state a small sample is taken of the liquid entering the top of the column from the condenser and of that flowing to the reboiler from the bottom of the column. The temperature is read at these points also, and usually the overhead (condenser) pressure and pressure drop across the column are measured. The two compositions of the samples taken, of course, do not represent the composition of vapor and liquid at equilibrium; they present the enrichment obtained after successive vapor-liquid contacting *N* times. [38]

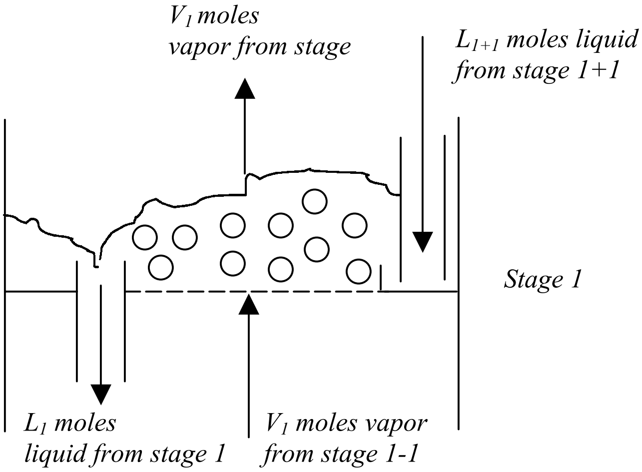


Figure 2-18: Schematic of a typical stage in a multi stage VLE apparatus

2.20 Brief Review of Similar Searches to Calculate VLE of n-Hydrocarbon Systems

2.20.1 Josep Vega Model With soft-SAFT EOS

It has been observed that n-alkanes show a great regularity in their behavior with respect to the carbon number. Therefore, the search of transferable parameters becomes an attractive route to obtain the thermodynamic properties and components *Transferable parameters* can be defined according to our model, n-alkanes need three molecular parameters, m, σ, and ϵ, to describe all thermodynamic properties. As mentioned already, one of the most promising results of applying the soft-SAFT EOS to these systems is that, these parameters increase linearly with the molecular weight. n-Alkanes are modeled as homonuclear chainlike molecules formed by tangentially banded Lennard-Jones (LJ) segments of equal diameter and the same dispersive energy. Phase equilibria calculations of heavy pure members of series, up to n-octatetracontane (n-$C_{48}H_{98}$), and of ethane/

n-decane and ethane/n-eicosane mixture are performed with the soft-SAFT (Statistical Associating Fluid Theory) EOS. The soft-SAFT EOS is a modification of the original SAFT equation proposed by Chapman et. al [13]. The main differences between the original SAFT and the soft-SAFT equations are that

(a). The latest uses the LJ potential for the reference fluid, hence accounting in a single term for dispersive and repulsive forces, while the original equation is based on hard-spheres reference fluid.

(b). The original SAFT uses the radial distribution function of hard spheres in the chain and association terms, while in soft-SAFT the radial distribution function of a LJ fluid is used.

This method based on molecular model in which n-alkanes are described as homonuclear chainlike molecules, modeled as *m* LJ segments of equal diameter which has unit $\overset{o}{A}$, and the same dispersive energy ϵ, bonded tangentially to form the chain.

$$m=0.0255\,M_w+0.628 \qquad \ldots(2\text{-}43)$$

$$m\sigma^3=1.34\,M_w+37.2 \qquad \ldots(2\text{-}44)$$

$$m\epsilon/K_B=7.17\,M_w+58.1 \qquad \ldots(2\text{-}45)$$

where ϵ/K_B has a unit (K)

M_w is the n-alkane molecular weight expressed (mg/mol).

K_B is Boltzmann constant

The phase equilibrium of light n-alkane predicted by this method is good and an accurate enough as PR-EOS. It is not surprising that PR-EOS used here predicts accurately the whole phase envelope. However, this equation does not explicitly consider the structure of the molecules and, in particular, the non-sphericity; hence, its performance deteriorates for compounds not included in its fitted parameters.

Predictions of phase equilibria of binary mixtures form the soft-SAFT equation as well as prediction form the PR-EOS are compared to experimental and simulation data. They found that, in general, the PR-EOS performs better than the original SAFT for these asymmetric mixtures, although predictions form both deteriorate as the chain length increases. Soft-SAFT equation greatly improves predictors for the phase equilibria behavior of these mixtures. So, it is concluded that SAFT-type equation explicitly accounts for repulsive and dispersive forces in the reference term through a LJ interaction potential, and it has been proved to accurately describe the phase behavior of light n-alkane. Using the new set of parameters, the soft-SAFT equation is able to accurately predict the phase behavior of pure heavy n-alkanes. [48]

2.20.2 CEOS by Richard Freze and Jean-Louis

A new cubic EOS is presented with a pseudo critical compressibility factor (Z_c^*) taken as substance-dependent. This equation leads to good phase behavior prediction for normal fluid mixtures up to the critical state, even in the case of binary systems involving a light and a heavy alkane.

Pseudo critical compressibility factor (Z_c^*) is taken as a constant value for a given compound in order to keep the EOS simple. Using VLE data for methane + n-alkane systems, Z_c^* factor optimal value for each n-alkane (C_2 to C_{10}) is determined by minimizing the error between the experimental and calculated pressures. For methane Z_c^* is fixed to 0.319, which is the value giving the best representation of the liquid volume in the range $0.55 < Tr < 0.95$, $P > 700$ atm. For compounds having an acentric factor greater than 0.09, the parameter Z_c^*, may be correlated with fairly good accuracy with ω by the relation.

$$Z_c^* = 0.2910 + 0.04421 \exp(-6.46361\,\omega) \qquad ...(2\text{-}46)$$

For compounds having $\omega < 0.090$, Z_c^* fixed to 0.319, because this value gives better results in VLE calculations than that obtained form Eq.*(2-46)*. [74]

The new CEOS, which fulfills the critical conditions, will be defined by only two parameters, Ω_c and Z_c^*. Ω_c will characterize the family of the EOS, and Z_c^* a particular member of the family. For each family, it is possible to define a basic term.

The new cubic EOS with its parameters will have the following form:

$$a=0.456533\alpha\,(R\,T_c)^2/P_c$$

$$b=(Z_c^*-0.23)\,R\,T_c/P_c$$

$$r_1=(Z_c^*-0.276106)\,R\,T_c/P_c$$

$$r_2=(Z_c^*-0.493894)\,R\,T_c/P_c$$

$$\alpha=[1+m\,(1-T_r^{1/2})]^2$$

$$m=0.381363+1.51188\,\omega-0.1993\,\omega^2$$

$$Z_c^*=0.319 \qquad (\omega\leq 0.090)$$

$$Z_c^*=0.2190+0.4421\exp(-6.46361\,\omega) \qquad (\omega>0.090)$$

The consistent correction for volumes

$$\overset{\frown}{V}=V+\sum_j\sum_j x_i x_j C_{ij}$$

$$C_{ij}=(C_i\,C_j)^{1/2}$$

$$C_i=d_i\,R\,T_{ci}/P$$

With $d_i=0.02802-0.02787\omega_i-0.04421\exp(-6.46461\omega_i)$

If $\omega_i>0.09$; otherwise, $d_i=0$

2.20.3 Sheng-Ping Formulation for Hydrocarbon VLE Estimation

The Cubic EOS of Patel and Teja [67] is used in this method for VLE calculations on straight-chain paraffin. Various modifications of the combinatorial part of UNIFAC tested as models of the excess Gibbs free energy at infinite pressure for calculating EOS parameters of mixtures. A new formulation is introduced, which was found to give improved VLE predictions for binary and ternary mixtures, especially for mixtures containing molecules of very different sizes and shapes. The results of this new formulation lead to a predictive cubic EOS with no adjustable parameters that depend on the characteristics of the binary pair for paraffinic hydrocarbons. The new formulation of excess Gibbs free energy has the form

$$\frac{G^E_\infty}{RT} = \sum_{i=1}^{N} x_i \ln\left(\frac{\psi'_i}{x_i}\right) - \frac{z}{2}\sum_{i=1}^{N} q_i x_i \ln\left(\frac{\psi'_i}{\vartheta_i}\right) \qquad ...(2\text{-}47)$$

$$\psi'_i = \frac{x_i r_i^{pi}}{\sum_{j=1}^{N} x_j r_j^{pj}} \qquad ...(2\text{-}48)$$

$$pi = 1 - \frac{1}{[0.8(\varepsilon - 1)^{0.2} + 1]} \qquad ...(2\text{-}49)$$

$$\varepsilon_i = r_i^{1/3}\left(\frac{q_i}{r_i}\right) \qquad ...(2\text{-}50)$$

For near spherical molecules the exponential factor *pi* is near zero; as the entropy of mixing of these molecules closely resembles that of an ideal solution. Chain like molecules are more flexible; therefore the entropy of mixing is larger than that of an ideal solution and the exponential factor *pi* becomes greater than zero. It should be noted, however, that the *pi* are properties of binary pair. While, ε_i is the ratio of the surface area of molecule '*i*' to the surface area of a spherical molecule that has the same van der Waals volume. By definition, the ε_i is close to 1.0, for spherical molecules of any size. As the size of chain molecules increases, the ε_i increase as the r_i become very large, but q_i/r_i remains close to unity. EOS parameters for mixtures were calculated using a group contribution model for calculating excess Gibbs free energy at infinite pressure. This model was found to be as good as the original cubic EOS with van der Waals mixing rules and optimal binary interaction coefficient but eliminates the need for adjustable binary parameters. [110]

2.21 Theoretical Background to Calculate VLE of n-Hydrocarbon Systems

Since hydrocarbons and hydrocarbon mixtures used as subsituent refrigerants in refrigeration. It is very important to know the behavior of hydrocarbons and their mixtures. Three factors which are of practical importance in the case of hydrocarbon mixtures make it possible and sometimes necessary to treat them in somewhat different manner from that which is most advantageous in the case of other systems:

1. It is seldom possible to analyze hydrocarbon mixtures by chemical methods on account of their lack of reactivity. Methods based on the physical propertis of such mixtures are not very sensitive at best, and as a result the accuracy of analysis is comparatively low, particularly for the components which are present in the smallest amounts.
2. From the few data available in the litrature regarding hydrocarbon mixtures, the indications are that many such systems follow closely the ideal solution laws. It is of particular importance to posses a simple and reliable method to determine whether a given system is ideal, since in that case the whole equilibrium curve can be calculated with far greater accuracy than it can be determined experimentally.
3. The hydrocarbon mixtures which are of practical interest are for the most part so complex that their analysis in terms of the individual constituents is well-nigh impossible. Hence it would be of great advantage to be able to predict the shape of the liquid-vapor equilibrium curve without having to resort to an analysis of the two phases. [37]

It is very important to know the behavior of hydrocarbon substituent properties. One of the most important property is the VLE behavior of hydrocarbons mixture.

The VLE behavior is investigated by two different methods which is:

a. Investigation of the ability of an EOS to calculate VLE of hydrocarbon mixtures.
b. Investigation of the effect of activity coefficient with the share of EOS to calculate VLE of hydrocarbons mixture.

2.22 Activity Coefficient Models

Activity coefficient models are much more empirical in nature when compared to the property prediction by EOS that is typically used in the hydrocarbon industry. For example, they can not be used as reliably as the equations of state for generalized application or extrapolating into untested operating conditions. Their tuning parameters should be fitted against a representative sample of experimental data and their application should be limited to moderate pressures. Consequently, more caution should be exercised when selecting these models for particular simulation. The individual activity coefficient for any system can be obtained from a derived expression for excess Gibbs free energy function coupled with Gibbs Duhem equation:

$$nG^E = R\,T \sum_i n_i \ln(\gamma_i) \qquad \ldots(2\text{-}12)$$

where G^E= excess Gibbs free energy

R= gas constant
T= temperature
n_i= number of moles of component 'i'
γ_i= activity coefficient for component 'i'

The early models (Margules, Van Lear) provide an empirical representation of the excess function that limits their application. The newer models such as Wilson, NRTL UNIQUAC and UNIFAC utilize the local composition concept and provide an improvement in their general application and reliability. All of these models involve the concept of binary interaction parameters and require that they be fitted to experimental data. [43]

The use of activity-coefficient models as a tool for phase equilibrium calculations is introduced. All such models are empirical in nature and represent the activity coefficient of a component in a mixture (and hence its fugacity) in terms of an equation that contains a set of parameters. Two general approaches are employed:

a. The parameters of the activity coefficient model are determined in a fit to experimental VLE data in a binary mixture, usually at a single temperature. Provided that parameters are determined for all possible binary pairs, the model may then be applied in the prediction of activity coefficients in a multi-component mixture over a range of temperature and pressure. In this sense the model is only a correlation for binary systems (although it may allow extrapolation with respect to temperature or pressure) but it is truly predictive for multicomponent systems. Examples of this approach are Wilson, T-K-Wilson, NRTL, and UNIQUAC activity-coefficient models. This general approach is to be preferred from the point of view of reliability but the need for experimental data on binary sub-systems can be demanding.

b. An alternative approach, which requires no experimental data, is one in which the parameters of the activity-coefficient model are estimated by a group-contribution method. Several such schemes have been developed with functional-group parameters determined by regression against a very large data base of experimental VLE results.

In application, group-contribution models are predictive but generally offer inferior accuracy. Examples of this approach are the ASOG and UNIFAC models. [59]

Group contribution method, which has been extensively developed, can be used to predict VLE, and some models can estimate LLE, or even solid-liquid equilibria and polymer-liquid equilibria. Except at high pressures, dependency of K-values on composition is due primarily to non-ideal solution behavior in the liquid phase. The *simple regular solution theory* of Scatchard and Hildebrand [40] can be used to estimate the deviation due to non ideal behavior for hydrocarbon-liquid mixtures.

Simple models for the liquid-phase activity coefficient, γ_i^L, based only on properties of pure species are not generally accurate however, for hydrocarbon mixtures; regular solution theory is convenient and widely applied. The theory is based in the premise that non-ideality is due to differences in van der Waals forces of attraction among the different molecular present. Regular solutions have an endothermic heat of mixing, and all activity coefficients are greater than 1. These solutions are regular in the sense that molecules are assumed to be randomly dispersed. Unequal attractive forces between like and unlike molecules pairs tend to cause segregation of molecules. However, for regular solutions the species concentrations on a molecular level are identical to overall solution concentrations. Therefore, excess entropy due to segregation is zero and entropy of regular solutions is identical to that of ideal solutions, in which the molecules are randomly dispersed. [83]

2.23 Wilson Equation

The Wilson equation model, proposed by Grant M. Wilson [105] 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 [59]. It offers a thermodynamically consistent approach to predict multicomponent behavior from regressed binary equilibrium data [43]. 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 [59]. Although the Wilson equation is more complex and requires more computational time than other activity coefficient equations, it can represent almost non-ideal liquid solutions satisfactorily except electrolytes and solutions exhibiting limited miscibility

(LLE and VLE). It performs an excellent job of predicting ternary equilibrium using parameters regressed from binary data only. The Wilson equation will give similar results as the Margulas and van Lear equations for weak non-ideal systems. [43]

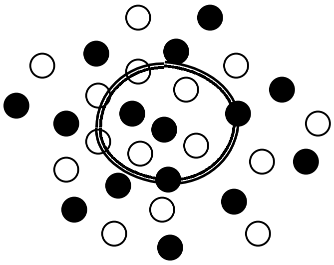
2.23.1 Local Composition Concept of Wilson Equation

Since its introduction in 1964, the Wilson equation has received wide attention because of its ability to fit strongly non-ideal, but miscible system. Wilson equation, with its binary interaction parameter fits experimental data well even in dilute regions where the variation of γ_i, becomes exponential.

In Wilson equation, the effects of differences both in molecular size and intermolecular forces are incorporated by an extension of the Flory-Huggins relation. Overall solution volume fraction are replaced by local volume fractions, which are related to local molecule segregations caused by differing energies of interaction between pairs of molecules. The local concept of local compositions that differ from overall compositions is shown schematically for overall equimolar binary solution in *Figure 2-19*, which is taken from Cukor and Prausentiz. [17]

○ Molecule of type *1*

● Molecule of type *2*



overall mole fractions : $x_1=x_2=1/2$

local mole fractions:

$$x_{12} = \frac{\textit{Molecules of type 2 about a central molecule}}{\textit{Total molecules about a central molecule of type 1}}$$

$x_{21}+x_{11}=1.0$, *as shown*

$x_{12}+x_{22}=1.0$

$x_{11} \approx 3/8$

$x_{21} \approx 5/8$

Figure 2-19: The concept of local compositions

About a central molecule of type 1, the local mole fraction of molecule of type 2 is shown as 5/8, while the overall composition is 1/2. [83]

2.23.2 Application of Wilson Equation to Mixture

Consider a binary mixture of component 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

$$\frac{x_{11}}{x_{21}} = \frac{x_1 \, exp(-\varepsilon_{11}/RT)}{x_2 \, exp(-\varepsilon_{21}/RT)} = \frac{x_1}{x_2} exp\left(-\lambda_{21}/RT\right) \qquad \ldots(2\text{-}51)$$

where ε_{11} and ε_{21} are energies interaction defined in a manner similar to the attractive part of van der Waals potential and $\lambda_{21} = \varepsilon_{21} - \varepsilon_{11}$. 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.*(2-51)* is next used to evaluate the local volume fraction, z_i, of species *'i'* around itself, with the result

$$z_i = \frac{x_{ii} V_i}{\sum_j x_{ji} V_j} = \frac{x_i}{\sum_j \Lambda_{ij} x_j} \qquad \ldots(2\text{-}52)$$

where

$$\Lambda_{ij} = V_{ij} \exp\left(-\frac{\lambda_{ij}}{RT}\right) \qquad \ldots(2\text{-}53)$$

$$V_{ij} = \frac{V_j}{V_i} \qquad \ldots(2\text{-}54)$$

here V_i and V_j are respectively the partial molar volumes of species '*i*' and '*j*' in the liquid mixture. It should be noted that Λ_{ij} can not be negative, that $\Lambda_{ii} = \Lambda_{jj} = 1.0$, and that, in general, $\Lambda_{ij} \neq \Lambda_{ji}$.

Excess Gibbs free energy G^E of a mixture, is obtained from the following equation

$$\frac{G^E}{RT} = \sum_i x_i \ln\left(\sum_j x_i \Lambda_{ij}\right) \qquad \ldots(2\text{-}55)$$

The activity coefficient is found to be:

$$\ln(\gamma_i) = 1 - \ln\left(\sum_{j=1}^{n} x_i \Lambda_{ij}\right) - \sum_{k=1}^{n} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{n} x_j \Lambda_{kj}} \qquad \ldots(2\text{-}56)$$

which is a generalized expression for multicomponent mixture and it may be used to obtain the activity coefficient of each component *'i'* in a mixture of '*n*' components provided that all binary parameter λ_{ij} and the partial molar volumes are known. No additional parameters are required. Typically molar volumes are approximated by the molar volumes of pure liquids and provided that this is done consistently in both parameter determination and application, the results are generally satisfactory.

In most cases, λ_{ij} parameters are assumed to be independent of temperature although, for the best accuracy, they should not be used at temperatures too far from that at which they were determined. These parameters are usually determined by fitting either experimentally determined excess Gibbs free energies or experimentally determined activity coefficients. In either case Eq.*(2-53)* is used to relate λ_{ij} and Λ_{ij}. Usually, results over a range of liquid compositions are employed and the optimum parameters found by non-linear regression analysis. However, it is possible, through 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.

The outstanding features of the Wilson equations include the generally superior representation of activity coefficients for both polar and non-polar mixtures, and the ability to treat multicomponent systems with only one binary parameters. One drawback of the model however, is its inability to handle either LLE or VLLE. This is a fundamental restriction imposed by the form of the Wilson equations and many modifications have been suggested to overcome this problem. [59]

2.24 UNIFAC Group Contribution

The fundamental idea of solution of group model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. In concept, the UNIFAC method follows the ASOG method, wherein activity coefficients in mixtures are related to interactions between structural groups.

The essential features are:

1. Suitable reduction of experimentally obtained activity coefficient data to yield parameters characterizing interactions between pairs of structural groups in non-electrolyte systems.

2. Use of those parameters to predict activity coefficients for other systems which have not been studied experimentally but which contain same functional groups. [76]

The UNIFAC (UNIQUAC Functional Group Activity Coefficient) group-contribution method proposed by Fredenslund, Jones, and Pransentiz at (1975) [26] has provided the design engineer with a rational and reliable basis for predicting activity coefficient in non-electrolyte liquid mixtures, non-polymeric mixtures at low to moderate pressures and temperatures between 300 and 425 K [34]. The reliability and the method are demonstrated by a large number prediction [27]. At present, UNIFAC represents more than 70% of the published VLE data at normal pressure [25, 27].

2.24.1 Local Area Fraction

A molecule of component 1 is represented by a set of bonded segments; the number of segments per molecule is r_1. While all segments, by definition, have the same size, they differ in their external contact area; for example, in n-Pentane, the two methyl end groups have a large external area than the three methylene groups. For a molecule of component 1, the number of external nearest neighbors is given by $z \times q_1$ where z is the coordination number of the lattice and q_1 is a parameter proportional to the molecule's external surface area. Similarly, for a molecule of component 2, we have structural parameters r_2 and q_2.

Let us focus attention on the composition of a region in the immediate vicinity of a molecule 1. The θ_{21} is the fraction of external sites around molecule 1 which are occupied by segments of molecule 2. Similarly, local area fraction θ_{11} is the fraction of external sites around molecule 1 which are occupied by segments of (another) molecule 1. Similarly when the attention is focused on the composition of molecule 2. So for a binary mixture, therefore, we have four local area fractions which describe the microstructure of the lattice; however, only two of these are independent because [1]

$$\theta_{11}+\theta_{21}=1 \qquad \text{and} \qquad \theta_{22}+\theta_{12}=1 \qquad \ldots(2\text{-}57)$$

2.24.2 UNIFAC Model Concepts

The UNIFAC method is based on the solution of group concept. The groups are structural units such as ($-CH_3$), ($-COCH_3$), ($-COCH_2-$), ($-CH_2Cl$), and others, which, when added, from the parent molecules. [29]

Derr and Deal [20] separate the molecular activity coefficient into two parts: one part provides the contribution due to differences in molecular size and the other provides the contribution due to molecular interactions. The first part is arbitrarily estimated by using the thermal Flory-Huggins equation, the Wilson equation, applied to functional groups, is chosen to estimate the second part. Much of the arbitrariness is removed by combining the solution of groups' concept with the UNIFAC equation. First, the UNIFAC model contains a combinatorial part, essentially due to difference in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions. Second, functional group sizes and interaction surface area are introduced from independently obtained pure-component, molecules structure data.

Abrams and Pransentiz (1976) show that the UNIFAC equation gives good representation of both VLE and LLE for binary and multicomponent mixtures containing a variety of non-electrolytes such as hydrocarbons, ketones, esters, water, amines, alcohols, nitriles, etc. In a multicomponent mixture, the UNIFAC equation for the activity coefficient of (molecular) component *i* is

$$\ln(\gamma_i) = \underbrace{\ln(\gamma_i^{C})}_{\text{Combinatorial part}} + \underbrace{\ln(\gamma_i^{R})}_{\text{Residual part}} \qquad \ldots(2\text{-}58)$$

where

$$\ln(\gamma_i^{C}) = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i \frac{\Phi_i}{x_i}\sum_j x_j l_j \qquad \ldots(2\text{-}59)$$

and

$$\ln(\gamma_i^{R}) = q_i\left[1 - \ln\left(\sum_j \theta_j \tau_{ji}\right) - \sum_j (\theta_j \tau_{ij} / \sum_k \theta_k \tau_{kj})\right] \qquad \ldots(2\text{-}60)$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad ; \quad z = 10 \qquad \ldots(2\text{-}61)$$

$$\theta_i \equiv \frac{q_i x_i}{\sum_i q_i x_i} \quad \text{and} \quad \Phi \equiv \frac{r_i\, x_i}{\sum_i r_i\, x_i} \qquad \ldots(2\text{-}62)$$

$$\tau_{ji} = exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) = exp\left(-\frac{a_{ij}}{RT}\right) \qquad \ldots(2\text{-}63)$$

where u_{ji} is a measure of the energy of interaction between groups j and i. The group interaction parameters a_{ij} (two parameters per binary mixture of groups) are the parameters which must be evaluated experimental phase equilibrium data. Note that a_{ij} has a unit Kelvin and that $a_{ij} \neq a_{ji}$.

In these equations, x_i is the mole fraction of component '*i*', θ_i is the area fraction, and Φ_i is the segment fraction which is similar to the volume fraction. Pure component parameters r_i and q_i are respectively, measures of molecular van der Waals volumes and molecular surface areas.

The two adjustable binary parameters τ_{ij} and τ_{ji} must be evaluated from experimental phase equilibrium data. No ternary (or higher) parameters are required for system containing three or more components.

Parameters r_i and q_i are calculated as the sum of the group volume and area parameters R_k and Q_k which are given in appendix *"B"*

$$r_i = \sum_k \nu_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k \nu_k^{(i)} Q_k \qquad \ldots(2\text{-}64)$$

where $\nu_k^{(i)}$, always an integer, is the number of groups of type k in molecule *'i'*. Group parameters R_k and Q_k are obtained from van der Waals group volume and surface area V_{wk} and A_{wk} given by Boudi [11]:

$$R_k = V_{wk} / 15.17 \ \text{and} \ \ Q_k = A_{wk} / 2.5 \times 10^9 \qquad \ldots(2\text{-}65)$$

The residual part of the activity coefficient can be calculated from the following equation:

$$ln\,(\gamma_i^R) = \sum_{k_{all-groups}} \nu_k^{(i)} \left(ln\,\Gamma_k - ln\,\Gamma_k^{(i)} \right) \qquad \ldots(2\text{-}66)$$

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

The group activity coefficient Γ_k is found from an expression similar to Eq.*(2-60)*

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \Theta_m \tau_{km} \right) - \sum_m \left(\frac{\Theta_m \tau_{km}}{\sum_n \Theta_n \tau_{nm}} \right) \right] \qquad \ldots(2\text{-}67)$$

In this equation, Θ_m is the area fraction of group m, and the sums area over all different groups. Θ_m is calculated in a manner similar to that for θ_i:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad \ldots(2\text{-}68)$$

where X_m is the mole fraction of group m in the mixture. [26]

2.24.3 Uses of UNIFAC

UNIFAC has become most popular model where liquid-phase activity coefficients are needed. Anderson et. al. [6] described a process simulator where UNIFAC is used for VLE, LLE, and VLLE flash computations and for distillation and extraction column calculations. Indeed, many commercially available process simulators have such programs. Also, other applications have been reported. Examples are:

(i) Estimation of solvent effects on chemical reaction rates (Lo and Paulaities) [55]

(ii) Estimation of flash point of flammable liquid mixtures (Gmeling and Rasmussen) [33].

(iii) Choice of solvent for extraction purposes (Tegtmeier and Misselhorn) [97]; and

(iv) Representation of petroleum fractions (Ruzika et.al.) [78].

With the introduction of small modifications, the method has also been used to describe phase equilibria of polymer solution [35], and quite recently it has been used for the calculation of gas solubility in pure mixture solvents (Sander et. al.) [63]. Gmehling et. al. [32] has shown that UNIFAC may be applied to solid liquid equilibria.

The UNIFAC group interaction parameters have been estimated mostly from experimental VLE data. The possibility of using infinite dilution activity coefficients from gas-liquid-chromatographic data has also been investigated (Alessi et. al) [2]. Conversely, Roth and Novak [77] have shown that UNIFAC may be used to predict GLC retention times. Finally, Jensen et. al. [47] has shown that UNIFAC may be used in connection with the prediction of pure component vapor pressures.

The populations of UNIFAC stems most probably from the fact that in general it gives reasonable good predictions of activity coefficients. The method also has a broad range of applicability due to the many parameters which are available. Other methods have been proposed. They are normally of accuracy comparable to UNIFAC, but they are not the same broad range of applicability. [28]

2.24.4 Limitations of UNIFAC

UNIFAC has some limitations. The range of applicability of UNIFAC is limited because of:

1. Limitations of the activity coefficient approach.
2. Restrictions stemming from the solution-of- groups approach.
3. Lack of flexibility of the UNIFAC functional expression.
4. Lack of reliable data.

The basic assumption in the group-contribution approach for the prediction of activity coefficients is that the functional groups, which together add to form the molecules in the mixtures, are independent from one another and thus do not know which were their neighboring group in the present molecules. This fundamental assumption is the basis of the wide applicability and the flexibility of the group contribution models. On the other hand, this assumption also renders the group contribution models known today unable to distinguish between details in the molecular structures as in isomers. Hence, unfortunately, group-contribution models are unable to predict separation factors for e.g. separation processes for Xylenes.

This same basic assumption also is the reason why a group-contribution approach can not describe “proximity effects”; i.e., the fact that two strongly polar groups situated on two neighboring carbon atoms will have different properties than groups are spaced far apart. [28]

One of the goals of all theories and correlations in phase equilibria studies is to predict properties of mixtures from pure-component data alone. This goal has remained largely elusive due to an inadequate fundamental understanding of the structures of liquids and intermolecular forces. Consequently, all of widely used existing methods, UNIFAC (universal functional activity coefficient) [26] derived from UNIQUAC (universal quasichemical) [1], needs experimental data for mixtures to deduce the values of at least two parameters for further, VLE prediction. This need for empirical information hampers the effectiveness and generality of these theories, particularly outside the range for which the data were originally determined. In addition, prediction and information on several important mixtures and of mixtures containing new compounds can not be obtained because experimental data for related mixtures are not available. [2]

Another common goal of phase equilibria studies is to develop models that can simultaneously correlate or predict VLE, enthalpy data and LLE. Several attempts have been made in this respect, because such models would truly advance the understanding of the thermodynamics of liquid mixtures. These attempts have been largely unsuccessful due mainly, to the inherent assumptions in the group-contribution approach used by most of the worker. [7]

2.25 Classification of Equation Of State

The need for accurate prediction of the thermodynamic properties of many fluids and mixtures has led to the development of a rich diversity of equations of state with differing degrees of empiricism, predictive capability and mathematical form. Before proceeding with the discussion of specific equations of state it is useful to make some general classifications into which they may fall.

The main types of EOS may be classified conveniently according to their mathematical form as follows:

1. Standard P-V-T forms:-.

This type of EOS may be written for pure fluids as

$$P=P\ (T,\ V_m) \qquad or \qquad Z=Z\ (T,\ V_m)$$

while, for mixture of *'n'* components, there are a further *'n-1'* independent composition variables. Sub-classifications may be introduced according to the structure of the function P or Z:

I. *Truncated virial equations* in which P is given by a polynomial in $1/V_m$ with temperature and composition dependent coefficients.

II. *Cubic equations* in which P is given by a cubic function of V_m containing two parameters which are functions of composition and possibly also of temperature.

III. *Complex empirical equations* which represent P by some combination of polynomial and other terms (e.g. BWR and related equations).

It is also possible to invert the functional relationship to give V_m or Z terms of T, P and the composition variables may be convenient in the analysis of experimental data for a single fluid phase, it is almost never used in thermodynamic modeling.

2. Fundamental form:-

A fundamental equation gives one of the state functions in terms of its natural independent variables. By far the most common choice is the molar Helmholtz energy A_m as a function of temperature and molar volume:

$$A_m = A_m (T, V_m)$$

In order to achieve a precise representation of the experimental data over a wide range of conditions, the structure of the functional relationship is often very complicated. Invariably, A_m is split into perfect-gas and residual parts which are parameterized separately. Although accurate fundamental equations of state exist for only about twenty of the most important pure fluids, one or more of these may form the basis of a corresponding-state treatment of the residual properties of a wide variety of other fluids including mixtures. [59]

2.26 Cubic Equation Of State

For an accurate description of the *PVT* behavior of fluids over wide ranges of temperature and pressure, an EOS required. Such an equation must be sufficiently general to apply to liquids as well as gases and vapors.

The first practical cubic EOS was proposed by J. D. van der Waals in 1873:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \text{...(2-69)}$$

Here, ‘a’ and ‘b’ are positive constants where ‘b’ is related to the size of the hard sphere while ‘a’ can be regarded as a measure of the intermolecular attraction force [88]. When ‘a’ and ‘b’ are zero, the ideal-gas equation is recovered. *Figure 2-2*0 is a schematic *PV* diagram showing three such isotherms. [84]

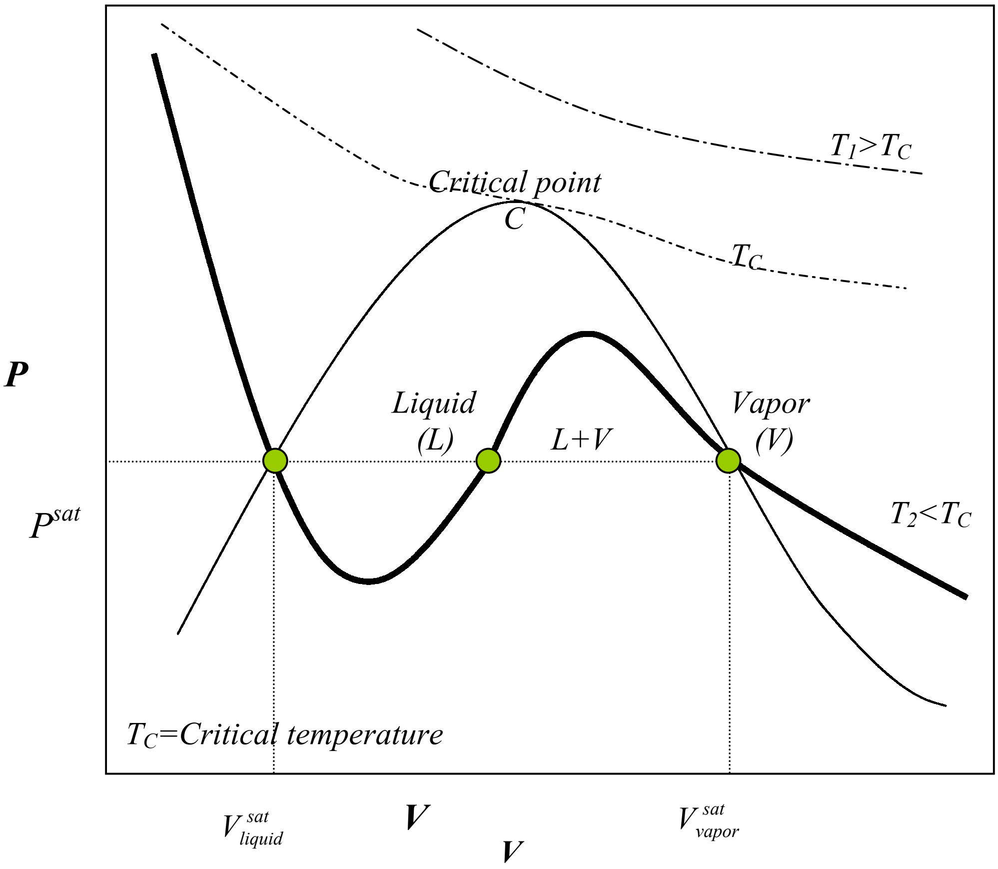


Figure 2-20: PV diagram showing three such isotherms

Where the solid line represent a smooth transition from liquid to vapor where each bolt point on the straight saturated pressure represent a root of cubic EOS. The need of simple models imposed by the computing tools existing at that time could be satisfied only by van der Waals EOS which is inaccurate enough and unable to treat liquid phase. The calculation of VLE could then be realized only by resorting to an unsymmetrical treatment of the phases, by which liquid-state fugacities were obtained through the use of activity coefficient. [86]

The EOS proposed by Redlich Kwong (RK) [73] is considered a good equation for the calculation of volumetric and thermal properties of pure compounds and mixtures. The RK-EOS does not, however, give as good results for the calculations of VLE, which is due to the relatively small temperature dependence of the parameters in the EOS. The original form of RK-EOS is

$$P = \frac{RT}{V-b} - \frac{a/T^{0.5}}{V(V+b)} \qquad \text{...(2-70)}$$

where the constants '*a*' and *'b*' can be expressed as:

$$a = \Omega_a \frac{R^2 T_C^{\ 2.5}}{P_C} \qquad \text{...(2-71)}$$

$$b = \Omega_b \frac{R T_C}{P_C} \qquad \text{...(2-72)}$$

where $\Omega_a = 0.42748$ and $\Omega_b = 0.08664$

The critical compressibility factor (Z_C) of RK-EOS is constant and its value equal (1/3) for all fluids. Because of this shortcoming, the RK equation is inaccurate around the critical region. Also in RK-EOS the expression "α" at the critical temperature has a value =1.0. In original RK equation, the "α" expression is:

$$\alpha = T_r^{-0.5} \qquad \text{...(2-73)}$$

where Redlich and Kwong determined the "α" expression as an integral part of their EOS development, without considering the variation of individual fluids. Noting that Redlich and Kowng developed their equation six years before the acentric factor was proposed. [23]

2.27 Soave and Peng Robinson Equation of State

The parameter $(a / T^{0.5})$ in RK-EOS was modified by Soave [89] in order to increase the influence of the temperature. The parameter, $a(T)$, was correlated to vapor pressure data by Soave who found a more appropriate form to be:

$$a(T) = a_C\, \alpha \qquad \text{...(2-74)}$$

Soave calculated the value of "α" over a temperature range of T_r=0.4 to 1.0 for a number of light hydrocarbons and found that $\alpha^{0.5}$ was a linear function of $T_r^{0.5}$ with a negative slope for each studied fluid.

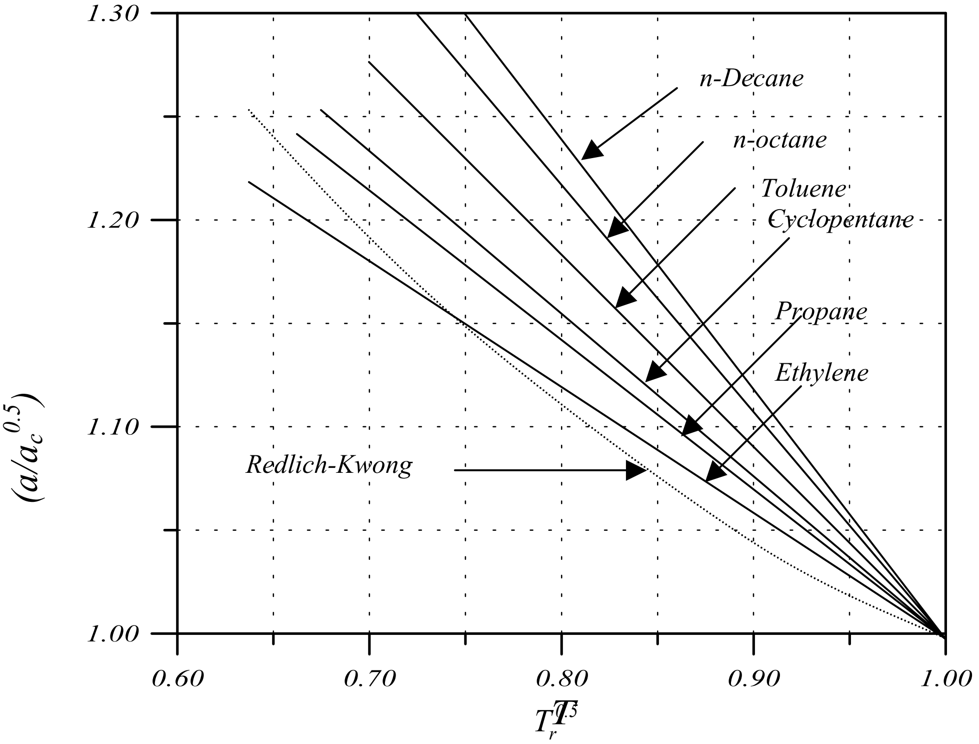


Figure 2-21: Shown Soave and Peng Robinson linear relationship through the derivation

$$\alpha^{0.5} = C - mT_r^{0.5} \qquad \text{...(2-75)}$$

where *C* and m are constants α *=1.0 at* T_r*=1.0* leads to

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 \qquad \text{...(2-76)}$$

$$m = 0.480 + 1.574\omega - 0.176\,\omega^2 \qquad \text{...(2-77)}$$

The constants a_C and *b* can be calculated in the same way as in the original RK-equation [52]. Soave for *Z*-factor in polynomial form is:

$$Z^3 - Z^2 + (A - B - B^2)\,Z - AB = 0 \qquad \text{...(2-78)}$$

The compressibility factor (*Z)* determined from the cubic EOS by solving it with iterative procedure using Newton-Raphson method [93]. Three real roots can be obtained; in the later case, the smallest root will be taken for the liquid phase and the highest one for the vapor phase. [88, 89]

It is interesting to note that Peng Robinson equation of state (PR-EOS) is similar to that obtained by Soave (1972) except that PR-EOS derived for each substance using vapor pressure data from the normal boiling point to the critical point whereas Soave works only in the range of T_r=0.4 to 1.0 and the calculated vapor pressure at T_r=0.7 based on the value of acentric factor. [22]

For all substances examined the relationship between α and T_r can be linearized by the following equation.

$$\alpha^{0.5} = C - mT_r^{0.5} \qquad ...(2\text{-}79)$$

The different choice of the integer parameter C and m results in improvement in the predicted critical compressibility factor to Z_C=0.307 and this leads to generally improved predictions of liquid density. [59]

$$\alpha = [1 + k\,(1 - T_r^{0.5})]^2 \qquad ...(2\text{-}80)$$

where k is a constant characteristic of each substance, as shown in *Figure 2-22*:

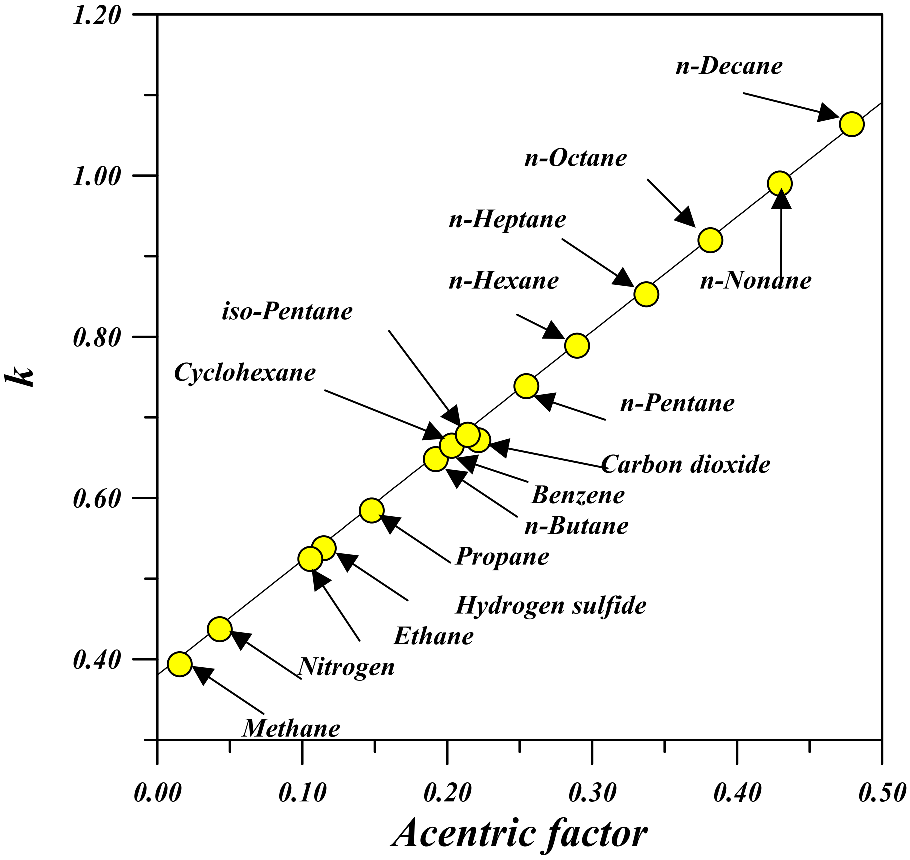


Figure 2-22: Peng-Robinson k factor vs. acentric factor

These constants have been correlated against the acentric factors. The resulting equation is

$$k= 0.37464 +1.54226\,\omega - 0.26992\,\omega^2 \qquad ...(2\text{-}81)$$

PR-EOS has the following form

$$P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)+b(V-b)} \qquad ...(2\text{-}82)$$

Also, it can be written in polynomial form as

$$Z^3-(1-B)Z^2+(A-3B^2-2B)Z-(AB-B^2-B^3)=0 \qquad ...(2\text{-}83)$$

$$\text{With}\quad a=0.457235\frac{R^2\,T_C^{\,2}}{P_C}\quad\text{and}\quad A=\frac{a\,P}{R^2\,T^2} \qquad ...(2\text{-}84)$$

$$b=0.077796\frac{R\,T_C}{P_C}\quad\text{and}\quad B=\frac{b\,P}{R\,T} \qquad ...(2\text{-}85)$$

2.28 Peng-Robinson-Stryjek-Vera Equation Of State (PRSV-EOS)

After careful examination by Stryjek and Vera for the deviation in the calculated vapor pressures at low reduced temperatures for compounds of a wide range of acentric factors, the functional dependence of *k* was modified. High percent deviations between experimental and calculated vapor pressures as a function of reduced temperature given by Peng-Robinson equation was reduced.

In PR-EOS, *k* was expressed as a function of acentric factor only; Stryjek and Vera have assumed *k* to be a function of acentric factor and reduced temperature. [96]

It may be observed that errors are large at all temperatures for compounds with large acentric factor even for non-polar compounds such as hexadecane, the error increases rapidly at low reduced temperatures for all compounds. A major improvement is obtained with the following simple expression for *k.*

$$k=k_o+k_1(1+T_r^{0.5})(0.7-T_r) \qquad ...(2\text{-}86)$$

$$\text{with}\quad k_o=0.378893+1.4897153\omega-0.17131848\,\omega^2+0.0196554\,\omega^3 \qquad ...(2\text{-}87)$$

and k_1, being an adjustable parameter characteristic of each pure compound given by Stryjek and Vera paper at (1986). [94, 95, 96]

PRSV-EOS has the potential to predict more accurately the phase behavior of hydrocarbon systems, particularly for systems composed of dissimilar components, and it can also be extended to handle non-ideal systems with accuracies that rival traditional activity coefficient models. The only compromise is increased computational time and the additional interaction parameter that is required for the equation. [43]

2.29 Some General Notes in Using EOS to Calculate VLE

Many authors investigating equations of state in order to apply them to high and low pressure phase equilibrium calculations [101]. In fact, the thermodynamic models on an EOS show some evident advantages with respect to VLE models, which can be summarized as follows:

1. They are developed from a theoretical based hypothesis concerning the interactions between molecules.

2. They have an explicit temperature-dependence for the pure component parameters, as they are able to describe PVT properties of pure components.

On the other hand, the composition-dependence of the mixture properties depends strongly on the assumptions concerning the mixing and combing rules used to calculate the mixture parameters from those of pure components. [24]

Cubic EOS has proved to be extremely useful. They are simple and can be solved with straight forward algebraic procedure, so that they lead to robust computer programs for the prediction of thermodynamic data to relatively short computing times. They contain only small number of adaptable parameters which can easily be related to the critical properties, so that the equations lend themselves well for generalization and application to mixtures. [36]

SRK and PR are the most successful cubic equations of state for phase equilibrium calculation. The critical compressibility factor for PR-EOS Z_C=0.307. This is a marked improvement over the (1/3) that is predicted by RK and Soave modifications. However, the value is still far from the actual critical compressibility factor of real fluids except for Hydrogen and Helium. On the other hand the failure point of both Soave and Peng-Robinson equations are the assumption of particular (fixed) value of the critical compressibility factor, as a result, the predicted densities of the saturated liquids and the predicted critical volumes differ considerably from their experimental values especially for substances whose critical compressibility is significantly different from the values assumed by these equations. [67, 23]

2.30 Application of Cubic Equation of State to Mixtures

Up to now, mixture properties usually predicted by a cubic EOS together with appropriate mixing rules [108]. The most important use of EOS is perhaps as thermodynamic property generators in chemical process simulators. Current simulator architectures are moving away from the traditional sequential modular to equation-oriented and simultaneous modular. Equations of state that yield simple analytical expression and derivatives for thermodynamic properties are desirable. From both theoretical and practical points of view, mixing rules are most useful when they:

1. are simple,
2. avoid excessive use of parameters,
3. require a light computational load for mixtures with many compounds,
4. reduce to the classical mixing rules for simple mixtures,
5. perform well for asymmetric non-polar mixtures, and
6. obey the quadratic dependency on composition of the second virial coefficient at low-density limits.

Many modifications and improvement of the van der Waals-type equations of state appear in the literature. These modifications incorporate new parameters to the equations and/or modify the classical mixing rules. [61]

There are two basic concepts in the developing of mixing rules which are:

2.30.1 Empirical Mixing Rules

The basic concept in developing a mixing rule is to use an equation given satisfactory results in modeling the liquid state, and then extend it to high pressure calculations and the vapor phase. Most models successfully describing the liquid phase are based on local composition concept: they are flexible enough to describe the complex behavior exhibited by systems containing polar compounds. Suffice it to say that it can quantitatively describe mixtures where non-randomness is involved.

The first attempts to introduce the local composition concept in EOS were empirical: Heyen [39] and Vidal [99]. Although their approaches represented a significant advance in modeling complex mixture phase equilibria, they suffer from several shortcomings. The parameters have no physical significance and do not depend on density; furthermore the equation does not meet the quadratic (theoretical correct) dependence of the second virial coefficient as pressure tends to zero. [58]

2.30.2 Statistical Mixing Rules

Local composition can also be derived from statistical thermodynamics and examined by using computer generator data for model fluids. Lee [53]; Sandler [70]; Diters [21] have investigated the development of statistical mechanics mixing rules in depth and compared their results with computer generated data for different kind of intermolecular potential. The agreement they found was very satisfactory. Furthermore they demonstrated that these models could rarely be applied to phase equilibria involving fluids of industrial interest.

In spite of success of some researchers in describing mixtures of real fluids, the rigorous statistical mechanics treatment of complex systems for which excess Gibbs free energy (G^E) models have customarily been used is not near; on the other hand, empiricism should be introduced at some point in the development. This theoretical approach, however, will be very useful in developing more theoretical based functional relationships for treatment of real fluids. [10, 58]

2.31 Introduction of Mixing and Combining Rules to Improve VLE Calculation

The introduction of new mixing and combining rules is very important in order to improve EOS mixing rules and as a result improve VLE calculated results. Many researchers and authors introduce different forms of mixing and combining rules as presented in the following sub-sections:

2.31.1 Conventional One- Binary- Parameter Form

The using of conventional mixing rule is one of the oldest method which tried by researchers in order to improve EOS results. The mixing or combining rules parameter contains an adjustable parameter. This adjustable parameter tried to decrease the error that might be associated with EOS used and shift the results to higher degree of accuracy. The conventional one binary parameter has the form:

$$a = \sum_i \sum_j x_i \, x_j \, a_{ij} \qquad \ldots(2\text{-}88)$$

$$a_{ij}=(a_{ii}\, a_{jj})^{0.5}(1-k_{ij}) \qquad \ldots(2\text{-}89)$$

$$b = \sum_i x_i \, b_i \qquad \ldots(2\text{-}90)$$

where k_{ij} is the binary interaction parameter or adjustable parameter.

The conventional one binary parameter combining rule in all cases produce not so accurate results for calculation [58, 65]. Such rules are adequate for low density components and regular solutions, such as approximate similar components in hydrocarbon mixtures. In presence of polar compounds they must be improved by introducing empirical correction terms. [87]

2.31.2 Quadratic Two- Binary- Parameter Form

The second modification to mixing rules in order to apply to mixture is required in the presence of dissimilar hydrocarbon mixtures which are greatly differ in their structure and in the case of presence polar compounds. Conventional mixing rules are no more adequate. A higher degree of flexibility must be given, for instance by an extension of the linear law of covolume parameter *'b'* to a quadratic rule, and the introduction of a second empirical binary constant:

$$b = \sum \sum x_i \, x_j \, b_{ij} \qquad \ldots(2\text{-}91)$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - h_{ij}) \quad \text{...(2-92)}$$

where h_{ij} is a second binary interaction parameter used to terminate the error associated with similarity assumption of mixture components shape and size.

Such rules, although theoretically well supported and completely adequate for binary systems, yet fail when applied to multicomponent mixtures. It is likely more complicated rules, involving ternary and higher order terms have to be considered, but it is an impractical route, owing to the extremely large number of terms and long computation times involved. [88]

2.31.3 Adachi-Sugie Type Two- Binary- Parameter Form (AS) Form

In order to increase the results accuracy obtained from any EOS used adjustable parameters which are proposed by Y. Adachi and H. Sugie [108] may be applied. With a linear mixing rule for a covolume parameter *'b'* of a cubic EOS, the calculated thermodynamic property depends on cohesion parameter '*a*' only at specific temperature, pressure, and mole fraction (*x*). Any thermodynamic property calculation is strongly depending on the binary interaction parameters of the modified conventional mixing rules expressed as:

$$a = \sum_i \sum_j x_i\, x_j\, a_{ij} \quad \text{...(2-88)}$$

$$a_{ij}=(a_{ii}\, a_{jj})^{0.5}(1-k_{ij}) \quad \text{...(2-89)}$$

$$k_{ij}=L_{ij}+ m_{ij}\,(x_i - x_j) \quad \text{...(2-93)}$$

where L_{ij} and m_{ij} are binary interaction parameters.

x_i, x_j are mole fractions of component '*i*' and '*j*' respectively

2.31.4 Huron and Vidal Mixing Rules (HV-Mixing Rules)

It is well known that a good reproduction of the VLE behavior of mixtures containing polar components can be obtained only with parameter mixing rules with a high degree of flexibility, i.e. containing a sufficient number (at least two) of adjustable binary parameters.

EOS mixing rules, based on local composition concepts for excess Gibbs energy, were introduced which opened a way to the rich field of the liquid state theories, was that by Huron and Vidal [42]. The original HV-mixing rule at infinite pressure was not largely used because the model parameters (in G^E at infinite pressure) must be adjust and not related to available parameters at low pressure.

The past decade seen a rapid growth in the number of ideas for the direct incorporation of existing model parameters of excess Gibbs energy models in equations of state. These so called G^E-EOS mixing rules use available activity coefficient model parameters from low-pressure data, without change, for predicting phase equilibrium at high pressures and temperatures.

The predictions for the systems containing hydrocarbons at high pressures which were based on UNIFAC pure component group parameters (r and q) in the estimation of the infinite dilution activity coefficients at P=0. This mixing rule opened a way to the rich field of the liquid state theories, by the simple, responsible assumption that, at infinite pressure, the excess Gibbs energy tends to a finite limit, a linear mixing rule of 'b' was confirmed and the following rule was derived:

$$a/b = \sum_i x_i \left[\frac{a_i}{b_i} - \frac{G^E_\infty}{\ln(2)} \right] = \sum_i x_i \left[\frac{a_i}{b_i} - \frac{\ln(\gamma_i \infty)}{\ln(2)} \right] \qquad \text{...(2-94)}$$

and $$b = \sum_i x_i b_i \qquad \text{...(2-90)}$$

This mixing rule in fact is useless in determining the interaction parameters, but it allows defining the analytical form of the mixing rules, by simply assuming for G^E_∞ one of the models available from liquid-sate theory.

Besides, connecting the mixing rules to an excess Gibbs energy make it possible even to predict G^E_∞ by applying the principle of group contributions (Just like in the well known UNIFAC method) [86, 96, 87, 83]. This new mixing rule is suitable for ternary mixtures and it does not contain any adjustable parameter.

Referring to the infinite pressure excess properties avoids any reference to a physical state and allows the treatment of supercritical components also, which was impossible with all the methods based on liquid phase activity coefficients. If a table of infinite pressure group contributions is developed, it can be thus extended to substances like hydrogen, nitrogen, carbon dioxide, etc. which was impossible with UNIFAC and similar methods. [96]

2.32 Adjustable or Interaction Parameter

Chemical engineers are continuously challenged to improve existing operations or design new process. The behavior of mixtures naturally is affected by interactions of unlike molecules, particularly if some are polar. Interactions between triplets and higher combinations usually are less important than those between pairs of components [92].

The simplest way of improving the binary and multicomponent data of a mixture is by the use of adjustable or interaction parameter.

In order to appreciate the limitations of a simple thermodynamic model, we always have to remember that we do not perform calculations from first principles. Our simple equation of sate, even through quite modest in its requirements of basic physical properties, still requires at least some experimental information (critical properties, vapor pressures, and acentric factors) and mixture vapor liquid equilibrium (VLE) or liquid liquid equilibrium (LLE) information. Even when we have this experimental information available, it is known that simple cubic equations of state do not always represent reality. While successful generalizations using a relatively small amount of experimental data can be accomplished for hydrocarbon systems, by the use of corresponding states parameters. [60]

k_{ij} is a binary constant, small compared to unity, characterizing the interaction between molecules '*i*' and '*j*'. For most non-polar system k_{ij} is essential independent of composition. Interaction parameter can be positive or negative, but it seldom gives quantitative good results. The parameter k_{ij} is especially significant for system containing chemically dissimilar components. However, even for systems of chemically similar components, k_{ij} can be different from zero as a result of differences in molecular shapes and sizes. In many cases the parameter k_{ij} is roughly independent of temperature when both components in the mixture are well below their critical temperatures [30]. Interaction parameters values may vary with temperature. In fact, VLE at lower temperatures are much more sensitive to the value of a binary parameter.

2.32.1 Estimating the Adjustable or Interaction Parameter

The interaction parameter for any EOS should be determined by regressing experimental VLE data. Two problems exist related to the regression procedure used to obtain the binary interaction parameter from VLE data [101, 49]:

1. The selection of the objective function to be minimized, and

2. The choice of the criteria which indicate the quantity of regression.

Interaction parameter used to eliminate the non-convergence which occasionally occurs in the calculation for those data points located in the vicinity of the critical point of the binary mixture. An adjustment of the interaction parameter value by excluding some points in that region would improve very much the representation of the remaining data points [107]. Also, any small change in the mixing rules or the binary interaction parameter affects VLE calculations significantly. Conversely, the fugacity coefficients depend on the integral of the *PVT* relation. Therefore, the VLE calculation will not be strongly dependent on the accuracy of the EOS used. Indeed, any small inaccuracies of an EOS can be compensated for by an adjustment in the interaction parameter. [19]

However, the interaction parameter where obtains by minimizing the vapor phase mole fraction values [61]. The optimal binary interaction parameters are those that minimize the difference between calculated and experimental values of an equilibrium related objective function. Popular objective functions used include the deviation in *k*-values, deviations in vapor mole fractions, and deviations in bubble point pressures [61]. For VLE estimation interaction parameter the vapor mole fraction objective function is used. There are several forms of vapor mole fraction objective function, which are:

$$OF = \sum_{i=1}^{N} \left| (y1_i^{exp.} - y1_i^{cal.}) \right| + \sum_{i=1}^{N} \left| (y2_i^{exp.} - y2_i^{cal.}) \right| \qquad \ldots(2\text{-}95)$$

$$OF = \sum_{i=1}^{N} \left| \left(\frac{y1_i^{exp.} - y1_i^{cal.}}{y1_i^{exp.}} \right) \right| + \sum_{i=1}^{N} \left| \left(\frac{y2_i^{exp.} - y2_i^{cal.}}{y2_i^{exp.}} \right) \right| \qquad \ldots(2\text{-}96)$$

$$OF = \sum_{i=1}^{N} \left| \left(\frac{y1_i^{exp.} - y1_i^{cal.}}{y1_i^{exp.}} \right)^2 \right| + \sum_{i=1}^{N} \left| \left(\frac{y2_i^{exp.} - y2_i^{cal.}}{y2_i^{exp.}} \right)^2 \right| \qquad ...(2\text{-}97)$$

and $$OF = \sum_{i=1}^{N} \left| (y1_i^{\exp.} - y1_i^{cal.})^2 \right| + \sum_{i=1}^{N} \left| (y2_i^{\exp.} - y2_i^{cal.})^2 \right| \qquad ...(2\text{-}98)$$

where N is the number of experimental data points. The last form of objective function equation is the more suitable objective function form for estimating the interaction parameter since its minimization procedure is based on the least square method.

Always the theoretical results depend on the main assumption that there is no systematic error either in the measurements or in the model. These conditions are never strictly satisfied in practice. The binary interaction parameters depend strongly on the property calculated but not on the cubic EOS form. [108]

3

Experimental Work and Results

It is necessary to have relevant experimental data in order to make a comparison possible between different theoretical areas of increasing interest for refrigerant mixtures. Although the process engineer is not often called on to obtain experimental VLE data, he must often exercise judgment on the validity of the data and the relative costs and risks to be balanced between designing without additional experimental data desired and insisting that the data can be obtained. In exercising such judgment it is advantageous for the engineer to be familiar with the type of laboratory apparatuses and techniques. The types of apparatus used may generally be classified as single-stage apparatus or multi-stage apparatus. The single-stage devices may be further classified into three types: static, recirculating, and flow. The multistage apparatus generally consists of a calibration laboratory column whose operation may be continuous or batch.

Experimental VLE data must be interpreted quantitively to yield the values of the pertinent parameters that allow the data to be used in process design calculations. Usually the design calculation involves the calculation of vapor composition at equilibrium with a liquid of known composition or vice versa. [38]

3.1 Vapor Liquid Equilibrium Rig

VLE is the foundation for a variety of separation methods that are essential to the process industries. The VLE measurement is difficult, so a high developed laboratory technique is needed in order to obtain more accurate and reliable measurements. The VLE rig used in this experimental work is recirculating single-stage type, which is shown in *Figure 3-1:*

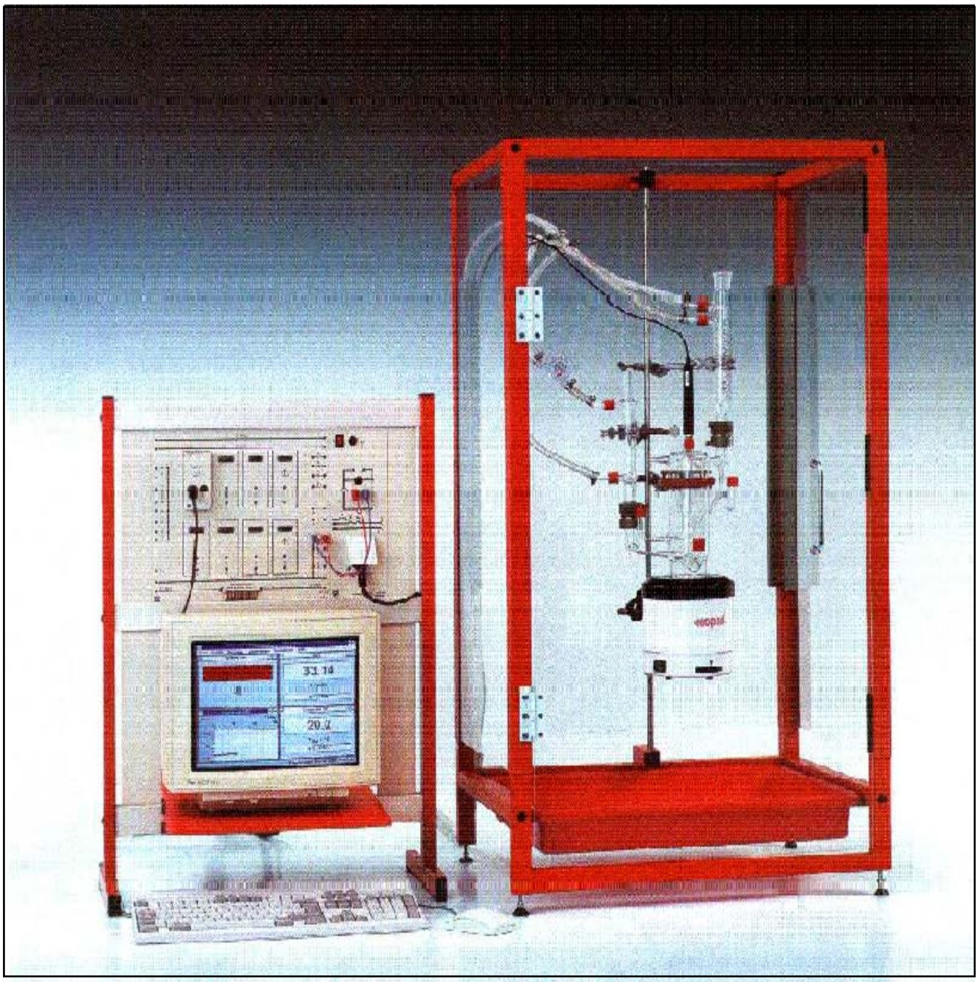


Figure 3-1: Vapor liquid equilibrium rig

The purpose of the stand system is support the equilibrium apparatus and to protect the experimenter.

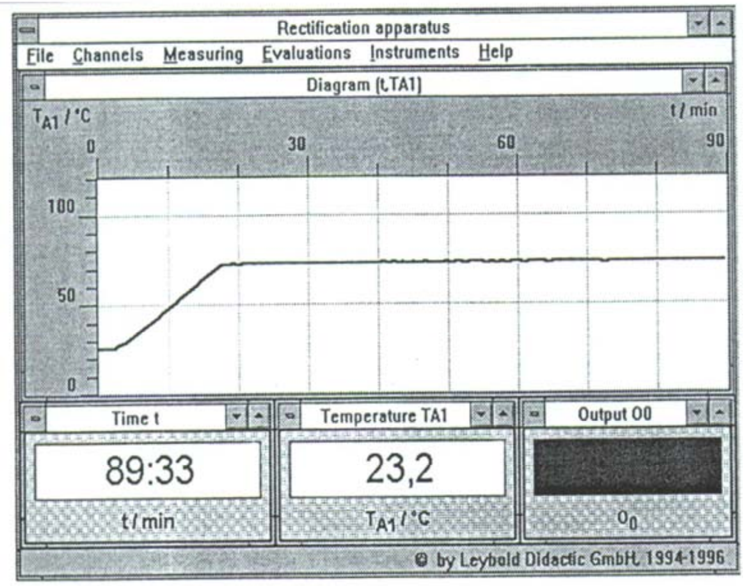
The equilibrium apparatus is used for experimentally determining equilibrium data of mixtures. The boiling temperature can be measured and the proportional material quantities of the liquid and vapor phases can be determined simultaneously.

Measurement, recording and graphical display of the boiling point and measuring time carried out using the *CASSY-C* module and a personal computer.

VLE rig consists of two essential parts, as described below:

3.1.1. Computer controlling and measuring device

This part is responsible for switching on the boiling mantel and start the experiment or switching off the heating mantel and shut down the experiment. Also, it is responsible on measuring the temperature of the mixture throughout the experiment as a function of time and shows a graphical representation of increasing the temperature with time till reaching the boiling point of the mixture as shown in Figure 3-2.



Time t: 89:33 t / min

Temperature TA1: 23,2 T_{A1} / °C

Output O0: O_0

Figure 3-2: Graphical representation of temperature with time by CASSY module

All these responsibilities are carried out by *CASSY* module interface (*Computer Assisted Science System*) with "*Universal Data Acquisition*" program. This is an extremely versatile software package for all purpose use in computer supported measurements and control in areas of chemical engineering and technology.

3.1.2. VLE apparatus

This equilibrium apparatus is used for measuring the equilibrium data point of specified or selected mixture experimentally. This part of VLE rig is made in glass.

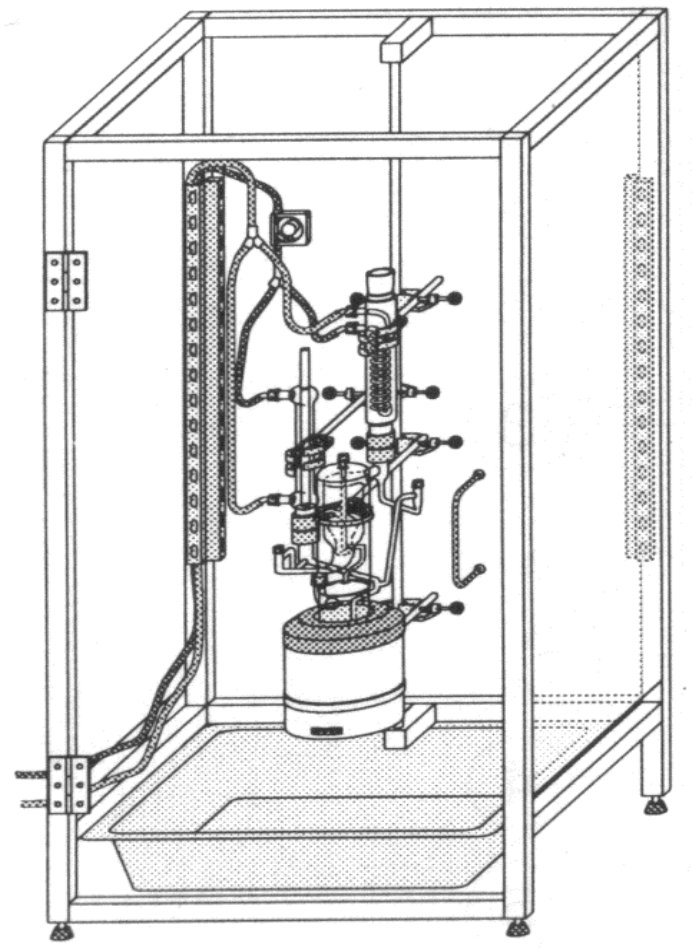


Figure 3-3: Vapor liquid equilibrium apparatus

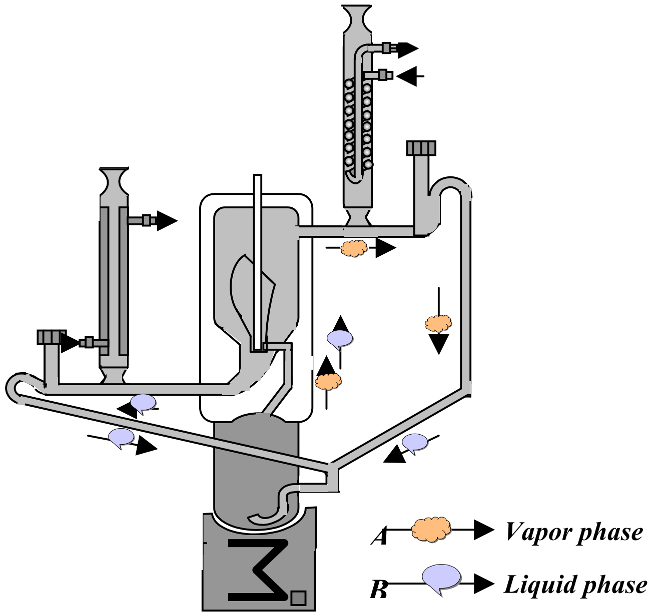


Figure 3-4: Vapor liquid equilibrium apparatus flow diagram

The VLE experiments are performed using an equilibrium apparatus (Figure 3-3) in which the vapor and liquid phases of a binary mixture are circulated continuously at a constant pressure. The binary mixture, whose composition is known, is brought to boil. When equilibrium has been established, samples are taken and the mole fractions of the liquid phase and of the condensed gaseous phase are determined.

Equilibrium has been reached when the number of molecules leaving the liquid equals the number of molecules entering the liquid.

3.1.2.1 Description, Technical Data of Equilibrium Apparatus

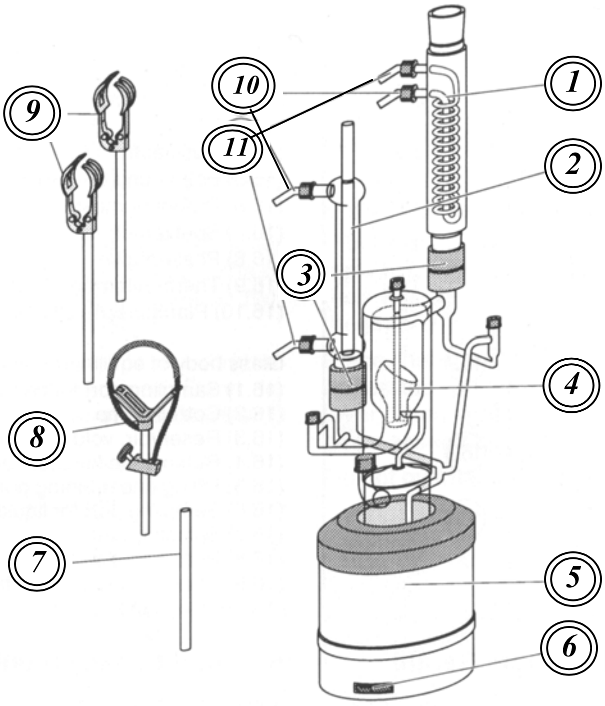


Figure 3-5: Description of technical vapor liquid equilibrium apparatus flow diagram

①	*Dimroth cooler, with 1 flat-ground joint (275 mm long)*
②	*Liebig cooler, with 1 flat-ground joint (250 mm long)*
③	*Double couplings with 1 Teflon seal each*
④	*Glass assembly of equilibrium apparatus, with evacuated double glass mantle (overall length 300 mm)*
⑤	*Housing heating mantle for 100 ml round-bottom flask, with on-off switch and built-in power controller*
⑥	*Power controller of housing heating mantle*

⑦ *Stand rod, 15 cm*
⑧ *Chain clamp*
⑨ *Clamps*
⑩ *Threaded connectors for cooling water outlet*
⑪ *Threaded connectors for cooling water inlet*

3.1.2.2 Scope of Supply of Equilibrium Apparatus

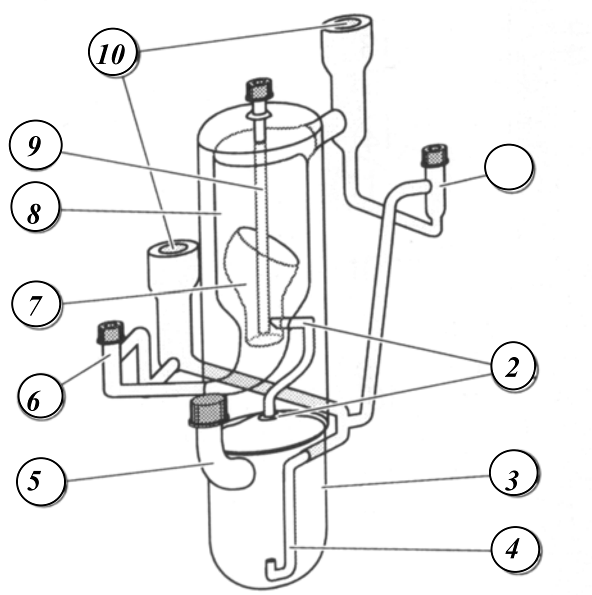


Figure 3-6: represent a scope on supplying equilibrium apparatus

① *Sampling port for condensed vapor phase*
② *Cotrell pump*
③ *Reservoir, volume approximately 175ml*
④ *Reflux tube for liquid and condensed vapor phase*
⑤ *Filling and draining ports of reservoir 3*
⑥ *Sampling port for liquid phase*
⑦ *Splash guard*
⑧ *Phase divider*
⑨ *Thermocouple protection tube*
⑩ *Flat flange*

3.1.2.3 Principle of the Equilibrium Apparatus

The liquid mixture in the reservoir③is heated to boiling by a housing heating mantle ⓹. The circulation caused by vapor bubbles ensure even heating and mixing.

When the vapor bubbles (*A*) pass the funnel-shaped constriction of the cotrell pump ②, they carry a large quantity of non vaporized liquid (*B*) to the phase divider ⑧. Here, the vapor liquid mixture pours over the thermocouple protection tube⑨. The splash guards⑦, which becomes wider higher up, prevents liquid splashes from being vaporized.

In the phase divider⑧, the vapor phase (*A*) and the liquid phase (*B*) are separated. The liquid phase (*B*) drains off laterally to the sampling port⑥, at which it can be sampled through the septum of the screw cap without having to open the apparatus. Sampling via a syringe also prevents contamination of the sample. To condense the vapor residues present in the liquid phase (*B*), the outlet flows into a small vessel, on which a Liebig cooler ⓶ is mounted.

The vapor (*A*) flows through the phase divider ⑧and a lateral outlet to the Dimroth cooler⓵, where it condenses. The condensate (*A*) drips down in a curved tube, which also terminates at a sampling port ①.

The liquid (*B*) and condensate reflux (*A*) flow into a common tube④. This enables remixing of the two phases before they are returned to the reservoir ③.

The tube extends into the reservoir ③and ends inside it with its opening facing upward. The liquid rising in the middle of the reservoir③draws the returned sample out of the tube④ and heats it.

3.2 Mode of Operation of VLE Apparatus

The mode of operation circulation stills provides isobaric data, with a complete *T-x-y* data generated by varying the composition of the initial mixture. [98]

The specified mixture is introduced into the equilibrium apparatus via the filler tube of the storage vessel and brought to the boiling using a heating mantle.

The heating mantle ensures that the number of vapor bubbles remains constant and that the mixture is heated uniformly. The ascending vapor bubbles thoroughly mix the entire volume of liquid, thus preventing a concentration gradient from forming and the boiling liquid from overheating.

When passing through the funnel-shaped taper and tube, the vapor bubbles (A) propel a large quantity of liquid which has not evaporated (B) to the phase separator, where the vapor/liquid mixture pours over the protective sleeve of the temperature sensor. The splashguard, which widens towards the top, ensures that the liquid spray does not evaporate completely, which would complicate establishment of stationary equilibrium. To prevent partial condensation on the glass walls of the phase separator, the equilibrium apparatus is equipped with an evacuated glass mantle consisting of two panes.

The gaseous phase (A) and liquid phase (B) are now separated in the phase separator. The liquid phase (B) runs down the side as far as the sampling point where samples can be taken through the septum without having to open the apparatus. Using a syringe can prevent contamination of the sample. The end of the curve tubing takes the form of a small vessel with a Liebig cooler for the condensation of any residual vapor in the liquid phase. The vapor (A) passes through the phase separator and a side outlet to Dimroth cooler, where it condenses. The condensate (A) drips down into a section of curved tubing, which also ends in a sampling vessel.

The arms for the reflux of liquid (B) and condensate (A), each fitted with a siphon, flow into a common tube allowing both phases to mix before entering the storage vessel once more. This tube extends into the storage vessel with the terminal opening, facing upwards, in the centre of the vessel. The ascending current of liquid in the middle of the storage vessel draws the liquid out of the sample reflux tube for subsequent heating.

3.3 Cleaning the Apparatus

Before starting a new distillation with different mixing proportions or other organic compounds dismount and drain the glass assembly ④. The residues should be captured and stored in a proper manner for future experiments. After draining the glass assembly ④, rinse it out with a little acetone and then allow it to dry.

3.4 Physical Properties of Used Materials

Three n-alkanes components are selected through the experimental work in which their physical properties can be tabulated as shown in *Table 3-1*.

Table 3-1: Physical properties of components used in the experimental work

Component	*Normal B.P. (^{O}C)*		*Density at T=20^{O}C (g/ml)*		*Refractive index ($n^{D}_{20^o}$)*	
	experimental	*literature*	*experimental*	*literature*	*experimental*	*literature*
n-Pentane	36.3	36.2	0.62907	0.626	1.3620	1.3600
n-Hexane	68.2	68.9	0.66043	0.659	1.3786	1.3750
n-Heptane	97.5	98.2	0.68685	0.685	1.3915	1.3900

3.5 Preparing the Experiments

3.5.1 Experiment Calibration Curve

When plotting a calibration curve “refractometric analysis”, the refractive indices at various mole fractions of a binary mixture were determined. This can be achieved most easily using a dilution series. Three binary systems were employed which are:
n-Pentane n-Hexane, n-Pentane n-Heptane, and n-Hexane n-Heptane systems. While, n-Pentane n-Hexane n-Heptane components are employed for ternary system.

I. __Binary Systems__

To prepare the calibration curve for certain mixture taking “n-Pentane n-Hexane n-Heptane” system as an example. The following steps were followed:

a. First placing a beaker on a precision balance, this weighs accurately up to four digits. Tarring the balance with the beaker. Weighting exactly 5 g of n-Pentane analytical grade. Setting the temperature of n-Pentane or refractrometer prism to 20^{o}C. Using a syringe, taking a sample (max. 0.1 ml) and then determining the refractive index $n^{D}_{20^o}$ with a laboratory refractrometer. The measured value now compared with the manufacture’s specifications for chemicals and noted.

b. Afterwards, pouring exactly 0.66359 g n-Hexane into the beaker, mixing briefly, taking a small sample and subjecting it to refractometric analysis. Covering the beaker with a watch glass between measurements. The determination of refractive index of a mixture containing the mole fractions

$$x_{n\text{-}Pentane}=0.9/x_{n\text{-}Hexane}=0.1$$

c. After these measurements, further 0.82957g of n-Hexane was added and proceeding in the same manner.

d. The same procedures are used for the other binary systems.

Upon completion of the total of eleven measurements, the determined refractive indices were plotted against the mole fractions to form the calibration curve "*refractometric analysis*" of the chosen system.

For the selected systems in this work, the following measurements were obtained:

1. For n-Pentane n-Hexane system

Table 3-2: Shows the n-Pentane n-Hexane system dilution series with system measurements for calibration curve at 101.325 kPa

$x_{n\text{-}C5}$	$x_{n\text{-}C6}$	Weight of n-Pentane (g)	Weight of n-Hexane (g)	Refractive index ($n^{D}_{20^o}$)
0.0	1.0	0	5	1.3786
0.1	0.9	5	53.75052	1.3767
0.2	0.8	5	23.88912	1.3760
0.3	0.7	5	13.93532	1.3740
0.4	0.6	5	8.95842	1.3727
0.5	0.5	5	5.97228	1.3716
0.6	0.4	5	3.98152	1.3703
0.7	0.3	5	2.559549	1.3685
0.8	0.2	5	1.49307	1.3670
0.9	0.1	5	0.66359	1.3645
1.0	0.0	5	0	1.3620

Calibration curve "*refractometric analysis*" for this system in *Figure 3*-7.

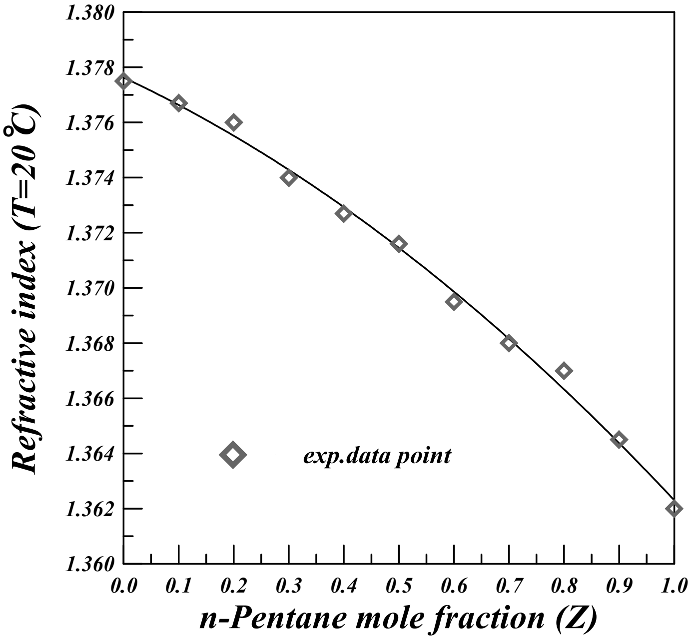


Figure 3-7: Calibration curve for n-Pentane n-Hexane system at 101.325 kPa

2. For n-Hexane n-Heptane system

Table 3-3: Shows the n-Hexane n-Heptane system dilution series with system measurements for calibration curve at 101.325 kPa

$x_{n\text{-}C6}$	$x_{n\text{-}C7}$	Weight of n-Hexane (g)	Weight of n-Heptane (g)	Refractive index ($n^{D}_{20^o}$)
0.0	1.0	0	5	1.3915
0.1	0.9	5	52.32072	1.3905
0.2	0.8	5	23.25365	1.3895
0.3	0.7	5	13.56463	1.3889
0.4	0.6	5	8.720121	1.3869
0.5	0.5	5	5.813420	1.3856
0.6	0.4	5	3.875609	1.3845
0.7	0.3	5	2.491463	1.3831
0.8	0.2	5	1.450453	1.3817
0.9	0.1	5	0.645935	1.3800
1.0	0.0	5	0	1.3786

Calibration curve "*refractometric analysis*" for this system as shown in *Figure 3-8*.

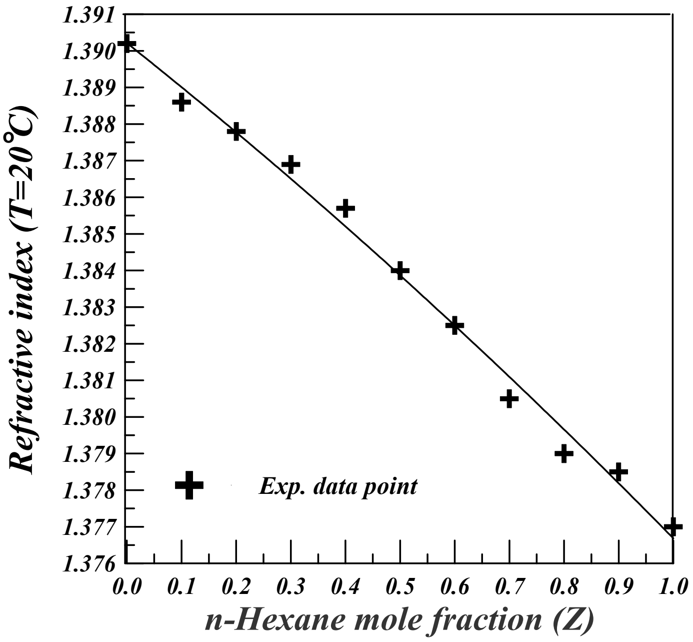


Figure 3-8: Calibration curve for n-Hexane n-Heptane system at 101.325 kPa

Table 3-4: Shows the n-Pentane n-Heptane system dilution series with system measurements for calibration curve at 101.325 kPa

$z_{n\text{-}C5}$	$z_{n\text{-}C7}$	*Weight of n-Pentane (g)*	*Weight of n-Hexane (g)*	*Refractive index* ($n^{D}_{20^o}$)
0.0	1.0	0	5	1.3915
0.1	0.9	5	62.49480	1.3893
0.2	0.8	5	27.77547	1.3875
0.3	0.7	5	16.20236	1.3853
0.4	0.6	5	10.4158	1.3830
0.5	0.5	5	6.43867	1.3800
0.6	0.4	5	4.629244	1.3768
0.7	0.3	5	2.975943	1.3739
0.8	0.2	5	1.735967	1.3705
0.9	0.1	5	0.771541	1.3666
1.0	0.0	5	0	1.3620

Calibration curve "*refractometric analysis*" for this system as shown in *Figure 3-9*.

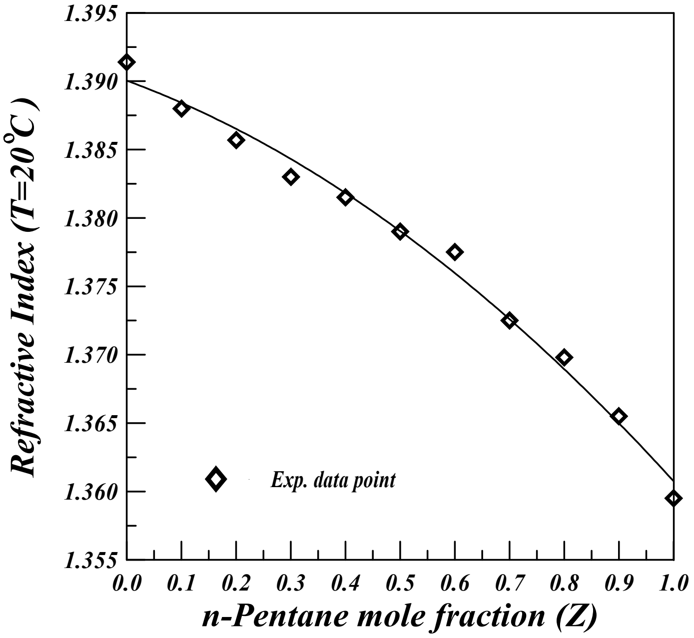


Figure 3-9: Calibration curve for n-Pentane n-Heptane system at 101.325 kPa

II. Ternary System

The calibration curve of ternary system measurements is more complex than the calibration curve of binary system. In this work n-Pentane, n-Hexane, n-Heptane are selected components with 66-measuring data points covering the whole axis's of the triangular diagram calibration curve.

In ternary system another new additional physical property should be measured in order to know the corresponding mole fractions since we have three components instead of two components in binary system. Density and refractive index at 20°C are the two selected measured properties for every point in the ternary system diagram. Following the same procedure as for preparing binary system of specified mole fractions and measuring its physical properties (density and refractive index). Schematic diagram of cross plot of calibration curve of “n-Pentane, n-Hexane, and n-Heptane” ternary system is illustrated in *Figure 3-10*:

— ***Refractive index***

— ***Density***

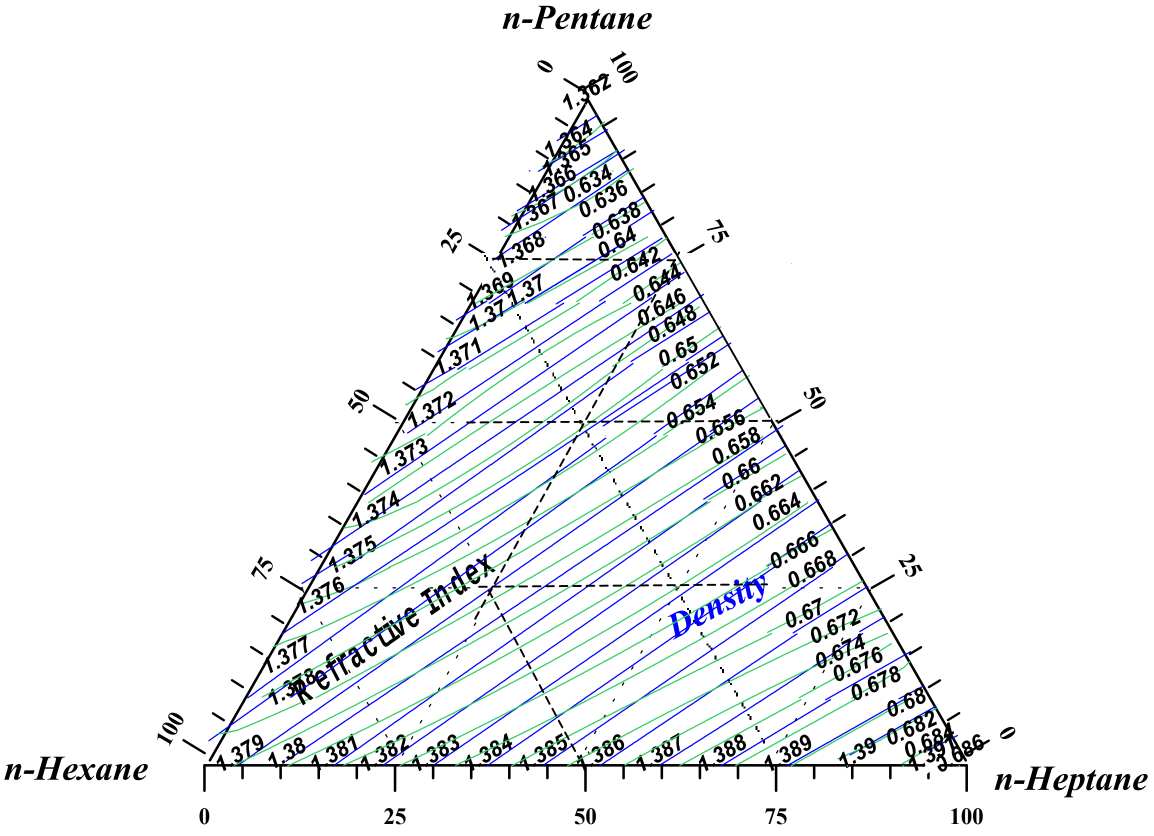


Figure 3-10: Calibration diagram for ternary system n-Pentane n-Hexane and n-Heptane at 101.325 kPa

The diagram shows the lines, which represent various composition of the ternary system at constant values of refractive index. It also shows the lines, which represent various compositions of ternary systems at constant density.

A computer program has been established for this cross plot diagram. That is to read the composition of the ternary system that has certain values of refractive index and density.

3.5.2 Preparing Mixtures with Specific Mole Fractions

The tables with dilution series in previous section also serve as a basis for calculating the exact quantities required to fill the storage vessel of the equilibrium apparatus and thus for selecting the required mole fractions.

As an example, n-Pentane and n-Hexane (system I) with a mole fractions $x_1=x_2=0.5$ are to be mixed. The density of n-Pentane is 0.62907 g/ml, and that of n-Hexane is 0.66043 g/ml. To obtain the above mole fractions 5 g of n-Pentane must be mixed with 5.97228 g n-Hexane. Dividing by the corresponding density gives the volumes (V_1, V_2) of the two components:

7.948241 ml of n-Pentane and 9.043017 ml of n-Hexane, addition of these two values gives the total volume of the mixture of 16.99126 ml.

The capacity of the storage vessel of the equilibrium apparatus is approximately 175 ml. Dividing the capacity by the volume of the mixture, we obtain the coefficient K_V:

$$175/\ 16.99126 = 10.29941 = K_V:$$

The individual volumes of the components now must be multiplied by K_V: in order to exactly fill the equilibrium apparatus with the desired mole fractions:

$$V_{n\text{-}C5}=V_1\,K_V= (7.948241)\ (10.29941) = 81.86221\ ml$$
$$V_{n\text{-}C6}=V_2\,K_V= (9.043017)\ (10.29941) = 93.13777\ ml$$

For the exact setting of the mole fractions $x_1=x_2=0.5$, it follows that 81.86221 ml of n-Pentane with 93.13777 ml of n-Hexane, are poured into a narrow necked vessel.

The same procedure is applied to each binary set in order to prepare it to the experiment. Also, this procedure is followed for ternary system with the corresponding required changes.

3.5.3 Filling the Storage Vessel of the Equilibrium Apparatus

Filling the mixture to be examined into the storage vessel in accordance with the preparations for the experiments described in the operating instructions for the equilibrium apparatus. Several boiling stones were placed in the storage vessel to prevent delayed boiling, which would complicate the establishment of equilibrium. Pouring the prepared mixture into the storage vessel of the equilibrium apparatus via a funnel in the filler tube. To ensure an adequate transport of the liquid and vapor phases to the phase separator, the storage vessel must be filled up as far as the narrowest section of the funnel-shaped taper. Then the filler tube is closed with the screw cap.

3.6 Operating the Equilibrium Apparatus

When the heating mantle has been switch on, the mixture is brought to boil after about 30 minutes. Approximately 20 minutes later, the entire glass apparatus has reached a sufficient temperature for sampling to be commenced. Stationary equilibrium is reached when the composition of the liquid and gaseous phase remains constant for at least two successive measurements.

3.7 Sampling

The most straightforward method of taking samples without influencing stationary equilibrium is to use suitable syringe. Samples (max. 0.1 ml) taking in this manner can now be analyzed for the concentration of the individual components by means of refractrometry for binary system while for ternary system, the samples can be analyzed for the concentration of the individual components in every phase by means of refractrometer for measuring of refractive index and by means of pycnometer for measuring density. The fact that small samples can be taken without opening the apparatus, which means that stationary equilibrium, is not affected.

3.8 Examining the Samples

3.8.1 Refractometric Analysis

Components with high vapor pressures must be subjected to refractometric analysis immediately after the samples have been taken otherwise the composition of the samples would change rapidly as a result of the high volatility.

Furthermore, attention must be paid to the temperature of the samples taken because the refractive index is temperature-dependence and it is generally specified for a reference temperature of 20^{o}C and it has the symbol ($\boldsymbol{n}_{20^o}^{D}$). The analysis is sufficient for binary system, while for the ternary system density measurement is also required.

3.8.2 Density Measurements

Density of liquid is measured by using suitable pycnometer at 20^{o}C, the sample temperature should be kept at this temperature since the density is affected by temperature. This temperature of the sample was kept constant at this temperature by using circulation thermostat with refrigerant unit associated with VLE rig.

3.9 Evaluating the Measured Values

Preparing an Equilibrium Diagram

The composition at equilibrium of the vapor phase y_i of one component is plotted against the composition of the corresponding liquid phase x_i in an equilibrium diagram, under the assumption that the working pressure remains constant, which is equal to the atmospheric pressure.

The experiments with the equilibrium apparatus are repeated for a series of different mole fractions of mixture.

In these experiments, the equilibrium temperature and refractive indices of binary mixture for vapor and liquid phases are determined as shown in *tables: 3-5 and 3-6* and *Figures: 3-11 and 3-12*.

1. n-Pentane n-Hexane System

Table 3-5: Shows the vapor liquid equilibrium experimental data points for n-Pentane n-Hexane system at 101.325 kPa

n-Pentane liquid phase mole fraction (x_1)	*n-Pentane vapor phase mole fraction (y_1)*	*Temperature (^oC)*
0.00000	0.00000	68.2
0.07084	0.17088	64.7
0.15560	0.33555	60.7
0.24288	0.47110	57.0
0.34842	0.60101	53.0
0.47708	0.72309	48.7
0.59189	0.80787	43.8
0.70429	0.87478	42.3
0.79843	0.92141	40.0
0.87293	0.95342	38.3
1.00000	1.00000	36.3

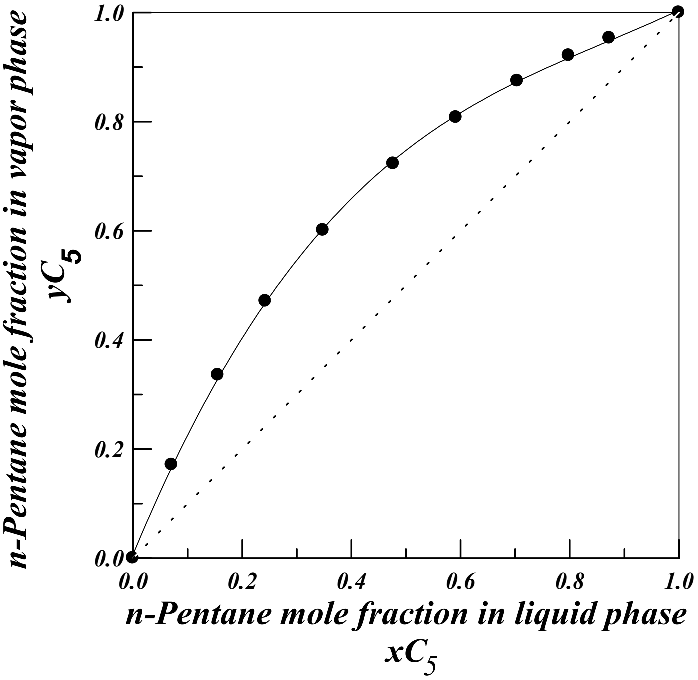


Figure 3-11: Vapor liquid equilibrium diagram (x, y) for n-Pentane n-Hexane system at 101.325 kPa

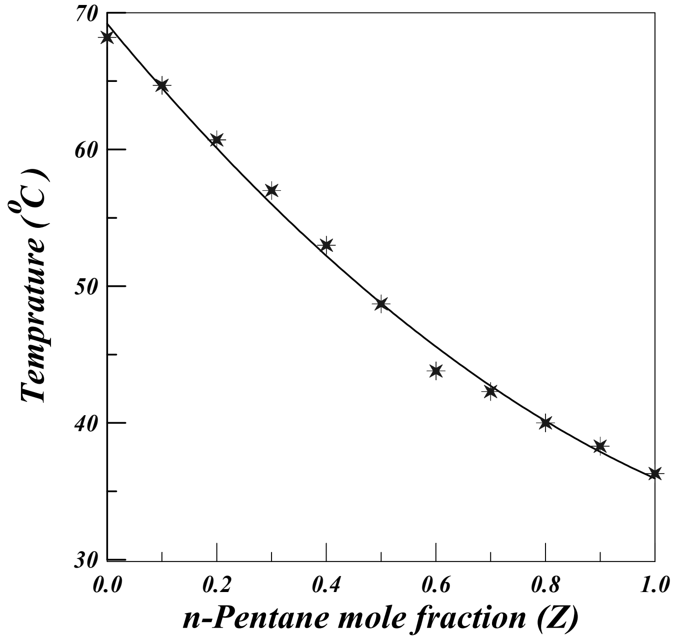


Figure 3-12: Boiling point temperature diagram vs., composition for n-Pentane n-Hexane system at 101.325 kPa

2. n-Hexane n-Heptane System

Table 3-6: Shows the vapor liquid equilibrium experimental data points for n-Hexane n-Heptane system at 101.325 kPa

n-Hexane liquid phase mole fraction (x_1)	***n-Hexane vapor phase mole fraction (y_1)***	***Temperature (^oC)***
0.00000	0.00000	97.5
0.04858	0.10556	96.0
0.12049	0.24200	93.0
0.17948	0.33907	90.7
0.27638	0.47498	87.2
0.37658	0.59090	83.9
0.46914	0.68057	81.1
0.56946	0.76278	78.3
0.66630	0.83024	75.8
0.78416	0.90000	73.1
1.00000	1.00000	68.2

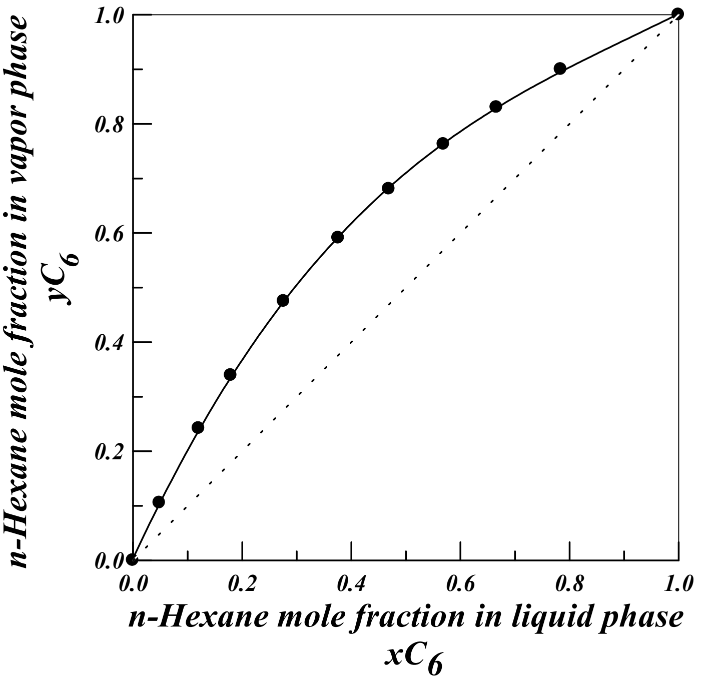


Figure 3-13: Vapor liquid equilibrium diagram (x, y) for n-Hexane n-Heptane system at 101.325 kPa

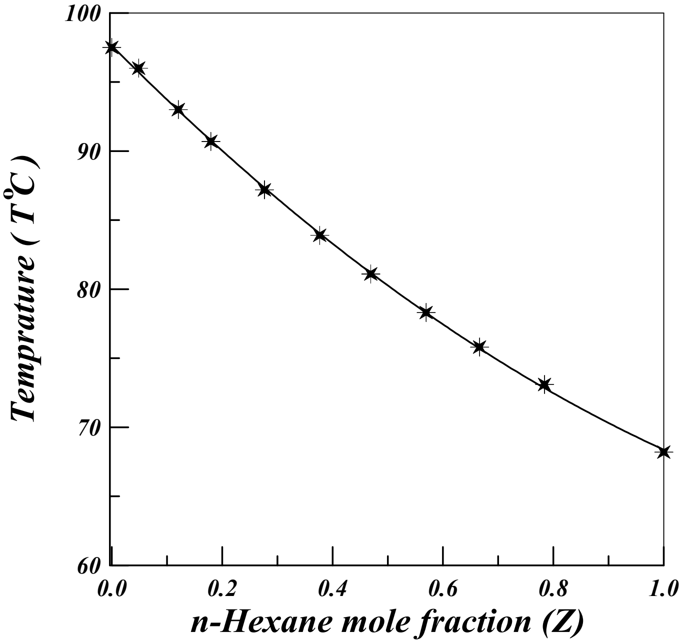


Figure 3-14: Boiling point temperature diagram vs. composition for n-Hexane n-Heptane system at 101.325 kPa

3. n-Pentane n-Heptane System

Table 3-6: Shows the vapor liquid equilibrium experimental data points for n-Pentane n-Heptane system at 101.325 kPa

n-Pentane liquid phase mole fraction (x_1)	*n-Pentane vapor phase mole fraction (y_1)*	*Temperature (^oC)*
0.00000	0.00000	97.5
0.07160	0.31412	87.8
0.13330	0.48818	80.5
0.18782	0.59735	75.0
0.28834	0.73285	66.6
0.38628	0.81665	60.0
0.55008	0.89341	52.3
0.64500	0.93369	47.2
0.75709	0.96143	43.0
0.86083	0.98069	39.6
1.00000	1.00000	36.3

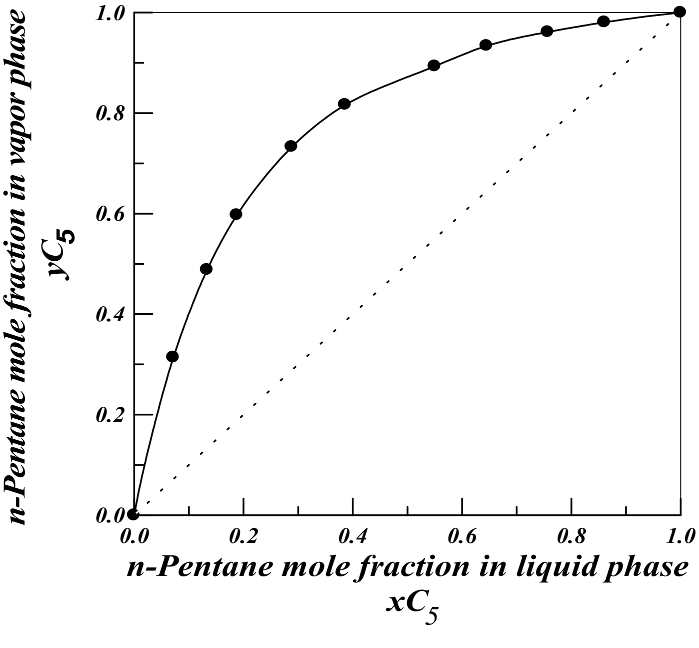


Figure 3-15: Experimental vapor liquid equilibrium curve (x, y) of n-Pentane n-Heptane System at 101.325 kPa

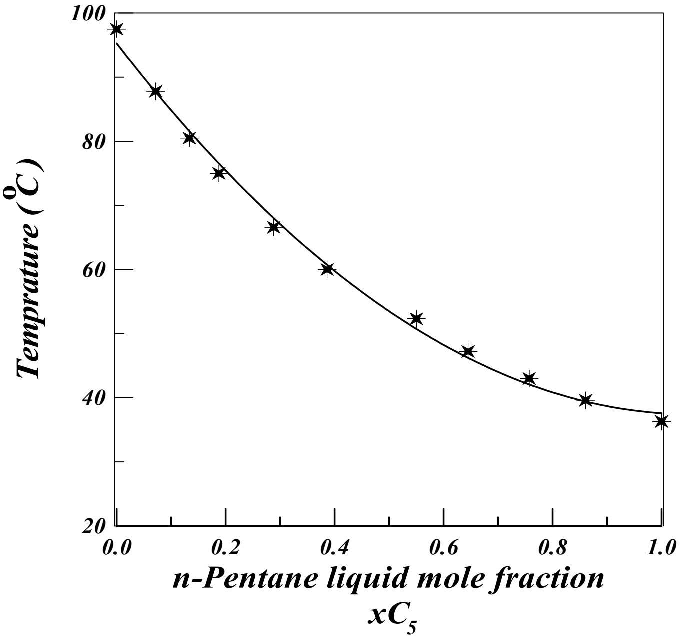


Figure 3-16: Boiling point temperature diagram vs. composition for n-Pentane n-Heptane system at 101.325 kPa

While for ternary system the equilibrium temperature, refractive indices and density are recorded. From the intersection between the density curve and refractive index curve the mole fractions of the liquid phase and vapor phase for each component in the ternary system are determined. The measurements and results of the ternary system are appeared in the following table:

Table 3-7 Vapor liquid equilibrium experimental data points for n-Pentane n-Hexane n-Heptane ternary system at 101.325 kPa

Exp. No.	$z_{n\text{-}C5}$	$z_{n\text{-}C6}$	$z_{n\text{-}C7}$	Refractive Index ($n^{D}_{20^o}$)	Density ρ (g/ml)	Temp. (^oC)	liquid phase mole fraction					Vapor phase mole fraction				
							Refractive Index ($n^{D}_{20^o}$)	Density (g/ml)	$x_{n\text{-}C5}$	$x_{n\text{-}C6}$	$x_{n\text{-}C7}$	Refractive Index ($n^{D}_{20^o}$)	Density (g/ml)	$y_{n\text{-}C5}$	$y_{n\text{-}C6}$	$y_{n\text{-}C7}$
1	0	0.0	1.0	1.3915	0.68685	97.5	1.3915	0.68685	0	0	1	1.3915	0.68684	0	0	1
2	0	0.1	0.9	1.3905	0.68348	96.0	1.3893	0.68477	0	0.04858	0.95142	1.3890	0.67985	0	0.10556	0.89444
3	0	0.2	0.8	1.3895	0.68096	93.0	1.3887	0.67943	0	0.12049	0.87951	1.3863	0.67393	0	0.24200	0.75800
4	0	0.3	0.7	1.3881	0.67861	90.7	1.3881	0.67842	0	0.17948	0.82052	1.3855	0.67186	0	0.33907	0.66093
5	0	0.4	0.6	1.3869	0.67562	87.2	1.3865	0.67432	0	0.27638	0.72362	1.3837	0.668360	0	0.47498	0.525056
6	0	0.5	0.5	1.3856	0.67101	83.9	1.3858	0.67262	0	0.37658	0.62342	1.3829	0.66658	0	0.59090	0.40910
7	0	0.6	0.4	1.3845	0.66974	81.1	1.3844	0.66973	0	0.46914	0.53086	1.3819	0.66454	0	0.68057	0.31943
8	0	0.7	0.3	1.3831	0.66654	78.3	1.3833	0.66740	0	0.56946	0.43054	1.3812	0.66395	0	0.76278	0.23722
9	0	0.8	0.2	1.3817	0.66426	75.8	1.3817	0.66451	0	0.6663	0.3337	1.3805	0.66292	0	0.83024	0.16976
10	0	0.9	0.1	1.3800	0.66158	73.1	1.3808	0.66320	0	0.78416	0.21526	1.3798	0.66173	0	0.90000	0.10000
11	0	1.0	0.0	1.3786	0.66043	68.2	1.3786	0.66043	0	1	0	1.3786	0.66043	0	1	0
12	0.1	0.0	0.9	1.3893	0.68076	87.8	1.3885	0.67965	0.0716	0	0.9284	1.3820	0.66170	0.31412	0	0.68588
13	0.1	0.1	0.8	1.3885	0.67760	84.7	1.3888	0.67949	0.07107	0.09257	0.83636	1.3835	0.66574	0.28903	0.14852	0.56245
14	0.1	0.2	0.7	1.3870	067498	80.9	1.3878	0.67622	0.07762	0.19098	0.7314	1.3820	0.662542	0.28716	0.27548	0.43736
15	0.1	0.3	0.6	1.3858	067203	77.9	1.3865	0.67380	0.07963	0.29009	0.63027	1.3815	0.66087	0.27298	0.38413	0.34289
16	0.1	0.4	0.5	1.3850	0.67015	75.1	1.3853	0.67091	0.08162	0.39111	0.52727	1.3764	0.65220	0.26026	0.47749	0.26225
17	0.1	0.5	0.4	1.3832	0.66709	72.2	1.3837	0.66741	0.08652	0.49523	0.41825	1.3760	0.65200	0.25567	0.55506	0.18928
18	0.1	0.6	0.3	1.3820	0.66560	70.0	1.3825	0.66560	0.08024	0.58962	0.33014	1.3758	0.65155	0.23421	0.62421	0.14158
19	0.1	0.7	0.2	1.3800	0.66052	68.7	1.3809	0.66231	0.07586	0.69882	0.22532	1.3754	065040	0.20413	0.70508	0.09079
20	0.1	0.8	0.1	1.3790	0.65813	66.7	1.3795	0.65909	0.0736	0.80953	0.11687	1.3750	0.64950	0.18758	0.76840	0.04402
21	0.1	0.9	0.0	1.3767	0.65520	64.7	1.3762	0.65495	0.07084	0.92916	0	1.3743	0.64781	0.17088	0.82912	0
22	0.2	0.0	0.8	1.3875	067455	80.5	1.3865	0.67232	0.1333	0	0.8667	1.3775	0.65300	0.48818	0	0.51182
23	0.2	0.1	0.7	1.3862	0.67134	77.0	1.3866	0.67410	0.1414	0.09513	0.76347	1.3755	0.65053	0.47365	0.12274	0.40361
24	0.2	0.2	0.6	1.3848	0.66865	73.7	1.3857	0.67081	0.14975	0.19459	0.65565	1.3745	0.64902	0.46037	0.22801	0.31163
25	0.2	0.3	0.5	1.3840	0.66604	70.4	1.3845	0.66745	0.16083	0.29752	0.54165	1.3735	0.64610	0.45302	0.31600	0.23098
26	0.2	0.4	0.4	1.3822	0.66340	68.2	1.3828	0.66541	0.16141	0.40036	0.43823	1.3730	0.64540	0.4285	0.39785	0.17364
27	0.2	0.5	0.3	1.3813	0.66075	65.9	1.3829	0.66595	0.1649	0.50532	0.32978	1.3725	0.64520	0.41113	0.46799	0.12089
28	0.2	0.6	0.2	1.3790	0.65863	63.9	1.3818	0.66395	0.16585	0.61202	0.22213	1.3723	0.64480	0.39128	0.53269	0.07603
29	0.2	0.7	0.1	1.3776	0.65551	61.8	1.3802	0.65975	0.17036	0.71892	0.11073	1.3722	0.64350	0.37898	0.58579	0.03524

Exp. No.	$z_{n\text{-}C5}$	$z_{n\text{-}C6}$	$z_{n\text{-}C7}$	*Refractive Index* ($n^{D}_{20^o}$)	*Density (g/ml)*	*Temp.* (°C)	*liquid phase mole fraction*					*Vapor phase mole fraction*				
							Refractive Index ($n^{D}_{20^o}$)	*Density (g/ml)*	$x_{n\text{-}C5}$	$x_{n\text{-}C6}$	$x_{n\text{-}C7}$	*Refractive Index* ($n^{D}_{20^o}$)	*Density (g/ml)*	$y_{n\text{-}C5}$	$y_{n\text{-}C6}$	$y_{n\text{-}C7}$
30	0.2	0.8	0.0	1.3760	0.65318	60.7	1.3785	0.65730	0.1556	0.8444	0	1.3720	0.64230	0.33555	0.66445	0
31	0.3	0.0	0.7	1.3853	0.66983	75.0	1.3768	0.65698	0.18782	0	0.81218	1.3740	0.64650	0.59735	0	0.40265
32	0.3	0.1	0.6	1.3839	0.66705	71.4	1.3873	0.67430	0.20203	0.09764	0.70034	1.3730	0.64531	0.58444	0.10686	0.30870
33	0.3	0.2	0.5	1.3830	0.66461	69.4	1.3848	0.66798	0.19959	0.19825	0.60216	1.3720	0.64352	0.54731	0.20431	0.24838
34	0.3	0.3	0.4	1.3811	0.66062	66.4	1.3833	0.66567	0.21069	0.30504	0.48428	1.3715	0.64319	0.53255	0.28688	0.18057
35	0.3	0.4	0.3	1.3791	0.65763	63.2	1.3816	0.66259	0.22796	0.41482	0.35722	1.3710	0.64192	0.52742	0.35323	0.11935
36	0.3	0.5	0.2	1.3778	0.65451	61.0	1.3795	0.65737	0.23334	0.5263	0.24035	1.3705	0.64103	0.50751	0.41811	0.07438
37	0.3	0.6	0.1	1.3765	0.65255	58.7	1.3775	0.65278	0.24318	0.63763	0.11919	1.3703	0.64099	0.49537	0.47062	0.03401
38	0.3	0.7	0.0	1.3740	0.65024	57.0	1.3740	0.64975	0.24288	0.75712	0	1.3701	0.64072	0.4711	0.52890	0
39	0.4	0.0	0.6	1.3830	0.66371	66.6	1.3855	0.66925	0.28834	0	0.71166	1.3703	0.64012	0.73285	0	0.26715
40	0.4	0.1	0.5	1.3815	0.66146	63.5	1.3836	0.66539	0.30491	0.1034	0.5917	1.3680	0.63703	0.71137	0.08888	0.19975
41	0.4	0.2	0.4	1.3800	0.65808	61.2	1.3820	0.66257	0.3124	0.20994	0.47766	1.3675	0.63562	0.6833	0.16785	0.14885
42	0.4	0.3	0.3	1.3785	0.65550	58.6	1.3805	0.66594	0.32751	0.31804	0.35445	1.3673	0.63500	0.66524	0.23399	0.10077
43	0.4	0.4	0.2	1.3768	0.65185	56.0	1.3778	0.65402	0.34725	0.42357	0.22918	1.3672	0.63480	0.65425	0.28639	0.05935
44	0.4	0.5	0.1	1.3749	0.64811	54.9	1.3760	0.65128	0.33802	0.54192	0.12005	1.3670	0.63450	0.61671	0.35341	0.02988
45	0.4	0.6	0.0	1.3727	064553	53.0	1.3735	0.64843	0.34842	0.65158	0	1.3668	0.63402	0.60101	0.39899	0
46	0.5	0.0	0.5	1.3800	0.65808	60.0	1.3830	0.66422	0.38628	0	0.61372	1.3675	0.63485	0.81665	0	0.18335
47	0.5	0.1	0.4	1.3786	0.65533	56.2	1.3810	0.65984	0.42487	0.10674	0.4684	1.3662	0.63452	0.80517	0.07264	0.12219
48	0.5	0.2	0.3	1.3774	0.65252	53.4	1.3785	0.65481	0.45237	0.21132	0.3363	1.3657	0.63392	0.78964	0.13114	0.07923
49	0.5	0.3	0.2	1.3758	0.64899	51.9	1.3766	0.65124	0.45632	0.31868	0.22501	1.3650	0.63240	0.76176	0.18809	0.5015
50	0.5	0.4	0.1	1.3738	0.64529	50.4	1.3744	0.64792	0.46214	0.42569	0.11217	1.3645	0.63180	0.7375	0.23886	0.2364
51	0.5	0.5	0.0	1.3716	0.64266	48.7	1.3720	0.64337	0.47708	0.52292	0	1.3643	0.63150	0.72309	0.27691	0
52	0.6	0.0	0.4	1.3768	0.65310	52.3	1.3787	0.65482	0.55008	0	0.44992	1.3646	0.63180	0.89341	0	0.10659
53	0.6	0.1	0.3	1.3755	0.65012	49.9	1.3770	0.65225	0.55401	0.10696	0.33903	1.3635	0.63165	0.87086	0.05901	0.07014
54	0.6	0.2	0.2	1.3740	0.64642	47.9	1.3748	0.64824	0.57532	0.20908	0.2156	1.3630	0.63143	0.85092	0.10772	0.04136
55	0.6	0.3	0.1	1.3724	0.64407	45.7	1.3719	0.64321	0.60988	0.2935	0.09663	1.3627	0.63115	0.84284	0.14012	0.01704
56	0.6	0.4	0.0	1.3703	0.64036	43.8	1.3697	0.63979	0.59189	0.40811	0	1.3625	0.63087	0.80787	0.19213	0
57	0.7	0.0	0.3	1.3739	0.64699	47.2	1.3729	0.64479	0.645	0	0.355	1.3640	0.63124	0.93369	0	0.06631
58	0.7	0.1	0.2	1.3725	0.64335	44.7	1.3705	0.64086	0.68386	0.10389	0.21225	1.3630	0.63091	0.9161	0.04789	0.03601

Exp. No.	$z_{n\text{-}C5}$	$z_{n\text{-}C6}$	$z_{n\text{-}C7}$	*Refractive Index* ($n^{D}_{20^o}$)	*Density* ρ *(g/ml)*	*Temp.* (°C)	*liquid phase mole fraction*					*Vapor phase mole fraction*				
							Refractive Index ($n^{D}_{20^o}$)	*Density* *(g/ml)*	$x_{n\text{-}C5}$	$x_{n\text{-}C6}$	$x_{n\text{-}C7}$	*Refractive Index* ($n^{D}_{20^o}$)	*Density* *(g/ml)*	$y_{n\text{-}C5}$	$y_{n\text{-}C6}$	$y_{n\text{-}C7}$
59	0.7	0.2	0.1	1.3705	0.64058	43.4	1.3695	0.63929	0.69542	0.20261	0.10197	1.3624	0.63084	0.89434	0.08922	0.01645
60	0.7	0.3	0.0	1.3685	0.63808	42.3	1.3677	0.63680	0.70429	0.29571	0	1.3622	0.63072	0.87478	0.12522	0
61	0.8	0.0	0.2	1.3705	0.64066	43.0	1.3683	0.63608	0.75709	0	0.24291	1.3632	0.63098	0.96143	0	0.03857
62	0.8	0.1	0.1	1.3690	0.63747	41.2	1.3690	0.63828	0.78421	0.10637	0.10942	1.3625	0.63043	0.94051	0.04331	0.01618
63	0.8	0.2	0.0	1.3670	0.63503	40.0	1.3675	0.63252	0.79843	0.20157	0	1.3621	0.63000	0.92141	0.07859	0
64	0.9	0.0	0.1	1.3666	0.63444	39.6	1.3645	0.63222	0.86083	0	0.13917	1.3625	0.63097	0.98069	0	0.01931
65	0.9	0.1	0.0	1.3645	0.63150	38.3	1.3635	0.63042	0.87293	0.12707	0	1.3621	0.62984	0.95342	0.04658	0
66	1.0	0.0	0.0	1.3620	0.62907	36.3	1.3620	0.62907	1	0	0	1.3620	0.62907	1	0	0

The boiling point diagram for ternary system n-Pentane n-Hexane and n-Heptane is shown in *Figure 3-17* below:

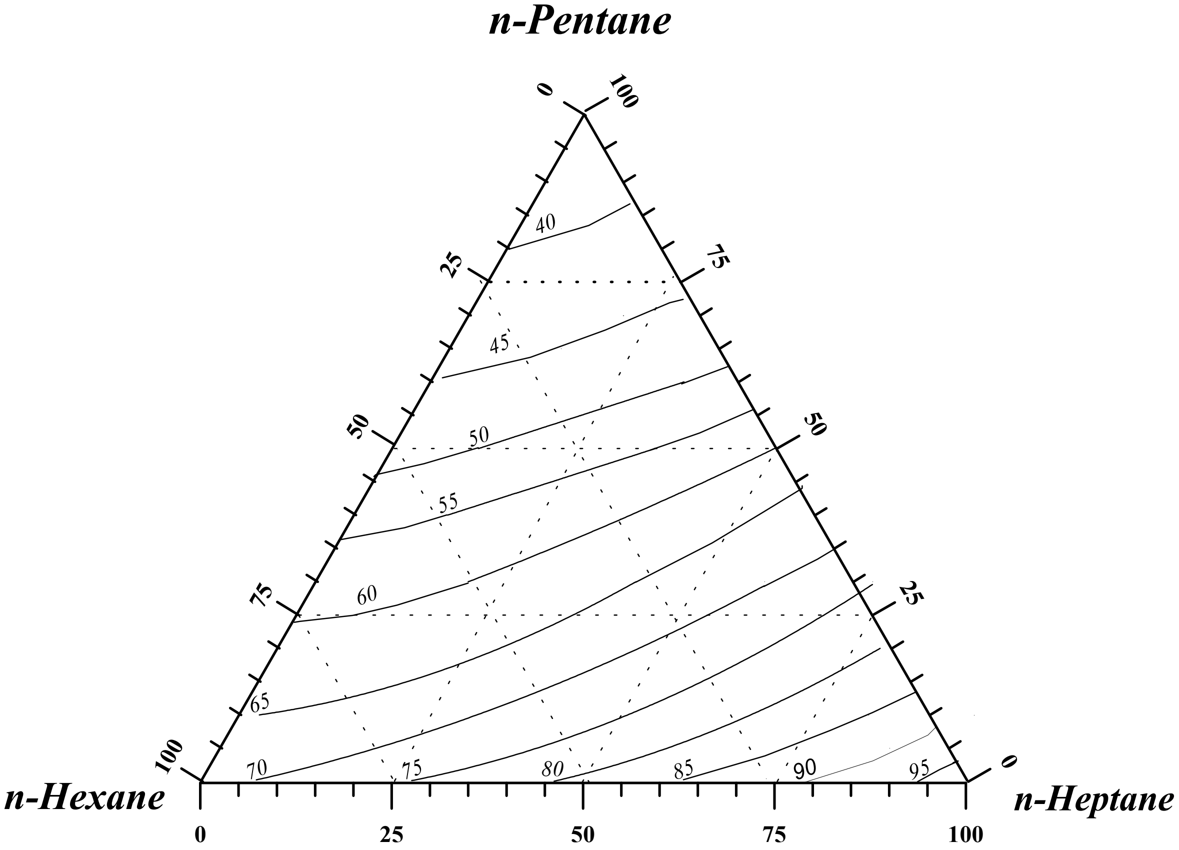


Figure 3-17: Boiling point temperature in Celsius degree of ternary system n-Pentane n-Hexane n-Heptane with mixture composition at 101.325 kPa

The density and refractive indices measurements for this ternary in two dimensional representations have the following shape as shown in *Figures: 3-18 and 3-19*.

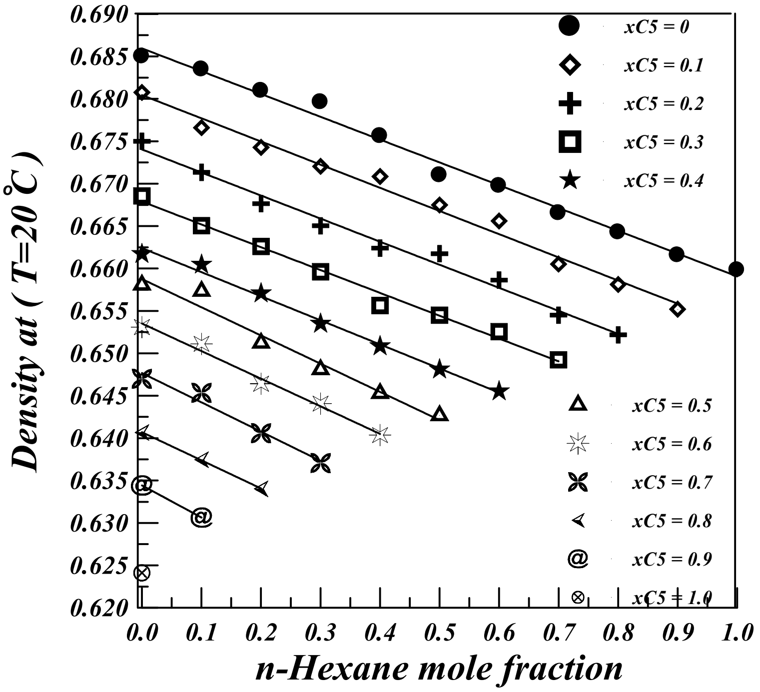


Figure 3-18: Two dimensional representation of density in (g/ml) with n-Hexane mole fraction for the ternary system

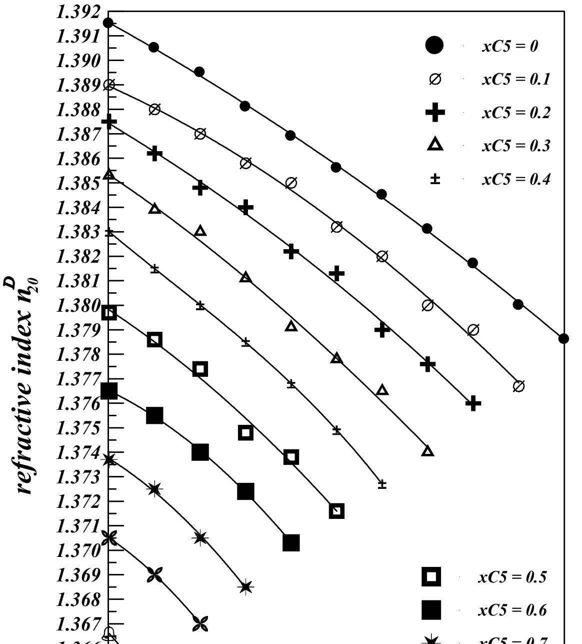


Figure 3-19: Two dimensional representations of refractive indices with n-Hexane mole fraction for the ternary system

While the boiling point temperature with density relationship for the binaries n-Pentane n-Hexane; n-Hexane n-Heptane; and n-Pentane n-Heptane systems for vapor and liquid phases are shown in the following Figures respectively

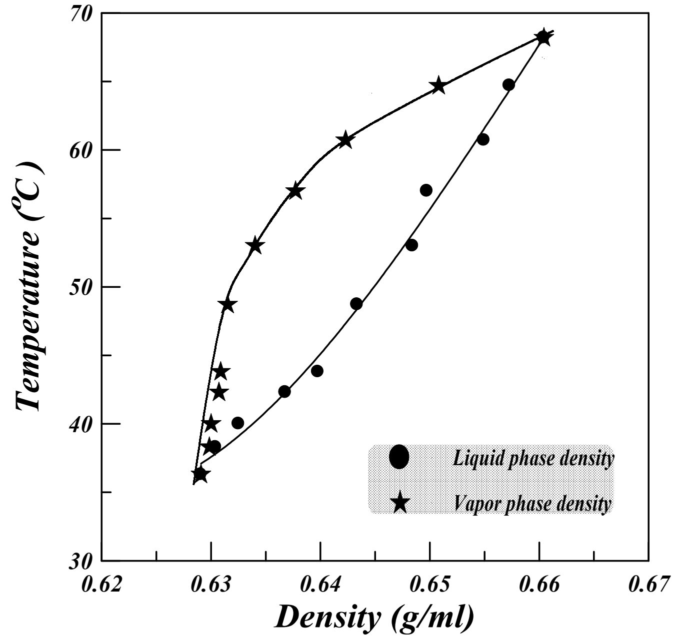


Figure 3-20: Graphical representation of temperature with density relationship for n-Pentane, n-Hexane system at 20^{o}C and 101.325 kPa

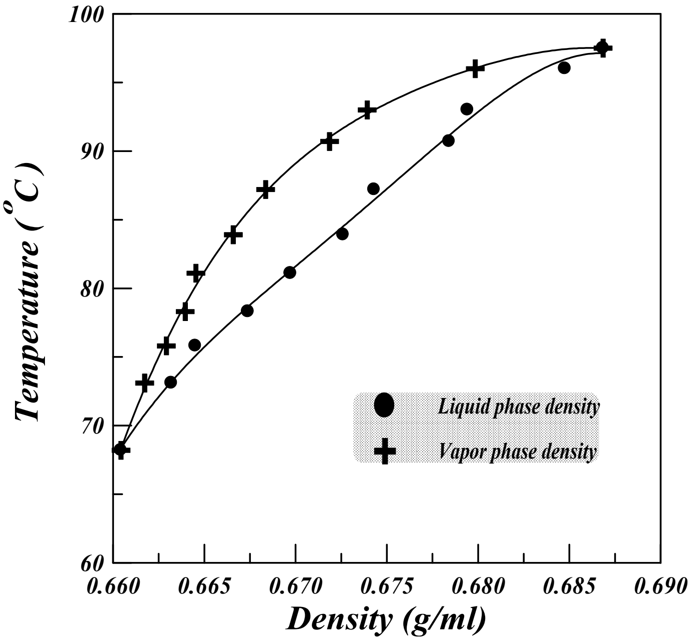


Figure 3-21: Graphical representation of temperature with density relationship for n-Hexane
n-Heptane system at 20^{o}C and 101.325 kPa

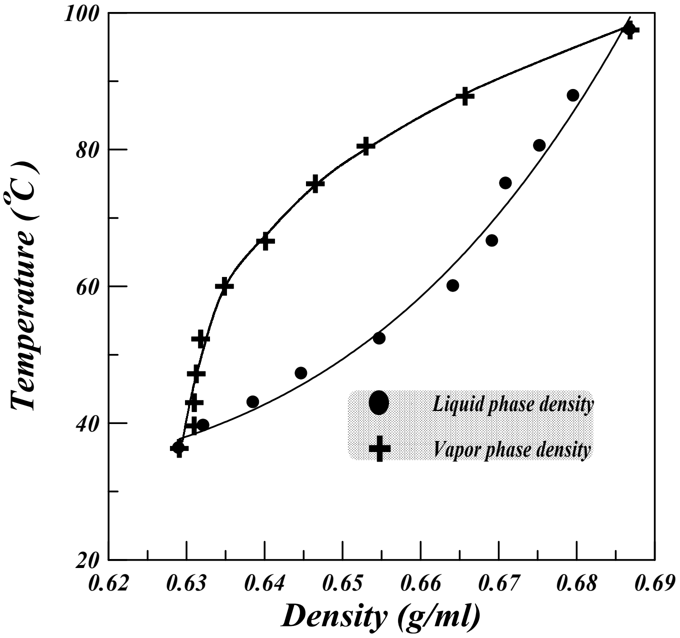


Figure 3-22: Graphical representation of temperature with density relationship for n-Pentane n-Heptane system at 20^{o}C and 101.325 kPa

The boiling point temperature with refractive indices relationship for the binaries n-Pentane n-Hexane; n-Hexane n-Heptane; and n-Pentane n-Heptane systems for vapor and liquid phases are shown in the following Figures respectively

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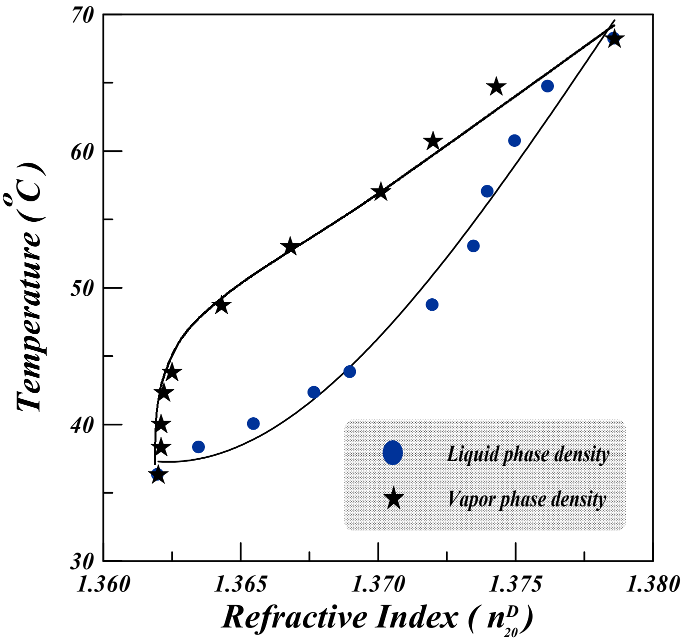

Figure 3-23: Graphical representation of temperature with refractive index relationship for n-Pentane n-Hexane system at 20^{o}C and 101.325 kPa

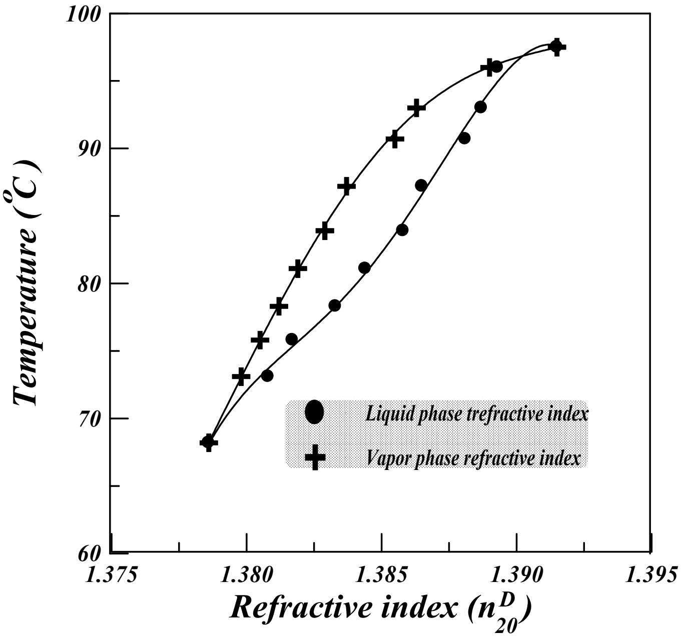

Figure 3-24: Graphical representation of temperature with refractive index relationship for n-Hexane n-Heptane system at 20^{o}C and 101.325 kPa

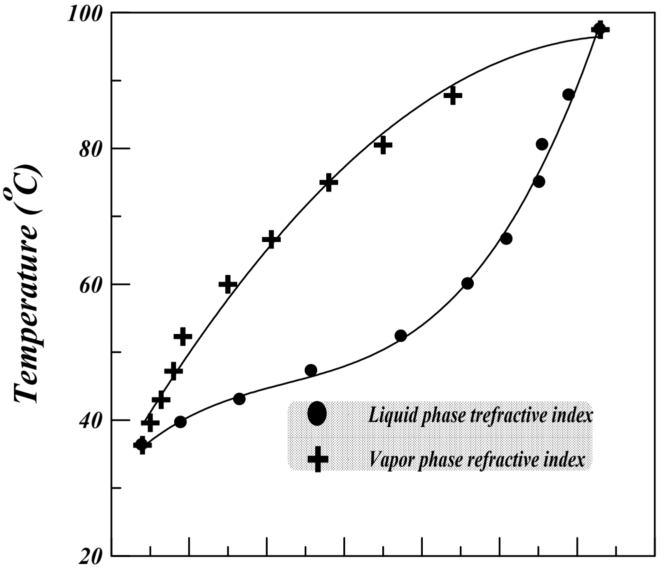

Figure 3-25: Graphical representation of temperature with refractive index relationship for n-Pentane n-Heptane system at 20^{o}C and 101.325 kPa

4

Investigation of a Suitable Model for VLE Calculation of Hydrocarbon Systems

4.1 Why Selecting The Redlich Kwong (RK) EOS Family?

The first, historical reason is that, when a systematic work on EOS was begun, the only available EOS combining ease of treatment and accuracy was those equations of states, which derived from RK equation. Cubic nature made it very practical to use, and unlike second order virial equations it could be applied to liquid phase also.

The availability of the RK-EOS and its derivatives equations were fortunate. Until now it remains one of the better of all two parameter cubic equations.

To prove that, it may be useful to consider the critical isotherms. Their shape varies according to the substance considered, while any two parameters EOS will give single critical isotherm. It is so necessary to accept a compromise, and it seems reasonable to have the best behavior with lighter compounds. For light compounds and far from the critical field (where no cubic EOS is satisfactory any way), Peng-Robinson equation, another two parameter EOS which is claimed to give accurate densities.

4.2 Investigation of a Suitable Method to Predict VLE Data of Hydrocarbon Systems

A number of industrially important processes, such as distillation, absorption, and extraction, bring two phases into contact. When the phases are not in equilibrium, mass transfer occurs between the phases. The rate of transfer of each species depends on the departure of the system from equilibrium. Quantitative treatment of mass transfer rates requires knowledge of the equilibrium states (T, P, and compositions) of the system.

In most industrial processes coexisting phases are vapor and liquid, although liquid/liquid, vapor/ solid, and liquid/ solid systems are also encountered. In this chapter, three different paths are employed in order to calculate and predict VLE then select the most suitable method for n-hydrocarbons VLE calculation. The paths which are followed for VLE of n-hydrocarbons are:

4.2.1 First Path "Prediction of VLE-Data for Both Phases By Means of Cubic Equation Of State"

A suitable EOS when applied to both phases and combined with appropriate mixing rules provides reasonable results in the predication of VLE [102]. The practically identical results in VLE calculations can be obtained form various cubic EOS, in spite of their differences in representing pure-component properties, and these results are frequently comparable to those obtained form more complex EOS calculations, the general practice is to treat the cohesion parameter "a" temperature-dependent in addition to the inclusion of an adjustable binary interaction coefficient k_{ij}.

Cubic EOS is widely used for computerized calculation of VLE data employed in engineering process design. Besides acceptable accuracy for wide-boiling multicomponent mixtures (including noncondensables and supercritical conditions), EOS presents these computational advantages:

1. It requires only values of Tc, Pc, and ω for each component. These are known for pure components and are computed for pseudo-components (petroleum fractions) by readily available correlations.
2. It converges to real roots for Z_V and Z_L in every case, except near the critical point.
3. It requires minimum computer to computes time for highly iterative processes such as distillation when K (equilibrium constant) values depending on liquid composition and vice versa. [101]

4.2.1.1 Selecting of an EOS for VLE Calculation

The RK equation which is modified by Soave, Peng-Robinson equations and their modification are the more current by popular equations for hydrocarbons and hydrocarbons mixture. VLE Calculation by PR-EOS extends the range of applicability over the SRK-EOS, where near the critical point many thermodynamic properties change drastically, apparently approaching either zero or infinity, and at the critical point itself it is no longer possible to distinguish vapor or gas form liquid.

A *critical point*, if it exists, is one at which the properties of that second fluid phase becomes identical to that of the parent phase. The consequences of adopting a classical thermodynamic model, such as most equations of state and the activity coefficient models for predicting phase compositions near to a critical point itself are likely to exhibit quite large errors. The predicted location of the critical point is to a considerable extent depends upon the binary interaction parameters in a particular thermodynamic model and it may be possible to force agreement with experimental data in that respect. When this is not done, there may be appreciable errors associated with the location of the critical point possibly leading to entirely incorrect predictions of the phase behavior in the critical region. As with pure fluids, non-classical equations of state can be constructed that give essentially correct critical behavior, however, their complexity is such that they are unlikely to find wide applications in the near future. Some of equations of state are derived essentially for low and moderate pressure and they can not predict mixture's VLE data under high pressure or compressed liquid.

Nonconvergence occasionally occurred in the calculation for those data points located in the vicinity of the critical point of the binary mixture. An adjustment of k_{ij} value by excluding some points in that region would improve very much the representation of the remaining data points.

Soave and Peng-Robinson equations are of roughly equal reliability for VLE calculations although the representation of *PVT* data. The vicinity of the critical point is better with the Peng-Robinson equation. So, Soave EOS is out of use because it is not capable to produce all the equation mixture roots, while PR-EOS is capable to produce larger number of roots and in region closer to the critical point as shown in *Figure 4-1*.

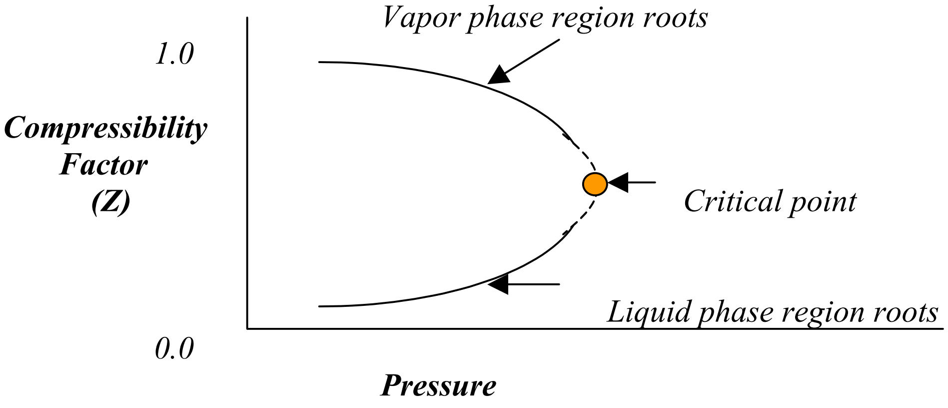

Figure 4-1: Values of Z-factor at temperature below critical temperature calculated with PR-EOS program

Soave EOS is used in order to be applied to calculate VLE data. It is found that this cubic EOS in not capable of producing all the compressibility factors values for a number of systems used in this investigation. While, PR-EOS and its modification PRSV-EOS are capable of representing all the compressibity factors of all investigated systems. So, SRK-EOS is not used in the investigation. PR-EOS and PRSV-EOS are applied to all hydrocarbon systems without using any adjustable parameter (k_{ij}=0) with reasonable accuracy for each EOS.

4.2.1.2 Applying Different Mixing Rules on the Selected EOS

Different forms of mixing rules are applied to 36 binary hydrocarbon mixtures with 376 data points and 14 ternary hydrocarbon systems with 368 data points. Investigation of these forms of mixing and combining rules ability to predict VLE data of hydrocarbons systems and to find the most suitable one to be used with PR-EOS and PRSV-EOS. When applying these forms of mixing and combining rules for VLE. The success of the predictions depends on the accuracy of the EOS used and on the mixing rules used at one hand; and the accuracy of experimental data point at the other hand. These forms of mixing and combining rules are:

1. Conventional Mixing Rules

The oldest method used to improve the VLE results obtained from using an EOS and conventional mixing rules with an adjustable parameter (k_{ij}) which is introduced in the attraction term of an EOS. The method used for determining k_{ij} is by using minimizing objective function (*OF*) method given by Eq.*(2-98)* which has the form

$$OF = \sum_{i=1}^{N} \left| (y1_i^{\exp.} - y1_i^{cal.})^2 \right| + \sum_{i=1}^{N} \left| (y2_i^{\exp.} - y2_i^{cal.})^2 \right| \qquad ...(2\text{-}98)$$

where k_{ij} value required to minimize the error associated from the first principles in the derivation of an EOS and the error from the assumption of equal share forces between like and unlike molecules in the mixture mixing rules. The optimal values of binary interaction coefficient are determined from binary VLE data by minimizing the square of the difference between calculated and experimental values of vapor mole fraction. k_{ij} value is introduced in the attraction term *"a"* parameter of an EOS as described by Eq.*(2-89)* which has the form

$$a_{ij}=(a_{ii}a_{jj})^{0.5}(1-k_{ij}) \qquad \text{...(2-89)}$$

(The values of k_{ij} parameter for the systems used in this work will be shown later)

This introduction of an adjustable parameter improves the EOS mixing rules and reduces the deviation of VLE calculation. This can be seen from the results shown in tables *5-1, 2, 3,* and *4* where for PR-EOS binary system the percent deviations are reduced from 2.84623% to 2.40001% and for ternary systems from 7.18732% to 4.45651%. While for PRSV-EOS binary systems the percent deviations are reduced from 2.6604% to 2.37989% and for ternary systems from 6.8071% to 4.26583%.

2. Quadratic Mixing Rules

This approach method involves the introduction of an adjustable parameter in each parameter of an EOS. The purpose of this mixing rule is to eliminate each parameter of an EOS assumption. The first one for the attraction term parameter, which is responsible for forces between like and unlike molecules where the original EOS derivation theory assumes equal shares of all molecules in the mixture. The second one for the covolume term parameter where the original derivation theory of an EOS assumed that all molecules have equal spherical volumes. This assumption thus corrected this term by the introduction of a new adjustable parameter h_{ij} in the covolume EOS parameter which eliminates the errors associated with this assumption. This adjustable parameter improves the results significantly for mixtures components which have shape far from spherical shape. The quadratic mixing rules have the form:

$$a=\sum_i\sum_j x_i x_j a_{ij} \qquad \text{...(2-88)}$$

$$a_{ij}=(a_{ii}a_{jj})^{0.5}(1-k_{ij}) \qquad \text{...(2-89)}$$

$$b=\sum\sum x_i x_j b_{ij} \qquad \text{...(2-91)}$$

$$b_{ij}=\frac{b_i+b_j}{2}(1-h_{ij}) \qquad \text{...(2-92)}$$

where k_{ij} *and* h_{ij} are adjustable parameters in the attraction and covolume terms respectively. These mixing rules are applied to PR-EOS and PRSV-EOS because these two equations give larger range of application and can cover all the data points range which are near the critical region. The over all average absolute deviations by applying PR-EOS to binary systems are reduced from 2.84623% to 1.82701% and for ternary systems from 7.18732% to 3.64523%. By applying PRSV-EOS the average absolute deviations are reduced from 6.80709% to 3.4558%.

The values of adjustable parameters in conventional and quadratic mixing rules are given in *tables 4-1, 4-2, 4-3, and 4-4:*

Table 4-1: Conventional and quadratic mixing rules adjustable parameters value when applying PR-EOS to binary systems

System	N_P	***Temp. (K)***	***Conventional mixing rules*** k_{ij}	***Quadratic mixing rules***	
				k_{ij}	h_{ij}
Methane + Ethane **[114] ✥**	6	130.3700	-0.07703	0.30519	0.21724
	9	144.2600	-0.07711	0.26319	0.18100
	12	158.1500	0.01552	0	0
	11	172.0400	-0.01316	0.15862	0.10098
	13	186.1100	-0.02310	0.07165	0.05895
	7	188.0400	0.01590	-0.09288	-0.10883
	15	189.6400	-0.01086	0.01739	0.01773
	18	190.9400	-0.01073	0	0
	14	192.3900	0.01030	-0.01828	-0.01822
	7	193.9200	-0.00759	0.12444	0.17202
	8	195.4400	0.00763	0.02463	0.01646
	15	199.9200	0.00167	-0.04063	-0.02876
Methane + Propane **[113]**	5	130.3700	-0.13110	0.16565-	0.14129
	8	144.2600	-0.17698	0.33090	0.25632
	10	158.1500	-0.21357	0.63538	0.43221
	10	172.0400	-0.12837	0.56967	0.38393
	11	187.5400	-0.10443	0.39390	0.27683
	6	190.5800	-0.02433	-0.17782	-0.20427
	13	190.9500	-0.03397	0.14645	0.11715
	14	192.3000	-0.09872	0.36205	0.25697
	15	195.2000	-0.03100	0.33776	0.24678
	14	213.7100	-0.01701	0.24652	0.17765
Ethane + Propane **[117]**	8	144.2611	0.03860	0.08759	0.02787
	9	172.03889	0.07594	0.00228	-0.04336
	9	199.81667	0.08325	0.03252	-0.03185
	8	227.5944	0.12090	0.07315	-0.03095
	11	255.3722	0.16719	-2.80707	-1.76628
Methane + n-Butane **[119]**	7	277.5944	-0.16694	-0.16694	0
	7	344.2611	-0.11046	0.12055	0.10931
	4	377.5944	0.00702	0.14846	0.15696
Propane + iso-Butane **[116]**	12	266.5389	0.00674	0.27254	0.17069
	12	299.8167	-0.19555	-0.23171	-0.02230
	15	338.7056	0.09581	-0.51682	-0.43931
		Pressure (kPa)			
n-Pentane + n-Hexane	11	101.325	0.00357	0	0.14015
n-Pentane + n-Heptane	11	101.325	-0.01572	1.35016	0.00209
n-Hexane + n-Heptane	11	101.325	-0.00563	-0.05195	0.08505

✥ ***Refers to reference which mixture data come from***

Table 4-2: Conventional and quadratic mixing rules adjustable parameters value when applying PR-EOS to ternary systems

System	N_p	***Temp (K).***	***Conventional mixing rules***			***Quadratic mixing rules***					
			k_{12}	k_{13}	k_{23}	k_{12}	k_{13}	k_{23}	h_{12}	h_{13}	h_{23}
Methane +Ethane +Propane **[115]**	6	158.1500	0.02858	-0.18164	-0.13022	-0.32569	0.19968	0.01722	-0.16870	0.16409	0.09407
	15	172.0400	0.03768	-0.142	-0.11816	0.14676	0.32927	0.21605	0.08724	0.25291	0.1734
	19	185.9300	-0.02288	-0.12267	-0.2741	0.01218	0.09783	-0.08907	0.02877	0.12838	0.05492
	29	199.8200	0.06891	-0.06496	-0.06009	-0.06443	0.24081	0.10474	-0.07364	0.18388	0.10013
	24	213.7100	0.02068	-0.0447	-0.06945	-0.07864	0.14791	0.10734	-0.05311	0.12160	0.11100
Methane + Propane+ n-Butane **[119]**	23	304.6200	0	0	0.00518	0.01050	0.01010	0.01010	-0.0100	0	0
	22	305.4500	0.0093	0	0.02379	0	0	0	-0.03761	0	0
	14	306.5000	0	0.05323	-0.17567	0.24604	-1.31045	0.53914	-0.17059	-0.77516	0.58565
Methane + Propane + n-Decane **[112] [118]**	31	244.2611	5.4964	-1.96927	-0.95972	0.38000	-0.64007	0.07236	-1.11223	0.22041	0.35908
	41	255.3722	3.69374	-1.70186	-0.71027	0.66851	-0.55981	0.05994	-0.90170	0.22669	0.29689
	60	294.2611	1.32189	-1.33667	-0.17379	0	-0.47000	0	-0.3	0.05178	0.10730
Methane + Propane + n-Heptane **[112]**	12	233.1500	2.61063	-0.67489	-0.37515	0.52909	0.17604	-0.13931	-0.31699	0.21004	0.08095
	12	244.2611	2.12828	-0.71899	-0.41761	0.63947	-0.02370	0.04372	-0.18153	0.16137	0.20230
		Press. (kPa)									
n-Pentane +n-Hexane +n-Heptane	66	101.325	0	0	-0.38023	-0.15000	-0.02500	-0.03000	0.06828	0.10000	0.06737

Table 4-3: Conventional and quadratic mixing rules adjustable parameters value when applying PRSV-EOS to binary systems

System	N_P	***Temp. (K)***	***Conventional mixing rules*** k_{ij}	***Quadratic mixing rules***	
				k_{ij}	h_{ij}
Methane + Ethane	6	130.3700	-0.08305	0.35693	0.24854
	9	144.2600	-0.07808	0.26069	0.17937
	12	158.1500	0.01630	-0.14884	-0.08897
	11	172.0400	-0.01168	0.14336	0.09049
	13	186.1100	-0.02185	0.06864	0.05551
	7	188.0400	0.01642	-0.10831	-0.12544
	15	189.6400	-0.00820	0.02091	0.01819
	18	190.9400	-0.01081	0.04844	0.03420
	14	192.3900	0.01303	-0.02173	-0.02220
	7	193.9200	-0.00704	0.07491	0.10898
	8	195.4400	0.00884	0.01540	0.00663
	15	199.9200	0.00419	-0.04268	-0.03380
Methane + Propane	5	130.3700	-0.12725	0.10000	0.10263
	8	144.2600	-0.17286	0.29790	0.23636
	10	158.1500	-0.20863	0.61160	0.41616
	10	172.0400	-0.12232	0.54041	0.36404
	11	187.5400	-0.09734	0.38084	0.26545
	6	190.5800	-0.02197	-0.20317	-0.24167
	13	190.9500	-0.02881	0.13247	0.10216
	14	192.3000	-0.09084	0.35224	0.24698
	15	195.2000	-0.06916	0.32978	0.23794
	14	213.7100	-0.03917	0.23950	0.16957
Ethane + Propane	8	144.2611	-0.20094	0.00338	-0.10419
	9	172.03889	0.08962	-0.00186	-0.05448
	9	199.81667	0.08834	0.00007	-0.05526
	8	227.5944	0.12382	0.09497	-0.01876
	11	255.3722	0.16754	-2.86489	-1.79901
Methane + n-Butane	7	277.5944	-0.15658	0.39256	0.26113
	7	344.2611	-0.10789	0.12999	0.11061
	4	377.5944	0.00702	0.15570	0.15504
Propane + iso-Butane	12	266.5389	0.00759	0.00800	0
	12	299.8167	-0.18488	0.05000	-0.09289
	15	338.7056	0.08316	-0.57115	-0.44014
		Pressure (kPa)			
n-Pentane + n-Hexane	11	101.325	0.00782	0.57601	0.36377
n-Pentane + n-Heptane	11	101.325	-0.00227	0.90000	0.55473
n-Hexane + n-Heptane	11	101.325	-0.00928	0.57307	0.36521

Table 4-4 Conventional and quadratic mixing rules adjustable parameters value when applying PRSV-EOS on ternary systems

System	N_p	Temp (K).	Conventional mixing rules			Quadratic mixing rules					
			k_{12}	k_{13}	k_{23}	k_{12}	k_{13}	k_{23}	h_{12}	h_{13}	h_{23}
Methane +Ethane +Propane	6	158.1500	0.027620	-0.17090	-0.12441	-0.19145	0.64459	0.01665	-0.09336	0.36147	0.08066
	15	172.0400	0.03709	-0.13611	-0.11044	0.12902	0.11773	0.07709	0.06663	0.14089	0.09313
	19	185.9300	-0.02240	-0.11642	-0.21512	-0.02546	0.27915	-0.00468	0.01621	0.22635	0.08541
	29	199.8200	0.06991	-0.05829	-0.05447	-0.01133	0.11380	0.04287	-0.04610	0.11009	0.06134
	24	213.7100	0.02127	-0.03887	-0.06278	-0.06018	0.25243	0.11776	-0.04125	0.18227	0.10429
Methane + Propane+ n-Butane	23	304.6200	0.06184	-0.01493	0.06792	0.06952	0.00600	0.01700	0	0.03500	-0.0400
	22	305.4500	0.02023	0	0.03162	0.00491	0	0	-0.02600	0	-0.02242
	14	306.5000	0	0.04876	-0.18377	-0.01038	0.00226	0.00398	-0.11547	-0.06230	0.15915
Methane + Propane + n-Decane	31	244.2611	3.87895	-1.50668	-0.73884	0.70932	0.95083	-0.47665	-0.96620	0.48609	0.13128
	41	255.3722	3.10932	-1.48001	-0.58419	-0.99544	-0.18740	-0.33860	-1.54317	0.28544	0.17018
	60	294.2611	1.00400	-1.16740	-0.12403	0.34098	-0.80587	-0.04929	-0.15261	0.06175	0.04353
Methane + Propane + n-Heptane	12	233.1500	2.42561	-0.61205	-0.33064	0.72253	0.25961	-0.07906	-0.13164	0.22194	0.06859
	12	244.2611	2.03152	-0.64848	-0.39306	0.48558	0.23732	-0.57109	-0.50289	0.21784	-0.06273
		Press. (kPa)									
n-Pentane +n-Hexane +n-Heptane	66	101.325	0.03709	-0.13611	-0.11044	0.12902	0.11773	0.07709	0.06663	0.14089	0.09313

3. Adachi-Sugie Mixing Rules

In this approach method Adachi-Sugie (AS) increased the accuracy of VLE results obtained from any EOS by using binary adjustable parameters in attraction term of an EOS which combines a CEOS for VLE data and a correlation method. AS-mixing rules has the form

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad \text{...(2-88)}$$

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \qquad \text{...(2-89)}$$

$$k_{ij} = L_{ij} + m_{ij}(x_i - x_j) \qquad \text{...(2-93)}$$

Adachi and Sugie directed their efforts on eliminating the errors resulted from the attraction term parameter. They discovered that an EOS is more sensitive to any changes in the value of *"a"* parameter than the change in the *"b"* parameter except for polar compounds. They related the adjustable parameter to composition and two new adjustable parameters that are introduced which are L_{ij} and m_{ij} respectively. The value of L_{ij} and m_{ij} for all systems used are shown in the following tables for both types of equations of state. This mixing rules were applied also to PR-EOS and PRSV-EOS with a linear mixing rules for a covolume parameter *"b"* of a CEOS, the calculated VLE data depend on the cohesion parameter *"a"* only at specified temperature, pressure and mole fraction. The over all averages absolute deviations for binary systems were reduced from 2.8463% to 1.840398% by applying PR-EOS and from 2.66045% to 1.70525% by applying PRSV-EOS. While, for ternary systems they were reduced from 7.18732% to 3.41616% by applying PR-EOS and from 6.80709% to 2.86145% by applying PRSV-EOS.

Table 4-5: Adachi-Sugie mixing rules constants by applying PR-EOS and PRSV-EOS to Binary Systems

System	N_P	***Temp. (K)***	***PR-EOS***		***PRSV-EOS***	
			L_{ij}	m_{ij}	L_{ij}	m_{ij}
Methane + Ethane	6	130.3700	-0.10337	0.26851	-0.10660	0.23247
	9	144.2600	-0.05645	0.17904	-0.05927	0.16388
	12	158.1500	0.00629	-0.06013	0.00541	-0.07080
	11	172.0400	-0.00702	0.08486	-0.00619	0.07583
	13	186.1100	-0.02301	0.05527	-0.02067	0.04975
	7	188.0400	0	0	0.17920	-0.23000
	15	189.6400	-0.01033	0.02692	-0.00797	0.02207
	18	190.9400	-0.01392	0.033	-0.01136	0.02828
	14	192.3900	0.00985	-0.0169	0.01246	-0.02155
	7	193.9200	0	0	-0.0340	0.03100
	8	195.4400	0	0	0.01065	-0.00292
	15	199.9200	0.00326	-0.0194	0.00610	-0.02317
Methane + Propane	5	130.3700	-0.14490	0.17426	-0.13930	0.15391
	8	144.2600	-0.22339	0.33126	-0.21519	0.30492
	10	158.1500	-0.26672	0.66970	-0.26133	0.62515
	10	172.0400	-0.20218	0.59183	-0.19293	0.56204
	11	187.5400	-0.14895	0.40135	-0.13962	0.38403
	6	190.5800	0	0	0.02722	-0.05361
	13	190.9500	-0.07447	0.14439	-0.06737	0.13786
	14	192.3000	-0.13549	0.37150	-0.12531	0.35349
	15	195.2000	-0.14270	036637	-0.13257	0.35089
	14	213.7100	-0.07836	0.25545	-0.06996	0.24239
Ethane + Propane	8	144.2611	0.05327	-0.08158	-0.21263	0.09482
	9	172.03889	0.08867	-0.14147	0.09694	-0.19473
	9	199.81667	0.11704	-0.15446	0.13380	-0.20228
	8	227.5944	0.12347	-0.10745	0.12550	-0.11143
	11	255.3722	0.18878	-0.18262	0.18713	-0.17672
Methane + n-Butane	7	277.5944	-0.10816	0.48964	-0.10118	0.46123
	7	344.2611	-0.04077	0.19738	-0.03330	0.19740
	4	377.5944	0.02325	0.33407	0.01385	0.33017
Propane + iso-Butane	12	266.5389	0.00699	-0.00673	0.00801	-0.00777
	12	299.8167	0.00418	-0.51210	0.01392	-0.42698
	15	338.7056	0.10977	-0.15769	0.09568	-0.10920
		Pressure (kPa)				
n-Pentane + n-Hexane	11	101.325	0.00822	0.04284	0.27475	0.00738
n-Pentane + n-Heptane	11	101.325	0.141154	0.31364	-0.19565	0.04425
n-Hexane + n-Heptane	11	101.325	0.015910	0.05955	-0.10521	0.68689

Table 4-6: Adachi-Sugie mixing rules constants by applying PR-EOS and PRSV-EOS to Ternary Systems

System	N_p	**Temp (K).**	**PR-EOS**						**PRSV-EOS**					
			L_{12}	L_{13}	L_{23}	m_{12}	m_{13}	m_{23}	L_{12}	L_{13}	L_{23}	m_{12}	m_{13}	m_{23}
Methane +Ethane +Propane	6	158.1500	-0.04727	0.19851	-0.24919	-0.20654	1.62858	-1.11067	-0.04820	0.19575	-0.23852	-0.21922	1.56262	-1.06617
	15	172.0400	-0.00174	-0.17991	-0.07109	0.08256	0.55395	0.04593	0.00177	-0.17700	-0.06764	0.08966	0.45645	0.05206
	19	185.9300	-0.00053	-0.18312	-0.20596	0	0.26803	0	-0.00499	-0.17654	-0.19523	0	0.29753	0
	29	199.8200	0.02365	-0.08739	-0.04050	0.16230	0.08677	0.21207	0.02698	-0.07731	-0.03017	0.15718	0.06021	0.16815
	24	213.7100	0.00238	-0.08428	-0.03358	-0.03154	0.28555	0.04768	0.01873	-0.05777	-0.03376	0.01747	0.09854	0.08880
Methane + Propane+ n-Butane	23	304.6200	0	0	-0.00014	0	0	0	0.0096	0	0.06661	0	0	0
	22	305.4500	0.02033	0	0.03307	0	0	0	0.02087	0	0.02000	0	0	0
	14	306.5000	0	0.05617	-0.17650	0	0	0	0	0.05700	-0.12710	0	0	0
Methane + Propane + n-Decane	31	244.2611	-0.58921	0.02276	-0.40129	-11.5292	1.37007	2.09665	-2.05859	-0.53371	-0.48816	10.85368	1.26154	2.03711
	41	255.3722	-3.74565	0.84633	-0.14036	4.58576	6.41757	1.46385	-3.79259	0.79432	-0.09179	4.89665	5.79834	1.48859
	60	294.2611	0.33104	-0.33183	-0.25295	-0.68481	1.62755	0.23879	0.18568	-0.24342	-0.24606	-0.49439	1.18298	0.27628
Methane + Propane + n-Heptane	12	233.1500	-0.88112	-0.29485	0.15662	-0.41107	1.86515	0.42052	-0.09708	-0.33138	0.2679	0.09039	1.42752	0.18656
	12	244.2611	0.08813	-0.16426	-0.18772	-0.40491	1.84393	0.93178	0.33219	-0.25264	-0.19121	-0.08707	1.33524	0.90725
		Press. (kPa)												
n-Pentane+n-Hexane+n-Heptane	66	101.325	-0.05383	-0.14258	-0.19342	0.57623	0.69877	0.04494	-0.28008	-0.12265	-0.17355	-0.05184	0.64414	0.00289

4.2.2 Second Path: Prediction of VLE Data by Using CEOS for the Vapor Phase and Activity Coefficient Model for the Liquid Phase

An EOS has found wide application for the treatment of gaseous fluids, while still inapplicable to the liquid state and phase equilibria with different compounds of different chemical structures.

Another way of modeling VLE is to use activity coefficient models for the liquid phase and an EOS for the vapor phase. Activity coefficient methods are generally applied to low pressure VLE where pressure corrections are unimportant. Several liquid activity coefficient models are suitable and in this work UNIFAC and Wilson models are selected to represent the liquid phase activity coefficient, on the other hand, many equations of state models, including the two equations mentioned earlier with all kinds of mixing rules can be used to represent the vapor phase.

4.2.2.1 Selection of a Proper Model to Calculate VLE Data of Hydrocarbon Systems

In this study, mixtures that contain species that are similar in size and in the nature of their intermolecular forces are termed *homogeneous mixtures*. The accuracy of correlations of VLE data for a number of homogeneous binary and ternary systems using the CEOS and mixing models are shown in the discussion chapter.

PRSV-EOS with AS mixing rules are selected to represent the vapor phase since it gives approximately the more accurate results for binary and ternary systems used in this study. While, for the liquid phase UNIFAC and Wilson models are used as will be shown later.

In this path the equilibrium constant k_i for the binary and multicomponent systems is determined from Eq.*(2-33)* which has the following form:

$$k_i = \frac{\gamma_i \phi_i^{osat} P_i^{sat}}{\hat{\phi}_i^V P} \exp\left(\frac{V^L\left(P - P_i^{sat}\right)}{RT}\right) \qquad ...(2\text{-}33)$$

where the saturation pressure is calculated by applying Wagner equation. Liquid volume is calculated by assuming the liquid volume is equal to the saturated liquid volume and applying Rackett equation to calculate it.

4.2.2.2 PRSV-EOS with AS-Mixing Rules to Represent Vapor Phase and UNIFAC Model to Represent Liquid Phase

A cubic equation of state of PRSV with AS- mixing rules are used to represent the vapor phase fugacity coefficient while UNIFAC model is used to calculate the activity coefficient for binary and ternary hydrocarbon systems. The over all average absolute deviations using this method for 23 binary systems are 9.31151% while for the 5 ternary systems are 16.36047%.

4.2.2.3 PRSV-EOS with AS-Mixing Rules to Represent Vapor Phase While Wilson Model Is Used to Represent the Liquid Phase

In this part of the second path Wilson equation which is based on local composition is selected to represent the liquid phase activity coefficient. By using both Wagner equation for calculation of saturation pressure and Rackett equation to calculate the liquid volume as in the first part of the second path. This part is applied to the same binary and ternary hydrocarbon systems as in the first part of this path. The over all average absolute deviations for the binary hydrocarbon systems are 3.07893%. While for the ternary systems are 3.63660%. The systems detailed results will be shown in discussion chapter tables.

4.2.3 Third Path: Prediction of VLE Data from Activity Coefficient Model at Infinite Dilution

The description of the behavior of any system, both by the EOS route (path one) and activity coefficient route (path two), requires the use of specific interaction parameters, which are typical of the pair of components considered which must be determined by correlation of specific experimental data. It is impossible however to determine previously all the parameters required to describe any possible system, or even a sufficient number of systems, since the number of required parameters are proportional to the square of the number of substances.

The application of any cubic EOS to system components requires an approximate mixing rule for the EOS parameter *"a"*. Huron and Vidal (HV) pioneered linking the EOS parameter *"a"* to excess Gibbs free energy at infinite dilution which has the following form when HV proposed their new mixing rules and applied it to RK-EOS and NRTL model excess Gibbs free energy.

$$\frac{a}{RTb}=\sum_{i=1}^{N}x_i\frac{a_i}{RTb_i}-\frac{G_\infty^E}{RT} \qquad \ldots(2\text{-}94)$$

These equation parameters can be for any type of CEOS where PR and PRSV equations are used. While, the excess Gibbs free energy involving in the HV-mixing rules can be determined from any model of activity coefficient where in this path UNIFAC and Wilson equation model are used. The models of combinatorial excess Gibbs free energy of mixing rules at infinite dilution G_∞^E are given as:.

Model	**Equation**	***Reference***
UNIFAC	$\frac{G_\infty^E}{RT}=\sum_{i=1}^{N}x_i\ln(\frac{\Psi_i}{x_i})-\frac{z}{2}\sum q_ix_i\ln(\frac{\Psi_i}{\vartheta_i})$	[108]
Wilson	$\frac{G_\infty^E}{RT}=-\sum_i x_i\,ln\left(\sum_j(x_j\Lambda_{ij})\right)$	[26]

4.2.3.1 Using UNIFAC Activity Coefficient Model

The predictions of VLE data for the systems containing hydrocarbons at normal and high pressures with the share of PRSV-EOS since it gives the more accurate results and based only on UNIFAC pure component parameters (R_k and Q_k). The over all average absolute deviations of VLE data of 36 binary hydrocarbon systems are 2.60706 %. While, the over all average absolute deviations for 14 ternary hydrocarbon systems are 6.08109 %.

It must be mentioned that in alkane-alkane systems only the combinatorial part of the UNIFAC model is used, since no interaction coefficients are involved. There is no residual term for alkane-alkane systems i.e there is no residual part. The UNIFAC model is used in this path for generating the excess Gibbs free energy at infinite dilution on the whole scale of mole fractions of any selected system.

A modified procedure of using HV-mixing rules based on UNIFAC activity coefficients at infinite dilution is also tried in order to get more accurate VLE predictive data for the hydrocarbon systems. These modifications are:

1. Trying to use quadratic mixing rule for *(a/b)* term of modified HV-mixing rules i.e the mixing rules will have the following form

$$a/b=\sum_i\sum_j x_i x_j\left[\frac{a_{ij}}{b_i}-\frac{G^E_\infty}{ln(2)}\right]=\sum_i\sum_j x_i x_j\left[\frac{a_{ij}}{b_i}-\frac{ln(\gamma_i^\infty)}{ln(2)}\right] \qquad \ldots(4\text{-}1)$$

where

$$a_{ij}=(a_{ii}a_{jj})^{0.5}(1-k_{ij}) \qquad \ldots(2\text{-}89)$$

$$b=\sum_i\sum_j x_i x_j b_{ij} \qquad \ldots(2\text{-}91)$$

$$b_{ij}=\frac{b_i+b_j}{2}(1-h_{ij}) \qquad \ldots(2\text{-}92)$$

Noting that h_{ij} in this path was taking equal to zero.

The results are improved since an adjustable parameter k_{ij} was introduced the over all average absolute percent deviation are reduced from 3.97047% to 2.22391% for the 36 binary systems and they are reduced from 10.22861 % to 3.633341 % when the adjustable parameter was introduced in the ternary hydrocarbon systems.

The values of the new adjustable parameter (k_{ij}) when UNIFAC model was used for the binary and ternary systems will be shown in the following tables respectively

Table 4-6: Values of an adjustable parameter when quadratic mixing rules applied on third path and using UNIFAC model for binary hydrocarbon systems

System	N_P	***Temp. (K)***	k_{ij}
Methane + Ethane	6	130.3700	-0.14954
	9	144.2600	-0.14031
	12	158.1500	-0.04128
	11	172.0400	-0.07157
	13	186.1100	-0.07970
	7	188.0400	-0.03360
	15	189.6400	-0.06475
	18	190.9400	-0.06867
	14	192.3900	-0.04193
	7	193.9200	-0.05611
	8	195.4400	-0.04236
	15	199.9200	-0.04967
Methane + Propane	5	130.3700	-0.30181
	8	144.2600	-0.36254
	10	158.1500	-0.41352
	10	172.0400	-0.31393
	11	187.5400	-0.27333
	6	190.5800	-0.17516
	13	190.9500	-0.18653
	14	192.3000	-0.26489
	15	195.2000	-0.24457
	14	213.7100	-0.20144
Ethane + Propane	8	144.2611	-0.22805
	9	172.03889	0.07381
	9	199.81667	0.07409
	8	227.5944	0.10748
	11	255.3722	0.15491
Methane + n-Butane	7	277.5944	-0.46983
	7	344.2611	-0.43711
	4	377.5944	-0.36277
Propane + iso-Butane	12	266.5389	0.06128
	12	299.8167	0.17975
	15	338.7056	0.08144
		Press. (kPa)	
n-Pentane +n-Hexane	11	101.325	-0.29099
n-Pentane+n-Heptane	11	101.325	-0.01048
n-Hexane+ n-Heptane	11	101.325	-0.19844

Table 4-7: Values of an adjustable parameter when quadratic mixing rules applied on third path and using UNIFAC model for ternary hydrocarbon systems

System	N_P	Temp. (K)	k_{12}	k_{13}	k_{23}
Methane +Ethane +Propane	6	158.1500	-0.03139	-0.32136	-0.15460
	15	172.0400	-0.01888	-0.30443	-0.13142
	19	185.9300	-0.08204	-0.28291	-0.22054
	29	199.8200	0.02615	-0.21040	-0.07920
	24	213.7100	-0.02247	-0.18095	-0.08534
Methane + Propane+ n-Butane	23	304.6200	-0.01000	0.05713	0.05000
	22	305.4500	0.01404	0	0.02082
	14	306.5000	0.03887	0	-0.16576
Methane + Propane + n-Decane	31	244.2611	-2.73051	-2.71244	-1.12814
	41	255.3722	1.97815	-2.50727	-0.89265
	60	294.2611	0.72223	-1.85319	-0.43177
Methane + Propane + n-Heptane	12	233.1500	1.09121	-1.21216	-0.36630
	12	244.2611	0.97744	-1.15755	-0.49514
		Press. (kPa)			
n-Pentane+n-Hexane+n-Heptane	66	101.325	-0.23737	-0.21682	-0.18866

2. Trying to get a new value substituted in place of the constant value (2) where Eq.*(4-1)* will be

$$a/b=\sum_i\sum_j x_i x_j\left[\frac{a_{ij}}{b_i}-\frac{G^E_\infty}{\ln(d)}\right]=\sum_i\sum_j x_i x_j\left[\frac{a_{ij}}{b_i}-\frac{\ln(\gamma_i^\infty)}{\ln(d)}\right] \qquad ...(4\text{-}2)$$

d is the new constant whose value is to be found in order to make the results more accurate.

The values of the new constant *d* are listed in tables *4-7* and *4-8* for the binary and ternary systems respectively. The over all average absolute error for 36 binary hydrocarbon systems are 2.23338%. While, for the 14 ternary systems are 5.71417%.

The value of the new constant is obtained by using an optimization technique with a suitable mathematical computer program. The value of the new constant which is obtained by this mathcad computer program is 1.72956. The substitution of this new constant in Eq.*(4-2)* will give an average absolute over all error for the 36 binary hydrocarbon systems are 2.59685% while, for the ternaries used in this work are 5.88957%.

Table 4-8: d values by applying UNIFAC and model for binary hydrocarbon systems

System	N_P	***Temp. (K)***	***d values by applying UNIFAC model***
Methane + Ethane	6	130.3700	1.10053
	9	144.2600	1.12563
	12	158.1500	2
	11	172.0400	2
	13	186.1100	2.2908
	7	188.0400	2
	15	189.6400	2
	18	190.9400	2
	14	192.3900	2
	7	193.9200	2
	8	195.4400	2
	15	199.9200	2
Methane + Propane	5	130.3700	1.15503
	8	144.2600	1.12125
	10	158.1500	1.10800
	10	172.0400	1.21371
	11	187.5400	1.30742
	6	190.5800	2
	13	190.9500	3.15813
	14	192.3000	1.74019
	15	195.2000	1.44611
	14	213.7100	1.95350
Ethane + Propane	8	144.2611	1.01070
	9	172.03889	2
	9	199.81667	2
	8	227.5944	2
	11	255.3722	2
Methane + n-Butane	7	277.5944	1.10688
	7	344.2611	1.21320
	4	377.5944	1.21520
Propane + iso-Butane	12	266.5389	2.18338
	12	299.8167	1.01897
	15	338.7056	2
		Press. (kPa)	
n-Pentane +n-Hexane	11	101.325	1.00358
n-Pentane+n-Heptane	11	101.325	1.01521
n-Hexane+ n-Heptane	11	101.325	1.00401

Table 4-9: d values by applying UNIFAC model for ternary hydrocarbon systems

System	N_P	*Temp. (K)*	*d values by applying UNIFAC model*
Methane +Ethane +Propane	6	158.1500	1.22710
	15	172.0400	1.32583
	19	185.9300	1.26441
	29	199.8200	3.43609
	24	213.7100	3.18372
Methane + Propane+ n-Butane	23	304.6200	1.46384
	22	305.4500	1.06391
	14	306.5000	2.31100
Methane + Propane + n-Decane	31	244.2611	1.94582
	41	255.3722	1.60288
	60	294.2611	2.26683
Methane + Propane + n-Heptane	12	233.1500	1.96192
	12	244.2611	1.73700
		Press. (kPa)	
n-Pentane+n-Hexane+n-Heptane	66	101.325	1.01762

3. Trying to rise the term $\left(\frac{G_{\infty}^{E}}{\ln(2)}\right)$ to power *'n'* in order to improve the accuracy and obtain results proximately near or equal the experimental VLE data. The over all average absolute error for the binary hydrocarbon systems when the power value is changed according to the system components are 2.97558% while, for the ternary systems are 6.31553%. The new value of *'n'* instead of '1' will be 0.92847. By applying this new power value the over all average absolute deviations for the binary systems are 2.56157% and for the ternary hydrocarbon systems are 6.16821%. Also, in this modification path the new *"n"* value is obtained by using an optimization technique with suitable mathcad computer program. The new power values of this model for binary and ternary systems are listed in tables *4-8*, and *4-9* respectively

Table 4-10: Third path; trying to find the real power value for the term $\left(\frac{G_{\infty}^{E}}{\ln(2)}\right)$ when applying UNIFAC and Wilson models in PRSV-EOS and AS mixing rules for binary systems

System	N_P	Temp. (K)	Values of "n" power by applying UNIFAC model
Methane + Ethane	6	130.3700	1.10053
	9	144.2600	1.12563
	12	158.1500	2
	11	172.0400	2
	13	186.1100	2.29080
	7	188.0400	2
	15	189.6400	2
	18	190.9400	2
	14	192.3900	2
	7	193.9200	2
	8	195.4400	2
	15	199.9200	2
Methane + Propane	5	130.3700	1.15503
	8	144.2600	1.12125
	10	158.1500	1.10800
	10	172.0400	1.21371
	11	187.5400	1.30742
	6	190.5800	2
	13	190.9500	3.15813
	14	192.3000	1.74019
	15	195.2000	1.44611
	14	213.7100	1.95350
Ethane + Propane	8	144.2611	1.01070
	9	172.03889	2
	9	199.81667	2
	8	227.5944	2
	11	255.3722	2
Methane + n-Butane	7	277.5944	1.10688
	7	344.2611	1.21320
	4	377.5944	1.21520
Propane + iso-Butane	12	266.5389	2.18338
	12	299.8167	1.01897
	15	338.7056	2
		Press. (kPa)	
n-Pentane +n-Hexane	11	101.325	1.00358
n-Pentane +n-Heptane	11	101.325	1.01521
n-Hexane + n-Heptane	11	101.325	1.00401

Table 4-11: Third path; trying to find the real power value for the term $\left(\frac{G_{\infty}^{E}}{\ln(2)}\right)$ ***when applying UNIFAC models in PRSV-EOS and AS mixing rules for ternary systems***

System	N_P	***Temp. (K)***	***Values of "n" power by applying UNIFAC model***
Methane +Ethane +Propane	6	158.1500	1.22710
	15	172.0400	1.32583
	19	185.9300	1.26441
	29	199.8200	3.43609
	24	213.7100	3.18372
Methane + Propane+ n-Butane	23	304.6200	1.46384
	22	305.4500	1.06391
	14	306.5000	2.31100
Methane + Propane + n-Decane	31	244.2611	1.94582
	41	255.3722	1.60288
	60	294.2611	2.26683
Methane + Propane + n-Heptane	12	233.1500	1.96192
	12	244.2611	1.73700
		Press. (kPa)	
n-Pentane+n-Hexane+n-Heptane	66	101.325	1.01762

4.2.3.2 Using Wilson Activity Coefficient Model

In this section Wilson activity coefficient model at infinite dilution is applied with the share of PRSV-EOS. The same procedure is applied as with the UNIFAC activity coefficient at infinite dilution model. When applying this model to the hydrocarbons binaries used in this work the over all average absolute deviations are reduced to 2.01276%. While, for the ternary hydrocarbon systems they are reduced to 5.20716%. Noting that these results are obtained without using any adjustable parameters.

The same modified procedure as UNIFAC model is also adopted in this work by Wilson model in order to find the more accurate model capable to generate VLE data of hydrocarbon systems. These modification routes are:

1. Quadratic mixing rules for *(a/b)* term in order to insert the k_{ij} adjustable parameter to increase the VLE data of hydrocarbon systems accuracy. With the same equations as in UNIFAC modification model, the results for binary systems used in this work are reduced from 3.10182% to 1.97773%. While, for the ternaries the over all average absolute deviations are reduced from 12.30291% to 3.55501%.

The values of the new adjustable parameter (k_{ij}) for the binary and ternary systems when Wilson model was used will be shown in the following tables respectively.

Table 4-12: Values of an adjustable parameter when quadratic mixing rules applied on third path and using Wilson model for binary hydrocarbon systems

System	N_P	Temp. (K)	k_{ij}
Methane + Ethane	6	130.3700	-0.07567
	9	144.2600	-0.07494
	12	158.1500	-0.08142
	11	172.0400	-0.07808
	13	186.1100	-0.08028
	7	188.0400	-0.08100
	15	189.6400	-0.07105
	18	190.9400	-0.08719
	14	192.3900	-0.08514
	7	193.9200	-0.09268
	8	195.4400	-0.08807
	15	199.9200	-0.08249
Methane + Propane	5	130.3700	-0.19969
	8	144.2600	-0.19140
	10	158.1500	-0.16018
	10	172.0400	-0.13724
	11	187.5400	-0.13967
	6	190.5800	-0.20826
	13	190.9500	-0.19438
	14	192.3000	-0.17329
	15	195.2000	-0.15218
	14	213.7100	-0.18478
Ethane + Propane	8	144.2611	-0.02469
	9	172.03889	-0.02690
	9	199.81667	-0.02627
	8	227.5944	-0.02532
	11	255.3722	-0.02435
Methane + n-Butane	7	277.5944	-0.35834
	7	344.2611	-0.34083
	4	377.5944	-0.26535
Propane + iso-Butane	12	266.5389	-0.01060
	12	299.8167	-0.01044
	15	338.7056	-0.01158
		Press. (kPa)	
n-Pentane + n-Hexane	11	101.325	-0.00666
n-Pentane + n-Heptane	11	101.325	-0.01801
n-Hexane + n-Heptane	11	101.325	-0.00484

Table 4-13: Values of an adjustable parameter when quadratic mixing rules applied on third path and using Wilson model for ternary hydrocarbon systems

System	N_P	**Temp. (K)**	k_{12}	k_{13}	k_{23}
Methane +Ethane +Propane	6	158.1500	0.07311	-0.13844	0.45646
	15	172.0400	0.06891	-0.17523	0.43013
	19	185.9300	0.02304	-0.20002	0.50246
	29	199.8200	-0.00959	-0.01572	0.60441
	24	213.7100	-0.05643	-0.19888	0.48010
Methane + Propane+ n-Butane	23	304.6200	-0.01000	-0.01000	0.00523
	22	305.4500	-0.01000	-0.01000	0.17146
	14	306.5000	0	0	0
Methane + Propane + n-Decane	31	244.2611	-3.63091	-3.53070	-1.44825
	41	255.3722	1.68426	-2.75115	0.13050
	60	294.2611	-0.18705	-1.46429	0.36487
Methane + Propane + n-Heptane	12	233.1500	1.26452	-1.19598	0.33744
	12	244.2611	1.09672	-1.10013	0.30864
		Press. (kPa)			
n-Pentane +n-Hexane+n-Heptane	66	101.325	0.14655	0.04719	0.35669

2. Trying to find new constant value (*d*) in Eq.*(4-2)* i.e. to replace in place of the constant “2” in the original mixing rule equation. The value of the new constant is varied from system to system as shown in table (4-14). The over all average absolute deviations for the binary hydrocarbon systems are reduced to 2.05383%. While, for the ternaries they are reduced to 5.09225% as shown in table 4-15.

Table 4-14: The values of the constant "d" when applying UNIFAC and Wilson model for the binary systems

System	N_P	Temp. (K)	Values of constant "d" when applying Wilson model
Methane + Ethane	6	130.37	2.02746
	9	144.26	2.04128
	12	158.15	1.99997
	11	172.04	3.06373
	13	186.11	2.00710
	7	188.04	1.99977
	15	189.65	2.08243
	18	190.94	2.11276
	14	192.39	2.20635
	7	193.92	1.67108
	8	195.44	2.30308
	15	199.92	2.00239
Methane + Propane	5	130.37	2.00211
	8	144.26	1.32865
	10	158.15	1.75905
	10	172.04	1.99512
	11	187.54	1.99647
	6	190.58	2.00094
	13	190.95	2.00735
	14	192.3	2.02624
	15	195.2	2.15291
	14	213.71	2.56171
Ethane + Propane	8	144.2611	1.87921
	9	172.0390	2.23824
	9	199.8167	2.04248
	8	227.594	2.19089
	11	255.3700	2.02962
Methane + n-Butane	7	277.5944	2.02207
	7	344.2611	2.05527
	4	377.5944	2.02917
Propane + iso-Batane	12	266.4833	1.99989
	12	299.8167	1.97358
	12	338.7056	1.99006
		Press. (kPa)	
n-Pentane +n-Hexane	11	101.325	1.99988
n-Hexane +n-Heptane	11	101.325	2
n-Pentane +n-Heptane	11	101.325	1.03240

Table 4-15: The values of the constant "d" when applying UNIFAC and Wilson model for the ternary systems

System	N_P	Temp. (K)	Values of constant "d" when applying Wilson model
Methane +Ethane +Propane	6	158.1500	2.07239
	15	172.0400	2.00054
	19	185.9300	2.01698
	29	199.8200	10.12346
	24	213.7100	1.99815
Methane +Propane +n-Butane	23	304.6200	2
	22	305.4500	3.13682
	14	306.5000	2.02014
Methane +Propane +n-Decane	31	244.2611	1.86958
	41	255.3722	1.42472
	60	294.2611	2.00424
Methane +Propane +n-Heptane	12	233.1500	1.99428
	12	244.2611	1.97680
		Press. (kPa)	
n-Pentane +n-Hexane +n-Heptane	66	101.325	2.01266

3. The last modification is trying to rise $\left(\frac{G_{\infty}^{E}}{\ln(2)}\right)$ term to power *"n"* in order to find the more suitable power value required for generating more accurate VLE data of hydrocarbon systems (binary and ternary mixtures). The values of power *"n"* are tabulated in the following tables for each binary and ternary system respectively. The over all average absolute percent of deviations for 36 binary systems they were 2.082324%. While, for the 14 ternary hydrocarbon systems they were 5.36877%.

Table 4-16: The values of the power "n" when applying Wilson model for the binary systems

System	***N_P***	***Temp. (K)***	***Values of power "n" when applying Wilson model***
Methane +Ethane	6	130.37	0.99842
	9	144.26	0.99283
	12	158.15	1.00004
	11	172.04	1.51137
	13	186.11	1.34489
	7	188.04	1.01584
	15	189.65	1.00148
	18	190.94	2.87327
	14	192.39	0.95268
	7	193.92	0.95768
	8	195.44	0.94750
	15	199.92	0.96956
Methane +Propane	5	130.37	1.00050
	8	144.26	1.00070
	10	158.15	0.99763
	10	172.04	0.98109
	11	187.54	0.94418
	6	190.58	1.53737
	13	190.95	0.96931
	14	192.3	0.99201
	15	195.2	0.97066
	14	213.71	0.98200
Ethane +Propane	8	144.2611	0.99928
	9	172.0390	1.13538
	9	199.8167	1.03823
	8	227.594	1.00121
	11	255.3700	1.00060
Methane +n-Butane	7	277.5944	0.99585
	7	344.2611	0.98577
	4	377.5944	0.98580
Propane +iso-Batane	12	266.4833	1.00167
	12	299.8167	1
	12	338.7056	1.00145
		Press. (kPa)	
n-Pentane +n-Hexane	11	101.325	0.99998
n-Hexane +n-Heptane	11	101.325	1.14538
n-Pentane +n-Heptane	11	101.325	1

Table 4-17: The values of the power “n” when applying Wilson model for the ternary systems

System	N_P	***Temp.***	***Values of power “n” when applying Wilson model***
Methane +Ethane +Propane	6	158.1500	0.98517
	15	172.0400	0.99379
	19	185.9300	0.99493
	29	199.8200	0.83221
	24	213.7100	0.99749
Methane +Propane +n-Butane	23	304.6200	1
	22	305.4500	0.32342
	14	306.5000	1
Methane +Propane +n-Decane	31	244.2611	1
	41	255.3722	1.21827
	60	294.2611	0.99791
Methane +Propane +n-Heptane	12	233.1500	1.00004
	12	244.2611	1.00323
		Press. (kPa)	
n-Pentane +n-Hexane +n-Heptane	66	101.325	1

5 Discussion

This study concerned mixtures that contain species that are not so different in size and the nature of their intermolecular forces which are termed *homogeneous mixtures*. The need of a simplest and more accurate method to calculate the VLE data of hydrocarbon systems from the theoretical base which can be applied for each phase without needing any experimental data point is important. Simple models imposed by the computing tools which can satisfy the engineering design needs and fulfill the requirements of both simplicity and accuracy are required. Several paths are tried and their results are tabulated in this chapter. Some notes are made for each path model as shown in details of this chapter.

5.1 <u>Path One:</u> "Applying EOS to Calculate VLE Data for Both Phases"

The first path examined the ability of an EOS for generating VLE data and the role played by mixing rules in EOS calculation of VLE for various types of binary and ternary hydrocarbon mixtures. Several types of mixing rules are used. Through the work in this path three types of mixing rules conventional, quadratic and Adachi-Sugie mixing rules with two types of equations of state which are PR-EOS and PRSV-EOS are used.

In order to increase any EOS accuracy k_{ij} is introduced. The parameter k_{ij} is a symmetric ($k_{ij}= k_{ji}$) binary interaction parameter obtained from experimental data that applied in MathCAD optimization program prepared in this work. In general, k_{ij} is constant for specified system at certain temperature and pressure. For non-ideal systems, however, k_{ij} depends on temperature, and small changes in its value can cause large changes in the properties predicted by the EOS. Each system mixture has a k_{ij} value that represents that system. The effect of this adjustable parameter is to shift the VLE data results to higher degree of accuracy.

In order to appreciate the limitations of a simple thermodynamic model, we always have to remember that we do not perform calculations from first principles. Simple EOS, even through quite modest in the requirements of basic physical information. This experimental information can be divided into pure component information (critical properties, vapor pressure, and acentric factor) and mixtures VLE information. Even when we have this experimental information available, it is known that simple cubic equations of state do not always represent reality. So, for these reasons several methods which are tried to improve the VLE results of hydrocarbon systems.

Improvement to VLE calculations has been increased by the increasing the number of adjustable parameters in the mixing rules. Therefore, the fitting effects might cause those improvements, i.e. by increasing the flexibility of the mixing rules to fit the data. However, the issue of how many parameters are necessary for the practical applications is not well defined. For example if mixing rules have one, two, or three adjustable parameters in the cohesion parameter of an EOS *"a"* the results shows that for the same system:

1. The difference between the VLE result of the two, three and higher number of adjustable parameters are quite small. Indicating that more than two and sometimes three adjustable are not necessary; and
2. The VLE results of the one parameter and those of the two parameters are fairly different. However, the VLE results of the two parameters and those of three parameters are close to each other.

These phenomena indicate that the parameters required in the mixing rules for binary systems are two. So, AS mixing rules is quite enough for VLE calculation. While, for the covolume parameter of an EOS *"b"* an adjustable parameter has very small effect if it is compared to results of non-ideal systems. Since, systems which are adopted in this work are hydrocarbons which have approximately similar shape and size and this can be seen in the table results of quadratic mixing rules. The adjustable parameter in this part of any EOS will be important if the systems which work with are non-ideal systems with a great difference between molecules shape and size.

PR and PRSV equations give excellent results at high pressure, over a wide range of temperatures, from above the critical temperature down through the cryogenic range.

While, SRK-EOS predicts phase behavior poorly. For simulation near the critical region, the PR and PRSV-EOS yields better results.

Since this work adopted homogeneous mixtures vdW mixing rules may be adequate. Since, the effect of orientation and packing of molecules can be neglected for approximately similar compounds in the mixture.

It is generally believed that CEOS can be applied successfully to calculate VLE of non polar mixtures using the conventional vdW one fluid mixing rules. However, for non ideal mixtures in which polar intermolecular forces or hydrogen bonding can be found, these mixing rules are insufficient.

For non polar systems attraction term parameter of an EOS are more sensitive to any change or adjustment than the covolume parameter term and this can be discovered from the results of AS mixing rules with PR and PRSV equations of state for binary and ternary systems.

Conventional mixing rules eliminate the error associated in the assumption of equal forces of attraction between the like and unlike molecules in each individual component in the mixture. The adjustable parameter "k_{ij}" is one of the oldest and till know is used depending on the required accuracy of the calculation and design purposes. While, quadratic mixing rules try to cancel out the deviation from the real covolume parameter of an EOS "b" value due to the assumption of molecules spherical shape. The introduction of h_{ij} adjustable parameter tries to cancel out the effect of shape and size of molecules and their deviations from the assumption of having a spherical shape type. The use of this type of mixing rules modified the results over the conventional mixing rules.

The results of using PR and PRSV equations with these three different types of mixing rules for binary and ternary systems are shown *tables 5-1, 5-2, 5-3, and 5-4:*

Table 5-1: Application of conventional, quadratic, and Adachi-Sugie mixing rules on PR-EOS for binary systems

System	N_P	***Temp. (K)***	***Mixing rules type %AAD***			
			$k_{ij}=0$	***Conventional***	***Quadratic***	***Adachi-Sugie***
Methane +Ethane	6	130.37	1.73259	1.71937	0.81347	0.70038
	9	144.26	2.42105	1.64344	0.58213	0.52487
	12	158.15	2.04234	2.04654	2.04234	2.15026
	11	172.04	0.97326	1.01137	0.69500	0.69173
	13	186.11	0.76125	0.76203	0.64983	0.65087
	7	188.04	0.23254	0.20794	0.15695	0.23254
	15	189.65	0.95050	0.93998	0.91890	0.90357
	18	190.94	0.62992	0.60775	0.57825	0.56253
	14	192.39	1.01594	0.95979	0.93759	0.93925
	7	193.92	0.25330	0.23092	0.20080	0.25330
	8	195.44	0.21851	0.19037	0.20013	0.21851
	15	199.92	1.39861	1.39976	1.39672	1.38604
Methane +Propane	5	130.37	3.81335	1.61414	0.80025	0.81246
	8	144.26	4.54200	3.15132	1.43707	1.42077
	10	158.15	5.60810	5.26322	2.39833	2.11441
	10	172.04	4.68442	4.53599	2.60703	2.48859
	11	187.54	3.04593	2.98919	1.93927	1.87976
	6	190.58	0.12843	0.12490	0.11210	0.12806
	13	190.95	0.67328	0.72224	0.29315	0.27284
	14	192.3	3.36612	3.14171	2.11027	1.98245
	15	195.2	3.62349	3.59703	2.88868	2.71585
	14	213.71	3.03808	2.97959	2.16142	2.06110
Ethane +Propane	8	144.2611	2.16829	2.11768	2.11841	2.09418
	9	172.039	6.88410	6.78386	6.778381	6.72283
	9	199.8167	3.42716	3.23768	3.23443	3.15589
	8	227.594	7.70015	7.31829	7.31083	7.22564
	11	255.3700	5.53237	4.78913	1.61856	4.62874
Methane +n-Butane	7	277.5944	4.81169	2.65808	2.65807	0.55271
	7	344.2611	4.78839	3.48893	2.62535	2.68102
	4	377.5944	6.57457	6.60780	3.59885	3.59869
Propane +iso-Butane	12	266.4833	1.40004	1.39860	1.39866	1.39812
	12	299.8167	1.52476	1.20409	1.18824	1.09960
	12	338.7056	3.42007	3.22430	2.49444	3.13270
System		***Pressure (kPa)***				
n-Pentane +n-Hexane	11	101.325	2.80387	1.07865	1.43801	0.99486
n-Hexane +n-Heptane	11	101.325	3.67272	1.378325	2.04010	2.49525
n-Pentane +n-Heptane	11	101.325	2.50322	1.38110	1.36143	1.37941
% overall average absolute deviation			***2.84623***	***2.40001***	***1.82701***	***1.84040***

Table 5-2: Application of conventional, quadratic, and Adachi-Sugie mixing rules on PRSV-EOS for binary systems

System	***N_P***	***Temp. (K)***	***Mixing rules type %AAD***			
			k_{ij}=0	***Conventional***	***Quadratic***	***Adachi-Sugie***
Methane +Ethane	6	130.37	1.69729	1.47550	0.69788	0.72723
	9	144.26	2.36739	1.50251	0.49313	0.50171
	12	158.15	1.99212	2.01598	2.10342	2.12810
	11	172.04	0.92424	0.95799	0.69319	0.69317
	13	186.11	0.76614	0.76177	0.67299	0.67065
	7	188.04	0.23606	0.21061	0.15218	0.13374
	15	189.65	0.96606	0.95836	0.93824	0.92909
	18	190.94	0.62807	0.61065	0.58160	0.58250
	14	192.39	1.05647	0.98717	0.96581	0.96569
	7	193.92	0.24588	0.22494	0.19420	0.21852
	8	195.44	0.22027	0.18792	0.19215	0.18571
	15	199.92	1.40711	1.41038	1.39997	1.39403
Methane +Propane	5	130.37	3.65467	1.38485	0.67503	0.70333
	8	144.26	4.44748	2.88510	1.41805	1.40533
	10	158.15	5.39465	5.04282	2.34278	2.08282
	10	172.04	4.48347	4.35946	2.47584	2.37180
	11	187.54	2.88862	2.86953	1.85415	1.80250
	6	190.58	0.12457	0.14293	0.10993	0.12331
	13	190.95	0.63110	0.69404	0.26599	0.26549
	14	192.3	3.14515	2.97792	1.98162	1.85857
	15	195.2	3.46045	3.34835	2.76060	2.60168
	14	213.71	2.86233	2.91156	2.03632	1.94533
Ethane +Propane	8	144.2611	2.33079	1.08033	1.03936	0.86501
	9	172.039	5.01171	4.90335	4.89663	4.51273
	9	199.8167	3.15359	2.95240	2.94673	2.86437
	8	227.594	7.95169	7.55515	7.55024	7.30575
	11	255.3700	5.88532	5.12785	1.74345	4.90004
Methane +n-Butane	7	277.5944	4.51513	2.51372	0.65791	0.49911
	7	344.2611	4.62336	3.31754	2.48224	2.54661
	4	377.5944	6.57457	6.60780	3.53060	3.56089
Propane +iso-Batane	12	266.4833	1.71580	1.71350	1.71380	1.56113
	12	299.8167	1.46162	1.16021	0.98702	0.85103
	12	338.7056	3.66538	3.23345	2.59273	3.16077
System		***Pressure (kPa)***				
n-Pentane +n-Hexane	11	101.325	2.73578	1.58575	1.08392	1.17717
n-Hexane +n-Heptane	11	101.325	2.97519	1.57265	2.54980	1.57314
n-Pentane +n-Heptane	11	101.325	1.57062	1.28473	1.57636	1.32304
% overall average absolute deviation			***2.66045***	***2.37989***	***1.61868***	***1.70525***

Table 5-3: Application of conventional, quadratic, and Adachi-Sugie mixing rules on PR-EOS for ternary systems

System	***N_P***	***Temp.***	***Mixing rules type %AAD***			
			k_{ij}=0	***Conventional***	***Quadratic***	***Adachi-Sugie***
Methane +Ethane +Propane	6	158.1500	5.89520	3.58575	2.51149	0.04874
	15	172.0400	4.20206	2.95447	1.65906	1.62628
	19	185.9300	5.33112	3.0105	2.62278	2.72087
	29	199.8200	3.11808	3.10663	2.40916	2.91942
	24	213.7100	2.05205	1.96325	1.39757	1.35577
Methane +Propane +n-Butane	23	304.6200	3.25747	3.25634	3.21467	3.26574
	22	305.4500	1.83077	1.82514	1.74662	1.81019
	14	306.5000	4.44909	4.40982	3.59719	4.40343
Methane +Propane +n-Decane	31	244.2611	20.88142	12.10122	12.03606	14.23731
	41	255.3722	18.14335	11.06620	8.93367	6.85545
	60	294.2611	9.23573	4.50493	4.72007	3.71307
Methane +Propane +n-Heptane	12	233.1500	9.23513	4.45753	3.50630	2.00973
	12	244.2611	10.27015	3.65812	3.09997	1.18272
		Pressure (kPa)				
n-Pentane+n-Hexane+n-Heptane	66	101.325	3.71364	2.49128	2.051581	1.67343
% overall average absolute deviation			***7.18732***	***4.45651***	***3.64523***	***3.41616***

Table 5-4: Application of conventional, quadratic, and Adachi-Sugie mixing rules on PRSV-EOS for ternary systems

System	***N_P***	***Temp.***	***Mixing rules type %AAD***			
			k_{ij}=0	***Conventional***	***Quadratic***	***Adachi-Sugie***
Methane +Ethane +Propane	6	158.1500	5.69637	3.49322	2.27167	0.03260
	15	172.0400	4.00039	2.83585	2.09071	1.59115
	19	185.9300	5.15830	2.94051	2.50971	2.65666
	29	199.8200	3.07457	3.04097	2.56660	2.94023
	24	213.7100	1.97349	1.91284	1.39249	1.47283
Methane +Propane +n-Butane	23	304.6200	3.25992	3.27653	3.28098	3.27173
	22	305.4500	1.83627	1.80841	1.80104	1.80775
	14	306.5000	4.44960	4.38733	3.99271	4.36158
Methane +Propane +n-Decane	31	244.2611	19.71095	10.92098	8.97505	7.73849
	41	255.3722	16.94388	9.80771	8.14369	6.42180
	60	294.2611	8.09632	3.82594	3.59641	3.23264
Methane +Propane +n-Heptane	12	233.1500	8.32203	4.14069	3.23875	1.98989
	12	244.2611	9.41724	3.34918	2.82413	1.20797
		Pressure (kPa)				
n-Pentane+n-Hexane+n-Heptane	66	101.325	3.35999	1.73160	1.71231	1.33492
% overall average absolute deviation			***6.80709***	***4.26583***	***3.45578***	***2.86145***

By the application of "conventional, quadratic, and Adachi-Sugie" mixing rules for PR and RPSV equations of state, PRSV-EOS shows slightly better results than PR-EOS for both binary and ternary systems for each mixing rules type. So, the results indicate that PRSV-EOS is slightly better than PR-EOS in representing VLE data for n-hydrocarbon systems and the most successful mixing rules is Adachi-Sugie mixing rules. The results also show the effect of mixing rules on an EOS. It can be concluded that both the nature of CEOS and the type of mixing rules used with it have influence on the accuracy of the calculated VLE data. It seems clearly from the results that the type of mixing rules has more influence on the accuracy of the calculated data rather than the nature of EOS.

It can be noticed that the mixing rules type which contain two adjustable parameters in the attraction term *"a"* of an EOS give more accurate results than the mixing rules type that contain one adjustable parameter for the same EOS. An attempted way of introducing three adjustable parameters mixing rules type increases only slightly the accuracy of results as compared with the mixing rules type of two parameters. So, the mixing rules of three adjustable parameters are disappointed and AS-mixing rules with two adjustable parameters in the attraction term of an EOS is the best used mixing rules for VLE generating data.

5.2 Second Path: "Prediction of VLE Data by Using CEOS for Vapor Phase and Activity Coefficient for the Liquid Phase"

Another way of calculating phase equilibria feature is the use of an EOS for predicting the vapor fugacity coefficients (PRSV-EOS with AS mixing rules is used) and an activity coefficient model is used for the liquid phase. The liquid state fugacities are obtained through the use of activity coefficient while, the vapor phase can be obtained through the use of EOS. This method has proven to be accurate in the low to moderate pressure VLE region and thus can be used to represent highly non-ideal systems where pressure corrections are unimportant. It is evident to know that the use of more complicated equation of state does not improve VLE correlation to any significant extent. This is not an expected since the composition dependence of the fugacity coefficients, which is so important in phase equilibrium calculations. Therefore, a small change in the mixing rules or binary interaction coefficient affects VLE calculations significantly. Conversely, the fugacity coefficients depend on the integral of *PVT* relation i.e. cubic equation of state. Therefore, the VLE calculation will not be strongly dependent on the accuracy of the EOS used. Indeed, any small inaccuracy in the EOS can be compensated for by an adjustment in the interaction coefficient. However, activity coefficient models have limitations. Difficulties and inaccuracies arise when calculating high pressure equilibria and equilibria for mixtures that contain supercritical compounds and this can be seen for systems containing light hydrocarbons such as methane. This can be noticed from the high percentage of deviation from experimental data when it compared with other hydrocarbon systems which not contain methane. In addition, the number of parameters used in the activity coefficient models ranges from two to four parameters per binary, a characteristic that leads to errors when extrapolating experimental data, while, CEOS do not inherently suffer from these limitations. So, because of these limitations this path is not capable to produce all the systems roots i.e. some systems mathematical representation leads to trivial solution. For this reason the number of binary systems used in this path is reduced to 23 while the number of ternary systems is only 5. The over all average absolute deviation for each binary and ternary as shown in *tables 5-5, 5-6, and 5-7*:

Table 5-5: PRSV-EOS with AS mixing rules for vapor phase while UNIFAC and Wilson activity coefficient models for the liquid phase binary systems

System	N_P	***Temp. (K)***	***First Path with PRSV-EOS with AS mixing rules %AAD***	***Second Path with***	
				UNIFAC model %AAD	***Wilson model %AAD***
Methane +Ethane	6	130.37	0.72723	10.78798	1.32995
	9	144.26	0.50171	18.08936	2.49691
	12	158.15	2.12810	18.23141	3.26376
	11	172.04	0.69317	18.85337	1.78800
	13	186.11	0.67065	9.00346	0.90528
	7	188.04	0.13374	12.68565	1.25152
	15	189.65	0.92909	9.39949	1.17358
Methane +Propane	5	130.37	0.70333	15.12261	1.90530
	8	144.26	1.40533	16.52061	2.46354
	10	158.15	2.08282	17.78422	3.05145
	10	172.04	2.37180	18.92888	3.10616
	11	187.54	1.80250	16.66619	4.07630
Ethane +Propane	8	144.2611	0.86501	1.25283	3.42972
	9	172.039	4.51273	4.81251	3.48958
	9	199.8167	2.86437	2.35647	2.64868
	8	227.594	7.30575	6.88991	5.50355
	11	255.3700	4.90004	5.30297	6.57482
Propane +iso-Batane	12	266.4833	1.56113	1.44657	4.17630
	12	299.8167	0.85103	1.86381	3.01788
	12	338.7056	3.39741	4.86799	4.55092
		Pressure (kPa)			
n-Pentane +n-Hexane	11	101.325	1.17717	1.32452	1.65221
n-Hexane +n-Heptane	11	101.325	1.57314	1.77550	7.23096
n-Pentane +n-Heptane	11	101.325	1.32304	0.19849	1.72892
% overall average absolute deviation			***2.86145***	***9.31151***	***3.07893***

Table 5-6: PRSV-EOS with AS mixing rules for vapor phase while UNIFAC and Wilson activity coefficient models for the liquid phase ternary systems

System	N_P	Temp. (K)	First Path with PRSV-EOS with AS mixing rules %AAD	Second Path with	
				UNIFAC model %AAD	Wilson model %AAD
Methane +Ethane +Propane	6	158.1500	0.03260	28.15440	4.025053
	15	172.0400	1.59115	23.67867	3.092718
	19	185.9300	2.65666	24.39503	3.561945
Ethane +Propane +n-Butane	23	304.6200	3.27173	4.23770	4.33117
		Pressure (kPa)			
n-Pentane+n-Hexane+n-Heptane	66	101.325	1.33492	1.33657	3.17210
% overall average absolute deviation			***2.86145***	***16.36047***	***3.63660***

UNIFAC has become a most popular model whenever liquid phase activity coefficients are needed. In UNIFAC group interaction parameters have been estimated mostly from experimental VLE data. The popularity of UNIFAC stems most probably good predictions of activity coefficients. UNIFAC activity coefficient method also has a broad range of applicability due to the many parameters which are available.

The basic assumption in the group contribution approach for the prediction of activity coefficient is that the fundamental groups, which together added to form the molecules in the mixture, are independent from one another and thus do not know which were their neighboring groups in the parent molecules. This fundamental assumption is the basis of the wide applicability and the flexibility of the group contribution models. On the other hand, this assumption also renders the group contribution models know today unable to distinguish between details in the molecular structures as in isomers.

Unfortunately the activity coefficient based method has a major limitation if UNIFAC model is used. It can not treat systems containing supercritical components (and it tends to become inaccurate with light components and/ or at high pressure conditions). This feature can be observed from the systems results in the previous tables for binary and ternary systems of this path. Results for binary and ternary systems that not containing methane are comparable with those of binary and ternary mixtures containing methane. Noting that methane r_i and q_i values are calculated according to method described in reference [108 and 111].

If UNIFAC model is used the over all average absolute deviation for the 23 binaries used in this work with mixtures that containing methane are 9.311513%. While, the 11 binary hydrocarbon mixtures that not contain methane the over all average absolute deviation are 2.91742%. For ternary systems (5 systems) the over all average absolute deviation are 16.36047%. The over all average absolute deviation for the 2 ternary hydrocarbon systems which are not contain methane are 2.78714%. These results show the limitation of UNIFAC equation to treat supercritical fluids such as methane.

When Wilson model is adopted the methane component present in the hydrocarbon system mixture has no effect. It is like any other component in the system. So, this is an improvement point of Wilson model over UNIFAC model but UNIFAC model parameters (r_i and q_i) are widely available in a large number of references approximately for all components. While, Wilson equation parameters (λ_{ij}) are not available sufficiently for all systems. λ_{ij} parameters depend on the type of experimental data and on its accuracy. So, for the systems which do not have its value a suitable mathcad program with the aid of reference [116] is prepared. The over all average absolute deviation for the 23 binary hydrocarbon systems are 3.07893%. While, the over all average absolute deviation for the five ternary hydrocarbon systems is reduced to 3.63660%. For the individual systems the overall average absolute deviations for the binary and ternary systems for UNIFAC and Wilson models are shown in tables *5-5* and *6* respectively.

5.3 Third Path: "Prediction of VLE Data by Applying Activity Coefficient Models at Infinite Dilution in PRSV-EOS"

Conventional and quadratic mixing rules, although theoretically well supported and completely adequate for binary systems, yet fail when applied to multicomponent mixtures. It is likely that more complicated rules, involving ternary and higher order terms have to be considered, but it is an impractical route, owing to the extremely large number of terms and long computation times involved. It is then necessary to adopt mixing rules of new type, avoiding the introduction of higher order terms, and can apply both to binary and multicomponent systems.

EOS mixing rules, based on local composition concepts for excess Gibbs free energy, are introduced by Huron and Vidal. The original HV-mixing rules at infinite pressure are not largely used because the model parameters (in G^E_∞ at infinite pressure) must be adjusted and not related to available parameters at low pressure.

The past few years have seen a rapid growth in the number of ideas for direct incorporation of existing model parameters of excess Gibbs free energy models in an EOS.

Excess Gibbs free energy model in an EOS mixing rules use available activity coefficient model parameters from low pressure data, without change, for predicting phase equilibria at high pressures and temperatures.

The connection of EOS with group contribution methods such as UNIFAC and Wilson, allow EOS to become predictive tools.

This path links the EOS parameters *"a"* and *"b"* to excess Gibbs free energy at infinite dilution by applying UNIFAC and Wilson models. Where in this path EOS use UNIFAC and Wilson models by substituting their excess Gibbs free energy term at infinite dilution without losing accuracy of the classical UNIFAC and Wilson methods, for the VLE data calculation.

Such approach is probably applicable to any CEOS, on condition that it can reproduce correctly the pure-component phase equilibrium behavior. This linking makes it possible to exploit the main advantage of the EOS route over the activity coefficient route that is the possibility of treating systems containing supercritical compounds.

With the classical method (second path), this can be done only by adopting a complex unsymmetrical convention, that is referring the activity coefficients to the pure liquid compounds for supercritical components, and to infinite dilution conditions for supercritical ones (which can lead to lack of convergence in the search of a phase equilibrium states, due to the jumping of some components between either states).

The introduction of a temperature dependence of the attraction term allows reproducing accurately pure compounds vapor pressure. The modification of the mixing rules, with the infinite dilution excess Gibbs free energy expressed by UNIFAC and Wilson models, allows reproducing accurately phase equilibria of polar and non polar systems if it is present. Finally, the introduction of a volume correction improves markedly the calculated liquid densities, without changing the phase equilibrium conditions.

It is generally believed that CEOS can be applied successfully to calculate VLE of non polar mixtures using the conventional vdW mixing rules. Since the systems adopted in this search are hydrocarbons and classified as homogeneous mixtures. Conventional mixing rules with one adjustable parameter are sufficient since it proposed a linear combination between molecules and neglect the effect of orientation and packing size of molecules. The results of using this new method are illustrated in tables (5-7and 5-8) with the aid of UNIFAC excess Gibbs free energy at infinite dilution for the binary and ternary systems respectively. Noting that there is no adjustable parameter present.

Table 5-7: Third path approach results by using PRSV-EOS with UNIFAC and Wilson models excess Gibbs free energy at infinite dilution for binary systems

System	***N_P***	***Temp. (K)***	***Third path %AAD using***	
			UNIFAC model	***Wilson model***
Methane +Ethane	6	130.37	1.37969	1.25429
	9	144.26	1.98188	1.17539
	12	158.15	2.06158	2.38548
	11	172.04	0.98936	0.96463
	13	186.11	0.77695	0.76110
	7	188.04	0.31951	0.20524
	15	189.65	1.00166	1.13066
	18	190.94	0.67702	0.61043
	14	192.39	1.29236	0.98309
	7	193.92	0.25956	0.22990
	8	195.44	0.43963	0.18464
	15	199.92	1.62955	1.38820
Methane +Propane	5	130.37	2.84768	0.84824
	8	144.26	3.82831	1.93772
	10	158.15	5.05501	2.85249
	10	172.04	4.23776	3.62326
	11	187.54	2.77186	2.93855
	6	190.58	0.13739	0.12445
	13	190.95	0.74049	0.64150
	14	192.3	2.93568	2.58187
	15	195.2	3.44908	3.37078
	14	213.71	2.81438	2.69533
Ethane +Propane	8	144.2611	2.32192	0.76200
	9	172.0390	5.02384	4.79889
	9	199.8167	3.17566	2.81100
	8	227.594	7.98733	7.44951
	11	255.3700	5.94364	4.97125
Methane +n-Butane	7	277.5944	3.86008	1.08307
	7	344.2611	3.93376	2.30124
	4	377.5944	5.99858	4.62111
Propane +iso-Batane	12	266.4833	1.82536	1.71356
	12	299.8167	1.09661	0.83844
	12	338.7056	3.68877	3.42435
System		***Pressure (kPa)***		
n-Pentane +n-Hexane	11	101.325	2.73326	1.57752
n-Hexane +n-Heptane	11	101.325	2.47314	2.49575
n-Pentane +n-Heptane	11	101.325	2.14577	1.05908
% overall average absolute deviation			***2.60706***	***2.01276***

Table 5-8: Third path approach results by using PRSV-EOS with UNIFAC and Wilson models excess Gibbs free energy at infinite dilution for ternary systems

System	N_P	*Temp. (K)*	*Third path %AAD using*	
			UNIFAC model	*Wilson model*
Methane +Ethane +Propane	6	158.1500	4.73909	3.90391
	15	172.0400	3.45435	3.30520
	19	185.9300	4.56160	2.74894
	29	199.8200	3.55153	5.20758
	24	213.7100	2.34360	1.82453
Methane +Propane +n-Butane	23	304.6200	3.47220	3.28678
	22	305.4500	2.20460	1.95690
	14	306.5000	6.94561	4.25509
Methane +Propane +n-Decane	31	244.2611	17.85925	18.96851
	41	255.3722	14.24443	14.35421
	60	294.2611	4.89912	2.82615
Methane +Propane +n-Heptane	12	233.1500	6.06395	5.35786
	12	244.2611	7.45047	5.63284
		Pressure (kPa)		
n-Pentane+n-Hexane+n-Heptane	66	101.325	3.34544	1.66878
% overall average absolute deviation			***6.08109***	***5.20716***

It is found that this path results is accurate enough in predictions and correlations for a wide range of mixtures. The generality and simplicity of this new mixing model has a great advantage in engineering applications. Also, this path benefit from EOS specification in representing VLE data. Where the EOS method, offers internal consistency as one of its advantages. Also, it is valid over a wide range of temperatures and pressures, including ones in the mixture critical region. This path is therefore, attractive for VLE data calculations, including once involving high pressure. The agreement between calculated and experimental values is very good, comparable to the other good methods used in this work. Noting that there is no adjustable parameter present in this mixing rule (k_{ij}). Moreover, this mixing rule is simpler in the VLE calculations.

A limitation of HV-mixing rules during the using of UNIFAC model is determined by unavailable group contribution parameters for gases such as CO_2, H_2, etc. if it is applied to system mixture containing these light compounds. This path was found to be good as original CEOS with conventional mixing rules with optimal binary interaction parameter but this path eliminate the need for adjustable binary interaction parameter. Also, the results of this path for VLE calculation of hydrocarbons binary and ternary systems are reasonably good with minor efforts in calculation. This is due to the using of more simple mixing rules if it is compared to other types of mixing rules which are probably need an additional prepared optimizing mathcad program for the adjustable parameter in order to increase the accuracy of the obtained VLE data.

The advantage of this path over the classical activity coefficient route lies in the possibility of treating systems at extreme physical conditions and systems containing supercritical components. It is found that this model is comparable in accuracy with that of the conventional vdW mixing rules model with k_{ij} adjust in the conventional mixing rules to optimal value, while this model do not need adjustable parameter. It is much better than the vdW mixing model with k_{ij} set to zeros, especially when there are great disparities in size and shape of molecules which are present in the system mixture.

A different modified procedure of using HV-mixing rule based on UNIFAC activity coefficients at infinite dilution at low and high pressures is tried. The results of the used paths shows that the third path with no addition of adjustable parameter is very suitable for binary systems as it is compared with other used paths and various types of mixing rules which are applied in different equations of states keeping in mind that all studied methods except one which is named as third path required an adjustable parameter. While, for ternary systems the over all average absolute deviations for the third path shows slightly larger percent deviation if it is compared to other methods. Different tried modifications methods are applied for this path. The first tried method is the introduction of quadratic mixing rules with one adjustable parameter "k_{ij}" in *(a/b)* calculated term of an EOS. This introduction of the new rout of calculation *(a/b)* term introduced one adjustable parameter in the attraction term of an EOS "k_{ij}". While, the covolume parameter *"b"* still does not contain an adjustable parameter. This new adjustable parameter increases the accuracy of the calculated VLE data of hydrocarbon systems significantly especially for ternary systems. This modified procedure with this high accuracy with minimum efforts and minimum number of adjustable parameters can also be applied in the same time with the same simplicity to ternary and multicomponent systems. This developed approach in this path put this path as a first selected path for designed purposes with higher degree of accuracy. Also, this modified path is applied to Wilson model which shows slightly higher degree of accuracy when it is compared to UNIFAC model. Remembering that Wilson parameter determination depend on the experimental data accuracy. The results of UNIFAC and Wilson models are shown in tables (5-9, and 5-10) for binary and ternary systems respectively.

Table 5-9: Applying quadratic mixing rules for the third path with the share of UNIFAC and Wilson models for binary systems

System	N_P	***Temp. (K)***	***EOS with quadratic mixing rules sharing with***					
			UNIFAC model			***Wilson model***		
			%AAD when k_{ij}=0	k_{ij}	***%AAD***	***%AAD when k_{ij}=0***	k_{ij}	***%AAD***
Methane +Ethane	6	130.37	2.70124	-0.14954	1.40831	1.48661	-0.07567	1.22814
	9	144.26	3.75362	-0.14031	1.41206	2.20289	-0.07494	1.15629
	12	158.15	2.14723	-0.04128	2.02061	2.82188	-0.08142	2.38526
	11	172.04	1.40491	-0.07157	0.93093	1.46952	-0.07808	0.95882
	13	186.11	1.22089	-0.07970	0.76973	1.23508	-0..08028	0.75585
	7	188.04	0.33145	-0.03360	0.20819	0.55524	-0.08100	0.20531
	15	189.65	1.47407	-0.06475	0.96239	1.32792	-0.07105	0.79987
	18	190.94	1.04982	-0.06867	0.62232	1.18482	-0.08719	0.61975
	14	192.39	1.31031	-0.04193	0.98425	1.65707	-0.08514	0.96778
	7	193.92	0.42558	-0.05611	0.27131	0.52277	-0.09268	0.20044
	8	195.44	0.55112	-0.04236	0.21394	0.96972	-0.08807	0.15320
	15	199.92	1.97639	-0.04967	1.43409	2.44057	-0.08249	1.8750
Methane +Propane	5	130.37	7.100207	-0.30181	1.09233	5.12068	-0.19969	0.83842
	8	144.26	7.24796	-0.36254	2.51926	4.16151	-0.19140	1.79796
	10	158.15	7.35587	-0.41352	4.59674	3.45713	-0.16018	2.72960
	10	172.04	6.34322	-0.31393	4.34285	3.54808	-0.13724	3.16178
	11	187.54	5.05746	-0.27333	2.82674	3.18675	-0.13967	2.57744
	6	190.58	0.27157	-0.17516	0.12978	0.30220	-0.20826	0.12617
	13	190.95	2.31902	-0.18653	0.69790	2.43031	-0.19438	0.63695
	14	192.3	5.23026	-0.26489	2.83330	3.77571	-0.17329	2.46187
	15	195.2	5.75227	-0.24457	3.57739	4.10577	-0.15218	2.96616
	14	213.71	5.53782	-0.20144	2.81259	5.16353	-0.18478	2.59012

System	N_P	Temp. (K)	EOS with quadratic mixing rules sharing with					
			UNIFAC model			Wilson model		
			%AAD when k_{ij}=0	k_{ij}	%AAD	%AAD when k_{ij}=0	k_{ij}	%AAD
Ethane +Propane	8	144.2611	2.37555	-0.22805	1.01089	0.85034	-0.02469	0.76122
	9	172.0390	4.95623	0.07381	4.89130	4.82637	-0.02690	4.79776
	9	199.8167	3.07498	0.07409	2.93811	2.83844	-0.02627	2.81038
	8	227.594	7.84599	0.10748	7.52912	7.43963	-0.02532	7.44986
	11	255.3700	5.74280	0.15491	5.09404	4.97762	-0.02435	4.97103
Methane +n-Butane	7	277.5944	12.24055	-0.46983	2.22766	8.93256	-0.35834	1.12252
	7	344.2611	11.09833	-0.43711	2.70567	8.88811	-0.34083	2.33836
	4	377.5944	11.09736	-0.36277	5.87223	8.66708	-0.26535	5.13221
Propane +iso-Batane	12	266.4833	1.79500	0.06128	1.71378	1.71488	-0.01060	1.71351
	12	299.8167	1.10647	0.17975	0.98245	0.83222	-0.01044	0.83789
	12	338.7056	3.64667	0.08144	3.46139	3.41947	-0.01158	3.42473
System		***Pressure (kPa)***						
n-Pentane +n-Hexane	11	101.325	2.74264	-0.29099	1.34131	1.57537	-0.00666	1.57749
n-Hexane +n-Heptane	11	101.325	2.50038	-0.01048	2.49639	2.50394	-0.01801	2.49671
n-Pentane +n-Heptane	11	101.325	2.15182	-0.19844	1.12953	1.07356	-0.00484	1.05985
% overall average absolute deviation			***2.60706***		***2.22391***	***2.01276***		***1.97773***

Table 5-10: Applying quadratic mixing rules for the third path with the share of UNIFAC and Wilson models for ternary systems

System	N_P	Temp. (K)	EOS with quadratic mixing rules sharing with									
			UNIFAC model					Wilson model				
			%AAD when $k_{ij}=0$	k_{12}	k_{13}	k_{23}	%AAD	%AAD when $k_{ij}=0$	k_{12}	k_{13}	k_{23}	%AAD
Methane +Ethane +Propane	6	158.1500	8.18432	-0.03139	-0.32136	-0.15460	3.28538	18.95679	0.07311	-0.13844	0.45646	3.10935
	15	172.0400	5.92047	-0.01888	-0.30443	-0.13142	2.76403	12.63711	0.06891	-0.17523	0.43013	2.51204
	19	185.9300	7.07917	-0.08204	-0.28291	-0.22054	2.88362	11.80467	0.02304	-0.20002	0.50246	2.65240
	29	199.8200	4.00074	0.02615	-0.21040	-0.07920	3.02572	19.36311	-0.00959	-0.01572	0.60441	3.42709
	24	213.7100	3.80893	-0.02247	-0.18095	-0.08534	1.87475	9.41139	-0.05643	-0.19888	0.48010	2.15837
Methane +Propane +n-Butane	23	304.6200	3.21586	-0.01000	0.05713	0.05000	3.26908	5.10691	-0.01000	-0.01000	0.00523	5.05318
	22	305.4500	1.76165	0.01404	0	0.02082	1.78172	8.06679	-0.01000	-0.01000	0.17146	4.37285
	14	306.5000	4.39159	0.03887	0	-0.16576	4.27857	8.92546	0	0	0	8.92546
Methane +Propane +n-Decane	31	244.2611	27.80161	-2.73051	-2.71244	-1.12814	8.53823	21.20122				
	41	255.3722	24.44526	1.97815	-2.50727	-0.89265	8.10793	15.13905	1.68426	-2.75115	0.13050	8.36567
	60	294.2611	14.83995	0.72223	-1.85319	-0.43177	3.22896	5.63530	-0.18705	-1.46429	0.36487	2.68009
Methane +Propane +n-Heptane	12	233.1500	17.23236	1.09121	-1.21216	-0.36630	3.40895	12.33046	1.26452	-1.19598	0.33744	3.11751
	12	244.2611	17.13571	0.97744	-1.15755	-0.49514	2.74717	16.15995	1.09672	-1.10013	0.30864	1.89583
		Pressure (kPa)										
n-Pentane+n-Hexane+n-Heptane	66	101.325	3.38285	-0.23737	-0.21682	-0.18866	1.67364	7.50252	0.14655	0.04719	0.35669	1.50030
% overall average absolute deviation			***6.08109***				***3.63341***	***5.20716***				***3.55501***

A second modified procedure is also adopted in this path. This new approach tried to find the more accurate constant *"d"* in the original HV-mixing rules constant based on the hypothetical aspects assumption during the derivation of HV-mixing rules. This approach is applied at first to UNIFAC model making a variable *"d"* values (each system has its own value) instead of using a constant number for all the systems in order to find the exact constant value for each system. This approach is applied to the binary and ternary systems. The obtained new constants for each system are entered in a suitable way in this work as an optimization MathCAD computer program. The new obtained value for all the binary and ternary hydrocarbon systems now is 1.72956 instead of (2) in the modified HV-mixing rules. The results are only slightly modified. So, depending on the required accuracy this modified procedure can be used or not. Because of the little improvement when applying this modified route on UNIFAC model the optimization procedure was not applied on Wilson model except the variable value instead of constant value (2) in the modified HV-mixing rules. The results of variable value *"d"* for Wilson model show also slight modified VLE results when it is compared to the modified HV-mixing rules.

The results of this new tried approach are shown in tables 5-11, and 5-12 when it is applied on the binary and ternary systems respectively:

Table 5-11: Third path with second approach modified route for binary systems

System	N_P	**Temp. (K)**	**%AAD when applying**				
			UNIFAC model			**Wilson model**	
			d=2	*d=variable value*	*d=1.72956*	*d=2*	*d=variable value*
Methane +Ethane	6	130.37	1.37969	1.45433	1.33319	1.25429	1.24987
	9	144.26	1.98188	1.47329	1.93203	1.17539	1.17557
	12	158.15	2.06158	2.06158	2.07283	2.38548	2.38552
	11	172.04	0.98936	0.98936	1.01192	0.96463	0.95896
	13	186.11	0.77695	0.76689	0.79327	0.76110	0.76087
	7	188.04	0.31951	0.31951	0.33942	0.20524	0.20524
	15	189.65	1.00166	1.00166	1.03300	1.13066	1.10301
	18	190.94	0.67702	0.67702	0.71767	0.61043	0.61074
	14	192.39	1.29236	1.29236	1.33933	0.98309	0.96855
	7	193.92	0.25956	0.25956	0.25956	0.22990	0.23543
	8	195.44	0.43963	0.43963	0.48339	0.18464	0.16612
	15	199.92	1.62955	1.62955	1.70552	1.38820	1.38822
Methane +Propane	5	130.37	2.84768	1.26897	2.67491	0.84824	0.76120
	8	144.26	3.82831	2.76054	3.71292	1.93772	6.09784
	10	158.15	5.05501	4.89535	5.01699	2.85249	2.89267
	10	172.04	4.23776	4.36502	4.23178	3.62326	7.44885
	11	187.54	2.77186	2.84961	2.75541	2.93855	4.97081
	6	190.58	0.13739	0.13739	0.13845	0.12445	0.84756
	13	190.95	0.74049	0.68169	0.83559	0.64150	1.92434
	14	192.3	2.93568	2.93125	2.93116	2.58187	2.87037
	15	195.2	3.44908	3.57127	3.49448	3.37078	3.58505
	14	213.71	2.81438	0.66962	2.86882	2.69533	2.70755
Ethane +Propane	8	144.2611	2.32192	1.05421	2.31954	0.76200	0.12493
	9	172.0390	5.02384	5.02384	5.02707	4.79889	0.64145
	9	199.8167	3.17566	3.17566	3.18157	2.81100	2.57634
	8	227.594	7.98733	7.98733	7.99685	7.44951	3.32169
	11	255.3700	5.94364	5.94364	5.95918	4.97125	2.69335
Methane +n-Butane	7	277.5944	3.86008	1.65391	3.72753	1.08307	1.11426
	7	344.2611	3.93376	2.56238	3.78027	2.30124	2.35027
	4	377.5944	5.99858	4.83651	5.86216	4.62111	4.65261
Propane +iso-Batane	12	266.4833	1.82536	1.80528	1.88041	1.71356	1.71356
	12	299.8167	1.09661	0.98578	1.09549	0.83844	0.83214
	12	338.7056	3.68877	3.68877	3.69403	3.42435	3.42368
System		**Pressure (kPa)**					
n-Pentane +n-Hexane	11	101.325	2.73326	1.32788	2.73266	1.57752	1.57752
n-Hexane +n-Heptane	11	101.325	2.47314	2.74878	2.97614	2.49575	2.49575
n-Pentane +n-Heptane	11	101.325	2.14577	1.11214	1.57207	1.05908	1.10587
% overall average absolute deviation							

Table 5-12: Third path with second approach modified route for ternary systems

System	***N_P***	***Temp. (K)***	***%AAD when applying***				
			UNIFAC model			***Wilson model***	
			d=2	***d=variable value***	***d=1.72956***	***d=2***	***d=variable value***
Methane +Ethane +Propane	6	158.1500	4.73909	4.69632	4.57784	3.90391	3.85058
	15	172.0400	3.45435	3.48628	3.41473	3.30520	3.30497
	19	185.9300	4.56160	4.08870	4.46395	2.74894	2.73485
	29	199.8200	3.55153	3.32893	3.66365	5.20758	3.30262
	24	213.7100	2.34360	2.07259	2.52610	1.82453	1.82489
Methane +Propane +n-Butane	23	304.6200	3.4722	3.26081	3.37074	3.28678	3.28678
	22	305.4500	2.2046	3.37719	1.95198	1.95069	1.86368
	14	306.5000	6.94561	4.44216	4.50128	4.25509	4.25050
Methane +Propane +n-Decane	31	244.2611	17.85925	17.69100	18.49823	20.74006	18.66546
	41	255.3722	14.24443	14.22714	14.60097	14.35421	12.83353
	60	294.2611	4.89912	4.49055	4.48023	2.82615	2.83018
Methane +Propane +n-Heptane	12	233.1500	6.06395	5.96895	6.00490	5.35786	5.34047
	12	244.2611	7.45047	6.60525	7.05756	5.63284	5.53250
		Pressure (kPa)					
n-Pentane +n-Hexane +n-Heptane	66	101.325	3.34544	2.26246	3.34176	1.668781	1.67044
% overall average absolute deviation			***6.08109***	***5.71417***	***5.88957***	***5.20716***	***5.09225***

The final tried approach method is the founding of a real power value of the term $\left(\frac{G_{\infty}^{E}}{\ln(2)}\right)$ where this tried approach assumed that this term is raised to power *"n"*. At first this approach indicates the real power value of each binary and multicomponent system. The obtained power values of these systems are considered as an input data for a suitable prepared in this work MathCAD computer program. This program leads to the more suitable constant power value for all binary and ternary systems. The new constant value is applied again to all binary and ternary systems. The over all average absolute error shows very slight modification over the modified HV-mixing rules. The optimization program therefore is applied only on UNIFAC model. The obtained value from the optimization program for UNIFAC model is 0.92847 for all 36 binary and 14 ternary systems. The over all average absolute deviation for binary and ternary systems for this approach in this path will be shown in tables 5-13, and 5-14 respectively.

Table 5-13: Third path with third approach modification route for binary systems

System	N_P	***Temp. (K)***	***%AAD when applying***				
			UNIFAC model			***Wilson model***	
			n=1	***n=variable***	***n=0.92847***	***n=1***	***n=variable***
Methane +Ethane	6	130.37	1.37969	1.45799	1.42431	1.25429	1.25284
	9	144.26	1.98188	2.01618	2.02954	1.17539	1.17825
	12	158.15	2.06158	2.01618	2.05474	2.38548	2.38599
	11	172.04	0.98936	0.96517	0.98151	0.96463	1.25355
	13	186.11	0.77695	0.73406	0.76454	0.76110	1.13099
	7	188.04	0.31951	0.26340	0.30475	0.20524	0.20448
	15	189.65	1.00166	0.95674	0.98578	1.13066	1.13591
	18	190.94	0.67702	0.93373	0.64727	0.61043	0.60884
	14	192.39	1.29236	1.11900	1.25221	0.98309	0.96871
	7	193.92	0.25956	0.21755	0.24934	0.22990	0.22805
	8	195.44	0.43963	0.27632	0.40366	0.18464	0.16406
	15	199.92	1.62955	1.43681	1.57940	1.38820	1.38848
Methane +Propane	5	130.37	2.84768	6.33061	3.04229	0.84824	0.85139
	8	144.26	3.82831	6.08355	3.96026	1.93772	1.94881
	10	158.15	5.05501	5.83378	5.11663	2.85249	2.87220
	10	172.04	4.23776	6.38701	4.25646	3.62326	3.59323
	11	187.54	2.77186	4.56879	2.79661	2.93855	2.76282
	6	190.58	0.13739	0.12616	0.13226	0.12445	0.14990
	13	190.95	0.74049	0.69876	0.70596	0.64150	0.64827
	14	192.3	2.93568	4.54066	2.94677	2.58187	2.50866
	15	195.2	3.44908	5.98337	3.41732	3.37078	3.30639
	14	213.71	2.81438	2.79702	2.80927	2.69533	2.68645
Ethane +Propane	8	144.2611	2.32192	2.31893	2.32361	0.76200	0.75946
	9	172.0390	5.02384	6.75629	5.02151	4.79889	6.21740
	9	199.8167	3.17566	3.15230	3.17100	2.81100	2.93247
	8	227.594	7.98733	5.74993	7.97955	7.44951	7.44813
	11	255.3700	5.94364	5.88274	5.93020	4.97125	4.97058
Methane +n-Butane	7	277.5944	3.86008	3.79498	4.00175	1.08307	1.13509
	7	344.2611	3.93376	4.69013	4.10207	2.30124	2.42532
	4	377.5944	5.99858	6.84065	6.14418	4.62111	4.73874
Propane +iso-Batane	12	266.4833	1.82536	1.71589	1.76723	1.71356	1.71355
	12	299.8167	1.09661	1.09528	1.09742	0.83844	0.83844
	12	338.7056	3.68877	3.66782	3.68460	3.42435	3.42358
		Pressure (kPa)					
n-Pentane +n-Hexane	11	101.325	2.73326	1.07264	1.07238	1.57752	1.57752
n-Hexane +n-Heptane	11	101.325	2.47314	2.49507	2.49505	2.49575	2.49603
n-Pentane +n-Heptane	11	101.325	2.14577	2.14549	1.57163	1.05908	1.05908
% overall average absolute deviation			***2.60706***	***2.97558***	***2.56175***	***2.01276***	***2.08232***

Table 5-14: Third path with third approach modification route for ternary systems

System	N_P	**Temp. (K)**	**%AAD when applying**				
			UNIFAC model			**Wilson model**	
			n=1	***n=variable***	***n=0.92847***	***n=1***	***n=variable***
Methane +Ethane +Propane	6	158.1500	4.73909	7.11401	4.94503	3.90391	3.81243
	15	172.0400	3.45435	5.58360	3.57255	3.30520	3.28248
	19	185.9300	4.56160	6.62384	4.70966	2.74894	2.71432
	29	199.8200	3.55153	3.34360	3.41844	5.20758	3.62208
	24	213.7100	2.34360	2.14034	2.18694	1.82453	1.82174
Methane +Propane +n-Butane	23	304.6200	3.4722	3.25068	3.31738	3.28678	3.28678
	22	305.4500	2.2046	2.58956	2.48169	1.95069	1.83618
	14	306.5000	6.94561	4.41477	4.46962	4.25509	4.25509
Methane +Propane +n-Decane	31	244.2611	17.85925	17.65031	17.92127	20.74006	18.96851
	41	255.3722	14.24443	14.23053	14.97956	14.35421	16.17031
	60	294.2611	4.89912	4.86492	5.97485	2.82615	2.84426
Methane +Propane +n-Heptane	12	233.1500	6.06395	5.95880	6.83403	5.35786	5.35690
	12	244.2611	7.45047	7.30699	8.19891	5.63284	5.52296
		Pressure (kPa)					
n-Pentane +n-Hexane +n-Heptane	66	101.325	3.34544	3.34544	3.34570	1.668781	1.66878
% overall average absolute deviation			***6.08109***	***6.31553***	***6.16821***	***5.20716***	***5.36877***

So, depending on the required accuracy an engineer or scientist can select suitable required path for the design purposes. The third path is one of the most important paths used in industrial field since it is not contain any additional adjustable parameter with good accuracy when it is compared to other previous methods. Also, an additional benefit is appeared in this path that programs are simple in programming and they are not time consuming since an optimizing program is not required. If higher degree of accuracy is required an engineer or scientist can select one of the modified tried methods which are adopted in this work.

6

Conclusions and Recommendation for Future Work

A common goal of phase equilibria studies is to develop models that can simultaneously correlate or predict VLE. Several attempts have been made in this respect, because such models would truly advance the understanding of the thermodynamics of liquid mixtures.

For rational design of separation equipment, reliable thermodynamic properties of mixtures are essential. In the petroleum, petrochemical, and related industries of hydrocarbon mixtures of interest frequently include those containing saturated hydrocarbon mixtures. Such mixtures are only modestly non ideal, but for efficient design, departures from ideal behavior must be taken into account.

The binary and multicomponent hydrocarbons systems and any system, with a minimum of empirical parameters are needed with the use of an accurate and simplest equation is very important to cover the engineering interest.

6.1 Conclusions

An engineer or scientist can predict or calculate VLE data of hydrocarbon systems by different methods or paths. The paths which adopted in this work are:

- Prediction of VLE data for both phases by means of CEOS.
- Prediction of VLE data by using CEOS for the vapor phase and activity coefficient model for the liquid phase.
- Prediction of VLE data from activity coefficient model at infinite dilution.

Depending on the petroleum cut, the region which works with, available data and calculation time; an engineer or scientist can select suitable path for VLE data prediction.

1. When first path is selected for generating VLE data PR-EOS and its modified versions including one adjustable parameter has been previously shown to be the best CEOS for the representation of VLE data. PRSV-EOS were originally designed for non polar light hydrocarbons coupled with AS mixing rules give the more accurate results when compared with other types of mixing rules adopted in this work (conventional and quadratic mixing rules). These mixing rules tried to eliminate the error in the attraction term of an EOS. Addition of an empirical binary interaction constant allows for correction between dissimilar components. Use of this constant enable EOS to accurately simulate not only non polar light hydrocarbons, but heavy hydrocarbons also. The results of calculation for 36 binary systems with 376 data points and 14 ternary hydrocarbon systems with 368 data points are agreed with the AS mixing rules assumption for homogeneous systems mixtures. Also, *table 6-1* results shows the effect of mixing rules on an EOS is more than the type of EOS used. Where the over all percent deviation for all systems are changed only slightly from one EOS to another. While, for the same EOS but using different mixing rules the over all percent deviation are improved much greatly than the EOS type.

2. When the second path is selected for VLE prediction, two models are used for this path namely: the UNIFAC and Wilson activity coefficient models. By applying these two models on hydrocarbon systems, Wilson model shows better results than those of UNIFAC model. The activity coefficient models can not be applied on systems near the critical region. This can be discovered from the reduction in the number of systems. The numbers of hydrocarbon systems in this path are reduced from 36 binary to 23 systems only. While, for the ternary systems they have been reduced from 14 to 5 systems only. While, far from the critical region and for systems under low to moderate pressure very reasonable accuracy are obtained. In fact, except for vapor composition, EOS results are in most cases better than the activity coefficient model results.

3. Finally when the last tried path is selected for VLE data prediction. PRSV-EOS is coupled with modified HV-mixing rules model at infinite dilution activity coefficients calculated from UNIFAC and Wilson models. This path can be applied on all hydrocarbon systems and can represent the VLE data for all mixtures under high pressure because of the generality of an EOS. Also, this path is very simple in use and does not required additional separated computer program with the EOS as in the second path. This path does not contain any additional adjustable parameter and has very good accuracy. So, there is no need for computer optimization program. This method is found to be as good as the original CEOS with conventional mixing rules including binary interaction parameter but eliminates the need for adjustable interaction parameter when it is applied for binary systems. For the ternary systems it also gives reasonable percent deviation. However, it is slightly less accurate when it compared with CEOS (first path) contain adjustable parameter in the conventional mixing rules. So, this search tried to modify these results for ternary systems. Several approaches are tried; one of them are the most suitable one for the binary and ternary systems where the over all average absolute deviation for the 36 binary hydrocarbon and 14 ternary hydrocarbon systems which are greatly modified. This approach method used the quadratic mixing rules on modified HV mixing rules but with $h_{ij=}0$ This mixing rule made it possible to insert an adjustable parameter (k_{ij}) which reduces all the error associated with the deviation of CEOS and mixing rules assumption through the Huron and Vidal assumption. While, raise the calculated VLE data to higher degree of accuracy. This new approach offered a suitable simulator computer program with high accuracy for VLE data calculation of hydrocarbon systems.

So, if binary systems are present; third path without any adjustable parameter saves considerably computing time and effort because it avoids iterations in objective function calculations. For ternary systems, third path with quadratic mixing rules gives high degree of accuracy which is very difficult to obtain with other calculation methods with the same accuracy. Also, this approach can be applied to binary systems with very good accuracy.

Table 6-1: Summarized over all average deviations for VLE data calculation for all paths and approaches

method			***PR-EOS***		***PRSV-EOS***	
			Binary systems %ABD	***Ternary systems %ABD***	***Binary systems %ABD***	***Ternary systems %ABD***
First path		***k_{ij}=0***	2.84623	7.18732	2.66045	6.80709
		Conventional mixing rules	2.40001	4.45651	2.37989	4.26583
		Quadratic mixing rules	1.82701	3.64523	1.61868	3.45578
		Adachi- Sugie mixing rules	1.84040	3.41616	1.70525	2.86145
Second path	***UNIFAC model***	***For all hydrocarbon systems***	_	_	9.31151	16.36047
		for systems not containing methane	_	_	2.91742	2.78714
	Wilson model	***For all hydrocarbon systems***	_	_	3.07893	3.63660
Third path	***UNIFAC model***	***Modified HV-mixing rules with k_{ij}=0***	_	_	2.60706	6.08109
		Using modified HV-quadratic mixing rules	_	_	2.22391	3.63341
		Try to find "d" value d=variable number.	_	_	2.23338	5.71417
		d=1.72956	_	_	2.59685	5.88957
		Try to find new "n" power value	_	_	2.97558	6.31553
		n=0.92847	_	_	2.56175	6.16821
	Wilson model	***Modified HV-mixing rules with k_{ij}=0***	_	_	2.01276	5.20716
		Using modified HV-quadratic mixing rules	_	_	1.97773	3.55501
		Try to find "d" value d=variable number	_	_	2.05383	5.09225
		Try to find new "n" power value	_	_	2.08232	5.36877

6.2 Recommendations for Future Work

In spite of the development of high speed computers, enabling the use of more complex (and more accurate) equations of state, cubic equations, and in particular the PR-EOS in its many versions, it seems still far from having concluded their way. Not particularly accurate, but easy to solve and program, moderate in computer requirements, easy to adjust, they remain the work horse of students, researchers and designers.

Further developments are still needed any way, in particular to improve their predictive ability; some of them are outlined here:

a) Improving the vapor pressure prediction in the low temperature range: expression used normally for $\alpha(T_r)$ is usually accurate in pressure range from, say, 1/100 bar upwards, but the heaviest components of a mixture can have much lower saturation pressures and any error in their evaluation can affect seriously in development of new α functions which can be extrapolated with confidence to much lower reduced temperatures than presently.

b) Improvement the treatment of heavy hydrocarbons: first, by making their parameters in the α function predictable from available properties. Second, the methods for the estimation of pseudo component binary interaction constants should keep into account their higher or lower aromatic nature, by the use of parameters bound to it (e.g. , the Watson *k* factor).

c) Considering special case of high temperature, high pressure behavior: current $\alpha(T_r)$ functions are usually fitted to vapor pressure data, neglecting their trend over the critical temperature (some functions even diverge); a recent work on the SRK-EOS has shown that fugacity coefficients at high temperature and pressure (which are used to predict compositions of chemical reactions at equilibrium) are quite sensitive to the $\alpha(T_r)$ function adopted, and that a proper choice of $\alpha(T_r)$ even makes their prediction possible.

d) A more extensive study of the model predictions in the multicomponent high pressure VLE would evidently be desirable in path three.

e) In path three HV-modified mixing rules set a connection between $(a / R\,T\,b)$ and the excess Gibbs free energy at infinite pressure.

Once an expression *f* or $\frac{G^E_\infty}{RT}$ is assigned, the mixing rules are completely defined. The simplest case is that of an ideal solution at infinite pressure:

Whence: $G^E_\infty = 0$; $\frac{G^E_\infty}{RT} = \sum_i x_i \frac{a_i}{RTb_i}$

This equation is a good starting point for more accurate mixing rules for mixtures near an ideal solution and then can be extended to slightly polar mixtures. Also, a more extensive study of the model predictions in multicomponent high pressure VLE would evidently be desirable.

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Appendix "A"

Components Physical Properties

Component	**Formula**	ω	T_C (K)	P_C (bar)	Z_C	V_C (cm^3/mole)	k_1^*
Methane	CH_4	0.012	190.6	45.99	0.286	98.6	-0.00159
Ethane	C_2H_6	0.100	305.3	48.72	0.279	145.5	0.02669
n-Propane	C_3H_8	0.152	369.8	42.48	0.276	200.0	0.03136
n-Butane	C_4H_{10}	0.200	425.1	37.96	0.274	255.	0.03443
Iso-Butane	C_4H_{10}	0.181	408.1	36.48	0.282	262.7	0.03443
n-Pentane	C_5H_{12}	0.252	469.7	33.70	0.270	313.	0.03946
n-Hexane	C_6H_{14}	0.301	507.6	30.25	0.266	371	0.05104
n-Heptane	C_7H_{16}	0.350	540.2	27.40	0.261	428.	0.04648
n-Decane	$C_{10}H_{22}$	0.492	617.7	21.10	0.247	600.	0.04510

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* *This column refers to PRSV adjustable parameter constant value for each pure component*

الخلاصة

أختيرت مسارات وطرق مختلفة للتنبؤ بقيم توازن البخار مع السائل بصورة دقيقة لستة وثلاثون مزيج ثنائي مع ٣٧٦ نقطة توازن واربعة عشر خليط ثلاثي مع ٣٦٨ نقطة توازن وخاصة تلك الامزجة ذات الاهمية الصناعية لوحدات التبريد.

هذا ادى الى أختيار نموذج لحساب توازن البخار مع السائل بالنسبة للانظمة الهيدروكاربونية بدون الحاجة الى توليف متغير وطريقة اخرى تحتاج الى توليف متغير واحد لضبط قيم النتائج واختيار الطريقة هنا يعتمد على الدقة الصناعية المطلوبة.

المسار الأول يتناول حساب توازن البخار مع السائل للانظمة الهيدروكاربونية من خلال استخدام معادلة الحالة PR ومعادلة الحالة المشتقة منها PRSV مع قواعد خلط متعددة لكل من الطورين البخاري و السائل. نتيجة هذا المسار ذو المتغيرين من خلال تطبيق قواعد الخلط AS تعطي تقريبا افضل درجة دقة للانظمة الثنائية و الثلاثية مع قواعد الخلط الباقية المتبناة في هذا البحث لمعادلتي الحالة PR و PRSV .

وكان مقدار معدل الانحراف الكلي من خلال تطبيق قاعدة الخلط AS مع معادلة الحالة PRSV لستة و ثلاثون مركب ثنائي ٣٧٦ قراءة توازن كان% ١,٧٠٥٢٥ بينما كان للاربعة عشر خليط ثلاثي ٣٦٨ قراءة توازن كان معدل الانحراف الكلي %٢,٨٦١٤٥ .

المسار الثاني يتعامل مع حساب توازن البخار مع السائل للمركبات الهيدروكاربونية عن طريق تطبيق معادلة الحالة PRSV مع قاعدة الخلط AS للطور البخاري (لكون قاعدة الخلط AS مع معادلة الحالة PRSV تعطي افضل النتائج لحساب توازن البخار مع السائل لكلا الطورين) .

بينما استخدم نموذج معامل الفعالية لنموذجي UNIFAC و WILSON للطور السائل لحساب توازن البخار مع السائل للانظمة الهيدروكاربونية. حيث ان هذا المسار له بعض المحددات عند تطبيقه في الظروف فوق الحرجة و المركبات تحت الضغوط العالية لذلك خفضت الانظمة المطبقة على هذا المسار الى ٢٣ نظام ثنائي و ٥ انظمة ثلاثية فقط.

وكان مقدار معدل الانحراف الكلي للانظمة الثنائية من خلال تطبيق نماذج معامل فعالية في نموذجي UNIFAC و Wilson هو %٩,٣١١٥١ و%٣,٧٨٠٣ على التوالي .بينما للانظمة الثلاثية كان معدل الانحراف الكلي عند تطبيق نموذج UNIFAC هو %١٦,٣٦٠٤٧ ولنموذج Wilson %٣,٦٣٦٦. كذلك ان لنموذج معامل الفعالية في UNIFAC له تحديدات اضافية عند تطبيقها ، حيث ان تواجد مركب الميثان في الخليط يعطي دقة اقل في حساب قيم توازن البخار مع

السائل و بغياب هذا المركب كان معدل الانحراف الكلي للانظمة الثنائية و الثلاثية ٢,٩١٧٤٢% ، ٢,٧٨٧١٤% على التوالي.

المسار الثالث في هذا المسار طبقت معادلة الحالة PRSV مع قاعدة خلط جديدة لكلا الطورين البخاري مع السائل. قاعدة الخلط هذه اشتقت من معادلة Gibbs للطاقة الحرة عند التخفيف العالي و التي اشتقت بدورها من معامل الفعالية تحت ظروف التخفيف العالي. المسار الثالث يربط بين معادلة الحالة PRSV و معادلة Gibbs للطاقة الحرة عند التخفيف العالي الذي يتبنى نموذجي UNIFAC و Wilson. هذا الربط يمكن من الاستفادة من فوائد معادلة الحالة التي تتميز بها عن معامل الفعالية حيث ان لها القدرة على التعامل مع المركبات تحت الظروف الحرجة. وكان مقدار معدل الانحراف الكلي لستة و ثلاثون مزيج ثنائي هيدروكاربوني بتطبيق نموذجي UNIFAC و Wilson هو ٢,٦٠٧٠٦% و ٢,٠١٢٢٧٦% على التوالي. معدل الانحراف الكلي لاربعة عشر نظام ثلاثي هيدروكاربوني باستخدام نموذجي UNIFAC و Wilson هو ٦,٠٨١٠٩% و ٥,٢٠٧١٦% على التوالي. هذه النتائج للانظمة الثنائيه و الثلاثية كانت بدون استخدام اي متغير توليفي ($k_{ij}=0$) .

النتائج الخاصة بالمسار الأول و التي استخدمت قاعدة الخلط AS والتي تحتوي على متغيرين توليفيين في حد التجاذب التابع لمعادلة الحالة PRSV اعطت تقريبا نفس الدقة عند مقارنتها بنتائج المسار الثالث بدون استخدان المتغير التوليفي بالنسبة للانظمة الثنائية. بينما للانظمة الثلاثية كانت قاعدة الخلط AS مع معادلة الحالة PRSV تعطي دقة اعلى قليلاً في حساب توازن البخار مع السائل .لذا طور المسار الثالث لغرض اعطاء دقة اعلى للانظمة الثلاثية.

عديد من التعديلات اجريت على قواعد الخلط مع نموذج معامل الفعالية في حد التجاذب التابع لمعادلة الحالة. وكانت افضل النتائج لهذه التعديلات في حساب توازن البخار مع السائل قد استحصلت عند تطوير قاعدة الخلط الى قاعدة خلط رباعية مع متغير توليفي واحد (k_{ij}). هذا التعديل يسمح باعادة حساب التوازن الطوري للخلائط غير القطبية حتى بوجود اثار لمركبات قطبية. معدل الانحراف الكلي للانظمة الثنائية من خلال تطبيق نموذجي UNIFAC و Wilson كان ٢,٢٢٣٩١% و ١,٩٧٧٧٣% على التوالي ، بينما للانظمة الثلاثية كان معدل الانحراف الكلي ٣,٦٣٣٤١% لنموذج UNIFAC و ٣,٥٥٥٠١% لنموذج Wilson .هذا المسار كان الافضل عند مقارنته مع المسارين المتبنيان سابقا لحساب توازن البخار مع السائل للمركبات الهيدروكاربونية الخاصة بالانظمة الثلاثية حيث ان ندرة الدقة العالية بدون او مع اقل عدد من المتغيرات التوليفية في الاستخدامات الصناعية ميز هذا المسار عن غيره .

Appendix "B"

Wagner Vapor Pressure Equation Constants

Component	**Formula**	**A**	**B**	**C**	**D**	$T_{min.}$	$T_{max.}$
Methane	CH_4	-6.00435	1.18850	-0.83408	-1.22833	91	T_C
Ethane	C_2H_6	-6.34307	1.01630	-1.19116	-2.03539	133	T_C
n-Propane	C_3H_8	-6.72219	1.33236	-2.13868	-1.38551	145	T_C
n-Butane	C_4H_{10}	-6.88709	1.15157	-1.99873	-3.13003	170	T_C
Iso-Butane	C_4H_{10}	-6.95579	1.50090	-2.52717	-1.49776	165	T_C
n-Pentane	C_5H_{12}	-7.28936	1.53679	-3.08367	-1.02456	195	T_C
n-Hexane	C_6H_{14}	-7.46765	1.44211	-3.28222	-2.50941	220	T_C
n-Heptane	C_7H_{16}	-7.67468	1.37068	-3.53620	-3.20243	240	T_C
n-Decane	$C_{10}H_{22}$	-8.56523	1.97756	-5.81971	-0.29982	368	T_C

Wagner equation formula is:

$$ln(P_{vap}/P_C) = (1-x)^{-1}\left[(A)x + (B)x^{1.5} + (C)x^3 + (D)x^6\right]$$

where: $x = 1 - (T/T_C)$
P_{vap} = *vapor pressure, in bars*
P_C = *critical pressure, in bars*
T = *temperature, in Kelvin*
T_C = *critical temperature, in Kelvin*