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Theme

Calculation methods investigation, of some thermodynamic and volumetric properties for two light hydrocarbons

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Symbols & Abbreviations

Symbols

a: Constant in Equation of State; may be Function of Temperature.	**Mpa. (m3/kmol)2**
b: Constant in Equation of State.	**m3/kmol**
k_B: is the Boltzmann constant ($k_B = R/\mathcal{N}_A = 1{,}38.10^{-23}$ J/K.).	**J/K**
m: Constant; (may be Substance Dependent).	
n: is the number of moles of the gas.	**mol**
N: is the number of molecules (in term of Avogadro's number ($\mathcal{N}_A$) of molecules).	**mol^{-1}**
P: Pressure.	**MPa**
Pc: critical pressure.	MPa
Pr: the values of reduced pressure.	
Pi: actual pressure value.	**MPa**
Pp: predicted pressure value**.**	**MPa**
R: is the universal (or perfect) gas constant (8.314×10 -03).	**MJ/kmol.K**
T: Absolute Temperature.	**K**
Tc: critical temperature.	**K**
***Tr*:** is the reduced temperature.	
V: Molar Volume.	**m3/kmol**
Vc: the critical molar volume**.**	**m3/kmol**
Vr: reduced volume.	
w: Pitzer's Acentric Factor.	
Z: The compressibility factor.	
α(T): is a temperature-dependent function in the equation.	
ΔH_{vap}: is the difference between the enthalpies of saturated vapor and saturated liquid	**KJ/mol**

Abbreviations

P-R: Peng and Robinson Equation.
PVT: Pressure-Volume-Temperature.
R-K: Redl ich-Kwong Equation.
S-R-K: Soave-Redlich-Kwong Equation.
VDW: van der Waals Equation.

VLE: Vapour-Liquid Equilibrium.

PCS: The principle of corresponding states.

EOS: Equations of State.

RMSE: Root Mean Squared Error.

RE: Relative Error.

General Introduction

The study of gases, both ideal and real, plays a pivotal role in the field of chemical engineering, particularly when examining the thermodynamic and volumetric properties of substances. Ideal gas laws provide a foundational understanding of gas behavior under theoretical conditions where interactions between molecules are negligible and the volume occupied by the gas particles themselves is insignificant compared to the container volume. However, these assumptions rarely hold true in practical applications, especially under high pressure or low temperature conditions where deviations from ideality become significant. [1]

To bridge the gap between the simplicity of ideal gas laws and the complexity of real gas behavior, cubic equations of state (EOS) have been developed. These mathematical models are designed to describe the state of matter under a given set of conditions: pressure, volume, and temperature. They account for intermolecular forces and the finite size of molecules, offering a more accurate representation of real gases. [2]

The necessity for equations of state arises from their wide-ranging applications in the design and optimization of chemical processes. Accurate predictions of thermodynamic properties such as phase equilibria, enthalpy, and entropy are essential for process modeling, simulation, and control. Volumetric properties like density and compressibility factor are equally critical for equipment sizing and safety analysis.[2]

In this thesis, we focus on n-butane and propane. These compounds find applications in various industrial processes, from fuel to refrigerants. And to evaluate their behavior, we delve into the comparative analysis of four prominent equations of state (Van Der Waals, Redlich-Kwong, Soave Redlich-Kwong, and Peng Robinson) against experimental data for these light hydrocarbons. Our objective is to evaluate their predictive capabilities and determine which equation provides the most reliable correlation with empirical observations, such as PV isotherm plotting and, mainly, the calculation of saturation molar volumes. This investigation not only improves our understanding of gas behavior but also informs the selection of appropriate EOS for industrial applications involving light hydrocarbons.

In order to try finding some answers to all that, our manuscript will be sequenced as it follows:

The first chapter is devoted to the theoretical section, which presents:

- PVT diagrams and their relations
- A generalization of equations of states starting with the ideal gas low and passing to the two parameters Ending with the three parameters Eos
- A review of the corresponding state principle and acentric factor

The second chapter contains an experimental section, which comprises:

- A list of the experimental PVT data
- The calculated isotherms and the molar volumes using Eos
- An application of the corresponding state principle and acentric factor

Finally, we will end up this work by a general conclusion, where our main finding will be presented.

Chapter One:

PVT Relations & Equations of State Evolution

I.1 Introduction:

Understanding the fundamental principles that govern the behavior of gases and liquids is crucial in many fields of science and engineering. This chapter delves into the essential concepts of Pressure-Volume-Temperature (PVT) relations and the evolution of equations of state, which are pivotal in describing the physical properties and behavior of substances.

Equations of state (EOS) are mathematical models that describe the state of matter under a given set of physical conditions. They are derived from empirical observations and theoretical foundations, providing a bridge between microscopic properties and macroscopic behavior. The evolution of these equations has seen significant advancements from the simplistic ideal gas law to more sophisticated models like the Van der Waals equation, Redlich-Kwong equation, and Peng-Robinson equation. Each evolution has brought about improved accuracy and applicability to a wider range of substances and conditions.

The study of PVT (pressure-volume-temperature) relations and equations of state provides critical insights into the properties of both ideal and real gases. By examining theoretical frameworks such as the kinetic theory for ideal gases, and more complex equations of state, we can predict and describe the behavior of substances with increasing accuracy.

Additionally, concepts like the corresponding state principle and the acentric factor further refine our understanding, allowing for better predictions of fluid behavior across different conditions. This comprehensive exploration will begin with the fundamental PVT relations for pure substances and progressively delve into the various equations of state and their specific parameters, providing a robust foundation for understanding fluid behavior in diverse scenarios.

This chapter will explore the historical context and theoretical foundations of PVT relations and equations of state. We will discuss the key equations that have shaped our understanding, their derivations, and their limitations. Additionally, we will highlight the practical applications and implications of these concepts in various industries.

And by the end of this, readers will have a comprehensive understanding of PVT relations and the progression of equations of state, equipping them with the knowledge to apply these principles in both academic and professional settings.

I.2 PVT Diagrams for Pure Substance

A pure substance is one that has the same chemical composition throughout. It can exist in more than one phase, but each phase's chemical makeup must be the same, for example, a mixture of liquid water and steam or ice and water.

The behavior of a substance under different pressure and temperature conditions is described by the pressure-volume-temperature (PVT) phase diagram for a pure substance, these diagrams are essential to comprehending a substance's characteristics and phase transitions. Those diagrams are represented by property tables, T-V, P-V, and P-T diagrams. This is meant to provide an explanation of how to determine a system's state using property tables and PVT diagrams. To calculate the heat and work interactions of a system conducting a process, the initial and final states must be specified. [3]

I.2.1 P-T diagram (phase change)

A phase diagram is a graphical representation of the phases (solid, liquid, gas) of a substance and the conditions (temperature, pressure) under which each phase exists. In a phase diagram, the three phases are separated by three lines, indicating the conditions where phase transitions occur. Most pure substances, such as water have a similar phase diagram structure with three phases and three phase transition lines.

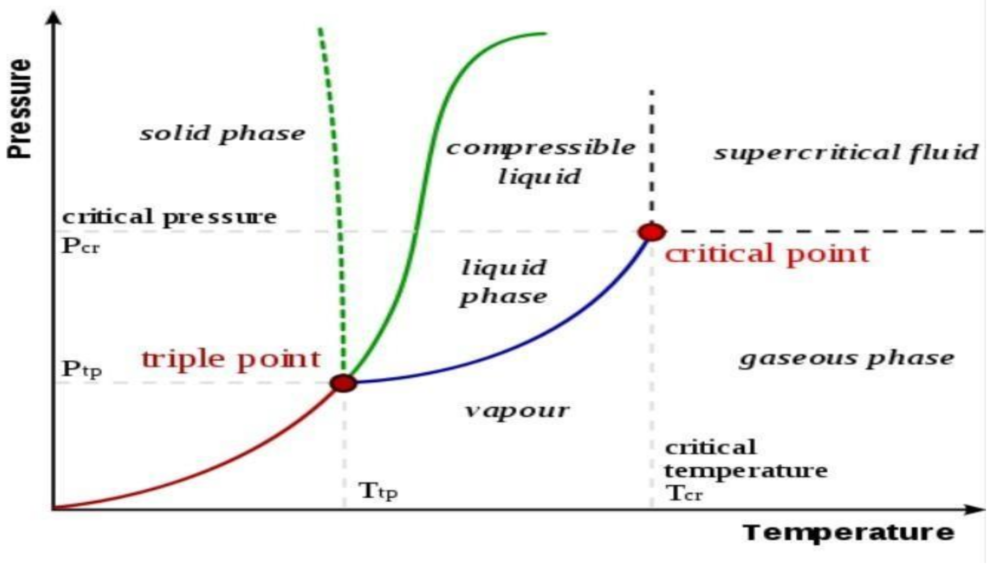

Figure I.2-1: Phase diagram for a pure substance [4]

I.2.1.a Experimental PT diagram for propane & butane

The next figure (I-2-2) represents the experimental diagram for propane, where it shows the phase behavior with changes in temperature and pressure. The curve between the critical point and the triple point shows the propane boiling point with changes in pressure. It also shows the saturation pressure with changes in temperature.[5]

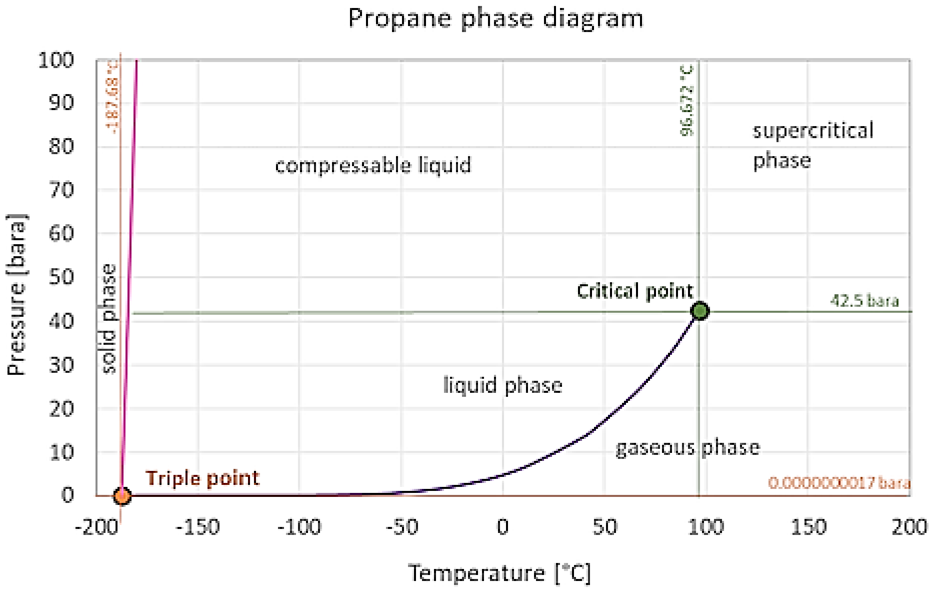

Figure I.2-2: P-T phase diagram for propane [2]

The phase diagram for butane, in figures I-2-3, feature distinct curves that connect their respective critical point and triple point. These curves, known as vapor pressure curves or saturation lines, depict the equilibrium between the liquid and vapor phases of each substance.

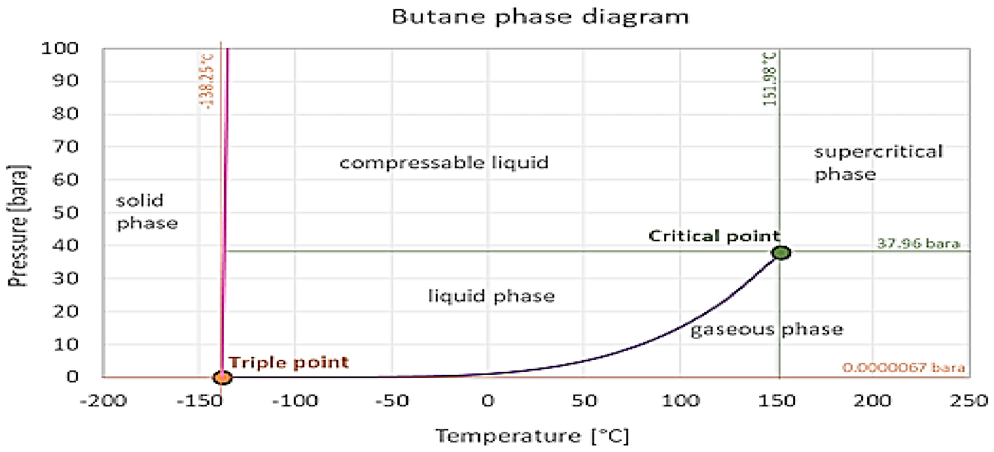

Figure I.2-3: P-T phase diagram for butane [4]

Along these curves: The boiling point temperatures of propane and butane, at which they transition from liquid to vapor, vary with changes in pressure.

The saturation pressures of propane and butane, at which they condense from vapor to liquid, vary with changes in temperature.

I.2.2 P-V diagram of Pure Substance

A Pressure-Volume diagram commonly referred to as P-V diagram, serves as a graphical depiction illustrating the relations between pressure and volume for a specific pure substance, characterized by its uniform. Proficiency in interpreting a P-V diagram is instrumental in comprehending the fundamental properties of pure substances, a pivotal facet of thermodynamics. [6}

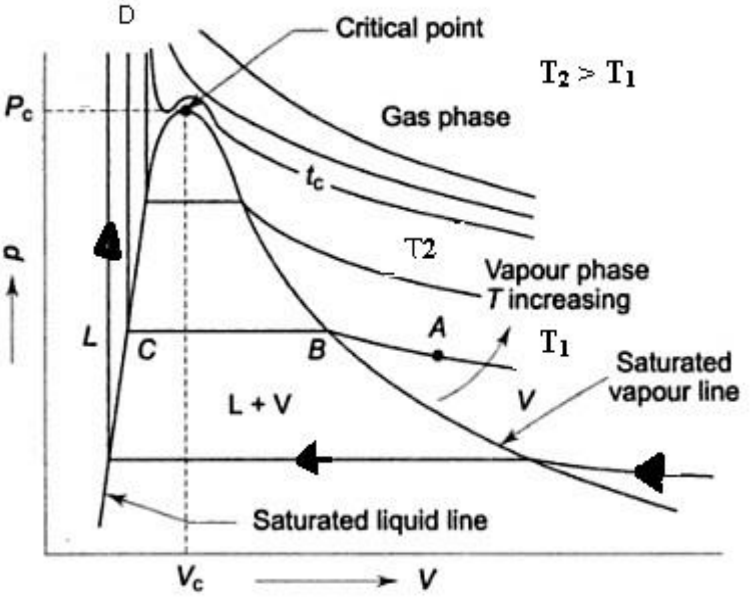

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Figure I.2-4:P-V for a pure substance ***[6]***

I.2.2.a **Experimental PV diagram for methane**:

The following figure (I-2-5) represents the van der Waals isotherms of (CH 4) near critical temperature. Shaded region represents vapor-liquid equilibrium.[6] The critical temperature of CH4 is 190.564 K. [7]

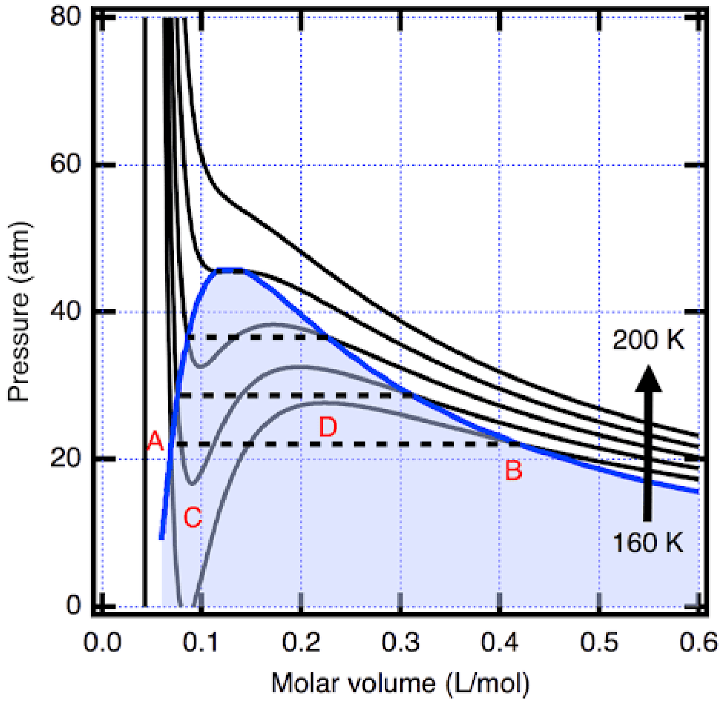


Figure I.2-5:P-V diagram for methane [6]

I.3 PVT Relations & Equations of State (EOS)

The PVT relations elucidate the interplay of these fundamental state variables within a pure substance at thermodynamic equilibrium. This relation is commonly articulated through an equation of state, the complexity of which is contingent upon the specific substance and prevailing conditions [9]

Equations of State (EOS) are mathematical representations that characterize the characteristics of substances, notably gases and liquids, across varying thermodynamic scenarios. Prominent EOS encompasses the ideal gas law, Van Der Waals equation, Redlich-Kwong equations, and Peng-Robinson equation.

The first equation of state was introduced by Johannes van der Waals in 1873 [10] , and he based in the kinetic theory of ideal gases which was established in the 19th century by the scientist James Clerk Maxwell and physicist Ludwig Boltzmann, and the relation between them is that both describe the behavior of gases[11].

In the next title we are going to give you an overview about the kinetic theory of ideal gases.

I.3.1 Kinetic Theory for Ideal Gases (zero parameters):

The kinetic theory of ideal gases is a theoretical framework that describes the behavior of an ideal gas at the molecular level, without relying on any adjustable parameters. Their experience fully elastic collisions in which no energy is lost when they crash into one to other or the walls of their container. The theory makes the assumption that there are no forces of attraction or repulsion between the particles, and that the volume of the container is much larger than the volume of the particles. A microscopic picture of temperature as a metric of microscopic motion is provided by the direct relation between the temperature of the gas and the average kinetic energy of the molecules. This parameter free method offers profound insights into the nature of gaseous states and enables the formulation of fundamental gas laws.

The ideal gas law serves as a fundamental equation of state linking: Pressure, Volume, and Temperature (PVT) for ideal gases, outlining their behavior under standard conditions. This law operates on the premise that gas particles possess insignificant volume and exhibit no mutual interactions, as a Macroscopic picture.[12]

The two version of the ideal gas law, can be written as:

$$\mathrm{PV} = \mathrm{Nk_BT} \quad ; \qquad \text{Microspic Version} \tag{1}$$

$$\mathrm{PV} = \mathrm{nRT} \quad ; \qquad \text{Macrosopic Version} \tag{2}$$

Where:

n: is the number of moles of the gas.

R: is the universal (or perfect) gas constant.

N: is the number of molecules (in term of Avogadro's number ($\mathcal{N}_\mathrm{A}$) of molecules.

$\mathbf{k_B}$: is the Boltzmann constant ($\mathrm{k_B} = \mathrm{R}/\mathcal{N}_\mathrm{A} = 1{,}38.10^{-23}$ J/K.).

However, real substances frequently require more intricate equations of state to precisely model their PVT characteristics, particularly in the vicinity of the critical point or during phase transitions. Some of the more widely recognized equations of state for real substances include:

I.3.2 Van der WAALS Theory (Two parameters EOS):

The VAN DER WAALS equation of state (EOS) is a basic, but crucial, model in statistical mechanics and thermodynamics. It was intended to better reflect the ideal gas law by taking into consideration the finite size of gas molecules and the attractive forces that exist between them.

The Van der Waals equation can be written as:

$$(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2})(\mathrm{V} - \mathrm{b}) = \mathrm{RT} \tag{3}$$

Where the constants a and b have an approximate physical meaning which is:

- *a:* (molecular attraction): It represents the strength of the molecular interactions or the attraction forces between molecules. This constant is a measure of the energy required to separate two molecules from each other to infinity.[13] [14]
- b: (molecular volume): It represents the excluded molar volume due to the finite size of molecules. This constant is related to the molecular size and is calculated as the volume of a sphere with a diameter equal to the distance between the centers of two molecules. It accounts for the fact that the centers of two molecules cannot be closer than their diameter.[13][14]

The equation (1) indicates some important characteristics, at low pressures; the gas phase volume is large compared with the molecule's volume. So, the term b is negligible when compared with V, and the attractive force term a/V^2 turn to be negligible. So, the VdW EOS goes back to the original ideal gas equation.

At high pressure (P→ ∞), volume V, tend to be extremely small, and will have almost the same value of b, which is the actual molecular volume, can be expressed as:

$$\lim_{P\to\infty} V(P) = b \tag{4}$$

Van der Waals, or any other type of EOS could be represented in a more general formula:

$$\mathrm{P} = P_{repulsion} - P_{attraction} \tag{5}$$

The repulsion pressure terms defined by:

$$P_{repulsion} = \frac{RT}{v-b} \tag{6}$$

The attraction pressure terms defined by:

$$P_{attraction} = \frac{a}{v^2} \tag{7}$$

To determine the values of (a) and (b), for pure substances, van der Waals realized that the critical isotherm has an inflection point and a horizontal slope at the critical point, and can be calculated as:

$$a= \Omega_a \frac{R^2T_C^2}{P_C} \tag{8}$$

$$b=\Omega_b \frac{RT_C}{P_C} \tag{9}$$

The formulation of a and b can be determined using the critical point mathematical properties of the substance, that's Because the critical point on a P-V plot is a point of inflection the usual first two pressure-volume derivatives are set to zero:

$$(\frac{\partial P}{\partial V})_{T_C} = \frac{-RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3}=0 \tag{10}$$

$$(\frac{\partial^2 P}{\partial V^2})_{T_C} = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4}=0 \tag{11}$$

After resolution of the system of those 3 equations, we obtain those formulations:

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \tag{12}$$

$$b = \frac{RT_c}{8P_c} \tag{13}$$

$$V_c = 3b = \frac{3}{8}\frac{RT_c}{8P_c} \tag{14}$$

The VdW EOS importance could be summarized in few points**:**

- Its prediction ability was successfully better than ideal gas EOS.
- The first equation predicts continuous behavior of matter between liquid and gas
- It helped to formulate the Principle of Corresponding States (PCS).
- It became basis for other developed cubic EOS. [15]

As conclusion, while the Van der Waals equation of state may not have direct practical applications in modern times, its historical significance, theoretical basis, and role as a foundation for the derivation of contemporary EOSs ensure its enduring importance in the field of thermodynamics.

The van der Waals equation of state has been reformulated and improved upon by several researchers over time. One significant improvement was made by the Redlich and Kwong brothers, who introduced a temperature-dependent attractive parameter and a co-volume term to enhance the accuracy of the equation, whereas:[16]

I.3.3 Redlich &Kwong Equation of State (Two parameters):

The equation of state of Redlich-Kwong was published in 1949, marking the first significant and successful adjustment to the attraction parameter. Van der Waals EOS was updated by Redlich and Kwong (R-K) equation of state is one of the simplest forms that need only the critical pressure and temperature:

$$P = \frac{RT}{(V-b)} - \frac{a}{T^{0.5}V(V+b)} \tag{15}$$

Where the constants a and b are obtained by equating the two pressure-volume derivatives to zero at the critical point, as in the case of the VdW equation. In terms of (Tc) and (Pc) a and b are:

$$a = 0.42748\frac{R^2T_c^{2.5}}{P_c} \tag{16}$$

$$b = 0.08664\frac{RT_c}{P_c} \tag{17}$$

An important consideration in the derivation of the Redlich-Kwong (R-K) equation was the experimental observation that the volume of all gases approaches a limiting value at high pressures. Redlich and Kwong assumed this limiting volume to be proportional to the critical volume of the substance: [17]

$$\mathrm{b} = 0.26\mathrm{V_c} \tag{18}$$

I.3.3.a Advantages of the R-K Equation

The R-K equation is remarkably simple and can be employed in a wide range of property calculations. It has achieved widespread application and acceptance in chemical engineering practice, primarily due to the good degree of approximation it provides through comparatively simple means. Like the vdW, the R-K equation is a well-behaved function that can be used to represent gas phase properties over a broad range of pressures. [17]

I.3.3.b Limitations of the R-K Equation:

However, like any other equation of state, the R-K equation has its shortcomings. It cannot provide accurate predictions for widely different types of fluids over extensive ranges of temperature, pressure, and density conditions. The original R-K equation was proposed for non-polar fluids in the gaseous state only, and its application to polar fluids, their mixtures, and the liquid state is not recommended. Additionally, the fundamental criterion of the equality of fugacity is not implicit in the equation, and therefore, it should not be strictly applied for the calculation of vapor-liquid equilibrium.

[19] [20] [21] [22]

Despite these limitations, the R-K equation is still a useful tool in chemical engineering, offering a balance of simplicity and precision for a variety of applications incorporating intrusive phase characteristics and volumetric behavior. However, this does not diminish the need of strengthening and developing this equation, which we will discuss in the following title.

I.3.4 Soave Redlich &Kwong Equation of State (Three parameters):

The Soave adaptation of the Redlich-Kwong equation of state, introduced by Giorgio Soave in 1972, entailed refining the original equation to more effectively capture the characteristics of substances, particularly in vapor-liquid equilibrium (VLE) scenarios. This enhancement involved replacing the $T^{1/2}$ term in the attractive term's denominator with a sophisticated temperature-dependent expression. The objective of the Soave modification was to enhance the precision and versatility of the Redlich-Kwong equation, specifically in forecasting phase equilibria and thermodynamic attributes of gases and liquids.

The SRK EOS model is defined by:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{19}$$

Where: a and b are the EOS model parameters. for pure component parameters can be calculated:

$$a = \Omega_a \frac{R^2 T_C^2}{P_C} \alpha(T) \tag{20}$$

$$b = \Omega_b \frac{RT_C}{P_C} \tag{21}$$

$$\alpha(T) = [1 + m(\omega)(1 - \sqrt{\frac{T}{T_C}})]^2 \qquad (22)$$

In equations **(20)**,**(21)** and**(22)** the coefficients Ω_a and Ω_b , and the value of $\boldsymbol{\alpha(T)}$ can be calculated by: [23] [24] [25]

$$\Omega_a = 0.42748 \ldots. \qquad (23)$$

$$\Omega_b = 0.08664 \ldots. \qquad (24)$$

$$m(\omega) = 0.480 + 1.57\omega - 0.57\omega^2 \qquad (25)$$

The modified SRK equation retains the simplicity of the original R-K equation, requiring only the critical pressure, critical temperature, and molecular weight as input parameters. Additionally, the modified SRK equation is simpler in form compared to the original R-K equation. [27]

In summary, the adjustments made to the SRK equation, such as modifying the co-volume parameter, represent a significant advancement over the R-K equation for predicting vapor pressures and VLE (vapor-liquid-equilibrium) properties across a wide range of compounds. This improved accuracy and ease of use make the modified SRK equation a valuable tool for various thermodynamic calculations and process simulations. [28]

I.3.5 Peng & Robinson Equation of State (Three parameters):

The Peng-Robinson (PR) equation of state (EOS) is a widely used cubic equation in the field of petroleum and chemical engineering. Developed by Peng and Robinson in 1976, the original PR EOS was later modified in 1978 to improve its accuracy in predicting the phase behavior of substances.

This equation can be written in the following form:

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{V(V + b) + b(V - b)} \qquad (26)$$

Where (a) and (b) are the EOS model parameters. The pure component parameters (a and b) can be calculated by:

$$a = 0.45724 \frac{R^2 T_C^2}{P_C} \alpha(T) \qquad (27)$$

$$b = 0.07780 \frac{RT_C}{P_C} \qquad (28)$$

$$\alpha(T) = [1 + m(\omega)(1 - \sqrt{\frac{T}{T_C}})]^2 \qquad (29)$$

$$m(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2,\ \omega \leq 0.49 \tag{30}$$

$$m(\omega) = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3, \omega > 0.49 \tag{31}$$

With: **[26]**

α : is a function of temperature*;*

ω: is the acentric factor*;*

Tr: is the reduced temperature $\frac{T}{T_C}$ with *Tc* being the critical temperature.

I.4 Corresponding State Principle & Acentric Factor

The principle of corresponding states and the acentric factor are significant concepts within the realms of thermodynamics and fluid mechanics, especially concerning the study of gas and liquid behaviors across diverse conditions.

I.4.1 The principle of corresponding states (PCS):

It’s a fundamental concept applied within equations of state (EOS) to compare the behavior of diverse fluids under similar reduced conditions. Initially introduced by van der Waals**,** this principle posits that substances demonstrate analogous behavior when assessed at equivalent reduced states. Reduced parameters, including reduced pressure (Pr), reduced temperature (Tr), and reduced volume (Vr), are utilized to establish corresponding states. Through the PCS, fluids can be effectively compared by accounting for their deviation from critical conditions, enabling the estimation of properties and behaviors based on data from analogous fluids. [27] [28] [29]

Within the domain of EOS, the PCS plays a pivotal role in establishing thermodynamic relation, facilitating the formulation of generalized equations that are universally applicable across different substances. By adhering to the principle of corresponding states, equations like the van der Waals EOS can be formulated and utilized to predict fluid behavior independent of their specific molecular makeup. This principle enables the prediction of properties such as reduced volume (Vr) for any fluid at identical reduced pressure and temperature conditions, underscoring the consistent behavior of gases at corresponding states. [28] [29] [30]

Reduced properties provide a measure of the “departure” of the conditions of the substance from its own critical conditions and are defined as follows: [31]

$$\mathrm{P_r} = \frac{\mathrm{P}}{\mathrm{P_C}} \tag{32}$$

$$\mathrm{T_r} = \frac{\mathrm{T}}{\mathrm{T_c}} \tag{33}$$

$$V_r = \frac{V}{V_c} \tag{34}$$

When a substance is at its critical condition, the values of reduced pressure (Pr), reduced temperature (Tr), and reduced volume (Vr) are all equal to unity.

Beyond the critical point, the reduced parameters exceed 1, with Tr > 1, Pr > 1, and Vr > 1. Conversely, when all conditions are subcritical, the reduced parameters fall below 1, such that Tr< 1, Pr< 1, and Vr< 1.

The critical point serves as a reference point, providing a scaling factor that enables the comparison of substances based on their "departure from criticality" or reduced properties.

By normalizing the pressure, temperature, and volume with respect to their critical values, the PCS allows for the comparison of fluids across different molecular structures and compositions. This approach is particularly useful in the context of equations of state (EOS), where generalized correlations can be developed based on the reduced properties of substances. [32] [33] [30]

Upon CSP, the VdW EOS can be written as the next new form:

$$(P_r + \frac{3}{V_r^2})(3V_r - 1) = 8T_r \tag{35}$$

Equation (35) represents the reduced form of the van der Waals equation of state (EOS). This equation demonstrates its universality by being independent of the specific fluid under consideration. By inputting the reduced conditions of reduced pressure (Pr) and reduced temperature (Tr) into this equation, it yields the reduced volume (Vr) irrespective of the fluid being analyzed. Consequently, calculating Vr for a particular fluid using the van der Waals reduced EOS (Equation 35) with specific Pr and Tr values will yield the same Vr for any other fluid at identical Pr and Tr conditions.

An excellent example is the popular Z-chart of Standing and Katz, shown in Figure

I-4-1. In fact, most of the correlations that we use in thermodynamics are based on this principle. This explains why “Pr” and “Tr” so often appear in thermodynamic correlations. The main reason for using “Pr” and “Tr” is to obtain the most generalized correlation possible, so that it is suitable for use with most substances.

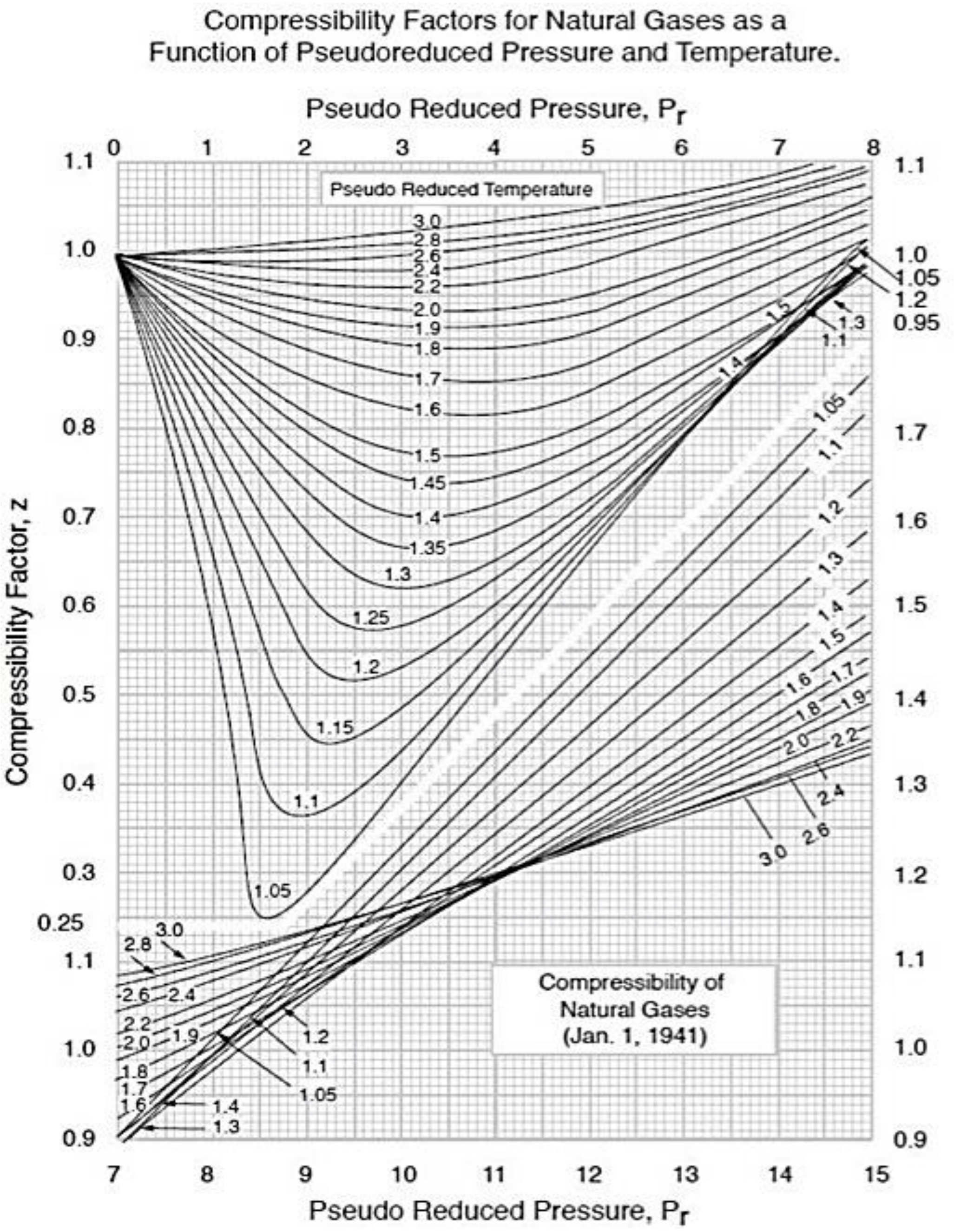


Figure I.4-1: compressibility factors for natural gases as a function of pseudo reduced pressure and temperature [34]

I.4.2 Acentric factor

The acentric factor: denoted as "ω", is a dimensionless parameter that was introduced by the renowned scientist **Pitzer** in 1955. This concept has since proven to be highly valuable in the comprehensive characterization of various substances.

I.4.3 Significance of the Acentric Factor

The acentric factor has become a standard property, alongside other commonly used characteristics, for the proper and complete description of any single pure component. These other properties typically include:

- Molecular weight.
- Critical temperature.
- Critical pressure.
- Critical volume.

Pitzer came up with this factor by analyzing the vapor pressure curves of various pure substances. From thermodynamic considerations, the vapor pressure curve for pure components can be mathematically described by the Clausius–Clapeyron equation:

$$\frac{1}{P}\frac{dP}{dT}=\frac{\Delta H_{vap}}{RT^2} \tag{36}$$

The utilization of the integrated form of Equation (36) is a prevalent practice in the mathematical modeling of vapor pressure data. This integrated version of the equation (36) reveals a linear relationship between the logarithm of vapor pressure and the reciprocal of absolute temperature. When expressed in reduced conditions, vapor pressure data tends to exhibit an approximately linear trend when graphed as "logPr" against "1/Tr," or equivalently:

$$\log_{10}\mathrm{P_r}=\mathrm{a}\left(\frac{1}{\mathrm{T_r}}\right)+\mathrm{b} \tag{37}$$

This linear correlation observed in the reduced representation of vapor pressure data provides a valuable tool for analyzing and predicting the behavior of substances across a range of temperatures. By leveraging this linear relationship, researchers and practitioners can effectively fit vapor pressure data mathematically, enabling the extrapolation and interpolation of vapor pressure values with confidence. The simplicity and predictive power of this linear relationship in reduced conditions enhance the accuracy and efficiency of modeling vapor pressure behavior in various systems. [35]

While the principle of corresponding states does imply that the reduced vapor pressure curves of different substances should demonstrate a similar linear trend when plotted as "log Pr" versus "$\frac{1}{T_r}$" it does not necessarily mean that the specific slope (a) and intercept (b) of these linear relations will be identical across all substances.

Recognizing the need to quantify the deviations of substances from the two-parameter corresponding states predictions, **Pitzer** analyzed the vapor pressure data for noble gases. He observed that a value of log (Pr) = -1 was achieved at approximately Tr = 0.7 for these substances. Pitzer then proposed that if the vapor pressure data of a substance show

log(Pr) = -1 at Tr = 0.7, it can be considered to behave similarly to the noble gases, and comply with the two-parameter corresponding states. If not, the difference can be computed and used as a measure of the deviation. [36] [37]

By establishing this reference point and quantifying the deviations, Pitzer introduced the acentric factor, a valuable tool for characterizing the thermodynamic properties of fluids and accounting for their non-ideal behavior, through the following equation:

$$\omega = -\log_{10}(P_r)_{T_{r=0.7}} - 1 \tag{38}$$

Noble gases, being the reference themselves, have an acentric factor value of zero (ω=0). Substances with an acentric factor of zero are called “simple” substances. The acentric factor is said to be a measure of the non-sphericity (acentricity) of the molecules. Therefore, the three-parameter corresponding state theory of Pitzer reads: *“Fluids that have the same value of ω, will behave alike, at the same conditions of reduced pressure and temperature”.*

To make this more comprehensible, we will provide you the next table as an example of the critical pressure, temperature, and the acentric factor:

Table I.4-1: Example of EOS component properties for a multi-component fluid mixture [38]

Component Properties			
Component Name	Tc (°F)	Pc (psia)	ω
C1	-116.66	667.0	0.011
C2	89.91	706.6	0.099
C3	206.02	616.1	0.152
i-C4	274.5	527.9	0.186
n-C4	305.5	550.6	0.200
i-C5	369.0	490.4	0.229
n-C5	385.8	488.8	0.252
C6	464.4	490.0	0.240
C7	529.0	455.3	0.274
C8	585.2	420.4	0.312

In summary, the principle of corresponding states and the acentric factor provide a powerful tool for understanding and predicting the behavior of substances in the chemical and petroleum industries. These principles facilitate phase equilibrium calculations, thermodynamic property estimation, and the design and simulation of industrial processes, ultimately contributing to the optimization of industrial operations and the development of more efficient technologies.[39]

I.5 Conclusion

In conclusion, the exploration of PVT relations and the evolution of equations of state underscore the complexity and depth of understanding required to accurately model the behavior of substances under varying conditions. PVT relationships are foundational to thermodynamics and provide critical insights into how substances respond to changes in pressure, volume, and temperature.

This chapter has traced the development of these concepts, and delineated the progression of these fundamental concepts, from the foundational ideal gas law to more sophisticated equations of state like the Van der Waals equation and beyond. This evolution underscores the ongoing endeavor to enhance our models to accommodate the pure and non-pure substance complexities.

The development of equations of state, has been driven by the need to accurately describe the behavior of real fluids, particularly in the petroleum industry. The field continues to evolve, with ongoing research aimed at improving the accuracy and applicability of these thermodynamic expressions.

II.

Chapter Two:

Evaluation of Cubic EOS Ability to Represent PVT Relations, for n-Butane and propane

II.1 Introduction

Within reservoirs, a vast array of substances with varying chemical compositions can be found in the fluids. These substances encompass both hydrocarbons and nonhydrocarbons, with hydrocarbons ranging from simple methane to complex compounds containing up to 100 carbon atoms. The chemistry of hydrocarbon reservoir fluids is highly intricate. Despite this complexity, equations of state have demonstrated remarkable accuracy in predicting the phase behavior of these intricate fluids.

An equation of state (EOS) is a mathematical expression that establishes a relationship between pressure, volume, and temperature. It is utilized to describe the volumetric properties, vapor-liquid equilibria (VLE), and thermal characteristics of both pure substances and mixtures. Since Van der Waals introduced his equation in 1873, numerous equations of state have been proposed. Currently, in chemical engineering, several equations of state are employed for reservoir fluid calculations due to their proven reliability.

In this part, we explore the strength of these equations on two pure substances, which are n-Butane and propane, by calculating the pressure and the molar volume for each molecule.

First let’s take a look of the experimental data of the two components:

II.2 Experimental PVT Data

The following table represent the experimental data of n-Butane, taken from NIST web site, to illustrate the PV diagram.

Table II.2-1:saturation curves for n-Butane [40]

Temperature (K)	**Pressure (MPa)**	**Molar volume(m3/kmol)**	
		Liquid state	gaseous state
240	0.2582	0.091546	81.85915
260	0.2582	0.094587	34.39053
280	1.1718	0.097992	16.6533
300	1.1718	0.101877	8.91411
360	2.4892	0.118767	1.977543

400	2.4892	0.142444	0.801213
425.15	**3.796**	**0.25508**	**0.25508**

From the same web site, we're collect the experimental PVT data for Propane.

Table II.2-2:saturation curves for propane.[40]

Temperature (K)	**Pressure (MPa)**	**Molar volume(m3/kmol)**	
		Liquid state	gaseous state
90	9.69E-10	6.05×10^{-02}	7.72×10^{08}
150	0.00028345	6.61×10^{-02}	$4.40\times 10^{+03}$
250	0.21796	7.90×10^{-02}	8.93
290	0.76914	8.74×10^{-02}	2.65
310	1.2724	9.32×10^{-02}	1.58
350	2.9514	$1.15\times 10-^{01}$	5.72×10^{-01}
369.89	4.2512	2.00×10^{-01}	2.00×10^{-01}

The experimental PVT diagram that follows, was obtained using previously collected experimental data for each component, it will be serve as a reference for comparing the calculated parameters.

II.2.1 Experimental PT & PV Diagrams Plotting

Initially, for n-butane we plot the experimental PV diagram at different temperatures below and above the critical temperature.

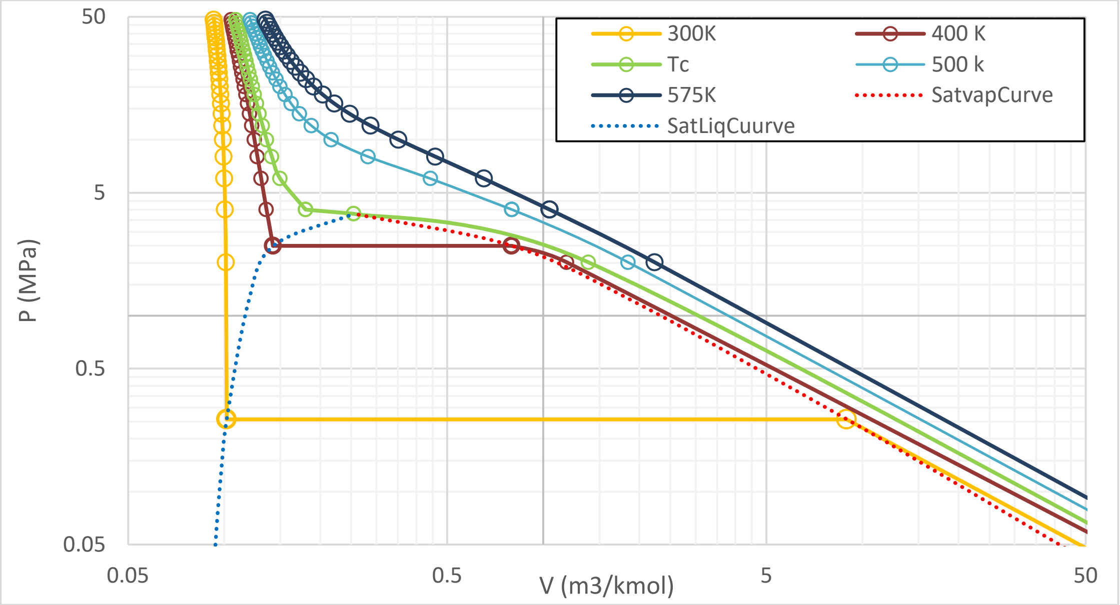


Figure II.2-1:Experimental PV diagram plotting for n-Butane

With the same way we will plot propane’s experimental PV diagram at different temperature, as it shown bellow

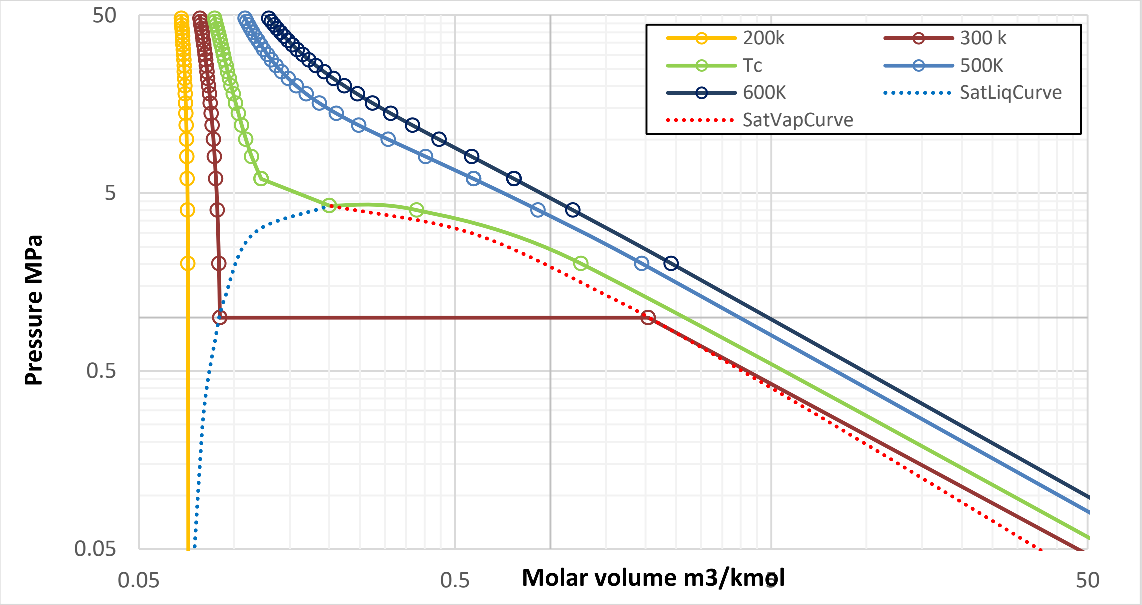


Figure II.2-2:Experimental PV diagram plotting for propane

In the next section, we will primarily focus on isotherm plotting, and to achieve this, we will calculate the pressure using the cubic equations of state which are VDW, RK, SRK, and the PR equation. For each of those equations, we need their specific parameters and the critical parameter for the two components.

II.3 Van der WAALS (VdW) Isotherms Plotting

We will use the equation (3) to determine the pressure in MPa using the parameters of van der Waals (a) and (b) that are calculated by the critical pressure and temperature. Additionally, we will choose an interval of molar volume values, ensuring that V cannot be less than b as this will lead to negative values of P, which is not physically acceptable

II.3.1 Parametrization

As table II.3-1 shows, we listed the critical parameter values for the two substances that we will use in each equation of state:

Table II.3-1:critical point for n-Butane and propane [40]

	Propane	n-Butane
Critical pressure Pc [MPa]	4.2512	3.7960
Critical temperature [K]	369.89	425.125
Critical Vm [m3/kmol]	0.200	0.255

The next table presents Van der Waals's calculated parameters:

Table II.3-2:Van der Waals's parameters

	propane	n-Butane
a [Mpa. (m3/kmol)2]	0.93850691	*1.38862*
b [m3/kmol]	0.09042345	*0.1164*
R [MJ/kmol.K]	8.314×10^{-03}	

II.3.2 Calculation

Now, we can smoothly calculate the pressure for n-butane and Propane (***Appendix A***) at different temperatures after we set the VDW's parameters.

II.3.3 Plotting

After we get the computed van der Waals pressure values, we will plot the isotherms and the calculated PV diagram for n-butane, as shown below:

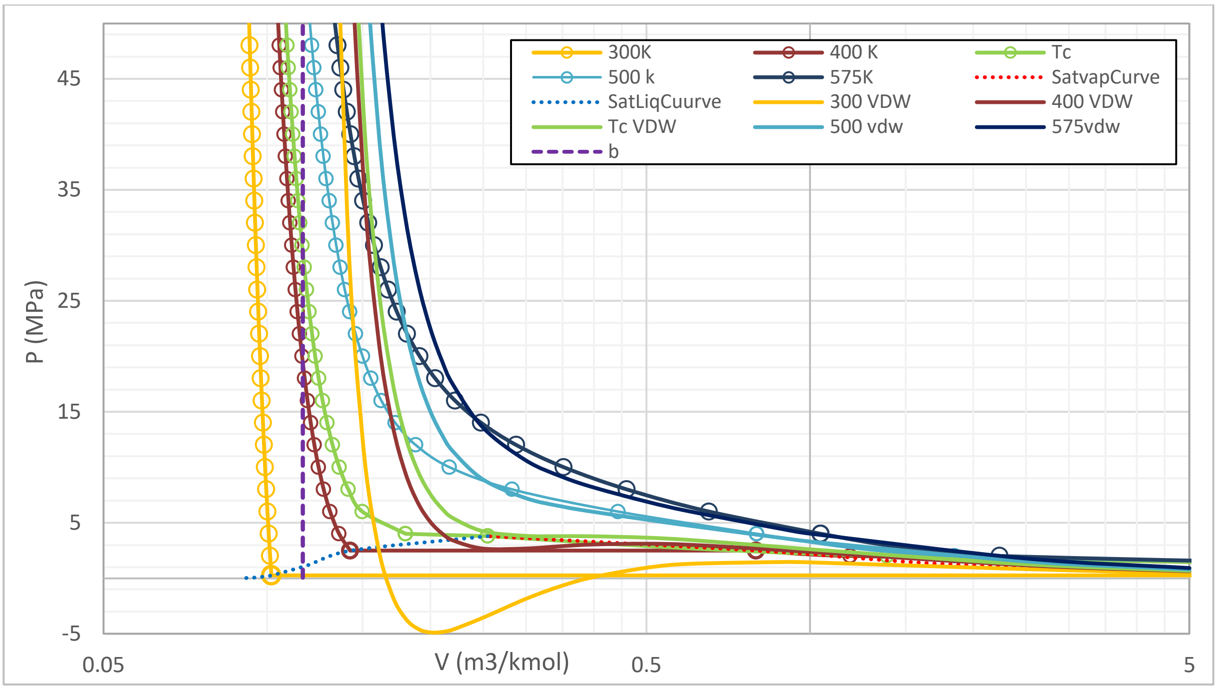


Figure II.3-1:Isotherms computed using VDW for n-Butane

By doing the same thing for propane, we get the following PV diagram:

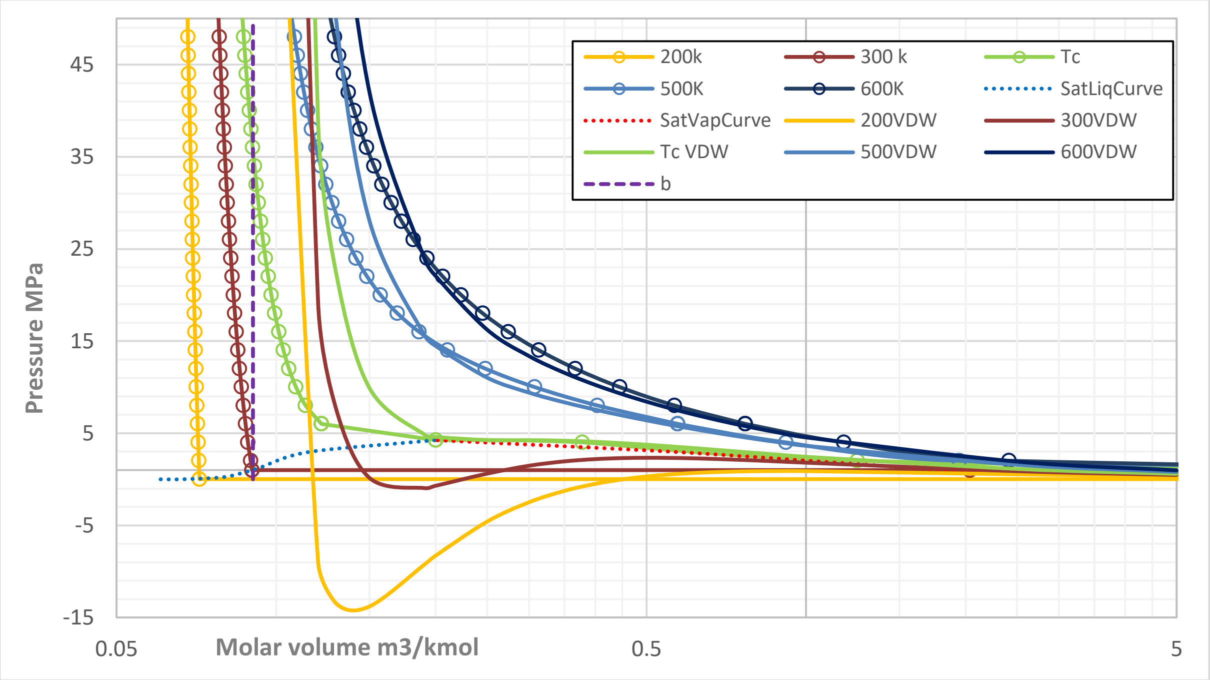


Figure II.3-2:Isotherms computed using VDW for Propane

The next step will evaluate the performances of this model compared to the experimental data.

II.3.4 Van der Waals performances evaluations

We will use the statistical metric Root Mean Squared Error (RMSE) to detect the average difference between two modules (the experimental and calculated models). It is defined with the next formula:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(P_a - P_p)}{n}}$$

Where Pa: actual pressure value

Pp: predicted pressure value

n: number of values

Using our experimental data (see ***Appendix E*** and ***F***), we've performed the RMSE calculations for all isotherms for the two components. Starting with n-butane, we've got:

Table II.3-3:VDW's RMSE results for n-butane

		300 K	400 K		Tc	500 K	575 K
VDW's RMSE	vapor	0.005866	0.13645	Before Vc	0.206323	0.209298	0.498573
	liquid	309.6791	1744.63	After Vc	1960.858	8037.151	238.1663

Going to propane had the following outcomes:

Table II.3-4:VDW's RMSE results for propane

		200 K	300 K		Tc	500 K	600 K
VDW's RMSE	vapor	0.0000846	0.040111	Before Vc	0.186092	0.469287	0.828166
	liquid	311.0099	1460.954	After Vc	4789.174	157.8519	41.77357

II.3.5 VdW Results description & interpretation

Figures II.3-1 and II.3-2 show the experimental and van der Waals 'isotherm plots, where we clearly can remark the mismatching of VDW isotherms to the experimental at the liquid state also we notice that (b) is over estimated, and for the vapor state they are fairly paralleling well, and to detect the exact average, we will notice it by the RMSE outcomes as indicated in the previous tables (II.3-3 and II.3-4). Hence, for the low temperatures, we got results approaching zero. And it started gradually moving away from the zero values as the temperature increased.

This gives us a general view of how the van der Waals model reacts. Where it appears that it has limitations, especially in the liquid phase due to the strong intermolecular forces are generated from the high pressure and low temperature, in this case, the term(a) it doesn't capture the complex interactions.

II.4 Redlich & Kwong (RK) Isotherms Plotting

After we determine the pressure using the van der Waals' equation, we move on to the second model, the Redlich-Kwong equation.

II.4.1 Parametrization

First, we need to calculate the specific parameters (a) and (b) for this model using the critical parameters mentioned in Table II.4-1 for each component, as shown:

Table II.4-1: Redlich Kwong's Parameters

	propane	n-Butane
a [Mpa. (m3/kmol)2]	*18.2896662*	*29.01287*
b [m3/kmol]	*0.0626743*	*0.08068*
R [MJ/kmol.K]	8.314×10^{-03}	

II.4.2 Calculation

Depending on equation (15), we have the calculations results for n-butane and Propane (see ***Appendix B***)

II.4.3 Plotting

The following is the RK's isotherm plot compared to the experimental for n-butane:

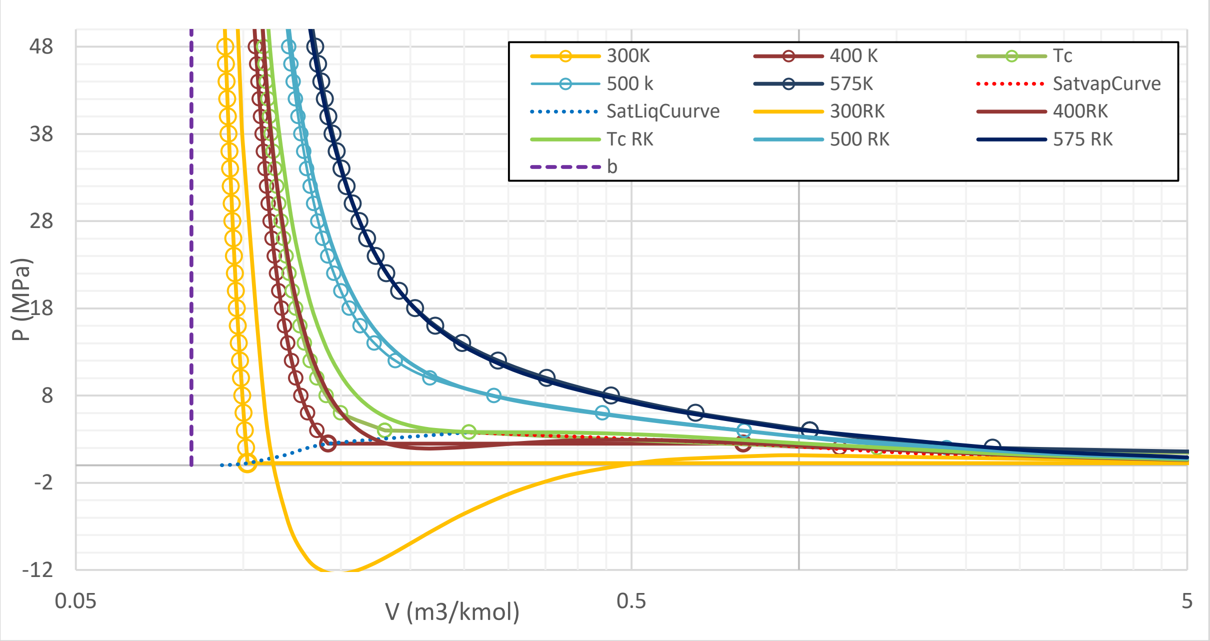


Figure II.4-1:Isotherms computed using RK for n-Butane

And the next plot is for propane:

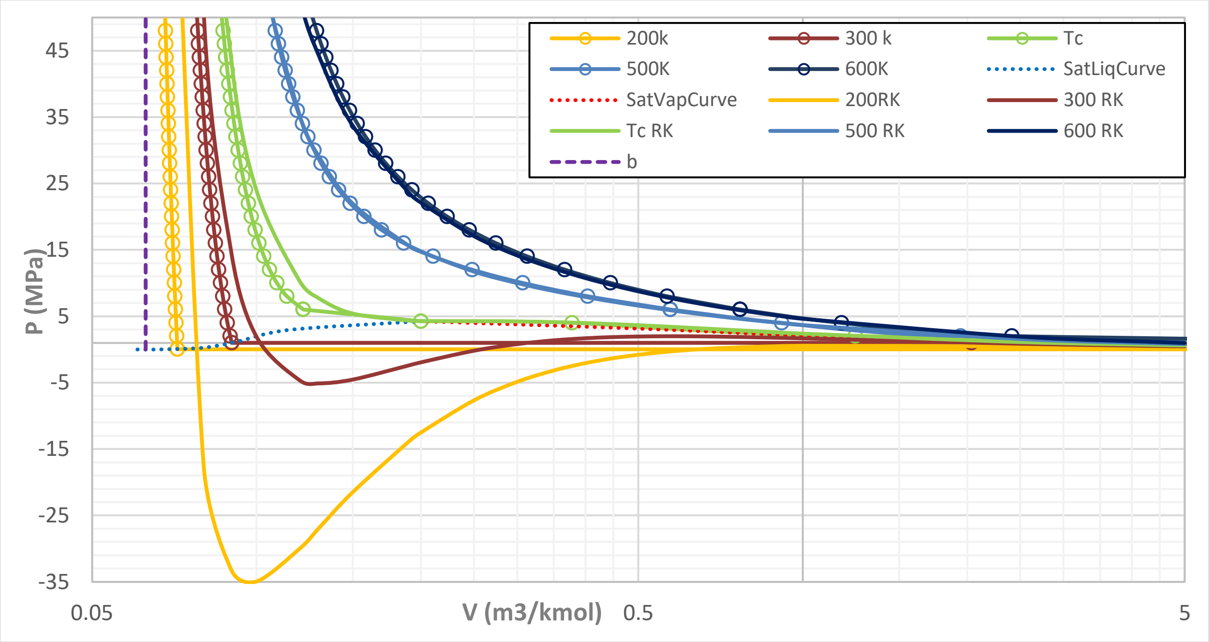


Figure II.4-2:Isotherms computed using RK for Propane

By applying the RMSE to the RK for n-butane and propane, we've got the following results:

II.4.4 Redlich-Kwong performances evaluations

Table II.4-2:RK's RMSE results (a) n-butane, (b) propane

(a)

		300 K	400 K		Tc	500 K	575 K
RK's RMSE	vapor	0.00264339	0.048033	Before Vc	0.025363	0.070228	0.196223
	liquid	47.409438	12.06	After Vc	8.145043	2.09105	1.740711

(b)

		200 K	300 K		Tc	500 K	600 K
RK's RMSE	vapor	4.0697×10^{-5}	0.012775	Before Vc	0.026573	0.128587	0.37944
	liquid	99.95730555	16.84256	After Vc	5.821002	1.799059	3.481756

II.4.5 RK Results description & interpretation

The former figures (II.4-1 and II.4-2) indicate the plot of different isotherms that have been computed using the Redlich-Kwong equation and also describe the plot of the experimental isotherm that we collected from the NIST web site (see ***Appendices E*** and ***F***).At first glance, we can see at the liquid state that the RK's isotherms approach the experimental one in an acceptable manner due to the adjustment of the parameter (a), which made the RK equation heed the attractive forces more effectively, but they still haven't achieved perfection. In the other phase, which is the vapor state, all we can see is that the isotherms are superposed on the experimental isotherms, and with RMSE calculations (Tabel II.4-2), they come with the same remark; hence, all those results approach the zero value, starting with the lower temperature to the highest. And this was achieved owing to the dependences of (a) temperature.

II.5 Soave Redlich & Kwong (SRK) Isotherms Plotting

After considering the VDW and RK equations, we will proceed to the three parameter equations. Starting with the SRK model, we have to calculate its special empirical parameters.

II.5.1 Parametrization

In the following table, we set the SRK's parameters:

Table II.5-1:Soave Redlic&Kwong's Parameters

	propane	n-Butane
a_c	0.95097584	*1.407065887*
b [m3/kmol]	0.0626743	*8.068×10^{-05}*
M	0.71670202	*0.7893*
R [MJ/kmol.K]	*8.314×10^{-03}*	
Ω	0.153	0.201

II.5.2 Calculation

The pressure results for both n-Butane and Propane are obtained using equation (19), we listed them in ***Appendix C***.

II.5.3 Plotting

By using the previous calculated pressure, we plot the n-butane and propane's isotherms, adding to them their empirical isotherms as shown for n-Butane:

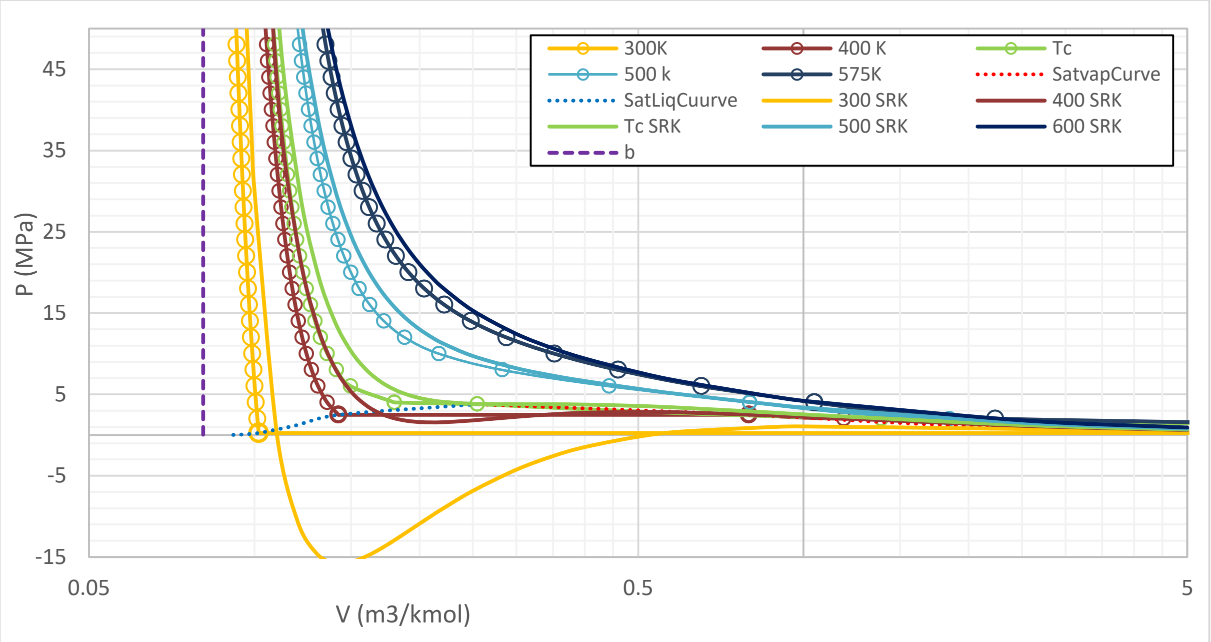


Figure II.5-1:Isotherms computed using SRK for n-Butane

And for the propane:

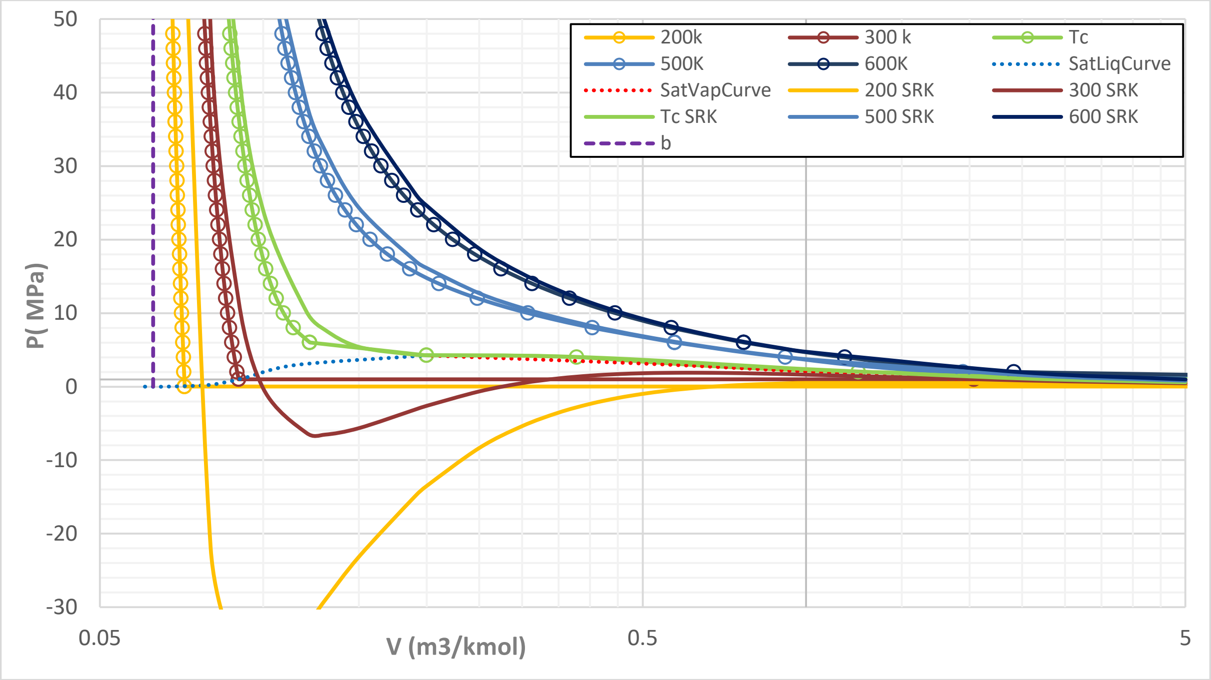


Figure II.5-2:Isotherms computed using SRK for Propane

II.5.4 Soave Redlich Kwong performances evaluations

To see the average difference between the empirical and calculated isotherms, we applied the RMSE to the two components, and we got the listed results below:

Table II.5-2:SRK's RMSE results (a) n-butane, (b) propane

(a)

		300 K	400 K		Tc	500 K	575 K
SRK's RMSE	vapor	0.00169	0.026407	Before Vc	0.025363	0.246881	0.39869
	liquid	41.1306	10.94281	After Vc	8.145043	4.664725	3.094861

(b)

		200 K	300 K		Tc	500 K	600 K
SRK's RMSE	vapor	3.4914×10^{-5}	0.006938	Before Vc	0.026573	0.481674	0.746401
	liquid	94.44816603	13.79032	After Vc	5.821002	2.732624	2.137642

II.5.5 SRK Results description & interpretation

Table II.5-2 describes the average difference between the SRK's calculated and experimental isotherms for n-butane and propane, where for the lower temperatures and at the vapor state, we see that this model gives a nice approaching result to zero, which indicates the satisfaction of paralleling the calculated isotherms to the empirical isotherms, and the same thing is indicated with the highest temperature when the V is higher than the critical volume. and the figures II.5-1 and II.5-2 determinant the same RMSE's description for both components.

However, in the liquid state compared to the vapor state, there is a difference between the experimental and SRK plots. Hence, the Soave Redlich-Kwong expressed the parameter (a) as a product of the constant coefficient a_c=a (T_c) and alpha function $\alpha(T)$, where the proposed modification of the attractive term fails to predict exactly the behavior of our components in the liquid state, which means the complexes attraction still is not captured.

II.6 Peng & Robinson (PR) Isotherms Plotting

With the same procedure, we'll calculate the pressure using the last model, which is the Peng-Robinson equation.

II.6.1 Parameterizations

As with all equations, we need to determine its specific parameters using the critical pressure and temperature for n-butane and propane, as shown in the below table:

Table II.6-1: Peng Robinson's Parameters

	propane	n-Butane
a_c	1.01709122	*1.505022004*
b [m3/kmol]	0.05627956	7.245×10^{-05}
M	0.60428722	*0.6737*
R [MJ/kmol.K]	8.314×10^{-03}	
Ω	0.153	0.201

II.6.2 Calculation

And for the last model, we use the equation (26) to calculate the pressure of n-butane and propane at different temperatures (see ***Appendix D)***

II.6.3 Plotting

The results obtained from equation (26) have been compared with experimental data for n-butane:

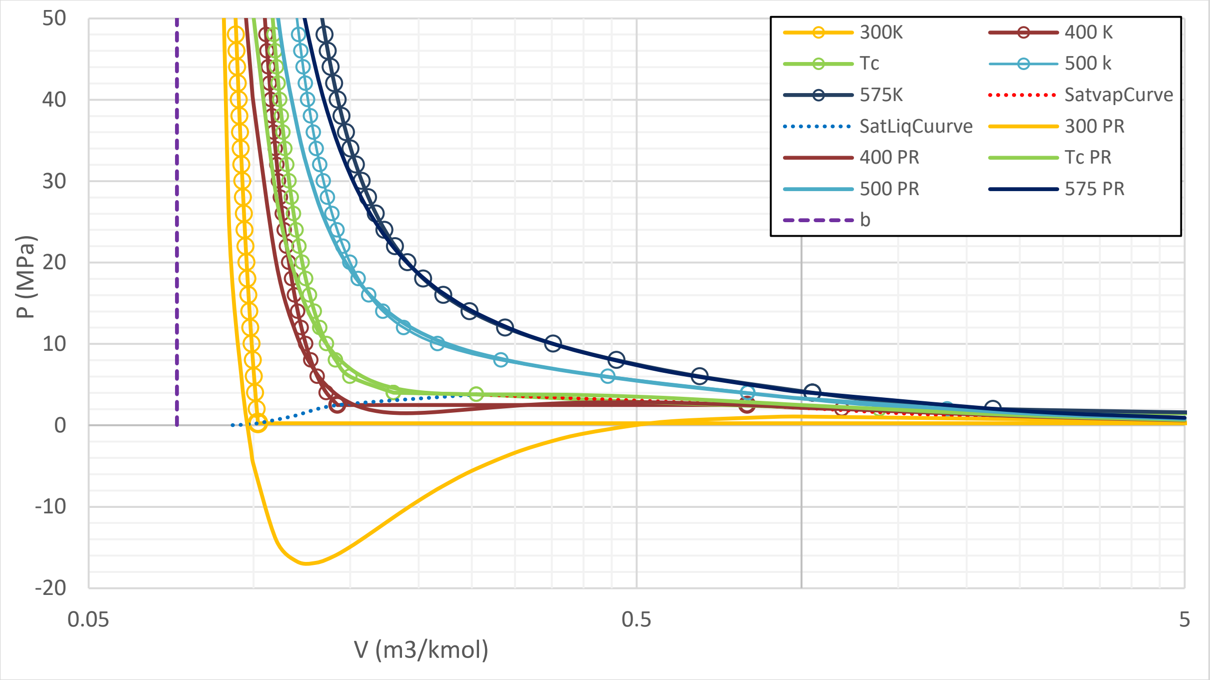


Figure II.6-1:Isotherms computed using PR for n-Butane

And for Propane:

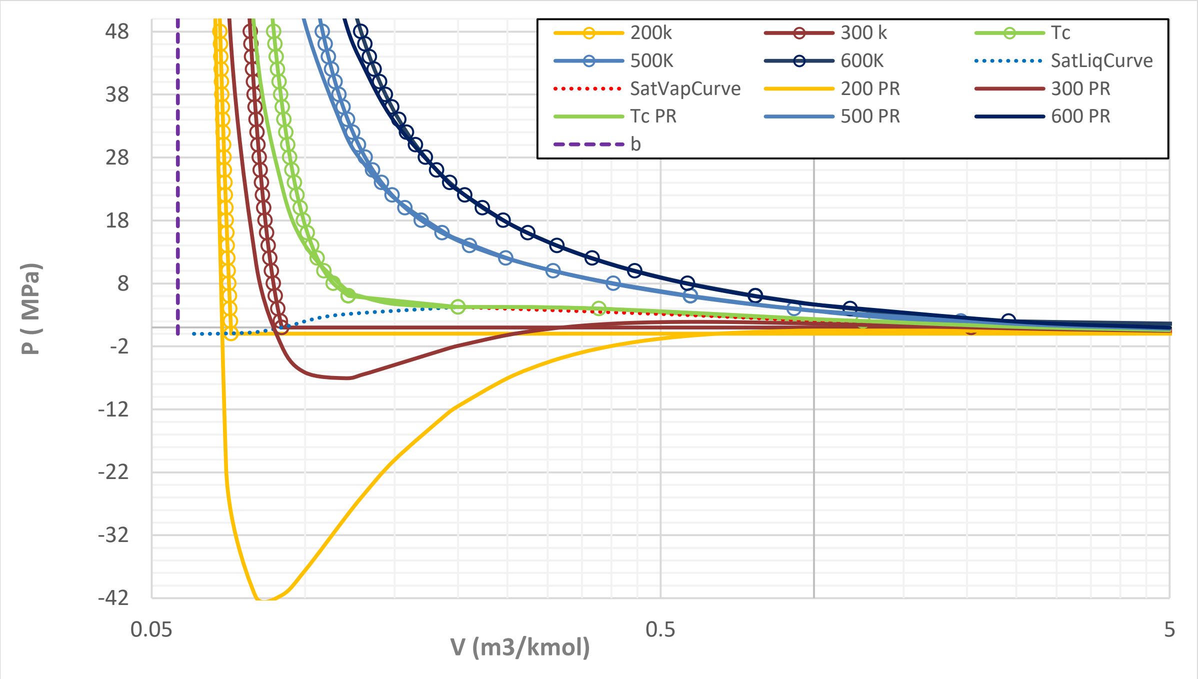


Figure II.6-2:Isotherms computed using PR for Propane

II.6.4 Peng Robinson performances evaluations

The root mean squared errors for the Perng-Robinson equation are given in the following table:

Table II.6-2:PR's RMSE results (a) n-butane, (b) propane

(a)

		300 K	400 K		Tc	500 K	575 K
PR’s RMSE	vapor	0.001154368	0.010046	Before Vc	0.01755	0.07807	0.06970
	liquid	30.04249377	18.14296	After Vc	15.53585	11.91876	9.05454

(b)

		200 K	300 K		Tc	500 K	600 K
PR’s RMSE	vapor	5.61×10^{-05}	0.000241	Before Vc	0.022261	0.082531	0.044224
	liquid	28.07434	26.48333	After Vc	16.65359	8.938069	6.240153

II.6.5 PR Results description & interpretation

A comparison of the empirical data with the PR equation of state is shown in figures II.6-1 and II.6-2. For the respective components of n-butane and propane. Considering the limitation imposed in this model where the liquid state doesn’t match perfectly the experimental isotherm, the approximation obtained by equation (26) is satisfactory, especially for the vapor state, where the RMSE results (Table II.6-2) describe the difference between the PR isotherm plot and the experimental plot; hence, all values at all temperatures and especially at low temperatures are approaching zero, thus the modification of the temperature-dependent function α(T) in the attractive term proposed by PR did an acceptable job at this state.

II.7 Cubic EOS Performances Evaluation

After studying the performance of the EOs separately, we'll move on to a second performance evaluation to get a better view of how these equations predict the experimental behavior.

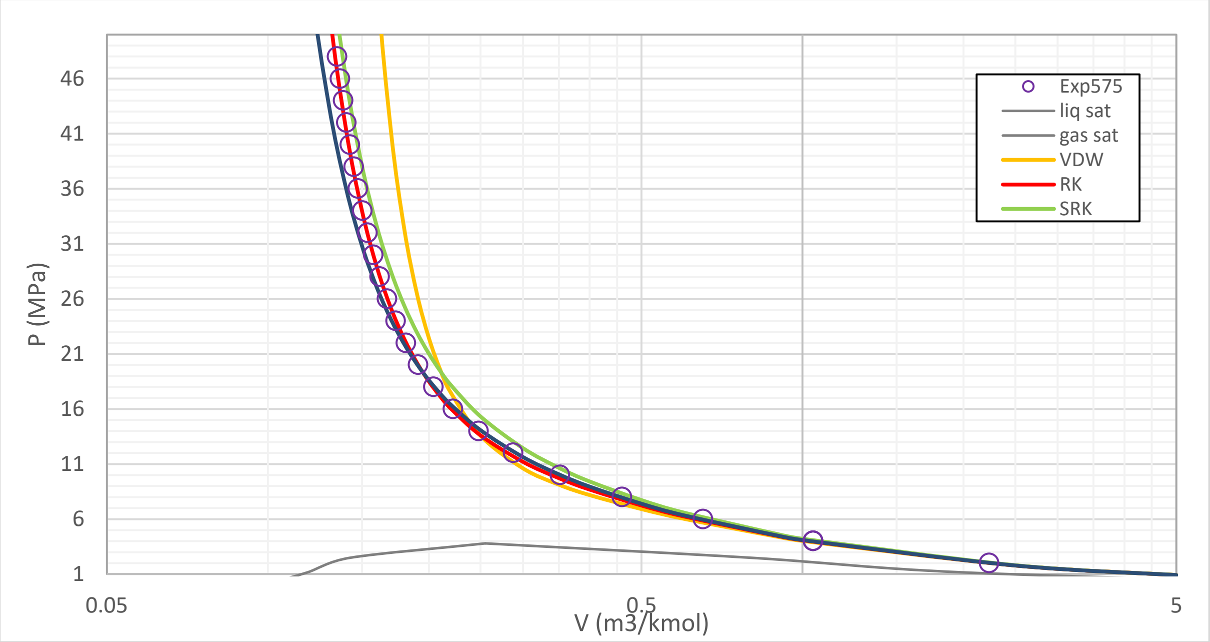
II.7.1 Experimental Isotherms Prediction

In this section, we will discuss the development and performance of the calculated isotherms compared to the experimental isotherms of n-butane and propane.

II.7.1.a T>Tc

In the first area, we will plot the different models' isotherms when temperatures are greater than the critical temperature for the n-butane, as shown below:

(a)



(b)

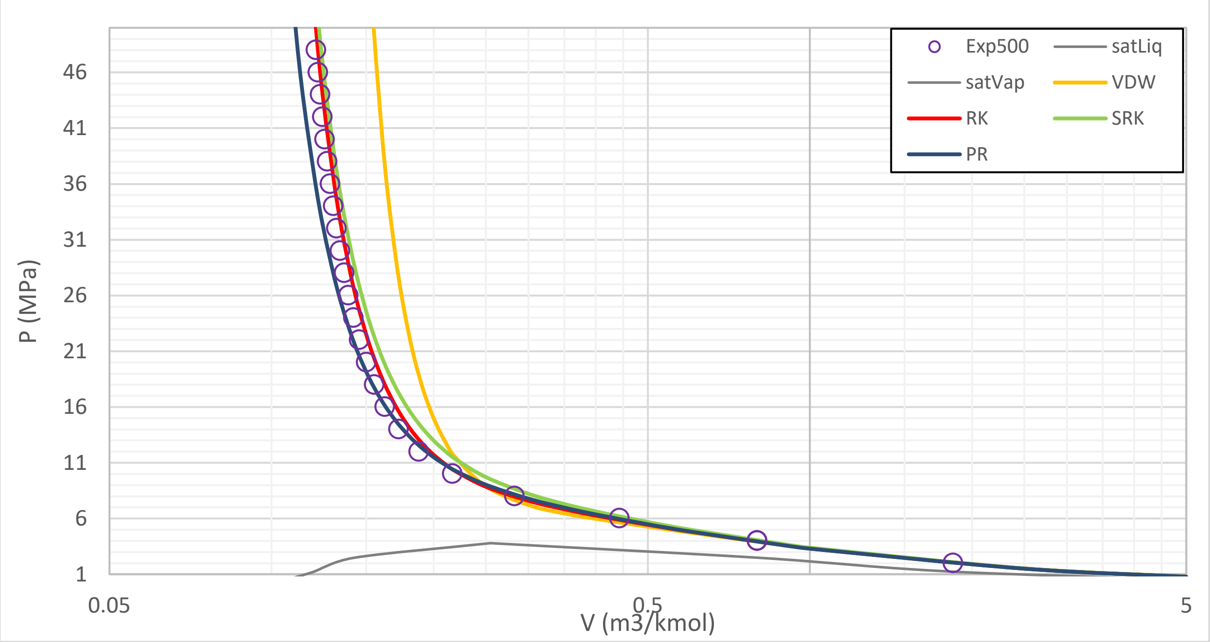
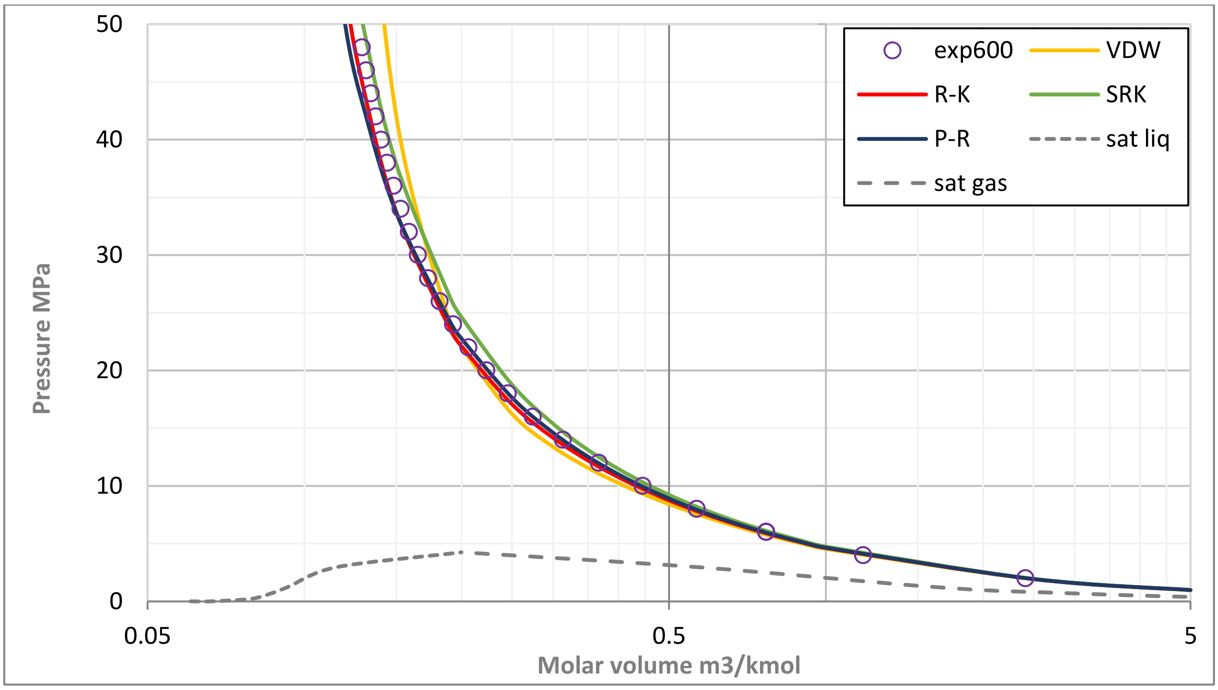


Figure II.7-1:Cubic EOS isotherms when T>Tc of n-butane (a):575K & (b): 500K

And for propane, we got the following plots:

(a)



(b)

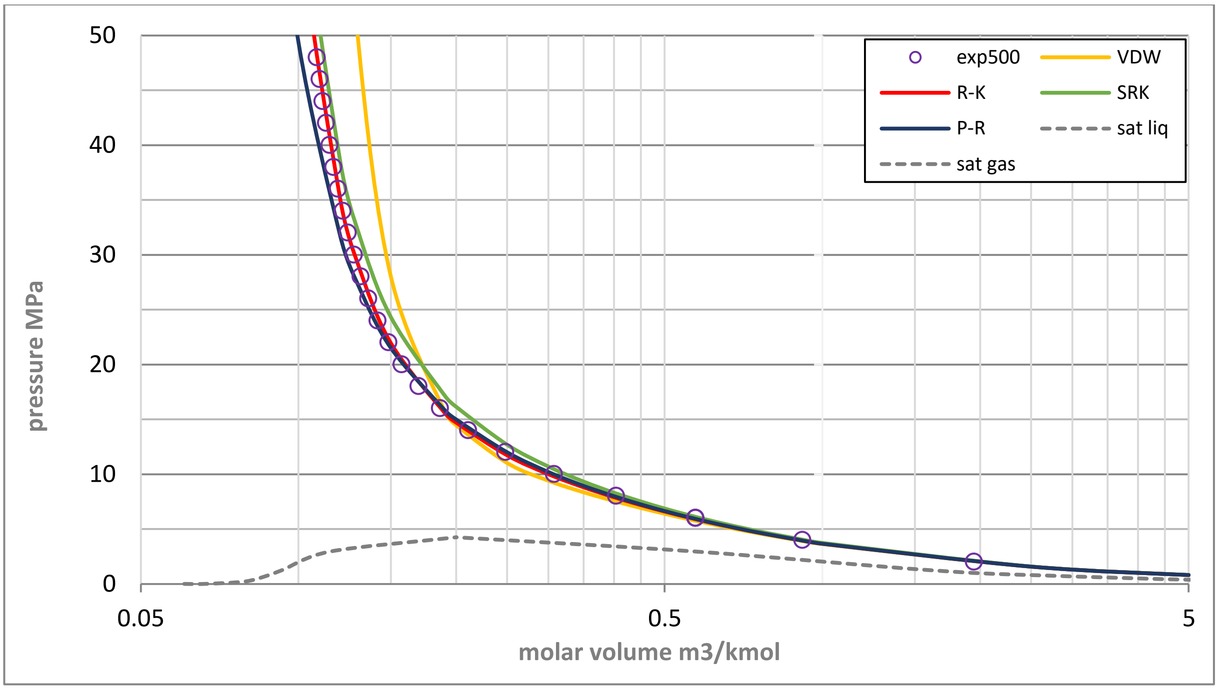


Figure II.7-2:Cubic EOS isotherms when T>Tc of propane (a):500K & (b): 600K

II.7.1.a.a Result's Description & Interpretation

Refer to figures II.7-1 and II.7-2, where we have depicted the isotherms of VDW, RK, SRK, and PR when T was greater than Tc, to see their behavior compared to the empirical isotherms. Whereas, we notice that when the temperature was above 500K, the behavior of the experimental isotherms for the two molecules resembled that of the perfect gas. That's why we expect that, at this level, all models can disproportionately predict the empirical one. However, when the temperature is lowered to 500K, experimental isotherms exhibit distortion, which gradually increases. This signifies a deviation from the perfect gas character.

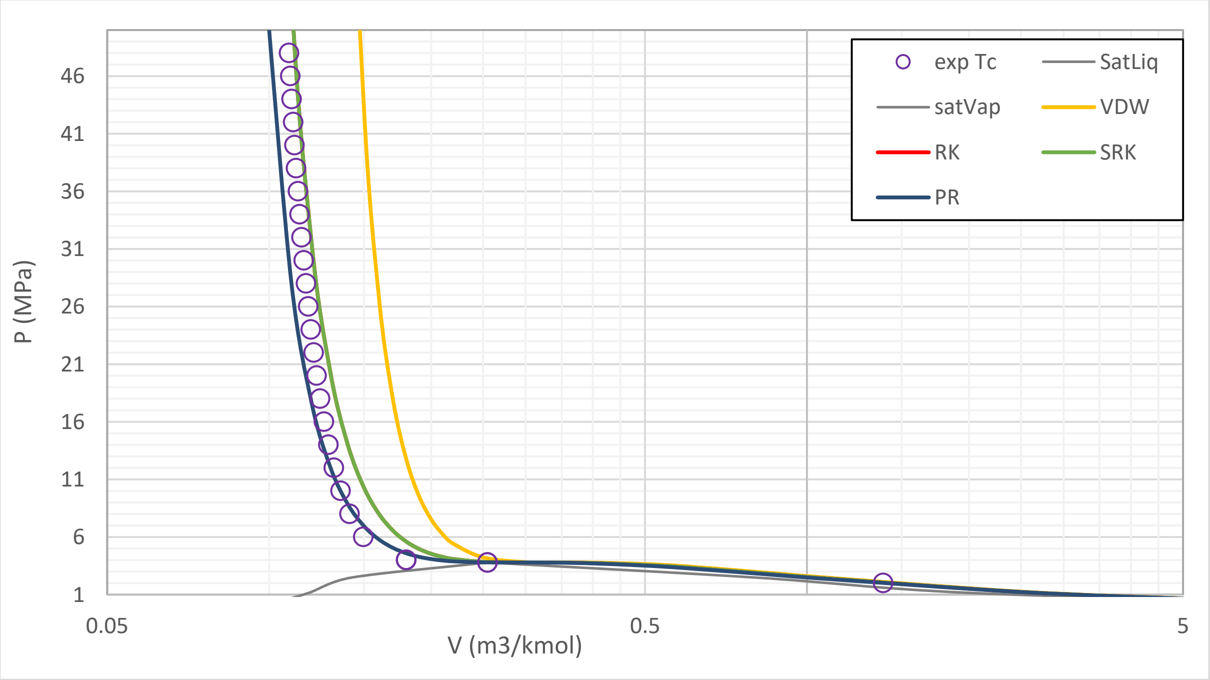
At the interval when V>Vc, we noticed for the two components and for their two superior temperatures that the Peng-Robinson predicts the behavior of the experimental isotherm better than the others.

And when V<Vc, apparently there is a little competition between RK and PR.

II.7.1.b Tc

In the second area, we will plot the different models' isotherms when temperatures are equal to the critical temperature for the n-butane and Propane, as shown below:

(a)



(b)

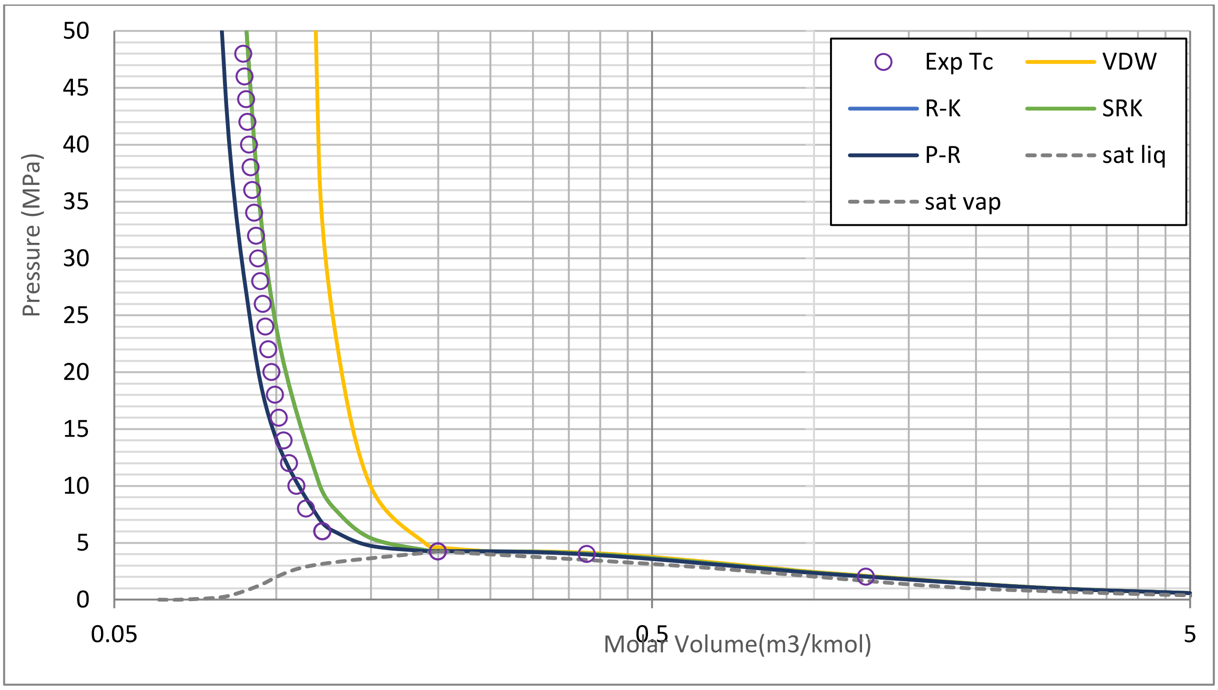


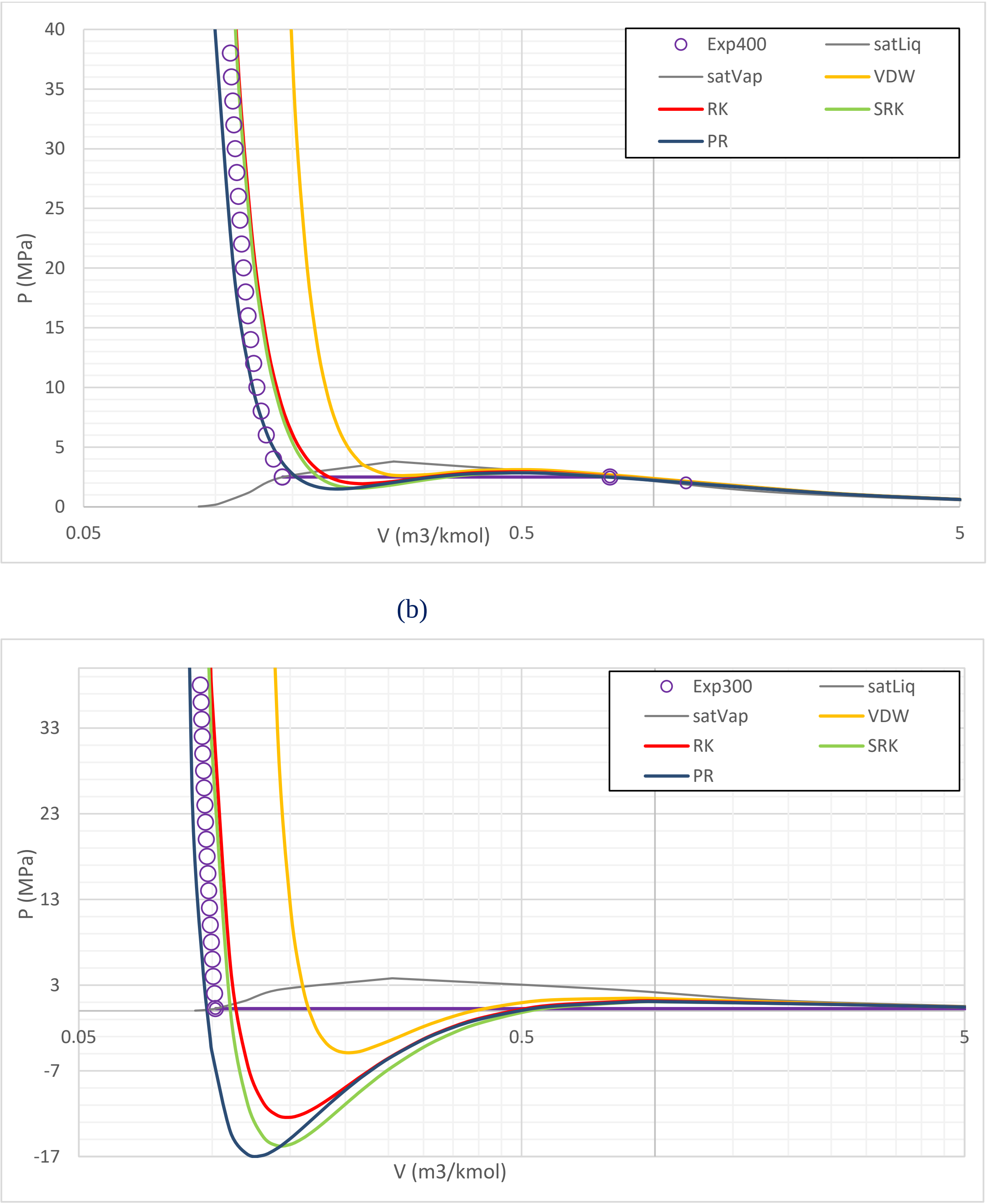
Figure II.7-3:EOS isotherms at Tc (a) n-Butane, (b) Propane

II.7.1.b.a Result's Description & Interpretation

Figure II.7-3 shows the experimentally and the calculated critical isotherm plots for n-butane and propane, where we observe a kink in the empirical curve of the two components at 425.16K for n-butane and 369.89K for propane, which suggests that gas can be liquefied under compression. Above these temperatures, liquefaction cannot be produced, however high the pressure may be. Back to the calculated critical pressure with the four equations, none of them predicts the exact value where the kink exists, and as a general behavior, Peng-Robinson did a satisfactory job compared to the others. Also, we can see that RK and SRK give the same values because at this point the alpha function is unity($\alpha=1$), which means SRK becomes the same as RK's equation.

II.7.1.c T<Tc

In the third area, we will plot the different models' isotherms when temperatures are lower than the critical temperature for the n-butane, as shown below:

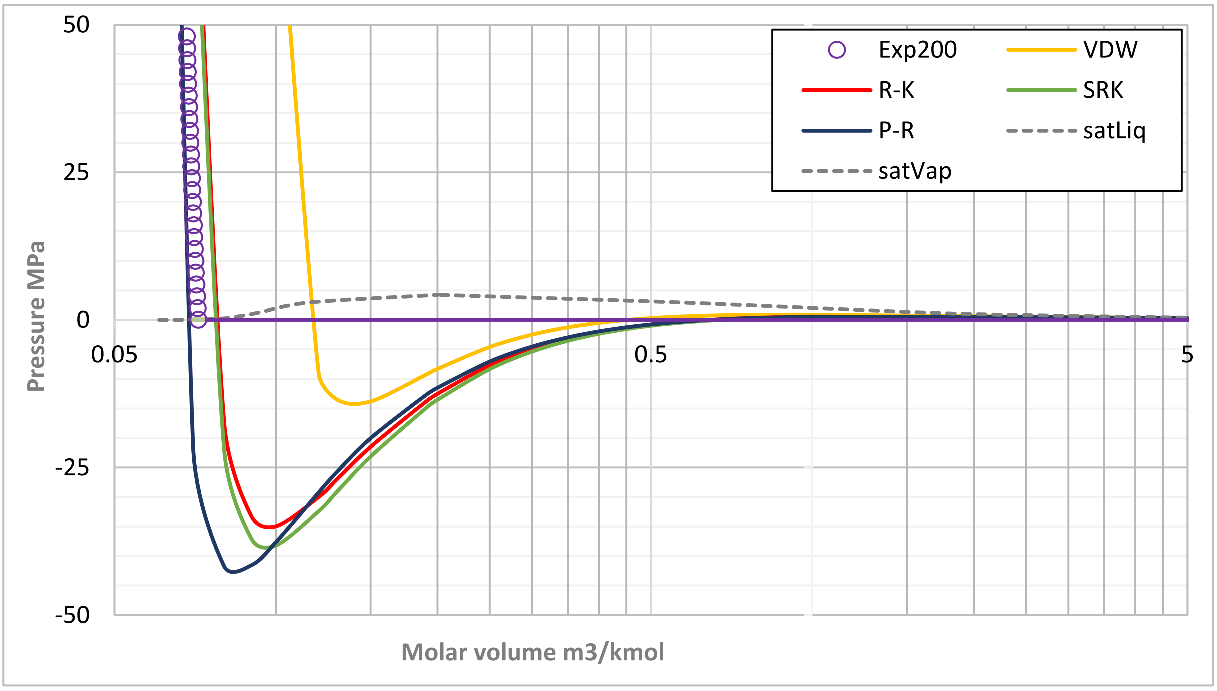


(a)

(b)

Figure II.7-4:EOS isotherms at Tc (a) n-Butane, (b) Propane

(a)



(b)

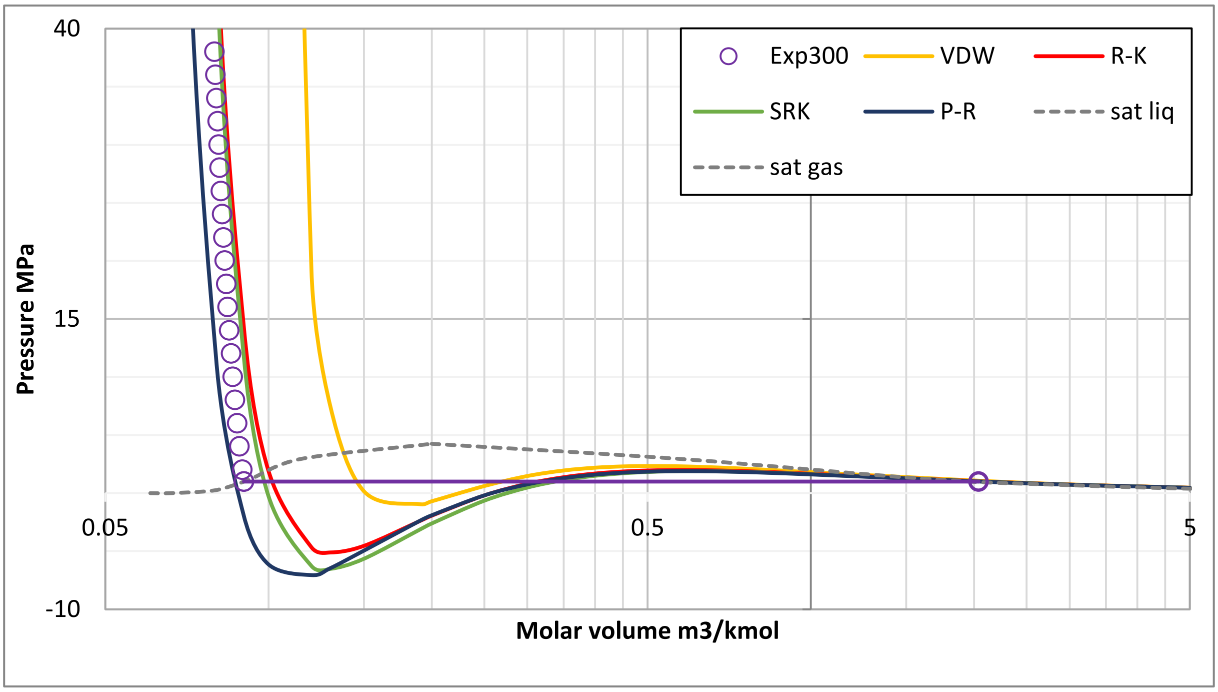


Figure II.7-5:Cubic EOS isotherms when T>Tc of Propane (a):200K & (b): 300K

II.7.1.c.a Result's Description & Interpretation

At low temperatures, we plot the computed isotherms using different equations of state and the experimental isotherms for n-butane and propane, as shown in figures II.7-4 and II.7-5, respectively. Hence, as the temperature is lowered further, say to 400 K for n-butane and 300 K for propane, with regard to their experimental plots, we observe that the kink spreads into a horizontal line (in other words, compression produces liquefaction). However, all models form curves with negative pressure, which doesn't have a physical meaning. For that, we'll focus on the equation's predictions for the vapor and liquid states.

For vapor state, it seems like all models predict the experimental behavior, but using the RMSE tables (see table II.3-3, II.3-4 , II.4-2, II.5-2, and II.6-2), we found that PR gave values that approached zero. However, the liquid state, we can see that VDW is extremely deviated from the experimental, the rest did a good job of approaching the empirical one, especially PR.

II.7.2 Cubic EOS Saturation volume Prediction

After we studied the performance of the different isotherm's models, we moved on to calculate the saturated volume at T<Tc, where the equations (3) (15), (19), and (26) turn to a cubic equation. At this level of temperature, the cubic equation of state that we had to determine the molar volume has one or three real roots; in the latter case, the largest corresponds to the vapor phase and the smallest to the liquid. The intermediate word has no physical meaning. To determine the molar volume, we need a numeric method. For that, we used the solver in Excel that works with the Newton-Raphson method.

II.7.2.a Cubic EOS Liquid Saturation volume Prediction (2 phase Region)

In the following table, we list the liquid saturation molar values determined by VDW, RK, SRK, and PR for n-butane:

Table II.7-1: n-Butane's Liquid Saturation volume prediction evaluation (RE: Relative Error)

T [K]	Vapor Pressure [MPa]	Liquid Saturation molar Volume Predicted Values v_{liq}^{sat} in m^3/kmol								
		Database	VdW	RE %	RK	RE %	SRK	RE %	PR	RE %
400	2.49540	0.14229	/	/	/	/	0.1720	20.90	0.15244	7.13
300	0.258	0.10185	0.1651	62	0.1275	25	0.110	8	0.0970	-5

And for propane:

Table II.7-2:Propane's Liquid Saturation volume prediction evaluation (RE: Relative Error)

T [K]	Vapor Pressure [MPa]	Liquid Saturation molar Volume Predicted Values v_{liq}^{sat} in m^3/kmol								
		Database	VdW	RE %	RK	RE %	SRK	RE %	PR	RE %
300	0.99768	0.09009	0.14523	61	0.1155	28.2	0.0983	9.17	0.0866	-3.8
200	0.02019	0.071651	0.11307	58	0.06976753	-2.6	0.0855	19.33	0.072	0.487

II.7.2.b Cubic EOS Vapor Saturation volume Prediction (2 phase Region)

The following tables indicate the vapor saturation volume for n-butane:

Table II.7-3: n-Butane's Vapor Saturation Molar prediction evaluation (RE: Relative Error)

T [K]	Vapor Pressure [MPa]	Vapor Saturation molar Volume Predicted Values v_{liq}^{sat} in m^3/kmol								
		Database	VdW	RE %	RK	RE %	SRK	RE %	PR	RE %
400	2.4954	0.79536	0.92163	15.9	0.88061	10.7	0.82485	3.71	0.79260	-0.3
300	0.2576	8.9194	9.22176	3.4	9.17848	2.90	9.00844	1.00	8.97589	0.63

And the next table indicates the saturation molar volume for propane:

Table II.7-4:Propane's Vapor Saturation Molar volume prediction evaluation (RE: Relative Error)

T [K]	Vapor Pressure [MPa]	Vapor Saturation molar Volume Predicted Values v_{liq}^{sat} in m^3/kmol								
		Database	VdW	RE %	RK	RE %	SRK	RE %	PR	RE %
300	0.99768	2.0387	2.1761	6.7	2.14320	5.1	2.06392	1.2	2.03782	**-0.04**
200	0.020192	81.401	81.8728	0.58	81.83751	0.54	81.59644	0.24	81.57659	0.2

II.7.3 Result's Description & Interpretation

Tables II.7.1, II.7.2, II.7.3, and II.7.4 describe the values of the saturated liquid and vapor molar volumes when T<Tc for n-butane and propane, where the relative error outcomes of each model give results of which equation predicts the database saturated molar volume better than the others, and we notice that actually PR and SRK, which means the three parameters equation provide a good prediction due to the third parameter (ω), which takes into account the shape of the molecule.

II.8 Corresponding State Principle (Pitzer's Theory)

This principle relies on the concept of reduced properties, where the pressure and temperature of a substance are expressed as function of their critical values, thus when two different substances have the same reduced conditions, they are said to be in corresponding states and should behave similarly.

II.8.1 Reduced Coordinates (Back to Zero Parameters Model)

Because we come back to the zero-parameter models after studying the two- and three-parameter' models, using (P, T) values from [41] (see Appendix G), we will calculate the reduced parameters (Tr, Pr) for n-butane as follows:

Table II.8-1:n-Butane's reduced parameters

Tr	Pr	Tr	Pr	Tr	Pr	Tr	Pr	Tr	Pr
0.3172	1.78E-07	0.4589	3.48E-04	0.57625	0.0081	0.6921	0.05685	0.82943	0.26322
0.32929	4.54E-07	0.47041	5.12E-04	0.57981	0.0088	0.7705	0.14663	0.83232	0.27244
0.34105	1.05E-06	0.48217	7.47E-04	0.58801	0.0103	0.7835	0.16864	0.83517	0.27792
0.35281	2.29E-06	0.49393	1.07E-03	0.59977	0.0129	0.7913	0.18271	0.83973	0.28928
0.36457	4.71E-06	0.50021	1.27E-03	0.60261	0.0137	0.7914	0.18164	0.84444	0.30229
0.37633	9.22E-06	0.50569	1.49E-03	0.61153	0.0161	0.8019	0.20262	0.84893	0.31675
0.38809	1.72E-05	0.51745	2.06E-03	0.61687	0.0177	0.8069	0.21306	0.84942	0.31599
0.39985	3.09E-05	0.52921	2.79E-03	0.62329	0.0198	0.8097	0.21976	0.84959	0.31786
0.41161	5.32E-05	0.53221	3.01E-03	0.6275	0.0212	0.8108	0.22085	0.85485	0.33138
0.42337	8.88E-05	0.54097	3.72E-03	0.63506	0.0241	0.8121	0.22703	0.86015	0.34626
0.43513	1.43E-04	0.55273	4.89E-03	0.63599	0.0245	0.8188	0.23917	0.86231	0.35298
0.4469	2.25E-04	0.55467	5.11E-03	0.63982	0.0261	0.8201	0.24098	0.8652	0.36212
0.45865	3.44E-04	0.56449	6.34E-03	0.64165	0.0269	0.8208	0.24386	0.86551	0.36328

And using the (P, T) parameters from [42] (see ***Appendix H***), we get the next reduced properties for propane:

Table II.8-2:Propane's reduced parameters

Tr	Pr	Tr	Pr	Tr	Pr	Tr	Pr
0.23122	4.05E-11	0.42756	1.65E-04	0.62461	0.02383	0.81957	0.25381
0.23831	1.14E-10	0.44108	2.74E-04	0.63032	0.02614	0.83309	0.28648
0.25183	6.91E-10	0.45459	4.39E-04	0.64384	0.03228	0.84660	0.32212
0.26535	3.43E-09	0.468112	6.82E-04	0.65736	0.03948	0.86012	0.36091
0.27887	1.44E-08	0.48163	1.03E-03	0.67088	0.04785	0.87364	0.40302
0.29238	5.23E-08	0.49515	1.52E-03	0.68439	0.05752	0.88716	0.44863
0.30590	1.68E-07	0.50866	2.18E-03	0.69791	0.06860	0.90067	0.49793
0.31942	4.83E-07	0.52218	3.07E-03	0.71143	0.08122	0.91419	0.55114
0.33294	1.27E-06	0.53570	4.24E-03	0.72495	0.09551	0.92771	0.60849
0.34645	3.05E-06	0.54922	5.74E-03	0.73846	0.11161	0.94123	0.67023
0.35997	6.83E-06	0.56273	7.65E-03	0.75198	0.12964	0.95474	0.73671
0.37349	1.43E-05	0.57625	0.01	0.76550	0.14975	0.96826	0.80827
0.38701	2.84E-05	0.58977	0.01300	0.77902	0.17207	0.98178	0.88542
0.40052	5.34E-05	0.60329	0.01660	0.79253	0.19676	0.99530	0.96902
0.41404	9.59E-05	0.61680	0.02095	0.80605	0.22395	1	1

II.8.1.a Plotting

The next plot explained well the concept of corresponding states:

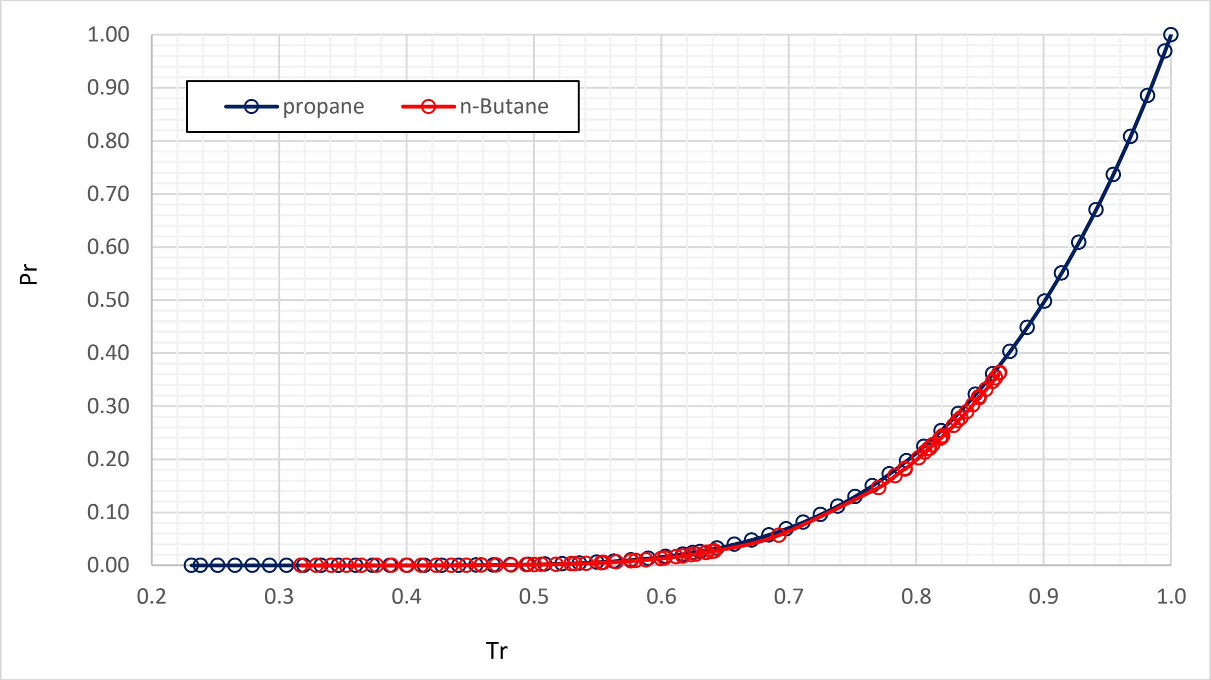


Figure II.8-1:Reduced Parameters Plot

Where we obtain a clear correspondence between the 2 diagrams is obvious.

II.8.2 Acentric Factor Determination (Linear Interpolation)

Apparently the most useful tool in the prediction of the PVT behavior is the theory of corresponding states, where Pitzer developed and termed the acentric factor to reformulate the PT relationship to a linear equation (38), which helps us to establish the acentric factor by interpolating the vapor pressure at the reduced temperature of 0.7.

In the following, we plot Log Pr using the reciprocal of the reduced temperature (1/Tr) for n-butane and propane.

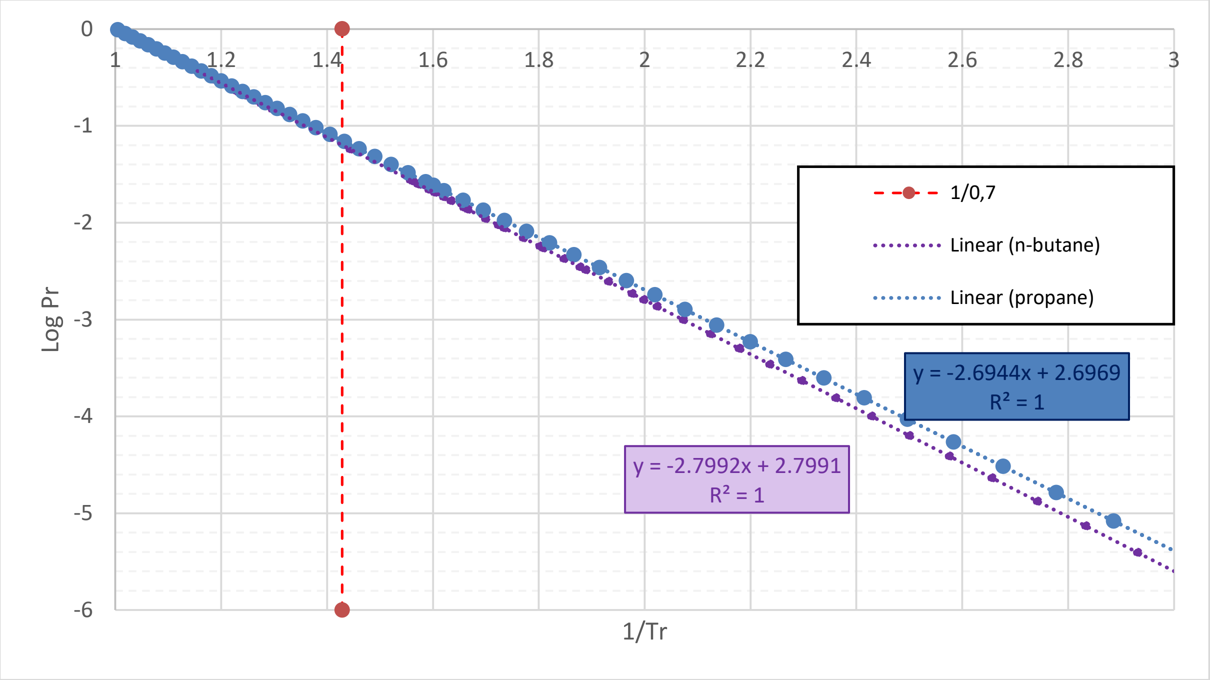


Figure II.8-2:linear interpolation (n-Butane and propane)

Using equation (38), we'll determine the acentric factor for n-butane and propane, as listed in the next table.

Table II.8-3:calculated acentric factor for n-butane and propane

	n-Butane	Propane
Log (Pr (Tr=0.7)	**-1.1997225**	-1.1521674
$w^{Calculated}$	*0.1997*	0.15216739
$w^{Database}$	*0.201*	0.153
RE	-0.64%	-0.54%

II.8.3 Result's Description & Interpretation

Figure II.8-1 explains and demonstrates the concept of the corresponding state principle, where the plots of the reduced parameters (Pr, Tr) of propane and n-butane are perfectly accurate to each other. Which gives us the ability to treat the two components similarly.

And figure II.8-2 shows the linear plot of the reduced parameters that contributed to calculating (ω), where the data points fit well the regression line (R2 = 1) for both components, and we set at table II.8-3 the calculated omega, where the relative error shows how much the results of omega we had satisfactorily apportion the database value of (ω). All this gives us a hint that the reliance on NIST was a good choice.

II.9 Conclusion

In this chapter, the VDW, RK, SRK, and PR EOSs were critically compared with the experimental data for a non-polar component. Hence, the calculation results unfortunately revealed that all these equations had no adequate results for the tow liquid/vapor state simultaneously.

And as a specific conclusion, cubic Eos, where the attractive parameter (a) is not a function of temperature, such as the RK and the VDW, fail to give reliable predictions of vapor pressures.

On the other hand, very good predictions for vapor pressure are obtained by SRK and PR for nonpolar compounds, where (a) is made an appropriate function of temperature.

Also, SRK and PR provide nice predictions of saturation vapor volumes.

Due to the adjustment of PR and SRK using the acentric factor, they made nice predictions where this factor represents, therefore, a measure of the acentricity (non-sphericity) of the molecule. It is therefore equal to zero for monoatomic gases, very small for methane, and increases with molecular weight. It is also affected by the polar character of the molecule. It thus reflects the geometry and polarity of the molecule.

General Conclusion

In this study, we investigated the evolution of the cubic equation of state Eos from the relatively simple model of Van der WAALS, to the more sophisticated ones, as Redlich-Kwong,Soave-Redlich-Kwong, and Peng Robinson equations of state. Our focus centered on light hydrocarbons, and our findings shed light on their predictive capabilities and practical applications. The quest from VDW to PR has been a fascinating evolution. Each step addressed limitations and improved predictions for real gases. The ideal gas equation, while foundational. The VdW, model introduced corrections, accounting for molecular size and attractive interactions. Then it refined by RK, SRK and PR modifications successively over the years.

For non-polar compounds, SRK and PR give nice predictions; PR consistently demonstrated superior performance. It provided better predictions for vapor-liquid properties, including isotherms, vapor pressure, and molar volume.

Where concerning the isotherms results, especially at low temperatures we get these root mean squared error values (RMSE of propane at 200 K goes to 3.4914×10-5, and for n-butane it comes with a value of 0.00169 when T = 300 K).

Also, PR accurately predicted molar volumes, where the RE value for the saturated liquid volume gave a deviation from the empirical value by 5% in the negative direction at T =300K for n-butane and 0.487% for propane at T = 200K. The same results come with the saturated vapor volume (RE = 0.63% for n-butane at T = 300K, RE = 0.2% for propane at T=200K).

The corresponding state principle (CSP) is a fundamental concept in thermodynamics; it suggests that the behavior of fluids at different conditions can be related if we express their properties in terms of reduced variables. The Pitzer's theory refined our understanding by considering additional parameters. Notably, it introduces a third parameter, called the acentric factor, present in the SRK and PR equations, where it plays a significant role in predicting the phase behavior of pure substances.

The obtained values, deduced using linear interpolation, confirms the reliability of our experimental data, illustrated in the PT diagrams for both fluids.

Taking into consideration the fact that we have obtained relatively deviated liquid saturation volumes, we can say that this is just the starting of a big journey, in the field, aiming to continue this quest, seeking for other EOS, with better performances. And the present work, can be considered as a good starting point. For that, more attention must be pointed out for the b parameter, which is related to molecules volume, and can be considered as the main responsible for the bigger values of the liquid saturation volumes, due to the asymptote $v = b$, present in all EOS studied in this our work, and if it’s dependence to temperature was studied for example, very probably will enhance the modeling ability of this kind of EOS.

Appendix A

n-Butane

T [K] →	**300**	**400**	**425.125**	**500**	**575**
V [m3/kmol] ↓		P^{VDW}[MPa]	↓		
0.117	4092.074	5489.916	5841.124	6887.758	7936.140
0.118	1464.302	1985.650	2116.638	2506.997	2898.008
0.119	863.213	1183.641	1264.149	1504.070	1744.391
0.12	597.432	828.724	886.836	1060.016	1233.485
0.13	101.302	162.461	177.827	223.620	269.490
0.14	34.860	70.098	78.952	105.337	131.766
0.15	12.524	37.274	43.492	62.023	80.585
0.16	2.967	22.040	26.831	41.112	55.416
0.17	-1.514	14.000	17.898	29.513	41.149
0.18	-3.641	9.433	12.718	22.507	32.313
0.19	-4.577	6.720	9.559	18.018	26.491
0.2	-4.881	5.065	7.564	15.011	22.471
0.21	-4.841	4.042	6.274	12.926	19.588
0.22	-4.616	3.410	5.427	11.436	17.456
0.25	-3.550	2.674	4.238	8.898	13.566
0.3	-1.845	2.684	3.822	7.213	10.609
0.35	-0.659	2.900	3.795	6.460	9.129
0.4	0.116	3.047	3.784	5.979	8.178
0.5	0.947	3.115	3.660	5.282	6.908
0.6	1.300	3.020	3.451	4.739	6.028
0.9	1.469	2.530	2.796	3.591	4.387
1	1.434	2.375	2.612	3.316	4.022
2.5	0.824	1.173	1.261	1.522	1.784
5	0.455	0.625	0.668	0.796	0.923

Propane

T [K]→	**200**	**300**	**369.89**	**500**	**600**
V [m3/kmol]↓		P^{VDW}[MPa]	↓		
0.1	79.782	166.598	227.274	340.231	427.047
0.12	-8.954	19.156	38.802	75.376	103.487
0.13	-13.518	7.489	22.171	49.504	70.511
0.15	-13.801	0.154	9.907	28.064	42.020
0.19	-9.299	-0.949	4.886	15.749	24.099
0.2	-8.288	-0.701	4.602	14.474	22.062
0.25	-4.596	0.614	4.255	11.034	16.244

0.3	-2.494	1.473	4.246	9.407	13.374
0.35	-1.255	1.947	4.186	8.353	11.556
0.4	-0.494	2.191	4.068	7.562	10.248
0.45	-0.010	2.302	3.918	6.926	9.238
0.5	0.306	2.336	3.754	6.395	8.425
0.55	0.516	2.325	3.589	5.943	7.752
0.6	0.656	2.288	3.428	5.551	7.182
0.65	0.750	2.236	3.274	5.208	6.693
0.7	0.812	2.176	3.130	4.904	6.268
0.75	0.853	2.113	2.994	4.634	5.895
0.8	0.877	2.049	2.868	4.392	5.564
0.9	0.895	1.922	2.640	3.976	5.003
1	0.890	1.804	2.442	3.632	4.546
2.5	0.540	0.885	1.126	1.575	1.920
5	0.301	0.470	0.589	0.809	0.979

Appendix B

n-Butane

T [K] →	**300**	**400**	**425.125**	**500**	**575**
V [m3/kmol] ↓		P^{RK}[MPa]	↓		
0.09	158.657	262.506	287.760	361.715	434.345
0.095	73.844	145.365	162.564	212.616	261.419
0.099	41.999	100.008	113.859	154.010	192.977
0.1	36.407	91.871	105.094	143.390	180.519
0.11	5.212	44.273	53.474	79.936	105.382
0.12	-6.123	24.344	31.464	51.851	71.349
0.13	-10.588	14.466	20.291	36.917	52.759
0.14	-12.172	9.109	14.040	28.084	41.431
0.15	-12.430	6.051	10.323	22.473	34.000
0.16	-12.055	4.256	8.020	18.716	28.852
0.17	-11.384	3.192	6.552	16.095	25.132
0.18	-10.587	2.567	5.598	14.203	22.349

0.2	-8.937	2.029	4.555	11.726	18.513
0.21	-8.155	1.951	4.280	10.890	17.147
0.22	-7.421	1.940	4.097	10.223	16.023
0.25	-5.532	2.093	3.853	8.856	13.599
0.3	-3.296	2.461	3.794	7.593	11.203
0.35	-1.852	2.724	3.789	6.828	9.724
0.4	-0.901	2.870	3.750	6.270	8.679
0.5	0.179	2.935	3.583	5.445	7.234
0.6	0.701	2.852	3.361	4.828	6.243
0.9	1.146	2.415	2.720	3.604	4.464
1	1.163	2.275	2.543	3.321	4.081
2.5	0.771	1.150	1.243	1.517	1.789
5	0.441	0.619	0.663	0.794	0.924

Propane

T [K] →	**200**	**300**	**369.89**	**500**	**600**
V[m3/kmol]↓		P^{RK}[MPa]	↓		
0.1	79.781827	166.598085	227.273968	340.230603	427.046861
0.12	-8.953871	19.156240	38.802396	75.376460	103.486570
0.13	-13.518171	7.489220	22.171285	49.504002	70.511393
0.15	-13.801107	0.154049	9.907308	28.064361	42.019517
0.19	-9.298710	-0.949355	4.886010	15.749357	24.098712
0.2	-8.287893	-0.700503	4.602324	14.474277	22.061667
0.25	-4.596033	0.614006	4.255302	11.034083	16.244122
0.3	-2.493761	1.473286	4.245855	9.407380	13.374427
0.35	-1.255463	1.947445	4.185958	8.353263	11.556172
0.4	-0.494460	2.191144	4.068112	7.562352	10.247956
0.45	-0.010274	2.301890	3.917862	6.926219	9.238383
0.5	0.305775	2.335677	3.754375	6.395479	8.425381
0.55	0.515611	2.324668	3.589017	5.942781	7.751838
0.6	0.656138	2.287689	3.427979	5.550790	7.182341
0.65	0.750215	2.235981	3.274383	5.207514	6.693280
0.7	0.812475	2.176373	3.129601	4.904168	6.268065
0.75	0.852555	2.113060	2.994028	4.634072	5.894577
0.8	0.876952	2.048637	2.867528	4.392007	5.563691
0.9	0.895263	1.922219	2.639959	3.976133	5.003089

1	0.889597	1.803648	2.442479	3.631752	4.545803
2.5	0.539919	0.884959	1.126107	1.575038	1.920078
5	0.301145	0.470487	0.588841	0.809172	0.978515

Appendix C

n-Butane

T (K)	**300**	**360**	**400**	**425.125**	**500**	**575**
α →	1.26741	1.129449	1.047796	1	0.871613	0.72628
a(T) →	1.783544	1.5894	1.474496	1.407235	1.226564	1.022046
V m3/kmol ↓			**P^{SRK}**	**(Mpa)**		
0.09	151.608	217.789	260.965	287.758	366.342	443.478
0.095	67.356	113.833	143.947	162.562	216.875	269.825
0.099	35.912	74.061	98.677	113.857	158.006	200.865
0.1	30.414	66.984	90.561	105.092	147.324	188.284
0.11	0.050	26.322	43.144	53.472	83.325	112.071
0.12	-10.620	10.130	23.361	31.463	54.803	77.175
0.13	-14.542	2.662	13.601	20.289	39.513	57.882
0.14	-15.677	-0.983	8.343	14.039	30.385	45.973
0.15	-15.559	-2.752	5.367	10.322	24.527	38.055
0.16	-14.867	-3.536	3.641	8.019	20.562	32.496
0.17	-13.925	-3.784	2.636	6.551	17.763	28.424
0.18	-12.895	-3.735	2.063	5.598	15.718	25.339
0.19	-11.862	-3.523	1.753	4.970	14.180	22.933
0.2	-10.866	-3.227	1.607	4.555	12.992	21.012
0.21	-9.929	-2.891	1.563	4.279	12.054	19.445
0.22	-9.058	-2.542	1.582	4.097	11.298	18.145
0.25	-6.842	-1.547	1.807	3.853	9.716	15.296
0.3	-4.244	-0.269	2.253	3.794	8.215	12.432
0.35	-2.570	0.570	2.567	3.788	7.299	10.655
0.4	-1.465	1.107	2.747	3.750	6.640	9.408
0.5	-0.194	1.664	2.853	3.583	5.690	7.717
0.6	0.436	1.872	2.794	3.361	5.002	6.587
0.9	1.024	1.853	2.389	2.720	3.684	4.623
1	1.063	1.785	2.253	2.543	3.387	4.211
2.5	0.755	0.991	1.146	1.243	1.528	1.810

5	0.437	0.546	0.618	0.663	0.797	0.930

Propane

T (K)	**200**	**300**	**369.89**	**500**	**600**
α →	1.4153715	1.14757976	1	0.78044675	0.6462506
a(T) →	1.34598411	1.09132063	0.95097584	0.742186	0.6145687
V m3/kmol ↓			**P^{SRK}**	**(Mpa)**	
0.07	82.05291	222.96473	317.39517	487.53966	614.77177
0.08	-21.95148	48.34665	94.18034	174.90814	234.07549
0.09	-37.10495	11.85416	43.33240	98.11412	137.82725
0.10	-38.19264	-0.26364	23.93115	65.74695	95.86611
0.12	-32.39563	-6.27516	10.26338	38.65804	58.98285
0.13	-29.03907	-6.52299	7.71079	32.11367	49.55758
0.15	-23.15098	-5.64741	5.40596	24.33822	37.85929
0.19	-14.97717	-3.14287	4.34410	17.18896	26.37692
0.20	-13.51234	-2.61061	4.29215	16.14361	24.62702
0.25	-8.34247	-0.64634	4.25097	12.69661	18.76746
0.30	-5.36451	0.47930	4.21759	10.69459	15.37073
0.35	-3.53174	1.12500	4.11900	9.32939	13.10653
0.40	-2.34349	1.49723	3.97813	8.31310	11.46734
0.45	-1.54123	1.70914	3.81767	7.51551	10.21519
0.50	-0.98204	1.82425	3.65178	6.86744	9.22215
0.55	-0.58227	1.87952	3.48836	6.32771	8.41247
0.60	-0.29065	1.89714	3.33152	5.86982	7.73808
0.65	-0.07446	1.89086	3.18316	5.47568	7.16673
0.70	0.08785	1.86938	3.04398	5.13237	6.67593
0.75	0.21091	1.83835	2.91401	4.83039	6.24939
0.80	0.30487	1.80146	2.79289	4.56253	5.87503
0.90	0.43232	1.71918	2.57511	4.10799	5.24821
1	0.50738	1.63402	2.38600	3.73654	4.74363
2.5	0.47213	0.85299	1.11330	1.58971	1.95074
5	0.28361	0.46206	0.58529	0.81263	0.98607

Appendix D

n-Butane

T (K)	**300**	**360**	**400**	**425. 125**	**500**	**575**
α →	1.219844	1.106947	1.039614	1	0.892759	0.769613
a(T) →	1.836113	1.66618	1.56483	1.505203	1.343784	1.158423
V m3/kmol ↓			**P^{PR}**	**(Mpa)**		
0.08	186.315	265.732	317.739	350.083	445.220	538.950
0.09	26.596	65.716	91.044	106.695	152.331	196.789
0.095	5.945	37.756	58.282	70.941	107.756	143.495
0.099	-3.212	24.570	42.460	53.480	85.475	116.468
0.1	-4.886	22.054	39.393	50.071	81.062	111.068
0.11	-14.138	6.604	19.908	28.085	51.750	74.581
0.12	-16.727	0.167	10.981	17.618	36.796	55.255
0.13	-16.881	-2.639	6.464	12.047	28.162	43.650
0.14	-16.084	-3.792	4.057	8.869	22.748	36.074
0.15	-14.932	-4.140	2.748	6.969	19.139	30.819
0.16	-13.685	-4.083	2.044	5.797	16.618	26.998
0.17	-12.457	-3.824	1.685	5.059	14.786	24.116
0.18	-11.299	-3.469	1.528	4.589	13.411	21.873
0.19	-10.230	-3.076	1.490	4.287	12.349	20.083
0.2	-9.254	-2.677	1.521	4.093	11.508	18.622
0.21	-8.369	-2.289	1.592	3.970	10.827	17.408
0.22	-7.567	-1.921	1.684	3.893	10.265	16.382
0.25	-5.594	-0.966	1.991	3.805	9.039	14.068
0.3	-3.358	0.160	2.412	3.794	7.789	11.636
0.35	-1.944	0.865	2.666	3.774	6.978	10.069
0.4	-1.017	1.305	2.797	3.715	6.375	8.945
0.5	0.046	1.748	2.846	3.522	5.487	7.393
0.6	0.571	1.902	2.761	3.292	4.838	6.341
0.9	1.051	1.835	2.346	2.662	3.587	4.492
1	1.078	1.765	2.213	2.490	3.303	4.100
2.5	0.750	0.981	1.133	1.228	1.509	1.787
5	0.435	0.543	0.614	0.659	0.791	0.923

Propane

T (K)	**200**	**300**	**369.89**	**500**	**600**
α →	1.34546165	1.12376046	1	0.81308661	0.69665045
a(T) →	1.36845723	1.1429669	1.01709122	0.82698325	0.70855706
V m3/kmol ↓			**P^{PR}**	**(Mpa)**	

0.06	256.50643	511.35287	685.05107	1002.26004	1242.20782
0.07	-21.18196	62.87362	118.31998	216.93977	289.85646
0.08	-41.72649	11.74987	46.53246	107.67100	152.39839
0.09	-41.53800	-1.91245	23.67605	68.37645	100.89422
0.10	-37.62079	-6.13858	14.11076	49.36271	74.92602
0.12	-29.21897	-7.05684	7.15014	31.81072	49.64523
0.13	-25.68859	-6.46133	5.85835	27.23395	42.68672
0.15	-20.04336	-4.94611	4.72952	21.52087	33.66189
0.19	-12.75815	-2.38947	4.27326	15.86263	24.26029
0.20	-11.48989	-1.90536	4.25877	14.98890	22.76931
0.25	-7.06094	-0.19135	4.24719	12.00454	17.65016
0.30	-4.52447	0.75655	4.18444	10.19921	14.59246
0.35	-2.96022	1.29097	4.06229	8.94286	12.51953
0.40	-1.94171	1.59420	3.90831	7.99724	11.00275
0.45	-1.25087	1.76280	3.74216	7.25011	9.83550
0.50	-0.76728	1.85033	3.57514	6.64020	8.90461
0.55	-0.42032	1.88784	3.41320	6.13045	8.14224
0.60	-0.16650	1.89395	3.25925	5.69673	7.50489
0.65	0.02203	1.88020	3.11448	5.32244	6.96323
0.70	0.16373	1.85394	2.97916	4.99570	6.49663
0.75	0.27118	1.81992	2.85306	4.70770	6.09013
0.80	0.35314	1.78125	2.73572	4.45175	5.73257
0.90	0.46391	1.69761	2.52491	4.01635	5.13215
1	0.52844	1.61268	2.34186	3.65947	4.64720
2.5	0.47082	0.84558	1.10264	1.57442	1.93278
5	0.28281	0.45980	0.58226	0.80851	0.98132

Appendix E

T= 300 K		
Pressure (MPa)	Volume (m3/kmol)	Phase
0.01	248.73	vapor
0.2576	8.9194	vapor
0.2576	0.10185	liquid
2.0097	0.10131	liquid
4.0094	0.10073	liquid
6.0091	0.10018	liquid
8.0088	0.099672	liquid
10.008	0.099187	liquid
12.008	0.098728	liquid
14.008	0.098291	liquid
16.008	0.097873	liquid

T= 400 K		
Pressure (MPa)	Volume (m3/kmol)	Phase
0.01	332.22	vapor
2.0097	1.1856	vapor
2.4954	0.79536	vapor
2.4954	0.14229	liquid
4.0094	0.13575	liquid
6.0091	0.13067	liquid
8.0088	0.12716	liquid
10.008	0.12445	liquid
12.008	0.12224	liquid
14.008	0.12037	liquid
16.008	0.11874	liquid

18.007	0.097474	liquid
20.007	0.097092	liquid
22.007	0.096725	liquid
24.006	0.096372	liquid
26.006	0.096032	liquid
28.006	0.095704	liquid
30.006	0.095387	liquid
32.005	0.095081	liquid
34.005	0.094784	liquid
36.005	0.094496	liquid
38.004	0.094217	liquid
40.004	0.093946	liquid
42.004	0.093683	liquid
44.003	0.093427	liquid
46.003	0.093177	liquid
48.003	0.092934	liquid
50.002	0.092697	liquid
52.002	0.092466	liquid
54.002	0.092241	liquid
56.002	0.09202	liquid
58.001	0.091805	liquid
60.001	0.091594	liquid
62.001	0.091388	liquid
64	0.091186	liquid
66	0.090989	liquid
68	0.090795	liquid
69.999	0.090605	liquid

18.007	0.11731	liquid
20.007	0.11602	liquid
22.007	0.11486	liquid
24.006	0.11379	liquid
26.006	0.11281	liquid
28.006	0.11191	liquid
30.006	0.11106	liquid
32.005	0.11028	liquid
34.005	0.10953	liquid
36.005	0.10884	liquid
38.004	0.10818	liquid
40.004	0.10755	liquid
42.004	0.10696	liquid
44.003	0.10639	liquid
46.003	0.10585	liquid
48.003	0.10533	liquid
50.002	0.10483	liquid
52.002	0.10436	liquid
54.002	0.1039	liquid
56.002	0.10346	liquid
58.001	0.10303	liquid
60.001	0.10262	liquid
62.001	0.10223	liquid
64	0.10184	liquid
66	0.10147	liquid
68	0.10111	liquid
69.999	0.10076	liquid

T= 425.125 K		
Pressure (MPa)	Volume (m3/kmol)	Phase
0.01	353.16	vapor
2.0097	1.3859	vapor
3.796	0.25492	vapor
3.796	0.25492	liquid
4.0094	0.18003	liquid
10.008	0.13587	supercritical
12.008	0.13205	supercritical
14.008	0.12904	supercritical
16.008	0.12657	supercritical
18.007	0.12448	supercritical

T= 500 K		
Pressure (MPa)	Volume (m3/kmol)	Phase
0.01	415.51	vapor
2.0097	1.8455	vapor
4.0094	0.79833	vapor
4.0094	0.79833	supercritical
4.0094	0.79833	supercritical
6.0091	0.44319	supercritical
8.0088	0.28285	supercritical
10.008	0.2168	supercritical
12.008	0.18787	supercritical
14.008	0.17229	supercritical

20.007	0.12266	supercritical
22.007	0.12105	supercritical
24.006	0.11961	supercritical
26.006	0.11831	supercritical
28.006	0.11713	supercritical
30.006	0.11604	supercritical
32.005	0.11503	supercritical
34.005	0.11409	supercritical
36.005	0.11322	supercritical
38.004	0.11239	supercritical
4.0094	0.18003	supercritical
4.0094	0.18003	supercritical
40.004	0.11162	supercritical
42.004	0.11089	supercritical
44.003	0.1102	supercritical
46.003	0.10955	supercritical
48.003	0.10893	supercritical
50.002	0.10833	supercritical
52.002	0.10776	supercritical
54.002	0.10722	supercritical
56.002	0.1067	supercritical
58.001	0.1062	supercritical
6.0091	0.14982	supercritical
60.001	0.10571	supercritical
62.001	0.10525	supercritical
64	0.1048	supercritical
66	0.10437	supercritical
8.0088	0.14116	supercritical

16.008	0.16237	supercritical
18.007	0.15531	supercritical
20.007	0.14993	supercritical
22.007	0.14562	supercritical
24.006	0.14206	supercritical
26.006	0.13903	supercritical
28.006	0.13641	supercritical
30.006	0.13411	supercritical
32.005	0.13206	supercritical
34.005	0.13022	supercritical
36.005	0.12854	supercritical
38.004	0.12702	supercritical
40.004	0.12561	supercritical
42.004	0.12432	supercritical
44.003	0.12311	supercritical
46.003	0.12199	supercritical
48.003	0.12093	supercritical
50.002	0.11994	supercritical
52.002	0.11901	supercritical
54.002	0.11813	supercritical
56.002	0.1173	supercritical
58.001	0.1165	supercritical
60.001	0.11575	supercritical
62.001	0.11503	supercritical
64	0.11434	supercritical
66	0.11369	supercritical
68	0.11306	supercritical
69.999	0.11245	supercritical

T= 575 K		
Pressure (MPa)	Volume (m3/kmol)	Phase
0.01	415.51	vapor
2.0097	1.8455	vapor
4.0094	0.79833	vapor
4.0094	0.79833	supercritical
4.0094	0.79833	supercritical
6.0091	0.44319	supercritical
8.0088	0.28285	supercritical
10.008	0.2168	supercritical
12.008	0.18787	supercritical
14.008	0.17229	supercritical
16.008	0.16237	supercritical
18.007	0.15531	supercritical
20.007	0.14993	supercritical
22.007	0.14562	supercritical
24.006	0.14206	supercritical
26.006	0.13903	supercritical
28.006	0.13641	supercritical
30.006	0.13411	supercritical
32.005	0.13206	supercritical
34.005	0.13022	supercritical
36.005	0.12854	supercritical
38.004	0.12702	supercritical
40.004	0.12561	supercritical
42.004	0.12432	supercritical
44.003	0.12311	supercritical
46.003	0.12199	supercritical
48.003	0.12093	supercritical
50.002	0.11994	supercritical
52.002	0.11901	supercritical
54.002	0.11813	supercritical
56.002	0.1173	supercritical
58.001	0.1165	supercritical
60.001	0.11575	supercritical
62.001	0.11503	supercritical
64	0.11434	supercritical
66	0.11369	supercritical
68	0.11306	supercritical
69.999	0.11245	supercritical

Appendix F

T= 200 K		
Pressure (MPa)	**Volume (m3/kmol)**	**Phase**
0.01	165.34	vapor
0.020192	81.401	vapor
0.020192	0.071651	liquid
2.0097	0.071463	liquid
4.0094	0.071279	liquid
6.0091	0.071101	liquid
8.0088	0.070927	liquid
10.008	0.070758	liquid
12.008	0.070593	liquid
14.008	0.070432	liquid
16.008	0.070275	liquid
18.007	0.070122	liquid
20.007	0.069972	liquid
22.007	0.069826	liquid
24.006	0.069683	liquid
26.006	0.069543	liquid
28.006	0.069405	liquid
30.006	0.069271	liquid
32.005	0.069139	liquid
34.005	0.06901	liquid
36.005	0.068883	liquid
38.004	0.068759	liquid
40.004	0.068636	liquid
42.004	0.068516	liquid
44.003	0.068398	liquid
46.003	0.068282	liquid
48.003	0.068168	liquid
50.002	0.068056	liquid
52.002	0.067946	liquid
54.002	0.067837	liquid
56.002	0.06773	liquid
58.001	0.067625	liquid
60.001	0.067522	liquid
62.001	0.06742	liquid
64	0.067319	liquid
66	0.06722	liquid
68	0.067122	liquid
69.999	0.067026	liquid

T= 300 K		
Pressure (MPa)	**Volume (m3/kmol)**	**Phase**
0.01	249.05	vapor
0.99768	2.0387	vapor
0.99768	0.090093	liquid
2.0097	0.089507	liquid
4.0094	0.088471	liquid
6.0091	0.08756	liquid
8.0088	0.086746	liquid
10.008	0.08601	liquid
12.008	0.085336	liquid
14.008	0.084715	liquid
16.008	0.084139	liquid
18.007	0.083601	liquid
20.007	0.083097	liquid
22.007	0.082622	liquid
24.006	0.082173	liquid
26.006	0.081748	liquid
28.006	0.081343	liquid
30.006	0.080957	liquid
32.005	0.080589	liquid
34.005	0.080236	liquid
36.005	0.079897	liquid
38.004	0.079572	liquid
40.004	0.079259	liquid
42.004	0.078957	liquid
44.003	0.078666	liquid
46.003	0.078384	liquid
48.003	0.078112	liquid
50.002	0.077848	liquid
52.002	0.077592	liquid
54.002	0.077344	liquid
56.002	0.077103	liquid
58.001	0.076869	liquid
60.001	0.076641	liquid
62.001	0.076419	liquid
64	0.076202	liquid
66	0.075991	liquid
68	0.075786	liquid
69.999	0.075585	liquid

T= 369.89 K		
Pressure (MPa)	**Volume (m3/kmol)**	**Phase**
0.01	307.3	vapor
2.0097	1.2489	vapor
4.0094	0.37816	vapor
4.2512	0.2	vapor
4.2512	0.2	liquid
6.0091	0.12183	liquid
6.0091	0.12183	supercritical
6.0091	0.12183	supercritical
8.0088	0.11367	supercritical
10.008	0.10901	supercritical
12.008	0.10573	supercritical
14.008	0.10321	supercritical
16.008	0.10116	supercritical
18.007	0.099435	supercritical
20.007	0.097945	supercritical
22.007	0.096636	supercritical
24.006	0.095469	supercritical
26.006	0.094416	supercritical
28.006	0.093458	supercritical
30.006	0.092579	supercritical
32.005	0.091768	supercritical
34.005	0.091014	supercritical
36.005	0.090311	supercritical
38.004	0.089652	supercritical
40.004	0.089032	supercritical
42.004	0.088447	supercritical
44.003	0.087894	supercritical
46.003	0.087368	supercritical
48.003	0.086868	supercritical
50.002	0.086391	superc

T= 500 K		
Pressure (MPa)	**Volume (m3/kmol)**	**Phase**
0.01	415.6	vapor
2.0097	1.9469	vapor
4.0094	0.91571	vapor
6.0091	0.57261	vapor
6.0091	0.57261	supercritical
6.0091	0.57261	supercritical
8.0088	0.40403	supercritical
10.008	0.30739	supercritical
12.008	0.24819	supercritical
14.008	0.21069	supercritical
16.008	0.18615	supercritical
18.007	0.1694	supercritical
20.007	0.15742	supercritical
22.007	0.14847	supercritical
24.006	0.14152	supercritical
26.006	0.13595	supercritical
28.006	0.13137	supercritical
30.006	0.12753	supercritical
32.005	0.12424	supercritical
34.005	0.12139	supercritical
36.005	0.11888	supercritical
38.004	0.11666	supercritical
40.004	0.11466	supercritical
42.004	0.11286	supercritical
44.003	0.11122	supercritical
46.003	0.10971	supercritical
48.003	0.10833	supercritical
50.002	0.10705	supercritical
52.002	0.10586	supercritical
54.002	0.10475	superc

		ritical
52.002	0.085935	supercritical
54.002	0.085499	supercritical
56.002	0.085081	supercritical
58.001	0.084679	supercritical
60.001	0.084292	supercritical
62.001	0.08392	supercritical
64	0.08356	supercritical
66	0.083214	supercritical

		ritical
56.002	0.10372	supercritical
58.001	0.10274	supercritical
60.001	0.10183	supercritical
62.001	0.10096	supercritical
64	0.10014	supercritical
66	0.099362	supercritical
68	0.098623	supercritical
69.999	0.097918	supercritical

T= 600 K		
Pressure (MPa)	**Volume (m3/kmol)**	**Phase**
0.01	498.8	vapor
2.0097	2.4139	vapor
4.0094	1.1787	vapor
6.0091	0.76808	vapor
6.0091	0.76808	supercritical
6.0091	0.76808	supercritical
8.0088	0.56479	supercritical
10.008	0.4449	supercritical
12.008	0.36696	supercritical
14.008	0.3131	supercritical
16.008	0.27428	supercritical
18.007	0.24542	supercritical
20.007	0.22342	supercritical
22.007	0.20627	supercritical
24.006	0.19264	supercritical
26.006	0.18161	supercritical
28.006	0.17253	supercritical
30.006	0.16494	supercritical
32.005	0.15851	supercritical
34.005	0.15299	supercritical
36.005	0.14819	supercritical
38.004	0.144	supercritical
40.004	0.14028	supercritical
42.004	0.13697	supercritical
44.003	0.13399	supercritical
46.003	0.13131	supercritical
48.003	0.12886	supercritical
50.002	0.12663	supercritical
52.002	0.12458	supercritical
54.002	0.12269	supercritical
56.002	0.12093	supercritical
58.001	0.11931	supercritical
60.001	0.11779	supercritical
62.001	0.11637	supercritical
64	0.11504	supercritical
66	0.11378	supercritical
68	0.1126	supercritical
69.999	0.11148	supercritical

Appendix G

T_{exp} (K)	P_{exp}(MPa)	T_{exp} (K)	P_{exp}(MPa)	T_{exp} (K)	P_{exp}(MPa)	T_{exp} (K)	P_{exp}(MPa)
134. .86	6.74E-07	210	4.05E-03	262.267	6.71E-02	345.65	8.62E-01
140	1.72E-06	212.668	4.83E-03	265	7.50E-02	348.14	9.08E-01
145	3.99E-06	215	5.67E-03	266.789	8.07E-02	348.66	9.15E-01
150	8.69E-06	220	7.81E-03	270	9.15E-02	348.99	9.26E-01
155	1.79E-05	225	1.06E-02	270.397	9.29E-02	352.64	9.99E-01
160	3.50E-05	226.276	1.14E-02	272.027	9.90E-02	353.87	1.03
165	6.54E-05	230	1.41E-02	272.806	1.02E-01	355.08	1.06
170	1.17E-04	235	1.86E-02	294.26	2.16E-01	357.02	1.10
175	2.02E-04	235.822	1.94E-02	327.59	5.57E-01	359.02	1.15
180	3.37E-04	240	2.41E-02	333.13	6.40E-01	360.93	1.20
185	5.44E-04	245	3.09E-02	336.42	6.94E-01	361.14	1.20
190	8.54E-04	246.511	3.33E-02	336.48	6.90E-01	361.21	1.21
195	1.30E-03	250	3.91E-02	340.94	7.69E-01	363.45	1.26
195.107	1.32E-03	255	4.91E-02	343.07	8.09E-01	365.7	1.31
200	1.94E-03	256.204	5.18E-02	344.26	8.34E-01	366.62	1.34
205	2.84E-03	260	6.10E-02	344.71	8.38E-01	367.85	1.37
						367.98	1.38

Appendix H

T_{exp} (K)	P_{exp}(MPa)	T_{exp} (K)	P_{exp}(MPa)	T_{exp} (K)	P_{exp}(MPa)	T_{exp} (K)	P_{exp}(MPa)
85.525	1.720E-10	158.15	7.022E-04	231.036	1.013E-01	303.15	1.079
88.15	4.853E-10	163.15	1.164E-03	233.15	1.111E-01	308.15	1.2179
93.15	2.939E-09	168.15	1.866E-03	238.15	0.13723	313.15	1.3694
98.15	1.460E-08	173.15	2.899E-03	243.15	0.16783	318.15	1.5343
103.15	6.126E-08	178.15	4.380E-03	248.15	0.20343	323.15	1.7133
108.15	2.225E-07	183.15	6.448E-03	253.15	0.24452	328.15	1.9072
113.15	7.137E-07	188.15	9.272E-03	258.15	0.29162	333.15	2.1168
118.15	2.054E-06	193.15	1.305E-02	263.15	0.34528	338.15	2.343
123.15	5.380E-06	198.15	1.801E-02	268.15	0.40604	343.15	2.5868
128.15	1.297E-05	203.15	2.440E-02	273.15	0.47446	348.15	2.8493
133.15	2.904E-05	208.15	3.253E-02	278.15	0.55112	353.15	3.1319
138.15	6.095E-05	213.15	4.269E-02	283.15	0.6366	358.15	3.4361
143.15	1.207E-04	218.15	5.525E-02	288.15	0.73151	363.15	3.7641
148.15	2.271E-04	223.15	7.057E-02	293.15	0.83646	368.15	4.1195
153.15	4.077E-04	228.15	8.905E-02	298.15	0.95207	369.89	4.2512

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عنوان المذكرة : التحقيق في طرق حساب بعض الخصائص الحرارية، الديناميكية والحجمية للهيدروكربونات الخفيفة

اللقب: عبابسة **الإسم:** بسمة **المؤطر:** **بورزق محمد الطاهر**

اللقب: حمامي **الإسم:** عائشة إكرام

ملخص: تستخدم معادلات الحالة للتنبؤ بسلوك السوائل عند مختلف الضغوط ودرجات الحرارة. ويعتمد اختيار المعادلة على نوع المكون، الضغط ،نطاق الحرارة والخواص التي يجرى حسابها. وفي هذا العمل، تم اختبار أربع معادلات (بينغ - روبينسون، فان دير والز، ريدليك وكونغ وسوافي ريدليك وكونغ) على مركبين هيدروكربونيين خفيفين هما البوتان الطبيعي والبروبان، من أجل دراسة أدائهما بحساب بعض الخصائص الكمية والحراروديناميكية. وكانت النتائج المتحصل عليها مرضية إلى حد كبير عند استخدام PR و SRK في الحالة الغازية عند حساب الضغط . بسبب تعديل المصطلح (أ) بإضافة البارامتر الثالث إليه، الذي تم الحصول عليه من نظرية Pitzer. وبالنسبة لتنبؤات حجم المولي المشبع المتحصل عليها بواسطة PR العامة ، كانت النتائج مقاربة إلى قيم الحجم التجريبية.

كلمات مفتاحية: معادلة الحالة،متساوي الحرارة، الحجم المولي، العامل اللا مركزي.

Titre du mémoire : Méthodes de calcul d'enquête, de certaines propriétés thermodynamiques et volumétriques pour les hydrocarbures légers

Nom : ABABSA **Prénom : Basma** **Encadrant :** Bourzeg Med Tahar

Nom : HAMAMI **Prénom :** Aicha Ikram

Résumé : Les équations d'état sont utilisées pour prédire le comportement des fluides à diverses pressions et températures. Le choix de l'équation dépend du type de composant, de la pression et de la plage de température, et des propriétés qui sont calculées. Dans ce travail, quatre équations (Peng-Robinson, van der Waals, Redlich et Kwong, et Soave Redlich et Kwong) sont testées sur deux hydrocarbures légers, qui sont le n-butane et le propane, afin d'enquêter sur leurs performances pour le calcul de certaines propriétés volumétriques et thermodynamiques. Les résultats obtenus ont été très satisfaisants lors de l'utilisation de PR et SRK pour l'état gazeux lors du calcul de la pression, en raison de la modification du terme (a) en y ajoutant le troisième paramètre (ω), qui a été obtenu par la théorie de Pitzer. Et pour le volume molaire saturé, les prévisions de PR étaient extrêmement proches des valeurs de volume empiriques.

Mots clés : équations de l'état, isotherme, volume molaire, facteur acentrique

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Thesis title: Calculation methods investigation, of some thermodynamic and volumetric properties for two light hydrocarbons
Name: ABABSA **First name: Basma** **Directed by:** Bourzeg Med Tahar

Name: HAMAMI **First name:** Aicha Ikram

Abstract: Equations of state are used to predict the behavior of fluids at various pressures and temperatures. The choice of equation depends on the type of component, the pressure and temperature range, and the properties being calculated. In this work, four equations (Peng-Robinson, van der Waals, Redlich and Kwong, and Soave Redlich and Kwong) are tested on two light hydrocarbons, which are n-butane and propane, in order to investigate their performances for the calculation of some volumetric & thermodynamic properties. The results obtained were highly satisfactory when using PR and SRK for the gaseous state when calculating the pressure, due to the adjustment of the term (a) by adding to it the third parameter (ω), that was obtained by Pitzer's theory. And for the saturated molar volume predictions by PR were extremely approached to the empirical volume values.

Key words: equations of state, isotherm, molar volume, acentric factor.

Le résumé doit être rédigé en deux langues différentes au moins