Isothermal Graphical Method For Determining An Equation Of State In A Gas Mixture

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Abstract.
This article presents a theoretical framework and methodological strategy for determining an equation of state in a gas mixture, focusing specifically on Camisea natural gas in Peru. The research highlights the lack of previous studies on this topic and proposes the development of an isothermal graphical method for this determination. The general and specific objectives of the research focus on determining the equation of state for the gas mixture, selecting the appropriate isothermal graphical method, and relating the chemical composition of the gas mixture to the equation of state. The methodology is described as technological research of explanatory-correlational level, with a multivariate-correlational design. The study population is Camisea natural gas, with the sample being the chemical composition of the gas. Data are collected from official chromatographic analysis reports from the Camisea Consortium. The technique for data processing, analysis, and interpretation involves the use of Excel spreadsheets and Matlab. The conclusions reveal that the equation of state that best fits Camisea natural gas is the Soave Redlinch-Kwong equation, followed by the Peng-Robinson equation. Additionally, the simplicity of the proposed isothermal graphical method is highlighted, which can be implemented in Excel and provides a relationship between the fundamental study variables.

Keyboards: Gas, Equation of State, Camisea.

Introduction

1. Theoretical framework

1.1. Background of the Research Problem

At present, ther[1]e are no studies regarding the determination of an equation of state of a gas mixture, although there is information on the use of software to choose one of the models that the program has as an application, but there is no methodology to determine the equation of state for a mixture such as air or natural gas specifically. What has been collected is the article "Determination of optimal constants for the Peng Robinson Stryjec-Vera (PRSV) equation of state at elevated pressures", whose author is Zavaleta (2010), who presents the research work based on the following proposals:

The PRSV equation of state in the two-phase zone (liquid and gas) is developed to calculate the eccentricity factor (ω) and constant value (k1) that characterizes the PRSV model, which is specific for each gas and was included to better regulate the data obtained from the vapor pressure (Pv) at low temperatures, especially for compounds that are not

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hydrocarbons. This improvement in Pv prediction also has important applications for improving the values obtained in vapor-liquid phase equilibrium (L-V). When more than 60 chemical compounds are involved, the results obtained, ω and k1, reduce the average error over a pressure range from 1 atmosphere to the critical pressure [1].

1.2   Theoretical Basis of the Research

Natural Gas
Natural gas is a fossil fuel formed by a group of hydrocarbons that, in reservoir conditions, are usually found in a gaseous state or, to a certain extent, in solution with petroleum. It is usually found in nature in two ways as "associated natural gas" when it is accompanied by oil and as "non-associated natural gas" when it is not accompanied by oil [2].
It usually consists mostly of compounds of the kerosene series, mainly methane, with minor amounts of ethane, propane, and butane, and may also contain very small percentages of heavier compounds. Variable quantities of certain non-hydrocarbon gases such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitrogen (N_2), helium (He_2), water vapor, and others can be found in natural gas [3].

Properties of Natural Gas
- This gas can be considered as consisting of particles without volume and between which there are no forces of attraction or repulsion.
- It is a homogeneous mixture, generally of low density and viscosity, without defined volume, which occupies independently of the place in which it is found.

Natural Gas Characteristics
- It is composed mainly of methane (CH_4)
- It is a source of fossil fuel energy.
- It has a relative density of less than 1, so it is lighter than air and dissipates quickly.
- Liquefies at a temperature below -160°C
- It has a calorific value between 9000 and 1000 Kcal/m^3

Camisea Natural Gas
Camisea, also known as Camisea natural gas, is one of the most important natural reserves on the Peruvian coast and is ten times larger than any other discovered in the country. Its proven and probable reserves of natural gas usually amount to 11 trillion cubic feet, with associated liquids of around 600 million barrels [4].
Within the production of natural gas, to obtain the necessary resources that will be used, a series of components follow, among which are:
Exploitation
The extraction and production of natural gas is recapitulated in a contract whose module specifies an exploitation time of 40 years assigned to the Consortium led by Pluspetrol Peru.
Transportation
Once the gas has been exploited in the main gas fields, it is transported together with the liquids to different congenital plants which include the Malvina Cryogenic Plant (Camisea) to the "City Gate" in Lurin located in Lima, likewise, there is a pipeline that transports the natural gas liquids from the Malvinas Gas Plant (Camisea) to the fractionation plant and terminal in Pisco.
Distribution
This is done through a network of pipelines that supply the Peruvian coast.

Ideal Gas

An ideal gas is a model composed of imaginary molecules of zero volume that do not interact. Each chemical species in an ideal gas mixture has therefore its particular properties [5].

The definition of an ideal gas derives from a rationale that proposes, in the absence of molecular interactions, that the internal energy of the gas depends exclusively on the temperature; considering also that the pressure values tend to zero. The macroscopic behavior of an ideal gas is characterized by the following equation:

$$PV = nRT$$

Where:
- P: Pressure (atm)
- V: Volume (L)
- n: Number of moles (mol)
- R: Universal gas constant (atm-l/mol-K)
- T: Temperature (K)

Equations of state

The equations of state are used to correlate pressure, volume, and temperature data and to calculate different physical and thermodynamic properties of hydrocarbon systems over a wide range of pressure and temperature values [5].

The equation of state obeys a behavior from a certain point of view focused on molecular theory and are generally empirical equations. A classification of these equations is as follows:

Cubic equations usually represent the phase behavior (L-V) of non-polar molecules in a limited range of pressure versus temperature. They are relatively simple from a mathematical point of view [5].

Models of cubic equations

Van der Waals equation (VDW)

It is a cubic equation of state developed in 1873 by VDW and is the first equation capable of predicting the behavior of gas and liquid, taking into account attractive and repulsive molecular interactions. It was proposed to correct the two worst assumptions of the ideal gas law [5].

The expression of the Van Der Waals equation is as follows:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

Where:
- **P:** Gas pressure.
- **v:** Specific volume of gas.
- **R:** Universal gas constant.
- **T:** Temperature.

  In addition, a is the corrected value of the intermolecular forces expressed as a function of critical pressure (P_c), critical temperature (T_c), and R as follows:

$$a = \frac{27}{64}\left(\frac{(RT_c)^2}{P_C}\right)$$

Similarly, it can be expressed ε   on b:

$$b = \frac{1}{8}\left(\frac{RT_C}{P_C}\right)$$

Where:
- Tc: Critical Temper
- Pc: Critical pressure (atm)

Redlich-Kwong Equation (R-K)

This equation also contains two constants and can be determined from the variation of the equation of state at critical conditions of pressure and temperature. It is possibly the most accurate two-constant equation at high pressures. R-K proposes to modify the attraction term by including temperature to a square root power. However, the (R-K) equation is more accurate and has wider application [5].

The R-K equation is expressed as follows:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{T^{\frac{1}{2}}\overline{V}(\overline{V} + b)}$$

Where:
- P: Pressure.
- v: Specific volume.
- R: Universal gas constant.
- T: Temperature.

In addition:

$$a = \frac{0.42748R^2 T_C^{2.5}}{P}$$
$$b = \frac{0.0866RT_C}{P_C}$$

Peng-Robinson Equation

This cubic equation of state was proposed in 1976 to express the parameters as functions of critical properties and the eccentricity factor. This gives very similar results to those obtained using the SRK model but is highly recommended for liquid phase density prediction, especially in non-polar compounds, where it outperforms the SRK equation in this respect. The P-R equation is expressed as [5].

Being:

$$\frac{R * T}{} \qquad a$$
$$a = 0.45724\frac{R^2 Tcm^2}{Pcm}[1 + f_\omega(1 - Tr^{0.5}]^2$$
$$b = 0.0778\frac{RTcm}{Pcm}$$
$$f_\omega = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

2. Problem

Air is a mixture of gases very important for the preservation of life; even in these last years as a consequence of the pandemic, the lack of oxygen in the Health Centers was evidenced, the reason for which it was necessary to use the technology for the liquefaction of oxygen from air. This could allow, according to its chemical composition and graphics, to relate them with state equations that allow to improve the processes related to the separation treatment of air components.

Similarly, natural gas has allowed almost all sectors of production and households, that there is an important energy migration in the country, due to cost reduction and its massification in Lima and Ica; but like air natural gas is a mixture of gases, and to evaluate their physical and chemical properties for proper processing, it is necessary to know the equation of state that fits these mixtures.

So, it is important to know the equation of state of a mixture of gases to evaluate it and then submit it to the various physical and chemical processes.

For these reasons, it is necessary to raise the following question.

How does the isothermal graphical method determine the equation of state in a mixture of gases?

3. Justification and importance of the research

The ideal gas is applied at low pressures below 1 atm. of pressure. In this condition, its application is extremely simple because the data is simply replaced, and simplifies the calculation to find one of its variables. This allows that if the equation of an equal gas is plotted isothermally in a pressure-volume relationship, a reference line will be obtained.

If the pressures are values greater than one, then the gas ceases to behave as an ideal gas and is an equation of state of a real gas that science has been studying to obtain various equations of state that apply to real gases.

At present, no method directly suggests which equation of state is applicable for a given mixture of gases, taking into account that there is a diversity of equations of state.

The present study proposes a mathematical treatment model to relate the chemical composition of a gas mixture to an equation of state and isothermically apply a graphical method, giving pressure and volume values and superimposing it on the trend line of the ideal gas.

The equation of state that most closely approximates the trend line of the ideal gas will be the equation of state to be used for the various processes to which the mixture will be subjected.

Its scope of application could be, for example: air, natural gas, liquefied petroleum gas, and others.

For the reasons mentioned above, the present study is technically justified due to the importance it would have in the data processing and evaluation of properties of a gas mixture.

4. Hypotheses and variables (if applicable to the type of study).

Hypotheses
The isothermal graphical method determines an equation of state in a gas mixture.
Variables
Independent variable = Isothermal Graph Method
Dependent variable = Determination of an equation of state in a gas mixture.

5. Research objectives

General Objective
The general objective is to develop an isothermal graphical method for the determination of an equation of state in a mixture of gases.
Specific objectives
- Determine the equation of state for a mixture of gases.
- Select the appropriate isothermal graphical method that relates the variables of an equation of state.
- Relate the chemical composition of the gas mixture to the equation of state.

6. Methodological strategy

6.1 Type, level, and design of investigation

Based on the criteria set forth by authors in methodology, such as Espinoza Montes [6], and with this criterion the project is of the Technological research type.

Technological research aims to apply knowledge to solve various problems that will benefit society [6]. Accordingly, the level of the research is Explanatory-Correlational.

According to the criteria of the same author [6], research design, as a schematic organization to link and control research variables, intended to establish controlled restrictions to the observation of phenomena; it is a directional tool for the researcher that includes steps or actions to find possible solutions to problems.

According to these considerations, the design will be multivariate-correlational.

6.2 Population, sample, and sampling
Population: Camisea natural gas
Sample: Chemical composition of Camisea natural gas.
Sampling: According to current conditions, the sample will be taken from the official chromatographic analysis reports of the Camisea Consortium of the chemical composition of Camisea natural gas.

6.3 Data collection techniques and instruments
6.4 There are two general methods of data collection: documentary and empirical [6]. This project is part of a documentary approach since the sample collection and sampling will be taken from the official chromatographic analysis reports of the Camisea Consortium on the chemical composition of Camisea natural gas.

6.5 Data collection procedure
The data collection procedure will be organized by Consorcio Camisea reports on the chemical composition of natural gas at the wellhead and after gas conditioning processes.

6.6 Data processing, analysis, and interpretation techniques
For data processing, the Excel spreadsheet will be used to determine the equation of state in a gas mixture employing simple graphs or Matlab, which is one of the open-source programs available at the Computer Center Laboratory of the School of Chemical and Petrochemical Engineering.

The analysis and interpretation of the data will be performed by applying the Conceptual Design based on the fundamentals of thermodynamics in the chapter on equations of state.

6.7 Scope of study
The scope of the study is the hydrocarbon sector, specifically the Camisea natural gas extracted in the fields; and also after the conditioning stages in the Malvinas plant located in the Convention of the Cusco Region.

7. Experimental Procedure:
Determining the equation of state for a mixture of gases from a generalized Camisea gas report:

Table 1 Composition of Camisea Natural Gas

Component	%
Methane	82.9
Ethane	8.65
Propane	3.19

Pentane	3.02
Butane	1.38
Nitrogen	0.76
Carbon dioxide	0.2
Total	100

Source: Luis Espinoza Quiñonez "Camisea: Impacto en el sector energético"

Ideal Gas Equation

This equation follows the formula:

$$PV = nRT$$

$$P\frac{V}{n} = RT$$

$$P\overline{V} = RT$$

$$P = \frac{RT}{\overline{V}} \dots (1)$$

Working conditions:

❖ Molar volume: Volume values w
❖ Temperature: A standard temperature of 25°C – 298K Will be taken.
❖ Universal constant of ideal gases: $0.08215 \frac{atm-L}{mol-k}$
❖ Pressure: A pressure of 30 atm is proposed

First of all, with the values of the working conditions, it will be possible to determine volume values in order to achieve a given range:

$$\overline{V} = \frac{RT}{P}$$

$$\overline{V} = \frac{(0.08215 \frac{atm-L}{mol-k})(298 \text{ K})}{30 \text{ atm}}$$

$$\overline{V} = \mathbf{0.82} \frac{\mathbf{L}}{\mathbf{mol}}$$

With the determined value, a final value in the range of volume values was found; after that, the mathematical model was determined according to molar volume values applying the ideal gas equation:

Replacing values in the equation (1)

$$P = \frac{RT}{\overline{V}}$$

$$P = \frac{(0.08215 \frac{atm-L}{mol-k})(298 \text{ K})}{\overline{V}}$$

$$P = \frac{24.4807 \text{ atm} - L}{\overline{V}}$$

With the mathematical model obtained it is possible to give molar volume values up to a maximum of $0.82 \frac{L}{mol}$, which are shown in Table 2.

Table 2 Pressure - Molar Volume Data for the Equation of Ideal Gases

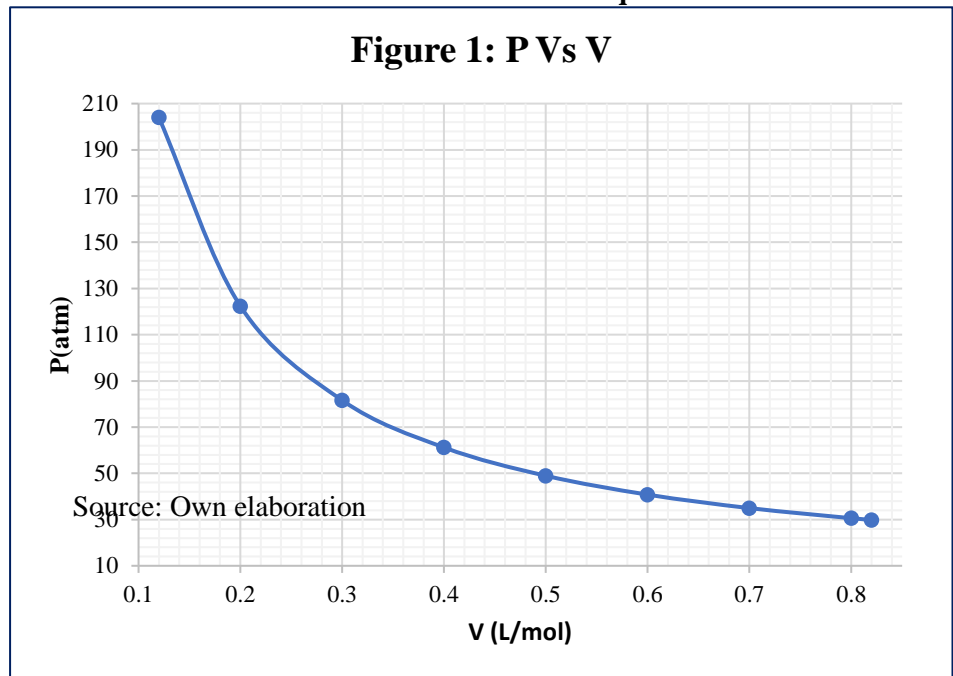| V(L/mol)	P(atm)

0.12	204.005833
0.2	122.4035
0.3	81.6023333
0.4	61.20175
0.5	48.9614
0.6	40.8011667
0.7	34.9724286
0.8	30.600875
0.82	29.8545122

Source: Own elaboration

Plotting the values:

Figure 1 Pressure versus Molar Volume for the Ideal Gas Equations

Figure 1: P Vs V

Source: Own elaboration

Equation of Corresponding States

In this equation of state, the Z factor known as the compressibility factor is used as a corrective to the ideal gas equation.
The equation is as follows:

$$P = \frac{ZRT}{\overline{V}} \dots (2)$$

Where it must be taken into account that the value of Z is a function of the reduced pressure as well as the reduced temperature.

$$Z = f(Pr, Tr)$$

This value is calculated using a Figure. The values of reduced pressure and reduced temperature will have to be a function of the mixture of the reservoir components; these values are calculated by the following formulas:

$$P_{rm} = \frac{P}{P_{cm}}$$

$$T_{rm} = \frac{T}{T}$$

In order to calculate the values of the reduced pressure of the mixture and the reduced temperature of the mixture, Table 3 was developed.

Table 3 Calculations of critical pressure and critical temperature of the mixture of components:

| Components:	Chemical Formula	yi	Pc(atm)	Tc(K)	yi*Pc(atm)	yi*Tc(K)
Methane	CH4	0.829	45.379	190.53	37.619191	157.94937
Ethane	C2H6	0.0865	48.077	305.34	4.1586605	26.41191
Propane	C3H8	0.0319	41.922	369.85	1.3373118	11.798215
Pentane	C5H12	0.0302	33.203	469.69	1.0027306	14.184638
Butane	C4H10	0.0138	37.464	425.16	0.5170032	5.867208
Nitrogen	N2	0.0076	33.555	126.2	0.255018	0.95912
Carbon Anhydride	CO2	0.002	72.877	304.14	0.145754	0.60828
TOTAL:		1			45.0356691	217.778741

Source: Own elaboration

Therefore:

$$P_{rm} = \frac{P}{P_{cm}} \rightarrow P_{rm} = \frac{30 \text{ atm}}{45.0357 \text{ atm}} = 0.67$$

$$T_{rm} = \frac{T}{T_{cm}} \rightarrow T_{rm} = \frac{298 \text{ K}}{217.779 \text{ K}} = 1.37$$

Having the corresponding data of the reduced pressure of the mixture and the reduced temperature of the mixture, the value of the compressibility factor can be calculated using Figure 2.

Figure 2 Representation of the Compressibility Factor
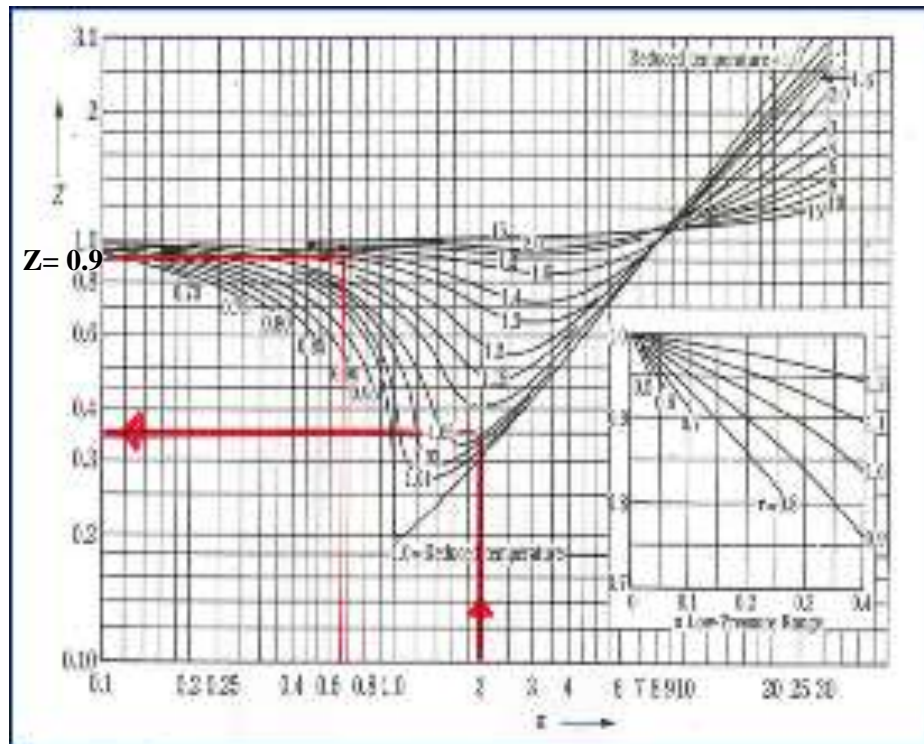
Source: Smith et al. [5]

From Figure 2, a value of Z = 0.9 is obtained, which is replaced in the equation (2):

$$P = \frac{ZRT}{\overline{V}}$$

$$P = \frac{(0.9)(0.08215\,\frac{atm - L}{mol - k})(298\ K)}{\overline{V}}$$

With the mathematical model obtained, it is possible to give molar volume values up to a maximum of $0.82\ \frac{L}{mol}$, which are shown in Table 3.

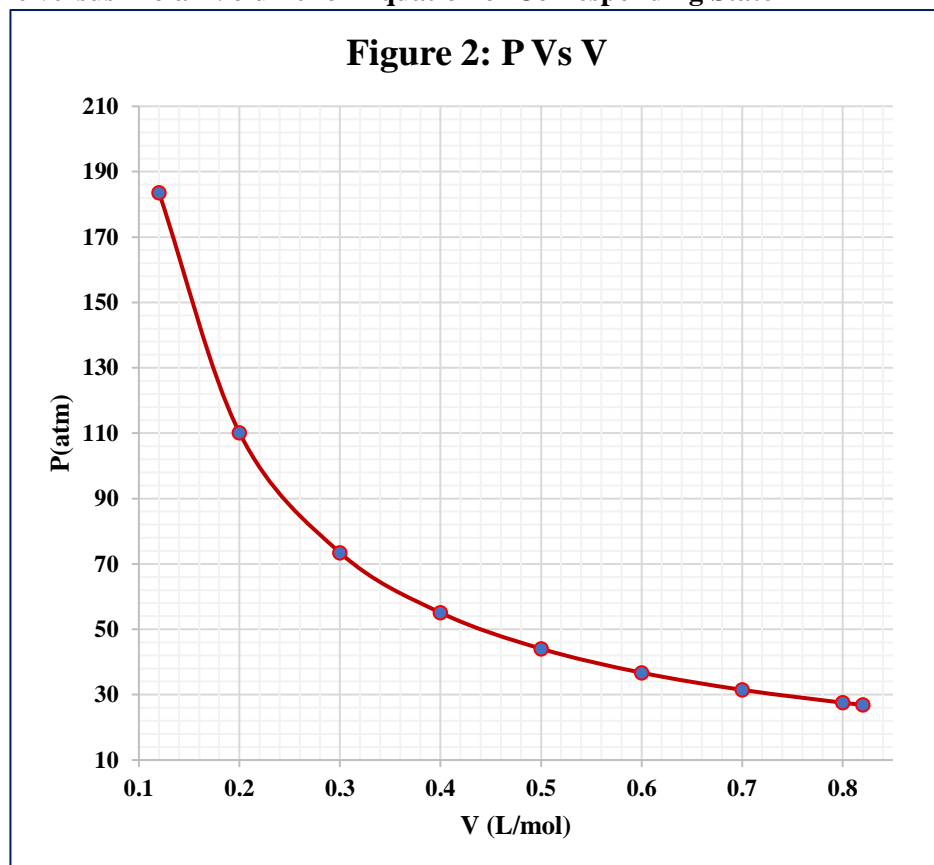**Table 3 Pressure - Molar Volume data for the corresponding Equation of States**

V(L/mol)	P(atm)
0.12	183.60525
0.2	110.16315
0.3	73.4421
0.4	55.081575
0.5	44.06526

0.6	36.72105
0.7	31.4751857
0.8	27.5407875
0.82	26.869061

Source: Own elaboration

Graphing the values:

Figure 3 Pressure versus Molar Volume for Equation of Corresponding State

Source: Own elaboration

Van der Waals equation:

The Van der Waals equation has the following mathematical model, where the parameters a and b are determined with the following formulas:

$$P = \frac{RT}{(\overline{V} - b)} - \frac{a}{\overline{V}^2} \dots (3)$$

$$a = \frac{27R^2 T cm^2}{64 P cm}$$

$$b = \frac{RT cm}{8 P cm}$$

Pseudocritical values for the mixture were obtained in the previous section:

$$P_{cm} = 45.0357 \text{ atm}$$

$$T_{cm} = 217.779 \, K$$

It is then proposed to calculate the values of a and b respectively:

Finding "a":

$$a = \frac{27(0.08215 \frac{\text{atm} - \text{L}}{\text{molK}})^2 (217.779\text{K})^2}{64(45.0357\text{atm})}$$

$$a = 2.99829 \frac{\text{atm.Lt}^2}{\text{mol}^2}$$

Finding "b":

$$b = \frac{(0.08215 \frac{\text{atm} - \text{L}}{\text{molK}})(217.779)}{8(45.0357\text{atm})}$$

$$b = 0.04966 \frac{\text{Lt}}{\text{mol}}$$

Once the values of a and b have been obtained, the mathematical model that is a function of molar volume data can be determined using the equation (3).

Replacing:

$$P = \frac{RT}{(\overline{V} - b)} - \frac{a}{\overline{V}^2}$$

$$P = \left[\frac{(0.08215 \frac{\text{atm} - \text{L}}{\text{molK}})(298\text{K})}{\overline{V} - (0.04966 \frac{\text{L}}{\text{mol}})}\right] - \left[\frac{2.99829 \frac{\text{atm} - \text{L}^2}{\text{mol}^2}}{\overline{V}^2}\right]$$

$$P = \left[\frac{24.4807\text{atm} - \text{L}}{\overline{V} - 0.04966 \text{ L}}\right] - \left[\frac{2.99829\text{atm L}^2}{\overline{V}^2}\right]$$

With the mathematical model obtained, it is possible to give molar volume values up to a maximum of $0.82 \frac{\text{L}}{\text{mol}}$, which are shown in Table 5.

Table 5
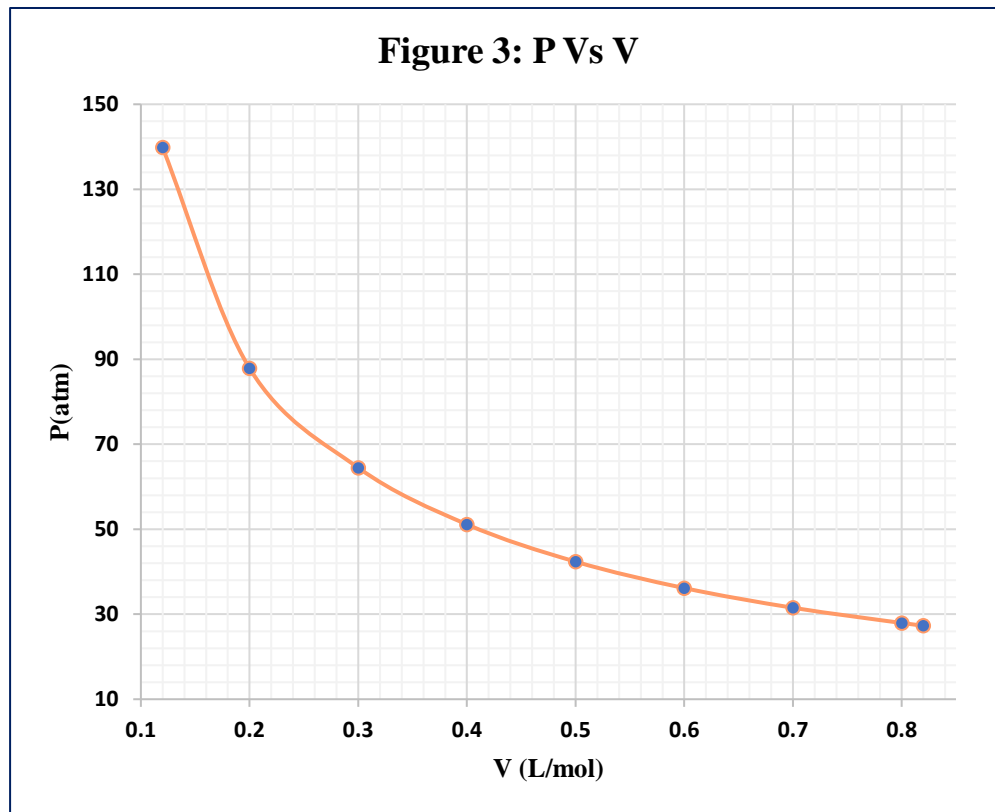**Pressure - Molar Volume data for the Van der Waals Equation**

V(L/mol)	P(atm)
0.12	139.8192523
0.2	87.8783227

0.3	64.47547253
0.4	51.13766415
0.5	42.36732319
0.6	36.1542818
0.7	31.52396606
0.8	27.94131469
0.82	27.31999771

Source: Own elaboration

Graphing the data:

Figure 3 Pressure versus Molar Volume for the Van der Waals Equation

Source: Own elaboration

Redlich - Kwong Equation:

The Redlich - Kwong equation has the following mathematical model:

$$P = \frac{RT}{V - b} - \frac{a}{T^{\frac{1}{2}}V(V + b)} \ldots (4)$$

Where the parameters a and b ar

$$a = \frac{0.42748 * R^2 * Tc^{2.5}}{Pc}$$

$$b = \frac{0.08664 * R * Tc}{Pc}$$

The pseudocritical values of the mixture were obtained in the previous section:

$$P_{cm} = 45.0357 \text{ atm}$$

$$T_{cm} = 217.779 \text{ K}$$

It is then proposed to calculate the values of a and b respectively:

Finding "a"

$$a = \frac{27(0.08215\frac{atm-L}{molK})^2(217.779K)^2}{64(45.0357atm)}$$

$$a = 2.99829\frac{atm.Lt^2}{mol^2}$$

Finding "b"

$$b = \frac{(0.08215\frac{atm-L}{molK})(217.779)}{8(45.0357atm)}$$

$$b = 0.04966\frac{Lt}{mol}$$

Once the values of a and b are obtained, the mathematical model based on molar volume data is determined by means of the equation (3).

Replacing:

$$P = \frac{RT}{(\overline{V} - b)} - \frac{a}{\overline{V}^2}$$

$$P = \left[\frac{(0.08215\frac{atm-L}{molK})(298K)}{\overline{V} - (0.04966\frac{L}{mol})}\right] - \left[\frac{2.99829\frac{atm-L^2}{mol^2}}{\overline{V}^2}\right]$$

$$P = \left[\frac{24.4807atm - L}{\overline{V} - 0.04966 \text{ L}}\right] - \left[\frac{2.99829atm \text{ } L^2}{\overline{V}^2}\right]$$

With the mathematical model obtained, molar volume values are given up to a maximum of 0.82 $\frac{L}{mol}$, which are shown in Table 6.

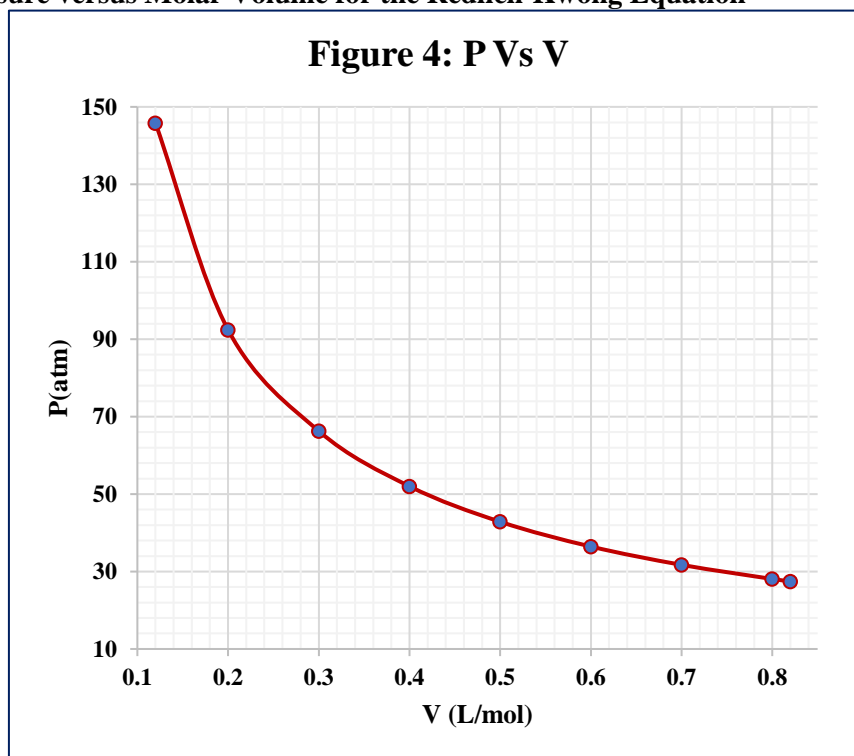**Table 6 Pressure - Molar Volume data for the Redlich - Kwong Equation**

V(L/mol)	P(atm)
0.12	145.8232511
0.2	92.43355633
0.3	66.28414916
0.4	52.01443677
0.5	42.85951165
0.6	36.459989
0.7	31.72815492
0.8	28.08531581
0.82	27.45500677

Source: Own evaluation

Graphing the data:

Figure 5 Pressure versus Molar Volume for the Redlich-Kwong Equation

Source: Own elaboration

Peng - Robinson Equation:

The Peng - Robinson Equation has the following mathematical model, where the acentric factor is introduced, which will be introduced in a function taking into account the components of the given sample.

Corresponding equation:

$$P = \frac{R * T}{\overline{V} - b} - \frac{a}{\overline{V}^2 + 2b\overline{V} - b^2} \ldots (5)$$

The value of a is a fu

$$a = 0.45724 \frac{R^2 Tcm^2}{Pcm} [1 + f_\omega(1 - Tr^{0.5}]^2$$

The function con   is follows:

$$f_\omega = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

The value of b is determined by the following model:

$$b = 0.0778 \frac{RTcm}{Pcm}$$

The values of the acentric factors of the components of the sample studied are shown in Table 7.

Table 7 Values of acentric factors

Acentric factors	ω
CH$_4$	0.012
C$_2$H$_6$	0.1
C$_3$H$_8$	0.152
C$_5$H$_{12}$	0.252
	0.2
N$_2$	0.038
CO$_2$	0.224

Source: Smith Van Ness [5]

Pseudocritical values for the mixture were obtained in the previous section:

$$P_{cm} = 45.0357 \text{ atm}$$

$$T_{cm} = 217.779 \text{ K}$$

In order to determine the value of the constant, the value of the reduced temperature of the mixture is needed, which is calculated by the following equation:

$$T_{rm} = \frac{T}{T_{cm}}$$

$$T_{rm} = \frac{298 \text{ K}}{217.779 \text{ K}} = 1.3684$$

It is then proposed to calculate the values of a and b respectively:

Calculating the constant "a":

$$a = 0.45724 \frac{R^2 Tcm^2}{Pcm}[1+\ f_\omega(1-Tr^{0.5}]^2$$

$$f_\omega = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

Adding the values of the acentric factors, the following value is obtained:

$$\sum \omega = \omega_{CH_4} + \omega_{C_2H_6} + \omega_{C_3H_8} + \omega_{C_4H_{10}} + \omega_{C_5H_{12}} + \omega_{N_2} + \omega_{CO_2}$$

$$\sum \omega = 0.012 + 0.1 + 0.152 + 0.2 + 0.252 + 0.038 + 0.224$$

$$\sum \omega = 0.978$$

Solving the mathematical function as a function of the sum of the values of the acentric factors:

$$f_\omega = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

$$f_\omega = 0.37464 + 1.5422(0.978) - 0.26992(0.978)^2$$

$$f_\omega = 1.6247$$

Finally, by replacing the values in the equation that determines the value of the constant a:

$$a = 0.45724 \frac{\left(0.08215\ \frac{atm-L}{mol-K}\right)^2 (217.779K)^2}{(45.03567\ atm)}[1+\ (1.6247)(1-1.3684^{0.5}]^2$$

$$a = 1.6988$$

Calculating the constant "b"

$$b = 0.0778 \frac{RTcm}{Pcm}$$

$$b = 0.0778 \frac{(0.08215\ \frac{atm*L}{mol*K})(217.779K)}{(45.0357\ atm)}$$

$$b = 0.0309$$

Finally, replacing the values of the constants a and b in equation (5), the appropriate mathematical model for the Peng-Robinson equation is obtained:

$$P = \frac{R*T}{\bar{V}-b} - \frac{a}{\bar{V}^2 + 2b\bar{V} - b^2}$$

$$P = \frac{(0.08215\ \frac{atm-L}{mol-K})(298\ K)}{\bar{V} - 0.0309} - \frac{1.6988}{\bar{V}^2 + 2(0.0309)\bar{V} - (0.0309)^2}$$

$$P = \frac{(24.4807\frac{atm-L}{mol})}{\overline{V}-0.0309} - \frac{1.6988}{\overline{V}^2 + 2(0.0309)\overline{V} - (0.0309)^2}$$

With the mathematical model obtained, molar volume values are given up to a maximum of $0.82 \frac{L}{mol}$, which are shown in Table 8.

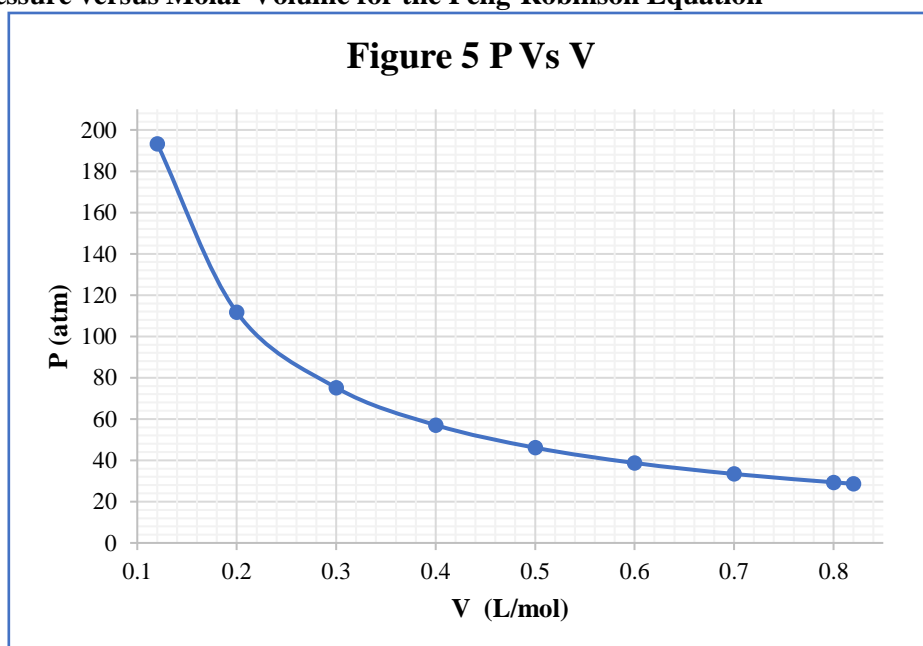**Table 8 Pressure - Molar Volume Data for the Peng - Robinson Equation**

V(L/mol)	P(atm)
0.12	193.3436322
0.2	111.7292891
0.3	75.18448615
0.4	57.0821346
0.5	46.11888748
0.6	38.72843062
0.7	33.39642615
0.8	29.36311494
0.82	28.67128442

Source: Own elaboration

Graphing the data:

Figure 6 Pressure versus Molar Volume for the Peng-Robinson Equation

Source: Own elaboration

Soave Redlich - Kwong Equation:

The Soave Redlich-Kwong equation usually handles a mathematical model that is a function of pseudo-critical values as seen above. Like the Peng-Robinson equation, this equation introduces the acentric factor which will be introduced in a function taking into account the components of the given sample.

The Soave Redlich - Kwong equation is as follows:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}(\overline{V} + b)}$$

The value of a is a function of the following model:

$$a = 0.42748 \frac{R^2 Tcm^2}{Pcm} [1 + f_\omega (1 - Tr^{0.5}]^2$$

The function contair   s follows:

$$f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$$

The value of b is determined by t

$$b = \frac{0.08664 * R * Tc}{Pc}$$

The values of the acentric factors of the components of the sample studied are as follows:

Table 9 Values of acentric factors

Acentric factors	ꞷ
CH_4	0.012
C_2H_6	0.1
C_3H_8	0.152
C_5H_{12}	0.252
C_4H_{10}	0.2
N_2	0.038
CO_2	0.224

Source: Smith Van Ness [5]

The pseudocritical values of the mixture were obtained in the previous section:

$$P_{cm} = 45.0357 \text{ atm}$$

$$T_{cm} = 217.779 \text{ K}$$

For the determination of the value   of the reduced temperature of the mixture is needed, which is determined by the following equation:

$$T_{rm} = \frac{T}{T_{cm}}$$

$$T_{rm} = \frac{298 \text{ K}}{217.779 \text{ K}} = 1.3684$$

It is then proposed to calculate the values of a and b respectively:

Calculating the constant "a":

$$a = 0.42748 * \frac{R^2 Tcm^2}{Pcm}[1 + f_\omega(1 - Tr^{0.5}]^2$$

$$f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$$

Adding the values of the acentric factors gives the following value:

$$\sum \omega = \omega_{CH_4} + \omega_{C_2H_6} + \omega_{C_3H_8} + \omega_{C_4H_{10}} + \omega_{C_5H_{12}} + \omega_{N_2} + \omega_{CO_2}$$

$$\sum \omega = 0.012 + 0.1 + 0.152 + 0.2 + 0.252 + 0.038 + 0.224$$

$$\sum \omega = 0.978$$

Solving the mathematical function as a function of the sum of the values of the acentric factors:

$$f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$$

$$f_\omega = 0.48 + 1.57(0.978) - 0.176(0.978)^2$$

$$f_\omega = 1.8510$$

Finally, by replacing the values in the equation that determines the value of the constant "a":

$$a = 0.42748 * \frac{\left(0.08215 \frac{atm - L}{mol - K}\right)^2 (217.779K)^2}{(45.03567 \, atm)}[1 + (1.8510)(1 - 1.3684^{0.5}]^2$$

$$a = 1.5224$$

Calculating the constant "b"

$$b = 0.08664 \frac{RTcm}{Pcm}$$

$$b = 0.0778 * \frac{(0.08215 \frac{atm * L}{mol * K})(217.779K)}{(45.0357 \, atm)}$$

$$b = 0.0344$$

Finally, by replacing the values of the constants a and b in equation (5), the appropriate mathematical model for the Peng-Robinson equation is obtained:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}(\overline{V} + b)}$$

$$P = \frac{(0.08215\,\frac{atm-L}{mol-K})(298\ K)}{\overline{V} - 0.0309} - \frac{1.5224}{\overline{V}^2 + 2(0.0309)\overline{V} - (0.0344)^2}$$

$$\boxed{P = \frac{(24.4807\,\frac{atm-L}{mol})}{\overline{V} - 0.0309} - \frac{1.5224}{\overline{V}^2 + 2(0.0309)\overline{V} - (0.0344)^2}}$$

With the mathematical model obtained, molar volume values are given up to a maximum of $0.82\ \frac{L}{mol}$, which are shown in Table 10.

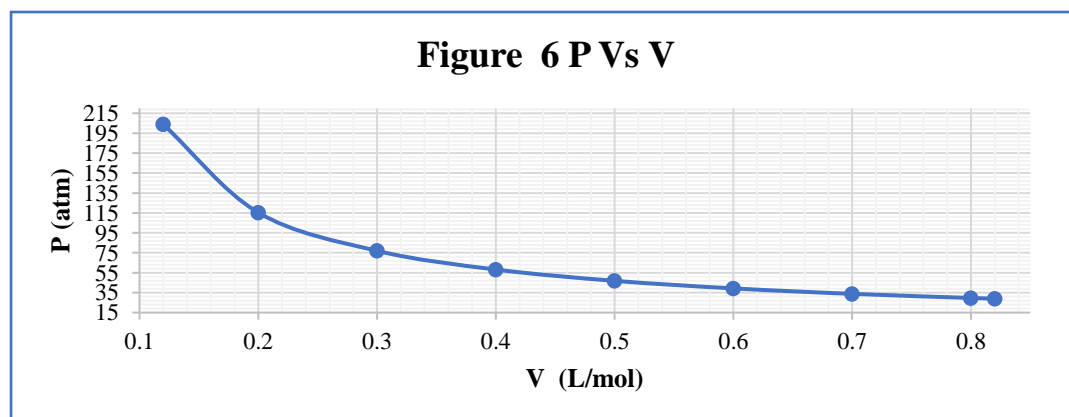**Table 10 Pressure - Molar volume data for the Soave Redlich - Kwong Equation**

V(L/mol)	P(atm)
0.12	203.8925
0.2	115.374828
0.3	77.0031055
0.4	58.2025885
0.5	46.8835082
0.6	39.284666
0.7	33.8195925
0.8	29.6959826
0.82	28.9896024

Fuente: Investigadores

Graphing the data:

Figure 7 Pressure versus Molar Volume for the Soave Redlich - Kwong Equation

Figure 6 P Vs V

The following table shows the different calculations that were made using the different mathematical models:

Table 11 Calculations of critical pressure and critical temperature of the mixture of components

	Ideal Gas	Factor Z	VDV	R-K	PR	S-R-K
V(lt/mol)	P(atm)	P(atm)	P(atm)	P(atm)	P(atm)	P(atm)
0.12	204.006	183.605	139.819	145.823	193.344	203.893
0.2	122.404	110.163	87.878	92.434	111.729	115.375
0.3	81.602	73.442	64.475	66.284	75.184	77.003
0.4	61.202	55.082	51.138	52.014	57.082	58.203
0.5	48.961	44.065	42.367	42.860	46.119	46.884
0.6	40.801	36.721	36.154	36.460	38.728	39.285
0.7	34.972	31.475	31.524	31.728	33.396	33.820
0.8	30.601	27.541	27.941	28.085	29.363	29.696
0.82	29.855	26.869	27.320	27.455	28.671	28.990

Source: Own elaboration

Finally, all the mathematical models made can be represented in a final figure (Figure 8), where the curve closest to the ideal gas curve can be distinguished.

Figure 8 Comparison of Equations by means of the developed curves
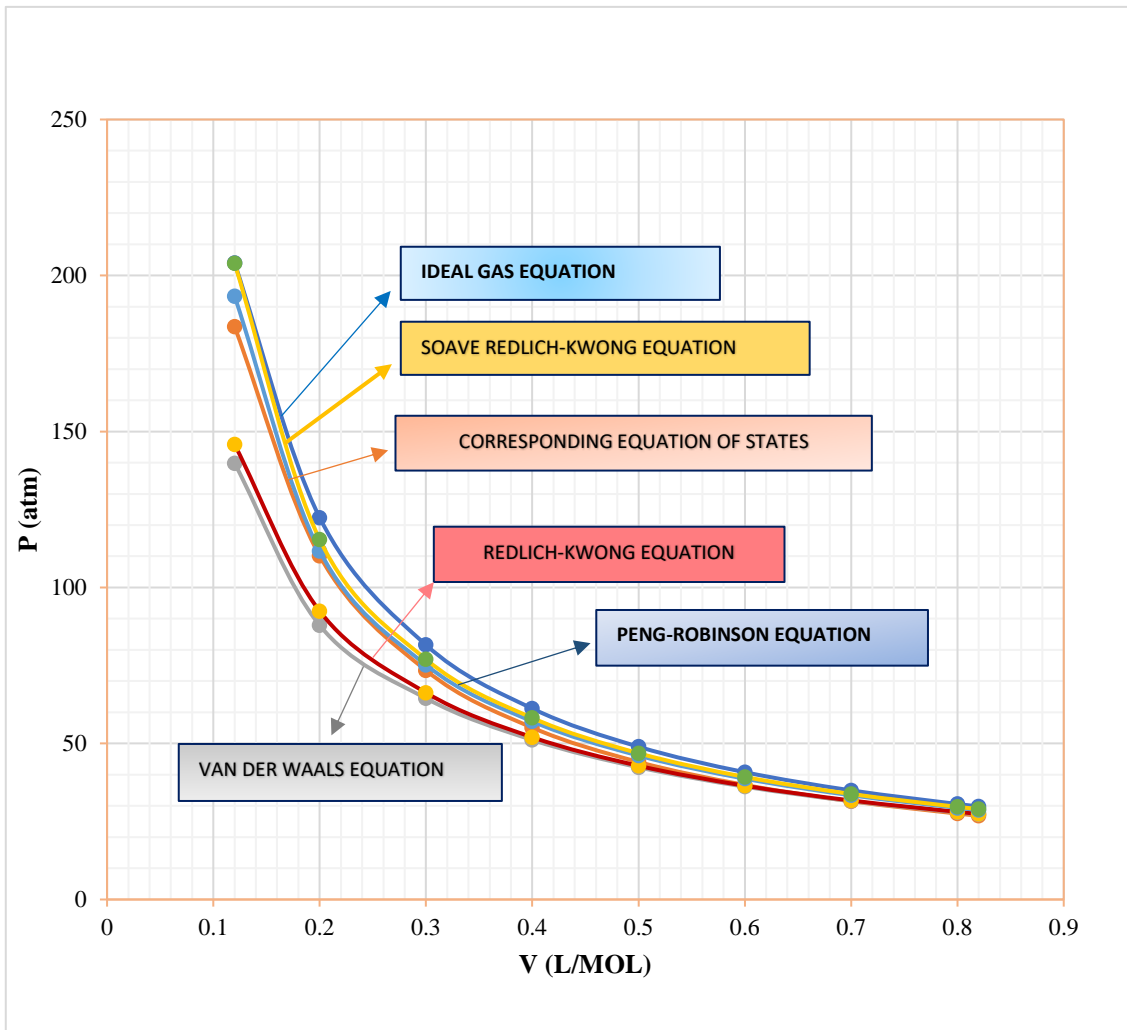
Source: Own elaboration

ANALYSIS OF RESULTS

- The final figure shows that the Van der Waals Equation is too far away from the concentration zone of the other curves, and it can be deduced that this equation of state does not apply to Camisea natural gas. Likewise, the Soave Redlich - Kwong Equation gets closer to the concentration zone of curves, with greater proximity to the curve of the Ideal Gases Equation, thus being considered the Equation that governs and applies to Camisea natural gas.
- The mathematical results show the similarity between the result obtained with the Soave Redlich-Kwong equation and the results of the values obtained in the Ideal Gas Equation.

CONCLUSIONS

1. By means of the graphic method and using Excel graphs, the equation of state that most closely resembles the general equation of Ideal Gases was determined, taking as a study point the gas mixture of a sample corresponding to Camisea Natural Gas.

2. After calculating each of the equations of state for a mixture of gases, it was determined that the thermodynamic equation governing Camisea natural gas is the Soave Redlinch-Kwong equation, followed by the Peng-Robinson equation of state.

3. The isothermal graphic method used in this research is a simple graphic method that can be developed in the Excel program, which can be expressed in the form of curves through the use of data that relate fundamental variables in the study of each equation of state.

4. After developing the corresponding calculations for each type of equation of state, the corresponding composition of the Camisea natural gas was related to the models of the equations studied, after which the equation of the corresponding Camisea natural gas was determined with the use of Excel graphics.

9. References

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