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Research Article

Use the Thermodynamic State Equations to Analyze the Non-ideality of Gas Mixtures

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Abstract

The assessment of gas behavior in chemical engineering systems necessitates a profound understanding of thermodynamic principles that govern the interactions among the components within a given system. To this end, the deviation from ideality in a single gas or gas mixture is associated with the disparity between the actual behavior of the gas or gas mixture and the behavior anticipated by the ideal gas model. This study is aimed at scrutinizing the deviation from ideal behavior in a gas mixture composed of CH_4 and CO_2. The analysis employs the cubic equations of state: Van Der Waals, Soave-Redlich-Kwong, and generalized Virial equations, truncated to the third term. These equations are widely recognized for their utility in characterizing substance behavior under specific thermodynamic conditions. The investigation involves an evaluation of the mixture's behavior by assessing variations in the compressibility factor concerning pressure, volume, and pressure, using a thermodynamic calculator at 296.15 K and 15 bar. The findings of this study reveal the prevalence of attractive intermolecular forces at higher pressures and repulsive interactions at lower pressures. An analogous examination of the effect of altering the composition of CH_4 was undertaken using the Soave-Redlich-Kwong equation, which incorporates parameters allowing for an evaluation of the impact of molecule size and intermolecular interactions within the mixture. Furthermore, experimental data were employed to validate the results obtained in this study. Consequently, it can be inferred that these equations provide insight into the influence of pressure on molecular interaction forces, encompassing repulsive and attractive forces, which in turn can define the new volume of a real system. Thus, based on the corroboration established herein, these equations demonstrate a high degree of consistency and applicability, thereby expanding the realm of thermodynamic inquiry.

Keywords: *Equation of state; real gas; ideal gas; compressibility factor.*

1. Introduction

The instruction of Chemical Engineering is founded on the examination of predicting the thermodynamic properties of both pure substances and mixtures of components within a given phase, which play a crucial role in separation systems capable of achieving phase equilibrium. The majority of the properties under discussion here pertain to the behavior of pure components, disregarding molecular interaction forces among various constituents within a given mixture.

Furthermore, separation operations, notably distillation, absorption, and liquid-liquid extraction, entail mixing phases in equilibrium, with process performance heavily contingent on an understanding of the thermodynamic interactions between these phases. In such cases, employing equations of state for ideal gases (of the cubic, Virial-type, or generalized variety) is a common practice to enhance comprehension of the thermodynamic relationships at play. These equations establish a connection between the compressibility factor (Z) of either a pure substance or mixture and macroscopic, measurable parameters—Pressure, Volume, and Temperature, commonly referred to as PVT.

As posited by Muachia et al. [1], the thermodynamic relationships associated with PVT provide the means to assess the thermodynamic behavior of systems, as they offer mechanisms for experimental determination that yield knowledge of various physical relationships linked to perturbations of each one. The authors contend that pressurized systems, characterized by elevated pressure levels, lead to a reduction in system volume, thereby intensifying molecular interactions and augmenting the attractive and repulsive forces between the system's molecules.

Consequently, an examination of thermodynamic systems should initially be grounded in an understanding of the behavior of an ideal gas—a theoretical gas characterized by the absence of intermolecular forces, where collisions are non-existent or negligible. These phenomena are rooted in the principles of conservation of momentum and kinetic energy [2].

To comprehensively determine the state of a system composed of a mixture of pure components, it is imperative to possess knowledge of the intensive variables, with particular emphasis on pressure (P), volume (V), and temperature (T), as well as an understanding of the composition of the constituent components of the mixture slated for separation. The relationships between these intensive properties remain constant within the system as long as the composition remains unaltered. These

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relationships are predicated on the connections between volume, pressure, and work, as established by the principles of the first law of thermodynamics.

However, it is important to note that the behavior of most gas mixtures deviates from ideality, primarily due to the diverse interactions occurring among their constituent molecules. Moreover, variations in the shapes and sizes of the molecules within the mixture can also exert influence on the non-ideal behavior observed in gas-liquid mixtures.

In such cases, Mamedov et al. [3] posit that the ideal behavior of gases can be represented by Clapeyron's equation (Equation 1), which is grounded in the fundamental principles of physics and frequently applied to address a wide array of practical challenges, particularly in the domain of chemical engineering. Equation 1 establishes a direct correlation between its principal parameters, thus characterizing thermodynamic ideality.

$$PV = nRT \tag{1}$$

When analyzing the ideal gas equation (Equation 1), Costa [4] asserts that it describes a gas composed of numerous molecules represented as rigid spheres with a diameter 'd.' These molecules exhibit random or disordered motion, governed by Newton's Laws. The author further contends that these particles possess a non-zero mass 'm' while their individual volumes are negligible relative to the container's volume.

In this context, intermolecular interactions involving attraction and repulsion are considered negligible, except during collisions with each other and with the container walls. Within this analytical framework, it is evident that the internal energy of the involved molecules is associated with translational kinetic energy, which propagates in a linear fashion. Finally, according to Costa [4], the collisions among these molecules are perfectly elastic, as kinetic energy is not converted into other forms of energy.

In alignment with this analysis, Mahan & Myers [11] propose that the macroscopic properties of an ideal gas entail the independent motion of molecules, particularly evident when measurements of pressure, molar volume, and temperature deviate from the behavior described by the Clapeyron equation, which represents non-ideal behavior. Deviations from ideality are observed in pure gases and mixtures of unreacted gases. At room temperature and low pressures, deviations from ideality are nearly nonexistent. However, as pressure increases, gas behavior deviates from that of ideal gases.

Under known temperature and pressure conditions, a real or non-ideal gas comprises material particles engaged in chaotic motion, subject to forces of attraction and repulsion, with significant mass and volume [6].

To assess the PVT (Pressure-Volume-Temperature) behavior of real gases, cubic equations of state and generalized correlations are employed. These mathematical models account for intermolecular interactions and describe actual behavior across various pressure ranges. Notable among these equations of state are Van der Waals, Redlich-Kwong, and Soave-Redlich-Kwong, alongside the Pitzer and Virial correlations [7].

The fundamental premise underlying deviations from ideality is attributed to intermolecular forces, both attractive and repulsive, which exert a predominant influence on the PVT behavior of a given fluid (Equation 2).

$$\mathrm{P} = \mathrm{P_R} + \mathrm{P_A} \tag{2}$$

In this scenario, repulsive forces contribute positively to pressure ($P_R > 0$), while attractive forces yield a negative contribution to pressure ($P_A < 0$). Consequently, the cubic Van der Waals (VDW) equation of state alters the ideal gas equation by incorporating the intermolecular forces present in a specific gas or gas mixture. Equation (3) characterizes this approach, taking into account intermolecular interactions, albeit with certain limitations. Nonetheless, Equation (3) proves valuable for depicting the behavior of real gases under conditions closely approximating those of ideal gases [8].

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

Equation (2) can be applied to compute the thermodynamic parameters for gas mixing, which entails the utilization of the mixing parameters a_m and b_m, as detailed in Equation (3).

$$\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V-b_m}} - \frac{\mathrm{a_m}}{\mathrm{V^2}} \tag{4}$$

Where P represents the pressure of the gas in atm, V is the molar volume of the gas in cm^3/mol, T is the temperature of the system in Kelvin (K), and R is the universal gas constant. Additionally, a_m and b_m are the Van der Waals constants, which are defined according to Equations 5, 6, 7, 8, and 9.

$$\mathrm{a} = \frac{27(\mathrm{RT_c})^2}{64\mathrm{P_c}} \tag{5}$$

$$\mathrm{b} = \frac{\mathrm{RT_c}}{8\mathrm{P_c}} \tag{6}$$

$$\mathrm{a_m} = \sum\sum \mathrm{y_i}\,\mathrm{y_j}\mathrm{a_{ij}} \tag{7}$$

$$\mathrm{a_{ij}} = \left(\mathrm{a_i a_j}\right)^{0,5} \tag{8}$$

$$\mathrm{b_m} = \sum \mathrm{y_i b_i} \tag{9}$$

In the collision of gas molecules with any surface, the unopposed attractive forces of the molecules diminish the collision velocity. The additional term incorporated into the pressure equation serves to rectify the absence of counterbalancing attractive forces.

Conversely, the equation put forth in 1972 by Soave-Redlich-Kwong (SRK) represents one of the most extensively employed equations of state for elucidating the characteristics of both pure substances and gas mixtures (Equation 10). It is distinguished as an extension of the Van der Waals equation [6].

$$\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V-b}} - \frac{\mathrm{a}}{\mathrm{V^2+Vb}} \tag{10}$$

The utilization of Equation (10) is expanded to compute the thermodynamic properties of gas mixtures, encompassing the incorporation of mixing parameters a_m and b_m, as delineated by Equation (11).

$$\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V-b_m}} - \frac{\mathrm{a_m}}{\mathrm{V^2+Vb_m}} \tag{11}$$

In this context, P represents the gas pressure (in atm), V stands for the molar volume of the gas (in cm^3/mol), T denotes the system's temperature (in K), while R signifies the universal gas constant. Additionally, a and b represent the substance-specific constants, and α serves as a temperature-dependent correction factor, in accordance with the descriptions provided in Equations (12), (13), (14), (15), and (16).

$$a_m = \alpha a_c \tag{12}$$

$$a_c = \frac{0,42748(RT_c)^2}{P_c} \tag{13}$$

$$\alpha = [1 + m(1 - T_r)^{0,5}]^2 \tag{14}$$

$$m = 0,048508 + 1,55171w - 0,15613w^2 \tag{15}$$

$$b = 0,008664\frac{RT_c}{P_c} \tag{16}$$

For Van Wylen et al. [9], assessing the departure from gas ideality involves the computation of the compressibility factor. This thermodynamic property quantifies the deviation of real gas behavior from ideal gas behavior. It is defined as the ratio between the molar volumes of real and ideal gases under identical temperature and pressure conditions. A compressibility factor of 1 (one) indicates ideal gas behavior, while values different from 1(one) suggest non-ideal behavior.

Given the aforementioned complexity, numerous equations of state have been developed to study gas behavior. Prominent among these are the cubic equations, including Van Der Waals, Redlich-Kwong, and Soave-Redlich-Kwong, among others [10].

Notably, Pitzer's correlation stands out among various approaches. It expresses the compressibility factor (Z) as a function of temperature (Tr), reduced pressure (Pr), and the acentric factor (w) for each component.

The generalized Pitzer correlation serves as an empirical model that aids in comprehending molecular interaction forces, particularly in solutions where interactions occur between molecules of different sizes. Kenneth Pitzer introduced this correlation [10], which elucidates molecular or ionic interactions in solution using linear combinations of parameters in a Virial-type expansion of the excess Gibbs free energy.

Consequently, the virial-type equation with emphasis on the third coefficient is employed to calculate the compressibility factor, as defined in Equation (17).

$$Z = 1 + (B^O + wB^1)\frac{P_r}{T_r} + (C^o + wC^1)\frac{{P_r}^2}{{T_r}^2} \tag{17}$$

$$P_r = \frac{P}{P_c} \tag{18}$$

$$T_r = \frac{T}{T_c} \tag{19}$$

On the contrary, the generalized equation incorporates the acentric factor (w), a parameter inherent to the molecular structure of the gas, which exhibits a significant correlation with the system's pressure and temperature. This factor is also interconnected with the dimensions of the constituent molecules within the examined mixture [14]. All functions herein are interdependent with the reduced pressure and temperature, as elucidated in Equations (20), (21), (22), and (23) [11].

$$B^o = 0,083 - \frac{0,422}{T^{1,6}} \tag{20}$$

$$B^1 = 0,139 - \frac{0,172}{T^{4,2}} \tag{21}$$

$$C^o = 0,01407 + \frac{0,02432}{T_r} - \frac{0,00313}{T^{10,5}} \tag{22}$$

$$C^1 = -0,02676 + \frac{0,05539}{{T_r}^{2,7}} - \frac{0,00242}{T^{10,5}} \tag{23}$$

Based on the provided theoretical framework, a thermodynamic assessment was conducted to analyze the behavior of the compressibility factor as a function of gas mixture pressure consisting of carbon dioxide (CO_2) and methane (CH_4). This investigation explored the influence of varying proportions of these gas components. The obtained results were evaluated within the context of attractive and repulsive forces under isothermal conditions, employing two distinct cubic equations of state and a generalized equation of state.

2. Procedure and Methodology

To carry out this study, a logical algorithm was developed for solving a sequence of equations essential for determining properties such as volume, compressibility factor, entropy, internal energy, enthalpy, Gibbs free energy, and Helmholtz free energy for a binary gas mixture. These calculations were performed under predefined conditions of temperature, composition, and pressure.

The algorithm incorporates a comprehensive database, facilitating the exploration of diverse gas mixtures with varying compositions and the assessment of concentration effects on the compressibility factor within a specified pressure range under isothermal conditions. Additionally, it permits an examination of the impacts of molecular size and attractive/repulsive forces on the behavior of the compressibility factor, irrespective of the equation of state or correlation utilized. Figure 1 illustrates the algorithm created.

For the implementation of this algorithm, a software program was developed using Microsoft Excel, creating a thermodynamic calculator with a user-friendly graphical interface. This interface enables adjustment of input parameters, evaluation of output conditions, and correlation of various types of equations of state, thereby enhancing comprehension of the parametric interactions involved in the evaluated cases.

The thermodynamic calculator investigated the cubic Van Der Waals equation, the Soave-Redlich-Kwong (SKW) equation of state and the generalized Virial-type equation truncated to its third term.

This exploration was conducted to assess the parametric attributes associated with each equation, elucidating the physical and molecular interactions within the system, and their impact on the mixing behavior.

2.1 Resolution Method

To derive the compressibility factor and molar volume using the cubic equations outlined in this study, the first step involved determining the constants 'a' and 'b' for each equation. These constants were calculated through the correlations provided by Equations (5), (6), (13), and (16), respectively, as specified in the Van der Waals and Soave Redlich-Kwong equations.

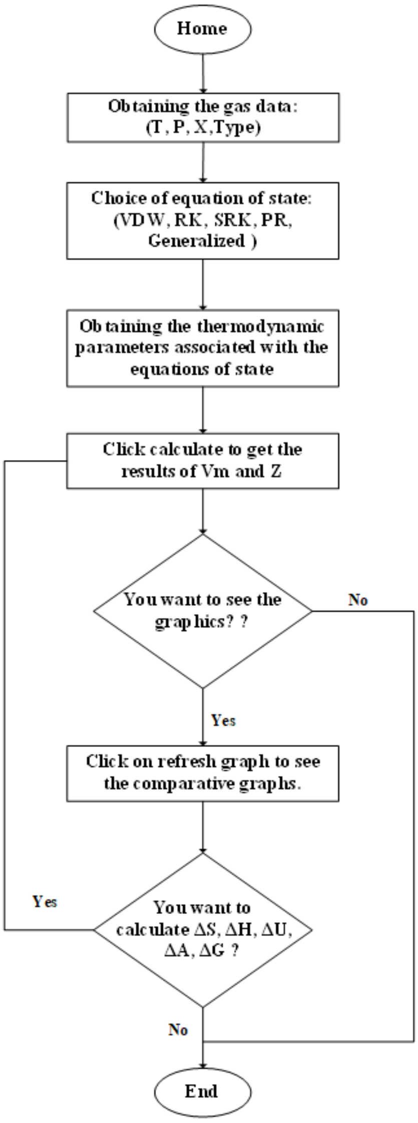


Figure 1. Proposed algorithm for determining the thermodynamic parameters of gas mixtures.

Subsequently, armed with the known operating conditions in terms of pressure (P) and temperature (T), the equations were restructured into a cubic equation format, with the molar volume (V_m) serving as the variable of interest.

Upon structuring the cubic equation, the Newton-Raphson method was employed to ascertain the mixture's volume using the Taylor series expansion. In this context, the maximum volume identified corresponds to the volume of the gas under examination. This value was employed in determining the compressibility factor (Z), as supported by Equation (24).

$$Z = \frac{P}{V_m RT} \tag{24}$$

Maxwell's relations were employed to compute the energy variation within the system. This process entailed utilizing the definitions stemming from the equations of the first and second laws of thermodynamics. The outcomes obtained through these calculations provided valuable insights into the behavior of these parameters within the systems under investigation.

3. Results and Discussions

The thermodynamic calculator, developed in the context of this study, systematically investigates the parametric behavior of a mixture consisting of carbon dioxide (CO2) and methane (CH4) under the prescribed initial conditions, as detailed and specified in Table 1.

Table 1. CO_2 and CH_4 mixture conditions used in this article.

Components	**Composition (%)**	**Temperature (K)**	**Pressure (Bar)**
CO_2	68	296.15	15
CH_4	32		

The algorithm proposed (Figure 1) served as a foundation for the development of the Thermodynamic Calculator (Figure 2), which was utilized for data input and solution display for the specified problem. Under the operational conditions employed, the molar volumes and compressibility factors were determined under the prescribed conditions. Furthermore, the behavior of the compressibility factor was assessed over a predefined pressure range (0 to 1000 bar), utilizing the three aforementioned equations of state.

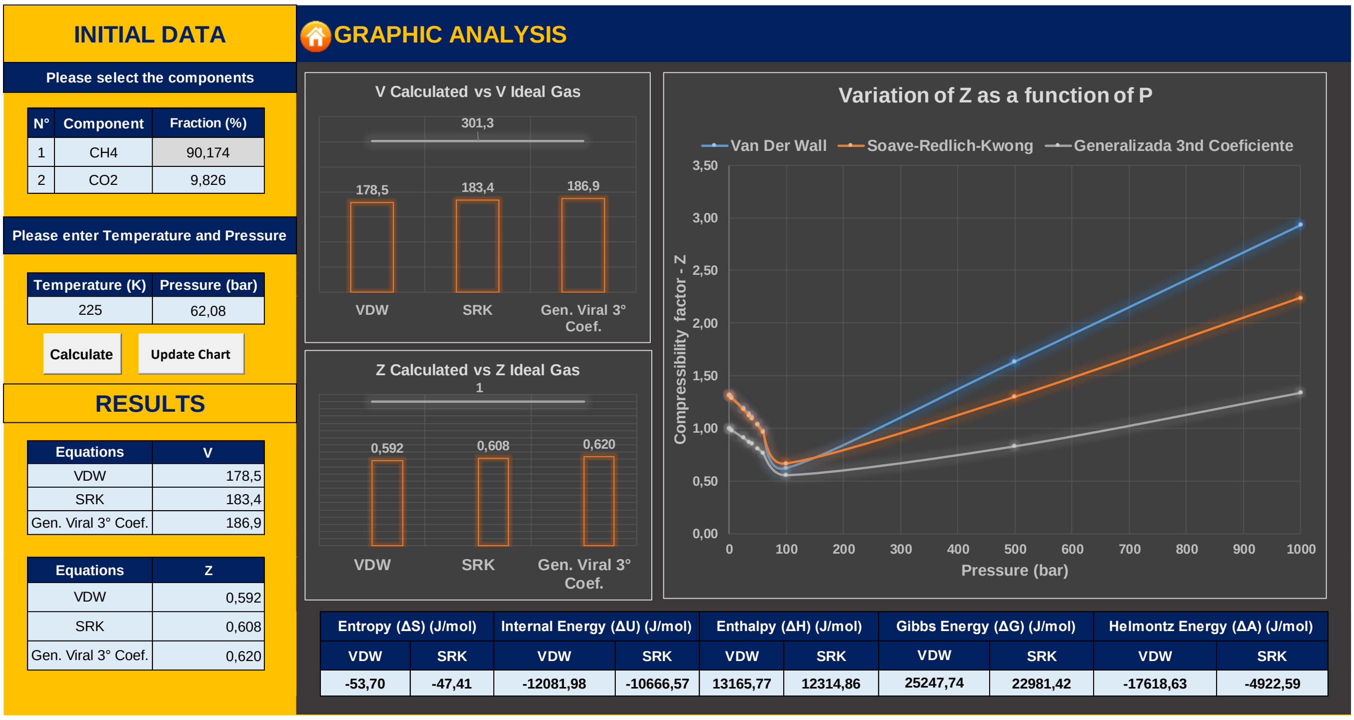
The acquired data exhibited notable similarity, yielding an average compressibility factor of 0.944 for the three equations, resulting in an average deviation of merely 0.5% from this computed average.

An analysis of the compressibility factor profile indicated analogous qualitative patterns: attractive forces were substantial up to 500 bar, with repulsive forces assuming greater significance beyond this pressure range. Conversely, when employing the cubic Van der Waals equation of state, attractive forces exhibited reduced significance, while repulsive forces became more pronounced. This discrepancy can be attributed to the absence of parameters related to molecular size in the Van der Waals equation.

In contrast, the Soave-Redlich-Kwong equation of state incorporates the acentric factor as a parameter, accounting for molecular sizes within the mixture. This leads to a diminished influence of both repulsive and attractive forces compared to the results obtained with the Van der Waals equation.

At lower pressures, molecules are generally distanced from one another in these scenarios, with negligible intermolecular forces at play, causing the fluid to behave akin to an ideal gas (Z=1). As pressure increases, molecules draw closer together, and attractive intermolecular forces dominate. Consequently, the gas's volume decreases more significantly than it would if no intermolecular attraction forces were present, resulting in Z<1.

Conversely, at very high pressures, molecules approach each other to an extent where repulsive forces become dominant, causing a more substantial increase in volume than expected in the absence of intermolecular repulsive forces, leading to Z > 1. While a value of Z=1 is attained at high pressures in all cases, it does not correspond to ideal gas behavior [9], [11], and [12].



INITIAL DATA

Please select the components

N°	Component	Fraction (%)
1	CH4	90,174
2	CO2	9,826

Please enter Temperature and Pressure

Temperature (K)	Pressure (bar)
225	62,08

Calculate

Update Chart

RESULTS

Equations	V
VDW	178,5
SRK	183,4
Gen. Viral 3° Coef.	186,9

Equations	Z
VDW	0,592
SRK	0,608
Gen. Viral 3° Coef.	0,620

GRAPHIC ANALYSIS

Entropy (ΔS) (J/mol)		Internal Energy (ΔU) (J/mol)		Enthalpy (ΔH) (J/mol)		Gibbs Energy (ΔG) (J/mol)		Helmontz Energy (ΔA) (J/mol)	
VDW	SRK	VDW	SRK	VDW	SRK	VDW	SRK	VDW	SRK
-53,70	-47,41	-12081,98	-10666,57	13165,77	12314,86	25247,74	22981,42	-17618,63	-4922,59

Figure 2. Thermodynamic calculator interface.

The examination of the results presented in Figure 2 and Table 1 unveils a level of molecular disarray characterized by the entropy change (ΔS). This observed molecular disarray emanates from the reduced operational pressures and temperatures taken into account under the assessed operating conditions. These factors significantly impact the stochastic movement of the molecules. A similar pattern is discerned when analyzing the changes in internal energy (ΔU) and Helmholtz free energy (ΔA), both of which exhibit negative values, as recorded in Table 2, acquired at 296.15 K and 15 bar.

Table 2. Thermodynamic energies evaluated in this paper.

Equation	Temperature (K)	Pressure (Bar)	ΔS (J/mol.K)	ΔU (J/mol)	ΔH (J/mol)	ΔG (J/mol)	ΔA (J/mol)
VDW	296.15	15.0	-4.81	-1432.64	1468.56	2901.2	-1545.81
SRK			-5.20	-1539.16	1583.21	3122.37	-1418.72

The analysis of enthalpy (ΔH) and Gibbs Free Energy (ΔG), which represent the energies associated with the system, provides insights into non-spontaneous processes. This analysis supports the molecular behavior of the system, which is influenced by both attractive and repulsive forces between the system molecules. It elucidates the disparities in values between the Van der Waals (VDW) and Soave-Redlich-Kwong (SRK) equations.

Numerical results derived from these equations reveal a deviation of approximately 7%. This deviation is noticeable when comparing data from these two equations, with the cubic Soave-Redlich-Kwong equation demonstrating greater accuracy. This enhanced accuracy is attributed to its consideration of the molecular size as a dominant factor in dictating the thermodynamic behavior of gas mixtures.

3.1. Non-ideality Analysis

The deviation from gas ideality can be observed through the analysis of the compressibility factor (Z), which is a dimensionless measure describing the behavior of a gas concerning its pressure and volume. According to Elechi et al. [9], when the compressibility factor (Z) deviates from the ideal gas standard, the gas or gas mixture exhibits non-ideal behavior.

Figure 3 illustrates the behavior of the compressibility factor (Z) as a function of pressure (P) for the cubic Van Der Waals, Soave-Redlich-Kwong, and generalized Virial-type truncated equations of state at a temperature of 296.15 K.

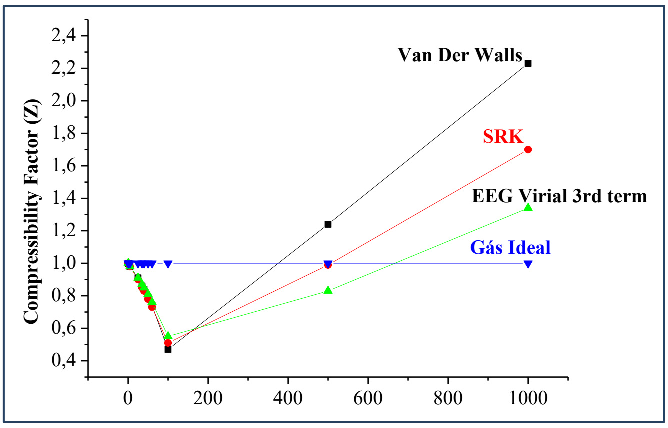


Figure 3. Behavior of the compressibility factor as a function of pressure mixture of 32% CH_4 and 68% CO_2.

The operational conditions employed for the Z calculations (Figure 3) are elucidated within Table 1. The scrutiny of Figure 3 unveils that when subjected to elevated pressures, the methane (CH_4) and carbon dioxide (CO_2) gas amalgamation demonstrates non-ideal gas behavior, characterized by the preeminence of repulsive intermolecular forces.

Conversely, under reduced pressures, attractive forces hold sway, marked by their heightened efficacy in the intermolecular collisions between CH_4 and CO_2 molecules, manifesting as a counterintuitive phenomenon at lower pressures.

Furthermore, an examination was conducted to assess the pressure-volume relationship of the studied gas mixture. This analysis indicated that within the high-pressure regime, spanning from 600 to 1000 bar, negligible fluctuations in volume were observed with incremental pressure increments within the stipulated range. Conversely, a conspicuous volume fluctuation was noted within the pressure range of 0 to 300 bar. This phenomenon is attributable to the increased intermolecular spacing induced by compression, leading to pronounced volume alterations within the system. Notably, for all three equations of state examined, a confluence in volume behavior as a function of system pressure was ascertained across the considered pressure spectrum.

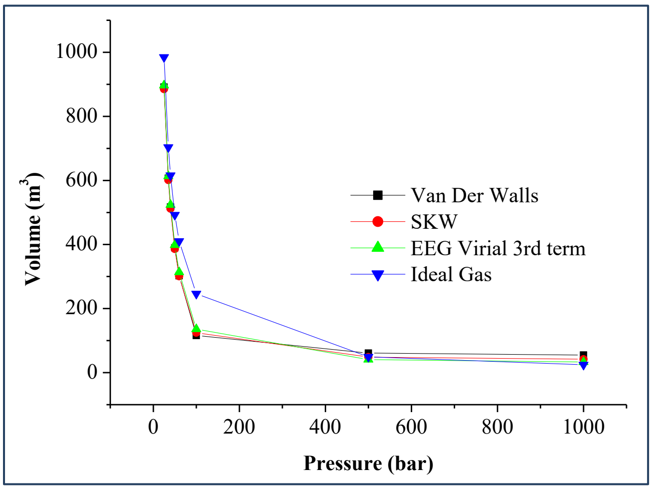


Figure 4. Volume profile as a function of pressure for a mixture of 32% CH_4 *and 68%* CO_2*.*

Nevertheless, the ideal gas model exhibited more pronounced deviations within the pressure range of 100 to 400 bar, possibly owing to its inherent gas properties.

Figure 4 presents an analysis of gas mixing, entailing the blending of two gases comprising 32% and 68% fractions of CH_4 and CO_2, respectively. These studies were conducted to gain deeper insights into the mixing phenomena across various compositional ratios.

3.2 Influence of Composition on the Compressibility Factor

For the analysis of the influence of the gas mixture composition, CH_4 and CO_2, data from the Soave-Redlich-Kwong equation were utilized due to the qualitative similarity in the behavior of the three equations studied and the incorporation of the acentric factor into this correlation.

Thus, the effects of mixture concentration were investigated, with an examination of systems containing pure CH_4 and the progressive increment of CO_2, up to maximum CO_2 purity. This analysis was conducted under isothermal conditions at 296.15K, as indicated in Figure 5.

In general, it is observed that the compressibility factor of pure CH_4 is higher than that of pure CO_2, indicating a greater prevalence of attractive forces in CO_2 gas compared to CH_4 gas.

Conversely, repulsion forces become more significant when analyzing the behavior of CH_4 gas, predominating above 300 bars. This phenomenon is also noted for pure CO_2 gas at pressures exceeding 580 bars.

The 25% CH_4 and 75% CO_2 mixture exhibits a pronounced influence of attractive forces, surpassing the behavior observed when analyzing the compressibility factor of the individual components, prevailing up to a pressure of 530 bars.

Beyond this threshold, it is observed that this parameter behaves more prominently than that of pure CO_2 but less so than pure CH_4. The other curves obtained from this evaluation demonstrate mixing effects based on the proportions established in each analysis of this process.

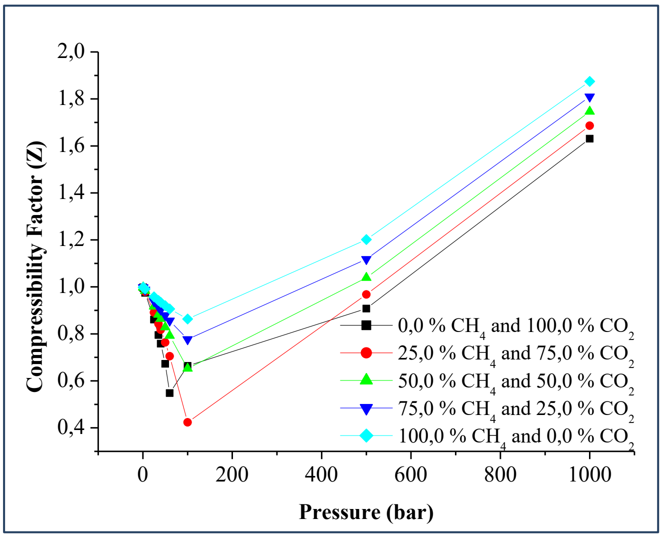


Figure 5. Behavior of Z as a function of pressure for the mixture of CH_4 and CO_2.

The evaluation depicted in Figure 5 illustrates the behavior of an ideal gas mixture comprising CO_2 and CH_4 at varying proportions as the system pressures approach zero. As pressure increases, the effects of attractive forces become increasingly apparent, irrespective of the gas fractions' composition within the mixture.

Conversely, when pressures exceed 400 bar, the influence of repulsive forces becomes dominant across all compositions considered and persists throughout the entire range of operating conditions investigated in this study. For all cases analyzed, a transition point is discernible, marking the shift from attraction to repulsion phenomena. This transition point is characterized by a calculated compressibility factor equal to 1 (one), indicating a departure from the conditions of an ideal gas.

3.3 Validation of State Equations

The consistency of the data derived from the state equations employed in this study was validated through a comparison with experimental data obtained by Hwang et al. [13]. This comparison was conducted for two distinct cases, with a focus on the specific weight of the gas mixture. In the first case, the data was extracted from experiments conducted at a temperature of 225K, utilizing a mixture composed of 9.826% CO_2 and 90.174% methane, respectively. In the second case, experiments were performed under different thermal conditions, specifically at 350K, while maintaining the same composition ratios for the components.

The results for the first case are presented in Figure 6, where a noteworthy approximation between the experimental data and the Soave-Redlich-Kwong (SRK) model data is observed, with an average deviation of 2.27%.

On the other hand, the comparison between experimental data and Van der Waals data in these analyses exhibited an average deviation of 11.59%. In this scenario, smaller deviations in specific mass values were observed for pressures exceeding 100 bar.

Regarding the data derived from the generalized Virial-type equation truncated to its third term (EEG), within the pressure range assessed in this study, the deviation was

10.68% when comparing experimental data with GEE-derived data.

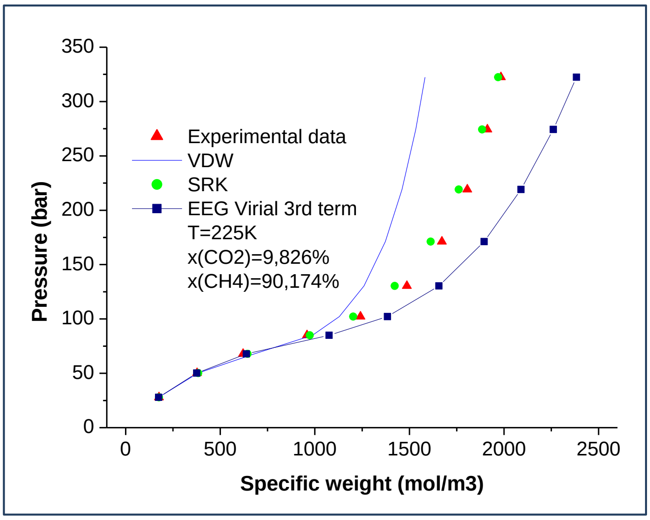


Figure 6. Behavior of specific weight as a function of pressure for the mixture of CH_4 and CO_2 with 225 K.

In the second case, when comparing experimental data with state equation data at 350 K, a significant approximation was observed for all cases evaluated, as depicted in Figure 7. Nevertheless, the Van der Waals equation displayed an average deviation of 3.69%, whereas the Soave-Redlich-Kwong (SRK) and EEG exhibited deviations of 1.78% and 1.74%, respectively.

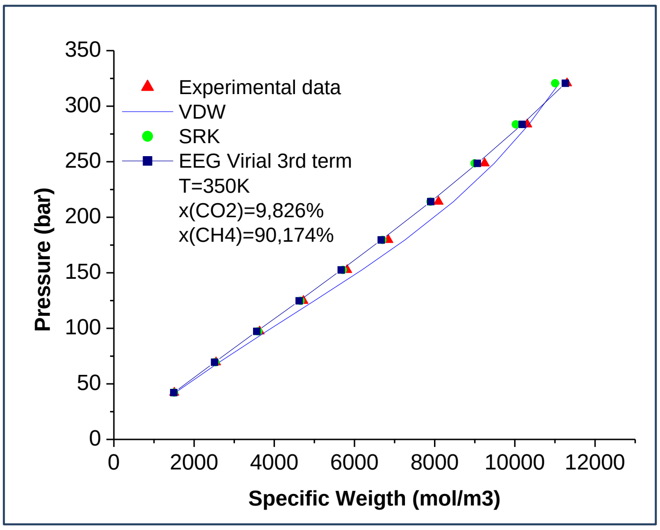


Figure 7. Behavior of specific weight as a function of pressure for the mixture of CH_4 and CO_2 with 350 K.

The results presented in Figure 7 demonstrate a high degree of consistency when utilizing state equations to evaluate the thermodynamic profiles of gas mixtures, particularly when employing the SRK equation.

On the other hand, both the EEG and SRK equations rely on the acentric factor, a parameter associated with molecular size, as a crucial determinant for assessing the thermodynamic characteristics of gas mixtures.

4. Conclusions

Based on the results obtained in this study, the following conclusions can be drawn:

a) Real gases exhibit ideal gas behavior as system pressures approach zero.
b) The influence of gas mixtures can be assessed by examining the behavior of compressibility factors. These factors depend on the fractions of each component in the mixture and the specific type of gas involved in the process.
c) The equations of state analyzed in this study demonstrate compatibility with the analysis of gas mixing behavior. They account for both attractive and repulsive forces between constituent molecules within the system and consider the size of molecules as predominant factors influencing the thermodynamic behavior of gases.
d) The behavior of gases can be characterized by examining the relationship between pressure and volume. Under high pressures, significant changes in system volume are not observed due to the strong interaction between system molecules, resulting in their close proximity and alterations in the system's physical state.
e) Experimental data corroborate the equations studied in this work, with the best consistency observed when employing the SRK equation within the evaluated temperature and pressure range.
f) At low pressures, the impact of pressure on the system's volume becomes significant, primarily due to the increased distance between constituent molecules within the system under investigation.

Nomenclature:

P: pressure of the gas (bar);
V: molar volume of the gas (cm^3/mol);
V_m: molar volume of the gas mixture (cm^3/mol);
T: temperature of the system (K);
R: universal gas constant;
a_m and b_m: mixture constants of state equations;
P_A and P_B: attractive and repulsive pressure;
SRK: Soave-Redlich-Kwong cubic equation;
VDW: Van Der Waals cubic equation;
P_C: critical pressure (Bar);
T_C: critical temperature (Kelvin);
a and b: pure constants of state equations;
W: acentric factor;
Z: compressibility factor;
T_r: reduced temperature;
PVT: pressure, volume and temperature;
ΔS: variation of entropy (Joule/(mol K));
ΔU: variation of internal energy (Joule/mol);
ΔA: variation of Helmholtz free energy (Joule/mol);
ΔH: variation of enthalpy (Joule/mol);
ΔG: variation of Gibbs Free Energy (Joule/mol).

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