



## Thermodynamic Analysis of a Gas Mixture Utilizing Peng-Robinson and Soave-Redlich-Kwong Cubic Equations of State

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Cubic equations of state are mathematical models used to describe the thermodynamic behavior of pure substances or mixtures of substances by calculating physical and chemical properties under different pressure and temperature conditions. These equations are widely employed in various scientific fields, particularly in chemical engineering, for the thermodynamic study of physical and chemical processes involving phase equilibrium. Thus, the knowledge derived from these studies enables the development of industrial processes, the synthesis of new processes and materials, the study of chemical reaction kinetics, analysis of experimental data, and more. Therefore, this study aims to describe deviations from ideality in real gases, evaluated based on the behavior of the compressibility factor ( $Z$ ) as a function of pressure ( $P$ ) for a binary mixture involving hydrogen ( $H_2$ ) and carbon dioxide ( $CO_2$ ). In ideal gases, the system has a compressibility factor equal to one at any pressure, unlike real gases, where the compressibility factor can assume values smaller or larger than unity. To achieve this, a logical algorithm was developed for evaluating the compressibility factor using the Peng-Robinson (P-R) and Soave-Redlich-Kwong cubic equations of state, with mathematical resolution carried out using the Microsoft EXCEL SOLVER. The calculation procedure involved transforming the initial equations into cubic equations through linearization, followed by the calculation of compressibility factors that determine the phenomena associated with molecular attraction and repulsion within the referenced gas mixtures for different compositions, temperatures, and within a specific pressure range. The results of this analysis revealed the predominance of attractive and repulsive forces within the studied pressure range, with the transition occurring in the pressure range of 400 to 450 atm for both mathematical equations under evaluation. Furthermore, these attraction and repulsion phenomena are strongly influenced by the proportion of each gas in the mixture and the operating temperature. Therefore, understanding these phenomena enhances the scientific understanding of industrial processes involving phase equilibrium, especially when implemented in separation operations.

### 1. Introduction

Cubic equations of state are integral mathematical models for characterizing the thermodynamic properties of either pure substances or their mixtures, by calculating their physical and chemical attributes under varied pressure and temperature conditions. These equations are extensively utilized in numerous scientific fields, especially in chemical engineering, for thermodynamic analysis of phase equilibrium in separation processes. The insights derived from these studies significantly advance the development of industrial processes, synthesis of new materials, analysis of chemical reactions, and interpretation of experimental data.

The application of cubic equations of state is particularly vital in addressing thermodynamic cycle challenges. For complex fluids like refrigerants, often used in these cycles, properties may not be readily available in standard thermodynamic tables or diagrams. This scarcity increases the complexity of problem-solving in the chemical industry. Cubic equations of state provide an essential mathematical framework for deriving thermodynamic insights critical for system analysis involving these complex fluids, thereby optimizing industrial processes and tackling complex chemical industry challenges.

Utilization of cubic equations of state in scientific research enables the analysis of data and outcomes from industrial processes, thereby enriching the knowledge base across various scientific and technological domains. These equations are especially useful in understanding gas behavior under high pressure and low temperature, accounting for intermolecular forces and non-idealities.

This study focuses on real gases' deviation from ideality, evaluated through the compressibility factor ( $Z$ ) as a function of pressure ( $P$ ). Unlike ideal gases, where  $Z$  is uniformly one at any pressure, real gases exhibit  $Z$  values diverging from this norm due to attractive and repulsive intermolecular forces. These forces, influenced by system pressure, alter the collision rates of fluid particles with the system walls.

Despite advancements in cubic equations of state for gas property determination, experimental validation remains a gap. Manuel et al. conducted a validation study on the compressibility factor behavior of  $CO_2$  and  $CH_4$  systems, finding that the Soave-Redlich-Kwong equation more accurately fits experimental data for a broad pressure range, with a minor average deviation.

This study aims to develop an algorithm for assessing the compressibility factor using two cubic equations of state via Microsoft Excel's SOLVER tool. This

algorithm also calculates other thermodynamic properties, including fugacity coefficients, entropy, enthalpy, Gibbs free energy, and Helmholtz free energy. The results are graphically presented to elucidate the influence of molecular interactions on the thermodynamic behavior of gases in both pure and mixed states.

#### 1.1. Soave-Redlich-Kwong Equation of State

In 1972, Soave introduced a significant modification to the Van der Waals Equation of State, incorporating a specific parameter to account for the molecular size in a gas system. Prior modifications to this equation primarily concentrated on the temperature dependence of the gas's attractive forces. Soave's modification, grounded in the Redlich-Kwong equation of state, extended the parametric dependence by correlating the constant "a" with both temperature and the acentric factor. This acentric factor, a concept introduced by Pitzer in 1955[9,10], encapsulates the deviation of a substance's behavior from that of an ideal gas, as indicated in Equation (1). The integration of the acentric factor into the equation of state marked a pivotal advancement in the thermodynamic modeling of real gases, enhancing the equation's ability to predict gas behavior under various conditions more accurately.

$$a = a(T, \omega) \quad (1)$$

The acentric factor, referenced here, is characterized as a measure of the configuration, sphericity, or deformation of the constituent molecule in the gas system under investigation, whose influence extends to critical temperature conditions.

On the other hand, Soave assessed the use of binary interaction parameters ( $k_{ij}$ ) as an empirical factor employed to adjust the results of equations of state with experimental data when the system involves a mixture of gases. This proposal allows for a better understanding of the interaction measures between molecular pairs with distinct characteristics. Therefore, the determination of  $k_{ij}$  is based on experimental data from binary systems, resulting in the best approximation between theoretical and experimental data, especially for multicomponent systems and, consequently, those of greater phenomenological complexity [12,13].

#### 1.2. Peng-Robinson Equation of State

The Peng-Robinson equation of state has been characterized as the most widely applied in gaseous systems, particularly in the petroleum industry. During the 1970s, Peng, a doctoral student under the guidance of Prof. D. B. Robinson at the University

of Alberta, conducted studies funded by the Canadian Energy Board that led to the proposition of the Peng-Robinson cubic equation of state. This equation demonstrates a strong mathematical similarity to the equation proposed by Soave-Redlich-Kwong, but it exhibits better performance at the critical point. This aspect broadens the application of the Peng-Robinson equation in systems involving phase change phenomena, such as gas/condensate [12,13,14,17,20].

Therefore, the Peng-Robinson equation of state retained the temperature dependence of the attractive term and the acentric factor introduced by Soave. However, the authors presented different adjustment parameters for a better description of this dependence, with significant modifications in the denominator of the term relating to attractive forces. Nevertheless, in the analysis of phenomena associated with

intermolecular forces, the mixture parameters are calculated using the procedures described in the cubic equation of state of Soave-Redlich-Kwong, which involve binary interaction ( $k_{ij}$ ), considering the physical phenomena described earlier [15,16,18,19].

## 2. Methodological Procedures

The study conducted in this context systematically investigates the parametric behavior of a mixture composed of Carbon Dioxide ( $\text{CO}_2$ ) and Hydrogen ( $\text{H}_2$ ) under the initial conditions described in Table 1. Thus, the developed study explores the thermodynamic behavior of binary gas systems, utilizing the cubic state equations of Soave-Redlich-Kwong and Peng-Robinson, as detailed throughout this work.

Table 1.  $\text{CO}_2$  and  $\text{CH}_4$  mixture and physical conditions used in this study.

Components	Composition (%)	Temperature (K)	Pressure (Atm)
$\text{CO}_2$	60	296.15	19,74 – 700
$\text{H}_2$	40		

### 2.1. Algorithm Description

The methodology employed for the development of this work adheres to the description outlined in the block diagram depicted in Figure 1.

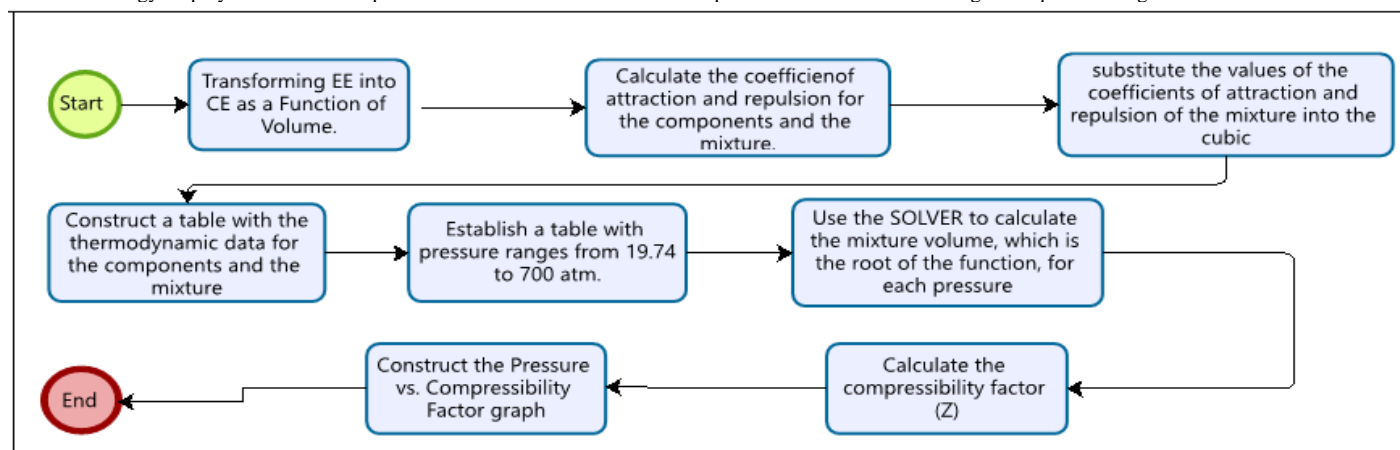


Figure 1: Block Diagram depicting the algorithm used for solving the equations of state.

### 2.2. Equation Resolution Procedure

The Solver is a mathematical programming tool integrated into spreadsheet software, specifically utilized for solving linear programming problems and seamlessly integrated into Excel. It represents a sophisticated tool that facilitates the resolution of problems involving multiple variables and parameter constraints through sensitivity analysis.

For its utilization, it is enabled in the Excel spreadsheet add-ins options, contingent on its corresponding availability. Following the activation of the Solver and the definition of the objective cell for the cubic state equation intended to be solved, along with the assigned value (zero), since the goal is to nullify the equation with a predefined minimal error, with the variable cells designated for modification, the cell representing the volume to be calculated, resulting in the equation being equated to zero, is selected. This process is iteratively performed for each proposed pressure. In the present study, a pressure range between 19,74 and 700 atm was explored, using a variable scale, and the outcomes of this exploration are detailed in Figure 1.

## 3. Results and Discussion

The investigation of the compressibility factor ( $Z$ ) as a function of pressure for the two cubic equations of state [Soave-Redlich-Kwong (S-R-K) and Peng-Robinson (P-R)] at 303.15 K was undertaken in this study. It was observed that the dominance of attractive and repulsive forces, and the transition thereof, is contingent upon the specific equation of state employed. This transition was found to occur within the pressure range of 400 to 450 atm.

The data depicted in Figure 2 illustrate the variation of the compressibility factor as a function of pressure for the two equations assessed in this study. The figure highlights the influence of system pressure on the attractive and repulsive forces among the constituent molecules of the mixture under isothermal conditions, as outlined in Table 1. For both equations of state explored in this research, the SRK equation exhibits a more pronounced impact of molecular interactive forces, encompassing both attractive and repulsive interactions. This observation is likely attributed to a heightened adherence to the physical phenomena incorporated within the equation model.

Therefore, based on the data presented in Figure 2, the SRK equation of state demonstrates greater predominance and representation of phenomenological performance. This is the rationale for its utilization in assessing the influence of gas composition in the mixture on the compressibility factor's behavior as a function of pressure (Figure 3).

Thus, the results presented in Figure 3 stem from the assessment of the influence of gas composition in the mixture, ranging from pure gases such as  $\text{CO}_2$  or  $\text{H}_2$ . The obtained values delineate the scope of the study, specifically within the evaluated pressure range. In the case of molecular hydrogen, within this pressure range, only the effects of repulsive forces are evident, characterized by compressibility factors greater than 1 (one).

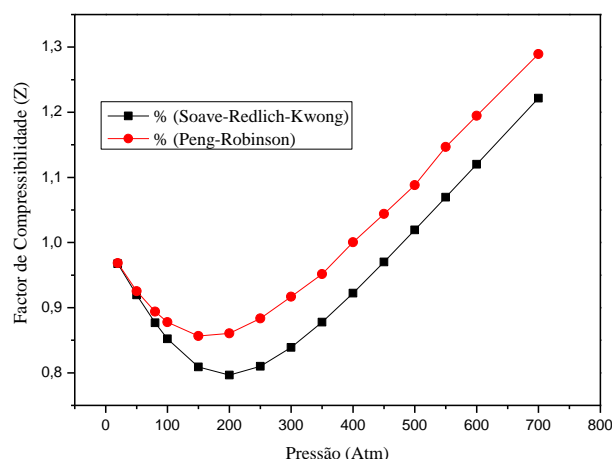
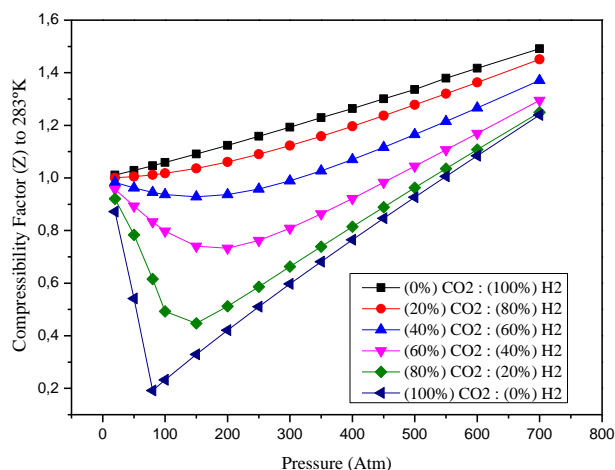


Figure 2: Compressibility Factor Behavior as a Function of System Pressure.

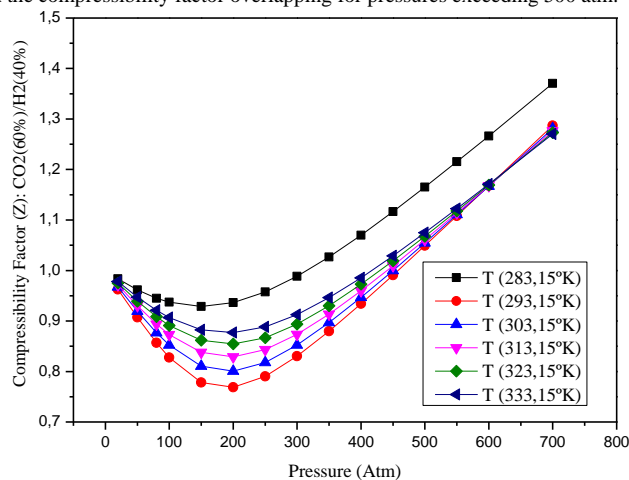
Conversely, with pure  $\text{CO}_2$ , attractive forces predominantly occur up to a pressure of 600 atm, with an inversion observed beyond this pressure. The introduction of a reduced percentage of  $\text{H}_2$  into the mixture, specifically 20% and 40%, reflects the predominance of  $\text{CO}_2$  molecule behavior in the mixture, influenced by the presence of  $\text{H}_2$ . This behavior mirrors the analysis of  $\text{H}_2$  with the introduction of reduced percentages of  $\text{CO}_2$ , resulting in the predominance of hydrogen molecule behavior in the mixture.

With the level of knowledge derived from this analysis, the study extended to investigate the influence of temperature on the compressibility factor's behavior within the pressure domain for a mixture of 60%  $\text{CO}_2$  and 40%  $\text{H}_2$ .



**Figure 3:** Compressibility Factor Behavior as a Function of Gas Composition

The results are depicted in Figure 4. A qualitative analysis of the compressibility factor's behavior reveals similarity across the studied temperatures, with more pronounced deviations observed when the compressibility factor is assessed at 283.15 K and 293.15 K identified as the upper and lower limits of the obtained parameters. However, the highlighted temperatures exhibited analogous behavior, with the compressibility factor overlapping for pressures exceeding 500 atm.



**Figure 4:** Compressibility Factor Behavior as a Function of Temperature (60% CO<sub>2</sub> and 40% H<sub>2</sub>)

Therefore, even with this analysis, considering the mathematical models describing the equations of state studied in this work, temperature emerges as a parameter of significant importance in the behavior of the compressibility factor. It should always be considered in gas mixture studies due to its impact on the predominant attractive and repulsive forces within the gas mixture system.

### 3. Conclusions

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

- Cubic equations of state serve as fundamental tools for investigating the behavior of gas mixtures, enabling the identification of the influence of molecular attractive and repulsive forces through an understanding of the compressibility factor's behavior in the mixture.
- The proportion of each component in the gas mixture directly affects the profile of the compressibility factor's behavior, with the behavior of pure gases prevailing when the fractions of other components are reduced.
- Temperature is a crucial parameter for comprehending gas behavior, as it is a variable present in all studied equations and directly influences the pressure range under investigation.
- Building upon previous studies, it was affirmed that the acentric factor incorporated into cubic equations of state enhances the analytical performance of behavior in gas mixtures. This is attributed to the fact that the size of molecules directly impacts the attractive and repulsive forces present in gas mixtures.
- Comparison of the obtained data with literature values allowed the assertion that the cubic equation of state proposed by SRK demonstrates closer alignment with experimental data. Consequently, it was employed in studying the compressibility factor's behavior as a function of pressure for different fractions and temperatures within the system.

### Nomenclature:

w: Acentric factor;

PVT: Pressure, Volume, and Temperature;

P: Gas pressure (atm);

T: System temperature (K);

a and b: Constants in the cubic equations of state utilized.

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