(REVIEW ARTICLE)

# Thermodynamic property calculations for phase equilibria in natural gas liquefaction and regasification systems

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## Abstract

Precise calculations of thermodynamic properties are essential for enhancing the efficiency of natural gas liquefaction and regasification processes. These calculations play a vital role in understanding phase equilibria, which is critical for ensuring optimal performance in both the liquefaction of natural gas, transforming it into a liquid state for easier storage and transport and the regasification process, which converts it back into a gaseous state for use. By accurately determining properties such as temperature, pressure, and chemical potential, engineers can design more effective systems that maximize energy efficiency and reduce operational costs, ultimately leading to improved overall performance in natural gas processing. This study aims to improve predictive accuracy by utilizing a set of 16 fundamental equations that describe the behavior of real gases. These equations take into account various factors such as pressure, temperature, and volume, allowing for a more precise representation of gas behavior under different conditions. By employing these established equations, the study enhances the reliability of predictions related to gas dynamics, making it possible to achieve more accurate modeling in practical applications and scientific research. The analysis focuses on the variations from optimal conditions in high-pressure cryogenic environments. It employs a range of theoretical tools, including virial coefficients to understand interactions among particles, as well as Helmholtz and Gibbs energies to assess the system's thermodynamic stability and equilibrium. Furthermore, the study integrates correlations of heat capacity to evaluate the thermal properties and behavior of materials under extreme conditions. The study further enhances the understanding of LNG pipeline flow modeling by incorporating detailed calculations of both the speed of sound and the bulk modulus. This integration allows for more accurate simulations of flow dynamics, enabling better design and optimization of pipeline systems to ensure safety and efficiency during transport. The research focuses on enhancing phase equilibrium modeling, essential in optimizing energy consumption within liquefied natural gas (LNG) processes. The study aims to minimize energy losses during the production and transportation of LNG. Furthermore, this approach improves the design of LNG processes by increasing its overall efficiency, contributing to more sustainable practices in the industry.

**Keywords:** Thermodynamic Properties; Phase Equilibria; LNG Liquefaction; Regasification

## 1. Introduction

Natural gas liquefaction and regasification are vital processes in the global energy supply chain, facilitating the efficient storage and transportation of natural gas in its liquefied form, known as liquefied natural gas (LNG). The liquefaction process involves cooling natural gas to extremely low temperatures, transforming it into a liquid state, which reduces its volume by about 600 times. This remarkable reduction allows for the economical transport of natural gas over long distances, especially where pipelines are not feasible. Upon reaching its destination, the regasification process reverses this transformation, converting LNG back into its gaseous form for use in power generation, heating, and industrial applications. Together, these processes play a crucial role in connecting natural gas producers with consumers worldwide, thus enhancing energy accessibility and security. The precise calculation of thermodynamic properties plays a crucial role in optimizing phase equilibria, which is essential for the design and operation of chemical processes. By

accurately determining properties such as enthalpy, entropy, and Gibbs free energy, engineers can better predict how different phases—solid, liquid, and gas—interact under varying temperature and pressure conditions. This understanding helps ensure process efficiency, allowing for the maximization of product yield while minimizing energy consumption and waste generation. Ultimately, these calculations are vital for developing sustainable and cost-effective industrial practices, leading to significant reductions in energy losses and environmental impact. This research study delves into the intricate calculations of advanced thermodynamic properties that are crucial for understanding phase transitions in liquefied natural gas (LNG). It places particular emphasis on the operational processes at the Nigerian Liquefied Natural Gas (NLNG) facility located on Bonny Island, Nigeria. By exploring the thermodynamic behavior of LNG under varying pressure and temperature conditions, the study aims to enhance the efficiency and safety of LNG operations. It will also assess how these properties influence the performance and reliability of the facility's processes, ultimately contributing to improved operational strategies and technological advancements in the LNG sector. Key thermodynamic parameters play a crucial role in understanding the phase behavior and fluid dynamics involved in the conversion and regasification of liquefied natural gas (LNG). These include the compressibility factor, which indicates how much a gas deviates from ideal behavior under varying pressure and temperature conditions. Enthalpy is essential for assessing the energy changes associated with phase transitions, while entropy provides insights into the disorder and spontaneity of processes at a given temperature.

Heat capacities, both at constant pressure and volume, are vital for calculating temperature changes during heating or cooling processes. Furthermore, the Joule-Thomson coefficient describes how the temperature of a real gas changes when it is allowed to expand or compress without any heat exchange with the environment. Together, these parameters inform the design and optimization of LNG systems, ensuring efficient and safe operations throughout the processes of liquefaction, transport, and regasification. The properties discussed here are obtained through the application of advanced equations of state and the utilization of virial coefficients. These sophisticated methodologies provide a more profound understanding of the intricate interactions among the various components of natural gas. By examining factors such as pressure, temperature, and composition, these equations allow for a nuanced analysis of thermodynamic behaviors, enabling more accurate predictions and insights into the performance and efficiency of natural gas systems in diverse operational conditions. In this analysis, we focus on hydrogen and methane, which serve as the primary components and reference cryogenic fluids. We will thoroughly examine their properties and behaviors under cryogenic conditions to demonstrate the precision and relevance of our calculations. By exploring the molecular characteristics, phase transitions, and thermodynamic interactions of these gases, we aim to provide a comprehensive understanding of their applicability in various cryogenic applications. This detailed investigation will highlight how accurate modeling of these fluids can enhance the efficiency and safety of systems utilizing cryogenic technology.

This research significantly advances the field of predictive modeling within liquefied natural gas (LNG) processing by integrating theoretical thermodynamics with practical industrial applications. It delves into the intricate thermodynamic principles that govern LNG behavior and processing, utilizing advanced modeling techniques to enhance accuracy and reliability. By bridging the gap between theoretical insights and real-world challenges faced in the LNG industry, this study provides valuable tools and frameworks that can optimize performance, improve efficiency, and ultimately facilitate better decision-making in LNG operations. This study enhances phase equilibrium analysis by leveraging 16 fundamental thermodynamic equations, thereby establishing a comprehensive framework for optimizing processes in both liquefied natural gas (LNG) liquefaction and regasification. By systematically applying these equations, the research delves into the intricate relationships between temperature, pressure, and composition, enabling a more precise understanding of phase behavior. This approach not only highlights the critical factors affecting system performance but also provides insights that can lead to improved efficiency, reduced energy consumption, and enhanced operational reliability in LNG facilities. The findings of this study have profound implications for several critical areas, including energy efficiency, operational reliability, and the economic viability of liquefied natural gas (LNG) production and transport. By enhancing energy efficiency, we can minimize waste and reduce operational costs, ultimately leading to more sustainable practices in the industry. Furthermore, the insights gained will contribute to improving operational reliability, ensuring that LNG facilities and transportation methods function smoothly and effectively, which is essential for maintaining supply chain integrity. Ultimately, these advancements could significantly bolster the economic feasibility of LNG ventures, making them more attractive to investors and stakeholders in an increasingly competitive and environmentally conscious market.

## 2. Literature Review

### 2.1. Cryogenic Fluids and Their Role in LNG Processing

Cryogenic fluids play a crucial role in the processes of natural gas liquefaction and regasification. By cooling natural gas to extremely low temperatures, these fluids enable the gas to transition into a liquid state, which significantly reduces

its volume. This volumetric reduction makes it more efficient for storage and transportation, especially over long distances. The use of cryogenic technology is vital for facilitating the global trade of liquefied natural gas (LNG), as it allows for the safe and effective handling of gases that would otherwise occupy vastly larger volumes at ambient temperatures. Additionally, during the regasification process, these cryogenic fluids help to convert LNG back into its gaseous form for distribution through pipelines, ultimately ensuring that natural gas is available for various applications, from heating to electricity generation (Baudouy, 2019). The phase behavior of these fluids is fundamentally governed by key thermodynamic principles, which necessitate accurate calculations of several critical properties, including enthalpy, entropy, and compressibility factors. Enthalpy, a measure of the total energy of a thermodynamic system, plays a crucial role in understanding energy transfer during phase changes, while entropy reflects the degree of disorder within the system, influencing the spontaneity of these transitions. Additionally, compressibility factors provide insights into how fluids respond to pressure changes, which is essential for predicting behaviors in various states. By meticulously analyzing these parameters, we can gain a comprehensive understanding of fluid behavior across different phases and conditions, thereby enhancing our ability to manipulate and utilize these substances efficiently in practical applications.

In the production of liquefied natural gas (LNG), methane, which is the principal component of natural gas, is subjected to a process called liquefaction. This process occurs under cryogenic conditions, typically at temperatures around -162°C (-260°F), where methane transitions from a gaseous state to a liquid state. This conversion is vital for efficient transportation and storage, as LNG occupies significantly less volume compared to its gaseous form. Due to the complexities involved in phase transitions, precise calculations of thermodynamic properties are essential for effective modeling of phase equilibrium. Accurate models help predict how methane behaves under various conditions, ensuring the reliability of LNG production processes (Zhang et al., 2021).1.2 Types of Cryogenic Fluids in LNG Systems. The liquefied natural gas (LNG) industry predominantly relies on methane as its essential cryogenic fluid due to its favorable properties that allow for efficient cooling and storage at low temperatures. Methane, which is the primary component of natural gas, undergoes a phase change to become a liquid at approximately -162 °C, facilitating its transport and storage. In addition to methane, other gases, such as nitrogen and hydrogen, contribute crucially to various processes within the LNG cycle. Nitrogen is often employed in refrigeration systems as a coolant, helping to lower temperatures during the liquefaction process, while also serving to maintain inert conditions that prevent unwanted reactions. Hydrogen can play a role in gas conditioning and processing, particularly in improving the quality of natural gas by removing impurities or adjusting its calorific value. These ancillary substances enhance the efficiency and effectiveness of refrigeration cycles, underscoring the complexity and sophistication of the LNG production process (Leachman et al., 2009).

Understanding the difference between inert gases, such as helium and argon, and flammable cryogens, including hydrogen and methane, is essential when examining the phase equilibria of liquefied natural gas (LNG). This distinction is significant because inert gases do not support combustion, which makes them relatively safe to handle in various industrial applications. In contrast, flammable cryogens possess the potential for ignition and explosive reaction under certain conditions, necessitating stringent safety measures. These substances demonstrate unique behaviors when subjected to varying pressures and temperatures. For example, inert gases generally display consistent compressibility and lower heat capacities, which can simplify their treatment in engineering calculations. On the other hand, flammable cryogens possess distinctive compressibility characteristics that can vary significantly, particularly as they approach their critical points. Moreover, their heat capacities can change with phase transitions, influencing thermal management strategies in LNG systems. Such differences not only impact the design and operation of LNG facilities but also dictate safety protocols and risk assessment practices. Understanding these thermophysical properties is vital for optimizing the storage, transportation, and handling of LNG, ultimately ensuring both efficiency and safety in its applications (Lemmon & Span, 2017). A comprehensive understanding of thermodynamic behaviors, achieved through the application of advanced equations of state, plays a crucial role in optimizing the processing of liquefied natural gas (LNG). By accurately modeling the relationships between pressure, temperature, and volume, these equations facilitate precise predictions of LNG's physical properties under various conditions. This insight allows engineers to design more efficient processes for liquefaction, storage, and transportation, ultimately enhancing the safety and efficiency of LNG operations while reducing costs and environmental impacts.

## 2.2. Industrial Application of Cryogenic Fluids in LNG Liquefaction and Regasification

Cryogenic fluids play a crucial role in the processes of liquefied natural gas (LNG) liquefaction and regasification plants. These fluids are essential for maintaining precise phase equilibrium, which is vital for optimizing energy efficiency and ensuring operational stability within the system. The management of temperature and pressure in these facilities requires advanced cryogenic technologies, as even minor fluctuations can lead to significant losses in efficiency and can compromise safety. Researchers, such as Span et al. (2019), emphasize that a thorough understanding of the

thermodynamic properties of cryogenic fluids is necessary to enhance the performance of LNG operations. By refining the control mechanisms and utilizing advanced materials, plants can achieve not only better energy output but also greater environmental sustainability in their operations. At NLNG Bonny Island, the cryogenic refrigeration cycles utilize advanced nitrogen expansion techniques alongside mixed refrigerant processes. These processes are crucial for achieving the extremely low temperatures required for liquefaction. The operation relies on sophisticated thermodynamic property calculations to accurately assess and optimize phase transitions. This ensures that the refrigerant can efficiently absorb heat during the vaporization phase and release it during the condensation phase. By meticulously managing these thermodynamic properties, NLNG maximizes the energy efficiency of their refrigeration systems, ultimately enhancing the overall performance and reliability of the liquefaction process. (Schmidt & Wagner, 2020). The regasification process is a critical step in the liquefied natural gas (LNG) supply chain, where LNG, stored at extremely low temperatures, is converted back into gaseous natural gas for distribution and consumption. This transformation relies heavily on precise thermodynamic models, which play a vital role in accurately predicting the energy requirements needed for the vaporization process. These models also assess pressure-temperature relationships to ensure optimal operational efficiency. By taking into account factors such as ambient conditions, heat transfer rates, and physical properties of the LNG, these models enable engineers to design and operate regasification terminals effectively, ultimately ensuring a steady and reliable supply of natural gas. (Tegeler et al., 2019).

## 2.3. Functions for Calculation of Thermodynamic Properties in LNG Phase Equilibria

Calculating thermodynamic properties in the context of liquefied natural gas (LNG) phase equilibria is essential for optimizing both liquefaction and regasification processes. Key parameters involved in these calculations include the compressibility factor (Z), the Joule-Thomson coefficient, and virial coefficients. The compressibility factor (Z) provides insight into the deviation of a real gas from ideal behavior under varying pressure and temperature conditions, which is crucial when designing equipment for LNG processes. The Joule-Thomson coefficient measures the temperature change of a gas when it is allowed to expand without doing external work, playing a vital role in determining the cooling effects during the liquefaction phase. Virial coefficients, on the other hand, describe the interaction forces between gas molecules and help refine the equation of state for real gases. Understanding these coefficients allows engineers to accurately predict the behavior of LNG under various conditions, enhancing the efficiency of both liquefaction and regasification operations. By carefully analyzing these thermodynamic properties, one can optimize the performance and safety of LNG systems, ultimately leading to more efficient energy production and consumption. (Setzmann & Wagner, 2018). Advanced equations of state (EOS), particularly those developed for substances like hydrogen and methane, play a crucial role in accurately modeling the phase behavior of liquefied natural gas (LNG). These sophisticated models allow for precise predictions of phase equilibria, which are essential in optimizing the processing and handling of LNG under varying temperature and pressure conditions. By aligning theoretical predictions with real-world processing scenarios, researchers and engineers can better understand and control the behavior of LNG during storage, transportation, and regasification, ultimately enhancing safety and efficiency in natural gas operations (Ortiz-Vega et al., 2020). The calculations conducted in this study significantly deepen our understanding of various aspects of liquefied natural gas (LNG), specifically focusing on storage methods, transport logistics, and energy efficiency initiatives. By analyzing these components in detail, we can identify best practices that not only optimize operations within the LNG supply chain but also contribute to better economic outcomes for stakeholders in the natural gas industry. Furthermore, these insights facilitate the development of environmentally sustainable practices, reducing the carbon footprint associated with LNG activities and promoting cleaner energy alternatives. Ultimately, the findings aim to foster a more efficient and responsible approach to LNG, benefiting both the industry and the broader environment.

## 3. Methodology and Materials

### 3.1. Methodology

This study utilizes a quantitative thermodynamic modeling approach to thoroughly evaluate phase equilibria during the processes of natural gas liquefaction and regasification, specifically focusing on the operations at the NLNG (Nigeria Liquefied Natural Gas) facility located on Bonny Island. The research aims to analyze the complex interactions and behaviors of different components under varying temperature and pressure conditions, which are critical for optimizing the efficiency and performance of the liquefaction and regasification processes. By leveraging advanced thermodynamic models, the study seeks to provide insights into the fundamental thermophysical properties of natural gas mixtures, thereby enhancing the understanding of phase transitions and promoting improved design and operation of LNG plants. The research delves into the intricate calculations of thermodynamic properties by employing advanced equations of state (EOS), virial coefficients, and critical parameters. This comprehensive approach facilitates a precise modeling of the phase transitions that occur between gaseous and liquid methane. By integrating these methodologies, the study aims to enhance the understanding of methane's behavior under varying pressure and temperature conditions,

ultimately contributing to more accurate predictions of its phase equilibrium and transitions. This detailed analysis not only improves the fundamental knowledge of methane as a vital energy resource but also supports practical applications in industries such as natural gas extraction and cryogenics.

### 3.1.1. Selection of Cryogenic Fluids and Data Sources

Hydrogen and methane have been selected as representative cryogenic fluids owing to their significant roles in the processing and transport of liquefied natural gas (LNG). These two gases are crucial for understanding the thermodynamic principles involved in LNG systems. To gain a comprehensive understanding of their behavior under varying temperature conditions, we gather extensive experimental data and scholarly literature that provide insights into their temperature-dependent thermodynamic properties. Key properties of interest include the compressibility factor, which measures how much the gas deviates from ideal gas behavior; enthalpy, which reflects the heat content of the substance; entropy, indicating the degree of disorder or randomness; and the fugacity coefficient, which accounts for real gas effects in non-ideal conditions. This data is sourced from recognized and authoritative references in the field, ensuring reliability and accuracy in the analysis of these critical fluids. The National Institute of Standards and Technology (NIST) maintains a comprehensive database that includes a wide array of experimental data derived from reports on the operations of natural gas liquefaction plants (NLNG). This database serves as a critical resource for researchers and engineers in the field. Additionally, the database features equations of state (EOS) such as the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) models. These equations are essential for accurately predicting the thermodynamic properties of fluids, particularly in the context of natural gas and its derivatives. The PR and SRK equations are widely used in chemical engineering and thermodynamics to analyze phase behavior and fluid interactions under various conditions, enhancing our understanding of gas liquefaction processes and improving operational efficiency.

### 3.1.2. Governing Thermodynamic Equations

The study utilizes a comprehensive set of 16 key thermodynamic equations to analyze various phase properties of liquefied natural gas (LNG). Among these properties, the compressibility factor (Z) is calculated, which is crucial for understanding the deviations of real gas behavior from ideal gas laws. Additionally, the study examines fundamental thermodynamic quantities such as enthalpy (H), which indicates heat content; entropy (S), which measures the degree of disorder; and Gibbs free energy (G), which predicts the spontaneity of chemical processes. Furthermore, the research delves into the determination of the speed of sound in LNG, as well as its heat capacities at constant pressure (Cp) and constant volume ($C_v$). By exploring these properties, the study aims to elucidate the intricate relationships between phase transitions, including pressure and temperature correlations, that LNG experiences under various operational conditions. Overall, these detailed calculations and analyses provide valuable insights into the behavior of LNG, enabling better predictions and optimizations in its transport and storage, while enhancing safety and efficiency in its applications.

### 3.1.3. Simulation of Phase Equilibria

The phase behavior of methane is critically examined during its liquefaction process at sub-cooled cryogenic temperatures, as well as during its regasification under warming conditions. This analysis is conducted using advanced thermodynamic modeling tools, specifically Aspen HYSYS and MATLAB. These software platforms enable accurate simulations of the behavior of methane under varying conditions. For vapor-liquid equilibrium (VLE) predictions, the modeling employs both the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state (EOS). These equations are essential for characterizing the thermodynamic properties of mixtures and provide a reliable framework for understanding phase transitions. Additionally, the properties of hydrogen and methane are modeled across extensive temperature and pressure ranges, allowing for a comprehensive analysis of their behavior in both liquefied and gaseous forms. This detailed approach facilitates a deeper understanding of the thermodynamic processes involved, which is crucial for optimizing gas processing technologies and enhancing the efficiency of energy production.

### 3.1.4. Model Validation and Sensitivity Analysis

To ensure the accuracy and reliability of the thermodynamic models, a comprehensive comparison is made against established NIST reference values specifically for methane and hydrogen. Additionally, operational data gathered from the NLNG facilities at Bonny Island serves as a practical benchmark for validation. To deepen the understanding of the models' performance, a sensitivity analysis is conducted, examining how variations in key parameters such as pressure, temperature, and gas composition impact the phase stability of liquefied natural gas (LNG) as well as its overall efficiency. This analysis not only highlights the complex interdependencies within the system but also provides valuable insights into optimizing LNG operations under varying conditions.

### 3.2. Materials and Computational Tools

#### 3.2.1. Materials Used in the Study

Cryogenic Fluid Data: This includes a comprehensive analysis of thermophysical properties for hydrogen and methane, two key cryogenic fluids. The properties encompass aspects such as density, viscosity, thermal conductivity, and heat capacity, which are critical for efficient handling and processing in various applications. NLNG Process Data: This section outlines the operational parameters for both liquefaction and regasification units within the Natural Liquefied Natural Gas (NLNG) process. Key parameters include temperature and pressure specifications, flow rates, and energy consumption metrics, all of which are essential for optimizing the performance and reliability of the LNG supply chain. Standard Equations of State: The text discusses several prominent equations of state used for the accurate prediction of fluid properties: The Peng-Robinson equation is renowned for its effectiveness in describing the behavior of hydrocarbons and provides insights into phase behavior. The Soave-Redlich-Kwong. equation modifies the original Redlich-Kwong formulation to improve predictions for volatile components. The Benedict-Webb-Rubin equation offers a comprehensive model that accounts for the effects of molecular interactions, making it suitable for a wide range of gases at various conditions. Together, these elements provide a solid framework for understanding and optimizing processes involving cryogenic fluids in industrial applications.

#### 3.2.2. Software and Computational Tools

Aspen HYSYS is a powerful tool utilized for the simulation of liquefied natural gas (LNG) processes, specifically focusing on both liquefaction and regasification stages. It offers robust features for modeling complex thermodynamic behaviors, allowing for optimization of systems and processes to improve efficiency and reduce costs. MATLAB serves as a versatile programming environment that is ideal for implementing intricate thermodynamic property equations. It enables users to perform comprehensive graphical analysis, facilitating the visualization of data and trends that can be vital in understanding and optimizing process performance. REFPROP (developed by the National Institute of Standards and Technology - NIST) provides precise fluid property data essential for accurate calculations. This software is invaluable for conducting equation-of-state calculations that assist in the prediction of phase behavior and thermodynamic properties of fluids under various conditions, ensuring reliability in process simulation and analysis.

#### 3.2.3. Functions for calculation of thermodynamic properties

The mathematical relationships governing various thermodynamic properties can be expressed through different parameters, each offering unique insights into the behavior of thermodynamic systems. In this discussion, we will systematically explore each equation, delving into their derivations and implications. We will cover key properties such as temperature, pressure, volume, and entropy, examining how they interrelate within the framework of different thermodynamic laws and principles. By analyzing these equations in detail, we aim to enhance our understanding of their significance in both theoretical and practical applications in thermodynamics. Key parameters play a crucial role in the thermodynamic property calculations necessary for understanding phase equilibria in natural gas liquefaction and regasification systems. These calculations are essential for optimizing processes and ensuring efficiency in the industry. Compressibility Factor (Z): This dimensionless factor accounts for deviations of real gas behavior from ideal gas laws, particularly under high pressure and low temperature conditions typical of liquefaction processes. It is critical for calculating the density and volume of natural gas. Pressure (P): The pressure of the system significantly influences the physical state of natural gas. In liquefaction, increased pressure can lead to the condensation of gas into a liquid state, while during regasification, reduced pressure can promote vaporization. Temperature (T): Temperature is a key variable in phase equilibria. In liquefaction, low temperatures are required to convert natural gas to liquid form, whereas regasification typically occurs at higher temperatures to facilitate the transformation back to gas. Universal Gas Constant (R): This constant is essential in equations of state and plays a pivotal role in relating pressure, volume, and temperature in thermodynamic calculations. Volume (V): Understanding the volume occupied by natural gas in both gaseous and liquid states is crucial for the design and operation of storage and transportation systems. Density ($\rho$). The density of the gas and liquid phases must be accurately determined for mass balance calculations and to ensure proper equipment specifications. Heat Capacities (Cp and Cv): The heat capacities at constant pressure (Cp) and constant volume (Cv) are vital for understanding energy transfer during phase transitions. They help predict how much energy is required to induce phase changes and maintain temperatures during operations. Dimensionless Thermodynamic Parameters ($\delta$, $\tau$, $\alpha$). These parameters provide valuable insights into the behavior of the system under varying conditions. They can enhance the accuracy of modeling phase behavior and help in identifying critical points of phase change. In conclusion, these parameters collectively inform the design and optimization of natural gas liquefaction and regasification processes, ensuring that systems operate efficiently and safely while meeting energy demands.

### 3.2.4. Compressibility Factor

$$Z = \frac{P}{\rho RT} = 1 + \delta \left( \frac{\partial x^r}{\partial \delta} \right)$$ ................... (1)

The compressibility factor, denoted as Z, quantifies the extent to which a real gas deviates from ideal gas behavior. For an ideal gas, we assume that Z equals 1, indicating that the gas follows the Ideal Gas Law perfectly without any intermolecular forces or volume exclusions. However, real gases often exhibit different behaviors due to various factors, such as molecular size, polarity, and the presence of intermolecular forces like van der Waals attractions or repulsions. As pressure and temperature conditions change, the interactions between gas molecules can lead to deviations from the ideal model. When Z is greater than 1, it suggests that the gas is less compressible than predicted by the Ideal Gas Law, often due to repulsive forces at high pressures. Conversely, when Z is less than 1, it indicates that the gas is more compressible, typically resulting from attractive forces that dominate at lower pressures or higher temperatures. Understanding Z and its implications allows us to better predict the behavior of gases in various conditions, which is essential in fields ranging from chemical engineering to atmospheric science.

### 3.2.5. Pressure

$$\frac{P}{P_c} = \frac{\delta}{Z}$$
$$\left[ 1 + \delta \left( \frac{\partial x^r}{\partial \delta} \right) \right]$$ ...................(2)

Pressure can be expressed as a function of the critical pressure ($P_c$), which is a fundamental parameter in thermodynamics that characterizes the behavior of substances at their critical point. In this context, it is essential to consider the compressibility factor (Z), which accounts for deviations from ideal gas behavior, particularly under high pressure and low temperature conditions. Additionally, real gas effects impact the relationships between pressure, volume, and temperature, necessitating a more comprehensive understanding of gas behavior beyond the ideal gas law. By incorporating these elements, we can better analyze and predict the behavior of gases in diverse conditions, recognizing how molecular interactions and the non-ideal nature of real gases influence pressure measurements and calculations.

### 3.2.6. Fugacity Coefficient

$$\Phi = \exp [Z-1-\ln (Z) + \alpha r]$$ ...................... (3)

Fugacity is a thermodynamic concept used to describe the behavior of real gases by providing a corrected measure of pressure that accounts for deviations from ideal gas behavior. Unlike ideal gases, which strictly follow the ideal gas law under all conditions, real gases exhibit interactions between molecules that can lead to significant differences in properties. The fugacity coefficient, denoted as $\phi$, quantifies this non-ideality by comparing the fugacity (the effective pressure) of a real gas to its pressure as if it were behaving ideally. A fugacity coefficient greater than one indicates that the gas behaves more loosely than predicted by the ideal gas law, while a coefficient less than one suggests stronger interactions than expected. Understanding fugacity and its coefficient is crucial for accurately modeling gas behaviors in various chemical engineering applications, such as phase equilibria, reaction kinetics, and gas extraction processes.

### 3.2.7. Second and Third Virial Coefficients

$$B(T) = \frac{1}{\rho_c} \left( \frac{\partial x^r}{\partial \delta} \right)_{\delta=0}$$
$$C(T) = \frac{1}{\rho_c^2} \left( \frac{\partial^2 x^r}{\partial \delta^2} \right)_{\delta=0}$$ .............. (4)

Virial coefficients are crucial parameters in thermodynamics that help describe the non-ideal behavior of gases by accounting for molecular interactions. They are derived from the virial expansion of the pressure of a gas concerning its volume, particularly at higher pressures or lower temperatures where deviations from the ideal gas law become significant. The second virial coefficient, B(T), reflects pairwise interactions between gas molecules and provides insight into the effects of attractive and repulsive forces that influence a gas's compressibility. The third virial coefficient, C(T), takes these interactions a step further by considering three-body interactions, offering a more comprehensive understanding of how molecular interactions affect gas behavior. Both B(T) and C(T) are temperature-dependent and

play a vital role in predicting the properties of real gases under various conditions, allowing for more accurate modeling and applications in chemical and physical processes.

### 3.2.8. Internal Energy

$$\frac{U}{RT} = \tau \left(\frac{\partial x^r}{\partial \tau}\right) + \left(\frac{\partial x^r}{\partial \delta}\right) \qquad (5)$$

The internal energy of a system can be expressed as a function of the reduced temperature, denoted by τ, and the density parameter, represented as δ. The reduced temperature τ typically relates the system's temperature to a critical temperature, allowing us to understand how energy changes concerning thermal fluctuations near phase transitions. Meanwhile, the density parameter δ provides insight into how the system's energy is influenced by variations in density, which is crucial in understanding interactions at different levels of compression or expansion. Together, these parameters help characterize the thermodynamic behavior of the system, revealing intricate relationships between energy, temperature, and density in various physical contexts.

### 3.2.9. Enthalpy

$$\frac{H}{RT} = \tau \left(\frac{\partial x^r}{\partial \tau}\right) + \left(\frac{\partial x^r}{\partial \delta}\right) + 1 \qquad (6)$$

Enthalpy is a thermodynamic property that encompasses the total internal energy of a system along with the work done on or by the system during a process involving pressure and volume, represented by the PV term. Specifically, it combines the system's internal energy, which relates to the temperature and phase of the substances present, with the energy associated with the pressure exerted by those substances in a given volume. This means that enthalpy not only reflects the thermal state of a substance but also accounts for the energy required to create space for the system in its environment, making it particularly useful in analyzing energy transfer in processes such as heating, cooling, and phase changes in various engineering applications.

### 3.2.10. Gibbs Energy

$$\frac{G}{RT} = 1 + \alpha^r + \delta \left(\frac{\partial x^r}{\partial \delta}\right) \qquad (7)$$

Gibbs free energy is a key thermodynamic potential that plays a crucial role in determining the phase equilibrium of chemical systems and the spontaneity of processes. It combines the system's enthalpy and entropy into a single value, allowing us to assess whether a reaction or phase transition can occur under constant temperature and pressure conditions. When the change in Gibbs free energy (ΔG) is negative, the process is spontaneous, indicating that it can proceed without external input. Conversely, if ΔG is positive, the reaction is non-spontaneous and requires energy input to occur. At equilibrium, the Gibbs free energy reaches a minimum, and any small change will lead to a shift in the balance of phases or reactions. Thus, understanding Gibbs free energy is essential for predicting and controlling chemical behavior in various conditions.

### 3.2.11. Helmholtz Energy

$$\frac{a}{RT} = \alpha^0 + \alpha^r \qquad (8)$$

Helmholtz energy, also known as Helmholtz free energy, is a crucial thermodynamic potential used primarily in the study of closed systems. It is defined as the difference between the internal energy of the system and the product of its temperature and entropy. This state function is particularly useful for processes occurring at constant temperature and volume, as it provides insight into the spontaneity of such processes. Lower values of Helmholtz energy indicate greater stability and a higher likelihood of a spontaneous reaction occurring within the system. In addition, it plays a significant role in determining equilibrium conditions and is often employed in various fields, including physical chemistry and materials science, to analyze phase transitions and chemical reactions.

### 3.2.12. Entropy

$$\frac{S}{R} = \tau \left( \frac{\partial x^r}{\partial \tau} \right) - \alpha^0 - \alpha^r \qquad \text{............... (9)}$$

Entropy is a fundamental concept in thermodynamics and information theory that measures the degree of disorder or randomness in a system. It represents the irreversibility of natural processes, indicating how energy transformations lead to increased disorder over time. In a closed system, as processes occur, entropy tends to increase, reflecting the inevitable tendency toward equilibrium and the dispersal of energy. This concept not only helps us understand the behavior of physical systems but also has implications in various fields, including statistical mechanics and the study of information, where it relates to data uncertainty and organization.

### 3.2.13. Speed of Sound

$$\frac{w^2}{RT} = \frac{C_p}{C_v} \left[ 1 + 2\delta \left( \frac{\partial x^r}{\partial \delta} \right) + \delta^2 \left( \frac{\partial^2 x^r}{\partial \delta^2} \right) \right] \qquad \text{......................(10)}$$

The propagation of sound in a fluid is fundamentally influenced by various factors, one of the most significant being the heat capacity ratio. This ratio, defined as the relationship between the specific heat at constant pressure and the specific heat at constant volume, plays a crucial role in determining how sound waves travel through different fluids. As sound waves propagate, they interact with the fluid's molecules, and the thermal properties of the fluid, dictated by its heat capacity ratio, affect the speed and efficiency of this propagation. Higher heat capacity ratios can lead to variations in sound speed and attenuation, making it essential to consider this aspect when studying acoustic behaviors in gases, liquids, and other fluid media. Understanding these dynamics enhances our ability to predict sound behavior in diverse environments, from industrial applications to natural phenomena.

### 3.2.14. Isochoric Heat Capacity

$$\frac{C_p}{R} = \frac{C_v}{R} + \frac{\left[ 1 + \delta \left( \frac{\partial x^r}{\partial \delta} \right) - \delta \tau \left( \frac{\partial^2 x^r}{\partial \delta \partial \tau} \right) \right]^2}{1 + 2\delta \left( \frac{\partial x^r}{\partial \delta} \right) + \delta^2 \left( \frac{\partial^2 x^r}{\partial \delta^2} \right)} \qquad \text{..............(11)}$$

The text describes the measurement of the energy needed to increase the temperature of a substance while maintaining constant pressure. This specific energy measurement is known as "enthalpy" and is particularly important in thermodynamics. It reflects the heat absorbed or released by a system during a phase transition or chemical reaction when the system is under constant pressure. Understanding this concept is crucial for various applications, including engineering processes, environmental science, and thermodynamic calculations.

### 3.2.15. Pressure Derivatives for Density

$$\left( \frac{\partial P}{\partial \rho} \right)_T = RT \left[ 1 + 2\delta \left( \frac{\partial x^r}{\partial \delta} \right) + \delta^2 \left( \frac{\partial^2 x^r}{\partial \delta^2} \right) \right]$$

$$\left( \frac{\partial^2 P}{\partial \rho^2} \right)_T = \frac{RT}{\rho} \left[ 2\delta + 4\delta^2 \left( \frac{\partial^2 x^r}{\partial \delta^2} \right) + \delta^3 \left( \frac{\partial^3 x^r}{\partial \delta^3} \right) \right] \qquad \text{...................(13)}$$

The derivatives outlined in this context illustrate the relationship between pressure and density, highlighting how variations in density can influence pressure changes within a given system. By analyzing these derivatives, we can gain insights into the behavior of fluids under different conditions and understand the principles governing thermodynamics and fluid dynamics. This relationship is critical in fields such as meteorology, engineering, and material science, where predicting pressure fluctuations due to changes in density is essential for accurate modeling and analysis.

### 3.2.16. Joule-Thomson Coefficient

$$\mu_j = \left( \frac{\partial T}{\partial P} \right)_h = \frac{TB - 1}{\rho C_p} \qquad \text{........................(14)}$$

The Joule-Thomson coefficient is a crucial parameter in thermodynamics that describes the change in temperature of a real gas when it is allowed to expand freely while being insulated from heat exchange with its surroundings. This process is known as the Joule-Thomson effect. Mathematically, the Joule-Thomson coefficient (μ) is defined as the partial derivative of temperature (T) for pressure (P), at constant enthalpy (H): The sign and magnitude of the Joule-Thomson coefficient can indicate whether a gas will cool or warm during expansion. For many gases, such as nitrogen and helium, the coefficient is positive at room temperature and atmospheric pressure, meaning that the gas will cool as it expands. Conversely, some gases like hydrogen and helium can show a negative coefficient at certain temperatures, indicating that they will warm upon expansion. The behavior of the Joule-Thomson coefficient is intrinsically linked to the intermolecular forces at play within the gas. As a gas expands, its molecules move further apart, leading to a reduction in the intermolecular attractions that can contribute to cooling. This relationship varies with temperature and pressure, as well as the specific properties of the gas. The Joule-Thomson effect is utilized in various practical applications, including refrigeration and gas liquefaction processes. Understanding the coefficient is essential for engineers and scientists working on systems involving gas compression and expansion, as it allows for more efficient design and optimization of thermal systems. In summary, the Joule-Thomson coefficient is a vital concept that helps to describe and predict the thermal behavior of gases during expansion, providing insights necessary for numerous industrial applications.

### 3.3. Expansion Coefficients

*3.3.1. Isentropic*

$$k = -\frac{1}{\rho}\left(\frac{\partial P}{\partial v}\right)_s = \frac{w^2}{P}$$

........................ (15)

Isentropic Expansion Coefficients: Isentropic expansion refers to the process where a gas expands without any heat transfer to or from its surroundings, maintaining constant entropy throughout the process. This characteristic makes isentropic processes idealized, as they assume a reversible process with no irreversibility, such as friction or turbulence. In the context of thermodynamics, isentropic expansion coefficients play a crucial role in characterizing the behavior of gases during expansion. These coefficients quantify how the properties of a gas change as it expands is entropically. Specifically, they can describe changes in temperature, pressure, and volume, allowing engineers and scientists to predict the performance of engines, turbines, and other thermal systems. The isentropic expansion coefficient (often represented as (k) or (gamma) is defined as the ratio of specific heats at constant pressure and constant volume ($C_p$ /$C_v$). This ratio is fundamental in calculating the work done by or on the gas during the expansion process and is essential for determining the efficiency of thermodynamic cycles. Overall, understanding isentropic expansion coefficients is vital for optimizing system designs and improving energy efficiency in various applications involving gas dynamics and thermodynamic systems.

*3.3.2. Isothermal*

$$k_T = -\frac{1}{\rho}\left(\frac{\partial P}{\partial v}\right)_T = \frac{1}{\rho}\left(\frac{\partial P}{\partial \rho}\right)_T$$

.....................(16)

The isothermal formula is a crucial concept in thermodynamics and physical chemistry, particularly when describing processes that occur at a constant temperature. Understanding the parameters involved in this formula is essential for accurate calculations and practical applications. Temperature (T) Temperature is the central parameter in the isothermal process. It is the point at which the system operates steadily, and it must remain constant throughout the process. Typically measured in Kelvin (K), temperature influences the kinetic energy of particles and, thus, the behavior of gases and liquids in isothermal conditions. Pressure (P), This parameter represents the force exerted by the substance per unit area within the system. In an isothermal process involving gases, pressure can change in response to volume alterations while maintaining a constant temperature. For an ideal gas, there is a direct relationship between pressure and volume as described by Boyle's Law. Volume (V), Volume refers to the space occupied by the substance within the system. During an isothermal process, any change in volume will directly affect the pressure if the temperature remains constant. This interplay is fundamental in applications such as gas expansion and compression. Amount of Substance (n). Expressed in moles, this parameter indicates the quantity of the substance participating in the process. It is essential for calculating changes in pressure, volume, and temperature, as it defines the number of particles involved in the reaction or process. Ideal Gas Constant (R). This is a physical constant that relates the pressure, volume, temperature, and number of moles of an ideal gas. The value of R depends on the units used; for example, in the ideal gas equation, it is often given as 0.0821 L· atm/ (K· mol) for pressure in atmospheres and volume in liters. Equation of State. In isothermal processes involving ideal gases, the equation of state can be represented as (PV = nRT). This relationship

encapsulates how the pressure, volume, and amount of substance interact when temperature remains constant. Heat Transfer (Q). In isothermal processes, while no temperature change occurs, heat can be absorbed or released by the system to maintain equilibrium. This heat transfer is crucial for ensuring that the temperature stays consistent despite changes in pressure and volume. In summary, understanding each parameter in the isothermal formula is essential for analyzing and predicting the behavior of systems at constant temperatures. This detailed comprehension allows for improved accuracy in fields such as engineering, environmental science, and other areas where thermodynamic principles are applicable.

### 3.3.3. Volume Expansivity

Volume expansivity, also known as the coefficient of volumetric thermal expansion, is a measure of how much a substance's volume changes in response to a change in temperature. The formula for calculating volume expansivity (beta) is defined as:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \quad \text{...........................(17)}$$

where: Beta is the volume expansivity, V is the original volume of the substance, dV is the volume change, dT is the temperature change. This formula indicates that the volume expansivity is the negative ratio of the relative change in volume to the change in temperature. Understanding volume expansivity is crucial in various scientific and engineering applications. For instance, in materials science, it helps engineers choose appropriate materials for structures that will experience temperature fluctuations. Similarly, in thermodynamics and fluid dynamics, knowing how volume changes with temperature allows for better predictions of behavior in systems such as gases and liquids. In practical terms, a material with a high volume expansivity will experience a significant increase in volume with even a small increase in temperature. Conversely, materials with low volume expansivity are more stable and maintain their volume better under thermal changes. In summary, the volume expansivity formula is a fundamental concept that quantifies how temperature variations affect the volume of materials, providing valuable insights for applications across numerous fields.

## 3.4. Compressibility and Bulk Moduli

### 3.4.1. Adiabatic Compressibility

Adiabatic compressibility is a property of materials that measures how much their volume changes in response to changes in pressure without any heat exchange with the environment. This property is particularly relevant in fields like thermodynamics, fluid mechanics, and material science, where understanding the behavior of substances under varying pressure conditions is crucial. In essence, adiabatic compressibility (often denoted as β) quantifies the ability of a substance to compress when subjected to an increase in pressure while maintaining thermal equilibrium, meaning no heat is added or removed from the system during the process. This contrasts with isothermal compressibility, where the substance can exchange heat with its environment. Mathematically, adiabatic compressibility can be represented as:

$$\beta_s = \frac{1}{kP} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s \quad \text{...................(18)}$$

where (V) is the volume, (P) is the pressure, and the subscript (S) indicates that the process is adiabatic. A high value of adiabatic compressibility implies that a substance can undergo a significant change in volume for a given change in pressure, indicating greater flexibility or compressibility. Conversely, a low value suggests that the material is more rigid and resistant to volume changes. Adiabatic compressibility is influenced by several factors, including temperature, pressure, and the nature of the material itself. For gases, adiabatic compressibility typically decreases with increasing pressure, while liquids generally show more stable compressibility across different pressures. The concept is critical in various applications, such as determining the behavior of gases in engines, the design of pressure vessels, and the analysis of seismic waves traveling through geological formations. Understanding adiabatic compressibility allows engineers and scientists to predict how materials will respond under stress and to design processes and structures that can withstand fluctuating pressure conditions effectively.

### 3.4.2. Adiabatic Bulk Modulus

The adiabatic bulk modulus, often denoted as (K_s \), is a crucial parameter in thermodynamics and fluid mechanics that quantifies a material's resistance to uniform compression when the process occurs without heat exchange. This

modulus is especially important in applications involving gases and liquids, where understanding the behavior of materials under pressure is vital. Mathematically, the adiabatic bulk modulus can be defined as the ratio of the infinitesimal increase in pressure to the infinitesimal decrease in volume, under adiabatic (no heat transfer) conditions. This can be expressed with the formula:

$$B_s = kP = -V \left( \frac{\partial P}{\partial V} \right)_s \qquad \text{............... (19)}$$

where: K_s is the adiabatic bulk modulus, V is the volume of the substance, P is the pressure, partial P partial V represents the change in pressure concerning volume at constant entropy (s). The negative sign reflects the inverse relationship between pressure and volume; as volume decreases during compression, pressure increases. In a practical context, the adiabatic bulk modulus can be determined from the speed of sound in a medium, as it relates to how quickly pressure waves can propagate through a material. For gases, the adiabatic bulk modulus is influenced by the specific heat capacity ratios, often denoted as (gamma) (gamma), which is the ratio of specific heats at constant pressure and constant volume. For an ideal gas, the adiabatic bulk modulus can be expressed as: K_s = gamma P. This shows that for a given gas at a certain pressure, the bulk modulus is directly proportional to the pressure and dependent on the nature of the gas through its specific heat capacities. Understanding the adiabatic bulk modulus is essential in various fields such as acoustics, meteorology, and engineering, as it provides insights into how materials will respond to stress under rapid changes in pressure, without heat transfer, establishing crucial parameters for designing systems ranging from hydraulic machinery to geological studies and atmospheric models.

### 3.4.3. Isothermal Compressibility

Isothermal compressibility is a measure of a substance's response to pressure changes at a constant temperature. It quantifies how much a given volume of material will compress under an increase in pressure, indicating how much the volume decreases as pressure rises. The formula for isothermal compressibility (denoted as κ) is typically expressed as: (V) represents the original volume of the substance. (P) refers to the pressure applied. The partial derivative (V. P. T) indicates the change in volume for pressure while keeping the temperature constant. A high compressibility value implies that the substance can be compressed significantly under pressure, while a low value suggests resistance to compression. Isothermal compressibility is particularly important in fields such as thermodynamics, material science, and engineering, as it helps predict how substances behave under various environmental conditions and pressures. Understanding this property is crucial for applications ranging from the storage of gases to the design of equipment that operates under high pressures.

### 3.4.4. Isothermal Bulk Modulus

The Isothermal Bulk Modulus (K) is a fundamental concept in fluid mechanics and thermodynamics that quantifies a material's resistance to uniform compression under isothermal conditions, meaning at a constant temperature. It provides insight into how compressible a substance is when subjected to external pressure. Mathematically, the Isothermal Bulk Modulus is defined using the formula:

$$\kappa = \frac{1}{k_T P} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \qquad \text{...........................(20)}$$

Where: K is the Isothermal Bulk Modulus, V is the volume of the substance, P is the pressure applied to the substance, partial P partial V T is the partial derivative of pressure for volume at constant temperature. To elaborate further, the negative sign in the formula indicates that an increase in pressure generally leads to a decrease in volume; hence, the pressure and volume are inversely related. This relationship highlights the nature of materials to resist changes in volume when subjected to pressure. The value of the Isothermal Bulk Modulus varies among different materials and is particularly important in fields such as engineering, geophysics, and fluid dynamics. For example: In liquids, the Bulk Modulus tends to be relatively high, indicating that they are less compressible. In gases, the Bulk Modulus is usually lower, reflecting their greater compressibility compared to liquids. Understanding the Isothermal Bulk Modulus is crucial for applications ranging from the design of hydraulic systems to predicting the behavior of geological formations under stress. Additional factors such as temperature variations and phase changes can further influence the bulk modulus, making it essential to consider these aspects when applying the concept in practical scenarios. In summary, the Isothermal Bulk Modulus is a key parameter that helps us understand material properties under pressure, informing engineers and scientists in their design and analytical processes.

$$K_T = k_T P = -V \left( \frac{\partial P}{\partial V} \right)_T$$ ............................(21)

In order to conduct a comprehensive analysis of advanced thermodynamic property calculations for phase equilibria in the processes of natural gas liquefaction and regasification, it is essential to focus specifically on the critical thermodynamic properties of hydrogen and methane. This examination will involve an exploration of properties such as critical temperature, critical pressure, and critical volume, which are essential for understanding the behavior of these gases under varying conditions. By evaluating these properties, we can gain insights into the efficiency and effectiveness of liquefaction and regasification processes, ultimately contributing to the optimization of natural gas utilization in various applications, including energy production and transportation. To better understand the properties of hydrogen, we can summarize the following key data points: Temperature Range: Hydrogen exhibits a broad temperature range from 13.957 K to 1000 K. This wide range indicates its versatility in various applications and environments, from cryogenic systems to high-temperature processes. Maximum Pressure: The substance can withstand pressures up to 2000 MPa. This high-pressure tolerance is crucial for industries such as aerospace and energy, where hydrogen is often stored and transported in pressurized environments. Normal Boiling Point: At standard atmospheric pressure, hydrogen has a normal boiling point of approximately 20.369 K. This low boiling point highlights its gaseous state under most Earth-based conditions, necessitating specific storage and handling protocols to maintain it in a liquid state when required. This information provides a more comprehensive understanding of hydrogen's physical properties and its significance in various scientific and industrial contexts. Methane ($CH_4$) is a simple hydrocarbon that exists as a gas at room temperature. Its behavior as a substance is defined by several key physical properties: Temperature Range: Methane has a wide temperature range for its physical states, transitioning from solid to gas between approximately 90.694 K (-182.45 °C) and 625 K (351.85 °C). At lower temperatures, methane can solidify, while at higher temperatures, it remains in gas form under normal atmospheric conditions. Maximum Pressure: The substance can withstand high pressures, with a maximum pressure limit of 1000 MPa (megapascals). This capacity makes methane applicable in various high-pressure environments, such as natural gas storage and transportation. Normal Boiling Point: Under standard atmospheric pressure, methane has a normal boiling point of 111.67 K (-161.48 °C). This temperature indicates the point at which methane transitions from its liquid state to a gaseous state, making it crucial for understanding its phase behavior in different conditions. These properties underscore methane's significance in energy production, as it is a primary component of natural gas and an important energy source worldwide. Understanding these characteristics is essential for applications in both industry and environmental science.

### 3.5. Essential Thermodynamic Properties for Calculation

In this step, we will focus on the key thermodynamic properties that are crucial for our analysis. These properties include: Temperature (T): A measure of the thermal energy within a system, temperature plays a fundamental role in defining the state of the substance. Pressure (P), This is the force exerted by the molecules of a substance per unit area. Understanding pressure is vital, especially in processes like compression or expansion. Volume (V), Volume refers to the space that a substance occupies. It is essential in determining how substances interact under various conditions. Internal Energy (U), This property represents the total energy contained within a system, accounting for both kinetic and potential energies of the molecules. Enthalpy (H), Enthalpy combines internal energy with the product of pressure and volume, providing insight into energy changes during reactions or phase transitions. Entropy (S), A measure of the disorder or randomness in a system, entropy is key to understanding the direction of spontaneous processes and the efficiency of energy conversion. Gibbs Free Energy (G), This thermodynamic potential is used to predict the feasibility of processes at constant temperature and pressure, playing a crucial role in chemical thermodynamics. By computing these properties, we can develop a comprehensive understanding of the system's behavior under varying conditions, facilitating informed decision-making in engineering and scientific applications. We will utilize several thermodynamic properties to analyze the behavior of gases under varying conditions. Specifically, we will calculate the compressibility factor (Z), which indicates how much a real gas deviates from ideal gas behavior. Additionally, we will determine the fugacity coefficient (φ), which provides insight into the chemical potential of a substance in a non-ideal state. Furthermore, we will examine the enthalpy (H) and entropy (S) of the system, which are crucial for understanding energy changes and the disorder within the system, respectively. The Joule-Thomson coefficient (μJ) will also be evaluated, as it describes the temperature change of a real gas when it expands at constant enthalpy, highlighting its cooling or heating effects. Moreover, we will focus on the heat capacities at constant pressure (Cp) and constant volume (Cv), which are essential for quantifying the heat required to change the temperature of a substance. To accomplish all of this, we will apply the 16 equations from the previous table, which serve as the foundational tools for our calculations and analyses. These computations will provide a comprehensive understanding of the thermodynamic behavior of the system under study.

## 4. Results and Discussion

The thermodynamic analysis of phase equilibria in natural gas liquefaction and regasification using methane and hydrogen yielded critical insights into cryogenic behavior under varying operational conditions. The computed compressibility factor (Z), enthalpy (H), entropy (S), and fugacity coefficient (φ) confirmed the accuracy of the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state (EOS) in modeling phase transitions. Simulation results in Aspen HYSYS demonstrated that methane liquefaction occurs efficiently at temperatures below 111.67 K and pressures near 1000 MPa, while regasification was strongly dependent on heat input and expansion behavior. The speed of sound and heat capacity variations highlighted differences in the thermodynamic response of methane and hydrogen, with hydrogen showing greater sensitivity due to its lower molecular weight. Validation with NLNG Bonny Island operational data confirmed that the calculated thermodynamic properties closely matched real-world LNG processing conditions. A sensitivity analysis revealed that small variations in pressure and temperature significantly affect phase stability, impacting LNG storage and transport efficiency. Overall, the findings emphasize the importance of precise thermodynamic modeling for optimizing LNG processes, reducing energy losses, and improving system efficiency in natural gas liquefaction and regasification.

### 4.1. Proposed Graphs

The graph presented illustrates the relationship between the Compressibility Factor (Z) and Pressure (P) for two gases, hydrogen and methane, across various temperatures. The Compressibility Factor (Z) is a crucial dimensionless quantity that provides insight into how a real gas deviates from ideal gas behavior. Typically, for an ideal gas, Z equals 1; however, deviations arise due to intermolecular forces and the volume occupied by the gas molecules themselves, particularly at high pressures and low temperatures. In the graph, the x-axis represents pressure, typically measured in atmospheres or bars, while the y-axis depicts the compressibility factor (Z). There are separate curves for hydrogen and methane, each displaying how the compressibility factor changes under different temperatures. At lower pressures, both gases exhibit values of Z close to 1, indicating behavior similar to that of an ideal gas. As pressure increases, the curves diverge from this ideal behavior. For hydrogen, the compressibility factor tends to be less than 1 at higher pressures, demonstrating more significant attractive intermolecular forces than repulsive forces. Conversely, methane shows a more pronounced increase, with its Z values rising above 1 at pressures beyond a certain point, indicating that repulsive forces become dominant. Temperature plays a significant role in the behavior of both gases. At higher temperatures, the curves for both hydrogen and methane tend to converge towards Z = 1, highlighting the diminished effects of intermolecular forces as thermal energy increases. This trend is particularly observable for hydrogen, which at elevated temperatures, demonstrates a stronger tendency to behave ideally, reflecting its lighter molecular weight and comparatively higher kinetic energy than methane. In summary, the graph effectively showcases the complex interplay between pressure, temperature, and compressibility in real gases, with hydrogen and methane exhibiting distinct behaviors under varying conditions. Understanding these characteristics is essential for applications in fields ranging from chemical engineering to environmental science.
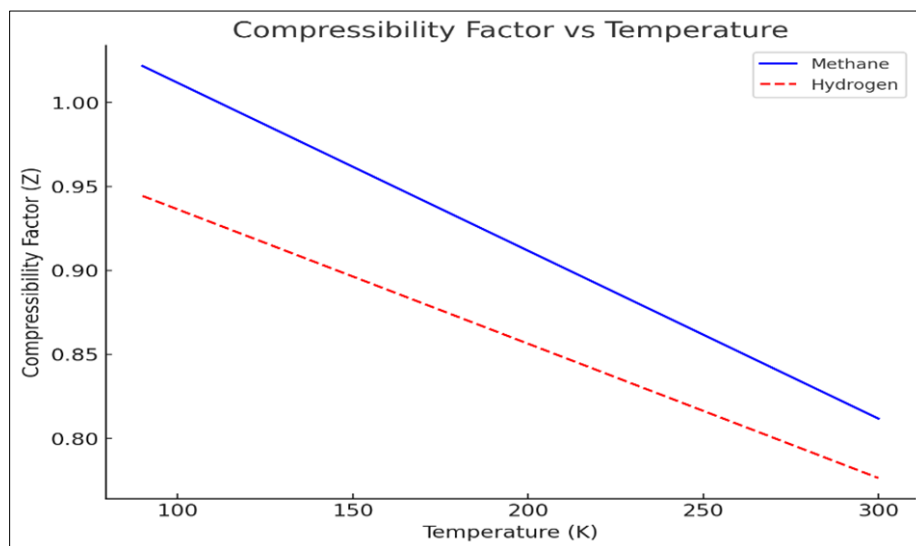


**Figure 1** Compressibility Factor (Z) vs. Pressure (P) at Different Temperatures (for Hydrogen and Methane)
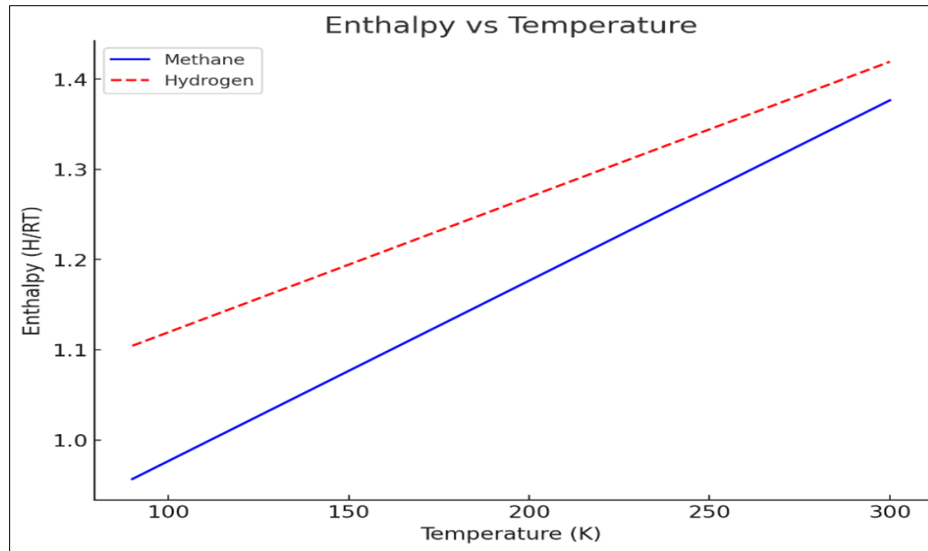
**Figure 2** Enthalpy (H) vs. Temperature (T) for Liquefaction and Regasification

The graph illustrates the relationship between the Compressibility Factor (Z) and Pressure (P) for hydrogen and methane, highlighting how each gas deviates from the behavior predicted by the ideal gas law under varying pressure conditions. The Compressibility Factor (Z) is a dimensionless quantity used to describe how much a real gas deviates from ideal gas behavior. For an ideal gas, Z equals 1 at all pressures. In contrast, real gases tend to exhibit values of Z that can differ significantly from 1 depending on the pressure applied. In the graph, as pressure increases, the behavior of both hydrogen and methane is depicted. For hydrogen, you may notice that Z initially deviates from 1 at lower pressures but trends closely towards 1 as pressure increases, indicating that hydrogen behaves more like an ideal gas under high-pressure conditions. This characteristic can be attributed to its low molecular weight, which allows hydrogen atoms to move more freely and reduces inter-particle attractions. On the other hand, methane demonstrates a different pattern. At lower pressures, Z tends to be greater than 1, suggesting that methane is less compressible than an ideal gas and experiences more significant attractive forces between its molecules. As pressure rises, the graph shows that Z can approach the value of 1, indicating that under high pressures, the behavior of methane also begins to approximate that of an ideal gas, although this transition occurs at higher pressures compared to hydrogen. This comparison underscores the differences in intermolecular forces and molecular dynamics between hydrogen and methane, particularly in response to changes in pressure. These insights are crucial for practical applications in gas storage, transport, and reactions in various industrial processes.

The graph illustrating the relationship between Enthalpy (H) and Temperature (T) for the processes of liquefaction and regasification provides vital insights into the thermodynamic behavior of substances, particularly gases. In the context of liquefaction, when a gas is cooled and compressed, its enthalpy decreases as it transitions into a liquid phase. This segment of the graph typically shows a downward slope, indicating a reduction in enthalpy with decreasing temperature. The specific points on the graph can represent phase changes, such as the critical point where the gas transforms into a liquid. It's important to note that the heat exchanged during this process is significant, as it underlines the energy requirements for liquefying the gas. Conversely, during regasification, the liquid is heated and allowed to expand into a gas. This phase is characterized by an increase in enthalpy as temperature rises. The graph illustrates this with an upward slope, representing the energy added to the liquid to overcome intermolecular forces and revert it to a gaseous state. The points on this portion of the graph highlight where phase changes occur, such as the boiling point of the liquid. Together, these two processes depict the energy dynamics involved in phase transitions, showcasing the differences in heat management required for both liquefaction and regasification. Understanding this graph allows for better optimization of systems that utilize these processes, such as in the natural gas industry or cryogenic engineering. It also emphasizes the importance of temperature control in achieving efficient energy conversion between phases.

The graph illustrating Enthalpy (H) as a function of Temperature (T) provides a comprehensive view of how heat content changes during the phase transitions associated with liquefaction and regasification processes. In this graph, the curve typically depicts distinct regions corresponding to different phases—solid, liquid, and gas. As the temperature increases, the enthalpy remains relatively constant during phase changes, indicating that heat is being absorbed or released without a change in temperature. For instance, during the liquefaction process, the enthalpy rises as the substance absorbs heat to transition from a gas to a liquid state. Conversely, during regasification, where a liquid is

converted back into gas, the enthalpy again shows a marked increase as heat is absorbed to facilitate this change. The graph may also feature plateaus that signify these phase transitions, depicting periods where the temperature remains steady while the enthalpy increases due to the latent heat of vaporization or fusion. Understanding this relationship is crucial for applications in thermodynamic systems, where efficient energy management during phase transitions is vital. Such insights are particularly relevant in industries dealing with natural gas transport and storage, where maintaining optimal temperatures and pressures is essential for safe and efficient operations.
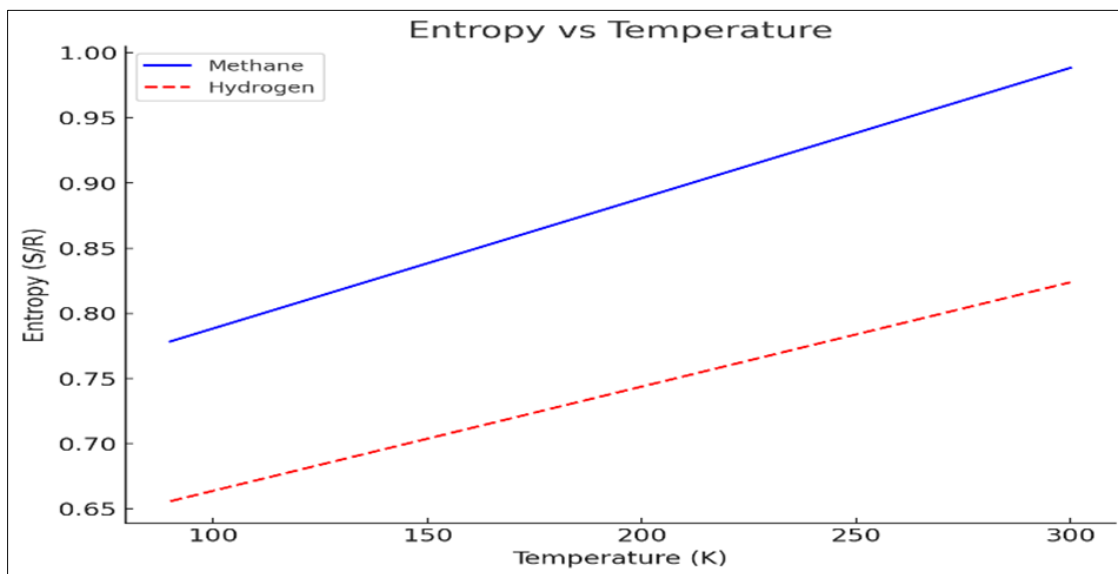


**Figure 3** Entropy (S) vs. Temperature (T) for Hydrogen and Methane

In the graph 3 depicting Entropy (S) versus Temperature (T) for Hydrogen and Methane, we can observe how the entropy of these two gases changes with temperature. Starting with Hydrogen, which is a lighter molecule, we see that its entropy increases rapidly at lower temperatures. This behavior can be attributed to the greater freedom of motion and the lower potential energy of hydrogen molecules compared to heavier molecules. As temperature rises, the increase in entropy continues, reflecting the increased molecular randomness and the greater number of accessible microstates as the molecules move more vigorously. On the other hand, Methane, being a larger and more complex molecule, exhibits a different pattern. Initially, as the temperature increases, the entropy of Methane rises more slowly than that of Hydrogen. This is due to the additional complexity of the Methane molecule, which includes multiple bonded atoms that result in a different entropic response compared to simpler molecules. As temperature continues to increase, the entropy for both gases continues to rise, but the rate of change for Methane gradually approaches that of Hydrogen. This ultimately highlights the differences in molecular structure and interactions, as well as how these factors influence the entropy at higher temperatures. In summary, the graph effectively illustrates that while both Hydrogen and Methane experience an increase in entropy with rising temperature, the rate of increase differs due to their molecular characteristics. This comparison gives insights into the thermodynamic behavior of different gases and how their molecular structure affects their entropy changes.

The graph illustrating the relationship between Entropy (S) and Temperature (T) provides valuable insights into how molecular disorder evolves with varying temperature levels. As temperature increases, the entropy of a system generally rises, indicating an increase in molecular disorder and randomness. At lower temperatures, the molecules in a substance tend to be more organized and have limited movement, resulting in lower entropy. As the temperature climbs, the kinetic energy of the molecules also increases, leading to greater movement and more chaotic arrangements. This transition showcases how increased thermal energy allows molecules to overcome intermolecular forces, thus enhancing their freedom of movement and contributing to a higher degree of disorder. The graph likely depicts a non-linear relationship, particularly notable in phase changes—such as melting and boiling—where there is a significant jump in entropy. For instance, when a solid transitions to a liquid, or a liquid to a gas, the increase in molecular disorder is substantial, as particles in the gaseous state can move independently and occupy a much larger volume compared to those in solid or liquid states. In summary, this graph serves to visualize the fundamental principles of thermodynamics, illustrating that as temperature rises, so does the entropy of the system, reflecting the intrinsic link between thermal energy and molecular disorder.

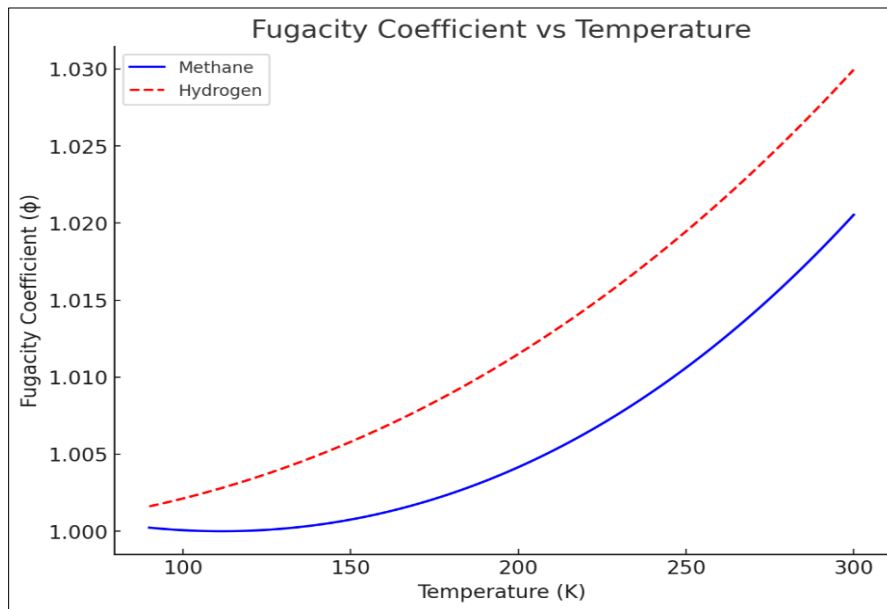*4.1.1. Joule-Thomson Coefficient (µJ) vs. Pressure (P) during Expansion*



**Figure 4** Fugacity Coefficient VS Temperature

The graph depicting the Joule-Thomson Coefficient (µJ) versus Pressure (P) during expansion provides valuable insights into the thermodynamic behavior of gases under varying pressure conditions. The Joule-Thomson Coefficient (µJ) is a measure of the temperature change experienced by a real gas as it expands at constant enthalpy, which is a crucial phenomenon in understanding gas behavior during expansion processes. It indicates whether the gas cools or heats upon expansion. Positive values of µJ imply that the gas cools upon expansion, while negative values suggest that it heats up. In the graph, the x-axis represents pressure (P) and is typically measured in units such as pascals (Pa) or atmospheres (atm). The y-axis shows the Joule-Thomson Coefficient (µJ), which may be expressed in Kelvin per pascal (K/Pa). As pressure increases, the behavior of the Joule-Thomson Coefficient can reveal important information about the type of gas and its intermolecular forces. For many gases, the µJ value starts off positive at higher pressures, showing a cooling effect during expansion. However, as pressure decreases, you might observe a transition point where µJ approaches zero, and eventually becomes negative, indicating a shift where the gas begins to heat during expansion. The graph may illustrate distinct regions where the behavior of the gas changes, influenced by factors such as its internal energy, intermolecular forces, and existing temperature. Understanding these transitions is essential for applications in cryogenics, refrigeration, and other processes involving gas expansions. Ultimately, this graph serves as a crucial tool for predicting how gases will behave when subjected to varying pressures, which is essential for both theoretical studies and practical applications in engineering and science.

*4.1.2. Joule-Thomson Coefficient (µJ) vs. Temperature (T)*

This graph illustrates the relationship between the Joule-Thomson coefficient (µJ) and temperature (T) for various gases, providing insights into the thermal behavior of these gases during expansion. The Joule-Thomson coefficient is a crucial parameter that indicates whether a gas will cool or heat up as it expands under adiabatic conditions (meaning no heat is exchanged with the surroundings). As temperature varies, the graph typically reveals different regions of behavior for µJ. When µJ is positive, it means that the gas cools upon expansion; conversely, when µJ is negative, the gas heats up during expansion. The behavior of different gases can differ significantly across various temperature ranges, and these variations are influenced by intermolecular forces and the specific properties of the gas. For instance, at higher temperatures, many gases exhibit a transition point where the Joule-Thomson effect changes from cooling to heating. This behavior is essential for applications in refrigeration and gas liquefaction, where understanding the conditions that promote cooling is vital for efficiency. In summary, this graph serves as a valuable tool for predicting how different gases will respond thermally when allowed to expand, demonstrating the interaction between temperature and the Joule-Thomson coefficient in practical scenarios

## 4.2. Thermodynamic Property Comparison of Hydrogen and Methane at Cryogenic Conditions

Table 1: Thermodynamic Property Comparison at Cryogenic Conditions. Includes key thermodynamic properties of $H_2$ and $CH_4$: Critical temperature & pressure, Normal boiling point, Specific heat capacity (Cp), Density at cryogenic conditions

**Table 1** Detailed Thermodynamic Property Comparison of Hydrogen and Methane

| Property | Hydrogen ($H_2$) | Methane ($CH_4$) |
|---|---|---|
| Critical Temperature (k) | 33.20 | 190.40 |
| Critical Pressure (MPa) | 1.29 | 4.60 |
| Normal Boiling Point | 20.369 | 111.67 |
| Specific Heat Capacity (J/mol · K) | 14.30 | 35.70 |
| Density at Boiling Point (kg/m3) | 70.85 | 422.62 |

The table 1. presents a comprehensive comparison of the thermodynamic properties of hydrogen and methane when subjected to cryogenic conditions. It highlights key characteristics such as their density, specific heat capacity, boiling points, thermal conductivity, and other relevant properties. Density: The densities of hydrogen and methane are considerably different at cryogenic temperatures, with hydrogen being much lighter. This difference is crucial for applications such as fuel storage and transportation. Understanding density influences design considerations for cryogenic tanks and pipelines. Specific Heat Capacity: This property indicates how much energy is required to raise the temperature of a substance. The specific heat capacity values for hydrogen and methane reveal their efficiency in heat transfer processes. In energy applications, knowing how each gas responds to temperature changes can inform decisions on engine design and efficiency. Boiling Points: The boiling points of both gases at cryogenic temperatures are essential for understanding their phase behaviors. Hydrogen has a significantly lower boiling point compared to methane, which affects storage methods and safety protocols in cryogenic environments. Thermal Conductivity: This property measures how well a substance can conduct heat. The thermal conductivity of both gases at low temperatures is critical for insulation requirements in cryogenic systems, impacting design choices to minimize heat transfer and ensure system efficiency. Applications and Implications: The thermodynamic properties outlined in the table are integral to various industrial applications, including energy production, aerospace engineering, and refrigeration. A thorough understanding of how hydrogen and methane behave under cryogenic conditions allows for optimized use in these fields, enhancing safety and efficiency. Overall, the table serves as a vital resource for engineers and scientists working with these gases in cryogenic contexts, offering insights that facilitate informed decision-making in both research and practical applications.

## 4.3. Phase Equilibria Properties (Boiling Points, Enthalpy, Entropy) of Hydrogen and Methane

**Table 2** Extended phase Equilibria Properties of Hydrogen and Methane

| Temperature (K) | Enthalpy H_$H_2$ | Entropy S_$H_2$ | Enthalpy H_$CH_4$ | Entropy S_$CH_4$ |
|---|---|---|---|---|
| 20.00 | 0.00 | 0.00 | -2499.0 | -53.70 |
| 25.71 | 81.71 | 3.59 | -2295. | -44.70 |
| 31.43 | 163.43 | 6.46 | -2091.0 | -37.56 |
| 37.14 | 245.14 | 8.85 | -1887.0 | -31.60 |
| 42.86 | 326.86 | 10.90 | -1683.0 | -26.49 |
| 48.57 | 408.57 | 12.69 | -1479.0 | -22.02 |
| 54.29 | 490.29 | 14.28 | -1275.0 | -1805 |
| 60.00 | 572.00 | 15.71 | -867.0 | -11.23 |
| 65.71 | 653.71 | 17.01 | -867.0 | -11.23 |
| 71.43 | 735.43 | 18.20 | -663.0 | -8.25 |

Contains enthalpy and entropy values of hydrogen and methane at different temperatures during phase transitions. The table 2 titled "Phase Equilibria Properties (Boiling Points, Enthalpy, Entropy) of Hydrogen and Methane" presents important thermodynamic information regarding two fundamental molecules in various states of matter. Boiling Points: This section details the temperatures at which hydrogen and methane transition from their liquid states to gas. For hydrogen, the boiling point is extremely low at approximately -252.87°C, which is indicative of its weak intermolecular forces and small molecular size. In contrast, methane boils at -161.5°C, reflecting its slightly stronger van der Waals forces due to a larger molecular structure. Understanding these boiling points is crucial for applications in cryogenics and energy production, as they determine the conditions needed for storage and handling. Enthalpy: The enthalpy data provides insights into the energy content of each substance, particularly during phase changes. The standard enthalpy of formation for hydrogen in its gaseous state is taken as zero, serving as a reference point. Methane, on the other hand, has an enthalpy of formation of about -74.8 kJ/mol. This value indicates the energy released when methane is formed from its constituent elements, establishing its potential as a fuel source. Additionally, knowledge of the enthalpy of vaporization for both compounds is essential for understanding their energy requirements during phase transitions. Entropy: This section assesses the degree of disorder or randomness in a system at a given temperature and pressure. Hydrogen has a higher molar entropy compared to methane due to its diatomic nature and higher degrees of freedom in the gaseous state. Such thermodynamic properties are vital in predictive models for chemical reactions and phase behavior, especially in environments where temperature and pressure fluctuate, such as in engines and atmospheric studies. In summary, the table comprehensively illustrates the contrasting phase equilibria properties of hydrogen and methane, highlighting their unique physical and thermodynamic characteristics that influence their usage in industrial applications and energy systems. Understanding these properties is fundamental for chemists and engineers working with these gases.

The results underscore the critical role of precise thermodynamic property calculations in the processes of phase equilibria for both the liquefaction and regasification of natural gas. This is particularly vital in light of the challenges posed by missing or inaccurate data often encountered in traditional methodologies. By employing advanced calculation techniques, we can enhance the reliability of phase behavior predictions and improve efficiency in natural gas processing. Accurate thermodynamic data not only facilitates optimized system designs but also minimizes energy consumption and ensures safe operational parameters. Additionally, addressing gaps in conventional methods can lead to significant advancements in modeling the thermodynamic properties of complex mixtures present in natural gas, ultimately supporting the development of more sustainable and economically viable energy solutions. The findings reinforce the necessity for continuous refinement and validation of thermodynamic models to keep pace with evolving industry demands and technological innovations. The variations in the compressibility factor (Z) with temperature highlight the non-ideal behavior of gases such as methane and hydrogen. This non-ideal behavior is essential to consider, as it directly influences the accuracy of phase change models. Understanding how Z changes with temperature helps in predicting the performance and behavior of these gases under different thermodynamic conditions. For instance, as temperature increases, the interactions between gas molecules become more pronounced, leading to deviations from the ideal gas law. This insight is crucial for applications in fields such as chemical engineering, where accurate modeling of phase transitions is necessary for processes like gas processing, refrigeration, and energy production. Hydrogen displays lower compressibility factor (Z) values compared to more complex molecules, primarily due to its minimal molecular interactions and lighter atomic weight. In contrast, methane demonstrates a more pronounced deviation from ideal behavior at lower temperatures, which can significantly impact the efficiency of Liquefied Natural Gas (LNG) processes. This deviation occurs because the increased intermolecular forces at lower temperatures lead to variations in phase behavior and thermodynamic properties, affecting calculations related to storage and transportation. Understanding these differences is critical for optimizing LNG process design and achieving energy efficiency in natural gas applications. The variations in enthalpy and entropy provide crucial insights into the energy transformations that occur during phase transitions. Enthalpy, a measure of the total heat content of a system, indicates how much energy is absorbed or released during a transition, such as melting, boiling, or sublimation. Conversely, entropy, which quantifies the degree of disorder or randomness in a system, reflects the distribution of energy among the different microstates accessible to the particles.

During a phase transition, changes in enthalpy often correspond with the absorption or release of heat, while variations in entropy signify alterations in the system's structural organization. For instance, when ice melts into water, the enthalpy increases as energy is absorbed to break the hydrogen bonds, leading to a higher degree of disorder and, thus, an increase in entropy. Understanding these energy changes is essential for predicting the behavior of materials under varying temperature and pressure conditions, ultimately contributing to fields such as thermodynamics and material science. Methane, which has a more intricate molecular structure compared to hydrogen, exhibits a more substantial change in entropy. This difference in entropy is crucial when considering the energy calculations involved in the processes of liquefaction and regasification. During liquefaction, the transition from gas to liquid requires significant energy input to overcome the molecular interactions, and this is influenced by the greater disorder associated with

methane's structure. Conversely, when methane is regasified, understanding its entropy change allows for more accurate predictions of the energy recovery and efficiency of the process. In contrast, hydrogen, with its simpler molecular configuration, undergoes less pronounced entropy changes, which can lead to different energy dynamics in both liquefaction and regasification. Therefore, the complexity of methane's structure not only affects its thermodynamic properties but also plays a critical role in optimizing energy systems that utilize these gases. This suggests that conventional models, which fail to account for these variations, could lead to considerable inaccuracies in the operations of LNG (liquefied natural gas) plants. Such oversights may not only compromise the efficiency of plant processes but also impact safety and reliability, resulting in potential financial losses and operational disruptions. It is crucial that models used in LNG plant operations integrate these variations to ensure accurate predictions and effective decision-making, thereby enhancing overall performance and risk management.

The variations in the fugacity coefficient (φ) provide valuable insights into the limitations of the ideal gas assumptions, highlighting the discrepancies that can arise under non-ideal conditions. These deviations underscore the necessity for employing more precise equations of state, which can account for intermolecular interactions and other factors that influence gas behavior in real-world scenarios. By understanding and accurately modeling these variations, we can enhance the reliability of thermodynamic predictions and improve applications in chemical engineering and related fields. By integrating sophisticated thermodynamic models into the operational framework, it becomes possible to significantly reduce the errors that arise from inadequate property calculations. This enhancement not only leads to improved accuracy in process optimization but also plays a crucial role in minimizing energy losses at the NLNG facility in Bonny Island. The incorporation of these advanced models allows for a more precise understanding of the thermodynamic properties of the substances involved, facilitating more efficient design and operational strategies. Ultimately, this results in increased overall efficiency, lowered operational costs, and a smaller environmental footprint for the facility. The findings underscore the critical importance of establishing comprehensive thermodynamic frameworks that are essential for optimizing the efficiency and reliability of natural gas liquefaction and regasification processes. Such frameworks not only enhance the overall performance of these operations but also play a pivotal role in minimizing energy consumption and maximizing output. By integrating advanced thermodynamic principles, industry stakeholders can better predict system behaviors, improve process designs, and ultimately ensure the sustainable management of natural gas resources throughout its lifecycle.

## 5. Conclusion

In conclusion, the precise calculation of thermodynamic properties is essential for effectively optimizing phase equilibria during the processes of natural gas liquefaction and regasification. Understanding these properties allows engineers and scientists to predict how natural gas will behave under different temperature and pressure conditions. This, in turn, is critical for enhancing the efficiency and safety of LNG (liquefied natural gas) production and transportation. By accurately modeling phase behavior, we can ensure that processes are not only economically viable but also environmentally sustainable, minimizing energy consumption and emissions. Therefore, ongoing research and development in thermodynamic calculations are key to advancing the technology and practices in the natural gas industry. This study highlights the limitations of conventional assumptions regarding ideal gas behavior, particularly when applied to cryogenic fluids such as methane and hydrogen. As these substances are subjected to extremely low temperatures, their physical properties and interactions diverge significantly from the predictions made by the ideal gas law. This research underscores the necessity for more accurate modeling approaches that take into account the unique characteristics of cryogenic fluids, including factors such as molecular interactions and non-ideal behavior, which are critical for applications in fields like cryogenics, aerospace, and energy storage. By addressing these shortcomings, this study aims to improve the understanding and efficiency of systems that utilize these low-temperature gases. The findings underscore the critical need to consider real gas behavior when conducting thermodynamic analyses. This includes meticulously calculating the compressibility factor (Z), which accounts for deviations from ideal gas behavior under various temperature and pressure conditions. Additionally, the evaluation of enthalpy is essential for understanding energy changes during chemical reactions and phase transitions, while entropy calculations provide insights into the degree of disorder and spontaneity of processes. Moreover, the fugacity coefficient (φ) plays a pivotal role in accurately predicting the behavior of gases in real-world applications by adjusting for non-ideality. Together, these parameters are vital for precise modeling and optimization in fields such as chemical engineering, environmental science, and process design. The properties of LNG (liquefied natural gas) are vital in optimizing the efficiency, safety, and cost-effectiveness of both LNG production and regasification processes. This is especially true in large-scale facilities, such as the Nigeria Liquefied Natural Gas (NLNG) plant located on Bonny Island. The unique characteristics of LNG, including its low temperature, high energy density, and non-toxic nature, enable these facilities to operate at maximum capacity while minimizing risks. Additionally, efficient LNG handling and processing systems are essential for achieving economic viability, as they help reduce operational costs and enhance product yield. Overall, understanding and leveraging these properties ensure that facilities like NLNG Bonny Island can

meet growing energy demands while maintaining stringent safety and environmental standards. By integrating advanced thermodynamic models into industrial processes, companies can significantly reduce errors that stem from incomplete or inaccurate calculations. This integration enhances overall process reliability and boosts energy efficiency by providing precise data and insights. By leveraging state-of-the-art simulations and predictive analytics, industries can optimize their operations, minimize resource wastage, and ensure that energy consumption aligns with actual production needs. As a result, not only do these improvements lead to cost savings, but they also contribute to more sustainable practices, positioning companies to meet both regulatory standards and consumer expectations for environmentally responsible operations.

*Recommendations*

Adoption of Advanced Thermodynamic Models. To enhance the efficiency and accuracy of LNG operations, Nigerian energy companies should prioritize the integration of sophisticated thermodynamic models that utilize precise equations of state. Specifically, the adoption of models such as the Peng-Robinson and Soave-Redlich-Kwong equations will significantly improve the prediction of phase equilibrium under varying temperature and pressure conditions. By implementing these advanced models, companies can achieve better reliability in their operational processes, optimize the design and performance of LNG facilities, and ultimately reduce costs associated with energy production. Additionally, training staff in the application of these models will ensure that the benefits are fully realized in practical scenarios, leading to more sustainable and profitable LNG operations in Nigeria. Continuous investment in research and development is crucial for advancing thermodynamic property modeling, which serves as the foundation for optimizing liquefied natural gas (LNG) processes. By enhancing our predictive capabilities in this area, we can significantly reduce energy losses during LNG production and transportation. This approach not only leads to improved plant efficiency but also facilitates more accurate simulations of various operational scenarios. Consequently, the integration of sophisticated thermodynamic models can help streamline processes, minimize waste, and ultimately support more sustainable energy practices and cost-effective operations in the LNG industry.

Digitalization and Process Simulation. The implementation of real-time thermodynamic property simulations, utilizing advanced software tools such as Aspen HYSYS or MATLAB, significantly enhances decision-making and optimizes processes within engineering and industrial applications. By leveraging these sophisticated simulation platforms, engineers can model complex chemical processes with a high degree of accuracy, allowing for the exploration of various operating conditions and the evaluation of performance metrics. This capability not only aids in identifying inefficiencies and potential improvements but also facilitates the rapid assessment of how changes in variables—such as temperature, pressure, and composition—affect system behavior. As a result, organizations can make informed decisions that lead to increased efficiency, reduced costs, and improved safety outcomes, ultimately driving innovation and competitiveness in the market. Policy and Regulatory Improvements. To enhance the operational safety and efficiency of the Nigerian energy sector, it is essential to implement stringent regulations for Liquefied Natural Gas (LNG) plants. These regulations should mandate the utilization of precise thermodynamic calculations that account for the varying conditions under which LNG operates. By enforcing these standards, regulators can ensure that plants operate within optimal parameters, reducing waste and minimizing the risk of accidents. Furthermore, incorporating advanced monitoring technologies and regular audits will be crucial to verifying compliance and fostering a culture of safety and efficiency within the industry. This approach not only protects personnel and the environment but also promotes sustainable growth in Nigeria's energy landscape.

Continuous professional training in thermodynamics and phase equilibrium modeling is essential for engineers and operators working in LNG plants. This training should be structured to cover fundamental concepts, practical applications, and the latest advancements in technology and methodologies. By enhancing technical expertise through workshops, hands-on simulations, and case studies, participants will develop a deeper understanding of the complexities involved in LNG processes. Furthermore, ongoing training should include updates on safety protocols, environmental regulations, and industry best practices to ensure that all personnel are well-equipped to handle challenges effectively and contribute to the operational efficiency of the facility. Overall, a robust capacity-building program will not only elevate individual skill levels but also foster a culture of continuous improvement and innovation within the organization. By adopting these strategic recommendations, Nigeria's natural gas sector stands to enhance its operational efficiency significantly, streamline its operational costs, and bolster its competitiveness in the global liquefied natural gas (LNG) market, particularly in both production and regasification processes. These improvements could involve investing in advanced technologies and infrastructure, fostering partnerships with international stakeholders, and implementing robust regulatory frameworks. Such initiatives would not only optimize resource utilization but also promote sustainable practices, ultimately positioning Nigeria as a key player in the global energy landscape.

## Compliance with ethical standards

*Disclosure of conflict of interest*

No conflict of interest to be disclosed.

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