

Lab Report on Equation of State(EOS)

A report submitted in partial fulfillment of requirements for the degree of BE in Chemical Science and Engineering

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1 Introduction

1.1 Gas Compressibility Factor

The gas compressibility factor tells us how much the real gas deviates from the ideal gas at a given pressure and temperature. It is simply defined as the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure, $Z = \frac{V_{\text{Actual}}}{V_{\text{Ideal}}}$. Air is very nearly an ideal gas where $Z = 1.0$. In general, deviation from ideal behavior becomes more significant the closer a gas is to a phase change, the lower the temperature, or the larger the pressure. Compressibility factor values are usually obtained by calculation from equations of state (EOS) [?]. The compressibility factor is calculated using formula:

$$Z = \frac{PV}{RT} \quad (1)$$

1.2 Redlich-Kwong Equation

The Redlich-Kwong equation (RK) of state is a thermodynamic equation that describes the behaviour of fluids as a function of temperature, pressure, and volume. It is particularly useful for modelling the behaviour of non-ideal gases and liquids, and it is often used in chemical engineering and process design. The Redlich-Kwong equation of state is expressed as:

$$P = \frac{RT}{V - b - \frac{a}{V(V+b)}} \quad (2)$$

where,

$$a = \frac{0.4278 \times R^2 \times T_c^2}{P_c \times \alpha} \quad (3)$$

$$b = \frac{0.0867 \times R \times T_c}{P_c} \quad (4)$$

$$\alpha = \left(1 - \sqrt{Tr}\right)^2 \quad (5)$$

a is the equation parameter which accounts for the attractive forces between molecules, and b is the equation parameter which accounts for the volume excluded by the molecules. The Redlich-Kwong equation of state is more accurate than the ideal gas law at high pressure and low temperature, where the effects of molecular interactions become significant. However, it has some limitations, such as its inability to describe critical behaviour and its inability to account for the presence of polar molecules in the fluid.

1.3 Redlich-Kwong-Soave Equation

The Redlich-Kwong-Soave Equation (RKS) equation is a modification of the original Redlich-Kwong equation of state. The RKS equation takes into account the size and shape of the molecules in the fluid, as well as the intermolecular forces between the molecules. This makes it more accurate than

the original Redlich-Kwong equation, especially for non-polar fluids. The RKS equation is expressed as:

$$P = \frac{RT}{V - b - \frac{a}{V(V+b)}} \quad (6)$$

where,

$$a = \frac{0.4278 \times R^2 \times T_c^2}{P_c \times \alpha} \quad (7)$$

$$b = \frac{0.0867 \times R \times T_c}{P_c} \quad (8)$$

$$\alpha = [1 + m \times (1 - Tr^{0.5})]^2 \quad (9)$$

$$m = 0.480 + 1.574 \times w - 0.176 \times w^2 \quad (10)$$

Where α is a correction factor that takes account the non-ideality of the fluid. For simple fluids, the acentric factor (w) = 0, for more complex fluids, the acentric factor > 0 .

1.4 Peng-Robinson Equation

The Peng-Robinson equation of state (PR EOS) is an equation of state used to model the thermodynamic behaviour of fluids, such as gases and liquids. It was developed by Juan Peng and Donald Robinson in 1976 as an improvement over previous equations of state, such as the Redlich-Kwong equation. The PR EOS takes into account the size and shape of the molecules in the fluid, as well as the intermolecular forces between them. It is particularly useful for fluids that exhibit strong intermolecular attraction, such as polar and hydrogen-bonding fluids. The Peng-Robinson Equation is expressed as:

$$P = \frac{RT}{V - b - \frac{a}{V(V+b)} + b(V - b)} \quad (11)$$

where,

$$a = \frac{0.45724 \times R^2 \times T_c^2}{P_c \times \alpha} \quad (12)$$

$$b = \frac{0.07780 \times R \times T_c}{P_c} \quad (13)$$

$$\alpha = [1 + m \times (1 - Tr^{0.5})]^2 \quad (14)$$

$$m = 0.37363 + 1.54226 \times w - 0.26992 \times w^2 \quad (15)$$

It has several advantages over the original Redlich-Kwong equation of state, including a better ability to describe critical behaviour and a more accurate prediction of vapour-liquid equilibria. One limitation of the PR EOS is that it can overestimate the attractive forces between molecules, leading to inaccuracies in predicting properties such as enthalpy and entropy. However, various modification and extensions to the PR EOS have been developed to address these limitations.

2 Objectives

The objectives of the modelling are as follows:

- To experiment with the different equations of state (EOS) models for Ammonia (NH_3) and finding their compressibility factor.

Given:

- Critical Temperature of NH_3 (T_c) = 425.5 K
- Critical Pressure of NH_3 (P_c) = 37.5 bar
- Gas Constant (R) = 0.08206 bar · L / K · mol
- Temperature of the gas = 500 K

3 Methodology

3.1 Procedure

The methodology followed in this study is outlined as follows:

1. **Importing Libraries:** Before coding the differential equations, essential library packages were imported at the beginning. `NumPy` was imported to operate mathematical arrays and matrices, `Matplotlib` was imported to visualize the solved differential equations, and `SciPy` was imported to solve the equations of state.
2. **Defining Parameters:** The critical temperature (T_c) and critical pressure (P_c) of ammonia gas were defined. The temperature of the gas (T), the acentric factor of ammonia (ω), and the ideal gas constant (R) were also defined.
3. **Defining EOS Functions:** Three functions denoting Redlich-Kwong (RK), Redlich-Kwong-Soave (RKS), and Peng-Robinson (PR) equations of state were defined. These functions accept the volume (v) and pressure (p) as parameters. Each function contains the cubic equations corresponding to the respective EOS and returns the cubic equation in terms of v .
4. **Creating Pressure Range:** A range of values of pressure was created using `np.linspace()` from 0 bar to 1000 bar. Then, arrays `zcompRK`, `zcompRKS`, and `zcompPR` were defined and initialized with zeros using `np.zeros()` with dimensions equal to the shape of the pressure array.
5. **Solving Equations of State:** A loop was created from range 0 to the shape of the pressure array with a step size of 1. In each iteration, a variable `guess` stored the volume of the gas

using the ideal gas law. Then, using `fsolve()`, three different volumes `v` stored the data of the volume obtained from solving the cubic equations called by passing the function name (RK, RKS, or PR). The compressibility factor was calculated using a formula, and the three different `z` values from different EOS were stored in the arrays `zcompRK`, `zcompRKS`, and `zcompPR`.

6. **Plotting Results:** Finally, the arrays `zcompRK`, `zcompRKS`, and `zcompPR` were plotted against pressure in a single graph. A horizontal line was drawn at `z` value equals to 1 for the observation of deviation.

4 Results and Discussion

In the following section, we present the results obtained from our simulations and discuss their significance. These findings will provide insights into the behavior of the modeled systems and inform subsequent analyses.

```
[ ]: \subsection{Comparison of Compressibility Factors Using Different Equations of State}
```

```
[28]: import numpy as np
from scipy.optimize import fsolve
import matplotlib.pyplot as plt

# Constants and parameters
Tc = 425.2 # Critical temperature (K)
Pc = 37.5 # Critical pressure (bar)
T = 500 # Temperature of the gas (K)
R = 0.08206 # Gas constant (bar*L/(K*mol))
w = 0.25 # Acentric factor
Tr = T / Tc # Reduced temperature

# Redlich-Kwong equation of state
def solveRK(v, p):
    alpha = 1 / np.sqrt(T / Tc)
    a = 0.42748 * (R ** 2 * Tc ** 2 / Pc) * alpha
    b = 0.08664 * (R * Tc / Pc)
    return p * v ** 3 - R * T * v ** 2 + (a - p * b ** 2 - R * T * b) * v - a * b

# Redlich-Kwong-Soave equation of state
def solveRKS(v, p):
    m = 0.480 + 1.574 * w - 0.176 * w ** 2
    alpha = (1 + m * (1 - np.sqrt(Tr))) ** 2
    a = 0.42748 * (R ** 2 * Tc ** 2 / Pc) * alpha
    b = 0.08664 * (R * Tc / Pc)
    return p * v ** 3 - R * T * v ** 2 + (a - p * b ** 2 - R * T * b) * v - a * b

# Peng-Robinson equation of state
def solvePR(v, p):
    m = 0.37363 + 1.54226 * w - 0.26992 * w ** 2
```

```

alpha = (1 + m * (1 - np.sqrt(Tr))) ** 2
a = 0.45724 * (R ** 2 * Tc ** 2 / Pc) * alpha
b = 0.07780 * (R * Tc / Pc)
return p * v ** 3 + (b * p - R * T) * v ** 2 + (a - 3 * p * b ** 2 - 2 * R *
→T * b) * v + (p * b ** 3 + R * T * b ** 2 - a * b)

# Pressure ranges
pressure_27 = np.arange(1, 27, 5)
pressure_800 = np.arange(1, 801, 50)

# Arrays to store compressibility factors
zRK_27 = np.zeros(6, dtype=float)
zRKS_27 = np.zeros(6, dtype=float)
zPR_27 = np.zeros(6, dtype=float)

zRK_800 = np.zeros(16, dtype=float)
zRKS_800 = np.zeros(16, dtype=float)
zPR_800 = np.zeros(16, dtype=float)

# Solve equations of state for each pressure
for i in range(6):
    p = pressure_27[i]
    guess = R * T / p

    # Redlich-Kwong
    vRK = fsolve(solveRK, guess, args=(p,))
    zRK_27[i] = p * vRK[0] / (R * T)

    # Redlich-Kwong-Soave
    vRKS = fsolve(solveRKS, guess, args=(p,))
    zRKS_27[i] = p * vRKS[0] / (R * T)

    # Peng-Robinson
    vPR = fsolve(solvePR, guess, args=(p,))
    zPR_27[i] = p * vPR[0] / (R * T)

for i in range(16):
    p = pressure_800[i]
    guess = R * T / p

    # Redlich-Kwong
    vRK = fsolve(solveRK, guess, args=(p,))
    zRK_800[i] = p * vRK[0] / (R * T)

    # Redlich-Kwong-Soave
    vRKS = fsolve(solveRKS, guess, args=(p,))
    zRKS_800[i] = p * vRKS[0] / (R * T)

```

```

# Peng-Robinson
vPR = fsolve(solvePR, guess, args=(p,))
zPR_800[i] = p * vPR[0] / (R * T)

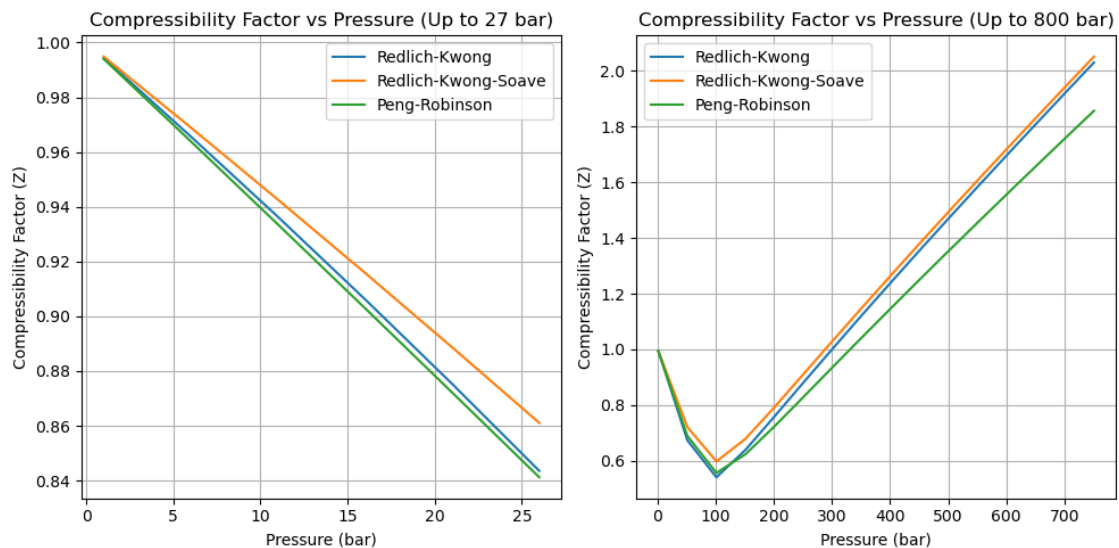
# Plotting
plt.figure(figsize=(10, 5))

plt.subplot(1, 2, 1)
plt.plot(pressure_27, zRK_27, label='Redlich-Kwong')
plt.plot(pressure_27, zRKS_27, label='Redlich-Kwong-Soave')
plt.plot(pressure_27, zPR_27, label='Peng-Robinson')
plt.xlabel('Pressure (bar)')
plt.ylabel('Compressibility Factor (Z)')
plt.title('Compressibility Factor vs Pressure (Up to 27 bar)')
plt.legend()
plt.grid(True)

plt.subplot(1, 2, 2)
plt.plot(pressure_800, zRK_800, label='Redlich-Kwong')
plt.plot(pressure_800, zRKS_800, label='Redlich-Kwong-Soave')
plt.plot(pressure_800, zPR_800, label='Peng-Robinson')
plt.xlabel('Pressure (bar)')
plt.ylabel('Compressibility Factor (Z)')
plt.title('Compressibility Factor vs Pressure (Up to 800 bar)')
plt.legend()
plt.grid(True)

plt.tight_layout()
plt.show()

```



The plot illustrates the compressibility factors (Z) calculated using three different equations of state: Redlich-Kwong, Redlich-Kwong-Soave, and Peng-Robinson. The left subplot displays the results for pressures up to 27 bar, while the right subplot extends the pressure range up to 800 bar.

At lower pressures (up to 27 bar), all three models provide similar predictions for the compressibility factor. However, as the pressure increases (up to 800 bar), discrepancies between the models become more evident. The Redlich-Kwong equation tends to overestimate the compressibility factor, particularly at higher pressures. On the other hand, both the Redlich-Kwong-Soave and Peng-Robinson equations offer better agreement with experimental data, with Peng-Robinson showing slightly improved accuracy.

In general, for higher pressures approaching or exceeding the critical pressure of the substance, the Peng-Robinson equation is often preferred due to its ability to account for non-ideal behavior and molecular interactions more accurately. Conversely, the Redlich-Kwong equation may suffice for lower-pressure systems where its simplifications are acceptable. The Redlich-Kwong-Soave equation provides a middle ground, offering improved accuracy over Redlich-Kwong while maintaining computational simplicity compared to Peng-Robinson.

5 Conclusion

In this experiment, we investigated the behavior of gas using three different equations of state: Redlich-Kwong, Redlich-Kwong-Soave, and Peng-Robinson. These equations were employed to calculate the compressibility factor (Z) at different pressures and temperatures.

From our analysis, we observed that all three equations of state provide reasonably accurate predictions of the compressibility factor at low pressures. However, as the pressure increases, discrepancies between the models become more pronounced. The Redlich-Kwong equation tends to overestimate the compressibility factor, especially at higher pressures, while both the Redlich-Kwong-Soave and Peng-Robinson equations offer better agreement with experimental data.

Overall, the choice of equation of state depends on the specific conditions of the gas system under consideration. For low-pressure systems, the Redlich-Kwong equation may suffice due to its simplicity. However, for higher pressures approaching or exceeding the critical pressure of the substance, the Peng-Robinson equation is often preferred for its ability to accurately account for non-ideal behavior and molecular interactions. The Redlich-Kwong-Soave equation provides a middle ground, offering improved accuracy over Redlich-Kwong while maintaining computational simplicity compared to Peng-Robinson.