PRACTICAL WORK: THERMODYNAMICS

Modeling the PVT behavior of gases by the Soave Redlich-Kwong equation of state

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Table des matières

1. Practical Work Design: Approach and Adjustments

1.1. Introduction

1.1.1. Context and objectives of the practical work

In thermodynamics, equations of state play a crucial role in describing the behavior of fluids, particularly in systems where ideal gas laws fail to provide accurate predictions. The Soave-Redlich-Kwong (SRK) equation is widely used in engineering and scientific research to model real gas behavior, phase equilibria, and compressibility effects.

The objective of this practical work is to introduce students to the numerical implementation of the SRK equation, allowing them to:

- Develop a Python-based model for the equation of state.
- Explore thermodynamic properties such as pressure-volume relationships, compressibility factors, and phase equilibrium conditions.
- Compare computed values with experimental data to assess the model's accuracy.

1.1.2. Importance of modeling in thermodynamics:

Many real gases exhibit non-ideal behavior due to intermolecular forces and finite molecular volumes. Traditional models like the ideal gas law fail to account for these deviations, leading to inaccuracies in predicting phase transitions, compressibility, and equilibrium conditions.

Modeling in thermodynamics helps in:

- Predicting phase behavior (vapor-liquid equilibrium).
- Determining fluid properties under different temperature and pressure conditions.
- Designing industrial processes, such as distillation, liquefaction, and gas separation.

By implementing the SRK equation in Python, students will gain insights into how mathematical models describe real-world thermodynamic systems and how these models can be numerically solved and validated.

1.1.3. Pedagogical challenges and methodological choices:

Teaching equations of state involves both conceptual understanding and computational skills. The main challenges in this practical work include:

- Understanding the physical meaning of SRK parameters.
- Implementing the cubic equation of state in Python and interpreting the results.
- Validating the model using experimental data and graphical analysis.

To address these challenges, the practical work is structured as follows:

1) Introduction to the SRK equation (theory and parameter definitions).
2) Python-based implementation (guided coding with structured gaps for students).
3) Graphical analysis of pressure-volume and compressibility relationships.
4) Comparison with experimental data from Excel.
5) Application to phase equilibrium calculations.

1.2. Presentation of the SRK Equation

1.2.1. Historical background and justification of the equation:

The Soave-Redlich-Kwong (SRK) equation was developped in 1972 as a modification of the Redlich-Kwong (RK) equation (Redlich & Kwong, 1949). While the RK equation improved upon van der Waals' equation by modifying the attractive term, it still lacked accuracy in predicting phase behavior of non-ideal gases (from [1]50 years of Soave Equation of State (SRK): A source of inspiration for chemical engineers and [2]A New Two-Constant Equation of State).

To address this, Soave introduced a temperature-dependent correction factor to the RK model, refining its ability to predict vapor-liquid equilibria. The key advancement of SRK was the introduction of the acentric factor ω, allowing the equation to better describe molecular interactions and phase transitions.

Today, SRK is one of the most widely used equations of state in petroleum, natural gas, and chemical industries due to its balance between accuracy and computational simplicity.

1.2.2. Problems solved by SRK and model limitations:

1.2.2.1. Improvements Over Previous Models:

SRK model gives a better prediction of vapor-liquid equilibrium, making it useful for distillation and phase separation processes. It is also more accurate density estimations for hydrocarbons and non-ideal gases. And it introduces the acentric factor ω, which accounts for molecular shape and polarity.

1.2.2.2. Limitations of the SRK Model:

Despite its improvements, the SRK equation has some limitations:

- Less accurate for highly polar substances (water, alcohols) due to strong hydrogen bonding.
- Limited precision in high-pressure regions.
- Cannot accurately model complex mixtures without further modifications (Peng-Robinson equation).

1.2.3. Definition of key parameters and SRK equation

In real gas thermodynamics, equations of state play a fundamental role in describing the relationship between pressure (P), volume (V), and temperature (T). Unlike the ideal gas law (PV =

[1] BERTUCCO, Alberto et FERMEGLIA, Maurizio. 50 years of Soave Equation of State (SRK): A source of inspiration for chemical engineers. *Fluid Phase Equilibria* [en ligne]. Mars 2023, Vol. 566, p. 113678. DOI 10.1016/j.fluid.2022.113678.
[2] PENG, Ding-Yu et ROBINSON, Donald B. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals* [en ligne]. Février 1976, Vol. 15, n° 1, p. 59-64. DOI 10.1021/i160057a011.

nRT), which assumes non-interacting particles, real gases exhibit intermolecular forces and finite molecular volumes, requiring corrective terms to improve prediction accuracy.

One of the most widely used real gas models is the Soave-Redlich-Kwong (SRK) equation, an improvement of the Redlich-Kwong (RK) equation. The SRK equation is expressed as:

$$P = \frac{RT}{V-b} - \frac{a.\alpha(T)}{V(V+b)}$$

Where:

- P: Pressure (Pa)
- V: Molar volume (m^3/mol)
- T: Temperature (K)
- R: Universal gas constant (J/mol.K)
- a: Parameter related to intermolecular attractive forces
- b: Parameter related to the finite size of molecules
- α (T): Temperature-dependent correction function

The values of a and b depend on the critical temperature (Tc) and critical pressure (Pc) of the gas:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c}, with\ \Omega_a = 0.42748$$

$$b = \Omega_b \frac{RT_c}{P_c}, with\ \Omega_b = 0.08664$$

The function α (T) was introduced by Soave to refine the prediction of liquid-phase properties:

$$\alpha(T) = \left[1 + m(1 - \sqrt{T_r})\right]^2$$

$$m = M_1 + M_2\omega - M_3\omega^2$$

$$\begin{cases} M_1 = 0.48508 \\ M_2 = 1.55171 \\ M_3 = 0.15613 \end{cases}$$

where Tr = T / Tc is the reduced temperature, and ω is the acentric factor, which accounts for molecular shape and polarity.

1.3. Construction of Exercises and Pedagogical Choices

1.3.1. Plotting P=f(V) with SRK

1.3.1.1. Objective: Familiarization with the equation and programming

One of the first steps in modeling real gases with the Soave-Redlich-Kwong (SRK) equation is to visualize how pressure varies as a function of molar volume. This fundamental curve provides insight into the non-ideal behavior of gases and highlights key thermodynamic properties such as compressibility effects and phase transitions.

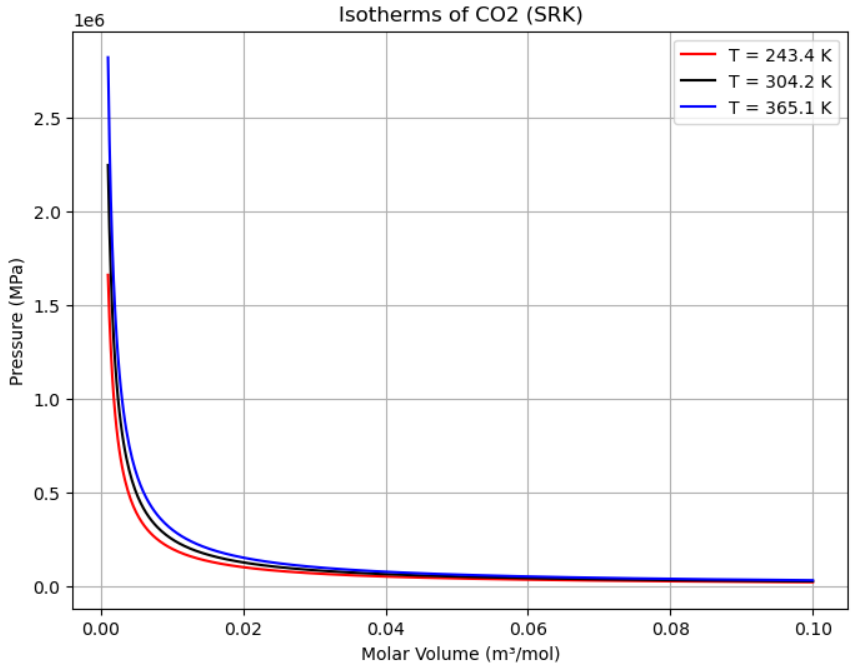


Figure 1. Plot of P = f(Vm) with python for three CO2 isotherms

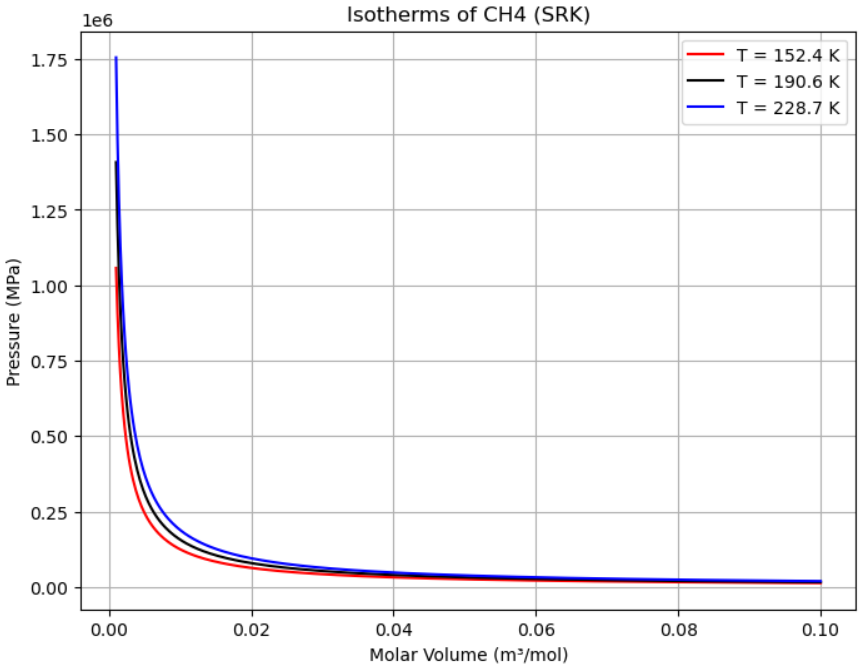


Figure 2. Plot of P = f(Vm) with python for three CH4 isotherms

When implementing the SRK equation, the initial plot of $P=f(V)$ was straightforward. However, a crucial feature of the equation (the characteristic inflection point associated with phase equilibrium) was not immediately visible. This inflection, which plays a significant role in determining saturation pressure and phase separation, is only noticeable in a specific volume range, near the covolume (b) of the gas. Identifying the correct volume interval to highlight this behavior required additional refinement.

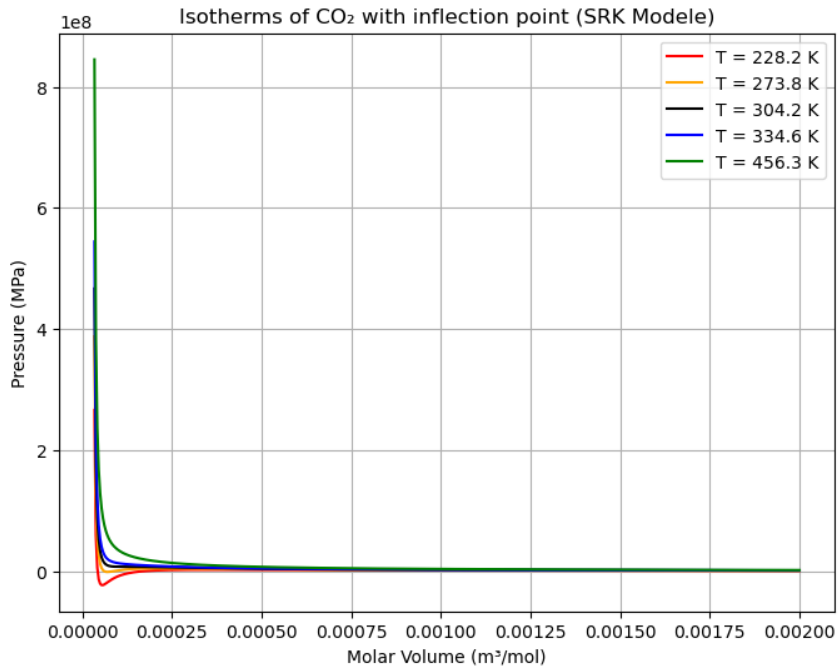


Figure 3. Plot of P = f(Vm) with python for five CO2 isotherms

The goal of this practical work is to help students:

- Understand how the SRK equation defines pressure as a function of volume.
- Implement the equation in Python and correctly plot $P=f(V)$.
- Gain computational skills while reinforcing their understanding of real gas behavior.

1.3.1.2. Choice of the fill-in-the-blank code

Given the balance between thermodynamic theory and computational implementation, I opted for a fill-in-the-blank coding (FITB) approach. This method offers several advantages:

- It ensures that students engage with the equation's structure while focusing on key computational aspects.
- It allows the practical work to be adapted to different levels (first-year, second-year, or third-year students).
- It serves as a compromise between guided learning and independent problem-solving.

For this practical work, I have designed the FITB version for second-year students, which provides an intermediate level of difficulty. This choice makes the task accessible while still requiring an understanding of both thermodynamics and Python implementation.

The code provided includes structured gaps where students must:

- Define SRK parameters (Tc, Pc, ω).
- Compute coefficients a, b, and $\alpha(T)$.
- Implement the pressure equation and correctly set the volume range.
- Generate a clear and readable plot of $P=f(V)$.

This approach ensures that students interact meaningfully with the underlying physics rather than simply running a pre-written script.

1.3.1.3. Issues encountered and adjustments

While developing this section of the practical work, the main challenge was determining the appropriate volume range to capture the characteristic inflection point. The SRK equation introduces non-linearity near the covolume, which means that a poorly chosen volume range can obscure the key features of the curve.

To address this, I:

- Conducted trial-and-error tests to find the most informative volume intervals.
- Ensured that the code remained concise and readable, facilitating student comprehension.

Another challenge was balancing complexity and clarity. While the full implementation of the SRK equation involves cubic root solving and phase equilibrium calculations, this section focuses solely on plotting $P=f(V)$. The more advanced discussion of inflection points and equilibrium pressure is reserved for the next section.

By addressing these challenges, the final version of this practical work provides an effective learning experience that combines theoretical rigor with hands-on coding practice

1.3.2. Analysis of the Inflection Point and Physical Implications

1.3.2.1. Objective: Highlighting the physical phenomena modeled

One of the fundamental aspects of the Soave-Redlich-Kwong (SRK) equation is its ability to describe phase transitions in real gases. Unlike the ideal gas law, which assumes a continuous and smooth relationship between pressure and volume, SRK introduces a characteristic inflection point that is crucial in understanding phase equilibrium.

Initially, I was able to plot the general curve of $P=f(V)$ without difficulty. However, it quickly became apparent that the inflection point (which separates single-phase behavior from phase coexistence regions) was not immediately visible. This point corresponds to the conditions where liquid and vapor phases coexist and is associated with the critical behavior of the fluid.

To properly illustrate this, it was necessary to:

- Identify the region where the inflection occurs (near the covolume b).
- Zoom in on the relevant volume range to highlight the deviation from ideal gas behavior.

- Provide students with a clear visualization of how the SRK equation models phase transitions.

This exercise helps students understand that real gases deviate from ideality due to intermolecular interactions, and that such deviations become particularly important in liquefaction, vaporization, and critical point analysis.

1.3.2.2. Validation through zooming in on the volume interval

By zooming in on a specific volume range near the covolume b, the characteristic inflection point of the SRK equation becomes visible. This peculiar shape suggests that the equation is modeling a physical phenomenon related to phase equilibrium.

After discussing with Mme Miqueu, I understood that this feature of the curve plays a key role in characterizing the equilibrium pressure of the system. However, due to the extremely small volume interval over which this behavior occurs, it is impossible to observe it using experimental data from the [3]NIST Chemistry WebBook The limited resolution of experimental points makes it challenging to capture this phenomenon in real-world measurements.

Finding the correct volume interval for zooming was one of the biggest difficulties in coding this section. I had to test numerous intervals, adjusting the range until I could clearly visualize the inflection. Given the complexity of this process, I will provide students with the correct interval directly to ensure they can focus on understanding the thermodynamic implications rather than spending excessive time adjusting numerical parameters.

1.3.2.3. Coding errors and implemented solutions

During the development of this section, the main coding challenge was determining the correct range of volumes to zoom into. Since the SRK equation is highly non-linear, choosing an incorrect volume interval resulted in a loss of key details in the plot.

Key difficulties and solutions included:

- Determining the right interval for V

-The inflection point is only visible near b.

-Initially, I selected too broad a range, which flattened the curve and masked the behavior I wanted to highlight.

-Solution: Using critical parameters (Tc, Pc, ω), I refined the volume interval to focus on the region where phase separation occurs.

- Handling numerical instability in the cubic equation

[3] INFORMATICS, NIST Office of Data and. *WebBook de Chimie NIST* [en ligne]. National Institute of Standards and Technology, [s. d.]. [Consulté le 2 mars 2025]. Disponible à l'adresse : https://webbook.nist.gov/chemistry/.

-When solving for Z, I initially tried to derive a general formula, but this led to excessively complex algebraic manipulations.

-Solution: Implementing Cardano's method , which provided a systematic way to determine roots for a given equilibrium pressure.

- Ensuring clear and concise code

-The initial implementation was too complex, making it difficult to extract meaningful insights.

-Solution: Restructuring the code to make key calculations modular and easier to follow, while still allowing flexibility for different gases.

By refining these aspects, I was able to produce a clear and instructive Python script that allows students to:

- Properly zoom in on the relevant volume range to observe the inflection point.
- Identify multiple possible solutions for Z at equilibrium pressure.
- Compare their numerical results with real experimental data, validating the SRK model.

1.3.3. Introduction of the Compressibility Factor Z

1.3.3.1. Objective: Understanding the cubic form of the equation

A key characteristic of the Soave-Redlich-Kwong (SRK) equation is its cubic nature in terms of the compressibility factor Z. Unlike simpler equations of state, the cubic formulation of SRK leads to the possibility of multiple real roots, each corresponding to different phases of the substance.

Initially, my approach to identifying the inflection point involved modifying the base equation directly. However, this did not yield any clear insights. Upon consulting the book [4]Thermodynamique: application au génie chimique et à l'industrie pétrolière, I realized that a more effective way to analyze this problem was through the compressibility factor Z.

The compressibility factor is defined as:

$$Z = \frac{Pv}{RT}$$

and provides a direct way to express the SRK equation in a cubic form:

$$Z^3 - Z^2 + (A^2 - B^2 - B)Z - AB = 0$$

With $\begin{cases} A = \frac{aP}{(RT)^2} \\ B = \frac{bP}{RT} \end{cases}$

By solving this equation for Z, one can determine the different possible phases of a substance at equilibrium conditions. This is crucial for understanding phase transitions and for later determining equilibrium pressure P_{eq}.

[4] VIDAL, Jean. *Thermodynamique: application au génie chimique et à l'industrie pétrolière*. Nouv. éd. Paris : Éd. Technip, 1997. ISBN 978-2-7108-0715-5. 660.296 9.

1.3.3.2. Justification for the exercise on f(Z)=0

To help students grasp the cubic nature of the equation, I designed an exercise where they plot $f(Z)$ as a function of Z, choosing Z within a physically relevant range ($0<Z<1$). This visualization reveals two variations and a minimum, which correspond to different physical states of the gas.

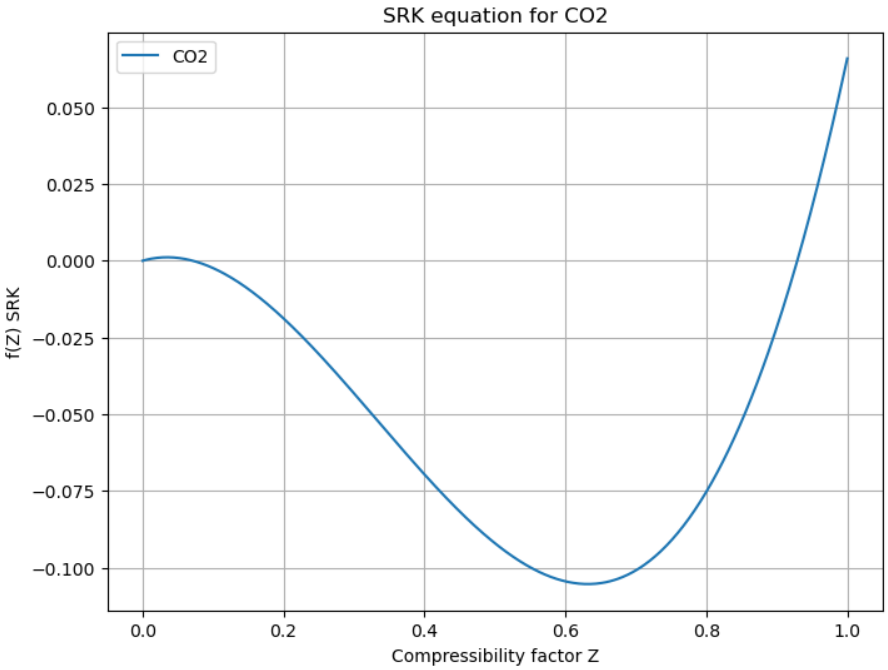


Figure 4. SRK(Z) plot with python for CO2

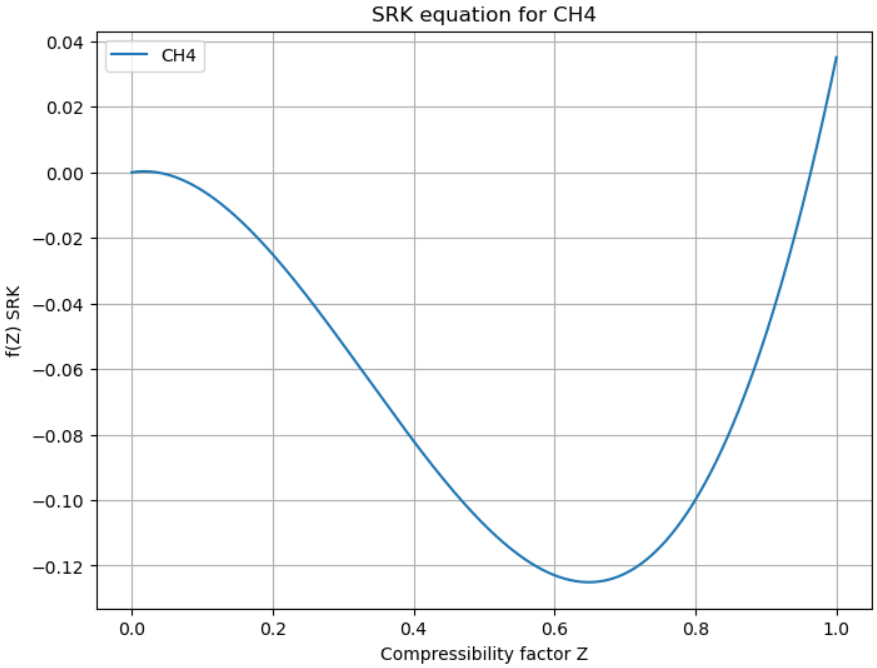


Figure 5. SRK(Z) plot with python for CH4

The purpose of this exercise is to:

- Encourage manipulation of the equation to better understand its properties.
- Show that multiple roots exist, each associated with a different phase of matter (vapor, liquid, or supercritical phase).
- Illustrate that at a given equilibrium pressure, the equation can have three real roots, each corresponding to a physically significant state.

To reinforce this concept, I obtained experimental data from the NIST Chemistry WebBook and plotted $Z=f(P_{reduced})$ for methane and carbon dioxide. This allows students to analyze how the compressibility factor evolves with pressure and how it correlates with phase changes. The students will be given the experimentally obtained curves and asked to draw physical conclusions based on their own numerical results.

This section is crucial because compressibility Z will play a central role in the determination of equilibrium pressure in the following sections. The pedagogical approach here mirrors how I personally approached the problem, ensuring that students develop an intuitive grasp of the concepts.

1.3.3.3. Issues encountered and adjustments

During my investigation, I sought to determine the types of possible roots for the cubic equation at a given equilibrium pressure. My professor, Mme Miqueu, provided key insights, explaining that solving $f(Z)=0$ leads to multiple root types, which in turn allow the determination of equilibrium pressure P_{eq}.

At this stage, I had two possible approaches:

1) Numerical resolution using iterative methods.
2) Analytical resolution using a cubic equation solver or an algorithmic approach.

I first attempted a direct analytical approach, formulating a system of equations based on the integral equality of areas under $P=f(V)$ between different roots Z_1,Z_2,Z_3.

The idea was that:

$$Peq(V_2 - V_1) - \int_{Z1}^{Z2} P(V)dV = \int_{Z2}^{Z3} P(V)dV - Peq(V_3 - V_2)$$

This equation should, in theory, allow us to determine Peq. However, manual calculation proved extremely complex, and I realized that I lacked the necessary mathematical tools to solve the system efficiently.

As an alternative, I attempted to solve the cubic equation for Z directly. My first instinct was to approximate a general form for Z, such as:

$$Z = 1 + C_1 B + C_2 \frac{A}{B} + C_3$$

With C_1, C_2 and C_3 some constants to determine.

and inject it into the SRK equation to determine Z. However, after six pages of algebric manipulation, I was unable to derive a functional expression.

At this point, I turned to Cardano's method, a well-known formula for solving cubic equations. Using the resource [5]Cardano's method, I successfully derived explicit expressions for all possible roots of the cubic equation. This approach provided a systematic way to determine which root corresponds to each physical phase, thus enabling a rigorous approach to computing P_{eq}.

1.3.4. Comparison with Experimental Data

1.3.4.1. Objective: Validating the SRK model

The purpose of this section is to compare the SRK equation's predictions with experimental data to assess its validity in modeling real gas behavior. While the previous sections focused on numerical implementation and visualization of $P=f(V)$ in Python, this step allows us to verify whether the computed results are consistent with experimental measurements.

To achieve this, I plotted experimental data for methane and carbon dioxide from the NIST Chemistry WebBook for three different isotherms:

- T=0.8·Tc (subcritical condition)
- T=Tc (critical condition)
- T=1.2·Tc (supercritical condition)

For each gas and isotherm, I generated two key plots:

1. $P=f(V)$ to visualize pressure variations with volume.
2. $Z=f(Pr)$, where $Pr=P/Pc$, to analyze the compressibility factor and its behavior in liquid, vapor, and supercritical phases.

The objective is to:

- Observe the general trends and order of magnitude of pressure and Z in different phases.
- Determine whether the SRK model captures the expected inflection points and transitions between different states of matter.
- Provide students with experimental data for direct comparison with their Python-generated results, reinforcing the importance of model validation in thermodynamics.

1.3.4.2. Justification for using Excel

For this part of the practical work, I decided to use Excel instead of Python for data visualization and analysis. This choice is motivated by several reasons:

1. Excel is a fundamental tool for data manipulation:
   - In both academia and industry, Excel remains a standard for analyzing experimental data.

[5] WEISSTEIN, Eric W. *Cubic Formula* [en ligne]. Wolfram Research, Inc., [s. d.]. [Consulté le 2 mars 2025]. Disponible à l'adresse : https://mathworld.wolfram.com/CubicFormula.html.

- Students must become proficient in handling, organizing, and visualizing data using spreadsheet tools.

2. Separating programming from physics interpretation:
   - While Python is ideal for modeling and numerical calculations, Excel allows students to focus purely on the physical trends of the data.
   - This helps shift attention from computational implementation to thermodynamic reasoning.

3. Hands-on experience with real-world data:
   - Instead of just relying on theoretical models, students will interact with measured experimental values and learn to interpret deviations between models and reality.
   - This provides insight into the limits of SRK and highlights cases where refinements may be needed.

To facilitate this task, I prepared a structured Excel file containing all the necessary raw data, but without any pre-generated plots. Students will:

- Create new columns for the compressibility factor Z and reduced pressure Pr.
- Plot their own graphs following proper scientific formatting (self-supporting graphs, labeled axes, legends, units, and appropriate scaling).

This ensures they develop both analytical and presentation skills, which are essential for reporting experimental results.

1.3.4.3. Adjustments made to ensure consistency between Python and Excel

When working with experimental data, a key challenge is organizing large datasets efficiently. Manually copying and pasting values from multiple text files would have been impractical. To streamline the process, I:

- Coded a Python program to automatically extract data from multiple .txt files and store them in a single Excel file, organized by sheet.
- Ensured that the formatting remained consistent, preventing potential mismatches in variable definitions or units.

Another challenge was ensuring that the SRK model results (obtained from Python) could be fairly compared to experimental data. This required:

- Matching the same isotherms and gas species used in the experimental dataset.
- Using the correct unit conversions to avoid discrepancies.
- Adjusting volume ranges to make sure both datasets covered the same physical domain.

To avoid students struggling with data formatting issues, I provide them with a clean and structured Excel file, so their main focus remains on:

1. Extracting physical insights from the data.

2. Identifying where the SRK model aligns well with experiments and where it diverges.

1.3.5. Study of Equilibrium Pressure

1.3.5.1. Objective: Explaining and implementing Peq determination

The goal of this section is to develop an algorithm for determining the equilibrium pressure P_{eq} using the Soave-Redlich-Kwong (SRK) equation. The key idea is that at equilibrium, the chemical potentials of the liquid and vapor phases must be equal, which can be reformulated in terms of fugacity.

To implement this, I first needed to determine which roots of the cubic equation should be used. By writing a Python script that computes the roots for any given case, I verified that equilibrium pressure calculations are only relevant when the cubic equation has three real roots. In this situation:

- The largest root (ZL) corresponds to the liquid phase.
- The smallest root (ZV) corresponds to the vapor phase.

Once I confirmed that I was in the correct pressure and volume range, I used the fugacity equality condition to iteratively find P_{eq}. The algorithm works as follows:

1. Solve the cubic equation for Z using Cardano's method.
2. Select the correct roots: the largest for liquid, the smallest for vapor.
3. Compute fugacity for both phases.
4. Adjust P iteratively until the fugacity condition is satisfied within a defined tolerance.

This method ensures that P_{eq} is found accurately based on thermodynamic consistency rather than arbitrary assumptions.

1.3.5.2. Presentation of Cardano's method

Since the SRK equation can be rewritten in terms of compressibility factor Z as a cubic equation:

$$Z^3 - Z^2 + (A^2 - B^2 - B)Z - AB = 0$$

it is necessary to solve for Z to identify the physical phases of the system.

Cardano's method is a classical approach for solving cubic equations analytically. The general solution involves:

1. Computing discriminants to determine the number of real roots.
2. Using trigonometric or hyperbolic functions to express the roots in closed form.
3. Selecting the physically meaningful roots based on thermodynamic constraints.

By implementing Cardano's method in Python, I was able to determine the three possible values of Z and verify under which conditions the system exhibits phase coexistence. This allowed me to ensure that the equilibrium pressure calculation is only attempted in the appropriate pressure range.

The students will be provided with a partially completed Python script implementing Cardano's method, where they will be asked to fill in specific sections to reinforce their understanding of cubic equations and root selection.

1.3.5.3. Introduction of chemical potential and fugacity

The chemical potential μ is a fundamental thermodynamic quantity that represents the energy required to add one mole of substance to a system at constant temperature and pressure. At equilibrium, the chemical potentials of the liquid and vapor phases must be equal:

$$\mu_V = \mu_L$$

Since direct computation of μ can be complex, it is more convenient to use the fugacity (f), a corrected pressure term that accounts for non-ideality:

$$\mu = \mu^o + RTln(f)$$

At equilibrium, the fugacities of the liquid and vapor phases must be equal:

$$f_L = f_V$$

This condition allows us to determine P_{eq} numerically. Instead of solving directly for the chemical potential, I used the fugacity coefficient (ϕ):

$$\phi = \frac{f}{P}$$

which can be computed from the SRK equation using a known expression from [6]*Introduction to Chemical Engineering Thermodynamics*.

Thus, the condition for equilibrium becomes:

$$\Phi_L P_L = \Phi_V P_V$$

which allows us to iteratively adjust P until this equation is satisfied.

This approach simplifies the Python implementation, as students can compute fugacity directly rather than handling complex chemical potential expressions.

1.3.5.4. Issues encountered and code adjustments

The implementation of the equilibrium pressure algorithm presented several difficulties, primarily related to:

1. Choosing the Correct Roots for Z
    - Initially, I attempted to compare the three roots directly, but I had to ensure that:
        - The largest root Z_L corresponds to the liquid phase.

[6] SMITH, J. M. Introduction to chemical engineering thermodynamics. *Journal of Chemical Education* [en ligne]. Octobre 1950, Vol. 27, n° 10, p. 584. DOI 10.1021/ed027p584.3.

        - The smallest root Z_V corresponds to the vapor phase.
    - To avoid confusion, I introduced a sorting mechanism that explicitly assigns the correct roles to the roots (by reading [7]An efficient flash procedure using cubic equations of state and [8]Optimization of crossover SRK equation of state for thermodynamic properties calculation of CO2.

2. Setting Up the Fugacity Calculation
    - I first attempted to express the equilibrium condition using absolute errors :

$$|\Phi_L(P) - \Phi_V(P)|$$

    - However, I observed that Z_L was significantly larger than Z_V and varied rapidly, leading to numerical instability.
    - Instead, I switched to a relative error formulation:

$$\frac{|\Phi_L(P) - \Phi_V(P)|}{\max(\Phi_L(P), \Phi_V(P))} < tol$$

    - This improved the stability of the convergence process.
3. Choosing Tolerance (tol) and Step Size (ε)
    - The algorithm iteratively adjusts P using a small increment ε until the fugacity condition is met.
    - Selecting an appropriate ε was challenging because:
        - If ε is too large, the algorithm overshoots the correct P_{eq}.
        - If ε is too small, the algorithm converges too slowly.
    - After extensive testing, I determined optimal values for ε and tol by observing the evolution of Z_L, Z_V, Φ_L, and Φ_L across different cases.
4. Convergence Issues
    - Early implementations of the algorithm exhibited poor convergence, requiring excessive iterations.
    - Adjusting the step size dynamically based on the rate of change of fugacity significantly improved efficiency.

By overcoming these challenges, I was able to develop a robust Python algorithm for equilibrium pressure determination, which will be provided as a fill-in-the-blank exercise for students. They will complete small sections of the code to ensure they understand:

- How to solve cubic equations for Z.

[7] VÁZQUEZ-ROMÁN, Richart, GARCÍA-SÁNCHEZ, Fernando, SALAS-PADRÓN, Alejandrina, et al. An efficient flash procedure using cubic equations of state. *Chemical Engineering Journal* [en ligne]. Décembre 2001, Vol. 84, nº 3, p. 201-205. DOI 10.1016/S1385-8947(00)00276-X.
[8] DONG, Ao, CHEN, Yuhang, ZHAN, Taotao, et al. Optimization of crossover SRK equation of state for thermodynamic properties calculation of CO2. *Fluid Phase Equilibria* [en ligne]. Janvier 2025, Vol. 587, p. 114200. DOI 10.1016/j.fluid.2024.114200.

- How to compute fugacity coefficients.
- How to iterate P to satisfy the equilibrium condition.

CO2 Data	Value
Critical temperature (K)	304.21
Critical pressure (Pa)	7.3825e+06
Acentric factor	0.225
Soave parameter : m	0.82524
Soave corrective factor : α	1.08885
Gas attraction parameter at Tcritical : a_c	0.370407
Gas attraction parameter : a	0.403316
Covolume : b	2.96824e-05
Liquid fugacity at equilibrium at 273 K : ΦL	0.724071
Vapour fugacity at equilibrium at 273 K : ΦV	0.724788
Equilibrium pressure at 273 K : Peq	3.4898e+06

Figure 6. Data table given by the SRK resolution code to find Peq of CO2 at an isotherm

CH4 Data	Value
Critical temperature (K)	190.55
Critical pressure (Pa)	4.64e+06
Acentric factor	0.011
Soave parameter : m	0.497293
Soave corrective factor : α	1.05592
Gas attraction parameter at Tcritical : a_c	0.231226
Gas attraction parameter : a	0.244156
Covolume : b	2.95814e-05
Fugacité liquide : ΦL	0.715532
Fugacité vapeur : ΦV	0.71624
Pression d'équilibre à 170 K : Peq	2.381e+06

Figure 7. Data table given by the SRK resolution code to find Peq of CH4 at an isotherm

1.3.6. Extension to the Saturation Curve Plotting

1.3.6.1. Objective: Further exploration through a loop on T

The goal of this section is to extend the equilibrium pressure calculation to construct the saturation curve P_{sat}=f(T). Instead of determining P_{eq} for a single isotherm, the process is repeated over a range of temperatures to map out the phase boundary between liquid and vapor.

In this practical work, students will not have to code this part themselves. Instead, they will be provided with:

1. A precomputed Python-generated saturation curve P_{sat}=f(T).
2. An Excel file containing experimental data on P_{sat} for methane (CH_4) and carbon dioxide (CO_2).

Their task will be to:

- Use Excel to plot P_{sat}=f(T) from the experimental dataset.
- Compare their graph to the one generated by the Python model.
- Analyze the differences, identifying:
    - The regions of the graph (subcritical, near critical, and supercritical).
    - The temperature limits and justify them in Python.

This task allows students to validate the SRK model by directly confronting numerical results with experimental reality.

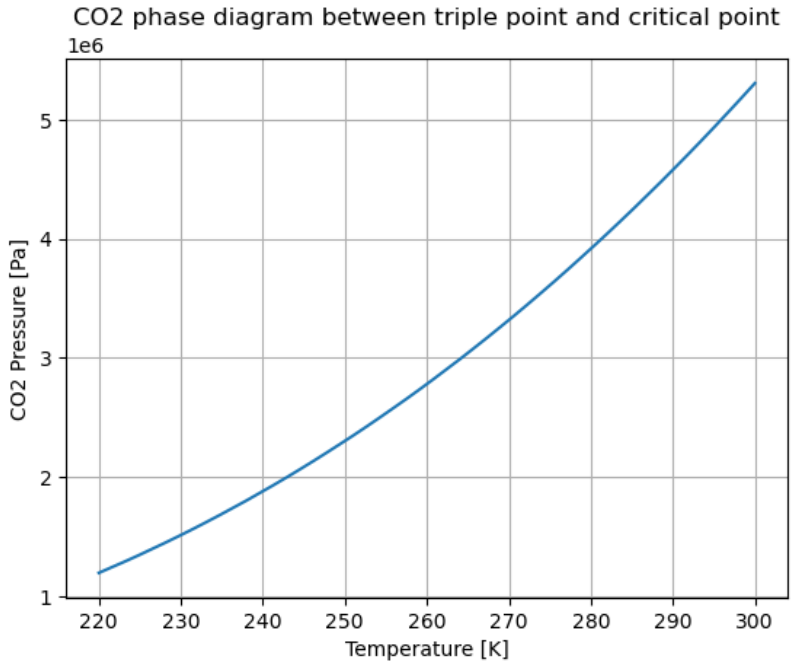


Figure 8. CO2 saturation curve plotted with python.

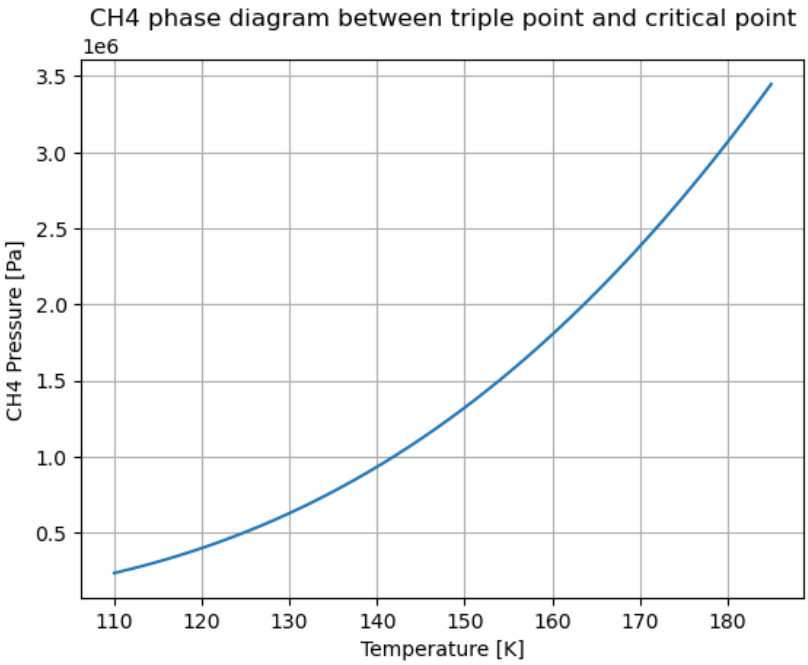


Figure 9. CH4 saturation curve plotted with python.

1.3.6.2. Justification for the bonus and pedagogical interest

I chose to include this section as a bonus exercise because the practical work already contains multiple analytical and computational steps. However, plotting the saturation curve brings additional physical meaning to the numerical results and allows students to:

- Visualize the phase boundary between liquid and vapor.
- Compare their results to experimental data and analyze deviations.
- Assess the impact of numerical parameters such as tol and ϵ on accuracy.

A final optional task is provided:

- Students modify the Python script to generate the saturation curve directly.
- This only requires embedding the existing code into a loop over T and storing results, making it a manageable challenge while reinforcing Python scripting skills.

I did not encounter particular difficulties when implementing this extension, but the comparison with experimental points provides useful insights into the accuracy of the SRK model and the choice of numerical parameters. This part helps students connect theoretical models to real-world data, an essential skill in thermodynamic modeling.

1.4. Conclusion

1.4.1. Summary of adjustments and relevance of the practical work

The development of this practical work required several iterations and refinements to balance theoretical understanding, numerical implementation, and experimental validation. Initially, plotting P=f(V) was straightforward, but identifying the inflection point and its physical significance required careful selection of volume ranges. Further, the transition to the compressibility factor Z provided a clearer framework for understanding the cubic nature of the SRK equation.

Key adjustments included:

- Identifying the correct volume interval to observe the inflection point, after extensive testing.
- Implementing Cardano's method to rigorously compute the roots of the cubic equation.
- Using fugacity instead of chemical potential for equilibrium pressure determination, simplifying computations.
- Switching to relative error in fugacity calculations to improve numerical convergence.
- Providing students with precomputed saturation curves to focus on physical interpretation rather than coding complexity.

These refinements ensured that the practical work remains accessible while exposing students to advanced thermodynamic modeling concepts. The overall approach successfully links theory, computation, and experimental validation, reinforcing the importance of equations of state in real-world applications.

1.4.2. Pedagogical contributions and improvement perspectives

This practical work was designed to provide students with a comprehensive learning experience, combining thermodynamic theory, Python programming, and experimental data analysis. The following pedagogical aspects were prioritized:

- Progressive learning structure:
    - Starting with basic SRK modeling.
    - Introducing compressibility factor analysis.
    - Moving towards equilibrium pressure determination.
    - Concluding with saturation curve validation using experimental data.
- Hands-on coding experience through guided fill-in-the-blank exercises, allowing students to actively engage with numerical methods.
- Real-world application by comparing Python-generated results with experimental data from the NIST Chemistry WebBook.
- Data visualization skills using Excel, an essential tool in scientific analysis.

For future improvements, several aspects could be refined:

- Enhancing code modularity to allow easier modifications and extensions.
- Investigating alternative numerical solvers for the cubic equation to improve stability.
- Extending the practical work to multi-component systems, demonstrating the SRK model's application in mixtures.

By completing this practical work, students gain a solid foundation in thermodynamic modeling, numerical problem-solving, and data interpretation key skills for further studies and professional applications in physics and engineering.

2. Appendix: Practical Workbook for Students

2.1. Understanding the SRK Equation

2.1.1. Presentation of the equation and its parameters

In real gas thermodynamics, equations of state (EoS) play a fundamental role in describing the relationship between pressure (P), volume (V), and temperature (T). Unlike the ideal gas law (PV = nRT), which assumes non-interacting particles, real gases exhibit intermolecular forces and finite molecular volumes, requiring corrective terms to improve prediction accuracy.

One of the most widely used real gas models is the Soave-Redlich-Kwong (SRK) equation, an improvement of the Redlich-Kwong (RK) equation. The SRK equation is expressed as:

$$P = \frac{RT}{V-b} - \frac{a.\alpha(T)}{V(V+b)}$$

Where:

- P: Pressure (Pa)
- V: Molar volume (m^3/mol)
- T: Temperature (K)
- R: Universal gas constant (J/mol.K)
- a: Parameter related to intermolecular attractive forces
- b: Parameter related to the finite size of molecules
- α (T): Temperature-dependent correction function

The values of a and b depend on the critical temperature (T_c) and critical pressure (P_c) of the gas:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c}, with\ \Omega_a = 0.42748$$

$$b = \Omega_b \frac{RT_c}{P_c}, with\ \Omega_b = 0.08664$$

The function α (T) was introduced by Soave to refine the prediction of liquid-phase properties:

$$\alpha(T) = \left[1 + m(1 - \sqrt{T_r})\right]^2$$

$$m = M_1 + M_2\omega - M_3\omega^2$$

$$\begin{cases} M_1 = 0.48508 \\ M_2 = 1.55171 \\ M_3 = 0.15613 \end{cases}$$

where $T_r = T / T_c$ is the reduced temperature, and ω is the acentric factor, which accounts for molecular shape and polarity.

Preliminary Questions:

1. How were the parameters Ω_a and Ω_b determined in the SRK equation?

2. Demonstrate that the units of a and b are consistent with the equation of state.
3. What is the physical meaning of the acentric factor ω? How does it influence the equation?

2.1.2. Theoretical background and application

The van der Waals equation was one of the first attempts to describe real gases, introducing terms for molecular volume and intermolecular attractions. The Redlich-Kwong equation improved upon this by refining the attractive term, but it still lacked accuracy for liquids and phase equilibrium calculations. The SRK equation, proposed by Soave in 1972, introduced a temperature-dependent correction function α(T) to account for non-ideal phase behavior, significantly improving its accuracy in vapor-liquid equilibrium calculations.

Why is the SRK Equation Important?

- It provides a simple yet effective model for real gases, widely used in chemical engineering, petroleum industries, and thermodynamic simulations.
- It is particularly useful for predicting phase transitions, compressibility, and equilibrium conditions.
- Unlike the Peng-Robinson equation, which improves density predictions, SRK focuses on accurate phase equilibrium modeling.

Practical Applications:

- Modeling natural gas and hydrocarbon behavior in pipelines and refineries.
- Determining phase diagrams for multi-component mixtures.
- Designing distillation and liquefaction processes.

Preliminary Questions:

4. Explain the main difference between the Redlich-Kwong equation and the SRK equation.
5. Why does the SRK equation perform better than van der Waals for phase equilibrium modeling?

2.1.3. Problematic and scope of the model

Although the SRK equation is widely used, it is important to understand its limitations:

- It is less accurate for highly polar substances (water, alcohols) due to strong hydrogen bonding.
- It may fail at very high pressures, where additional repulsive interactions become significant.
- It assumes that molecular interactions can be represented by a single attraction term, which is not always the case.

This practical work focuses on:

- Understanding the SRK equation and its fundamental parameters.
- Implementing it in Python to analyze gas behavior through numerical simulations.
- Comparing SRK results with experimental data, to evaluate its accuracy.

Preliminary Questions:

6. In which cases would the SRK equation fail to accurately predict gas behavior? How could it be improved?
7. Given an unknown gas, how would you determine whether SRK is an appropriate model?

This introductory section provides the theoretical background necessary to begin the practical work. In the next sections, you will implement and analyze the SRK model in Python to explore real gas behavior in detail.

2.2. Numerical Implementation and Model Validation

2.2.1. Python Modeling of the SRK Equation

2.2.1.1. First implementation: Plotting P=f(V)

In this section, you will implement the Soave-Redlich-Kwong (SRK) equation in Python to visualize how pressure varies with molar volume at different temperatures. The provided fill-in-the-blank code will guide you in completing the missing parts and generating isothermal curves for CO_2 and CH_4.

Objectives:

- Implement the SRK equation to compute P=f(V).
- Observe the behavior of real gases compared to ideal gas predictions.
- Identify how temperature influences the pressure-volume relationship.

Instructions:

1. Complete the missing parts in the provided Python script.
2. Run the script to generate isotherms for CO_2 and CH_4.
3. Analyze the generated curves and answer the following questions:
    - How do the isotherms behave at different temperatures?
    - What differences can you observe between CO_2 and CH_4?

2.2.1.2. Zooming in on the inflection point

A key characteristic of real gas behavior is the inflection point, which indicates the transition between liquid and vapor phases. The SRK equation models this phenomenon, but it is only visible within a very narrow volume range near the covolume (b).

Objectives:

- Modify the given code to zoom in on the region where the inflection point appears.
- Analyze how the curve behaves near the critical region.
- Comment on the choice of the volume interval, explaining why this range is appropriate.

Instructions:

1. Adjust the volume range in the provided script to focus on the region near the covolume.
2. Re-run the simulation and observe how the inflection point appears.
3. Answer the following questions:
    - Why does the curve exhibit this particular shape?
    - How does the inflection point relate to the equilibrium pressure and phase transition?
    - Why is it difficult to observe this inflection using experimental data?

Key Observations:

- The inflection point only appears in a specific range of volume and pressure.
- It cannot be directly observed in experimental datasets due to resolution limits.
- Understanding this behavior is crucial for determining phase equilibrium conditions.

This section provides the foundation for the next part, where you will analyze the compressibility factor Z and its implications for phase transitions.

2.2.2. Compressibility Factor Analysis

2.2.2.1. Theoretical background on Z

The compressibility factor Z is a fundamental quantity in real gas thermodynamics, defined as:

$$Z = \frac{PV_m}{RT}$$

where P is the pressure, V_m is the molar volume, R is the gas constant, and T is the temperature.

For real gases, Z varies due to intermolecular interactions and finite molecular volume effects, leading to deviations from ideality.

One limitation of the previous representation P=f(V) is that volume scales are drastically different between phases (liquid, vapor, supercritical). To better visualize phase behavior, we rewrite the SRK equation in terms of Z:

$$Z^3 - Z^2 + (A^2 - B^2 - B)Z - AB = 0$$

With $\begin{cases} A = \frac{aP}{(RT)^2} \\ B = \frac{bP}{RT} \end{cases}$

This cubic form allows us to determine three possible roots, corresponding to different gas phases.

By solving f(Z)=0, we can:

- Observe the structure of the cubic equation.
- Understand phase transitions in terms of Z.
- Determine which roots correspond to liquid and vapor phases.

Preliminary Questions:

1. Why do we use Z instead of V_m to analyze phase behavior?
2. What does Z=1 correspond to? Why does this value change for real gases?

2.2.2.2. Python modeling of the cubic SRK equation

To visualize the cubic nature of the SRK equation, students will modify the provided fill-in-the-blank code to:

- Compute f(Z) and plot it for CO_2 and CH_4.
- Observe the number of real roots depending on the pressure and temperature conditions.

Instructions:

1. Complete the missing parts of the provided Python script.
2. Run the code and generate f(Z) for CH_4 and CO_2.
3. Analyze the curve and answer:
    - Why is 0<Z<1 in this context?
    - How many real roots appear in different cases?
    - What do these roots represent physically?

Key Observations:

- The cubic structure of the equation confirms that real gases can exhibit multiple phases.
- When three real roots exist, the gas is in a phase equilibrium condition.
- The smallest root corresponds to vapor, the largest root to liquid, and the middle root is metastable.

2.2.2.3. Comparison of Z=f(P) and P=f(Vm) for different gases

Once Z has been computed using Python, students will compare their results to experimental data using an Excel file containing real measurements for CH_4 and CO_2.

Instructions:

1. Open the provided Excel file containing experimental data for different isotherms.
2. Create two new columns:
    - Z using the experimental values: $Z=PV_m/RT$

- $Pr=P/P_c$ to express pressure in reduced form.

3. Plot the following graphs:
   - $P=f(V_m)$ for CH_4 and CO_2.
   - $Z=f(P_r)$ for CH_4 and CO_2.
4. Compare the trends between the SRK model and the experimental data.

Analysis Questions:

1. How does Z behave in the liquid, vapor, and supercritical phases?
2. What are the main differences between CH_4 and CO_2 in terms of compressibility?
3. How well does the SRK model agree with experimental data? What are its limitations?

Key Observations:

- The experimental values of Z confirm deviations from ideality.
- The liquid phase exhibits much lower compressibility than the vapor phase.
- The SRK model captures the general trends, but deviations can occur, especially for highly polar gases.

2.3. Study of Equilibrium Pressure and Further Analysis

2.3.1. Theoretical Framework of Equilibrium Pressure

2.3.1.1. Definition using area equality under P=f(V)

When a substance undergoes a phase transition between liquid and vapor, the equilibrium pressure (P_{eq}) is the pressure at which both phases coexist in equilibrium. In thermodynamics, this pressure can be determined using the Maxwell construction, which states that at equilibrium, the areas under the isothermal P=f(V) curve must be equal for the liquid and vapor phases.

This condition arises from the fact that during a phase transition, the work done by the system in expanding from liquid to vapor must be equal to the work done in compressing from vapor to liquid. Mathematically, this means:

$$Peq(V_2 - V_1) - \int_{V_1}^{V_2} P(V)dV = \int_{V_2}^{V_3} P(V)dV - Peq\,(V_3 - V_2)$$

where:

- V_1 and V_3 are the molar volumes of the liquid and vapor phases, respectively.
- Peq is the equilibrium pressure at which the areas above and below the curve are equal.

Why is this method not used in practice?

Although this method is theoretically correct, computing the integral analytically is extremely complex because:

- The exact equation of state must be integrated.

- The limits V_1 and V_3 depend on the roots of the cubic equation.
- It is difficult to solve numerically without introducing significant approximations.

Thus, in practical applications, alternative methods based on chemical potential and fugacity are preferred to determine P_{eq}.

2.3.1.2. Understanding chemical potential and fugacity

Since direct calculation using area equality is not feasible, we rely on the chemical potential (μ) and its practical equivalent, fugacity (f), to determine the equilibrium pressure.

Chemical Potential and Phase Equilibrium :

The chemical potential μ represents the thermodynamic potential per mole of a substance. At equilibrium, a system minimizes its free energy, which means that for two coexisting phases, the chemical potential must be equal:

$$\mu_L = \mu_V$$

where:

- μ_L is the chemical potential of the liquid phase.
- μ_V is the chemical potential of the vapor phase.

If this condition is not met, matter will flow from one phase to another to equalize the chemical potential, thereby shifting the phase equilibrium.

Fugacity: A Practical Alternative to Chemical Potential :

The fugacity f is introduced as a corrected pressure term that accounts for real gas deviations from ideal behavior:

$$\mu = \mu^o + RTln(f)$$

Since the chemical potential is difficult to measure directly, we use fugacity because at equilibrium:

$$f_L = f_V$$

This means that instead of comparing chemical potentials, we can compare fugacities, which are directly calculable from the SRK equation.

Why Use Fugacity Instead of Pressure ?

For an ideal gas, fugacity is equal to pressure (f=P), but for real gases, interactions modify the pressure, requiring a fugacity coefficient (ϕ):

$$f = \Phi P$$

Thus, the equilibrium condition simplifies to:

$$\Phi_L P_L = \Phi_V P_V$$

This is the condition we will use numerically to determine P_{eq} in the next section.

2.3.2. Algorithm for Peq Calculation

2.3.2.1. Implementation using Cardano's method

To determine the equilibrium pressure P_{eq}, we must first solve the cubic equation in compressibility factor Z derived from the SRK equation:

$$Z^3 - Z^2 + (A^2 - B^2 - B)Z - AB = 0$$

With $\begin{cases} A = \frac{aP}{(RT)^2} \\ B = \frac{bP}{RT} \end{cases}$

Solving this equation allows us to identify the possible phases (liquid, vapor) at a given temperature and pressure. Since it is a cubic equation, it can have either:

- One real root (single-phase behavior, gas or liquid only).
- Three real roots (two stable phases and one metastable phase, indicating phase coexistence).

To solve this equation analytically, we use Cardano's method, a classical technique for solving cubic equations. The full derivation of Cardano's method will be provided in the annex, but the main steps are:

1. Compute the coefficients p and q from the SRK equation.
2. Evaluate the discriminant Δ :

$$\Delta = \left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3$$

With $\begin{cases} p = -\frac{1}{3} + (A - B^2 - B) \\ q = \frac{A - B^2 - B}{3} - AB - \frac{2}{27} \end{cases}$

3. Depending on the sign of Δ, classify the roots:
    - If Δ>0: One real root, no phase equilibrium.
    - If Δ=0: Two real roots (one double root), critical behavior.
    - If Δ<0: Three real roots, corresponding to liquid, vapor, and a metastable phase.

Student Task:

- Complete the fill-in-the-blank Python script to implement Cardano's method in Python.
- Run the script to compute the roots and classify them.

- Answer:
    - What happens when there is only one real root?
    - Why do we need three real roots for equilibrium calculations?

2.3.2.2. Root analysis and selection criteria

Once the cubic equation is solved, we must identify which roots correspond to the liquid and vapor phases. When three real roots exist, they are ordered as follows:

- Z_V (smallest root) → Vapor phase.
- Z_M (middle root) → Metastable region, physically irrelevant.
- Z_L (largest root) → Liquid phase.

Since we are interested in phase equilibrium, we select:

- Z_L for the liquid phase.
- Z_V for the vapor phase.

Student Task:

- Modify the code to extract the correct roots for Z_L and Z_V.
- Answer:
    - Why is the middle root Z_M ignored in phase equilibrium calculations?
    - How do the values of Z_L and Z_V compare at different pressures?

2.3.2.3. Scan-based algorithm to find Peq

Now that we can compute Z_L and Z_V, we use the fugacity equality condition to determine P_{eq}:

$$\Phi_L P_L = \Phi_V P_V$$

Since ϕ depends on pressure, we must scan for the correct P iteratively:

1. Set an initial guess $P=P_{init}$.
2. Compute Z_L and Z_V at this pressure.
3. Compute fugacity coefficients ϕ_L and ϕ_V.
4. Compute the relative error:

$$\frac{|\Phi_L(P) - \Phi_V(P)|}{\max(\Phi_L(P), \Phi_V(P))} < tol$$

5. If the error is larger than a tolerance tol, adjust P by a small increment ε.
6. Repeat until the error is within the tolerance.

Algorithm Parameters :

- tol $=10^{-3}$: Ensures sufficient accuracy.
- ε =100 Pa : Avoids overshooting or slow convergence.

Student Task :

- Complete the fill-in-the-blank Python script for the scan algorithm.
- Answer:
    - Why is a relative error used instead of an absolute one?
    - What happens if ε is too large or too small?

2.3.3. Bonus: Saturation Curve Calculation

2.3.3.1. Final plotting of Psat=f(T)

In this bonus section, you will extend the previous calculations to construct the saturation curve $P_{sat}=f(T)$, which represents the phase boundary between liquid and vapor. This step reinforces the importance of equilibrium pressure calculations and provides a direct comparison between theoretical predictions and experimental data.

Objectives:

- Modify the existing Python script to loop over multiple temperatures and compute P_{sat}.
- Generate the theoretical saturation curve for CO_2 and CH_4.
- Use an Excel file containing experimental values of P_{sat} for these gases.
- Compare the Python-generated curves with experimental data.

Instructions:

1. Modify the provided Python script to:
    - Implement a loop over a range of temperatures.
    - Compute P_{sat} at each temperature using the equilibrium pressure algorithm from the previous section.
    - Store the results and plot $P_{sat}=f(T)$.
2. Open the Excel file containing experimental Psat values.
3. In Excel, create:
    - A column for reduced temperature $T_r=T/T_c$.
    - A plot of experimental P_{sat} as a function of T.
4. Compare the SRK model predictions with the experimental data by overlaying both curves.

Analysis Questions:

1. How well does the SRK-predicted saturation curve match the experimental data?

2. In which temperature regions (low, near critical, high) does the SRK model deviate the most?
3. What are possible sources of error in the SRK predictions?

Key Observations:

- The SRK model generally follows experimental trends but may show deviations near the critical point.
- The difference between CO_2 and CH_4 highlights the role of the acentric factor ω.
- Comparing Python and Excel results provides insight into model accuracy and limitations.

2.4. Conclusion

2.4.1. Summary of key takeaways from the practical work

This practical work explored the Soave-Redlich-Kwong (SRK) equation as a refined model for real gas behavior, emphasizing its ability to describe phase transitions and deviations from ideality. By implementing the equation in Python, you were able to analyze pressure-volume relationships, compressibility factors, and equilibrium conditions. One of the key insights was the need to move beyond direct volume-based analysis to a compressibility factor approach, which better captures phase behavior. The practical work also introduced fugacity-based equilibrium pressure calculations, showing that the traditional area equality method is impractical for real applications. Finally, by constructing the saturation curve $P_{sat}=f(T)$ and comparing it to experimental data, you assessed the accuracy and limitations of the SRK model, highlighting its strengths and areas where refinements are needed.

2.4.2. Expected learning outcomes for students

By completing this practical work, you should now have a comprehensive understanding of real gas thermodynamics and the numerical tools needed to model it. You have implemented a cubic equation of state, explored root analysis to distinguish physical phases, and applied fugacity calculations to determine equilibrium conditions. The ability to compare theoretical predictions with experimental data is a crucial skill in scientific research and engineering, reinforcing the importance of both computational modeling and physical interpretation. This practical work serves as a foundation for more advanced thermodynamic studies, giving you the analytical and coding skills necessary to tackle more complex systems in future coursework and research.

3. Calculus Appendix

3.1. Cubic equation form

$$(SRK): P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

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

$$\Leftrightarrow PV(V^2-b^2) = RTV(V+b) - a(T)(V-b)$$

$$\Leftrightarrow PV^3 - Pvb^2 = RTV^2 + RTVb - a(T)V + a(T)b$$

$$\Leftrightarrow PV^3 + (a(T) - RTb - Pb^2)V - RTV^2 - a(T)b = 0$$

$$\Leftrightarrow PV^3 - RTV^2 + (a(T) - Pb^2 - RTb)V - a(T)b = 0$$

$$\times \frac{P^2}{(RT)^3}$$

$$\Leftrightarrow \frac{P^3V^3}{(RT)^3} - \frac{P^2V^2}{(RT)^2} + \left(\frac{a(T)P^2}{(RT)^3} - \frac{P^3b^2}{(RT)^3} - \frac{P^2b}{(RT)^2}\right)V - \frac{a(T)bP^2}{(RT)^3} = 0$$

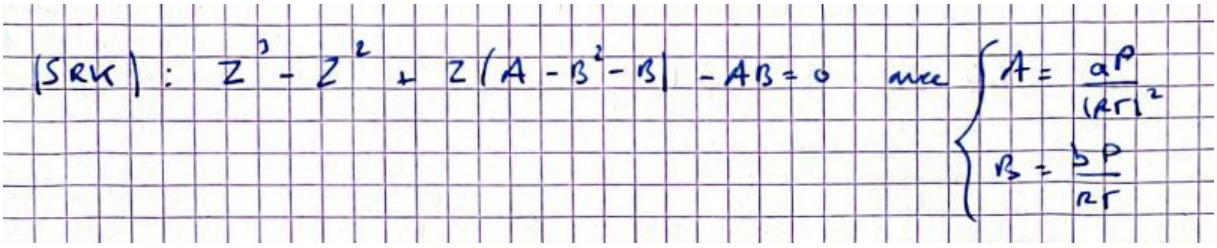
let $Z = \frac{PV}{RT}$

$$\Leftrightarrow \boxed{Z^3 - Z^2 + (A - B^2 - B)Z - AB = 0}$$

$$\begin{cases} A = \frac{aP}{(RT)^2} \\ B^2 = \left(\frac{Pb}{RT}\right)^2 \\ B = \frac{Pb}{RT} \end{cases}$$

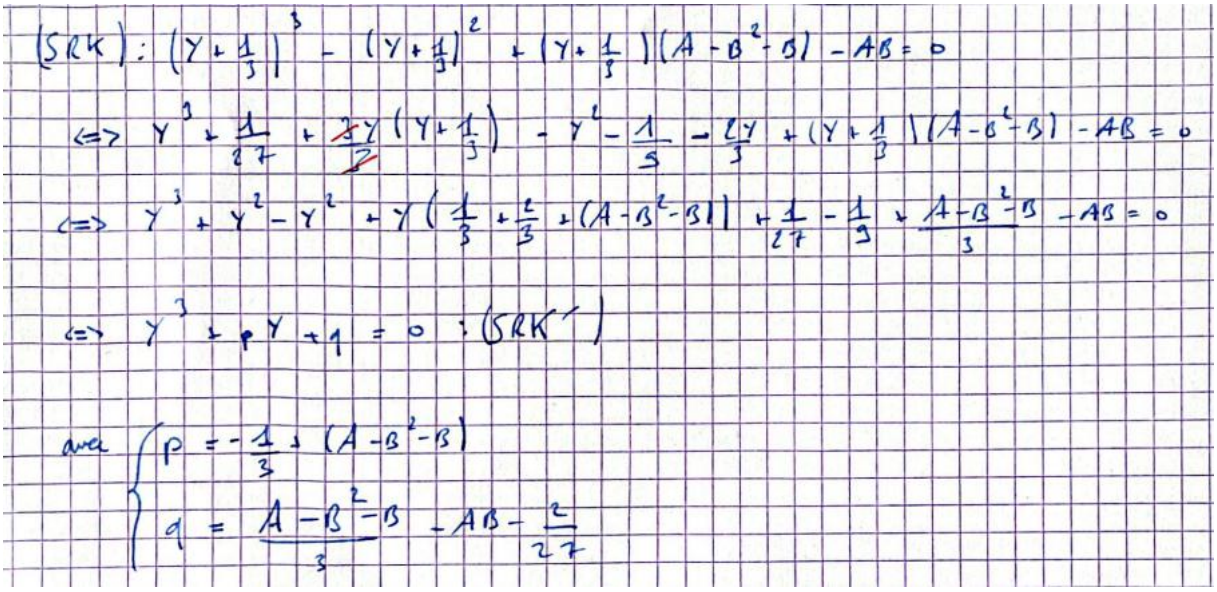
$$\hookrightarrow \left[\frac{a(T)P^2}{(RT)^3} - \frac{P^3b^2}{(RT)^3} - \frac{P^2b}{(RT)^2}\right]V = \left[\underbrace{\frac{a(T)P}{(RT)^2}}_{A} - \underbrace{\frac{P^2b^2}{(RT)^2}}_{B^2} - \underbrace{\frac{Pb}{RT}}_{B}\right]\underbrace{\frac{PV}{RT}}_{Z}$$

3.2. Resolution of SRK equation my Cardan's method



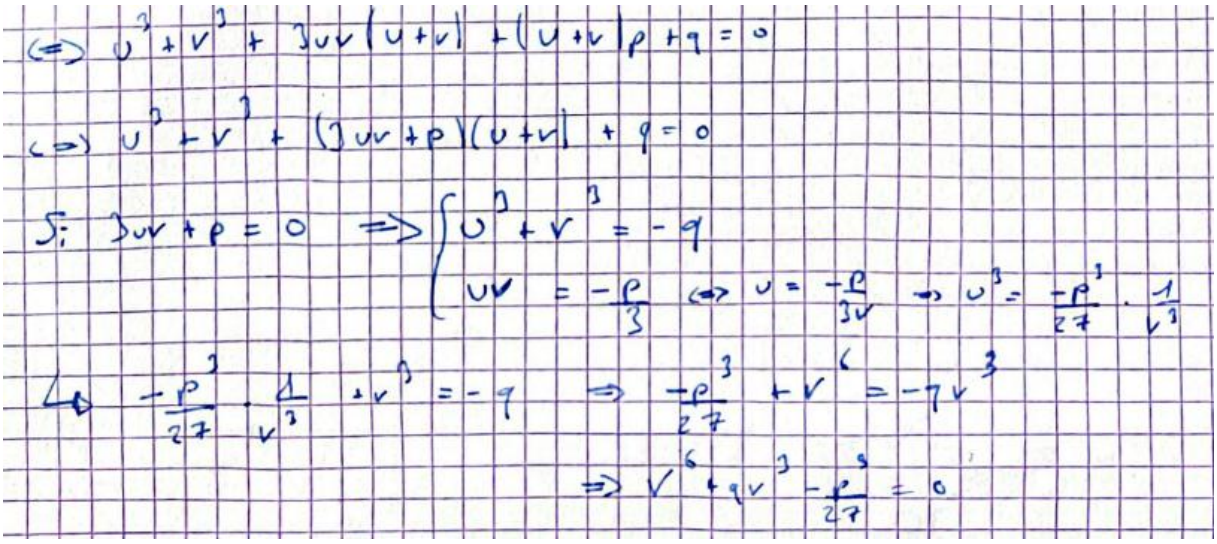
Put in the form $Y^3 + pY + q = 0$

Let $Y = Z - \frac{1}{3} \Leftrightarrow Z = Y + \frac{1}{3}$

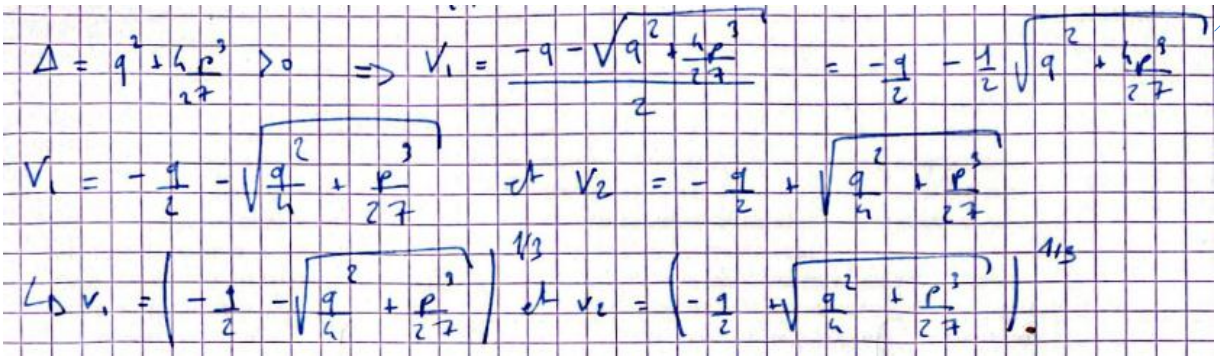


Definition of Δ :

Let $Y = u + v \Rightarrow (SRK) : (u+v)^3 + p(u+v) + q = 0$



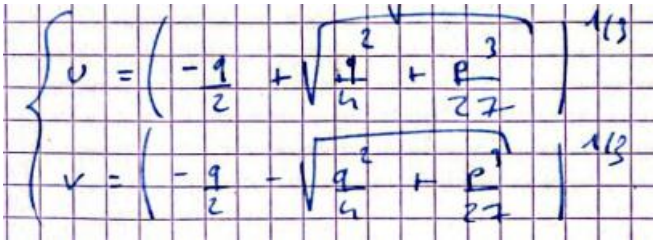
Let $V = v^3 \Rightarrow V^2 + qV - \frac{p^3}{27} = 0$



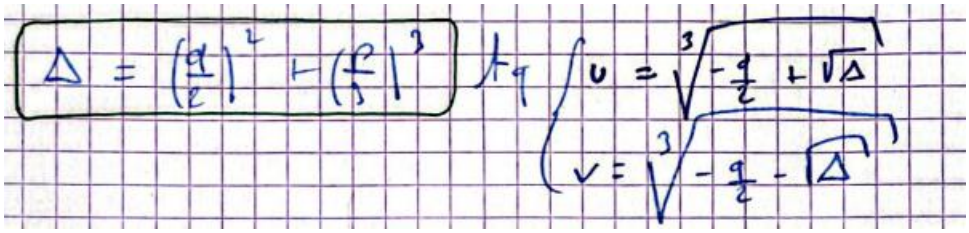
Know we have : $u_1^3 + v_1^3 = -q \Leftrightarrow u_1^3 = -\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}$

Furthermore $u_1 = v_2 \; and \; u_2 = v_1$

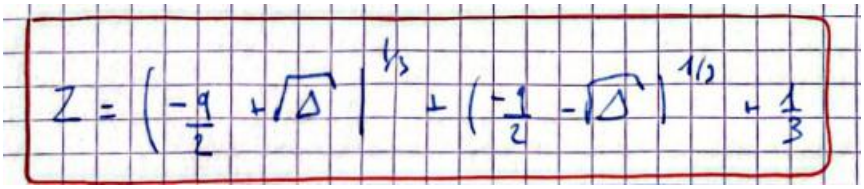
So :



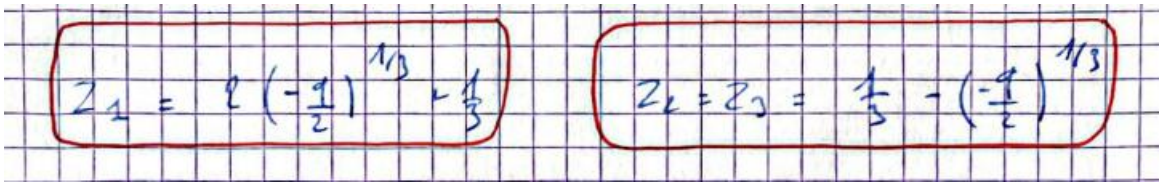
And finally :



3.2.1. If Δ>0:

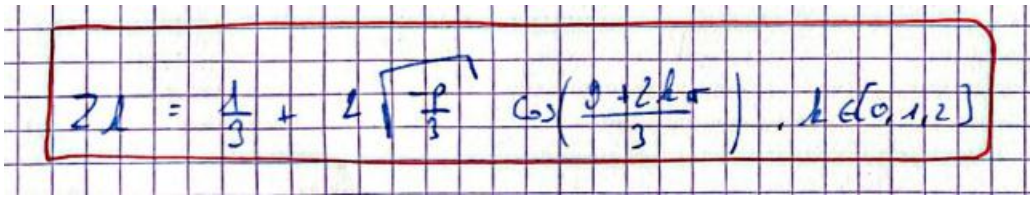


3.2.2. If Δ=0:



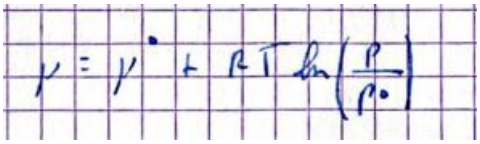
3.2.3. If Δ<0:

$$with\ \cos\theta = -\frac{q}{2}\left(\frac{-3}{p}\right)^{\frac{3}{2}}$$

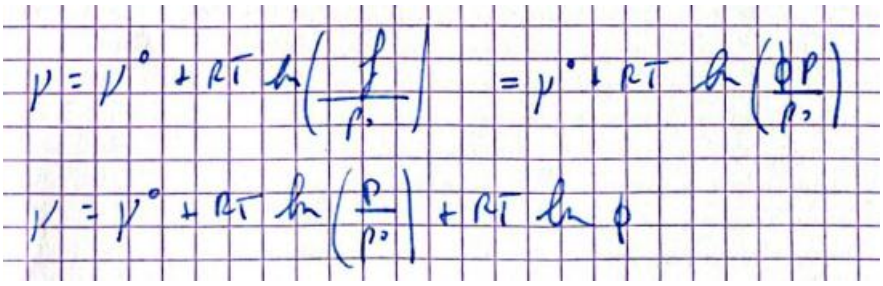


3.3. Chemical potential/Fugacity equilibrium

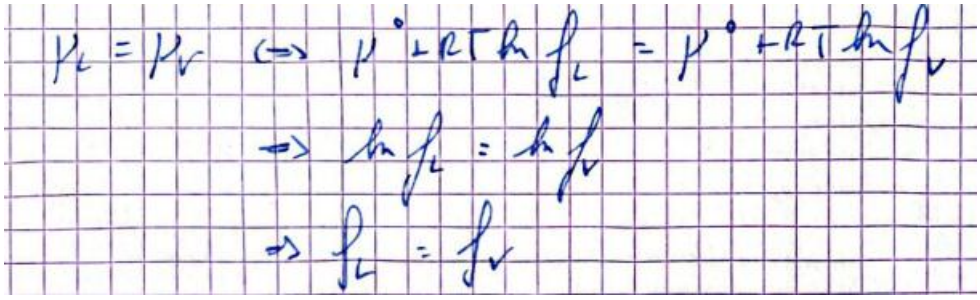
For perfect gas :



For real gas :

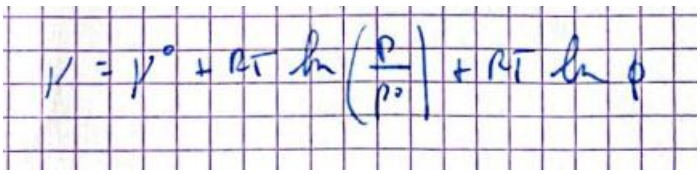


So we have at equilibrium :

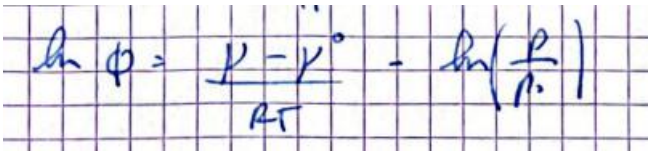


3.4. Fugacity coefficient expression

By :

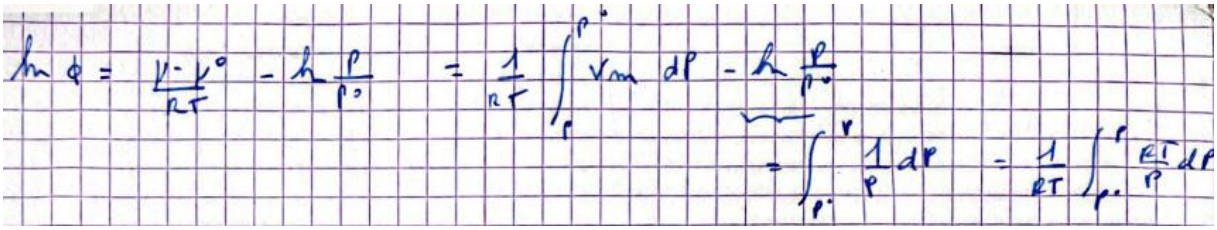


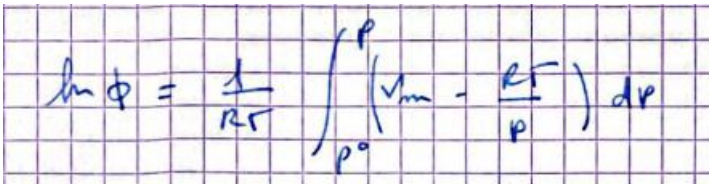
We can deduce :



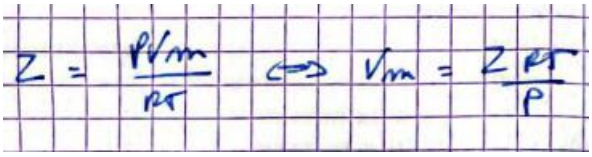
And by the Schwarz theorem : $\left(\frac{\partial \mu}{\partial P}\right)_T = V_m \Rightarrow \mu(P) - \mu(P°) = \int_{P°}^{P} V_m dP$

So by implementing that in ln(Φ) expression we have :

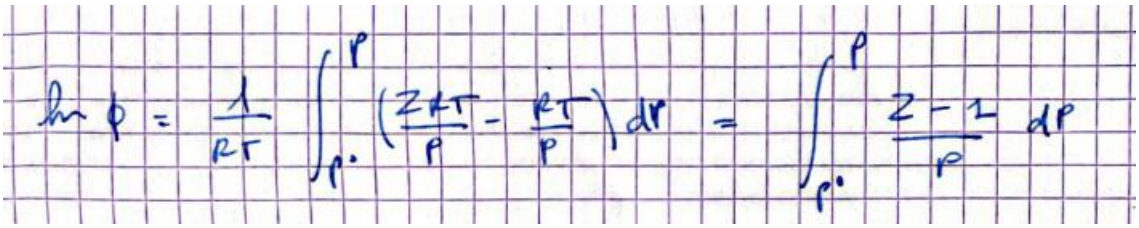




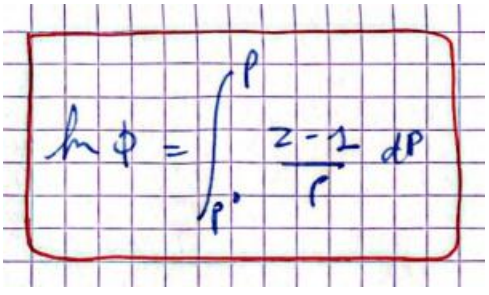
With :



Thus :



Finally :



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