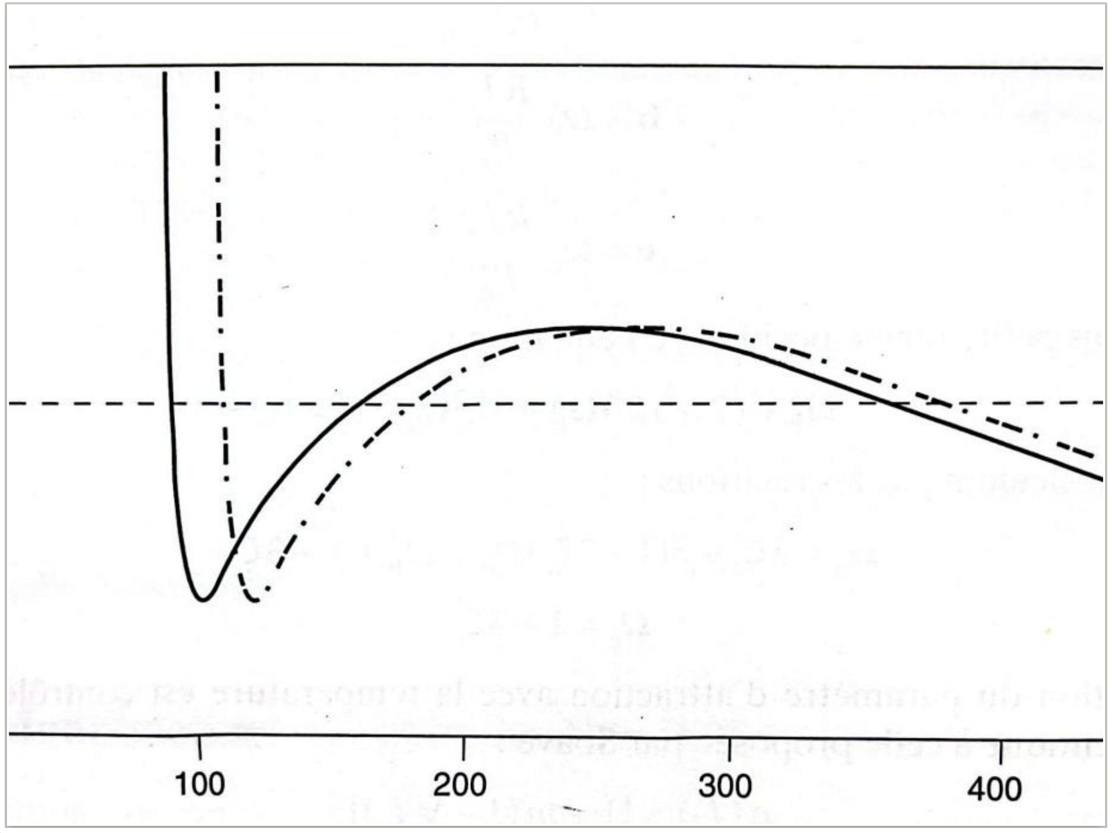
THERMODYNAMICS PRACTICAL WORK : CHALLENGES AND ADJUSTMENTS

Modeling the PVT behavior of gases using the SRK Equation



SUMMARY

1°) Introduction & Objectives

Main goals of the project :

- Develop a pedagogical approach combining thermodynamics and Python
- Overcome key learning challenges

Why this project ?

- Importance of modeling in thermodynamics
- Need for a practical work to teach students numerical methods

2°) Initial Concept & Pedagogical Approach

Starting point :

- Implementing the SRK equation in a student-friendly way

Key pedagogical choices :

- Balance between theoretical understanding and programming
- Use of fill-in-the-blank (FITB) coding for guided learning

3°) First Challenge :
Visualizing P = f(V) and Understanding the Inflection Point

Problem encountered :

The phase transition inflection point was not clearly visible

Solution :

Refining the volume range selection

Adjusting code structure for better visualization

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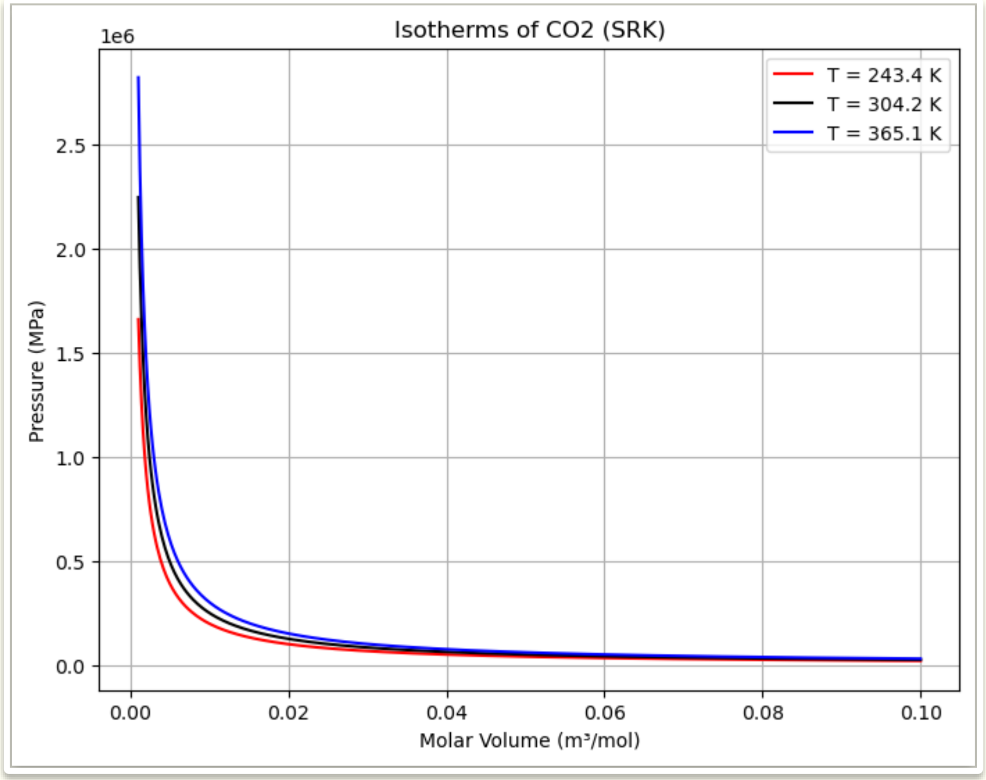
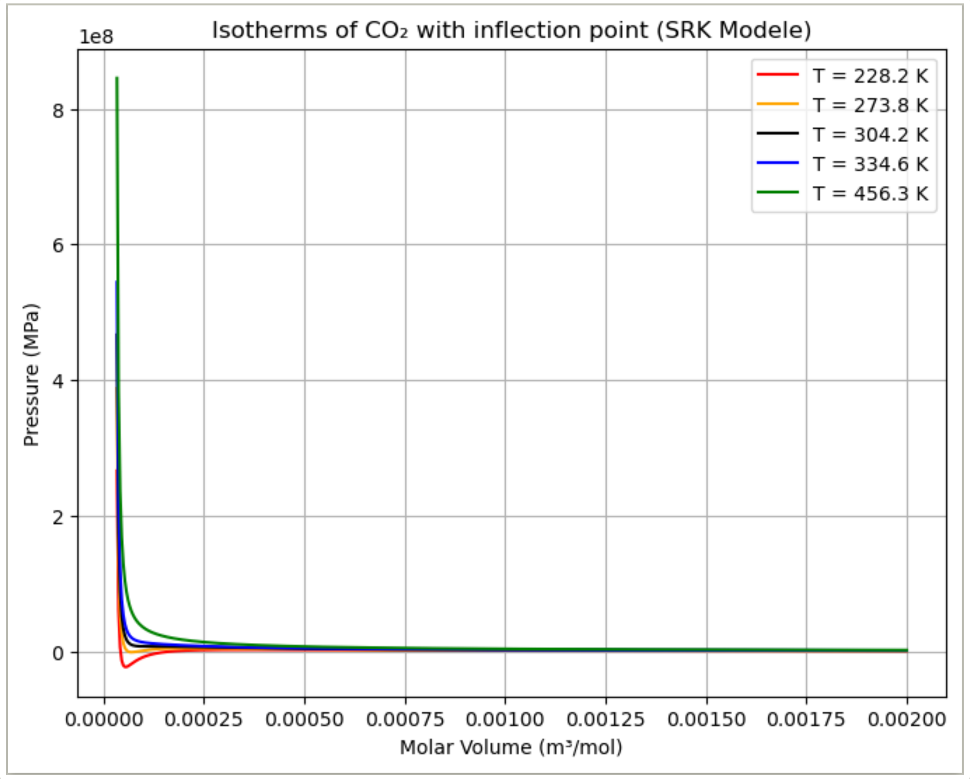
Visualizing P = f(V) and Understanding the Inflection Point



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



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

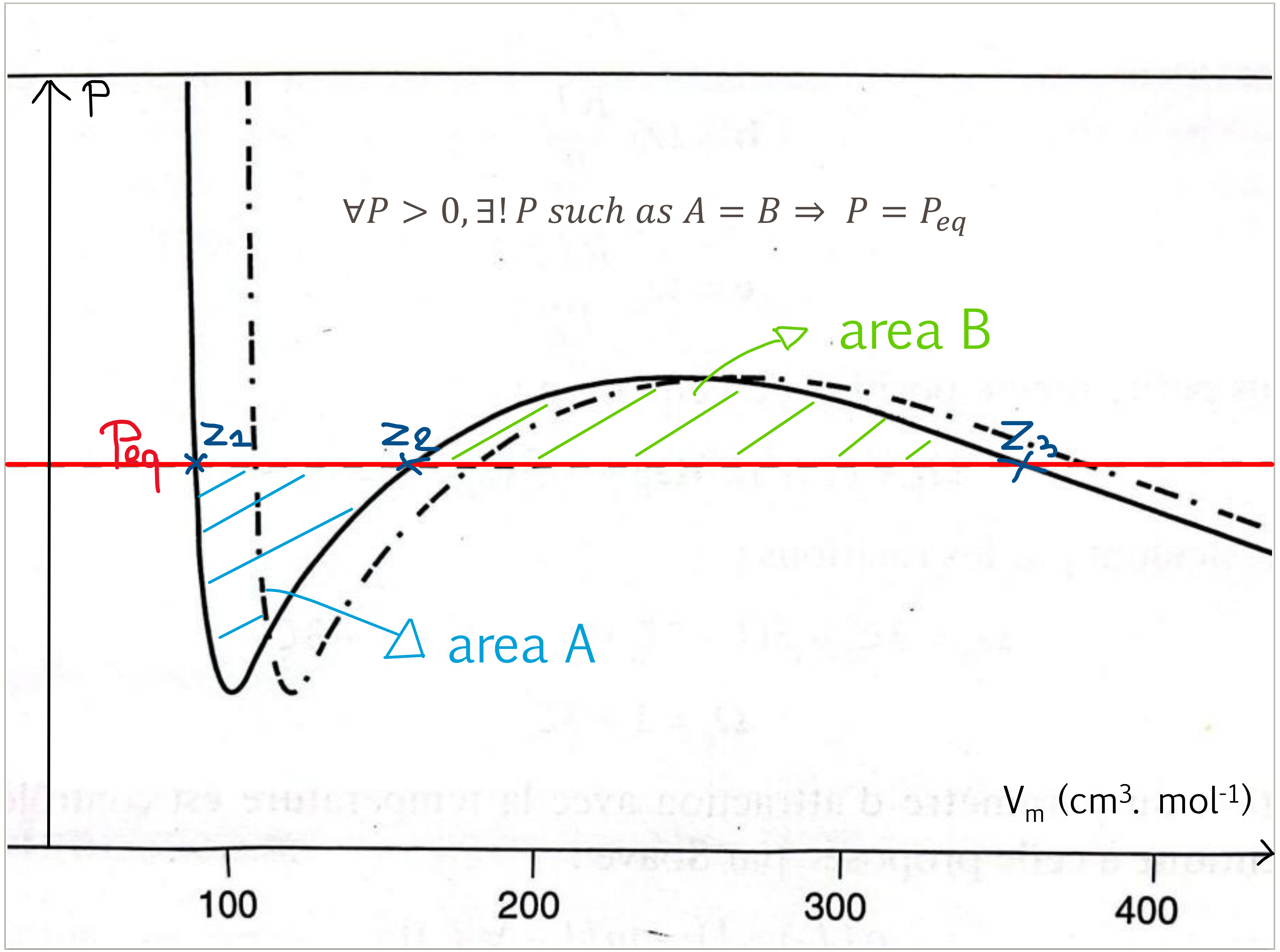
4°) Second Challenge : Compressibility Factor Z

Why introduce Z ?

- ⟶ P-V graphs were hard to interpret for phase behavior
- ⟶ Z=f(P) gives a clearer insight into real gas deviations

Solution implemented :

- ⟶ Reformulated SRK as a cubic equation in Z
- ⟶ Used root analysis to link Z to phase transitions



PV diagram from « Thermodynamique : application eu génie chimique et à l'industrie pétrolière by J.Vidal »

5°) Numerical Issues and Algorithmic Adjustments

Challenge :

Finding the correct roots for equilibrium pressure

Initial attempts :

Manual algebraic solutions (too complex)

Final solution :

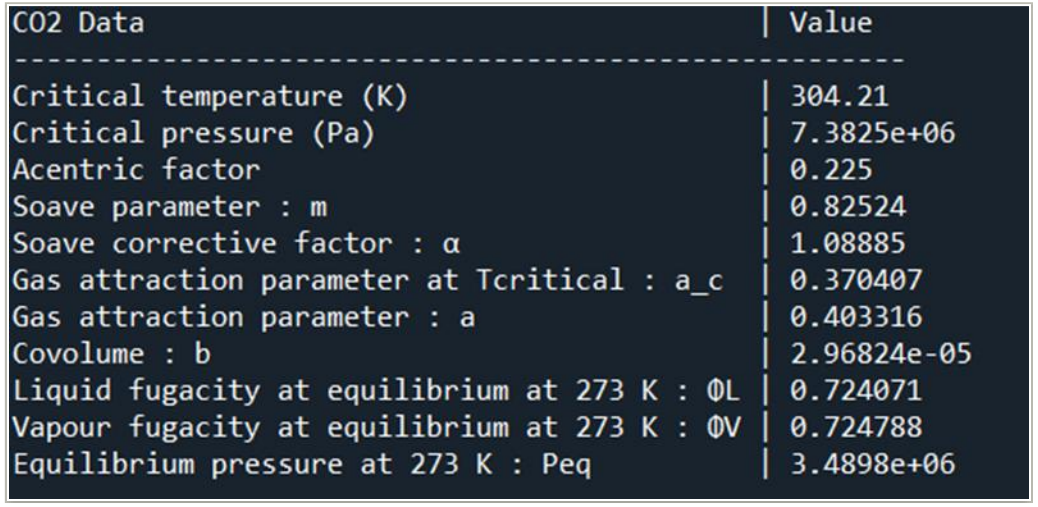
Implementation of Cardano’s method for cubic equation

5°) Numerical Issues and Algorithmic Adjustments

- $(SRK): \; Z^3 - Z^2 + Z(A - B^2 - B) - AB = 0$
- $(SRKC): Y^3 + pY + q = 0, \begin{cases} Y = Z - {}^{1}/_{3} \\ p = -{}^{1}/_{3} + (A - B^2 - B) \\ q = \frac{A - B^2 - B}{3} - AB - {}^{2}/_{27} \end{cases}$
- $\Delta = \left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3$
- $\Delta > 0 \Rightarrow Z = \left(\frac{-q}{2} + \sqrt{2}\right)^{1/3} + \left(\frac{-q}{2} - \sqrt{\Delta}\right)^{1/3} + \frac{1}{3}$
- $\Delta = 0 \Rightarrow Z_1 = 2\left(\frac{-q}{2}\right)^{1/3} + \frac{1}{3} \; and \; Z_2 = \frac{1}{3} - \left(\frac{-q}{2}\right)^{1/3}$
- $\Delta < 0 \Rightarrow Z_k = \frac{1}{3} + 2\sqrt{\frac{-p}{3}} cos\left(\frac{\theta + 2k\pi}{3}\right),$

$$\begin{cases} k \in [0,1,2] \\ \theta = arcos\left(\frac{-q}{2}\left(\frac{3}{-p}\right)^{3/2}\right) \end{cases}$$

Cardano's method



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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
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Fugacity coefficients

6°) Equilibrium Pressure Calculation – Overcoming Instabilities

algorithm for solving P_{eq} :

- $T = C^{ste}, \begin{cases} P_L = P_V = P_{sat} \\ \mu_L = \mu_V \Leftrightarrow \Phi_L = \Phi_V \end{cases}$
- $$\begin{tikzcd} P = P_{ini} \arrow[r] & \mu_L - \mu_V = 0 \arrow[r, "yes"] \arrow[d, "\text{no}"] & return\ P \\ & P = P_{ini} + \varepsilon \arrow[ul, bend left] & \end{tikzcd}$$

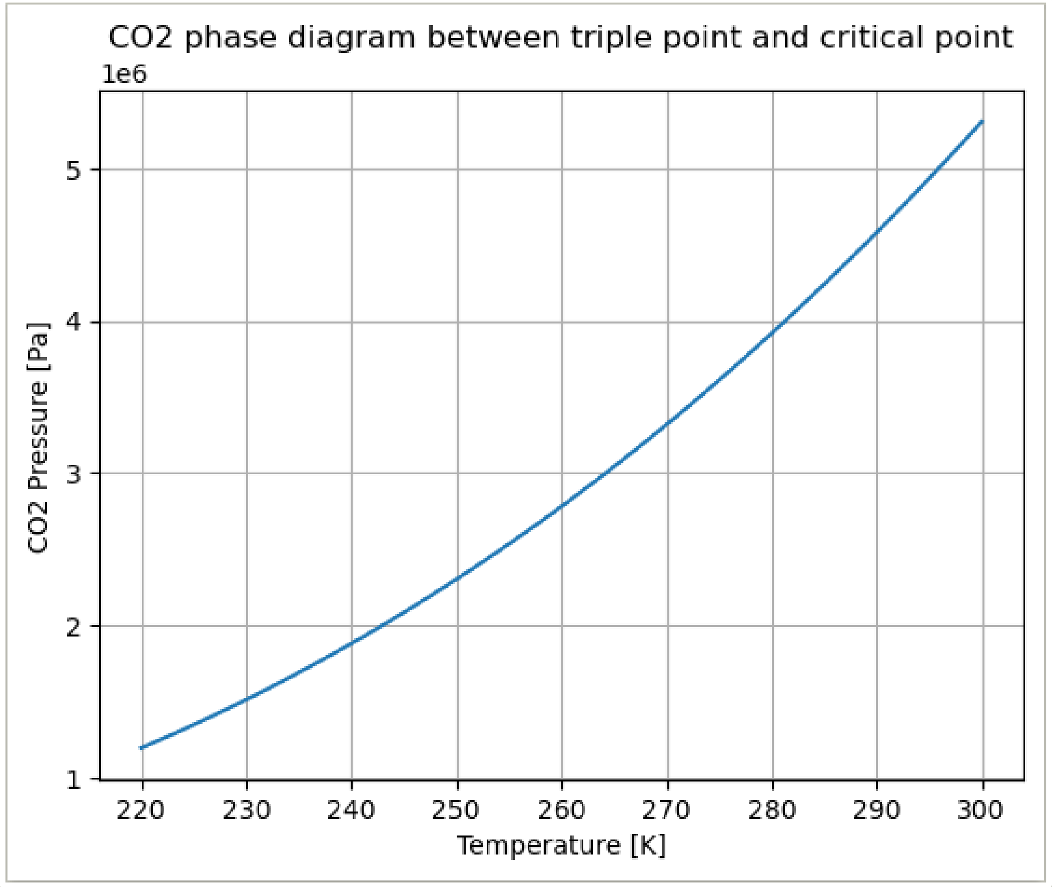
Challenge :

Poor convergence in fugacity-based equilibrium calculations

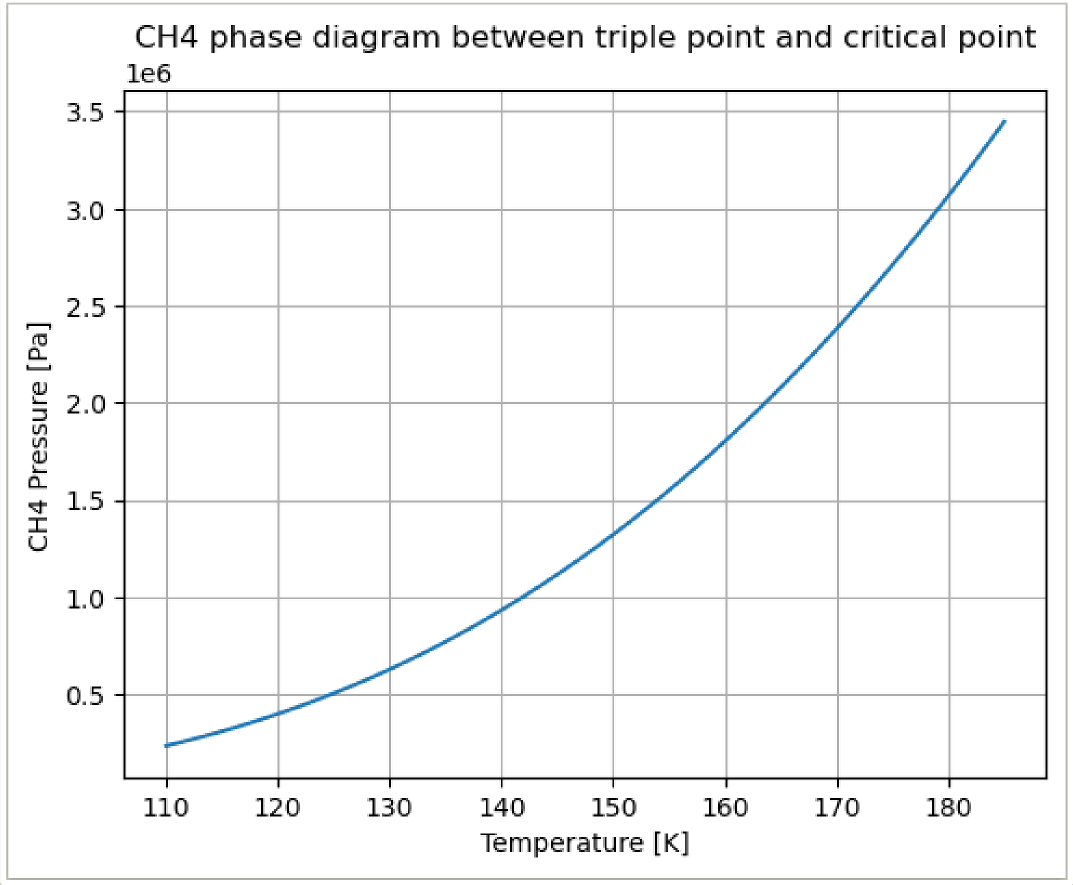
Solutions :

Switching from absolute to relative error	Adjusting the step size & tolerance dynamically

6°) Equilibrium Pressure Calculation – Overcoming Instabilities

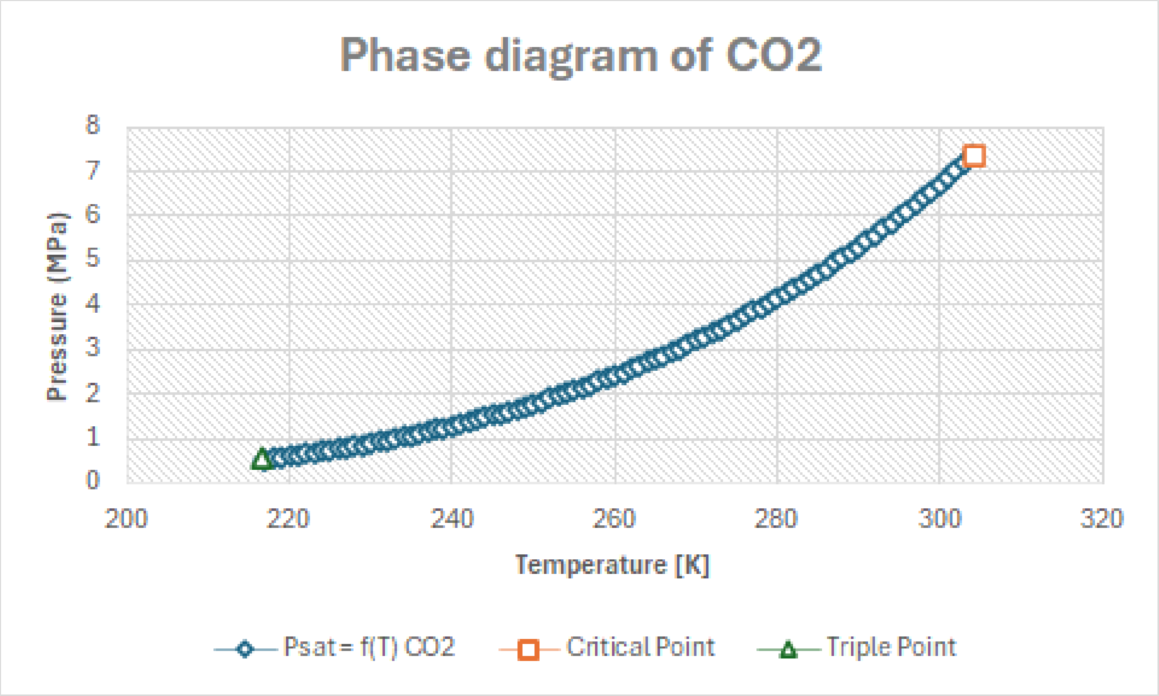


CO2 saturation curve plotted with python



CH4 saturation curve plotted with python

7°) Model Validation – Comparing with Experimental Data



CO2 saturation curve plotted with experimental data from NIST WebBook

Goal :

- Ensure the SRK model aligns with real data

Approach taken :

- Using NIST experimental datasets for CH_4 and CO_2
- Comparing Python results with Excel-generated experimental plots

8°) Final Refinements & Lessons Learned

- Structured the PW for progressive learning
- Provided precomputed data where coding was too complex
- Used real-world data to make results more meaningful

Key refinements:

- Iterative design is key in pedagogy
- Balancing complexity and accessibility is challenging but essential

What I learned from this project:

9°) Conclusion & Perspectives

What this project brings to students :

- A structured approach to thermodynamic modeling
- Hands-on experience in Python & data analysis

Possible improvements :

- Extending the PW to multi-component gas mixtures
- Implementing alternative cubic equations (e.g., Peng-Robinson)

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