Problem 2

The ideal gas equation of state is valid only for a limited range of pressures and temperatures. An alternative equation of state for gases is the van der Waals equation:

$$(p + \frac{a}{v^2})(v - b) = RT$$

where v is the molar volume, and a and b are the empirical constants for a gas. A chemical engineering design project requires you to accurately estimate the molar volume of ethyl alcohol (a = 12.02 and b = 0.08407) at a temperature of 400 K and pressure of 2.5 atm. Use the false position method. Compare your results with the ideal gas law.

Description of Problem:

The problem involves estimating the molar volume of ethyl alcohol (a specific gas) using the van der Waals equation of state. The problem addresses the behavior of gases under non-ideal conditions, where deviations from the ideal gas law become significant. The ideal gas equation ($pv = nRT$) accurately describes gas behavior at low pressures and high temperatures, but it fails to capture interactions between gas molecules, molecular volume, and attraction under conditions where these effects are pronounced. This is where the van der Waals equation of state comes into play.

Van der Waals Equation:

The van der Waals equation provides a more realistic model for gases by accounting for two factors: molecular volume and intermolecular forces. The equation is given by:

$$\boxed{(p + \frac{a}{v^2})(v - b) = RT}$$

Here:

- p is the pressure.
- v is molar volume.
- R is the real gas constant.
- T is temperature.
- a and b are empirical constants specific to the gas.

To Find: We need to compute molar volume v using the False position method and then need to compare the result with the ideal gas law.

Given: $T = 400k, p = 2.5\ atm$, $a = 12.02$, $b = 0.08407$,
$R = 0.082057338\ L.atm.K^{-1}mol^{-1}$.

NOTE: We are using the units of the parameters as given in the problem and according to that the unit of molar volume(v) will be in $L.mol^{-1}$.

Procedure:

- Rearrange the Van der Waals equation to solve for molar volume v.

$$(p + \frac{a}{v^2})(v - b) - RT = 0$$

$$\Rightarrow pv^3 - (pb + RT)v^2 + av - ab = 0$$

,Domain $\forall\ v \in \Re - \{0\}$

- Substitute the given values of p, T, a and b into the equation.

$$2.5v^3 - ((2.5)(0.08407) + (0.082057338)(400))v^2 + 12.02v - (12.02)(0.08407) = 0$$

$$\Rightarrow 2.5v^3 - 33.03375v^2 + 12.02v - 1.0105214 = 0$$

- Let us define a function f of v for the above equation as $f(v)$.

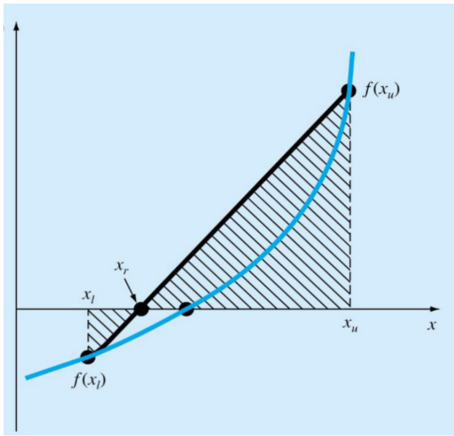
$$f(v) = 2.5v^3 - 33.03375v^2 + 12.02v - 1.0105214$$

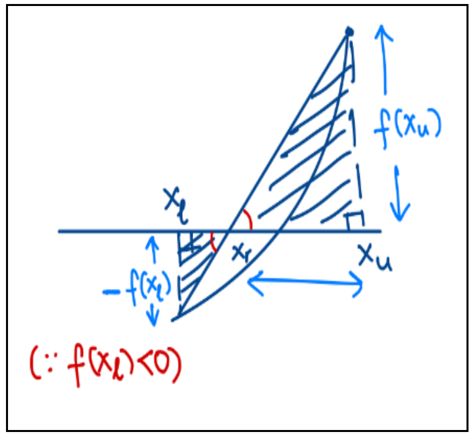
False Position Method:

Step 1: Choose lower x_l and upper x_r guesses for the root such that the function changes sign over the interval. This can be checked by ensuring that $f(x_l)f(x_u) < 0$.

Step 2: An estimate of the root x_r is determined by $x_r = x_l - \frac{f(x_l)(x_u - x_l)}{f(x_u) - f(x_l)}$.

Deriving the formula for x_r:





We can see two shaded triangles in the above figures which are similar to each other i.e. $\Delta_1 \sim \Delta_2$.

Therefore,

$$\frac{f(x_u)}{x_u - x_l} = \frac{-f(x_l)}{x_r - x_l} = \frac{f(x_l)}{x_l - x_r}$$

By cross multiplying and simplifying we get,

$$\boxed{x_r = x_l - \frac{f(x_l)(x_u - x_l)}{f(x_u) - f(x_l)}}$$

Step 3: Make the following evaluations to determine in which subinterval the root lies:

1. If $f(x_l)f(x_r) < 0$, the root lies in the lower subinterval. Therefore, set $x_u = x_r$ and return to step 2.
2. If $f(x_l)f(x_r) > 0$, the root lies in the upper subinterval. Therefore, set $x_l = x_r$ and return to step 2.
3. If $f(x_l)f(x_r) = 0$, the root equals x_r; terminate the computation.

❖ To compute the above procedure of the False Position method, we can either use the recursion process where we will call the function after each iteration, or we can use the looping process. For the sake of this problem, we will use a looping process using a while loop.

- Using the False Position method, we know that we might be unable to reach the exact true answer of the equation. For example, if the root is 12.3426789 or any irrational number, the computer will require many iterations, which might cause a runtime error.
- So, there need to be some stopping criteria within the loop after which the program will exit, and we can get a sufficiently close answer to our actual solution.
- So we can use two ways or criteria as a threshold condition in our program.
  - I. Set a limit to the number of iterations that our program will perform by defining a $itermax$ variable such that if $iter >= itermax$ then stop the loop and return x_r.
  - II. Use approximation error(ε_a) to keep track on x_r. Define a value for the variable ε_s such that if $\varepsilon_a < \varepsilon_s$ the loop ends, it will return the optimized root x_r.

    Where $\varepsilon_a(\%) = \frac{x_r^{new} - x_r^{old}}{x_r^{new}} \times 100.$

Solution :

- So to solve the problem we first need to define the values of stopping criteria for our program.
- Let us take the max number of iterations to 100 and the minimum value of approximation error ε_a that we want to achieve to be 0.05%.

$$itermax = 100 \; and \; \varepsilon_s = 0.005$$

- The next step is to guess a lower x_l and upper x_u such that $f(x_l)f(x_u) < 0$.

> **Note:** If we notice the equation,
>
> $$f(v) = 2.5v^3 - 33.03375v^2 + 12.02v - 1.0105214$$
>
> we can see that it is a cubic polynomial equation. So, there will be three roots of the equation. Therefore, we need to find 3 subintervals for the 3 roots.

So, let's perform some hit-and-trial methods to get the guesses.

- As zero is not in the domain, let's start with taking $x_l = 0.01$ and $x_u = 0.1$

$$f(x_l)f(x_u) = f(0.01)f(0.1) \approx 121847.624 > 0$$

- Take $x_l = 0.1$ and $x_u = 0.2$

$$f(x_l)f(x_u) = f(0.1)f(0.2) \approx -31.413 < 0$$

The condition is satisfied, and therefore one root is between 0.1 and 0.2

The root found by our program is $v = 0.1302\ L.mol^{-1}$ in 17 iterations.

Iteration	x_l	x_u	x_r	ea(%)
1	0.1	0.200000	0.185546	-
2	0.1	0.185546	0.170713	8.688977
3	0.1	0.170713	0.157512	8.380486
4	0.1	0.157512	0.147306	6.928975
5	0.1	0.147306	0.140316	4.981701
6	0.1	0.140316	0.135949	3.211806
7	0.1	0.135949	0.133386	1.921387
8	0.1	0.133386	0.131939	1.096908
9	0.1	0.131939	0.131140	0.609269
10	0.1	0.131140	0.130704	0.333212
11	0.1	0.130704	0.130469	0.180684
12	0.1	0.130469	0.130342	0.097521
13	0.1	0.130342	0.130273	0.052502
14	0.1	0.130273	0.130236	0.028227
15	0.1	0.130236	0.130217	0.015165
16	0.1	0.130217	0.130206	0.008144
17	0.1	0.130206	0.130200	0.004373

- Now take $x_l = 0.2$ and $x_u = 0.3$

$$f(x_l)f(x_u) = f(0.2)f(0.3) \approx -7.935 < 0$$

The condition is satisfied again, and therefore one root is between 0.2 and 0.3

The root found by our program is $v = 0.241772\ L.mol^{-1}$ in 4 iterations.

Iteration	x_l	x_u	x_r	ea(%)
1	0.200000	0.300000	0.240079	-
2	0.240079	0.300000	0.241798	0.71086
3	0.240079	0.241798	0.241772	0.010415
4	0.241772	0.241798	0.241772	0.000011

- Now take $x_l = 1$ and $x_u = 20$

$$f(x_l)f(x_u) = f(1)f(20) \approx -342.93 < 0$$

The condition is satisfied again, and therefore one root is between 1 and 20.

The root found by our program is $v = 12.841275\ L.mol^{-1}$ in 4 iterations.

Iteration	x_l	x_u	x_r	ea(%)
1	1.000000	20	11.001592	-
2	11.001592	20	12.818794	14.176076
3	12.818794	20	12.841042	0.17326
4	12.841042	20	12.841275	0.001814

➢ So we have 3 roots of the equation now that are $v_1 = 0.1302$, $v_2 = 0.241772$ and $v_3 = 12.841275$.

Ideal Gas Equation:

The ideal gas equation, often referred to as the equation of state for ideal gases, is a fundamental relation that describes the behavior of ideal gases under specific conditions. The equation is given by:

$$\boxed{pv = RT}$$

Here:

- p is the pressure.
- v is molar volume.
- R is the real gas constant.
- T is temperature.

Now assuming the ideal behavior of gas, the molar volume we get is

$$v_{ideal} = \frac{RT}{p}$$

$$\Rightarrow v_{ideal} = \frac{(0.082057338)(400)}{2.5} = 13.12917\ L.mol^{-1}$$

To compare our results for Van der Waals equation with ideal gas we can use compressibility factor Z which is defined as

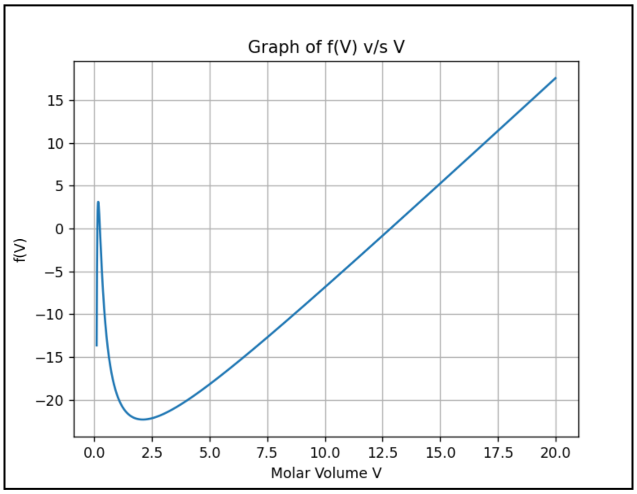
$$\boxed{Z = \frac{v_{real}}{v_{ideal}}}$$

If we substitute the values of v_1, v_2, v_3 in v_{real} one by one, we get

$$Z_1 = \frac{v_1}{v_{ideal}} \qquad Z_2 = \frac{v_2}{v_{ideal}} \qquad Z_3 = \frac{v_3}{v_{ideal}}$$

$$\Rightarrow Z_1 = 9.92 \times 10^{-3} \qquad \Rightarrow Z_2 = 1.8 \times 10^{-2} \qquad \Rightarrow Z_3 = 0.9787$$

Now looking at Z_1 and Z_2, we can say that the gas deviates a lot from ideal gas behavior. But the pressure and temperature that are given in the problem tend gas to ideal behavior. Therefore, the value of Z should be near 1 which is in the case of Z_3. Hence we can conclude our answer to be $V_3 = 12.841275\ L.mol^{-1}$.


Graph of f(V) v/s V
f(V)
Molar Volume V
15
10
5
0
−5
−10
−15
−20
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0