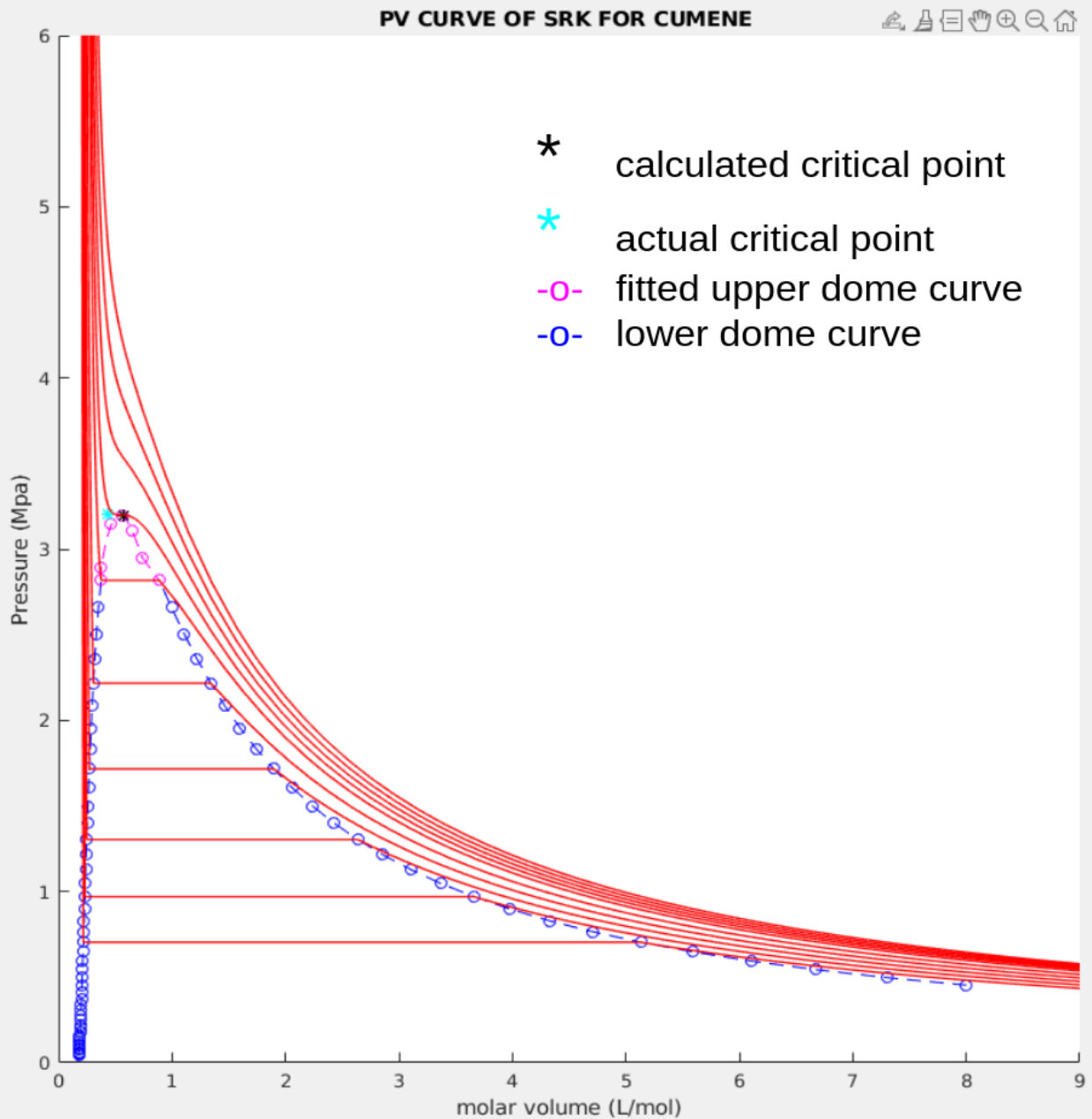


# COMPUTATIONAL ASSIGNMENT

## PV DIAGRAM OF SRK EOS FOR CUMENE



---

## Introduction

The **Soave-Redlich-Kwong (SRK) equation** of state (EoS), proposed by Soave (1972), is one of the most popular EoS in simulations and optimizations in which vapor-liquid equilibrium (VLE) properties are required.

## EQUATIONS

These are the equations which are mainly used to solve the assignment.

$$1. P = \frac{RT}{v-b} - \frac{\alpha a}{v(v+b)}$$

$$2. Z = \frac{1}{1-\rho b} - \frac{\alpha a \rho}{RT(1+\rho b)}$$

$$3. \int_0^\rho (z-1) \frac{d\rho}{\rho} = -\ln(1-\rho b) - \frac{\alpha a}{RTb} \ln(1+\rho b)$$

$$4. \frac{G-G^{ig}}{NRT} = -\ln(1-\rho b) - \frac{\alpha a}{RTb} \ln(1+\rho b) + (z-1) - \ln(z)$$

## BRIEF APPROACH

According to data available on internet for cumene -

Source - <https://pubchem.ncbi.nlm.nih.gov/compound/Cumene#section=Flammable-Limits>

Critical Temperature - 631.15k      Critical Pressure - 3.2 Mpa      Critical Volume - 0.4370 L/mol

Acentric factor - 0.3377

As we know nearly all equations of state are yet unable to predict the correct nature of two phase regions and also have some problems around critical temperature. So, for plotting the complete dome shaped curve for cumene, I have divided it into two parts: lower dome shaped curve and upper dome shaped curve.

### Lower Dome Shape Curve -

---

Lower dome shaped curve is plotted for a temperature range of 400 to 620 kelvin. The methodology for plotting the curve is straight forward. For a particular temperature , we have to find the saturation pressure. At saturation pressure , we know  $\mu^l - \mu^g \rightarrow 0$ .

So , we can use the bisection method and by observing some properties we can guess two initial value of P such that  $(\mu^l - \mu^g)_{P_1,T} * (\mu^l - \mu^g)_{P_2,T} < 0$  , which ensures that the root of this equation lies in this interval.

We can observe from the graphs that above the saturation region , difference in chemical potential ( $\mu^l - \mu^g$ ) above the saturation pressure is negative and below the saturation pressure is positive.

For finding limits , we know that saturation pressure will always be less than critical pressure. So , to get the upper limit , we can start with P\_critical and decrease it until we get three real roots. And , to get a lower limit , we can start from very less temperature (like 0.0001 Mpa) and increase temperature until we get three roots for the equation of state.

Using , bisection method we can get a very accurate value of Psat for the temperature range and corresponding molar volume of liquid and gas.

**Figure(a)** shows the lower dome region.

### **Upper Dome Region Plotting & Finding Critical Point -**

This is the region in which the equation of state has some problems. Upper dome curved is plotted for a temperature range of 620 to T critical in my case. In this region the above method cannot be used since we don't get correct chemical\_potential\_diff around this temperature. For my system , I found that near this temperature , chemical potential difference above and below psat is negative in both cases sometimes so we cannot apply the bisection method.

To tackle this problem , My approach is ->

1. At this point, we can check that  $(v^g - v^l) < 0.65$  , so we are near our critical points.
2. To make our algorithm faster , we can subdivide it into three parts that are as.
  - a) When  $(v^g - v^l) > 0.3$  , for this we can assume psat to be average of upper\_limit and lower\_limit where upper\_limit and lower\_limit are as maximum pressure and minimum pressure we get three real roots for volume. For , this loop we increase the temperature by 1k.

- 
- b) When  $(v^g - v^l) > 0.1$  , for this we can assume  $p_{sat}$  to be equal to `upper_limit` as at this point `upper_limit` and `lower_limit` are nearly equal. For this loop we increase the temperature by 0.1k.
  - c) When  $(v^g - v^l) > 0.01$  , for this we can also assume  $p_{sat}$  equal to `upper_limit` but in this case we increase temperature by 0.001k as at this point we are very near to the critical point and when we get  $(v^g - v^l)$  nearly equal to 0.01 we can end the loop and the corresponding points will be our critical points for the system.

Since , in this algorithm we are just approximating  $p_{sat}$  but not calculating it exactly .So , we will not get the correct behaviour for this part.

**Figure(b)** shows the upper dome region we get after applying this algorithm.

Values of critical points we get are as ->

Critical Pressure - 3.1975 Mpa

Critical Temperature - 631.08 K

Critical Volume - 0.571 L/mol

Since , we do not get the correct behaviour. So ,for this we can fit a curve in the upper dome region. In my case I have fitted a cubic curve using matlab inbuilt functions such as `polyfit` and `polyval`.

**Figure (c)** shows the fitted curve and `upper_dome_region`.

**Figure (d)** only shows the fitted curve for `upper_dome_region`..

## ERROR ANALYSIS IN CRITICAL POINTS

Percentage error in critical temperature =  $(\text{abs}(631.15 - 631.08) / 631.15) * 100 = 0.011 \%$

Percentage error in critical pressure =  $(\text{abs}(3.2 - 3.1975) / 3.2) * 100 = 0.0781 \%$

Percentage error in critical volume =  $(\text{abs}(0.4370 - 0.571) / 0.4370) * 100 = 30.66 \%$

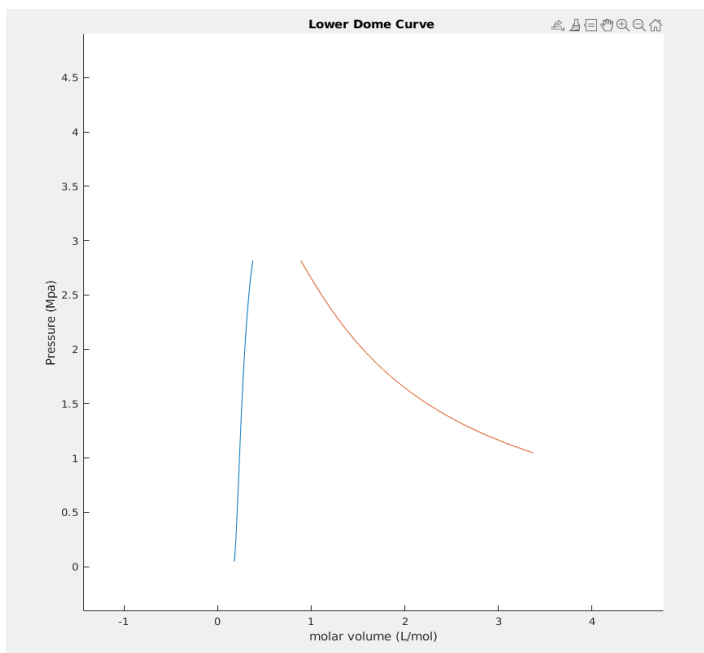


Figure (a)

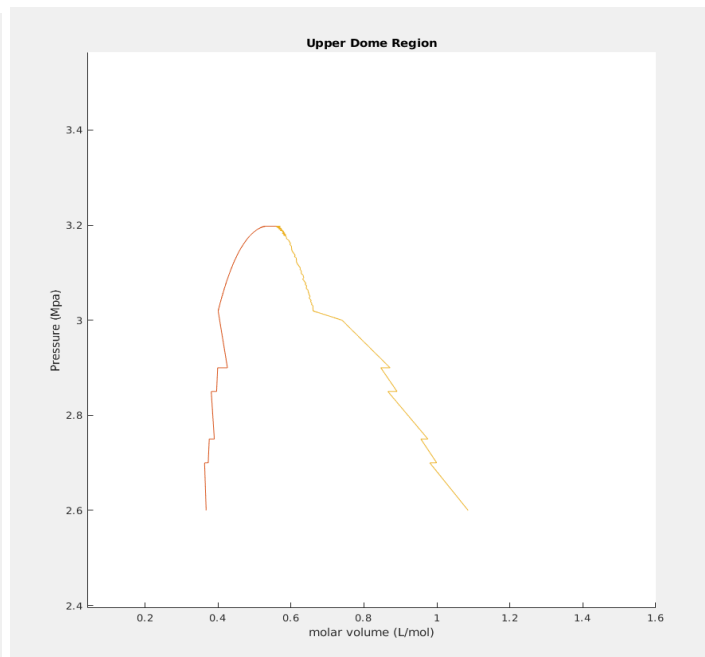


Figure (b)

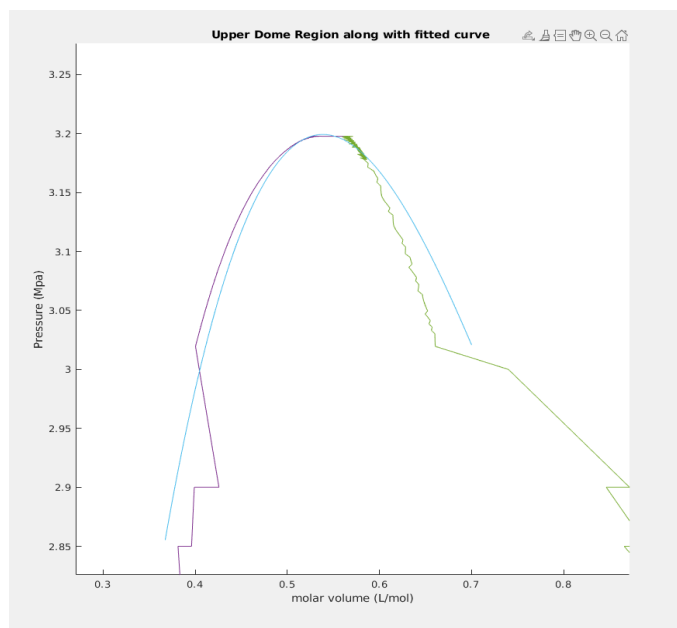


Figure (c)

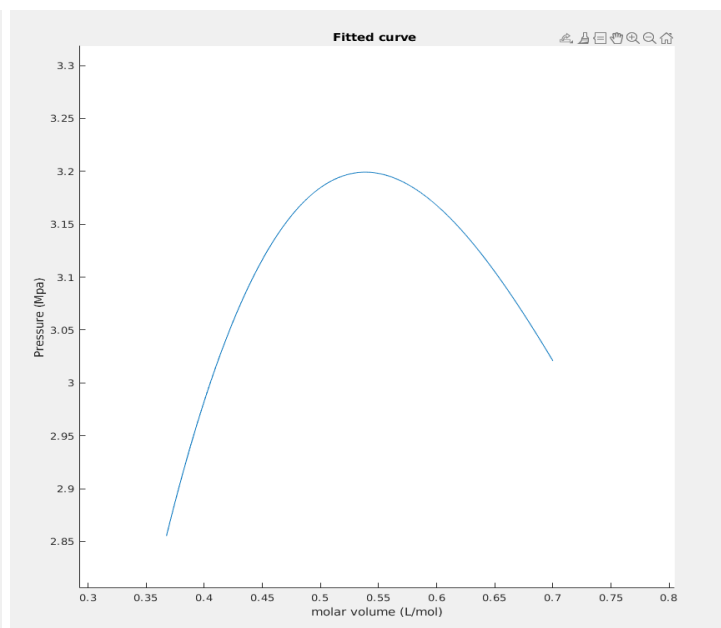


Figure (d)

---

## CODE DESCRIPTION -

**srk.m** - A custom class is defined for the srk equation of state which has methods to solve for psat ,critical points and other important parameters.

**plot\_iso.m** - This file uses an object of srk class and plot the required isotherm using methods of the class.

## How to run the code -

Put these both files in the same folder and add the path of the folder to matlab path and , then run plot\_iso.m file only.

## CODE OUTPUT -

This is the list of some of the values that are outputted by the code.

T(K)	Psat(Mpa)	vol_liquid(L/mol)	vol_gas(L/mol)
400	0.047	0.1778	68.6286
440	0.141	0.1870	24.6868
480	0.339	0.2001	10.6227
520	0.7036	0.2189	5.1304
560	1.3035	0.2485	2.6362
600	2.2169	0.3068	1.3408
620	2.817	0.375549	0.8871
631.08	3.1975	0.57128	0.57128