

# **CHE221: COMPUTATIONAL ASSIGNMENT**

## **Equation of state: Soave Redlich Kwong**

### **System: Toluene**

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An equation of state is a thermodynamic relation between various state variables of a system, which describe the state of a particular system completely. These are empirical relations given on basis of extensive experimentation. The very basic equation of state is the **Ideal Gas Equation**. This equation was corrected and many modified versions were given. The first significant modification was with **Van der Waal's Real gas equation**. This was among the very first cubic equations of state. Van der Waal's equation captures the presence of intermolecular interactions between the gas molecules, which was assumed to be absent in the formulation of the ideal gas equation. It behaved more nicely than the ideal gas equations, but still not perfect.

**Redlich Kwong Equation** was modelled while Otto Redlich and Kwong were working at Shell Development Company, California. They were mostly concerned with non-polar gases and slightly polar hydrocarbons. And the equations of state like Van der Waal's, Benedict-Webb-Rubin equation, Beattie- Bridgeman equation, were either unable to capture the behaviour correctly(VW) or they were too complicated and involved more parameters. In 1972, Soave proposed a modification to the equation by introducing a temperature-dependent parameter  $\alpha_{SRK}$ . The modified equation is given as -

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$

where

$$\bullet \alpha = \left(1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - \sqrt{T_r})\right)^2,$$

$$\bullet a = \frac{1}{9(\sqrt[3]{2} - 1)} \frac{R^2 T_c^2}{P_c} = 0.42748 \frac{R^2 T_c^2}{P_c},$$

$$\bullet b = \frac{\sqrt[3]{2} - 1}{3} \frac{RT_c}{P_c} = 0.08664 \frac{RT_c}{P_c},$$

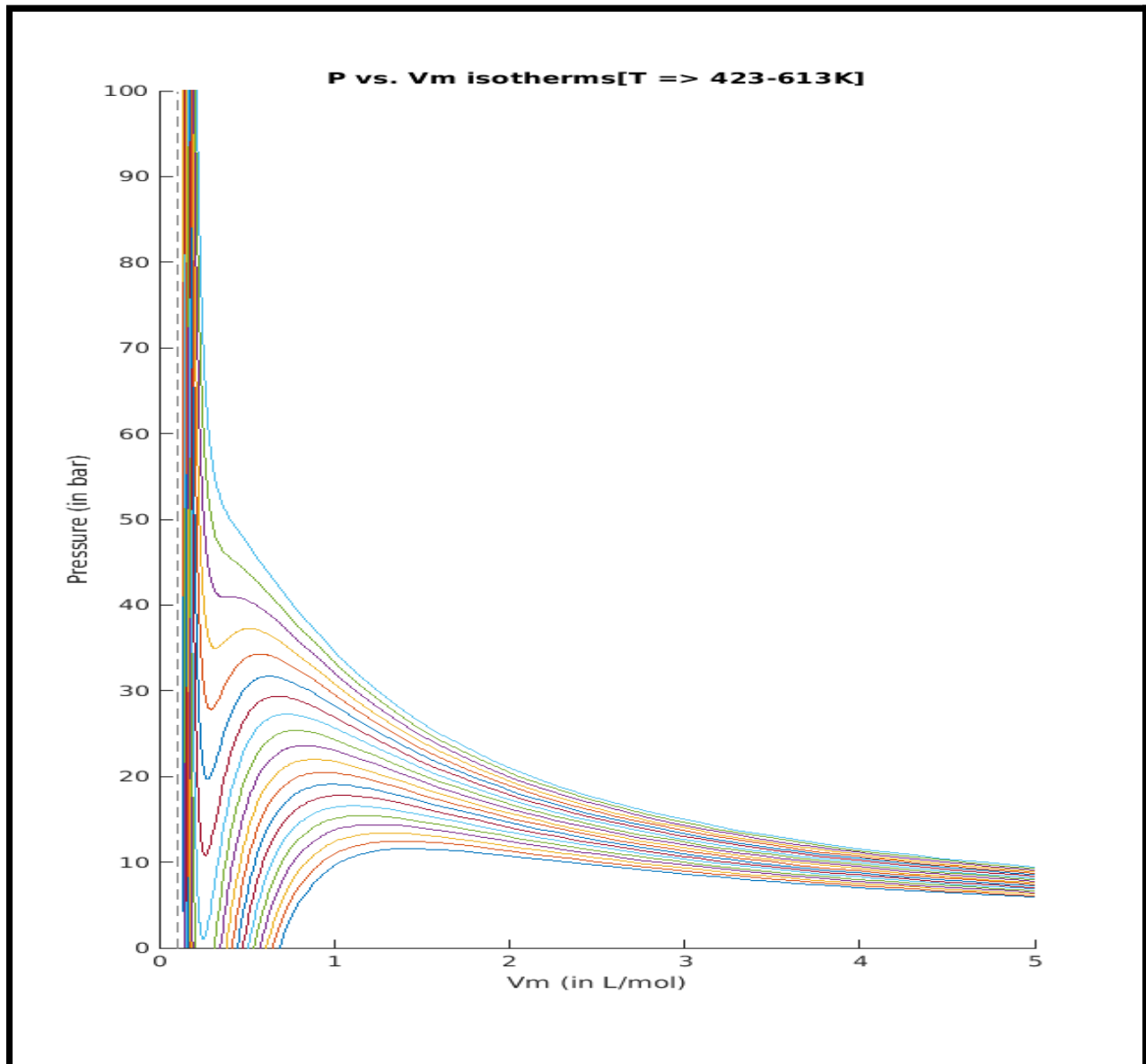
here,  $T_r$  is the reduced temperature, given by  $T/T_c$ .

**Approach-** To plot the isotherms for various temperatures over the range 420-590K, we follow this procedure-

- Obtain the acentric factor for toluene, which is  $\omega = 0.263$  for toluene. From acentric factor, calculate  $\alpha_{SRK} = (1 + (0.48 + 1.564\omega - 0.176\omega^2)(1 - T_R))^2$ .

- The critical point for Toluene is 593K and 41 bar, according to the NIST database.
- Calculate the constant  $b = \phi \cdot R \cdot T_c / P_c$ .  $\phi = 0.08664$ ,  $R = 0.08314$  bar L/mol. K.
- Calculate constant  $a(T) = \Omega \cdot \alpha_{\text{SRK}} \cdot (R \cdot T_c)^2 / P_c$ .  $\Omega = 0.42748$ .
- Now having obtained all the values, we will plot P by varying  $V_m$  over a range, after putting all the values in SRK EOS.

We get the following plot by following the above procedure-



After watching this plot carefully, one can observe the change in the shape of the isotherm at some intermediate stage. From our studies, we know that the point at which

such inflexion takes place, i.e. the point at which convexity of the isotherm changes is the critical point. We know the following properties of the critical point-

- Above the critical point, liquid-vapour equilibrium doesn't exist. Only one phase exists at a critical point.
- The isotherm passing through the critical point, **critical isotherm**, undergoes an inflexion at a critical point. This gives us -

$$\left( \frac{\partial p}{\partial V} \right)_T = 0,$$

$$\left( \frac{\partial^2 p}{\partial V^2} \right)_T = 0.$$

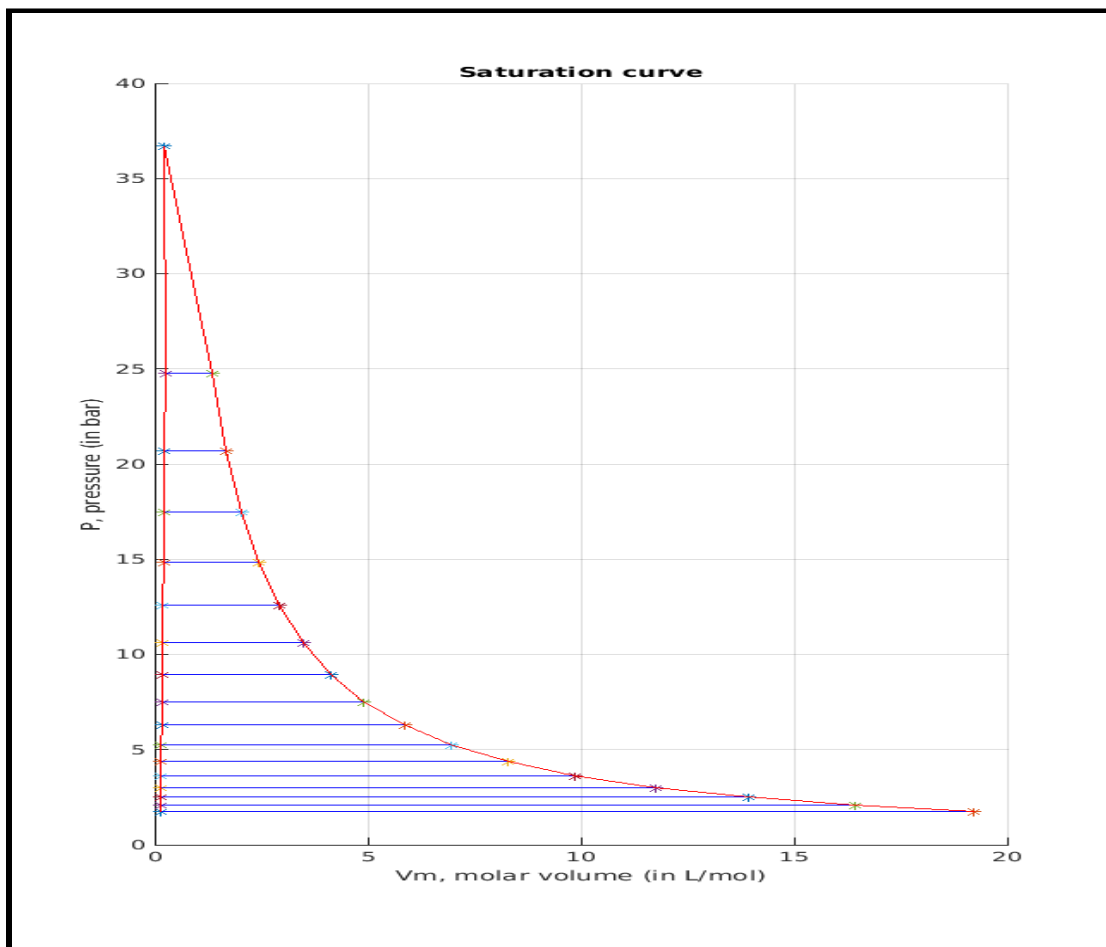
The first relation implies that, if we collect a locus of saturation points at different temperatures, then the only point at which the derivative of  $P_{\text{sat}}$  w.r.t. volume is 0, must be the critical point. The reasoning behind this can be given as above critical point no saturation point exists. At a critical point, only one phase exists and we have the first derivative of  $p$  with respect to  $v$  at constant  $T$  is 0. That means, the locus must converge on a critical point, and the above property applies to the locus too.

To find the  $P_{\text{sat}}$ , for a given temperature we follow the given procedure-

1. Choose a temperature range over which we will find the saturation curve. For my calculations, I have chosen 423-593 Kelvin since, there are no saturation points above the critical point, and we have a fair range to predict the behaviour.
2. For a given temperature, we will guess  $P_{\text{sat}}$ . In this case, I have used the Antoine equation to find the guess value. One point which I would like to highlight here is, since we are only guessing  $P_{\text{sat}}$ , we can use this equation slightly above the given range for the parameters too.
3. This guess value is named and used as  $P_g$  in the program. Calculation of the coefficients of various powers of volume when the equation is expressed in standard cubic form.
4. For the given value of  $P_g$ , roots of the equation, i.e. values of volume that the substance can take, are calculated. There are two possibilities,
  - a. One real root and two imaginary roots- then we are in one root region and we have to vary  $P_g$  such that we fall in three root region.

- b. Three real roots may be equal or unequal- out of the three roots, the lowest one corresponds to liquid saturated volume at  $P_{\text{sat}}$  and the highest one to vapour volume, when pressure is  $P_{\text{sat}}$ .
5. From these two volumes, we can calculate the chemical potential of saturated liquid and saturated vapour phase. From our studies, we know that these chemical potentials must be equal at equilibrium. So we will calculate these two chemical potentials, and then find their difference. If magnitude of difference is below some tolerance value, say 0.001 for my program, then these two are equal, and the corresponding guess for pressure is the  $P_{\text{sat}}$  for the given temperature.
6. We mark these points on a plot for the given temperature, and repeat steps 1 to 5 for different temperature values to collect data for various temperatures.

I have written my code using the general outline approach given above, and using Desmos graphing calculator to simulate the equations by varying different parameters. The output plot is given below-



From the two plots above, we can draw following conclusions.

1. **The critical point follows two derivative properties as given above. From the isotherms shown above, the violet line (3rd from top) seems to show inflexion as well as flatness at same point. The point is approximately 41 bar, 0.402 L/mol and since it is third line from top,  $T = 593\text{ K}$ .**
2. **From saturation curve, the saturated liquid line and saturated vapour line converge at  $P = 36.72\text{ bar}$ ,  $V_m = 0.2416\text{ L/mol}$  and  $T = 583\text{ K}$ .**

First result agrees with the experimental data collected from standard database. Second result shows some deviation. The actual data from NIST database is -

$T_c = 593\text{ K}$ ,  $P_c = 41\text{ bar}$ ,  $V_c = 0.316\text{ L/mol}$ .

Ascentric factor was taken from the following website -

- [http://www.kaylaiacovino.com/Petrology\\_Tools/Critical\\_Constants\\_and\\_Acentric\\_Factors.htm](http://www.kaylaiacovino.com/Petrology_Tools/Critical_Constants_and_Acentric_Factors.htm)
- <https://webbook.nist.gov/cgi/cbook.cgi?ID=C108883&Mask=4> (NIST database for toluene.)

**\*\*\*\*\* Thank You \*\*\*\*\***

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