

COMPUTATIONAL ASSIGNMENT

EQUATION OF STATE - SOAVA REDLICH KWONG

SYSTEM – NAPHTHALENE

EQUATION OF STATE

Soave Redlich Kwong is a modified version of Redlich Kwong equation obtained by replacing the $1/\sqrt{T}$ term with a function $\alpha(T, \omega)$ involving the temperature and the acentric factor. The α function was devised to fit the vapor pressure data of hydrocarbons and the equation does well for these materials. It is a cubic polynomial in V.

SRK EOS is given by:

$$P = \frac{NRT}{V - Nb} - \frac{N^2 a(T)}{(V + \epsilon Nb)(V + \sigma Nb)} \quad \sigma = 1, \epsilon = 0$$

$$a(T) = \psi \alpha(T_r) R^2 T_c^2 / P_c \quad \psi = 0.42748$$

$$b = \frac{\Omega R T_c}{P_c} \quad \Omega = 0.08664$$

$$\alpha(T_r) = [1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5})]^2$$

VALUES USED

Napthalene is a polycyclic aromatic hydrocarbon with formula $C_{10}H_8$ and molecular weight of 128.1705 g/mol.

Napthalene have a critical temperature of 784 K and a critical pressure of 40 atm and an acentric value ω of 0.302.

These values have been used from the NSIT Webbook

PROCEDURE

At the start we will be declaring all the essential variable and their values. We will then also be declaring vector to store the values of Psat and corresponding V_l and V_v. We will also be taking an array of guesses of Psat. We will also be making a departure function which will be later called to calculate the condition $\mu_l = \mu_v$

ISOTHERM

1. Firstly, start a for loop of T and initiate a counter.
2. Now using given values also calculate alpha which is a function of temperature and other required values.

3. Now use all the values in the EOS to get a equation of P in terms of only V.
4. For plotting the isotherm, we simply graph the P vs by using the given equation of state at a particular temperature.
5. This plot can be plotted by using fplot. Add other functions to get the graph in the required scale.

We can see the behavior of isotherm from the plot.

Below the critical temperature, the isotherms follow a cubic trend i.e., in this region, the isotherms three positive roots for a particular given pressure. The maximum is the volume of saturated vapor, and the minimum is the volume of saturated liquid.

At the critical temperature, the distinct roots merges into a single root. This point of inflection is the critical point.

Above the critical temperature the curve seems to have no real root. Physically above the critical temperature, there is no distinction between the solid-liquid-gas phases.

DOME SHAPED CURVE

1. For this we need some initial guesses of Psat. The choice of guess is very important as better the guess faster it converges, and this also helps in getting real roots. This choice can be taken using Antoine equation, but the equation is valid only up to a particular temperature. So, a better choice is to take the guesses by analyzing the isotherm and selecting the points, when a horizontal line is drawn through it, it intersects the curve at exactly three points.
2. Now for the given T and Psat we find the roots of the cubic polynomial in V. We will get three real roots of V. Out of this the maximum one corresponds to V_v and the minimum is V_l. These roots can be found using function roots and then sorted to the maximum and minimum value of the found roots.
3. Now we know that for at the point of saturation chemical potential of both liquid and gas is equal i.e., $\mu_l = \mu_v$.
4. To check if the above condition is satisfied or not, we will be using departure function.

$$\frac{G(T, P) - G^{ig}(T, P)}{NRT} = \frac{\mu(T, P) - \mu^{ig}(T, P)}{NRT} = \int_0^P \frac{(Z - 1)dP}{P} + (Z - 1) - \log Z$$

For vapor, $\rho = 1/v_v$ and for liquid, $\rho = 1/v_l$.

5. After doing the integration, the equation comes out to be:

$$-\log(1 - \rho^l b) - \frac{a \log(1 + \rho^l b)}{bRT} - Z_l - 1$$

$$-\log(Z_l) = \log(1 - \rho^v b) - \frac{a \log(1 + \rho^v b)}{bRT} - Z_v - 1 - \log(Z_v)$$

6. The departure function of both liquid and gas can be calculated by using a separate function, let's name it dep , this would give $depl$ which is departure function of liquid and $depv$ which is departure function of vapor.
7. Now we will be taking a tolerance value which helps us converge $psat$ to a particular value where absolute difference between these departure functions should be less than this tolerance.
8. First, we will increase the value of $Psat$ and check if the absolute difference decreases or does it decrease.
9. If it increases, we must slowly decrease the value of $Psat$ and if it decreases, we will continue increasing the value of $Psat$.
10. Now, we will again calculate roots and then calculate departure function and then their absolute difference. This loop continues till the tolerance value.
11. We will then be storing the final converged $Psat$ and corresponding values of $Vsat$ in the earlier declared array.
12. For plotting we will be marking $Psat$ and $Vsat$ on the graph and then drawing a spline through these points.
13. For drawing the spline, we will be using spline function.

COMPARISON TO THE EXPERIMENTAL VALUE

By comparing the result with the experimental values, we can clearly see some deviation. The primary reason for this deviation is the limitation of equation of state. Moreover, using a tolerance value for absolute difference of departure function also adds to this deviation. Taking significant values and rounding off also deviates the calculated value from the experimental values.

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