CHE221: CHEMICAL ENGINEERING THERMODYNAMICS

COMPUTATIONAL ASSIGNMENT

- Manvendra Singh, 190487

System : Carbon Disulphide

Equation : Peng Robinson

Theory:

General Equation of State for real gases:

$$P = NRT/(V - Nb) - N^2 a(T)/((V + \varepsilon Nb)(V + \sigma Nb))$$

$$a(T) = \psi \cdot \alpha(T) \cdot R^2 T_c^2 / P_c$$

$$b = \Omega \cdot RT_c / P_c$$

For Carbon Disulfide,

Acentric Factor : $\omega = 0.1107$

Antoine Equation Coefficients : A = 6.94219

B = 1169.11

C = 241.59

For Peng Robinson Equation,

N = 1, ψ = 0.45724 , Ω = 0.07760, $\varepsilon = 1 - \sqrt{2}$, $\sigma = 1 + \sqrt{2}$

$$\alpha(T) = [1 + (0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2) \cdot (1 - \sqrt{(T/T_c)}]$$

Simplified Equation : $P = RT/(V - b) - a(T)/(V^2 + 2bV - b^2)$

Cubic Form:

$$PV^3 + (Pb - RT)V^2 + (a(T) - 2bRT - 3pb^2 + (Pb^3 + RTb^2 - ab) = 0$$

Chemical Potential Calculation :

$$(G - G^{ig})/NRT = \int_0^{\rho} ((z-1)d\rho)/\rho + (Z-1) - ln(Z)$$

where Z = PV/RT

$$\Rightarrow -log(1 - b/V) - alog((V + 2.414b)/(V - 0.414b))/(2.828bRT) + ((VP)/(RT) - 1) - log((VP)/(RT))$$

Fugacity Calculation :

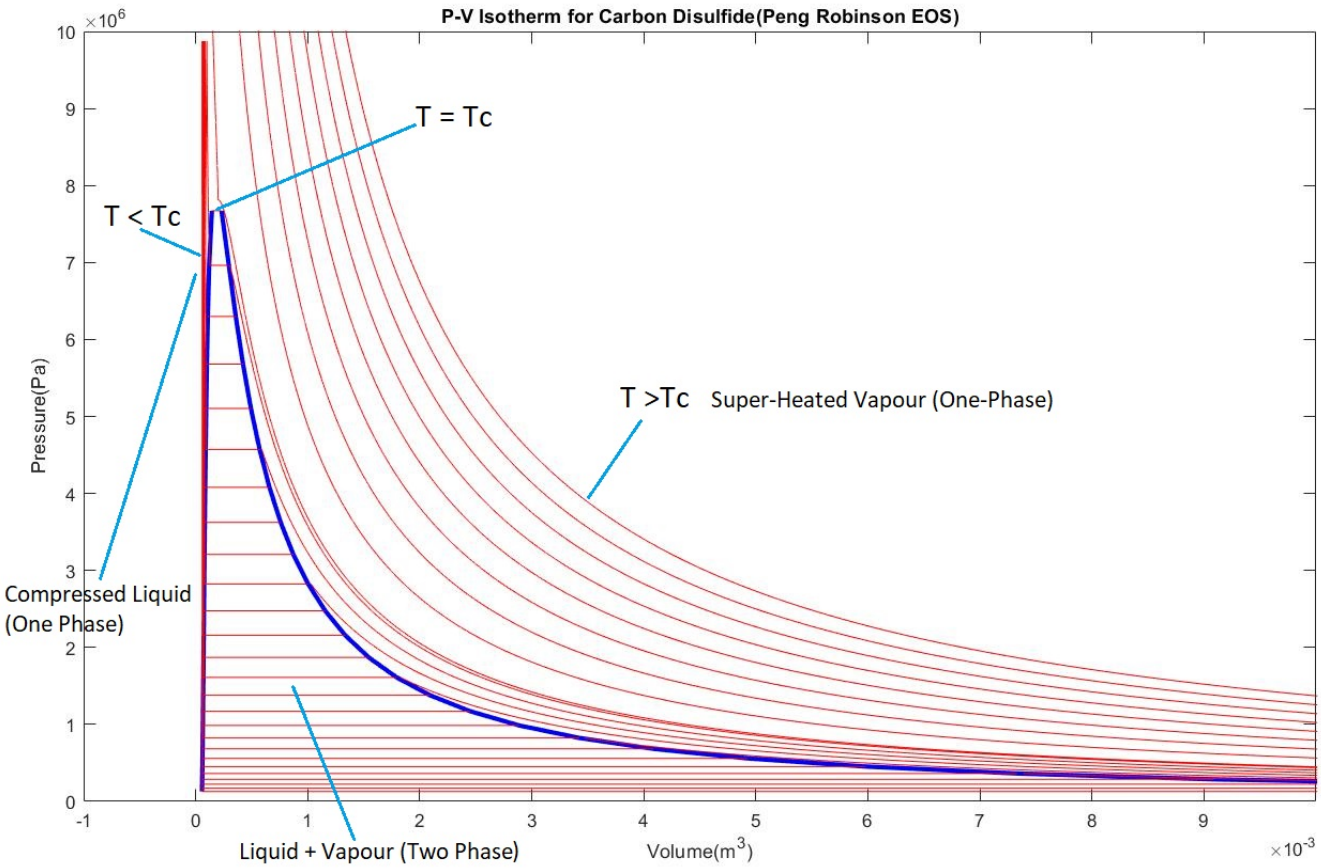
$$f = P \cdot e^{(G - G^{ig})/NRT}$$

FLOW DIAGRAM:

1. Defining Constants.
2. Varying T over a range to get isotherms.
3. Find the Parameters and Coefficients.
4. Use a nested loop to vary Psat with initial guess from antoine equation to get Vliq and Vvap (Antoine equation is avoided as it was giving imaginary roots. Rather, some low initial pressure is taken as guess values and then slowly increased till all real roots are found). The max value in the roots corresponds to Vvap while min value corresponds to Vliq.
5. Storing the Vliq, Vvap, Psat values in separate vectors.
6. Plotting the dome by taking Psat and corresponding volume values for different temperatures.
7. Plotting the lines inside the dome by joining the values of Vliq and Vvap for corresponding Psat.

8. Plotting the lines for T<Tc by varying the pressure from Psat to 1.25Psat by increasing by an amount of 1000Pa and plotting the corresponding value of Volume by finding the real root.
9. Plotting the lines for the right side of dome by varying the pressure from Psat to 250000 Pa by decreasing by an amount of 1000Pa and plotting the corresponding value of Volume by finding the real root.
10. Plotting the lines for T>Tc by varying the pressure from 1.5Psat to 50000Pa and temperature from Tc to 3Tc plotting the corresponding value of Volume by finding the real root.
11. Finally comprising all plots in one to find the final plot.

RESULT :



Explanation:

From the graph, we can infer that below the critical point, there exists a liquid-vapour equilibrium where the isotherms are parallel to the volume axis. This is due to pressure being saturated.

At T>>Tc, it becomes a vapour phase system(superheated) and pressure and volume varies inversely. Only one real root exists for EOS.

At T<Tc, it becomes a Liquid phase systeem(Compressed) and here also only one root exists.

At the critical point, There exist 3 real roots of the EOS which are all unique. This is because at the critical point, no specific liquid or vapour phase exists.

Appendix:

```
clc;
%Defining Constants value in SI Units
R = 8.314;
Tc = 552;
Pc = 7900000;
Omega = 0.1107;
A = 6.94219;
B = 1169.11;
C = 241.59;
Psat = 300000;          %Initial guess Psat for finding Psat for corresponding temperatures

%Arrays to store values of Volume of liquid, vapor and Saturation Pressure
%for corresponding temperature
Vliq = zeros(26,1);
Vvap = zeros(26,1);
PSAT = zeros(26,1);
VOLR = zeros(7,1);
PssR = zeros(7,1);
c = 1;
```

```
%for loop to calculate Psat at different temperatures till Tc
for T = 300:10:550
    alpha = 1+(0.37464 + 1.54226*Omega - 0.26992*Omega*Omega)*(1-sqrt(T/Tc));
    a = (0.45724*alpha*(R*Tc)^2)/Pc;
    b = 0.0775*R*Tc/Pc;

    %Antoine equation is not being used as the guess value provided by it
    %is giving imaginary values
    %Psat = 10^(A - B/(C+T-273.15));
    %Psat = (Psat*101.325)/760;



    flag = 0;
    while flag == 0
        c1 = Psat;
        c2 = (Psat*b - R*T);
        c3 = (a - 2*b*R*T -3*b*b*Psat);
        c4 = (Psat*(b^3) + R*T*b*b - a*b);
        p = [c1 c2 c3 c4];
        V = roots(p);
        if (isreal(V)) == 1
            Vg = max(V);
            Vl = 10000;
            for i = 1:3
                if V(i)<Vl && V(i)>0
                    Vl = V(i);
                end
            end
            %fugacity(similar to chemical potential) is calculated for
            %liquid and vapour
            LHS = Psat*exp(Value(Vl,a,b,R,T,Psat));
            RHS = Psat*exp(Value(Vg,a,b,R,T,Psat));
            if abs(LHS - RHS) < 1000
                flag = 1;
            elseif RHS > LHS
                Psat = Psat - 1000;
```

```
        else
            Psat = Psat + 1000;
        end
    else
        %if the roots are imaginary
        Psat = Psat + 100000;
    end
  end
  Vliq(c,1) = Vl;
  Vvap(c,1) = Vg;
  PSAT(c,1) = Psat;
  c = c+1;
end

%plot for dome
plot(Vliq,PSAT,'color','blue','LineWidth',2.5);
hold on;
plot(Vvap,PSAT,'color','blue','LineWidth',2.5);
hold on;

%plot for lines inside the dome
for i = 1:26
  x(1) = Vvap(i,1);
  x(2) = Vliq(i,1);
  y = [PSAT(i,1) PSAT(i,1)];
  plot(x,y,'color','red');
  hold on;
end

%plot for lines at T<Tc
T1 = [300:10:550];
for i = 1:4:26
  Ps1 = PSAT(i,1);
  j = 1;
  while(Ps1 <= 1.25*Pc)
    C1 = Ps1;
```

```
        C2 = (Ps1*b - R*(T1(i)));
        C3 = (a - 2*b*R*(T1(i)) -3*b*b*Ps1);
        C4 = (Ps1*(b^3) + R*(T1(i))*b*b - a*b);
        p = [C1 C2 C3 C4];
        r = roots(p);
        for k =1:3
            if isreal(r(k))
                VOLL(j) = r(k);
            end
        end
        PssL(j) = Ps1;
        Ps1 = Ps1 + 1000;
        j = j+1;
    end
    plot(VOLL,PssL,'color','red');
    hold on;
end

%plot for Right side of dome
T2 = [300:10:550];
for i = 1:4:26
    Ps2 = PSAT(i,1);
    j = 1;
    while(Ps2 >= 250000)
        C1 = Ps2;
        C2 = (Ps2*b - R*(T2(i)));
        C3 = (a - 2*b*R*(T2(i)) -3*b*b*Ps2);
        C4 = (Ps2*(b^3) + R*(T2(i))*b*b - a*b);
        p = [C1 C2 C3 C4];
        r = roots(p);
        r = real(r);
        VOLR(j) = r(1);
        PssR(j) = Ps2;
        Ps2 = Ps2 - 1000;
        j = j+1;
    end
```

```
    plot(VOLR,PssR,'color','red');
    hold on;
end

%plot for T>Tc
for i = 1:0.25:3
    j = 1;
    for Ps = (1.5*Pc):-1000:50000
        C1 = Ps;
        C2 = (Ps*b - R*i*Tc);
        C3 = (a - 2*b*R*i*Tc -3*b*b*Ps);
        C4 = (Ps*(b^3) + R*i*Tc*b*b - a*b);
        p = [C1 C2 C3 C4];
        r = roots(p);
        r = real(r);
        VOLT(j) = r(1);
        PssT(j) = Ps;
        j = j+1;
    end
    plot(VOLT,PssT,'color','red');
    xlim([-0.001 0.01]);
    ylim([0 10^7]);
    title('P-V Isotherm for Carbon Disulfide(Peng Robinson EOS)');
    xlabel('Volume(m^3)');
    ylabel('Pressure(Pa)');
    hold on;
end

%function to calculate chemical potential
function Y = Value(V,a,b,R,T,P)
    A1 = log(abs(1 - b/V));
    B1 = a*log(abs((V + 2.414*b)/(V - 0.414*b)))/(2.828*b*R*T);
    C1 = ((V*P)/(R*T) - 1) - log(abs((V*P)/(R*T)));
    Y = -A1 -B1 +C1;
end
```

REFERENCES

- Properties Of Carbon Disulphide:

  ~Appendix, Perry's Chemical Engineer Handbook

- Equation Of State and Values for Peng Robinson Equation :

  ~CHE221 Course Lecture 11

- Chemical Potential Calculation :

  ~CHE221 Course Lecture 15