Quiz 3: Thermodynamic property calculation for oxygen [Due for submission at 5 pm September 30, 2022]

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The Peng-Robinson equation of state is

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}\left(\underline{V} + b\right) + b\left(\underline{V} - b\right)}$$ where

$$a(T) = 0.45724\frac{R^2T_c^2}{P_c}\left[1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \qquad b = 0.0778\frac{RT_c}{P_c}$$

For oxygen

$$\kappa = 0.4069 \qquad T_c = 154.6\ K \qquad P_c = 5.046\ MPa$$

This EOS can be written in a cubic polynomial form as

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$$

where

$$\alpha = B - 1 \qquad \beta = A - 3B^2 - 2B \qquad \gamma = B^3 + B^2 - AB$$

$$A = aP/(RT)^2 \qquad B = bP/RT \qquad Z = P\underline{V}/RT.$$

MAIN PROGRAM

```
%options
%1)the vapor pressure P(T) at temperatures T = –125, –150 and –175 °C
%2)Plot the isotherm P – V curve at temperatures T = –125, –150 and –175 °C
%3)Make a plot for Pvap versus T for the vapor-liquid coexistence for given
%temperatures
%4)Fit a polynomial curve to Pvap versus T,also for ΔV(T)
%5)Plot ΔH and ΔS as a function of temperature
%6)Enthalpy calculations
%7)Entropy calculations

option = input("Enter the option no.:- ");

if option == 1
   temp = [148.15 123.15 98.15];
   p_vap = zeros(3,1);
   for i = 1:3
      p_vap(i) = P_vap(temp(i));
   end
   for i = 1 : 3
      fprintf('The vapor pressure at %.2f K is %.4f bar \n',temp(i),p_vap(i))
   end
end

if option == 2
   temp = [148.15 123.15 98.15];
   p_vap = zeros(3,1);
   c = ['r' 'b' 'g'];
   for i = 1:3
```

```
    p_vap(i) = P_vap(temp(i));
  end
  PVplot(p_vap(1),temp(1),c(1));
  hold on
  PVplot(p_vap(2),temp(2),c(2));
  hold on
  PVplot(p_vap(3),temp(3),c(3));
  hold off


end

if option == 3
  temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
  p_vap = zeros(9,1);
  for i = 1:9
    p_vap(i) = P_vap(temp(i));
  end
  plot(temp,p_vap,'linewidth',2.5)
  hold on
  plot(temp,p_vap,'.r',MarkerSize=15)
  hold off
  title("P_v_a_p vs T","FontSize",20)
  xlabel("Temperature(K)","FontSize",20)
  ylabel("P_v_a_p(bar)","FontSize",20)

end

if option == 4
  curve_fitting
  temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
  delH = zeros(9,1);
  delS = zeros(9,1);
```

```
    for i = 1:9
        [dH,dS] = clapeyron(temp(i));
        delH(i) = dH*10^-3;
        delS(i) = dS*10^-3;
    end

    for j = 1:9
        fprintf('At T = %.2f K,  ΔH/mole is %.4f (KJ/mole) and  ΔS/mole is %.4f (KJ/K/mol) \n',temp(j),delH(j),delS(j));
    end
end



if option == 5
    temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
    delH = zeros(9,1);
    delS = zeros(9,1);
    for i = 1:9
        [dH,dS] = clapeyron(temp(i));
        delH(i) = dH*10^-3;
        delS(i) = dS*10^-3;
    end

    figure(1)
    plot(temp,delH,'linewidth',2.5)
    hold on
    plot(temp,delH,'.r',MarkerSize=15)
    hold off
    title("ΔH/mol vs T","FontSize",20)
    xlabel("Temperature(K)","FontSize",20)
    ylabel("ΔH/mol(KJ/mol)","FontSize",20)

    figure(2)
    plot(temp,delS,'linewidth',2.5)
```

```
    hold on
    plot(temp,delS,'.r',MarkerSize=15)
    hold off
    title("ΔS/mol vs T","FontSize",20)
    xlabel("Temperature(K)","FontSize",20)
    ylabel("ΔS/mol(KJ/mol/K)","FontSize",20)



end
if option == 6
    pressenthalpy
end

if option == 7
    pressentropy
end
```

(a) Find the vapor pressure $P_{vap}(T)$ at temperatures $T = -125,\ -150$ and -175 °C.

Hint: To find the vapor pressure you require T and a guess value of P. Figure 6.4-3 can be used to obtain a guess value. Solve for Z^L and Z^V using the cubic equation $Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$. We shall employ fugacity. For vapor, calculate the vapor fugacity f^V with the help of

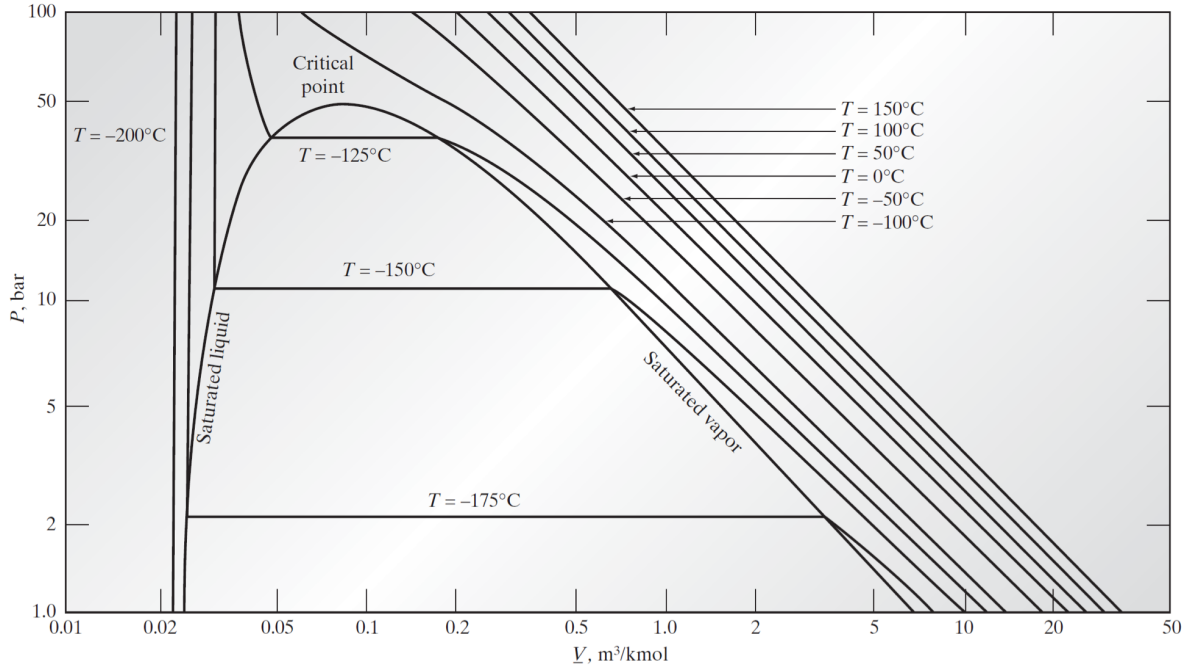


Figure 6.4-3 Pressure-volume diagram for oxygen calculated using the Peng-Robinson equation of state.

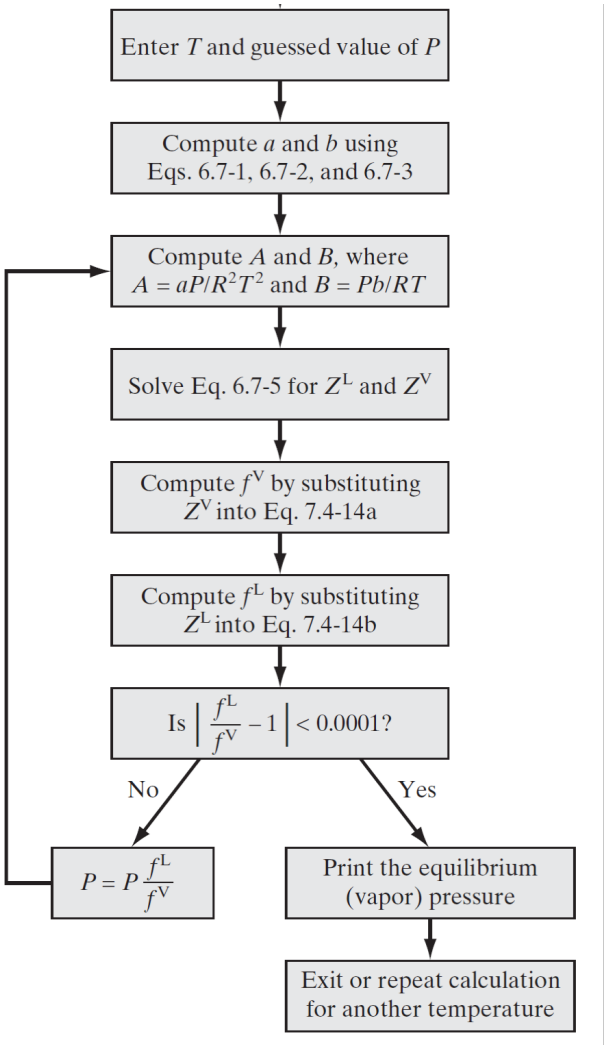
$$\ln\frac{f^V}{P} = \left(Z^V - 1\right) - \ln\left(Z^V - B\right) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z^V + \left(1+\sqrt{2}\right)B}{Z^V + \left(1-\sqrt{2}\right)B}\right].$$

For liquid, calculate the liquid fugacity f^L with the help of

$$\ln\frac{f^L}{P} = \left(Z^L - 1\right) - \ln\left(Z^L - B\right) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z^L + \left(1+\sqrt{2}\right)B}{Z^L + \left(1-\sqrt{2}\right)B}\right].$$

Recall that A and B depend on T and P. Therefore, they have to be calculated each time for a new value of T and P.

For vapor-liquid coexistence we require $f^V(T,P) = f^L(T,P)$. Therefore, check whether $\left|\frac{f^L}{f^V} - 1\right| < 0.0001$. If so, then you can stop – you have a solution for P_{vap} at the selected temperature. Otherwise, set $P = P\frac{f^L}{f^V}$. The flowchart below will help:



CODE:- PART A

P_vap.m :-

```
function y = P_vap(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
```

```
    P = P*(f_l/f_v);
    b = 0.0778*R*Tc*(1/Pc);
    A = (a(T)*P)/(R*T)^2;
    B = (b*P)/(R*T);

    alpha = B-1;
    beta = A - 3*B^2 - 2*B;
    gamma = B^3 + B^2 - A*B;

    c = [1 alpha beta gamma];
    z = real(roots(c));
    Zv = max(z);
    Zl = min(z);
    f_l = fug(Zl,P,T);
    f_v = fug(Zv,P,T);
end
y = P/10^5;
```

fug.m:-

```
function y = fug(Z , P , T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);
sq = sqrt(2);
y = exp(Z-1-log(Z-B)-A/B/2/sq*log((Z + (1+sq)*B)./(Z + (1-sq)*B)));
```

a.m:-

```
function y = a(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
k = 0.4069;
r = (T/Tc);
b =sqrt(r);

y = 0.45724*(R^2)*((Tc)^2)*(1/Pc)*(1 + k*(1-b))^2;
```

PR_main_program.m :-

```
if option == 1
   temp = [148.15 123.15 98.15];
   p_vap = zeros(3,1);
   for i = 1:3
      p_vap(i) = P_vap(temp(i));
   end
   for i = 1 : 3
      fprintf('The vapor pressure at %.2f K is %.4f bar \n',temp(i),p_vap(i))
   end
end
```

FIGURES(OUTPUT):-

```
>> PR_main_program
Enter the option no.:- 1
The vapor pressure at 148.15 K is 39.4240 bar
The vapor pressure at 123.15 K is 12.2929 bar
The vapor pressure at 98.15 K is 2.1931 bar
>>
```

COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**
  - **1)P_vap.m**
  - **2)fug.m**
  - **3)a.m**
  - **4)PR_main_program.m**
- **Run the main program :- PR_main_program.m**
- **Enter 1 as the option no.**

(b) Plot the isotherm $P - \underline{V}$ curve at temperatures $T = -125,\ -150$ and -175 °C as shown in Figure 6.4-3 (page 1).

CODE:- PART B

P_vap.m :-

```
function y = P_vap(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
   P = P*(f_l/f_v);
   b = 0.0778*R*Tc*(1/Pc);
   A = (a(T)*P)/(R*T)^2;
```

```
    B = (b*P)/(R*T);

    alpha = B-1;
    beta = A - 3*B^2 - 2*B;
    gamma = B^3 + B^2 - A*B;

    c = [1 alpha beta gamma];
    z = real(roots(c));
    Zv = max(z);
    Zl = min(z);
    f_l = fug(Zl,P,T);
    f_v = fug(Zv,P,T);
end
y = P/10^5;
```

fug.m:-

```
function y = fug(Z , P , T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);
sq = sqrt(2);
y = exp(Z-1-log(Z-B)-A/B/2/sq*log((Z + (1+sq)*B)./(Z + (1-sq)*B)));
```

a.m:-

```
function y = a(T)
Tc = 154.6;
Pc = 5.046*10^6;
```

```
R = 8.314;
k = 0.4069;
r = (T/Tc);
b =sqrt(r);

y = 0.45724*(R^2)*((Tc)^2)*(1/Pc)*(1 + k*(1-b))^2;
```

PV_plot.m:-

```
function y = PVplot(P,T,c)
k = linspace(P,50,20);
j = linspace(1,P,20);
v1 = zeros(20,1);
v2 = zeros(20,1);
p_sat = [P ,P];
for i = 1:20
   z = Z(k(i),T,'l');
   v1(i) = Vbar(z,T,k(i));
end
v_sat = zeros(2,1);
[zl,zv] = Z_sat(T);
z_sat = [zl,zv];
for i = 1:2
   v_sat(i) = Vbar(z_sat(i),T,P);
end
for i = 1:20
   z = Z(j(i),T,'v');
   v2(i) = Vbar(z,T,j(i));
end
loglog(v1,k,c,'Linewidth',1.5)
```

```
hold on
loglog(v_sat,p_sat,c,'Linewidth',1.5)
hold on
loglog(v2,j,c,'Linewidth',1.5)
hold off

xlabel("Volume/mole(m^3/kmol)",FontSize=20)
ylabel("Pressure(bar)",FontSize=20)
title('PRESSURE VS MOLAR VOLUME',FontSize=25)
```

Vbar.m:-

```
function y = Vbar(Z,T,P)
R = 8.314;
P = P*10^5;
y = (Z*R*T*10^3)/P;
```

Z.m:-

```
function y = Z(P,T,phase)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
P = P*10^5;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;
s = 0;
c = [1 alpha beta gamma];
```

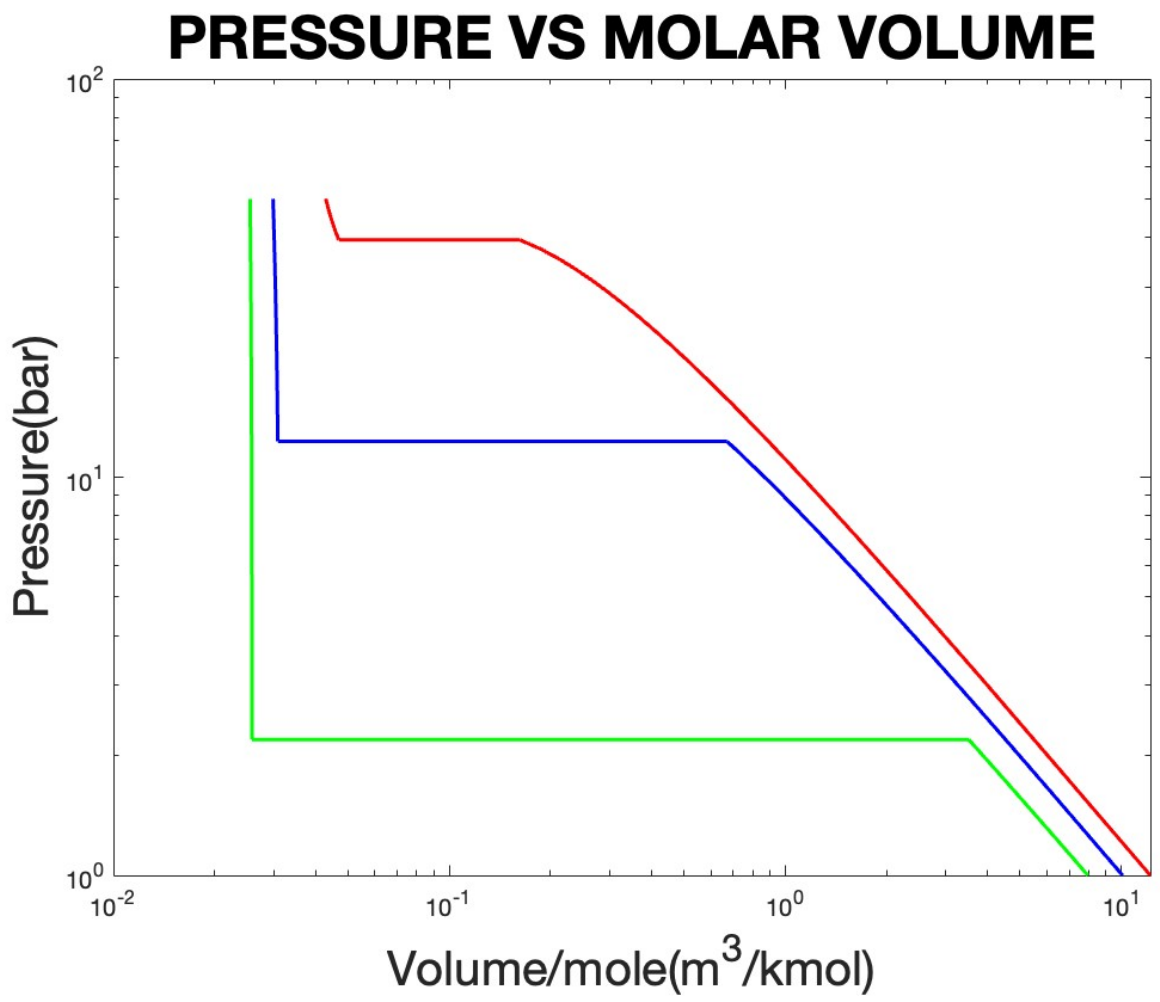
```
z = roots(c);
for i = 1:3
   if imag(z(i)) == 0
      s = s+1;
      k = z(i);
   end
end
if s == 3

   if phase == 'l'
      k = min(z);
   end
   if phase == 'v'
      k = max(z);
   end
end
if phase == 'n'
   k = real(k);
end
y = k;
```

PR_main_program.m :-

```
if option == 2
   temp = [148.15 123.15 98.15];
   p_vap = zeros(3,1);
   c = ['r' 'b' 'g'];
   for i = 1:3
      p_vap(i) = P_vap(temp(i));
   end
   PVplot(p_vap(1),temp(1),c(1));
   hold on
```

```
    PVplot(p_vap(2),temp(2),c(2));
    hold on
    PVplot(p_vap(3),temp(3),c(3));
    hold off
end
```

FIGURES(OUTPUT):-



COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**
  - **1)P_vap.m**
  - **2)fug.m**

3)a.m

4)Z.m

5)Vbar.m

6)PVplot.m

7)PR_main_program.m

- Run the main program :- PR_main_program.m
- Enter 2 as the option no.

(c) Make a plot for P_{vap} versus T for the vapor-liquid coexistence. Choose temperatures $T = -125,\ -130,\ -140,\ -150,\ -160,\ -170,\ -175,\ -180$ and -183 °C.

CODE:- PART C

P_vap.m :-

```
function y = P_vap(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
```

```
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
   P = P*(f_l/f_v);
   b = 0.0778*R*Tc*(1/Pc);
   A = (a(T)*P)/(R*T)^2;
   B = (b*P)/(R*T);

   alpha = B-1;
   beta = A - 3*B^2 - 2*B;
   gamma = B^3 + B^2 - A*B;

   c = [1 alpha beta gamma];
   z = real(roots(c));
   Zv = max(z);
   Zl = min(z);
   f_l = fug(Zl,P,T);
   f_v = fug(Zv,P,T);
end
y = P/10^5;
```

fug.m:-

```
function y = fug(Z , P , T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);
```

```
sq = sqrt(2);
y = exp(Z-1-log(Z-B)-A/B/2/sq*log((Z + (1+sq)*B)./(Z + (1-sq)*B)));
```

a.m:-

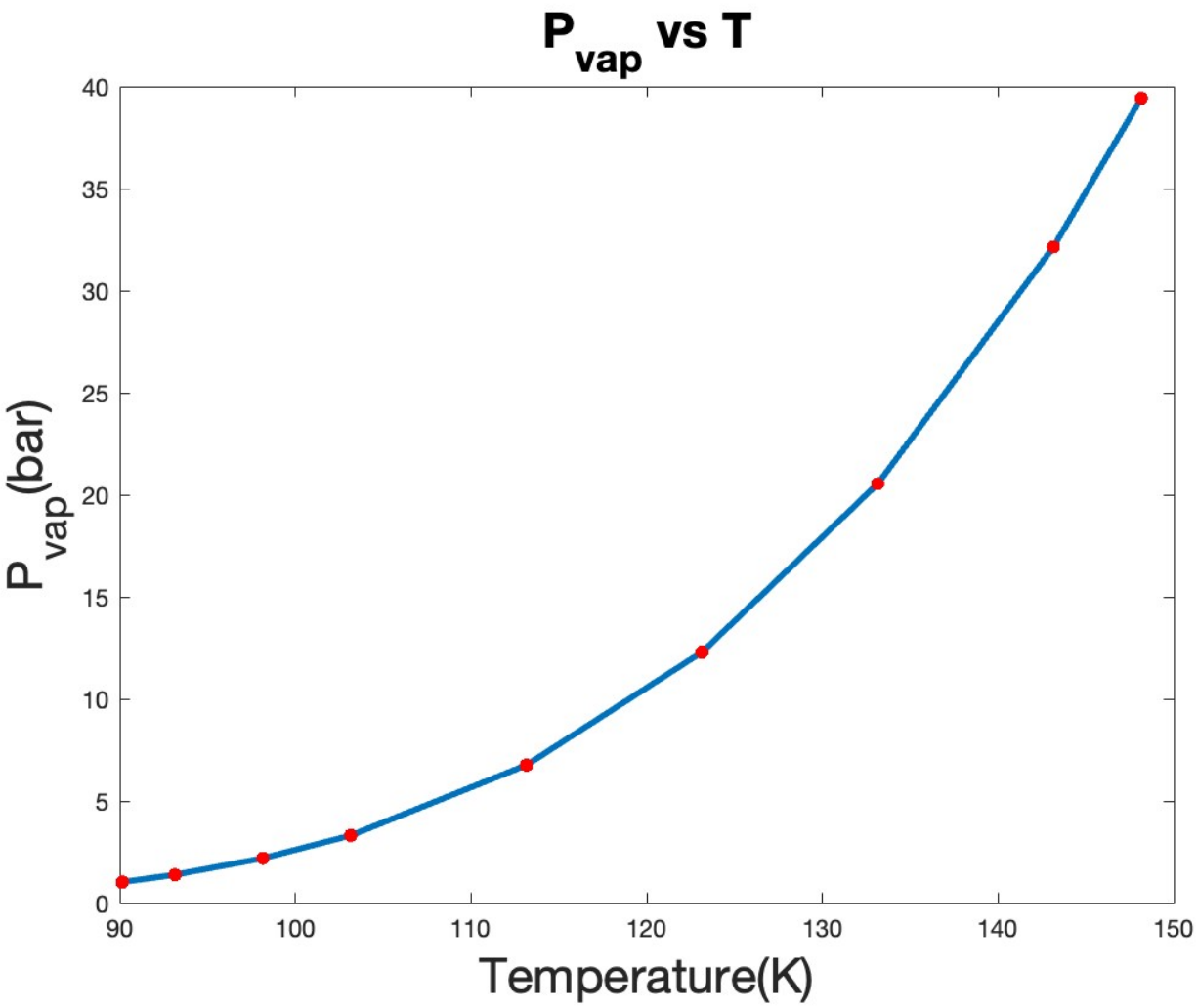
```
function y = a(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
k = 0.4069;
r = (T/Tc);
b =sqrt(r);

y = 0.45724*(R^2)*((Tc)^2)*(1/Pc)*(1 + k*(1-b))^2;
```

PR_main_program.m :-

```
if option == 3
   temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
   p_vap = zeros(9,1);
   for i = 1:9
      p_vap(i) = P_vap(temp(i));
   end
   plot(temp,p_vap,'linewidth',2.5)
   hold on
   plot(temp,p_vap,'.r',MarkerSize=15)
   hold off
   title("P_v_a_p vs T","FontSize",20)
   xlabel("Temperature(K)","FontSize",20)
   ylabel("P_v_a_p(bar)","FontSize",20)
```

```
end
```

FIGURES(OUTPUT):-



COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**

  1)P_vap.m

2)fug.m

3)a.m

2)Z.m

3)PR_main_program.m

- **Run the main program :- PR_main_program.m**
- **Enter 3 as the option no.**

(d) Fit a polynomial curve to P_{vap} versus T. Make sure that the polynomial curve fits your data well. Recall that according to the Clapeyron equation

$$\frac{dP_{vap}}{dT} = \frac{\Delta \underline{S}}{\Delta \underline{V}} = \frac{\Delta \underline{H}}{T \Delta \underline{V}}.$$

Calculate $\Delta \underline{H} = \underline{H}^V - \underline{H}^L$, $\Delta \underline{S} = \underline{S}^V - \underline{S}^L$ and $\Delta \underline{V} = \underline{V}^V - \underline{V}^L$ from the information you have collected so far. For this you can also fit a curve through $\Delta \underline{V}(T)$.Compare your value of $\Delta \underline{H}$ to the

value given in the figure below:

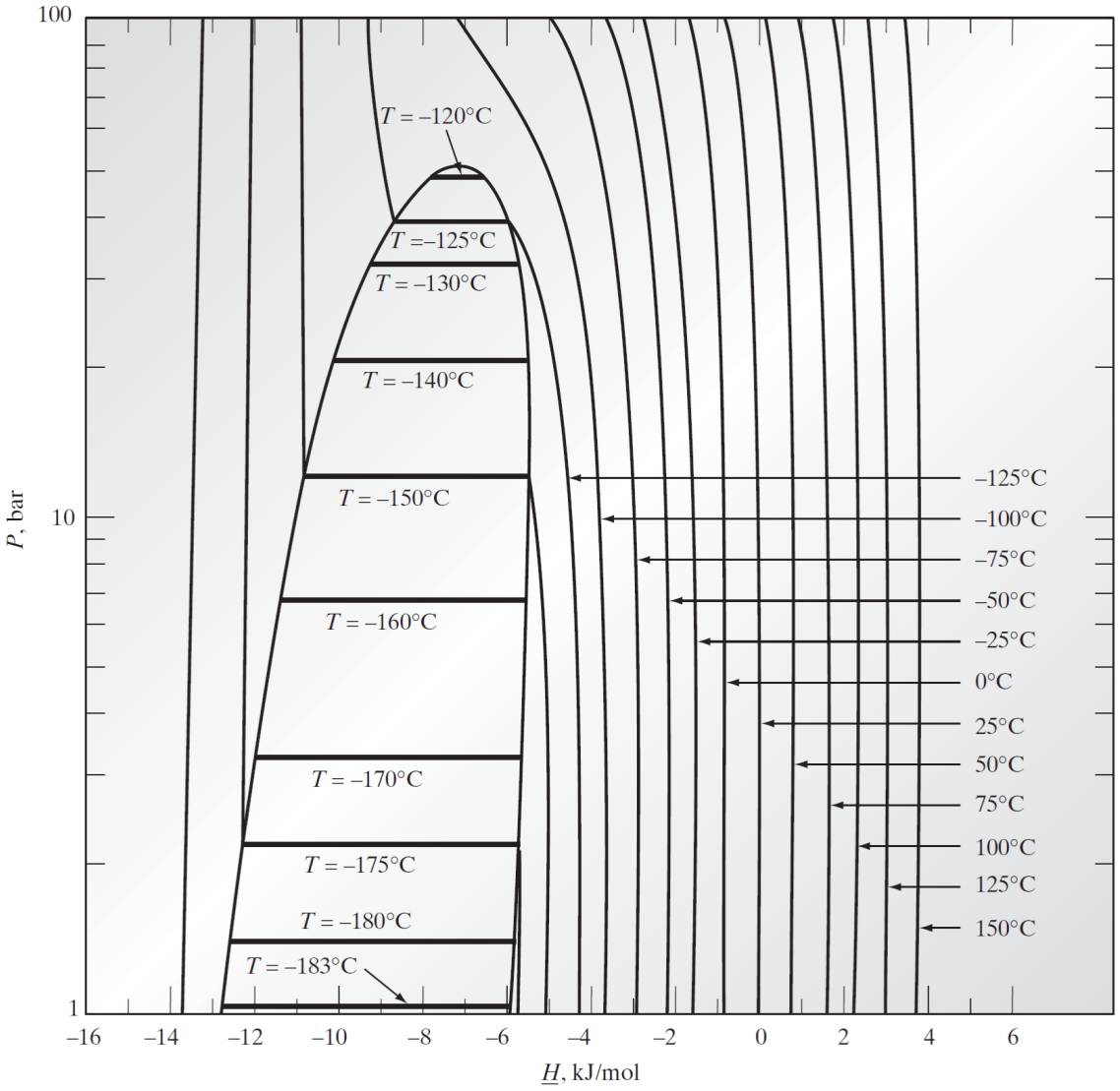


Figure 6.4-4 Pressure-enthalpy diagram for oxygen calculated using the Peng-Robinson equation of state.

Note that in general the pressure where the transition happens from one phase to another is also called saturation pressure $P^{sat}(T)$. For vapor-liquid equilibrium (VLE) $P^{sat}(T) \equiv P^{vap}(T)$.

CODE:- PART D

P_vap.m :-

```
function y = P_vap(T)

Tc = 154.6;
```

```
Pc = 5.046*10^6;
R = 8.314;
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
   P = P*(f_l/f_v);
   b = 0.0778*R*Tc*(1/Pc);
   A = (a(T)*P)/(R*T)^2;
   B = (b*P)/(R*T);

   alpha = B-1;
   beta = A - 3*B^2 - 2*B;
   gamma = B^3 + B^2 - A*B;

   c = [1 alpha beta gamma];
   z = real(roots(c));
   Zv = max(z);
   Zl = min(z);
```

```
   f_l = fug(Zl,P,T);
   f_v = fug(Zv,P,T);
end
y = P/10^5;
```

fug.m:-

```
function y = fug(Z , P , T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);
sq = sqrt(2);
y = exp(Z-1-log(Z-B)-A/B/2/sq*log((Z + (1+sq)*B)./(Z + (1-sq)*B)));
```

a.m:-

```
function y = a(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
k = 0.4069;
r = (T/Tc);
b =sqrt(r);

y = 0.45724*(R^2)*((Tc)^2)*(1/Pc)*(1 + k*(1-b))^2;
```

curve_fitting.m:-

```
x = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
```

```
y = zeros(9,1);
for i = 1:9
   y(i) = P_vap(x(i));
end
p = polyfit(x,y,3);
x2 = 148.15:-5:88.15;
y2 = polyval(p,x2);
figure(1)
plot(x,y,'o')
hold on
plot(x2,y2)
hold off
xlabel("Temperature(K)","FontSize",20)
ylabel("P_v_a_p(bar)","FontSize",20)
s = sprintf('P_v_a_p = %.8f T^3 + %.8f T^2 + %.8f T + %.8f',p(1),p(2),p(3),p(4));
title(s);

y1 = zeros(9,1);
for i = 1:9
   y1(i) = delVbar(x(i))*10^-6;
end
p1 = polyfit(x,y1,4);
x_2 = 148.15:-5:88.15;
y_2 = polyval(p1,x_2);
figure(2)
plot(x,y1,'o')
hold on
plot(x_2,y_2)
hold off
xlabel("Temperature(K)","FontSize",20)
ylabel("V/mol(m^3/mol)","FontSize",20)
s1 = sprintf('V/mol = %.8f T^4 + %.8f T^3 + %.8f T^2 + %.8f T + %.8f ',p1(1),p1(2),p1(3),p1(4),p1(5));
title(s1);
```

clapeyron.m:-

```
function [dH , dS ] = clapeyron(T)
dH = diffPvap(T)*T*delVbar(T);
dS = diffPvap(T)*delVbar(T);
```

delVbar.m:-

```
function y = delVbar(T)
[zl,zv] = Z_sat(T);
z = zv - zl;
R = 8.314;
y = (z*R*T)/P_vap(T);
```

diffPvap.m:-

```
function y = diffPvap(T)
x = 0.0001;
y1 = P_vap(T-x);
y2 = P_vap(T+x);
y = (y2-y1)/(2*x);
```

H.m:-

```
function y = H(P,T,phase)
z = Z(P,T,phase);
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);
```

```
B = (b*P*10^5)/(R*T);


Tr = 298.15;

c = 25.46*(T -Tr) + (0.7595*10^(-2))*(T^2 - (Tr)^2) - (0.7151*(1/3)*10^(-5))*(T^3 -(Tr)^3) + (0.32775*10^(-9))*(T^4-(Tr)^4);

d = T*diff_a(T);

sq = sqrt(2);

s = ((d-a(T))/(b*2*sq))*log((z + (1+sq)*B)./(z + (1-sq)*B));

v = R*T*(z-1);


y = v + s + c;
```

S.m:-

```
function y = S(P,T,phase)

z = Z(P,T,phase);

Tc = 154.6;

Pc = 5.046*10^6;

R = 8.314;

b = 0.0778*R*Tc*(1/Pc);


B = (b*P*10^5)/(R*T);


Tr = 298.15;

c = 25.46*log(T/Tr) + (1.519*10^(-2))*(T - (Tr)) - (0.7151*(1/2)*10^(-5))*(T^2 -(Tr)^2) + (1.311*(1/3)*10^(-9))*(T^3-(Tr)^3);

d = diff_a(T);

e = R*log(P);

sq = sqrt(2);

s = (d/(b*2*sq))*log((z + (1+sq)*B)./(z + (1-sq)*B));

v = R*log(z-B);


y = v + s + c - e;
```

Z_sat.m:-

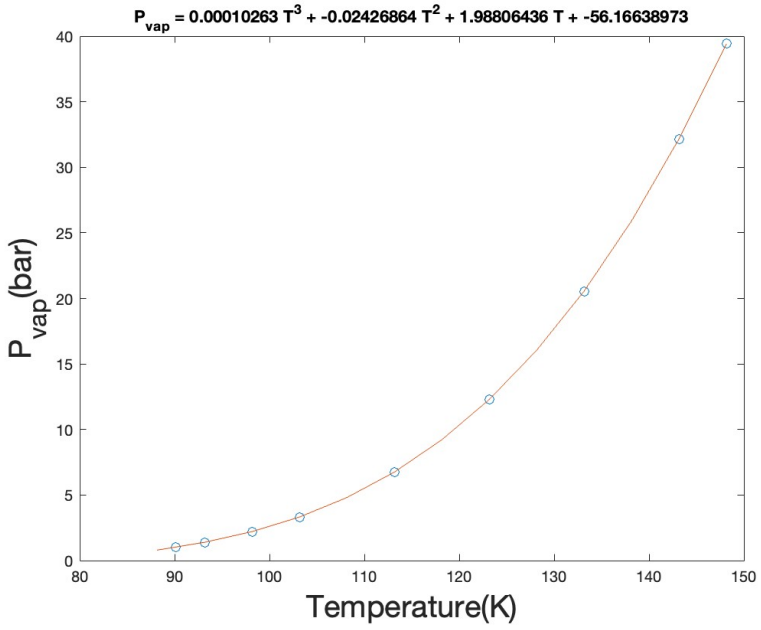
```
function [zl,zv] = Z_sat(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
   P = P*(f_l/f_v);
   b = 0.0778*R*Tc*(1/Pc);
   A = (a(T)*P)/(R*T)^2;
   B = (b*P)/(R*T);

   alpha = B-1;
   beta = A - 3*B^2 - 2*B;
```

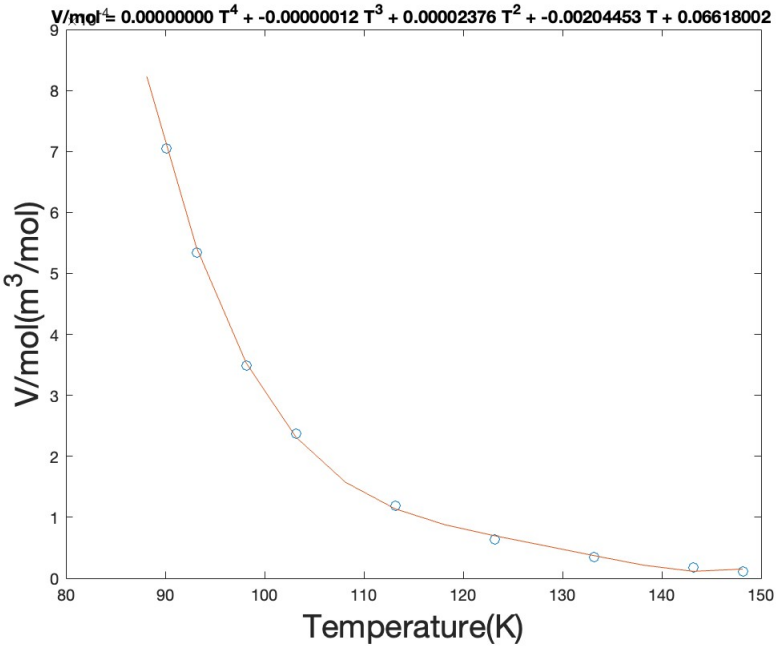
```
    gamma = B^3 + B^2 - A*B;

    c = [1 alpha beta gamma];
    z = real(roots(c));
    Zv = max(z);
    Zl = min(z);
    f_l = fug(Zl,P,T);
    f_v = fug(Zv,P,T);
end
zl = Zl;
zv = Zv;
```

PR_main_program.m:-

```
if option == 4
    curve_fitting
    temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
    delH = zeros(9,1);
    delS = zeros(9,1);
    for i = 1:9
        [dH,dS] = clapeyron(temp(i));
        delH(i) = dH*10^-3;
        delS(i) = dS*10^-3;
    end

    for j = 1:9
        fprintf('At T = %.2f K,  ΔH/mole is %.4f (KJ/mole) and  ΔS/mole is %.4f (KJ/K/mol) \n',temp(j),delH(j),delS(j));
    end
end
```

FIGURES(OUTPUT):-






```
Enter the option no.:- 4
At T = 148.15 K,  ΔH/mole is 2.6798 (KJ/mole) and  ΔS/mole is 0.0181 (KJ/K/mol)
At T = 143.15 K,  ΔH/mole is 3.4984 (KJ/mole) and  ΔS/mole is 0.0244 (KJ/K/mol)
At T = 133.15 K,  ΔH/mole is 4.6016 (KJ/mole) and  ΔS/mole is 0.0346 (KJ/K/mol)
At T = 123.15 K,  ΔH/mole is 5.3562 (KJ/mole) and  ΔS/mole is 0.0435 (KJ/K/mol)
At T = 113.15 K,  ΔH/mole is 5.9128 (KJ/mole) and  ΔS/mole is 0.0523 (KJ/K/mol)
At T = 103.15 K,  ΔH/mole is 6.3398 (KJ/mole) and  ΔS/mole is 0.0615 (KJ/K/mol)
At T = 98.15 K,  ΔH/mole is 6.5168 (KJ/mole) and  ΔS/mole is 0.0664 (KJ/K/mol)
At T = 93.15 K,  ΔH/mole is 6.6764 (KJ/mole) and  ΔS/mole is 0.0717 (KJ/K/mol)
At T = 90.15 K,  ΔH/mole is 6.7634 (KJ/mole) and  ΔS/mole is 0.0750 (KJ/K/mol)
```

COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**
  - **1)P_vap.m**
  - **2)fug.m**
  - **3)a.m**
  - **4)curve_fitting.m**
  - **5)claypeyron.m**
  - **6)delVbar.m**
  - **7)diffPvap.m**
  - **8)H.m**
  - **9)S.m**
  - **10)Z_sat.m**
  - **11)Z.m**
  - **11)PR_main_program.m**
- **Run the main program :- PR_main_program.m**
- **Enter 4 as the option no.**

(e) Plot ΔH and ΔS as a function of temperature.

CODE:- PART E

P_vap.m :-

```
function y = P_vap(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
```

```
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
   P = P*(f_l/f_v);
   b = 0.0778*R*Tc*(1/Pc);
   A = (a(T)*P)/(R*T)^2;
   B = (b*P)/(R*T);

   alpha = B-1;
   beta = A - 3*B^2 - 2*B;
   gamma = B^3 + B^2 - A*B;

   c = [1 alpha beta gamma];
   z = real(roots(c));
   Zv = max(z);
   Zl = min(z);
   f_l = fug(Zl,P,T);
   f_v = fug(Zv,P,T);
```

```
end
y = P/10^5;
```

fug.m:-

```
function y = fug(Z , P , T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);
sq = sqrt(2);
y = exp(Z-1-log(Z-B)-A/B/2/sq*log((Z + (1+sq)*B)./(Z + (1-sq)*B)));
```

a.m:-

```
function y = a(T)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
k = 0.4069;
r = (T/Tc);
b =sqrt(r);

y = 0.45724*(R^2)*((Tc)^2)*(1/Pc)*(1 + k*(1-b))^2;
```

clapeyron.m:-

```
function [dH , dS ] = clapeyron(T)
dH = diffPvap(T)*T*delVbar(T);
dS = diffPvap(T)*delVbar(T);
```

delVbar.m:-

```
function y = delVbar(T)
[zl,zv] = Z_sat(T);
z = zv - zl;
R = 8.314;
y = (z*R*T)/P_vap(T);
```

diffPvap.m:-

```
function y = diffPvap(T)
x = 0.0001;
y1 = P_vap(T-x);
y2 = P_vap(T+x);
y = (y2-y1)/(2*x);
```

H.m:-

```
function y = H(P,T,phase)
z = Z(P,T,phase);
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
b = 0.0778*R*Tc*(1/Pc);

B = (b*P*10^5)/(R*T);

Tr = 298.15;
c = 25.46*(T -Tr) + (0.7595*10^(-2))*(T^2 - (Tr)^2) - (0.7151*(1/3)*10^(-5))*(T^3 -(Tr)^3) + (0.32775*10^(-9))*(T^4-(Tr)^4);
d = T*diff_a(T);
sq = sqrt(2);
```

```
s = ((d-a(T))/(b*2*sq))*log((z + (1+sq)*B)./(z + (1-sq)*B));

v = R*T*(z-1);


y = v + s + c;
```

S.m:-

```
function y = S(P,T,phase)

z = Z(P,T,phase);

Tc = 154.6;

Pc = 5.046*10^6;

R = 8.314;

b = 0.0778*R*Tc*(1/Pc);


B = (b*P*10^5)/(R*T);


Tr = 298.15;

c = 25.46*log(T/Tr) + (1.519*10^(-2))*(T - (Tr)) - (0.7151*(1/2)*10^(-5))*(T^2 -(Tr)^2) + (1.311*(1/3)*10^(-9))*(T^3-(Tr)^3);

d = diff_a(T);

e = R*log(P);

sq = sqrt(2);

s = (d/(b*2*sq))*log((z + (1+sq)*B)./(z + (1-sq)*B));

v = R*log(z-B);


y = v + s + c - e;
```

Z_sat.m:-

```
function [zl,zv] = Z_sat(T)

Tc = 154.6;

Pc = 5.046*10^6;

R = 8.314;
```

```
P = Pc;

b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;

c = [1 alpha beta gamma];
z = real(roots(c));
Zv = max(z);
Zl = min(z);
f_l = fug(Zl,P,T);
f_v = fug(Zv,P,T);

while abs(f_l/f_v - 1) > 10^(-4)
   P = P*(f_l/f_v);
   b = 0.0778*R*Tc*(1/Pc);
   A = (a(T)*P)/(R*T)^2;
   B = (b*P)/(R*T);

   alpha = B-1;
   beta = A - 3*B^2 - 2*B;
   gamma = B^3 + B^2 - A*B;

   c = [1 alpha beta gamma];
   z = real(roots(c));
   Zv = max(z);
   Zl = min(z);
   f_l = fug(Zl,P,T);
   f_v = fug(Zv,P,T);
```

```
end
zl = Zl;
zv = Zv;
```

Z.m:-

```
function y = Z(P,T,phase)
Tc = 154.6;
Pc = 5.046*10^6;
R = 8.314;
P = P*10^5;
b = 0.0778*R*Tc*(1/Pc);
A = (a(T)*P)/(R*T)^2;
B = (b*P)/(R*T);

alpha = B-1;
beta = A - 3*B^2 - 2*B;
gamma = B^3 + B^2 - A*B;
s = 0;
c = [1 alpha beta gamma];
z = roots(c);
for i = 1:3
   if imag(z(i)) == 0
      s = s+1;
      k = z(i);
   end
end
if s == 3

   if phase == 'l'
      k = min(z);
   end
```

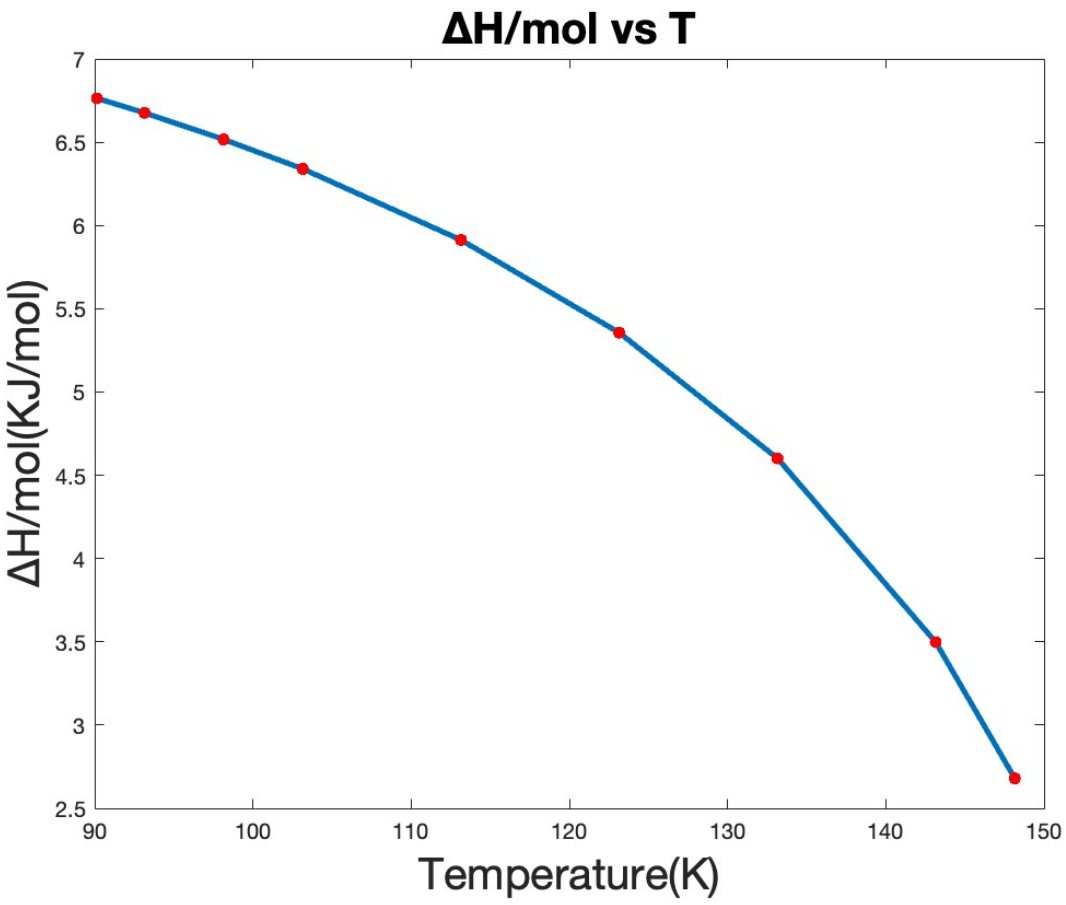
```
    if phase == 'v'
        k = max(z);
    end
end
if phase == 'n'
    k = real(k);
end
y = k;
```

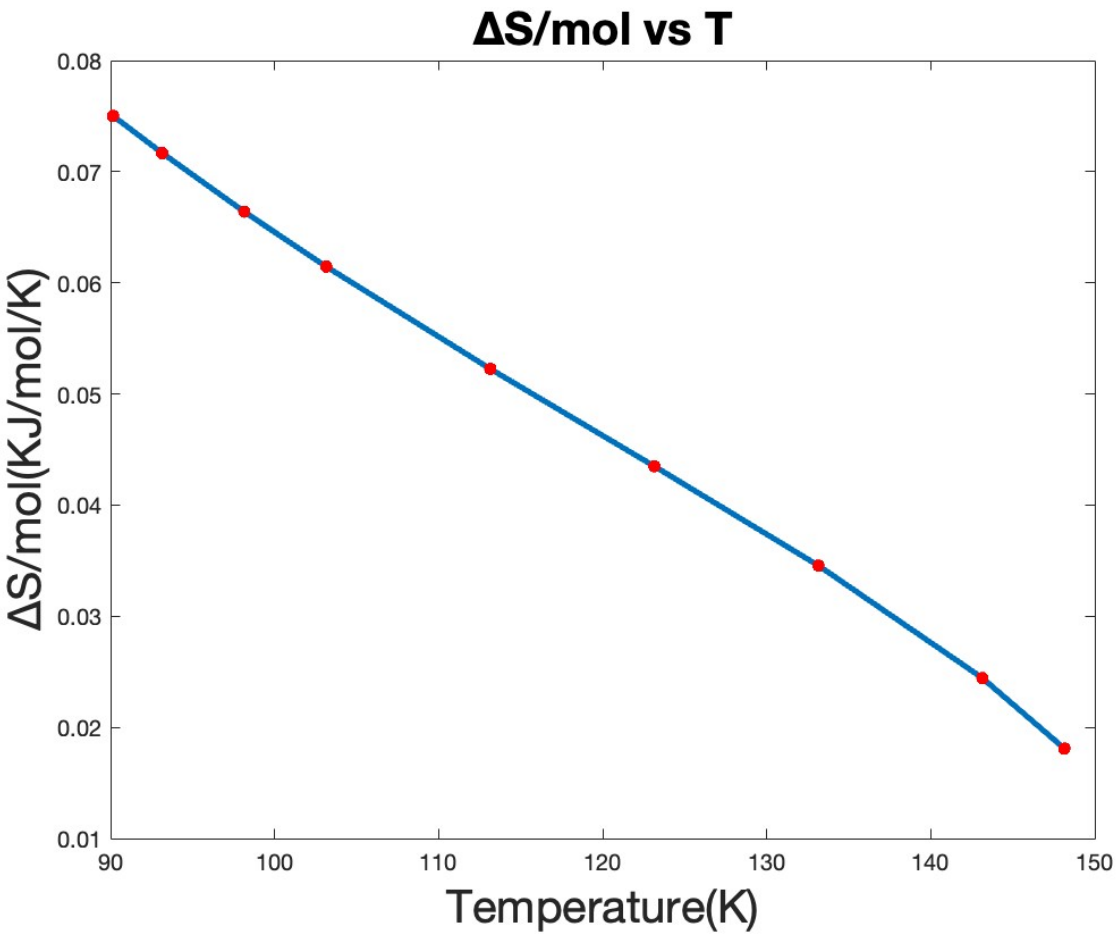
PR_main_program.m:-

```
if option == 5
    temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
    delH = zeros(9,1);
    delS = zeros(9,1);
    for i = 1:9
        [dH,dS] = clapeyron(temp(i));
        delH(i) = dH*10^-3;
        delS(i) = dS*10^-3;
    end

    figure(1)
    plot(temp,delH,'linewidth',2.5)
    hold on
    plot(temp,delH,'.r',MarkerSize=15)
    hold off
    title("ΔH/mol vs T","FontSize",20)
    xlabel("Temperature(K)","FontSize",20)
    ylabel("ΔH/mol(KJ/mol)","FontSize",20)

    figure(2)
    plot(temp,delS,'linewidth',2.5)
    hold on
```

```
plot(temp,delS,'.r',MarkerSize=15)
hold off
title("ΔS/mol vs T","FontSize",20)
xlabel("Temperature(K)","FontSize",20)
ylabel("ΔS/mol(KJ/mol/K)","FontSize",20)

end
```

FIGURES(OUTPUT):-




ΔS/mol vs T
ΔS/mol(KJ/mol/K)
Temperature(K)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
90
100
110
120
130
140
150

COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**
  - **1)P_vap.m**
  - **2)fug.m**
  - **3)a.m**
  - **4)curve_fitting.m**
  - **5)claypeyron.m**
  - **6)delVbar.m**
  - **7)diffPvap.m**
  - **8)H.m**
  - **9)S.m**
  - **10)Z_sat.m**
  - **11)Z.m**
  - **11)PR_main_program.m**
- **Run the main program :- PR_main_program.m**
- **Enter 5 as the option no.**

(f) Enthalpy calculations:

Choose $\underline{H}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = 0.$ ***IG*** **implies ideal gas. This sets our reference state. Now calculate enthalpy as**

$$\underline{H}(T,P) - \underline{H}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = \left\{ \underline{H}(T,P) - \underline{H}^{IG}(T,P) \right\} + \left\{ \underline{H}^{IG}(T,P) - \underline{H}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) \right\}$$

Here $\underline{H}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right)$ **has a value zero therefore it has been struck through.**

For Peng-Robinson equation, the departure function for enthalpy or residual enthalpy

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2}b} \ln\left[\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right].$$

Also

$$\underline{H}^{IG}(T,P) - \underline{H}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = \int_{T=298.15\ K}^{T} C_P^* dT$$

where

$$C_P^* = 25.46 + 1.519 \times 10^{-2} T - 0.7151 \times 10^{-5} T^2 + 1.311 \times 10^{-9} T^3 \left(\frac{J}{mol\,.\,K}\right)$$

for oxygen and T is in K.

Obtain the pressure-enthalpy along the isotherm as shown in Figure 6.4-4 in page 3.

Hint:

For saturated liquid, we write

$$\underline{H}^{L}(T, P_{vap}(T)) = \underline{H}^{V}(T, P_{vap}(T)) - \Delta\underline{H}(T)\,.$$

For liquid,

$$\underline{H}(T,P) - \underline{H}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = \left\{ \underline{H}(T,P) - \underline{H}^{L}(T, P_{vap}(T)) \right\} + \underline{H}^{L}(T, P_{vap}(T))$$

where

$$\underline{H}(T,P) - \underline{H}^{L}\left(T, P_{vap}(T)\right) = \left\{ RT(Z-1) + \frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2}b} \ln\left[\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right] \right\}_{T,P} - \left\{ RT(Z-1) + \frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2}b} \ln\left[\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right] \right\}_{T,P_{vap}(T)}$$

CODE:- PART F

- **ALL SUBPROGRAMS USED IN PART e IS REQUIRED**

pressenthalpy.m:-

```
temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
h_1 = zeros(9,1);
h_2 = zeros(9,1);
p_2 = zeros(9,1);
for i = 1:9
```

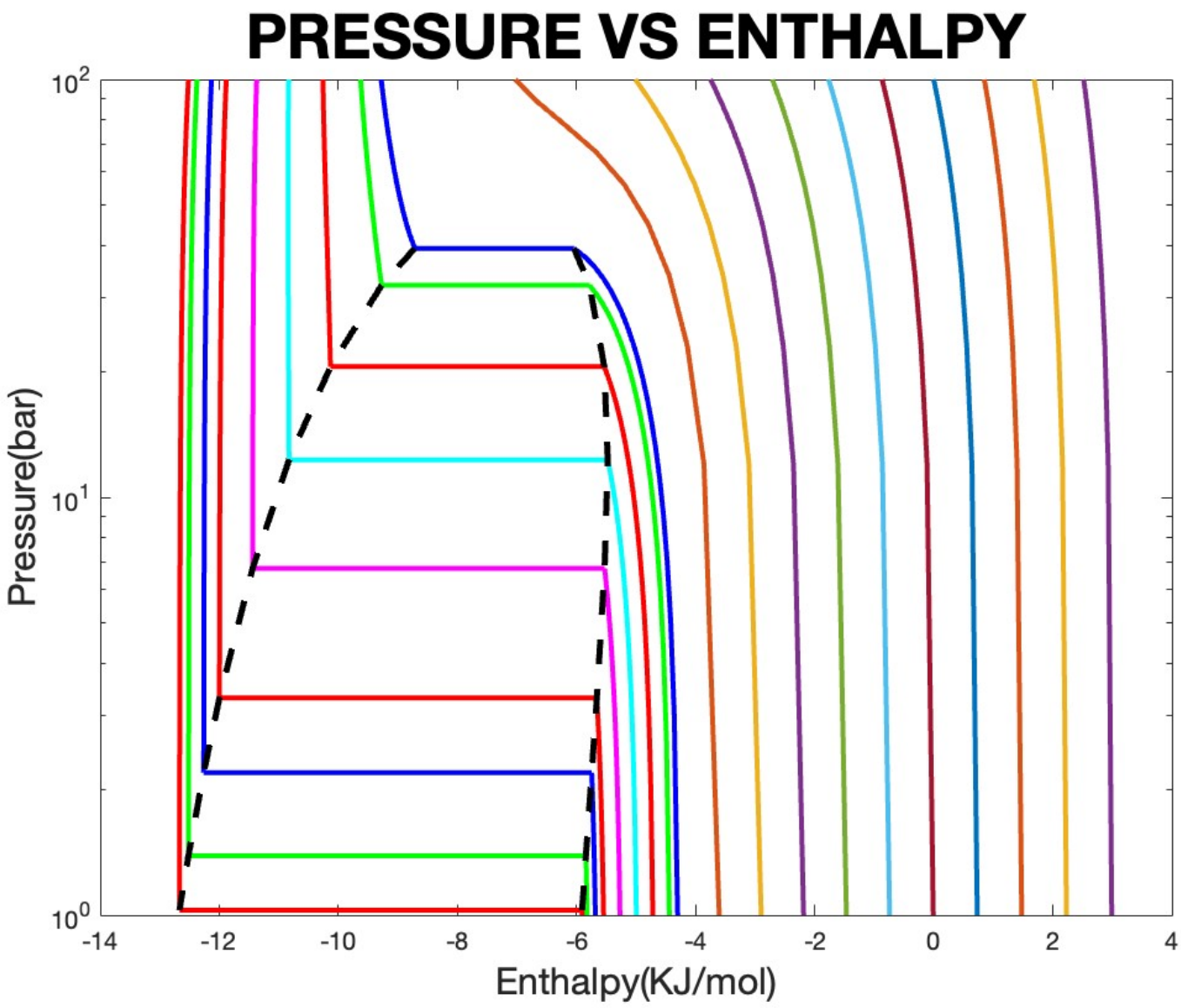
```
    p = P_vap(temp(i));
    p1 = linspace(p,1,20);
    p2 = linspace(100,p,20);
    p3 = [p,p];
    h1 = zeros(20,1);
    h2 = zeros(20,1);
    h3 = [H(p,temp(i),'l') H(p,temp(i),'v')];
    h_1(i) = H(p,temp(i),'l')*10^-3;
    h_2(i) = H(p,temp(i),'v')*10^-3;
    p_2(i) = p;
    c = ['b' 'g' 'r' 'c' 'm' 'r' 'b' 'g' 'r'];
    for j = 1:20
        h1(j) = H(p1(j),temp(i),'v');
    end
    for k = 1:20
        h2(k) = H(p2(k),temp(i),'l');
    end
    h1 = h1*10^-3;
    h2 = h2*10^-3;
    h3 = h3*10^-3;
    semilogy(h1,p1,c(i),'LineWidth',2)
    hold on
    semilogy(h2,p2,c(i),'LineWidth',2)
    hold on
    semilogy(h3,p3,c(i),'LineWidth',2)
    hold on

    title("PRESSURE VS ENTHALPY",'FontSize',25)
    xlabel("Enthalpy(KJ/mol)",'FontSize',15)
    ylabel("Pressure(bar)",'FontSize',15)
end
semilogy(h_1,p_2,'--k','LineWidth',2.5)
hold on
```

```
semilogy(h_2,p_2,'--k','LineWidth',2.5)
hold on



temp2 = [-100 -75 -50 -25 0 25 50 75 100 125 150]+273.15;
p_1 = linspace(100,1,10);
for i = 1:10
   h = zeros(10,1);
   for j = 1:10
      h(j) = H(p_1(j),temp2(i),'n');
   end
   h = h*10^-3;
   semilogy(h,p_1,'LineWidth',2)
   hold on
end
hold off
```

PR_main_program.m:-

```
if option == 6
   pressenthalpy
end
```

FIGURES(OUTPUT):-



COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**

  1)pressenthalpy

  2)PR_main_program.m

- **Run the main program :- PR_main_program.m**
- **Enter 6 as the option no.**

(g) Entropy calculations:

Choose $\underline{S}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = 0.\ IG$ **implies ideal gas. This sets our reference state. Now calculate entropy as**

$$\underline{S}(T,P) - \underline{S}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = \left\{\underline{S}(T,P) - \underline{S}^{IG}(T,P)\right\} + \left\{\underline{S}^{IG}(T,P) - \underline{S}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right)\right\}$$

Here $\underline{S}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right)$ **has a value zero therefore it has been struck through.**

For Peng-Robinson equation, the departure function for entropy or the residual entropy

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = R\ln(Z - B) + \frac{\frac{da}{dT}}{2\sqrt{2}b}\ln\left[\frac{Z + \left(1 + \sqrt{2}\right)B}{Z + \left(1 - \sqrt{2}\right)B}\right].$$

Also

$$\underline{S}^{IG}(T,P) - \underline{S}^{IG}\left(T = 25°\text{C}, P = 1\ bar\right) = \int_{T=298.15\ K}^{T} \frac{C_P^*}{T}dT - R\ln\left(\frac{P}{1\ bar}\right).$$

Obtain the pressure-entropy along the isotherm.

CODE:- PART G

- **ALL SUBPROGRAMS USED IN PART e IS REQUIRED**

pressentropy.m:-

```
temp = [148.15 143.15 133.15 123.15 113.15 103.15 98.15 93.15 90.15];
s_1 = zeros(9,1);
s_2 = zeros(9,1);
p_2 = zeros(9,1);

for i = 1:9
   p = P_vap(temp(i));
```

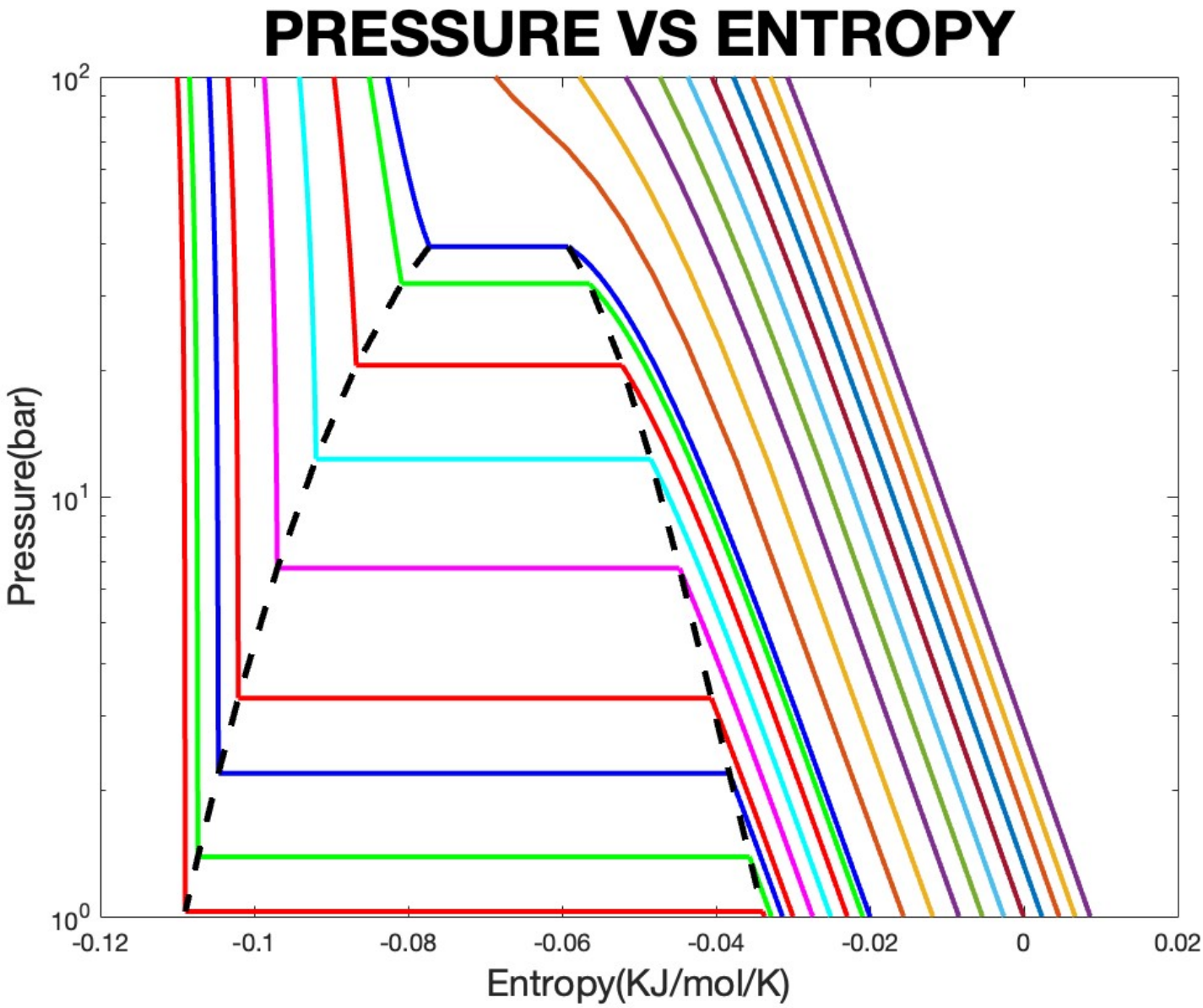
```
    p1 = linspace(p,1,20);
    p2 = linspace(100,p,20);
    p3 = [p,p];
    s1 = zeros(20,1);
    s2 = zeros(20,1);
    s3 = [S(p,temp(i),'l') S(p,temp(i),'v')];
    s_1(i) = S(p,temp(i),'l')*10^-3;
    s_2(i) = S(p,temp(i),'v')*10^-3;
    p_2(i) = p;
    c = ['b' 'g' 'r' 'c' 'm' 'r' 'b' 'g' 'r'];
    for j = 1:20
        s1(j) = S(p1(j),temp(i),'v');
    end
    for k = 1:20
        s2(k) = S(p2(k),temp(i),'l');
    end
    s1 = s1*10^-3;
    s2 = s2*10^-3;
    s3 = s3*10^-3;
    semilogy(s1,p1,c(i),'LineWidth',2)
    hold on
    semilogy(s2,p2,c(i),'LineWidth',2)
    hold on
    semilogy(s3,p3,c(i),'LineWidth',2)
    hold on

    title("PRESSURE VS ENTROPY",'FontSize',25)
    xlabel("Entropy(KJ/mol/K)",'FontSize',15)
    ylabel("Pressure(bar)",'FontSize',15)

end
semilogy(s_1,p_2,'--k','LineWidth',2.5)
hold on
```

```
semilogy(s_2,p_2,'--k','LineWidth',2.5)
hold on

temp2 = [-100 -75 -50 -25 0 25 50 75 100 125 150]+273.15;
p_1 = linspace(100,1,10);
for i = 1:10
   s = zeros(10,1);
   for j = 1:10
      s(j) = S(p_1(j),temp2(i),'n');
   end
   s = s*10^-3;
   semilogy(s,p_1,'LineWidth',2)
   hold on
end
hold off
```

PR_main_program.m:-

```
if option == 7
   pressentropy
end
```

FIGURES(OUTPUT):-



COMMENTS/INSTRUCTIONS:-

- **FILES(PROGRAMS) TO BE OPENED:-**

  1)pressentropy

  2)PR_main_program.m

- **Run the main program :- PR_main_program.m**
- **Enter 7 as the option no.**