# Scilab Textbook Companion for Chemical Engineering Thermodynamics by Y. V. C. Rao[1]

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# Book Description

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Scilab numbering policy used in this document and the relation to the above book.

**Exa** Example (Solved example)

**Eqn** Equation (Particular equation of the above book)

**AP** Appendix to Example(Scilab Code that is an Appednix to a particular Example of the above book)

For example, Exa 3.51 means solved example 3.51 of this book. Sec 2.3 means a scilab code whose theory is explained in Section 2.3 of the book.

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# Chapter 1

# Introduction

**Scilab code Exa 1.1** weight of payload

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-1,Example 1,Page 6
//Title:Weight of payload
//================================================================================

clear
clc

//INPUT
weight=981; //weight of payload in N
gmoon=1.62;//acceleration due to gravity on the moon in m/s^2
g=9.81;//acceleration due to gravity on earth

//CALCULATION
mass=weight/g;//calculation of mass of the payload in kg (calculated as F=m*g)
```

```
weightmoon=mass*gmoon;//calculation of weight of payload on the moon in N

//OUTPUT
mprintf('\n The weight of payload on the moon= %d N',weightmoon);

//================================================END OF PROGRAM==============================================================
```

**Scilab code Exa 1.2** Force due to atmospheric air

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-1,Example 2,Page 7
//Title:Force due to atmospheric air
//================================================================================================================

clear
clc

//INPUT
l=15;//length of the child's head in cm
b=12;//breadth of the child's head in cm
p=101325;//atmospheric pressure in Pa

//CALCULATION
area=(l*b)/(10^4);//calculation of area of the child's head in m^2
force=p*area;//calculation of force exerted on the
```

```
child's head due to atmospheric air in N

//OUTPUT
mprintf('\n The force exerted on the childs head due to atmospheric air= %f N',force);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 1.3** pressure drop

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-1,Example 3,Page 7
//Title:Pressure drop
//==========================================================================================

clear
clc

//INPUT
rho_water=1000;//density of water flowing through the pipeline in kg/m^3
rho_manomtr=1595;//density of manometric fluid (carbon tetrachloride) in kg/m^3
l=40;//length between the selected sections in cm
theta=45;//inclination of the manometer in degrees
g=9.81;//acceleration due to gravity in m/s^2

//CALCULATION
```

```
delp=(l/100)*sin((theta*%pi)/180)*g*(rho_manomtr-rho_water);//calculation of pressure drop between the required sections in Pa

//OUTPUT
mprintf('\n The pressure drop between the required sections= %f Pa',delp);

//==========================================================END OF PROGRAM==========================================================
```

# Chapter 2

# Review of basic concepts

**Scilab code Exa 2.1** work done by gas

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-2,Example 1,Page 29
//Title:Work done by gas
//================================================================================================================

clear
clc

//INPUT
R=8.314;//universal gas constant in J/molK
t1=300;//initial temperature of gas in K
p1=0.1;//initial pressure of the gas in MPa
p2=0.5;//pressure of gas after heating in MPa
p3=0.1;//pressure of gas after expansion in MPa
n=1;//number of moles of gas in mole

//CALCULATION
```

```
w1=0*n;//calculation of work done by the gas during heating in kJ (since dv=0)
t2=t1*(p2/p1);//calculation of temperature of gas after heating in K
t3=t2;//calculation of temperature of gas after expansion in K (constant temperature expansion)
volume2=p2/p3;//calculation of  ratio of volume of gas after expansion to the volume of gas after heating (no unit)
w2=(R*t2*log(volume2)*n)/1000;//calculation of work done  by the gas during expansion in kJ
volume3= t3/t1;//calculation of ratio of volume of gas after expansion to the final volume of gas (no unit)
w3=(R*t1*(1-volume3)*n)/1000;//calculation of work done by the gas during constant pressure compression in kJ
work_net=w1+w2+w3;//calculation of net work done by the gas for the process in kJ

//OUTPUT
mprintf('\n Work done during heating process:Work from 1-2= %d kJ \n',w1);
mprintf('\n Work done during constant temperature expansion: Work from 2-3= %f kJ \n',w2);
mprintf('\n Work done during constant pressure compression: Work from 3-1= %f kJ \n',w3);
mprintf('\n Net work done by the gas during the process= %f kJ \n',work_net);
//==============================================================END OF PROGRAM================================================================
```

---

**Scilab code Exa 2.2** work done by gas in piston cylinder assembly

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-2,Example 2,Page 30
//Title:Work done by gas in piston cylinder assembly
//================================================================================

clear
clc

//INPUT
v1=0.1;//volume of gas initially present in the cylinder in m^3
p1=0.1;//initial pressure of gas in MPa
p_atm=0.1;//atmospheric pressure acting on the piston in MPa
v2=0.3;//volume of gas after heating in m^3
p2=0.6;//pressure of gas after heating in MPa

//CALCULATION
work=((p1+p2)*(v2-v1)*10^6)/(2*1000);//calculation of work done by the gas in kJ
//calculation is done by using reversible work done as integral of Pdv followed by a force balance taken on the piston

//OUTPUT
mprintf('\n The work done by the gas = %d kJ',work);

//===============================================END OF PROGRAM=================================================
```

# Chapter 3

# PvT relations of fluids

**Scilab code Exa 3.1** Specific volume and Specific internal energy

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 1,Page 48
//Title:Specific volume and Specific internal energy
//================================================================================================

clear
clc

//INPUT
X=0.8;//Quality of wet steam (no unit)
T=150;//Temperature of the wet steam in degree celsius
vf=0.0010908;//molar volume of saturated liquid in m^3/kg
vg=0.3924;//molar volume of saturated vapour in m^3/kg
uf=631.63;//molar internal energy of the saturated
```

```
liquid in kJ/kg
ug=2558.6;//molar internal energy of the saturated vapour in kJ/kg

//CALCULATION
V=(X*vg)+((1-X)*vf);//calculation of specific volume in m^3/kg using Eq.(3.3)
U=(X*ug)+((1-X)*uf);//calculation of specific internal energy in kJ/kg using Eq.(3.6)

//OUTPUT
mprintf('\n The specific volume of wet steam= %0.4f m^3/kg \n',V);
mprintf('\n The specific internal energy of wet steam= %0.1f kJ/kg \n',U);

//===================================================END OF PROGRAM====================================================
```

---

**Scilab code Exa 3.2** Quality of wet steam

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 2,Page 49
//Title:Quality of wet steam
//================================================================================================================

clear
clc

```

```
//INPUT
V=1.42;//specific volume of wet steam in m^3/kg
T=100;//temperature of wet steam in degree celsius
vf=0.0010437;//molar volume of saturated liquid in m^3/kg
vg=1.673;//molar volume of saturated vapour in m^3/kg

//CALCULATION
X=(V-vf)/(vg-vf);//calculation of the quality of wet steam using Eq.(3.3) (no unit)

//OUTPUT
mprintf('\n The quality of wet steam= %0.4f \n',X);

//===================================================END OF PROGRAM======================================================
```

**Scilab code Exa 3.3** Volume ratio

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 3,Page 49
//Title:Volume ratio
//==================================================================================================================

clear
clc

//INPUT
```

```
T=100;//temperature inside the vessel in degree celsius
V=0.00317;//specific volume of water at the critical point in m^3/kg
vf=0.0010437;//molar volume of saturated liquid in m^3/kg
vg=1.673;//molar volume of saturated vapour in m^3/kg

//CALCULATION
X=(V-vf)/(vg-vf);//calculation of the quality of wet steam using Eq.(3.3) (no unit)
ratio=(X*vg)/((1-X)*vf);//calculation of volume ratio of saturated vapour to the saturated liquid (no unit)

//OUTPUT
mprintf('\n The volume ratio of saturated vapour to the saturated liquid= %0.2f \n',ratio);

//================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 3.4** Mass ratio

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 4,Page 49
//Title:Mass ratio
//================================================================================================================
```

```
clear
clc

//INPUT
U=2000;//specific internal energy of liquid-vapour mixture in kJ/kg
uf=850.6;//specific internal energy of saturated liquid in kJ/kg
ug=2593.2;//specific internal energy of saturated vapour in kJ/kg

//CALCULATION
mass_ratio=(U-uf)/(ug-U);//calculation of the mass ratio of vapour to liquid using the lever rule (no unit)

//OUTPUT
mprintf('\n The mass ratio of vapour to liquid= %0.4f \n',mass_ratio);

//==================================================END OF PROGRAM==================================================
```

**Scilab code Exa 3.5** Volume using ideal gas law

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 5,Page 52
//Title:Volume using ideal gas law
//
```

```
clear
clc

//INPUT
n=1;//number of moles of n-octane vapour in mol
T=427.85;//tempearture of n-octane vapour in K
P=0.215;//pressure n-octane vapour in MPa
R=8.314;//universal gas constant in (kPa m^3)/(kmol K)

//CALCULATION
V=((n*10^-3)*R*T)/(P*10^3);//calculation of volume using ideal gas law-Eq.(3.9) in m^3

//OUTPUT
mprintf('\n The volume occupied by n-octane vapour= %f m^3 \n',V);

//==============================================END OF PROGRAM
```

---

**Scilab code Exa 3.6** Volume using van der Waals equation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 6,Page 54
//Title:Volume using van der Waals equation
//
```

```
clear
clc

//INPUT
n=1;//number of moles occupied by n-octane vapour in mol
T=427.85;//temperature in K
P=0.215;//saturation pressure in MPa
a=3.789;//van der Waals constant in Pa(m^3/mol)^2
b=2.37*10^-4;//van der Waals constant in m^3/mol
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
Vguess=(n*R*T)/(P*10^6);//taking the vguess as volume from ideal gas (in m^3/mol) for the iteration process in van der Waals equation
Vnew=(R*T)/((P*10^6)+(a/Vguess^2))+b;//getting the initial value of volume (in m^3/mol) using van der Waals equation to start the iteration process
tolerance=1e-6;//defining the tolerance limit for the convergence of the iteration process
while abs(Vguess-Vnew)>tolerance
    Vguess=Vnew;
    Vnew=(R*T)/((P*10^6)+(a/Vguess^2))+b;//the iteration process to solve the system of equation
end
V=Vnew;//The volume calculated using the van der Waals equation in m^3/mol
//OUTPUT
mprintf('\n The volume occupied by n-octane vapour obtained by van der Waals equation= %f m^3/mol\n',V);

//==============================================END OF PROGRAM==============================================
```

**Scilab code Exa 3.7** Volume of liquid using van der Waals equation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 7,Page 55
//Title:Volume of liquid using van der Waals equation
//
clear
clc

//INPUT
n=1;//number of moles occupied by n-octane liquid in mol
T=427.85;//temperature in K
P=0.215;//saturation pressure in MPa
a=3.789;//van der Waals constant in Pa(m^3/mol)^2
b=2.37*10^-4;//van der Waals constant in m^3/mol
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
Vguess=b;//taking vguess (in m^3/mol) for the iteration process in van der Waals equation
Vnew=(R*T)/((P*10^6)+(a/Vguess^2))+b;//getting the initial value of volume (in m^3/mol) using van der Waals equation to start the iteration process
tolerance=1e-6;//defining the tolerance limit for the convergence of the iteration process
while abs(Vguess-Vnew)>tolerance
```

```
    Vguess=Vnew;
    Vnew=(R*T)/((P*10^6)+(a/Vguess^2))+b;//the iteration process to solve the system of equation
end
V=Vnew;//The volume calculated using the van der Waals equation in m^3/mol

//OUTPUT
mprintf('\n The volume occupied by n-octane liquid obtained by van der Waals equation= %e m^3/mol\n',V);

//===========================================================END OF PROGRAM ===============================================================
```

**Scilab code Exa 3.8** Volume using Cardans method

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 8,Page 57
//Title:Volume using Cardan's method
//================================================================================

clear
clc

//INPUT
T=427.85;//temperature in K
P=0.215;//saturation pressure in MPa
```

```
a=3.789;//van der Waals constant in Pa(m^3/mol)^2
b=2.37*10^-4;//van der Waals constant in m^3/mol
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
//The Cardan's method simplifies the equation of state into a cubic equation which can be solved easily
//The general form of the cubic equation is (Z^3)+(alpha*Z^2)+(beeta*Z)+gaamma=0, where alpha,beeta and gaamma are determined using established relations

A=(a*P*10^6)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*P*10^6)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1-B;//calculation of alpha for van der Waals equation of state using Table (3.2)
beeta=A;//calculation of beeta for van der Waals equation of state using Table (3.2)
gaamma=-(A*B);//calculation of gaamma for van der Waals equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)
if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
        vf=((Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=((Z)*R*T)/(P*10^6);//Volume of saturated
```

```
vapour calculated as vg=(Z*R*T)/P in m^3/mol
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
    else
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol

    end
end

//OUTPUT
mprintf('\n The volume occupied by n-octane (
```

```
   saturated liquid) obtained by Cardans method= %e
   m^3/mol\n',vf);
mprintf('\n The volume occupied by n-octane (
   saturated vapour) obtained by Cardans method= %f
   m^3/mol\n',vg);


//==============================================================END
    OF PROGRAM
   ==================================================================

//DISCLAIMER: THE COMPUTED VALUE OF Z2 IS 0.0213 AND
    NOT 0.0187 AS PRINTED IN THE TEXTBOOK. THIS HAS
   BEEN CORRECTED IN THE ABOVE PROGRAM.
```

**Scilab code Exa 3.9** Volume using Redlich Kwong equation of state by implementing Cardans method

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-3,Example 9,Page 60
//Title:Volume using Redlich-Kwong equation of state
    by implementing Cardan's method
//
   ==========================================================================

clear
clc

//INPUT
T=427.85;//temperature in K
P=0.215;//saturation pressure in MPa
```

```
R=8.314;//universal gas constant in (Pa m^3)/(mol K)
Pc=24.97;//critical pressure of n-octane in bar
Tc=569.4;//critical temperature of n-octane in K

//CALCULATION
a=(0.42748*R^2*Tc^2.5)/(Pc*100*10^3*sqrt(T));//calculation of Redlich-Kwong constant in (m^6 Pa mol^-2)
b=(0.08664*R*Tc)/(Pc*100*10^3);//calculation of Redlich-Kwong constant in m^3/mol
//The Cardan's method simplifies the equation of state into a cubic equation which can be solved easily
//The general form of the cubic equation is (Z^3)+(alpha*Z^2)+(beeta*Z)+gaamma=0, where alpha,beeta and gaamma are determined using established relations

A=(a*P*10^6)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*P*10^6)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1;//calculation of alpha for Redlich-Kwong equation of state using Table (3.2)
beeta=A-B-B^2;//calculation of beeta for Redlich-Kwong equation of state using Table (3.2)
gaamma=-(A*B);//calculation of gaamma for Redlich-Kwong equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D))
```

```
)^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
      vf=((Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
      vg=((Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
else if D==0 then
      Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
      Z2=((q/2)^(1/3))-(alpha/3);
      Z3=((q/2)^(1/3))-(alpha/3);
      Z=[Z1 Z2 Z3];
      vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
      vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
   else
      r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
      theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
      Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
      Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
      Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
      Z=[Z1 Z2 Z3];
      vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
      vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
```

```

    end
end

//OUTPUT
mprintf('\n The volume occupied by n-octane (saturated vapour) using Redlich-Kwong equation of state= %f m^3/mol\n',vg);
mprintf('\n The volume occupied by n-octane (saturated liquid) using Redlich-Kwong equation of state= %f m^3/mol\n',vf);

//==================================================END OF PROGRAM======================================================

//DISCLAIMER:THE COMPUTED VALUE OF Z2 IS 0.0147 AND NOT 0.0163 AS PRINTED IN THE TEXTBOOK. THIS HAS BEEN CORRECTED IN THE ABOVE PROGRAM.
```

**Scilab code Exa 3.10** Acentric factor

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 10,Page 67
//Title:Acentric factor
//=================================================================================================

clear
clc

```

```
//INPUT
T=180;//temperature of water in degree celsius
P=1.0027;//saturation pressure of water in MPa
Tc=647.3;//critical temperature of water in K
Pc=221.2;//critical pressure of water in bar
Tr=0.7;//reduced temperature at which acentric factor was defined by Pitzer

//CALCULATION
T1=Tr*Tc;//calculating temperature  in K using reduced temperature value
T1=T1-273.15;//conversion to degree celsius
Pr=(P*10)/Pc;//calculation of reduced pressure (no unit) using saturation pressure at t1. In this case t1 equals t, therefore the given saturation pressure is taken
w=-log10(Pr)-1.0;//calculation of acentric factor using Eq.(3.62)

////OUTPUT
mprintf('\n The acentric factor of water= %f \n',w);


//=======================================================END OF PROGRAM=======================================================
```

---

**Scilab code Exa 3.11** Volume using two paramter and three parameter compressibility factor correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

```

```
//Chapter-3,Example 11,Page 72
//Title:Volume using two paramter and three parameter compressibility factor correlation
//==================================================================================

clear
clc

//INPUT
T=409.41;//temperature of n-octane in degree celsius
P=4.98;//pressure in bar
Tc=569.4;//critical temperature of n-octane in K
Pc=24.97;//critical pressure of n-octane in bar
w=0.398;//acentric factor (no unit)
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
Tr=(T+273.15)/Tc;//calculation of reduced temperature (no unit)
Pr=P/Pc;//calculation of reduced pressure (no unit)
z0=0.96;//value of compressibilty factor at tr and pr obtained from Fig.3.11
V1=(z0*R*(T+273.15))/(P*10^5);//calculation of volume in m^3/mol using the two parameter compressibilty factor correlation
z1=0.01;//value of compressibilty factor at tr and pr obtained from Fig.3.12
z=z0+(w*z1);//calculation of compressibility factor using Eq.3.64
V2=(z*R*(T+273.15))/(P*10^5);//calculation of volume in m^3/mol using the three parameter compressibility factor correlation

//OUTPUT
mprintf('\n The volume occupied by n-octane obtained by the two parameter compressibilty factor correlation= %f m^3/mol\n',V1);
```

```
mprintf('\n The volume occupied by n-octane obtained by the three parameter compressibility factor correlation= %f m^3/mol\n',V2);


//====================================================END OF PROGRAM ==========================================================
```

---

**Scilab code Exa 3.12** Pressure developed using two paramter compressibility factor correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 12,Page 72
//Title:Pressure developed using two paramter compressibility factor correlation
//================================================================================================

clear
clc

//INPUT
V=1;//volume of the tank in m^3
m=180;//mass of carbon dioxide in kg
T=91.8;//temperature of the tank in degree celsius after it is placed in the vicinity of a furnace
Tc=304.2;//critical temperature of carbon dioxide in K
Pc=73.87;//critical pressure of carbon dioxide in bar
```

```
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
mwt=44*10^-3;//molecular weight of carbon dioxide in kg/mol
n=m/mwt;//calculation of number of moles of carbon dioxide in the tank in moles
MV=V/n;//calculation of molar volume in m^3/mol
slope=(MV*Pc*10^5)/(R*(T+273.15));//slope of the straight line formed when z0 is plotted against Pr formed by using the relation z0=(V*Pc*Pr)/(R*T)
Tr=(T+273.15)/Tc;//calculation of reduced temperature (no unit)

//At the given conditions, the state of CO2 must lie on the curve corresponding to the obtained value of Tr. To determine the state of CO2, a straight line passing through the origin, with the obtained value of slope is drawn on the z0 vs Pr plot of Fig.3.12 and the point of intersection of this straight line with the Tr curve is obtained to get the value of z0

z0=0.725;//value of compressibilty factor obtained by doing the above mentioned procedure
P=(z0*R*10^-6*(T+273.15))/(MV)//calculation of pressure in MPa using Eq.(3.59)

//OUTPUT
mprintf('\n The pressure developed by carbon dioxide = %.0f MPa\n',P);



//==============================================END OF PROGRAM==============================================
```

---

**Scilab code Exa 3.13** Pressure developed using three paramter compressibility factor correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-3,Example 13,Page 73
//Title:Pressure developed using three paramter
   compressibility factor correlation
//
   ================================================================================

clear
clc

//INPUT
V=1;//volume of the tank in m^3
m=180;//mass of carbon dioxide in kg
T=91.8;//temperature of the tank in degree celsius
   after it is placed in the vicinity of a furnace
Tc=304.2;//critical temperature of carbon dioxide in
    K
Pc=73.87;//critical pressure of carbon dioxide in
   bar
R=8.314;//universal gas constant in (Pa m^3)/(mol K)
w=0.239;//acentric factor (no unit)

//CALCULATION
mwt=44*10^-3;//molecular weight of carbon dioxide in
    kg/mol
n=m/mwt;//calculation of number of moles of carbon
   dioxide in the tank in mol
```

```
MV=V/n;//calculation of molar volume in m^3/mol
Tr=(T+273.15)/Tc;//calculation of reduced temperature (no unit)
z0=0.725;//the value of z0 as computed in Example 3.12 (no unit)
z_init=z0;//taking the initial guess value of z as z0
slope=(MV*Pc*10^5)/(R*(T+273.15));//slope of the straight line formed when z is plotted against Pr formed by using the relation  z0=(V*Pc*Pr)/(R*T)
Prguess=z_init/slope;//Calculation of an initial guess value of reduced pressure (no unit) to compute the value of z
z1guess=0.1;//z1 read from Fig.3.14 for the value of Tr and Prguess (no unit)
tolerance=1e-6;//framing the tolerance limit for the convergence of the equation
function[fn]=solver_function(zi)
    fn=zi-(z0+(w*z1guess));//Function defined for solving the system using Eq.(3.64)
endfunction
[z]=fsolve(z1guess,solver_function,tolerance)//using inbuilt function fsolve for solving the system of equations
Pr=z/slope;//calculation of the proper reduced pressure (no unit)
P=((Pc*10^5)*Pr)*10^-6;//calculation of pressure exerted by carbon dioxide in MPa

//OUTPUT
mprintf('\n The pressure developed by carbon dioxide = %f MPa\n',P);



//===============================================================END OF PROGRAM===============================================================
```

**Scilab code Exa 3.14** Volume using generalized form of the Redlich Kwong equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 14,Page 75
//Title:Volume using generalized form of the Redlich-Kwong equation of state
//

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-ocatne vapour in MPa
Tc=569.4;//critical temperature of n-octane in K
Pc=2.497;//critical pressure of n-octane in MPa
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=P/Pc;//calculation of reduced pressure (no unit)
z_init=1;//taking a guess value of z (compressibilty factor) to get a value of h for solving the system
h=(0.08664*Pr)/(z_init*Tr);//calculation of h using Eq.(3.68)
tolerance=1e-6;//Framing the tolerance limit for the
```

```
convergence of the equation
function[fn]=solver_func(zi)
    fn=zi-((1/(1-h))-((h/(1+h))*(4.93398/(Tr^(3/2)))));//Function defined for solving the system using Eq.(3.67)
endfunction
[z]=fsolve(h,solver_func,tolerance)//using inbuilt function fsolve for solving the system of equations
V=(z*R*T)/(P*10^6);//calculation of volume in m^3/mol using Eq.(3.59)

//OUTPUT
mprintf('\n The volume occupied by n-octane vapour obtained by the generalized form of Redlich-Kwong equation of state= %f m^3/mol\n',V);


//==========================================================END OF PROGRAM==============================================================
```

**Scilab code Exa 3.15** Volume using Soave Redlich Kwong equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 15,Page 77
//Title:Volume using Soave-Redlich-Kwong equation of state
//================================================================================
```

```
clear
clc

//INPUT
T=427.85;//temperature in K
P=0.215;//saturation pressure in MPa
Tc=569.4;//critical temperature of n-octane in K
Pc=24.97;//critical pressure of n-octane in bar
w=0.398;//acentric factor (no unit)
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
//The Cardan's method simplifies the equation of state into a cubic equation which can be solved easily
//The general form of the cubic equation is (Z^3)+(alpha*Z^2)+(beeta*Z)+gaamma=0, where alpha,beeta and gaamma are determined using established relations

Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=(P*10^6)/(Pc*10^5);//calculation of reduced pressure (no unit)
S=0.48+(1.574*w)-(0.176*w^2);//calculation of S using Eq.(3.73)
alpha1=(1+(S*(1-sqrt(Tr))))^2;//calculation of alpha1 using Eq.(3.72)
a=(0.42748*R^2*Tc^2*alpha1)/(Pc*10^5);//calculation of the Soave-Redlich-Kwong constant in (m^6 Pa mol^-2) using Eq.(3.70)
b=(0.08664*R*Tc)/(Pc*10^5);//calculation of the Soave-Redlich-Kwong constant in m^3/mol using Eq.(3.71)
A=(a*P*10^6)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*P*10^6)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
```

```
alpha=-1;//calculation of alpha for Soave-Redlich-Kwong equation of state using Table (3.2)
beeta=A-B-B^2;//calculation of beeta for Soave-Redlich-Kwong equation of state using Table (3.2)
gaamma=-(A*B);//calculation of gaamma for Soave-Redlich-Kwong equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
        vf=((Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=((Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
    else
        r=sqrt((-(p^3)/27));//calculation of r using
```

```
Eq.(3.38)
      theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
      Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
      Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
      Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
      Z=[Z1 Z2 Z3];
      vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
      vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol

   end
end

//OUTPUT
mprintf('\n The volume occupied by n-octane (saturated vapour) obtained by Soave-Redlich-Kwong equation of state= %f m^3/mol\n',vg);
mprintf('\n The volume occupied by n-octane (saturated liquid) obtained by Soave-Redlich-Kwong equation of state= %f m^3/mol\n',vf);



//====================================================END OF PROGRAM======================================================
```

**Scilab code Exa 3.16** Volume using Peng Robinson equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-3,Example 16,Page 78
//Title:Volume using Peng-Robinson equation of state
//================================================================================

clear
clc

//INPUT
T=427.85;//temperature in K
P=0.215;//saturation pressure in MPa
Tc=569.4;//critical temperature of n-octane in K
Pc=24.97;//critical pressure of n-octane in bar
w=0.398;//acentric factor (no unit)
R=8.314;//universal gas constant in (Pa m^3)/(mol K)

//CALCULATION
//The Cardan's method simplifies the equation of state into a cubic equation which can be solved easily
//The general form of the cubic equation is (Z^3)+(alpha*Z^2)+(beeta*Z)+gaamma=0, where alpha,beeta and gaamma are determined using established relations

Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=(P*10^6)/(Pc*10^5);//calculation of reduced pressure (no unit)
S=0.37464+(1.54226*w)-(0.26992*w^2);//calculation of S using Eq.(3.79)
alpha1=(1+(S*(1-sqrt(Tr))))^2;//calculation of
```

```
alpha1 using Eq.(3.78)
a=(0.45724*R^2*Tc^2*alpha1)/(Pc*10^5);//calculation of the Peng−Robinson constant in (m^6 Pa mol^−2) using Eq.(3.76)
b=(0.07780*R*Tc)/(Pc*10^5);//calculation of the Peng−Robinson constant in m^3/mol using Eq.(3.77)
A=(a*P*10^6)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*P*10^6)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1+B;//calculation of alpha for Peng−Robinson equation of state using Table (3.2)
beeta=A-(2*B)-(3*B^2);//calculation of beeta for Peng−Robinson equation of state using Table (3.2)
gaamma=-(A*B)+(B^2)+(B^3);//calculation of gaamma for Peng−Robinson equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
        vf=((Z)*R*t)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=((Z)*R*t)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
```

```
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol
    else
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        vf=(min(Z)*R*T)/(P*10^6);//Volume of saturated liquid calculated as vf=(Z*R*T)/P in m^3/mol
        vg=(max(Z)*R*T)/(P*10^6);//Volume of saturated vapour calculated as vg=(Z*R*T)/P in m^3/mol

    end
end

//OUTPUT
mprintf('\n The volume occupied by n-octane (saturated vapour) obtained by Peng-Robinson equation of state= %f m^3/mol\n',vg);
mprintf('\n The volume occupied by n-octane (saturated liquid) obtained by Peng-Robinson equation of state= %f m^3/mol\n',vf);
```

```



//====================================================================================END OF PROGRAM=====================================================================================
```

# Chapter 4

# First law of thermodynamics and its applications

**Scilab code Exa 4.1** Net work done by the system

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 1,Page 94
//Title:Net work done by the system
//================================================================================================

clear
clc

//INPUT
Q1=50;//Energy added as heat in kJ when the system undergoes a process 1-2
W1=30;//Work done by the system in kJ during the process 1-2
Q2=-40;//Energy rejected as heat in kJ during the process 2-3
```

```
W2=-50;//Work done on the system in kJ during the process 2-3
Q3=0;//System undergoes an adiabatic process to return to initial state

//CALCULATION
U2_1=Q1-W1;//calculation of net change in energy in kJ during process 1-2 using Eq.(4.5)
U3_2=Q2-W2;//calculation of net change in energy in kJ during process 2-3 using Eq.(4.5)
U1_3=(-U2_1)-(U3_2);//calculation of net change in energy in kJ during process 3-1 using Eq.(4.5)
W3=Q3-U1_3;//calculation of work by the system in kJ using Eq.(4.5)
net_work=W1+W2+W3;//calculation of net work done in kJ

//OUTPUT
mprintf('\n The net work done by the system= %d kJ\n',net_work);

//==================================END OF PROGRAM==================================
```

---

**Scilab code Exa 4.3** Final temperature and final pressure

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 3,Page 96
//Title:Final temperature and final pressure
//
```

```
clear
clc

//INPUT
V=1;//volume of tank in m^3;
N=200;//number of moles of carbon dioxide in tank in
    mol
T1=25;//ambient temperature in degree celsius
I=5;//current in amperes passed through the resistor
    place in the tank
Voltage=440;//voltage in volts existing across the
   resistor
t=10;//time in minutes for which the current is
   passed
a=363.077*10^-3;//van der waals constant in Pa (m^3/
   mol)^2
b=0.043*10^-3;//van der waals constant in m^3/mol
Cv=32.34;//molar heat capacity at constant volume in
    J/molK
R=8.314;//universal gas constant in J/molK

//CALCULATION
MV=V/N;//calculation of molar volume in m^3/mol
Q=0;//energy transfer as heat during the process
W_Pdv=0;//mechanical work done by the system
W_elec=-(Voltage*I*t*60)*(10^-6);//calculation of
   electrical work done on the system in MJ
U2_1=Q-(W_Pdv+W_elec);//calculation of internal
   energy in MJ using Eq.(4.5)
T2=((U2_1*10^6)/(N*Cv))+(T1+273.15);//calculation of
    final temperature in K using the relation du=
   CvdT+(a/v^2)dv, where dv is zero
P=(((R*T2)/(MV-b))-(a/(MV^2)))*10^-3;//calculation
   of final pressure in kPa using Eq.(3.18)

//OUTPUT
```

```
mprintf('\n The final pressure= %0.3f kPa \n',P);
mprintf('\n The final temperature= %0.2f K\n',T2);


//==========================================================END OF PROGRAM==========================================================
```

**Scilab code Exa 4.4** Energy transferred and final state masses of liquid and vapour

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 4,Page 97
//Title:Energy transferred and final state masses of liquid and vapour
//========================================================================================================

clear
clc

//INPUT
V=0.1;//volume of tank in m^3
T1=200;//initial temperature of saturated steam inside the tank in degree celsius
T2=150;//temperature in degree celsius that the tank attains after some time due to poor insulation
P1=15.549;//pressure in bar obtained from steam tables corresponding to T1
vg1=0.1272;//specific volume of saturated vapour in m^3/kg obtained from steam tables corresponding
```

```
to T1
hg1=2790.9;//specific enthalpy of saturated vapour in kJ/kg obtained from steam tables corresponding to T1
P2=4.76;//pressure in bar obtained from steam tables corresponding to T2
vf=0.0010908;//specific volume of saturated liquid in m^3/kg obtained from steam tables corresponding to T2
vg2=0.3924;//specific volume of saturated vapour in m^3/kg obtained from steam tables corresponding to T2
hf=632.15;//specific enthalpy of saturated liquid in kJ/kg obtained from steam tables corresponding to T1
hg2=2745.4;//specific enthalpy of saturated vapour in kJ/kg obtained from steam tables corresponding to T1

//CALCULATION
ug1=((hg1*10^3)-(P1*10^5*vg1))*10^-3;//calculation of internal energy of vapour corresponding to T1 in kJ/kg
uf=((hf*10^3)-(P2*10^5*vf))*10^-3;//calculation of internal energy of liquid corresponding to T2 in kJ/kg
ug2=((hg2*10^3)-(P2*10^5*vg2))*10^-3;//calculation of internal energy of vapour corresponding to T2 in kJ/kg
v2=vg1;//since constant volume process
X2=(v2-vf)/(vg2-vf);//calculation of the final quality of steam (no unit)
u2=(X2*ug2)+((1-X2)*uf);//calculation of the internal energy at the final state in kJ/kg
m=V/vg1;//calculation of the mass of steam in kg
Q=m*(u2-ug1);//calculation of energy transferred as heat in kJ, using the first law of thermodynamics
mf=m*(1-X2);//calculation of mass of liquid in the
```

```
tank in the final state in kg
mg=m*X2;//calculation of mass of vapour in the tank in the final state in kg

 //OUTPUT
mprintf('\n The energy transferred as heat= %f kJ\n',Q);
mprintf('\n The mass of liquid in the tank in the final state= %0.3f kg\n',mf);
mprintf('\n The mass of vapour in the tank in the final state= %0.3f kg\n',mg);
//==================================================END OF PROGRAM======================================================
```

---

**Scilab code Exa 4.5** Work done and energy transferred

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 5,Page 102
//Title:Work done and energy transferred
//================================================================================================================

clear
clc

//INPUT
W=1;//weight of steam in kg in the piston cylinder assembly
X=0.8;//quality of steam (no unit)
T1=150;//initial temperature of steam in degree
```

```
   celsius
T2=200;//final temperature of steam in degree
   celsius
P1=476;//pressure in kPa obatined from steam tables
   (corresponding to T1)
vf=0.0010908;//specific volume of saturated liquid
   in m^3/kg obatined from steam tables (
   corresponding to T1)
vg=0.3924;//specific volume of satuarted vapour in m
   ^3/kg obatined from steam tables (corresponding
   to T1)
hf=632.15;//specific enthalpy of saturated liquid in
    kJ/kg obtained from steam tables (corresponding
   to T1)
hg=2745.4;//specific enthalpy of saturated vapour in
    kJ/kg obtained from steam tables (corresponding
   to T1)

//CALCULATION
V1=(X*vg)+((1-X)*vf);//calculation of specific
   volume of steam in m^3/kg
h1=(X*hg)+((1-X)*hf);//calculation of specific
   enthalpy of steam in kJ/kg
P2=0.476;//Pressure in MPa is held constant during
   the process
P_int1=0.4;//Pressure in MPa from steam tables at T2
    taken for interpolation to find V2 and h2
   corresponding to P2
P_int2=0.5;//Pressure in MPa from steam tables at T2
    taken for interpolation to find V2 and h2
   corresponding to P2
V_int1=0.5343;//specific volume in m^3/kg at P_int1
   obtained from steam tables at T2 taken for
   interpolation to find V2 and h2 corresponding to
   P2
V_int2=0.4250;//specific volume in m^3/kg at P_int2
   obtained from steam tables at T2 taken for
   interpolation to find V2 and h2 corresponding to
```

```
P2
h_int1=2860.4;//specific enthalpy in kJ/kg at P_int1 obtained from steam tables at T2 taken for interpolation to find V2 and h2 corresponding to P2
h_int2=2855.1;//specific enthalpy in kJ/kg at P_int2 obtained from steam tables at T2 taken for interpolation to find V2 and h2 corresponding to P2
V2=(((P2-P_int1)/(P_int2-P_int1))*(V_int2-V_int1))+V_int1;//specific volume of superheated steam in m^3/kg obtained by interpolation (corresponding to T2 and P2)
h2=(((P2-P_int1)/(P_int2-P_int1))*(h_int2-h_int1))+h_int1;//specific enthalpy of superheated steam in kJ/kg obtained by interpolation (corresponding to T2 and P2)
Q=(h2-h1)*W;//calculation of net heat transferred in kJ using Eq.(4.15)
W=P1*(V2-V1)*W;//calculation of work done by steam in kJ using Eq.(4.14)

//OUTPUT
mprintf('\n The work done by steam= %0.2f kJ \n',W);
mprintf('\n The net energy transferred as heat = %0.2f kJ\n',Q);
mprintf('\n The final state of superheated steam, Pressure=%0.3f MPa \n',P2);
mprintf('\n The final state of superheated steam, Temperature=%d degree celsius \n',T2);

//==========================================END OF PROGRAM==========================================
```

**Scilab code Exa 4.6** Work done and final temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 6,Page 103
//Title:Work done and final temperature
//================================================================================

clear
clc

//INPUT
W=1;//weight of steam in kg in the piston cylinder assembly
X=0.8;//quality of steam (no unit)
T1=150;//initial temperature  of steam in degree celsius
I=5;//current passed in Amperes
V=220;//voltage in volts across the resistor
t=10;//time for which the current is passed in minutes
P1=476;//pressure in kPa obatined from steam tables (corresponding to T1)
vf=0.0010908;//specific volume of saturated liquid in m^3/kg obatined from steam tables (corresponding to T1)
vg=0.3924;//specific volume of satuarted vapour in m^3/kg obatined from steam tables (corresponding to T1)
hf=632.15;//specific enthalpy of saturated liquid in kJ/kg obtained from steam tables (corresponding
```

```
to T1)
hg=2745.4;//specific enthalpy of saturated vapour in kJ/kg obtained from steam tables (corresponding to T1)

//CALCULATION
V1=(X*vg)+((1-X)*vf);//calculation of specific volume of steam in m^3/kg
h1=(X*hg)+((1-X)*hf);//calculation of specific enthalpy of steam in m^3/kg
Ws=-V*I*t*60*10^-3;//calculation of electrical work done on the system in kJ
h2=h1-Ws;//calculation of the specific enthalpy of steam in the final state in kJ/kg
P2=0.476;//Pressure in MPa is held constant during the process
T_int1=200;//Temperature in degree celsius obtained from steam tables at P2 taken for interpolation to find V2 and T2 corresponding to P2
T_int2=300;//Temperature in degree celsius obtained from steam tables at P2 taken for interpolation to find V2 and T2 corresponding to P2
V_int1=0.4512;//specific volume in m^3/kg at T_int1 from steam tables at P2 taken for interpolation to find V2 and T2 corresponding to P2
V_int2=0.5544;//specific volume in m^3/kg at T_int2 from steam tables at P2 taken for interpolation to find V2 and T2 corresponding to P2
h_int1=2856.37;//specific enthalpy in kJ/kg at T_int1 obtained from steam tables at P2 taken for interpolation to find V2 and T2 corresponding to P2
h_int2=3065.38;//specific enthalpy in kJ/kg at T_int2 obtained from steam tables at P2 taken for interpolation to find V2 and T2 corresponding to P2
V2=(((h2-h_int1)/(h_int2-h_int1))*(V_int2-V_int1))+V_int1;//specific volume of superheated steam in
```

```
m^3/kg obtained by interpolation (corresponding to T2 and P2)
//Temperature of superheated steam in degree celsius obtained by interpolation (corresponding to T2 and P2)
T2=(((h2-h_int1)/(h_int2-h_int1))*(T_int2-T_int1))+T_int1;
W=(P1*10^3*(V2-V1)*W)*10^-3;//calculation of work done by steam in kJ using Eq.(4.14)

//OUTPUT
mprintf('\n The work done by steam= %0.2f kJ \n',W);
mprintf('\n The final temperature= %0.2f degree celsius\n',T2);

//===========================================================END OF PROGRAM===========================================================
```

---

**Scilab code Exa 4.7** Amount of energy

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 7,Page 104
//Title:Amount of energy
//===========================================================================

clear
clc

//INPUT
```

```
N=1;//number of moles of carbon dioxide in kmol
T1=298;//initial temperature in K
T2=600;//final raised temperature in K
a=45.369;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
b=8.688*10^-3;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
e=-9.619*10^5;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
//Where Cp is in J/molK

//CALCULATION
Q=N*10^3*((a*(T2-T1)+((b/2)*(T2^2-T1^2))-(e*((1/T2)-(1/T1)))))*10^-6;//calculation of the amount of energy to be transferred in MJ using Eq.(4.25)

//OUTPUT
mprintf('\n The amount of energy to be transferred as heat= %0.3f MJ\n',Q);

//===================================================END OF PROGRAM=======================================================
```

---

**Scilab code Exa 4.8** Isobaric molar heat capacity

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 8,Page 104
//Title:Isobaric molar heat capacity
//==========================================================================================
```

```
clear
clc

//INPUT
T1=298;//initial temperature in K
T2=600;//final raised temperature in K
a=45.369;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
b=8.688*10^-3;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
e=-9.619*10^5;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
//Where Cp is in J/molK

//CALCULATION
Cpm=((a*(T2-T1))+((b/2)*(T2^2-T1^2))-(e*((1/T2)-(1/T1))))/(T2-T1);//calculation of isobaric molar heat capacity in J/molK using Eq.(4.26)

//OUTPUT
mprintf('\n The isobaric molar heat capacity= %0.2f J/molK\n',Cpm);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 4.9** Amount of energy transferred using isobaric molar heat capacity

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.
```

```

//Chapter-4,Example 9,Page 105
//Title:Amount of energy transferred using isobaric molar heat capacity
//================================================================================

clear
clc

//INPUT
N=1;//number of moles of carbon dioxide in kmol
T1=298;//initial temperature in K
T2=600;//final raised temperature in K
a=45.369;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
b=8.688*10^-3;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
e=-9.619*10^5;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
//Where Cp is in J/molK

//CALCULATION
Cpm=((a*(T2-T1))+((b/2)*(T2^2-T1^2))-(e*((1/T2)-(1/T1))))/(T2-T1);//calculation of isobaric molar heat capacity in J/molK using Eq.(4.26)
Q=N*10^3*Cpm*(T2-T1)*10^-6;//calculation of the amount of energy to be transferred in MJ using Eq.(4.25)

//OUTPUT
mprintf('\n The amount of energy to be transferred as heat= %0.3f MJ \n',Q);

//==============================================================END OF PROGRAM==============================================================
```

**Scilab code Exa 4.10** Final temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 10,Page 105
//Title:Final temperature
//
clear
clc

//INPUT
N=100;//number of moles of carbon dioxide in mol
T1=298;//initial temperature in K
Q=1;//energy added as heat in MJ
a=45.369;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
b=8.688*10^-3;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
e=-9.619*10^5;//coefficient in the specific heat capacity expression where Cp=a+bT+eT^-2
//Where Cp is in J/molK

//CALCULATION
delh=Q*10^6/N;//calculation of enthalpy in J
Tguess=520;//The final temperature guess value in K used for solving the system of equations
//The system of equations are defined by :
//T2=T1+(delh/Cpm)--->A
//Cpm=a+(b*Tm)+(e/T1T2)--->B
Cpm_guess=a+(b*((T1+Tguess)/2))+(e/(T1*Tguess));//
```

```
calculation of Cpm guess (in J/molK) to be used to determine T2 from Equation A
T2_guess=T1+(delh/Cpm_guess);//calculation of T2 using Equation A (in K) based on the value of Cpm guess computed using Equation B
tolerance=1e-6;//defining the tolerance limit to obtain convergence
while abs(T2_guess-Tguess)>tolerance
    Tguess=T2_guess;
    Cpm_guess=a+(b*((T1+Tguess)/2))+(e/(T1*Tguess));
    T2_guess=T1+(delh/Cpm_guess);//the iteration process to solve the system of equations
end
T2=T2_guess;//value of the final temperature of CO2 obtained upon solving the system of equations(A and B) in K

//OUTPUT
mprintf('\n The final temperature= %0.1f K\n',T2);

//===========================================================END OF PROGRAM===================================================================
```

---

**Scilab code Exa 4.11** Final temperature Pressure and work done in adiabatic process

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 11,Page 107
//Title:Final temperature,Pressure and work done in adiabatic process
```

```
//==============================================================================================
clear
clc

//INPUT
volume_ratio=1/15;//final volume to the initial volume of air at the end of compression stroke (no unit)
gaamma=1.4;//ratio of the molar heat capacities at constant pressure and constant volume for air (no unit)
T1=300;//initial temperature of air in K
P1=0.1;//initial pressure of air in MPa
R=8.314;//universal gas constant in J/molK

//CALCULATION
T2=T1*((1/volume_ratio)^(gaamma-1));//calculation of final temperature in K using Eq.(4.32)
P2=P1*((1/volume_ratio)^(gaamma));//calculation of final pressure in MPa using Eq.(4.34)
W=(R*(T1-T2)*10^-3)/(gaamma-1);//calculation of work to be done on the system in kJ/mol using Eq.(4.31)

//OUTPUT
mprintf('\n The final temperature= %0.2f K\n',T2);
mprintf('\n The final pressure= %0.4f MPa\n',P2);
mprintf('\n Work done per mole of air= %0.3f kJ/mol\n',W);

//===========================================================END OF PROGRAM=====================
```

**Scilab code Exa 4.12** Final temperature Pressure work done and heat interaction in polytropic process

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 12,Page 110
//Title:Final temperature Pressure work done and heat interaction in polytropic process
//================================================================================

clear
clc

//INPUT
volume_ratio=1/15;//final volume to the initial volume of ideal gas at the end of compression (no unit)
T1=300;//initial temperature of ideal gas in K
P1=0.1;//initial pressure of ideal gas in MPa
R=8.314;//universal gas constant in J/molK
n=1.2;//index of expansion (no unit)
gaamma=1.4;//ratio of the molar heat capacities at constant pressure and constant volume for ideal gas (no unit)

//CALCULATION
P2=P1*((1/volume_ratio)^n);//calculation of final pressure in MPa using Eq.(4.37)
T2=T1*(P2/P1)*(volume_ratio);//calculation of final temperature in K (since the gas is taken to be ideal, (P1*V1)/T1=(P2*V2)/T2))
```

```
W=(R*(T1-T2)*10^-3)/(n-1);//calculation of work to be done on the system in kJ/mol using Eq.(4.38)
del_u=(R*(T2-T1)*10^-3)/(gaamma-1);//calculation of the change in the internal energy in kJ/mol using Eq.(4.28 and 4.29) (del_u=Cv*(T2-T1) and Cv=R/(gaamma-1))
q=del_u+W;//calculation of the heat interaction during the process in kJ/mol using the first law of thermodynamics

//OUTPUT
mprintf('\n The final pressure= %0.3f MPa\n',P2);
mprintf('\n The final temperature= %0.1f K\n',T2);
mprintf('\n Work done on the gas= %f kJ/mol\n',W);
mprintf('\n Heat interaction during the process= %f kJ/mol\n',q);

//========================================================END OF PROGRAM===============================================================
```

---

**Scilab code Exa 4.13** Final temperature and amount of gas entering the tank

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 13,Page 112
//Title:Final temperature and amount of gas entering the tank
//================================================================================================
```

```
clear
clc

//INPUT
V=1;//volume of tank in m^3
T0=300;//initial temperature of ideal gas in K
P0=0.1;//initial pressure of ideal gas in MPa
T=500;//temperature of ideal gas in the pipeline in K
P=3;//pressure of ideal gas in the pipeline in MPa
R=8.314;//universal gas constant in J/molK
gaamma=1.4;//ratio of the molar heat capacities at constant pressure and constant volume for ideal gas (no unit)

//CALCULATION
Pf=3;//final pressure reached in the tank in MPa
//calculation of final temperature of the gas in the tank in K using Eq.(4.44) (and applying u=Cv*T, h=Cp*T and N=P*V/R*T as the gas is taken to be ideal)
Tf=(Pf*10^6)/((((Pf*10^6)-(P0*10^6))/(gaamma*T))+((P0*10^6)/T0));
//calculation of the moles of ideal gas entering into the tank using Eq.(4.44) (and applying u=Cv*T, h=Cp*T and N=P*V/R*T as the gas is taken to be ideal)
N=(V/R)*(((Pf*10^6)/Tf)-((P0*10^6)/T0));

//OUTPUT
mprintf('\n The final temperature= %0.1f K\n',Tf);
mprintf('\n The amount of gas that has entered the tank= %0.2f mol\n',N);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 4.14** Final state and mass of steam that entered the tank

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 14,Page 113
//Title:Final state and mass of steam that entered the tank
//================================================================================

clear
clc

//INPUT
V=3;//volume of tank in m^3
T0=100;//initial temperature of steam in degree celsius
T=300;//temperature of superheated steam in the pipeline in degree celsius
P=3;//pressure of superheated steam in the pipeline in MPa
R=8.314;//universal gas constant in J/molK

//CALCULATION
Ps=101.33;//pressure of saturated steam in kPa from steam tables corresponding to T0
vg=1.673;//specific volume of saturated vapour in m^3/kg obtained from steam tables corresponding to T0
hg=2676.0;//specific enthalpy of saturated vapour in kJ/kg obtained from steam tables corresponding to T0
```

```
h=2995.1;//specific enthalpy of superheated steam in kJ/kg obtained from superheated steam tables corresponding to T and P
u0=((hg*10^3)-(Ps*10^3*vg))*10^-3;//calculation of initial internal energy of steam in kJ/mol using the first law of thermodynamics for the adiabatic charging of a tank
m0=V/vg;//calculation of mass of steam initially in the tank in kg
//The first law of thermodynamics for the adiabatic charging of a tank is given by:
//mfuf-m0u0=(mf-m0)h. This equation is to be solved to determine mf

Tf=418;// assuming final temperature of superheated steam in degree celsius
//For superheated steam at P and Tf
vf=0.102329;//specific volume of superheated steam in m^3/kg
uf=2965.78;//internal energy of the superheated steam in kJ/kg

mf_guess=V/vf;//taking a guess value for the mass of steam inside the tank at the end of the charging operation,in kg

function[fn]=solver_func(ui)
//Function defined for solving the system to determine the internal energy of steam inside the tank at the end of the charging operation in kJ/kg using Eq.(4.44, where Q=0 as the process is adiabatic)
    fn=(mf_guess*ui)-(m0*u0)-((mf_guess-m0)*h);
endfunction
[uf_solved]=fsolve(mf_guess,solver_func,1e-6)//using inbuilt function fsolve for solving the system of equations
mf=mf_guess//mass of the steam inside the tank at
```

```
the end of the charging operation , in kg
mass=mf-m0;//calculation of mass of steam that entered the tank in kg

//OUTPUT
mprintf("\n The final state of steam(superheated), Pressure=%d MPa\n",P);
mprintf("\n The final state of steam(superheated), Temperature=%d degree celsius\n",Tf);
mprintf("\n The mass of steam that entered the tank=%0.3f kg\n",mass);

//===========================================================END OF PROGRAM==================================================================
```

---

**Scilab code Exa 4.15** Final temperature and amount of gas escaping the cylinder

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 15,Page 115
//Title:Final temperature and amount of gas escaping the cylinder
//================================================================================================================

clear
clc

//INPUT
V=0.1;//volume of cylinder in m^3
```

```
T0=300;//initial temperature of nitrogen in K
P0=14;//initial pressure of nitrogen in MPa
P=0.1;//ambient pressure in MPa
Pf=2;//final pressure of nitrogen in MPa
R=8.314;//universal gas constant in J/molK
gaamma=1.4;//ratio of the molar heat capacities at constant pressure and constant volume for nitrogen (no unit)

//CALCULATION
//calculation of final temperature of the gas in the tank in K using Eq.(4.51) (and applying u=Cv*T, h=Cp*T and N=P*V/R*T as the gas is taken to be ideal)
function[fn]=solver_func(Ti)
    //Function defined for solving the system to determine the final temperature
    fn=((P0*10^6)-(Pf*10^6))-((gaamma/2)*(T0+Ti)*(((P0*10^6)/T0)-((Pf*10^6)/Ti)));
endfunction
Tguess=300;//The final temperature guess value in K used for solving the system of equations
[Tf]=fsolve(Tguess,solver_func,1e-6)//using inbuilt function fsolve for solving the system of equations

//calculation of the moles of nitrogen escaping from the tank using Eq.(4.51) (and applying u=Cv*T, h=Cp*T and N=P*V/R*T as the gas is taken to be ideal)
N=(V/R)*(((P0*10^6)/T0)-((Pf*10^6)/Tf));

//OUTPUT
mprintf('\n The final temperature= %0.1f K\n',Tf);
mprintf('\n The amount of gas that has escaped from the cylinder= %0.2f mol\n',N);

//=========================================================================END
```

```
OF PROGRAM
```

**Scilab code Exa 4.16** Percentage error

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 16,Page 118
//Title:Percentage error
//

clear
clc

//INPUT
T0=300;//initial temperature of superheated steam in degree celsius
P0=3;//initial pressure of superheated steam in MPa
Xe=0.85;//quality of steam leaving the turbine (no unit)
Tf=45;//final temperature of steam leaving the turbine in degree celsius
Vi=10;//velocity of steam at the entrance in m/s
Ve=40;//exit velocity of steam in m/s
Zi=10;//elevation at the entrance in m
Ze=4;//elevation at the exit in m
m=1;//mass flow rate of steam through turbine in kg/s
g=9.81;//accleration due to gravity in m/s^2

//CALCULATION
```

```
hi=2995.1;//specific enthalpy of superheated steam in kJ/kg obtained from superheated steam tables corresponding to T0 and P0
hf=188.35;//specific enthalpy of saturated liquid in kJ/kg obtained from steam tables corresponding to Tf
hg=2583.3;//specific enthalpy of saturated vapour in kJ/kg obtained from steam tables corresponding to Tf
he=((1-Xe)*hf)+(Xe*hg);//calculation of specific enthalpy of steam at the exit in kJ/kg using Eq.(3.6)
Q=0;//adiabatic process
enthalpy_change=(he*10^3)-(hi*10^3);//calculation of the enthalpy change between the entrance and exit in J/kg
KE_change=((Ve^2)-(Vi^2))/2;//calculation of the kinetic energy change between the entrance and exit in J/kg
PE_change=g*(Ze-Zi);//calculation of the potential energy change between the entrance and exit in J/kg
Ws=Q-(m*(enthalpy_change+KE_change+PE_change)*10^-3);//calculation of power output in kW using Eq.(4.61)
err_KE=((KE_change)/(Ws*10^3))*100;//calculation of percentage error when kinetic energy change is ignored
err_PE=((abs(PE_change)/(Ws*10^3)))*100;//calculation of percentage error when potential energy change is ignored
err=err_KE+err_PE;//calculation of percentage error when both potential kinetic energy changes are ignored

//OUTPUT
mprintf('\n The percentage error when Kinetic energy change is ignored= %0.3f \n',err_KE);
```

```
mprintf('\n The percentage error when Potential
    energy change is ignored= %0.4f \n',err_PE);
mprintf('\n The percentage error when both Kinetic
    and Potential energy changes are ignored= %f \n',
    err);

//==========================================================END
    OF PROGRAM
    ===========================================================
```

---

**Scilab code Exa 4.17** Exit velocity

```
// Y.V.C.Rao ,1997.Chemical Engineering
    Thermodynamics.Universities Press,Hyderabad,India
    .

//Chapter-4,Example 17,Page 119
//Title:Exit velocity
//
    ===========================================================

clear
clc

//INPUT
Pi=5;//pressure of dry saturated steam at the
    entrance in bar
Pe=2;//pressure of dry saturated steam at the exit
    in bar
Vi=3;//velocity of dry saturated steam at the
    entrance in m/s
m=1;//flow rate of steam through the nozzle in kg/s
g=9.81;//acceleration due to gravity in m/s^2

```

```
//CALCULATION
hi=2747.5;//specific enthalpy in kJ/kg of the dry saturated steam at the entrance taken from steam tables corresponding to Pi
he=2706.3;//specific enthalpy in kJ/kg of the dry saturated steam at the exit taken from steam tables corresponding to Pe
ve=0.8854;//specific volume in m^3/kg of the dry saturated steam at the exit taken from steam tables corresponding to Pe
Zi=0;//assuming that the nozzle is horizontal
Ze=0;//assuming that the nozzle is horizontal
Q=0;//adiabatic process
Ws=0;//since no shaft work is done
Ve=sqrt (2*(((Q-Ws)/m)-(g*(Zi-Ze))-((he*10^3)-(hi*10^3)))+(Vi^2));//calculation of velocity at the exit in m/s using Eq.(4.61)
A=(m*ve)/Ve;//calculation of cross sectional area of the nozzle at the exit in m^2

//OUTPUT
mprintf('\n The velocity of dry saturated steam at the exit= %0.2f m/s\n',Ve);
mprintf('\n The cross sectional area of the nozzle at the exit= %0.3e m^2\n',A);

//==============================================END OF PROGRAM ==========================================================
```

---

**Scilab code Exa 4.18** Quality of wet steam

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India
```

```
.

//Chapter-4,Example 18,Page 123
//Title:Quality of wet steam
//==============================================================================

clear
clc

//INPUT
T1=270;//temperature of wet steam in degree celsius
T2=120;//final temperature of superheated steam in degree celsius
P=0.1;//pressure of superheated steam in MPa

//CALCULATION
hf=1185.2;//specific enthaply of saturated liquid in kJ/kg obtained from steam tables corresponding to T1
hg=2789.9;//specific enthalpy of saturated vapour in kJ/kg obtained from stean tables corresponding to T1
he=2716.04;//specific enthalpy of superheated steam in kJ/kg obtained from superheated steam tables corresponding to T2 obtained by interpolation
Xi=(he-hf)/(hg-hf);//calculation of quality of steam using Eq.(3.6) (no unit)

//OUTPUT
mprintf('\n The quality of wet steam= %0.3f \n',Xi);

//===================================END OF PROGRAM==============================
```

**Scilab code Exa 4.20** Standard enthalpy change

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 20,Page 128
//Title:Standard enthalpy change
//================================================================================

clear
clc

//INPUT
del_H=-90.135;//standard enthalpy change for the reaction CO(g)+2H2(g)--->CH3OH(g) at 298.15K in kJ

//CALCULATION
del_H1=2*del_H;//calculation of standard enthalpy change for the reaction 2CO(g)+4H2(g)--->2CH3OH(g) at 298.15K in kJ
del_H2=(1/2)*del_H;//calculation of standard enthalpy change for the reaction (1/2)CO(g)+H2(g)--->(1/2)CH3OH(g) at 298.15K in kJ

//OUTPUT
mprintf('\n The standard enthalpy change for the reaction 2CO(g)+4H2(g)---->2CH3OH(g) at 298.15K= %0.2f kJ\n',del_H1);
mprintf('\n The standard enthalpy change for the reaction (1/2)CO(g)+H2(g)---->(1/2)CH3OH(g) at 298.15K= %0.4f kJ\n',del_H2 );
```

```

//===================================================END OF PROGRAM=======================================================
```

---

**Scilab code Exa 4.22** Standard enthalpy change for the reaction from standard enthalpies of formation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 22,Page 130
//Title:Standard enthalpy change for the reaction from standard enthalpies of formation
//==========================================================================================================================

clear
clc

//INPUT
del_Hf_C4H10=-74.943;//standard enthalpy of formation of C4H10(g) at 298.15K in kJ
del_Hf_CO2=-393.978;//standard enthalpy of formation of CO2(g) at 298.15K in kJ
del_Hf_H2O=-241.997;//standard enthalpy of formation of H2O(g) at 298.15K in kJ

//CALCULATION

//calculation of the standard enthalpy change for the reaction C4H10(g)+(13/2)O2(g)--->4CO2(g)+5H2O(g) at 298.15K in kJ
```

```
// by using the standard enthalpy of formation data where the formation reactions are:
// 4C(s)+5H2(g)--->C4H10(g)--->A
//C(s)+O2(g)--->CO2(g)---->B
//H2(g)+(1/2)O2(g)--->H2O(g)---->C
//del_Hr=5(C)+4(B)-(A)

del_Hr=(5*del_Hf_H2O)+(4*del_Hf_CO2)-(del_Hf_C4H10);

//OUTPUT
mprintf('\n The standard enthalpy change for the reaction C4H10(g)+(13/2)O2(g)---->4CO2(g)+5H2O(g) at 298.15K= %0.3f kJ\n',del_Hr);

//===================================================END OF PROGRAM=========================================================
```

**Scilab code Exa 4.23** Standard enthalpy change for the reaction from standard enthalpies of formation 2

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 23,Page 131
//Title:Standard enthalpy change for the reaction from standard enthalpies of formation (2)
//==========================================================================================

clear
clc

```

```
//INPUT
del_Hf_C4H10=-74.943;//standard enthalpy of formation of C4H10(g) at 298.15K in kJ
del_Hf_CO2=-393.978;//standard enthalpy of formation of CO2(g) at 298.15K in kJ
del_Hf_H2O=-241.997;//standard enthalpy of formation of H2O(g) at 298.15K in kJ
del_H_vap=43.966;//enthalpy of vaporization of H2O at 298.15K in kJ/mol

//CALCULATION

//calculation of the standard enthalpy change for the reaction C4H10(g)+(13/2)O2(g)--->4CO2(g)+5H2O(l)--->A at 298.15K in kJ
//The above reaction A can be expressed as a sum of the following two reactions:
//C4H10(g)+(13/2)O2(g)--->4CO2(g)+5H2O(g) --->B
//5H2O(g)--->5H2O(l)--->C
//Reaction C represents the physical change H2O((g);25 degree celsius,1 bar)--->H2O((l);25 degree celsius,1 bar), which can be expressed as:
//a-->H2O((g);25 degree celsius,1 bar)--->H2O((g);25 degree celsius,Ps)---->del_H1
//b-->H2O((g);25 degree celsius,Ps)--->H2O((l);25 degree celsius,Ps)--->del_H2
//c-->H2O((l);25 degree celsius,Ps)--->H2O((l);25 degree celsius,1 bar)--->del_H3, where Ps is the saturation pressure at 25 degree celsius
//The overall enthalpy change therefore is given as del_H0=del_H1+del_H2+del_H3

del_H1=0;//vapour phase at low pressures behaves like an ideal gas therefore the enthalpy change is zero
del_H2=5*(-del_H_vap);//calculation of the enthalpy of reaction b in kJ
del_H3=0;//effect of pressure on the enthalpy of
```

```
liquids is negligible

//calculation of the standard enthalpy change for the reaction C4H10(g)+(13/2)O2(g)--->4CO2(g)+5H2O(g) at 298.15K in kJ, from Example (4.22)
//by using the standard enthalpy of formation data where the formation reactions are:
//4C(s)+5H2(g)--->C4H10(g)
//C(s)+O2(g)--->CO2(g)
//H2(g)+(1/2)O2(g)--->H2O(g)
del_H=(5*del_Hf_H2O)+(4*del_Hf_CO2)-(del_Hf_C4H10);
del_net_H=(del_H)+(del_H1)+(del_H2)+(del_H3);//calculation of the standard enthalpy change for the reaction C4H10(g)+(13/2)O2(g)-->4CO2(g)+5H2O(l) at298.15K in kJ

//OUTPUT
mprintf('\n The standard enthalpy change for the reaction C4H10(g)+(13/2)O2(g)---->4CO2(g)+5H2O(l) at 298.15K= %0.3f kJ\n',del_net_H);

//==============================================================END OF PROGRAM==============================================================
```

---

**Scilab code Exa 4.24** Standard enthalpy change of formation of n butane gas

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 24,Page 132
//Title:Standard enthalpy change of formation of n-
```

```
butane gas
//==================================================================

clear
clc

//INPUT
del_H_comb=2880.44;//gross heating value of n-buatne gas at 298.15K in kJ/mol
del_Hf_CO2=-393.978;//standard enthalpy of formation of CO2(g) at 298.15K in kJ
del_Hf_H2O=-285.958;//standard enthalpy of formation of H2O(l) at 298.15K in kJ
del_Hf_O2=0;//standard enthalpy of formation of O2(g) at 298.15K in kJ
//CALCULATION

//The combustion reaction is given by:
//C4H10(g)+(13/2)O2(g)--->4CO2(g)+5H2O(l)
//del_H_comb=(4*del_Hf_CO2)+(5*del_Hf_H2O)-(del_Hf_C4H10), from which del_Hf_C4H10 is computed
n_CO2=4;//stoichiometric coefficient (no unit)
n_H2O=5;//stoichiometric coefficient (no unit)
n_O2=-13/2;//stoichiometric coefficient (no unit)
n_C4H10=-1;//stoichiometric coefficient (no unit)
//computation of the standard enthaply of formation of n-butane gas at 298.15K in kJ
del_Hf_C4H10=(n_CO2*del_Hf_CO2)+(n_H2O*del_Hf_H2O)+(n_O2*del_Hf_O2)-(-del_H_comb);


//OUTPUT
mprintf('\n The standard enthalpy of formation of n-butane gas at 298.15K= %0.3f kJ\n',del_Hf_C4H10);

//=========================================================END
```

```
OF PROGRAM
=====================================================
```

**Scilab code Exa 4.25** Standard enthalpy change

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 25,Page 133
//Title:Standard enthalpy change
//=====================================================

clear
clc

//INPUT

//The reaction is: CH4(g)+H2O(g)--->CO(g)+3H2(g)
//The standard enthalpy change for the above reaction is determined by using the individual combustion reactions
//The combustion reactions are:
//A--->CH4(g)+2O2(g)--->CO2(g)+2H2O(l)--->del_Hc_A
//B--->CO(g)+(1/2)O2(g)--->CO2(g)--->del_Hc_B
//C--->H2(g)+(1/2)O2(g)--->H2O(l)--->del_Hc_C
//D--->H2O(g)--->H2O(l)--->del_H_vap

del_Hc_A=-890.94;//enthalpy change accompanying reaction A in kJ
del_Hc_B=-283.18;//enthalpy change accompanying reaction B in kJ
del_Hc_C=-286.03;//enthalpy change accompanying
```

```
reaction C in kJ
del_H_vap=-43.966;//enthalpy change of vaporization of H2O at 298.15K in kJ/mol

//CALCULATION
del_H0=(del_Hc_A)-(del_Hc_B)-(3*del_Hc_C)+(del_H_vap);//calculation of the standard enthalpy change of the reaction in kJ

//OUTPUT
mprintf('\n The standard enthalpy change at 298.15K for the reaction CH4(g)+H2O(g)--->CO(g)+3H2(g)=%0.3f kJ\n',del_H0);

//================================================END OF PROGRAM=====================================================
```

---

**Scilab code Exa 4.26** Standard enthalpy change at 400K

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 26,Page 135
//Title:Standard enthalpy change at 400K
//==================================================================================================

clear
clc

//INPUT

```

```
//The reaction is : C2H4(g)+H2O(g)--->C2H5OH(g)

del_H_vap=43.82;//enthalpy of vaporization of ethanol at 298.15K in kJ/mol

//Data taken from Appendix tables A.3 and A.4 have been given below:

del_Hf=[52.335;-241.997;0;-277.819];//standard enthalpies of formation of C2H4(g),H2O(g),C2H5OH(g),C2H5OH(l) at 298.15K in kJ
a=[4.196;28.850;20.691;0]//coefficients to compute isobaric molar heat capacity of C2H4(g),H2O(g),C2H5OH(g),C2H5OH(l) in J/molK
b=[154.565*10^-3;12.055*10^-3;205.346*10^-3;0]//coefficients to compute isobaric molar heat capacity of C2H4(g),H2O(g),C2H5OH(g),C2H5OH(l) in J/molK
c=[-81.076*10^-6;0;-99.793*10^-6;0]//coefficients to compute isobaric molar heat capacity of C2H4(g),H2O(g),C2H5OH(g),C2H5OH(l) in J/molK
d=[16.813*10^-9;0;18.825*10^-9;0]//coefficients to compute isobaric molar heat capacity of C2H4(g),H2O(g),C2H5OH(g),C2H5OH(l) in J/molK
e=[0;1.006*10^5;0;0];//coefficients to compute isobaric molar heat capacity of C2H4(g),H2O(g),C2H5OH(g),C2H5OH(l) in J/molK
//where Cp0=a+bT+cT^2+dT^3+eT^-2

T1=298.15;//Ambient temeprature in K
T2=400;//temperature at which the standard enthalpy change has to be determined in K
n_C2H4=-1;//stoichiometric coefficient (no unit)
n_H2O=-1;//stoichiometric coefficient (no unit)
n_C2H5OH=1;//stoichiometric coefficient (no unit)

//CALCULATION

```

```
//The standard enthalpy of formation of C2H5OH(g) can be obtained from the following reactions:
//2C(s)+3H2(g)+(1/2)O2(g)--->C2H5OH(l)
//C2H5OH(l)--->C2H5OH(g)

del_Hf_C2H5OH_g=del_Hf(4,:)+del_H_vap;//calculation of standard enthalpy of formation of C2H5OH(g) at 298.15K in kJ
del_Hr=(n_C2H5OH*del_Hf_C2H5OH_g)+(n_C2H4*del_Hf(1,:))+(n_H2O*del_Hf(2,:));//calculation of standard enthalpy change of reaction in kJ
del_a=(n_C2H4*a(1,:))+(n_H2O*a(2,:))+(n_C2H5OH*a(3,:));//calculation of del_a using Eq.(4.83)
del_b=(n_C2H4*b(1,:))+(n_H2O*b(2,:))+(n_C2H5OH*b(3,:));//calculation of del_b using Eq.(4.83)
del_c=(n_C2H4*c(1,:))+(n_H2O*c(2,:))+(n_C2H5OH*c(3,:));//calculation of del_c using Eq.(4.83)
del_d=(n_C2H4*d(1,:))+(n_H2O*d(2,:))+(n_C2H5OH*d(3,:));//calculation of del_d using Eq.(4.83)
del_e=(n_C2H4*e(1,:))+(n_H2O*e(2,:))+(n_C2H5OH*e(3,:));//calculation of del_e using Eq.(4.83)
del_H0=(del_Hr*10^3)-((del_a*T1)+((del_b/2)*T1^2)+((del_c/3)*T1^3)+((del_d/4)*T1^4)-(del_e/T1));//calculation del_H0 in kJ using Eq.(4.82)
//calculation of the standard enthalpy of reaction at 400K in kJ
del_Hr_T2=(del_H0+((del_a*T2)+((del_b/2)*T2^2)+((del_c/3)*T2^3)+((del_d/4)*T2^4)-(del_e/T2)))*10^-3;

//OUTPUT
mprintf('\n The standard enthalpy change at 400K for the reaction C2H4(g)+H2O(g)--->C2H5OH(g)= %f kJ\n',del_Hr_T2);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 4.28** Flame temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 28,Page 137
//Title:Flame temperature
//

clear
clc

//INPUT

//The combustion reaction of methane is given by:
// CH4(g)+2O2(g)--->CO2(g)+2H2O(g)

n_O2=2;// stoichiometric amount of oxygen required for combustion
n_CH4=1;//number of moles of CH4(g) in moles
n_CO2=1;//number of moles of CO2(g) formed in the combustion reaction in moles
n_H2O=2;//number of moles of H2O(g) formed in the combustion reaction in moles
del_Hf=[-74.943;0;-393.978;-241.997];// standard enthalpies of formation of CH4(g),O2(g),CO2(g),H2O(g) at 298.15K in kJ
a=[45.369;28.850;30.255;27.270];//coefficients to compute isobaric molar heat capacity of CO2(g),H2O(g),O2(g),N2(g) in J/molK
b
```

```
=[8.688*10^-3;12.055*10^-3;4.207*10^-3;4.930*10^-3];//coefficients to compute isobaric molar heat capacity of CO2(g),H2O(g),O2(g),N2(g) in J/molK
c=[0;0;0;0];//coefficients to compute isobaric molar heat capacity of CO2(g),H2O(g),O2(g),N2(g) in J/molK
d=[0;0;0;0];//coefficients to compute isobaric molar heat capacity of CO2(g),H2O(g),O2(g),N2(g) in J/molK
e=[-9.619*10^5;1.006*10^5;-1.887*10^5;0.333*10^5];//coefficients to compute isobaric molar heat capacity of CO2(g),H2O(g),O2(g),N2(g) in J/molK
per_excess_air=50; //percentage excess of air supplied to the adiabatic burner
T_amb=298.15;// temperature at which air and methane enter the burner in K
per_N2=79;//percentage of N2 in the air supplied
per_O2=21;//percentage of O2 in the air supplied

//CALCULATION
n_O2_actual=(1+(per_excess_air/100))*n_O2;//calculation of the number of moles of oxygen actually present in the system in moles
n_N2=n_O2_actual*(per_N2/per_O2);//calculation of the number of moles of nitrogen actually present in the system in moles
n_O2_residual=n_O2_actual-n_O2;//calculation of excess oxygen leaving as product in moles
// The actual combustion reaction can be written as:
// CH4(g)+3O2(g)+11.286N2(g)--->CO2(g)+2H2O(g)+O2(g)+11.286N2(g)


del_Hr=(n_CO2*del_Hf(3,:))+(n_H2O*del_Hf(4,:))-(n_O2*del_Hf(2,:))-(n_CH4*del_Hf(1,:));//standard enthalpy of reaction at 298.15K in kJ

//-delH_r=del_Hp
```

```
//deriving an expression for del_Hp:

del_a=(n_CO2*a(1,:))+(n_H2O*a(2,:))+(n_O2_residual*a(3,:))+(n_N2*a(4,:));//calculation of del_a using Eq.(4.83)
del_b=(n_CO2*b(1,:))+(n_H2O*b(2,:))+(n_O2_residual*b(3,:))+(n_N2*b(4,:));//calculation of del_b using Eq.(4.83)
del_c=(n_CO2*c(1,:))+(n_H2O*c(2,:))+(n_O2_residual*c(3,:))+(n_N2*c(4,:));//calculation of del_c using Eq.(4.83)
del_d=(n_CO2*d(1,:))+(n_H2O*d(2,:))+(n_O2_residual*d(3,:))+(n_N2*d(4,:));//calculation of del_d using Eq.(4.83)
del_e=(n_CO2*e(1,:))+(n_H2O*e(2,:))+(n_O2_residual*e(3,:))+(n_N2*e(4,:));//calculation of del_a using Eq.(4.83)
tguess=500;//giving a guess value of temperature in K for using the inbuilt solver, fsolve to solve the system of equations below
function[fn]=solver_func(ti)
    //Function defined for solving the system
fn=(-(del_Hr*10^3))-((del_a*(ti-T_amb))+((del_b/2)*((ti^2)-(T_amb^2)))+((del_c/3)*((ti^3)-(T_amb^3)))+((del_d/4)*((ti^4)-(T_amb^4)))+(del_e*((1/T_amb)-(1/ti))));
endfunction
[T]=fsolve(tguess,solver_func,1e-6)//using inbuilt function fsolve for solving the system of equations to get the flame temperaure in K

 //OUTPUT
mprintf('\n The flame temperature when methane is burned with 50 percent excess air in an adiabatic burner= %f K\n',T);

//====================================================END OF PROGRAM
```

**Scilab code Exa 4.29** Amount of energy transferred as heat in the boiler

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-4,Example 29,Page 139
//Title: Amount of energy transferred as heat in the boiler
//

clear
clc

//INPUT
T_exit=550;//temperature in K at which the combustion products leave the boiler
percent_molar_comp_prdct=[6.28;3.14;7.85;82.73];//percentage molar composition of the combustion products CO2(g),CO(g),O2(g),N2(g) on dry basis
T_ent=298.15;//temperature in K at which Propane and air enter the combustion chamber
del_Hf=[-393.978;-110.532;-241.997;0;0;-103.833];//standard enthalpies of formation of CO2(g),CO(g),H2O(g),O2(g),N2(g),C3H8(g) at 298.15K in kJ
a=[45.369;28.068;30.255;27.270;28.850];//coefficients to compute isobaric molar heat capacity of CO2(g),CO(g),O2(g),N2(g),H2O(g) in J/molK
//coefficients to compute isobaric molar heat capacity of CO2(g),CO(g),O2(g),N2(g),H2O(g) in J/
```

```
molK
b=[8.688*10^-3;4.631*10^-3;4.207*10^-3;4.930*10^-3;12.055*10^-3];

c=[0;0;0;0;0];//coefficients to compute isobaric molar heat capacity of CO2(g),CO(g),O2(g),N2(g),H2O(g) in J/molK
d=[0;0;0;0;0];//coefficients to compute isobaric molar heat capacity of CO2(g),CO(g),O2(g),N2(g),H2O(g) in J/molK
e=[-9.619*10^5;-0.258*10^5;-1.887*10^5;0.333*10^5;1.006*10^5];//coefficients to compute isobaric molar heat capacity of CO2(g),CO(g),O2(g),N2(g),H2O(g) in J/molK
per_N2=79;//percentage of nitrogen in air
per_O2=21;//percentage of oxygen in air
molar_mass_propane=44*10^-3;//molar mass of propane in kg/mole

//CALCULATION
// TAKE BASIS AS 100 mol OF  DRY COMBUSTION PRODUCTS
n_CO2=percent_molar_comp_prdct(1,:);//number of moles of CO2(g) in the product stream
n_CO=percent_molar_comp_prdct(2,:);//number of moles of CO(g) in the product stream
n_O2=percent_molar_comp_prdct(3,:);//number of moles of O2(g) in the product stream
n_N2=percent_molar_comp_prdct(4,:);//number of moles of N2(g) in the product stream

//The combustion reaction can be given as:
// x C3H8+ y O2+ (79/21)y N2--->6.28CO2+3.14CO+7.85O2+82.73N2+ zH2O

//Determination of x, y, z

//carbon atom balance:
```

```
x=(n_CO2+n_CO)/3;

//Nitrogen atom balance:
y=(2*n_N2)/(2*(per_N2/per_O2));

//oxygen atom balance
z=(2*y)-(2*n_CO2)-(n_CO)-(2*n_O2);

//The actual combustion reaction becomes:
//3.14C3H8+ 21.992O2+ 82.73N2--->6.28CO2+3.14CO+7.85O2+82.73N2+ 12.584H2O

n_H2O=z;//number of moles of H2O determined after the balance done on the carbon,oxygen,and nitrogen atoms
n_C3H8=x;//number of moles of C3H8 determined after the balance done on the carbon,oxygen,and nitrogen atoms

//calculation of the standard enthalpy of the reaction at 298.15K in kJ
//del_hf=0, for oxygen and nitrogen,therefore they are omitted in the expression
del_Hr=(n_CO2*del_Hf(1,:))+(n_CO*del_Hf(2,:))+(n_H2O*del_Hf(3,:))-(n_C3H8*del_Hf(6,:));

del_a=(n_CO2*a(1,:))+(n_CO*a(2,:))+(n_O2*a(3,:))+(n_N2*a(4,:))+(n_H2O*a(5,:));//calculation of del_a using Eq.(4.83)
del_b=(n_CO2*b(1,:))+(n_CO*b(2,:))+(n_O2*b(3,:))+(n_N2*b(4,:))+(n_H2O*b(5,:));//calculation of del_b using Eq.(4.83)
del_c=(n_CO2*c(1,:))+(n_CO*c(2,:))+(n_O2*c(3,:))+(n_N2*c(4,:))+(n_H2O*c(5,:));//calculation of del_c using Eq.(4.83)
del_d=(n_CO2*d(1,:))+(n_CO*d(2,:))+(n_O2*d(3,:))+(n_N2*d(4,:))+(n_H2O*d(5,:));//calculation of del_d using Eq.(4.83)
```

```
del_e=(n_CO2*e(1,:))+(n_CO*e(2,:))+(n_O2*e(3,:))+(n_N2*e(4,:))+(n_H2O*e(5,:));//calculation of del_e using Eq.(4.83)

//calulation of del_Hp J
        del_Hp=(del_a*(T_exit-T_ent))+((del_b/2)*((T_exit^2)-(T_ent^2)))+((del_c/3)*((T_exit^3)-(T_ent^3)))+((del_d/4)*((T_exit^4)-(T_ent^4)))-(del_e*((1/T_exit)-(1/T_ent)));
        del_H=((del_Hr*10^3)+(del_Hp))*10^-3;//calculation of total energy transferred as heat in kJ
        mass_propane=n_C3H8*molar_mass_propane;//calculation of amount of propane in the system in kg
        energy=(-(del_H*10^3)/mass_propane)*10^-6;//energy transferred as heat per kg propane in MJ

//OUTPUT
mprintf('\n The energy transferred as heat per kg propane= %f MJ\n',energy);

//=================================================END OF PROGRAM=================================================
```

# Chapter 5

# Second law of thermodynamics and its applications

**Scilab code Exa 5.2** Inventor and the heat engine

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 2,Page 161
//Title: Inventor and the heat engine
//

clear
clc

//INPUT
Q=1000;//amount of energy absorbed by the heat engine in kJ/s
W=650;//work delivered by the heat engine in kW
T_source=500;//temperature of the source in degree celsius
T_sink=25;//temperature of the sink in degree
```

```
celsius

//CALCULATION
n_claimed=W/Q;//calculation of the efficiency of the heat engine invented by the inventor (no unit)
T1=T_source+273.15;//conversion of source temperature in K
T2=T_sink+273.15;//conversion of sink temperature in K
n_carnot=1-(T2/T1);//calculation of the efficiency of a carnot engine from Eg.(5.1) (no unit)

//OUTPUT
mprintf("\n The efficiency of the Carnot engine=%0.3f \n",n_carnot);
mprintf("\n The efficiency of the engine claimed by the inventor=%0.2f \n",n_claimed);
if n_claimed<n_carnot then
    mprintf("\n The claimed heat engine is theoretically feasible as the efficiency of the engine is lesser than that of a Carnot engine\n");
else
    mprintf("\n The claimed heat engine is not theoretically feasible as the efficiency of the engine is greater than that of a Carnot engine\n");
end

//==========================================================END OF PROGRAM==========================================================
```

**Scilab code Exa 5.3** Minimum power required

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 3,Page 165
//Title: Minimum power required
//
clear
clc

//INPUT
T_source_summer=42;//temperature in the summer months in degree celsius
T_sink_winter=0;//temperature in the winter months in degree celius
T_amb=25;//temperature at which the house is to be maintained during both the months in degree celsius
//rate of energy loss from the windows,walls and roof, in kW per degree celsius difference between the ambient temperature and the conditions inside the room
energy_loss=0.5;

//CALCULATION
T_H_summer=T_source_summer+273.15;//conversion of temperature in K
T_L_summer=T_amb+273.15;//conversion of temperature in K
T_H_winter=T_amb+273.15;//conversion of temperature in K
T_L_winter=T_sink_winter+273.15;//conversion of temperature in K
W_summer=(energy_loss*((T_H_summer-T_L_summer)^2))/(T_L_summer);//calculation of the minimum power required to operate the device in summer using Eq
```

```
.(5.20) in kW
W_winter=(energy_loss*((T_H_winter-T_L_winter)^2))/(T_H_winter);//calculation of the minimum power required to operate the device in winter using Eq.(5.21) in kW

//OUTPUT
mprintf("\n The minimum power required to operate the device in summer=%f kW \n",W_summer);
mprintf("\n The minimum power required to operate the device in winter=%f kW \n",W_winter);

//================================================END OF PROGRAM=====================================================

//DISCLAIMER: THE ANSWER GIVEN FOR THE MINIMUM POWER REQUIRED TO OPERATE THE DEVICE IN WINTER, IS NUMERICALLY INCORRECT IN THE TEXTBOOK.
```

**Scilab code Exa 5.4** Minimum work and maximum possible COP

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 4,Page 166
//Title: Minimum work and maximum possible COP
//================================================================================================================

clear
clc

```

```
//INPUT
T_L=4.25;//normal boiling point of helium in K
Q_L=0.083;//latent heat of vaporization of helium in kJ/mol
n=1;//amount of liquid helium to be produced in kmol
T_amb=42;//ambient temperature in summer in degree celsius

//CALCULATION
T_H=T_amb+273.15;//conversion of temperature in K
COP=(T_L)/(T_H-T_L);//calculation of COP of the refrigerator using Eq.(5.20)(no unit)
W=(Q_L)/COP;//calculation of work to be done on the refrigerator unit using Eq.(5.20) in kJ

//OUTPUT
mprintf("\n The maximum possible COP of the unit=%0.4f \n",COP);
mprintf("\n The minimum amount of work to be done on the refrigerating unit=%f kJ \n",W);

//=================================================END OF PROGRAM=====================================================
```

**Scilab code Exa 5.5** Minimum power and maximum efficiency

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 5,Page 166
//Title: Minimum power and maximum efficiency
//
```

```
clear
clc

//INPUT
T_ice=0;//temperature of the ice to be produced in degree celsius
m=5000;//rate at which ice is to be produced in kg/hour
T_water=0;//temperature of water used to produce ice in degree celsius
T_amb=40;//ambient temperature in degree celsius
T_source=100;//temperature of the source for operating heat engine in degree celsius
lambda_fusion=6.002;//latent heat of fusion of water in kJ/mol at 0 degree celsius
molar_mass=18*10^-3;//molar mass of water in kg/mol

//CALCULATION
T_L=T_water+273.15;//sink temperature of the refrigerating unit in K
T_H=T_amb+273.15;//source temperature of the refrigerating unit in K
COP=(T_L)/(T_H-T_L);//calculation of COP of the refrigerating unit using Eq.(5.20) (no unit)
Q_L=((m/3600)/molar_mass)*(lambda_fusion);//calculation of the energy from the sink taken up by the refrigerator in kW
W=(Q_L)/(COP);//calculation of the minimum power required to operate the refrigerator using Eq.(5.20) in kW
T1=T_source+273.15;//temperature of the source of the heat engine in K
T2=T_amb+273.15;//temperature of the sink of the heat engine in K
n_heatengine=(T1-T2)/T1;//calculation of the efficiency of heat engine using Eq.(5.18) (no
```

```
unit)
Q1=W/n_heatengine;//calculation of the energy absorbed by the heat engine using Eq.(5.1) in kW
//calculation of the ratio of energy rejected by both the devices to ambient atmosphere to the energy absorbed by the refrigerator (no unit)
energy_ratio=(Q1+Q_L)/Q_L;

//OUTPUT
mprintf("\n The minimum power required to operate the refrigerator=%0.2f kW\n",W);
mprintf("\n The maximum possible efficiency of the heat engine=%0.4f \n",n_heatengine);
mprintf("\n Ratio of the energy rejected to the ambient atmosphere to the energy absorbed from the water=%0.4f \n",energy_ratio);

//==========================================================END OF PROGRAM==================================================================
```

**Scilab code Exa 5.6** Inventor and the claim

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 6,Page 169
//Title: Inventor and the claim
//================================================================================================================

clear
clc
```

```

//INPUT
T1=800;//temperature of reservoir 1 in K
T2=400;//temperature of reservoir 2 in K
Q1=1000;//energy absorbed from reservoir maintained at T1 in kJ
Q2=400;//energy absorbed from reservoir maintained at T2 in kJ
W=1000;//work delivered by the heat engine in kJ
T3=300;//temperature of the sink in K

//CALCULATION
Q3=(Q1+Q2)-W;//calculation of the energy rejected to the sink using the first law of thermodynamics in kJ
clausius_inequality=(Q1/T1)+(Q2/T2)-(Q3/T3);//application of the second law of thermodynamics in the form of the Clausius inequality using Eq.(5.28)

//OUTPUT
mprintf("\n The LHS of the Clausius inequality=%0.4f\n",clausius_inequality);
if clausius_inequality<0 | clausius_inequality==0 then
    mprintf("\n The given process does not violate the second law of thermodynamics, therefore the claim is correct\n");
else
    mprintf("\n This is a violation of the second law of thermodynamics, and hence the claim cannot be justified\n");
end

//===================================================END OF PROGRAM===================================================
```

**Scilab code Exa 5.7** Change in the entropy of the reactor contents

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-5,Example 7,Page 172
//Title: Change in the entropy of the reactor
   contents
//
   ================================================================================

clear
clc

//INPUT
T_system=200;//temperature of the contents of
   reactor in degree celsius
t=15;//operation time of agitator in minutes
P=750;//power of the operating motor in W

//CALCULATION
dQ=P*t*60*10^-3;//calculation of energy added as
   heat in kJ
T=T_system+273.15;//conversion of temperature in K
del_S=dQ/T;//calculation of entropy change using Eq
   .(5.32) in kJ/K

//OUTPUT
mprintf("\n The change in the entropy of the reactor
    contents=%0.4f kJ/K \n",del_S);


//===============================================================END
```

```
OF PROGRAM
==================================================
```

---

**Scilab code Exa 5.8** Entropy change

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 8,Page 172
//Title: Entropy change
//==================================================

clear
clc

//INPUT
P=0.101325;//pressure in the piston cylinder assembly in MPa
T1=300;//temperature of the piston cylinder assembly in K
T2=400;//final temperature of the piston cylinder assembly in K
a=45.369;//coefficients to compute isobaric molar heat capacity of CO2(g) in J/molK
b=8.688*10^-3;//coefficients to compute isobaric molar heat capacity of CO2(g) in J/molK
e=-9.619*10^5;//coefficients to compute isobaric molar heat capacity of CO2(g) in J/molK
//Cpo for CO2(g) is given as a+bT+eT^-2

//CALCULATION

```

```
del_S=(a*log(T2/T1))+(b*(T2-T1))-((e/2)*((1/T2^2)-(1/T1^2)));//calculation of entropy change for the constant pressure expansion in J/molK

//OUTPUT
mprintf("\n The change in entropy of CO2=%f J/molK\n",del_S);


//===============================================END OF PROGRAM===============================================
//DISCLAIMER: THE AUTHOR HAS NOT DIVIDED 'e' IN THE INTEGRATED EXPRESSION USED TO COMPUTE del_S BY 2, WHICH IS AN ERROR.THE INTEGRATION OF (eT^-3)dT IS -(e/2)*T^-2 THIS ERROR HAS BEEN RECTIFIED IN THIS PROGRAM.
```

**Scilab code Exa 5.9** Change in entropy of water

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 9,Page 173
//Title: Change in entropy of water
//================================================================================================================

clear
clc

//INPUT
m=1;//amount of saturated liquid water in kg
```

```
T_initial=100;//initial temperature of water in degree celsius
T_body=500;//temperature of body which is brought into contact with the cylinder in degree celsius
hfg=2256.94;//enthalpy of vaporization taken from steam tables corresponding to T1 in kJ/kg

//CALCULATION
T=T_initial+273.15;//conversion of temperature in K
del_S=hfg/T;//calculation of the entropy change during the process using Eq.(5.34) in kJ/kgK

//OUTPUT
mprintf("\n The change in entropy of water=%0.4f kJ/kgK\n",del_S);


//===========================================================END OF PROGRAM=================================================================
```

**Scilab code Exa 5.10** Change in entropy of steel and water

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 10,Page 173
//Title: Change in entropy of steel and water
//================================================================================================================

clear
clc
```

```

//INPUT
m_steel=10;//mass of steel casting in kg
T_steel=800;//temperature of steel casting in degree celsius
m_water=100;//mass of water used for quenching in kg
T_water=30;//temperature of water used for quenching in degree celsius
Cp_steel=0.461;//heat capacity of steel in kJ/kgK
Cp_water=4.23;//heat capacity of water in kJ/kgK

//CALCULATION
Ti_steel=T_steel+273.15;//conversion of temperature in K
Ti_water=T_water+273.15;//conversion of temperature in K
//calculation of final temperature of steel and water usung the first law of thermodynamics in K
T_final=((m_steel*Cp_steel*Ti_steel)+(m_water*Cp_water*Ti_water))/((m_steel*Cp_steel)+(m_water*Cp_water));
del_S_steel=m_steel*Cp_steel*log(T_final/Ti_steel);//calculation of the entropy change of steel using Eq.(5.32) in kJ/K
del_S_water=m_water*Cp_water*log(T_final/Ti_water);//calculation of the entropy change of water using Eq.(5.32) in kJ/K

//OUTPUT
mprintf("\n The change in entropy of steel = %0.4f kJ/K\n",del_S_steel);
mprintf("\n The change in entropy of water = %f kJ/K\n",del_S_water);

//==============================================================END OF PROGRAM==============================================================
```

**Scilab code Exa 5.11** Entropy change of the gas

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 11,Page 175
//Title: Entropy change of the gas
//================================================================================================
clear
clc

//INPUT
V=2;//volume of insulated tank in m^3
Ta=400;//temperature of gas in compartment (a) in K
Pa=3;//pressure of gas in compartment (a) in MPa
Tb=600;//temperature of gas in compartment (b) in K
Pb=1;//pressure of gas in compartment (b) in MPa
R=8.314;//universal gas constant in J/molK

//CALCULATION
Va=V/2;//calculation of volume of compartment (a) in m^3
Vb=V/2;//calculation of volume of compartment (b) in m^3
Na=(Pa*10^6*Va)/(R*Ta);//calculation of number of moles of gas in compartment (a) in mol
Nb=(Pb*10^6*Vb)/(R*Tb);//calculation of number of moles of gas in compartment (b) in mol
//From the first law of thermodynamics, del_U=Q-W=0; since Q=0 and W=0. This implies that Na*Cv*(T-Ta)+Nb*Cv*(T-Tb)=0, therefore, Na*(T-Ta)+Nb*(T-Tb)
```

```
=0
T=((Na*Ta)+(Nb*Tb))/(Na+Nb);//calculation of final temperature using the above equation in K
N=Na+Nb;//calculation of total number of moles of gas in mol
P=((N*R*T)/V)*10^-6;//calculation of final pressure of gas in MPa
Cp=(5/2)*R;//calculation of isobaric molar heat capacity as given in the problem statement in J/molK
del_S=((Na*((Cp*log(T/Ta))-(R*log(P/Pa))))+(Nb*((Cp*log(T/Tb))-(R*log(P/Pb)))))*10^-3;//calculation of the change in entropy using Eq.(5.43) in kJ/K

//OUTPUT
mprintf("\n Entropy change of the gas=%0.2f kJ/K\n",del_S);


//==========================================END OF PROGRAM==========================================
```

---

**Scilab code Exa 5.12** Minimum work to be done for separation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 12,Page 177
//Title: Minimum work to be done for separation
//==========================================================================================
```

```
clear
clc

//INPUT
N=1;//amount of air to be separated into its components in kmol
P=0.1;//pressure of air in MPa
T=300;//temperature of air in K
per_oxygen=21;//percentage of oxygen in air
per_nitrogen=79;//percentage of nitrogen in air
R=8.314;//universal gas constant in J/molK

//CALCULATION

//From the first law of thermodynamics, del_U=Q-W. As air is considered as an ideal gas, U is a function of temperature alone.Here, both pure nitrogen and
//pure oxygen are at the same temperature in the initial and the final states. Therefore, del_U=0. This implies that W=Q

//From the second law of thermodynamics ,Eq.(5.32), ds=(dQ/T), therefore, Q=T*del_S, hence, W=T*del_s
x1=per_nitrogen/100;//calculation of mole fraction of nitrogen (no unit)
x2=per_oxygen/100;//calculation of mole fraction of oxygen (no unit)
W=(T*N*10^3*R*((x1*log (x1))+(x2*log (x2))))*10^-3;//calculation of the work to be done based on the above formula in kJ, del_S is computed using Eq.(5.47)

//OUTPUT
mprintf("\n Minimum work to be done to separate 1 kmol of air at 0.1MPa and 300K into pure oxygen and nitrogen at the same temperature and pressure=%0.2f kJ\n",abs(W));
```

```


//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 5.13** Change in the entropy of the mixture

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 13,Page 179
//Title: Change in the entropy of the mixture
//================================================================================================================

clear
clc

//INPUT
m_ice=10;//mass of the block of ice in kg
T_ice=0;//temperature of the ice in degree celsius
m_water=100;//mass of watre in the tank in kg
T_water=30;//temperature of the water in the tank in degree celsius
Cp=4.23;//heat capacity of water in kJ/kgK
lambda_melting=333.44;//latent heat of melting of ice in kJ/kg

//CALCULATION
Ti_ice=T_ice+273.15;//conversion of temperature in K
Ti_water=T_water+273.15;//conversion of temperature in K
```

```

//applying the first law of thermodynamics, an energy balance on the system is established from which the final temperature of water is determined

T_final=((m_water*Cp*Ti_water)+(m_ice*Cp*Ti_ice)-(m_ice*lambda_melting))/((m_ice*Cp)+(m_water*Cp));//calculation of final temperature of water in K
del_S_ice=((m_ice*lambda_melting)/(Ti_ice))+(m_ice*Cp*log(T_final/Ti_ice));//calculation of entropy change of ice in kJ/K
del_S_water=m_water*Cp*log(T_final/Ti_water);//calculation of entropy change of water in kJ/K
del_S_G=del_S_ice+del_S_water;//calculation of entropy generated using Eq.(5.54) in kJ/K

//OUTPUT
mprintf("\n The change in entropy of ice = %f kJ/K\n",del_S_ice);
mprintf("\n The change in entropy of water = %f kJ/K\n",del_S_water);
mprintf("\n The entropy generated= %f kJ/K\n",del_S_G);

//==========================================================END OF PROGRAM==========================================================
```

**Scilab code Exa 5.14** Power output of turbine

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.
```

```

//Chapter-5,Example 14,Page 182
//Title: Power output of turbine
//
clear
clc

//INPUT
P=3;//pressure of superheated steam in MPa
T_enter=300;//entrance temperature of superheated steam in degree celsius
T_exit=45;//final temperature at which the steam leaves in degree celsisus
m=1;//mass flow rate of steam in kg/s

//CALCULATION

//From steam tables corresponding to P and T_enter
si=6.5422;//entropy of steam at the entrance in kJ/kgK
hi=2995.1;//entahlpy of steam at the entrance in kJ/kg

//From steam tables corresponding to T_exit
sf=0.6383;//entropy of saturated liquid in kJ/kgK
hf=188.35;//enthalpy of saturated liquid in kJ/kg
sg=8.1661;//entropy of saturated vapour in kJ/kgK
hg=2583.3;//entahlpy of saturayed vapour in kJ/kg

Xe=(si-sf)/(sg-sf);//calculation of quality of steam at the exit (no unit)
he=((1-Xe)*hf)+(Xe*hg);//calculation of enthalpy of steam at the exit in kJ/kg
Ws=-m*(he-hi);//calculation of power output from turbine using the first law of thermodynamics on the control-volume in kW
```

```

//OUTPUT
mprintf("\n The power output from the turbine=%0.1f kW\n",Ws);


//=================================================END OF PROGRAM====================================================
```

---

**Scilab code Exa 5.15** Exit velocity of steam

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 15,Page 183
//Title: Exit velocity of steam
//================================================================================================================

clear
clc

//INPUT
Pi=3;//pressure of dry saturated steam when it enters the nozzle in bar
Pe=2;//pressure of dry saturated steam at the exit in bar

//CALCULATION
//From steam tables corresponding to Pi
si=6.9909;//entropy of steam at the entrance in kJ/kgK
```

```
hi=2724.7;//entahlpy of steam at the entrance in kJ/kg

//From steam tables corresponding to Pe
sf=1.5301;//entropy of saturated liquid in kJ/kgK
hf=504.70;//enthalpy of saturated liquid in kJ/kg
sg=7.1268;//entropy of saturated vapour in kJ/kgK
hg=2706.3;//entahlpy of saturayed vapour in kJ/kg

se=6.9909;//From Eq.(5.67), se=si (i.e. entropy of the fluid remains constant), where se is in kJ/kgK
Xe=(se-sf)/(sg-sf);//calculation of the quality of steam at the exit (no unit)
he=((1-Xe)*hf)+(Xe*hg);//calculation of enthalpy of steam at the exit in kJ/kg
Ve=sqrt (2*(hi-he)*10^3);//calculation of exit velocity of steam in m/s by applying the first law of thermodynamics

//OUTPUT
mprintf("\n The exit velocity of steam=%f m/s\n",Ve);


//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 5.16** Rate at which entropy is generated

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.
```

```

//Chapter-5,Example 16,Page 183
//Title: Rate at which entropy is generated
//==========================================================================================================
clear
clc

//INPUT
N_glycerol=100;//molar flow rate of glycerol in mol/s
Ti_gly=227;//inlet temperature of glycerol in degree celsius
Te_gly=40;//outlet temperature of glycerol in degree celsius
Ti_water=25;//inlet temperature of cooling water in degree celsius
Te_water=50;//outlet temperature of cooling water in degree celsius
Cp_gly=280;//heat capacity of glycerol in J/molK
Cp_water=77;//heat capacity of water in J/molK

//CALCULATION
Ti_gly=Ti_gly+273.15;//conversion of temperature in K
Te_gly=Te_gly+273.15;//conversion of temperature in K
Ti_water=Ti_water+273.15;//conversion of temperature in K
Te_water=Te_water+273.15;//conversion of temperature in K
//calculation of the molar flow rate of water in mol/s by applying the first law of thermodynamics on the control-volume
N_water=-(N_glycerol*Cp_gly*(Te_gly-Ti_gly))/(Cp_water*(Te_water-Ti_water));
del_S_gly=N_glycerol*Cp_gly*log (Te_gly/Ti_gly)
```

```
*10^-3;//calculation of change in entropy of glycerol in kJ/K s
del_S_water=N_water*Cp_water*log (Te_water/Ti_water)*10^-3;//calculation of change in entropy of water in kJ/K s
S_G=del_S_gly+del_S_water;//calculation of the rate at which entropy is generated  in the heat exchanger in kJ/K s

//OUTPUT
mprintf("\n The rate at which entropy is generated in the heat exchanger=%0.3f kJ/K s\n",S_G);


//===================================================================END OF PROGRAM===================================================================
```

**Scilab code Exa 5.17** Device and its feasibility

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 17,Page 183
//Title: Device and its feasibility
//================================================================================================

clear
clc

//INPUT
T_i=150;//temperature of saturated steam taken up by
```

```
the device in degree celsius
T_e=200;//temperature of superheated steam delivered by the device in degree celsius
P_e=0.2;//pressure of superheated steam delivered by the device in MPa
me2=0.949;//mass of superheated steam leaving the device in kg
me1=0.051;//mass of saturated liquid leaving the device in kg
T_liq=100;//temperature of saturated liquid leaving the device in degree celsius
mi=1;//mass of saturated steam fed to the device in kg

//CALCULATION
//From steam tables corresponding to T_i
hi=2745.4//enthalpy of saturated vapour in kJ/kg
si=6.8358;//entropy of saturated vapour in kJ/kgK

//For saturated liquid at T_liq
he1=419.06;//enthalpy of saturated liquid in kJ/kg
se1=1.3069;//entropy of saturated vapour in kJ/kgK

//For superheated steam at P_e and T_e
he2=2870.5;//enthalpy of superheated steam in kJ/kg
se2=7.5072;//entropy of superheated steam in kJ/kgK

//Test to see if the device obeys the first law of thermodynamics
//Application of the first law of thermodynamics to the flow device gives: mi*hi=(me1*he1)+(me2*he2)
LHS=mi*hi;
RHS=(me1*he1)+(me2*he2);

//Test to see if the device obeys the second law of thermodynamics
//Application of the second law of thermodynamics to the flow device gives: (Ne1*se1)+(Ne2*se2)-(Ni*
```

```
si)>|0
S_G=(me1*se1)+(me2*se2)-(mi*si);

//OUTPUT
mprintf(”\n The LHS of the equation applied to the flow device to check if the first law of thermodynamics is satisfied= %0.1f kJ\n”,LHS);
mprintf(”\n The RHS of the equation applied to the flow device to check if the first law of thermodynamics is satisfied=%0.1f kJ\n”,RHS);
mprintf(”\n The entropy generated by applying the second law of thermodynamics to the flow device=%0.4f kJ/kgK\n”,S_G);
if int(LHS)== int(RHS)& S_G>0 | S_G==0 then
   mprintf(”\n As the first and second law of thermodynamics are satisfied , the device is theoretically feasible \n”);
else
mprintf(”\n As both the first and second law or either the first or second law of thermodynamics are not satisfied , the device is not feasible \n”);
end


//============================================================END OF PROGRAM==============================================================
```

**Scilab code Exa 5.18** Isentropic efficiency

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.
```

```

//Chapter-5,Example 18,Page 185
//Title: Isentropic efficiency
//
clear
clc

//INPUT
Pi=30;//pressure of superheated steam entering the turbine in bar
Ti=300;//temperature of superheated steam entering the turbine in degree celsius
Pe=0.1;//pressure at which steam exits the turbine in bar
Xe=0.9;//quality of steam at the exit (no unit)(for the actual turbine)

//CALCULATION
//For superheated steam at Pi and Ti
hi=2995.1;//enthalpy of superheated steam at the entrance in kJ/kg
si=6.5422;//entropy of superheated steam at the entrance in kJ/kgK

//For steam at Pe
hf=191.83;//enthalpy of saturated liquid in kJ/kg
hg=2584.8;//enthalpy of saturated vapour in kJ/kg
sf=0.6493;//entropy of saturated liquid in kJ/kgK
sg=8.1511;//entropy of saturated vapour in kJ/kgK

//For isentropic turbine s1=s2 i.e. si=se, where si is the entropy at the entrance and se is the entropy at the exit
X2=(si-sf)/(sg-sf);//calculation of the quality of steam at the exit for the isentropic process (no unit)
```

```
h2=(hf*(1-X2))+(X2*hg);//calculation of the enthalpy of steam at the exit for the isentropic process in kJ/kg
he=(hf*(1-Xe))+(Xe*hg);//calculation of the enthalpy of steam at the exit for the actual turbine in kJ/kg
n_T=(hi-he)/(hi-h2);//calculation of isentropic efficiency of the turbine using Eq.(5.68) (no unit)

//OUTPUT
mprintf("\n The isentropic efficiency of the turbine =%f \n",n_T);


//==================================================END OF PROGRAM=======================================================
```

---

**Scilab code Exa 5.19** Power consumed by the compressor

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 19,Page 186
//Title: Power consumed by the compressor
//==================================================================================================

clear
clc

//INPUT
```

```
Ti=25;//temperature of air taken in by the adiabatic air compressor in degree celsius
Pi=0.1;//pressure of air taken in by the adiabatic air compressor in MPa
Pe=1;//discharge pressure of air in MPa
n_c=0.8;//isentropic efficiency of the compressor (no unit)
gaamma=1.4;//ratio of molar specific heat capacities (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
Ti=Ti+273.15;//conversion of temperature in K
Te=Ti*(((Pe*10^6)/(Pi*10^6))^((gaamma-1)/gaamma));//calculation of the discharge temperature of air using Eq.(4.35) in K (for reversible and adiabatic compression)
W_s=(((R*gaamma)/(gaamma-1))*(Te-Ti))*10^-3;//calculation of the power consumed by the isentropic compressor using Eq.(5.69) in kW
Ws=W_s/n_c;//calculation of the power consumed by an actual compressor per mole of air using Eq.(5.68) in kW
Te_actual=((Ws*10^3*(gaamma-1))/(R*gaamma))+Ti;//calculation of the exit temperature of air in K

//OUTPUT
mprintf("\n The exit temperature of air=%0.2f K\n",Te_actual);
mprintf("\n The power consumed by the compressor =%f kW/mol\n",Ws);


//==========================================================END OF PROGRAM==========================================================
```

**Scilab code Exa 5.20** Power consumed by the pump

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 20,Page 187
//Title: Power consumed by the pump
//================================================================================

clear
clc

//INPUT
Ti=30;//temperature of saturated liquid water in degree celsius
m=500;//mass flow rate of water being pumped in kg/s
P2=3;//preesure maintained in the boiler in MPa
n_p=0.75;//isentropic efficiency of the pump (no unit)

//CALCULATION
//For saturated liquid water at Ti
vf=0.0010043;//specific volume in m^3/kg
P1=4.241;//pressure in kPa

//Assuming that the liquid is incompressible, the power input required for an isentropic pump is calculated as:
Ws_m=(vf*((P2*10^6)-(P1*10^3)))*10^-3;//power input required by the isentropic pump in kJ/kg
Ws_act_m=Ws_m/n_p;//power input required by an actual pump in kJ/kg
```

```
P=((Ws_act_m*10^3)*m)*10^-6;//calculation of the total power consumed by the pump in MW

//OUTPUT
mprintf("\n The power consumed by the pump = %d MW\n",P);


//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 5.21** Isentropic efficiency of nozzle

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-5,Example 21,Page 188
//Title: Isentropic efficiency of nozzle
//================================================================================

clear
clc

//INPUT
Pi=3;//pressure of dry saturated steam entering the nozzle in bar
Xe=0.98;//quality of steam exiting the nozzle (no unit)
Pe=2;//pressure of steam exiting the nozzle in bar

//CALCULATION
```

```
//For steam at Pi
hi=2724.7;//enthalpy of dry saturated steam in kJ/kg
he=2652.8;//enthalpy of steam at the exit for an isentropic nozzle,from Example 5.15,in kJ/kg
V2_2_s=hi-he;//calculation of the specific kinetic energy of steam at the nozzle exit (for isentropic nozzle) in kJ/kg

//For steam at Pe
hf=504.70;//enthalpy of saturated liquid in kJ/kg
hg=2706.3;//enthalpy of saturated vapour in kJ/kg
he_act=((1-Xe)*hf)+(Xe*hg);//calculation of enthalpy of steam at the exit in kJ/kg
V2_2=hi-he_act;//calculation of the actual specific kinetic energy of steam leaving the nozzle in kJ/kg
n_N=(V2_2)/(V2_2_s);//calculation of isentropic efficiency of the nozzle using Eq.(5.72) (no unit)

//OUTPUT
mprintf("\n The isentropic efficiency of the nozzle= %0.3f \n",n_N);


//==================================================END OF PROGRAM==================================================
```

# Chapter 6

# Thermodynamic potentials

**Scilab code Exa 6.6** Work done by steam

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-6,Example 6,Page 218
//Title: Work done by steam
//
   ==================================================================

clear
clc

//INPUT
m=0.1;//mass of superheated steam in the piston
   cylinder assembly in kg
P1=1;//initial pressure of superheated steam in MPa
T1=300;//initial temperature of superheated steam in
    degree celsius
P2=0.1;//pressure of steam after expansion in MPa
T2=200;//temperature of steam after expansion in
   degree celsius
```

```

//CALCULATION
//For steam at P1 and T1:
h1=3052.1;//specific enthalpy of steam in kJ/kg
v1=0.2580;//specific volume of steam in m^3/kg

//For steam at P2 and T2:
h2=2875.4;//specific enthalpy of steam in kJ/kg
v2=2.1720;//specific volume of steam in m^3/kg

del_u=(((h1*10^3)-(P1*10^6*v1))-((h2*10^3)-(P2*10^6*v2)))*10^-3;//calculation of the change in internal energy of the steam in kJ/kg
W=m*(del_u);//calculation of the work done by  using Eq.(6.77)steam in kJ

//OUTPUT
mprintf("\n The work done by steam=%0.2f kJ\n",W);

//==========================================================END OF PROGRAM==========================================================
```

**Scilab code Exa 6.8** Power output of the turbine

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-6,Example 8,Page 220
//Title: Power output of the turbine
//================================================================================
```

```
clear
clc

//INPUT
P=3;//pressure of superheated steam in MPa
Ti=300;//temperature at which the steam enters the turbine in degree celsius
m=1;//mass flow rate of steam in kg/s
Te=60;//temperature of dry saturated steam when it leaves the turbine in degree celsius

//CALCULATION
//For steam at P and Ti:
h1=2995.1;//specific entahlpy of steam in kJ/kg

//For saturated steam at Te:
h2=2609.7;//specific enthalpy of saturated vapour in kJ/kg

Ws=m*(h1-h2);//calculation of the power output of the turbine using Eq.(6.83) in kW

//OUTPUT
mprintf("\n The power output of the turbine=%0.1f kW\n",Ws);

//===============================================END OF PROGRAM===============================================
```

---

**Scilab code Exa 6.10** Maximum work obtained from steam

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India
```

```
.

//Chapter-6,Example 10,Page 223
//Title: Maximum work obtained from steam
//

clear
clc

//INPUT
m=0.1;//mass of superheated steam in the piston cylinder assembly in kg
P1=3;//initial pressure of superheated steam in MPa
T1=300;//initial temperature of superheated steam in degree celsius
T0=300;//temperature of the reservoir which is placed in thermal contact with the piston-cylinder assembly in degree celsius
P2=0.1;//pressure of steam after expansion in MPa

// ADDITIONAL DATA PROVIDED
//For steam at P1 and T1:
h1=2995.1;//specific enthalpy of steam in kJ/kg
v1=0.08116;//specific volume of steam in m^3/kg
s1=6.5422;//entropy of steam in kJ/kgK

//For steam at P2 and T2:
h2=3074.5;//specific enthalpy of steam in kJ/kg
v2=2.6390;//specific volume of steam in m^3/kg
s2=8.2166;//entropy of steam in kJ/kgK

//CALCULATION
T0=T0+273.15;//conversion of temperature in K

//The maximum work can be carried out if the process is carried out reversibly, which is given by:
W=m*(h1-h2-(((P1*v1)-(P2*v2))*10^3)-(T0*(s1-s2)));//
```

```
calculation of maximum work obtained from the steam using Eq.(6.90) in kJ

//OUTPUT
mprintf("\n The maximum work obtained from steam=%0.2f kJ\n",W);

//===========================================================END OF PROGRAM===============================================================
```

---

**Scilab code Exa 6.12** Minimum power for compression

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-6,Example 12,Page 226
//Title: Minimum power for compression
//================================================================================================================

clear
clc

//INPUT
P1=0.1;//pressure at which air enters the compressor in MPa
T1=300;//temperature at which air enters the compressor in K
P2=1;//pressure at which air leaves the compressor in MPa
T2=300;//temperature at which air leaves the compressor in K
```

```
T0=300;//ambient temperature in K
N=1;//molar flow rate of air in mol/s
gaamma=1.4;//ratio of specific heat capacities (no
    unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION

//T0=T1=T2 and h2-h1=Cp*(T2-T1)=0 as T2=T1

Ws=(-N*T0*(-R*log (P2/P1)))*10^-3;//calculation of
    minimum power required for compression using Eq
    .(6.99) in kW

//OUTPUT
mprintf("\n The minimum power required to compress
    one mole per second of air=%0.3f kW\n",Ws);

//=================================================END
     OF PROGRAM
    ==================================================
```

# Chapter 7

# Thermodynamic property relations

**Scilab code Exa 7.10** Pressure at which boiler is to be operated

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-7,Example 10,Page 259
//Title: Pressure at which boiler is to be operated
//================================================================================

clear
clc

//INPUT
T2=150;//temperature at which water it is desired to boil water in degree celsius
P1=0.10133;//ambient pressure in MPa
T1=100;//temperature at which water boils corresponding at pressure P1 in degree celsius
del_hv=2256.94;//enthalpy of vaporization in kJ/kg
```

```
R=8.314;//universal gas constant in J/molK
M=18*10^-3;//molar mass of water in kg/mol

//CALCULATION
T1=T1+273.15;//conversion of temperature in K
T2=T2+273.15;//conversion of temperature in K
P2=P1*(exp (((del_hv*10^3*M)*((1/T1)-(1/T2)))/(R)));//calculation of the approximate pressure at which the boiler is to be operated using Eq.(7.92) in MPa

//OUTPUT
mprintf("\n The approximate pressure at which the boiler is to be operated=%0.3f MPa\n",P2);

//===================================================END OF PROGRAM===================================================
```

---

**Scilab code Exa 7.11** The skating problem

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-7,Example 11,Page 259
//Title: The skating problem
//================================================================================================================

clear
clc

//INPUT
```

```
m=60;//mass of the person who wants to skate in kg
T=-2;//temperature of the ice in degree celsius
A=15;//area of contact between the skate edges and ice in mm^2
vs=1.091*10^-3;//specific volume of ice in m^3/kg (at Tref)
vf=1.0*10^-3;//specific volume of water in m^3/kg (at Tref)
del_hf=6.002;//enthalpy of melting of ice in kJ/mol
g=9.81;//accleration due to gravity in m/s^2
Tref=0;//reference temperature at which the specific enthalpy of ice and water are taken in degree celsius

//CALCULATION
Tref=Tref+273.15;//conversion of temperature in K
del_P=((m*g)/(A*10^-6))*10^-6;//calculation of the pressure exerted on the ice by the skater in MPa
del_v=(vf-vs)*(18*10^-3);//calculation of the change in volume in m^3/mol
del_T=(del_P*10^6)/((del_hf*10^3)/(Tref*del_v));//calculation of the reduction in melting point of ice using Eq.(7.86)(Clapeyron equation) in degree celsius

//OUTPUT
mprintf("\n The temperature of ice originally = %d degree celsius \n",T);
mprintf("\n The reduction in melting point of ice due to the additional pressure,computed using the Clayperon equation = %0.2f degree celsius \n",del_T);
if del_T<T then
    mprintf ("\n The ice can melt due to the additional pressure and therefore it will be possible to skate \n");
else
    mprintf ("\n The ice will not melt and therefore
```

```
it will be difficult to skate \n");
end

//=========================================================================END OF PROGRAM=========================================================================
```

---

**Scilab code Exa 7.12** Enthalpy of vaporization

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-7,Example 12,Page 261
//Title: Enthalpy of vaporization
//==========================================================================================================

clear
clc

//INPUT
T1=100;//temperature of water in degree celsius
del_hv1=2256.94;//enthalpy of vaporization at T1 in kJ/kg
T2=150;//temperature at which the enthalpy of vaporization is to be determined in degree celsius
Cp_f=4.26;//isobaric heat capacity of liquid in kJ/kgK
Cp_g=1.388;//isobaric heat capacity of vapour in kJ/kgK

//CALCULATION
```

```
del_hv2=((Cp_g-Cp_f)*(T2-T1))+del_hv1;//calculation of the enthalpy of vaporization at T2 using Eq.(7.98) (Kirchhoff equation) in kJ/kg

//OUTPUT
mprintf(”\n The enthalpy of vaporization at 150 degree celsius=%0.2f kJ/kg\n”,del_hv2);

//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 7.13** Enthalpy of vaporization using Watsons correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-7,Example 13,Page 261
//Title: Enthalpy of vaporization using Watson's correlation
//================================================================================================================

clear
clc

//INPUT
T1=100;//temperature of water in degree celsius
del_hv1=2256.94;//enthalpy of vaporization at T1 in kJ/kg
T2=150;//temperature at which the enthalpy of vaporization is to be determined in degree celsius
```

```
del_hv_kirchoff=2113.34;//enthalpy of vaporization predicted by the Kirchhoff relation taken from Example 7.12 for comparison, in kJ/kg
del_hv_steam_tables=2113.25;//enthalpy of vaporization taken from the steam tables corresponding to T2,for comparison, in kJ/kg
Tc=647.3;//critical temperature of water in K

//CALCULATION
T1=T1+273.15;//conversion of temperature in K
T2=T2+273.15;//conversion of temperature in K
Tr1=T1/Tc;//calculation of reduced temperature corresponding to state 1 (no unit)
Tr2=T2/Tc;//calculation of reduced temperature corresponding to state 2 (no unit)
del_hv2=del_hv1*(((1-Tr2)/(1-Tr1))^0.38);//calculation of enthalpy of vaporization at T2 using Eq.(7.101) in kJ/kg

//OUTPUT
mprintf("\n The enthalpy of vaporization at 150 degree celsius using \n");
mprintf("\n Watson correlation \t = %f kJ/kg\n",del_hv2);
mprintf("\n Kirchhoffs relation \t = %f kJ/kg\n",del_hv_kirchoff);
mprintf("\n From steam tables \t = %f kJ/kg\n",del_hv_steam_tables);

//===========================================END OF PROGRAM======================================
```

**Scilab code Exa 7.14** Enthalpy of vaporization using Riedels correlation

```
//Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-7,Example 14,Page 262
//Title: Enthalpy of vaporization using Riedel's correlation
//
clear
clc

//INPUT
T=373.15;//normal boiling point of water in K (temperature at which the enthalpy of vaporization is to be determined)
Pc=221.2//critical pressure of water in bar
Tc=647.3;//critical temperature of water in K
R=8.314;//universal gas constant in J/molK
del_hvn_steam_tables=2256.94;//enthalpy of vaporization at the normal boiling point taken from the steam tables, for comparison, in kJ/kg

//CALCULATION
Tbr=T/Tc;//calculation of the reduced normal boiling point (no unit)
//calculation of the enthalpy of vaporization at the normal boiling point using Eq.(7.102) in kJ/kg
del_hvn=((1.093*R*Tc*(Tbr*((log (Pc)-1.013)/(0.930-Tbr))))*10^-3)/(18*10^-3);
err=abs ((del_hvn-del_hvn_steam_tables)/del_hvn_steam_tables)*100;//calculation of percentage error

//OUTPUT
mprintf(”\n The enthalpy of vaporization at the normal boiling point \n”);
```

```
mprintf("\n Using Riedels correlation \t = %f kJ/kg\n",del_hvn);
mprintf("\n From the steam tables \t \t = %f kJ/kg\n",del_hvn_steam_tables);
mprintf("\n Error \t \t \t \t = %f %% \n",err);

//============================================================END OF PROGRAM==============================================================
```

---

# Chapter 8

# Thermodynamic properties of real gases

**Scilab code Exa 8.2** Enthalpy and entropy departure

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 2,Page 275
//Title: Enthalpy and entropy departure
//================================================================================

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
a=3.789;//van der Waals constant in Pa (m^3/mol)^2
b=2.37*10^-4;//van der Waals constant in m^3/mol
v=15.675*10^-3;//volume occupied by n-octane vapour taken from Example (3.8) in m^3/mol
```

```
R=8.314;//universal gas constant in J/molK

//CALCULATION
//n-octane obeys the van der Waals equation of state
dep_h=(P*10^6*v)-(R*T)-(a/v);//calculation of the enthalpy departure using Example(8.1) in J/mol
dep_s=R*log ((P*10^6*(v-b))/(R*T));//calculation of the entropy departure using Example(8.1) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for n-octane vapour = %0.2f J/mol\n",dep_h);
mprintf("\n The entropy departure for n-octane vapour = %0.4f J/mol K\n",dep_s);

//===========================================================END OF PROGRAM==============================================================
```

---

**Scilab code Exa 8.3** Enthalpy departure using Beattie Bridgman equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 3,Page 276
//Title: Enthalpy departure using Beattie-Bridgman equation of state
//==========================================================================================================================

clear
```

```
clc

//INPUT
T=100;//temperature of carbon dioxide in degree celsius
P=10;//pressure of carbon dioxide in MPa
A0=0.5073;//Beattie-Bridgman constant for carbon dioxide in (Pa m^3)/mol^2
B0=104.76*10^-6;//Beattie-Bridgman constant for carbon dioxide in m^3/mol
a=71.32*10^-6;//Beattie-Bridgman constant for carbon dioxide in m^3/mol
b=72.35*10^-6;//Beattie-Bridgman constant for carbon dioxide in m^3/mol
C=660.0;//Beattie-Bridgman constant for carbon dioxide in (m^3 K^3)/mol
R=8.314;//universal gas constant in J/molK

//CALCULATION
//The virial form of the Beattie-Bridgman equation of state from Eq.(8.25) is given as:
//P=(A1/v)+(A2/v^2)+(A3/v^3)+(A4/v^4)

T=T+273.15;//conversion of temperature in K
A1=(R*T);//calculation of A1 using Eq.(8.27)
A2=(B0*R*T)-A0-((C*R)/T^2);//calculation of A2 using Eq.(8.28)
A3=(a*A0)-(b*B0*R*T)-((B0*C*R)/T^2);//calculation of A3 using Eq.(8.29)
A4=((b*C*B0*R)/T^2);//calculation of A4 using Eq.(8.30)
vguess=0.01;//taking a guess value of the volume,to be used for solving Eq.(8.25) using the function defined below, in m^3/mol
tolerance=1e-6;//Framing the tolerance limit for the convergence of the equation
function[fn]=solver_func(vi)
    fn=(P*10^6)-((A1/vi)+(A2/vi^2)+(A3/vi^3)+(A4/vi
```

```
^4));//Function defined for solving the system given by Eq.(8.25)
endfunction
[v]=fsolve(vguess,solver_func,tolerance)//using inbuilt function fsolve for solving the system of equations, to determine the volume in m^3/mol
Z=(P*10^6*v)/(R*T);//calculation of compressibility factor (no unit)
//calculation of the enthalpy departure using Eq.(8.37) in J/mol
dep_h=(((B0*R*T)-(2*A0)-((4*C*R)/(T^2)))*(1/v))+((((3/2)*a*A0)-(b*B0*R*T)-((5*B0*C*R)/(2*(T^2))))*(1/(v^2)))+((2*b*C*B0*R)/((T^2)*(v^3)));

//OUTPUT
mprintf("\n Molar volume of CO2 at %0.f MPa and %0.2f K = %f m^3/mol \n",P,T,v);
mprintf("\n The compressibility factor=%f \n",Z);
mprintf("\n The enthalpy departure for carbon dioxide using the Beattie-Bridgman equation of state = %f J/mol\n",dep_h);


//==================================================END OF PROGRAM==================================================

//DISCLAIMER: THE PROBLEM STATEMENT GIVES THE TEMPERATURE AS 100 DEGREE CELSIUS, WHICH CORRESPONDS TO A TEMPERATURE OF 373.15K. HOWEVER, IN THE COMPUTATION OF THE SECOND TERM IN THE ENTHALPY DEPARTURE EXPRESSION, THE AUTHOR HAS TAKEN THE TEMPERATURE TO BE 313.15K, WHICH CLEARLY IS A PRINTING ERROR. THE CODE ABOVE HAS BEEN WRITTEN FOR THE TEMPERATURE OF 373.15K, AS GIVEN IN THE PROBLEM STATEMENT.
```

**Scilab code Exa 8.4** Entropy departure using Beattie Bridgman equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 4,Page 278
//Title: Entropy departure using Beattie-Bridgman equation of state
//==========================================================================================

clear
clc

//INPUT
T=100;//temperature of carbon dioxide in degree celsius
P=10;//pressure of carbon dioxide in MPa
B0=104.76*10^-6;//Beattie-Bridgman constant for carbon dioxide in m^3/mol
b=72.35*10^-6;//Beattie-Bridgman constant for carbon dioxide in m^3/mol
C=660.0;//Beattie-Bridgman constant for carbon dioxide in (m^3 K^3)/mol
R=8.314;//universal gas constant in J/molK
v=0.233*10^-3;//volume calculated in Example (8.3) in m^3/mol
Z=0.751;//compressibility factor as calculated in Example (8.3) (no unit)

//CALCULATION
T=T+273.15;//conversion of temperature in K
```

```
//calculation of entropy departure using Eq.(8.38) in J/molK
dep_s=(R*log (Z))-(((B0*R)+((2*C*R)/(T^3)))*(1/v))+(((b*B0*R)-((2*C*B0*R)/(T^3)))*(1/(2*(v^2))))+((2*b*C*B0*R)/(3*(T^3)*(v^3)));

//OUTPUT
mprintf("\n The entropy departure for carbon dioxide using the Beattie-Bridgman equation of state = %f J/mol K\n",dep_s);


//===================================================END OF PROGRAM===================================================

//DISCLAIMER: THE PROBLEM STATEMENT MENTIONS THE TEMPERATURE TO BE 100 DEGREE CELSIUS, WHICH CORRESPONDS TO A TEMPERATURE OF      373.15K. HOWEVER, THE AUTHOR HAS EVALUATED THE ENTROPY DEPARTURE FOR A TEMPERATURE OF 313.15K, WHICH IS CLEARLY A PRINTING ERROR. THE CODE ABOVE HAS BEEN WRITTEN FOR THE TEMPERATURE OF 373.15K  AS GIVEN IN THE PROBLEM STATEMENT.
```

**Scilab code Exa 8.5** Enthalpy and entropy departure using the generalized Redlich Kwong equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 5,Page 281
//Title: Enthalpy and entropy departure using the
```

```
generalized Redlich-Kwong equation of state
//==========================================================================

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
a=4.426;//Redlich-Kwong constant taken from Example (3.9) in (m^6 Pa mol^-2)
b=164.3*10^-6;//Redlich-Kwong constant taken from Example(3.9) in m^3/mol
Z=0.9308;//compressibility factor taken from Example (3.9) (no unit)
B=9.9306*10^-3;//value of B, used in the Cardan's method in Example (3.9)
R=8.314;//universal gas constant in J/molK

//CALCULATION
dep_h=(R*T*(Z-1))-(((3*a)/(2*b))*log ((Z+B)/Z));//calculation of the enthalpy departure using Eq.(8.39) in J/mol
dep_s=(R*log(Z-B))-((a/(2*b*T))*log((Z+B)/Z));//calculation of the entropy departure using Eq.(8.40) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for n-octane vapour using the generalized Redlich-Kwong equation of state = %0.2f J/mol\n",dep_h);
mprintf("\n The entropy departure for n-octane vapour using the generalized Redlich-Kwong equation of state = %0.4f J/mol K\n",dep_s);

//==========================================================END OF PROGRAM
```

**Scilab code Exa 8.6** Enthalpy and entropy departure using the SRK equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 6,Page 281
//Title: Enthalpy and entropy departure using the SRK equation of state
//
clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
S=1.0786;//constant used in the SRK equation of state,from Example(3.15)
alpha=1.3079;//constant used in the SRK equation of state,from Example(3.15)
a=5.0180;//constant used in the SRK equation of state,from Example(3.15) in (m^6 Pa mol^-2)
b=1.6426*10^-4;//constant used in the SRK equation of state,from Example(3.15) in m^3/mol
B=9.9282*10^-3;//factor used in the Cardan's method for solving the SRK equation of state,from Example(3.15) (no unit)
Z=0.9191;//compressibility factor taken from Example (3.15) (no unit)
```

```
R=8.314;//universal gas constant in J/molK
Tc=569.4;//critical temperature of n-octane in K

//CALCULATION
da_dT=(-a*S)/(sqrt (alpha*T*Tc));//calculation of da/dT using Eq.(8.44)
dep_h=(R*T*(Z-1))+((((T*da_dT)-a)/b)*log ((Z+B)/Z));//calculation of the enthalpy departure using Eq.(8.42) in J/mol
dep_s=(R*log (Z-B))+((1/b)*(da_dT)*log ((Z+B)/Z));//calculation of the entropy departure using Eq.(8.43) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for n-octane vapour using the SRK equation of state = %f J/mol\n",dep_h);
mprintf("\n The entropy departure for n-octane vapour using the SRK equation of state = %0.4f J/mol K\n",dep_s);

//==================================================================END OF PROGRAM ==================================================================

// DISCLAIMER: NUMERICAL ERROR OBSERVED IN ENTHALPY DEPARTURE FUNCTION CALCULATION. FOR THE GIVEN INPUT DATA, THE ANSWER GIVEN IN THE BOOK "-890.22 J/mol" WAS FOUND TO BE NUMERICALLY INCORRECT.
```

**Scilab code Exa 8.7** Enthalpy and entropy departure using the Peng Robinson equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering
```

```
Thermodynamics. Universities Press, Hyderabad, India.

//Chapter-8,Example 7,Page 282
//Title: Enthalpy and entropy departure using the Peng-Robinson equation of state
//

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
S=0.9457;//constant used in the Peng-Robinson equation of state,from Example(3.16)
alpha=1.2677;//constant used in the Peng-Robinson equation of state,from Example(3.16)
a=5.2024;//constant used in the Peng-Robinson equation of state,from Example(3.16) in (m^6 Pa mol^-2)
b=1.4750*10^-4;//constant used in the Peng-Robinson equation of state,from Example(3.16) in m^3/mol
B=8.9151*10^-3;//factor used in the Cardan's method for solving the Peng-Robinson equation of state, from Example(3.16) (no unit)
Z=0.9151;//compressibility factor taken from Example (3.16) (no unit)
R=8.314;//universal gas constant in J/molK
Tc=569.4;//critical temperature of n-octane in K

//CALCULATION
da_dT=(-a*S)/(sqrt (alpha*T*Tc));//calculation of da/dT using Eq.(8.47)
//calculation of the enthalpy departure using Eq.(8.45) in J/mol
dep_h=(R*T*(Z-1))+(((((T*da_dT)-a)/(2*sqrt(2)*b)))*(
```

```
log((Z+(B*(1+sqrt(2))))/(Z+(B*(1-sqrt(2))))))
;
dep_s=(R*log(Z-B))+((1/(2*sqrt(2)*b))*(da_dT)*(log((Z+(B*(1+sqrt(2))))/(Z+(B*(1-sqrt(2)))))));//calculation of the entropy departure using Eq.(8.46) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for n-octane vapour using the Peng-Robinson equation of state = %0.1f J/mol\n",dep_h);
mprintf("\n The entropy departure for n-octane vapour using the Peng-Robinson equation of state = %0.3f J/mol K\n",dep_s);

//==========================================================END OF PROGRAM===============================================================
```

**Scilab code Exa 8.8** Enthalpy and entropy departure using the Edmister charts

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 8,Page 284
//Title: Enthalpy and entropy departure using the Edmister charts
//================================================================================

clear
clc
```

```

//INPUT
T=339.7;//temperature of ethylene in K
P=30.7;//pressure of ethylene in bar
Tc=283.1;//critical temperature of ethylene in K
Pc=51.17;//critical pressure of ethylene in bar
w=0.089;//acentric factor (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
Pr=P/Pc;//calculation of reduced pressure (no unit)
Tr=T/Tc;//calculation of reduced temperature (no unit)
del_h0=0.45;//value of ((h0-h)/RTc)_0 read from Fig.(8.2) corresponding to Pr and Tr (no unit)
del_h1=0.18;//value of ((h0-h)/RTc)_1 read from Fig.(8.3) corresponding to Pr and Tr (no unit)
del_s0=0.26;//value of ((s0-s)/R)_0 read from Fig.(8.4) corresponding to Pr and Tr (no unit)
del_s1=0.20;//value of ((s0-s)/R)_1 read from Fig.(8.5) corresponding to Pr and Tr (no unit)
dep_h=((del_h0)+(w*del_h1))*R*Tc;//calculation of the enthalpy departure using Eq.(8.52) in J/mol
dep_s=((del_s0)+(w*del_s1))*R;//calculation of the entropy departure using Eq.(8.56) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for ethylene using the Edmister charts = %0.3f J/mol\n",dep_h);
mprintf("\n The entropy departure for ethylene using the Edmister charts = %0.4f J/mol K\n",dep_s);

//==================================================END OF PROGRAM==================================================
```

**Scilab code Exa 8.9** Enthalpy and entropy departure using the Lee Kesler data

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 9,Page 297
//Title: Enthalpy and entropy departure using the Lee-Kesler data
//================================================================================

clear
clc

//INPUT
T=339.7;//temperature of ethylene in K
P=30.7;//pressure of ethylene in bar
Tc=283.1;//critical temperature of ethylene in K
Pc=51.17;//critical pressure of ethylene in bar
w=0.089;//acentric factor (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
Pr=P/Pc;//calculation of reduced pressure (no unit)
Tr=T/Tc;//calculation of reduced temperature (no unit)
del_h0=0.474;//value of ((h0-h)/RTc)_0 read from Fig.(8.6) corresponding to Pr and Tr (no unit)
del_h1=0.232;//value of ((h0-h)/RTc)_1 read from Fig.(8.8) corresponding to Pr and Tr (no unit)
del_s0=0.277;//value of ((s0-s)/R)_0 read from Fig.(8.10) corresponding to Pr and Tr (no unit)
```

```
del_s1=0.220;//value of ((s0-s)/R)_1 read from Fig.(8.12) corresponding to Pr and Tr (no unit)
dep_h=((del_h0)+(w*del_h1))*R*Tc;//calculation of the enthalpy departure using Eq.(8.62) in J/mol
dep_s=((del_s0)+(w*del_s1))*R;//calculation of the entropy departure using Eq.(8.65) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for ethylene using the Lee-Kesler data = %f J/mol\n",dep_h);
mprintf("\n The entropy departure for ethylene using the Lee-Kesler data = %f J/mol K\n",dep_s);

//=========================================================END OF PROGRAM=========================================================
```

---

**Scilab code Exa 8.10** Enthalpy and entropy departure using the generalized virial coefficient correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-8,Example 10,Page 299
//Title: Enthalpy and entropy departure using the generalized virial coefficient correlation
//==========================================================================================

clear
clc

//INPUT
```

```
T=339.7;//temperature of ethylene in K
P=1;//pressure of ethylene in bar
Tc=283.1;//critical temperature of ethylene in K
Pc=51.17;//critical pressure of ethylene in bar
w=0.089;//acentric factor (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
Pr=P/Pc;//calculation of reduced pressure (no unit)
Tr=T/Tc;//calculation of reduced temperature (no unit)
dep_h=R*Tc*Pr*((0.083-(1.097/(Tr^1.6)))+(w*(0.139-(0.894/(Tr^4.2)))));//calculation of the enthalpy departure using Eq.(8.75) in J/mol
dep_s=-Pr*R*((0.675/(Tr^2.6))+(w*(0.722/(Tr^5.2))));//calculation of the entropy departure using Eq.(8.76) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure for ethylene using the generalized virial coefficient correlation = %f J/mol\n",dep_h);
mprintf("\n The entropy departure for ethylene using the generalized virial coefficient correlation = %e J/mol K\n",dep_s);

//===================================================END OF PROGRAM======================================================
```

---

**Scilab code Exa 8.11** Volume Enthalpy and Entropy departure using the Peng Robinson equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering
```

```
Thermodynamics. Universities Press, Hyderabad, India
.

//Chapter-8,Example 11,Page 299
//Title: Volume, Enthalpy and entropy departure using
 the Peng-Robinson equation of state
//
==================================================================

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
T_ref=0;//reference state saturated liquid
temperature in degree celsius
h0=0;//enthalpy of saturated liquid in J/mol (
reference state)
s0=0;//entropy of saturated liquid in J/molK (
reference state)
Tc=569.4;//critical temperature of n-octane in K
Pc=24.97;//critical pressure of n-octane in bar
w=0.398;//acentric factor (no unit)
NBP=398.8;//normal boiling point of n-octane (
saturated liquid)
[Cp
]=[6.907;741.770*10^-3;-397.204*10^-6;82.629*10^-9;0];
//coefficients to compute the isobaric molar heat
 capacity, where Cp=a+bT+cT^2+dT^3+eT^-2,in J/
molK
S=0.9457;//value of S taken from Example (3.16)
b=1.4750*10^-4;//value of the Peng-Robinson constant
 in m^3/mol from Example (3.16)
v=15.14*10^-3;//volume of saturated vapour in m^3/
mol from Example (3.16)
R=8.314;//universal gas constant in J/molK
P_amb=101.325;//pressure at which the normal boiling
```

```
point is computed in kPa

//CALCULATION

//Step a: Vaporization of n-octane at T_ref
T_ref=T_ref+273.15;//conversion of temperature in K
//calculation of the enthalpy of vaporization using Eq.(7.92)(Clausius-Clayperon equation) in kJ/mol
del_hv=((R*log ((Pc*10^5)/(P_amb*10^3)))/((1/NBP)-(1/Tc)))*10^-3;
P2=P_amb*exp (((del_hv*10^3)/(R))*((1/NBP)-(1/T_ref)));//calculation of the vapour pressure at T_ref using Eq.(7.92)(Clausius-Clayperon equation) in kPa
Tbr=NBP/Tc;//calculation of the reduced normal boiling point (no unit)
//calculation of the enthalpy of vaporization at the normal boiling point using Eq.(7.102)(Riedel's correlation) in kJ/mol
del_hvn=(1.093*R*Tc*(Tbr*(((log (Pc))-1.013)/(0.930-Tbr))))*10^-3;
Tr2=T_ref/Tc;//calculation of the reduced temperature with reference to T_ref (no unit)
//calculation of the enthalpy of vaporization (Step a)at T_ref using Eq.(7.101)(Watson's correlation) in kJ/mol
del_ha=((del_hvn*10^3)*(((1-Tr2)/(1-Tbr))^(0.38)))*10^-3;
del_sa=(del_ha*10^3)/T_ref;//calculation of the entropy change in the conversion from saturated liquid to saturated vapour (Step a) at T_ref in J/molK

//Step b:Change from real state of n-octane at T_ref and P2 to ideal gas state at the same temperature and pressure
alpha=(1+(S*(1-sqrt (Tr2))))^2;//calculation of alpha so as to compute the Peng-Robinson constant
```

```
(a)
a=(0.45724*(R^2)*(Tc^2)*alpha)/(Pc*10^5);//calculation of the Peng-Robinson constant using Eq.(3.76) in Pa(m^3/mol)^2
//Using the Cardan's method to evaluate Z
A=(a*P2*10^3)/(R*T_ref)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*P2*10^3)/(R*T_ref);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1+B;//calculation of alpha for Peng-Robinson equation of state using Table (3.2)
beeta=A-(2*B)-(3*B^2);//calculation of beeta for Peng-Robinson equation of state using Table (3.2)
gaamma=-(A*B)+(B^2)+(B^3);//calculation of gaamma for Peng-Robinson equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Za=[Z1 Z2 Z3];
        Z=max(Za);
    else
```

```
        theta=acos((-(q)/2)*(sqrt((-27)/(((p)^3)))));//calculation of theta in radians using Eq.(3.37)
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Za=[Z1 Z2 Z3];
        Z=max(Za);
    end
end
da_dT=(-a*S)/(sqrt (alpha*T_ref*Tc));//calculation of da/dT using Eq.(8.47)
//calculation of the enthalpy departure using Eq.(8.45) in J/mol
dep_h=(R*T_ref*(Z-1))+(((((T_ref*da_dT)-a)/(2*sqrt (2)*b)))*(log ((Z+(B*(1+sqrt (2))))/(Z+(B*(1-sqrt (2)))))));
//calculation of the entropy departure using Eq.(8.46)in J/molK
dep_s=(R*log (Z-B))+((1/(2*sqrt (2)*b))*(da_dT)*(log ((Z+(B*(1+sqrt (2))))/(Z+(B*(1-sqrt (2)))))));
del_hb=-dep_h;//calculation of the enthalpy change corresponding to Step b in J/mol
del_sb=-dep_s;//calculation of the entropy change corresponding to Step b in J/molK

//Step c:Change n-octane in the ideal gas state at T_ref and P2 to n-octane in the ideal gas state at T and P
//Calculation of the enthalpy change corresponding to Step c using Eq.(4.25) in kJ/mol
 del_hc=((Cp(1,:)*(T-T_ref))+(((Cp(2,:))/2)*((T^2)-(T_ref^2)))+(((Cp(3,:))/3)*((T^3)-(T_ref^3)))+(((
```

```
Cp(4,:))/4)*((T^4)-(T_ref^4)))-((Cp(5,:))*((1/T)-(1/T_ref))))*10^-3;
del_sc=((Cp(1,:))*log (T/T_ref))+((Cp(2,:))*(T-T_ref))+(((Cp(3,:))/2)*((T^2)-(T_ref^2)))+(((Cp(4,:))/3)*((T^3)-(T_ref^3)))-(((Cp(5,:))/2)*((1/(T^2))-(1/(T_ref^2))))-(R*log ((P*10^6)/(P2*10^3)));//calculation of the entropy change corresponding to Step c using Eq.(5.43) in J/molK

//Step d: Change n-octane from the ideal gas state to the real state at T and P
Z=0.9151;//compressibility factor taken from Example (3.16) (no unit)
da_dT=(-a*S)/(sqrt (alpha*T*Tc));//calculation of da/dT using Eq.(8.47)
//calculation of the enthalpy change corresponding to Step d using Eq.(8.45) in J/mol
del_hd=(R*T*(Z-1))+((((T*da_dT)-a)/(2*sqrt(2)*b))*log ((Z+(B*(1+sqrt (2))))/(Z+(B*(1-sqrt (2))))));
//calculation of the entropy change corresponding to Step d using Eq.(8.46)in J/molK
del_sd=(R*log (Z-B))+((1/(2*sqrt (2)*b))*(da_dT)*(log ((Z+(B*(1+sqrt (2))))/(Z+(B*(1-sqrt (2)))))));

h=h0+del_ha+(del_hb*10^-3)+del_hc+(del_hd*10^-3);//calculation of the enthalpy of n-octane vapour at T and P in kJ/mol
s=s0+del_sa+del_sb+del_sc+del_sd;//calculation of the entropy of n-octane vapour at T and P in J/molK

//OUTPUT
mprintf("\n The enthalpy of n-octane vapour at 427.85K and 0.215MPa using the Peng-Robinson equation of state = %f kJ/mol\n",h);
mprintf("\n The entropy of n-octane vapour at 427.85K and 0.215MPa using the Peng-Robinson equation
```

```
of state = %f J/mol K\n",s);
mprintf("\n The volume of n-octane vapour at 427.85K and 0.215MPa using the Peng-Robinson equation of state = %f m^3/mol\n",v)

//==================================================END OF PROGRAM==================================================

//DISCLAIMER: THE VOLUME OF n-OCTANE VAPOUR AS COMPUTED IN EXAMPLE 3.16 IS 15.14*10^-3 m^3/mol AND NOT 15.41*10^-3 m^3/mol AS PRINTED IN THIS EXAMPLE IN THE TEXTBOOK.
```

# Chapter 9

# Multicomponent mixtures

**Scilab code Exa 9.1** Partial molar volume

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 1,Page 313
//Title: Partial molar volume
//================================================================================

clear
clc

//INPUT
per_ethanol=60;//mole percent of ethanol in a ethanol-water system
per_water=40;//mole percent of water in a ethanol-water system
v1=57.5*10^-6;//partial molar volume of ethanol in the ethanol-water system in m^3
rho=849.4;//density of the mixture in kg/m^3
M_ethanol=46*10^-3;//molar mass of ethanol in kg/mol
```

```
M_water=18*10^-3;//molar mass of ethanol in kg/mol

//CALCULATION
X1=per_ethanol/100;//calculation of the mole fraction of ethanol (no unit)
X2=per_water/100;//calculation of the mole fraction of water (no unit)
M=(X1*M_ethanol)+(X2*M_water);//calculation of the molar mass of the ethanol-water mixture in kg/mol
v=M/rho;//calculation of the molar volume of the mixture in m^3/mol
v2=(v-(X1*v1))/(X2);//calculation of the partial molar volume of water using Eq.(9.10) in m^3/mol

//OUTPUT
mprintf("\n The partial molar volume of water = %f m^3/mol\n",v2);

//==========================================END OF PROGRAM==============================================
```

**Scilab code Exa 9.2** Volumes to be mixed

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 2,Page 313
//Title: Volumes to be mixed
//================================================================================================
clear
```

```
clc

//INPUT
V=3;//volume of mixture to be prepared in m^3
per_ethanol=60;//mole percent of ethanol in a ethanol-water system
per_water=40;//mole percent of water in a ethanol-water system
v1=57.5*10^-6;//partial molar volume of ethanol in the ethanol-water system in m^3/mol
v2=16*10^-6;//partial molar volume of water in the ethanol-water system in m^3/mol
v1_pure=57.9*10^-6;//molar volume of pure ethanol in m^3/mol
v2_pure=18*10^-6;//molar volume of pure water in m^3/mol

//CALCULATION
X1=per_ethanol/100;//calculation of the mole fraction of ethanol (no unit)
X2=per_water/100;//calculation of the mole fraction of water (no unit)
v=(X1*v1)+(X2*v2);//calculation of the molar volume of the solution using Eq.(9.10) in m^3/mol
N=V/v;//calculation of the mole number of solution required in mol
N1=N*X1;//calculation of the mole number of ethanol in solution in mol
N2=N*X2;//calculation of the mole number of water in solution in mol
V1=N1*v1_pure;//calculation of the volume of pure ethanol required in m^3
V2=N2*v2_pure;//calculation of the volume of pure water required in m^3

//OUTPUT
mprintf("\n The volume of pure ethanol required = %0.3f m^3\n",V1);
```

```
mprintf("\n The volume of pure water required = %0.3
   f m^3\n",V2);

//=====================================================END
    OF PROGRAM
   ==========================================================
```

---

**Scilab code Exa 9.3** Fugacity and fugacity coefficient

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-9,Example 3,Page 318
//Title: Fugacity and fugacity coefficient
//
   ==========================================================================

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
a=3.789;//van der Waals constant in Pa(m^3/mol)^2
b=2.37*10^-4;//van der Waals constant in m^3/mol
v=15.675*10^-3;//molar volume of n-octane saturated
   vapour taken from Example 3.8 in m^3/mol
R=8.314;//universal gas constant in J/molK

//CALCULATION
Z=(P*10^6*v)/(R*T);//calculation of the
   compressibility factor (no unit)
//calculation of the fugacity coefficient (f/P)
```

```
using the expression derived in Example 9.3 (no unit)
phi=exp (Z-1-log (((P*10^6)*(v-b))/(R*T))-a/(R*T*v));
f=(P*10^6*phi)*10^-6;//calculation of fugacity using Eq.(9.37) in MPa

//OUTPUT
mprintf("\n The fugacity coefficient of n-octane vapour = %0.2f \n",phi);
mprintf("\n The fugacity of n-octane vapour = %0.4f MPa\n",f);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 9.5** Fugacity and fugacity coefficient from the Lee Kesler data

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 5,Page 322
//Title: Fugacity and fugacity coefficient from the Lee-Kesler data
//==========================================================================

clear
clc

//INPUT
```

```
T=427.85;//temperature of n-octane vapour in K
P=0.215;//pressure of n-octane vapour in MPa
Tc=569.4;//critical temperature of n-octane in K
Pc=24.97;//critical pressure of n-octane in bar
w=0.398;//acentric factor (no unit)

//CALCULATION
Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=(P*10^6)/(Pc*10^5);//calculation of reduced pressure (no unit)
log_phi0=-0.032;//value of log_phi0 taken from Figure(9.2) (no unit)
log_phi1=-0.025;//value of log_phi1 taken from Figure(9.4) (no unit)
phi=10^(log_phi0+(w*log_phi1));//calculation of the fugacity coefficient using Eq.(9.54) (no unit)
f=P*phi;//calculation of the fugacity using Eq.(9.37) in MPa

//OUTPUT
mprintf("\n The fugacity coefficient of n-octane vapour = %f \n",phi);
mprintf("\n The fugacity of n-octane vapour = %f MPa \n",f);

//==============================================================END OF PROGRAM==================================================================


// DISCLAIMER: THE VALUE OF FUGACITY COEFFICIENT AS CALCULATED IN THE TEXTBOOK UPON TAKING THE ANTILOG IS WRONG. THE ANTILOG OF -0.042 IS A VALUE LESS THAN 1. THIS HAS BEEN CORRECTED ACCORDINGLY IN THIS PROGRAM AND THE VALUE OF FUGACITY COEFFICIENT AND FUGACITY HAVE BEEN COMPUTED.
```

**Scilab code Exa 9.6** Fugacity and fugacity coefficient using the virial coefficient correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 6,Page 327
//Title: Fugacity and fugacity coefficient using the virial coefficient correlation
//

clear
clc

//INPUT
T=339.7;//temperature of ethylene in K
P=1;//pressure of ethylene in bar
Tc=283.1;//critical temperature of ethylene in K
Pc=51.17;//critical pressure of ethylene in bar
w=0.089;//acentric factor (no unit)

//CALCULATION
Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=P/Pc;//calculation of reduced pressure (no unit)
B0=0.083-(0.422/(Tr^1.6));//calculation of B0 using Eq.(3.95) so as to compute fugacity coefficient using Eq.(9.58)
B1=0.139-(0.172/(Tr^4.2));//calculation of B1 using Eq.(3.96) so as to compute fugacity coefficient using Eq.(9.58)
phi=exp ((B0+(w*B1))*(Pr/Tr));//calculation of the
```

```
fugacity coefficient using Eq.(9.58) (no unit)
f=P*phi;//calculation of the fugacity using Eq.(9.37) in bar

//OUTPUT
mprintf("\n The fugacity coefficient of ethylene = %0.4f \n",phi);
mprintf("\n The fugacity of ethylene = %0.4f bar\n",f);

//==================================================END OF PROGRAM ======================================================
```

---

**Scilab code Exa 9.7** Second virial coefficient

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 7,Page 330
//Title: Second virial coefficient
//================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
Tc=[425.2;569.4];//critical temperature of n-butane and n-octane in K
Pc=[37.97;24.97];//critical pressure of n-butane and
```

```
n-octane in bar
vc=[255.0*10^-6;486.0*10^-6];//critical molar volume of n-butane and n-octane in m^3/mol
Zc=[0.274;0.256];//compressibility factor of n-butane and n-octane corresponding to Tc,Pc (no unit)
w=[0.199;0.398];//acentric factor of n-butane and n-octane (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
K_12=1-((8*((vc(1,:)*vc(2,:))^(1/2)))/((((vc(1,:))^(1/3))+((vc(2,:))^(1/3)))^3));//calculation of the binary interaction parameter using Eq.(9.94)
Tc_12=(((Tc(1,:))*(Tc(2,:)))^(1/2))*(1-K_12);//calculation of Tc_ij using Eq.(9.89) in K
w_12=(w(1,:)+w(2,:))/2;//calculation of w_ij using Eq.(9.92) (no unit)
Zc_12=(Zc(1,:)+Zc(2,:))/2;//calculation of Zc_ij using Eq.(9.91) (no unit)
vc_12=((((vc(1,:))^(1/3))+((vc(2,:))^(1/3)))/2)^3;//calculation of vc_ij using Eq.(9.90) in m^3/mol
Pc_12=((Zc_12*R*Tc_12)/vc_12)*10^-6;//calculation of Pc_ij using Eq.(9.93) in MPa
Tr_12=T/Tc_12;//calculation of reduced temperature for computing the mixture interaction virial coefficient (no unit)
B_12_0=0.083-(0.422/(Tr_12^(1.6)));//calculation of B_ij0 using Eq.(9.87)
B_12_1=0.139-(0.172/(Tr_12^(4.2)));//calculation of B_ij1 using Eq.(9.88)
B_12=((R*Tc_12)/(Pc_12*10^6))*(B_12_0+(w_12*B_12_1))
```

```
;//calculation of the mixture interaction virial coefficient using Eq.(9.86) in m^3/mol
Tr1=T/Tc(1,:);//calculation of reduced temperature of n-butane (no unit)
B_11_0=0.083-(0.422/(Tr1^(1.6)));//calculation of B_i0 for the pure component (n-butane) using Eq.(9.87)
B_11_1=0.139-(0.172/(Tr1^(4.2)));//calculation of B_i1 for the pure component (n-butane) using Eq.(9.88)
B_11=((R*Tc(1,:))/(Pc(1,:)*10^5))*(B_11_0+(w(1,:)*B_11_1));//calculation of the pure component (n-butane) second virial coefficient using Eq.(9.86) in m^3/mol
Tr2=T/Tc(2,:);//calculation of reduced temperature of n-octane (no unit)
B_22_0=0.083-(0.422/(Tr2^(1.6)));//calculation of B_i0 for the pure component (n-octane) using Eq.(9.87)
B_22_1=0.139-(0.172/(Tr2^(4.2)));//calculation of B_i1 for the pure component (n-octane) using Eq.(9.88)
B_22=((R*Tc(2,:))/(Pc(2,:)*10^5))*(B_22_0+(w(2,:)*B_22_1));//calculation of the pure component (n-octane) second virial coefficient using Eq.(9.86) in m^3/mol
Bm=((y1^2)*B_11)+((2*y1*y2)*B_12)+((y2^2)*B_22);//calculation of the second virial coefficient using Eq.(9.85) in m^3/mol

//OUTPUT
mprintf("\n The second virial coefficient for an equimolar mixture of n-butane and n-octane at 600 K = %f m^3/mol\n",Bm);

//=====================================================END OF PROGRAM=====================================================
```

---

**Scilab code Exa 9.8** van der Waals constants

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 8,Page 331
//Title: van der Waals constants
//
clear
clc

//INPUT
a=[1.3874;3.7890];//van der Waals constant of n-butane and n-octane in Pa(m^3/mol)^2
b=[0.1163*10^-3;0.237*10^-3];//van der Waals constant of n-butane and n-octane in m^3/mol

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
//Set K_ij=0 in Eq.(9.64) to compute the van der Waals constant (a_m) for an equimolar mixture of n-butane and n-octane
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
a_m=((y1^2)*a(1,:))+((2*y1*y2)*sqrt (a(1,:)*a(2,:)))+((y2^2)*a(2,:));//calculation of the van der Waals constant (a_m) using Eq.(9.64) in Pa(m^3/
```

```
mol)^2
b_m=(y1*b(1,:))+(y2*b(2,:));//calculation of the van der Waals constant (b_m) using Eq.(9.65) in m^3/mol

//OUTPUT
mprintf(”\n The van der Waals constant for an equimolar mixture of n-butane and n-octane, a_m = %0.4f Pa(m^3/mol)^2\n”,a_m);
mprintf(”\n The van der Waals constant for an equimolar mixture of n-butane and n-octane, b_m = %f m^3/mol\n”,b_m);

//==============================================================END OF PROGRAM==============================================================
```

---

**Scilab code Exa 9.9** Molar volume of an equimolar mixture

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 9,Page 333
//Title: Molar volume of an equimolar mixture
//================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
```

```
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
Tc=[425.2;569.4];//critical temperature of n-butane and n-octane in K
Pc=[37.97;24.97];//critical pressure of n-butane and n-octane in bar
R=8.314;//universal gas constant in J/molK

//CALCULATION
//Calculation by Amagat's law of additive volumes
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
Tr1=T/Tc(1,:);//calculation of reduced temperature of n-butane (no unit)
Pr1=P/Pc(1,:);//calculation of reduced pressure of n-butane (no unit)
Z1_0=0.95;//value of Z1_0 taken from the generalized compressibility chart, Figure(3.11) corresponding to Tr1 and Pr1 (no unit)
Tr2=T/Tc(2,:);//calculation of reduced temperature of n-octane (no unit)
Pr2=P/Pc(2,:);//calculation of reduced pressure of n-octane (no unit)
Z2_0=0.785;//value of Z2_0 taken from the generalized compressibility chart, Figure(3.11) corresponding to Tr2 and Pr2 (no unit)
//Part a: Using the Amagat's law of additive volumes
Zm=(y1*Z1_0)+(y2*Z2_0);//calculation of the compressibility of the mixture using Eq.(9.96) (no unit)
vm=(Zm*R*T)/(P*10^5);//calculation of the molar volume of the equimolar mixture in m^3/mol

//Calculation by Dalton's law of additive pressures
```

```
//The compressibility factors for the pure
   components are to be evaluated at the mixture
   temperature and pure component pressure in Dalton
   's law of additive pressures. As the pure
   component pressures are not known, they are
   assumed to be equal to the partial pressure
P1=y1*P;//pure component pressure in bar
P2=y2*P;//pure component pressure in bar
Pr1=P1/Pc(1,:);//calculation of reduced pressure of
   n-butane (no unit)
Pr2=P2/Pc(2,:);//calculation of reduced pressure of
   n-octane (no unit)
Z1_0=0.97;//value of Z1_0 taken from the generalized
    compressibility chart, Figure(3.11)
   corresponding to Tr1 and Pr1 (no unit)
Z2_0=0.91;//value of Z2_0 taken from the generalized
    compressibility chart, Figure(3.11)
   corresponding to Tr2 and Pr2 (no unit)
Zm=(y1*Z1_0)+(y2*Z2_0);//calculation of the
   compressibility of the mixture using Eq.(9.96) (
   no unit)
vm_dalton=(Zm*R*T)/(P*10^5);//calculation of the
   molar volume of the equimolar mixture in m^3/mol
//Recalculation of P1 and P2 to verify the initial
   assumption
P1=((Z1_0*y1*R*T)/(vm_dalton))*10^-2;//P1
   recalculated in bar
P2=((Z2_0*y2*R*T)/(vm_dalton))*10^-2;//P2
   recalculated in bar
Pr1=P1/Pc(1,:);//recalculation of reduced pressure
   of n-butane (no unit)
Pr2=P2/Pc(2,:);//recalculation of reduced pressure
   of n-octane (no unit)
Z1_0_new=0.97;//value of Z1_0_new taken from the
   generalized compressibility chart, Figure(3.11)
   corresponding to Tr1 and Pr1 (no unit)
Z2_0_new=0.91;//value of Z2_0_new taken from the
   generalized compressibility chart, Figure(3.11)
```

```
corresponding to Tr2 and Pr2 (no unit)
if Z1_0_new==Z1_0 & Z2_0_new==Z2_0 then
    vm_new=vm_dalton;//molar volume of the equimolar mixture in m^3/mol
else
    Zm=(y1*Z1_0_new)+(y2*Z2_0_new);//calculation of the compressibility of the mixture using Eq.(9.96) (no unit)
    vm_new=(Zm*R*T)/(P*10^5);//calculation of the molar volume of the equimolar mixture in m^3/mol
end

//OUTPUT
mprintf("\n The molar volume of an equimolar mixture of n-butane and n-octane found using the Amagats law of additive volumes = %0.4e m^3/mol\n",vm);
mprintf("\n The molar volume of an equimolar mixture of n-butane and n-octane found using the Daltons law of additive pressures = %0.2e m^3/mol\n",vm_new);

//===========================================END OF PROGRAM===============================================
```

---

**Scilab code Exa 9.10** Molar volume of an equimolar mixture using pseudocritical properties

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 10,Page 334
```

```
//Title: Molar volume of an equimolar mixture using pseudocritical properties
//

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
Tc=[425.2;569.4];//critical temperature of n-butane and n-octane in K
Pc=[37.97;24.97];//critical pressure of n-butane and n-octane in bar
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
Tcm=(y1*Tc(1,:))+(y2*Tc(2,:));//calculation of pseudocritical temperature of mixture using Eq.(9.100) in K
Pcm=(y1*Pc(1,:))+(y2*Pc(2,:));//calculation of pseudocritical pressure of mixture using Eq.(9.101) in bar
Trm=T/Tcm;//calculation of pseudoreduced temperature of the mixture using Eq.(9.102) (no unit)
Prm=P/Pcm;//calculation of pseudoreduced pressure of the mixture using Eq.(9.103) (no unit)
Zm0=0.9;//value of Zm0 is taken from the generalized compressibility chart, Figure(3.11)
```

```
    corresponding to Trm and Prm (no unit)
vm=(Zm0*R*T)/(P*10^5);//calculation of the molar volume of the equimolar mixture in m^3/mol

//OUTPUT
mprintf("\n The molar volume of an equimolar mixture of n-butane and n-octane using the pseudocritical properties estimated through Kays rule = %0.2e m^3/mol\n",vm);

//===============================================================END OF PROGRAM===============================================================
```

---

**Scilab code Exa 9.11** Molar volume of mixture using Prausnitz Gunn rule

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 11,Page 335
//Title: Molar volume of mixture using Prausnitz-Gunn rule
//
================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
```

```
Tc=[425.2;569.4];//critical temperature of n-butane and n-octane in K
Pc=[37.97;24.97];//critical pressure of n-butane and n-octane in bar
vc=[255.0*10^-6;486.0*10^-6];//critical molar volume of n-butane and n-octane in m^3/mol
Zc=[0.274;0.256];//compressibility factor of n-butane and n-octane corresponding to Tc,Pc (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
Tcm=(y1*Tc(1,:))+(y2*Tc(2,:));//calculation of pseudocritical temperature of mixture using Eq.(9.104) in K
Pcm=((R*((y1*Zc(1,:))+(y2*Zc(2,:)))*Tcm)/((y1*vc(1,:))+(y2*vc(2,:))))*10^-5;//calculation of the pseudocritical pressure of mixture using Eq.(9.105) in bar
Trm=T/Tcm;//calculation of pseudoreduced temperature using Eq.(9.102) (no unit)
Prm=P/Pcm;//calculation of pseudoreduced pressure using Eq.(9.103) (no unit)
Zm0=0.89;//value of Zm0 is taken from the generalized compressibility chart, Figure(3.11) corresponding to Trm and Prm (no unit)
vm=(Zm0*R*T)/(P*10^5);//calculation of the molar volume of the equimolar mixture in m^3/mol

//OUTPUT
mprintf("\n The molar volume of an equimolar mixture of n-butane and n-octane at 600K and 16bar
```

```
estimated using the Prausnitz-Gunn rule = %0.2e m^3/mol\n",vm);

//========================================================================END OF PROGRAM========================================================================
```

---

**Scilab code Exa 9.12** Molar volume of mixture using van der Waals equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 12,Page 335
//Title: Molar volume of mixture using van der Waals equation of state
//================================================================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
a_m=2.4405;//van der Waals constant for the mixture as determined in Example 9.8 in Pa(m^3/mol)^2
b_m=0.1767*10^-3;//van der Waals constant for the mixture as determined in Example 9.8 in m^3/mol
R=8.314;//universal gas constant in J/molK

```

```
//CALCULATION
//The problem is solved by using the Cardan's method
A=(a_m*P*10^5)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b_m*P*10^5)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1-B;//calculation of alpha for van der Waals equation of state using Table (3.2)
beeta=A;//calculation of beeta for van der Waals equation of state using Table (3.2)
gaamma=-(A*B);//calculation of gaamma for van der Waals equation of state using Table (3.2)
p=beeta-((alpha^2)/3);//calculation of p to determine the roots of the cubic equaton using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equaton using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=(((-(q)/2)+(sqrt(D)))^(1/3))+(((-(q)/2)-(sqrt(D)))^(1/3))-(alpha/3);//One real root given by  Eq.(3.32)
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Za=[Z1 Z2 Z3];
        Z=max(Za);
    else
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
```

```
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Za=[Z1 Z2 Z3];
        Z=max(Za);
    end
end
vm=(Z*R*T)/(P*10^5);//calculation of the molar volume of the equimolar mixture in m^3/mol

//OUTPUT
mprintf("\n The molar volume of an equimolar mixture of n-butane and n-octane at 600K and 16bar found using the van der Waals equation of state = %e m^3/mol\n",vm);

//===================================================END OF PROGRAM===================================================

// DISCLAIMER: VALUE OF Z COMPUTED IN PROGRAM IS NOT AS THAT REPORTED IN THE TEXTBOOK. HOWEVER, VALUES OF ALL OTHER PERTINENT VARIABLES A, B, alpha, beeta, p, q etc. AGREE WELL WITH THE TEXTBOOK ANSWER. COMPUTATION WAS ALSO VERIFIED MANUALLY AND GAVE THE ANSWER AS COMPUTED IN PROGRAM. ONE POSSIBLE REASON FOR DEVIATION COULD BE ROUND OFF ERROR.
```

**Scilab code Exa 9.13** Molar volume of mixture using the generalized virial coefficient correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 13,Page 336
//Title: Molar volume of mixture using the generalized virial coefficient correlation
//==================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
Bm=-309*10^-6;//second virial coefficient for the mixture taken from Example(9.7) in m^3/mol
R=8.314;//universal gas constant in J/molK

//CALCULATION
Zm=1+((Bm*P*10^5)/(R*T));//calculation of the compressibility factor for the mixture (no unit)
vm=(Zm*R*T)/(P*10^5);//calculation of the molar volume of the equimolar mixture in m^3/mol

//OUTPUT
mprintf("\n The molar volume of an equimolar mixture of n-butane and n-octane found using the generalized virial coefficient correlation = %0.4e m^3/mol\n",vm);

//============================================END OF PROGRAM============================================
```

---

**Scilab code Exa 9.14** Enthalpy and entropy departure

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 14,Page 337
//Title: Enthalpy and entropy departure
//================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
am=2.4405;//van der Waals constant for the mixture taken from Example 9.8 in Pa(m^3/mol)^2
bm=0.1767*10^-3;//van der Waals constant for the mixture taken from Example 9.8 in m^3/mol
vm=2.8933*10^-3;//molar volume of the mixture taken from Example 9.12 in m^3/mol
R=8.314;//universal gas constant in J/molK

//CALCULATION
dep_h=((P*10^5*vm)-(R*T)-(am/vm))*10^-3;//calculation of the enthalpy departure using Example(8.1) in kJ/mol
dep_s=R*(log ((P*10^5*(vm-bm))/(R*T)));//calculation of the entropy departure using Example(8.1) in J/molK
```

```

//OUTPUT
mprintf("\n The enthalpy departure of an equimolar mixture of n-butane and n-octane = %0.3f kJ/mol\n",dep_h);
mprintf("\n The entropy departure of an equimolar mixture of n-butane and n-octane = %0.3f J/mol K\n",dep_s);

//==================================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 9.15** Enthalpy and entropy departure using the generalized compressibility factor correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 15,Page 338
//Title: Enthalpy and entropy departure using the generalized compressibility factor correlation
//==========================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
```

```
Tcm=497.3;//pseudocritical temperature of mixture taken from Example(9.10) in K
Pcm=31.47;//pseudocritical pressure of mixture taken from Example(9.10) in bar
Trm=1.21;//pseudoreduced temperature of the mixture taken from Example(9.10) (no unit)
Prm=0.51;//pseudoreduced pressure of the mixture taken from Example(9.10) (no unit)
w_butane=0.199;//acentric factor for n-butane (no unit)
w_octane=0.398;//acentric factor for n-octane (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
wm=(y1*w_butane)+(y2*w_octane);//calculation of the acentric factor for the mixture (no unit)
del_h0=0.380;//value of ((h0-h)/RTcm)_0 read from Fig.(8.6) corresponding to Prm and Trm (no unit)
del_h1=0.188;//value of ((h0-h)/RTcm)_1 read from Fig.(8.8) corresponding to Prm and Trm (no unit)
del_s0=0.22;//value of ((s0-s)/R)_0 read from Fig.(8.10) corresponding to Prm and Trm (no unit)
del_s1=0.18;//value of ((s0-s)/R)_1 read from Fig.(8.12) corresponding to Prm and Trm (no unit)
dep_h=((R*Tcm)*(del_h0+(wm*del_h1)))*10^-3;//calculation of the enthalpy departure using Eq.(8.62) in kJ/mol
dep_s=(R)*(del_s0+(wm*del_s1));//calculation of the entropy departure using Eq.(8.65) in J/molK

//OUTPUT
```

```
mprintf("\n The enthalpy departure of an equimolar mixture of n-butane and n-octane using the generalized compressibility factor correlation = %0.3f kJ/mol\n",dep_h);
mprintf("\n The entropy departure of an equimolar mixture of n-butane and n-octane using the generalized compressibility factor correlation = %f J/mol K\n",dep_s);

//=====================================================================END OF PROGRAM======================================================================
```

---

**Scilab code Exa 9.16** Enthalpy and entropy departure using the virial coefficient correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 16,Page 339
//Title: Enthalpy and entropy departure using the virial coefficient correlation
//================================================================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
```

```
Tc=[425.2;569.4];//critical temperature of n-butane and n-octane in K
Pc=[37.97;24.97];//critical pressure of n-butane and n-octane in bar
w=[0.199;0.398];//acentric factor of n-butane and n-octane (no unit)
Tr1=1.411;//reduced temperature of n-butane (no unit) taken from Example (9.7)
Tr2=1.054;//reduced temperature of n-octane (no unit) taken from Example (9.7)
Tr_12=1.24;//reduced temperature for computing the mixture interaction virial coefficient (no unit) taken from Example(9.7)
Pc_12=2.978;//Pc_ij in MPa taken from Example(9.7)
Tc_12=483.9;//Tc_ij in K taken from Example(9.7)
w_12=0.2985;// w_ij (no unit) taken from Example (9.7)
Bm=-309*10^-6;//second virial coefficient in m^3/mol taken from Example (9.7)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
dB0_dTr1=0.675/(Tr1^2.6);//calculation of dBij0/dTrij using Eq.(8.73) (no unit)
dB0_dTr2=0.675/(Tr2^2.6);//calculation of dBij0/dTrij using Eq.(8.73) (no unit)
dB1_dTr1=0.722/(Tr1^5.2);//calculation of dBij1/dTrij using Eq.(8.74) (no unit)
dB1_dTr2=0.722/(Tr2^5.2);//calculation of dBij1/dTrij using Eq.(8.74) (no unit)
dB0_dTr12=0.675/(Tr_12^2.6);//calculation of dBij0/dTrij using Eq.(9.114) (no unit)
```

```
dB1_dTr12=0.722/(Tr_12^5.2);//calculation of dBij1/dTrij using Eq.(9.115) (no unit)
dB1_dT=(R/(Pc(1,:)*10^5))*((dB0_dTr1)+(w(1,:)*(dB1_dTr1)));//calculation of dBij/dT using Eq.(9.112) (m^3/molK)
dB2_dT=(R/(Pc(2,:)*10^5))*((dB0_dTr2)+(w(2,:)*(dB1_dTr2)));//calculation of dBij/dT using Eq.(9.112) (m^3/molK)
dB12_dT=(R/(Pc_12*10^6))*((dB0_dTr12)+(w_12*(dB1_dTr12)));//calculation of dBij/dT using Eq.(9.112) (m^3/molK)
dBm_dT=((y1^2)*(dB1_dT))+((2*y1*y2)*(dB12_dT))+((y2^2)*(dB2_dT));//calculation of dBm/dT using Eq.(9.110) (m^3/molK)
dep_h=((Bm-(T*dBm_dT))*P*10^5)*10^-3;//calculation of enthalpy departure using Eq.(8.69) in kJ/mol
dep_s=-P*10^5*(dBm_dT);//calculation of entropy departure using Eq.(8.70) in J/molK

//OUTPUT
mprintf("\n The enthalpy departure of an equimolar mixture of n-butane and n-octane using the virial coefficient correlation = %f kJ/mol\n",dep_h);
mprintf("\n The entropy departure of an equimolar mixture of n-butane and n-octane using the virial coefficient correlation = %0.3f J/mol K\n",dep_s);

//===================================================END OF PROGRAM===================================================
```

**Scilab code Exa 9.17** Fugacity and fugacity coefficient using van der Waals equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-9,Example 17,Page 340
//Title: Fugacity and fugacity coefficient using van
    der Waals equation of state
//
  ================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-
   octane mixture in K
P=16;//pressure of the equimolar n-butane and n-
   octane mixture in bar
a_m=2.4405;//van der Waals constant (a_m) in Pa(m^3/
   mol)^2 taken from Example(9.8)
b_m=0.1767*10^-3;//van der Waals constant (b_m) in m
   ^3/mol taken from Example(9.8)
Z=0.928;//compressibility factor taken from Example
   (9.12)
vm=2.8933*10^-3;//molar volume of the equimolar
   mixture in m^3/mol taken from Example(9.12)
R=8.314;//universal gas constant in J/molK

//CALCULATION
phi=exp (Z-1-log ((P*10^5*(vm-b_m))/(R*T))-(a_m/(R*T
   *vm)));//calculation of the fugacity coefficient
   (f/P) using the expression derived in Example 9.3
    (no unit)
f=phi*P;//calculation of fugacity using Eq.(9.37) in
    bar


//OUTPUT
```

```
mprintf("\n The fugacity coefficient of an equimolar mixture of n-butane and n-octane using the van der Waals equation of state = %0.4f \n",phi);
mprintf("\n The fugacity of an equimolar mixture of n-butane and n-octane using the van der Waals equation of state = %0.2f bar\n",f);

//===============================================END OF PROGRAM===============================================
```

---

**Scilab code Exa 9.18** Fugacity and fugacity coefficient using the pseudocritical constants method

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 18,Page 341
//Title: Fugacity and fugacity coefficient using the pseudocritical constants method
//==================================================================================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
Tcm=497.3;//pseudocritical temperature of mixture in K taken from Example(9.10)
```

```
Pcm=31.47;//pseudocritical pressure of mixture in bar taken from Example(9.10)
Trm=1.21;//pseudoreduced temperature of the mixture (no unit) taken from Example(9.10)
Prm=0.51;//pseudoreduced pressure of the mixture (no unit) taken from Example(9.10)
w=[0.199;0.398];//acentric factor of n-butane and n-octane (no unit)

//CALCULATION
wm=(w(1,:)+w(2,:))/2;//calculation of the acentric factor for the mixture (no unit)
log_phi0=-0.042;//value of log_phi0 taken from Figure(9.2) (no unit)
log_phi1=0.01;//value of log_phi1 taken from Figure (9.4) (no unit)
phi=10^(log_phi0+(wm*log_phi1));//calculation of the fugacity coefficient using Eq.(9.54) (no unit)
f=P*phi;//calculation of the fugacity using Eq.(9.37) in bar

//OUTPUT
mprintf("\n The fugacity coefficient of an equimolar mixture of n-butane and n-octane using the pseudocritical constants method = %0.3f \n",phi);
mprintf("\n The fugacity of an equimolar mixture of n-butane and n-octane using the pseudocritical constants method = %f bar\n",f);

//==========================================END OF PROGRAM==========================================
```

**Scilab code Exa 9.19** Fugacity and fugacity coefficient using the virial coefficient correlation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 19,Page 341
//Title: Fugacity and fugacity coefficient using the virial coefficient correlation
//================================================================================
clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
Bm=-309*10^-6;//second virial coefficient in m^3/mol taken from Example (9.7)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//Using Eq.(3.91) and Eq.(9.58) ln(phi)=BP/RT, which is used to compute phi
phi=(exp((Bm*P*10^5)/(R*T)));//calculation of the fugacity coefficient using the above expression (no unit)
f=phi*P;//calculation of the fugacity using Eq.(9.37) in bar

//OUTPUT
mprintf("\n The fugacity coefficient of an equimolar mixture of n-butane and n-octane using the virial coefficient correlation = %f \n",phi);
```

```
mprintf("\n The fugacity of an equimolar mixture of n-butane and n-octane using the virial coefficient correlation = %f bar\n",f);

//==============================================================END OF PROGRAM==============================================================

//DISCLAIMER: THE VALUE OF FUGACITY COEFFICIENT AS CALCULATED IN THE TEXTBOOK IS WRONG.THIS HAS BEEN CORRECTED IN THIS PROGRAM.
```

**Scilab code Exa 9.20** Fugacity coefficients of the components in a mixture using Redlich Kwong Equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 20,Page 344
//Title: Fugacity coefficients of the components in a mixture using Redlich-Kwong Equation of state
//==============================================================

clear
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
Tc=[425.2;569.4];//critical temperature of n-butane
```

```
and n-octane in K
Pc=[37.97;24.97];//critical pressure of n-butane and n-octane in bar
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
a1=(0.42748*R^2*Tc(1,:)^2.5)/(Pc(1,:)*10^5*sqrt(T));//calculation of Redlich-Kwong constant for n-butane in (m^6 Pa mol^-2)
a2=(0.42748*R^2*Tc(2,:)^2.5)/(Pc(2,:)*10^5*sqrt(T));//calculation of Redlich-Kwong constant for n-octane in (m^6 Pa mol^-2)
b1=(0.08664*R*Tc(1,:))/(Pc(1,:)*10^5);//calculation of Redlich-Kwong constant for n-butane in m^3/mol
b2=(0.08664*R*Tc(2,:))/(Pc(2,:)*10^5);//calculation of Redlich-Kwong constant for n-octane in m^3/mol
//Set Kij=0 and evaluate a using Eq.(9.64)
a=((y1^2)*a1)+(2*y1*y2*sqrt(a1*a2))+((y2^2)*a2);//calculation of Redlich-Kwong constant for the mixture using Eq.(9.64) in (m^6 Pa mol^-2)
b=(y1*b1)+(y2*b2);//calculation of Redlich-Kwong constant for the mixture using Eq.(9.65) in m^3/mol

//The Cardans method can be used to determine Z
A=(a*P*10^5)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*P*10^5)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1;//calculation of alpha for Redlich-Kwong equation of state using Table (3.2)
beeta=A-B-B^2;//calculation of beeta for Redlich-
```

```
Kwong equation of state using Table (3.2)
gaamma=-(A*B);//calculation of gaamma for Redlich-Kwong equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Za=[Z1 Z2 Z3];
        Z=max(Za);
    else
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Za=[Z1 Z2 Z3];
        Z=max(Za);
    end
end
//calculation of the fugacity coefficient of n-
```

```
butane in the mixture using Eq.(9.126) (no unit)
phi1=exp (((b1/b)*(Z-1))-log(Z-B)+((a/(b*R*T))*((b1/b)-(2*sqrt(a1/a)))*log((Z+B)/Z)));
//calculation of the fugacity coefficient of n-octane in the mixture using Eq.(9.126) (no unit)
phi2=exp (((b2/b)*(Z-1))-log(Z-B)+((a/(b*R*T))*((b2/b)-(2*sqrt(a2/a)))*log((Z+B)/Z)));

//OUTPUT
mprintf("\n The fugacity coefficient of n-butane in the equimolar mixture using the Redlich-Kwong Equation of state = %0.4f \n",phi1);
mprintf("\n The fugacity coefficient of n-octane in the equimolar mixture using the Redlich-Kwong Equation of state = %0.4f \n",phi2);

//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 9.21** Fugacity coefficients of the components in a mixture using the Virial Equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 21,Page 346
//Title: Fugacity coefficients of the components in a mixture using the Virial Equation of state
//==========================================================================
clear
```

```
clc

//INPUT
T=600;//temperature of the equimolar n-butane and n-octane mixture in K
P=16;//pressure of the equimolar n-butane and n-octane mixture in bar
B_11=-131*10^-6;//pure component (n-butane) second virial coefficient in m^3/mol taken from Example (9.7)
B_22=-577*10^-6;//pure component (n-octane) second virial coefficient in m^3/mol taken from Example (9.7)
B_12=-264*10^-6;//mixture interaction virial coefficient in m^3/mol taken from Example(9.7)
Bm=-309*10^-6;//second virial coefficient in m^3/mol taken from Example(9.7)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//For convenience, n-butane is taken as 1 and n-octane as 2
y1=0.5;//mole fraction of n-butane in the equimolar mixture
y2=0.5;//mole fraction of n-octane in the equimolar mixture
Zm=(1/2)*(1+sqrt(1+((4*Bm*P*10^5)/(R*T))));//calculation of compressibility for the mixture(Zm) using Eq.(9.136) (no unit)
phi1=exp((((2*P*10^5)/(Zm*R*T))*((y1*B_11)+(y2*B_12)))-log(Zm));//calculation of the fugacity coefficient of n-butane in the mixture using Eq.(9.135) (no unit)
phi2=exp((((2*P*10^5)/(Zm*R*T))*((y1*B_12)+(y2*B_22)))-log(Zm));//calculation of the fugacity coefficient of n-octane in the mixture using Eq.(9.135) (no unit)

```

```
//OUTPUT
mprintf("\n The fugacity coefficient of n-butane in the equimolar mixture using the Virial Equation of state = %0.3f \n",phi1);
mprintf("\n The fugacity coefficient of n-octane in the equimolar mixture using the Virial Equation of state = %f \n",phi2);

//==================================================END OF PROGRAM======================================================
```

---

**Scilab code Exa 9.22** Fugacity of liquid n octane

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-9,Example 22,Page 349
//Title: Fugacity of liquid n-octane
//================================================================================================================

clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
Psat=0.215;//saturation pressure of n-octane vapour at T in MPa
P=1;//pressure at which the fugacity of liquid n-octane is to be determined in MPa
f_sat=0.2368;//fugacity of n-octane vapour at T and Psat taken from Example(9.5) in MPa
```

```
vl=0.2003*10^-3;//molar volume of n-octane liquid at T and Psat taken from Example(3.16) in m^3/mol
R=8.314;//universal gas constant in J/molK

//CALCULATION
f_l=(0.2368*exp((vl*(P-Psat)*10^6)/(R*T)));//calculation of fugacity of n-octane liquid using Eq.(9.150) in MPa

//OUTPUT
mprintf("\n The fugacity of liquid n-octane at 427.85K and 1MPa = %0.4f MPa\n",f_l);

//=====================================================================END OF PROGRAM ====================================================================
```

# Chapter 10

# Stability and phase transition in thermodynamic systems

**Scilab code Exa 10.2** Number of degrees of freedom

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-10,Example 2,Page 369
//Title:Number of degrees of freedom
//================================================================================================================

clear
clc

//INPUT
P=2;//number of phases (no unit)
C=2;//number of components (no unit)

//CALCULATION
F=C+2-P;//calculation of the number of degrees of freedom using Eq.(10.35) (no unit)
```

```

//As the number of degrees of freedom is 2, two intensive properties of the system are to be specified to describe the thermodynamic state of the system.Therefore, the fundamental relation in the Gibbs free energy representation for this system is of the type G=G(T,P,N1,N2)

//OUTPUT
mprintf("\n The number of degrees of freedom = %d \n",F);
mprintf("Two intensive properties are required to be specified to describe the thermodynamic state of the system,and \nthe fundamental relation in the Gibbs free energy representation for this system is of the type, G=G(T,P,N1,N2)");

//==================================================END OF PROGRAM=======================================================
```

---

**Scilab code Exa 10.3** Vapour Pressure of n octane using the Peng Robinson equation of state

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-10,Example 3,Page 370
//Title:Vapour Pressure of n-octane using the Peng-Robinson equation of state
//=======================================================================================
```

```
clear
clc

//INPUT
T=427.85;//temperature of n-octane vapour in K
R=8.314;//universal gas constant in J/molK
Tc=569.4;//critical temperature of n-octane in K
Pc=24.97;//critical pressure of n-octane in bar
w=0.398;//acentric factor (no unit)

//CALCULATION
Pguess=0.215;//taking a guess value of vapour pressure (P) to check the criterion of equilibrium given by Eq.(10.37) in MPa
//Using the Cardans method to calculate Z_l and Z_v
Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=(Pguess*10^6)/(Pc*10^5);//calculation of reduced pressure (no unit)
S=0.37464+(1.54226*w)-(0.26992*w^2);//calculation of S using Eq.(3.79)
alpha1=(1+(S*(1-sqrt(Tr))))^2;//calculation of alpha1 using Eq.(3.78)
a=(0.45724*R^2*Tc^2*alpha1)/(Pc*10^5);//calculation of the Peng-Robinson constant in (m^6 Pa mol^-2) using Eq.(3.76)
b=(0.07780*R*Tc)/(Pc*10^5);//calculation of the Peng-Robinson constant in m^3/mol using Eq.(3.77)
A=(a*Pguess*10^6)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*Pguess*10^6)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1+B;//calculation of alpha for Peng-Robinson equation of state using Table (3.2)
beeta=A-(2*B)-(3*B^2);//calculation of beeta for Peng-Robinson equation of state using Table (3.2)
```

```
gaamma=-(A*B)+(B^2)+(B^3);//calculation of gaamma for Peng−Robinson equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
        Z_l=Z;
        Z_v=Z;
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        Z_l=min(Z);
        Z_v=max(Z);
    else
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        Z_l=min(Z);
```

```
        Z_v=max(Z);

    end
end
//calculation of fugacity coefficient for the liquid using Eq.(9.48) (no unit)
phi_l=exp (Z_l-1-log(Z_l-B)-((a/(2*sqrt(2)*b*R*T))*log((Z_l+(B*(1+sqrt(2))))/(Z_l+(B*(1-sqrt(2))))));
//calculation of fugacity coefficient for the vapour using Eq.(9.48) (no unit)
phi_v=exp (Z_v-1-log(Z_v-B)-((a/(2*sqrt(2)*b*R*T))*log((Z_v+(B*(1+sqrt(2))))/(Z_v+(B*(1-sqrt(2))))));
fl=Pguess*phi_l;//calculation of the fugacity of the liquid in MPa
fv=Pguess*phi_v;//calculation of the fugacity of the vapour in MPa
tolerance=1e-6;//defining the tolerance to compare fl and fv
if abs(fl-fv)<tolerance then
    P=Pguess;//the vapour pressure (in MPa) is taken as the guess value as the criterion of equilibrium given by Eq.(10.37) is established
else
    Prevised=Pguess*(fl/fv);//calculation of the revised value of P to check for the criterion of equilibrium given by Eq.(10.37) in MPa, if it fails for Pguess
while abs(fl-fv)>tolerance
    //Using the Cardans method to calculate Z_l and Z_v
Tr=T/Tc;//calculation of reduced temperature (no unit)
Pr=(Prevised*10^6)/(Pc*10^5);//calculation of reduced pressure (no unit)
S=0.37464+(1.54226*w)-(0.26992*w^2);//calculation of
```

```
S using Eq.(3.79)
alpha1=(1+(S*(1-sqrt(Tr))))^2;//calculation of alpha1 using Eq.(3.78)
a=(0.45724*R^2*Tc^2*alpha1)/(Pc*10^5);//calculation of the Peng-Robinson constant in m^6*Pa*mol^-2 using Eq.(3.76)
b=(0.07780*R*Tc)/(Pc*10^5);//calculation of the Peng-Robinson constant in m^3/mol using Eq.(3.77)
A=(a*Prevised*10^6)/(R*T)^2;//calculation of A to determine alpha,beeta and gaamma by using Eq.(3.25)
B=(b*Prevised*10^6)/(R*T);//calculation of B to determine alpha,beeta and gaamma by using Eq.(3.26)
alpha=-1+B;//calculation of alpha for Peng-Robinson equation of state using Table (3.2)
beeta=A-(2*B)-(3*B^2);//calculation of beeta for Peng-Robinson equation of state using Table (3.2)
gaamma=-(A*B)+(B^2)+(B^3);//calculation of gaamma for Peng-Robinson equation of state using Table (3.2)
p=beeta-(alpha^2)/3;//calculation of p to determine the roots of the cubic equation using Eq.(3.29)
q=((2*alpha^3)/27)-((alpha*beeta)/3)+gaamma;//calculation of q to determine the roots of the cubic equation using Eq.(3.30)
D=(((q)^2)/4)+(((p)^3)/27);//calculation of D to determine the nature of roots using Eq.(3.31)

if D>0 then
        Z=((-q/2)+(sqrt(D)))^(1/3)+((-q/2)-(sqrt(D)))^(1/3)-(alpha/3);//One real root given by  Eq.(3.32)
        Z_l=Z;
        Z_v=Z;
else if D==0 then
        Z1=((-2*(q/2))^(1/3))-(alpha/3);//Three real roots and two equal given by Eq.(3.33)
```

```
        Z2=((q/2)^(1/3))-(alpha/3);
        Z3=((q/2)^(1/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        Z_l=min(Z);
        Z_v=max(Z);
    else
        r=sqrt((-(p^3)/27));//calculation of r using Eq.(3.38)
        theta=acos((-(q)/2)*(1/r));//calculation of theta in radians using Eq.(3.37)
        Z1=(2*(r^(1/3))*cos(theta/3))-(alpha/3);
        Z2=(2*(r^(1/3))*cos(((2*%pi)+theta)/3))-(alpha/3);//Three unequal real roots given by Eqs.(3.34,3.35 and 3.36)
        Z3=(2*(r^(1/3))*cos(((4*%pi)+theta)/3))-(alpha/3);
        Z=[Z1 Z2 Z3];
        Z_l=min(Z);
        Z_v=max(Z);

    end
end
//calculation of fugacity coefficient for the liquid using Eq.(9.48) (no unit)
phi_l=exp (Z_l-1-log(Z_l-B)-((a/(2*sqrt(2)*b*R*T))*log((Z_l+(B*(1+sqrt(2))))/(Z_l+(B*(1-sqrt(2))))))
);
//calculation of fugacity coefficient for the vapour using Eq.(9.48) (no unit)
phi_v=exp (Z_v-1-log(Z_v-B)-((a/(2*sqrt(2)*b*R*T))*log((Z_v+(B*(1+sqrt(2))))/(Z_v+(B*(1-sqrt(2))))))
);
fl=Prevised*phi_l;//calculation of the fugacity of the liquid in MPa
fv=Prevised*phi_v;//calculation of the fugacity of the vapour in MPa
Prevised=Prevised*fl/fv;//updating the value of Prevised for the next iteration
```

```
end
P=Prevised;//the vapour pressure (in MPa) is taken
    as the revised value as the criterion of
    equilibrium given by Eq.(10.37) is established
end

//OUTPUT
mprintf("\n The vapour pressure of n-octane at
    427.85K = %f MPa\n",P);


//==========================================================END
    OF PROGRAM
   ==============================================================
```

---

# Chapter 11

# Properties of solutions

**Scilab code Exa 11.1** Pxy and Txy diagram for a Benzene Toluene system

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 1,Page 378
//Title:P-x-y and T-x-y diagram for a Benzene Toluene system
//================================================================================

clear
clc

//INPUT
antoine_const_benzene=[6.87987;1196.760;219.161];//Antoine's constants for Benzene from Table A.7
antoine_const_toluene=[6.95087;1342.310;219.187];//Antoine's constants for Toluene from Table A.7
t=95;//temperature at which the P-x-y diagram has to be prepared in degree celsius
P=101.325;//pressure at which the T-x-y diagram has
```

```
to be prepared in kPa

//CALCULATION
//P-x-y diagram:
//For convenience Benzene is denoted as 1 and Toluene as 2
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius

P1_s=10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(t+antoine_const_benzene(3,:))));//calculation of saturation pressure of benzene at t in Torr
P2_s=10^(antoine_const_toluene(1,:)-(antoine_const_toluene(2,:)/(t+antoine_const_toluene(3,:))));//calculation of saturation pressure of toluene at t in Torr
x1=0:0.1:1;//mole fraction of benzene in the liquid phase (no unit)
i=1;//iteration parameter
n=length(x1);//iteration parameter
while i<n |i==n
    P_tot(i)=P2_s+((P1_s-P2_s)*x1(:,i));//calculation of the total pressure using Eq.B, Page 379 in Torr
        y1(i)=(x1(:,i)*P1_s)/(P_tot(i));//calculation of the mole fraction of Benzene in the vapour phase (no unit)
      i=i+1;
end

//T-x-y diagram:
P=760;//converting pressure from kPa to Torr. 760 Torr=101.325 kPa
//calculation of the saturation temperature of benzene at P in degree celsius
t1_s=((antoine_const_benzene(2,:))/(
```

```
antoine_const_benzene(1,:)-log10(P)))-antoine_const_benzene(3,:);
//calculation of the saturation temperature of toluene at P in degree celsius
t2_s=((antoine_const_toluene(2,:))/(antoine_const_toluene(1,:)-log10(P)))-antoine_const_toluene(3,:);
//calculation of the saturation vapour pressures of Benzene (P1s) and Toluene (P2s)
//At T=t1_s, P=P1s=760.0 Torr, and at T=t2_s, P=P2s=760.0 Torr.
//X1 is given by X1=(P-P2s)/(P1s-P2s). Therefore at T=t1_s, X1=1.0 and at T=t2_s, X1=0.0
//As Y1=X1*P1s/P, Y1=1.0, when X1=1.0 and Y1=0.0, when X1=0.0.Therefore x1_initial=y1_initial=0.0(corresponding to t=t2_s) and x1_final=y1_final=1.0(corresponding to t=t1_s) where X1,x1_initial,x1_final are  the mole fractions of benzene in the liquid phase (no unit) and Y1,y1_initial,y1_final are the mole fractions of benzene in the vapour phase (no unit).
x1_initial=0.0;
y1_initial=0.0;
x1_final=1.0;
y1_final=1.0;
// An intermediate temperature is chosen such that t1_s<T<t2_s, and at different temperatures upto t2_s, the values of P1s, P2s, X1 and X1 are found out
T=85:5:105;//temepertaures at which P1s, P2s, X1 and Y1 are to be determined in degree celsius. The initial T is taken as 85 degree celsius, such that t1_s<T<t2_s
k=1;
l=length(T);
while k<l|k==l
P1s(k)=10^((antoine_const_benzene(1,:))-((antoine_const_benzene(2,:))/(T(:,k)+
```

```
antoine_const_benzene(3,:))));//calculation of saturation pressure of benzene in Torr
P2s(k)=10^((antoine_const_toluene(1,:))-((antoine_const_toluene(2,:))/(T(:,k)+antoine_const_toluene(3,:))));//caclculation of saturation pressure of toluene in Torr
    X1(k)=(P-P2s(k))/(P1s(k)-P2s(k));//calculation of mole fraction of Benzene in liquid phase (no unit)
    Y1(k)=(X1(k)*P1s(k))/P;//calculation of mole fraction of Benzene in vapour phase (no unit)
    k=k+1;
end
//Generating the T-x-y data
    j=1;
    while j<l+2|j==l+2
        if j==1 then
            temp(j)=t1_s;
            x1_benzene(j)=x1_final;
            y1_benzene(j)=y1_final;
        else if j==l+2 then
                temp(j)=t2_s;
                x1_benzene(j)=x1_initial;
                y1_benzene(j)=y1_initial;
            else
                temp(j)=T(j-1);
                x1_benzene(j)=X1(j-1);
                y1_benzene(j)=Y1(j-1);
            end
        end
        j=j+1;
    end

//OUTPUT
mprintf('P-x-y results \n');
i=1;
for i = 1 : n
      mprintf('x1=%f \t y1=%f\t P=%f Torr \n\n',x1(i
```

```
),y1(i),P_tot(i));
 end
 mprintf('T-x-y results \n t=%f degree celsius\t P1_s=760.0 Torr \t P2_s=(-) Torr \t\t x1=1.0 \t y1=1.0 \n\n',t1_s);
 k=1;
 for k= 1:l
      mprintf('t=%f degree celsius\t P1_s=%f Torr \t P2_s=%f Torr \t x1=%f \t y1=%f \n\n',T(k),P1s(k),P2s(k),X1(k),Y1(k));
 end
  mprintf('t=%f degree celsius\t P1_s=(-)Torr \t\t P2_s=760.0 Torr \t x1=0.0 \t y1=0.0 \n',t2_s);
  f1=scf(1);
  scf(f1);
plot(x1,P_tot,y1,P_tot);//generating the P-x-y plot
 xtitle('P-x-y diagram for benzene-toluene system at 95 degree celsius','x1,y1','P(Torr)');
 f2=scf(2);
 scf(f2);
 plot(x1_benzene,temp,y1_benzene,temp);//generating the T-x-y plot
 xtitle('T-x-y diagram for benzene-toluene sytem at 760 Torr','x1,y1','t (degree celsius)');

//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 11.2** Composition of liquid

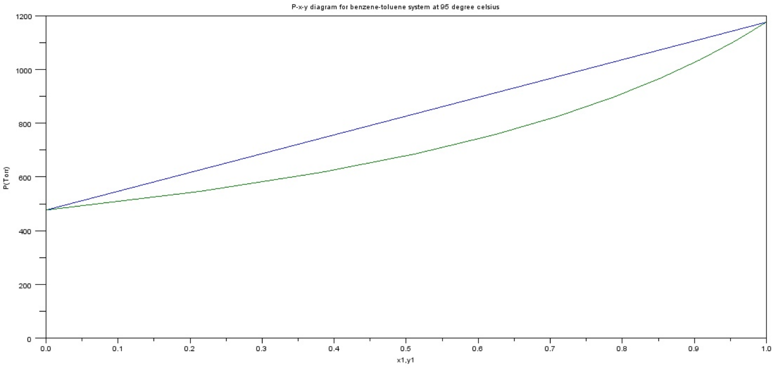

Figure 11.1: Pxy and Txy diagram for a Benzene Toluene system

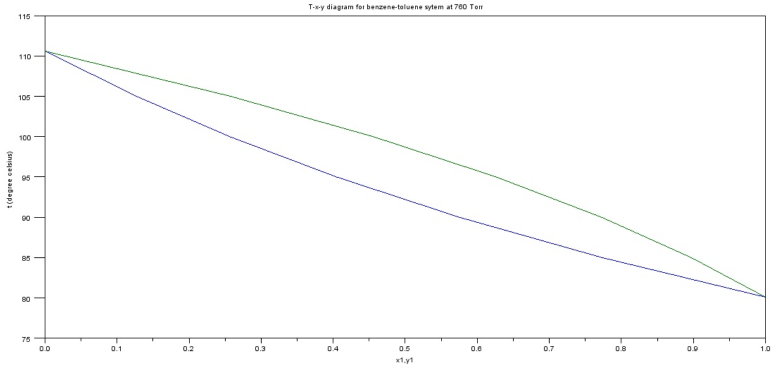

Figure 11.2: Pxy and Txy diagram for a Benzene Toluene system

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 2,Page 384
//Title:Composition of liquid
//================================================================================

clear
clc

//INPUT
//For convenience, benzene is taken as 1 and toluene as 2
T=95;//temperature of the equimolar vapour mixture of benzene and toluene in degree celsius
y1=0.5;//mole fraction of benzene in vapour phase (no unit)
y2=0.5;//mole fraction of toluene in vapour phase (no unit)
P1_s=1176.21;//saturation pressure of benzene at T, taken from Example 11.1 in Torr
P2_s=477.03;//saturation pressure of toluene at T, taken from Example 11.1 in Torr

//CALCULATION
P=1/((y1/P1_s)+(y2/P2_s));//calculation of the total pressure using Eq.(11.21) in Torr
x1=(y1*P)/P1_s;//calculation of mole fraction of benzene in liquid phase using Eq.(11.15)(no unit)
x2=1-x1;//calculation of mole fraction of toluene in liquid phase using Eq.(11.15)(no unit)

//OUTPUT
mprintf('The composition of the liquid which is in equilibrium with the equimolar vapour mixture of benzene and toluene at 95 degree celsius is \n
```

```
mole fraction of benzene in liquid phase (x1)=%f \n mole fraction of toluene in liquid phase (x2)=%f \n',x1,x2);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 11.3** Bubble temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 3,Page 384
//Title:Bubble temperature
//==================================================================================================================

clear
clc

//INPUT
//For convenience, benzene is taken as 1 and toluene as 2
P=760;//pressure of the binary liquid mixture of benzene and toluene in Torr
x1=0.4047;//mole fraction of benzene in liquid phase (no unit)
antoine_const_benzene=[6.87987;1196.760;219.161];//Antoine's constants for Benzene from Table A.7
antoine_const_toluene=[6.95087;1342.310;219.187];//Antoine's constants for Toluene from Table A.7

```

```
//CALCULATION

//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
//Based on the procedure given in the texbook, the criterion of summation of (y_i)=1.0 will be checked, where y_i=(x_i*Pi_s)/P, where Pi_s is the saturation pressure obtained from the Antoine's equation.

x2=1-x1;//mole fraction of toluene in liquid phase (no unit)
tol=1e-6;//tolerance limit for convergence of the system using fsolve
tguess=100;//taking a guess value for the bubble temperature to be used in the fsolve function in degree celsius
function[fn]=solver_func(ti)
 fn=(((x1/P)*(10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(ti+antoine_const_benzene(3,:))))))+((x2/P)*(10^(antoine_const_toluene(1,:)-(antoine_const_toluene(2,:)/(ti+antoine_const_toluene(3,:)))))))-1.0;//Function defined for solving the system
endfunction
[t]=fsolve(tguess,solver_func,tol)//using inbuilt function fsolve for solving the system of equations

//OUTPUT
mprintf('The bubble temperature of a binary liquid mixture of benzene and toluene at 760 Torr=%d degree celsius \n',t);

//==================================================END OF PROGRAM
```

**Scilab code Exa 11.4** Dew temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .

//Chapter-11,Example 4,Page 385
//Title:Dew temperature
//
   ================================================================================

clear
clc

//INPUT
//For convenience, benzene is taken as 1 and toluene
    as 2
P=760;//pressure of the binary liquid mixture of
   benzene and toluene in Torr
y1=0.6263;//mole fraction of benzene in vapour phase
    (no unit)
antoine_const_benzene=[6.87987;1196.760;219.161];//
   Antoine's constants for Benzene from Table A.7
antoine_const_toluene=[6.95087;1342.310;219.187];//
   Antoine's constants for Toluene from Table A.7

//CALCULATION

//The form of the Antoine's equation used is logP=A
   -(B/(t+C)), where P is in Torr and t is in degree
    celsius
//Based on the procedure given in the texbook, the
```

```
criterion of summation of (x_i)=1.0 will be checked, where x_i=(y_i*P)/(Pi_s), Pi_s is the saturation pressure obtained from the Antoine's Equation.

y2=1-y1;//mole fraction of toluene in vapour phase (no unit)
tol=1e-6;//tolerance limit for convergence of the system using fsolve
tguess=100;//taking a guess value for the dew temperature to be used in the fsolve function in degree celsius
function[fn]=solver_func(ti)
 fn=(((y1*P)/(10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(ti+antoine_const_benzene(3,:))))))+((y2*P)/(10^(antoine_const_toluene(1,:)-(antoine_const_toluene(2,:)/(ti+antoine_const_toluene(3,:)))))))-1.0;//Function defined for solving the system
endfunction
[t]=fsolve(tguess,solver_func,tol)//using inbuilt function fsolve for solving the system of equations

//OUTPUT
mprintf('The dew temperature of a binary vapour mixture of benzene and toluene at 760 Torr=%d degree celsius \n',t);

//=========================================================================END OF PROGRAM==========================================================================
```

**Scilab code Exa 11.5** Composition of the liquid and vapor streams leaving the flash unit

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 5,Page 386
//Title:Composition of the liquid and vapor streams leaving the flash unit
//================================================================================

clear
clc

//INPUT
//For convenience, n-pentane is taken as 1 , n-hexane as 2, and n-heptane as 3
P=200;//pressure at which the flash vaporizer is maintained in kPa
T=90;//temperature at which the flash vaporizer is maintained in degree celsius
zf1=0.3//mole fraction of n-pentane in feed stream (no unit)
zf2=0.3//mole fraction of n-hexane in feed stream (no unit)
zf3=0.4//mole fraction of n-heptane in feed stream (no unit)
antoine_const_pentane=[6.87632;1075.780;233.205];//Antoine's constants for n-pentane from Table A.7
antoine_const_hexane=[6.91058;1189.640;226.280];//Antoine's constants for n-hexane from Table A.7
antoine_const_heptane=[6.89386;1264.370;216.640];//Antoine's constants for n-heptane from Table A.7

//CALCULATION

```

```
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
P1_s=10^(antoine_const_pentane(1,:)-(antoine_const_pentane(2,:)/(T+antoine_const_pentane(3,:))));//calculation of saturation pressure of n-pentane at T in Torr
P1_s=P1_s*133.322*10^-3;//conversion from Torr to kPa
P2_s=10^(antoine_const_hexane(1,:)-(antoine_const_hexane(2,:)/(T+antoine_const_hexane(3,:))));//calculation of saturation pressure of n-hexane at T in Torr
P2_s=P2_s*133.322*10^-3;//conversion from Torr to kPa
P3_s=10^(antoine_const_heptane(1,:)-(antoine_const_heptane(2,:)/(T+antoine_const_heptane(3,:))));//calculation of saturation pressure of n-heptane at T in Torr
P3_s=P3_s*133.322*10^-3;//conversion from Torr to kPa
K1=P1_s/P;//calculation of K factor using Eq.(11.22)(no unit)
K2=P2_s/P;//calculation of K factor using Eq.(11.22)(no unit)
K3=P3_s/P;//calculation of K factor using Eq.(11.22)(no unit)
tol=1e-6;//tolerance limit for convergence of the system using fsolve
L_F_guess=0.1;//taking a guess value for the L/F ratio, where L is the mole number of liquid stream leaving the unit at T and P, and F is the mole number of feed stream
function[fn]=solver_func(L_F)
 fn=((zf1/((L_F)+((1-L_F)*K1)))+(zf2/((L_F)+((1-L_F)*K2)))+(zf3/((L_F)+((1-L_F)*K3))))-1.0;//Function defined for solving the system
endfunction
```

```
[L_F]=fsolve(L_F_guess,solver_func,tol)//using inbuilt function fsolve for solving the system of equations
x1=(zf1/((L_F)+((1-L_F)*K1)));//calculation of mole fraction of n-pentane in liquid stream leaving the unit at T and P (no unit)
x2=(zf2/((L_F)+((1-L_F)*K2)));//calculation of mole fraction of n-hexane in liquid stream leaving the unit at T and P (no unit)
x3=(zf3/((L_F)+((1-L_F)*K3)));//calculation of mole fraction of n-heptane in liquid stream leaving the unit at T and P (no unit)
y1=K1*x1;//calculation of mole fraction of n-pentane in the vapour stream leaving the unit at T and P (no unit)
y2=K2*x2;//calculation of mole fraction of n-hexane in the vapour stream leaving the unit at T and P (no unit)
y3=K3*x3;//calculation of mole fraction of n-heptane in the vapour stream leaving the unit at T and P (no unit)
V_F=1-(L_F);//calculation of the fraction that has vaporized

//OUTPUT
mprintf('The composition of the liquid leaving the flash unit is : x1=%f \t\t x2=%f \t\t x3=%f\n',x1,x2,x3);
mprintf('The composition of the vapour leaving the flash unit is : y1=%f \t\t y2=%f \t\t y3=%f\n',y1,y2,y3);
mprintf('The fraction of feed that has vaporized in the unit=%f \n ',V_F);

//====================================================================END OF PROGRAM========================================================================
```

## Scilab code Exa 11.7 Activity coefficients

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 7,Page 397
//Title:Activity coefficients
//================================================================

clear
clc

//INPUT
//For convenience, nitromethane is taken as 1 and carbon tetrachloride as 2
T=45;//temperature of the mixture in degree celsius
A=2.230;//van laar constant for the system at T (no unit)
B=1.959;//van laar constant for the system at T (no unit)
n1=30;//mole percentage of nitromethane in the mixture ( in percentage)

//CALCULATION
n2=100-n1;//calculation of mole percentage of carbon tetrachloride in the mixture (in percentage)
x1=n1/100;//calculation of mole fraction of nitromethane in the mixture (no unit)
x2=1-x1;//calculation of mole fraction of carbon tetrachloride in the mixture(no unit)
gaamma1=exp (A/(1+((A/B)*(x1/x2)))^2);//calculation of activity coefficient using Eq.(11.82) (no unit
```

```
)
gaamma2=exp (B/(1+((B/A)*(x2/x1)))^2);//calculation of activity coefficient using Eq.(11.83) (no unit )

//OUTPUT
mprintf('The activity coefficients for the system using van laar equation is : gamma1=%f \t gamma2=%f \t\n ', gaamma1,gaamma2);

//==========================================================END OF PROGRAM==============================================================
```

---

**Scilab code Exa 11.8** van Laar constants and Activity coefficients

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 8,Page 397
//Title:van Laar constants and Activity coefficients
//================================================================================

clear
clc

//INPUT
//For convenience, ethanol is taken as 1 and benzene as 2
n_azeo=44.8;//azeotropic composition given as mole percentage
Tb=68.24;//boiling point of mixture in degree
```

```
celsius
P=760;//pressure in Torr
P1_s=506;//saturation pressure of ethanol at Tb in Torr
P2_s=517;//saturation pressure of benzene at Tb in Torr
n1=10;//mole percentage of ethanol in the mixture (in percentage)

//CALCULATION
//At azeotropic composition, y_i=x_i, therefore gaamma_i=P/Pi_s
x1=n_azeo/100;//calculation of the mole fraction of ethanol (azeotropic composition) (no unit)
x2=1-x1;//calculation of the mole fraction of benzene (azeotropic composition) (no unit)
gaamma1=P/P1_s;//calculation of the activity coefficient at the azeotropic composition (no unit)
gaamma2=P/P2_s;//calculation of the activity coefficient at the azeotropic composition (no unit)
A=log(gaamma1)*(1+((x2*log(gaamma2))/(x1*log(gaamma1))))^2;//calculation of the van Laar constant using Eq.(11.84) (no unit)
B=log(gaamma2)*(1+((x1*log(gaamma1))/(x2*log(gaamma2))))^2;//calculation of the van Laar constant using Eq.(11.85) (no unit)
x1=n1/100;//calculation of the mole fraction of ethanol (no unit)
x2=1-x1;//calculation of the mole fraction of benzene (no unit)
gaamma1=exp (A/(1+((A/B)*(x1/x2)))^2);//calculation of activity coefficient at the given composition using Eq.(11.82) (no unit)
gaamma2=exp (B/(1+((B/A)*(x2/x1)))^2);//calculation of activity coefficient at the given composition using Eq.(11.83) (no unit)
```

```


//OUTPUT
mprintf('The van Laar constants for the system are : A=%f \t B=%f \n',A,B)
mprintf('The activity coefficients for the system using van laar equation are : gamma1=%f \t gamma2=%f \t\n ', gaamma1,gaamma2);

//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 11.9** Activity coefficients using the Wilsons parameters

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 9,Page 399
//Title: Activity coefficients using the Wilson's parameters
//================================================================================================

clear
clc

//INPUT
//For convenience, nitromethane is taken as 1 and carbon tetrachloride as 2
T=45;//temperature of the system in degree celsius
A_12=0.1156;//Wilson's parameter for the system at T (no unit)
```

```
A_21=0.2879;//Wilson's parameter for the system at T
    (no unit)
x1=0.3;//mole fraction of nitromethane in the liquid
    mixture (no unit)

//CALCULATION
x2=1-x1;//calculation of the mole fraction of carbon
    tetrachloride in the liquid mixture (no unit)
ln_gaamma1=-log(x1+(A_12*x2))+(x2*((A_12/(x1+(A_12*
   x2)))-(A_21/((A_21*x1)+x2))));//calculation of ln
   (activity coefficient) using Eq.(11.89) (no unit)
gaamma1=exp(ln_gaamma1);//calculation of activity
   coefficient (no unit)
ln_gaamma2=-log(x2+(A_21*x1))-(x1*((A_12/(x1+(A_12*
   x2)))-(A_21/((A_21*x1)+x2))));//calculation of ln
   (activity coefficient) using Eq.(11.90) (no unit)
gaamma2=exp(ln_gaamma2);//calculation of activity
   coefficient (no unit)

//OUTPUT

mprintf('The activity coefficients for the system
   using Wilsons parameters are : gamma1=%f \t
   gamma2=%f \t\n ', gaamma1,gaamma2);

//=========================================END
    OF PROGRAM
   ================================================
```

---

**Scilab code Exa 11.10** Activity coefficients using the UNIQUAC equation

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
   .
```

```

//Chapter-11,Example 10,Page 401
//Title: Activity coefficients using the UNIQUAC equation
//================================================================
clear
clc

//INPUT
//For convenience, ethanol is taken as 1 and benzene as 2
T=345;//temperature of the mixture in K
x1=0.8;//mole fraction of ethanol in the liquid phase (no unit)

//Ethanol (CH3CH2OH) has 1 CH3 group, 1 CH2 group and 1 OH group, while Benzene has 6 ACH groups. The group identification and the parameters R_k and Q_k are given below:
//Molecule: Ethanol : Group identification: Name: CH3, Main No. 1, Sec.No.1, Name: CH2, Main No. 1, Sec.No.2, Name: OH, Main No.5 ,Sec.No.14
//Molecule: Benzene : Group identification: Name: ACH, Main No. 3, Sec.No. 9
nu_ki=[1;1;1;6];//number of groups of type: CH3, CH2, OH and ACH respectively (no unit)
R_k=[0.9011;0.6744;1.0000;0.5313];//Group volume parameter for CH3, CH2, OH and ACH respectively (no unit)
Q_k=[0.848;0.540;1.200;0.400];//Area parameter for CH3, CH2, OH and ACH respectively (no unit)
R=8.314;//universal gas constant in J/molK
u12_u22=-241.2287;//UNIQUAC parameter for the system in J/molK
u21_u11=2799.5827;//UNIQUAC parameter for the system in J/molK
```

```
z=10;//co-ordination number usually taken as 10 (no unit)

//CALCULATION
x2=1-x1;//calculation of mole fraction of benzene in liquid phase (no unit)
r1=(nu_ki(1,:)*R_k(1,:))+(nu_ki(2,:)*R_k(2,:))+(nu_ki(3,:)*R_k(3,:));//calculation of volume parameter using Eq.(11.108) (no unit)
r2=(nu_ki(4,:)*R_k(4,:));//calculation of volume parameter using Eq.(11.108) (no unit)
phi1=(x1*r1)/((x1*r1)+(x2*r2));//calculation of volume fraction of component using Eq.(11.101) (no unit)
phi2=(x2*r2)/((x2*r2)+(x1*r1));//calculation of volume fraction of component using Eq.(11.101) (no unit)
q1=(nu_ki(1,:)*Q_k(1,:))+(nu_ki(2,:)*Q_k(2,:))+(nu_ki(3,:)*Q_k(3,:))//calculation of surface area parameter using Eq.(11.109) (no unit)
q2=(nu_ki(4,:)*Q_k(4,:))//calculation of surface area parameter using Eq.(11.109) (no unit)
theta1=(x1*q1)/((x1*q1)+(x2*q2));//calculation of area fraction of component using Eq.(11.102) (no unit)
theta2=(x2*q2)/((x1*q1)+(x2*q2));//calculation of area fraction of component using Eq.(11.102) (no unit)
l1=((z/2)*(r1-q1))-(r1-1);//calculation of l_i using Eq.(11.107) (no unit)
l2=((z/2)*(r2-q2))-(r2-1);//calculation of l_i using Eq.(11.107) (no unit)
tau_12=exp(-(u12_u22)/(R*T));//calculation of the adjustable parameter using Eq.(11.103) (no unit)
tau_21=exp(-(u21_u11)/(R*T));//calculation of the adjustable parameter using Eq.(11.103) (no unit)
tau_11=1.0;//by convention taken as 1.0
tau_22=1.0;//by convention taken as 1.0
```

```
//calculation of the combinatorial part of the activity coefficient using Eq.(11.105) (no unit)
ln_gaamma1_c=log(phi1/x1)+((z/2)*q1*log(theta1/phi1))+l1-((phi1/x1)*((x1*l1)+(x2*l2)));
//calculation of the combinatorial part of the activity coefficient using Eq.(11.105) (no unit)
ln_gaamma2_c=log(phi2/x2)+((z/2)*q2*log(theta2/phi2))+l2-((phi2/x2)*((x1*l1)+(x2*l2)));
//calculation of the residual part of the activity coefficient using Eq.(11.106) (no unit)
ln_gaamma1_r=q1*(1-log((theta1*tau_11)+(theta2*tau_21))-(((theta1*tau_11)/((theta1*tau_11)+(theta2*tau_21)))+((theta2*tau_12)/((theta1*tau_12)+(theta2*tau_22)))));
//calculation of the residual part of the activity coefficient using Eq.(11.106) (no unit)
ln_gaamma2_r=q2*(1-log((theta1*tau_12)+(theta2*tau_22))-(((theta1*tau_21)/((theta1*tau_11)+(theta2*tau_21)))+((theta2*tau_22)/((theta1*tau_12)+(theta2*tau_22)))));
ln_gaamma1=ln_gaamma1_c+ln_gaamma1_r;//calculation of the ln(activity coefficient) using Eq.(11.104) (no unit)
ln_gaamma2=ln_gaamma2_c+ln_gaamma2_r;//calculation of the ln(activity coefficient) using Eq.(11.104) (no unit)
gaamma1=exp(ln_gaamma1);//calculation of the activity coefficient (no unit)
gaamma2=exp(ln_gaamma2);//calculation of the activity coefficient (no unit)

//OUTPUT

mprintf('The activity coefficients for the system using the UNIQUAC equation are : gamma1=%f \t gamma2=%f \t\n ', gaamma1,gaamma2);

//==================================================================END
```

```
OF PROGRAM
=====================================================
```

---

**Scilab code Exa 11.11** Activity coefficients using the UNIFAC method

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-11,Example 11,Page 405
//Title: Activity coefficients using the UNIFAC method
//================================================================================

clear
clc

//INPUT
//For convenience, acetone is taken as 1 and n-pentane as 2
T=307;//temperature of the mixture in K
x1=0.3;//mole fraction of acetone in the liquid phase (no unit)

//Acetone (CH3COCH3) has 1 CH3 group and 1 CH3CO group, while n-Pentane (C5H12) has 2 CH3 groups and 3 CH2 groups.
//The group identification and the parameters R_k and Q_k are given below:
//Componenet: Acetone : Group identification: Name: CH3, Main No. 1, Sec.No. 1, Name: CH3CO, Main No. 9, Sec.No. 18
//Component: n-Pentane : Group identification: Name:
```

```
CH3, Main No. 1, Sec.No. 1, Name: CH2, Main No. 1, Sec.No. 2
nu_ki=[1;1;2;3];//no.of groups of type : CH3, CH3CO, CH3, CH2 respectively in the two components making up the systen (no unit)
R_k=[0.9011;1.6724;0.6744];//Group volume parameter for CH3, CH3CO and CH2 respectively (no unit)
Q_k=[0.848;1.488;0.540];//Area parameter for CH3, CH3CO and CH2 respectively (no unit)
a_19=476.40;//group interaction parameter for the system in K
a_91=26.760;//group interaction parameter for the system in K
z=10;//co-ordination number usually taken as 10 (no unit)

//CALCULATION
x2=1-x1;//calculation of mole fraction of benzene in liquid phase (no unit)
r1=(nu_ki(1,:)*R_k(1,:))+(nu_ki(2,:)*R_k(2,:));//calculation of volume parameter using Eq.(11.108) (no unit)
r2=(nu_ki(3,:)*R_k(1,:))+(nu_ki(4,:)*R_k(3,:));//calculation of volume parameter using Eq.(11.108) (no unit)
phi1=(x1*r1)/((x1*r1)+(x2*r2));//calculation of volume fraction of component using Eq.(11.101) (no unit)
phi2=(x2*r2)/((x2*r2)+(x1*r1));//calculation of volume fraction of component using Eq.(11.101) (no unit)
q1=(nu_ki(1,:)*Q_k(1,:))+(nu_ki(2,:)*Q_k(2,:))//calculation of surface area parameter using Eq.(11.109) (no unit)
q2=(nu_ki(3,:)*Q_k(1,:))+(nu_ki(4,:)*Q_k(3,:))//calculation of surface area parameter using Eq.(11.109) (no unit)
theta1=(x1*q1)/((x1*q1)+(x2*q2));//calculation of
```

```
area fraction of component using Eq.(11.102) (no unit)
theta2=(x2*q2)/((x1*q1)+(x2*q2));//calculation of area fraction of component using Eq.(11.102) (no unit)
l1=((z/2)*(r1-q1))-(r1-1);//calculation of l_i using Eq.(11.107) (no unit)
l2=((z/2)*(r2-q2))-(r2-1);//calculation of l_i using Eq.(11.107) (no unit)
//calculation of the combinatorial part of the activity coefficient using Eq.(11.105) (no unit)
ln_gaamma1_c=log(phi1/x1)+((z/2)*q1*log(theta1/phi1))+l1-((phi1/x1)*((x1*l1)+(x2*l2)));
//calculation of the combinatorial part of the activity coefficient using Eq.(11.105) (no unit)
ln_gaamma2_c=log(phi2/x2)+((z/2)*q2*log(theta2/phi2))+l2-((phi2/x2)*((x1*l1)+(x2*l2)));
a_11=0;//by convention taken as 0.0,in K
a_99=0;//by convention taken as 0.0,in K
psi_19=exp(-(a_19)/(T));//calculation of psi_mn using Eq.(11.119) (no unit)
psi_91=exp(-(a_91)/(T));//calculation of psi_mn using Eq.(11.119) (no unit)
psi_11=1;//as a_11=0, psi_11=1 (no unit)
psi_99=1;//as a_99=0, psi_99=1 (no unit)
//calculation of the residual activity coefficient(tau_k) of group k, in a reference solution containing molecules of type i
x1_1=nu_ki(1,:)/(nu_ki(1,:)+nu_ki(2,:));//calculation of mole fraction of CH3 group (pure acetone(1)) (no unit)
x1_18=nu_ki(2,:)/(nu_ki(1,:)+nu_ki(2,:));//calculation of mole fraction of CH3CO group (pure acetone(1)) (no unit)
theta1_1=(Q_k(1,:)*x1_1)/((Q_k(1,:)*x1_1)+(Q_k(2,:)*x1_18));//calculation of surface area fraction of CH3 group (pure acetone) using Eq.(11.118) (no unit)
```

```
theta1_18=(Q_k(2,:)*x1_18)/((Q_k(2,:)*x1_18)+(Q_k(1,:)*x1_1));//calculation of surface area fraction of CH3CO group (pure acetone) using Eq.(11.118) (no unit)
//calculation of the residual activity coefficient(tau_k(i))of CH3 group,in a reference solution of (pure acetone) using Eq.(11.117)(no unit)
ln_tau1_1=Q_k(1,:)*(1-log((theta1_1*psi_11)+(theta1_18*psi_91))-(((theta1_1*psi_11)/((theta1_1*psi_11)+(theta1_18*psi_91)))+((theta1_18*psi_19)/((theta1_1*psi_19)+(theta1_18*psi_11)))));
//calculation of the residual activity coefficient(tau_k(i))of CH3CO group,in a reference solution of (pure acetone) using (Eq.11.117)(no unit)
ln_tau1_18=Q_k(2,:)*(1-log((theta1_1*psi_19)+(theta1_18*psi_99))-(((theta1_1*psi_91)/((theta1_1*psi_99)+(theta1_18*psi_91)))+((theta1_18*psi_99)/((theta1_1*psi_19)+(theta1_18*psi_99)))));
x2_1=nu_ki(3,:)/(nu_ki(3,:)+nu_ki(4,:));//calculation of mole fraction of CH3 group (pure n-pentane(2)) (no unit)
x2_2=nu_ki(4,:)/(nu_ki(3,:)+nu_ki(4,:));//calculation of mole fraction of CH2 group (pure n-pentane(2)) (no unit)
//As n-pentane contains only one main group (1)
ln_tau2_1=0;
ln_tau2_2=0;
//calculation of group residual activity coefficients for the given mole fraction of acetone in liquid phase (x1)(no unit)
//calculation of group mole fraction for CH3 group in Acetone and n-pentane using Eq.(11.115)(no unit)
x_1=((x1*nu_ki(1,:))+(x2*nu_ki(3,:)))/((((x1*nu_ki(1,:))+(x1*nu_ki(2,:))))+((x2*nu_ki(3,:))+(x2*nu_ki(4,:))));
//calculation of group mole fraction for CH2 group in n-Pentane using Eq.(11.115)(no unit)
```

```
x_2=((x2*nu_ki(4,:)))/((((x1*nu_ki(1,:))+(x1*nu_ki(2,:))))+((x2*nu_ki(3,:))+(x2*nu_ki(4,:))));
//calculation of group mole fraction for CH3CO group in Acetone using Eq.(11.115)(no unit)
x_18=((x1*nu_ki(2,:)))/((((x1*nu_ki(1,:))+(x1*nu_ki(2,:))))+((x2*nu_ki(3,:))+(x2*nu_ki(4,:))));
theta_1=(Q_k(1,:)*x_1)/((Q_k(1,:)*x_1)+(Q_k(2,:)*x_18)+(Q_k(3,:)*x_2));//calculation of surface area fraction of CH3 group (using Eq.11.118)(no unit)
theta_2=(Q_k(3,:)*x_2)/((Q_k(1,:)*x_1)+(Q_k(2,:)*x_18)+(Q_k(3,:)*x_2));//calculation of surface area fraction of CH2 group (using Eq.11.118)(no unit)
theta_18=(Q_k(2,:)*x_18)/((Q_k(1,:)*x_1)+(Q_k(2,:)*x_18)+(Q_k(3,:)*x_2));//calculation of surface area fraction of CH3CO group (using Eq.11.118)(no unit)
//calculation of group residual activity coefficient of CH3 using Eq.(11.117)(no unit)
ln_tau_1=Q_k(1,:)*(1-log((theta_1*psi_11)+(theta_2*psi_11)+(theta_18*psi_91))-((((theta_1*psi_11)+(theta_2*psi_11))/((((theta_1*psi_11)+(theta_2*psi_11))+(theta_18*psi_91)))+((theta_18*psi_19)/((theta_1*psi_19)+(theta_2*psi_19)+(theta_18*psi_11))))));
//calculation of group residual activity coefficient of CH2 using Eq.(11.117)(no unit)
ln_tau_2=Q_k(3,:)*(1-log((theta_1*psi_11)+(theta_2*psi_11)+(theta_18*psi_91))-((((theta_1*psi_11)+(theta_2*psi_11))/((((theta_1*psi_11)+(theta_2*psi_11))+(theta_18*psi_91)))+((theta_18*psi_19)/((theta_1*psi_19)+(theta_2*psi_19)+(theta_18*psi_11))))));
//calculation of group residual activity coefficient of CH3CO using Eq.(11.117)(no unit)
ln_tau_18=Q_k(2,:)*(1-log((theta_1*psi_19)+(theta_2*psi_19)+(theta_18*psi_99))-(((((theta_1+theta_2)*
```

```
psi_91)/((theta_1*psi_11)+(theta_2*psi_11)+(theta_18*psi_91)))+((theta_18*psi_99)/((theta_1*psi_19)+(theta_2*psi_19)+(theta_18*psi_11))))));
//calculation of the residual contributions to the activity coefficients using Eq.(11.116)(no unit)
ln_gaamma1_r=(nu_ki(1,:)*(ln_tau_1-ln_tau1_1))+(nu_ki(2,:)*(ln_tau_18-ln_tau1_18));
ln_gaamma2_r=(nu_ki(3,:)*(ln_tau_1-ln_tau2_1))+(nu_ki(4,:)*(ln_tau_2-ln_tau2_2));
ln_gaamma1=ln_gaamma1_c+ln_gaamma1_r;//calculation of the ln(activity coefficient) using Eq.(11.104)(no unit)
ln_gaamma2=ln_gaamma2_c+ln_gaamma2_r;//calculation of the ln(activity coefficient) using Eq.(11.104)(no unit)
gaamma1=exp(ln_gaamma1);//calculation of the activity coefficient (no unit)
gaamma2=exp(ln_gaamma2);//calculation of the activity coefficient (no unit)

//OUTPUT

mprintf('The activity coefficients for the system using the UNIFAC method are : gamma1=%f \t gamma2=%f \t\n ', gaamma1,gaamma2);

//=========================================================END OF PROGRAM==========================================================
```

# Chapter 12

# Vapor liquid Equilibrium

**Scilab code Exa 12.1** Margules parameters

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-12,Example 1,Page 423
//Title: Margules parameters
//================================================================================

clear
clc

//INPUT
//For convenience Benzene is taken as 1 and heptane is taken as 2
T=60;//temperature of the system in degree celsius
P=[237.60;265.20;317.50;333.00;368.70;387.20];//Pressure data in Torr (from Danneil et al.)
x1=[0.0870;0.1800;0.4040;0.4790;0.7130;0.9070];//mole fraction of benzene in the liquid phase corresponding to the given pressure (no unit) (
```

```
from Danneil et al.)
y1=[0.1870;0.3400;0.5780;0.6420;0.7960;0.9220];//mole fraction of benzene in the vapour phase corresponding to the given pressure (no unit) (from Danneil et al.)
antoine_const_benzene=[6.87987;1196.760;219.161];//Antoine's constants for Benzene from Table A.7
antoine_const_heptane=[6.89386;1264.370;216.640];//Antoine's constants for heptane from Table A.7

//CALCULATION
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
P1_s=10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(T+antoine_const_benzene(3,:))));//calculation of saturation pressure of benzene at T in Torr
P2_s=10^(antoine_const_heptane(1,:)-(antoine_const_heptane(2,:)/(T+antoine_const_heptane(3,:))));//calculation of saturation pressure of heptane at T in Torr
l=length(P);//iteration parameter
i=1;//iteration parameter
while i<l|i==l
    gaamma1(i)=(y1(i,:)*P(i,:))/(x1(i,:)*P1_s);//calculation of activity coefficient using the data points (no unit)
    gaamma2(i)=((1-y1(i,:))*P(i,:))/((1-x1(i,:))*P2_s);//calculation of activity coefficient using the data points (no unit)
    ln_gaamma1_expt(i)=log(gaamma1(i));
    ln_gaamma2_expt(i)=log(gaamma2(i));
    gE_RTx1x2(i)=((x1(i,:)*ln_gaamma1_expt(i))+((1-x1(i,:))*ln_gaamma2_expt(i)))/(x1(i,:)*(1-x1(i,:)));//calculation of gE/RT using Eq.(11.36) (no unit)
    i=i+1;
```

```
end
plot(x1,gE_RTx1x2,'o');//Plot of gE/RTx1x2 vs x1 to determine A12 and A21
 xtitle('Plot of gE/RTx1x2 vs x1','x1','gE/RTx1x2');
//The three suffix Margules equation is given by gE/RTx1x2=(A21*x1)+(A12*x2), upon plotting gE/RTx1x2 vs x1 , the values of A12 and A21 were found (corresponding to x1=0 and x1=1.0. At x1=0, we get the value of A12 and at x1=1.0 i.e. x2=0, we get A21)
A21=0.555;//value of A21 obtained from the plot of gE/RTx1x2 vs x1 (no unit)
A12=0.315;//value of A12 obtained from the plot of gE/RTx1x2 vs x1 (no unit)
//From the Margules equations (Eq. 11.79 and 11.80), the activity coefficients, Pressure and the mole fraction of benzene in the vapour phase in the vapour phase are recalculated using the experimental values of the mole fraction of benzene in the liquid phase (x1)repoerted earlier and the Margules paramters found above.
j=1;//iteration parameter
while j<l|j==l
    ln_gaamma1(j)=((1-x1(j,:))^2)*(A12+(2*(A21-A12)*x1(j,:)));//calculation of ln(activity coefficient) (no unit)
    ln_gaamma2(j)=(x1(j,:)^2)*(A21+(2*(A12-A21)*(1-x1(j,:))));//calculation of ln(activity coefficient) (no unit)
    gaamma1(j)=exp(ln_gaamma1(j));//calculation of the activity coefficient (no unit)
    gaamma2(j)=exp(ln_gaamma2(j));//calculation of the activity coefficient (no unit)
    P_calc(j)=(gaamma1(j)*x1(j,:)*P1_s)+(gaamma2(j)*(1-x1(j,:))*P2_s);//pressure recalculated in Torr
    y1_calc(j)=(gaamma1(j)*x1(j,:)*P1_s)/P(j);//recalculation of mole fraction of benzene in
```

```
vapour phase (no unit)
    j=j+1;
end

//OUTPUT
mprintf('Data for the plot of gE/RTx1x2 vs x1: \n\n');
i=1;
for i=1:l
    mprintf('P=%f Torr\t x1=%f\t y1=%f \t ln(gamma1)=%f\t\t ln(gamma2)=%f\t\t gE/RTx1x2=%f\n\n',P(i),x1(i),y1(i),ln_gaamma1_expt(i),ln_gaamma2_expt(i),gE_RTx1x2(i));
end
mprintf('Results: \n\n');
i=1;
for i=1:l
    mprintf('x1=%f \t gamma1=%f \t gamma2=%f \t P_Exptl.=%f Torr\t P_Calc=%f Torr\t y1_Exptl=%f \t y1_calc=%f \n\n',x1(i),gaamma1(i),gaamma2(i),P(i),P_calc(i),y1(i),y1_calc(i));
end

//==========================================================END OF PROGRAM==========================================================

//DISCLAIMER:ONE OF THE VALUES OF y1(Exptl) GIVEN IN THE ANSWER HAS A TYPO ERROR. THE VALUE AS GIVEN IN THE QUESTION IS 0.7960,WHILE WHAT IS GIVEN IN THE ANSWER IS 0.7920 THIS HAS BEEN CORRECTED IN THIS CODE.
```

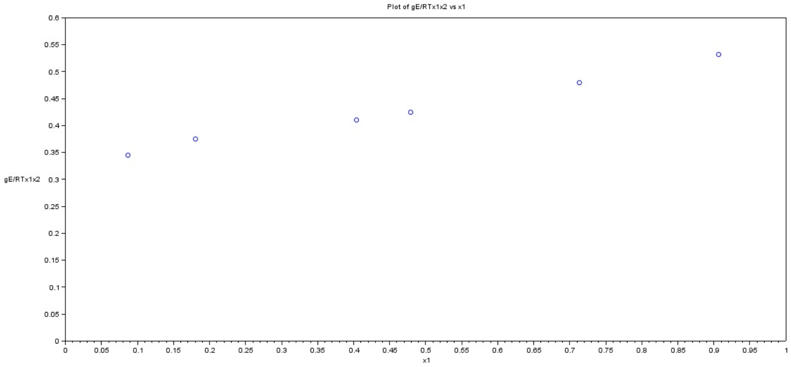

Figure 12.1: Margules parameters

**Scilab code Exa 12.2** van Laar parameters and txy data

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-12,Example 2,Page 427
//Title: van Laar parameters and t-x-y data
//================================================================================================================

clear
clc

//INPUT
//For convenience methanol is taken as 1 and nitromethane is taken as 2
P=760;//pressure of the system in Torr
t=[96.90;68.20;65.10;64.50];//temperature of the system in degree celsius (from Nakanishi et al.)
x1=[0.0150;0.4260;0.7470;0.9140];//mole fraction of methanol in the liquid phase corresponding to the given temperature (no unit) (from Nakanishi et
```

```
    al.)
y1=[0.1330;0.7470;0.8380;0.9210];//mole fraction of
    methanol in the vapour phase corresponding to the
     given temperature (no unit) (from Nakanishi et
    al.)
antoine_const_methanol=[8.08097;1582.271;239.726];//
    Antoine's constants for methanol from Table A.7
antoine_const_nmethane=[7.28166;1446.937;227.600];//
    Antoine's constants for nitromethane from Table A
    .7

//CALCULATION
//The form of the Antoine's equation used is logP=A
    -(B/(t+C)), where P is in Torr and t is in degree
     celsius
l=length(t);//iteration parameter
i=1;
while i<l|i==l
//calculation of saturation pressure of methanol at
    t in Torr
P1_s(i)=10^(antoine_const_methanol(1,:)-(
    antoine_const_methanol(2,:)/(t(i,:)+
    antoine_const_methanol(3,:))));
//calculation of saturation pressure of nitromethane
     at t in Torr
P2_s(i)=10^(antoine_const_nmethane(1,:)-(
    antoine_const_nmethane(2,:)/(t(i,:)+
    antoine_const_nmethane(3,:))));
gaamma1(i)=(y1(i,:)*P)/(x1(i,:)*P1_s(i));//
    calculation of activity coefficient using the
    data points (no unit)
gaamma2(i)=((1-y1(i,:))*P)/((1-x1(i,:))*P2_s(i));//
    calculation of activity coefficient using the
    data points (no unit)
ln_gaamma1(i)=log(gaamma1(i));//calculating the
    value of ln(activity coefficient) (no unit)
ln_gaamma2(i)=log(gaamma2(i));//calculating the
    value of ln(activity coefficient) (no unit)
```

```
gE_RT(i)=((x1(i,:)*ln_gaamma1(i))+((1-x1(i,:))*ln_gaamma2(i)));//calculation of gE/RT using Eq.(11.36) (no unit)
x1x2_gE_RT(i)=(x1(i,:)*(1-x1(i,:)))/gE_RT(i);//function for plotting againt x1 to determine the van Laar paramters (no unit)
i=i+1;
end
plot(x1,x1x2_gE_RT,'o');//Plot of RTx1x2/gE vs x1 to determine A and B
 xtitle('Plot of RTx1x2/gE vs x1','x1','RTx1x2/gE');
 //The values of the intercepts are read from Plot 12.2. From the intercepts ,the value of A and B are determined as given below
intercept_A=0.6725;//value of 1/A at x1=0, read from the plot (no unit)
intercept_B=0.710;//value of 1/B at x1=1.0, read from the plot (no unit)
A=1/intercept_A;//calculation of A (no unit)
B=1/intercept_B;//calculation of B (no unit)
//From the van Laar equations and using the van Laar parameters determined above along with the reported values of the mole fraction of methanol in the liquid  phase (x1), the activity coefficients and the mole fraction of methanol in the vapour phase (y1) are found out.
j=1;//iteration parameter
tol=1e-6;//tolerance limit for convergence of the system  when using fsolve
while j<l|j==l
    ln_gaamma1_new(j)=A/(1+((A/B)*(x1(j,:)/(1-x1(j,:)))))^2;//calculation of ln(activity coefficient) (no unit)
    ln_gaamma2_new(j)=B/(1+((B/A)*((1-x1(j,:))/x1(j,:))))^2;//calculation of ln(activity coefficient) (no unit)
    gaamma1(j)=exp(ln_gaamma1_new(j));//calculation of the activity coefficient (no unit)
```

```
    gaamma2(j)=exp(ln_gaamma2_new(j));//calculation of the activity coefficient (no unit)
    tguess(j)=100;//taking a guess value for the temperature to be used in the fsolve function in degree celsius
function[fn]=solver_func(ti)
 fn=((gaamma1(j)*(x1(j,:)/P)*(10^(antoine_const_methanol(1,:)-(antoine_const_methanol(2,:)/(ti+antoine_const_methanol(3,:))))))+((gaamma2(j))*((1-x1(j,:))/P)*(10^(antoine_const_nmethane(1,:)-(antoine_const_nmethane(2,:)/(ti+antoine_const_nmethane(3,:)))))))-1.0;//Function defined for solving the system
endfunction
[t_calc(j)]=fsolve(tguess(j),solver_func,tol)//using inbuilt function fsolve for solving the system of equations
j=j+1;
end
//Recalculation of the mole fraction of methanol in the vapour phase using the temperature recalculated above and the activity coefficients calculated above
j=1;//iteration paramter
while j<l|j==l
//recalculation of saturation pressure of methanol at t in Torr
P1_s_calc(j)=10^(antoine_const_methanol(1,:)-(antoine_const_methanol(2,:)/(t_calc(j,:)+antoine_const_methanol(3,:))));
//recalculation of saturation pressure of nitromethane at t in Torr
P2_s_calc(j)=10^(antoine_const_nmethane(1,:)-(antoine_const_nmethane(2,:)/(t_calc(j,:)+antoine_const_nmethane(3,:))));
y1_calc(j)=(gaamma1(j)*x1(j,:)*P1_s_calc(j))/P;//recalculation of the mole fraction of methanol in
```

```
    vapour phase (no unit)
j=j+1;
end

//OUTPUT
mprintf('Data for the plot of RTx1x2/gE vs x1: \n\n'
   );
i=1;
for i=1:l
    mprintf('t=%f degree celsius\t P1_s=%f Torr \t
       P2_s=%f Torr \t x1=%f\t y1=%f \n ln(gamma1)=
       %f\t\t ln(gamma2)=%f\t\t RTx1x2/gE=%f\n\n',t(
       i),P1_s(i),P2_s(i),x1(i),y1(i),ln_gaamma1(i),
       ln_gaamma2(i),x1x2_gE_RT(i));
end
mprintf('Txy data recalculated: \n \n');
i=1;
for i=1:l
    mprintf('x1=%f \n t_exptl=%f degree celsius \t
       t_calc=%f degree celsius \n y1_exptl=%f \t\t\
       t y1_calc=%f \n\n ',x1(i),t(i),t_calc(i),y1(i
       ),y1_calc(i));
end

//==================================================END
   OF PROGRAM
   ======================================================
```

---

**Scilab code Exa 12.3** Pxy data using the Margules parameters

```
// Y.V.C.Rao ,1997.Chemical Engineering
   Thermodynamics.Universities Press,Hyderabad,India
```

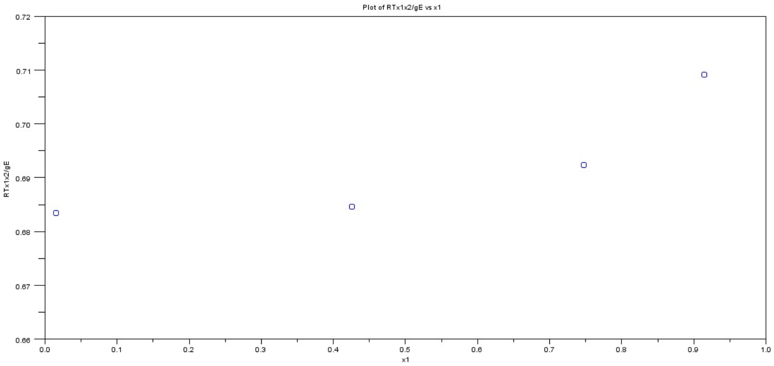

Figure 12.2: van Laar parameters and txy data

```
.

//Chapter-12,Example 3,Page 430
//Title: P-x-y data using the Margules parameters
//==================================================================

clear
clc

//INPUT
//For convenience acetone is taken as 1 and cyclohexane is taken as 2
T=25;//temperature of the system in degree celsius
A12=2.0522;//three suffix Margules parameters for the system (no unit)
A21=1.7201;//three suffix Margules parameters for the system (no unit)
P=[118.05;207.70;246.35;259.40;261.50;262.00;261.90;258.70;252.00]//Pressure data in Torr (from Tasic et al.)
//mole fraction of acetone in the liquid phase corresponding to the given pressure (no unit) (
```

```
from Tasic et al.)
x1=[0.0115;0.1125;0.3090;0.5760;0.6920;0.7390;0.7575;0.8605;0.9250]
//mole fraction of acetone in the vapour phase corresponding to the given pressure (no unit) (from Tasic et al.)
y1=[0.1810;0.5670;0.6550;0.7050;0.7250;0.7390;0.7460;0.8030;0.8580]
antoine_const_acetone=[7.11714;1210.595;229.664];//Antoine's constants for acetone from Table A.7
antoine_const_chexane=[6.85146;1206.470;223.136];//Antoine's constants for cyclohexane from Table A.7

//CALCULATION
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
P1_s=10^(antoine_const_acetone(1,:)-(antoine_const_acetone(2,:)/(T+antoine_const_acetone(3,:))));//calculation of saturation pressure of acetone at T in Torr
//calculation of saturation pressure of cyclohexane at T in Torr
P2_s=10^(antoine_const_chexane(1,:)-(antoine_const_chexane(2,:)/(T+antoine_const_chexane(3,:))));

//From the Margules equations (Eq. 11.79 and 11.80), the activity coefficients are found out
l=length(P);//iteration parameter
j=1;//iteration parameter
while j<l|j==l
    ln_gaamma1(j)=((1-x1(j,:))^2)*(A12+(2*(A21-A12)*x1(j,:)));//calculation of ln(activity coefficient) (no unit)
```

```
    ln_gaamma2(j)=(x1(j,:)^2)*(A21+(2*(A12-A21)*(1-x1(j,:))));//calculation of ln(activity coefficient) (no unit)
    gaamma1(j)=exp(ln_gaamma1(j));//calculation of the activity coefficient (no unit)
    gaamma2(j)=exp(ln_gaamma2(j));//calculation of the activity coefficient (no unit)
    P(j)=(gaamma1(j)*x1(j,:)*P1_s)+(gaamma2(j)*(1-x1(j,:))*P2_s);//calculation of pressure in Torr
    y1_calc(j)=(gaamma1(j)*x1(j,:)*P1_s)/P(j);//calculation of mole fraction of acetone in vapour phase (no unit)
    j=j+1;
end

//OUTPUT
mprintf('P-x-y data: \n\n');
i=1;
mprintf('x1 \t gamma1\t gamma2 \t P (Torr) \t y1 \n');
for i=1:l
    mprintf('%0.4f \t %f \t %f \t %f  \t %f \n',x1(i),gaamma1(i),gaamma2(i),P(i),y1_calc(i));
end

//==================================================END OF PROGRAM==================================================
```

**Scilab code Exa 12.4** Pxy data using the van Laar model

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India
```

```
   .

//Chapter-12,Example 4,Page 432
//Title: P-x-y data using the van Laar model
//
   ==================================================================

clear
clc

//INPUT
//For convenience acetone is taken as 1 and
   cyclohexane is taken as 2
T=25;//temperature of the system in degree celsius
A=2.0684;//the van Laar parameters for the system (
   no unit)
B=1.7174;//the van Laar parameters for the system (
   no unit)
P
   =[118.05;207.70;246.35;259.40;261.50;262.00;261.90;258.70;252.00]
   //Pressure data in Torr (from Tasic et al.)
//mole fraction of acetone in the liquid phase
   corresponding to the given pressure (no unit) (
   from Tasic et al.)
x1
   =[0.0115;0.1125;0.3090;0.5760;0.6920;0.7390;0.7575;0.8605;0.9250]

//mole fraction of acetone in the vapour phase
   corresponding to the given pressure (no unit) (
   from Tasic et al.)
y1
   =[0.1810;0.5670;0.6550;0.7050;0.7250;0.7390;0.7460;0.8030;0.8580]

antoine_const_acetone=[7.11714;1210.595;229.664];//
   Antoine's constants for acetone from Table A.7
antoine_const_chexane=[6.85146;1206.470;223.136];//
   Antoine's constants for cyclohexane from Table A
   .7
```

```

//CALCULATION
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
P1_s=10^(antoine_const_acetone(1,:)-(antoine_const_acetone(2,:)/(T+antoine_const_acetone(3,:))));//calculation of saturation pressure of acetone at T in Torr
//calculation of saturation pressure of cyclohexane at T in Torr
P2_s=10^(antoine_const_chexane(1,:)-(antoine_const_chexane(2,:)/(T+antoine_const_chexane(3,:))));
//From the van Laar equations(Eq. 11.82 and 11.83), the activity coefficients are found out
l=length(P);//iteration parameter
j=1;//iteration parameter
while j<l|j==l
    ln_gaamma1(j)=A/(1+((A*x1(j,:))/(B*(1-x1(j,:)))))^2;//calculation of ln(activity coefficient) (no unit)
    ln_gaamma2(j)=B/(1+((B*(1-x1(j,:)))/(A*x1(j,:))))^2;//calculation of ln(activity coefficient) (no unit)
    gaamma1(j)=exp(ln_gaamma1(j));//calculation of the activity coefficient (no unit)
    gaamma2(j)=exp(ln_gaamma2(j));//calculation of the activity coefficient (no unit)
    P(j)=(gaamma1(j)*x1(j,:)*P1_s)+(gaamma2(j)*(1-x1(j,:))*P2_s);//calculation of pressure in Torr
    y1_calc(j)=(gaamma1(j)*x1(j,:)*P1_s)/P(j);//calculation of mole fraction of acetone in vapour phase (no unit)
    j=j+1;
end

```

```
//OUTPUT
mprintf('P-x-y data: \n\n');
i=1;
mprintf('x1 \t  gamma1 \t gamma2 \t P(Torr) \t y1 \n');
for i=1:l
    mprintf('%0.4f \t %f \t %f \t %f  \t %f \n',x1(i),gaamma1(i),gaamma2(i),P(i),y1_calc(i));
end

//==============================================================END OF PROGRAM==============================================================
```

---

**Scilab code Exa 12.5** VLE data using the van Laar model

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-12,Example 5,Page 435
//Title: VLE data using the van Laar model
//==========================================================================================================

clear
clc

//INPUT
//For convenience chloroform is taken as 1 and methanol is taken as 2
P=760;//pressure in Torr at which chloroform and methanol form an azeotrope
T=53.5;//temperature in degree celsius at which
```

```
chloroform and methanol form an azeotrope
x1=0.65;//mole fraction of chloroform in the liquid phase (no unit) (corresponding to azeotropic composition)
antoine_const_chloroform=[6.95465;1170.966;226.232];//Antoine's constants for acetone from Table A.7
antoine_const_methanol=[8.08097;1582.271;239.726];//Antoine's constants for acetone from Table A.7

//CALCULATION
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
x2=1-x1;//calculation of the mole fraction of methanol in the liquid phase (no unit) (corresponding to azeotropic composition)
//calculation of saturation pressure of chloroform at T in Torr
P1_s=10^(antoine_const_chloroform(1,:)-(antoine_const_chloroform(2,:)/(T+antoine_const_chloroform(3,:))));
//calculation of saturation pressure of methanol at T in Torr
P2_s=10^(antoine_const_methanol(1,:)-(antoine_const_methanol(2,:)/(T+antoine_const_methanol(3,:))));
//At the azeotropic conditions, the activity coefficients are determined using Eq.(12.15 and 12.16)
gaamma1=P/P1_s;//calculation of activity coefficient using Eq.(12.15) (no unit)
gaamma2=P/P2_s;//calculation of activity coefficient using Eq.(12.16) (no unit)
A=log(gaamma1)*(1+((x2*log(gaamma2))/(x1*log(gaamma1))))^2;//calculation of the van Laar parameter (no unit) using Eq.(11.84)
B=log(gaamma2)*(1+((x1*log(gaamma1))/(x2*log(gaamma2))))^2;//calculation of the van Laar parameter (
```

```
no unit) using Eq.(11.85)
x1=0.1:0.1:0.9;//taking the values of mole fraction of chloroform in the liquid phase to compute the VLE data (no unit)
l=length(x1);//iteration parameter
j=1;//iteration parameter
while j<l|j==l
    ln_gaamma1(j)=A/(1+((A*x1(:,j))/(B*(1-x1(:,j)))))^2;//calculation of ln(activity coefficient) (no unit)
    ln_gaamma2(j)=B/(1+((B*(1-x1(:,j)))/(A*x1(:,j))))^2;//calculation of ln(activity coefficient) (no unit)
    gaamma1(j)=exp(ln_gaamma1(j));//calculation of the activity coefficient (no unit)
    gaamma2(j)=exp(ln_gaamma2(j));//calculation of the activity coefficient (no unit)
    P(j)=(gaamma1(j)*x1(:,j)*P1_s)+(gaamma2(j)*(1-x1(:,j))*P2_s);//calculation of pressure in Torr
    y1(j)=(gaamma1(j)*x1(:,j)*P1_s)/P(j);//calculation of mole fraction of chloroform in vapour phase (no unit)
    j=j+1;
end

//OUTPUT
mprintf('VLE data: \n\n');
i=1;
mprintf('x1 \tgamma1 \t\t gamma2  \t P (Torr) \t y1 \n\n');
for i=1:l
    mprintf('%0.1f \t %f \t %f \t %f \t %f \n',x1(i),gaamma1(i),gaamma2(i),P(i),y1(i));
end

//==================================================END OF PROGRAM
```

**Scilab code Exa 12.6** Dew pressure and liquid composition

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-12,Example 6,Page 443
//Title: Dew pressure and liquid composition
//================================================================================

clear
clc

//INPUT
//For convenience ethane is taken as 1 and propane is taken as 2
y1=0.3;//mole fraction of ethane in the vapour phase (no unit)
T=30;//temperature in degree celsius

//CALCULATION
//An assumption for the total Pressure is taken and the K factors are read from Fig.12.6. Using the K factor value, the value of x1 and x2 are computed.If x1 and x2 add up to 1, the assumption of total pressure is correct. Otherwise, the pressure is suitably adjusted
y2=1-y1;//calculation of the mole fraction of propane in the vapour phase (no unit)
P_guess=1;//assuming the value of pressure in MPa to compute the K factors
```

```
K1=3.4;//K factor taken from Fig.(12.6) corresponding to T and P_guess (no unit)
K2=1.1;//K factor taken from Fig.(12.6) corresponding to T and P_guess (no unit)
x1_calc=y1/K1;//calculation of the mole fraction of ethane in the liquid phase (no unit)
x2_calc=y2/K2;//calculation of the mole fraction of propane in the liquid phase (no unit)
tot=x1_calc+x2_calc;//checking if x1 and x2 add upto 1
if tot==1 then
    P=P_guess;//if the total of x1 and x2 sum up to 1, then the assumed pressure is the Dew pressure (in MPa)
   x1=x1_calc;//if the total of x1 and x2 sum up to 1, then the calculated value of x1 is the correct liquid composition of ethane (no unit)
   x2=x2_calc;//if the total of x1 and x2 sum up to 1, then the calculated value of x2 is the correct liquid composition of propane (no unit)
else
    P=1.5;//assuming a higher value of P in MPa to compute the K factors from Fig.(12.6), as in this case, the sum total of x1 and x2 are less than 1
    K1=2.4;//K factor taken from Fig.(12.6) corresponding to T and P (no unit)
    K2=0.8;//K factor taken from Fig.(12.6) corresponding to T and P (no unit)
    x1=y1/K1;//calculation of the mole fraction of ethane in the liquid phase (no unit)
    x2=y2/K2;//calculation of the mole fraction of propane in the liquid phase (no unit)
end

//OUTPUT
mprintf('The Dew pressure and the liquid composition
```

```
of a binary vapour mixture of ethane and propane was found to be P=%0.2f MPa\t x1=%0.3f\t x2=%0.3f \t',P,x1,x2);

//==================================================END OF PROGRAM==================================================
```

**Scilab code Exa 12.7** Bubble temperature and vapour composition

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-12,Example 7,Page 443
//Title: Bubble temperature and vapour composition
//================================================================================================================

clear
clc

//INPUT
//For convenience ethane is taken as 1 and propane is taken as 2
x1=0.4;//mole fraction of ethane in the liquid phase (no unit)
P=1.5;//pressure in MPa

//CALCULATION
//An assumption for the temperature is taken and the K factors are read from Fig.12.6. Using the K factor value, the value of y1 and y2 are computed. If y1 and y2 add up to 1, the assumption of the
```

```
temperature is correct. Otherwise, the temperature is suitably adjusted
x2=1-x1;//calculation of the mole fraction of propane in the liquid phase (no unit)
t_guess=10;//assuming the value of temperature in degree celsius to compute the K factors
K1=1.8;//K factor taken from Fig.(12.6) corresponding to t_guess and P (no unit)
K2=0.5;//K factor taken from Fig.(12.6) corresponding to t_guess and P (no unit)
y1_calc=K1*x1;//calculation of the mole fraction of ethane in the vapour phase (no unit)
y2_calc=K2*x2;//calculation of the mole fraction of propane in the vapour phase (no unit)
tot=y1_calc+y2_calc;//checking if y1 and y2 add upto 1
if tot==1 then
    t=t_guess;//if the total of y1 and y2 sum up to 1, then the assumed temperature is the bubble temperature (in degree celsius)
   y1=y1_calc;//if the total of y1 and y2 sum up to 1, then the calculated value of y1 is the correct vapour composition of ethane (no unit)
   y2=y2_calc;//if the total of y1 and y2 sum up to 1, then the calculated value of y2 is the correct vapour composition of propane (no unit)
else
    t=9;//assuming a lower value of t in degree celsius to compute the K factors from Fig.(12.6), as in this case, the sum total of y1 and y2 are greater than 1
    K1=1.75;//K factor taken from Fig.(12.6) corresponding to t and P (no unit)
    K2=0.5;//K factor taken from Fig.(12.6) corresponding to t and P (no unit)
    y1=K1*x1;//calculation of the mole fraction of ethane in the vapour (no unit)
```

```
    y2=K2*x2;//calculation of the mole fraction of propane in the vapour phase (no unit)
end

//OUTPUT
mprintf('The bubble temperature and the vapour composition of a binary vapour mixture of ethane and propane was found to be t=%d degree celsius\n y1=%f\t y2=%f\t',t,y1,y2);

//============================================================END OF PROGRAM ===================================================================
```

---

**Scilab code Exa 12.8** Thermodynamic consistency

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-12,Example 8,Page 449
//Title: Thermodynamic consistency
//==================================================================================

clear
clc

//INPUT
//For convenience 1-Propanol is taken as 1 and chlorobenzene is taken as 2
P=[350.00;446.00;518.00;574.50;609.00;632.50;665.00;681.50;691.50]//pressure data in Torr, taken from (Ellis et al
```

```
.)
x1=[0.0550;0.1290;0.2120;0.3130;0.4300;0.5200;0.6380;0.7490;0.8720]//mole fraction of 1-propanol in the liquid phase, taken from (Ellis et al.) (no unit)
y1=[0.3500;0.5110;0.5990;0.6500;0.6970;0.7260;0.7590;0.8130;0.8830]//mole fraction of 1-propanol in the vapour phase, taken from (Ellis et al.) (no unit)
antoine_const_propanol=[8.37895;1788.020;227.438];//Antoine's constants for 1-Propanol from Table A.7
antoine_const_cbenzene=[7.17294;1549.200;229.260];//Antoine's constants for Chlorobenzene from Table A.7
T=95;//temperature of the system in degree celsius

//CALCULATION
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is is Torr and t is in degree celsius
P1_s=10^(antoine_const_propanol(1,:)-(antoine_const_propanol(2,:)/(T+antoine_const_propanol(3,:))));//calculation of saturation pressure of propanol at T in Torr
//calculation of saturation pressure of chlorobenzene at T in Torr
P2_s=10^(antoine_const_cbenzene(1,:)-(antoine_const_cbenzene(2,:)/(T+antoine_const_cbenzene(3,:))));
l=length(P);//iteration parameter
i=1;//iteration paramter
while i<l|i==l
    gaamma1(i)=(y1(i,:)*P(i,:))/(x1(i,:)*P1_s);//calculation of activity coefficient using Eq.(12.15) (no unit)
    gaamma2(i)=((1-y1(i,:))*P(i,:))/((1-x1(i,:))*P2_s);//calculation of activity coefficient using Eq.(12.16) (no unit)
```

```
    lngamma1_gamma2(i)=log(gaamma1(i)/gaamma2(i));//calculation of ln(activity coefficient1/activity coefficient 2) (no unit), to check for the consistency
    i=i+1;
end
plot(x1,lngamma1_gamma2);//Plot of ln(gamma1/gamma2) vs x1 to determine A12 and A21
xtitle('Plot of ln(gamma1/gamma2) vs x1','x1','ln(gamma1/gamma2)');
//From the figure, the area above the x-axis and the area below the x-axis are determined and the thermodynamic consistency is checked
area_above=1515;//area above the x-axis from the above plot (no unit)
area_below=1540;//area below the x-axis (absolute value) from the above plot (no unit)
consistency_parameter=abs((area_above-area_below)/(area_above+area_below));//calculating the paramter for checking the thermodynamic consistency (no unit)


//OUTPUT
mprintf('Values of ln(gamma1/gamma2): \n\n');
i=1;
mprintf('x1 \t gamma1 \t gamma2 \t ln(gamma1/gamma2) \n');

for i=1:l
    mprintf('%0.4f \t %f \t %f \t %f \n',x1(i),gaamma1(i),gaamma2(i),lngamma1_gamma2(i));
end
mprintf('\nThe value of the consistency parameter=%f \n',consistency_parameter);
//0.02 is taken as the checking paramter for the consistency as prescribed by the author in the book on Page 449
```

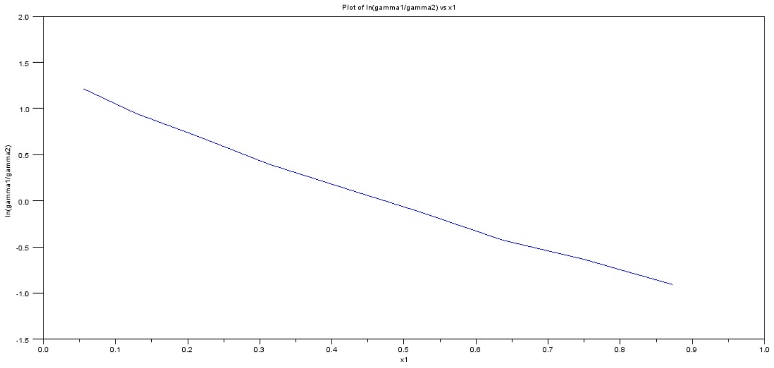

Figure 12.3: Thermodynamic consistency

```
if consistency_parameter<0.02|consistency_parameter==0.02 then
    mprintf('The VLE data is thermodynamically consistent');
else
    mprintf('The VLE data is not thermodynamically consistent');
end

//===========================================================END OF PROGRAM=====================================================
```

---

**Scilab code Exa 12.9** Temperature composition diagram

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.
```

```

//Chapter-12,Example 9,Page 464
//Title: Temperature-composition diagram
//

clear
clc

//INPUT
//For convenience benzene is taken as 1 and water is taken as 2. They form a completely immiscible system
P=760;//pressure of the system in Torr
antoine_const_benzene=[6.87987;1196.760;219.161];//Antoine's constants for Benzene from Table A.7
t=60:5:100;//temperature range in degree celsius
//saturation pressure of water(in torr)in the temperature range given by t (from steam tables)
P2_s=[149.40;187.58;233.71;289.13;355.21;433.51;525.84;634.00;760.00]

x1=0:0.2:1;//mole fraction of benzene in the liquid phase (no unit) (taken in an arbitrary manner)

//CALCULATION
//The form of the Antoine's equation used is logP=A-(B/(t+C)), where P is in Torr and t is in degree celsius
//The three phase equilibrium temperature is estimated using the saturation pressure values, such that at the three phase equilibrium temperature,P=P1_s+P2_s=P as given by Eq.(12.57) Torr
l=length(t);//iteration parameter
i=1;//iteration parameter
while i<l|i==l
//calculation of saturation pressure of benzene at T
```

```
in Torr
P1_s(i)=10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(t(:,i)+antoine_const_benzene(3,:))));
//calculating the total pressure in Torr so as to narrow down the temperature range for estimating the three phase equilibrium temperature
P_tot(i)=P1_s(i)+P2_s(i,:);
i=i+1;
end
//From the P_tot values calculated above, it is observed that the temperature range in which the three phase equilibrium temperature lies,is in between 65 and 70  degree celsius. Using linear interpolation , the three phase equilibrium temperature is determined in degree celsius
T=(((t(:,3)-t(:,2))*(760-P_tot(2,:)))/(P_tot(3,:)-P_tot(2,:)))+t(:,2);//linear interpolation to determine the three phase equilibrium temperature in degree celsius
//calculation of saturation pressure of benzene at the three phase temperature in Torr
P1_s_three_phase=10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(T+antoine_const_benzene(3,:))));
P2_s_three_phase=760-P1_s_three_phase;//calculation of the saturation pressure of water at the three phase temperature in Torr
y1_three_phase=P1_s_three_phase/760;//calculation of the mole fraction of benzene in the vapour phase at the three phase equilibrium point (no unit)
//redefining the temeprature range in degree celsius for computing the vapour compositions in the two phase regions. (As the three phase equilibrium temperature  lies between 65 and 70 degree celsius)
//The normal boiling point of benzene is given as 80.1 degree celsius (at a pressure of 760 Torr)
```

```
trange1=T:1:T+11;//temperature range for calculating vapour phase composition of benzene in the two phase region given by (L1+V)
n=length(trange1);//iteration parameter
i=1;//iteration parameter
while i<n|i==n
    if i==1 then
        y1(i)=y1_three_phase;//calculation of the vapour composition of benzene in the two phase region (L1+V) using Eq.(12.59) (no unit)
    else
         P1_s_calc(i)=10^(antoine_const_benzene(1,:)-(antoine_const_benzene(2,:)/(trange1(:,i)+antoine_const_benzene(3,:))));
    y1(i)=(P1_s_calc(i))/P;//calculation of the vapour composition of benzene in the two phase region (L1+V) using Eq.(12.59) (no unit)
    end
    i=i+1;
end
trange2=[70;75;80;85;90;95;100];//temperature range for calculating vapour phase composition of benzene in the two phase region given by (L2+V)
P2_s_range=[233.71;289.13;355.21;433.51;525.84;634.00;760.00];//saturation pressure of water(in torr)in the temperature range given by trange2 (from steam tables)
p=length(trange2);//iteration parameter
i=1;//iteration parameter
//calculation of the vapour composition of benzene in the two phase region (L2+V) using Eq.(12.61) (no unit)
y_one(i)=y1_three_phase;
trange2(i)=T;
i=i+1;
```

```
while i<p|i==p
        y_one(i)=(P-P2_s_range(i,:))/P;
    i=i+1;
end
i=1;//iteration parameter
k=length(x1);//iteration parameter
while i<k|i==k
    t_3phase(i)=T;//creating a vector for generating the plot at the three phase temperature
    i=i+1;
end

//OUTPUT
//Generating the T-x-y plot for the benzene-water system
plot(y1,trange1);
plot(y_one,trange2);
plot(x1,t_3phase);
 xtitle('t-x-y diagram for benzene-water sytem at 760 Torr','x1,y1','t (degree celsius)');
q=length(t);//iteration parameter
i=1;//iteration parameter
mprintf('Calculations performed for determining the three phase equilibrium temperature\n');
mprintf('t(degree celsius) \t P1_s (Torr) \t P2_s (Torr) \t P1_s+P2_s (Torr) \n');
for i=1:q
    mprintf('%d \t \t \t %f \t %0.2f \t %f \n',t(i),P1_s(i),P2_s(i),P_tot(i));
end
mprintf('The three phase equilibrium temperature=%0.2f degree celsius \n',T);
mprintf('The vapour phase composition of benzene at the three phase equilibrium point=%0.4f \n',y1_three_phase);
//=====================================================================END OF PROGRAM =====================================================================
```

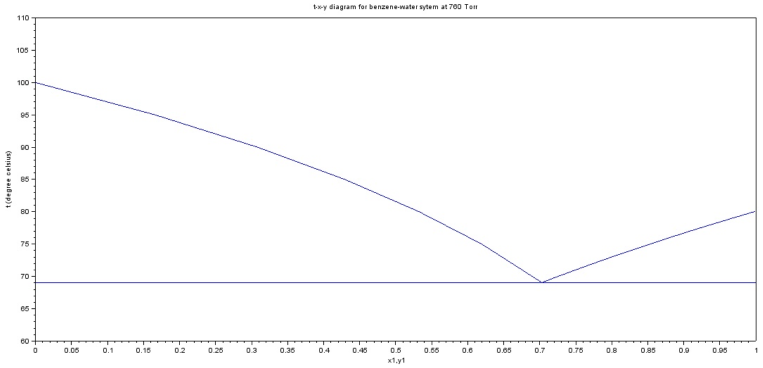

Figure 12.4: Temperature composition diagram

# Chapter 13

# Dilute solution laws

**Scilab code Exa 13.1** Depression in freezing point

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-13,Example 1,Page 478
//Title:Depression in freezing point
//==================================================================================

clear
clc

//INPUT
weight=10; //weight of NaCl in grams
volume=1; //volume of water in litres
weight_water=1000; //  weight of water in grams (Weight=Volume*Density, density of water =1g/cc=1g/ml=1000g/l)
molwt_NaCl=58.5; //molecular weight of NaCl in grams
molwt_water=18; //molecular weight of water in grams
hf=6.002; //enthalpy change of fusion in kJ/mol at 0
```

```
degree celsius
P=101.325; //pressure in kPa
T=273.15; // freezing point temperature of water at the given pressure in K
R=8.314; //universal gas constant in J/molK;

//CALCULATION
x2=(weight/molwt_NaCl)/((weight/molwt_NaCl)+(weight_water/molwt_water));// calculation of mole fraction of solute NaCl (no unit)
delt=(R*T^2*x2)/(hf*10^3);//calculation of depression in freezing point of water using Eq.(13.14)

//OUTPUT
mprintf('\n The depression in freezing point of water when 10g of NaCl solute is added = %0.2f K',delt);

//===========================================================================END OF PROGRAM===========================================================================
```

---

**Scilab code Exa 13.2** Elevation in Boiling Point

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-13,Example 2,Page 480
//Title:Elevation in Boiling Point
//===========================================================================
```

```
clear
clc

//INPUT
weight=10; //weight of NaCl in grams
volume=1; //volume of water in litres
weight_water=1000; //  weight of water in grams (Weight=Volume*Density, density of water =1g/cc=1g/ml=1000g/l)
molwt_NaCl=58.5; //molecular weight of NaCl in grams
molwt_water=18; //molecular weight of water in grams
lat_ht=2256.94; //latent heat of vaporization in kJ/kg at 100 degree celsius (obtained from steam tables)
P=101.325; //pressure in kPa
T=373.15; //boiling point temperature of water at the given pressure in K
R=8.314; //universal gas constant in J/molK

//CALCULATION
x2=0.0031;//mole fraction of solute NaCl (From Example 13.1)(no unit)
hv=(lat_ht*molwt_water)/1000; //conversion of latent heat from kJ/kg to kJ/mol
delt=(R*T^2*x2)/(hv*10^3); //calculation of elevation in boiling point of water using Eq.(13.24)

//OUTPUT
mprintf('\n The elevation in boiling point of water when 10g of NaCl solute is added = %0.2f K',delt);

//================================================END OF PROGRAM================================================
```

**Scilab code Exa 13.3** Osmotic pressure

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-13,Example 3,Page 481
//Title:Osmotic pressure
//================================================================================

clear
clc

//INPUT
weight=10; //weight of NaCl in grams
weight_water=1000; //  weight of water in grams
molwt_NaCl=58.5; //molecular weight of NaCl in grams
molwt_water=18; //molecular weight of water in grams
T=300; //prevailing temperature of water in K
R=8.314; //universal gas constant in (Pa m^3)/(mol K);
v=18*10^-6;//molar volume in m^3/mol
//CALCULATION
x2=0.0031;//mole fraction of solute NaCl (From Example 13.1)(no unit)
pi=((R*T*x2)/v)*10^-3; // calulation of osmotic pressure using Eq(13.30)(in kPa)

//OUTPUT
mprintf('\n The osmotic pressure of a solution conatining 10g of NaCl in 1000g of water at 300K = %0.2f kPa',pi);

```

```
//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 13.4** Ideal solubility

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-13,Example 4,Page 483
//Title:Ideal solubility
//================================================================================================================

clear
clc

//INPUT
temp=20; // prevailing tempearture in degree celsius
melt_temp=80.05; // melting point of naphthalene in degree celsius
hf=18.574; // enthalpy of fusion in kJ/mol
R=8.314; // universal gas constant in J/molK

//CALCULATION
t=temp+273.15; // convesion of prevailing temperature to K
melt_t=melt_temp+273.15; //conversion of melting point of naphtalene to K
x2=exp(((hf*10^3)/R)*((1/melt_t)-(1/t))); // calculation of ideal solubility using Eq.(13.40)(no unit)

```

```
//OUTPUT
mprintf('\n The ideal solubility of naphthalene at 20 degree celsius= %0.4f',x2);

//=====================================================================END OF PROGRAM=====================================================================
```

---

**Scilab code Exa 13.5** Solubility of gas

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-13,Example 5,Page 483
//Title:Solubility of gas
//==========================================================================================

clear
clc

//INPUT
t=295.43; //prevailing temperature in K
sat_p=6.05; //Sasturation pressure of carbon dioxide at the prevailing temperature in MPa
p=0.1; //pressure at which solubility has to be determined in MPa

//CALCULATION
x2=p/sat_p; //calculation of solubility using Eq.(13.44)(no unit)

//OUTPUT
```

```
mprintf('\n The solubility of carbon dioxide expressed in mole fraction of carbon dioxide in solution at 0.1MPa= %0.4f',x2);

//==========================================================END OF PROGRAM===========================================================
```

---

# Chapter 14

# Chemical reaction equilibrium

**Scilab code Exa 14.1** Standard Gibbs free energy change and equilibrium constant

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 1,Page 489
//Title: Standard Gibbs free energy change and equilibrium constant
//================================================================================================================================

clear
clc

//INPUT
//The water gas shift reaction is given by : CO2(g)+H2(g)--->CO(g)+H2O(g)
T=298.15;//temperature in K
del_Gf=[-137.327;-228.600;-394.815;0];//the standard Gibbs free energy of formation of CO(g),H2O(g),CO2(g) and H2(g) in kJ
```

```
n=[1;1;-1;-1];//stoichiometric coefficients of CO(g),H2O(g),CO2(g) and H2(g) respectively (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
//calculation of the standard Gibbs free energy of reaction at 298.15K using Eq.(14.1) in kJ
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:))+(n(4,:)*del_Gf(4,:));
Ka=exp((-(del_G*10^3))/(R*T));//calculation of the equilibrium constant using Eq.(14.9) (no unit)

//OUTPUT
mprintf('The standard Gibbs free energy of the water gas shift reaction at 298.15K=%0.3f kJ \n',del_G);
mprintf('The equilibrium constant of the water gas shift reaction at 298.15K=%0.3e \n',Ka);

//==========================================================END OF PROGRAM==========================================================
```

---

**Scilab code Exa 14.2** Standard Gibbs free energy of formation

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 2,Page 490
//Title: Standard Gibbs free energy of formation
//==========================================================
```

```
clear
clc

//INPUT
T=298.15;//temperature in K
P_s=0.16716;//saturation pressure of CH3OH in bar at T
//The reactions can be written down as:
//C(s)+2H2(g)+(1/2)O2(g)---->CH3OH(l)--->del_G1
//CH3OH(l)--->CH3OH(g)--->del_G2
//Overall: C(s)+2H2(g)+(1/2)O2(g)--->CH3OH(g)--->del_G=del_G2+del_G1
del_G1=-166.215;//standard Gibbs free energy of formation of CH3OH(l) in kJ
R=8.314;//universal gas constant in J/molK

//CALCULATION
//Now, the value of del_G2 has to be computed, from which del_G can be determined. The standard state for CH3OH(l) is 1 bar and 298.15K
//del_G2 is given by, del_G2=RTln(f_v/f_l), where f_v and f_l are the fugacities of the vapour and liquid phases respectively
//At 1 bar pressure, the vapour is an ideal gas and hence its fugacity is equal to pressure
f_v=1;//fugacity of the vapour in bar
f_l=P_s;//fugacity of the liquid is the saturation pressure at T, in bar
del_G2=R*T*log(f_v/f_l)*10^-3;//calculation of the value of del_G2 in kJ
del_G=del_G2+del_G1;//calculation of the standard Gibbs free energy of formation of CH3OH(g) in kJ

//OUTPUT
mprintf('The standard Gibbs free energy of formation of CH3OH(g)=%0.3f kJ \n',del_G);


```

```
//==================================================END OF PROGRAM==================================================
```

---

**Scilab code Exa 14.3** Equilibrium constant

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 3,Page 491
//Title: Equilibrium constant
//================================================================================================

clear
clc

//INPUT
//The water gas shift reaction is given by: CO2(g)+H2(g)--->CO(g)+H2O(g)
T1=298.15;//initial temperature in K
Ka1=8.685*10^-6;//equilibrium constant for the water-gas shift reaction at T1 (no unit)
T2=1000;//temperature at which the equilibrium constant has to be determined in K
R=8.314;//universal gas constant in J/molK
del_Hf=[-110.532;-241.997;-393.978;0];//the standard enthalpy of formation of CO(g),H2O(g),CO2(g) and H2(g) in kJ
n=[1;1;-1;-1];//stoichiometric coefficients of CO(g),H2O(g),CO2(g) and H2(g) respectively (no unit)

//CALCULATION
```

```
//It is assumed that del_H is constant in the temperature range T1 and T2
del_H=(n(1,:)*del_Hf(1,:))+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:))+(n(4,:)*del_Hf(4,:));//calculation of the standard enthalpy of the reaction in kJ
Ka2=Ka1*exp(((del_H*10^3)/R)*((1/T1)-(1/T2)));//calculation of the equilibrium constant at T2 (no unit)

//OUTPUT
mprintf('The equilibrium constant for the water gas shift reaction at 1000K=%f \n',Ka2);


//===================================================END OF PROGRAM===================================================
```

---

**Scilab code Exa 14.4** Equilibrium constant with enthalpy of reaction varying with temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 4,Page 492
//Title: Equilibrium constant with enthalpy of reaction varying with temperature
//================================================================================================================
clear
clc
```

```

//INPUT
//The water gas shift reaction is given by: CO2(g)+H2(g)--->CO(g)+H2O(g)
P=0.1;//pressure in MPa
T1=298.15;//initial temperature in K
Ka1=8.685*10^-6;//equilibrium constant for the water-gas shift reaction at T1 (no unit) (from Example 14.1)
T2=1000;//temperature at which the equilibrium constant is to be found, in K
del_H=41.449;//standard enthalpy of the reaction at T1 in kJ (from Example 14.3)
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K from Appendix A.3
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CO(g),H2O(g),CO2(g),H2(g) respectively)
a=[28.068;28.850;45.369;27.012];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CO(g),H2O(g),CO2(g),H2(g) respectively)
b=[4.631*10^-3;12.055*10^-3;8.688*10^-3;3.509*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CO(g),H2O(g),CO2(g),H2(g) respectively)
c=[0;0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CO(g),H2O(g),CO2(g),H2(g) respectively)
d=[0;0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CO(g),H2O(g),CO2(g),H2(g) respectively)
e=[-0.258*10^5;1.006*10^5;-9.619*10^5;0.690*10^5];
```

```
n=[1;1;-1;-1];//stoichiometric coefficients of CO(g),H2O(g),CO2(g) and H2(g) respectively (no unit)
R=8.314;//universal gas constant in J/molK
Ka2_prev=1.0855;//equilibrium constant calculated in Example (14.3) without considering the variation of del_H between T1 and T2 (no unit)


//CALCULATION
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:))+(n(4,:)*a(4,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:))+(n(4,:)*b(4,:));
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:))+(n(4,:)*c(4,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:))+(n(4,:)*d(4,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:))+(n(4,:)*e(4,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=(del_H*10^3)-((del_a*T1)+((del_b/2)*T1^2)+((del_c/3)*T1^3)+((del_d/4)*T1^4)-(del_e/T1));
//Calculation of the integration constant using Eq.(14.22) (no unit)
I=(log(Ka1))-((1/R)*((-del_H0/T1)+(del_a*log(T1))+((del_b/2)*T1)+((del_c/6)*T1^2)+((del_d/12)*T1^3)+((del_e/(2*T1^2)))));
//calculation of the equilibrium constant at T2 using Eq.(14.22) (no unit)
Ka2=exp(((1/R)*((-del_H0/T2)+(del_a*log(T2))+((del_b/2)*T2)+((del_c/6)*T2^2)+((del_d/12)*T2^3)+((del_e/(2*T2^2)))))+I);

//OUTPUT
mprintf('The equilibrium constant for the water gas
```

```
shift reaction at 1000K by taking into account the variation of del_H with temperature=%f \n',Ka2);
mprintf('The equilibrium constant for the water gas shift reaction at 1000K without considering the variation of del_H with temperature as given by Example(14.3)=%0.4f \n',Ka2_prev);


//=========================================================================END OF PROGRAM=========================================================================
```

---

**Scilab code Exa 14.5** Conversion and composition of the equilibrium mixture

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 5,Page 494
//Title: Conversion and composition of the equilibrium mixture
//================================================================================================================================

clear
clc

//INPUT
//Industrial methanol is produced by the following reaction:
//CO(g)+2H2(g)--->CH3OH(g)
T0=298.15;//standard temperature in K
```

```
T=500;//temperature in K
P=5;//pressure in bar
del_Hv=37.988;//enthalpy of vapourization of CH3OH at 298.15K in kJ/mol
R=8.314;//universal gas constant in J/molK
del_Gf=[-161.781;-137.327;0]//Standard Gibbs free energies of formation of CH3OH(g) from Example (14.2),CO(g) and H2(g) respectively in kJ
del_Hf=[-238.648;-110.532;0]//Standard enthalpies of formation of CH3OH(l), CO(g) and H2(g) respectively in kJ
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K from Appendix A.3
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
a=[18.382;28.068;27.012];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
b=[101.564*10^-3;4.631*10^-3;3.509*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
c=[-28.683*10^-6;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
d=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
e=[0;-0.258*10^5;0.690*10^5];
n=[1;-1;-2];//stoichiometric coefficients of CH3OH(g),CO(g) and H2(g) respectively (no unit)
m=[0;1;2];//mole number in feed (for CH3OH(g),CO(g),H2(g) respectively)
```

```

//CALCULATION
del_Hf_CH3OH_g=del_Hf(1,:)+del_Hv;//calculation of the standard enthalpy of formation of CH3OH(g) in kJ
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:));//calculation of the Gibbs free energy of reaction in kJ
del_H=del_Hf_CH3OH_g+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:));//calculation of the enthalpy of the reaction in kJ
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:));
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))*10^-3;
//Using Eq.14.23 to compute the integration constant (no unit)
I=(1/(R*T0))*((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3));
//Using Eq.14.23 to compute the Gibbs free energy of the reaction at T in kJ
del_G_T=((del_H0*10^3)-(del_a*T*log(T))-((del_b/2)*T^2)-((del_c/6)*T^3)-((del_d/12)*T^4)-((del_e/2)*(1/T))-(I*R*T))*10^-3;
```

```
Ka=exp((-del_G_T*10^3)/(R*T));//calculation of the equilibrium constant (no unit)
del_n=n(1,:)+n(2,:)+n(3,:);//calculation of the total mole number (no unit)
Ky=Ka/((P)^del_n);//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (K_phi=1.0,assuming ideal gas behaviour)
mtot=m(1,:)+m(2,:)+m(3,:);//calculation of the total mole number of feed entering (no unit)
//To determine the degree of conversion, the inbuilt function fsolve is used to solve the equation given by Ky=(y_CH3OH)/(y_CO*y_H2^2), where y_CH3OH,y_CO,y_H2  are the mole fractions of CH3OH,CO,H2 respectively. Let the equilibrium conversion be denoted as E
E_guess=0.1;//taking a guess value for the degree of conversion,to be used in the inbuilt function fsolve (no unit)
tol=1e-6;//tolerance limit for convergence of the system  when using fsolve
function[fn]=solver_func(Ei)
    //Function defined for solving the system
 fn=Ky-((((m(1,:)+(n(1,:)*Ei))/(mtot+(del_n*Ei)))^n(1,:))*(((m(2,:)+(n(2,:)*Ei))/(mtot+(del_n*Ei)))^n(2,:))*(((m(3,:)+(n(3,:)*Ei))/(mtot+(del_n*Ei)))^n(3,:)));
endfunction
[E]=fsolve(E_guess,solver_func,tol)//using inbuilt function fsolve for solving the system of equations
//Calculation of the composition of the equilibrium mixture (for CH3OH(g),CO(g),H2(g) respectively)(no unit)
y_CH3OH=(m(1,:)+(n(1,:)*E))/(mtot+(del_n*E));
y_CO=(m(2,:)+(n(2,:)*E))/(mtot+(del_n*E));
y_H2=(m(3,:)+(n(3,:)*E))/(mtot+(del_n*E));

```

```
//OUTPUT
mprintf('The degree of conversion at 500K and 5bar pressure=%0.4f\n',E);
mprintf('The composition of the equilibrium mixture at 500K and 5bar pressure: y_CH3OH=%0.4f\t y_CO=%0.4f\t y_H2=%0.4f\n',y_CH3OH,y_CO,y_H2);

//=========================================================END OF PROGRAM===========================================================
```

---

**Scilab code Exa 14.6** Conversion and composition of the equilibrium mixture at 5 and 100 bar Pressures

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 6,Page 496
//Title: Conversion and composition of the equilibrium mixture at 5 and 100 bar Pressures
//================================================================================================================================
clear
clc

//INPUT
//Industrial methanol is produced by the following reaction:
//CO(g)+2H2(g)--->CH3OH(g)
T0=298.15;//standard temperature in K
T=500;//temperature in K
P1=5;//pressure in bar
```

```
P2=100;//pressure in bar
del_Hv=37.988;//enthalpy of vapourization of CH3OH at 298.15K in kJ/mol
R=8.314;//universal gas constant in J/molK
del_Gf=[-161.781;-137.327;0]//Standard Gibbs free energies of formation of CH3OH(g) from Example(14.2),CO(g) and H2(g) respectively in kJ
del_Hf=[-238.648;-110.532;0]//Standard enthalpies of formation of CH3OH(l), CO(g) and H2(g) respectively in kJ
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K from Appendix A.3
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
a=[18.382;28.068;27.012];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
b=[101.564*10^-3;4.631*10^-3;3.509*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
c=[-28.683*10^-6;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
d=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
e=[0;-0.258*10^5;0.690*10^5];
n=[1;-1;-2];//stoichiometric coefficients of CH3OH(g),CO(g) and H2(g) respectively (no unit)
m=[0;1;2];//mole number in feed (for CH3OH(g),CO(g),H2(g) respectively)

```

```
//CALCULATION
//From Example 14.5, the conversion and the equilibrium composition has been determined and this is given below:
E1=0.0506;
y_CH3OH_1=0.0175;
y_CO_1=0.3275;
y_H2_1=0.6550;
//Calculation of conversion and equilibrium composition for the pressure of 100 bars(P2)
del_Hf_CH3OH_g=del_Hf(1,:)+del_Hv;//calculation of the standard enthalpy of formation of CH3OH(g) in kJ
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:));//calculation of the Gibbs free energy of reaction in kJ
del_H=del_Hf_CH3OH_g+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:));//calculation of the enthalpy of the reaction in kJ
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:));
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))*10^-3;
//Using Eq.14.23 to compute the integration constant (no unit)
```

```
I=(1/(R*T0))*((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3));
//Using Eq.14.23 to compute the Gibbs free energy of the reaction at T in kJ
del_G_T=((del_H0*10^3)-(del_a*T*log(T))-((del_b/2)*T^2)-((del_c/6)*T^3)-((del_d/12)*T^4)-((del_e/2)*(1/T))-(I*R*T))*10^-3;
Ka=exp((-del_G_T*10^3)/(R*T));//calculation of the equilibrium constant (no unit)
del_n=n(1,:)+n(2,:)+n(3,:);//calculation of the total mole number (no unit)
Ky=Ka/((P2)^del_n);//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (K_phi=1.0,assuming ideal gas behaviour)
mtot=m(1,:)+m(2,:)+m(3,:);//calculation of the total mole number of feed entering (no unit)
//To determine the degree of conversion, the inbuilt function fsolve is used to solve the equation given by Ky=(y_CH3OH)/(y_CO*y_H2^2), where y_CH3OH,y_CO,y_H2  are the mole fractions of CH3OH,CO,H2 respectively. Let the equilibrium conversion be denoted as E
E_guess=0.1;//taking a guess value for the degree of conversion,to be used in the inbuilt function fsolve (no unit)
tol=1e-6;//tolerance limit for convergence of the system  when using fsolve
function[fn]=solver_func(Ei)
    //Function defined for solving the system
 fn=Ky-((((m(1,:)+(n(1,:)*Ei))/(mtot+(del_n*Ei)))^n(1,:))*(((m(2,:)+(n(2,:)*Ei))/(mtot+(del_n*Ei)))^n(2,:))*(((m(3,:)+(n(3,:)*Ei))/(mtot+(del_n*Ei)))^n(3,:)));
endfunction
[E2]=fsolve(E_guess,solver_func,tol)//using inbuilt function fsolve for solving the system of
```

```
equations
//Calculation of the composition of the equilibrium mixture (for CH3OH(g),CO(g),H2(g) respectively)(no unit)
y_CH3OH_2=(m(1,:)+(n(1,:)*E2))/(mtot+(del_n*E2));
y_CO_2=(m(2,:)+(n(2,:)*E2))/(mtot+(del_n*E2));
y_H2_2=(m(3,:)+(n(3,:)*E2))/(mtot+(del_n*E2));

//OUTPUT
mprintf('The degree of conversion at 500K and 5bar pressure=%0.4f\n',E1);
mprintf('The composition of the equilibrium mixture at 500K and 5bar pressure: y_CH3OH=%0.4f\t y_CO=%0.4f\t y_H2=%0.4f\n',y_CH3OH_1,y_CO_1,y_H2_1);
mprintf('The degree of conversion at 500K and 100bar pressure=%0.3f\n',E2);
mprintf('The composition of the equilibrium mixture at 500K and 100bar pressure: y_CH3OH=%0.4f\t y_CO=%0.4f\t y_H2=%f\n',y_CH3OH_2,y_CO_2,y_H2_2);
//===========================================================================END OF PROGRAM===========================================================================
```

---

**Scilab code Exa 14.7** Conversion and composition of the equilibrium mixture with inerts

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 7,Page 497
//Title: Conversion and composition of the equilibrium mixture with inerts
//
```

```
clear
clc

//INPUT
//Industrial methanol is produced by the following
    reaction:
//CO(g)+2H2(g)--->CH3OH(g)
T0=298.15;//standard temperature in K
T=500;//temperature in K
P=5;//pressure in bar
del_Hv=37.988;//enthalpy of vapourization of CH3OH
    at 298.15K in kJ/mol
R=8.314;//universal gas constant in J/molK
del_Gf=[-161.781;-137.327;0]//Standard Gibbs free
    energies of formation of CH3OH(g) from Example
    (14.2),CO(g) and H2(g) respectively in kJ
del_Hf=[-238.648;-110.532;0]//Standard enthalpies of
     formation of CH3OH(l), CO(g) and H2(g)
    respectively in kJ
//The isobaric molar capacity is given by Cp=a+bT+cT
    ^2+dT^3+eT^-2 in J/molK and T is in K from
    Appendix A.3
//coefficient in the expression for computing the
    isobaric molar heat capacity from Appendix A.3 (
    for CH3OH(g),CO(g),H2(g) respectively)
a=[18.382;28.068;27.012];
//coefficient in the expression for computing the
    isobaric molar heat capacity from Appendix A.3 (
    for CH3OH(g),CO(g),H2(g) respectively)
b=[101.564*10^-3;4.631*10^-3;3.509*10^-3];
//coefficient in the expression for computing the
    isobaric molar heat capacity from Appendix A.3 (
    for CH3OH(g),CO(g),H2(g) respectively)
c=[-28.683*10^-6;0;0];
//coefficient in the expression for computing the
    isobaric molar heat capacity from Appendix A.3 (
```

```
for CH3OH(g),CO(g),H2(g) respectively)
d=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
e=[0;-0.258*10^5;0.690*10^5];
n=[1;-1;-2];//stoichiometric coefficients of CH3OH(g),CO(g),H2(g) respectively (no unit)
//The inert is denoted as A
m=[0;1;2;5];//mole number in feed (for CH3OH(g),CO(g),H2(g),A(g) respectively)

//CALCULATION
del_Hf_CH3OH_g=del_Hf(1,:)+del_Hv;//calculation of the standard enthalpy of formation of CH3OH(g) in kJ
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:));//calculation of the Gibbs free energy of reaction in kJ
del_H=del_Hf_CH3OH_g+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:));//calculation of the enthalpy of the reaction in kJ
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:));
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))
```

```
*10^-3;
//Using Eq.14.23 to compute the integration constant (no unit)
I=(1/(R*T0))*((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3));
//Using Eq.14.23 to compute the Gibbs free energy of the reaction at T in kJ
del_G_T=((del_H0*10^3)-(del_a*T*log(T))-((del_b/2)*T^2)-((del_c/6)*T^3)-((del_d/12)*T^4)-((del_e/2)*(1/T))-(I*R*T))*10^-3;
Ka=exp((-del_G_T*10^3)/(R*T));//calculation of the equilibrium constant (no unit)
del_n=n(1,:)+n(2,:)+n(3,:);//calculation of the total mole number (no unit)
Ky=Ka/((P)^del_n);//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (K_phi=1.0,assuming ideal gas behaviour)
mtot=m(1,:)+m(2,:)+m(3,:)+m(4,:);//calculation of the total mole number of feed entering (no unit)
//To determine the degree of conversion, the inbuilt function fsolve is used to solve the equation given by Ky=(y_CH3OH)/(y_CO*y_H2^2), where y_CH3OH,y_CO,y_H2 are the mole fractions of CH3OH,CO,H2 respectively. Let the equilibrium conversion be denoted as E
E_guess=0.1;//taking a guess value for the degree of conversion,to be used in the inbuilt function fsolve (no unit)
tol=1e-6;//tolerance limit for convergence of the system when using fsolve
function[fn]=solver_func(Ei)
    //Function defined for solving the system
 fn=Ky-((((m(1,:)+(n(1,:)*Ei))/(mtot+(del_n*Ei)))^n(1,:))*(((m(2,:)+(n(2,:)*Ei))/(mtot+(del_n*Ei)))^n(2,:))*(((m(3,:)+(n(3,:)*Ei))/(mtot+(del_n*Ei)))^n(3,:)));
```

```
endfunction
[E]=fsolve(E_guess,solver_func,tol)//using inbuilt function fsolve for solving the system of equations
//Calculation of the composition of the equilibrium mixture (for CH3OH(g),CO(g),H2(g),A(g) respectively)(no unit)
y_CH3OH=(m(1,:)+(n(1,:)*E))/(mtot+(del_n*E));
y_CO=(m(2,:)+(n(2,:)*E))/(mtot+(del_n*E));
y_H2=(m(3,:)+(n(3,:)*E))/(mtot+(del_n*E));
y_A=m(4,:)/(mtot+(del_n*E));
//OUTPUT
mprintf('The degree of conversion at 500K and 5bar pressure=%0.5f\n',E);
mprintf('The composition of the equilibrium mixture at 500K and 5bar pressure: y_CH3OH=%0.5f\t y_CO=%0.5f\t y_H2=%0.5f\t y_A=%0.4f \n',y_CH3OH,y_CO,y_H2,y_A);
//=================================================END OF PROGRAM=================================================
```

**Scilab code Exa 14.8** Degree of conversion for different feed conditions

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 8,Page 498
//Title: Degree of conversion for different feed conditions
//================================================================================
```

```
clear
clc

//INPUT
//Industrial methanol is produced by the following reaction:
//CO(g)+2H2(g)--->CH3OH(g)
T0=298.15;//standard temperature in K
T=500;//temperature in K
P=5;//pressure in bar
del_Hv=37.988;//enthalpy of vapourization of CH3OH at 298.15K in kJ/mol
R=8.314;//universal gas constant in J/molK
del_Gf=[-161.781;-137.327;0]//Standard Gibbs free energies of formation of CH3OH(g) from Example (14.2),CO(g) and H2(g) respectively in kJ
del_Hf=[-238.648;-110.532;0]//Standard enthalpies of formation of CH3OH(l), CO(g) and H2(g) respectively in kJ
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K from Appendix A.3
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
a=[18.382;28.068;27.012];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
b=[101.564*10^-3;4.631*10^-3;3.509*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
c=[-28.683*10^-6;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
d=[0;0;0];
```

```
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
e=[0;-0.258*10^5;0.690*10^5];
n=[1;-1;-2];//stoichiometric coefficients of CH3OH(g),CO(g) and H2(g) respectively (no unit)
//The degree of conversion has been determined for 3 different feed conditions:
//a) an equimolar mixture of CO(g) and H2(g) is fed to the reactor
//b) stoichiometric mixture of CO(g) and H2(g) is fed to the reactor
//c) CO(g) and H2(g) in the ratio 1:4 enter the reactor
m_a=[0;1;1];//mole number in feed (for CH3OH(g),CO(g),H2(g) respectively for condition (a))
m_b=[0;1;2];//mole number in feed (for CH3OH(g),CO(g),H2(g) respectively for condition (b))
m_c=[0;1;4];//mole number in feed (for CH3OH(g),CO(g),H2(g) respectively for condition (c))

//CALCULATION
del_Hf_CH3OH_g=del_Hf(1,:)+del_Hv;//calculation of the standard enthalpy of formation of CH3OH(g) in kJ
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:));//calculation of the Gibbs free energy of reaction in kJ
del_H=del_Hf_CH3OH_g+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:));//calculation of the enthalpy of the reaction in kJ
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:));
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:)
```

```
);
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))*10^-3;
//Using Eq.14.23 to compute the integration constant (no unit)
I=(1/(R*T0))*((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3));
//Using Eq.14.23 to compute the Gibbs free energy of the reaction at T in kJ
del_G_T=((del_H0*10^3)-(del_a*T*log(T))-((del_b/2)*T^2)-((del_c/6)*T^3)-((del_d/12)*T^4)-((del_e/2)*(1/T))-(I*R*T))*10^-3;
Ka=exp((-del_G_T*10^3)/(R*T));//calculation of the equilibrium constant (no unit)
del_n=n(1,:)+n(2,:)+n(3,:);//calculation of the total mole number (no unit)
Ky=Ka/((P)^del_n);//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (K_phi=1.0,assuming ideal gas behaviour)
mtot_a=m_a(1,:)+m_a(2,:)+m_a(3,:);//calculation of the total mole number of feed entering (no unit) (for condition (a))
mtot_b=m_b(1,:)+m_b(2,:)+m_b(3,:);//calculation of the total mole number of feed entering (no unit) (for condition (b))
mtot_c=m_c(1,:)+m_c(2,:)+m_c(3,:);//calculation of the total mole number of feed entering (no unit) (for condition (c))
//To determine the degree of conversion , the inbuilt
```

```
function fsolve is used to solve the equation given by Ky=(y_CH3OH)/(y_CO*y_H2^2), where y_CH3OH,y_CO,y_H2  are the mole fractions of CH3OH,CO,H2 respectively. Let the equilibrium conversion be denoted as E. This is done for all the three conditions (a,b and c)
E_guess=0.1;//taking a guess value for the degree of conversion,to be used in the inbuilt function fsolve (no unit)
tol=1e-6;//tolerance limit for convergence of the system  when using fsolve
//For condition (a)
function[fn]=solver_func1(Ei)
    //Function defined for solving the system
 fn=Ky-((((m_a(1,:)+(n(1,:)*Ei))/(mtot_a+(del_n*Ei)))^n(1,:))*(((m_a(2,:)+(n(2,:)*Ei))/(mtot_a+(del_n*Ei)))^n(2,:))*(((m_a(3,:)+(n(3,:)*Ei))/(mtot_a+(del_n*Ei)))^n(3,:)));
endfunction
[E_a]=fsolve(E_guess,solver_func1,tol)//using inbuilt function fsolve for solving the system of equations
//For condition (b)
function[fn]=solver_func2(Ei)
    //Function defined for solving the system
 fn=Ky-((((m_b(1,:)+(n(1,:)*Ei))/(mtot_b+(del_n*Ei)))^n(1,:))*(((m_b(2,:)+(n(2,:)*Ei))/(mtot_b+(del_n*Ei)))^n(2,:))*(((m_b(3,:)+(n(3,:)*Ei))/(mtot_b+(del_n*Ei)))^n(3,:)));
endfunction
[E_b]=fsolve(E_guess,solver_func2,tol)//using inbuilt function fsolve for solving the system of equations
//For condition (c)
function[fn]=solver_func3(Ei)
    //Function defined for solving the system
 fn=Ky-((((m_c(1,:)+(n(1,:)*Ei))/(mtot_c+(del_n*Ei)))^n(1,:))*(((m_c(2,:)+(n(2,:)*Ei))/(mtot_c+(
```

```
del_n*Ei)))^n(2,:))*(((m_c(3,:)+(n(3,:)*Ei))/(mtot_c+(del_n*Ei)))^n(3,:)));
endfunction
[E_c]=fsolve(E_guess,solver_func3,tol)//using inbuilt function fsolve for solving the system of equations

//OUTPUT
mprintf('The degree of conversion at 500K and 5bar pressure, for an equimolar mixture of CO(g) and H2(g) as feed=%f\n',E_a);
mprintf('The degree of conversion at 500K and 5bar pressure, for a stoichiometric mixture of CO(g) and H2(g) as feed=%0.4f\n',E_b);
mprintf('The degree of conversion at 500K and 5bar pressure, for a feed of CO(g) and H2(g) in the ratio of 1:4=%f\n',E_c);


//========================================================END OF PROGRAM========================================================
```

---

**Scilab code Exa 14.9** Degree of conversion

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 9,Page 499
//Title: Degree of conversion
//==========================================================================
```

```
clear
clc

//INPUT
//Industrial methanol is produced by the following reaction:
//CO(g)+2H2(g)--->CH3OH(g)
T0=298.15;//standard temperature in K
T=500;//temperature in K
P=5;//pressure in bar
del_Hv=37.988;//enthalpy of vapourization of CH3OH at 298.15K in kJ/mol
R=8.314;//universal gas constant in J/molK
del_Gf=[-161.781;-137.327;0]//Standard Gibbs free energies of formation of CH3OH(g) from Example (14.2),CO(g) and H2(g) respectively in kJ
del_Hf=[-238.648;-110.532;0]//Standard enthalpies of formation of CH3OH(l), CO(g) and H2(g) respectively in kJ
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K from Appendix A.3
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
a=[18.382;28.068;27.012];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
b=[101.564*10^-3;4.631*10^-3;3.509*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
c=[-28.683*10^-6;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
d=[0;0;0];
```

```
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for CH3OH(g),CO(g),H2(g) respectively)
e=[0;-0.258*10^5;0.690*10^5];
n=[1;-1;-2];//stoichiometric coefficients of CH3OH(g),CO(g) and H2(g) respectively (no unit)
m=[0.02;1;2];//mole number in feed (for CH3OH(g),CO(g),H2(g) respectively)

//CALCULATION
del_Hf_CH3OH_g=del_Hf(1,:)+del_Hv;//calculation of the standard enthalpy of formation of CH3OH(g) in kJ
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:));//calculation of the Gibbs free energy of reaction in kJ
del_H=del_Hf_CH3OH_g+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:));//calculation of the enthalpy of the reaction in kJ
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:));
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))*10^-3;
//Using Eq.14.23 to compute the integration constant (no unit)
```

```
I=(1/(R*T0))*((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3));
//Using Eq.14.23 to compute the Gibbs free energy of the reaction at T in kJ
del_G_T=((del_H0*10^3)-(del_a*T*log(T))-((del_b/2)*T^2)-((del_c/6)*T^3)-((del_d/12)*T^4)-((del_e/2)*(1/T))-(I*R*T))*10^-3;
Ka=exp((-del_G_T*10^3)/(R*T));//calculation of the equilibrium constant (no unit)
del_n=n(1,:)+n(2,:)+n(3,:);//calculation of the total mole number (no unit)
Ky=Ka/((P)^del_n);//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (K_phi=1.0,assuming ideal gas behaviour)
mtot=m(1,:)+m(2,:)+m(3,:);//calculation of the total mole number of feed entering (no unit)
//To determine the degree of conversion, the inbuilt function fsolve is used to solve the equation given by Ky=(y_CH3OH)/(y_CO*y_H2^2), where y_CH3OH,y_CO,y_H2  are the mole fractions of CH3OH,CO,H2 respectively. Let the equilibrium conversion be denoted as E
E_guess=0.1;//taking a guess value for the degree of conversion,to be used in the inbuilt function fsolve (no unit)
tol=1e-6;//tolerance limit for convergence of the system  when using fsolve
function[fn]=solver_func(Ei)
    //Function defined for solving the system
 fn=Ky-((((m(1,:)+(n(1,:)*Ei))/(mtot+(del_n*Ei)))^n(1,:))*(((m(2,:)+(n(2,:)*Ei))/(mtot+(del_n*Ei)))^n(2,:))*(((m(3,:)+(n(3,:)*Ei))/(mtot+(del_n*Ei)))^n(3,:)));
endfunction
[E]=fsolve(E_guess,solver_func,tol)//using inbuilt function fsolve for solving the system of
```

```
equations


//OUTPUT
mprintf('The degree of conversion at 500K and 5bar pressure=%f\n',E);

//==========================================================END OF PROGRAM==============================================================
```

**Scilab code Exa 14.10** Adiabatic reaction temperature

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 10,Page 500
//Title: Adiabatic reaction temperature
//================================================================================================

clear
clc

//INPUT
T0=298.15;//temperature at the entrance (feed) in K
P=0.1;//pressure (operating) in MPa
//The reaction is given by: H2(g)+(1/2)O2(g)--->H20(g)
n=[1;-1;-0.5];//stoichiometric coefficients of H2O(g),H2(g)and O2(g) respectively (no unit)
n_r=[1;0.5];//stochiometric coefficients on the reactant side alone for computing the right hand
```

```
side of Eq.(A)
m=[0;1;0.5];//inlet mole number of H2O(g),H2(g) and O2(g) respectively
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K from Appendix A.3
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for H2O(g),H2(g),O2(g) respectively)
a=[28.850;27.012;30.255];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for H2O(g),H2(g),O2(g) respectively)
b=[12.055*10^-3;3.509*10^-3;4.207*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for H2O(g),H2(g),O2(g) respectively)
c=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for H2O(g),H2(g),O2(g) respectively)
d=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity from Appendix A.3 (for H2O(g),H2(g),O2(g) respectively)
e=[1.006*10^5;0.690*10^5;-1.887*10^5];
del_H=-241.997;//enthalpy of reaction at 298.15K in kJ
del_G=-228.600;//Gibbs free energy of reaction at 298.15K in kJ
R=8.314;//universal gas constant in J/molK

//CALCULATION
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:)
```

```
);
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
mtot=m(1,:)+m(2,:)+m(3,:);//calculation of the total mole number of feed entering (no unit)
del_n=n(1,:)+n(2,:)+n(3,:);//calculation of the total mole number (no unit)
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))*10^-3;
//Using Eq.14.23 to compute the integration constant
I=(1/(R*T0))*(((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3)));
//The conversion is computed by using Eq.(A) and by Eq.(B) and the two are plotted with respect to temperature. The point of intersection gives the adiabatic reaction temeperature and from that the conversion and the composition are determined. Let E_A denote the conversion obtained by using Eq.A and E_B denote the conversion obtained by using Eq.B (no unit)
//For both the equations, conversion is determined for a temperature range of 2000 to 3800K, by incrementing temperature by 100K every time.
T=2000:100:3800;//framing the temperature range in K
l=length(T);//iteration parameter (no unit)
i=1;//iteration parameter
tol=1e-4;//tolerance limit for convergence of the system when using fsolve
while i<l|i==l
    del_H_T(i)=((del_H0*10^3)+((del_a*T(:,i))+((
```

```
del_b/2)*T(:,i)^2)+((del_c/3)*T(:,i)^3)+((del_d/4)*T(:,i)^4)-(del_e/T(:,i)))))*10^-3;
del_G_T(i)=((del_H0*10^3)-(del_a*T(:,i)*log(T(:,i)))-((del_b/2)*T(:,i)^2)-((del_c/6)*T(:,i)^3)-((del_d/12)*T(:,i)^4)-((del_e/2)*(1/T(:,i)))-(I*R*T(:,i)))*10^-3;
  Ka(i)=exp(-(del_G_T(i)*10^3)/(R*T(:,i)));//calculation of the equilibrium constant (no unit)
  //using Eq.A to determine the conversion(no unit)
E_A(i)=(1/del_H_T(i)*10^-3)*(-((((n_r(1,:)*a(2,:))+(n_r(2,:)*a(3,:)))*(T(:,i)-T0))+((((n_r(1,:)*b(2,:))+(n_r(2,:)*b(3,:)))/2)*((T(:,i))^2-(T0^2)))+((((n_r(1,:)*c(2,:))+(n_r(2,:)*c(3,:)))/3)*((T(:,i))^3-(T0^3)))+((((n_r(1,:)*d(2,:))+(n_r(2,:)*d(3,:)))/4)*((T(:,i))^4-(T0^4)))+(((n_r(1,:)*a(2,:))+(n_r(2,:)*a(3,:)))*((1/T(:,i))-(1/T0)))));
Eguess(i)=0.99;//taking a guess value for the conversion (no unit)
function[fn]=solver_func(Ei)
  //Function defined for solving the system (Using Eq.B to determine the conversion (no unit))
fn=((((m(1,:)+(n(1,:)*Ei))/(mtot+(del_n*Ei)))^n(1,:))*(((m(2,:)+(n(2,:)*Ei))/(mtot+(del_n*Ei)))^n(2,:))*(((m(3,:)+(n(3,:)*Ei))/(mtot+(del_n*Ei)))^n(3,:)))-Ka(i);
endfunction
[E_B(i)]=fsolve(Eguess(i),solver_func,tol)//using inbuilt function fsolve for solving the system of equations
i=i+1
end
//plotting the conversions determined above (using Eqs.A and B respectively) against temperature to determine the adiabatic reaction temperature in K
plot(T,E_A,T,E_B);
legends(['Equation (A)';'Equation (B)'],[2,3],opt=”
```

```
lr");
xtitle('Plot of degree of conversion versus adiabatic reaction temperature','T(K)','E');
//From the above plot, it is determined that the point of intersection occurs around 3440K, which is taken as the reaction temperature, where the conversion=0.68(no unit). Therefore, the conversion at the adiabatic reaction temperature is 0.68
T_adiabatic=3440;//the adiabatic reaction temperature in K
E_adiabatic=0.68;//conversion at the adiabatic reaction temperature (no unit)
//Calculation of the composition of the burned gas (H2,O2 and H2O respectively) at the adiabatic reaction temperature (no unit)
y_H2=((m(2,:)+(n(2,:)*E_adiabatic))/(mtot+(del_n*E_adiabatic)));
y_O2=((m(3,:)+(n(3,:)*E_adiabatic))/(mtot+(del_n*E_adiabatic)));
y_H2O=((m(1,:)+(n(1,:)*E_adiabatic))/(mtot+(del_n*E_adiabatic)));

//OUTPUT
mprintf('\n The adiabatic reaction temperature=%d K\n',T_adiabatic);
mprintf('\n The composition of the burned gases is given by: y_H2=%0.4f \t y_O2=%0.4f \t y_H2O=%0.4f \n',y_H2,y_O2,y_H2O);

//===================================================END OF PROGRAM===================================================
```

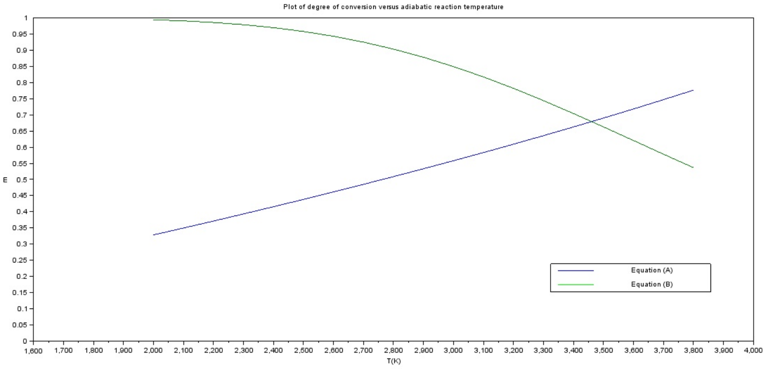

Figure 14.1: Adiabatic reaction temperature

**Scilab code Exa 14.11** Primary reactions

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 11,Page 506
//Title: Primary reactions
//================================================================================
clear
clc


//INPUT

//The reactions occuring during steam reformation are given by:
//CH4(g)+H2O(g)---->CO(g)+3H2(g)
```

```
//CO(g)+H2O(g)------>CO2(g)+H2(g)
//CH4(g)+2H2O(g)----->CO2(g)+4H2(g)
//CO2(g)----->CO(g)+(1/2)O2(g)
//CH4(g)+2O2(g)----->CO2(g)+2H2O(g)
//CH4(g)+O2(g)----->CO(g)+H2O(g)+H2(g)

//Let CH4=A1,H2O=A2,CO=A3,H2=A4,CO2=A5,O2=A6

stoichio_matrix=[-1 -1 1 3 0 0;0 -1 -1 1 1 0;-1 -2 0 4 1 0;0 0 1 0 -1 0.5;-1 2 0 0 1 -2;-1 1 1 1 0 -1]//Framing the stoichiometric coefficient matrix



//CALCULATION

r=rank(stoichio_matrix);//Determining the rank of the given matrix(number of independent row/columns),which is indicative of the number of primary reactions

//Performing elementary row operations to obtain diagonal elements as 0 or 1 and all elements below the diagonal as zero
stoichio_matrix(1,:)=-stoichio_matrix(1,:);
stoichio_matrix(3,:)=stoichio_matrix(3,:)+stoichio_matrix(1,:);
stoichio_matrix(5,:)=stoichio_matrix(5,:)+stoichio_matrix(1,:);
stoichio_matrix(6,:)=stoichio_matrix(6,:)+stoichio_matrix(1,:);
stoichio_matrix(2,:)=-stoichio_matrix(2,:);
stoichio_matrix(3,:)=stoichio_matrix(3,:)+stoichio_matrix(2,:);
stoichio_matrix(5,:)=stoichio_matrix(5,:)-(3*stoichio_matrix(2,:));
stoichio_matrix(6,:)=stoichio_matrix(6,:)-(2*
```

```
    stoichio_matrix(2,:));
x=stoichio_matrix(:,3);
y=stoichio_matrix(:,4);
stoichio_matrix(:,3)=y;
stoichio_matrix(:,4)=x;
stoichio_matrix(5,:)=stoichio_matrix(5,:)+(4*
    stoichio_matrix(4,:));
stoichio_matrix(6,:)=stoichio_matrix(6,:)+(2*
    stoichio_matrix(4,:));



//OUTPUT
mprintf('\n The stoichiometric coefficient matrix
    after performing the elementary row operations=\n
    ');
disp(stoichio_matrix);
mprintf('\n The number of primary reactions=%d\n',r)
    ;
mprintf('\n The non zero rows are (1,2,4)\n');
mprintf('\n The primary reactions are: CH4(g)+H2O(g)
    --->CO(g)+3H2(g), CO(g)+H2O(g)--->CO2(g)+H2(g),
    CO2(g)--->CO(g)+(1/2)O2(g)\n');

//==============================================END
    OF PROGRAM
    ===================================================
```

**Scilab code Exa 14.13** Equilibrium composition in a simultaneous reaction

```
// Y.V.C.Rao ,1997.Chemical Engineering
    Thermodynamics.Universities Press,Hyderabad,India
    .
```

```

//Chapter-14,Example 13,Page 510
//Title: Equilibrium composition in a simultaneous reaction
//================================================================================
clear
clc

//INPUT
//The simultaneous reactions are given as:
//A+B----->C+D =>1
//A+C----->D+E =>2
Ka1=0.1429;//equilibrium constant of reaction 1 (no unit)
Ka2=2;//equilibrium constant of reaction 2 (no unit)
P=1;//pressure in bar
m=[1;1;0;0;0];//mole number in the feed (for A,B,C,D and E respectively) (equimolar mixture of A and B are present in the feed)
n1=[-1;-1;1;1;0];//stoichiometric coefficients for reaction 1 (A,B,C D,E respectively) (no unit)
n2=[-1;0;-1;1;1];//stoichiometric coefficients for reaction 2 (A,B,C D E respectively) (no unit)

//CALCULATION
del_n1=n1(1,:)+n1(2,:)+n1(3,:)+n1(4,:);//calculation of the total mole number for reaction 1 (no unit)
del_n2=n2(1,:)+n2(2,:)+n2(3,:)+n2(4,:);//calculation of the total mole number for reaction 2 (no unit)
//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (for reaction 1) (K_phi=1.0,assuming ideal gas behaviour)
Ky1=Ka1/(P^del_n1);
```

```
//calculation of the equilibrium constant in terms of the mole fractions using Eq.(14.30) (no unit) (for reaction 2) (K_phi=1.0,assuming ideal gas behaviour)
Ky2=Ka2/(P^del_n2);
mtot=m(1,:)+m(2,:)+m(3,:)+m(4,:)+m(5,:);//calculation of the total mole number of feed entering (no unit)
//To determine the degree of conversion, a trial and error process is used to solve the equations given by Ky1=(y_C*y_D)/(y_A*y_B), and Ky2=(y_D*y_E)/(y_A*y_C)  where y_A,y_B,y_C,y_D,y_E are the mole fractions of A,B,C,D and E respectively. Let the equilibrium conversion be denoted as epsilon1 for reaction 1 and epsilon2 for reaction 2 respectively.
epsilon1_guess=0.3;//taking a guess value for the degree of conversion (reaction1) for the trial and error process (no unit)
tol=1e-6;//defining the tolerance limit for obtaining the convergence of the system using fsolve
E_guess=0.1;//taking a guess value for the degree of conversion (reaction2) to be used for solving the set of equations by the inbuilt function fsolve
function[fn1]=solver_func1(En)
    //The system of equations to be solved for reaction 1
    fn1=Ky1-((((m(3,:)+(n1(3,:)*epsilon1_guess)+(n2(3,:)*En))/(mtot))^n1(3,:))*(((m(4,:)+(n1(4,:)*epsilon1_guess)+(n2(4,:)*En))/(mtot))^n1(4,:))*(((m(1,:)+(n1(1,:)*epsilon1_guess)+(n2(1,:)*En))/(mtot))^n1(1,:))*(((m(2,:)+(n1(2,:)*epsilon1_guess)+(n2(2,:)*En))/(mtot))^n1(2,:)));
endfunction
[epsilon2]=fsolve(E_guess,solver_func1,tol);//using
```

```
inbuilt function fsolve for solving the system of equations
E_guess=0.2;//taking a guess value for the degree of conversion (reaction1) to be used for solving the set of equations by the inbuilt function fsolve
function[fn2]=solver_func2(Em)
    //For reaction 2, the degree of conversion(reaction2), determined above is used along with the guess value and the system of equations below are solved
fn2=Ky2-((((m(4,:)+(n1(4,:)*Em)+(n2(4,:)*epsilon2))/(mtot))^n2(4,:))*(((m(5,:)+(n1(5,:)*Em)+(n2(5,:)*epsilon2))/(mtot))^n2(5,:))*(((m(1,:)+(n1(1,:)*Em)+(n2(1,:)*epsilon2))/(mtot))^n2(1,:))*(((m(3,:)+(n1(3,:)*Em)+(n2(3,:)*epsilon2))/(mtot))^n2(3,:)));
endfunction
[epsilon1]=fsolve(E_guess,solver_func2,tol);//using inbuilt function fsolve for solving the system of equations
//calculation of the equilibrium composition at 1 bar pressure of A,B,C,D and E respectively (no unit)
y_A=((m(1,:)+(n1(1,:)*epsilon1)+(n2(1,:)*epsilon2)))/(mtot);
y_B=(m(2,:)+(n1(2,:)*epsilon1)+(n2(2,:)*epsilon2))/(mtot);
y_C=((m(3,:)+(n1(3,:)*epsilon1)+(n2(3,:)*epsilon2)))/(mtot);
y_D=(m(4,:)+(n1(4,:)*epsilon1)+(n2(4,:)*epsilon2))/(mtot);
y_E=((m(5,:)+(n1(5,:)*epsilon1)+(n2(5,:)*epsilon2)))/(mtot);

//OUTPUT
mprintf('\nThe degree of conversion :epsilon1=%0.1f\t epsilon2=%0.1f \n',epsilon1,epsilon2);
```

```
mprintf('\nThe equilibrium composition at 1 bar pressure for an equimolar mixture of A and B fed to the reactor:\n y_A=%0.2f \t y_B=%0.2f \t y_C=%0.2f \t y_D=%0.2f \t y_E=%0.1f\n',y_A,y_B,y_C,y_D,y_E);


//==========================================================END OF PROGRAM==========================================================
```

**Scilab code Exa 14.14** Equilibrium concentration

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 14,Page 515
//Title: Equilibrium concentration
//================================================================================================================

clear
clc

//INPUT
//The reaction is given by :
//CH3COOH(l)+C2H5OH(l)--->CH3COOC2H5(l)+H2O(l)
T=100;//temperature in degree celsius
Kc=2.92;//equilibrium constant (in terms of concentration) at T (no unit)
v=1;//volume of the aqueous solution in m^3
m=[0;10;10;5];//feed composition of CH3COOC2H5(l),H20(l),C2H5OH(l),CH3COOH(l) respectively in kmol
```

```
n=[1;1;-1;-1];//stoichiometric coefficient for the reaction (no unit)(CH3COOC2H5(l),H20(l),C2H5OH(l),CH3COOH(l) respectively)

//CALCULATION
//For convenience, CH3COOH(l) is denoted as A, C2H5OH(l) is denoted as B, CH3COOC2H5(l) is denoted as C and H2O(l) as D
//Calculation of the extent of the reaction, expressed in concentration units.The inbuilt function fsolve is used for solving the set of equations
tol=1e-6;//tolerance limit framed for the convergence of the system of equations by using fsolve
Eguess=1;//taking a guess value for the extent of reaction (no unit)
function[fn]=solver_func(Ei)
    //Function defined for solving the system
    fn=Kc-(((m(1,:)+n(1,:)*Ei)^n(1,:))*((m(2,:)+n(2,:)*Ei)^n(2,:))*((m(3,:)+n(3,:)*Ei)^n(3,:))*((m(4,:)+n(4,:)*Ei)^n(4,:)));
endfunction
[E]=fsolve(Eguess,solver_func,tol);//using inbuilt function fsolve for solving the system of equations
C_A=(m(4,:)+n(4,:)*E);//equilibrium concentration of CH3COOH(l) (no unit)
C_B=(m(3,:)+n(3,:)*E);//equilibrium concentration of C2H5OH(l) (no unit)
C_C=(m(1,:)+n(1,:)*E);//equilibrium concentration of CH3COOC2H5(l) (no unit)
C_D=(m(2,:)+n(2,:)*E);//equilibrium concentration of H2O(l) (no unit)

//OUTPUT
mprintf('\n The extent of reaction, expressed in concentration units=%0.4f\n',E);
```

```
mprintf('\n The equilibrium concentration:C_A=%0.4f kmol/m^3 \t C_B=%0.4f kmol/m^3 \t C_C=%0.4f kmol/m^3 \t C_D=%0.4f kmol/m^3 \n',C_A,C_B,C_C,C_D);

//================================================END OF PROGRAM ===========================================================
```

---

**Scilab code Exa 14.15** Decomposition pressure

```
// Y.V.C.Rao ,1997.Chemical Engineering Thermodynamics.Universities Press,Hyderabad,India.

//Chapter-14,Example 15,Page 517
//Title: Decomposition pressure
//================================================================================================================================

clear
clc

//INPUT
//The reaction is given by: CaCO3(s)--->CaO(s)+CO2(g)
T=1200;//temperature in K
T0=298.15;//reference temperature in K
//The isobaric molar capacity is given by Cp=a+bT+cT^2+dT^3+eT^-2 in J/molK and T is in K
//coefficient in the expression for computing the isobaric molar heat capacity (for CaO(s),CO2(g),CaCO3(s) respectively)
a=[41.84;45.369;82.34];
//coefficient in the expression for computing the
```

```
isobaric molar heat capacity (for CaO(s),CO2(g),CaCO3(s) respectively)
b=[20.25*10^-3;8.688*10^-3;49.75*10^-3];
//coefficient in the expression for computing the isobaric molar heat capacity (for CaO(s),CO2(g),CaCO3(s) respectively)
c=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity (for CaO(s),CO2(g),CaCO3(s) respectively)
d=[0;0;0];
//coefficient in the expression for computing the isobaric molar heat capacity (for CaO(s),CO2(g),CaCO3(s) respectively)
e=[-4.51*10^5;-9.619*10^5;-12.87*10^5];
del_Gf=[-604.574;-394.815;-1129.515]//Standard Gibbs free energies of formation of (CaO(s),CO2(g),CaCO3(s)) in kJ
del_Hf=[-635.975;-393.978;-1207.683]//Standard enthalpies of formation of (CaO(s),CO2(g),CaCO3(s))in kJ
n=[1;1;-1];//stoichiometric coefficients of CaO(s),CO2(g) and CaCO3(s) respectively (no unit)
R=8.314;//universal gas constant in J/molK

//CALCULATION
del_G=(n(1,:)*del_Gf(1,:))+(n(2,:)*del_Gf(2,:))+(n(3,:)*del_Gf(3,:));//calculation of the Gibbs free energy of reaction in kJ
del_H=(n(1,:)*del_Hf(1,:))+(n(2,:)*del_Hf(2,:))+(n(3,:)*del_Hf(3,:));//calculation of the enthalpy of the reaction in kJ
//Framing the isobaric molar heat capacity expression
del_a=(n(1,:)*a(1,:))+(n(2,:)*a(2,:))+(n(3,:)*a(3,:));
del_b=(n(1,:)*b(1,:))+(n(2,:)*b(2,:))+(n(3,:)*b(3,:));
```

```
del_c=(n(1,:)*c(1,:))+(n(2,:)*c(2,:))+(n(3,:)*c(3,:));
del_d=(n(1,:)*d(1,:))+(n(2,:)*d(2,:))+(n(3,:)*d(3,:));
del_e=(n(1,:)*e(1,:))+(n(2,:)*e(2,:))+(n(3,:)*e(3,:));
//Using Eq.14.21 to compute the value of del_H0 in kJ
del_H0=((del_H*10^3)-((del_a*T0)+((del_b/2)*T0^2)+((del_c/3)*T0^3)+((del_d/4)*T0^4)-(del_e/T0)))*10^-3;
//Using Eq.14.23 to compute the value of IR (no unit)
IR=(1/(T0))*((del_H0*10^3)-(del_a*T0*log(T0))-((del_b/2)*T0^2)-((del_c/6)*T0^3)-((del_d/12)*T0^4)-((del_e/2)*(1/T0))-(del_G*10^3));
//Using Eq.14.23 to compute the Gibbs free energy of the reaction at T in kJ
del_G_T=((del_H0*10^3)-(del_a*T*log(T))-((del_b/2)*T^2)-((del_c/6)*T^3)-((del_d/12)*T^4)-((del_e/2)*(1/T))-(IR*T))*10^-3;
Ka=exp((-del_G_T*10^3)/(R*T));//calculation of the equilibrium constant (no unit)
//Now, Ka=(a_CaO*a_CO2)/a_CaCO3. We get a_CaO=1 and a_CaCO3=1, if we choose the pure component solids CaO(s) and CaCO3(s) at 1200K(at T)and 1 bar pressure as the  standard states. Then, Ka=a_CO2=(f/f0)_CO2=((phi*y*P)/f0)_CO2. Assume the gas phase (pure CO2) is ideal. Then, phi=1 and y=1. The usual standard state for the gas gives f0=1 bar.Therefore, Ka=P
y=1;
phi=1;
f0=1;
P=(Ka*f0)/(phi*y);//calculation of the decomposition pressure in bar

//OUTPUT
```

```
mprintf('\n The decomposition pressure ,P=%f bar \n',
   P);

//=========================================================END
    OF PROGRAM
   ==============================================================


//DISCLAIMER: THE TEXTBOOK, GIVES A VALUE OF 2.42
   bar FOR THE VALUE OF THE DECOMPOSITION PRESSURE.
   HOWEVER, THE ACTUAL VALUE IS ONLY 2.38 bar AND
   NOT 2.42 bar AS PRINTED IN THE TEXTBOOK.
```