Solve each problem on separate sheets of paper, and clearly indicate the problem number and your name on each. Carefully and neatly document your answers. You may use a mathematical solver like Matlab or Mathematica. Use plotting software for all plots.

1 Partial molar concepts

Following is some data on the heat evolved when 1 mole of sulfuric acid (H_2SO_4) is isothermally mixed with H_2O at 298 K.

N_{H_2O} (mols)	0.25	1.0	1.5	2.33	4.0	5.44	9.0	10.1	19.0	20.0
$-\Delta H_{\text{mix}}$ (J)	8242	28200	34980	44690	54440	58370	62800	64850	70710	71970

1. Is this mixture ideal? Why?
2. Determine and plot the molar enthalpy of mixing as a function of mole fraction of H_2SO_4.
3. Estimate the heat evolved when 100 g of a 60%(w/w) sulfuric acid solution is mixed with 75 g of a 25%(w/w) sulfuric acid solution. *Hints*: What is the molar composition of the initial solutions? Of the final one?)
4. Estimate the partial molar enthalpies of H_2O and H_2SO in a 50%(w/w) solution.
5. The mixing enthalpy of a "regular" solution can be written as $\chi_{12}x_1x_2$. Fit the data to this model to estimate χ_{12} and to estimate the partial molar enthalpies of H_2O and H_2SO in a 50%(w/w) solution.

Problem 1. Partial molar concepts

1(a). For a mixture to be ideal, we need ΔHmix=0. However in this case ΔHmix≠0. The mixture is not ideal.

1(b). Plot molar enthalpy of mixing as a function of mole fraction of H2SO4.

In[9]:=
```
Nh2so4 = 1; MWh2so4 = 98.708;
Nh2o = {0.25, 1, 1.5, 2.33, 4, 5.44, 9, 10.1, 19, 20};
MWh2o = 18;
dHmix = -{8242, 28 200, 34 980, 44 690, 54 440, 58 370, 62 800, 64 850, 70 710, 71 970};
```

In[13]:=
```
xh2so4 = Nh2so4 / (Nh2so4 + Nh2o)
```

Out[13]= $\left\{0.8, \frac{1}{2}, 0.4, 0.3003, \frac{1}{5}, 0.15528, \frac{1}{10}, 0.0900901, \frac{1}{20}, \frac{1}{21}\right\}$

In[14]:=
```
dHmix = dHmix / (Nh2so4 + Nh2o)
```

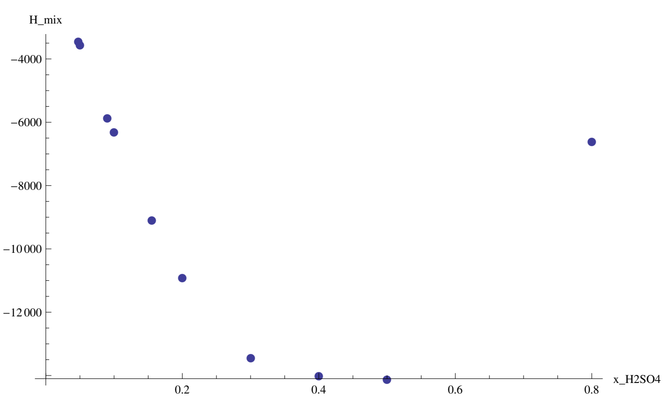
Out[14]= $\left\{-6593.6, -14\,100, -13\,992., -13\,420.4, -10\,888, -9063.66, -6280, -5842.34, -\frac{7071}{2}, -\frac{23\,990}{7}\right\}$

In[46]:=
```
dataset = Thread[{xh2so4, dHmix}]
```

Out[46]= $\left\{\{0.8, -6593.6\}, \left\{\frac{1}{2}, -14\,100\right\}, \{0.4, -13\,992.\}, \{0.3003, -13\,420.4\}, \left\{\frac{1}{5}, -10\,888\right\}, \{0.15528, -9063.66\}, \left\{\frac{1}{10}, -6280\right\}, \{0.0900901, -5842.34\}, \left\{\frac{1}{20}, -\frac{7071}{2}\right\}, \left\{\frac{1}{21}, -\frac{23\,990}{7}\right\}\right\}$

In[20]:=
```
ListPlot[%, AxesLabel → {x_H2SO4, H_mix}, PlotMarkers → {●, 10}]
```

Out[20]=



1(c) Heat evolved in mixing

2 Phase diagrams for liquids

Within the regular solution model, the free energy of mixing two liquids is given by

$$\Delta g_{\mathrm{mix}} = RT\left\{x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}} + \chi_{\mathrm{AB}} x_{\mathrm{A}} x_{\mathrm{B}}\right\}$$

1. Suppose $\chi_{\mathrm{AB}} = 5$ at 300 K for some mixture of liquids A and B. You prepare a mixture of 0.3 mol A and 0.7 mol B at this temperature. How many phases are present at equilibrium,

what are their compositions, and how much of each phase (if more than one) is present?

2. What are the spinodal compositions at 300 K of the A/B mixture?

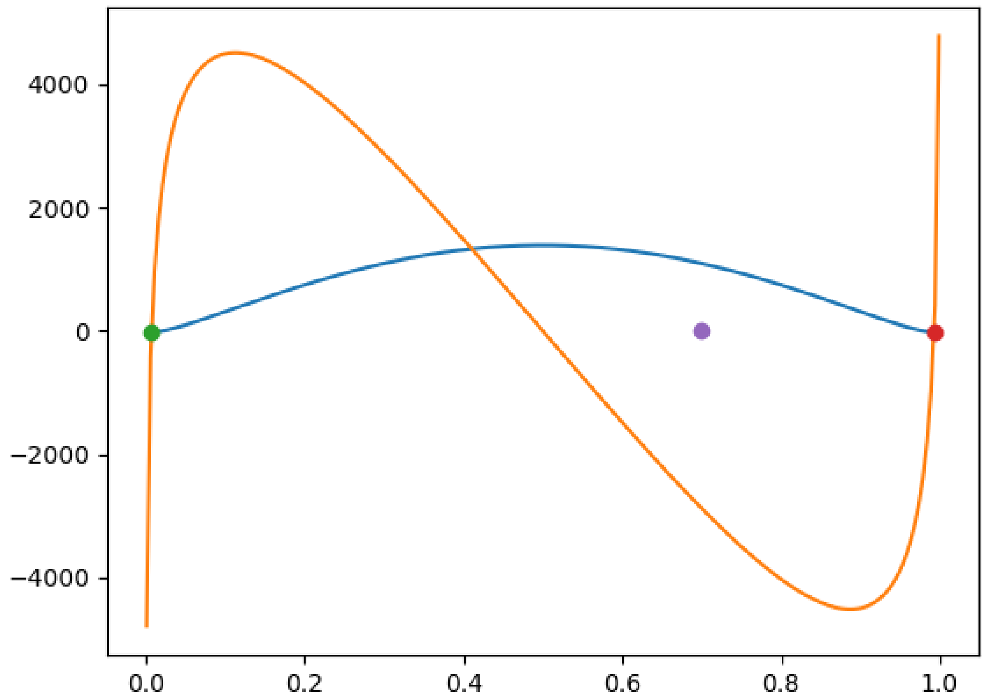
3. The binodal and spinodal curves meet at the critical point. The second and third derivatives of the free energy of mixing must vanish at this point. Find the critical composition and temperature of this mixture. Assume that $\chi_{AB} \propto 1/T$.

2.1 Solution

```
import numpy as np
import matplotlib.pyplot as plt
import scipy.optimize as opt

# free energy of mixing
def deltaf(xb):
    return R * T * ( xb * np.log(xb) + (1-xb) * np.log(1-xb)  + chi * xb * (1.-xb))

# first derivative
def ddeltaf(xb):
    return R * T * (np.log(xb) - np.log(1-xb) + chi * (1. - 2. * xb))

# second derivative
def dddeltaf(xb):
    return R * T * ((1./xb) + 1./(1.-xb) - 2. * chi)

# third derivative
def ddddeltaf(xb):
    return R * T * ( (-1./(xb*xb)) + 1./(1.-xb)**2)

R = 8.314
T = 300.
chi = 5.

xb = np.linspace(0.001,0.999,num=200)

plt.plot(xb,deltaf(xb))
plt.plot(xb,ddeltaf(xb))

arich = opt.newton(ddeltaf,0.01)
brich = opt.newton(ddeltaf,0.99)

plt.plot([arich],[deltaf(arich)],marker="o")
plt.plot([brich],[deltaf(brich)],marker="o")
plt.plot([0.7],[0.0],marker="o")
plt.savefig('mixture.png')

print("Two phases of composition {0:6.4f} and {1:6.4f}".format(arich,brich))

xb0 = 0.7

# Use lever rule:
amt1 = (xb0 - arich)/(brich - arich)
amt2 = (brich - xb0)/(brich - arich)

print("Of amounts {0:6.4f} and {1:6.4f}".format(amt2,amt1))

# find roots of second derivative of f
aspin = opt.newton(dddeltaf,0.05)
bspin = opt.newton(dddeltaf,0.95)

print("Spinodal composition {0:6.4f} and {1:6.4f}".format(aspin,bspin))

# find root of third derivative
x_crit = opt.newton(ddddeltaf,0.5)
```

```

# back substitute into second derivative
chi_crit = (1./x_crit + 1./(1.-x_crit))/2.

T_crit = 300.* ( chi/chi_crit)

print("Critical point composition {0:6.4f} and temperature {1:4.1f} K".format(x_crit,T_crit))
```

```
Two phases of composition 0.0072 and 0.9928
Of amounts 0.2971 and 0.7029
Spinodal composition 0.1127 and 0.8873
Critical point composition 0.5000 and temperature 750.0 K
```




```
0.00718806418267 0.992811935817
```

3 Funny phase diagrams

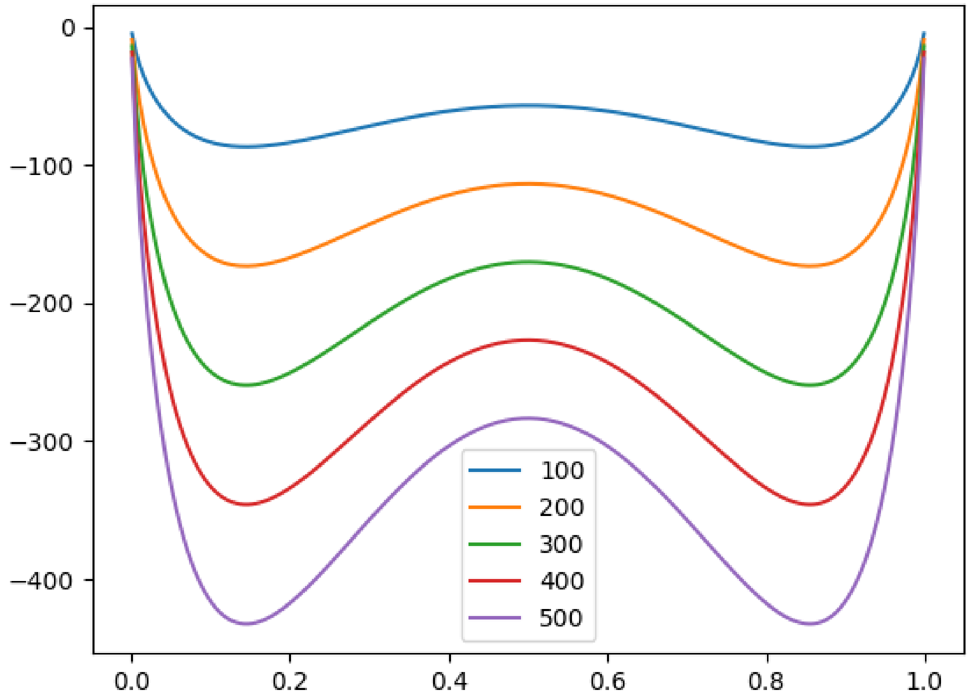
While $\chi_{\mathrm{AB}} \propto 1/T$ is the normal behavior, other dependencies are possible.

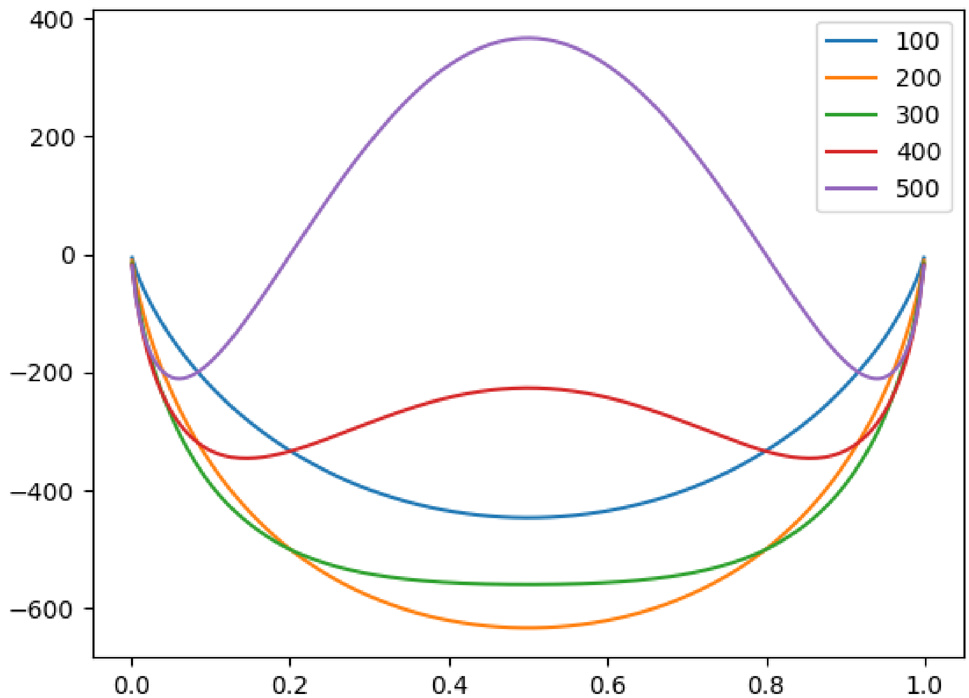
1. Construct a temperature vs. composition diagram for a system for which χ_{AB} is a positive constant independent of temperature.

2. Construct a temperature vs. composition diagram for a system for which $\chi_{\mathrm{AB}} \propto T$.

3.1 Solution

```
import numpy as np
import matplotlib.pyplot as plt
import scipy.optimize as opt

# free energy of mixing
def deltaf(xb):
    return R * T * ( xb * np.log(xb) + (1-xb) * np.log(1-xb)  + chi * xb * (1.-xb))

# first derivative
def ddeltaf(xb):
    return R * T * (np.log(xb) - np.log(1-xb) + chi * (1. - 2. * xb))

R = 8.314
chi = 2.5

xb = np.linspace(0.001,0.999,num=200)

plt.figure()
for T in [100,200,300,400,500]:
   plt.plot(xb,deltaf(xb),label=T)

plt.legend()
plt.savefig('ConstantComp.png')

plt.figure()
for T in [100,200,300,400,500]:
   chi = (T/100.) * 0.25 * 2.5
   plt.plot(xb,deltaf(xb),label=T)

plt.legend()
plt.savefig('Inverse.png')
```


0
−100
−200
−300
−400
0.0
0.2
0.4
0.6
0.8
1.0
100
200
300
400
500


400
200
0
−200
−400
−600
0.0
0.2
0.4
0.6
0.8
1.0
100
200
300
400
500

4 Two components, two phases, too much fun!

At 300 K, the saturation pressure of A is ten times the saturation pressure of B. A and B mix ideally.

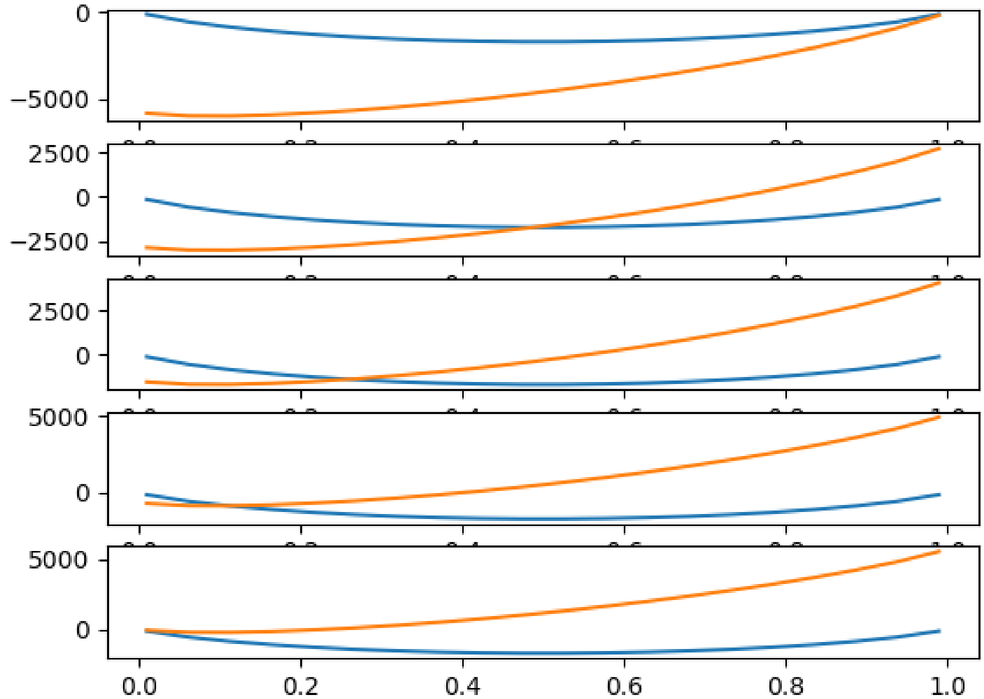
1. Write down an expression for the free energy of a two-component ideal liquid mixture as a function of pressure and composition, $g^l(P, x_B)$.

2. Write down an expression for the free energy of a two-component ideal gas mixture as a function of pressure and composition, $g^v(P, y_B)$.

3. Plot g^l and g^v vs composition at five pressure from $P = P^{sat,B}$ to $P = P^{sat,A}$. Identify the important regions on each plot.

4.1 solution

```python
import numpy as np
import matplotlib.pyplot as plt
from mpl_toolkits.mplot3d import Axes3D

def mu(mu0,x):
    return mu0 + RT * np.log(x)

# We are free to set chemical potential scale for A and B.
# Let chemical potentials of pure liquid A and B be 0. Can be any numbers
muAl0 = 0
muBl0 = 0

RT = 8.314*300
PBsat = 1
PAsat = 10

#P = np.linspace(PBsat,PAsat,num=10)
xB = np.linspace(0.01,0.99,num=20)
yB = np.linspace(0.01,0.99,num=20)

gl = (1-xB) * mu(muAl0,(1-xB)) + xB * mu(muBl0,xB)
for i in range(5):
   plt.subplot(5,1,i+1)
   P = PBsat + i*(PAsat-PBsat)/4.
   muAv0 = muAl0 + RT * np.log(P/PAsat)
   muBv0 = muBl0 + RT * np.log(P/PBsat)
   gv = (1-yB) * mu(muAv0,(1-yB)) + yB * mu(muBv0,yB)
   plt.plot(xB,gl)
   plt.plot(yB,gv)

plt.savefig('2phase.png')
```



5 Vapor-liquid equilibrium.

The partial pressure of CS_2 above a CS_2/dimethoxymethane (DMM) mixture at 35.2°C can be fit to the equation:

$$P_{CS_2} = x_{CS_2}(514.5\text{ torr})\exp(1.4967x_{\text{DMM}}^2 - 0.68175x_{\text{DMM}}^3)$$

1. Use the Gibbs-Duhem relation to determine the partial pressure of DMM as a function of composition. Assume the vapor is ideal.

2. Do CS_2 and DMM form a regular solution at these conditions? *Hint*: Determine the activities of each component and from these the excess free energy of mixing. Is it proportional to $x(1-x)$?

5.1 Solution

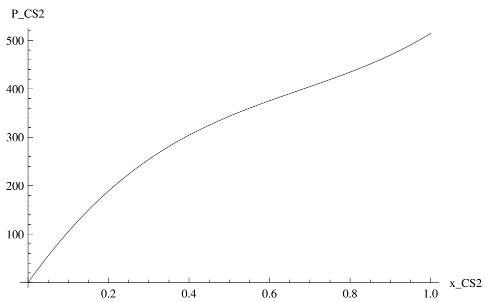
Problem 4. Vapor-liquid equilibrium

From the Gibbs-Duhem equation,

$$x_a \frac{\partial \ln(P_a)}{\partial x_a} = x_b \frac{\partial \ln(P_b)}{\partial x_b}$$

```
psatCS2 = 514.5;

In[52]:= PCS2 = xa * psatCS2 * Exp[1.4967 * (1 - xa) ^2 - 0.68175 * (1 - xa) ^3];

In[53]:= Plot[PCS2, {xa, 0, 1}, AxesLabel → {"x_CS2", "P_CS2"}]
```

Out[53]=



Simplify left side of Gibbs-Duhem equation

```
In[55]:= left = Simplify[xa * D[Log[PCS2], xa]]

Out[55]= 1. - 0.94815 xa - 1.0971 xa^2 + 2.04525 xa^3
```

change variable from xa to xb=1-xa

```
In[64]:= LHS = left /. xa → 1 - x

Out[64]= 1. - 0.94815 (1 - x) - 1.0971 (1 - x)^2 + 2.04525 (1 - x)^3
```

integrate from xb to 1

```
In[65]:= RHS = Integrate[LHS / x, {x, xb, 1}, Assumptions → xb > 0]

Out[65]= ConditionalExpression[
  -1.15583 + 2.9934 xb - 2.51933 xb^2 + 0.68175 xb^3 - 1. Log[xb], xb < 1]

In[66]:= right = -1.1558250000000003` + 2.9934000000000007` xb -
  2.5193250000000003` xb^2 + 0.6817499999999999` xb^3 - 1.` Log[xb]

Out[66]= -1.15583 + 2.9934 xb - 2.51933 xb^2 + 0.68175 xb^3 - 1. Log[xb]

In[67]:= Solve[Log[psatDMM / PDMM] == right, PDMM]
```

Out[67]= $\{\{PDMM \to 1866.91\, e^{-2.9934\, xb+2.51933\, xb^2-0.68175\, xb^3}\, xb^{1.000000000000000}\}\}$

In[70]:= PDMM = 1866.9131306545673\`

$e^{-2.9934000000000007`\, xb+2.5193250000000003`\, xb^2-0.6817499999999999`\, xb^3}\, xb^{1.`15.954589770191005}$

Out[70]= $1866.91\, e^{-2.9934\, xb+2.51933\, xb^2-0.68175\, xb^3}\, xb^{1.000000000000000}$