Problem 4. Vapor-liquid equilibrium
From the Gibbs-Duhem equation,

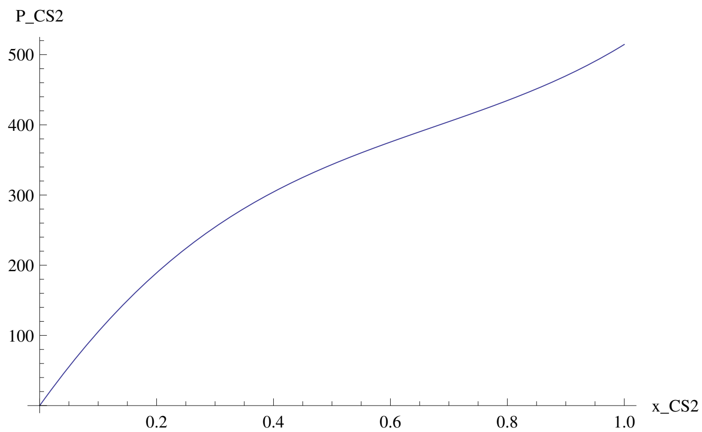
$$x_a \frac{\partial \ln(P_a)}{\partial x_a} = x_b \frac{\partial \ln(P_b)}{\partial x_b}$$

```
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[$-1.15583 + 2.9934\, xb - 2.51933\, xb^2 + 0.68175\, xb^3 - 1.\,\mathrm{Log}[xb]$, xb < 1]

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

Out[66]= $-1.15583 + 2.9934\, xb - 2.51933\, xb^2 + 0.68175\, xb^3 - 1.\,\mathrm{Log}[xb]$

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

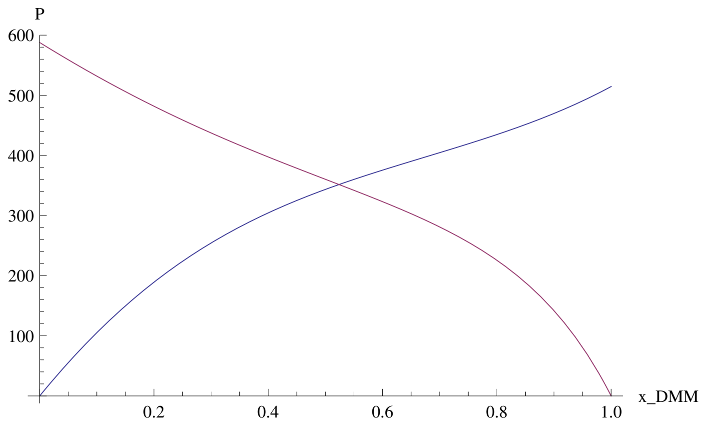
In[71]:=
```
PDMMxa = % /. xb → 1 - xa
```

Out[71]= $1866.91\, e^{-2.9934\,(1-xa)+2.51933\,(1-xa)^2-0.68175\,(1-xa)^3}\,(1-xa)^{1.000000000000000}$

Plot both pressures on the same plot

In[72]:=
```
Plot[{PCS2, PDMMxa}, {xa, 0, 1}, AxesLabel → {"x_DMM", "P"}]
```

Out[72]=



2(b)
Define activity using Raoult's Law
ai=γi xi =Pi / Psat

In[73]:=
```
γDMM = Simplify[PDMMxa / ((1 - xa) * psatDMM)]
```

Out[73]= $1.\, e^{xa\,(-4.44089\times10^{-16}+0.474075\,xa+0.68175\,xa^2)}$

In[74]:=
```
γCS2 = Simplify[PCS2 / (xa * psatCS2)]
```

Out[74]= $2.25906\, e^{xa\,(-0.94815-0.54855\,xa+0.68175\,xa^2)}$

Determine the excess free energy of mixing and plot it.

In[75]:=
```
gDMM = 8.314 * (273.15 + 35.2) * Log[γDMM]
```

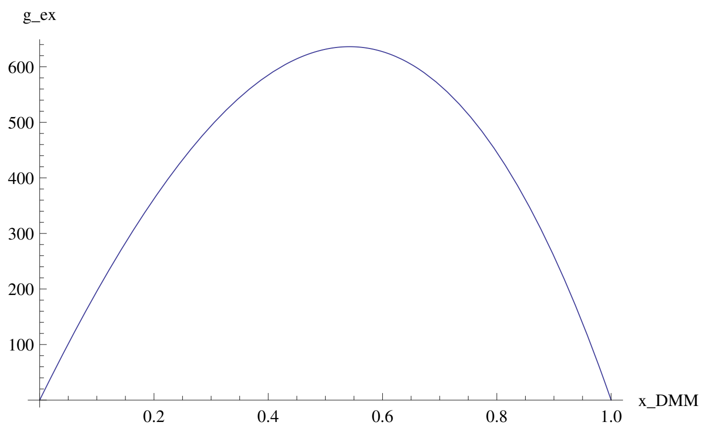
Out[75]= $2563.62\,\mathrm{Log}\left[1.\, e^{xa\,(-4.44089\times10^{-16}+0.474075\,xa+0.68175\,xa^2)}\right]$

In[76]:=
```
gCS2 = 8.314 * (273.15 + 35.2) * Log[γCS2]
```

Out[76]= $2563.62\,\mathrm{Log}\left[2.25906\, e^{xa\,(-0.94815-0.54855\,xa+0.68175\,xa^2)}\right]$

In[77]:= `Plot[{xa * gCS2 + (1 - xa) * gDMM}, {xa, 0, 1}, AxesLabel → {"x_DMM", "g_ex"}]`

Out[77]=



Try fitting the regular solution model to the curve above.

In[79]:= `xa = {0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0}`

Out[79]= {0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.}

In[81]:= `gex = xa * gCS2 + (1 - xa) * gDMM`

Out[81]= $\{-2.84619\times10^{-13}$, 195.895, 362.24, 493.791, 585.306, 631.54, 627.252, 567.197, 446.132, 258.814, $-2.84619\times10^{-13}\}$

In[82]:= `dataset2 = Thread[{xa, gex}]`

Out[82]= $\{\{0, -2.84619\times10^{-13}\}$, {0.1, 195.895}, {0.2, 362.24}, {0.3, 493.791}, {0.4, 585.306}, {0.5, 631.54}, {0.6, 627.252}, {0.7, 567.197}, {0.8, 446.132}, {0.9, 258.814}, $\{1., -2.84619\times10^{-13}\}\}$

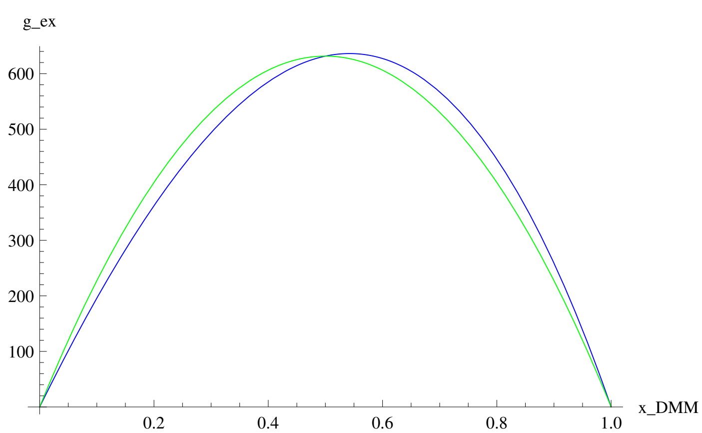
In[83]:= `solution = Fit[dataset2, {x * (1 - x)}, x]`

Out[83]= 2526.16 (1 - x) x

Plot the excess free energy curve in blue and the regular solution fitted curve in green.

In[88]:= `Show[Plot[{xa * gCS2 + (1 - xa) * gDMM}, {xa, 0, 1}, AxesLabel → {"x_DMM", "g_ex"}, PlotStyle → Blue], Plot[{solution}, {x, 0, 1}, PlotStyle → Green]]`

Out[88]=



From the plot we can see that the excess free energy of mixing is proportional to x(1-x), and χ=2526.16 is a pretty good fit of the regular solution model to the given partial pressure equations.