Part A: What is the reference state for each species?

Species A:

As $x_a \rightarrow 1$, $\ln\gamma_a \rightarrow 0$ which is equivalent to $\gamma_a \rightarrow 1$.

Thus the reference state is the pure species fugacity of species A. This is also known as the Lewis/Randall rule. (1 point)

Species B:

As $x_a \rightarrow 0$ ($x_b \rightarrow 1$), $\ln\gamma_b \rightarrow 0$ which is equivalent to $\gamma_b \rightarrow 1$.

Similarly, the reference state is the pure species fugacity of species B. This is also known as the Lewis/Randall rule. (1 point)

Part B: Show that the Gibbs-Duhem equation is satisfied at a mole fraction of x_a =0.6.

Gibbs-Duhem equation:

$$x_a\left(\frac{\partial \ln \gamma_a}{\partial x_a}\right)_{T,P} + (1-x_a)\left(\frac{\partial \ln \gamma_b}{\partial x_a}\right)_{T,P} = 0$$

At $x_a = 0.6$, draw a tangent to the curves and calculate the gradients of the slope.

$$\left(\frac{\partial \ln \gamma_a}{\partial x_a}\right)_{T,P} = 1.19 \quad \text{(graphical)} \qquad \text{(1 point)}$$

$$\left(\frac{\partial \ln \gamma_b}{\partial x_a}\right)_{T,P} = 1.786 \quad \text{(graphical)} \qquad \text{(1point)}$$

Now let's verify the value of $\left(\frac{\partial \ln \gamma_a}{\partial x_a}\right)_{T,P}$ using the Gibbs-Duhem equation and check whether it matches with the value obtained graphically.

$$(0.6)(1.19) + (0.4)\left(\frac{\partial \ln \gamma_b}{\partial x_a}\right)_{T,P} = 0$$

$$\left(\frac{\partial \ln \gamma_b}{\partial x_a}\right)_{T,P} = 1.923 \qquad \text{(1 point)}$$

The graphical result was within 10% of the calculated value. Thus we can conclude that the Gibbs-Duhem equation is satisfied.

Part C: Come up with an appropriate model for g^E for this system and find the values of the model parameters.

From the graph, it is observed that the activity coefficients are asymmetric. Thus we should employ the model for asymmetric activity coefficient, such as Three-suffix Margules, or Van Laar etc.

(1 point for any suitable model)

For this problem, the Three-suffix Margules model is used.

$$g^E = x_a x_b \left[A + B(x_a + x_b) \right]$$

Where the corresponding activity coefficients can be calculated by differentiation of the above equation:

$$RT \ln \gamma_a = (A + 3B) x_b^2 - 4B x_b^3 \qquad (1)$$

$$RT \ln \gamma_b = (A - 3B) x_a^2 + 4B x_a^3 \qquad (2)$$

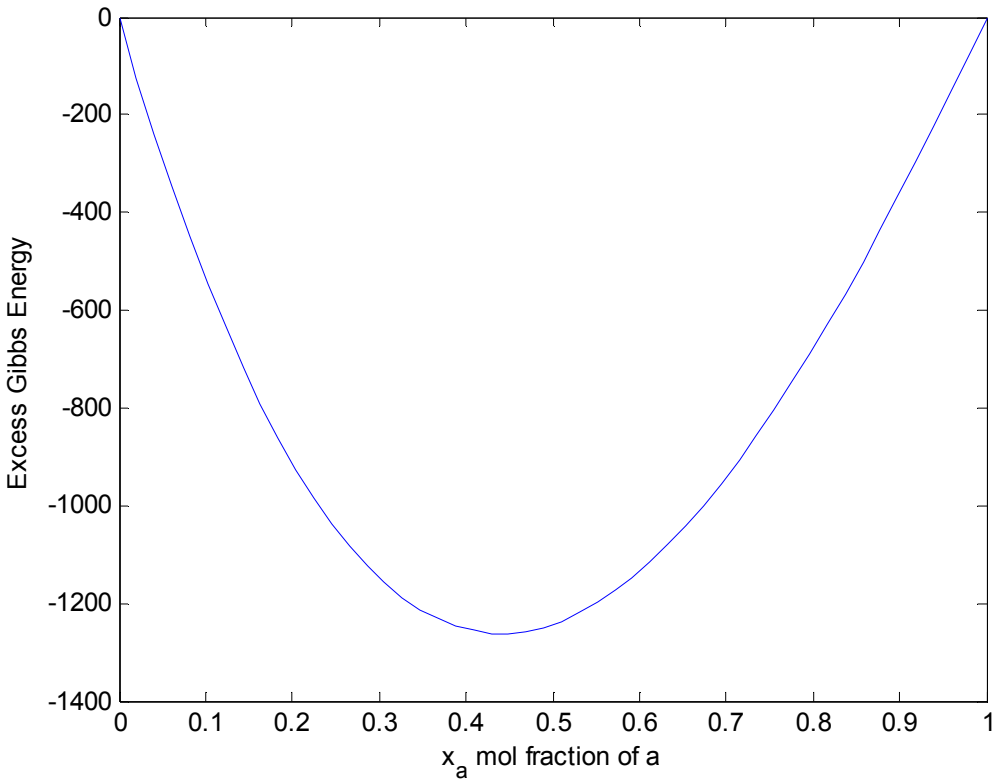
To determine the values of A and B, regression method is adopted. MATLAB was used to estimates values for A and B by minimizing the model predicted values and the data values.

(1 point for code and choice of regression method)

Substitute the above values into Equation (1) and (2), and solve them simultaneously:

$$\boxed{A = -4972.8 \frac{J}{mol}} \qquad \text{(1/2 point)}$$

$$\boxed{B = 1231.2 \frac{J}{mol}} \qquad \text{(1/2 point)}$$

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%Problem 7.28
%Determining the parameters of the Three-Suffix Margules equation using
%nonlinear regression
%3/31/08
%by Sarah Bashadi

function problem728

%Create a structure called param to pass data efficiently into functions
%Data for ln gamma a and ln gamma b, mol frac a and b
param.gb=[0 -.15 -.4 -.8 -1.2 -1.5];
param.ga=[-2.5 -1.35 -.6 -.23 -.08 0];
param.xa=[0 0.2 0.4 0.6 0.8 1];
param.xb=[1 .8 .6 .4 .2 0];

%Initial guess for A and B
xo=[1000 500];

%Gas Constant and Temp
R=8.314;
T=300;

%Minimize the objective function using fminunc
[beta]=fminunc(@(x) minobj(x,param),xo);

%Store solution
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```
A=beta(1);
B=beta(2);

%Display results on the screen
disp(['The parameter A is ',num2str(A)]);
disp(['The parameter B is ',num2str(B)]);

%Calculate predicted ln gamma-a, ln gamma-b
gamma_a=(1/(R*T))*((A+3*B)*param.xb.^2-4*B*param.xb.^3);
gamma_b=(1/(R*T))*((A-3*B)*param.xa.^2+4*B*param.xa.^3);


%Plot activity coefficients to compare fits
plot(param.xa,param.ga)
hold all
plot(param.xa,gamma_a)
plot(param.xa,param.gb)
plot(param.xa,gamma_b)

xlabel('xa mol fraction a')
ylabel('ln (gamma)i ')
title('Activity coefficient of species a and b vs. mol fraction a')
legend('gamma_a data','gamma_a fit using Three-suffix
Margules','gamma_b','gamma_b fit fit using Three-suffix Margules')

%Part d
molfrac_a=linspace(0,1,50);
molfrac_b=1-molfrac_a;
excessgibbs=molfrac_a.*molfrac_b.*(A+B*(molfrac_a-molfrac_b));

figure
plot(molfrac_a,excessgibbs);
xlabel('x_a mol fraction of a')
ylabel('Excess Gibbs Energy')

function Y=minobj(x,param)
%Contains the nonlinear least squares regression function to be minimized

%Rename variables
A=x(1);
B=x(2);

%Gas Constant and Temperature
R=8.314;
T=300;

%Unpack parameters
xa=param.xa;
xb=param.xb;
ga=param.ga;
gb=param.gb;

%Initialize
sum=0;
```

```
%Write the expression for the sum of squares
for i=1:length(xa)
    sum=sum+(ga(i)-(1/(R*T)*((A+3*B)*xb(i)^2-4*B*xb(i)^3)))^2+(gb(i)-
(1/(R*T)*((A-3*B)*xa(i)^2+4*B*xa(i)^3)))^2;
end

%Minimize nonlinear regression function
Y=sum;
```

Part D: Is it possible for species a and b to separate into two liquid phases? Explain.

A system always act spontaneously in order to reduce the free energy of the system. Thus the system will proceed in the direction to whichever state has a lower free energy.

In this system, we observe that both γ_a and γ_b values are less than 1. This means that the unlike interactions (a-b) is stronger than the like interactions (a-a, b-b). The A parameter (from part c) is negative, which reinforced the point that the mixture of a and b has a lower gibbs free energy. Thus it is impossible for the species to separate into two liquid phases.

1 point

- Mention that the species a and b will not separate into two liquid phases

1 point

- Mention that the mixture state has a lower gibbs free energy
- Proof of the mixture state has a lower gibbs free energy: γ_i is negative or A is negative