Homework 9 solutions

Exercise 1

Gold (15g) and Silver (25g) are mixed to form a single-phase ideal solid solution. The molar masses of gold and silver are 197 g/mol and 108 g/mol, respectively. R=8.314 J/mol K and Avogadro's number $N_A=6.02*10^{23}$ mol^{-1}.

a) How many moles of solution are there?

The moles of the solid solution

$$n_{Tot} = n_{Au} + n_{Ag} = \frac{15}{197} + \frac{25}{108} = 0.0761 + 0.231 = 0.308 \text{ mol}$$

b) What are the mole fractions of Gold and Silver?

The molar fraction of gold

$$x_{Au} = \frac{n_{Au}}{n_{Au} + n_{Ag}} = \frac{\frac{15}{197}}{\frac{15}{197} + \frac{25}{108}} = 0.248$$

The molar fraction of silver 15

$$x_{Ag} = \frac{n_{Ag}}{n_{Au} + n_{Ag}} = \frac{\frac{25}{108}}{\frac{15}{197} + \frac{25}{108}} = 0.752$$

c) What is the molar entropy of mixing?

The molar entropy of mixing

$$\Delta_{mix}s = -R\left(x_{Au}\ln x_{Au} + x_{Ag}\ln x_{Ag}\right) = -8.314 * (0.248 \cdot \ln 0.248 + 0.752 \cdot \ln 0.752)$$

$$\Delta_{mix}s = 4.66 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

d) What is the total entropy of mixing?

The total entropy of mixing

$$\Delta_{mix}S = -R\left(n_{Au}\ln x_{Au} + n_{Ag}\ln x_{Ag}\right) = -8.314 * (0.0761 * \ln 0.248 + 0.231 * \ln 0.752)$$

$$\Delta_{mix}S = 1.43 \frac{\text{J}}{\text{K}}$$

e) What is the molar free energy change at 500°C?

$$\Delta_{mix}g = RT\left(x_{Au}\ln x_{Au} + x_{Ag}\ln x_{Ag}\right)$$

$$= 8.314 * (500 + 273) * (0.248 * \ln 0.248 + 0.752 * \ln 0.752)$$

$$= -3.60 \frac{\text{kJ}}{\text{mol}}$$

f) What are the chemical potentials of Gold and Silver at 500°C, assuming free energies of pure Gold and Silver are zero?

$\Delta_{mix} g = RT\left(x_{Au} \ln x_{Au} + x_{Ag} \ln x_{Ag}\right) = g_{mix} - g_{pure} = g_{mix} - (\mu_{Au}^{*} x_{Au} + \mu_{Ag}^{*} x_{Ag})$

$$g_{mix} = RT\left(x_{Au} \ln x_{Au} + x_{Ag} \ln x_{Ag}\right) + \left(\mu_{Au}^{*} x_{Au} + \mu_{Ag}^{*} x_{Ag}\right)$$
$$= x_{Au}(\mu_{Au}^{*} + RT \ln x_{Au}) + x_{Ag}\left(\mu_{Ag}^{*} + RT \ln x_{Ag}\right) = x_{Au} \bar{G}_{Au} + x_{Ag} \bar{G}_{Ag}$$

Therefore,

$\bar{G}_{Au} = \mu_{Au} = \mu_{Au}^{*} + RT \ln x_{Au}$

$\bar{G}_{Ag} = \mu_{Ag} = \mu_{Ag}^{*} + RT \ln x_{Ag}$

The chemical potential is the partial molar Gibbs free energy. Since the pure free energies of Au and Ag are zero, μ_{Au}^{*} and μ_{Ag}^{*} are zero.

The chemical potential of gold

$$\mu_{Au} = RT \ln x_{Au} = 8.314 * (500 + 273) * \ln 0.248 = -8.96 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

The chemical potential of silver

$$\mu_{Ag} = RT \ln x_{Ag} = 8.314 * (500 + 273) * \ln 0.752 = -1.83 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

g) How much will the free energy of the solution change at 500°C if one Gold atom is added?

One gold atom expressed in moles is equal to:

$$n = \frac{N}{N_A} = \frac{1}{6.02 * 10^{23}} \text{ mol}$$

Adding of 1 atom to the composition does not influence the molar concentrations, because $\frac{1}{N_A} \sim 0$ - is a very small number:

$$x_{Au} = \frac{\left(n_{Au} + \frac{1}{N_A}\right)}{\left(n_{Au} + \frac{1}{N_A}\right) + n_{Ag}} \approx \frac{n_{Au}}{n_{Au} + n_{Ag}}$$

$$G_{mix} = n_{Au}(\mu_{Au}^{*} + RT \ln x_{Au}) + n_{Ag}\left(\mu_{Ag}^{*} + RT \ln x_{Ag}\right) = n_{Au}\mu_{Au} + n_{Ag}\mu_{Ag}$$

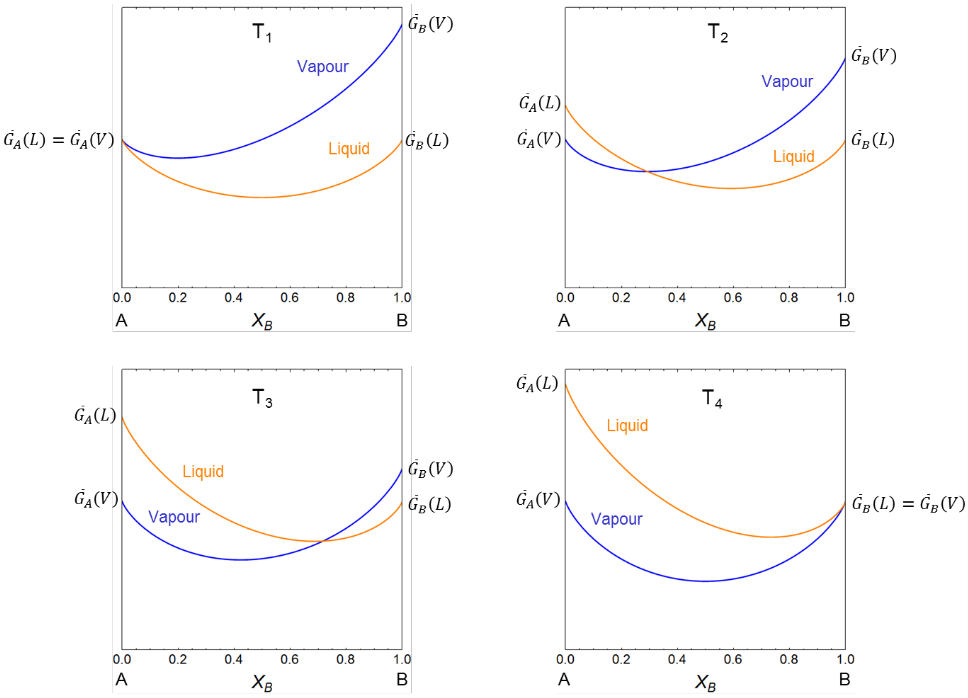
$$\Delta G = G_{mix+1\,atom} - G_{mix}$$

$$\Delta G = \left(n_{Au} + \frac{1}{N_A}\right)(\mu_{Au}^* + RT\ln x_{Au}) + n_{Ag}\left(\mu_{Ag}^* + RT\ln x_{Ag}\right) - n_{Au}(\mu_{Au}^* + RT\ln x_{Au}) - n_{Ag}\left(\mu_{Ag}^* + RT\ln x_{Ag}\right)$$

$$\Delta G = \frac{\mu_{Au}^* + RT\ln x_{Au}}{N_A} = \frac{0 - 8.96\cdot 10^3}{6.02\cdot 10^{23}} = -1.49 * 10^{-20}\ \mathrm{J}$$

Exercise 2

Imagine an ideal binary mixture at different temperatures (T_1, T_2, T_3 and T_4 of an increasing order). The respective molar Gibbs free energy G vs. X_B diagrams for liquid (L) and vapor (V) phases are given as:

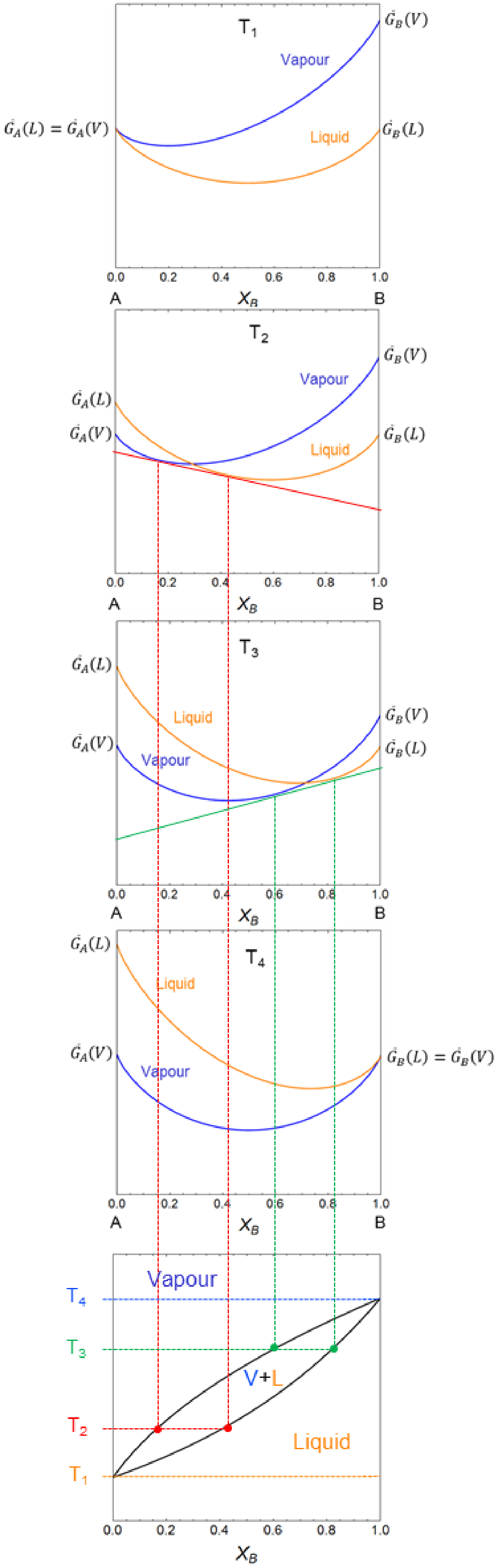


a) Given the information, draw a phase diagram (T vs X_B) and label all temperature and composition points. (You can use next page's sketch to draw your phase diagram)

At T_1 the liquid is a stable phase across all the composition so the phase diagram (T, X_B) at T_1 the line is all in liquid phase region (orange line). At $X_B = 0$, the chemical potential of pure A in the liquid state is equal to the chemical of pure A in the vapor state. Therefore, T_1 is the boiling point of A.

When the temperature increases to T_2, there is a phase separation V+L according to molar Gibbs free energy G vs. X_B diagram. In order to decide the composition range of phase separation region, one can draw a common tangent between liquid and vapor curves (red line). The intercepts of common tangent and molar free energy curves give the composition of two phases. Note that it is the composition not the ratio of two phases in the phase separation region. For example, the red common tangent in T_2 intercept with the molar vapor free energy curve at X_B~0.18. This means that the vapor composition is X_B~0.18. While the molar liquid free energy intercepts with red common tangent in X_B ~0.42 which is the liquid composition. Therefore, at T_2 the vapor composition is always X_B=0.18 and the liquid composition X_B =0.42 in the phase separation region.

At T_3, we can use a similar way to decide the phase separation region (green line). At T_4 the vapor is a stable phase across all the composition so in T, X_B phase diagram at T_4 the line is all in vapor phase region (blue line). At X_B = 1, the chemical potential of liquid B is equal to the chemical of vapor B. Therefore, T4 is the boiling point of B. Finally we can construct T, X_B phase diagram as shown below

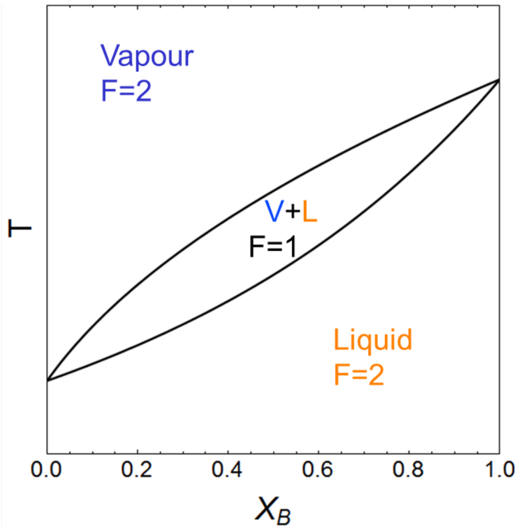

T$_1$
Vapour
Liquid
$\mathring{G}_A(L) = \mathring{G}_A(V)$
$\mathring{G}_B(V)$
$\mathring{G}_B(L)$
0.0
0.2
0.4
0.6
0.8
1.0
A
X_B
B
T$_2$
Vapour
Liquid
$\mathring{G}_A(L)$
$\mathring{G}_A(V)$
$\mathring{G}_B(V)$
$\mathring{G}_B(L)$
0.0
0.2
0.4
0.6
0.8
1.0
A
X_B
B
T$_3$
Liquid
Vapour
$\mathring{G}_A(L)$
$\mathring{G}_A(V)$
$\mathring{G}_B(V)$
$\mathring{G}_B(L)$
0.0
0.2
0.4
0.6
0.8
1.0
A
X_B
B
T$_4$
Liquid
Vapour
$\mathring{G}_A(L)$
$\mathring{G}_A(V)$
$\mathring{G}_B(L) = \mathring{G}_B(V)$
0.0
0.2
0.4
0.6
0.8
1.0
A
X_B
B
Vapour
T$_4$
T$_3$
V+L
T$_2$
Liquid
T$_1$
0.0
0.2
0.4
0.6
0.8
1.0
X_B

b) Apply the phase rule for the diagram you draw in (a) to find the degrees of freedom for each phase.

Gibbs phase rule: $F = n+1-\Phi$……. Here is +1 because p is fixed

Therefore, in liquid or vapor phase $F=2+1-1=2$,

and in V+L phase separation region $F=2+1-2=1$



c) Imagine you have a liquid mixture with a composition of $X_B = 0.7$. Practically, how would you obtain a liquid mixture with a composition $X_B < 0.1$? That is, explain one route to decrease the composition of B in the mixture.

This can be done by purifying the vapor composition within the phase separation region. First we start at $x_B=0.7$ and heat up to the temperature T_α. At T_α when it is at equilibrium, the vapor phase is with the composition x_α. We then collect the vapor and cool down to T_β. Again, the vapor has the composition x_β at T_β when the equilibrium is reached and collect the vapor to cool down to T_γ. Finally, we can have vapor with the composition $x_B=0.1$ and then cool down to have liquid phase. By keep doing the procedures, we can have the liquid composition $x_B<0.1$.