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

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

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

The molar fraction of gold

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

The molar fraction of silver 15

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

c) What is the molar entropy of mixing?

The molar entropy of mixing

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

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

d) What is the total entropy of mixing?

The total entropy of mixing

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

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

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

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

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

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

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

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

The chemical potential of silver

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

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:

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

Adding of 1 atom to the composition does not influence the molar concentrations, because $\frac{1}{N_A}$

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

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

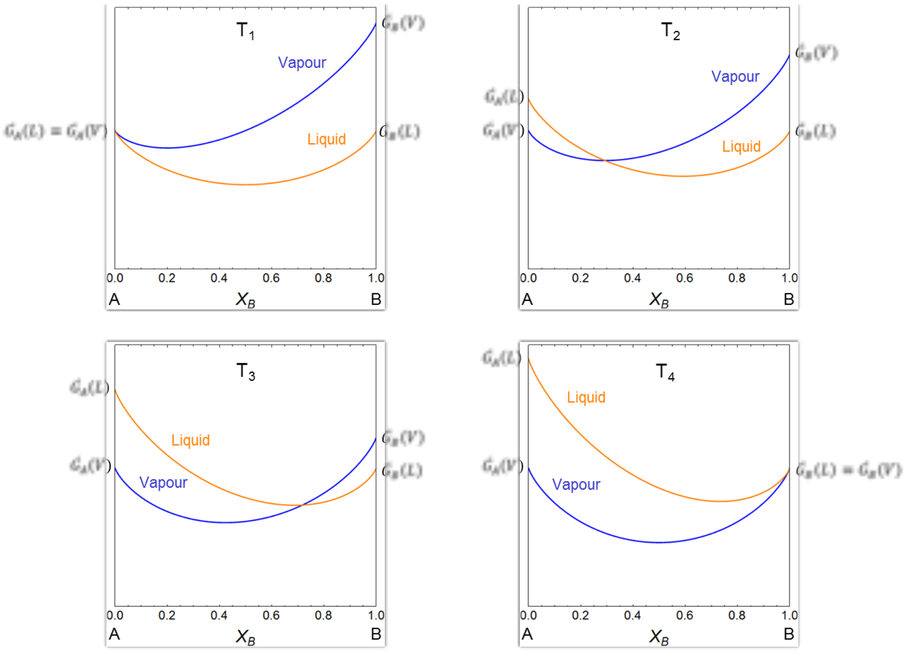
$$\Delta G = G_{mix+1\,atom} - G_{mix}$$

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

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

Exercise 2

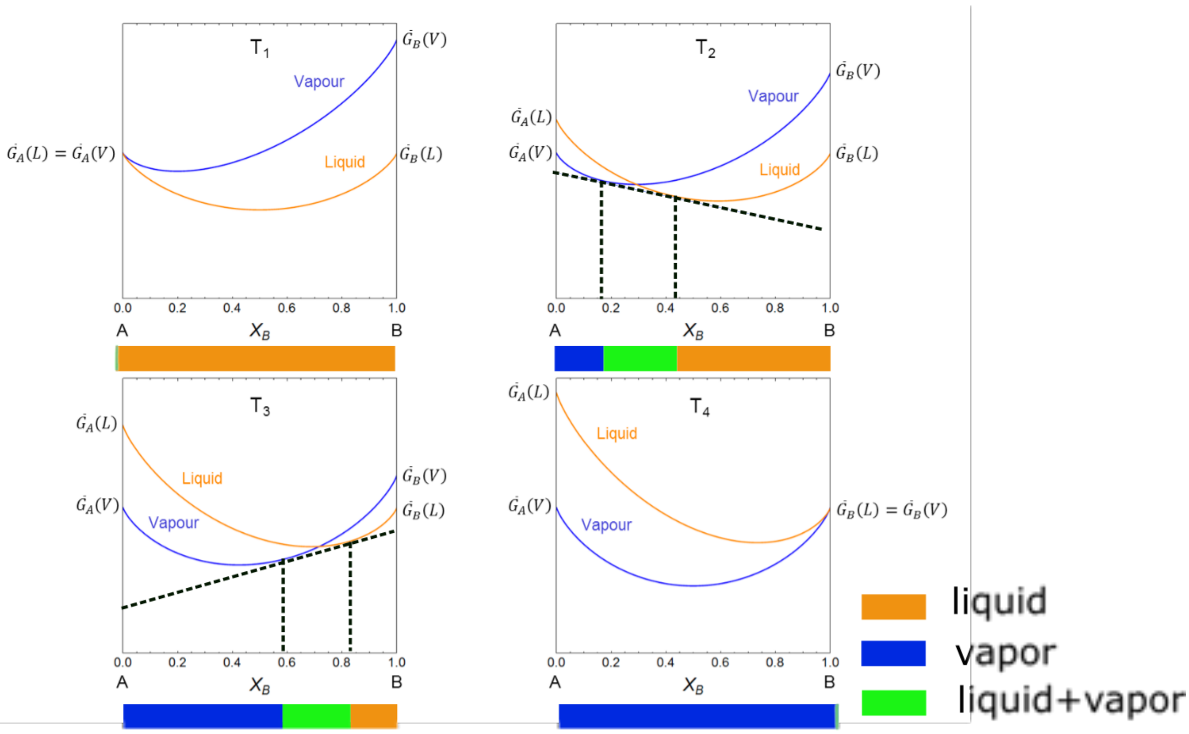
Imagine an ideal binary mixture at different temperatures (T_1, T_2, T_3 and T_4 of an increasing order). The respective molar Gibbs free energy G vs. X_B diagrams for liquid (L) and vapor (V) phases are given as:



a) Given the information, predict the vaporisation temperatures of the two components A and B

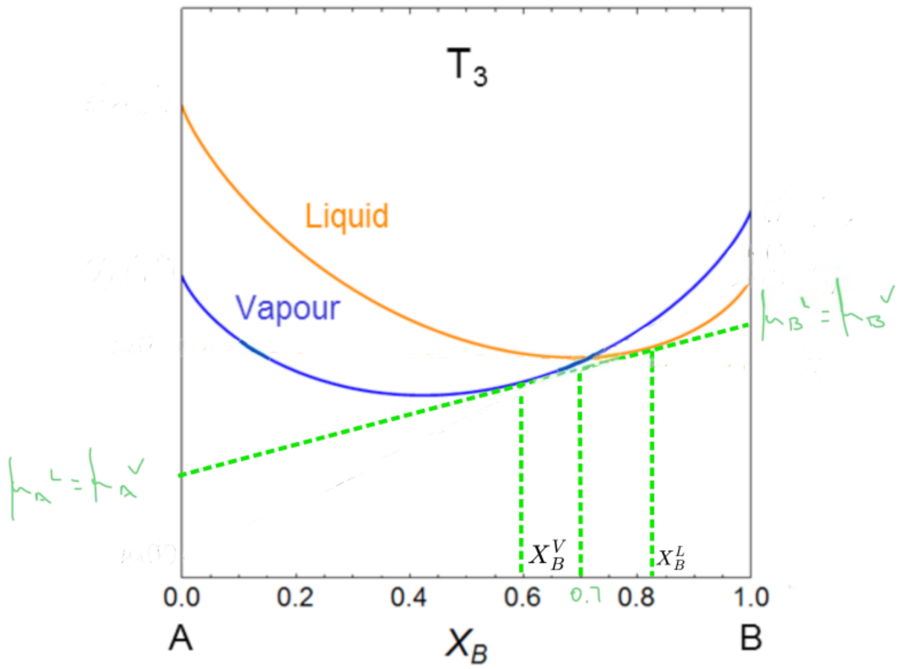
At T_1, $G_A(L) = G_A(V)$ for X_B=1 which means component A has equal chemical potential in vapor and liquid phase at T_1, therefore the vaporisation temperature for A is T_1. Similarly, the vaporisation temperature for B is T_4.

b) For each plot, make a rectangular box along XB and draw which phase(s) are present for all compositions.



c) For temperature T3 and composition XB=0.7, annotate on the plot the chemical potential of each component at each phase associated with these conditions. For the same conditions apply the lever rule to find the fractions of the liquid and vapor phases.

As shown below.



$$X_B = f^L X_B^L + (1 - f^L) X_B^V = 0.7$$

$$f^L = \frac{X_B - X_B^V}{X_B^L - X_B^V} = \frac{0.7 - 0.6}{0.825 - 0.6} = 0.44$$

The fraction of solid is therefore $f^V = 1 - f^L = 0.56$