Thermodynamics of Materials 3.00
Example Problems for Week 11

Example Problem 11.1

For a binary system at constant temperature and pressure with a molar gibbs free energy given by $\overline{G} = A(X_a - X_{a,0})^2(X_b - X_{b,0})^2$:

a. Calculate the chemical potentials of each component in terms of X_b.

b. For $X_{b,0} = X_{a,0} = 0.25$ plot the molar free energy and chemical potentials against X_b.

c. Plot the equilibrium chemical potential of component b at this temperature and pressure against X_b.

d. At this temperature and pressure calculate the composition and if appropriate phase-fractions for a bulk sample of composition $X_b^0 = 0.2$, $X_b^0 = 0.4$, $X_b^0 = 0.5$, $X_b^0 = 0.75$.

Solution 11.1

a. After substituting $X_a = 1 - X_b$, the chemical potentials are given by:

$$\mu_a = \overline{G} - X_b \frac{d\overline{G}}{dX_b} \text{ and } \mu_b = \overline{G} - (1 - X_b)\frac{d\overline{G}}{dX_b} \tag{1}$$

$$\mu_a = A(1-X_b-X_{a,0})^2(X_b-X_{b,0})^2 - X_b\left(2A(1 - X_b - X_{a,0})(X_b - X_{b,0})(1 - 2X_b + X_{b,0} - X_{a,0})\right) \tag{2}$$

$$\mu_b = A(1-X_b-X_{a,0})^2(X_b-X_{b,0})^2 + (1-X_b)\left(2A(1 - X_b - X_{a,0})(X_b - X_{b,0})(1 - 2X_b + X_{b,0} - X_{a,0})\right) \tag{3}$$

b. Substituting $X_{a,0} = X_{b,0} = 0.25$ into the above gives:

$$\overline{G} = A(0.75 - X_b)^2(X_b - 0.25)^2 \tag{4}$$

$$\mu_a = A(0.75 - X_b)^2(X_b - 0.25)^2 - X_b\left(2A(0.75 - X_b)(X_b - 0.25)(1 - 2X_b)\right) \tag{5}$$

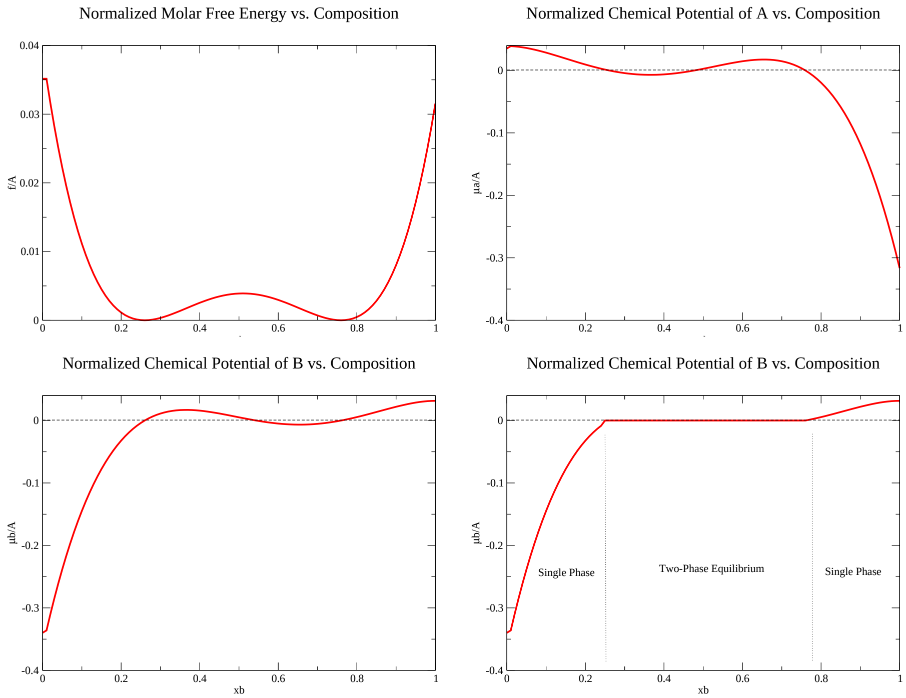
$$\mu_b = A(0.75 - X_b)^2(X_b - 0.25)^2 + (1 - X_b)\left(2A(0.75 - X_b)(X_b - 0.75)(1 - 2X_b)\right) \tag{6}$$

The plots are given below. Notice that on the chemical potential plots there are regions where different compositions have the same chemical potentials. This indicates that multi-phase equilibria occur.

c. This is a system with two phase equilibrium. Across the range of bulk compositions $0.25 \leq X_b \leq 0.75$ the equilibrium system is composed of two phases with fixed composition. The phase fraction of the phases does change, however, in order to accomodate the bulk composition. This is shown below by a constant chemical potential across this region.

d. At $X_b^0 = 0.2$, the system is in a single phase region with composition $X_b = 0.2$.

At $X_b^0 = 0.4$, the system is in a two-phase region. The composition of the two phases are $X_b^\alpha = 0.25$ and $X_b^\beta = 0.75$. The phase fractions are given by the lever rule: $f^\alpha = 0.70$ and $f^\beta = 0.30$.



At $X_b^0 = 0.5$, the system is in a two-phase region. The composition of the two phases are $X_b^\alpha = 0.25$ and $X_b^\beta = 0.75$ again. The phase fractions have changed, however, to accomodate the bulk composition change: $f^\alpha = 0.50$ and $f^\beta = 0.50$.

At $X_b^0 = 0.75$, the system is exactly at the phase boundary so is a single phase with composition $X_b = 0.75$.