Thermodynamics of Materials 3.00 Fall 2000
Solution for Problem Set 9

Problem 9 Consider a binary alloy comprised of two components A and B. Both pure A and pure B solidify into an FCC structure that will be designated as the γ-phase.

The molar Gibbs Free Energies[1] of the liquid and γ solutions are given as:

$$\overline{G^\gamma} = (X_B - \frac{1}{4})^2 \tag{1}$$

and

$$\overline{G^{liq}} = (X_B - \frac{3}{4})^2 + \frac{T - T_A}{T_B - T_A} - \frac{1}{2} \tag{2}$$

where T is the temperature, X_B is the composition, and T_A and T_B are constants.

1. Calculate the lowest and highest temperatures, T_L and T_H, that an equilibrium liquid can co-exist with an equilibrium solid phase and calculate the corresponding compositions of the liquid and solid phase at T_H and T_L.
2. For temperatures $T_1 = T_L + \frac{1}{3}(T_H - T_L)$ and $T_2 = T_L + \frac{2}{3}(T_H - T_L)$, calculate and plot μ_A as a function of X_B.
3. For temperatures $T_1 = T_L + \frac{1}{3}(T_H - T_L)$ and $T_2 = T_L + \frac{2}{3}(T_H - T_L)$, calculate the equilibrium composition of the liquid and the γ phase.
4. For the composition $X_B = \frac{1}{2}$, plot μ_A as a function of T, $T_L < T < T_H$.
5. Sketch the phase diagram of this alloy.

Solution to Problem 9

If the $\overline{G}$ curves had slopes with infinite magnitude at $X_B \to 0$ and $X_B \to 1$ then analysis of this problem would just entail equation of tangent lines. This is not the case here. Because this is a constrained problem, we must take a slightly different approach. The goal is to find the lowest total free energy of the system. The points where the common tangent touches each of the two curves must be within the range $0 \leq X_B \leq 1$. This is not true for all temperatures here.

For the unconstrained problem we derived the condition for the equality of the chemical potentials. In this constrained problem where $0 \leq X_B \leq 1$ the construction is like putting a rubber band around the outside of the free energy curves and taking this (the outer envelope) as the value of the free energy of the system.

9-1-i

Let's start the problem by applying the condition for a common tangent line to $\overline{G}^l$ and $\overline{G}^\gamma$. These are the equality of the intercepts with the $X_B = 0$ axis, $\mu_A^l(X^l) = \mu_A^\gamma(X^\gamma)$, and the equality of the slopes, $\frac{\partial \overline{G}^l}{\partial X_B}(X_l) = \frac{\partial \overline{G}^\gamma}{\partial X_B}(X^\gamma)$. Remember that the chemical potential of

[1] The energies that are given are artificial because, as will be shown in class, the derivatives with respect to composition of the free energy evaluated for pure components, must have infinite magnitude. However, this problem serves to illustrate how phase diagrams are constructed and how they follow from free energy curves. Because the expressions are artificial (they are picked to make the problem tractable) the resulting phase diagram will look a little unusual.

A in solution with composition X_B^* and molar Gibbs free energy $\overline{G}$ is given by $\mu_A(X_B^*) = \overline{G}(X_B^*) - X_B^* \frac{\partial \overline{G}}{\partial X_B}(X_B^*)$.

$$\begin{aligned} \mu_A^l(X^l) &= \mu_A^\gamma(X^\gamma) \\ (X_l - \frac{3}{4})^2 + \frac{T - T_A}{T_B - T_A} - \frac{1}{2} - 2X_l(X_l - \frac{3}{4}) &= (X_\gamma - \frac{1}{4})^2 - 2X_\gamma(X_\gamma - \frac{1}{4}) \\ -(X_l)^2 + \frac{1}{16} + T^* &= -(X_\gamma)^2 + \frac{1}{16} \\ -(X_l)^2 + T^* &= -(X_\gamma)^2 \end{aligned} \tag{3}$$

where $T^* = \frac{T - T_A}{T_B - T_A}$ and

$$\begin{aligned} \frac{\partial \overline{G}^l}{\partial X_B}(X_l) &= \frac{\partial \overline{G}^\gamma}{\partial X_B}(X^\gamma) \\ X_l - \frac{3}{4} &= X_\gamma - \frac{1}{4} \\ X_l &= X_\gamma + \frac{1}{2} \end{aligned} \tag{4}$$

The combination of the above yields an expression for the composition of the γ phase in equilibrium with liquid phase at every temperature from the common tangent construction.

$$X_\gamma = T^* - \frac{1}{4} \tag{5}$$

Now remember that by definition $0 \leq X_B \leq 1$ but also there is the constraint here that $X_l = X_\gamma + \frac{1}{2}$ so these combine to allow the above equation to evaluated at the largest allowed and smallest allowed values of X_γ, $X_\gamma = 0$ and $X_\gamma = \frac{1}{2}$, to give $T_H^* = \frac{3}{4}$ and $T_L^* = \frac{1}{4}$. These are the highest and lowest temperatures for co-existence using the common tangent construction.

The true highest and lowest values for co-existance come from the rubber band construction or convexification. From this technique the highest and lowest temperatures are the temperatures at which $\overline{G}^l(X_l = 0) = \overline{G}\gamma(X_\gamma = 0)$ and $\overline{G}^l(X_l = 1) = \overline{G}\gamma(X_\gamma = 1)$. So $T_L^* = 0$ and $T_H^* = 1$ or $T_L = T_A$ and $T_H = T_B$.

9-1-ii and 9-1-iii

At $T_1^* = \frac{1}{3}$ and $T_2^* = \frac{2}{3}$ the common tangent construction is valid. We want the chemical potential of A in the equilibrium phase as a function of the bulk composition of the system. This is $\mu_A^l(X_B)$ in the liquid singlephase field, a constant across the whole l-γ two-phase field, and $\mu_A^\gamma(X_B)$ in the γ single-phase field.

The limiting compositions for the single phase fields are given by evaluating Equations 5 and 4 at each temperature.

$$\begin{aligned} X_\gamma &= \frac{1}{3} - \frac{1}{4} = \frac{1}{12} \text{ and } X_l = \frac{7}{12} \text{ at } T_1 \\ X_\gamma &= \frac{2}{3} - \frac{1}{4} = \frac{5}{12} \text{ and } X_l = \frac{11}{12} \text{ at } T_2 \end{aligned} \tag{6}$$

So at T_1 the chemical potential of A is given by

$$\mu_A = \begin{cases} -(X_B)^2 + \frac{1}{16} & 0 \leq X_B \leq \frac{1}{12} \\ \frac{1}{18} & \frac{1}{12} \leq X_B \leq \frac{7}{12} \\ -(X_B)^2 + \frac{19}{48} & \frac{7}{12} \leq X_B \leq 1 \end{cases} \tag{7}$$

and at T_2 the chemical potential of A is given by

$$\mu_A = \begin{cases} -(X_B)^2 + \frac{1}{16} & 0 \leq X_B \leq \frac{5}{12} \\ -\frac{1}{9} & \frac{5}{12} \leq X_B \leq \frac{11}{12} \\ -(X_B)^2 + \frac{35}{48} & \frac{11}{12} \leq X_B \leq 1 \end{cases} \tag{8}$$

See Figure 1 for a plot.

9-1-iv

In order to find $\mu_A(X_B = \frac{1}{2}, T)$ we must identify the highest and lowest temparatures at which γ and liquid are in equilibrium. So the condition for two phase equilibrium is given by Equation 5 above. When $X_B = \frac{1}{2} = X_\gamma$ then $T^* = \frac{3}{4}$ and when $X_B = \frac{1}{2} = X_l$ then $T^* = \frac{1}{4}$. Above this temperature range $\mu_A = \mu_A^\gamma = -\frac{3}{16}$ and below $\mu_A = \mu_A^l = -\frac{3}{16} + T^*$. In this temperature range μ_A comes from the following expression.

$$\begin{gathered} \mu_A = -(X_\gamma)^2 + \frac{1}{16} \\ \text{where} \\ X_\gamma = T^* - \frac{1}{4} \\ \mu_A = -(T^*)^2 + \frac{1}{2}T^* \end{gathered} \tag{9}$$

In summary, μ_A as a function of temperature is given by the following.

$$\mu_A = \begin{cases} -\frac{3}{16} + T* & 0 \leq T^* \leq \frac{1}{4} \\ -(T^*)^2 + \frac{1}{2}T^* & \frac{1}{4} \leq T^* \leq \frac{3}{4} \\ -\frac{3}{16} & \frac{3}{4} \leq T^* \leq 1 \end{cases} \tag{10}$$

See Figure 2 for a plot.

9-1-v

In order to draw the whole phase diagram it is necessary to find the the equilibrium condition for the two phase region above $T^* = \frac{3}{4}$ and below $T^* = \frac{1}{4}$. This comes from equating the chemical potentials and using, for $T^* \geq \frac{3}{4}$, $X_l = 1$.

$$
\begin{aligned}
\mu_B^l = \overline{G}^l(X^l = 1) &= \mu_B^\gamma(X^\gamma) \\
T^* - \frac{7}{16} = (X_\gamma - \frac{1}{4})^2 &+ 2(1 - X_\gamma)(X_\gamma - \frac{1}{4}) \\
-\frac{23}{16} + T^* &= -(X_\gamma)^2 + 2X_\gamma - \frac{7}{16} \\
&\text{so} \\
X_\gamma &= 1 - \sqrt{1 - T^*}
\end{aligned} \tag{11}
$$

Now for $T^* \leq \frac{1}{4}$, $X_\gamma = 0$.

$$
\begin{aligned}
\mu_A^\gamma = \overline{G}^\gamma(X_\gamma = 0) &= \mu_A^l(X^l) \\
\frac{1}{16} &= -(X_l)^2 + \frac{1}{16} + T^* \\
&\text{so} \\
X_l &= +\sqrt{T^*}
\end{aligned} \tag{12}
$$

See Figure 3 for a plot.

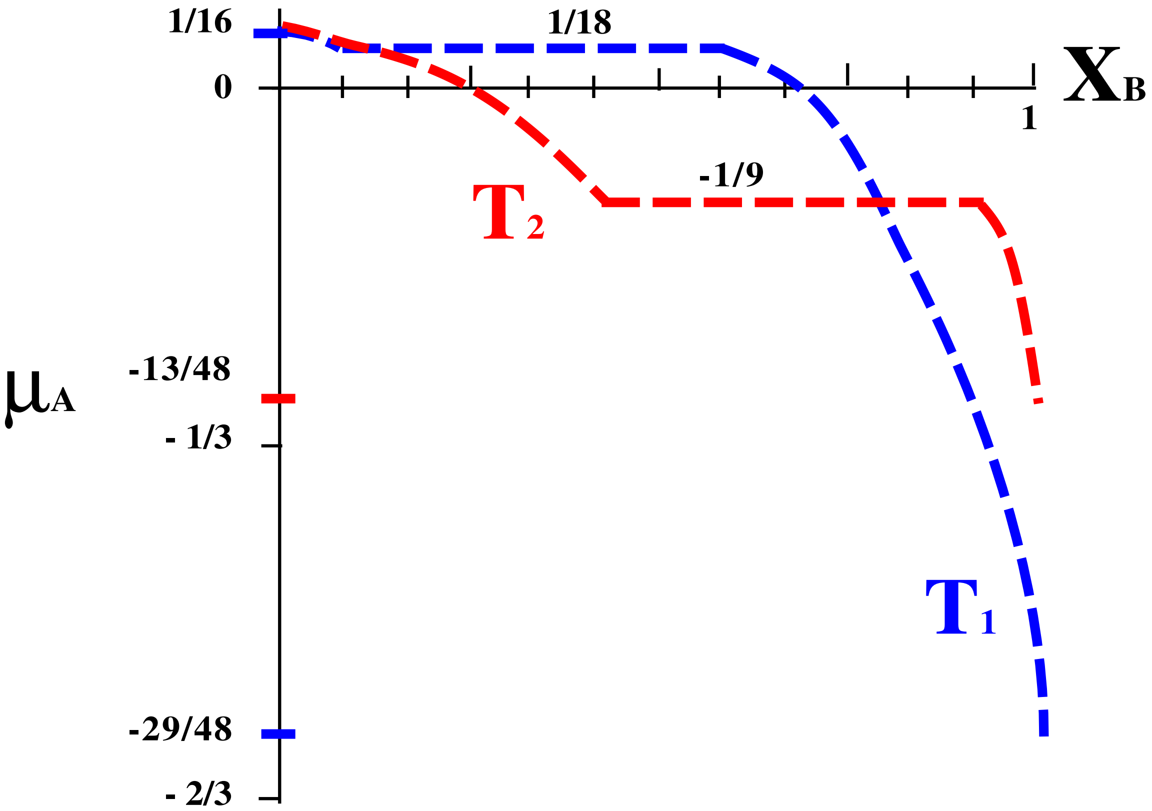

Figure 1: Plot of μ_A versus X_B at $T_1^* = \frac{1}{3}$ in blue and $T_2^* = \frac{2}{3}$ in red. Notice that the chemical potential is constant across the two phase regions.

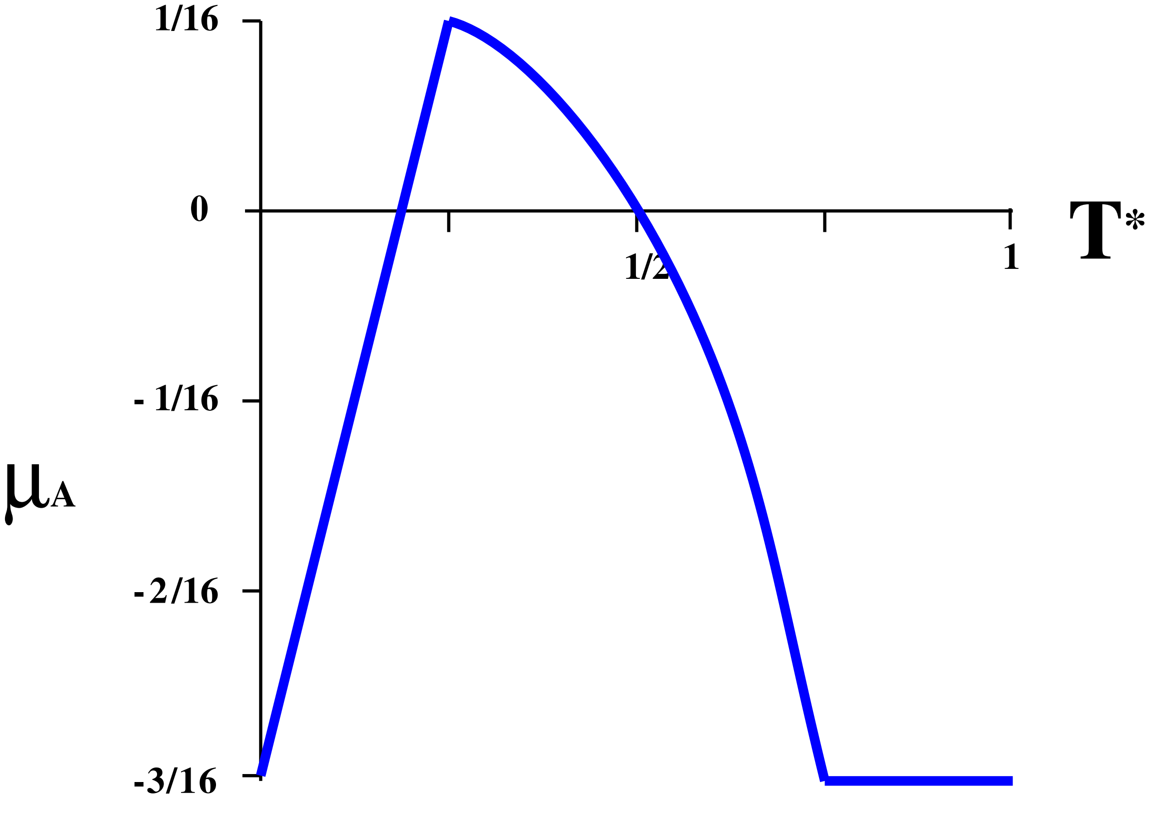

Figure 2: Plot of μ_A vs. $T^* = \frac{T - T_A}{T_B - T_A}$ at $X_B = \frac{1}{2}$.

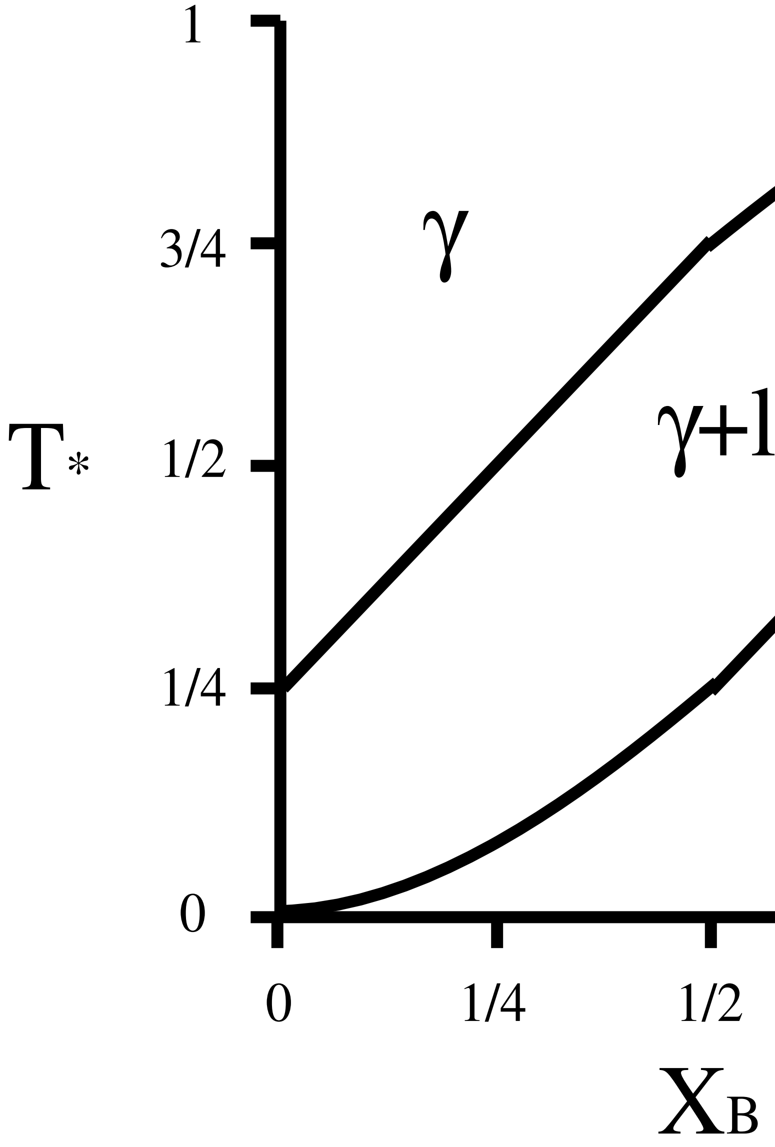

Figure 3: Binary phase diagram for γ and liquid phases where $T^* = \frac{T-T_A}{T_B-T_A}$. Notice that this isn't quite the classical lens shape because the $\overline{G}$ curves have finite slopes at $X_B = 1$ and $X_B = 0$.