Free Energy and Phase Diagrams

1 (25 points) In class, we showed that the number of possible microstates of a system of two types of atoms A and B, with numbers N_A and N_B, is as follows: $\Omega = \frac{(N_A+N_B)!}{N_A!N_B!}$. Using basic thermodynamic relations and the Boltzmann equation for entropy of a microstate: $S = k_B ln\Omega$, show that the molar entropy of mixing is most easily expressed in terms of the mole fractions of each atom (X_A and X_B) as: $T\Delta S = -RT\left(X_A ln X_A + X_B ln X_B\right)$, where R is the ideal gas constant and T is the temperature. (Hint: look up how R and k_B are related). Can the entropy of mixing (ΔS) ever be negative? Why or why not?

We need to find the entropy term, which can be expressed as::

$$S = k_B ln\left(\frac{(N_A + N_B)!}{N_A!N_B!}\right) \tag{1}$$

We can use Stirling's approximation, for very large x:

$$ln\left(x!\right) \approx x \cdot ln\left(x\right) - x \tag{2}$$

Using this approximation, we get:

$$S = k_B\left[(N_A + N_B)ln\left(N_A + N_B\right) - \cancel{N_A} - \cancel{N_B} - N_A ln\left(N_A\right) + \cancel{N_A} - N_B ln\left(N_B\right) + \cancel{N_B}\right] \tag{3}$$

Now each term $N_i = N_{Av}X_i$, where X_i is the molar fraction of substance i. We can therefore factor out Avogadro's number and combine terms:

$$S = R\left[N_A\left[ln\left(N_A + N_B\right) - ln\left(N_A\right)\right] + N_B\left[ln\left(N_A + N_B\right) - ln\left(N_B\right)\right]\right] \tag{4}$$

$$S = R\left[N_A\left[ln\left(\frac{N_A + N_B}{N_A}\right)\right] + N_B\left[ln\left(\frac{N_A + N_B}{N_B}\right)\right]\right] \tag{5}$$

$$S = -R\left[N_A\left[ln\left(\frac{N_A}{N_A + N_B}\right)\right] + N_B\left[ln\left(\frac{N_B}{N_A + N_B}\right)\right]\right] \tag{6}$$

$$S = -R\underbrace{(N_A + N_B)}_{N_{Av}}\left[\underbrace{\frac{N_A}{N_A + N_B}}_{X_A}\left[ln\left(\underbrace{\frac{N_A}{N_A + N_B}}_{X_A}\right)\right] + \underbrace{\frac{N_B}{N_A + N_B}}_{X_B}\left[ln\left(\underbrace{\frac{N_B}{N_A + N_B}}_{X_B}\right)\right]\right] \tag{7}$$

2 (25 points) Reconstructing free energy diagrams from phase diagrams: For each of the following binary phase diagrams, identify the number of unique phases present, and construct qualitative free energy diagrams for each phase at the following temperatures:
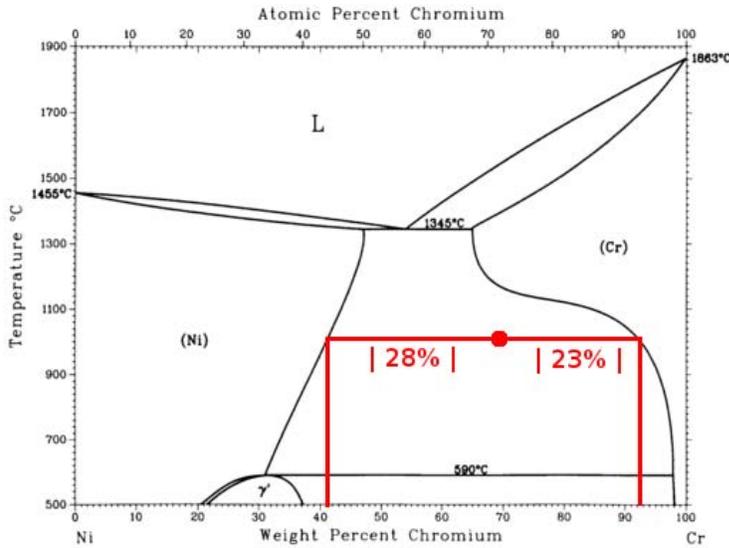

Ni-Cr (500°C, 1000°C, 1400°C, 1600°C)
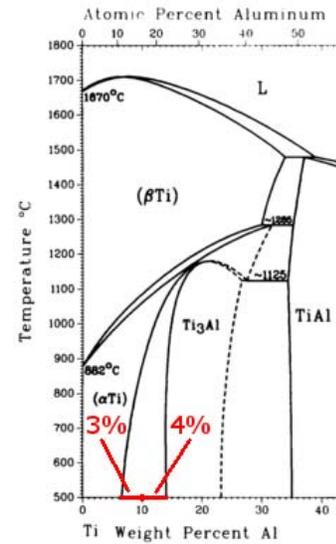
Al-Ti (700°C, 1100°C, 1300°C, 1800°C)

Source: ASM Handbook, Volume 3: Alloy Phase Diagrams.
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Ni-Cr: Has four distinct phases (Ni, Cr, γ', L)

Al-Ti: Has five distinct phases on the diagram shown (αTi, βTi, Ti$_3$Al, TiAl, L)

Each set of free energy diagrams should have a corresponding number of curves. Free energy diagrams are shown below:
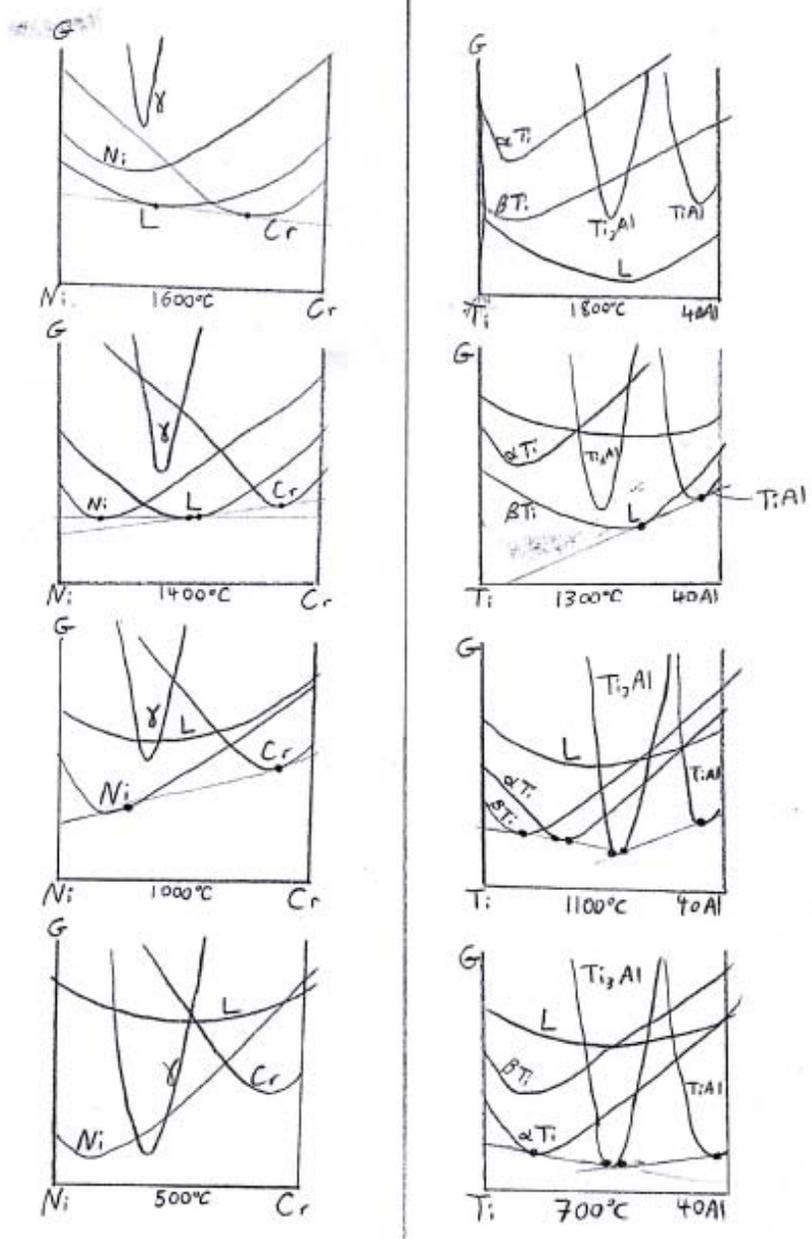
The exact shape isn't important, but the following general features should be observed:

1. Intermetallics should be sharp in proportion to their lack of compositional stability. The Ti-Al intermetallics have some tolerance to off-stoichiometry, so they shouldn't be razor sharp lines.

2. One side of each free energy curve will likely be lower than the other, this lower side should reside at the graph edge where the phase is more stable (see the Ti curves, for example).

3. All curve tangents should correspond to locations of changing phase stability on the binary phase diagram.

3 (25 points) Reading phase diagrams: For each composition (in weight percent) and temperature for the phase diagrams mentioned, use the lever rule to indicate the expected fractions, compositions, and crystal structures of each phase present. Next, answer the following questions to the best of your ability.

3.1 30Ni-70Cr, 1000°C: What does this tell you about the microstructural stability and compositional variability of Ni-based superalloys?

30Ni-70Cr lies squarely in the two-phase region. Therefore, there will be a Ni-rich phase and a Cr-rich phase. These will have compositions 58Ni-42Cr and 7Ni-93Cr. They will be present as follows:

$$\%Ni-rich = \frac{93-70}{93-42} = 45.1\% \tag{8}$$

$$\%Cr-rich = 1 - \$Ni-rich = 54.9\% \tag{9}$$

Nickel has a high solubility for Cr, making them quite stable to large compositional fluctuations. Nickel alloys form good solid solutions at a range of compositions.

3.2 Al-10Ti, 500°C: Look up the composition of Grade 6 titanium, commonly used in aircraft engines. Based on the Al-Ti phase diagram, why do you think the compositional limits for this alloy were chosen?

Al-10Ti lies almost in the middle of the two-phase region. Therefore, there will be a Ti-rich phase and a Ti_3Al intermetallic precipitate. These will have compositions 93Ti-7Al and 86Ti-14Al (which is Ti_3Al somewhat depleted in Al in atomic percent). They will be present in proportions as follows:

$$\%Ti-rich = \frac{14-10}{14-7} = 57\% \tag{10}$$

$$\%Ti_3Al = 1 - \$Ti-rich = 43\% \tag{11}$$

Grade 6 titanium has a composition of Ti-6Al-4V, which means 6% Al, 4% V, and the balance (90%) Ti. This composition was probably chosen to avoid the formation of Ti_3Al during long time service at temperatures around 500C, which could conceivably be reached for aircraft engine components.

4   (25 points) Constructing phase diagrams from the following free energy diagrams at indicated, arbitrary temperatures. Fill in what you expect the diagram to look like in between the specified temperatures.

(a)

(b)
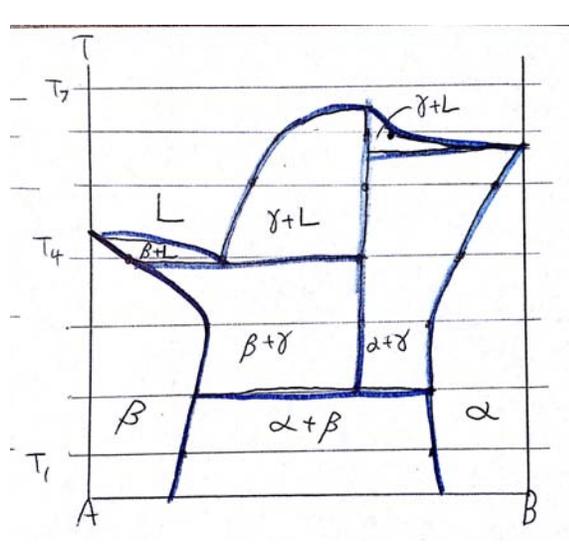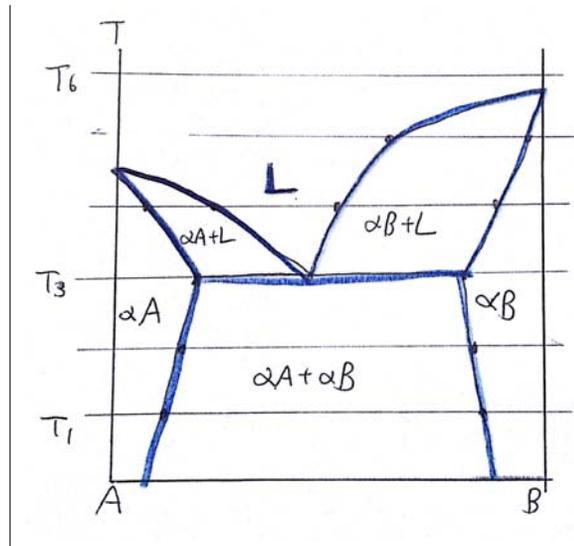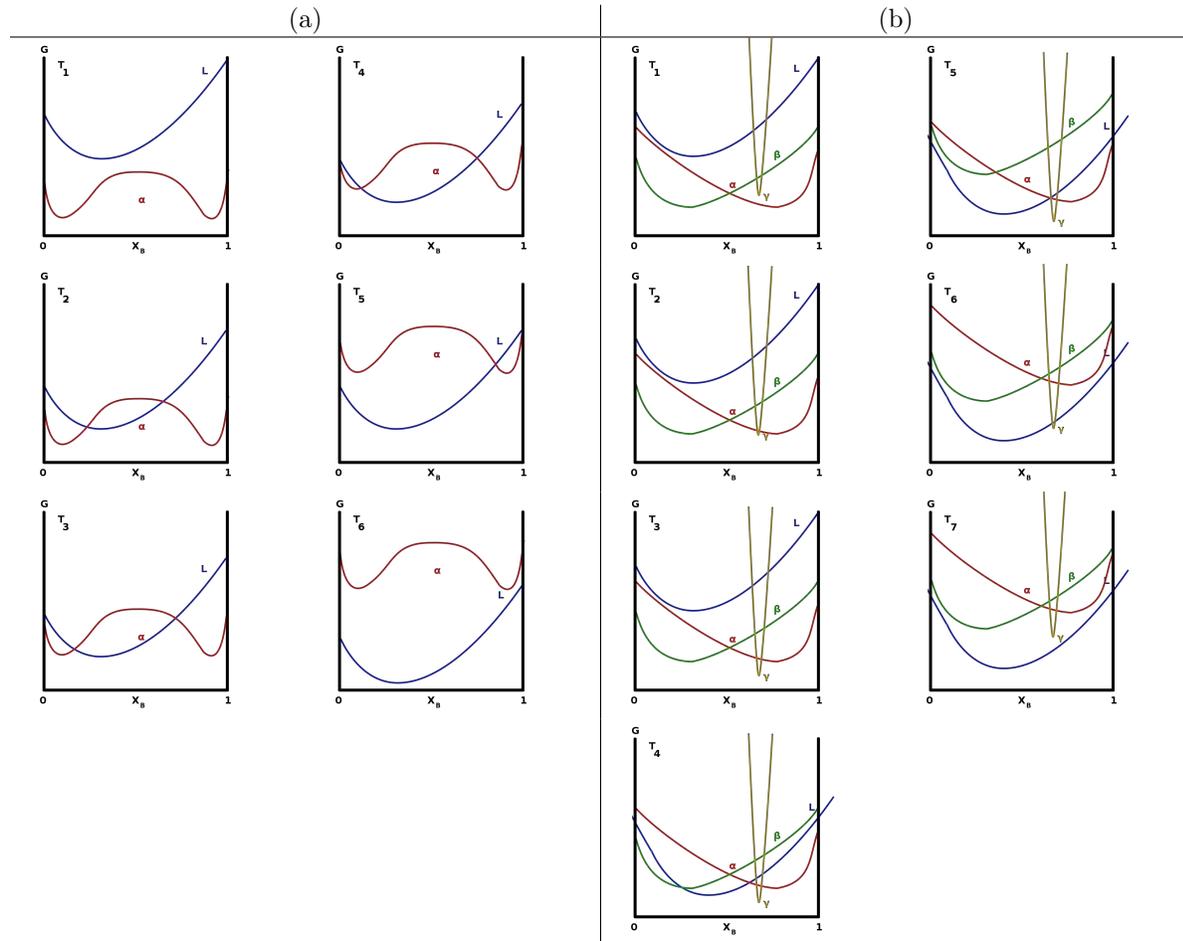
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