Mat Sci 103
Phase Transformations and Kinetics
First Midterm Exam
March 8, 2019

Name:

Instructions: Answer all questions and show your work. You will not receive partial credit unless you show your work. Good luck!

1a: 10 points	
1b: 10 points	
1c: 15 points	
1d: 15 points	
1e: 15 points	
2a: 10 points	
2b: 10 points	
2c: 15 points	
Total: 100 points	

1. Figure 1 shows the Cr-Ni phase diagram containing the following phases:

   L: Liquid
   (Cr): BCC solid solution
   (Ni): FCC solid solution

   Assume that the FCC (Ni) phase is a regular solution with $\Omega^{FCC} = 14.5\ \text{kJ mol}^{-1}$.

   a. (10 points) On the phase diagram label the two-phase regions, and circle and label the region of the phase diagram corresponding to the eutectic three-phase equilibrium.

   b. (10 points) Suppose an alloy containing 40 at. % Ni is cooled slowly from the liquid. What is the lowest temperature at which the liquid phase is present and what is the composition and phase fraction of the liquid at this temperature?

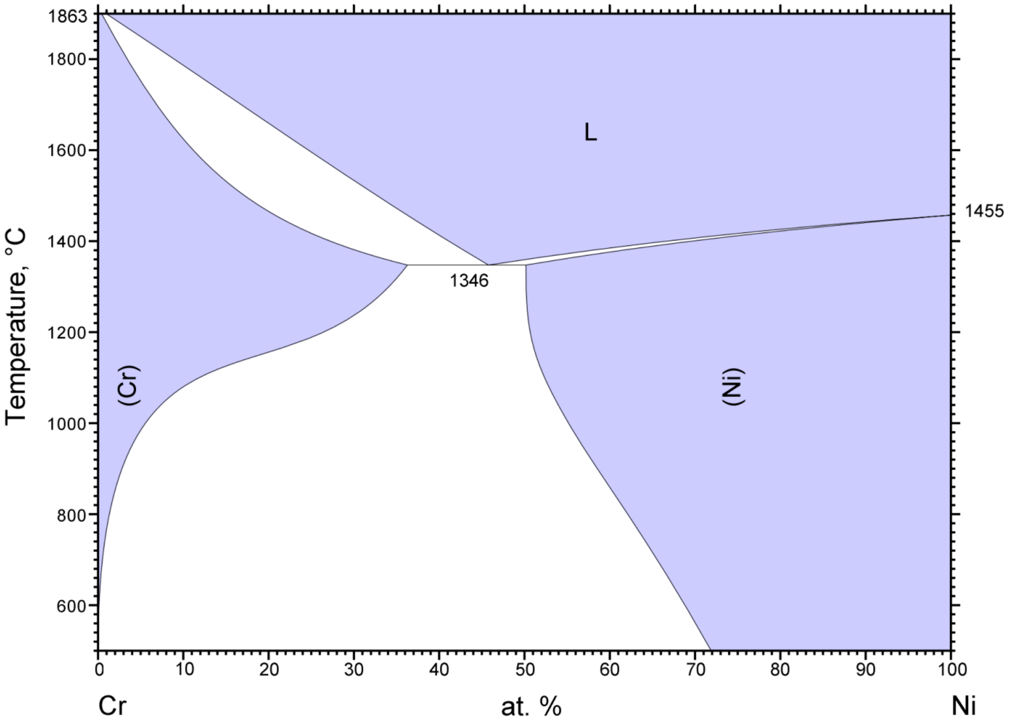
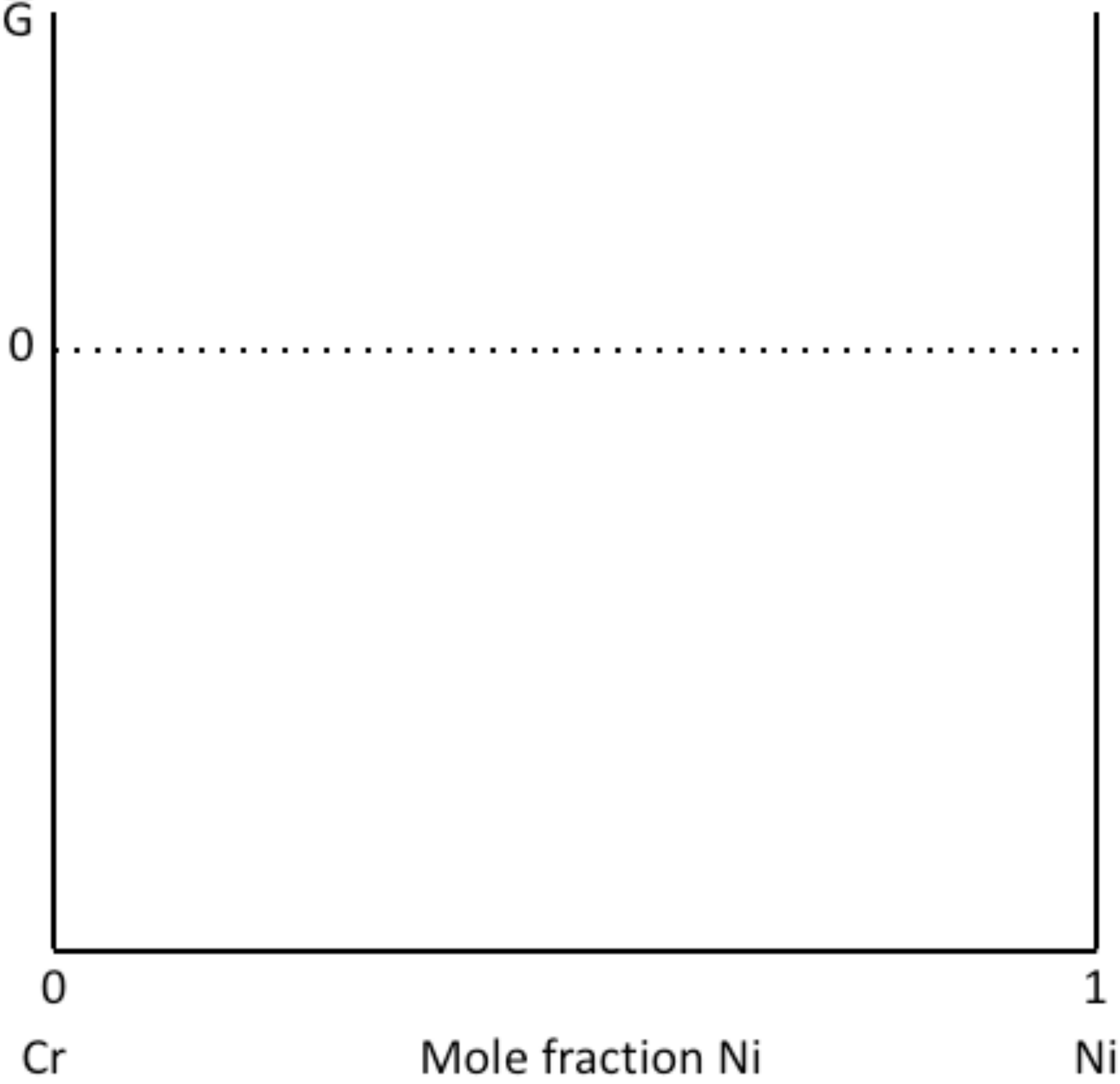


Figure 1: Composition-temperature phase diagram for Cr-Ni.

Problem 1 (cont.)

c. (15 points) In the space provided, sketch molar Gibbs free energy curves for the L, (Ni) and (Cr) phases at T=1346°C using L as the reference states for both pure Cr and pure Ni (i.e., set $\bar{G}_{Cr}^{0,L} = 0$ and $\bar{G}_{Ni}^{0,L} = 0$). On this sketch:
   i. Label the free energies for pure Cr and Ni in each of the three phases and sketch each free energy curve over the entire composition range.
   ii. Indicate the phase equilibria with a common tangent line. *Note*: since this is intended to be a sketch, your common-tangent compositions do not need to quantitatively match the phase diagram.



Problem 1 (cont.)

d. (15 points) At a temperature of T=800°C, compute the free energy difference between BCC and FCC phases of pure Cr. At this temperature, you can assume that the activity of Cr obeys Raoult's law over the compositional range of stability of the (Cr) phase. Recall from above that the (Ni) phase is a regular solution.

e. (15 points) Suppose that the BCC-FCC free energy difference $\Delta G^{FCC \rightarrow BCC}$ has the same magnitude (but opposite sign) for pure Ni and pure Cr. Suppose further that the BCC (Cr) phase is a regular solution with a positive interaction parameter Ω^{BCC}, similar to the FCC (Ni) phase. Based on the shape of the phase diagram, would you expect that $\Omega^{\mathrm{BCC}} > \Omega^{\mathrm{FCC}}$ or that $\Omega^{\mathrm{BCC}} < \Omega^{\mathrm{FCC}}$? Explain your answer.

2. Shown in Figure 2 on the next page is an isothermal section of the Al-Cr-Ni ternary phase diagram at a temperature of *T*=1150°C. There are 6 single-phase regions corresponding to the following phases:

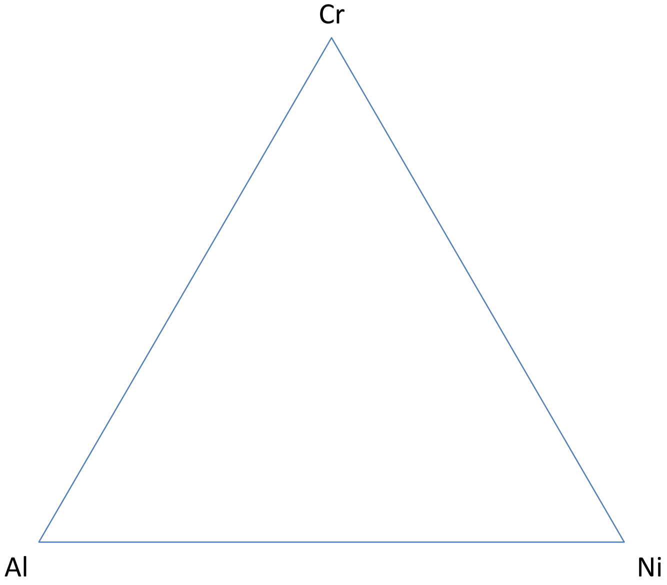
   (Cr): BCC Solid Solution
   Cr_5Al_8: Intermetallic Phase
   L: Liquid Phase
   NiAl: Intermetallic Phase
   Ni_3Al: Intermetallic Phase
   (Ni): FCC Solid Solution

   The white areas are two-phase regions and in some of these regions tie lines are drawn in by thin green lines.

   a. (10 points) On the phase diagram, label all of the 2-phase and 3-phase regions, and in the L+NiAl two-phase region draw in three plausible tie lines.

   b. (10 points) On the diagram label with a point the composition corresponding to $x_{Al}=x_{Ni}=0.25$. For this composition give the phases present in equilibrium, their compositions and phase fractions.

   c. (15 points) At *T*=1527°C the stable phases present are L, NiAl and (Cr). A vertical section from pure Al to a composition $x_{Ni}=x_{Cr}=0.5$ shows only L to be stable at this temperature. Given this information, sketch below a plausible isothermal section showing regions of the (Cr), NiAl, and L phases and associated two-phase fields.



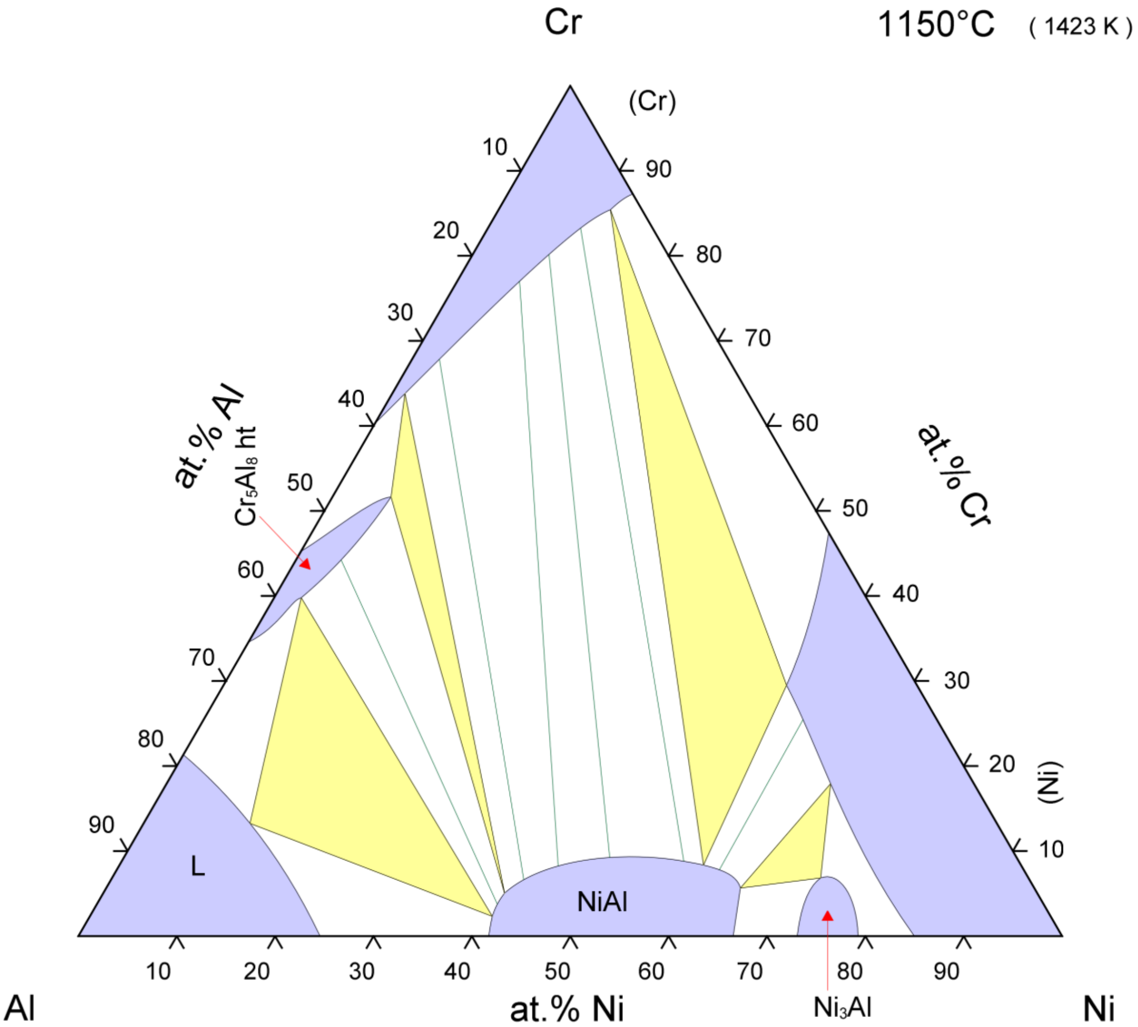


Figure 2: Al-Cr-Ni isothermal section at 1150°C.

Constants, Equations, Figures, Notation, Definitions

Ideal Gas Constant: $R = 8.314$ J mole^{-1} K^{-1}

Thermodynamic Relations:

$$G = H - TS$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P > 0$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T > 0$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P > 0$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T > 0$$

Free Energy Difference Between Solid and Liquid Phases for Single-Component System:

$$\Delta\bar{G}_0^{s\to l}(T) \approx \frac{\Delta\bar{H}^{s\to l}}{T_m}[T_m - T] = \Delta\bar{S}^{s\to l}[T_m - T]$$

Chemical Potentials:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

$$\mu_i^{\varphi} = \bar{G}_i^{0,\varphi} + RT\ln a_i^{\varphi}$$

$$a_i = \gamma_i x_i$$

Henry's Law: The activity coefficient for component *i* takes on a constant value (γ_i^{∞}) when *i* is dilute (i.e., $x_i \ll 1$)

Raoult's Law: The activity coefficient for component *i* takes the value of 1 when *i* is highly concentrated (i.e., $x_i \approx 1$)

Method of intercepts for a binary A-B mixture:

$$\mu_A(x_B) = \bar{G}(x_B) - \left(\frac{\partial\bar{G}}{\partial x_B}\right)x_B$$

$$\mu_B(x_B) = \bar{G}(x_B) + \left(\frac{\partial\bar{G}}{\partial x_B}\right)(1 - x_B)$$

Molar Gibbs Free Energy for Mixture:

$$\bar{G}^{\phi} = \left[(1 - x_B)\bar{G}_A^{0,\phi} + x_B \bar{G}_B^{0,\phi}\right] + \Delta\bar{G}_M^{\phi}$$

Mixing free energy: $\Delta\bar{G}_M$

Ideal Solution Model for Binary A-B Mixture:

$$\Delta\bar{G}_M \equiv \Delta\bar{G}_M^{id} = RT[x_B \ln(x_B) + (1 - x_B)\ln(1 - x_B)]$$

$$a_i = x_i$$

Regular Solution Model:

$$\Delta\bar{G}_M \equiv \Delta\bar{G}_M^{id} + \bar{G}^{xs}$$

$$\bar{G}^{xs} = \Omega x_B(1 - x_B)$$

$$a_i = \gamma_i x_i$$

$$\gamma_A = \exp\left(\frac{\Omega x_B^2}{RT}\right)$$

$$\gamma_B = \exp\left(\frac{\Omega x_A^2}{RT}\right)$$

$$T_c = \frac{\Omega}{2R}$$

Lever Rule for two-phase equilibrium between phases α and β in a binary A-B system with overall composition x_B:

$$f^{\alpha} = \frac{\left(x_B - x_B^{\beta}\right)}{\left(x_B^{\alpha} - x_B^{\beta}\right)}$$

$$f^{\beta} = \frac{\left(x_B^{\alpha} - x_B\right)}{\left(x_B^{\alpha} - x_B^{\beta}\right)}$$

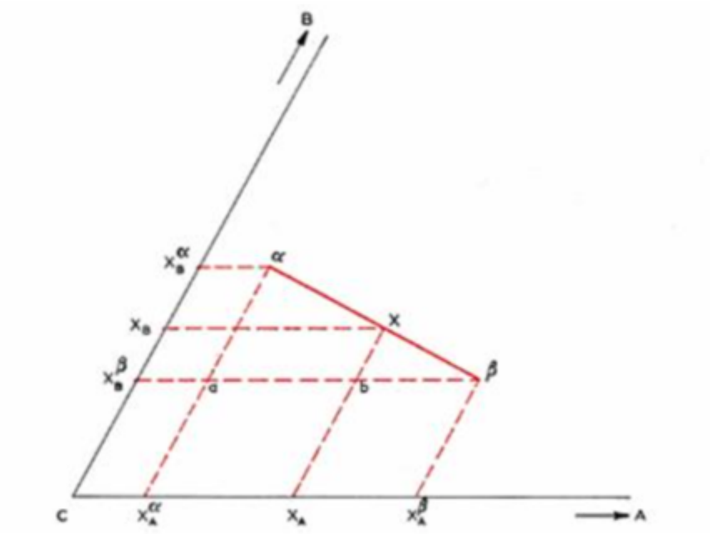
Gibbs Phase Rule at Fixed Pressure:

At fixed pressure: # degrees of freedom = # of components + 1 – # of phases

Invariant Equilibria in Binary Systems:

Euctectic: $L \Leftrightarrow \alpha + \beta$
Monotectic: $L_1 \Leftrightarrow L_2 + \alpha$
Peritectic: $L + \alpha \Leftrightarrow \beta$
Congruent: $L \Leftrightarrow \alpha$
Critical Point: $\alpha \Leftrightarrow \alpha_1 + \alpha_2$

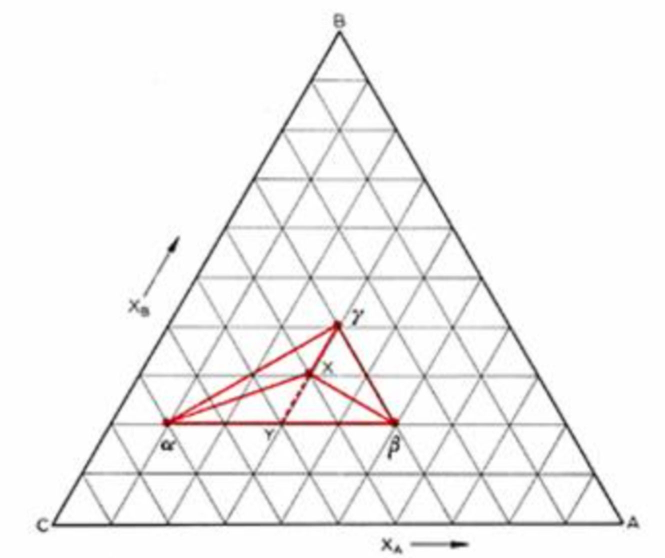
Two-Phase Lever Rule for Ternary Phase Diagram:



$$f^\alpha = \frac{\beta x}{\beta\alpha} = \frac{x_i - x_i^\beta}{x_i^\alpha - x_i^\beta}$$

$$f^\beta = 1 - f^\alpha$$

Three-Phase Lever Rule for Ternary Phase Diagram:



$$f^\gamma = \frac{XY}{\gamma Y}$$