

MS 115a, Problem Set #9

assigned 11/28/12  
 due **12/6/12**  
 will **not** be accepted late

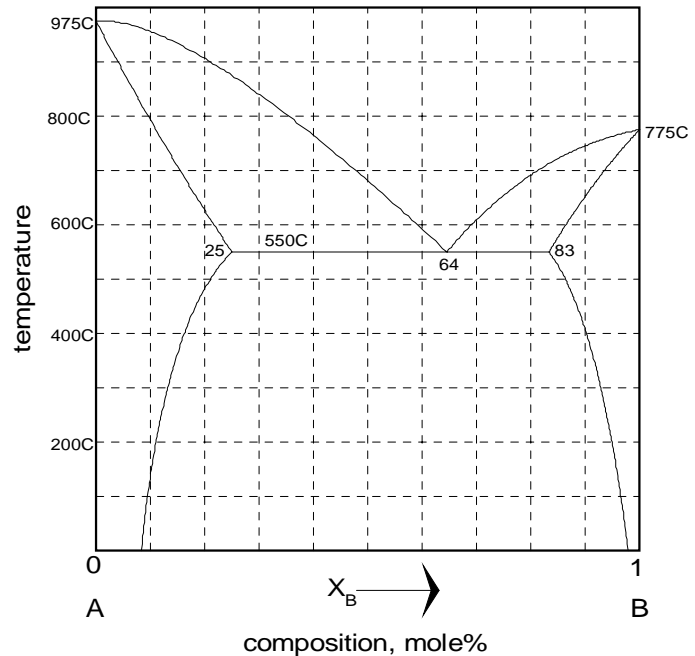
1. Show that the chemical potential of species A in an ideal solid solution is given by

$$\mu_A = \mu_A^0 + RT \ln(X_A) \quad \text{where } \mu_A^0 \text{ is the chemical potential in the pure state.}$$

2. The enthalpy of mixing of a regular solution is given by  $\Delta H^{\text{mix}} = \Omega X_A X_B$ , where  $\Omega$  is a constant that can be related to the energy parameter,  $\epsilon$ , of the quasichemical model of solutions. Show that for  $\Omega > 0$  (clustering) the maximum temperature at which phase separation occurs is given by  $T_{\text{max}} = \Omega/2R$ . Hints: (1) note that the maximum occurs at  $X_A = X_B = 0.5$ ; (2) note that phase separation occurs because  $\Delta G^{\text{mix}}$  has a double minima shape at low temperature, thus it changes from positive curvature to negative curvature at  $T_{\text{max}}$ .
3. The metallic elements A and D form a solid solution at room temperature. On cooling, phase separation occurs and the critical temperature,  $T_{\text{max}}$ , is 265K. What is the difference between the energy of A-D bonds and the average of the A-A and D-D bonds?

Problems 4-10 refer to the figure below and to the right. You will need to copy it onto your homework paper.

4. The melt temperatures of pure A and pure B are 975 and 775°C, respectively. Label these points as well as the regions and boundaries on the phase diagram.
5. What is the name given to this type of phase diagram?
6. If pure A has the hexagonal close-packed structure, what is the structure of pure B?
7. What is the composition of each phase (at equilibrium) at 450°C for an alloy with 35 mol% B? What is the phase fraction of each phase?
8. What is the maximum solubility of B into A? At what temperature is this maximum attained? What is the maximum solubility of A into B? At what temperature is this maximum attained?
9. Draw the Gibbs free energy curves of the liquid and the solid as a function of composition ( $X_B$ ), for the following temperatures:



$$T_1 > 975^\circ\text{C} \quad T_2 = 975^\circ\text{C} \quad 975^\circ\text{C} > T_3 > 775^\circ\text{C}$$

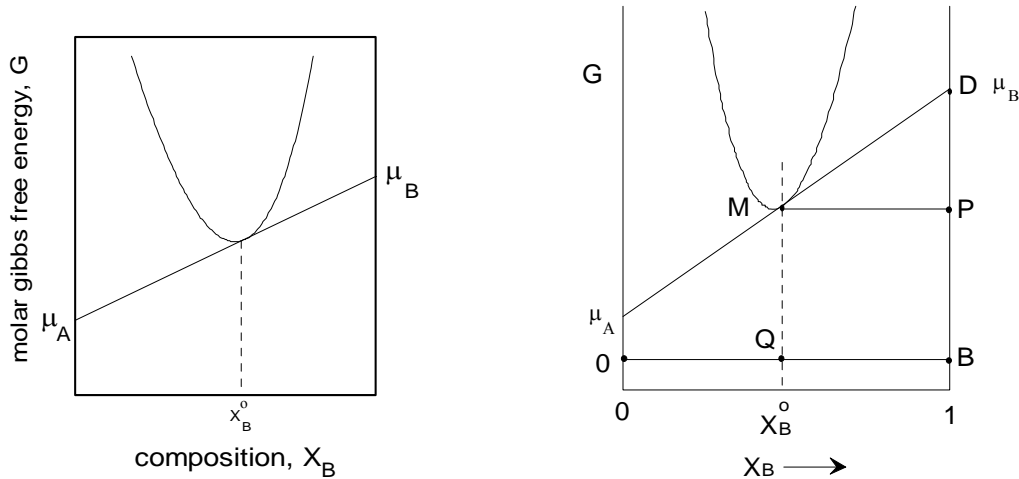
$$T_4 = 775^\circ\text{C} \quad 775^\circ\text{C} > T_5 > 550^\circ\text{C} \quad T_6 = 550^\circ\text{C}$$

$$T_7 < 550^\circ\text{C}$$

10. Using Gibbs free energy curves at  $850^\circ\text{C}$  (similar to  $T = T_3$  of problem 9):

- Show the chemical potentials of components A and B for an alloy with 20 mol% B.
- Show that in the two-phase region the chemical potential of A in the solid phase is equal to that in the liquid phase
- Plot  $\mu_A$  as a function of  $X_B$ . Pay close attention to the behavior of  $\mu_A$  within the two-phase region.

10. In class we noted the “Tangent Rule” for determining the chemical potential of a species in a solution from the Gibbs free energy curve as a function of composition. Specifically it was stated that the chemical potentials  $\mu_A$  and  $\mu_B$  are given by an extrapolation of a line, tangent to the Gibbs free energy curve at the composition of interest, to the compositions  $X_B = 0$  and  $X_B = 1$ , as shown in the left-side figure.



Derive this result by the following steps:

- Show that the differential molar Gibbs free energy of a two-component solution, at constant  $T$  and  $P$  is

$$dG = \mu_A dX_A + \mu_B dX_B$$

- Knowing that  $X_A + X_B = 1$ , show that

$$\mu_B = G + X_A(dG/dX_B)$$

- Use the right-side figure to demonstrate the equivalence of the tangent rule and the equation of step (b).

11. Show that for an ideal solution the slope of  $d\Delta G^{\text{mix}}/dX_B \rightarrow -\infty$  as  $X_B \rightarrow 0$ , and approaches infinity as  $X_B \rightarrow 1$ . Interpret this result in terms of the concentration of impurities present in any material.