MT 201 Phase Transformations

Spring 2007

Home Assignment 3

1. A long vertical column is closed at the bottom and open at the top. It is partially filled with a certain fluid and cooled to -5^o C. At this temperature, the fluid solidifies below a particular level, remaining liquid above this level. If the temperature is further lowered to -5.2^o C, the solid-liquid interface moves upward by 40 cm. The latent heat (per unit mass) is 2 cal/g, and the density of the liquid phase is 1 g/cm^3. Find the density of the solid phase (neglect thermal expansion of all the relevant phases).

   Hint: The pressure at the original position of the interface remains constant.

2. (Lupis: 1.14) Phase α of a species A transforms into phase β at 55 K and 1 atm. The heat capacities of A (at 1 atm) in the structures α and β are, respectively, $C_p^\alpha = 2.1 \times 10^{-5} T^3$ and $C_p^\beta = 5.7 \times 10^{-5} T^3$ cal/mol. Calculate the enthalpy and entropy of transformation at 55 K and 1 atm.

3. Using the same procedure as above, calculate the enthalpy and entropy of transformation at 50 K, and the free energy of transformation ΔG at 50 K.

   ΔG is often obtained using the approximation $\Delta G = \Delta H (T_t - T)/T_t$, where T_t is the transition temperature. Derive this approximation, and state all the assumptions that are used in the derivation.

   Compare the numerical results you obtained for ΔG using the two methods. What factors can explain the difference?

4. In a binary system exhibiting a continuous series of solid and liquid solutions, congruent melting (with a minimum in solidus and liquidus) is observed at an alloy composition of $x = 0.45$.

   Sketch this phase diagram. Apply Gibbs phase rule to this alloy at its melting point.

   Sketch schematic G_m vs x curves for the solid and liquid phases at a temperature just above the congruent melting point, and at just below it.

5. The Gibbs free energy (in calories per mole) of Al-Zn *fcc* α phase at 1 atm pressure may be represented by the equation:

$$\begin{aligned} G_m^\alpha &= (1-x)\, G_{Al}^\alpha + x\, G_{Zn}^\alpha + RT\,\{x \ln x + (1-x)\ln(1-x)\} \\ &\quad + x(1-x)\ \{3150(1-x) + 2300x\} \left\{1 - \frac{T}{4000}\right\} \end{aligned}$$

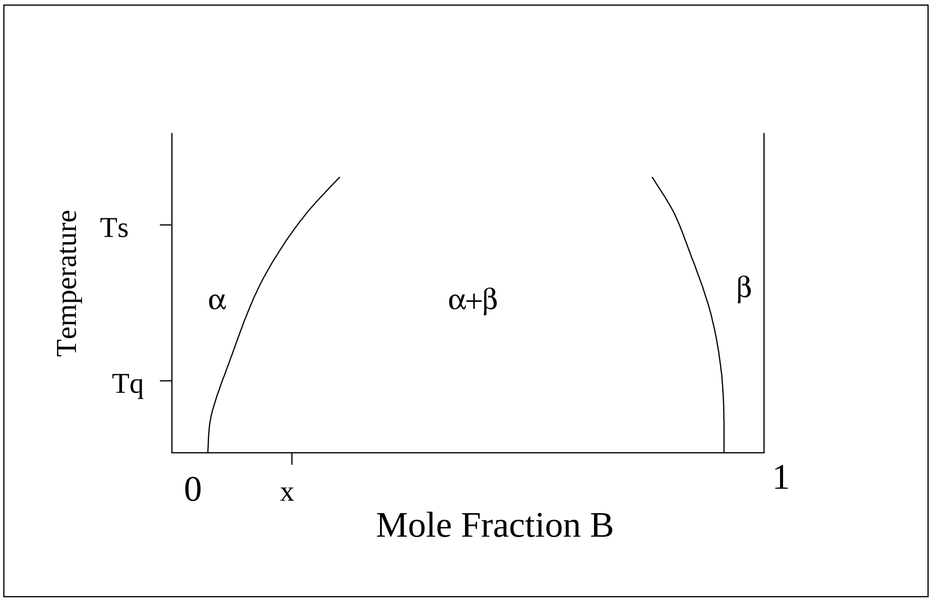
   where G_{Al}^α and G_{Zn}^α are Gibbs free energies of pure Al and Zn, and are functions of temperature. Derive expressions for the chemical potential of Al and Zn as a function of temperature and phase composition x, the mole fraction of Zn.

   Calculate the composition and temperature of the miscibility gap's critical point.

6. If a disordered phase α is an ideal solution, what do the following expressions evaluate to: $[\partial \mu_B^\alpha / \partial x]_{T,P}$, $[\partial \mu_B^\alpha / \partial P]_{T,x}$ and $[\partial \mu_B^\alpha / \partial T]_{P,x}$?

7. In a binary A-B system, the solid phase is found to be a regular solution with a positive regular solution parameter C. The phase diagram exhibits a miscibility gap, whose maximum temperature is T_c. For a temperature $T < T_c$, plot G, the first, second and third derivatives of G with respect to x, as a function of x from $x = 0$ to $x = 1$. Repeat this exercise for $T = T_c$. Find T_c and x_c, the composition at T_c.

8. Consider an alloy of composition x in the phase diagram in the following figure. This alloy is solutionized at T_s and quenched to T_q.



(a) What is the transformation which takes place in this alloy at T_q? Draw schematic G_m *vs* x curves for the α and β phases at T_q, and indicate on this diagram the free energy change ΔG_T (per mole of the alloy) for this transformation. Assuming ideal solution behaviour for the α phase (and for the β phase too, if necessary), find an expression for ΔG_T.

9. Derive, from the differential and integral forms of the fundamental relation, the equation: $\mu_B = G_m + (1 - x)\partial G_m/\partial x$.