1. True or false. Reason or prove your answer. (18%)
   (a) The internal energy of a system at constant entropy and volume must decrease in any spontaneous process.
   (b) For a single component system, the solid to liquid transition temperature always increases as the pressure is raised.
   (c) The thermal expansivity of a solid does approach zero as the temperature approaches zero.

2. An ideal monatomic gas occupies volume 10^{-3} m^3 at temperature 3 K and pressure 10^3 Pa. It undergoes the following cycle: The temperature is raised to 300 K at constant volume; the gas is then expanded adiabatically till the temperature is 3 K, followed by isothermal compression to the original volume. Calculate the work done, the heat transfer, and the change in the internal energy during this cycle. Note the specific heat at constant volume (c_V) for an ideal monatomic gas is 1.5R, where R is gas constant and equal to 8.314 J/mole K. (16%)

3. The van der Walls equation of state is

   $$(P+\frac{a}{V^2})(V-b)=RT$$

   where *a, b, R* are constant. Show that the specific heat at constant volume (c_V) for a van der Waals gas is independent of volume. (16%)

4. Consider the following electrochemical cell at 25°C:

   $$Pt, H_{2(g)} \mid H^+ \mid Fe^{2+} \mid Fe_{(s)}.$$

   The reaction is $H_{2(g)} + Fe^{2+}_{(aq)} = 2\,H^+_{(aq)} + Fe_{(s)}$. (5% each and 20% in total)
   (a) When all of the species are in their standard states, does this reaction proceed spontaneously to the right or to the left? [$\Delta G^\circ_f(Fe^{2+}) = -78.87$ kJ/mole]
   (b) Determine the cell voltage. [Faraday's constant is 96487]
   (c) Instead of constructing the cell described above, Fe is placed in natural water (PH = 7) at 25°C. Assuming the concentration of Fe^{2+} in water is 10^{-6} M (molarity) and the partial pressure of H_2 in the atmosphere is 5×10^{-7} atm. Is the Fe stable, or will it be oxidized under these conditions?
   (d) When dealing with ions in solution we often make the assumption that the activity coefficient, γ, is equal to one. Debye-Huckel theory allows us to estimate γ for dilute ionic solutions. Does the theory predict a value for γ greater than or less than one? Briefly discuss the physical origin of the effect.

5. The phase diagram for A-O indicates that two oxide compounds exist, AO and A_2O, and both appear to be stoichiometric. There is also very limited solubility of O in A. At 300K, $\Delta G^\circ_f(AO) = -130$kJ/mole, $\Delta G^\circ_f(A_2O) = -150$kJ/mole.
   (a) Sketch the integral Gibbs free energies at 300K, i.e. ΔG^M vs. X_O. (5%)
   (b) Determine the activity of A in a two-phase mixture consisting of AO and A_2O at 300K. (5%)

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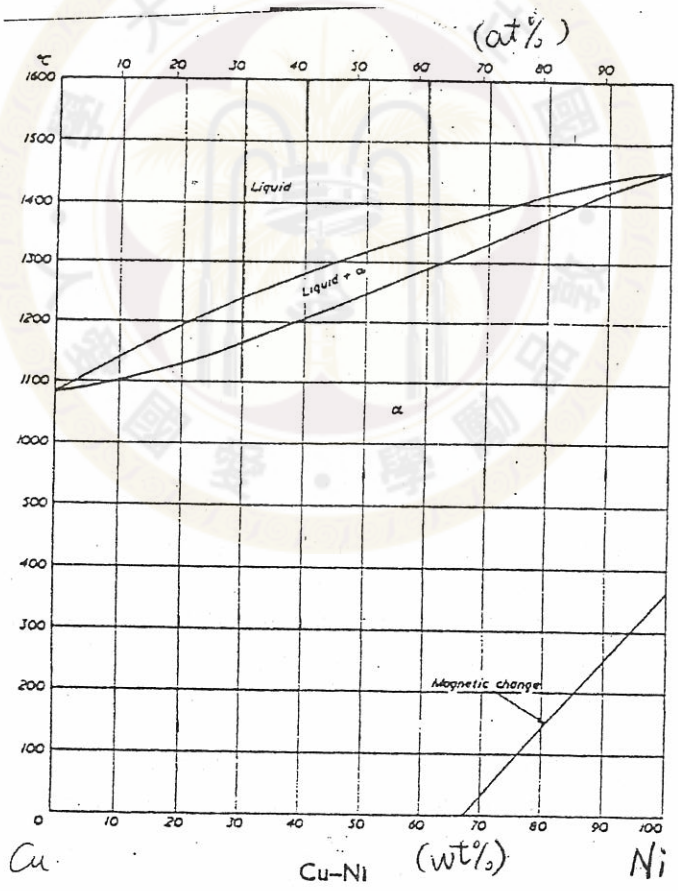
6. (a) Assume that the liquid and solid solutions in the Cu-Ni binary system are ideal. Determine the phase diagram from 1027 to 1527°C and compare with the attached phase diagram. Is the assumption that the solution are ideal a reasonable one? [melting point of Cu is 1084°C, ΔH_m°(Cu) = 13 kJ/mole; melting point of Ni is 1453°C, ΔH_m°(Ni) = 17.6 kJ/mole; assume $c_{p(s)} = c_{p(l)}$] (15%)

(b) What would be the effect of a larger value for ΔH_m on the separation of the liquidus and solidus curve? Explain using a Gibbs energy vs. composition diagram. (5%)



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