Physical Chemistry of Materials Final Exam June 18, 2008

1. (20pts) Answer the following questions.

(a) (5pts) Show that the solid-liquid phase boundary is given by

$$\frac{dp}{dT} = \frac{(\Delta H)_{fus}}{T(\Delta V)_{fus}}$$

Also, explain why the slope of *dp*/*dT* on the *p*-*T* phase diagram is very steep.

(b) (5pts) If the pressures are p and p^* at the melting points T and T^*, respectively, show that the phase boundary on the *p*-*T* phase diagram is given by

$$p \approx p^* + \frac{(\Delta H)_{fus}}{T^*(\Delta V)_{fus}}\left(T - T^*\right)$$

(c) (5pts) Assuming a vapour phase shows a perfect gas behavior, show that the liquid-vapour phase boundary is given by the Clausius-Clapeyron equation

$$\frac{d\ln p}{dT} = \frac{(\Delta H)_{vap}}{RT^2}$$

(d) (5pts) The normal boiling point of heptane is 98.4°C. Estimate its vapour pressure at 50°C by using the Trouton's rule (the standard entropy of vaporization ~ 85 $\mathrm{JK^{-1}mol^{-1}}$). Where $R = 8.314\ \mathrm{JK^{-1}mol^{-1}}$

2. (30pts) Answer the following questions.

(a) (5pts) Show that a change in Gibbs energy at constant pressure and temperature is given by the following Gibbs-Duhem equation,

$$d\mu_B = -\frac{n_A}{n_B}\,d\mu_A$$

(b) (10pts) For an ideal solution composed of two liquids (*A* and *B*), prove the following relations at constant *p* and *T*.

$$(\Delta G)_{mix} = nRT(x_A \ln x_A + x_B \ln x_B)$$
$$(\Delta S)_{mix} = -nR(x_A \ln x_A + x_B \ln x_B)$$

Also, describe the behavior of these quantities as a function of the mole fraction of A, x_A briefly.

(c) (5pts) Consider a container of volume 2.0 dm^3 that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.0 atm and 25 °C; in the right compartment there is oxygen at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect. 1 atm = 1.013×10^5 Pa

(d) (6pts) Explain the followings briefly.

(i) Raoult's law

(ii) Henry's law

(iii) regular solution

(e) (4pts) Given that $p^*(H_2O) = 0.02308$ atm and $p(H_2O) = 0.02171$ atm in a solution in which 0.207 kg of a non-volatile solute ($M = 298$ g mol^{-1}) is dissolved in 0.892 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

3.(15pts) Answer the following questions.

(a) (10pts) Justify the phase rule : $F = C - P + 2$ Where F is degree of freedom, C is the number of components, and P is the number of phases.

(b) (5pts) Derive the lever rule representing the relative amounts of two phases in equilibrium,

$$n_\alpha l_\alpha = n_\beta l_\beta$$

Where n_α is the amount of phase α, and n_β is that of phase β. l_α and l_β are the distances from a given composition to each equilibrium compositions on the tie line

4. (10pts) Answer the following questions.

(a) (5pts) Derive the following van't Hoff equation representing the response of the equilibria to temperature,

$$\frac{d\ln K}{d(1/T)} = -\frac{(\Delta H)_r^\circ}{R}$$

where $(\Delta H)_r^\circ$ is the standard reaction enthalpy. If the reaction is exothermic, reactants are favoured with increasing *T*. Explain the reason briefly.

(b) (5pts) What is the standard enthalpy of a reaction for which the equilibrium constant is doubled when the temperature is increased by 15 K at 310 K?

5. (10pts) Derive the following diffusion equation (Fick's second law of diffusion)

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

where *c* is the molar concentration, *t* is time, *D* is diffusion coefficient, and *x* is the coordinate along the direction of diffusion.

6. (15pts) Answer the following questions about the rates of chemical reactions.

(a) (6pts) Prove that integrated rate laws for the first-order and second-order reactions of the form A → P are given as the following, respectively. (6pts)

$$[A] = [A]_0 e^{-kt} \qquad \frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$(1^{st}\,order\,reactions) \qquad (2^{nd}\,order\,reactions)$$

Where [A] is the molar concentration of A after time *t*, $[A]_0$ is the initial molar concentration at $t = 0$, and *k* is the rate constant.

(b) (4pts) Derive the half-lives ($t_{1/2}$) of the first-order and second-order reactions, respectively.

(c) (5pts) Using the Arrhenius equation, plot the ln *k* versus $1/T$ for a positive activation energy E_a. Also explain the condition that the rate constant *k* of a chemical reaction decreases as the temperature is raised.