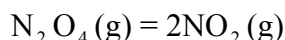**20.110/5.60/2.772 Fall 2005**
Homework #4
Due Friday October 14

1. Consider the dissociation of N_2O_4 (g) into NO_2 (g) described by

$$N_2O_4 (g) = 2NO_2 (g)$$

Assuming that we start with n_0 moles of N_2O_4 (g) and no NO_2 (g), show that the extent of reaction, ξ_{eq}, at equilibrium is given by

$$\frac{\xi_{eq}}{n_0} = \left(\frac{K_p}{K_p + 4p} \right)^{1/2}$$

Plot ξ_{eq}/n_0 against p given that $K_p = 6.1$ at 100° C. Is your result in accord with Le Châtelier's principle?

2. In Problem 1 you plotted the extent of reaction at equilibrium against the total pressure for the dissociation of N_2O_4 (g) to NO_2 (g). You found that ξ_{eq} decreases as p increases, in accord with Le Châtelier's principle. Now let's introduce n_{inert} moles of an inert gas into the system. Assuming that we start with n_0 moles of N_2O_4 (g) and no NO_2 (g), derive an expression for ξ_{eq}/n_0 in terms of p and the ratio $r = n_{inert}/n_0$. Let $K_P = 6.1$ and plot ξ_{eq}/n_0 verses p for $r = 0$, $r = 0.50$, $r = 1.0$, and $r = 2.0$. Show that introducing an inert gas into the reaction mixture at constant pressure has the same effect as lowering the pressure. What is the effect of introducing an inert gas into a reaction system at constant volume (your answer should be qualitative, no need for a calculation)?

3. The value of $K_P = 34.8$ at 1000° C for the decomposition of carbonyl dichloride (phosgene) according to

$$COCl_2 (g) = CO(g) + Cl_2 (g)$$

if the standard state is taken to be one bar. What would the value of K_P be if for some reason the standard state were taken to be 0.500 bar? What does this result say about the numerical values of equilibrium constants?

4. Use the Gibbs free energy of hydrolysis of ATP at 25 ˚C and 1 bar to answer the following questions. ATP hydrolysis proceeds according to

$$ATP + H_2O = ADP + Phosphate.$$

(a) Calculate the ΔG for the reaction when $[ATP] = 10^{-2}$ M and $[ADP] = 10^{-4}$ M and $[phosphate] = 10^{-1}$ M (ΔG^0 for this reaction is -31 kJ/mol).

(b) Calculate the maximum available work under the conditions of part (a) when 1 mole of ATP is hydrolyzed.

(c) Calculate ΔG and the maximum available work if $[ATP] = 10^{-7}$ M, $[ADP] = 10^{-1}$ M and $[phosphate] = 2.5$ x 10^{-1} M.

(d) What is the equilibrium constant? What are the equilibrium concentrations for the conditions given in aprt (a)?

(e) The value of ΔH^0 for ATP hydrolysis is -71 kJ/mol. What is the equilibrium constant at 37 ˚C? At 42 ˚C? At the temperature of thermophilic bacteria (60 ˚C)?

5. It is often easier to measure the free energy difference between two processes than to measure absolute changes in each process. For example, in the case of protein folding, one can look at the difference in free energy ($\Delta\Delta G$) upon making a point mutation.

(a) Show that for a protein, the difference in free energy for the protein unfolding process upon making a single mutation is $-RT \ln K_{mut}/K_{wt}$. (where mut is the mutated protein and wt is the wild type protein). The reaction for protein unfolding is $P_{folded} = P_{unfolded}$.

(b) For coiled-coil protein GCN4, a researcher claimed that mutation of Lys-54 to His, results in a net stability of 10 kcal/mol in the folding reaction $GCN4_{folded} = GCN4_{unfolded}$ (i.e., the equilibrium is shifted towards the folded protein). Write the equilibrium constant for mutated GCN4 in terms of wild type GCN4.

6. Chemical Potential.

(a) Using $dG = VdP - SdT + \Sigma\mu_i dn_i$ show that

$$\left(\frac{\partial}{\partial n_i}\right)\left(\frac{\partial V}{\partial T}\right) = \left(\frac{\partial}{\partial T}\right)\left(\frac{\partial \mu_i}{\partial P}\right)$$

(b) Consider the following reaction:

$$NO(g) + CO(g) = CO_2(g) + \tfrac{1}{2} N_2(g)$$
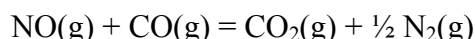
Calculate ΔG^0 and K at 25 ˚C at 1 bar assuming the Gibbs free energy of formation of NO is 86.7 kJ/mol, that of CO_2 is -394 kJ/mol and that of CO is -137 kJ/mol. (All values given for standard state reactions). Is the reaction favored to the right or the left?

7. In class we showed that $\left(\dfrac{\partial \ln K}{\partial T}\right)_P = \dfrac{\Delta H^0}{RT^2}$ (van't Hoff's Equation):

(a) Sow that this equation can be re-written as:

$$\left(\frac{\partial \ln K}{\partial (1/T)}\right)_P = \frac{-\Delta H^0}{R}$$

(b) Consider the following reaction:

$$N_2 + O_2 = 2NO$$
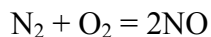
Estimate the partial pressure of NO in equilibrium with 0.8 bar N_2 and 0.2 bar O_2 at 25 °C and at 1000 °C. Assume that ΔH^0 is independent of temperature. The enthalpy of formation of NO is 90.35 kJ/mole and the Gibbs free energy of formation is 86.7 kJ/mole.

8. Consider the dissociation reaction of I_2 (g) described by

$$I_2(g) = 2I(g)$$
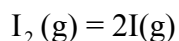
The total pressure and the partial pressure of I_2 (g) at 1400° C have been measured to be 36.0 torr and 28.1 torr, respectively. Use these data to calculate K_P (one bar standard state) and K_P (one mole • L^{-1} standard state) at 1400° C.