CHM 2046
HOMEWORK SET 1

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OFFICE HOURS: **ANNOUNCED IN CLASS AND POSTED ON OFFICE DOOR**

QUESTIONS ABOUT MEASURING REACTION RATES

1. Consider the following reaction; $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$. Express the rate of this reaction, separately, in terms of the change in concentration of each reactant and the product. Are these three rates equal to each other? Explain.

2. In the reaction of $2\,A + B \longrightarrow C + 3\,D$, reactant A was found to react at the rate of $2.8 \times 10^{-3}\ Ms^{-1}$.

   a) What is the rate of reaction of B?

   b) What is the rate of formation of D?

3. Consider the following reaction; $A(g) + 3\,B(g) \longrightarrow 2\,C(g) + 2\,D(g)$.
   Suppose that at some point in the reaction [A] = 0.9986 M and 15.00 minutes later [A] = 0.9689 M. What is the average rate of reaction of A during this time interval in Ms^{-1}? What is the average rate of reaction of B during this time interval in Ms^{-1}? What are the average rates of formation of C and D during this interval in Ms^{-1}?

4. Although rates may be determined by "following" the concentrations of any of the reactants or products, one of these is usually easier to monitor than the others and therefore the reaction (for practical reasons) is followed using this chemical. For each chemical reaction below determine in terms of which reagent would be easiest to measure the rate of the reaction and explain your reasoning.

   a) $C_2H_4(g) + Cl_2(g) \longrightarrow C_2H_4Cl_2(g)$

   b) $2\,H_2O_2(aq) \longrightarrow 2\,H_2O(\ell) + O_2(g)$

   c) $2\,H_2(g) + 2\,NO(g) \longrightarrow N_2(g) + 2\,H_2O(g)$

   d) $ClCH_2CH_2OH(aq) + OH^-(aq) \longrightarrow HOCH_2CH_2OH(aq) + Cl^-(aq)$

QUESTIONS ABOUT THE FACTORS THAT AFFECT REACTION RATES

5. Why cannot the reaction rate be calculated from the collision frequency alone?

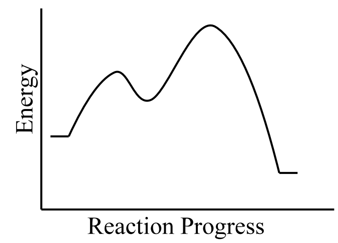
6. Increasing the pressure cause an increase in the reaction rates for gas phase reactions. Explain how the pressure increase cause the rate to increase.

7. How would an increase in temperature affect the rate of reaction? Explain the two factors involved.

8. The first step in the reaction of H_2 and I_2 involves the dissociation of I_2. I.e., $I_2 \longrightarrow 2\ I$.
   a) What would be the effect of replacing the I_2 with Br_2 on the rate of this reaction. Explain.
   b) What would be the effect of replacing the I_2 with N_2 on the rate of this reaction. Explain.

9. How does a catalyst change the reaction rate?

10. Consider the following potential energy diagram.



   a) How many elementary step are in the reaction mechanism?
   b) Which step is rate limiting?
   c) Is the overall reaction exothermic or endothermic?
   What about the first step? What about the second step?
   d) Locate on the graph the reactants, the reaction intermediates, the activated complexes, and the reaction products.

11. For the reversible reaction $A + B \rightleftharpoons C + D$, the enthalpy change of the forward reaction is +21 kJ/mol. The activation energy is 84 kJ/mol.
   a) Draw the potential energy diagram for this reaction.
   b) What is the activation energy for the reverse reaction?

12. Iodide ion (I^-) reacts with the peroxodisulfate ion ($S_2O_8^{-2}$) to form the sulfate ion (SO_4^{-2}) and the triiodide ion (I_3^-) by the following reaction.

   $$3\ I^- + S_2O_8^{-2} \longrightarrow 2\ SO_4^{-2} + I_3^-.$$

   The following rate data was collected for this reaction.

Expt	INITIAL CONCENTRATIONS, M $[S_2O_8^{-2}]$	$[I^-]$	INITIAL RATE OF REACTION $M \cdot s^{-1}$
1	$[S_2O_8^{-2}]_1 = 0.038$	$[I^-]_1 = 0.060$	$R_1 = 1.4 \times 10^{-5}$
2	$[S_2O_8^{-2}]_2 = 0.076$	$[I^-]_2 = 0.060$	$R_2 = 2.8 \times 10^{-5}$
3	$[S_2O_8^{-2}]_3 = 0.060$	$[I^-]_3 = 0.120$	$R_3 = 4.4 \times 10^{-5}$

   a) Use the data above to determine the order of the reaction with respect to I^- and $S_2O_8^{-2}$ as well as the overall order of the reaction.

   b) Determine the value of the rate constant for this reaction.

   c) What is the rate law for this reaction?

13. The following mechanism has been proposed for the peroxodisulfate - iodide ion reaction. The first step is slow and the others are fast.

$$I^- + S_2O_8^{-2} \longrightarrow IS_2O_8^{-3}$$

$$IS_2O_8^{-3} \longrightarrow 2\ SO_4^{-2} + I^+$$

$$I^+ + I^- \longrightarrow I_2$$

$$I_2 + I^- \longrightarrow I_3^-$$

Show that this mechanism is consistent with both the stoichiometry and the rate law. Explain why step one might be expected to be slower than the other steps.

14. For the reaction of NO and O_2 to give NO_2 the following rate data was obtained.

	INITIAL CONCENTRATIONS, M		INITIAL RATE OF REACTION
Expt	$[O_2]$	[NO]	$M{\bullet}s^{-1}$
1	$[O_2]_1 = 0.0110$	$[NO]_1 = 0.0130$	$R_1 = 3.20 \times 10^{-3}$
2	$[O_2]_2 = 0.0220$	$[NO]_2 = 0.0130$	$R_2 = 6.40 \times 10^{-3}$
3	$[O_2]_3 = 0.0110$	$[NO]_3 = 0.0260$	$R_3 = 1.28 \times 10^{-2}$

a) Determine the rate law for this reaction including the value of the rate constant.

b) Is this reaction likely to take place in a single step? Explain.

c) Is bond breaking likely to be the first step? Explain.

d) Propose then, a likely first step for this process which involves an fast equilibrium.

e) Is this first step endo or exothermic? Explain.

f) What then is the second step?

g) If the overall process is endothermic, what must the second step be, endo or exothermic? Explain.

h) Draw a potential energy diagram for this reaction.

15. In the following reaction: $OCl^- + I^- \longrightarrow OI^- + Cl^-$; one finds that the hydroxide ion is *involved* in the mechanism but is not consumed in the overall reaction.

The following rate data were obtained for this reaction.

	INITIAL CONCENTRATIONS, M			INITIAL RATE OF REACTION
Expt	$[OCl^-]$	$[I^-]$	$[OH^-]$	$M \bullet s^{-1}$
1	0.0040	0.0020	1.00	$R_1 = 4.8 \times 10^{-4}$
2	0.0020	0.0040	1.00	$R_2 = 5.0 \times 10^{-4}$
3	0.0020	0.0020	1.00	$R_3 = 2.4 \times 10^{-4}$
4	0.0020	0.0020	0.50	$R_4 = 4.6 \times 10^{-4}$
5	0.0020	0.0020	0.25	$R_5 = 9.6 \times 10^{-4}$

a) From the data given, determine the order of the reaction with respect to OCl^-, I^-, and OH^- as well as the over all order?

b) Write the rate equation for this reaction and determine the value of the rate constant.

c) Show that the following mechanism is consistent with the rate law determined in part a).

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad \text{(FAST)}$$
$$I^- + HOCl \longrightarrow HOI + Cl^- \quad \text{(SLOW)}$$
$$HOI + OH^- \longrightarrow OI^- + H_2O \quad \text{(FAST)}$$

d) The following equilibrium is present in any aqueous solution.

$$OH^- + H_3O^+ \rightleftharpoons 2\,H_2O \quad \text{(FAST)}$$

If this equilibrium is used as the first step, the mechanism would look like

$$OH^- + H_3O^+ \rightleftharpoons 2\,H_2O \quad \text{(FAST)}$$
$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad \text{(FAST)}$$
$$I^- + HOCl \longrightarrow HOI + Cl^- \quad \text{(SLOW)}$$
$$HOI + OH^- \longrightarrow OI^- + H_2O \quad \text{(FAST)}$$

What would the rate expression be for this mechanism now?

e) It should be evident from your rate expression in part c) as well as from the original data that increasing the $[OH^-]$ will result in the slowing of the reaction rate. What is the effect of increasing the $[H_3O^+]$ on the rate of this reaction?

f) Are these observations above similar to what you observed in lab in the bleach/dye kinetics experiment? What does that suggest as the mechanism for the bleach/dye reaction?

QUESTIONS ABOUT EQUILIBRIUM CONSTANTS EXPRESSIONS

16. Write the equilibrium constant expression in terms of concentrations for the following equilibria.

    a) $Sb_2S_3\ (s)\ +\ 3\ H_2\ (g) \rightleftharpoons 2\ Sb\ (s)\ +\ 3\ H_2S\ (g)$

    b) $SO_2Cl_2\ (g) \rightleftharpoons SO_2\ (g)\ +\ Cl_2\ (g)$

    c) $CaCO_3\ (s) \rightleftharpoons CaO\ (s)\ +\ CO_2\ (g)$

17. Based on the descriptions, write a balanced equation and the equilibrium constant expression, K_c , for the following equilibria.

    a) Hydrogen gas reacts with gaseous iodine to form gaseous hydrogen iodide.

    b) Potassium superoxide, KO_2 (s), reacts with gaseous carbon dioxide to form oxygen gas and solid potassium carbonate.

    c) Peroxodisulfate ions ($S_2O_8^{-2}$), oxidized triiodide ions (I_3^-) to iodine solid and sulfate ions in aqueous solution.

18. Based on the descriptions, write a balanced equation and the equilibrium constant expression, K_p , for the following equilibria.

    a) Carbonyl fluoride, COF_2 (g), decomposes into carbon dioxide gas and gaseous carbon tetrafluoride.

    b) Carbonyl chloride (also called phosgene), $COCl_2$ (g), decomposes into carbon monoxide gas and chlorine gas.

    c) Iron metal reacts with steam to produce iron(III) oxide and hydrogen gas.

19. a) For the reaction depicted in 17a) above K_c equals 50.2 at 445 °C. Calculate K_p for this reaction at 445 °C.

    b) For the reaction depicted in 17b) above K_p equals 28.5 atm at 25 °C. Calculate K_c for this reaction at 25 °C.

    c) For the reaction depicted in 18a) above K_c equals 2.00 at 1000 °C. Calculate K_p for this reaction at 1000 °C.

    d) For the reaction depicted in 18b) above K_p equals 22.5 atm at 668 °C. Calculate K_c for this reaction at 668 °C.

20. In the equilibrium $H_2\ (g)\ +\ I_2\ (g) \rightleftharpoons 2\ HI\ (g)$, an initial mixture contains 2 mol of H_2 and 1 mol I_2. Which of the following is the amount of HI expected at equilibrium?

    a) 1 mol   b) 2 mol   c) more than 2 but less than 4 mol   d) less than 2 mol

QUESTIONS ABOUT EVALUATING THE EQUILIBRIUM CONSTANT

21. For the equilibrium, $CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$,

    an equilibrium mixture contains 0.276 mol H_2, 0.276 mol CO_2, 0.224 mol CO, and 0.224 mol H_2O.

    a) Show that for this reaction K_c is independent of the container volume, V.

    b) Determine the value of K_c and K_p

22. The compounds PCl_3 and PCl_5 coexist in equilibrium through the reaction

    $PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$

    At 250 °C, an equilibrium mixture in a 2.50 L flask contains 0.105 g PCl_5 (g), 0.220 g PCl_3 (g), and 2.12 g Cl_2 (g). What are the values of K_c and K_p for this reaction at 250 °C?

23. The following questions are mainly math problems but they do illustrate important relationships between various equilibrium constants.

    K_c is equal to 23.2 at 600 K for the following equilibrium

    $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g) \qquad K_c = 23.2$ at 600 K

    What are the values of the equilibrium constants for the following reactions at 600 K?

    a) $CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$

    b) $2\ CO\ (g) + 2\ H_2O\ (g) \rightleftharpoons 2\ CO_2\ (g) + 2\ H_2\ (g)$

    c) $\frac{1}{2}\ CO\ (g) + \frac{1}{2}\ H_2O\ (g) \rightleftharpoons \frac{1}{2}\ CO_2\ (g) + \frac{1}{2}\ H_2\ (g)$

24. Determine the value of K_c for the following equilibrium

    $\frac{1}{2}\ N_2\ (g) + \frac{1}{2}\ O_2\ (g) + \frac{1}{2}\ Br_2\ (g) \rightleftharpoons NOBr\ (g)$

    from the following information at 25 °C.

    $2\ NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g) \qquad K_c = 2.4 \times 10^{30}$

    $NO\ (g) + \frac{1}{2}\ Br_2 \rightleftharpoons NOBr\ (g) \qquad K_c = 1.4$

SIMPLE CALCULATIONS INVOLVING THE EQUILIBRIUM CONSTANT

25. Consider the following information

$$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g) \qquad K_c = 4.61 \times 10^{-3}\ M$$

If the equilibrium concentration of N_2O_4 = 0.0277 M, what is the equilibrium concentration of NO_2?

26. Phosphorus forms two compounds with chlorine which are in equilibrium at 500 K according to the following equation

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

When 0.0820 moles of PCl_5 are introduced into a 1.00 L bulb at 500 K and it is found that after equilibrium is reached that the concentration of PCl_5 is 0.0420 M.

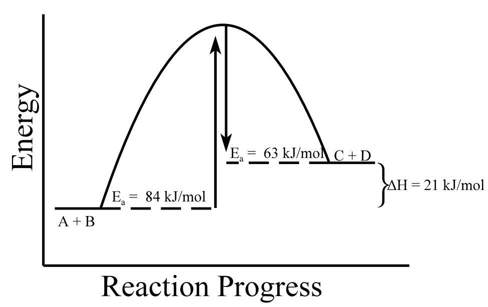
a) What are the equilibrium concentrations of PCl_3 and Cl_2?

b) What is the value of the equilibrium constant, K_c?

FACTORS THAT MAY AFFECT THE EQUILIBRIUM CONSTANT

27. Is K_{eq} very large or very small for a reaction which is highly exothermic?

28. Consider the following potential energy diagram



a) Are the reactants, A and B, or are the products, C and D more energetically stable? Explain.

b) What does that imply about the chemical bonding inside of A and B relative to those inside of C and D? Explain.

c) Does this graph represent a reaction in which K_{eq} is very small or very large? Explain.

d) If the bonding inside of C and D were stronger than those inside of A and B would the K_{eq} is very small or very large? Explain.

29. The halogens (F_2 , Cl_2 , Br_2 , and I_2) react with and reach equilibrium with hydrogen according to the following equation

$$H_2\,(g) + X_2\,(g) \rightleftharpoons 2\,HX\,(g) \qquad \text{where } X_2 \text{ is a halogen.}$$

In these reactions, the bond inside of the halogen must be broken as well as the bond holding H_2 together (we must avoid referring to this as the hydrogen bond since that has a different meaning!). Also 2 H-X bonds must be made during the reaction. With that in mind use the following data to predict the effect on the value of the equilibrium constant if the halogen , X_2 , is replaced first by I_2 then by Br_2 , Cl_2 and finally with F_2.

Bond Energies	Bond Energies
H_2 = 432 kJ/mol	
I_2 = 151 kJ/mol	HI = 295 kJ/mol
Br_2 = 193 kJ/mol	HBr = 363 kJ/mol
Cl_2 = 243 kJ/mol	HCl = 427 kJ/mol
F_2 = 159 kJ/mol	HF = 565 kJ/mol

SHIFTS IN THE EQUILIBRIUM POSITION

30. Le Châtelier's principle can be stated as "when a stress is applied to a chemical system which is in a state of equilibrium the system re-attains equilibrium by undergoing a net reaction that reduces the effect of the stress". Use this idea to explain

a) Why an increase in reactant concentration shifts the equilibrium position towards the right side but does not change the value of the equilibrium constant.

b) Why a decrease in volume shifts the equilibrium position towards the side with fewer moles of gas but does not change the value of the equilibrium constant.

c) Why an increase in temperature shifts the equilibrium position of an exothermic reaction towards the left side and decreases the value of the equilibrium constant.

31. Consider the following equilibrium which is present in the gas referred to as nitrogen dioxide (Note I said "referred" to as nitrogen dioxide since the sample is obviously a <u>mixture</u>!)

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

a) Is this reaction expected to be endo or exothermic? Explain your reasoning.

b) Is the value of K_{eq} expected to be large or small? Explain.

c) If K_p = 8.87 atm^{-1} at 25 °C, what is the pressure of N_2O_4 gas which is in equilibrium with 1.00 atm of NO_2 gas at 25 °C. Which gas is actually present in larger amount?

d) Do you find it curious that the sample is referred to as nitrogen dioxide? What is a more appropriate name for the sample if one "had" to name it?

32. Re-consider the equilibrium discussed in problem 31. If a **rigid** container is pressurized with 1.0 atm of pure NO_2 at 25°C, what would be the equilibrium pressures of each gas?

33. Re-consider the equilibrium discussed in problem 31. If a **flexible** container (such as a balloon) is pressurized with 1.0 atm of pure NO_2 at 25°C, what would be the equilibrium pressures of each gas?