Chem 260 – Third Exam

On the following pages are seven problems covering material in equilibrium chemistry and kinetics. Read each problem carefully and think about how best to approach the problem before you begin work. If you aren't sure how to begin a problem, then move on; working on a new problem may stimulate an idea that helps you solve the more troublesome one. For problems requiring a written response, be sure that your answer directly and clearly answers the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

Problem 1 _____/16	Problem 5 _____/12
Problem 2 _____/16	Problem 6 _____/12
Problem 3 _____/12	Problem 7 _____/16
Problem 4 _____/16	Total _____/100

A few constants are given here:

$d_{H_2O} = 1.00$ g/mL $\qquad S_{H_2O} = 4.184$ J/g·^oC

$R = 8.314$ J/mol$_{rxn}$·K $\qquad F = 96{,}485$ J/V·mol e^-

$$K_w = 1.00\times10^{-14}$$

Problem 1. The sulfide ion, S^{2-}, forms insoluble compounds with many metal ions. Given that the solubility product for Ag_2S is 1.6×10^{-49} and that for Bi_2S_3 is 1.1×10^{-73}, which compound will have the smallest molar solubility and which will have the smallest mass solubility? Place your answers in the appropriate blanks and provide your work and/or a one to three sentence explanation in the space below.

The compound with the smallest molar solubility is _____ with a value of _____. The compound with the smallest mass solubility is _____ and its value is _____.

Problem 2. The ligand EDTA, which forms strong complexes with many metal ions, is often used to keep a metal ion in solution under conditions in which it might otherwise precipitate. Suppose you add 0.010 moles of $Pb(NO_3)_2$ and 0.050 moles of Na_4EDTA to a 1-L volumetric flask and dilute to volume with a pH 13.00 buffer. Will a precipitate of $Pb(OH)_2$ form? The solubility product for $Pb(OH)_2$ is 1.2×10^{-15} and the formation constant for $Pb(EDTA)^{2-}$ is 1.1×10^{18}. Circle your answer and provide your work and a one sentence explanation for your choice of an answer in the space below.

A precipitate will form. A precipitate will not form.

Problem 3. The rate law for the reaction of methylacetate, CH_3COOCH_3, with water is known to be $R = k[CH_3COOCH_3][H_3O^+]$. For each of the following actions, will the reaction's rate constant increase, decrease or remain the same. Place an X in the appropriate box and explain your choice in one sentence.

action	increase	decrease	remain the same	explanation
increase the pH of the system				
shake the reaction mixture during reaction				
increase the temperature				

Problem 4. The oxidation of NO to NO_2 is an important reaction in the atmosphere. A study of the reaction's kinetics gives the following results:

Trial	[NO], M	$[O_2]$, M	Initial Rate (M/s)
1	4.5×10^{-2}	2.2×10^{-2}	8.00×10^{-3}
2	4.5×10^{-2}	4.5×10^{-2}	1.60×10^{-2}
3	9.0×10^{-2}	9.0×10^{-2}	0.128

What is the rate law and the rate constant for this reaction; limit yourself to any one trial when determining the rate constant. Place your answers in the appropriate blanks and provide your work in the space below.

The rate law is Rate = _____ with a rate constant of _____.

Problem 5. In the presence of a tungsten catalyst and at an elevated temperature, the decomposition of NH_3 to N_2 and H_2 occurs at a constant rate, with a rate constant of $3.7\times10^{-6}\ M^{-1}\ s^{-1}$. How long will it take for 99.9% of the NH_3 in a reaction vessel to undergo decomposition? Put your answer in the appropriate blank and provide your work in the space below.

It will take _____ seconds for 99.9% of the NH_3 to react.

Problem 6. Another important atmospheric reaction is the formation of CCl_4 from chloroform and chlorine

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

The following mechanism has been proposed for this reaction

$$Cl_2(g) \leftrightarrows 2Cl(g)$$
$$Cl(g) + CHCl_3(g) \rightarrow HCl(g) + CCl_3(g)$$
$$CCl_3(g) + Cl(g) \rightarrow CCl_4(g)$$

in which the second step is rate-determining with a rate constant of k_2. What is the rate law for the overall reaction? You may assume that the first step is at equilibrium with an equilibrium constant of K_{eq}. Write your rate law in terms of an observed rate constant, k_{obs}, and indicate how k_{obs} is related to k_2 and K_{eq}. Place your answers in the appropriate blanks and provide your work below. Your work must be logical and easy to follow!

The rate law is Rate = _____ with k_{obs} = _____.

Problem 7. Shown below are three graphs of kinetic data from a study of the reaction

$$A + B \rightarrow C$$

The first panel shows the original data as plots of [A] vs. time and [B] vs. time. The remaining two panels show transformations of this data. When studying the change in concentration of A, $[B]_o$ was set at 0.30 M, and when studying the change in [B] the initial concentration of A was set to 0.3 M. Using this data determine the reaction's rate law and rate constant. Place your answer in the appropriate blanks and provide your work in the space below.

The rate law is Rate = _____ and the rate constant is k = _____.