Chem 260 – Third Exam

On the following pages are six 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 _____/15	Problem 4 _____/15
Problem 2 _____/19	Problem 5 _____/17
Problem 3 _____/17	Problem 6 _____/17

Total_____

A few constants are given here:

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

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

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

Problem 1. Silver ion forms precipitates and complex ions with a variety of anions and ligands. Consider, for example, the following sequence of reactions:

a. adding NaCl to a solution of Ag^+ precipitates AgCl
b. adding NaI to a solution containing AgCl precipitates AgI
c. AgCl, but not AgBr, is soluble in 3 M NH_3
d. a solution of 3 M $Na_2S_2O_3$ will dissolve AgBr but not AgI

Based on these observations, which of the following solids has the smallest solubility product – AgBr, AgCl or AgI? Explain your reasoning in one or two sentences.

Based on these observations, which of the following complexes has the smallest overall formation constant – $Ag(NH_3)_2^+$ or $Ag(S_2O_3)_2^{3-}$? Explain your reasoning in one or two sentences.

Problem 2. As you saw in the pK_a lab, an equilibrium constant's value often depends on ionic strength. To calculate ionic strength one must know the concentrations of all ions in solution. This means that a solid's solubility reaction is a source of ionic strength that, in turn, affects its K_{sp}. Suppose you add 2.00 g of $AgNO_3$ and 3.00 g of K_2CrO_4 to a 50.00-mL volumetric flask, precipitating Ag_2CrO_4. How many grams of Ag_2CrO_4 will precipitate and what are the concentrations of the ions Ag^+, NO_3^-, K^+ and CrO_4^{2-} once equilibrium is established? The K_{sp} for Ag_2CrO_4 is 9.0×10^{-12}.

Problem 3. In a substitution reaction, one species, Y, replaces another species, X. The data on the last page of the exam show results for a kinetic study of the reaction

$$CH_3X + Y \rightarrow CH_3Y + X$$

where [R] is the concentration of CH_3X. The data in trial one (○) were obtained when $[Y]_o$ was 3.0 M and the data in trial two (Δ) when $[Y]_o$ was 4.5 M. What are the reaction orders for CH_3X and Y and the value of the rate constant (with units)? Show your work.

Problem 4. Many compounds undergo a dimerization reaction in which two molecules bind together. Isomers often dimerize at different rates, providing a means for studying the relationship between structure and chemical reactivity. For example, consider the two compounds A and B, which dimerize according to the reactions:

$$2A \rightarrow A_2 \qquad 2B \rightarrow B_2$$

The kinetics of both reactions are second order with, respectively, rate constants of k_A and k_B. When 1.22×10^{-2} moles of A were introduced into a 250.0 mL reaction flask, the concentration of A after 3.00 min was found to be 6.90×10^{-3} M. What is the value of the rate constant for this reaction (with units)?

Equimolar solutions of A and B are allowed to react, and after 3.00 min the concentration of B_2 is found to be less than that of A_2. What, if anything, can you conclude about the value of k_B? Explain your reasoning in one or two sentences.

Problem 5. In lab you studied the decomposition of hydrogen peroxide

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

As you observed, the rate of this thermodynamically favorable reaction is very slow unless a catalyst is present. In the presence of the catalyst Fe^{2+}, the activation energy is 42.0 kJ/mol$_{rxn}$; without a catalyst the activation energy is 70.0 kJ/mol$_{rxn}$. How many times larger is the rate constant for the catalyzed reaction, k_{cat}, relative to that for the uncatalyzed reaction, k_{uncat}? Assume a temperature of 20^{o}C. If you need to make any assumptions, be sure to state them.

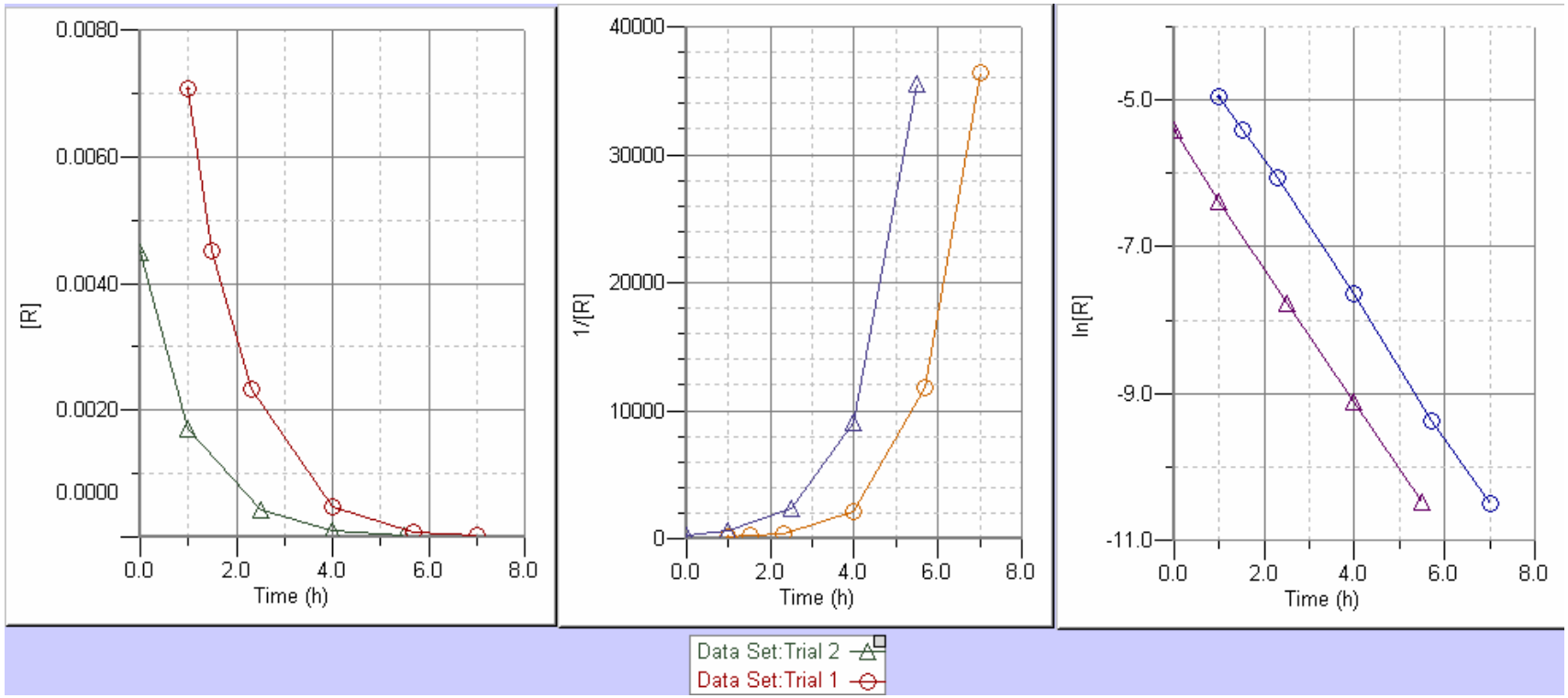
Problem 6. The concentration of ozone, O_3, in the atmosphere is important for many reasons (both good and bad). One of ozone's many reactions is its decomposition to O_2

$$2O_3 \rightarrow 3O_2$$

Shown below are two proposed mechanisms for this reaction:

Mechanism I	Mechanism II
$2O_3 \rightarrow 3O_2$	$O_3 \leftrightarrows O_2 + O$
	$O_3 + O \rightarrow 2O_2$

Clearly explain how a kinetic study of this reaction could distinguish between these two mechanisms. Be sure to fully support your answer!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Time (h)
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Data Set:Trial 2
Data Set:Trial 1