

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:

$$d_{\text{H}_2\text{O}} = 1.00 \text{ g/mL}$$

$$S_{\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot^\circ\text{C}$$

$$R = 8.314 \text{ J/mol}_{\text{rxn}}\cdot\text{K}$$

$$F = 96,485 \text{ J/V}\cdot\text{mol e}^-$$

$$K_w = 1.00 \times 10^{-14}$$

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

- adding NaCl to a solution of Ag^+ precipitates AgCl
- adding NaI to a solution containing AgCl precipitates AgI
- AgCl, but not AgBr, is soluble in 3 M NH_3
- a solution of 3 M $\text{Na}_2\text{S}_2\text{O}_3$ 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.

AgI – Observation (b) shows us that Ag I is less soluble than AgCl. Observation (d) shows us that AgI is less soluble than AgBr. Thus, AgI has the smaller solubility product.

Based on these observations, which of the following complexes has the smallest overall formation constant – $\text{Ag}(\text{NH}_3)_2^+$ or $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$? Explain your reasoning in one or two sentences.

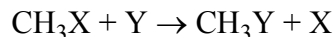
$\text{Ag}(\text{NH}_3)_2^+$ - Observations (c) and (d) show us that $\text{S}_2\text{O}_3^{2-}$ can dissolve AgBr but NH_3 cannot; thus, $\text{S}_2\text{O}_3^{2-}$ must form the stronger complex with Ag^+ and, therefore, has the larger overall formation constant.

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} .

Diluting 2.00 g of AgNO_3 (169.9 g/mol) to 50.00 mL gives a 0.235 M solution of AgNO_3 and diluting 3.00 g K_2CrO_4 (194.2 g/mol) to 50.00 mL gives a 0.309 M solution of K_2CrO_4 . Since neither NO_3^- nor K^+ have any chemistry here, their concentrations are 0.235 M and 0.618 M, respectively.

The precipitation reaction for Ag_2CrO_4 is $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4$. The limiting reagent is Ag^+ ; thus, 1.95 g of Ag_2CrO_4 (331.7 g/mole) are produced, with final concentrations for Ag^+ and CrO_4^{2-} of 0 M and 0.191 M, respectively. To find the equilibrium concentrations of Ag^+ and CrO_4^{2-} use an ICE table with the K_{sp} reaction $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$. Solving gives the equilibrium concentrations for Ag^+ and CrO_4^{2-} as 6.86×10^{-6} M and 0.191 M, respectively.

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



where [R] is the concentration of CH_3X . The data in trial one (\circ) were obtained when $[\text{Y}]_0$ was 3.0 M and the data in trial two (Δ) when $[\text{Y}]_0$ 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.

The reaction is studied using pseudo-order conditions; thus the rate law can be written as $\text{Rate} = k_{\text{obs}}[\text{CH}_3\text{X}]^\alpha$ with $k_{\text{obs}} = k[\text{Y}]^\beta$. Because a plot of $\ln[\text{CH}_3\text{X}]$ vs. t is linear, we know that α is 1. Changing the $[\text{Y}]$ has no effect on k_{obs} (slope of $\ln[\text{CH}_3\text{X}]$ vs. t remains unchanged); thus, we know that β is 0. The rate law, therefore, is $\text{Rate} = k[\text{CH}_3\text{X}]$. To find the value for k you can estimate the slope the plot of $\ln[\text{CH}_3\text{X}]$ vs. t , estimate the half-life using the plot of $[\text{CH}_3\text{X}]$ vs. t , or use the equation $\ln[\text{CH}_3\text{X}]_t = \ln[\text{CH}_3\text{X}]_0 - kt$. All methods yield a rate constant of approximately 0.9 hr^{-1} .

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:



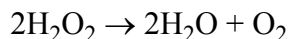
The kinetics of both reactions are second order with, respectively, rate constants of k_{A} and k_{B} . When 1.22×10^{-2} moles of A were introduced into a 250.0 mL reaction flask, the concentration of A after 3.00 min was found to be 6.90×10^{-3} M. What is the value of the rate constant for this reaction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

The initial concentration of A is 0.0488 M. For a second-order reaction, the integrated rate law is $[A]_t^{-1} = [A]_0^{-1} + kt$; thus, $(6.90 \times 10^{-3} \text{ M})^{-1} = (0.0488 \text{ M})^{-1} + k(3.00 \text{ min})$. Solving gives k as $41.48 \text{ M}^{-1} \text{ min}^{-1}$.

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.

Because $[\text{B}_2]$ is less than $[\text{A}_2]$ we know that the reaction $2\text{B} \rightarrow \text{B}_2$ must be slower than the reaction $2\text{A} \rightarrow \text{A}_2$; thus, k_{B} must be smaller than k_{A} .

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



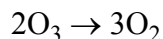
As you observed, the rate of this thermodynamically favorable reaction is very slow unless a catalyst is present. In the presence of the catalyst Fe^{2+} , the activation energy is $42.0 \text{ kJ/mol}_{\text{rxn}}$; without a catalyst the activation energy is $70.0 \text{ kJ/mol}_{\text{rxn}}$. How 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°C . If you need to make any assumptions, be sure to state them.

To solve we must assume that Z is unaffected by the presence of a catalyst and, therefore, has a constant value. Using the equation $k = Ze^{-E_a/RT}$ we arrive at

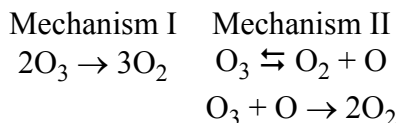
$$k_{\text{cat}}/k_{\text{uncat}} = e^{-(E_a)_{\text{cat}}/RT} / e^{-(E_a)_{\text{uncat}}/RT}$$

Taking $(E_a)_{\text{cat}}$ as 42000 J , $(E_a)_{\text{uncat}}$ as $70,000 \text{ J}$, R as $8.314 \text{ J/mol}_{\text{rxn}} \cdot \text{T}$ and T as 293 K gives the ratio $k_{\text{cat}}/k_{\text{uncat}}$ as $98,150$.

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



Shown below are two proposed mechanisms for this reaction:



Clearly explain how a kinetic study of this reaction could distinguish between these two mechanisms. Be sure to fully support your answer!

To distinguish between two mechanisms you must deduce their respective mechanisms. For mechanism I, which includes one step only, the rate law is $\text{Rate I} = k[\text{O}_3]^2$. In the case of mechanism II, if the second step is the RDS (as suggested by the arrows showing reaction direction), the rate law is $R = k[\text{O}_3][\text{O}]$. Taking the first step an equilibrium, we know that K_{eq} is $[\text{O}][\text{O}_2]/[\text{O}_3]$. Rearranging gives $[\text{O}] = K_{\text{eq}}[\text{O}_3]/[\text{O}_2]$. Substituting back gives the rate law for mechanism II as $\text{Rate II} = kK_{\text{eq}}[\text{O}_3]^2/[\text{O}_2]$. Both rate laws are second-order in O_3 , but mechanism II shows that the concentration of O_2 affects the rate. A kinetic experiment that varies the concentration of O_2 can determine which of the two mechanisms is plausible.

