Chem 260 – Third Exam

On the following pages are problems that cover material in equilibrium chemistry and kinetics. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer one question, then move on to another question; working on a new question may suggest an approach to that more troublesome question. If a question requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

Be sure to clearly state and verify any assumptions you make when solving an equilibrium problem.

Problem 1 _____/12	Problem 4 _____/12
Problem 2 _____/12	Problem 5 _____/12
Problem 3 _____/20	Problem 6 _____/12

Problem 7 _____/20

Total _____/100

A few constants and thermodynamics values are given here:

$d_{H_2O} = 1.00$ g/mL	$S_{H_2O} = 4.184$ J/g•°C
$R = 8.314$ J/mol$_{rxn}$•K	$F = 96{,}485$ J/V•mol e$^-$

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

Problem 1. Many metals are found in nature as insoluble phosphate salts. Because phosphate is a weak base, the solubility of a metal phosphate is pH-dependent. Given the following pK_a values for phosphoric acid, H_3PO_4

$$pK_{a,H_3PO_4} = 2.148 \qquad pK_{a,H_2PO_4^-} = 7.198 \qquad pK_{a,HPO_4^{2-}} = 12.319$$

and knowing that the solubility product for $FePO_4$ is 1.3×10^{-22}, write the reaction that controls the solubility of $FePO_4$ at a pH of 10.0 and report the reaction's equilibrium constant.

Problem 2. An analyst is asked to study the solubility of iron hydroxide and to report its molar solubility, S, and its solubility product, K_{sp}. The analyst prepares a saturated solution of iron hydroxide, filters the solution to remove the undissolved solid, and determines the concentration of iron in the supernatant, finding that its concentration is 2.17×10^{-10} M. The analyst reports the molar solubility and the K_{sp} values believing the precipitate is $Fe(OH)_2$ when it is, in fact, $Fe(OH)_3$. How will this error affect the reported molar solubility and K_{sp}? For each, circle the correct response and support your choice with either a written explanation of 2-4 sentences or a calculation.

The reported value for S is: too large too small correct there is insufficient information

The reported value K_{sp} is: too large too small correct there is insufficient information

Problem 3. In industrial chemistry, sometimes it is necessary to form a soluble metal-ligand complex to prevent a metal ion from precipitating under basic conditions. For example, ammonia is added to plating baths because the reaction

$$Zn^{2+}(aq) + 4NH_3(aq) \leftrightharpoons Zn(NH_3)_4^{2+} \qquad \beta_4 = 7.8 \times 10^8$$

prevents the precipitation of $Zn(OH)_2$. Suppose you mix 35.0 L of 0.0020 M Zn^{2+} with 15.0 L of 0.15 M NH_3. What percentage of the zinc remains uncomplexed at equilibrium?

Problem 4. Gaseous radon is sometimes found in the basements and crawlspaces of homes where it leaks out from the underlying bedrock. Radon is an environmental health hazard because one of its isotopes, ^{222}Ra, is radioactive with a first-order half-life of 3.82 days. Suppose a basement has 5.61×10^{12} atoms of ^{222}Ra when it is properly sealed to prevent further contamination. How many days will it take before there are fewer than 561 atoms of ^{222}Ra remaining in the basement?

Problem 5. Consider the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$, which is first order in H_2 and in I_2. Predict the effect of the following actions on the reaction's rate. For each, circle the correct response and provide an explanation in 1-3 sentences.

if you increase the temperature, the rate: increases decreases stays the same

if you increase the container's volume, the rate: increases decreases stays the same

if you add a catalyst, the rate: increases decreases stays the same

if you add an inert gas, such as Ar, the rate: increases decreases stays the same

Problem 6. As we saw in class, in the initial rate method for determining a reaction's rate law we design pairs of experiments in which we change the concentration of one species while holding constant the concentrations of all other species, and then observe the effect on the reaction's rate. Although many reactions follow simple kinetics where each species has a reaction order of 0, 1, or 2, there are reactions where a species' reaction order is fractional and/or negative.

(a) Predict what will happen to a reaction's rate if you double the concentration of a species that has a reaction order of 3/2.

(b) Predict what will happen to a reaction's rate if you double the concentration of a species that has a reaction order of –2.

Problem 7. One method for synthesizing metal-ligand complexes is to displace one ligand with another ligand. For example, the synthesis of $[Co(NH_3)_5Cl]^{2+}$ is shown here

$$[Co(NH_3)_5H_2O]^{3+}(aq) + Cl^{-}(aq) \leftrightarrows [Co(NH_3)_5Cl]^{2+}(aq) + H_2O(l)$$

The reaction's mechanism is known to occur in two steps, the first of which is

$$[Co(NH_3)_5H_2O]^{3+}(aq) \leftrightarrows [Co(NH_3)_5]^{2+}(aq) + H_2O(l)$$

(a) What is the mechanism's second step? In one sentence, explain how you arrived at your answer.

(b) Suppose the rate of the second step is slower than the rate of the first step and that the first step is in equilibrium. If you study the reaction in lab, what is the expected overall rate law and what terms make up the observed rate constant? Be sure to justify clearly how you arrived at your answer.

(c) Because the absorbance spectra for $[Co(NH_3)_5H_2O]^{2+}$ and for $[Co(NH_3)_5Cl]^{2+}$ are different, we can study the reaction's kinetics by monitoring the concentration of $[Co(NH_3)_5H_2O]^{2+}$ as a function of time at a wavelength where only $[Co(NH_3)_5H_2O]^{2+}$ absorbs. With this in mind, explain how you would complete a kinetic analysis for the reaction

$$[Co(NH_3)_5H_2O]^{2+}(aq) + Cl^{-}(aq) \leftrightarrows [Co(NH_3)_5Cl]^{2+}(aq) + H_2O(l)$$

to determine its rate law, including the reaction orders with respect to $[Co(NH_3)_5H_2O]^{2+}$ and Cl^{-}, and the observed rate constant. The strongest answers will include sketches of typical results that are consistent with your rate law from part (b) above and written in complete sentences. In the context of this question, it does not matter if your answer to part (b) above is correct; what matters is that your response is consistent with your answer to part (b) above. Use the space below to outline the points you wish to make and then use the other side of this page to write your response.