Chem 260 – Third Exam Key

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:

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

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

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

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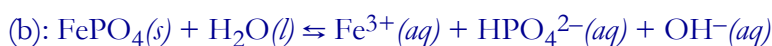
$$pK_{a,H_3PO_4} = 2.148 \qquad pK_{a,H_2PO_4^-} = 7.198 \qquad pK_{a,HPO_4^{2-}} = 12.319$$

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.

At a pH of 10.0, HPO_4^{2-} is the only important form of phosphate in solution; thus, the solubility reaction must show HPO_4^{2-} as the product instead of PO_4^{3-}. We can write two different reactions

(a): $FePO_4(s) + H_3O^+(aq) \leftrightharpoons Fe^{3+}(aq) + HPO_4^{2-}(aq) + H_2O(l)$

(b): $FePO_4(s) + H_2O(l) \leftrightharpoons Fe^{3+}(aq) + HPO_4^{2-}(aq) + OH^-(aq)$

Reaction (a) is the sum of the K_{sp} reaction for $FePO_4$ and the reverse of the K_a reaction for HPO_4^{2-}

$$FePO_4(s) \leftrightharpoons Fe^{3+}(aq) + PO_4^{3-}(aq) \qquad HPO_4^{2-}(aq) + H_2O(l) \leftrightharpoons PO_4^{3-}(aq) + H_3O^+(aq)$$

which gives $K = K_{sp}/K_{a3} = 1.3 \times 10^{-22}/4.80 \times 10^{-13} = 2.71 \times 10^{-10}$. Reaction (b) is the sum of the K_{sp} reaction for $FePO_4$ and the K_b reaction for PO_4^{3-}

$$FePO_4(s) \leftrightharpoons Fe^{3+}(aq) + PO_4^{3-}(aq) \qquad PO_4^{3-}(aq) + H_2O(l) \leftrightharpoons HPO_4^{2-}(aq) + OH^-(aq)$$

which gives $K = K_{sp}K_{b1} = K_{sp}K_w/K_{a3} = (1.3 \times 10^{-22})(1.00 \times 10^{-14})/4.80 \times 10^{-13} = 2.71 \times 10^{-24}$.

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

Given that the solubility reaction is $Fe(OH)_x(s) \leftrightharpoons Fe^{x+}(aq) + xOH^-(aq)$, where x is either 2 or 3, we know that the molar solubility of $Fe(OH)_x$ is equal to the $[Fe^{x+}]$ because each mole of $Fe(OH)_x$ yields one mole of dissolved Fe^{x+}; this is true whether x is 2 or 3. In this case, the error has no effect on what the analyst reports.

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

If the analyst assumes incorrectly that the solubility reaction is $Fe(OH)_2(s) \leftrightharpoons Fe^{2+}(aq) + 2OH^-(aq)$, then s/he reports the K_{sp} as $[Fe^{2+}][OH^-]^2 = [Fe^{2+}][2Fe^{2+}]^2 = 4[Fe^{2+}]^3 = 4.09 \times 10^{-29}$. The correct K_{sp} is $[Fe^{3+}][OH^-]^3 = [Fe^{3+}][3Fe^{3+}]^3 = 27[Fe^{3+}]^4 = 5.99 \times 10^{-38}$.

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

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

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?

The initial concentration of Zn^{2+} is 0.0020 M$\times$(35.0 L/50.0 L) = 0.00140 M, and the initial concentration of NH_3 is 0.15 M$\times$(15.0 L/50.0 L) = 0.0450 M. Setting up an ICE table, we let the reaction go to completion (because of the large value of β_2) and then let it move back to equilibrium; thus

	$Zn^{2+}(aq)$	+	$4NH_3(aq)$	$\rightleftharpoons$	$Zn(NH_3)_4^{2+}(aq)$
initial	0.0014		0.0450		0
change	−0.0014		−(4)(0.0014)		+0.0014
new initial	0		0.0394		0.0014
change	$+x$		$+4x$		$-x$
equilibrium	x		$0.0394 + 4x$		$0.0014 - x$

If we assume that $0.0394 + 4x \approx 0.0394$ and that $0.0014 - x \approx 0.0014$, then

$$\beta_2 = [Zn(NH_3)_4^{2+}]/\{[Zn^{2+}][NH_3]^4\} = (0.0014)/\{(x)(0.0394)^4\}$$

which gives x as 7.45×10^{-7}. The errors in the two assumptions are 0.0076% and 0.053%, respectively, so there is no need to iterate toward a more precise value for x. The percentage of Zn^{2+} that is uncomplexed is $100 \times (7.45 \times 10^{-7}/0.0014) = 0.053\%$.

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?

For first-order kinetics, we know that

$$\ln[^{222}Ra]_t = \ln[^{222}Ra]_0 - kt$$

where $[^{222}Ra]_t$ is 561 and $[^{222}Ra]_0$ is 5.61×10^{12}. To find the rate constant, k, we use the half-life and the relationship

$$k = 0.693/t_{1/2} = 0.693/3.82 \text{ d} = 0.1814 \text{ d}^{-1}$$

Substituting in

$$\ln(561) = \ln(5.61 \times 10^{12}) - (0.1814 \text{ d}^{-1})t$$

and solving for t gives its value as 127 days.

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.

Note: the factors that affect the reaction's rate are the rate constant, k, and the concentrations of H_2 and I_2; in turn, the rate constant depends on the activation energy and the temperature.

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

A higher temperature increases the kinetic energy of the molecules of H_2 and I_2, which means that more collisions will an energy greater than the reaction's activation energy.

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

The rate law is $R = k[H_2][I_2]$. Increasing the container's volume decreases the concentrations of H_2 and of I_2, which decreases the rate.

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

A catalyst decreases the reaction's activation energy and, therefore, increases the reaction's rate as a greater percentage of collisions will have an energy that exceeds the activation energy.

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

Adding an inert species does not affect the activation energy, the concentration of H_2 or I_2, or the energy of collisions between H_2 and I_2.

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.

If we double the concentration, then the rate increases by a factor of $2^{(3/2)}$ or 2.83.

(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.

If we double the concentration, then the rate decreases by a factor of 2^{-2} or 0.25.

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

$$[Co(NH_3)_5H_2O]^{3+}(aq) + Cl^-(aq) \rightleftharpoons [Co(NH_3)_5Cl]^{2+}(aq) + H_2O(l)$$
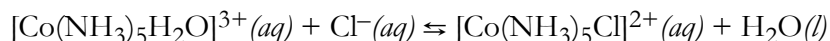
The reaction's mechanism is known to occur in two steps, the first of which is

$$[Co(NH_3)_5H_2O]^{3+}(aq) \rightleftharpoons [Co(NH_3)_5]^{3+}(aq) + H_2O(l)$$
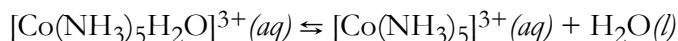
(a) What is the mechanism's second step? In one sentence, explain how you arrived at your answer.

The second step must be

$$[Co(NH_3)_5]^{3+}(aq) + Cl^-(aq) \rightarrow [Co(NH_3)_5Cl]^{2+}(aq)$$

as the sum of this reaction and the reaction for the mechanism's first step gives the overall reaction.

(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.

The rate law for the second step is

$$R = k_2[Co(NH_3)_5]^{3+}[Cl^-]$$

where k_2 is the rate constant for the second step. If the first step is in equilibrium, then we know

$$K = [Co(NH_3)_5]^{2+}/[Co(NH_3)_5H_2O]^{3+}$$

Solving for $[Co(NH_3)_5]^{3+}$

$$[Co(NH_3)_5]^{3+} = K[Co(NH_3)_5H_2O]^{3+}$$

and substituting back into the rate law gives the rate law as

$$R = k_2 K[Co(NH_3)_5H_2O]^{3+}[Cl^-] = k_{obs}[Co(NH_3)_5H_2O]^{3+}[Cl^-]$$

where k_{obs} is the product of k_2 and K.

(c) Because the absorbance spectra for $[Co(NH_3)_5H_2O]^{3+}$ and for $[Co(NH_3)_5Cl]^{2+}$ are different, we can study the reaction's kinetics by monitoring the concentration of $[Co(NH_3)_5H_2O]^{3+}$ as a function of time at a wavelength where only $[Co(NH_3)_5H_2O]^{3+}$ absorbs. With this in mind, explain how you would complete a kinetic analysis for the reaction

$$[Co(NH_3)_5H_2O]^{3+}(aq) + Cl^-(aq) \rightleftharpoons [Co(NH_3)_5Cl]^{2+}(aq) + H_2O(l)$$
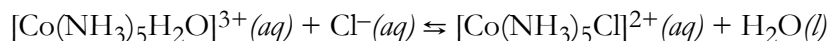
to determine its rate law, including the reaction orders with respect to $[Co(NH_3)_5H_2O]^{3+}$ and Cl^-, and the observed rate constant. The strongest answers will include sketches of typical results that are consistent with your rate law from part (b) above and written in complete sentences. In the 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.

Here are four key points you need to consider in designing your experiments. <u>First</u>, you are studying the kinetics of the system by following the change in concentration of $[Co(NH_3)_5H_2O]^{3+}$ as a function of time, which means all experiments must be run under pseudo-order conditions where

$$[Co(NH_3)_5H_2O]^{3+} \ll [Cl^-]$$

so that the rate law reduces to

$$R = k_{obs}[Co(NH_3)_5H_2O]^{3+}$$

where the observed rate constant is a function of the concentration of Cl^-

$$k_{obs} = k[Cl^-]$$

<u>Second</u>, every experiment you run will show first-order kinetics in $[Co(NH_3)_5H_2O]^{3+}$ as this is the only species that affects the reaction's rate. <u>Third</u>, to determine the effect of Cl^- on the reaction's rate, you will need to run the reaction for at least two different concentrations of Cl^- and observe its affect on k_{obs}. <u>Fourth</u>, you need to know that Beer's law applies and that there is a linear relationship between absorbance and concentration of $[Co(NH_3)_5H_2O]^{3+}$.

In terms of the data you will collect, here is a typical set of results. First, verify Beer's law by preparing several dilutions of a standard solution of $[Co(NH_3)_5H_2O]^{3+}$ and measure the absorbance of each; a straight-line plot of absorbance vs. concentration confirms Beer's law. Second, run a kinetic trial where the concentration of Cl^- is x. Follow the absorbance of $[Co(NH_3)_5H_2O]^{3+}$ as a function of time and then replot the data as ln(absorbance) vs. time, obtaining a straight-line consistent with first-order kinetics in $[Co(NH_3)_5H_2O]^{3+}$. The slope of this line is $(-k_{obs})_1$. Third, run a trial using the same concentration of $[Co(NH_3)_5H_2O]^{3+}$ but where the concentration of Cl^- is $2x$. Follow the absorbance of $[Co(NH_3)_5H_2O]^{3+}$ as a function of time and then replot the data as ln(absorbance) vs. time, obtaining a straight-line consistent with first-order kinetics in $[Co(NH_3)_5H_2O]^{3+}$. The slope of this line is $(-k_{obs})_2$ and it is $2\times(-k_{obs})_1$, consistent with first-order kinetics in Cl^-.