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 _____/14   Problem 5 _____/16

Problem 2 _____/10   Problem 6 _____/16

Problem 3 _____/16   Problem 7 _____/14

Problem 4 _____/14   Total _____/100

A few constants are given here:

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

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

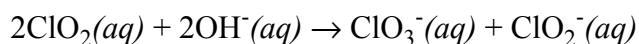$$K_w = 1.00\times10^{-14}$$

And a few additional equilibrium constants here:

$$\text{HF: } K_a = 7.2\times10^{-4}$$

$$\text{H}_3\text{PO}_4\text{: } K_{a1} = 7.1\times10^{-3} \quad K_{a2} = 6.3\times10^{-8} \quad K_{a3} = 4.2\times10^{-13}$$

Problem 1. Chlorine dioxide, ClO_2, is a reddish-yellow gas that is soluble in water. In basic solutions it reacts to form ClO_3^- and ClO_2^-

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq)$$

The following data were obtained in a study of this reaction's kinetics:

Trial	$[ClO_2]$, M	$[OH^-]$, M	Rate, M/s
1	0.060	0.030	2.48×10^{-2}
2	0.020	0.030	2.76×10^{-3}
3	0.020	0.090	8.28×10^{-3}

What will be the reaction's rate when the initial concentrations of ClO_2 and OH^- are 0.080 M and 0.110 M, respectively?

In going from Trial 2 to Trial 1 the $[ClO_2]$ increases by 3× and the rate increases by 9×; thus the rate order for ClO_2 is $3^\alpha = 9$, or an α of 2. In going from Trial 2 to Trial 3 the $[OH^-]$ increases by 3× and the rate increases by 3×; thus, the rate order for OH^- is $3^\beta = 3$, or a β of 1. The rate law, therefore, is Rate = $k[ClO_2]^2[OH^-]$. Substituting the rate and concentrations for any one trial gives the value of k as 229.6 M^{-2} s^{-1}. Finally, substituting in the provided concentrations into the rate law gives the rate as

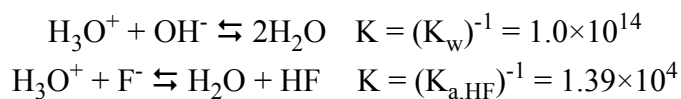$$\text{Rate} = (229.6 \ M^{-2} \ s^{-1}) \times (0.080 \ M)^2 \times (0.110 \ M) = 0.162 \ M/s$$

**Problem 2**. Tooth enamel consists mainly of $Ca_5(PO_4)_3OH$. Cavities are caused by the presence of acids; thus

$$Ca_5(PO_4)_3OH(s) + 4H_3O^+(aq) \leftrightarrows 5Ca^{2+}(aq) + 3HPO_4^{2-}(aq) + 5H_2O(l)$$

If fluoride is present, however, the $Ca_5(PO_4)_3OH$ is converted to $Ca_5(PO_4)_3F$, which is less soluble in acid. In one or two sentences, offer a suitable explanation for why $Ca_5(PO_4)_3F$ is less soluble than $Ca_5(PO_4)_3OH$.

The difference between the two compounds is the replacement of OH^- with F^-. The reaction of a strong base and a strong acid has a larger equilibrium constant than the corresponding reaction of a weak base with a strong acid

$$H_3O^+ + OH^- \leftrightarrows 2H_2O \quad K = (K_w)^{-1} = 1.0 \times 10^{14}$$
$$H_3O^+ + F^- \leftrightarrows H_2O + HF \quad K = (K_{a,HF})^{-1} = 1.39 \times 10^4$$

decreasing the ability of the strong acid to dissolve the compound.

Problem 3. Silver ion can be determined quantitatively by titrating with a standard solution of thiocyanate, the reaction for which is

$$Ag^+(aq) + SCN^-(aq) \leftrightarrows AgSCN(s)$$
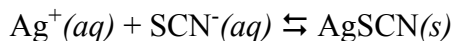
At the equivalence point for this titration, what is the equilibrium concentration of SCN^-? The K_{sp} for AgSCN is 1.0×10^{-12}.

At the equivalence point the Ag^+ and SCN^- have been reacted stoichiometrically. We can imagine, therefore, that the neither ion remains as they have combined to form AgSCN. The solid, of course, must exist in equilibrium with its ions and it must equilibrate to make equal concentrations of Ag^+ and SCN^-; thus

$$K_{sp} = [Ag^+][SCN^-] = [SCN^-]^2 = 1.0\times10^{-12} \qquad\qquad [SCN^-] = 1.0\times10^{-6}\ M$$

A solution of Fe^{3+} often is included in the titration described above because it forms the red-colored complex ion, $Fe(SCN)^{2+}$, with SCN^-. Knowing that K_1 for $Fe(SCN)^{2+}$ is 8.9×10^2 and that the smallest concentration of $Fe(SCN)^{2+}$ that can be seen visually is 6.5×10^{-6} M, what concentration of Fe^{3+} should be present if you are to be able to see the change in color at the equivalence point?

At the equivalence point we know the concentrations of SCN^- and $Fe(SCN)^{2+}$; thus

$$K_1 = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(6.5\times10^{-6})}{[Fe^{3+}](1.0\times10^{-6})} = 8.90\times10^2 \quad [Fe^{3+}] = 7.30\times10^{-3}\ M$$

An alternative approach for determining the amount of Ag^+ in a sample is to use a Ag electrode to measure the solution's potential during its titration with SCN^-. This potential is proportional to the concentration of Ag^+ remaining in solution. A plot of potential versus volume of titrant results in a titration curve similar to those that you have seen in lab. In a typical experiment a 25.00 mL portion of a

sample containing Ag^+ is placed in a beaker along with 15 mL of water and titrated with 0.0200 M KSCN yielding the titration curve shown here. What is the molarity of Ag^+ in the original sample?
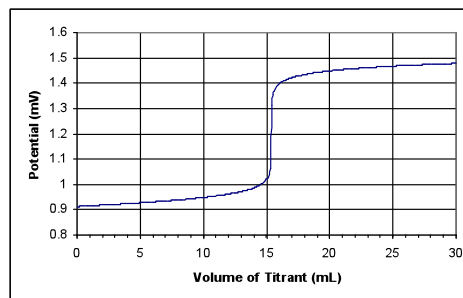
At the equivalence point we know that the moles of Ag^+ and SCN^- are equal:

$$M_{Ag} \times 25.0\ mL = M_{SCN} \times V_{SCN} = (0.0200\ M) \times (15.5\ mL) \qquad [Ag^+] = 0.0124\ M$$

Problem 4. A hundred years ago chemistry students at DePauw took a course in qualitative analysis in which they separated mixtures of ions by taking advantage of differences in their solubility chemistry. For example, Ca^{2+} and Ba^{2+} both form an insoluble precipitate with F^-, with K_{sp} values of 3.2×10^{-11} for CaF_2 and 1.5×10^{-6} for BaF_2. Suppose you had a solution containing 0.0438 M Ca^{2+} and 0.0375 M Ba^{2+}. If you add solid KF in small portions, will Ca^{2+} or Ba^{2+} be the first ion to precipitate from solution? Be sure to justify clearly your answer.

Because CaF_2 and BaF_2 have the same stoichiometry, we can make a decision by comparing the K_{sp} values. The concentrations of Ca^{2+} and Ba^{2+} are similar, but the K_{sp} for CaF_2 is smaller by more than 10^5; thus, Ca^{2+} will be the first ion to precipitate.

What is the equilibrium concentration of F^- when 99% of this cation has precipitated?

When 99% of the Ca^{2+} has precipitated, its concentration will be 0.01×0.0438 or 4.38×10^{-4} M. Substituting into the K_{sp} expression and solving for $[F^-]$ gives

$$K_{sp} = 3.2\times10^{-11} = [Ca^{2+}][F^-]^2 = (4.38\times10^{-4})[F^-]^2 \qquad [F^-] = 2.7\times10^{-4} \text{ M}$$

Given your answer to the previous question, will less than 1% of the other ion have precipitated? Be sure to support your answer with an appropriate calculation and/or explanation.

Knowing the concentration of F^- in the solution, we can calculate the value of Q_{sp} for BaF_2 and see if it has precipitated; thus

$$Q_{sp} = (Ba^{2+})(F^-)^2 = (0.0375) \times (2.7\times10^{-4})^2 = 2.73\times10^{-9}$$

This value is smaller than the K_{sp} for BaF_2, which means that BaF_2 has not yet formed. So, yes, less than 1% of the Ba^{2+} has precipitated.

Problem 5. For the chemical reaction

$$A + B \rightarrow C$$

the rate law can be expressed as

$$\text{Rate} = k[A]^{\alpha}[B]^{\beta}$$

The data in the following table were obtained for the reaction of a mixture containing 10.0 mM A and 1.0 M B. Determine the order of the rate law with respect to A and the value of the observed rate constant.

Time, sec	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
[A], mM	10.0	6.7	5.0	4.0	3.3	2.9	2.5	2.2	2.0	1.8	1.7	1.5	1.4	1.3	1.3	1.2

The first $t_{1/2}$ is 2 seconds from 10.0 mM to 5.0 mM and the second $t_{1/2}$ is 4 seconds from 5.0 mM to 2.5 mM; thus, the reaction must be second-order in A. The rate constant is

$$\frac{1}{[A]_t} = \frac{1}{5.0\ \text{mM}} = \frac{1}{[A]_o} - kt = \frac{1}{10.0\ \text{mM}} - k(2\ \text{sec}) \qquad k = 0.05\ \text{mM}^{-1}\ \text{s}^{-1}$$

Shown below are theoretical results for the reaction of 10.0 mM A with 1.0 M B, 2.0 M B and 6.0 M B. One of these figures represents a first-order dependence on B and one represents a second-order dependence on B. Identify B's reaction order for each figure and explain your choices.
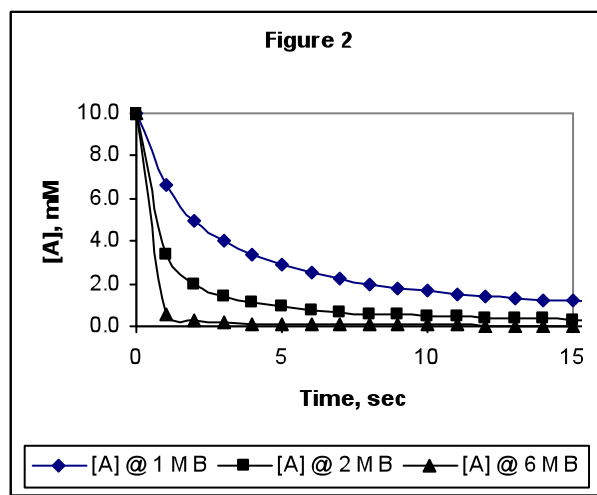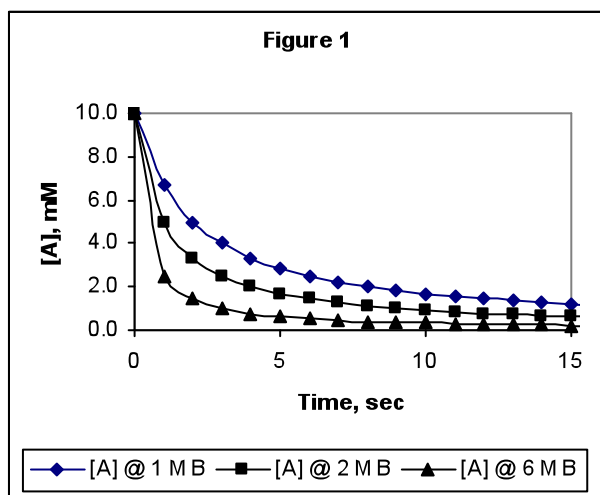

Figure 1

Figure 2

Figure 1 shows first-order dependence in B and Figure 2 is second-order in B. There are two pieces of evidence for this conclusion: First, the effect of B on the Δ[A] in the first

second is greater in Figure 2 than in Figure 1. Second, the effect of B on $t_{1/2}$ for A decreasing from 10 mM to 5 mM is greater in Figure 2 than in Figure 1.

Problem 6. The following elementary steps have been proposed as the mechanism for the reaction between hydrogen peroxide and bromide

$$H_2O_2(aq) + Br^-(aq) \rightarrow BrO^-(aq) + H_2O(l)$$

$$H_2O_2(aq) + BrO^-(aq) \rightarrow Br^-(aq) + H_2O(l) + O_2(g)$$
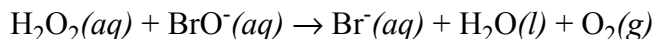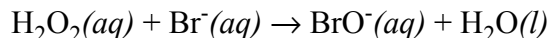
Identify each species in this mechanism (H_2O_2, Br^-, BrO^-, H_2O and O_2) as a reactant, a product, an intermediate, or a catalyst.

The net reaction is $2H_2O_2 \rightarrow 2H_2O + O_2$; thus, H_2O_2 is a reactant, Br^- is a catalyst, BrO^- is an intermediate, and H_2O and O_2 are products.

Explain how a kinetic study of this reaction can be used to determine whether (a) the first step is rate determining, (b) the second step is rate-determining or (c) the mechanism is completely wrong. You may assume that any step before a rate-determining step is in equilibrium.

If the first step is the RDS, then the rate law is

$$\text{Rate} = k_1[H_2O_2][Br^-]$$

If the second step is the RDS, then rate law is

$$\text{Rate} = k_2[H_2O_2][BrO^-]$$
$$[BrO^-] = K_{eq}[H_2O_2][Br^-]$$
$$\text{Rate} = k_2K_{eq}[H_2O_2]^2[Br^-]$$

To determine which step is the RDS do a kinetic study and see which, if any, of the two rate laws matches the experimental rate law.

Problem 7. Wilson's disease is a hereditary problem in which the body is unable to excrete copper, which subsequently becomes stored in the liver. To study treatments for the disease, doctor's inject patients with small doses of ^{64}Cu, a radioactive isotope that decays via first-order kinetics with a half-life of 12.7 hr. If 1.0 mL of a 2.5 µM solution of $^{64}Cu(CH_3CO_2)_2$ is injected into a patient, what percentage of the ^{64}Cu will remain in the body after 24 hours?

For a first-order reaction $k = 0.693/t_{1/2}$, or 5.46×10^{-2} hr^{-1}. The ratio of ^{64}Cu remaining is

$$\ln\left(\frac{[^{64}Cu]_t}{[^{64}Cu]_o}\right) = -kt = -(5.46 \times 10^{-2} \text{ hr}^{-1})(24 \text{ hr}) \qquad \frac{[^{64}Cu]_t}{[^{64}Cu]_o} \times 100 = 27.3\%$$