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 g/mL S_{H_2O} = 4.184 J/g·°C

R = 8.314 J/mol_{rxn}·K   F = 96,485 J/V·mol e^-

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

And a few additional equilibrium constants here:

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

H_3PO_4: $K_{a1} = 7.1\times10^{-3}$ $K_{a2} = 6.3\times10^{-8}$ $K_{a3} = 4.2\times10^{-13}$

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?

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 $Ca_5(PO_4)_3OH$.

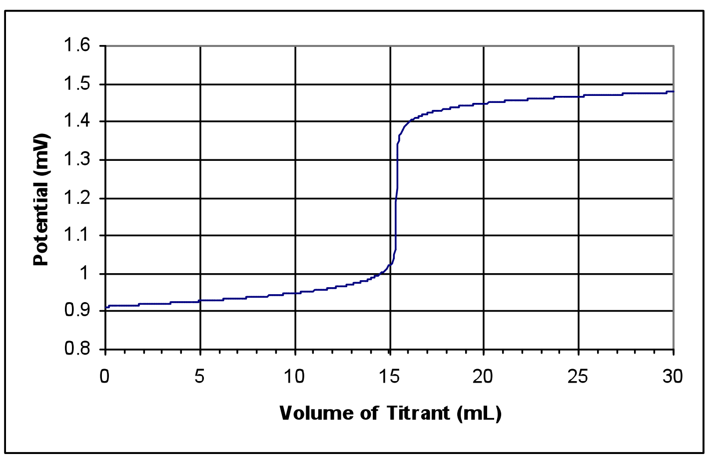
Problem 3. Silver ion can be determined quantitatively by titrating with a standard solution of thiocyanate, the reaction for which is

$$Ag^{+}(aq) + SCN^{-}(aq) \leftrightarrows AgSCN(s)$$

At the equivalence point for this titration, what is the equilibrium concentration of SCN^-? The K_{sp} for AgSCN is 1.0×10^{-12}.

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?

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?



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.

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

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.

Problem 5. For the chemical reaction

$$A + B \rightarrow C$$

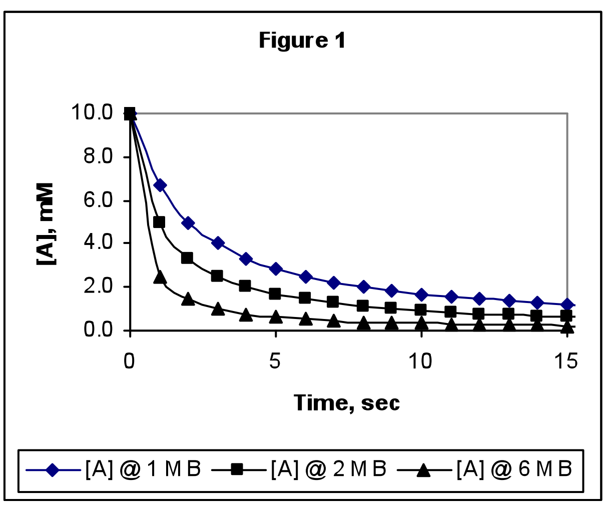
the rate law can be expressed as

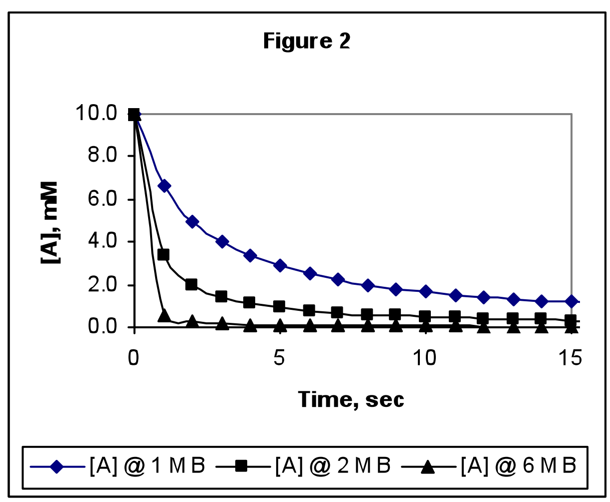
$$\text{Rate} = k[A]^{\alpha}[B]^{\beta}$$

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

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.





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.

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.

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?