

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 ____/16	Problem 5 ____/12
Problem 2 ____/16	Problem 6 ____/12
Problem 3 ____/12	Problem 7 ____/16
Problem 4 ____/16	Total ____/100

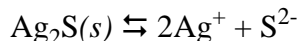
A few constants are given here:

$$d_{\text{H}_2\text{O}} = 1.00 \text{ g/mL} \qquad S_{\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot^\circ\text{C}$$

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

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

Problem 1. The sulfide ion, S^{2-} , forms insoluble compounds with many metal ions. Given that the solubility product for Ag_2S is 1.6×10^{-49} and that for Bi_2S_3 is 1.1×10^{-73} , which compound will have the smallest molar solubility and which will have the smallest mass solubility?

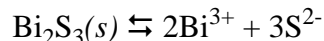


let x be the molar solubility

$$[Ag^+] = 2x \quad [S^{2-}] = x$$

$$K_{sp} = 1.6 \times 10^{-49} = (2x)^2(x) = 4x^3$$

$$x = 3.42 \times 10^{-17} \text{ M}$$



let x be the molar solubility

$$[Bi^{3+}] = 2x \quad [S^{2-}] = 3x$$

$$K_{sp} = 1.1 \times 10^{-73} = (2x)^2(3x)^3 = 108x^5$$

$$x = 1.00 \times 10^{-15} \text{ M}$$

The smaller molar solubility is that for Ag_2S . Multiplying the molar solubilities by molar mass gives the mass solubility of Ag_2S as $8.47 \times 10^{-15} \text{ g/L}$ (MM = 247.8 g/mol) and that for Bi_2S_3 as $5.14 \times 10^{-13} \text{ g/L}$ (MM = 513.8 g/mol). The smaller mass solubility is for Ag_2S .

Problem 2. The ligand EDTA, which forms strong complexes with many metal ions, is often used to keep a metal ion in solution under conditions in which it might otherwise precipitate. Suppose you add 0.010 moles of $Pb(NO_3)_2$ and 0.050 moles of Na_4EDTA to a 1-L volumetric flask and dilute to volume with a pH 13.00 buffer. Will a precipitate of $Pb(OH)_2$ form? The solubility product for $Pb(OH)_2$ is 1.2×10^{-15} and the formation constant for $Pb(EDTA)^{2-}$ is 1.1×10^{18} .

There are several approaches to solving this problem, all of which ultimately require comparing two numbers to each other, one based on an equilibrium calculation and one derived from the starting conditions. One approach begins by determining the $[Pb^{2+}]$ in equilibrium with EDTA and determining if that is sufficient to precipitate $Pb(OH)_2$.

Pb^{2+}	+	$EDTA^{4-}$	\rightleftharpoons	$Pb(EDTA)^{2-}$
0.010		0.050		0
-0.010		-0.010		+0.010
0		0.040		0.010
+X		+X		-X
X		0.040+X		0.010 - X

To solve we let the reaction proceed to completion and then relax back to equilibrium (see table to the left). To simplify, we assume that $0.040 + X$ is 0.040 and that $0.010 - X$ is 0.010. Substituting into K_1 and solving gives

$$K_1 = \frac{[Pb(EDTA)^{2-}]}{[Pb^{2+}][EDTA^{4-}]} = 1.1 \times 10^{18} = \frac{(0.010)}{(X)(0.040)}$$

for which X is $2.27 \times 10^{-19} \text{ M}$ (assumptions ok). Solving for Q_{sp}

$$Q_{sp} = (Pb^{2+})(OH^-)^2 = (2.27 \times 10^{-19})(0.1)^2 = 2.27 \times 10^{-21}$$

which is smaller than the K_{sp} ; thus, no precipitate forms. Another solution is at the end of this answer key.

Problem 3. The rate law for the reaction of methylacetate, $\text{CH}_3\text{COOCH}_3$, with water is known to be $R = k[\text{CH}_3\text{COOCH}_3][\text{H}_3\text{O}^+]$. For each of the following actions, will the reaction's rate constant increase, decrease or remain the same. Place an **X** in the appropriate box and explain your choice in one sentence.

action	increase	decrease	remain the same	explanation
increase the pH of the system			X	The rate constant depends upon activation energy and temperature as shown by the equation $k = Ze^{-E_a/RT}$. Increasing pH will decrease $[\text{H}_3\text{O}^+]$ and make the reaction slower, but it will not affect k . Shaking does not change E_a or T and has no affect on k . Increasing temperature makes k larger.
shake the reaction mixture during reaction			X	
increase the temperature	X			

Problem 4. The oxidation of NO to NO_2 is an important reaction in the atmosphere. A study of the reaction's kinetics gives the following results:

Trial	[NO], M	[O ₂], M	Initial Rate (M/s)
1	4.5×10^{-2}	2.2×10^{-2}	8.00×10^{-3}
2	4.5×10^{-2}	4.5×10^{-2}	1.60×10^{-2}
3	9.0×10^{-2}	9.0×10^{-2}	0.128

What is the rate law and the rate constant for this reaction; limit yourself to any one trial when determining the rate constant.

Comparing trials 1 and 2 shows that the rate increases by a factor of 2 when the concentration of O_2 increases by a bit more than a factor of 2. This is consistent with a reaction that is first order in O_2 . Comparing trials 2 and 3 shows that rate increases by a factor of 8 when the concentration of both NO and O_2 increase by a factor of 2. Since 2^3 is 8, the overall order must be 3. Knowing that the order for O_2 is 1 means that the order for NO must be 2. The rate law, therefore, is $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$. The rate constant using the data from trial 1 is $180 \text{ M}^{-2} \text{ s}^{-1}$.

Problem 5. In the presence of a tungsten catalyst and at an elevated temperature, the decomposition of NH_3 to N_2 and H_2 occurs at a constant rate, with a rate constant of $3.7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. How long will it take for 99.9% of the NH_3 in a reaction vessel to undergo decomposition?

A reaction that occurs at a constant rate is zero order, for which

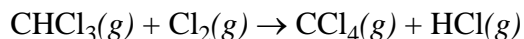
$$[\text{NH}_3]_t = [\text{NH}_3]_0 - kt$$

If we let the initial concentration be 1, then at time t the concentration will be 0.001; thus

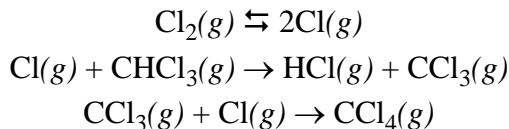
$$0.001 = 1 - (3.7 \times 10^{-6})t$$

Solving gives the time as $2.7 \times 10^5 \text{ s}$. Other choices for $[\text{NH}_3]_0$ will give different results.

Problem 6. Another important atmospheric reaction is the formation of CCl_4 from chloroform and chlorine



The following mechanism has been proposed for this reaction



in which the second step is rate-determining with a rate constant of k_2 . What is the rate law for the overall reaction? You may assume that the first step is at equilibrium with an equilibrium constant of K_{eq} . Write your rate law in terms of an observed rate constant, k_{obs} , and indicate how k_{obs} is related to k_2 and K_{eq} .

The rds is the second step, for which the rate law is

$$\text{Rate} = k_2[\text{Cl}][\text{CHCl}_3]$$

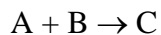
The concentration of Cl is given by the equilibrium constant for the first step; thus

$$K_{\text{eq}} = [\text{Cl}]^2/[\text{Cl}_2] \quad \text{and} \quad [\text{Cl}] = (K_{\text{eq}})^{1/2}[\text{Cl}_2]^{1/2}$$

Substituting back gives

$$\text{Rate} = k_2(K_{\text{eq}})^{1/2}[\text{Cl}_2]^{1/2}[\text{CHCl}_3] \quad \text{with} \quad k_{\text{obs}} = k_2(K_{\text{eq}})^{1/2}$$

Problem 7. Shown below are three graphs of kinetic data from a study of the reaction

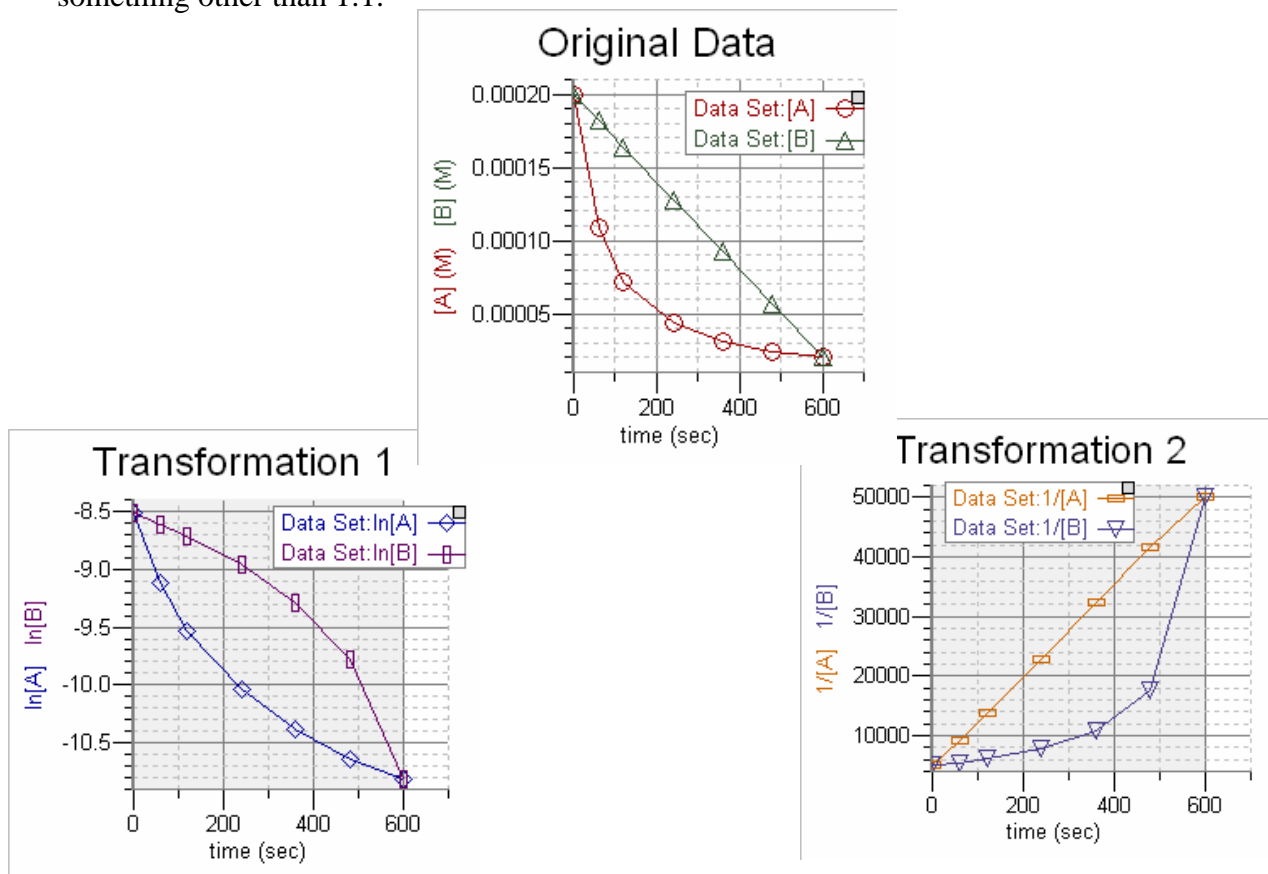


The first panel shows the original data as plots of $[A]$ vs. time and $[B]$ vs. time. The remaining two panels show transformations of this data. When studying the change in concentration of A, $[B]_0$ was set at 0.30 M, and when studying the change in $[B]$ the initial concentration of A was set to 0.3 M. Using this data determine the reaction's rate law and rate constant.

From the original data, the linear plot for $[B]$ vs. time indicates that the reaction is zero-order in B, and the plot of $[A]$ vs. time indicates that the reaction is not zero-order in A. The linear plot for $1/[A]$ vs. time, however, indicates that the reaction is second-order in A. The rate law, therefore, is

$$\text{Rate} = k[A]^2$$

The best way to find the value of k is to determine the slope for the plot of $1/[A]$ vs. time, which is 75.9, giving a rate constant of $75.9 \text{ M}^{-1} \text{ s}^{-1}$. An alternative approach is to find the slope of the plot of $[B]$ vs. time, for which the rate law is $R = k_{\text{obs}} = k[A]_0^2$. The slope is 3.0×10^{-7} , which, since the $[A]_0$ is 0.3 M, gives k as $3.3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. The fact that the rate constants are not identical means that the reaction's stoichiometry must be something other than 1:1.



Two Additional Approaches to Answering Problem 2.

If EDTA is added to a solution containing Pb(OH)_2 , then the following equilibrium might exist (note the use of word *might* as the equilibrium reaction can exist only if Pb(OH)_2 is present, a fact that we don't yet know):



Using an ICE table

$\text{Pb(OH)}_2(s)$	+	EDTA^{4-}	\rightleftharpoons	Pb(EDTA)^{2-}	+	2OH^-
-		0.050		0		0.1
-		-X		+X		-
-		$0.050 - X$		X		0.1

Substituting into the equation for K gives

$$1320 = \frac{(X)(0.1)^2}{(0.050 - X)}$$

Solving gives $X = 0.04999962$. This value, however, is impossible because it using up this many moles of EDTA requires dissolving the same number of moles of Pb(OH)_2 , of which we have only 0.010 moles. This means that there must not be any precipitate in the system and the equilibrium reaction does not in fact exist.

Another approach, which begins from the same reaction, recognizes that no more than 0.010 moles of EDTA can react and then determines if an equilibrium might exist; thus

$\text{Pb(OH)}_2(s)$	+	EDTA^{4-}	\rightleftharpoons	Pb(EDTA)^{2-}	+	2OH^-
-		0.050		0		0.1
-		-0.010		+0.010		-
-		0.040		0.010		0.1
-		+X		-X		-
-		$0.040 + X$		$0.010 - X$		0.1

If we solve for X we obtain a negative number for a result. A negative number, however, makes no sense as it means that when we let the reaction go back toward equilibrium by shifting to

the reactants side (the second-to-last row), the reaction actually shifted to the right. This contradiction occurs because the initial shift to the right (the change in EDTA of -0.010) dissolved all of the Pb(OH)_2 , destroying the equilibrium. Again, no solid is present.