

Key for Unit Exam: Equilibrium Chemistry

On the following pages are problems that consider equilibrium chemistry in the context of chemical or biochemical systems. 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 a question, then move on to another question; working on a new question may suggest an approach to a question that is more troublesome. 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 and that work is relevant to the question.

Problem	Points	Maximum	Problem	Points	Maximum
1	10.6	12	4	18.1	21
2	11.0	12	5	19.4	22
3	10.2	12	6	13.8	21
Total				82.5	100

high score	scores 100–90	scores 89–80	scores ≤ 79
95	6	8	10

A few constants are shown below; other information is included within individual problems. A periodic table and a sheet of equations also are available.

- the gas constant (R) is $8.314 \text{ J/mol}_{\text{rxn}} \cdot \text{K}$
- Faraday's constant (F) is $96,485 \text{ J/V} \cdot \text{mol e}^-$
- room temperature is 25°C or 298 K

Specific equilibrium constant and other potentially useful information are embedded within individual problems.

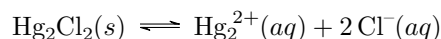
!!Special Note on Solutions to Equilibrium Problems!!

There are many options available to you when solving an equilibrium problem, including a rigorous algebraic solution, making an assumption to simplify the algebra, or using a calculator's ability to solve the equation. Each method requires some care and attention on your part; at a minimum this means that:

- *if you solve the problem rigorously, be sure your algebraic work is neat and easy to follow, and that you report all possible solutions before you identify the chemically meaningful solution*
- *if you make an assumption, be sure to test the validity of that assumption before you accept and report a final answer*
- *if you use your calculator's solver function, be sure to indicate the exact function you entered into your calculator and report all possible solutions before you identify the chemically meaningful solution*

Part A: Three Problems With Short Written Answers and/or With Short Calculations

Problem 1. The mercury (I) cation forms a precipitate with the chloride ion. The correct formula for the precipitate is Hg_2Cl_2 , with a solubility reaction of



Suppose you incorrectly think the formula is HgCl , with a solubility reaction of



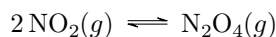
If you measure the equilibrium concentration of Cl^- and report a K_{sp} based on the incorrect solubility reaction, will you report a value that is greater than, less than, or equal to its true K_{sp} ? Support your answer with a 2-3 sentence explanation.

The correct equation for the solubility product is $K_{\text{true}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$ and the incorrect equation is $K_{\text{false}} = [\text{Hg}^+][\text{Cl}^-]$. Let's assume the equilibrium concentration for Cl^- is x ; then $K_{\text{true}} = [0.5x][x]^2 = 0.5x^3$ and $K_{\text{false}} = [x][x] = x^2$. We know x is small ($x \ll 1$) because Hg_2Cl_2 is insoluble; thus, x^2 is greater than $0.5x^3$ and we report a K_{sp} that is too big.

Problem 2. At a depth of 1200 meters, the pH of seawater shows a great deal more variability than it does at the surface, with a pH as low as 7.5 in the northern Pacific Ocean and as high as 8.1 in the Mediterranean Sea. An important acid-base system in seawater chemistry is that for carbonate, which is present in three forms: H_2CO_3 , HCO_3^- , and CO_3^{2-} . Given that the K_a values for H_2CO_3 are 4.5×10^{-7} and 4.7×10^{-11} , which of the three possible carbonate species is present at the highest concentration? Support your answer with a 2-3 sentence explanation.

The $\text{p}K_a$ values for carbonic acid are 6.35 and 10.33, with H_2CO_3 present at the highest concentration below a pH of 6.35, and CO_3^{2-} present at the highest concentration above a pH of 10.33. Between a pH of 6.35 and 10.33, bicarbonate, HCO_3^- , is present at the highest concentration; thus, given the pH of seawater, the species with the highest concentration is HCO_3^- .

Problem 3. Nitrogen dioxide, $\text{NO}_2(g)$, exists in equilibrium with dinitrogen tetroxide, $\text{N}_2\text{O}_4(g)$, as shown by the following equilibrium reaction



Nitrogen dioxide has a red color and dinitrogen tetroxide is colorless, which means we can use the color of the mixture to determine the relative position of the reaction at equilibrium. Suppose we suddenly decrease the volume in which the mixture resides; will the mixture turn a deeper shade of red, will it turn a lighter shade of red, or will it remain unchanged in color? Support your answer with a 2-3 sentence explanation.

Note: Although I made comments on most of your solutions, ultimately, I choose not to deduct points because the wording of the problem on my part was less than ideal. When we decrease volume the reaction shifts in the direction that produces the smallest number of particles; thus, the reaction shifts to the right, increasing the concentration of the colorless N_2O_4 and decreasing the concentration of the red NO_2 . As a result, the mixture turns a lighter shade of red than we might expect given that the concentration of both species increase when we decrease the volume.

When a mixture of nitrogen dioxide and dinitrogen tetroxide at room temperature is placed in a freezer, the mixture turns from a darker shade of red to a lighter shade of red. What can you conclude about ΔH° for the equilibrium reaction? Support your answer with a 2-3 sentence explanation.

Knowing that the reaction turned a lighter shade of red tells us that the reaction shifted to the right. When we cool a reaction mixture, it shifts in the direction that releases heat; thus, the reaction as written is exothermic and ΔH° is negative.

Part B: Three Problems With More Involved Calculations

Problem 4. Nicotinic acid, $\text{C}_6\text{H}_5\text{NO}_2$, is found in liver, yeast, milk, and corn. Pubmed reports that nicotinic acid has a mass solubility of 1.3 g per 100.0 mL of water, yielding a solution with a pH of 2.70. Based on this information, determine the K_a for nicotinic acid and report the $\text{p}K_b$ for nicotinic acid's conjugate weak base.

This problem is similar to the pharmaceutical compound worksheet and to Take-Home 05. Nicotinic acid is a weak acid, which we represent here as HA, with an acid dissociation reaction of



and an acid dissociation constant of

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The initial concentration of HA is

$$\frac{1.3 \text{ g HA}}{0.1000 \text{ L}} \times \frac{1 \text{ mol HA}}{123.11 \text{ g HA}} = 0.1056 \text{ M HA}$$

The measured pH gives the concentration of H_3O^+ at equilibrium as $10^{-2.70} = 1.995 \times 10^{-3} \text{ M}$. Now we can set up and complete an ICE table where starting values are shown in **bold** and values derived from the starting values are shown in *italics*.

	$\text{HA}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{A}^-(aq)$
initial	0.1056		—		0		0
change	<i>-0.001995</i>		—		<i>+0.001995</i>		<i>+0.001995</i>
equilibrium	<i>0.1036</i>		—		0.001995		<i>0.001995</i>

Substituting the equilibrium values into the K_a expression gives

$$K_a = \frac{(0.001995)(0.001995)}{0.1036} = 3.84 \times 10^{-5}$$

or a $\text{p}K_a$ of 4.41 and a $\text{p}K_b$ for the conjugate weak base of $14 - 4.41 = 9.59$.

Problem 5. One way to prepare a buffer is to store stock solutions of a weak acid and its conjugate weak base in separate digital dispensing bottles (listed at just \$1,165.00 each in the Cole-Parmer catalog!), which makes it easy to dispense precise amounts of each solution. Suppose you have stock solutions of 1.000 M acetic acid, CH_3COOH , and 1.500 M sodium acetate, CH_3COONa . How many mL of each solution do you need to prepare 0.1000 L of a buffer that has a pH of 4.850 subject to the limitation that the combined concentrations of the two buffering agents, CH_3COOH and CH_3COONa , cannot exceed 0.1250 M? The K_a for CH_3COOH is 1.754×10^{-5} .

This problem is similar to the designing a buffer worksheet, but here the buffering agents are provided as solutions instead of as solids.

Given a K_a of 1.754×10^{-5} for CH_3COOH , we know that its $\text{p}K_a$ is $-\log(1.754 \times 10^{-5})$, or 4.756. The ratio of the conjugate weak base, CH_3COONa , and the weak acid, CH_3COOH , needed to achieve a pH of 4.85 is given by the Henderson-Hasselbach equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$
$$4.85 = 4.756 + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

This equation has two unknowns, so we need an additional equation to find the exact amounts of buffering agents. The second equation comes from the combined concentrations of the buffering agents; thus

$$[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COONa}] = 0.1250 \text{ M}$$

Letting $[\text{CH}_3\text{COONa}] = x$ means that $[\text{CH}_3\text{COOH}] = 0.1250 - x$ and

$$4.85 = 4.756 + \log \frac{x}{0.1250 - x}$$

Solving for x

$$0.094 = \log \frac{x}{0.1250 - x}$$

$$10^{0.094} = 1.2417 = \frac{x}{0.1250 - x}$$

$$0.1552 - 1.2417x = x$$

$$x = [\text{CH}_3\text{COONa}] = 0.0692 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.1250 - [\text{CH}_3\text{COONa}] = 0.0558 \text{ M}$$

We need just 0.1000 L of buffer, which means we need to adjust the volume to arrive at the moles of each reagent

$$0.0692 \text{ M CH}_3\text{COONa} \times 0.1000 \text{ L} = 0.00692 \text{ mol CH}_3\text{COONa}$$

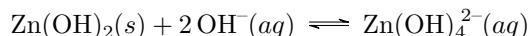
$$0.0558 \text{ M CH}_3\text{COOH} \times 0.1000 \text{ L} = 0.00558 \text{ mol CH}_3\text{COOH}$$

Finally, we determine the mL of each stock solution needed to make the buffer

$$0.00692 \text{ mol CH}_3\text{COONa} \times \frac{1000 \text{ mL}}{1.5 \text{ mol}} = 4.61 \text{ mL}$$

$$0.00558 \text{ mol CH}_3\text{COOH} \times \frac{1000 \text{ mL}}{1.0 \text{ mol}} = 5.58 \text{ mL}$$

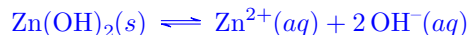
Problem 6. You may recall from Chem 130 that some metal hydroxide precipitates become soluble in the presence of excess hydroxide ions. This is true, for example, for zinc hydroxide, $\text{Zn}(\text{OH})_2$, which in concentrated solutions of NaOH dissolves to form $\text{Zn}(\text{OH})_4^{2-}$ as shown here



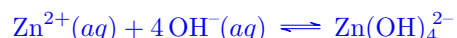
Given that the K_{sp} for $\text{Zn}(\text{OH})_2$ is 4.1×10^{-17} and that β_4 for $\text{Zn}(\text{OH})_4^{2-}$ is 2.9×10^{15} , what is the molar solubility of $\text{Zn}(\text{OH})_2$ in a solution of 0.50 M NaOH?

This problem is similar to an in-class problem on the solubility of CaF_2 in the presence of EDTA.

To begin, we need to determine the equilibrium constant for this reaction, which is the sum of two reactions with known equilibrium constants, the solubility of $\text{Zn}(\text{OH})_2$ as given by the K_{sp} reaction



and the overall formation of the metal-ligand complex $\text{Zn}(\text{OH})_4^{2-}$ as given by the β_4 reaction



When we add together two reactions we multiply their equilibrium constants; thus

$$K = K_{\text{sp}} \times \beta_4 = (4.1 \times 10^{-17})(2.9 \times 10^{15}) = 0.1189$$

Next, we use an ICE table to help us organize information

	$\text{Zn(OH)}_2(s)$	+	$2\text{OH}^-(aq)$	\rightleftharpoons	$\text{Zn(OH)}_4^{2-}(aq)$
initial	—		0.50		0
change	—		$-2x$		$+x$
equilibrium	—		$0.50 - 2x$		x

Substituting the equilibrium values into the equilibrium constant expression gives

$$K = \frac{[\text{Zn(OH)}_4^{2-}]}{[\text{OH}^-]^2} = \frac{x}{(0.50 - 2x)^2} = 0.1189$$

which we can solve using any of our available methods: a rigorous solution by expanding to a second-order polynomial and solving the quadratic equation; making a simplifying assumption; using a calculator's solver function; or graphing the function. The approach here makes use of simplifying assumptions, but all approaches yield the same result within the error tolerated by simplifying assumptions.

For our first pass, let's assume that $0.50 - 2x \approx 0.50$; thus

$$K = \frac{x}{(0.50)^2} = 0.1189$$

which gives $x = 0.029725$. Checking the assumption

$$\frac{0.5 - (0.5 - 2 \times 0.029725)}{0.5} \times 100 = 11.9\%$$

gives an error of 11.9%. This is too large of an error, so our second assumption is that $0.50 - 2x \approx 0.50 - 2 \times 0.029725 = 0.44055$; thus

$$K = \frac{x}{(0.44055)^2} = 0.1189$$

which gives $x = 0.023077$. Checking the assumption

$$\frac{(0.5 - 2 \times 0.029725) - (0.5 - 2 \times 0.023077)}{0.5 - 2 \times 0.029725} \times 100 = -3.0\%$$

an acceptable error of -3.0% . For this equilibrium reaction, the molar solubility of Zn(OH)_2 is equivalent to the concentration of Zn(OH)_4^{2-} , which, in turn, is equal to x or 0.0231 mol/L.