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		12	4		21
2		12	5		22
3		12	6		21
			Total		100

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 J/$\text{mol}_{\text{rxn}} \bullet$ K
- Faraday's constant (F) is 96,485 J/V $\bullet$ 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 simply 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

$$\mathrm{Hg_2Cl_2}(s) \rightleftharpoons \mathrm{Hg_2^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq)$$

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

$$\mathrm{HgCl}(s) \rightleftharpoons \mathrm{Hg^+}(aq) + \mathrm{Cl^-}(aq)$$

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.

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.

Problem 3. Nitrogen dioxide, $NO_2(g)$, exists in equilibrium with dinitriogen tetroxide, $N_2O_4(g)$, as shown by the following equilibrium reaction

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

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.

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.

Part B: Three Problems With More Involved Calculations

Problem 4. Nicotinic acid, $C_6H_5NO_2$, 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 pK_b for nicotinic acid's conjugate weak base.

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}.

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, $Zn(OH)_2$, which in concentrated solutions of NaOH dissolves to form $Zn(OH)_4^{2-}$ as shown here

$$Zn(OH)_2(s) + 2\,OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$$

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