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		11	4		20
2		11	5		23
3		11	6		24
			Total		100

A few constants are given here; other information is included within individual problems.

- density (d) of water is 1.00 g/mL
- specific heat (S) of water is 4.184 J/g • °C
- the gas constant (R) is 8.314 J/mol_{rxn} • K
- Faraday's constant (F) is 96,485 C/mol e^- or 96,485 J/V • mol e^-
- water's dissociation constant (K_w) is 1.00×10^{-14}

!!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. Good buffers (here Good is Norman Good, who was a plant biologist at Michigan State University) are a set of buffering reagents whose properties make them well-suited for work in phyiological systems. One such Good buffer is piperazine–N.N'–bis(2-ethanesulfonic acid), which commonly is refered to as PIPES. Its weak acid form is $HPIPES^+$ and it has a pK_a of 6.76 at 25°C. Suppose you prepare a PIPES buffer with a pH of 7.00. Does your buffer have a greater capacity to neutralize strong acid or strong base, or does it have an equal ability to neutralize both strong acid and strong base. Explain your answer in no more than three sentences.

Problem 2. As is the case with all buffer salts, the pK_a of $HPIPES^+$ changes with temperature, with a value of 6.66 reported at a temperature of 37°C and a value of 6.94 at a temperature of 4°C. What do these values imply about the sign of ΔH for its acid dissociation reaction? Is $\Delta H > 0$, $\Delta H < 0$, $\Delta H = 0$, or is there insufficient information to determine its sign? Explain your answer in no more than three sentences.

Problem 3. Ammonium acetate is an interesting compound because it consists of both a weak acid, NH_4^+, and a weak base, CH_3COO^-. When you dissolve CH_3COONH_4 in water the following equilibrium reaction determines the solution's composition.

$$NH_4^+(aq) + CH_3COO^-(aq) \rightleftharpoons CH_3COOH(aq) + NH_3(aq)$$

Given that the K_a for NH_4^+ is 5.6×10^{-10} and that the K_a for CH_3COOH is 1.8×10^{-5}, what is the equilibrium constant for the reaction above? Given your equilibrium constant, does a solution of ammonium acetate have a greater concentration of NH_3 or of NH_4^+? Explain your answer in one sentence.

Part B: Three Problems With More Involved Calculations

Problem 4. Most soaps contain long-chain fatty acids in the form of sodium salts, one example of which is sodium stearate, $CH_3(CH_2)_{16}COONa$. A solution is prepared by dissolving 5.0 g of $CH_3(CH_2)_{16}COONa$ in 1.00 L of water. The pH of the resulting solution is measured as 8.55. What is K_b for the stearate ion?

What is the pK_a for stearic acid, the conjugate weak acid of the stearate ion?

Problem 5. Commerical grape-flavored fruit juice powders usually include a mixture of tartaric acid, $H_2C_4H_4O_6$, and potassium tartrate, $KHC_4H_4O_6$, to fix the pH of the juice when the powder is dissolved in water. Suppose you work for a company that manufactures this beverage and are asked to devise a formulation with the following properties: when a package of the powdered mixture is added to 750 mL of water, the resulting pH is 3.20 and the total concentration of buffering agents is 0.100 M. How many grams of $H_2C_4H_4O_6$ and of $KHC_4H_4O_6$ do you need in each package of the powdered mixture? The K_a for tartaric acid is 9.20×10^{-4}.

What is the pH of a 250 mL portion of this solution if it is mixed with 100.00 mL of 0.0200 M HCl, which mimics the pH and volume of stomach acid?

Problem 6. The ligand EDTA forms strong metal-ligand complexes with most divalent metal ions. One of its important uses is to prevent a metal ion from precipitating as a hydroxide salt under basic conditions. Suppose you combine 0.0100 mol $Pb(NO_3)_2$ and 0.0500 mol of Na_4EDTA in a 1.00-L volumetric flask and diulte to volume using a pH 13.00 buffer. What is the concentration of uncomplexed Pb^{2+} in this solution given that the formation constant is 1.1×10^{18} for the reaction

$$\mathrm{Pb}^{2+}(aq) + \mathrm{EDTA}^{4-}(aq) \rightleftharpoons \mathrm{PbEDTA}^{2-}(aq)$$

Given your result for the concentration of Pb^{2+} and knowing that the K_{sp} for $Pb(OH)_2$ is 1.2×10^{-15}, is the amount of EDTA present sufficient to prevent the precipitation of $Pb(OH)_2(s)$? Support your answer with one sentence explanation and a suitable calculation.