

# 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  $\cdot$   $^{\circ}$ C
- the gas constant ( $R$ ) is 8.314 J/mol<sub>rxn</sub>  $\cdot$  K
- Faraday's constant ( $F$ ) is 96,485 C/mol e<sup>-</sup> or 96,485 J/V  $\cdot$  mol e<sup>-</sup>
- water's dissociation constant ( $K_w$ ) is  $1.00 \times 10^{-14}$

## !!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 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:*

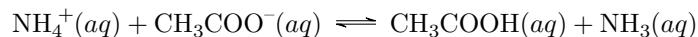
- *if you solve the problem rigorously, be sure your algebraic work is neat and easy to follow, and that you report all possible solutions before you identify the chemically meaningful solution*
- *if you make an assumption, be sure to test the validity of that assumption before you accept and report 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.** 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 physiological systems. One such Good buffer is piperazine–N,N'–bis(2-ethanesulfonic acid), which commonly is referred to as PIPES. Its weak acid form is HPIPES<sup>+</sup> and it has a p*K*<sub>a</sub> 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 p*K*<sub>a</sub> of HPIPES<sup>+</sup> 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 Δ*H* for its acid dissociation reaction? Is Δ*H* > 0, Δ*H* < 0, Δ*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<sub>4</sub><sup>+</sup>, and a weak base, CH<sub>3</sub>COO<sup>−</sup>. When you dissolve CH<sub>3</sub>COONH<sub>4</sub> in water the following equilibrium reaction determines the solution's composition.



Given that the *K*<sub>a</sub> for NH<sub>4</sub><sup>+</sup> is 5.6 × 10<sup>−10</sup> and that the *K*<sub>a</sub> for CH<sub>3</sub>COOH is 1.8 × 10<sup>−5</sup>, 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<sub>3</sub> or of NH<sub>4</sub><sup>+</sup>? Explain your answer in one sentence.

**Part B: Three Problems With More Involved Calculations**

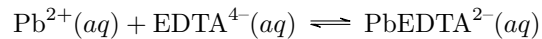
**Problem 4.** Most soaps contain long-chain fatty acids in the form of sodium salts, one example of which is sodium stearate,  $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$ . A solution is prepared by dissolving 5.0 g of  $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$  in 1.00 L of water. The pH of the resulting solution is measured as 8.55. What is  $K_b$  for the stearate ion?

What is the  $\text{p}K_a$  for stearic acid, the conjugate weak acid of the stearate ion?

**Problem 5.** Commercial grape-flavored fruit juice powders usually include a mixture of tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , and potassium tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ , 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  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  and of  $\text{KHC}_4\text{H}_4\text{O}_6$  do you need in each package of the powdered mixture? The  $K_a$  for tartaric acid is  $9.20 \times 10^{-4}$ .

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  $\text{Pb}(\text{NO}_3)_2$  and 0.0500 mol of  $\text{Na}_4\text{EDTA}$  in a 1.00-L volumetric flask and dilute to volume using a pH 13.00 buffer. What is the concentration of uncomplexed  $\text{Pb}^{2+}$  in this solution given that the formation constant is  $1.1 \times 10^{18}$  for the reaction



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