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		13	5		21
3		12	6		21
			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: Problems With Short Written Answers and/or With Short Calculations

Problem 1. Nitrogen dioxide, NO_2, is a reddish-brown gas and dinitrogen tetroxide, N_2O_4, is a colorless gas. The two gases form an equilibrium mixture defined by the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$. Suppose you have an equilibrium mixture of the two gases in a cylinder and note that the color of the mixture is a medium reddish-brown color. If you compress the gas by pushing down on the cylinder, will the gas mixture become a darker shade of reddish-brown or a lighter shade of reddish-brown, or will the color remain unchanged? In 2–3 sentences, explain this observation.

Problem 2. Equilibrium constants are temperature dependent. The value of K_w, for example, is 1.0×10^{-14} at 25° and is 0.29×10^{-14} at 10°. Based on this observation, is the dissocation of water exothermic or endothermic, or is there insufficient information to reach a conclusion. Limit your response to no more than 2–3 sentences.

What is the pH of water at 10°?

Problem 3. Many metals are found in nature as insoluble sulfide salts. Because sulfide is a weak base, the molar solubility of a metal sulfide depends on pH. Given the following information, write the reaction that controls the solubility of PbS in water at a fixed pH of 8.5, and report the value of its equilibrium constant.

$$K_\text{sp,PbS} = 8.0 \times 10^{-28} \qquad K_{\text{a1,H}_2\text{S}} = 1.0 \times 10^{-7} \qquad K_{\text{a2,H}_2\text{S}} = 1.3 \times 10^{-13}$$

Part B: Problems With More Involved Calculations

Problem 4. The weak acid N–(2–acetoamido)–2–aminoethanesulonic acid, which we abbreviate here as HACES, finds use in a variety of biological and biochemical research protocals, including the isoelectric focusing of proteins and SDS-PAGE separations. A publication by Interchim—a laboratory supply company that specializes in biological and biochemical reagents—notes that a 1.0 %w/v solution of HACES has a pH of 4.0 at 25°. Given this information, what is the pK_{a} for HACES? The molar mass for HACES is 182.2 g/mol.

What is the pK_{b} for the conjugate weak base of HACES?

Problem 5. The weak acid 2–(N–morpholino)ethanesulfonic acid monohydrate, which we abbreviate here as HMES, and its conjugate weak base, MES, are one of the so called "Good's buffers" that find use in biological and biochemical protocols. Suppose you need to prepare 500.0 mL of a pH 7.00 HMES/MES buffer in which the total concentration of buffering agents is 0.100 M. The following reagents are available to you: a solution of 0.500 M HMES, a solution of 1.00 M HCl, and a solution of 1.00 M NaOH. Explain how you will prepare this buffer. The molar mass for HMES is 195.24 g/mol and its pK_a is 6.16.

Will your buffer have a greater capcity to neutralize strong acid or strong base? Justify your answer in 1–3 sentences.

Problem 6. Sitting before you is a beaker that contains 500.0 mL of 0.300 M $Mg(NO_3)_2$ and a weigh boat with 15.0 g of NaOH pellets. If you add the NaOH to the beaker, what are the concentrations of Mg^{2+} and of OH^- when equilibrium is established at 25°? The K_{sp} for $Mg(OH)_2$ is 1.8×10^{-11} at 25°. You may assume there is no change in volume when you add the NaOH to the solution.

Suppose that adding solid NaOH to the beaker increases slightly the volume. What effect does this have on the equilibrium concentration for Mg^{2+} that you report above? Is that result too large or too small, or is your calculated result still correct? Justify your answer in 1–3 sentences.