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 | | 20 |
| 2 | | 6 | 5 | | 25 |
| 3 | | 12 | 6 | | 25 |
| | | | 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 $4.184 \text{ J/g} \bullet ^{\circ}\text{C}$
- 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 identifying the chemically meaningful solution
- *if you make an assumption, be sure to test the validity of that assumption before accepting and reporting 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 identifying the chemically meaningful solution

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

Problem 1. In the first unit on thermodynamics, we considered the reaction

$$\mathrm{NH}_3(g) + \mathrm{HCl}(g) \Longrightarrow \mathrm{NH}_4\mathrm{Cl}(s)$$

noting the following in regard to its thermodynamic values: $\Delta G < 0$, $\Delta H < 0$, and $\Delta S > 0$. Now, consider the reaction

$$NH_4Cl(s) \Longrightarrow NH_3(g) + HCl(g)$$

for which the equilibrium constant is 0.0167 at 500 K. Will K_{eq} increase, decrease, or remain the same if the temperature is increased to 1000 K? Explain your reasoning in 1–2 sentences.

A 1.00-L flask is charged with 0.0500 mol each of $NH_3(g)$, HCl(g), and $NH_4Cl(s)$ and heated to 500 K. Will the mass of $NH_4Cl(s)$ increase, decrease, or remain the same when equilibrium is reached? Explain your reasoning in 1–2 sentences.

A flask that contains $NH_3(g)$, HCl(g), and $NH_4Cl(s)$ is at equilibrium at 500 K. Will the concentration of $NH_3(g)$ increase, decrease, or remain the same if additional $NH_4Cl(s)$ is added to the flask? Explain your reasoning in 1–2 sentences.

Problem 2. The neutral weak acid, HY, has a pK_a of 8. Is the pH of a solution of NaY greater than, less than, or equal to 7, or is there insufficient information to make a decision. Briefly explain your reasoning in 1–2 sentences. If there is insufficient information, then indicate what additional information is needed.

Problem 3. Placed before you are two beakers. The first beaker contains 150 mL of HCl and has a pH of 2.15. The second beaker contains 100 mL of HNO_3 and has a pH of 1.35. If you pour one solution into the other, what is the pH of the resulting solution?

Part B: Problems With More Involved Calculations

Problem 4. Hippuric acid, $C_9H_9NO_3$, which is an acyl glycine, is a metabolite of aromatic compounds contained in food. It is found in horse urine—thus, its name, which is derived from the Greek *hippos* for horse. At higher concentrations, hippuric acid may have antibacterial properties. A saturated solution of hippuric acid contains 3.75 mg per 1.00 mL and has a pH of 3.60. What is the pK_a for hippuric acid?

Problem 5. A microbiologist needs a buffer with a pH of 7.00 to use when preparing bacterial cultures. Solutions of 0.10 M K₂HPO₄ and 0.10 M KH₂PO₄ are available. If you start with 100.0 mL of the K₂HPO₄ solution, how many mL of the KH₂PO₄ solution will you need to make this buffer? The p K_a values for H₃PO₄ are 2.15, 7.20, and 12.38.

Does your buffer have a greater capacity to neutralize strong acid or strong base? Explain your reasoning in 1-2 sentences.

Suppose the bacteria excretes 1.2×10^{-3} moles of H_3O^+ into your buffer. What is the resulting pH?

Problem 6. When you add NaOH to a solution of Zn^{2+} a precipitate of $Zn(OH)_2$ forms. If you continue to add NaOH, however, the amount of precipitate decreases as $Zn(OH)_2$ reacts to form $Zn(OH)_4^{2-}$.

Part A. First, consider only the solubility reaction

$$\operatorname{Zn}(\operatorname{OH})_2(s) \Longrightarrow \operatorname{Zn}^{2+}(aq) + 2\operatorname{OH}^-(aq)$$

How many grams of $\text{Zn}(\text{OH})_2$ will dissolve to make a 1.00 L aqueous saturated solution, and what is the pH of the resulting solution? The K_{sp} for $\text{Zn}(\text{OH})_2$ is 4.1×10^{-17} .

Part B. Next, consider the reaction

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

How many grams of Zn(OH)₂ will dissolve in 1.00 L of water if you fix the pH to 13 using a buffer? The overall formation constant, β_4 , for Zn(OH)₄^{2–} is 3.0×10^{15} .