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	9.9	12	4	16.5	20
2	5.3	6	5	21.7	25
3	9.9	12	6	20.7	25
			Total	83.0	100

high score	scores 100–90	scores 89–80	scores $\leq$ 79
96	3	7	4

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$_{\text{rxn}}$ • 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

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

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

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

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.

Answer. The decomposition of $NH_4Cl(s)$ is an endothermic reaction ($\Delta H > 0$), which means we can view heat as a reactant. Increasing the temperature is equivalent to adding heat, which shifts the reaction to the right, increasing the the concentrations of $NH_3(g)$ and $HCl(g)$. Given that $K_{eq} = [NH_3][HCl]$, the value of the equilibrium constant increases.

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.

Answer. Substituting the concentrations of $NH_3(g)$ and $HCl(g)$ into the equilibrium constant expression gives $Q = (0.0500)(0.0500) = 0.00225$. Given that $Q < K$, we know that the reaction must shift to the right to increase the concentrations of $NH_3(g)$ and $HCl(g)$, which, in turn, means that the mass of $NH_4Cl(s)$ will decrease.

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.

Answer. Because $NH_4Cl(s)$ is a solid, it does not appear in the equilibrium constant expression; thus, the mass of $NH_4Cl(s)$ does not affect the equilibrium reaction's position and the concentration of NH_3 remains the same.

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.

Answer. We know that HY is a weak acid, which means that NaY is a weak base. The pH of any solution that includee just a weak base must be greater than 7.

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?

Answer. To find the pH we calculate the moles of H_3O^+ in each solution, add them together, and then divide by their combined volumes. For a pH of 2.15 the H_3O^+ is 0.00708 M, and for a pH of 1.35 the $[H_3O^+]$ is 0.0447 M; thus

$$[H_3O^+] = \frac{0.150 \text{ L} \times 0.00708 \text{ M} + 0.100 \text{ L} \times 0.0447 \text{ M}}{0.150 \text{ L} + 0.100 \text{ L}} = 0.0221 \text{ M} H_3O^+$$

and the pH is 1.65.

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?

Answer. The information on the mass of hippuric acid that dissolves to make a saturated solution allows us to calculate its analytical concentration; thus

$$\frac{3.75 \times 10^{-3}\ \mathrm{g}}{1.00 \times 10^{-3}\ \mathrm{L}} \times \frac{1\ \mathrm{mol}}{179.17\ \mathrm{g}} = 0.0209\ \mathrm{mol/L}$$

The equilibrium pH is 3.60, which gives the concentration of H_3O^+ as 2.51×10^{-4} M. This also is the concentration of hippuric acid's conjugate base and is the change in concentration of hippuric acid at equilibrium. This leaves us with

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(2.51 \times 10^{-4})(2.51 \times 10^{-4})}{0.0209 - 2.51 \times 10^{-4}} = 3.05 \times 10^{-6}$$

or a pK_a of 5.52.

Problem 5. A microbiologist needs a buffer with a pH of 7.00 to use when preparing bacterial cultures. Solutions of 0.10 M K_2HPO_4 and 0.10 M KH_2PO_4 are available. If you start with 100.0 mL of the K_2HPO_4 solution, how many mL of the KH_2PO_4 solution will you need to make this buffer? The pK_a values for H_3PO_4 are 2.15, 7.20, and 12.38.

Answer. To find the volume of KH_2PO_4 we use the buffer equation; thus

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{\mathrm{mol\ K_2HPO_4}}{\mathrm{mol\ KH_2PO_4}} = 7.20 + \log \frac{(0.10\ \mathrm{M})(0.100\ \mathrm{L})}{(0.10\ \mathrm{M})(x)}$$

Solving for x gives the volume of KH_2PO_4 as 0.158 L or 158 mL. Note that this makes sense as we need more moles of the weak acid than of the weak base to have a pH that is less than the pK_a.

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

Answer. Because the pH is less than the pK_a, we know that there is more of the conjugate weak acid than the conjugate weak base; thus, the buffer has more ability to neutralize strong base than it does strong acid. Note that the answer here does not rely on the answer to the previous question.

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

Answer. Using the buffer equation and the answer to the first question, we have

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{\mathrm{mol\ K_2HPO_4} - \mathrm{mol\ SA}}{\mathrm{mol\ KH_2PO_4} + \mathrm{mol\ SA}} = 7.20 + \log \frac{(0.10\ \mathrm{M})(0.100\ \mathrm{L}) - 1.2 \times 10^{-3}\ \mathrm{mol\ SA}}{(0.10\ \mathrm{M})(0.158\ \mathrm{L}) + 1.2 \times 10^{-3}\ \mathrm{mol\ SA}} = 6.91$$

where SA is the strong acid; Note that this answer makes sense as we expect the pH to decrease when we add a strong acid.

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

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

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

Answer. An ICE table (not shown) tells us that the concentration of Zn^{2+} increases by x and the concentration of OH^- increases by $2x$. Substituting into the K_{sp} expression gives

$$(x)(2x)^2 = 4x^3 = 4.1 \times 10^{-17}$$

Solving for x gives the molar solubility of $Zn(OH)_2$ as 2.17×10^{-6} mol/L, or

$$2.17 \times 10^{-6}\ \mathrm{mol/L} \times \frac{99.396\ \mathrm{g}}{\mathrm{mol}} \times 1.0\ \mathrm{L} = 2.16 \times 10^{-4}\ \mathrm{gZn(OH)_2}$$

The concentration of OH^- is $2x$ or 4.35×10^{-6} M, which is equivalent to a pH of 8.64. Note that this pH makes sense as the dissolution of a hydroxide can only make a solution basic.

Part B. Next, consider the reaction

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

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}.

Answer. The reaction we are working with is not the β_4 reaction, which, instead, is

$$\mathrm{Zn^{2+}}(aq) + \mathrm{4OH^-}(aq) \rightleftharpoons \mathrm{Zn(OH)_4^{2-}}(aq)$$

To find the equilibrium constant for our reaction, we note that it is the sum of the K_{sp} reaction for $Zn(OH)_2$ and the β_4 reaction; thus, the equilibrium constant is

$$K_{\mathrm{sp}} \times \beta_4 = (4.1x10^{-17}) \times (3.0 \times 10^{15}) = 0.123$$

The concentration of OH^- is fixed at 0.10 M by the pH and the concentration of $Zn(OH)_4^{2-}$ is x; thus

$$\frac{x}{(0.1)^2} = 0.123$$

Solving for x gives its value as 0.00123 M, which, using the same approach above, gives the solubility of $Zn(OH)_2$ as 0.122 g/L.