Chem 260 – Second Exam

On the following pages are six problems covering material in equilibrium chemistry. Read each problem carefully and think about how best to approach it before you begin work. If you aren't sure how to begin a problem, then move on; working on a new problem may stimulate an idea that helps you solve the more troublesome one. For problems requiring a written response, be sure that your answer directly and clearly answers the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

When working equilibrium problems, be sure to clearly state and verify any assumptions.

Problem 1 _____/10   Problem 4 _____/20

Problem 2 _____/20   Problem 5 _____/20

Problem 3 _____/10   Problem 6 _____/20

Total_____

A few constants are given here:

$$d_{H_2O} = 1.00 \text{ g/mL} \qquad S_{H_2O} = 4.184 \text{ J/g} \cdot {}^oC$$

$$R = 8.314 \text{ J/mol}_{rxn} \cdot K \qquad F = 96,485 \text{ J/V} \cdot \text{mol e}^-$$

$$K_w = 1.00 \times 10^{-14}$$

Problem 1. In Michael Crichton's novel *The Andromeda Strain* a virus brought back to earth on a satellite proves fatal to anyone who comes in contact with it. There are two survivors in the town where the satellite lands: a wino and a crying baby. The scientists studying the virus discover that it can survive only within the normal pH range of blood, which is 7.35 to 7.45. Crying causes the concentration of $CO_2(g)$ in the baby's lungs to decrease. Knowing that $CO_2(g)$ and H_2O make H_2CO_3, was the baby saved by an increase or a decrease in the pH of his or her blood? Clearly explain your choice in two or three sentences. Include relevant equilibrium reactions in support of your answer.

Answer. The reactions to consider here are $CO_2(g) + H_2O(l) \leftrightarrows H_2CO_3(aq)$ and $H_2CO_3(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HCO_3^-(aq)$. Loss of CO_2 pushes the first reaction to the left, decreasing the concentration of H_2CO_3. The loss of H_2CO_3, in turn, pushes the second reaction to the left, decreasing the concentration of H_3O^+ and raising the pH. Crying saved the baby by making his or her blood more basic.

Problem 2. The pK_a values for several weak acids are shown below; use this information to answer the following:

If you prepare equimolar solutions of these weak acids, which will produce the smallest pH? Defend your choice in one sentence.

weak acid	formula	pK_a
benzoic acid	C_6H_5COOH	4.20
benzylammonium ion	$C_6H_5CH_2NH_3^+$	9.35
chloracetic acid	$ClCH_2COOH$	2.57
hydroxylamine hydrochloride	$H_2NOH\cdot HCl$	5.96
thioacetic acid	$HSCH_2COOH$	3.33

Answer. Chloracetic acid. The smallest pK_a corresponds to the largest K_a, which is the direct measure of a weak acid's relative strength.

Which of the weak acids has the strongest conjugate weak base and what is that base's K_b value? Defend your choice in one sentence.

Answer. Benzylammonium ion. The weaker an acid, the stronger the conjugate weak base; thus, the weak acid with the largest pK_a will have the strongest conjugate base. The K_b value for benzylamine is: $K_b = K_w/K_a = 1.00\times10^{-14}/4.47\times10^{-10} = 2.24\times10^{-5}$.

Will a solution of benzylammonium thioacetate be acidic, basic or neutral? Defend your choice in one or two sentences.

Answer. The solution is acidic. The K_a for benzylammonium is 4.47×10^{-10} and the K_b for thioacetate is 2.13×10^{-11}. Benzylammonium is a stronger weak acid than thioacetate is a weak base; thus, the solution is acidic.

Write the K_a reaction for hydroxylamine hydrochloride.

Answer. $^+H_3NOH + H_2O \leftrightarrows H_3O^+ + H_2NOH$

Problem 3. The simplest amino acid is glycine, which has the formula $H_2N\text{-}CH_2\text{-}COOH$. Glycine is a polyprotic weak acid with a K_a of 4.47×10^{-3} for the –COOH functional group and a K_b of 6.03×10^{-5} for the –NH_2 functional group. When dissolved in water at a pH of 7, in which of the following forms will glycine be present:

$^+H_3N\text{-}CH_2\text{-}COOH$ $\boxed{^+H_3N\text{-}CH_2\text{-}COO^-}$ $H_2N\text{-}CH_2\text{-}COOH$ $H_2N\text{-}CH_2\text{-}COO^-$

Circle your choice and, in two to four sentences, clearly explain why your choice is correct. <u>Your explanation must be grounded in equilibrium acid/base chemistry</u>.

Answer. The K_a value for –NH_3^+, the conjugate weak acid of the –NH_2 functional group is 1.65×10^{-10}. The two pK_a values, therefore, are 2.35 and 9.78. At a pH of 7, glycine will lose one of its two protons, which must be from the –COOH functional group as it is the stronger of the two weak acid sites. The correct structure, therefore, is

$$^+H_3N\text{-}CH_2\text{-}COO^-$$

Problem 4. The base putrescine, $H_2N(CH_2)_4NH_2$, plays a key role in the formation of the neurotransmitter GABA. A solution prepared by adding 0.882 g of putrescine to 100.0 mL of water has a pH of 11.32. What is the value of K_{b1} for putrescine? Although putrescine is dibasic, only the first base dissociation affects the solution's pH.

Answer. The molar mass of putrescine is 88.156 g/mol. The solution of putrescine, therefore, is 0.100 M. The pH of 11.32 corresponds to a pOH of 2.68, which gives [OH⁻] as 2.09×10^{-3}. Using an ICE table, with known values in **bold**, we have

$H_2N(CH_2)_4NH_2$	+	H_2O	⇆	OH^-	+	$H_2N(CH_2)_4NH_3^+$
0.100		-		**0**		**0**
-2.09×10^{-3}				$+2.09\times10^{-3}$		$+2.09\times10^{-3}$
0.09791				$\mathbf{2.09\times10^{-3}}$		2.09×10^{-3}

Substituting the equilibrium concentrations into the K_{b1} expression gives:

$$K_{b1} = \frac{[OH^-][H_2N(CH_2)_4NH_3^+]}{[H_2N(CH_2)_4NH_2]} = \frac{(2.09\times10^{-3})(2.09\times10^{-3})}{0.09791} = 4.46\times10^{-5}$$

Problem 5. In lab you standardized a solution of NaOH by titrating it against a solution containing the weak acid potassium hydrogen phthalate, $KC_8H_5O_4$, which also is known as KHP. Suppose that you dissolve 0.312 g of KHP in 51.2 mL of water. What is the pH of this solution? The pK_a for KHP is 5.408.

Answer. The molar mass of KHP is 204.22 g/mol. The solution of KHP, therefore, is 2.98×10^{-2} M. Using an ICE table, with known values in **bold**, we have

KHP	+	H_2O	$\leftrightarrows$	H_3O^+	+	KP^-
2.98×10⁻²		-		**0**		**0**
-X		-		+X		+X
$2.98 \times 10^{-2} - X$		-		X		X

Substituting the equilibrium concentrations into the K_a expression gives

$$K_a = \frac{[H_3O^+][KP^-]}{[KHP]} = \frac{(X)(X)}{2.98 \times 10^{-2} - X} = 3.91 \times 10^{-6}$$

Because KHP is a relatively weak acid, we can try the assumption that $2.98 \times 10^{-2} - X$ is approximately 2.98×10^{-2}; thus

$$K_a = \frac{[H_3O^+][KP^-]}{[KHP]} = \frac{(X)(X)}{2.98 \times 10^{-2}} = 3.91 \times 10^{-6}$$

Solving gives X as 3.41×10^{-4}. The error in the assumption is $100 \times (3.41 \times 10^{-4}/2.98 \times 10^{-2})$, or 1.15%, so the assumption is ok. The $[H_3O^+]$ is X, so the pH is 3.47.

Problem 6. Suppose that you need to prepare a buffer with a pH of 5.00. You already have 750 mL of a buffer that is 0.15 M in CH_3COOH and 0.50 M in CH_3COO^-. You also have access to 6.0 M HCl and 6.0 M NaOH. Clearly explain how you will prepare this buffer? The pK_a of CH_3COOH is 4.76.

Answer. First we must determine the pH of the original buffer, which is

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.76 + \log\left(\frac{0.50}{0.15}\right) = 5.28$$

Because we want to decrease the pH to 5.00 we must add a strong acid. To determine the moles of strong acid to add we first need to determine the moles of CH_3COOH and CH_3COO^- that are in the 750 mL of buffer; thus

$$\text{moles } CH_3COOH = 0.15 \text{ M} \times 0.750 \text{ L} = 0.1125$$

$$\text{moles } CH_3COO^- = 0.50 \text{ M} \times 0.750 \text{ L} = 0.375$$

Then

$$5.00 = pK_a + \log\left(\frac{\text{moles } CH_3COO^- - \text{moles } H_3O^+}{\text{moles } CH_3COOH + \text{moles } H_3O^+}\right) = 4.76 + \log\left(\frac{0.375 \text{ - X}}{0.1125 + X}\right)$$

$$0.24 = \log\left(\frac{0.375 \text{ - X}}{0.1125 + X}\right)$$

$$1.738 = \frac{0.375 \text{ - X}}{0.1125 + X}$$

Solving gives X as 0.06556 moles of H_3O^+. The necessary volume of 6.0 M HCl, therefore, is

$$0.06556 \text{ moles } H_3O^+ \times (1.0 \text{ L}/6.0 \text{ moles } H_3O^+) \times (1000 \text{ mL/L}) = 10.9 \text{ mL}$$