Chem 116 POGIL Worksheet - Week 10 - Solutions Weak Acid and Base Equilibria

Key Questions

1. A 0.0100 M solution of a weak acid HA has a pH of 2.60. What is the value of K_a for the acid? [Hint: What is the actual concentration of undissociated HA, [HA], in this solution?]

$$pH = 2.60 \Rightarrow [H_3O^+] = 2.5 \times 10^{-3} M$$

We can assume that the acid is the major source of hydronium ion and that water contributes little to the total $[H_3O^+]$. This concentration of hydronium ion, then, also represents the amount of the initial HA that is lost through hydrolysis. On this basis we have the following equilibrium concentrations:

Initial HA + H₂O
$$\Rightarrow$$
 H₃O⁺ + A⁻
Initial 0.0100 10⁻⁷ 0
Equilibrium 0.0100 - 0.0025 2.5 x 10⁻³ 2.5 x 10⁻³
= 0.0075 $K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(2.5 \times 10^{-3})^2}{7.5 \times 10^{-3}} = 8.3 \times 10^{-4}$

2. What is the pH of 4.0×10^{-2} M benzoic acid (C₆H₅CO₂H = HBz), for which $K_a = 6.46 \times 10^{-5}$? Is it necessary to solve the quadratic equation in this case?

$$HBz + H_2O \Rightarrow H_3O^+ + Bz^-$$

The concentration of the acid and the K_a fit our criteria to avoid needing the quadratic equation.

$$[H_3O^+] = \sqrt{(4.0 \times 10^{-2})(6.46 \times 10^{-5})} = \sqrt{2.5_{84} \times 10^{-6}} = 1.6 \times 10^{-3} M = [Bz^-]$$

pH = 2.79

The percent dissociation of the benzoic acid, based on our calculation, is

% dissociation =
$$\frac{1.6 \times 10^{-3}}{4.0 \times 10^{-2}} \times 100\% = 4.0\%$$

This is acceptable, so the quadratic equation was not necessary.

3. Find the concentrations of all species and pH for a 1.0×10^{-3} M HF solution. $K_a = 6.7 \times 10^{-4}$. You will need to find values for [HF], [H₃O⁺], [F⁻], and [OH⁻].

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

Trying the quick method, we obtain

$$[H_3O^+] = \sqrt{C_{HA}K_a} = \sqrt{(1.0 \times 10^{-3})(6.7 \times 10^{-4})} = 8.2 \times 10^{-4} M = [F^-]$$

% dissociation =
$$\frac{8.2 \times 10^{-4}}{1.0 \times 10^{-3}} \times 100\% = 82\%$$

This is not acceptable. Notice that $C_{\text{HA}} = 1.0 \text{ x } 10^{-3}$ and $K_a = 6.7 \text{ x } 10^{-4}$ are within two powers of 10 of each other, suggesting that HF is appreciably dissociated. We must solve the quadratic. This means that we will assume [HF] = $C_{\text{HF}} - [\text{H}_3\text{O}^+]$. Substituting into the K_a expression:

$$K_a = 6.7 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]^2}{1.0 \times 10^{-3} - [\text{H}_3\text{O}^+]}$$
$$[\text{H}_3\text{O}^+]^2 = 6.7 \times 10^{-7} - 6.7 \times 10^{-4} [\text{H}_3\text{O}^+]$$
$$[\text{H}_3\text{O}^+]^2 + 6.7 \times 10^{-4} [\text{H}_3\text{O}^+] - 6.7 \times 10^{-7} = 0$$

Solving the quadratic equation and ignoring the negative root (-1.22×10^{-3}) gives

$$[H_3O^+] = 5.4_9 \times 10^{-4} \text{ M} = [\text{F}^-] \implies \text{pH} = 3.26$$
$$[\text{HF}] = C_{\text{HF}} - [H_3O^+] = 1.0 \times 10^{-3} - 5.4_9 \times 10^{-4} = 4.5_1 \times 10^{-4} \text{ M}$$

To find [OH[–]], use K_w :

$$[OH^{-}] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{5.49 \times 10^{-4}} = 1.8_2 \times 10^{-11} M$$

4. What is the pH of a 0.120 M solution of $NH_3(aq)$? For ammonia, $K_b = 1.77 \times 10^{-5}$. Is it necessary to solve the quadratic equation? Justify the approach you took, either way.

The hydrolysis equilibrium and the equilibrium concentrations are as follows:

$$\begin{array}{rcl} \mathrm{NH}_3 &+& \mathrm{H}_2\mathrm{O} &\rightleftharpoons & \mathrm{NH}_4^+ &+& \mathrm{OH}^-\\ 0.120 - x & & x & x \end{array}$$

The analytical concentration of ammonia is 0.120 M, which is greater than $K_b = 1.77 \times 10^{-5}$ by much more than two powers of 10. Therefore, we can probably ignore the loss of NH₃ from hydrolysis. Thus, we can write

$$K_b = \frac{[\mathrm{NH}_4^+][\mathrm{OH}^-]}{[\mathrm{NH}_3]} = \frac{x^2}{0.120 - x} \approx \frac{x^2}{0.120} = 1.77 \times 10^{-5}$$

and

$$x = \sqrt{(0.120)(1.77 \times 10^{-5})} = 1.48 \times 10^{-3} \text{M} = [\text{OH}^{-}] = [\text{NH}_4^+]$$

From this result, the percent hydrolysis is much less than 5%:

% hydrolysis =
$$\frac{1.48 \times 10^{-3}}{0.120} \times 100\% = 1.23\%$$

Therefore, we are justified in ignoring loss of NH₃ from hydrolysis and avoiding the quadratic equation.

To obtain pH, we could calculate $[H_3O^+] = K_w/[OH^-]$, and then get pH; or we could calculate pOH from our value of $[OH^-]$, and get pH from pH = 14.000 – pOH. Taking the second approach, we have

 $pOH = -log(1.48 \times 10^{-3}) = 2.830 \implies pH = 14.000 - 2.830 = 11.170$

- 5. Sodium hypochlorite, NaOCl, is the active ingredient in chlorine bleach (e.g., Chlorox[©]). For hypochlorous acid, HOCl, $K_a = 3.0 \times 10^{-8}$.
 - a. Write the equation for the base hydrolysis equilibrium of the hypochlorite ion.

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

b. What is the value of K_b for the hypochlorite ion?

$$K_b^{\text{OCl}^-} = K_w / K_a^{\text{HOCl}} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3_3 \times 10^{-7}$$

c. What is the pH of a 0.10 M solution of sodium hypochlorite?

In solution, the 0.10 M NaOCl will break up into 0.10 M Na⁺ and 0.10 M OCl⁻. Therefore, the analytical concentration of the base is $C_{\text{OCl}^-} = 0.10 \text{ M}$.

$$NaOCl \rightarrow Na^{+} + OCl^{-}$$
$$OCl^{-} + H_2O \rightleftharpoons HOCl + OH^{-}$$
$$0.10 - x \qquad x \qquad x$$

Because the analytical concentration of the base is so much greater than K_b , loss of OCl⁻ is negligible, and we can assume [OCl⁻] $\approx C_{\text{OCl}^-} = 0.10$ M. Therefore,

$$[OH^{-}] = \sqrt{C_{OC1} - K_b^{OC1^{-}}} = \sqrt{(0.10)(3.3_3 \times 10^{-7})} = 1.8_{25} \times 10^{-4}$$

From this, pOH = 3.74, and pH = 14.00 – 4.24 = 10.26.

6. Trimethylamine, $(CH_3)_3N$, is a weak base $(K_b = 6.4 \times 10^{-5})$ that hydrolyzes by the following equilibrium:

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

a. Write the equation for the acid hydrolysis equilibrium of trimethylammonium ion, $(CH_3)_3NH^+$.

$$(CH_3)_3NH^+ + H_2O \rightleftharpoons (CH_3)_3N + H_3O^+$$

b. What is the value of K_a for the trimethylammonium ion, $(CH_3)_3NH^+$?

$$K_a^{(CH_3)_3NH^+} = K_w/K_b^{(CH_3)_3N} = 1.0 \times 10^{-14}/6.4 \times 10^{-5} = 1.5_6 \times 10^{-10}$$

c. What is the pH of a 0.12 M solution of trimethylammonium chloride, $((CH_3)_3NH)Cl?$

$$((CH_3)_3NH)Cl \Rightarrow (CH_3)_3NH^+ + Cl^-$$
$$(CH_3)_3NH^+ + H_2O \rightleftharpoons (CH_3)_3N + H_3O^+$$
$$0.12 - x \qquad x \qquad x$$

With $K_a = 1.5_6 \times 10^{-10}$, (CH₃)₃NH⁺ is a very weak acid, so we can definitely ignore hydrolysis and assume [(CH₃)₃NH⁺] = $C_{(CH_3)_3NH^+} = 0.12M$.

$$[H_{3}O^{+}] = \sqrt{C_{(CH_{3})_{3}NH^{+}}K_{a}^{(CH_{3})_{3}NH^{+}}} = \sqrt{(0.12)(1.5_{6} \times 10^{-10})} = 4.3 \times 10^{-6}M$$
$$pH = 5.36$$

- 7. Explain the following observations:
 - a. H_2Se is a stronger acid than H_2S Se is larger than S, so the Se–H bond is weaker, making H_2Se a stronger acid.

- b. HNO_2 is a weak acid, but HNO_3 is a strong acid HNO_2 has one terminal oxygen, but HNO_3 has two, making it a stronger acid.
- c. H_3PO_4 is a stronger acid than H_3AsO_4 P is more electronegative than As, making H_3PO_4 a stronger acid.
- FCH₂CO₂H is a stronger acid than CH₃CO₂H Electronegative fluorine withdraws electron density from the -OH bond of the carboxyl group, -CO₂H, making FCH₂CO₂H a stronger acid.
- 8. What is the pH of a solution prepared by adding 0.20 mole of formic acid, HCO₂H, and 0.25 mole of sodium formate, NaHCO₂, in enough water to make a liter of solution? The K_a of formic acid is 1.8×10^{-4} .

$$K_{a} = \frac{[\text{H}_{3}\text{O}^{+}][\text{HCO}_{2}^{-}]}{[\text{HCO}_{2}\text{H}]} = \frac{[\text{H}_{3}\text{O}^{+}](0.25)}{0.20} = 1.8 \times 10^{-4}$$
$$[\text{H}_{3}\text{O}^{+}] = 1.44 \times 10^{-4}$$
$$\text{pH} = 3.84$$

9. What is the pH of a solution prepared by adding 0.60 mole of formic acid and 0.75 mole of sodium formate in enough water to make a liter of solution? How does your answer compare to the answer you obtained in Key Question 8? Explain.

$$K_{a} = \frac{[H_{3}O^{+}][HCO_{2}^{-}]}{[HCO_{2}H]} = \frac{[H_{3}O^{+}](0.75)}{0.60} = 1.8 \times 10^{-4}$$
$$[H_{3}O^{+}] = 1.44 \times 10^{-4}$$
$$pH = 3.84$$

The pH is the same in both cases because the ratio $[HCO_2^-]/[HCO_2H]$ is the same in both cases.

10. The solution prepared in Key Question 9 was diluted with enough water to make ten liters of solution. What is the pH of the dilute solution? How does it compare to the previous two solutions? Explain.

Diluting to ten liters makes the analytical concentrations of both the acid and its conjugate base become one tenth what they were; i.e.,

 $C_{\rm HCO_2H} = 0.060 \,{\rm M}$. $C_{\rm HCO_2} = 0.075 \,{\rm M}$

But the ratio $[HCO_2^-]/[HCO_2H]$ remains the same as it was in the solutions in Key Questions 8 and 9, so the pH is still 3.84.

$$K_{a} = \frac{[\text{H}_{3}\text{O}^{+}][\text{HCO}_{2}^{-}]}{[\text{HCO}_{2}\text{H}]} = \frac{[\text{H}_{3}\text{O}^{+}](0.075)}{0.060} = 1.8 \times 10^{-4}$$
$$[\text{H}_{3}\text{O}^{+}] = 1.44 \times 10^{-4}$$
$$\text{pH} = 3.84$$

It is the ratio between the concentrations of the conjugate pair that fixes the pH in solutions of this type, not the actual concentrations themselves.

11. A student wishes to prepare a buffer with a pH of 4.52. She starts by preparing one liter of 0.10 M formic acid, HCO₂H. How many grams of sodium formate, NaHCO₂, must she add to the solution to achieve the desired pH? $K_a = 1.8 \times 10^{-4}$ for formic acid. The formula weight of sodium formate is 68.00 u.

First we need to determine what concentration of hydronium ion corresponds to pH = 4.54.

$$[H_3O^+] = 10^{-4.52} = 3.0 \times 10^{-5} \text{ M}$$

Next, by substituting into the K_a expression, we determine the ratio [HCO₂⁻]/[HCO₂H] that will give [H₃O⁺] = 3.0×10^{-5} M..

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = \frac{1.8 \times 10^{-4}}{3.0 \times 10^{-5}} = 6.0$$

One liter of 0.10 M HCO₂H contains 0.10 mol of the acid. Therefore,

g NaHCO₂ = (0.10 mol HCO₂H)
$$\left(\frac{6 \text{ mol NaHCO}_2}{1 \text{ mol HCO}_2\text{H}}\right) \left(\frac{68.00 \text{ g NaHCO}_2}{\text{mol NaHCO}_2}\right) = 40.8 \text{ g NaHCO}_2$$

12. A buffer solution is made by adding an equal number of moles of the base pyradine, C_5H_5N , and the chloride salt of it conjugate base, C_5H_5NHCl . What is the pH of the buffer solution? The K_b of C_5H_5N is 1.7×10^{-9} .

If $[C_5H_5N] = [C_5H_5NH^+]$, then substituting into the K_b expression gives

$$K_{b} = \frac{[C_{5}H_{5}NH^{+}][OH^{-}]}{[C_{5}H_{5}N]} = [OH^{-}]$$

For any equimolar mixture of a base and its conjugate acid, $[OH^-] = K_b$, from which it follows pOH = p K_b .

 $pOH = -\log(1.7 \times 10^{-9}) = 8.77$

pH = 14.00 - pH = 5.23