In Class Exercise for Chapter 17

1. Determine the pH for each of the following.

a.)
$$0.500 \ \underline{M} \ H_2SO_3 \ \text{with} \ K_{a1} = 1.5 \ \text{x} \ 10^{-2} \ \text{and} \ K_{a2} = 6.3 \ \text{x} \ 10^{-8}$$

$$H_2SO_{3(aq)} \rightleftharpoons H_{(aq)}^+ + HSO_{3(aq)}^-$$

$$H_2SO_{3(aq)} \qquad H_{(aq)}^+ \qquad HSO_{3(aq)}^-$$

$$I \qquad 0.500 \qquad 0 \qquad 0$$

$$C \qquad -x \qquad +x \qquad +x$$

$$E \qquad 0.500 - x \qquad +x \qquad +x$$

$$E \qquad 0.500 - x \qquad +x \qquad +x$$

$$K_{a1} = \frac{\left[H_{(aq)}^+\right] \left[HSO_{(aq)}^-\right]}{\left[H_2SO_{3(aq)}\right]} = 1.5 \times 10^{-2} = \frac{x^2}{0.500 - x} \rightarrow x^2 + 0.015x - 0.0075 = 0$$

$$\left[H_{(aq)}^+\right] = 7.94 \times 10^{-2} \ \underline{M} = \left[HSO_{(aq)}^-\right]$$

Since this is a polyprotic acid we are not done yet.

$$HSO_{3(aq)}^{-} \rightleftharpoons H_{(aq)}^{+} + SO_{3(aq)}^{2-}$$

$$HSO_{3(aq)}^{-} \qquad H_{(aq)}^{+} \qquad SO_{3(aq)}^{2-}$$

$$I \qquad 0.0794 \qquad 0.0794 \qquad 0$$

$$C \qquad -x \qquad +x \qquad +x$$

$$E \qquad 0.0794 - x \qquad 0.0794 + x \qquad +x$$

$$K_{a2} = \frac{\left[H_{(aq)}^{+}\right]\left[SO_{3(aq)}^{2-}\right]}{\left[HSO_{3(aq)}^{-}\right]} = 6.3 \times 10^{-8} = \frac{(0.0794 + x)x}{0.0794 - x} \sim x \text{ since } 10^{-8} << 10^{-2}$$

$$\left[H_{(aq)}^{+}\right] = 7.94 \times 10^{-2} \underline{M} \therefore pH = -\log(7.94 \times 10^{-2}) = 1.10$$

Therefore, the second deprotonation does not significantly contribute to our pH.

b.) 0.300 M Na₂SO₃

$$SO_{3(aq)}^{2-} + H_2O_{(l)} \rightleftharpoons OH_{(aq)}^{-} + HSO_{3(aq)}^{-}$$

$$SO_{3(aq)}^{2-} OH_{(aq)}^{-} HSO_{3(aq)}^{-}$$

$$I \quad 0.300 \quad 0 \quad 0$$

$$C \quad -x \quad +x \quad +x$$

$$E \quad 0.300 - x \quad +x \quad +x$$

$$K_b = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-8}} = 1.59 \times 10^{-7}$$

$$K_b = \frac{\left[OH_{(aq)}^{-}\right] \left[HSO_{3(aq)}^{-}\right]}{\left[SO_{3(aq)}^{2-}\right]} = 1.59 \times 10^{-7} = \frac{x^2}{0.300 - x} \sim \frac{x^2}{0.300} \text{ since } 10^{-7} << 10^{-1}$$

$$\left[OH_{(aq)}^{-}\right] = 2.18 \times 10^{-4} \underline{M} \therefore pH = 14 + \log(2.18 \times 10^{-4} \underline{M}) = 10.34$$

c.) 0.300 L solution containing 0.500 M NaHSO3 and 0.300 M Na₂SO₃

$$HSO_{3(aq)}^{-} \rightleftharpoons H_{(aq)}^{+} + SO_{3(aq)}^{2-}$$

$$pH = pK_{a} + \log \left(\frac{\left[SO_{3(aq)}^{2-} \right]}{\left[HSO_{3(aq)}^{-} \right]} \right)$$

$$pH = -\log(6.3 \times 10^{-8}) + \log \left(\frac{0.300}{0.500} \right)$$

$$pH = 6.98$$

2. Determine the molar solubility for each of the following:

a.)
$$0.500 \ \underline{M} \ \text{PbI}_2 \ \text{with} \ K_{sp} = 1.4 \times 10^{-8}$$

$$PbI_{2(s)} \rightleftharpoons Pb_{(aq)}^{2+} + 2I_{(aq)}^{-}$$

$$Pb_{(aq)}^{2+} \qquad I_{(aq)}^{-}$$

$$I \qquad 0 \qquad 0$$

$$C \qquad +s \qquad +2s$$

$$E \qquad +s \qquad +2s$$

$$K_{sp} = 1.4 \times 10^{-8} = s \left(2s\right)^2 = 4s^3$$

$$s = 0.0015 \ M \qquad \left[Pb_{(aq)}^{2+}\right] = 0.0015 \ M \qquad \& \qquad \left[I_{(aq)}^{-}\right] = 0.0030 \ M$$

b.) 0.300 <u>M</u> HI

$$HI_{(aq)} \rightarrow H_{(aq)}^+ + I_{(aq)}^-$$
 hence $\left[H_{(aq)}^+ \right] = \left[I_{(aq)}^- \right] = 0.300 M$

c.) 1 L solution containing 0.500 M PbI2 and 0.300 M HI

$$Pb_{(aq)}^{2+} \qquad I_{(aq)}^{-}$$

$$I \qquad 0 \qquad 0.300$$

$$C \qquad +s \qquad +2s$$

$$E \qquad +s \qquad 0.300+2s$$

$$K_{sp} = 1.4 \times 10^{-8} = s \left(0.300 + 2s\right)^{2}$$
since $10^{-8} << 10^{-1} \rightarrow 1.4 \times 10^{-8} \sim 0.0900s$ or $s = 1.56 \times 10^{-7} M$

$$ck \text{ assumption: } \frac{1.56 \times 10^{-7}}{0.300} \times 100\% = 5 \times 10^{-5} \%$$

$$\left[Pb_{(aq)}^{2+}\right] = 1.6 \times 10^{-7} M \qquad \& \qquad \left[I_{(aq)}^{-}\right] = 0.300 M$$

3. . Calculate the pOH and the concentrations of all species in a solution prepared by mixing equal volumes of 0.2 M HCl and 0.6 M H_2SO_4 ($K_{a2} = 1.2 \times 10^{-2}$).

we have two strong acids which completely dissociate:

$$HCl \rightarrow H^+ + Cl^-$$
 and $H_2SO_4 \rightarrow H^+ + HSO_4^-$

Initially:
$$\left[H^{+}\right] = \frac{1 \times 0.2 \frac{mol}{L} + 1 \times 0.6 \frac{mol}{L}}{2L} = 0.4 \frac{mol}{L} \text{ and } \left[HSO_{4}^{-}\right] = \frac{1 \times 0.6 \frac{mol}{L}}{2L} = 0.3 \frac{mol}{L}$$

since is a polyprotic acid we use the equation below to determine eq:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Initial 0.30 0.4 0
Change -x +x +x
Eq 0.30 - x 0.4+x +x
$$K_a = \frac{\left[H^+\right]\left[SO_4^{2-}\right]}{\left[HSO_4^{-}\right]} = \frac{x(0.4+x)}{0.3-x} = 1.2 \times 10^{-2} \rightarrow x^2 + 0.412x - 0.0036 = 0$$

$$x = \frac{-0.412 \pm \sqrt{0.412^2 - 4(1)(-0.0036)}}{2} \rightarrow x = 0.0085M \text{ or } x = -0.420M$$

$$\left[HSO_4^-\right] = 0.3 - x = 0.291M \rightarrow 0.3M$$

$$\left[H^+\right] = 0.4 + x = 0.409M \rightarrow 0.4M$$

$$\left[SO_4^{2-}\right] = 0.009M$$

$$pOH = 14 - pH = 14 + \log\left[H^+\right] = 13.60$$

4. What is the pH at the endpoint for titration of 0.20 M solutions of the following:

a.)
$$C_5H_{11}N$$
 (piperidine – $K_b = 1.3 \times 10^{-3}$) & HNO₃

When we add equal amounts of acid and base they react completely to produce salt and water: $C_5H_{11}N + HNO_3 \rightarrow C_5H_{11}NH^+NO_3^-$ or $C_5H_{11}N + H^+ \rightarrow C_5H_{11}NH^+$ Furthermore, addition of equal amounts will cut our concentrations in half. So, we start with the $0.10 \ \underline{M} \ C_5H_{11}NH^+$ in water.

$$C_{5}H_{11}NH^{+} + H_{2}O \rightleftharpoons C_{5}H_{11}N + H_{3}O^{+}$$

$$C_{5}H_{11}NH^{+} \qquad H_{(aq)}^{+} \qquad C_{5}H_{11}N$$

$$I \qquad 0.10 \qquad 0 \qquad 0$$

$$C \qquad -x \qquad +x \qquad +x$$

$$E \qquad 0.10 - x \qquad +x \qquad +x$$

$$K_{a} = \frac{K_{w}}{K_{b}} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-3}} = 7.7 \times 10^{-12}$$

$$K_{a} = 7.7 \times 10^{-12} = \frac{x^{2}}{0.10 - x} \sim \frac{x^{2}}{0.10} \text{ since } 10^{-12} <<10^{-1}$$

$$\left[H^{+}\right] = 8.8 \times 10^{-7} \underline{M} \therefore pH = 6.06$$

b.) NaHSO₃ ($K_a = 6.3 \times 10^{-8}$) & NaOH

Similar to the last problem in which our acid HSO_3^- has been completely neutralized by the hydroxide. So we have $0.10 \, \underline{M} \, SO_3^{2-}$ in water.

$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$$

$$SO_3^{2-} OH^- HSO_3^-$$

$$I 0.10 0 0 0$$

$$C -x +x +x +x$$

$$E 0.10 - x +x +x$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-8}} = 1.6 \times 10^{-7}$$

$$K_b = 1.6 \times 10^{-7} = \frac{x^2}{0.10 - x} \sim \frac{x^2}{0.10} \text{ since } 10^{-7} << 10^{-1}$$

$$OH^- = 1.26 \times 10^{-4} \underline{M} \therefore pH = 14 + \log(1.26 \times 10^{-4}) = 10.10$$

c.) Ba(OH)₂ & HBr

$$Ba(OH)_{2(aq)} \rightarrow Ba_{(aq)}^{2+} + 2OH_{(aq)}^{-}$$

$$HBr_{(aq)} \rightarrow H_{(aq)}^{+} + Br_{(aq)}^{-}$$
the rxn is really btwn $H_{(aq)}^{+}$ and $OH_{(aq)}^{-}$

$$H_{(aq)}^{+} + OH_{(aq)}^{-} \rightarrow H_{2}O_{(l)} \quad pH = 7.00$$