1) (20 pts) Consider the titration of 50.0ml of 0.10 M Chlorous acid (HClO₂) with 0.10 M NaOH.

\[
\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_2^- \\
K_a = 1.1 \times 10^{-2} \quad \text{p}K_a = 1.96
\]

a) (5 pts) Calculate the pH of the initial solution (50.0 ml of 0.10 M HClO₂).

\[
\begin{align*}
\text{HClO}_2 &\rightleftharpoons \text{H}^+ + \text{ClO}_2^- \\
[\text{HClO}_2] &= 0.1 \\
K_a &= 1.1 \times 10^{-2} \\
\frac{x^2}{0.1} &= 1.1 \times 10^{-2} \\
x &= [\text{H}^+] = 3.3 \times 10^{-2} \\
\text{pH} &= 1.48
\end{align*}
\]

b) (5 pts) What is the pH of the solution after the addition of 25.0 ml of the 0.10 M NaOH? (50.0ml of 0.10 M HClO₂ mixed with 25.0 ml of 0.10 M NaOH).

\[
\begin{align*}
\text{eq. pt.} &\quad \text{so} \quad \text{pH} = \text{p}K_a = 1.96 \\
0.10 \text{M} &\quad \left( \frac{50}{75} \right) = 0.066 \\
0.10 \text{M} &\quad \left( \frac{25}{75} \right) = 0.033 \text{M} \\
\text{majority} &\quad \text{HClO}_2 + \text{OH}^- \rightarrow \text{ClO}_2^- \\
\text{minority} &\quad \text{pH} = \text{p}K_a + \text{p}K_b = 1.96
\end{align*}
\]

\[
\begin{align*}
\text{pH} &= 1.96
\end{align*}
\]
c) (10 pts) Calculate the pH of the solution after the addition of 50.0 ml of the 0.10M NaOH. (50.0 ml of 0.10 M HClO₂ mixed with 50.0 ml of 0.10 M NaOH)

\[ \text{Majority} \quad \text{HClO}_2 + \text{OH}^- \rightarrow \text{ClO}_2^- \]
\[ \text{Minority} \quad \text{K}_a = \frac{10^{-14}}{10^{-5.4}} = 9.1 \times 10^{-11} \]

\[ \text{ClO}_2^- + \text{H}_2\text{O} \rightarrow \text{HClO}_2 + \text{OH}^- \]

\[ k_a = 9.1 \times 10^{-11} = \frac{x^2}{0.050} \]

\[ y \times = [\text{OH}^-] = 2.1 \times 10^{-7} \]

\[ \text{pH} = \frac{0.10 - 4.7}{2.0} \]

2) (25 pts)

a) (5 pts) Consider a weak acid, HA, with \( pK_a = 4.70 \). You want to make a buffer solution with \( \text{pH} = 5.00 \). What ratio of \([\text{A}^-]/[\text{HA}]\) do you want your buffer solution to have?

\[ \frac{[\text{A}^-]}{[\text{HA}]} = 10^{\text{pH} - \text{p}K_a} = 10^{5.0 - 4.7} = 2.0 \]

b) (5pts) Is this buffer more resistant to the addition of acid or base? (i.e. Is the buffer capacity greater for the addition of acid or addition of base?)

The buffer is more resistant to the addition of \( \text{acid} \)
c) (5 pts) Consider a weak acid, HA, with $pK_a = 4.70$. You want to make a buffer solution with $pH = 4.70$. You start with 100.0 ml of a 1.00 M solution of NaA. You can add either 1.00 M HCl or 1.00 M NaOH. Which do you add and how much (in ml)?

\[ A^- + H^+ \rightarrow HA \]

\[ 2 \rightarrow 1 \quad \text{RATIO} \]

So, 100 m\text{NaA} = \frac{50 \text{mL}}{1 \text{mHCl}}

Add: 1.00 M HCl \hspace{1cm} 1.00 M NaOH

volume added = \boxed{50} \text{ml}

(circle one)

---

d) (10 pts) Consider a weak acid, HA, with $pK_a = 5.20$. You start with 100.0 ml of a solution in which $[A^-] = 0.40 M$ and $[HA] = 0.60 M$. You add 100 ml of a 0.10 M NaOH solution. What is the change in pH caused by addition of the NaOH?

\[ \text{Initial} \]

\[ p\text{H} = pK_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) = 5.2 + \log_{10} \left( \frac{0.40}{0.60} \right) = 5.02 \]

\[ \text{Add OH}^- \]

\[ [\text{OH}^-] \rightarrow 0.05 M \]

\[ [\text{HA}] \rightarrow 0.30 M \]

\[ [A^-] \rightarrow 0.20 M \]

\[ \text{Dilution} \]

\[ \begin{array}{c|c|c|c}
  \text{I} & 0.30 & 0.050 & 0.20 \\
  \text{C} & -0.050 & -0.050 & +0.050 \\
  \hline
  k & 0.25 & 0 & 0.25 \\
\end{array} \]

\[ \text{Majority} \]

\[ \text{HA} + \text{OH}^- \rightarrow A^- \]

\[ \text{change} = +0.18 \]

\[ p\text{H} = pK_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) = 5.2 + \log_{10} \left( \frac{0.25}{0.25} \right) = 5.2 \]

\[ \text{change} \]

\[ \text{on addition of base} = \boxed{+0.18} \]
H₂A is a weak diprotic acid, whose sodium salt is Na₂A. The following shows the result of titrating 100ml of a solution of Na₂A with 1.0M HCl. The letters indicate some points along this titration curve. Circle the majority (or dominant) species present at each of these points (i.e. circle those species that are present with large concentrations at each of these points).

(circle the majority species present at each of the indicated points in the titration curve)
4) (35 pts)

a) (5pts) Calculate the solubility of PbI\(_2\) in distilled water (in mol/liter). \([K_{sp}(PbI_2) = 1.4 \times 10^{-8}]\)

\[
PbI_2 (s) \rightleftharpoons Pb^{2+} + 2I^{-} \\
K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}] [I^{-}]^2 = a (2a)^2 = 4a^3 \\
a = \sqrt[3]{1.4 \times 10^{-8}} = 1.5 \times 10^{-3} \\
solubility = 1.5 \times 10^{-3} \text{ mol/liter}
\]

b) (7pts) Calculate the solubility of PbI\(_2\) in 0.1 M NaI (in mol/liter).

\[
PbI_2 (s) \rightleftharpoons Pb^{2+} + 2I^{-} \\
K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}] [I^{-}]^2 \\
1.4 \times 10^{-8} = a (0.1)^2 \\
a = 1.4 \times 10^{-6} \\
solubility = 1.4 \times 10^{-6} \text{ mol/liter}
\]

c) (10 pts) Solid M(OH)\(_2\) is put into distilled water. The pH of the resulting solution is 11.2. What is the \(K_{sp}\) for M(OH)\(_2\)?

\[\text{M(OH)}_2 = M^{2+} + 2 \text{OH}^- \quad \text{K}_{sp} = ?\]

\[
\text{pH} = 11.2 \\
\text{pOH} = 14 - 11.2 = 3.8 \\
\text{[OH}^-\text{]} = 10^{-3.8} = 1.6 \times 10^{-4} \\
K_{sp} = (0.8 \times 10^{-4}) (1.6 \times 10^{-4})^2 \\
= 2.0 \times 10^{-12}
\]

\[
K_{sp} = 2.0 \times 10^{-12}
\]

d) (5pts) Consider making a buffer solution with the following pH's. In which buffer solutions is the above M(OH)\(_2\) salt more soluble than in distilled water? (circle all that apply)

Buffer pH:

1 2 3 4 5 6 7 8 9 10 11 12 13 14

(circle all buffer pH's in which M(OH)\(_2\) is more soluble than distilled water)
e) (8 pts)

50.0 ml of a solution containing lead ions with [Pb\(^{2+}\)] = 2.0 \times 10^{-4} \text{ M} is mixed with 50.0 ml of a solution containing iodide ions with a concentration [I\(^-\)] = 2.0 \times 10^{-2}. Does solid PbI\(_2\) form? [PbI\(_2\) has a K\(_{sp}\) of 1.4 \times 10^{-8}] (Please show your work.)

\[
Q = [Pb^{2+}][I^-]^2 = (1.0 \times 10^{-4})(1.0 \times 10^{-2})^2 = 1 \times 10^{-8}
\]

\[Q < K_{sp} \text{ so no precipitate forms.}\]

Solid PbI\(_2\) \(\text{does not}\) form.

5) (10 pts)

a) (5pts) A solution is formed by mixing the following three solutions together:

100 ml of 1.0M NaH\(_2\)PO\(_4\) 100 ml of 1.0M Na\(_2\)HPO\(_4\) 1.0 ml of 0.01M HAc.

What is the ratio of [Ac\(^-\)]/[HAc]? \(\text{H}_3\text{PO}_4\): pK\(_a1\) = 2.12  pK\(_a2\) = 7.21  pK\(_a3\) = 12.67  \(\text{HAc}\): pK\(_a\) = 4.75

\[\text{THE } \text{H}_3\text{PO}_4/\text{HPO}_4^\text{"}\text{H}\text{hold the } \text{pH AT } pK_{a2} = 7.21\]

\[\text{THEN } \frac{[\text{Ac}^-]}{[\text{HAc}]} = 10^{\frac{pK_{a2} - pK_{a}}{2}} = 10^{\frac{7.21 - 4.75}{2}} = 29.0\]

\[\frac{[\text{Ac}^-]}{[\text{HAc}]} = \frac{29.0}{10}\]

b) (5pts) A solution has the following ion concentrations:[Br\(^-\)] = 1.0 M and [Cl\(^-\)] = 1.0 M. You slowly add a solution with [Ag\(^+\)] = 0.01M. What salt forms first: AgCl or AgBr? [K\(_{sp}\) (AgCl) = 1.6 \times 10^{-10};  K\(_{sp}\) (AgBr) = 7.7 \times 10^{-13}]

AgCl \(\text{forms first}\)