Questions are worth 25 points each. OMIT ONE QUESTION by clearly writing OMIT in the space provided for your work. If you fail to mark OMIT on a question I will omit the last question of the test. Show your work and circle your answers for full credit.

1. Calculate the pH of the following solutions:

0.0025 M HClO₄

Since we have a strong acid, we can assume complete dissociation

\[ \text{pH} = \log \left( \frac{1}{0.0025} \right) = 2.60 \]

0.0025 M sodium benzoate

The species affecting the pH is the conjugate base of benzoic acid. \( K_b \) is therefore equal to \( \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} \), and

\[ [OH^-] = \sqrt{\frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}}} \times 0.0025 \]

\[ [OH^-] = 6.3 \times 10^{-7} \text{; pOH} = 6.20, \text{ and } \text{pH} = 7.80 \]

0.050 M NaHCO₃ (sodium bicarbonate)

Sodium bicarbonate is an acid salt, so

\[ [H^+] = \sqrt{K_1 K_2} = \sqrt{(4.3 \times 10^{-7})(4.8 \times 10^{-11})} \]

\[ [H^+] = 4.5 \times 10^{-8}; \text{ pOH} = 8.34 \]

A solution prepared by mixing 27.00 mL of 0.1004 M \( H_3PO_4 \) and 40.00 mL of 0.06777 M \( Na_2HPO_4 \)

\[ \text{Reaction : } \frac{1}{2} H_3PO_4 + HPO_4^{2-} \rightarrow 2 H_2PO_4^{2-} \]

\[ \begin{array}{c|ccc|c}
 & 2.7108 & 2.7108 & 0 \\
\hline
F & 0 & 0 & 5.4216 \\
\hline
\end{array} \]

\[ \Delta \begin{array}{c}
\end{array} -2.7108 -2.7108 +5.4216 \]

we have an acid salt in solution, and

\[ [H^+] = \sqrt{K_1 K_2} = \sqrt{(1.1 \times 10^{-2})(7.5 \times 10^{-8})} \]

\[ [H^+] = 2.9 \times 10^{-5}, \text{ and } \text{pH} = 4.54 \]

0.0250 M KI

Nothing causing ΔpH (Group I cation and conj. base of strong acid) \( \therefore \) pH = 7.00
2. Consider the titration of 50.0 mL of 0.050\(M\) salicylic acid with 0.050\(M\) NaOH. Calculate the pH of the solution at the following points along the titration curve:

a) Before any titrant is added;

The only species in solution is a weak acid; but since \(K_a \times 100 > C_{HA}\), we must use the quadratic form: \[ [H^+] = \frac{-K_a + \sqrt{K_a + 4K_a C_{HA}}}{2}; [H^+] = 6.6 \times 10^{-3} \]

\(\therefore \text{pH} = 2.18\)

b) After 25.0 mL of titrant is added;

From the reaction: \(HA + OH^- \rightarrow A^- + H_2O\)

\[
\begin{array}{c|ccc}
 & I & 2.5 & -1.25 & 0 \\
\Delta & 1.25 & -1.25 & +1.25 \\
\hline
F & 1.25 & 0 & 1.25
\end{array}
\]

we have a weak acid and its conjugate base in solution, and \(\text{pH} = pK_a + \log b/a\)

(Because the conjugate acid/base pair is in the same solution, we can ignore concentrations and use millimolar amounts) \(\text{pH} = 3.00 + \log (1.25 / 1.25), \therefore \text{pH} = 3.00\)

(assuming acid dissociation is negligible, which is borderline for this combination of acid/concentration.)

c) After 40.0 mL of titrant is added;

From the reaction: \(HA + OH^- \rightarrow A^- + H_2O\)

\[
\begin{array}{c|ccc}
 & I & 2.5 & 2.00 & 0 \\
\Delta & 2.00 & 2.00 & +2.00 \\
\hline
F & 0.50 & 0 & 2.00
\end{array}
\]

we have a weak acid and its conjugate base in solution; \(\text{pH} = 3.00 + \log (2.00 / 0.50), \therefore \text{pH} = 3.60\)

(assuming acid dissociation is negligible.)

d) After 50.0 mL of titrant is added;

Equivalence point - only \(A^-\) in solution, \(\therefore [OH^-] = \sqrt{K_b C_{A^-}} = \sqrt{\frac{1.0 \times 10^{-14}}{1.0 \times 10^{-13}}} \cdot \frac{2.5}{100} = \sqrt{500} \times 10^{-7}\)

\([OH^-] = 5.0 \times 10^{-7}; \text{pOH} = 6.30 \therefore \text{pH} = 7.70\)

e) After 60.0 mL of titrant is added.

Only strong base in solution; \([OH^-] = 0.5/110 = 0.0045, \therefore \text{pOH} = 2.34 \therefore \text{pH} = 11.66\)
3. Consider the titration of 25.0 mL of 0.10 M sodium phthalate [Na₂C₆H₄(COO)₂] with 0.10 M HCl. Calculate the pH of the solution at the following points along the titration curve:

a) Before any titrant is added:
   Assuming phthalic acid is H₂A, we have A²⁻ in solution, which is the conjugate base of HA⁻ (K₂), ∴ K_b = K_w / K₂, and:

   \[ [\text{OH}^-] = \sqrt{K_b \frac{C}{A^-}} = \sqrt{\left(\frac{10 \times 10^{-14}}{3.9 \times 10^{-6}}\right)(0.10)} \quad \text{[OH]} = 1.6 \times 10^{-5}; \text{pOH} = 4.80 \]

   ∴ pH = 9.20

b) After 12.5 mL of titrant is added:
   The reaction is A²⁻ + HCl → HA⁻ + Cl⁻
   \[
   \begin{array}{ccc}
   & I & 2.5 & 1.25 & 0 \\
   \Delta & -1.25 & -1.25 & +1.25 \\
   F & 1.25 & 0 & 1.25 \\
   \end{array}
   \]
   ∴ weak acid (HA⁻) and its conjugate base (A²⁻) in solution; pH = pK₂ + log (b/a) \[ \text{pH} = 5.40 + \log \left(\frac{1.25}{1.25}\right); \quad \text{pH} = 5.40 \]

c) After 25.0 mL of titrant is added:
   The reaction is A²⁻ + HCl → HA⁻ + Cl⁻
   \[
   \begin{array}{ccc}
   & I & 2.5 & 2.5 & 0 \\
   \Delta & -2.5 & -2.5 & +2.5 \\
   F & 0 & 0 & 2.5 \\
   \end{array}
   \]
   HA⁻ in solution (acid salt), ∴ \[ [\text{H}^+] = \sqrt{K_1 K_2} = \sqrt{(1.2 \times 10^{-3})(3.9 \times 10^{-6})} \]
   \[ [\text{H}^+] = 6.8 \times 10^{-5}; \quad \text{pH} = 4.16 \]

d) After 37.5 mL of titrant is added:
   The first reaction is A²⁻ + HCl → HA⁻ + Cl⁻
   \[
   \begin{array}{ccc}
   & I & 2.5 & 3.75 & 0 \\
   \Delta & -2.5 & -2.5 & +2.5 \\
   F & 0 & 1.25 & 2.5 \\
   \end{array}
   \]
   This gives us the conditions for the second reaction: HA⁻ + HCl → H₂A + Cl⁻
   (note that the initial conditions for the second reaction come from the final conditions for the first reaction)
   \[
   \begin{array}{ccc}
   & I & 2.5 & 1.25 & 0 \\
   \Delta & -1.25 & -1.25 & +1.25 \\
   F & 1.25 & 0 & 1.25 \\
   \end{array}
   \]
   ∴ weak acid (H₂A) and its conjugate base (HA⁻) in solution; pH = pK₁ + log (b/a) \[ \text{pH} = 2.92 + \log \left(\frac{1.25}{1.25}\right); \quad \text{pH} = 2.92 \]
   (Assuming acid dissociation is negligible, which is borderline for this combination of acid/concentration)

e) After 50.0 mL of titrant is added.
   Second equivalence point - only compound in solution is H₂A. Since H₂A < 100K₁, we need to use the quadratic form:

   \[ [\text{H}^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_{HA}}}{2} \quad \text{[H}^+] = 5.8 \times 10^{-3}; \text{pH} = 2.24 \]
4. The active ingredient in disulfiram, a drug used for the treatment of chronic alcoholism, is tetraethylthiurram disulfide. This drug has a molecular weight of 296.55, and contains four (4) sulfur atoms per molecule. The sulfur in a 0.4329 g sample of disulfiram preparation was oxidized to SO₂, which was absorbed in H₂O₂ to give H₂SO₄. The acid was treated with 22.13 mL of 0.03736 M NaOH. Calculate the percentage tetraethylthiurram disulfide in the preparation.

Starting with what we know...

\[
22.13 \text{ mL} \times 0.03736 \text{ mmol/mL} = 0.8268 \text{ mmol NaOH}
\]

The reaction with sulfuric acid:

\[
\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4
\]

\[
0.8268 \text{ mmol NaOH} / 2 = 0.4134 \text{ mmol H}_2\text{SO}_4 = 0.4134 \text{ mmol S}
\]

There are 4 atoms of sulfur per molecule of tetraethylthiurram disulfide (TET)

\[
0.4134 \text{ mmol S} / 4 = 0.1033 \text{ mmol TET}
\]

\[
0.1033 \text{ mmol TET} \times 296.55 \text{ mg/mmol} = 30.65 \text{ mg TET}
\]

\[
(30.65 \text{ mg TET} / 432.9 \text{ mg sample}) \times 100\% = 7.080\% \text{ TET}
\]
5. A 1.291 sample containing \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{NO}_3\), and inert material was diluted to 250.0 mL in a volumetric flask. A 50.00 mL aliquot was then made basic, and the liberated ammonia was distilled into 30.00 mL of 0.08421\(M\) HCl. After this reaction was complete, the excess HCl was titrated with 10.17 mL of 0.08802\(M\) NaOH. A 25.00 mL aliquot of the sample was then obtained, made basic, and the \(\text{NO}_3^-\) was reduced to \(\text{NH}_3\) with Devarda’s alloy. This aliquot was then distilled into 30.00 mL of the standard acid. It required 14.16 mL of the standard base to react with the excess acid from the second distillation. Calculate the percent \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{NO}_3\) present in the sample.

**FOR THE FIRST (50.00 mL) ALIQUOT:**

Initially, 30.00 mL \(\times 0.08421 \text{ mmol HCl/mL} = 2.526 \text{ mmol HCl}\)

Excess HCl was titrated with NaOH \([\text{Reaction: } \text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl}]\)

10.17 mL \(\times 0.08802 \text{ mmol NaOH/mL} = 0.8952 \text{ mmol NaOH} = 0.8952 \text{ mmol HCl}\)

HCl reacted: 2.526 - 0.8952 = 1.631 mmol HCl reacted

The reaction with the analyte: \(\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}; \therefore 1.631 \text{ mmol NH}_3\) were present.

**FOR THE SECOND (25.00 mL) ALIQUOT:**

Initially, 30.00 mL \(\times 0.08421 \text{ mmol HCl/mL} = 2.526 \text{ mmol HCl}\)

Excess HCl was titrated with NaOH \([\text{Reaction: } \text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl}]\)

14.16 mL \(\times 0.08802 \text{ mmol NaOH/mL} = 1.246 \text{ mmol NaOH} = 1.246 \text{ mmol HCl}\)

HCl reacted: 2.526 - 1.246 = 1.280 mmol HCl reacted

The reaction with the analyte: \(\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}; \therefore 1.280 \text{ mmol NH}_3\) were present.

Because the second aliquot was \(\frac{1}{2}\) the size of the first (25/50) we must multiply the mmol \(\text{NH}_3\) by 2 for comparison to the first aliquot:

1.280 mmol \(\text{NH}_3\) \(\times 2 = 2.560 \text{ mmol NH}_3\) in a 50.00 mL aliquot

‘Extra’ \(\text{NH}_3 = 2.560 - 1.631 = 0.929 \text{ mmol}\). The source of this ‘extra’ ammonia was the reduction of nitrate, \(\therefore\) there were 0.929 mmol \(\text{NO}_3^-\) in the 50.00 mL aliquot, \(\therefore 0.929 \text{ mmol NH}_4\text{NO}_3\) in the 50.00 mL aliquot.

0.929 mmol \(\times (250.0 \text{ mL}/50.00 \text{ mL}) = 4.64 \text{ mmol NH}_4\text{NO}_3\) in the original sample

4.64 mmol \(\text{NH}_4\text{NO}_3\) \(\times (80.0434 \text{ mg/mmol}) = 372 \text{ mg NH}_4\text{NO}_3\)

\((372 \text{ mg NH}_4\text{NO}_3 / 1,291 \text{ mg sample}) \times 100\% = 28.8\% \text{ NH}_4\text{NO}_3\) in the sample

For the first sample, the 1.631 mmol ammonia was from two sources \((\text{NH}_4\text{NO}_3\) and \((\text{NH}_4)_2\text{SO}_4\)). We have determined that 0.929 mmol was from the \(\text{NH}_4\text{NO}_3\), \(\therefore\) ammonia from \((\text{NH}_4)_2\text{SO}_4 = (1.631 - 0.929) = 0.702 \text{ mmol}\); however, because there are 2 \(\text{NH}_4^+\) ions in ammonium sulfate, 0.702 mmol \(\text{NH}_3\) / 2 = 0.351 mmol \((\text{NH}_4)_2\text{SO}_4\).

\(\therefore 0.351 \text{ mmol (NH}_4)_2\text{SO}_4 \times (250.0 \text{ mL} / 50.00 \text{ mL}) = 1.76 \text{ mmol (NH}_4)_2\text{SO}_4\) in sample.

1.76 mmol \((\text{NH}_4)_2\text{SO}_4 \times 132.1405 \text{ mg/mmol} = 232 \text{ mg (NH}_4)_2\text{SO}_4\)

232 mg \((\text{NH}_4)_2\text{SO}_4 \times 1,291 \text{ mg sample}) \times 100\% = 18.0\% \text{ (NH}_4)_2\text{SO}_4\) in sample.