Polyprotic Acids

- Acids that can donate more than 1 proton per molecule
  - Strong acid – H₂SO₄
  - Several weak acids
- ‘Well behaved’ dissociation
  - For most cases we can safely assume that protons are removed sequentially
    - All molecules will have their first proton removed before any will have the second removed, etc...

Polyprotic Acids

- Consider the dissociation of the weak polyfunctional acid H₂A
  - First step: H₂A ⇌ H⁺ + HA
    - \( K_1 = \frac{[H^+][HA]}{[H_2A]} \)
      - Subscript 1 indicates the first proton removed
  - Second Step: HA ⇌ H⁺ + A²⁻
    - \( K_2 = \frac{[H^+][A^-]}{[HA]} \)
      - Subscript 2 indicates the second proton removed
  - For higher order polyprotics, subscript indicated the number of the proton removed from the ‘parent’ molecule

Polyprotic Acids

- Possible combinations
  - H₂A
    - Since the protons dissociate sequentially, this is like any other weak acid
    - Calculate [H⁺] like any monoprotic acid using \( K_1 \).
  - H₂A / HA⁻
    - Buffer
    - Henderson-Hasselbalch using pK₁
  - H₂A / A²⁻
    - Will react
    - \( H_2A + A²⁻ \rightarrow 2HA \)
    - May have either of the two buffers OR HA

Homework

- 7-10, 12, 14, 18, 20, 27
Acid Salt

- Partially neutralized polyprotic acid
  - Only ‘new’ situation relative to monoprotic acids
  - Can act as either an acid or a base
  - $[H^+]$ a function of $K_a$ (acting as an acid) and $K_b$ (acting as a base)
    - Let $K_{n+1} = K_a$ as an acid, then $K_b = K_w / K_a$
    - For a diprotic acid, $K_a = K_{1n}$ and $K_{n+1} = K_{2n}$

- Deriving
  \[
  [H^+] = \frac{K_{n+1}C_{HA} + K_w}{1 + \frac{C_{HA}}{K_a}}
  \]
  - If $C_{HA} / K_1$ is much greater than 1, and also $K_{n+1}C_{HA}$ is much greater than $K_w$, then
  \[
  [H^+] \approx \sqrt{K_a K_{n+1}}
  \]

Acid Salt

- Final equation shows that under the assumed conditions, $[H^+]$ (and therefore pH) is independent of the concentration of the acid salt

Titration of Polyprotic Acids

![Polyprotic Titration Curve](image)

Legend

- **Point A**
  - Only a weak acid
  - Treat like any monoprotic acid using $K_1$

- **Region B** (blank)
  - First buffer region
  - pH from $pK_1$

- **Point C**
  - Acid Salt

Legend

- **Region D**
  - Second buffer region
  - Use $pK_2$ to calculate pH

- **Point E**
  - Conjugate base of ‘acid salt’
  - $K_b = K_w / K_2$

- **Region F**
  - Strong base
Calculations

- Consider the titration of 25.0 mL of 0.10 M o-phthalic acid with 0.10 M NaOH
  - Assume the formula of the acid is H₂A

Before any titrant is added

\[ [H^+] = \frac{(C_a + K_a)}{\sqrt{(C_a + K_a)^2 + 4K_aC_{Na}}} \]

\[ [H^+] = \frac{(0.5 + 1.12 \times 10^{-12}) + \sqrt{(0.5 + 1.12 \times 10^{-12})^2 + 4 \times 1.12 \times 10^{-12} \times \frac{2.0}{30}}} {2} \]

\[ [H^+] = 3.51 \times 10^{-12}; \text{pH} = 2.46 \]

Calculating with the 'short' form:

\[ \text{pH} = \text{pK}_a + \log\left(\frac{a}{[H^+]}\right) = 2.95 + \log(0.5/2.0) \]

\[ \text{pH} = 2.35 \text{ (significant difference)} \]

Titration of 25.0 mL of 0.10 M o-phthalic acid with 0.10 M NaOH

After 5.00 mL of titrant is added

\[ \text{HA} + \text{OH}^{-} \rightleftharpoons \text{A}^{-} + \text{H}_2\text{O} \]

| I | 2.50 | 0.50 | 0 | ~ ~ |
| Δ | -0.50 | -0.50 | +0.50 | ~ ~ |
| F | 2.00 | ~0 | 0.50 | ~ ~ |

Buffer, but with \( K_a > 10^{-3} \), we have to use the quadratic form for \([H^+]\)

Titration of 25.0 mL of 0.10 M o-phthalic acid with 0.10 M NaOH

After 25.0 mL of titrant is added

\[ \text{HA} + \text{OH}^{-} \rightleftharpoons \text{A}^{-} + \text{H}_2\text{O} \]

| I | 2.50 | 2.50 | 0 | ~ ~ |
| Δ | -2.50 | -2.50 | +2.50 | ~ ~ |
| F | ~0 | ~0 | 2.50 | ~ ~ |

Acid salt

Titration of 25.0 mL of 0.10 M o-phthalic acid with 0.10 M NaOH

After 35.0 mL of titrant is added

\[ \text{HA} + \text{OH}^{-} \rightleftharpoons \text{A}^{-} + \text{H}_2\text{O} \]

| I | 2.50 | 3.50 | 0 | ~ ~ |
| Δ | -2.50 | -2.50 | +2.50 | ~ ~ |
| F | ~0 | 1.00 | 2.50 | ~ ~ |

THEN

\[ \text{A}^{-} + \text{OH}^{-} \rightleftharpoons \text{A}^{2-} + \text{H}_2\text{O} \]

| I | 2.50 | 1.00 | 0 | ~ ~ |
| Δ | -1.00 | -1.00 | +1.00 | ~ ~ |
| F | 1.50 | ~0 | 1.00 | ~ ~ |
**Titration of 25.0 mL of 0.10 M \( \alpha \)-phthalic acid with 0.10 M NaOH**

- **Buffer with \( \text{HA}^- / \text{A}^2^- \)**
  - \( \text{pH} = \text{pK}_a + \log (b/a) \)
  - \( \text{pH} = 5.41 + \log (1.00 / 1.50) \)
  - \( \text{pH} = 5.23 \)

**Titration of 25.0 mL of 0.10 M \( \alpha \)-phthalic acid with 0.10 M NaOH**

- **Only species affecting the pH is \( \text{A}^2^- \)**
  - \( K_b = K_W / K_a \)
  - \( C_b = 2.5 / 75 \)
  
  \[
  [\text{OH}^-] = \sqrt{\frac{1.0 \times 10^{-14}}{3.91 \times 10^{-14}}} \times \left(\frac{2.5}{75}\right) 
  \]
  
  \( [\text{OH}^-] = 9.23 \times 10^{-4}; \text{pOH} = 5.03 \)
  
  \( \text{pH} = 14.00 - \text{pOH} = 8.97 \)

**Titration of 25.0 mL of 0.10 M \( \alpha \)-phthalic acid with 0.10 M NaOH**

- **After 50.0 mL of titrant is added**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 5.00 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 2.50 | 2.50 | ~   |
  
  **THEN**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 2.50 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 2.50 | 2.50 | ~   |

**Titration of 25.0 mL of 0.10 M \( \alpha \)-phthalic acid with 0.10 M NaOH**

- **After 75.0 mL of titrant is added**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 7.50 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 5.00 | 2.50 | ~   |
  
  **THEN**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 5.00 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 2.50 | 2.50 | ~   |

**Sulfuric Acid pH**

- **Unique situation**
  - First proton is completely dissociated (strong acid)
  - Second proton comes from a weak acid (partially dissociated)
  - Dissociation of the first proton affects the amount of dissociation for the second proton

- **What is the pH for a 0.010 M solution of sulfuric acid?**

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**Titration of 25.0 mL of 0.10 M \( \alpha \)-phthalic acid with 0.10 M NaOH**

- **After 50.0 mL of titrant is added**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 5.00 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 2.50 | 2.50 | ~   |
  
  **THEN**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 5.00 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 2.50 | 2.50 | ~   |

**Titration of 25.0 mL of 0.10 M \( \alpha \)-phthalic acid with 0.10 M NaOH**

- **After 75.0 mL of titrant is added**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 7.50 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 5.00 | 2.50 | ~   |
  
  **THEN**
  
  \[
  \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^2^- + \text{H}_2\text{O}
  \]
  
  | I   | 2.50 | 5.00 | 0   | ~   |
  | Δ   | 2.50 | 2.50 | +2.50 | ~   |
  | F   | ~0   | 2.50 | 2.50 | ~   |
Sulfuric Acid pH
Assume 1 mL of solution, then \( M = \text{mmol acid} \)
\[
\begin{align*}
\text{H}_2\text{SO}_4 & \rightarrow \text{HSO}_4^- + \text{H}^+ \\
I & 0.010 \\
\Delta & -0.010 \\
F & \sim 0 \\
\text{THEN} & \\
\text{HSO}_4^- & \rightarrow \text{SO}_4^{2-} + \text{H}^+ \\
I & 0.010 \\
\Delta \cdot x & +x +x \\
F & 0.010 \cdot x \quad x \quad 0.010+x
\end{align*}
\]

\[ K_2 = [\text{H}^+] [\text{SO}_4^{2-}] / [\text{HSO}_4^-]; \]
\[ K_2 = 0.0102 \]
\[ = (0.010+x)(x) / (0.010 - x) \]
\[ (0.0102)(0.010 - x) = (0.010+x)(x) \]
\[ 1.02 \times 10^{-4} - 0.0102x = x^2 + 0.010x \]

Rearranging:
\[ x^2 + 0.010x + 0.0102x - 1.02 \times 10^{-4} = 0 \]

Quadratic – solve for \( x \)
\[ x = 0.0042, [\text{H}^+] = 0.010+0.0042 = 0.0142 \]

\[ \text{pH} = 1.85 \]

Assume one proton dissociates, pH = 2.00
Assume both protons dissociate, pH = 1.70