**Acid-base Equilibria, Buffers and pH**

**Introduction**
This model focuses on approaches to estimating the pH of solutions of acids and bases. We will look at several cases; strong acids, strong bases, weak acids, weak bases and buffers.

**Case 1: Strong Acids**

Strong acids completely dissociate in water to form $\text{H}_3\text{O}^+$. So, the $[\text{H}_3\text{O}^+]$ can be taken directly from the formal concentration (the concentration at which it was prepared) of the strong acid.

Example: A 0.025 M solution of HCl has a pH of 1.60

\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+
\]

\[
[\text{H}_3\text{O}^+] = 0.025 \text{ M}
\]

\[
\text{pH} = -\log (0.025) = 1.60
\]

**Case 2: Strong Bases**

Strong bases completely dissociate in water to form $\text{OH}^-$. So, the $[\text{OH}^-]$ can be taken directly from the formal concentration (the concentration at which it was prepared) of the strong base.

Example: A 0.050 M solution of NaOH has a pH of 12.70

\[
\text{NaOH}^{(aq)} \rightarrow \text{OH}^- + \text{Na}^+
\]

\[
[\text{OH}^-] = 0.050 \text{ M}
\]

\[
K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \cdot 10^{-14}
\]

\[
[\text{H}_3\text{O}^+] = 1.0 \cdot 10^{-14} / 0.050 = 2.0 \cdot 10^{-13}
\]

\[
\text{pH} = -\log (2.0 \cdot 10^{-13}) = 12.70
\]
Case 3: Weak acids

Weak acids partially dissociate in water to form its conjugate base and $\text{H}_3\text{O}^+$, as dictated by its acid dissociation constant. We can set up an ICE table, simplify and solve for the $[\text{H}_3\text{O}^+]$.

Example: A 0.10 M solution of acetic acid (CH$_3$COOH, represented as HA) has a pH of 2.88.

$$K_a(\text{acetic acid}) = 1.76 \cdot 10^{-5}$$

$$\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{A}^- + \text{H}_3\text{O}^+$$

$$K_a = [\text{A}^-][\text{H}_3\text{O}^+] / [\text{HA}] = 1.76 \cdot 10^{-5}$$

From ICE Table

$$K_a = x^2 / 0.100 - x = 1.76 \cdot 10^{-5}$$

$$x << 0.10, \text{ so}$$

$$[\text{H}_3\text{O}^+] = x = (1.76 \cdot 10^{-5} \cdot 0.100)^{1/2} = 0.00132 \text{ M}$$

$$\text{pH} = -\log (0.00132) = 2.88$$

Case 4: Weak bases

Weak bases partially hydrolyze in water to form its conjugate acid and $\text{OH}^-$, as dictated by its base hydrolysis constant. We can set up an ICE table, simplify and solve for the $[\text{OH}^-]$.

Example: A 0.010 M solution of ammonia (NH$_3$) has a pH of 10.62.

$$K_b(\text{ammonia}) = 1.75 \cdot 10^{-5}$$

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$$

$$K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3] = 1.75 \cdot 10^{-5}$$

From ICE Table

$$K_b = x^2 \cdot 0.0100 - x = 1.75 \cdot 10^{-5}$$

$$x << 0.010, \text{ so}$$

$$[\text{OH}^-] = x = (1.75 \cdot 10^{-5} \cdot 0.010)^{1/2} = 0.0004184 \text{ M}$$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \cdot 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 1.0 \cdot 10^{-14} / 0.0004184 = 2.390 \cdot 10^{-11}$$

$$\text{pH} = -\log (2.390 \cdot 10^{-11}) = 10.62$$
Case 5: Buffers

A buffer is a mixture of a weak acid and its conjugate base. These solutions are resistant to pH change. The capacity to resist pH change upon the addition of acid or base is maximized at a high concentration of an equal mixture of the weak acid and the conjugate base. When the concentration of the weak acid and its conjugate base are equal the pH equals the pKa of the conjugate pair. Out of convenience the Henderson-Hasselbalch Equation is often used to handle buffers.

\[
pH = pK_a + \log \left( \frac{\text{conjugate base}}{\text{conjugate acid}} \right)
\]

Example 1: A mixture that is 0.050 M H$_2$PO$_4^-$ and 0.050 M HPO$_4^{2-}$ has a pH of 7.20. These two species are part of the phosphoric acid system. Phosphoric acid is a triprotic acid.

\[
K_{a1} \quad K_{a2} \quad K_{a3}
\]

\[
H_3PO_4 \leftrightarrow H_2PO_4^- \leftrightarrow HPO_4^{2-} \leftrightarrow PO_4^{3-}
\]

The acid dissociation reaction involving these two species is dictated by $K_{a2}$.

\[
K_{a2} = 6.32 \times 10^{-8}
\]

\[
H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+
\]

p$K_{a2}$ = -log ($K_a$) = 7.199

\[
pH = 7.199 + \log \left( \frac{0.050}{0.050} \right) = 7.20
\]

Example 2: 20.0 mL of 0.100 M Na$_2$HPO$_4$ is mixed with 10.0 mL of 0.100 M HCl. The resulting pH is 7.20. The reaction of weak bases with strong acids go to completion to produce its conjugate base and water.

\[
\text{HPO}_4^{2-} + H^+ \rightarrow H_2PO_4^- + H_2O
\]

Use a table to predict the mol ratio of the weak base and its conjugate.

<table>
<thead>
<tr>
<th></th>
<th>HPO$_4^{2-}$</th>
<th>H$^+$</th>
<th>H$_3$PO$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.00 mmol</td>
<td>1.00 mmol</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-1.00 mmol</td>
<td>-1.00 mmol</td>
<td>+1.00 mmol</td>
</tr>
<tr>
<td>Final</td>
<td>1.00 mmol</td>
<td>0</td>
<td>1.00 mmol</td>
</tr>
</tbody>
</table>

\[
pH = 7.199 + \log \left( \frac{1.00}{1.00} \right) = 7.199
\]
Objectives and Success Criteria

- Understand and predict how different types of acids and bases will act in water

Prerequisites

- pH, acid-base reactions, equilibrium
- pH = \(-\log [H_3O^+]\)
- \(pK_a = -\log K_a\)

EXERCISES

1. Calculate the pH of a 0.10 M solution of HBr. (1.00)

The \([\text{OH}^-]\) of the solution is \(1.0 \times 10^{-13}\) M. Explain the impact that adding a strong acid has on the Kw equilibrium in terms of LeChatlier’s Principle.
2. Calculate the pH of a 0.0050 M solution of Ca(OH)$_2$ (it is completely soluble at this concentration and acts as a strong base). (12.000)

3. Construct the ICE Table for the Case 3 example.
4. Estimate the pH of a 0.020 M solution of ammonium chloride (NH₄Cl). This salt completely dissociates to produce NH₄⁺ and Cl⁻. NH₄⁺ is the weak acid conjugate of ammonia (NH₃). Cl⁻ is just a spectator ion. (5.47)

\( K_a(NH_4^+) = 5.77 \times 10^{-10} \)

5. Construct the ICE Table for the Case 4 example.
6. Estimate the pH of a 0.0015 M solution of sodium formate, HCOONa. The $K_a$ of formic acid (HCOOH) is $1.8 \times 10^{-4}$). Sodium formate completely dissociates to produce $\text{Na}^+$ and the formate ion ($\text{HCOO}^-$), which is the conjugate base of formic acid. (7.46)

7. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.0100 M acetic acid (CH$_3$COOH) with 50.0 mL of 0.0100 M sodium acetate, the conjugate base of acetic acid. ($K_a$(acetic acid) = $1.75 \times 10^{-5}$). Sodium acetate completely dissociates in water to form $\text{Na}^+$ and the acetate ion (CH$_3$COO$^-$). The $\text{Na}^+$ is a spectator ion. HINT: when you mix the solutions you are diluting the concentrations! (4.46)
8. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.0100 M sodium benzoate \((C_6H_5COONa)\) with 50.0 mL of 0.0100 M HCl (a strong acid). \(K_a\) (benzoic acid, \(C_6H_5COOH\)) = 6.28 \(\times 10^{-5}\) Hint: The reaction of weak bases with strong acids goes to completion. (4.20)

9. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.100 M sodium dihydrogen phosphate \((\text{NaH}_2\text{PO}_4)\) with 50.0 mL of 0.0500 M NaOH (a strong base). Hint: The reaction of a weak acid with a strong base goes to completion. (6.722)