1. **Arrhenius Acid-Base Concept** (last semester)

   Acid: $\text{H}^+$ supplier  
   Base: $\text{OH}^-$ supplier

2. **Brønsted-Lowry Acid-Base Concept** (more general)

   (a) **Definition**  (H$^+$ transfer)

   **Acid:** $\text{H}^+$ donor  
   **Base:** $\text{H}^+$ acceptor

   **Conjugate Acid-Base Pairs:**

   $\text{Base} \xrightleftharpoons[+ \text{H}^+]{- \text{H}^+} \text{Acid}$

   **e.g.,**

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

   **more examples:**

<table>
<thead>
<tr>
<th>Conjugate Acids</th>
<th>Conjugate Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_2^-$</td>
<td>$\text{NH}_3$</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{O}_2^-$</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>$\text{HSO}_4^-$</td>
<td>$\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{CH}_3^-$</td>
<td>$\text{CH}_4$</td>
</tr>
<tr>
<td></td>
<td>&quot; $\text{CH}_5^+$ &quot;</td>
</tr>
</tbody>
</table>
(b) Amphoteric Substances -- molecules or ions that can function as both acids and bases (e.g., H₂O itself!)

* e.g., the bicarbonate ion, HCO₃⁻

\[
\begin{align*}
\text{HCO}_3^- + \text{OH}^- & \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-} \\
\text{acid} & \quad \text{base} \\
\text{HCO}_3^- + \text{HCl} & \rightarrow \text{H}_2\text{CO}_3 + \text{Cl}^- \\
\text{base} & \quad \text{acid}
\end{align*}
\]

(c) Relative Strengths of Brønsted Acids

* Binary Acids*  e.g., HCl, HBr, H₂S, etc.

* Acid Strength Increases*  Periodic Table

* e.g.,  relative acidity:  HCl > H₂S  (across a period)

* HI > HBr > HCl > HF  (up in a group)*
**Oxo acids**

- HNO₃, H₂SO₄, H₃PO₄, etc.

1. **for same central element,**
   acid strength increases with # of oxygens
   
   Acid Strength Increases
   
   HClO < HClO₂ < HClO₃ < HClO₄

2. **for different central element, but same # oxygens,**
   acid strength increases with electronegativity

   Acid Strength Increases
   
   Periodic Table

   e.g., H₂SO₄ > H₂SeO₄ > H₂TeO₄

(d) **Relative strengths of conjugate acid-base pairs**

For example,

HF + H₂O ⇌ H₃O⁺ + F⁻

acid base acid base

In this case, the equilibrium lies mainly on reactant side. Therefore, "HF is a weaker acid than H₃O⁺."

In general, weak Brønsted acids have strong conjugate bases. (vice versa)
3. **Lewis Acid-Base Concept** (most general)

(a) **Definition** (electron pair transfer)

**Acid:** e⁻ pair acceptor  **Base:** e⁻ pair donor

**Lewis acids** -- electron deficient molecules or cations.
**Lewis bases** -- electron rich molecules or anions.
(have one or more unshared e⁻ pairs)

(b) **Lewis acid-base reactions** (i.e., all non-redox reactions!)

\[
\text{OH}^- + \text{NH}_4^+ \rightarrow \text{H}_2\text{O} + \text{NH}_3
\]

\[
\text{OH}^- \quad \text{Lewis base} \quad \text{H}_2\text{O} \quad \text{Lewis acids} \quad \text{NH}_3
\]

\[
\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-
\]
4. Auto-ionization of Water and the pH Scale

(a) water undergoes self-ionization to slight extent:

\[
\begin{align*}
\text{H}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^- (\text{aq}) \\
\text{H}_3\text{O}^+ &= \text{hydronium ion} \\
\text{OH}^- &= \text{hydroxide ion}
\end{align*}
\]

or, in simplified form:

\[
\begin{align*}
\text{H}_2\text{O}(\text{l}) & \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^- (\text{aq}) \\
\text{equilibrium constant:} \\
K_c &= [\text{H}^+] [\text{OH}^-] / [\text{H}_2\text{O}] \\
&\text{but, } [\text{H}_2\text{O}] \sim \text{constant} \sim 55.6 \text{ mole/L at 25°C} \\
&\text{so, instead, use the "ion product" for water } = K_w \\
K_w &= [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at 25°C)} \\
in \text{pure water: } [\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}
\end{align*}
\]

(b) the pH scale: \[ \text{pH} = -\log [\text{H}^+] \]

in general: \[ \text{pX} = -\log X \]

\[ e.g., \quad \text{pOH} = -\log [\text{OH}^-] \]

and, in reverse: \[ [\text{H}^+] = 10^{-\text{pH}} \text{ mole/L} \]

\[ [\text{OH}^-] = 10^{-\text{pOH}} \text{ mole/L} \]

since \[ K_w = [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \]

\[ \text{pK}_w = \text{pH} + \text{pOH} = 14.00 \]

(c) relative acidity of solutions:

**neutral solution**

\[ [H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M} \]

\[ \text{pH} = \text{pOH} = 7.00 \]

**acidic solution**

\[ [H^+] > 10^{-7} \text{ (i.e., greater than in pure water)} \]

so, \( \text{pH} < 7.00 \)

\[ [OH^-] < 10^{-7} \text{ and } \text{pOH} > 7.00 \]

e.g., if \( [H^+] = 1.00 \times 10^{-3} \text{ M} \)

then \( \text{pH} = 3.00 \) and \( \text{pOH} = 11.00 \)

**basic solution**

\[ [H^+] < 10^{-7} \text{ (i.e., less than in pure water)} \]

so, \( \text{pH} > 7.00 \)

\[ [OH^-] > 10^{-7} \text{ and } \text{pOH} < 7.00 \]

e.g., if \( [OH^-] = 1.00 \times 10^{-3} \text{ M} \)

then \( \text{pOH} = 3.00 \) and \( \text{pH} = 11.00 \)

**Problem**

The water in a soil sample was found to have \( [OH^-] \) equal to \( 1.47 \times 10^{-9} \text{ mole/L} \). Determine \( [H^+] \), \( \text{pH} \), and \( \text{pOH} \)

\[ [H^+] = K_w / [OH^-] = (1.00 \times 10^{-14}) / (1.47 \times 10^{-9}) \]

\[ = 6.80 \times 10^{-6} \]

\[ \text{pH} = - \log [H^+] = - \log (6.80 \times 10^{-6}) = 5.17 \text{ (acidic !)} \]

\[ \text{pOH} = 14.00 - \text{pH} = 14.00 - 5.17 = 8.83 \]

\{ or, \( \text{pOH} = - \log [OH^-] = - \log (1.47 \times 10^{-9}) = 8.83 \} \]
5. **Strong acids and Bases**

(a) **Strong Acids** (e.g., HCl, HNO₃, etc.) -- 100% ionized

\[
\text{HNO}_3(aq) + \text{H}_2\text{O} \xrightarrow{100\%} \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)
\]

or, in simplified form:

\[
\text{HNO}_3(aq) \xrightarrow{100\%} \text{H}^+(aq) + \text{NO}_3^-(aq)
\]

\[\text{[H}^+\text{]} = \text{initial M of HNO}_3\]

e.g., in a 0.050 M HNO₃ solution:

\[\text{[H}^+\text{]} = 0.050\text{ and pH} = -\log (0.050) = 1.30\]

(b) **Strong Bases** (metal hydroxides) -- 100% ionized

\[
\text{NaOH}(aq) \xrightarrow{100\%} \text{Na}^+(aq) + \text{OH}^-(aq)
\]

\[\text{[OH}^-\text{]} = \text{initial M of NaOH}\]

**Problem**

What mass of Ba(OH)₂ (171.34 g/mole) is required to prepare 250 mL of a solution with a pH of 12.50?

First: What is the solution process?

\[
\text{Ba(OH)}_2(aq) \xrightarrow{100\%} \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq)
\]

so, \[\text{[OH}^-\text{]} = 2 \times \text{M of Ba(OH)}_2\text{ solution} \quad (2:1 \text{ ratio})\]

\[
\text{pOH} = 14.00\text{ - pH} = 14.00\text{ - 12.50} = 1.50
\]

\[\text{[OH}^-\text{]} = 10^{-1.50} = 0.0316 \text{ M}\]

Next: How much Ba(OH)₂ is needed for that much OH⁻?

250 mL \( \times \) (0.0316 mol OH⁻ / 1000 mL) = 0.00790 mol OH⁻

0.00790 mol OH⁻ \( \times \) [1 mol Ba(OH)₂ / 2 mol OH⁻] \( \times \) [171.34 g / mol Ba(OH)₂] = 0.677 g
6. **Weak Acids and Bases**

(a) **Weak Acids -- less than 100% ionized (equilibrium!)**

in general: HA is a weak acid, A\(^-\) is its conjugate base

\[ \text{HA(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

or, in simplified form:

\[ \text{HA(aq)} \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq) \]

**Acid Dissociation Constant:** \( K_a \)

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

relative acid strength:

- weak acid: \( K_a < \sim 10^{-3} \)
- moderate acid: \( K_a \sim 1 \) to \( 10^{-3} \)
- strong acid: \( K_a >> 1 \)

**Problem**

Hypochlorous acid, HOCl, has a \( pK_a \) of 7.52. What is the pH of 0.25 M solution of HOCl? What is the percent ionization?

\[ \text{pK}_a = -\log K_a \]
\[ K_a = 10^{-pK_a} = 10^{-7.52} = 3.02 \times 10^{-8} \]

\[ \begin{array}{c|c|c|c|}
\text{HOCl(aq)} & \rightleftharpoons & \text{H}^+ & + & \text{OCl}^-(aq) \\
\text{Initial} & 0.25 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equil} & 0.25 - x & x & x \\
\end{array} \]
now, substitute the appropriate equilibrium concentrations:

\[
K_a = \frac{[H^+][OCl^-]}{[HOCl]} = 3.02 \times 10^{-8}
\]

\[
(x) \frac{(x)}{(0.25 - x)} = \frac{x^2}{(0.25 - x)} = 3.02 \times 10^{-8}
\]

since \(K_a\) is very small, assume \(x \ll 0.25\)

\[
x^2 / (0.25) \approx 3.02 \times 10^{-8} \quad \Rightarrow \quad x \approx 8.69 \times 10^{-5}
\]

(assumption is OK)

\[
pH = - \log (8.69 \times 10^{-5}) = 4.06 \quad \text{(solution is acidic!)}
\]

\[
\% \text{ ionization} = \frac{\text{(amount HA ionized)}}{\text{(initial)}} \times 100%
\]

\[
= 100\% \times \frac{(8.69 \times 10^{-5})}{(0.25)} = 0.035 \%
\]

(b) Weak Bases

in general: B is a weak base, HB\(^+\) is its conjugate acid

\[
B(aq) + H_2O \rightleftharpoons HB^+(aq) + OH^-(aq)
\]

**Base Dissociation Constant: \(K_b\)**

\[
K_b = \frac{[HB^+][OH^-]}{[B]}
\]

e.g., \(NH_3\) is a weak base:

\[
NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)
\]

\[
K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}
\]

\[
pK_b = - \log K_b = 4.74
\]

**Note:** Since \(OH^-\) rather than \(H^+\) appears here, first find \([OH^-]\) or \(pOH\), and then convert to \(pH\)

sample problem: 0.25 M solution of \(NH_3\)

set up conc table as usual, solve for \(x = [OH^-]\)

\[
[OH^-] = 2.12 \times 10^{-3}
\]

\[
pOH = 2.67 \quad \Rightarrow \quad pH = 11.33 \quad \text{(basic !)}
\]
7. **Salts of Weak Acids and Bases**

(a) **Conjugate Acid - Base Pairs**  \((HA \text{ and } A^-)\)

\[
\begin{align*}
K_a & : \quad HA \rightleftharpoons H^+ + A^- \\
K_b & : \quad A^- + H_2O \rightleftharpoons HA + OH^- \\
\end{align*}
\]

**for any conjugate acid-base pair:**

\[
K_a K_b = K_w \quad \text{and} \quad pK_a + pK_b = 14.00
\]

(b) **Salt of a Weak Acid**  \((\text{e.g., } NaCN)\)  --  **Basic Solution**

**Anion acts as a weak base:**

\[
\begin{align*}
K_b & : \quad CN^- + H_2O \rightleftharpoons HCN + OH^- \\
K_b & = K_w / K_a = [OH^-] [HCN] / [CN^-] \\
\end{align*}
\]

e.g.,  \(K_a\) for HCN is \(6.2 \times 10^{-10}\)

What is \(pH\) of a 0.50 M NaCN solution?

\[
\begin{align*}
K_b & = K_w / K_a = (1 \times 10^{-14}) / (6.2 \times 10^{-10}) \\
& = 1.6 \times 10^{-5}
\end{align*}
\]

use a concentration table based on \(K_b\) reaction above:

\[
\begin{align*}
x & = [OH^-] = [HCN] \\
[CN^-] & = 0.50 - x \approx 0.50 \quad \text{(since } K_b \text{ is small)} \\
K_b & = [OH^-] [HCN] / [CN^-] \approx x^2 / 0.50 \approx 1.6 \times 10^{-5} \\
x & = [OH^-] \approx 2.8 \times 10^{-3} \\
pOH & = 2.55 \quad \text{and} \quad pH = 11.45 \quad \text{(basic !)}
\end{align*}
\]
(c) Salt of a Weak Base (e.g., NH₄Cl) -- Acidic Solution

Cation acts as a weak acid:

\[ \text{NH}_4^+ \xrightarrow{\text{H}^+ + \text{NH}_3} \]

\[ K_a = \frac{K_w}{K_b} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \]

e.g., \( K_b \) for \( \text{NH}_3 \) is \( 1.8 \times 10^{-5} \)

what is pH of a 0.50 M NH₄Cl solution?

\[ K_a = \frac{K_w}{K_b} = \frac{(1 \times 10^{-14})}{(1.8 \times 10^{-5})} \]
\[ = 5.56 \times 10^{-10} \]

use a concentration table based on \( K_a \) reaction above:

\[ x = [\text{H}^+] = [\text{NH}_3] \]

\[ [\text{NH}_4^+] = 0.50 - x \approx 0.50 \] (since \( K_a \) is small)

\[ K_a = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] \approx x^2/0.50 \approx 5.56 \times 10^{-10} \]

\[ x = [\text{H}^+] \approx 1.67 \times 10^{-5} \]

\[ \text{pH} = 4.78 \] (acidic !)

**Problem**

The pKₐ value for HCN is 9.21. What molar concentration of NaCN is required to make a solution with a pH of 11.75? [answer: 2.0 M NaCN]
8. **Polyprotic Acids**

E.g., diprotic acids, \( \text{H}_2\text{A} \), undergo stepwise dissociation:

\[
\begin{align*}
\text{H}_2\text{A} & \rightleftharpoons \text{HA}^- + \text{H}^+ & \text{K}_{a1} = \frac{[\text{HA}^-][\text{H}^+]}{[\text{H}_2\text{A}]} \\
\text{HA}^- & \rightleftharpoons \text{A}^{2-} + \text{H}^+ & \text{K}_{a2} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]}
\end{align*}
\]

Usually, \( \text{K}_{a1} \gg \text{K}_{a2} \) so that:

- The 1st equilibrium produces most of the \( \text{H}^+ \)
- But, the 2nd equilibrium determines \([\text{A}^{2-}]\)

**Problem**

Ascorbic acid (vitamin C), \( \text{H}_2\text{C}_6\text{H}_2\text{O}_6 \), is an example of a diprotic acid with \( \text{K}_{a1} = 7.9 \times 10^{-5} \) and \( \text{K}_{a2} = 1.6 \times 10^{-12} \). For a 0.10 M solution of ascorbic acid, determine the pH and the concentrations of the mono anion, \( \text{HC}_6\text{H}_2\text{O}_6^- \), and the dianion, \( \text{C}_6\text{H}_2\text{O}_6^{2-} \).

Based on the first equilibrium:

\[
x = [\text{H}^+] \approx [\text{HA}^-] \quad \text{and} \quad [\text{H}_2\text{A}] = 0.10 - x \approx 0.10
\]

\[
\text{K}_{a1} = 7.9 \times 10^{-5} \approx \frac{x^2}{0.10}
\]

\[
\therefore x \approx 2.8 \times 10^{-3} \quad \text{so,} \quad \text{pH} = 2.55
\]

Must use the 2nd equilibrium to find \([\text{A}^{2-}]\):

\[
\text{K}_{a2} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]} \quad \text{but, from above} \quad [\text{H}^+] \approx [\text{HA}^-]
\]

\[
\therefore \text{K}_{a2} \approx [\text{A}^{2-}] \quad \text{(a general result for \( \text{H}_2\text{A} \) !)}
\]

\[
[\text{A}^{2-}] \approx 1.6 \times 10^{-12}
\]