Chapter 16
Acid-Base Equilibria

Learning goals and key skills:
- Understand the nature of the hydrated proton, represented as either H⁺(aq) or H₂O⁺(aq)
- Define and identify Arrhenius acids and bases.
- Define and identify Bronsted-Lowry acids and bases, and identify conjugate acid-base pairs.
- Relate the strength of an acid to the strength of its conjugate base.
- Understand how the equilibrium position of a proton transfer reaction relates the strengths of acids and bases involved.
- Describe the autoionization of water and understand how [H₃O⁺] and [OH⁻] are related
- Calculate the pH of a solution given [H₃O⁺] or [OH⁻]
- Calculate the pH of a strong acid or strong base given its concentration
- Calculate Kₐ or Kₐ for a weak acid or weak base given its concentration and the pH of the solution
- Calculate pH of a weak acid or weak base or its percent ionization given its concentration and Kₐ or Kₐ
- Calculate Kₐ for a weak base given Kₐ of its conjugate acid, and similarly calculate Kₐ from Kₐ
- Predict whether an aqueous solution of a salt will be acidic, basic, or neutral
- Predict the relative strength of a series of acids from their molecular structures
- Define and identify Lewis acids and bases.
Acids and Bases

Arrhenius
- An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.
- A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.

Brønsted-Lowry
- An acid is a proton donor.
- A base is a proton acceptor.

Acids and bases may be **inorganic** (7 strong acids, 8 strong bases) or **organic** (acids have –COOH group):
- HCl, HNO₃, H₂SO₄, HBr, HI, HClO₃, HClO₄
- AOH (A = Li, Na, K, Rb, Cs); A(OH)₂ (A = Ca, Sr, Ba)

What happens when an acid dissolves in water?

- Water acts as a Brønsted-Lowry base and abstracts a proton (H⁺) from the acid.
- As a result, the **conjugate base** of the acid and a **hydronium ion** are formed.
Amphiprotic – a substance that is capable of acting as an acid or a base e.g. $\text{H}_2\text{O}$, $\text{HCO}_3^-$, $\text{HSO}_4^-$. 

\[ \text{:} \text{H} + \text{:} \text{O} \rightarrow \text{:} \text{H}^+ + \left[ \text{H} - \text{O} - \text{H} \right]^+ \]

Acid \hspace{1cm} Base

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \iff \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

Base \hspace{1cm} Acid

**Conjugate acids and bases**

\[ \text{HNO}_2(aq) + \text{H}_2\text{O}(l) \iff \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq) \]

Acid \hspace{1cm} Base \hspace{1cm} Conjugate base \hspace{1cm} Conjugate acid

\[ \text{HCN} (aq) + \text{H}_2\text{O} (l) \iff \text{CN}^- (aq) + \text{H}_3\text{O}^+ (aq) \]

\[ \text{HClO} (aq) + \text{H}_2\text{O} (l) \iff \text{ClO}^- (aq) + \text{H}_3\text{O}^+ (aq) \]

\[ \text{NH}_3 (aq) + \text{H}_2\text{O} (l) \iff \text{NH}_4^+ (aq) + \text{OH}^- (aq) \]
Acid and base strength

Strong acids are completely dissociated in water. Their conjugate bases are weak.

Weak acids only dissociate partially in water. Their conjugate bases are strong.

In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

A Strong acid

When HCl dissolves in water, it ionizes completely.

HCl(aq) + H₂O(l) → H₃O⁺(aq) + Cl⁻(aq)
**A Weak acid**

When HF dissolves in water, only a fraction of the molecules ionize.

\[
\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)
\]

**Autoionization of water**

Water is amphoteric. In pure water, some molecules act as bases and some as acids. This is referred to as **autoionization**.

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

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\rightleftharpoons
\begin{align*}
\cdot & \quad \cdot \\
\cdot & \quad \cdot
\end{align*}
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\cdot & \quad \cdot & \quad \cdot
\end{align*}

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-]
\]

- This equilibrium constant is referred to as the **ion-product constant** for water, \( K_w \).
- At 25°C, \( K_w = 1.0 \times 10^{-14} \)
Temperature dependence of $K_w$

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$K_w = [H_3O^+] [OH^-]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C</td>
<td>$0.114 \times 10^{-14}$</td>
</tr>
<tr>
<td>25 °C</td>
<td>$1.008 \times 10^{-14}$</td>
</tr>
<tr>
<td>50 °C</td>
<td>$5.476 \times 10^{-14}$</td>
</tr>
<tr>
<td>75 °C</td>
<td>$15.85 \times 10^{-14}$</td>
</tr>
<tr>
<td>100 °C</td>
<td>$51.3 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

Acidic, neutral, and basic solutions

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic</td>
<td>$[H^+] &gt; [OH^-]$</td>
</tr>
<tr>
<td></td>
<td>$[H^+][OH^-] = 1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>Neutral</td>
<td>$[H^+] = [OH^-]$</td>
</tr>
<tr>
<td></td>
<td>$[H^+][OH^-] = 1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>Basic</td>
<td>$[H^+] &lt; [OH^-]$</td>
</tr>
<tr>
<td></td>
<td>$[H^+][OH^-] = 1.0 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

neutral, $[H^+] = [OH^-]$
acidsic solution, $[H^+] > [OH^-]$
basic solution, $[H^+] < [OH^-]$
**pH and pOH scale**

\[
pH = -\log [H_3O^+] \\
pOH = -\log [OH^-]
\]

- At 25 °C in pure water,
  \[K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14}\]
  
  Since in pure water \([H_3O^+] = [OH^-]\),
  \[\sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M}\]
  
  \[\text{pH} + \text{pOH} = pK_w = 14.00\]

| TABLE 16.1 Relationships between \([H^+]\), \([OH^-]\), and pH at 25 °C for Acidic, Neutral, and Basic Aqueous Solutions |
|-----------------------------------------------|-----------------|-----------------|
| Acidic                                      | Neutral         | Basic           |
| pH   \(<7.00\)                               | 7.00            | \(>7.00\)       |
| \([H^+]\) (M) \(>1.0 \times 10^{-7}\)       | \(1.0 \times 10^{-7}\) | \(<1.0 \times 10^{-7}\) |
| \([OH^-]\) (M) \(<1.0 \times 10^{-7}\) \(= 1.0 \times 10^{-7}\) | \(>1.0 \times 10^{-7}\) |

Neutral pH is 7.00.

Acidic pH is below 7.00.

Basic pH is above 7.00.
Three ways to measure pH

- Litmus paper
  - red-to-blue: basic, pH > 8
  - blue-to-red: acidic, pH < 5
- An indicator
- A pH meter

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range for color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>0 2 4 6 8 10 12 14</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>Yellow Red Blue</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Red Yellow</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red Yellow</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless Pink</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>Yellow Red</td>
</tr>
</tbody>
</table>

Strong acids completely ionize.

\[ HA + H_2O \rightarrow H_3O^+ + A^- \]

For the monoprotic strong acids,

\[ [H_3O^+] = [\text{acid}] \]

- HCl, HNO_3, H_2SO_4, HBr, HI, HClO_3, HClO_4

Strong bases completely ionize.

\[ \text{MOH(aq)} \rightarrow \text{M}^+(aq) + \text{OH}^-(aq) \quad \text{or} \]
\[ \text{M(OH)}_2(aq) \rightarrow \text{M}^{2+}(aq) + 2 \text{OH}^-(aq) \]

- AOH (A = Li, Na, K, Rb, Cs); A(OH)_2 (A = Ca, Sr, Ba)
Weak Acids

• For a weak acid, the equation for its dissociation is
  \[ \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^- (aq) \]

• Since it is an equilibrium, there is an equilibrium constant related to it, called the acid-dissociation constant, \( K_a \):

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

Dissociation Constants

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structural Formula*</th>
<th>Conjugate Base</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorous (HClO)</td>
<td>( \text{H} \overset{\text{O}}{\text{O}} \overset{\text{Cl}}{\text{O}} )</td>
<td>( \text{ClO}_2^- )</td>
<td>( 1.0 \times 10^{-2} )</td>
</tr>
<tr>
<td>Hydrofluoric (HF)</td>
<td>( \text{H} \overset{\text{F}}{\text{F}} )</td>
<td>( \text{F}^- )</td>
<td>( 6.8 \times 10^{-4} )</td>
</tr>
<tr>
<td>Nitrous (HNO_2)</td>
<td>( \text{H} \overset{\text{O}}{\text{N}} \overset{\text{O}}{\text{O}} )</td>
<td>( \text{NO}_2^- )</td>
<td>( 4.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>Benzoic (C_6H_5COOH)</td>
<td><img src="image" alt="Benzoic Acid" /></td>
<td>( \text{C}_6\text{H}_5\text{COO}^- )</td>
<td>( 6.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>Acetic (CH_3COOH)</td>
<td>( \text{H} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{H}} )</td>
<td>( \text{CH}_3\text{COO}^- )</td>
<td>( 1.8 \times 10^{-5} )</td>
</tr>
<tr>
<td>Hypochlorous (HOCl)</td>
<td>( \text{H} \overset{\text{O}}{\text{O}} \overset{\text{Cl}}{\text{C}} )</td>
<td>( \text{OCl}^- )</td>
<td>( 3.0 \times 10^{-8} )</td>
</tr>
<tr>
<td>Hydrocyanic (HCN)</td>
<td>( \text{H} \overset{\text{C}}{\text{N}} )</td>
<td>( \text{CN}^- )</td>
<td>( 4.9 \times 10^{-10} )</td>
</tr>
<tr>
<td>Phenol (HOCl_2H_5)</td>
<td><img src="image" alt="Phenol" /></td>
<td>( \text{C}_6\text{H}_5\text{O}^- )</td>
<td>( 1.3 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

*The proton that ionizes is shown in red.

The greater the value of \( K_a \), the stronger is the acid.
Calculating $K_a$ from the pH

The pH of a 0.100 $M$ solution of formic acid, HCOOH, at 25°C is 2.38. Calculate $K_a$ for formic acid at this temperature.

$$\text{HCOOH} (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{HCOO}^- (aq)$$

We know that

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

To calculate $K_a$, we need the equilibrium concentrations of all three things. We can find $[\text{H}_3\text{O}^+]$, which is the same as $[\text{HCOO}^-]$, from the pH.

Calculating $K_a$ from pH

Now we can set up an ICE table...

<table>
<thead>
<tr>
<th></th>
<th>[HCOOH], M</th>
<th>[H$_3$O$^+$], M</th>
<th>[HCOO$^-$], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>0.100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Calculating Percent Ionization

\[
\text{Percent Ionization} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%
\]

In this example,
\[
\text{Percent Ionization} = \frac{[\text{H}_3\text{O}^+]_{eq}}{[\text{HA}]_{initial}} \times 100\%
\]

\[
[H_3O^+]_{eq} = 4.2 \times 10^{-3} \text{ M}
\]
\[
[\text{HCOOH}]_{initial} = 0.10 \text{ M}
\]
\[
\text{Percent Ionization} = \frac{4.2 \times 10^{-3}}{0.10} \times 100\%
\]
\[
= 4.2\%
\]

Method to Calculate pH Using \(K_a\)

1) Write the chemical equation for the ionization equilibrium.
2) Write the equilibrium constant expression.
3) Set up a table for Initial/Change in/Equilibrium Concentration to determine equilibrium concentrations as a function of change (\(x\)).
4) Substitute equilibrium concentrations into the equilibrium constant expression and solve for \(x\). (Make assumptions if possible)
Calculating pH from $K_a$

Calculate the pH of a 0.30 M solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, at 25°C.

$$\text{HC}_2\text{H}_3\text{O}_2 \ (aq) + \text{H}_2\text{O} \ (l) \rightleftharpoons \text{H}_3\text{O}^+ \ (aq) + \text{C}_2\text{H}_3\text{O}_2^- \ (aq)$$

$K_a$ for acetic acid at 25°C is $1.8 \times 10^{-5}$.

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Calculating pH from $K_a$

We next set up an ICE table...

<table>
<thead>
<tr>
<th></th>
<th>$[\text{HC}_2\text{H}_3\text{O}_2], \ M$</th>
<th>$[\text{H}_3\text{O}^+], \ M$</th>
<th>$[\text{C}_2\text{H}_3\text{O}_2^-], \ M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>0.30</td>
<td>$\approx0$</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td>- -</td>
<td>- -</td>
</tr>
</tbody>
</table>

We are assuming that $x$ will be very small compared to 0.30 and can, therefore, be ignored.

- $100*K_a = 100*(1.8 \times 10^{-5}) = 0.0018$
- $0.30-x = 0.30-0.0018 \approx 0.30$ (using sign. figures)

In general, the approximation that $[\text{HA}]_{eq}$ is effectively equal to $[\text{HA}]_0$ is valid whenever $[\text{HA}]_0$ is greater than $100*K_a$. 
**Strong vs. Weak Acids**

- Reaction proceeds more rapidly in strong acid, leading to formation of larger H₂ bubbles and rapid disappearance of metal.
- Reaction is complete in strong acid.
- H₂ bubbles show reaction still in progress in weak acid.
- Reaction eventually goes to completion in both acids.

Differences in conductivity and in rates of chemical reactions.

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As concentration increases, a smaller percentage of CH₃COOH molecules dissociates.

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**Percent ionized**

![Graph showing percent ionized versus acid concentration](image)

**Acid concentration (M)**

- 0.05
- 0.10
- 0.15

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Polyprotic Acids...

...have more than one acidic proton

Easier to remove the first proton than any successive proton.

If the difference between the $K_a$ for the first dissociation and subsequent $K_a$ values is $10^4$ or more, the pH generally depends only on the first dissociation.

**TABLE 16.3  Acid-Dissociation Constants of Some Common Polyprotic Acids**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_{a1}$</th>
<th>$K_{a2}$</th>
<th>$K_{a3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic</td>
<td>H$_2$C$_2$H$_2$O$_6$</td>
<td>$8.0 \times 10^{-3}$</td>
<td>$1.6 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>Carbonic</td>
<td>H$_2$CO$_3$</td>
<td>$4.3 \times 10^{-7}$</td>
<td>$5.6 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>Citric</td>
<td>H$_3$C$_6$H$_5$O$_7$</td>
<td>$7.4 \times 10^{-4}$</td>
<td>$1.7 \times 10^{-5}$</td>
<td>$4.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>Oxalic</td>
<td>HOOC—COOH</td>
<td>$5.9 \times 10^{-2}$</td>
<td>$6.4 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Phosphoric</td>
<td>H$_3$PO$_4$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>$6.2 \times 10^{-8}$</td>
<td>$4.2 \times 10^{-15}$</td>
</tr>
<tr>
<td>Sulfurous</td>
<td>H$_2$SO$_3$</td>
<td>$1.7 \times 10^{-2}$</td>
<td>$6.4 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>Sulfuric</td>
<td>H$_2$SO$_4$</td>
<td>Large</td>
<td>$1.2 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>Tartaric</td>
<td>C$_3$H$_2$O$_4$(COOH)$_2$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$4.6 \times 10^{-9}$</td>
<td></td>
</tr>
</tbody>
</table>

**Example (polyprotic acids)**

\[
\begin{align*}
\text{H}_3\text{PO}_4\ (aq) + \text{H}_2\text{O} \ (l) & \rightleftharpoons \text{H}_3\text{O}^+\ (aq) + \text{H}_2\text{PO}_4^-\ (aq) \\
K_{a1} & = 7.5 \times 10^{-3} \\
\text{H}_2\text{PO}_4^-\ (aq) + \text{H}_2\text{O} \ (l) & \rightleftharpoons \text{H}_3\text{O}^+\ (aq) + \text{HPO}_4^{2-}\ (aq) \\
K_{a2} & = 6.2 \times 10^{-8} \\
\text{HPO}_4^{2-}\ (aq) + \text{H}_2\text{O} \ (l) & \rightleftharpoons \text{H}_3\text{O}^+\ (aq) + \text{PO}_4^{3-}\ (aq) \\
K_{a3} & = 3.6 \times 10^{-13}
\end{align*}
\]

Successive $K_a$ values are smaller; it is less favorable to remove $\text{H}^+$ from an increasingly negatively charged ion.
Calculate the concentration of all species present at equilibrium in a 0.10 M oxalic acid solution at 25 °C.

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4(\text{aq}) & \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HC}_2\text{O}_4^-(\text{aq}) & K_{a1} = 6.5 \times 10^{-2} \\
\text{HC}_2\text{O}_4^-(\text{aq}) & \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) & K_{a2} = 6.1 \times 10^{-5}
\end{align*}
\]

**Weak Bases**

Bases react with water to produce hydroxide ion.

\[
\text{B} (\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{OH}^- (\text{aq})
\]

The equilibrium constant expression for this reaction is:

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

where \(K_b\) is the base-dissociation constant.
**Weak Bases**

$K_b$ can be used to find $[\text{OH}^-]$ and, through it, pH.

**Table 10.4 Some Weak Bases in Water at 25 °C**

<table>
<thead>
<tr>
<th>Base</th>
<th>Structural Formula</th>
<th>Conjugate Acid</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (NH$_3$)</td>
<td>H( \equiv )N( \equiv )H</td>
<td>NH$_4^+$</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pyridine (C$_5$H$_5$N)</td>
<td></td>
<td>C$_5$H$_5$NH$^+$</td>
<td>$1.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>Hydrazinium (HONH$_2$)</td>
<td></td>
<td>HONH$_3^+$</td>
<td>$1.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Methylamine (CH$_3$NH$_2$)</td>
<td></td>
<td>CH$_3$NH$_2^+$</td>
<td>$4.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrosulphide ion (HS$^-$)</td>
<td></td>
<td>HS$^-$(aq)</td>
<td>$1.8 \times 10^{-7}$</td>
</tr>
<tr>
<td>Carbonate ion (CO$_3^{2-}$)</td>
<td></td>
<td>CO$_3^{2-}$(aq)</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hypochlorite ion (ClO$^-$)</td>
<td></td>
<td>ClO$^-$(aq)</td>
<td>$3.3 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

*The atom that accepts the proton is shown in blue.

**pH of Basic Solutions**

What is the pH of a 0.15 $M$ solution of NH$_3$ at 25 °C?

\[
\text{NH}_3 (aq) + H_2O (l) \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq)
\]

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}
\]

Tabulate the data.

<table>
<thead>
<tr>
<th></th>
<th>$[\text{NH}_3]$, $M$</th>
<th>$[\text{NH}_4^+]$, $M$</th>
<th>$[\text{OH}^-]$, $M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Types of Weak Bases**

Two main categories

1) Neutral substances with an Atom that has a nonbonding pair of electrons that can accept H⁺ (e.g. ammonia and the amines)

2) Anions of weak acids

\[ \text{H}_3\text{N}(aq) + \text{H}_2\text{O}(l) \rightarrow \left[ \text{H}_3\text{N}^+ \left( \text{aq} \right) + \text{OH}^- \left( \text{aq} \right) \right] \]

### $K_a$ and $K_b$

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$</th>
<th>Base</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>(Strong acid)</td>
<td>NO₃⁻</td>
<td>(Negligible basicity)</td>
</tr>
<tr>
<td>HF</td>
<td>$6.8 \times 10^{-4}$</td>
<td>F⁻</td>
<td>$1.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>$1.8 \times 10^{-5}$</td>
<td>CH₃COO⁻</td>
<td>$5.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>$4.3 \times 10^{-7}$</td>
<td>HCO₃⁻</td>
<td>$2.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>$5.6 \times 10^{-10}$</td>
<td>NH₃</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>$5.6 \times 10^{-11}$</td>
<td>CO₃²⁻</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>OH⁻</td>
<td>(Negligible acidity)</td>
<td>O²⁻</td>
<td>(Strong base)</td>
</tr>
</tbody>
</table>

$K_a$ and $K_b$ are related in this way:

\[ K_a \times K_b = K_w \]

Therefore, if you know one of them, you can calculate the other.
Reactions of Anions with Water

• Anions are bases (conjugate base of an acid).
• As such, they can react with water in a hydrolysis reaction to form OH\(^{-}\) and the conjugate acid:

\[
X^- (aq) + H_2O (l) \rightleftharpoons HX (aq) + OH^- (aq)
\]

Reactions of Cations with Water

• Cations with acidic protons (like NH\(_4^+\)) will lower the pH of a solution.
• Most metal cations that are hydrated in solution also lower the pH of the solution.
Reactions of Cations with Water

- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O-H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic.

Effect of Cations and Anions

1. An anion that is the conjugate base of a strong acid will not affect the pH.
2. An anion that is the conjugate base of a weak acid will increase the pH.
3. A cation that is the conjugate acid of a weak base will decrease the pH.
4. Cations of the strong Arrhenius bases will not affect the pH.
5. Other metal ions will cause a decrease in pH.
6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the $K_a$ and $K_b$ values.
Factors Affecting Acid Strength

- The more polar the H-X bond and/or the weaker the H-X bond strength, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.

In oxyacids, in which an -OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.
Factors Affecting Acid Strength

For a series of oxyacids, acidity increases with the number of oxygens.
- Strength of an acid increases as additional electronegative atoms are added.

Arrange the following oxoacids in order of decreasing acid strength:

HClO, HClO₂, HClO₃, HBrO

(rank strongest to weakest)
Factors Affecting Acid Strength

Acidic behavior of carboxylic acids

- The additional oxygen attached to carbon draws electron density from the O-H bond, increasing polarity and stabilizing the conjugate base anion.
- **Resonance** in the conjugate bases of carboxylic acids stabilizes the anion by spreading the negative charge over several atoms.

Lewis Acids and Bases

- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted-Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.
Hydrated cations

\[ \text{M(H}_2\text{O)}_{6}^{n+}(\text{aq}) \rightleftharpoons \text{M(H}_2\text{O)}_{5}(\text{OH})^{(n-1)+}(\text{aq}) + \text{H}^+(\text{aq}) \]

\[ K_a = \frac{[\text{M(H}_2\text{O)}_{5}(\text{OH})^{(n-1)+}][\text{H}^+]}{[\text{M(H}_2\text{O)}_{6}^{n+}]} \]

\[ K_a \text{ values vary depending on the metal, meaning [H}^+] \text{ varies, thus pH depends on the metal.} \]

<table>
<thead>
<tr>
<th>Cation</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe^{3+}</td>
<td>6.3 \times 10^{-5}</td>
</tr>
<tr>
<td>Cr^{3+}</td>
<td>1.6 \times 10^{-6}</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>1.4 \times 10^{-5}</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>3.2 \times 10^{-10}</td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>2.5 \times 10^{-10}</td>
</tr>
<tr>
<td>Np^{3+}</td>
<td>2.5 \times 10^{-11}</td>
</tr>
</tbody>
</table>