Brønsted – Lowry Acids & Bases

- Brønsted-Lowry Acid: Proton (H⁺) Donor
- Brønsted-Lowry Base: Proton (H⁺) Acceptor
- General reaction:

\[ HA + B: \rightleftharpoons A^- + BH^+ \]

Conjugate Acid – Base Pairs

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>Conjugate Pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>H₂O</td>
<td>F⁻ + H₂O⁺</td>
</tr>
<tr>
<td>HCOOH</td>
<td>CN⁻</td>
<td>HCOO⁻ + HCN</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>CO₃²⁻</td>
<td>NH₃ + HCO₃⁻</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>OH⁻</td>
<td>HPO₄²⁻ + H₂O</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>SO₄²⁻</td>
<td>PO₄³⁻ + HSO₄⁻</td>
</tr>
</tbody>
</table>

Conjugate Pair

Acid + Base \rightleftharpoons Base + Acid
**Brønsted-Lowry Acids and Bases in Water**

A) Hydrochloric acid – Strong Acid – Complete dissociation in water
B) Ammonia – Weak Base – Partial deprotonation of water

**Examples of Brønsted-Lowry Acid-Base Reactions**

**General Reactivity**

These reactions illustrate a general pattern of reactivity:

- **Electron-rich** species react with electron-deficient species.
  - Bases are electron rich.
  - The H of an acid has a partial positive charge making it electron deficient.
  - Therefore, acids and bases tend to react with one another.

**Strong Acid – Strong Base Neutralization Reaction**

Consider the mixing of a solution of hydrochloric acid and sodium hydroxide.

- As discussed on a previous slide, hydrogen chloride fully dissociates in aqueous solution.
- Sodium hydroxide also fully dissociates.
- When the two solutions are mixed, the actual reaction is between hydronium and hydroxide ions.
**Autoionization of Water**

- $\text{H}_2\text{O}$ can function as both an ACID and a BASE.
- In pure water there can be **autoionization**:

$$2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$$

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

- Equilibrium constant for autoionization ($K_w$)

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

- In pure water, or in a neutral solution $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, so $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$

**pH – A Measure of Acidity**

**pH** = $-\log [\text{H}^+]$

- pH is a logarithmic scale commonly used to measure the [H$^+$] in solution.
- Because the pH scale is logarithmic, a change of one pH unit is equal to a $10 \times$ change in the [H$^+$] concentration.
- If the pH of a solution is known, the [H$^+$] can be easily determined by the following relationship, which is a rearrangement of the above equation:

$$[\text{H}^+] = 10^{(-\text{pH})}$$

**pH**

<table>
<thead>
<tr>
<th>[H$^+$]$^+$</th>
<th>pH</th>
<th>[OH$^-$]$^-$</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{-15}$</td>
<td>15.00</td>
<td>$1.0 \times 10^1$</td>
<td>$-1.00$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-14}$</td>
<td>14.00</td>
<td>$1.0 \times 10^0$</td>
<td>0.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-13}$</td>
<td>13.00</td>
<td>$1.0 \times 10^{-1}$</td>
<td>1.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-12}$</td>
<td>12.00</td>
<td>$1.0 \times 10^{-2}$</td>
<td>2.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-11}$</td>
<td>11.00</td>
<td>$1.0 \times 10^{-3}$</td>
<td>3.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
<td>$1.0 \times 10^{-4}$</td>
<td>4.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-9}$</td>
<td>9.00</td>
<td>$1.0 \times 10^{-5}$</td>
<td>5.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-8}$</td>
<td>8.00</td>
<td>$1.0 \times 10^{-6}$</td>
<td>6.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>7.00</td>
<td>$1.0 \times 10^{-7}$</td>
<td>7.00</td>
</tr>
</tbody>
</table>

**[H$^+$]$^+$**

**[OH$^-$]$^-$**

&

**powers of 10**

- **BASIC**
- **NEUTRAL**
- **ACIDIC**
Acid dissociation in water: $K_a$

- Consider the reaction of the weak acid, acetic acid:
  \[
  \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \\
  K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} \\
  \]

- In aqueous solution, $[\text{H}_2\text{O}] \approx 55 \text{ M}$ and is constant. It may be factored out of the equilibrium expression:
  \[
  K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.76 \times 10^{-5} \\
  \]

- In a general weak acid dissociation in water:
  \[
  \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \\
  K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \\
  \]

$pK_a$ scale

- In organic chemistry, we often talk about acid strength in terms of $pK_a$, where $pK_a = -\log K_a$
- Because this is a negative log relationship, the smaller the $pK_a$ value, the stronger the acid.

**Strengths of Acids: $K_a$**

- Larger $K_a$ values mean stronger acids.

<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure*</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorous acid (HClO2)</td>
<td>$\text{H}^-\text{Cl}=\text{O}^{-}$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Nitrous acid (HNO2)</td>
<td>$\text{H}^-\text{N}=\text{O}^{-}$</td>
<td>$7.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrofluoric acid (HF)</td>
<td>$\text{H}^-\text{F}$</td>
<td>$6.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Formic acid (HCOOH)</td>
<td>$\text{H}^-\text{C}=-\text{H}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Acetic acid (CH3COOH)</td>
<td>$\text{H}^-\text{C}(-\text{O})\text{H}$</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Propanoic acid (CH3CH2COOH)</td>
<td>$\text{H}^-\text{C}(-\text{O})\text{CH}_{2}\text{H}$</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hypochlorous acid (HClO)</td>
<td>$\text{H}^-\text{Cl}=$</td>
<td>$2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hydrocyanic acid (HCN)</td>
<td>$\text{H}^-\text{C}(-\text{N})\equiv\text{H}$</td>
<td>$6.2 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

**Predicting the Strengths of Bases**

- Because of the relationship between $K_a$, $K_b$, & $K_w$, the stronger an acid, the weaker its conjugate base will be.
  - An acid with a low $pK_a$ (stronger acid) will have a weaker conjugate base.
  - Chloride is a very weak base because its conjugate acid HCl is a very strong acid.
  - Acetate is a moderately weak base because its conjugate acid is a weak acid.

Increasing base strength

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a$ of conjugate acid</th>
<th>$pK_a$ value</th>
<th>Base strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>$-7$</td>
<td>Very weak</td>
<td>Very weak base</td>
</tr>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>4.75</td>
<td>Weak</td>
<td>Weak base</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>15.7</td>
<td>Strong</td>
<td>Strong base</td>
</tr>
</tbody>
</table>

Inorganic chemistry, we often talk about acid strength in terms of $pK_a$, where $pK_a = -\log K_a$ because this is a negative log relationship, the smaller the $pK_a$ value, the stronger the acid. Acetate is a moderately weak base because its conjugate acid is a weak acid. Chloride is a very weak base because its conjugate acid HCl is a very strong acid. Predicting the Strengths of Bases: Because of the relationship between $K_a$, $K_b$, & $K_w$, the stronger an acid, the weaker its conjugate base will be. Acid dissociation in water: $K_a$: Consider the reaction of the weak acid, acetic acid: $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$ $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} = 1.76 \times 10^{-5}$ In aqueous solution, $[\text{H}_2\text{O}] \approx 55 \text{ M}$ and is constant. It may be factored out of the equilibrium expression: $K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.76 \times 10^{-5}$ In a general weak acid dissociation in water: $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$ $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$ $pK_a$ scale: In organic chemistry, we often talk about acid strength in terms of $pK_a$, where $pK_a = -\log K_a$ because this is a negative log relationship, the smaller the $pK_a$ value, the stronger the acid. $\text{CH}_3\text{CO}_2\text{H} < \text{CF}_3\text{CO}_2\text{H} < \text{HCl}$ $pK_a = 4.75$ $pK_a = 0$ $pK_a = -7$ Weak acid Very strong acid Increasing acid strength
The position of the equilibrium depends on the relative strengths of the acids and bases.

Equilibrium always favors formation of the weaker acid and base.

Because the $pK_a$ of the starting acid (25) is lower than that of the conjugate acid (38), equilibrium favors the products.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a$</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>H−Cl</td>
<td>7</td>
<td>Cl−</td>
</tr>
<tr>
<td>CH₃COO−H</td>
<td>4.8</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>HO−H</td>
<td>15.7</td>
<td>HO⁺</td>
</tr>
<tr>
<td>CH₂CH₂O−H</td>
<td>16</td>
<td>CH₂CH₂O⁻</td>
</tr>
<tr>
<td>HCN</td>
<td>25</td>
<td>HCN⁻</td>
</tr>
<tr>
<td>H−H</td>
<td>35</td>
<td>H⁺</td>
</tr>
<tr>
<td>H₂N−H</td>
<td>38</td>
<td>H₂N⁺</td>
</tr>
<tr>
<td>CH₂=CH₂</td>
<td>44</td>
<td>CH₂=CH⁻</td>
</tr>
<tr>
<td>CH₃−H</td>
<td>50</td>
<td>CH₃⁻</td>
</tr>
</tbody>
</table>

1) Identify the acid and base in the starting materials. Assume $\text{NH}_2^-$ is the base because it bears a net negative charge. That makes HCN favored as the acid.

2) Draw the products of proton transfer and identify the conjugate acid and base in the products. Acetylene gives up its proton to $\text{NH}_2^-$.

3) Compare the $pK_a$ values of the acid and the conjugate acid. Equilibrium favors formation of the weaker acid with the higher $pK_a$. The $pK_a$ of NH₃ is higher; therefore products are favored.
Acid-base reaction always favor the formation of the weaker acid / weaker base pair.

The weaker acid / weaker base are always on the same side of the equation.

Example: Acetic acid reacts with sodium hydroxide to greatly favor products: water & sodium acetate

\[
\text{Stronger acid} \quad pK_a = 3-5 \quad \text{Stronger base} \quad \text{Weaker base} \quad \text{Weaker acid} \quad pK_a = 15.7
\]

Predicting K for an acid–base reaction

\[
K = 10^{[pK_a \text{ (product acid)} - pK_a \text{ (reactant acid)} ]}
\]

Factors that Determine Acid Strength

- Anything that stabilizes a conjugate base A:\(\text{^-}\) makes the starting acid H-A more acidic.

- Four factors affect the acidity of H-A. These are:
  - Element effects
  - Inductive effects
  - Resonance effects
  - Hybridization effects
Comparing the Acidity of Any Two Acids

- Always draw the conjugate bases.
- Determine which conjugate base is more stable.
- The more stable the conjugate base, the more acidic the acid.

Element Effects—Trends in the Periodic Table

Why does H₂O have a much lower pKₐ than CH₄?

Since oxygen is much more electronegative than carbon, it more readily accepts a negative charge.

Element Effects—Trends in the Periodic Table

Across a row of the periodic table, the acidity of H-A increases as the electronegativity of A increases.

\[
pK_a \approx 50 \quad \text{pK}_a = 38 \quad \text{pK}_a = 16 \quad \text{pK}_a = 3.2
\]

\[
\text{CH}_3^- \quad \text{H}_2\text{N}^- \quad \text{HO}^- \quad \text{F}^-
\]

Increasing electronegativity → Increasing acidity

Basicity increases

Element Effects Down a Column in the Periodic Table

- Down a column of the periodic table, size, and not electronegativity, determines acidity. The acidity of H-A increases as the size of A increases.

Positive or negative charge is stabilized when it is spread over a larger volume.

\[
pK_a = 3.2 \quad \text{pK}_a = 7 \quad \text{pK}_a = 9 \quad \text{pK}_a = 10
\]

\[
\text{H--F} \quad \text{H--Cl} \quad \text{H--Br} \quad \text{H--I}
\]

Increasing size → Increasing acidity
Summary of Acidity Trends

<table>
<thead>
<tr>
<th>Hybrid</th>
<th>C (H₂C−H)</th>
<th>N (H₂N−H)</th>
<th>O (HO−H)</th>
<th>F (F−H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKₐ</td>
<td>48</td>
<td>38</td>
<td>15.7</td>
<td>3.2</td>
</tr>
</tbody>
</table>

- An inductive effect is the pull of electron density through σ bonds caused by electronegativity differences of atoms.
- More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.
- The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.
- The acidity of H-A increases with the presence of electron withdrawing groups in A.

Inductive Effects in Trifluoroethanol

- In the example below, note that 2,2,2-trifluoroethanol is more acidic than ethanol.
  - CH₃CH₂O−H (ethanol) pKₐ = 16
  - CF₃CH₂O−H (2,2,2-trifluoroethanol) pKₐ = 12.4
  - The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.

Rationale for Inductive Effects

- CH₃CH₂O−
- CF₃CH₂O−

No additional electronegative atoms stabilize the conjugate base.

CF₃ withdraws electron density, stabilizing the conjugate base.

The dark red of the O atom indicates a region of high electron density.

The O atom is yellow, indicating it is less electron rich.
Resonance Effects

- Delocalization of charge through resonance influences acidity.
- Acetic acid is more acidic than ethanol, even though both conjugate bases have the negative charge on the same element, O.

\[ \text{Ethanol} \quad \text{Acetic acid} \]
\[ pK_a = 16 \quad pK_a = 4.8 \quad \text{stronger acid} \]

Comparison of Ethoxide and Acetate ions

- The conjugate base of ethanol has a localized charge.
- The conjugate base of acetic acid has the charge resonance delocalized.

Inductive effects also play a role

- Acetic acid:
The highly polarized carbonyl group draws electron density away from the acidic hydrogen.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Acetic acid: (stronger acid)
Ethanol: (weaker acid)

- Acetate ion:
Also the conjugate base of acetic acid is more stabilized by the carbonyl group.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{δ−} & \quad \text{δ−}
\end{align*}
\]

Acetate anion: Weaker base
Ethoxide anion: Stronger base

Electrostatic Potential Plots of Ethoxide and Acetate

- The negative charge is concentrated on the single oxygen atom, making this anion less stable.
- The negative charge is delocalized over both oxygen atoms, making this anion more stable.
Hybridization Effects

Consider the relative acidities of three different compounds containing C-H bonds.

- **CH₃CH₃** (ethane) pKₐ = 50
- **CH₂=CH₂** (ethylene) pKₐ = 44
- **H–C≡C–H** (acetylene) pKₐ = 25

**weakest acid** → **strongest acid**

Increasing acidity

- **CH₃CH₂** (sp³ hybridized C, 25% s-character)
- **CH₂=CH₂** (sp² hybridized C, 33% s-character)
- **H–C≡C⁻** (sp hybridized C, 50% s-character)

Increasing percent s-character → Increasing stability

Stability of Conjugate Bases

The higher the percent of s-character of the hybrid orbital, the more stable the conjugate base.

Figure 2.4

Summary of Factors that Determine Acid Strength

**Figure 2.5**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Example</th>
<th>Increasing acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. <strong>Element effects:</strong> The acidity of H–A increases both left-to-right across a row and down a column of the periodic table.</td>
<td>![C–H, N–H, O–H, H–F, H–Cl, H–Br, H–I]</td>
<td>![Increasing acidity]</td>
</tr>
<tr>
<td>2. <strong>Inductive effects:</strong> The acidity of H–A increases with the presence of electron-withdrawing groups in A.</td>
<td>CH₃CH₂O–H, CF₃CH₂O–H</td>
<td>![more acidic]</td>
</tr>
<tr>
<td>3. <strong>Resonance effects:</strong> The acidity of H–A increases when the conjugate base A⁻ is resonance stabilized.</td>
<td>CH₃CH₂O–H, CH₂COO–H</td>
<td>![more acidic]</td>
</tr>
<tr>
<td>4. <strong>Hybridization effects:</strong> The acidity of H–A increases as the percent s-character of A⁻ increases.</td>
<td>CH₃CH₃, CH₂=CH₂, H–C≡C–H</td>
<td>![Increasing acidity]</td>
</tr>
</tbody>
</table>

- As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.