Chapter 3
Acids and Bases
Acids and Bases

Brønsted-Lowry Acids and Bases
• A Brønsted-Lowry acid is a proton donor.
• A Brønsted-Lowry base is a proton acceptor.
• $H^+ = \text{proton}$
Reactions of Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid base reaction results in the transfer of a proton from an acid to a base.
- In an acid-base reaction, the electron pair of the base B: forms a new bond to the proton of the acid.
- The acid H—A loses a proton, leaving the electron pair in the H—A bond on A.
Acids and Bases

Every acid/base reaction has two acids and two bases.

Conjugate Acid/Base Pairs
Acids and Bases

There are two kinds of acids:

**Strong Acids** (completely dissociated in water)

Example:

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

**Weak Acids** (partly dissociated in water)

Example:

\[ \text{HAc} + \text{H}_2\text{O} \leftrightarrow \text{Ac}^- + \text{H}_3\text{O}^+ \]
Acids and Bases

There are only about 6 “STRONG ACIDS”:

HCl, HBr, HI, H$_2$SO$_4$, HNO$_3$, HClO$_4$

ALL other acids are “WEAK ACIDS”
For Weak (most) Acids

Acid Strength and $pK_a$

• Acid strength is the tendency of an acid to donate a proton.
• The more readily a compound donates a proton, the stronger an acid it is.
• Acidity is measured by an equilibrium constant.
• When a Brønsted-Lowry acid H—A is dissolved in water, an acid-base reaction occurs, and an equilibrium constant can be written for the reaction.

\[
K_{eq} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[H_3O^+][A^-]}{[H-A][H_2O]}
\]
Acids and Bases

Acid Strength and $pK_a$

Because the concentration of the solvent $H_2O$ is essentially constant, the equation can be rearranged and a new equilibrium constant, called the acidity constant, $K_a$, can be defined.

\[
\text{Acidity constant } = K_a = [H_2O]K_{eq} = \frac{[H_3O^+][A^{-}]}{[H-A]}
\]

Larger $K_a$, the further to the right, the stronger acid
Smaller $K_a$, the further to the left, the weaker the acid.

Therefore, the value of $K_a$ is a measure of acid strength
### Acids and Bases

#### Acid Strength and $pK_a$

It is generally more convenient when describing acid strength to use "$pK_a$" values than $K_a$ values.

<table>
<thead>
<tr>
<th>$K_a$</th>
<th>$pK_a = -\log K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$K_a$ values of typical organic acids</strong></td>
<td><strong>$pK_a$ values of typical organic acids</strong></td>
</tr>
<tr>
<td>$10^{-5}$ to $10^{-50}$</td>
<td>$+5$ to $+50$</td>
</tr>
<tr>
<td>larger number</td>
<td>smaller number</td>
</tr>
<tr>
<td>stronger acid</td>
<td>weaker acid</td>
</tr>
</tbody>
</table>

- Larger $K_a =$ stronger acid/Smaller $pK_a =$ stronger acid
- Smaller $K_a =$ weaker acid/Larger $pK_a =$ weaker acid
## Acids and Bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Approximate pK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongest acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;SiF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>&lt; -12</td>
<td>SbF&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>HI</td>
<td>-10</td>
<td>I&lt;sup&gt;-&lt;/sup&gt;</td>
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<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-9</td>
<td>HSO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>HBr</td>
<td>-9</td>
<td>Br&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>HCl</td>
<td>-7</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>-6.5</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C=O</td>
<td>-2.9</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C=O</td>
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<td>-2.5</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
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<td>-1.74</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>HNO&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>6.35</td>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;COCH&lt;sub&gt;2&lt;/sub&gt;COCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.0</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;COCH&lt;sub&gt;2&lt;/sub&gt;COCH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>9.2</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>9.9</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;O&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>18</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>19.2</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;COCH&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>HC≡CH</td>
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<td>HC≡C&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>35</td>
<td>H&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>38</td>
<td>NH&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>44</td>
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<td>50</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

## Increasing acid strength

## Increasing base strength

| Weakest acid | CH<sub>3</sub>CH<sub>3</sub> | 50 | CH<sub>3</sub>CH<sub>2</sub><sup>-</sup> | Strongest base |
Acids and Bases

Amphoteric or Amphiprotic Substances

Substances which can be either acids or bases.

For example: \( \text{H}_2\text{O} \)

Such compounds exist as two, independent conjugate acid/base pairs with two different \( \text{pK}_a \) values.

\( \text{H}_2\text{O} \) as an acid: \( \text{H}_2\text{O} / \text{HO}^- \) (\( \text{pK}_a = 15.7 \))

\( \text{H}_2\text{O} \) as a base: \( \text{H}_3\text{O}^+ / \text{H}_2\text{O} \) (\( \text{pK}_a = -1.74 \))
Factors that Determine Acid Strength

- Anything that stabilizes a conjugate base $A^-\,$ 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

- No matter which factor is discussed, the same procedure is always followed. To compare 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.
Factors that Determine Acid Strength

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.

$$pK_a = 50 \quad pK_a = 38 \quad pK_a = 16 \quad pK_a = 3.2$$

Increasing electronegativity

Increasing acidity

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

<table>
<thead>
<tr>
<th>Anion</th>
<th>H—A</th>
<th>pK_a</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>F^-</td>
<td>H—F</td>
<td>3.2</td>
<td>less stable conjugate base</td>
</tr>
<tr>
<td>Br^-</td>
<td>H—Br</td>
<td>-9</td>
<td>more stable conjugate base</td>
</tr>
</tbody>
</table>
Acids and Bases

Factors that Determine Acid Strength—Inductive Effects

- An inductive effect is the pull of electron density through $\sigma$ bonds caused by electronegativity differences in atoms.
- In the example below, when we compare the acidities of ethanol and 2,2,2-trifluoroethanol, we note that the latter is more acidic than the former.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{O}-\text{H} & \quad \text{CF}_3\text{CH}_2\text{O}-\text{H} \\
\text{ethanol} & \quad \text{2,2,2-trifluoroethanol} \\
pK_a = 16 & \quad pK_a = 12.4 \quad \text{(stronger acid)}
\end{align*}
\]
The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.

\[ \text{CH}_3\text{CH}_2\text{O}^- \]

No additional electronegative atoms stabilize the conjugate base. CF$_3$ withdraws electron density, stabilizing the conjugate base.
Factors that Determine Acid Strength—Inductive Effects

- When electron density is pulled away from the negative charge through $\sigma$ bonds by very electronegative atoms, it is referred to as an electron withdrawing inductive effect.
- 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 $A$.
Factors that Determine Acid Strength—Resonance Effects

- Resonance is a third factor that influences acidity.
- In the example below, when we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.

When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.

- The negative charge is localized on O.

Only one Lewis structure
Acids and Bases

Factors that Determine Acid Strength—Resonance Effects

• Resonance delocalization makes $\text{CH}_3\text{COO}^-$ more stable than $\text{CH}_3\text{CH}_2\text{O}^-$, so $\text{CH}_3\text{COOH}$ is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$.

• The acidity of $\text{H—A}$ increases when the conjugate base $\text{A}^-$ is resonance stabilized.
Factors that Determine Acid Strength—Hybridization Effects

- The final factor affecting the acidity of $H\text{--}A$ is the hybridization of A.

Let us consider the relative acidities of three different compounds containing $C\text{--}H$ bonds.

- The higher the percent of $s$-character of the hybrid orbital, the closer the lone pair is held to the nucleus, and the more stable the conjugate base.
Acids and Bases
Factors that Determine Acid Strength—Hybridization Effects

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

### Summary of Factors that Determine Acid Strength—Hybridization Effects

<table>
<thead>
<tr>
<th>Factor</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element effect</strong></td>
<td>The acidity of $H-A$ increases both left-to-right across a row and down a column of the periodic table.</td>
</tr>
</tbody>
</table>

- $\text{CH}_4 \quad \text{NH}_3 \quad \text{OH}^— \quad \text{F}^- \quad \text{Cl}^- \quad \text{Br}^- \quad \text{I}^-$

<table>
<thead>
<tr>
<th><strong>Inductive effects</strong></th>
<th>The acidity of $H-A$ increases with the presence of electron-withdrawing groups in $A$.</th>
<th>CH$_3$CH$_2$O—H, CF$_3$CH$_2$O—H (more acidic)</th>
</tr>
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<table>
<thead>
<tr>
<th><strong>Resonance effects</strong></th>
<th>The acidity of $H-A$ increases when the conjugate base $A^-\text{ is resonance stabilized.}$</th>
<th>CH$_3$CH$_2$O—H, CH$_3$COO—H (more acidic)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th><strong>Hybridization effects</strong></th>
<th>The acidity of $H-A$ increases as the percent $s$-character of $A$ increases.</th>
<th>Increasing acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_3$</td>
<td>CH$_2$=CH$_2$</td>
<td>H—C≡C—H</td>
</tr>
</tbody>
</table>
Acids and Bases

Acid/base equilibria always favor the side of the weaker acid and the weaker base

For Example:

\[
\text{HOAc} + \text{CN} \rightleftharpoons \text{AcO}^- + \text{HCN}
\]

Acid \quad \text{Base} \quad \text{Base} \quad \text{Acid}

Stronger \quad \text{Stronger} \quad \text{Weaker} \quad \text{Weaker}

\textit{ALWAYS}

\[
\text{HOAc/}\text{AcO}^- \quad \text{pKa} = 4.75
\]

\[
\text{HCN/}\text{CN}^- \quad \text{pKa} = 9.22
\]
What Makes a Compound Behave as a Base?

Any organic compound containing an atom with a lone pair (O,N) can act as a base.
Acids and Bases

Lewis Acids and Bases

• The Lewis definition of acids and bases is more general than the Brønsted-Lowry definition.

• A Lewis acid is an electron pair acceptor.

• A Lewis base is an electron pair donor.

• Lewis bases are structurally the same as Brønsted-Lowry bases. Both have an available electron pair—a lone pair or an electron pair in a \( \pi \) bond.

• A Brønsted-Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.
Lewis Acids and Bases

- A Lewis acid must be able to accept an electron pair, but there are many ways for this to occur.
- All Brønsted-Lowry acids are also Lewis acids, but the reverse is not necessarily true.
  - Any species that is electron deficient and capable of accepting an electron pair is also a Lewis acid.
- Common examples of Lewis acids (which are not Brønsted-Lowry acids) include BF$_3$ and AlCl$_3$. These compounds contain elements in group 3A of the periodic table that can accept an electron pair because they do not have filled valence shells of electrons.

Examples of Lewis acids

- H$_2$O
- CH$_3$OH
- BF$_3$
- AlCl$_3$

- These compounds are both Brønsted–Lowry acids and Lewis acids.
- These compounds are only Lewis acids.
Lewis Acids and Bases

- Any reaction in which one species donates an electron pair to another species is a Lewis acid-base reaction.
- In a Lewis acid-base reaction, a Lewis base donates an electron pair to a Lewis acid.
- In the simplest Lewis acid-base reaction one bond is formed and no bonds are broken. This is illustrated in the reaction of $\text{BF}_3$ with $\text{H}_2\text{O}$. $\text{H}_2\text{O}$ donates an electron pair to $\text{BF}_3$ to form a new bond.
Lewis Acids and Bases

- A Lewis acid is also called an electrophile.
- When a Lewis base reacts with an electrophile (other than a proton), the Lewis base is also called a nucleophile. In this example, BF$_3$ is the electrophile and H$_2$O is the nucleophile.
Nucleophiles and Electrophiles

The Organic chemistry terms for Lewis acids and bases

Electrophiles ("electron-loving" reagents): seek electrons to obtain a stable valence shell of electrons
  ➔ Are electron-deficient themselves

Some Examples are: \( \text{H}^+ \)  \( \text{Cl-Al-Cl} \)  \( \text{H-C}^+ \)

NOTE:
An electrophile can either be neutral or have a positive charge.

The important thing is that they have "room" for a pair of electrons.
Nucleophiles (“nucleus-loving” reagents): seek a proton or some other positively charged center

- Are electron-rich themselves

Some Examples are: 

\[
\begin{align*}
\text{H} & \text{N} & \text{H} \\
\text{H} \\
\text{H} & \text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{O} & \text{H} \\
\text{H} & \text{H} \text{CH}_2 & \text{CH}_2
\end{align*}
\]

NOTE:

A nucleophile can either be neutral or have a negative charge.

The important thing is that it be able to donate a pair of electrons (either from a lone pair or from a pi-bond)
Use of Curved Arrows in Illustrating Reactions

- Curved arrows show the movement of electrons in a reaction
- An arrow starts at site of higher electron density (a covalent bond or unshared electron pair) and points to site of electron deficiency
- Examples:

  \[
  \begin{align*}
  &\text{H} - \text{O}^\cdot + \text{H}^\cdot \text{Cl}^\cdot \rightarrow \text{H}^\cdot \text{O}^+ \text{H}^\cdot + \text{Cl}^- \\
  &\text{C} = \text{C}^\cdot + \text{H}^\cdot \text{Cl}^\cdot \rightarrow \text{C}^+ \text{C}^- \text{H}^- + \text{Cl}^-
  \end{align*}
  \]

  **Note:** Electron pairs move from the nucleophile to the electrophile
A Mechanism for an Organic Reaction
(The First Example of Many)

The Substitution Reaction of tert-Butyl Alcohol

This is the overall reaction:

\[
\begin{align*}
\text{CH}_3 & \quad \text{OH} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - & \quad \text{H} - \text{O}^+ - \text{H} + :\text{Cl}^- \\
\text{H}_3\text{C} - & \quad \text{H}_3\text{C} - \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

You will be doing this exact reaction in the lab this semester
The Mechanism Has Three Steps

All steps are actually acid-base reactions

Step 1:

- tert-Butyl alcohol acts as a base and accepts a proton from the hydronium ion. (Chloride anions are spectators in this step of the reaction.)

- tert-Butyloxonium ion

The products are a protonated alcohol and water (the conjugate acid and base).

Step 2:

- Carbocation

The bond between the carbon and oxygen of the tert-butyloxonium ion breaks heterolytically, leading to the formation of a carbocation and a molecule of water.

Step 3:

- tert-Butyl chloride

The carbocation, acting as a Lewis acid, accepts an electron pair from a chloride ion to become the product.
Acids and Bases in Nonaqueous Solutions

Sodium amide (NaNH₂) can be used as a strong base in solvents such as liquid NH₃.

\[
\begin{align*}
\text{H—C≡C—H} + \text{NH}_2^- & \xrightarrow{\text{liquid NH}_3} \text{H—C≡C}^+ + \text{NH}_3 \\
\text{Stronger acid} & \quad \text{Stronger base (from NaNH}_2) \\
pK_a = 25 & \quad \text{Weaker base} \\
\end{align*}
\]
Alkyl lithium reagents in hexane are extremely strong bases.

We need to use non-protic solvents when we use strong bases.