Arrhenius Acids and Bases

• In 1884, Svante Arrhenius proposed these definitions
  – **acid**: A substance that produces $\text{H}_3\text{O}^+$ ions aqueous solution.
  – **base**: A substance that produces $\text{OH}^-$ ions in aqueous solution.
  – this definition of an acid is a slight modification of the original Arrhenius definition, which was that an acid is a substance that produces $\text{H}^+$ in aqueous solution.
  – today we know that $\text{H}^+$ reacts immediately with a water molecule to give a **hydronium ion**.

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

**Hydronium ion**
**Brønsted-Lowry Definitions**

**Acid:** proton donor.  **Base:** proton acceptor.

![Acid and Base Diagram]

**Conjugate Acids & Bases**

- **Conjugate base:** The species formed from an acid when it donates a proton to a base.
- **Conjugate acid:** The species formed from a base when it accepts a proton from an acid.
- **Acid-base reaction:** A proton-transfer reaction.
- **Conjugate acid-base pair:** Any pair of molecules or ions that can be interconverted by transfer of a proton.
**Conjugate Acids & Bases**

- Brønsted-Lowry definitions do not require water as a reactant.
- Consider the following reaction between acetic acid and ammonia.

\[
\text{CH}_3\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{COO}^- + \text{NH}_4^+
\]

(conjugate acid-base pair)

**Acids & Bases**

- Use curved arrows to show the flow of electrons in an acid-base reaction.

\[
\text{CH}_3\cdot\text{C}\cdot\text{O}^- + \text{H}^+ \rightarrow \text{CH}_3\cdot\text{C} \cdot\text{O}^-
\]

(proton donor) (proton acceptor) (conjugate base of acetic acid) (conjugate acid of ammonia)

(conjugate acid-base pair)
Many organic molecules have two or more sites that can act as proton acceptors.

- In this chapter, discussion is limited to carboxylic acids, esters, and amides.
- In these molecules, the favored site of protonation is the one in which the charge is more delocalized.
- Question: Which oxygen of a carboxylic acid is protonated?

\[ \text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{HSO}_4^- \]

(protonated on the carbonyl oxygen)

(protonated on the hydroxyl oxygen)

Proton-transfer reactions occur with compounds having \( \pi \) electrons, as for example the \( \pi \) electrons of carbon-carbon double and triple bonds.

The pi electrons of 2-butene, for example, react with HBr by proton transfer to form a new C-H bond.

\[ \text{CH}_2=\text{CHCH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{C}^+\text{C}_\text{Br}^- \]

(2° carbocation)
The result is formation of a carbocation, a species in which one of its carbons has only six electrons in its valence shell and carries a charge of +1.

\[ \text{CH}_3-\text{CH}≡\text{CH}-\text{CH}_3 + \text{H}\text{Br} \rightarrow \text{CH}_3-\text{C}≡\text{C}-\text{CH}_3 + \text{Br}^- \]

2-Butene \hspace{1cm} sec-Butyl cation (a 2° carbocation)

**π Electrons As Basic Sites**

**Carbocation**
Sample Problem: Draw Lewis structures for the two possible carbocations formed by proton transfer from HBr to 2-methyl-2-butene.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3\text{C}==\text{CHCH}_3 + \text{H}^+\text{Br}^- \\
2\text{-Methyl-2-butene} & \\
\end{align*}
\]

Acids & Base Strengths

- The strength of an acid is expressed by an equilibrium constant.
  - The acid dissociation of acetic acid is given by the following equation.

\[
\begin{align*}
\text{CH}_3\text{COH} & + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}^- & + \text{H}_3\text{O}^+ \\
\text{Acetic acid} & \quad \text{Water} & \text{Acetate ion} & \text{Hydronium ion} \\
\end{align*}
\]
Weak Acids and Bases

An equilibrium expression for the dissociation of any uncharged acid, HA, is written as:

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

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

Weak Acids and Bases

- Water is a solvent and its concentration is a constant equal to approximately 55.5 mol/L.
- We can combine these constants to give a new constant, $K_a$, called an acid dissociation constant.

$$K_a = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
Acid-Base Equilibria

- Equilibrium favors reaction of the stronger acid and stronger base to give the weaker acid and weaker base.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>$pK_a$</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>$CH_2CH_3$</td>
<td>51</td>
<td>$CH_3CH_2^-$</td>
</tr>
<tr>
<td>Ethylene</td>
<td>$CH_2=CH_2$</td>
<td>44</td>
<td>$CH_3=CH^-$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$NH_3$</td>
<td>38</td>
<td>$NH_2^-$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$H_2$</td>
<td>35</td>
<td>$H^+$</td>
</tr>
<tr>
<td>Acetylene</td>
<td>$HC=CH$</td>
<td>25</td>
<td>$HC=CH^-$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$CH_3CH_2OH$</td>
<td>15.9</td>
<td>$CH_3CH_2O^-$</td>
</tr>
<tr>
<td>Water</td>
<td>$H_2O$</td>
<td>15.7</td>
<td>$HO^-$</td>
</tr>
<tr>
<td>Methylammonium ion</td>
<td>$CH_3NH_3^+$</td>
<td>10.64</td>
<td>$CH_3NH_2$</td>
</tr>
<tr>
<td>Bicarbonate ion</td>
<td>$HCO_3^-$</td>
<td>10.33</td>
<td>$CO_3^{2-}$</td>
</tr>
<tr>
<td>Phenol</td>
<td>$C_6H_5OH$</td>
<td>9.95</td>
<td>$C_6H_5O^-$</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>$NH_4^+$</td>
<td>9.24</td>
<td>$NH_3$</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>$H_2S$</td>
<td>7.04</td>
<td>$HS^-$</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>$H_2CO_3$</td>
<td>6.36</td>
<td>$HCO_3^-$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$CH_3COOH$</td>
<td>4.76</td>
<td>$CH_3COO^-$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$C_6H_5COOH$</td>
<td>4.19</td>
<td>$C_6H_5COO^-$</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>$H_3PO_4$</td>
<td>2.1</td>
<td>$H_2PO_4^-$</td>
</tr>
<tr>
<td>Hydronium ion</td>
<td>$H_3O^+$</td>
<td>-1.74</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>$H_2SO_4$</td>
<td>-5.2</td>
<td>$HSO_4^-$</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>$HCl$</td>
<td>-7</td>
<td>$Cl^-$</td>
</tr>
<tr>
<td>Hydrogen bromide</td>
<td>$HBr$</td>
<td>-8</td>
<td>$Br^-$</td>
</tr>
<tr>
<td>Hydrogen iodide</td>
<td>$HI$</td>
<td>-9</td>
<td>$I^-$</td>
</tr>
</tbody>
</table>

Acid: $CH_3COOH$ (stronger acid)  $pK_a$: 4.76
Base: $NH_3$ (stronger base)

Favors the side with the highest $pK_a$ (i.e. weaker acid)
Consider the reaction between acetic acid and sodium bicarbonate.

- write the equilibrium as a net ionic equation.
- omit Na\(^+\) because it does not undergo any chemical change in the reaction.

\[
\text{CH}_3\text{COH} + \text{HCO}_3^- \rightleftharpoons \text{CH}_3\text{CO}^- + \text{H}_2\text{CO}_3
\]

- Equilibrium lies to the right.
- Carbonic acid forms, which then decomposes to carbon dioxide and water.

**Thermochemistry & Mechanisms**

- **Reaction mechanism**: A step-by-step description of how a chemical reaction occurs.
- **Thermochemistry**: The study of the energy of an entire system at each and every instant of a reaction.
- **Reaction coordinate diagram**: A graph showing the energy changes that occur during a chemical reaction. Energy is plotted on the vertical axis and reaction progress (time) is plotted along the horizontal axis.
Most chemical reactions occur via collisions.

- During collisions, the structure of a molecule contorts and flexes. Collisions of higher energy lead to larger distortions in structure.
- During collisions, the kinetic energy of the reactants is converted to potential energy, which is stored in the chemical structures in the form of structural strains.

During a collision process that yields a reaction, a transition state (≠) is formed which possesses partially broken and partially formed bonds.

Chemists use reaction coordinate diagrams to show the changes in energy for the molecules involved in a chemical reaction.
Thermochemistry & Mechanisms

A reaction coordinate diagram for a one step reaction between H-A and B.

Thermochemistry & Mechanisms

• For reactions at constant pressure, the change in Gibbs free energy, $\Delta G^\circ$, is used.
  – This kind of energy controls the rates and equilibrium of reactions.
  – The change in Gibbs free energy between reactants and products is related to the equilibrium constant through this equation:
    
    $\Delta G^\circ = -RT \ln K_{eq}$
    
    where $R = 8.31\text{J/K mol}$ and $T$ is the temperature in kelvins.
  – Free energy of activation: The difference in energy between reactants and the transition state.
The overriding principle in determining the relative acidities of uncharged organic acids is the stability of the anion, $A^-$, resulting from the loss of a proton.

➢ the more stable the anion, the greater the acidity of HA

Ways to stabilize anions include having the negative charge:

1. on a more electronegative atom.
2. on a larger atom.
3. delocalized through resonance.
4. delocalized by the inductive effect.
5. in an orbital with more s character.
1. **Electronegativity of the atom bearing the negative charge**

   Within a period, the greater the electronegativity of the atom bearing the negative charge, the more strongly its electrons are held, the more stable the anion is, and the stronger the acid.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol pKₐ 16</td>
<td>CH₃⁻ + O⁻ - H⁻</td>
</tr>
<tr>
<td>Methylamine pKₐ 38</td>
<td>CH₃⁻ + N⁻ - H⁻</td>
</tr>
<tr>
<td>Ethane pKₐ 51</td>
<td>CH₃⁻ + C⁻ - H⁻</td>
</tr>
</tbody>
</table>

2. **Size of the atom**

   - The larger the atom bearing the charge, the greater its stability.

\[
\text{CH}_3\stackrel{\text{O}}{-}\text{H} + \text{CH}_3\stackrel{-}{\text{O}} - \rightarrow \text{CH}_3\stackrel{-}{\text{O}} - + \text{CH}_3\stackrel{\text{O}}{-}\text{H}
\]

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanethiol pKₐ 7.0</td>
<td>Methoxide ion</td>
</tr>
<tr>
<td>Methanol pKₐ 16</td>
<td>Methanethiolate ion</td>
</tr>
</tbody>
</table>
3. Resonance delocalization of charge in $A^-$

- The more stable the anion, the farther the position of equilibrium is shifted to the right.
- Compare the acidity alcohols and carboxylic acids.
- Ionization of the O-H bond of an alcohol gives an anion for which there is no resonance stabilization:

$$\text{CH}_3\text{CH}_2\text{O-H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+ \quad pK_a = 15.9$$

- Ionization of a carboxylic acid gives a resonance-stabilized anion.
- The $pK_a$ of acetic acid is 4.76

- Carboxylic acids are stronger acids than alcohols as a result of the resonance stabilization of the carboxylate anion.
4. Electron-withdrawing inductive effect
   – The polarization of electron density of a covalent bond due to the electronegativity of an adjacent covalent bond.

\[
\begin{align*}
\text{Ethanol} & \quad \text{pK}_a 15.9 \\
\text{2,2,2-Trifluoroethanol} & \quad \text{pK}_a 12.4
\end{align*}
\]

4. Electron-withdrawing inductive effect
   – Stabilization by the inductive effect falls off rapidly with increasing distance of the electronegative atom from the site of negative charge in the conjugate base.

\[
\begin{align*}
\text{CF}_3-\text{CH}_2-\text{OH} & \quad \text{CF}_3-\text{CH}_2-\text{CH}_2-\text{OH} & \quad \text{CF}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \\
2,2,2-\text{Trifluoroethanol} & \quad \text{3,3,3-Trifluoro-1-propanol} & \quad \text{4,4,4-Trifluoro-1-butanol} \\
(\text{pK}_a 12.4) & \quad (\text{pK}_a 14.6) & \quad (\text{pK}_a 15.4)
\end{align*}
\]
the operation of the inductive effect in the acidity of halogen substituted carboxylic acids is also observed:

\[
\begin{array}{ccc}
\text{Butanoic acid} & \text{4-Chlorobutanoic acid} & \text{3-Chlorobutanoic acid} & \text{2-Chlorobutanoic acid} \\
pK_a & 4.82 & 4.52 & 3.98 & 2.83 \\
\end{array}
\]

5. Hybridization

For anions differing only in the hybridization of the charged atom, the greater the percentage s character to the hybrid orbital of the charged atom, the more stable the anion.

<table>
<thead>
<tr>
<th>Weak Acid</th>
<th>Conjugate Base</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>HO-H</td>
<td>HO^-</td>
</tr>
<tr>
<td>Alkyne</td>
<td>HC≡C-H</td>
<td>HC≡C^-</td>
</tr>
<tr>
<td>Ammonia</td>
<td>H_2N-H</td>
<td>H_2N^-</td>
</tr>
<tr>
<td>Alkene</td>
<td>CH_2=CH-H</td>
<td>CH_2=CH^-</td>
</tr>
<tr>
<td>Alkane</td>
<td>CH_3CH_2-H</td>
<td>CH_3CH_2^-</td>
</tr>
</tbody>
</table>

Increasing acidity
**In summary:**

1. Negative charge on the more electronegative atom.
2. Negative charge on a larger atom.
3. Delocalization of the negative charge through resonance.
4. Delocalization of the negative charge onto electron-withdrawing groups by the inductive effect.
5. Have the negative charge in an orbital with more s character.