Acids and Bases—Chapter 4
Shriver et al.
MIT 3091 Video Lecture: Acids and Bases on You Tube

Acid-Base concepts

- stomach acid
- grapes
- bananas
- pure water
- baking soda
- ammonia
- oven cleaner
- lemon
- tomatoes
- milk
- eggs
- soap
- bleach

Acids

Bases
Gilbert Newton Lewis
1875 – 1946
Lewis Concept

Lewis, 1930s:

Base is a donor of an electron pair.

Acid is an acceptor of an electron pair.

For a species to function as a Lewis acid, it needs to have an accessible empty orbital.

For a species to function as a Lewis base it needs to have an accessible electron pair.

Examples of Lewis acids: $\text{BF}_3, \text{AlCl}_3, \text{SbF}_5, \text{Na}^+, \text{H}^+, \text{S}^{6+}$, etc.

Examples of Lewis bases: $\text{F}^-, \text{H}_2\text{O}, \text{Me}_3\text{N}, \text{C}_2\text{H}_4, \text{Xe}$, etc.
Lewis Concept—Connection to MO Theory

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A more general view also classifies compounds that can generate a species with an empty orbital as Lewis acids. Then we can include $\text{B}_2\text{H}_6$, $\text{Al}_2\text{Cl}_6$, $\text{HCl}$ etc.

Since $\text{H}^+$ and any cation from a solvent autodissociation is a Lewis acid, and anything that can add $\text{H}^+$ or a solvent-derived cation is a Lewis base, the Lewis acid concept effectively includes the ones discussed previously.
Lewis Continued

Acid-base reactions under the Lewis model is the reactions of forming adducts between Lewis acids and bases.

\[
\begin{align*}
\text{BF}_3 + \text{Me}_3\text{N} & \rightarrow \text{F}_3\text{B}-\text{NMe}_3 \\
\text{HF} + \text{F}^- & \rightarrow \text{FHF}^- \\
\text{SiF}_4 + 2\text{F}^- & \rightarrow \text{SiF}_6^{2-} \\
\text{CO}_2 + \text{OH}^- & \rightarrow \text{HCO}_3^- \\
\text{TiCl}_4 + 2\text{Et}_2\text{O} & \rightarrow \text{TiCl}_4(\text{OEt}_2)_2
\end{align*}
\]

In fact, any chemical compound can be mentally disassembled into Lewis acids and bases:

\[
\begin{align*}
\text{S}^{6+} + 6\text{F}^- & \rightarrow \text{SF}_6 \\
\text{C}^{4+} + 3\text{H}^- + \text{NH}_2^- & \rightarrow \text{CH}_3^+ + \text{NH}_2^- 
\end{align*}
\]
Tying this into MO Theory: Electrostatic Potential Plots: Red is negative; blue is positive
Formation of Lewis Acid-Base adduct
Another Look: Acid-Base concepts
Table 8.3 From Jolly, “Modern Inorganic Chemistry” Aqueous $pK_a$ values of the binary “hydrides” of the nonmetals

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th>NH$_3$</th>
<th>H$_2$O</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sim$ 44</td>
<td>39</td>
<td>15.74</td>
<td>3.15</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>$\sim$ 35</td>
<td>PH$_3$</td>
<td>H$_2$S</td>
<td>HCl</td>
</tr>
<tr>
<td>GeH$_4$</td>
<td>25</td>
<td>AsH$_3$</td>
<td>H$_2$Se</td>
<td>HBr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\leq$ 23</td>
<td>3.7</td>
<td>-8.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$_2$Te</td>
<td>HI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.6</td>
<td>-9.3</td>
</tr>
</tbody>
</table>

\[ pK_a = - \log_{10} [H^+] \quad K_a = [H^+][OH^-]/[H_2O] \]
Svante August Arrhenius
1859 – 1927
Arrhenius concept

Arrhenius, 1880s:

Acids form hydrogen ions $H^+(H_2O)_n$ in aqueous solution.

Bases form hydroxide ions in aqueous solution.

Examples of Arrhenius acids (in water): HCl, H$_2$SO$_4$, etc.

Examples of Arrhenius bases (in water): NaOH, NH$_3$, etc.

Arrhenius definitions only apply to aqueous solutions.

A general Arrhenius acid-base reaction is the reaction between $H^+$ and $OH^-$ to produce water.

$$\text{Acid + Base} \rightarrow \text{Salt + Water}$$

$$H^+ + NO_3^- + K^+ + OH^- \rightarrow K^+ + NO_3^- + H_2O$$
Johannes Nicolaus Brønsted
1879 – 1947

Thomas Martin Lowry
1874 – 1936
Johannes Nicolaus Brønsted 1879 – 1947

Thomas Martin Lowry 1874 – 1936
Brønsted-Lowry concept

Brønsted and Lowry, 1923:

**Acid** – a species with a capability to lose $\text{H}^+$.  
**Base** – a species with a capability to gain $\text{H}^+$.

[As often as not Lowry’s name is omitted and only Brønsted’s name is used.]

Brønsted’s acids and bases are by and large the same acids and bases as in the Arrhenius model but the model of Brønsted and Lowry is not restricted to aqueous solutions.

Brønsted’s model introduces the notion of conjugate acid-base pairs. It is logical that if something (an acid) exists and may lose a proton, then the product of such a proton loss is by definition a base since it has the capability to add a proton.
## Conjugate acids and bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{O}^+$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>$\text{O}^{2-}$</td>
</tr>
<tr>
<td>$\text{CH}_3^+$</td>
<td>$\text{CH}_2$</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>$\text{CH}_3^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$</td>
<td>$\text{H}_2\text{NCH}_2\text{CO}_2\text{O}^-$</td>
</tr>
<tr>
<td>$[\text{H}_3\text{NCH}_2\text{CO}_2\text{H}]^+$</td>
<td>$\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>$\text{H}^-$</td>
</tr>
</tbody>
</table>
Likewise, any compound with a pair of electrons may behave as a Brønsted base.

It is possible for the same compound to be able to behave as a Brønsted base and as a Brønsted acid.

Usually a compound is called acid or base depending on the circumstances.

Theoretically, any compound that has a hydrogen atom in it may behave as a Brønsted acid.
Brønsted continued

Under the Brønsted-Lowry model, an acid-base reaction is always a reaction between an acid and a base giving their conjugate base and acid, respectively.

\[
\text{EtOH} + \text{Me}_2\text{N}^- \text{Li}^+ \rightarrow \text{EtO}^- \text{Li}^+ + \text{Me}_2\text{NH}
\]

\[
\text{Acid}_1 + \text{Base}_2 \rightarrow \text{Base}_1 + \text{Acid}_2
\]

\[
\text{EtOH} + \text{H}_2\text{SO}_4 \rightarrow \text{EtOH}_{2}^+ + \text{HSO}_4^-
\]

\[
\text{Base}_1 + \text{Acid}_2 \rightarrow \text{Acid}_1 + \text{Base}_2
\]

Generally, the reactions proceed to form weaker acids and bases.
Solvent system concept

The solvent system concept is applicable to solvents that undergo autodissociation:

**Acids are compounds that increase the concentration of the cation.**
**Bases are compounds that increase the concentration of the anion.**

The Arrhenius model can be viewed as a part of the solvent system model.
Solvent system concept

The Arrhenius model can be viewed as a part of the solvent system model.

For instance, BrF₃ undergoes autodissociation:

\[ 2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^- \]

In BrF₃, KF will be classified as a base, and SbF₅⁻ as an acid.

\[ \text{KF} + \text{BrF}_3 \rightleftharpoons \text{K}^+ + \text{BrF}_4^- \]

\[ \text{SbF}_5^- + \text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{SbF}_6^- \]

An acid-base reaction in water is the reaction between H⁺ and OH⁻; an acid-base reaction in BrF₃ is the reaction between BrF₂⁺ and BrF₄⁻.