So far in this course, we have looked at processes in chemistry that deal with, or are best explained by, ionic salts or molecules.

Now we will turn our attention to a class of molecular compounds found in industry, nature and biological systems. We will now investigate acids and bases using what we have learned about chemical processes.

Acids and Bases

Arrhenius Acid = Any compound that increases the hydronium ion ($H_3O^+$) concentration in aqueous solution

Arrhenius Base = Any compound that increases the hydroxide ion concentration in aqueous solution

When we think of acids, we typically think of the Arrhenius definition.

Svante Arrhenius (1859-1927)
For any Acid:

\[ \text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{A}^-_{(aq)} \]

Acid + Water → Hydronium + Acid anion

The hydrogen of the acid is essentially a single proton that can bond through a coordination bond to water forming \( \text{H}_3\text{O}^+ \), called the hydronium ion.

\[ \begin{align*}
\text{H}^+_{(aq)} + \text{H}_2\text{O}_{(l)} &\rightarrow [\text{H}^+\text{O}^-]\text{H}_{(aq)}^+ \\
\text{H}^+_{(aq)} &\rightarrow \text{H}_3\text{O}^+_{(aq)}
\end{align*} \]

Examples:

1. \( \text{HCl}_{(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)} \)

   \[ \begin{array}{c}
   + \hspace{1cm} + \hspace{1cm} + \\
   \text{H}^+_{(aq)} + \text{H}_2\text{O}_{(l)} \hspace{1cm} \rightarrow \hspace{1cm} \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}
   \end{array} \]

2. \( \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{CO}_2^-_{(aq)} \)

Draw the Lewis structures for the acetic acid reaction above and show the proton movement with arrows.

A careless but often seen abbreviation for acid systems:

\( \text{HCl}_{(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)} \)

Could be written as:

\( \text{HCl}_{(g)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} \)

It is important to remember that water is still there and \( \text{H}^+_{(aq)} \) is truly in the form of \( \text{H}_3\text{O}^+_{(aq)} \).

Therefore, for any acid written, \( \text{H}_2\text{SO}_4_{(aq)} \), it really means:

\( \text{H}_2\text{SO}_4_{(l)} \rightarrow \text{H}^+_{(aq)} + \text{HSO}_4^-_{(aq)} \)

Or

\( \text{H}_2\text{SO}_4_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{HSO}_4^-_{(aq)} \)

Arrhenius’ understanding of acids and bases is limited to the presence of \( \text{H}^+ \) and \( \text{OH}^- \) ions.

This is true; however, this definition does not account for compounds that act as acids and bases in non-aqueous solutions, or in reversible processes.

A Brønsted-Lowry acid...

...must have a removable (acidic) proton.

A Brønsted-Lowry base...

...must have a pair of nonbonding electrons.

Johannes Bronsted – Thomas Lowry
(1923)

Independently expanded the definition of acids and bases

Bronsted-Lowry Acid = any chemical species that donates one or more protons

Bronsted-Lowry Base = any chemical species that accepts one or more protons
Some Definitions

• Arrhenius
  ➢ Acid: Substance that, when dissolved in water, increases the concentration of hydrogen ions.
  ➢ Base: Substance that, when dissolved in water, increases the concentration of hydroxide ions.

• Bronsted–Lowry
  ➢ Acid: Proton donor
  ➢ Base: Proton acceptor

If it can be either...
...it is amphiprotic or amphoteric.

\[ \text{HCO}_3^- \]
\[ \text{HSO}_4^- \]
\[ \text{H}_2\text{O} \]

Examine the formation of HCl\(_{(aq)}\) from HCl\(_{(g)}\)

\[
\begin{align*}
  &\text{Cl} - \text{H} + \text{O} - \text{H} \rightarrow \text{Cl} - \text{F} + \left[ \text{H} - \text{O} - \text{H} \right]^+ \\
  &\text{Cl} - \text{H} + \text{N} - \text{H} \rightarrow \text{Cl} - \text{F} + \left[ \text{H} - \text{N} - \text{H} \right]^+ \\
\end{align*}
\]

• We know HCl is an Arrhenius acid by the production of H+.
• HCl is also a Bronsted-Lowry (B-L) acid because it gives up a proton.
• Notice, water gains a proton (B-L Base).

Examples:

1. Hydrogen Chloride and Ammonia

Notice: No Water!

All Arrhenius acids are B-L acids, but not all B-L acids are Arrhenius. B-L bases and Arrhenius Bases are not necessarily interchangeable.

Examine:

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

• B-L acid / base, but neither are Arrhenius
• \( \text{NH}_3 \) autoionizes
• \( \text{NH}_3 \) is amphoteric

Examples:

2. Hydrogen cyanide and water
3. Ammonia and water
   * Notice, from rxn 2 and 3 that water can act as both an acid and a base. Water is amphoteric.
So far, we have only looked at acids and bases as strong electrolytes.

Remember electrolytes?
Strong electrolyte – strong acid/base
- 100% dissociation (ionization)
Weak electrolyte – weak acid/base
- <100% dissociation (ionization)

The Arrhenius theory only allows us to describe the acid as a function of $H_3O^+$, but does not allow for the reverse reaction.

The B-L definition not only allows us to describe acids in non-aqueous solutions, but it also allows us to describe both forward and reverse acid-base reactions for weak acid-base equilibriums using conjugate acid-base pairs.

Strong acids and bases react only in the forward direction but, weak acids and bases react in both the forward and reverse direction.
i.e. acetic acid
- $\text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2^- + H^+$
Equilibrium Exists (where $K\ll<1$)

Conjugate acid-base pairs

$$\text{acid}_1 + \text{base}_1 \rightleftharpoons \text{acid}_2 + \text{base}_2$$

Conjugate pairs

Conjugate means joined, or linked, as a pair

Notice, in the reverse reaction, the hydronium ion acts as an acid by donating a proton to the acetate ion, and the acetate ion acts as a base by accepting the proton.
Example 2:
\[
\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+
\]
B-L          B-L           Conj         Conj
acid         base          base         acid

The equilibrium always favors the weaker acid-base pair

1. Write the reaction for the following weak acid or base dissociations and identify all acid-base conjugate pairs.
   a. Ethanoic acid in water
   b. Ammonia in water
   c. Isopropyl alcohol in ammonia
   d. Phosphoric acid dissociating

2. Identify the correct conjugates of the following
   a. Conjugate base of HClO \textsubscript{3}
   b. Conjugate acid of CN\textsuperscript{-}
   c. Conjugate base of PH\textsubscript{4}\textsuperscript{+}
   d. Conjugate acid of HCO\textsubscript{3}\textsuperscript{-}

   You should notice that some acids have more than one proton to donate. These acids are called polyprotic acids.
   
   It is important to know that each proton is lost separately and with different degrees of difficulty

Example:
\[
\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}^+
\]

Strong acid (complete ionization)
\[
\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+
\]

Weak acid (K<<1)

Dissociation of a polyprotic acid works differently than a reaction with the polyprotic acid

Acid and Base Strength

- A \textit{strong acid} completely transfers its protons to water leaving no undissociated (ionized) molecules.
  - Its conjugate base is extremely weak.
  - Easily explained by Arrhenius
  - Concentration of H\textsuperscript{+} is defined stoichiometrically by initial acid concentration
**Acid and Base Strength**

- A weak acid only partially dissociates in aqueous solution and therefore exists in the solution as a mixture of the acid and its conjugate base.
  - Its conjugate base is fairly strong.
  - Explained by Arrhenius but better explained by BL.
  - Concentration of H\(^+\) must be determined applying equilibrium calculations.

**Acid and Base Strength**

- A molecule with negligible acidity contains hydrogen but does not demonstrate any acidic behavior in water.
  - Its conjugate base is extremely strong.
  - Possibly explained by Lewis theory.
  - No measurable H\(^+\).

**Acid and Base Strength**

- In any acid–base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base:
  \[
  \text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)
  \]
  - \(\text{H}_2\text{O}\) is a much stronger base than \(\text{Cl}^-\), so the equilibrium lies so far to the right that \(K\) is not measured (\(K \gg 1\)).

**Acid and Base Strength**

- In any acid–base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base:
  \[
  \text{CH}_3\text{CO}_2\text{H(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)
  \]
  - Acetate is a stronger base than \(\text{H}_2\text{O}\), so the equilibrium favors the left side (\(K << 1\)).

**G.N. Lewis (1920’s)**

Noticed that all bases contained an unshared electron pair and coordination bonds always form between this electron pair and the protons.

*Lewis acid – Electron pair acceptor*

*Lewis base – Electron pair donor*
Observe:

\[
\text{BF}_3 + :\text{NH}_3 \rightarrow \text{BF}_3\text{NH}_3
\]

Notice, no protons are transferred and \( \text{H}^+ \) does not increase

Lewis Acids

- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.

Lewis Bases

- 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.

Types of Acids

1. Oxyacids

   Acid species where the available proton is attached to oxygen.

   Examples:

   Nitric (monoprotic), sulfuric (diprotic), phosphoric (triprotic)

3. Identify the Lewis acids and bases in the following

   a. \( \text{Ni}^{2+} + 6\text{NH}_3 \rightarrow \text{Ni(NH}_3)_6^{2+} \)

   b. \( \text{H}^+ + \text{H}_2\text{O} \not\Rightarrow \text{H}_3\text{O}^+ \)

   c. \( \text{Fe(ClO}_4)_3(\text{s}) + 6\text{H}_2\text{O(}_l) \not\Rightarrow \text{Fe(H}_2\text{O}_6)^{3+}(\text{aq}) + 3\text{ClO}_4^-(\text{aq}) \)
2. Hydrohalic Acids

Acid species where the available proton is attached to a halogen

Examples:
HCl, HBr, HI, HF (all monoprotic)

3. Hydrides

Acid species where the available proton is attached to a non-metal other than halogens.

Examples:
H₂S, H₂Te, H₂O, H₃N, H₃P,
(all polyprotic)

4. Organic Acids

Acids formed from reactive groups on a long carbon chain that can donate a proton (or deprotonate).

Alcohols (extremely weak)
Carboxylic acids (most common)

Carboxyl group:
(stabilized by resonance)

*Named by replacing the -e on the parent name with -oic Acid

Examples:
Ethanoic Acid (acetic acid)
Hexanoic Acid

Types of Bases

1. Hydroxides

Hydroxides of alkali and heavy alkaline-earth metals

Examples:
LiOH, KOH, Sr(OH)₂
All strong bases

2. Ionic metal oxides

Oxides of alkali and alkaline-earth metals.

Examples:
Na₂O + H₂O → 2Na⁺ + 2OH⁻
CaO + H₂O → Ca²⁺ + 2OH⁻
3. Metal Hydrides

Hydrides of metals react in water to give hydroxide ions and hydrogen gas.

Example:
\[
\text{NaH} + \text{H}_2\text{O} \rightarrow \text{H}_2(\text{g}) + \text{Na}^+ + \text{OH}^-
\]

4. Organic Bases

Most common organic base is the nitrogen containing amine.

Amine – Ammonia molecule with substituted hydrocarbon groups.

Example: (Ethyl amine)
\[
\text{CH}_3\text{CH}_2\text{NH}_2 \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{OH}^-
\]

Tri-substituted ammonia molecule