Acids, Bases, Salts and Buffers
Centuries ago, certain substances were recognized for:

<table>
<thead>
<tr>
<th>Sour taste</th>
<th>Turned vegetable blues to red</th>
<th>Solvent power</th>
<th>Ability to neutralize alkalies to form salts</th>
</tr>
</thead>
</table>

These were called "acids" from "ac" which means sharp, as in *acetum*.

Other substances were recognized for:

<table>
<thead>
<tr>
<th>Soapiness</th>
<th>Cutting grease</th>
<th>Having the reverse effect of acids</th>
</tr>
</thead>
</table>

These were called "alkalies" which is from Arabic for plant ashes. They are also called bases.
Most Significant Properties

1) Their effect on acid/base indicators.
The table, below, summarizes the acid and base forms of 6 different acid/base indicators:

<table>
<thead>
<tr>
<th>Acid Form (color)</th>
<th>Indicator</th>
<th>Base Form (color)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Litmus</td>
<td>Blue</td>
</tr>
<tr>
<td>Clear</td>
<td>Phenolphthalein</td>
<td>Pink</td>
</tr>
<tr>
<td>Yellow</td>
<td>Bromocresol green</td>
<td>Green</td>
</tr>
<tr>
<td>Yellow</td>
<td>Phenol red</td>
<td>Red</td>
</tr>
<tr>
<td>Red</td>
<td>Methyl red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Yellow</td>
<td>Bromocresol purple</td>
<td>Purple</td>
</tr>
</tbody>
</table>

2) Their ability to react with each other to produce salts.
3) Their catalytic action.
4) Their ability to displace weaker acids or bases.
5) Aqueous solutions conduct an electrical current.
There are at least 4 definitions of acids and bases.

**Arrhenius Definition of Acids and Bases**

The first definitions are those of Arrhenius. By this set of definitions, an acid is a substance that dissociates in water to yield a proton (hydrogen ion). A base is a substance that dissociates in water to yield hydroxide ions. Examples of these sorts of reactions are summarized in the table, below:

<table>
<thead>
<tr>
<th>Acid Name</th>
<th>Acids</th>
<th>Base Name</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric</td>
<td>HCl $\rightarrow$ H$^+$ + Cl$^-$</td>
<td>Sodium hydroxide</td>
<td>NaOH $\rightarrow$ Na$^+$ + OH$^-$</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>$\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+$ + $\text{SO}_4^{2-}$</td>
<td>Potassium hydroxide</td>
<td>KOH $\rightarrow$ K$^+$ + OH$^-$</td>
</tr>
<tr>
<td>Nitric</td>
<td>HNO$_3 \rightarrow$ H$^+$ + NO$_3^-$</td>
<td>Magnesium hydroxide</td>
<td>Mg(OH)$_2 \rightarrow$ Mg$^{2+}$ + 2 OH$^-$</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>$\text{H}_3\text{PO}_4 \rightarrow 3\text{H}^+$ + PO$_4^{3-}$</td>
<td>Barium hydroxide</td>
<td>Ba(OH)$_2 \rightarrow$ Ba$^{2+}$ + 2 OH$^-$</td>
</tr>
<tr>
<td>Perchloric</td>
<td>HClO$_4 \rightarrow$ H$^+$ + ClO$_4^-$</td>
<td>Aluminum hydroxide</td>
<td>Al(OH)$_3 \rightarrow$ Al$^{3+}$ + 3 OH$^-$</td>
</tr>
<tr>
<td>Carbonic</td>
<td>$\text{H}_2\text{CO}_3 \rightarrow 2\text{H}^+$ + CO$_3^{2-}$</td>
<td>Tin (IV) hydroxide</td>
<td>Sn(OH)$_4 \rightarrow$ Sn$^{4+}$ + 4OH$^-$</td>
</tr>
</tbody>
</table>
By this set of definitions, an acid is a proton donor and a base is a proton acceptor when they dissociate in water. Representative reactions are summarized in the table, below:

<table>
<thead>
<tr>
<th>Acid dissociation in water</th>
<th>Reaction of Hydroxide with an Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HCl + H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$</td>
<td>$\text{HCl + OH}^- \rightarrow \text{H}_2\text{O} + \text{Cl}^-$</td>
</tr>
<tr>
<td>$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$</td>
<td>$\text{HNO}_3 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{NO}_3^-$</td>
</tr>
<tr>
<td>$\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$</td>
<td>$\text{H}_2\text{SO}_4 + \text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{SO}_4^{2-}$</td>
</tr>
</tbody>
</table>
Species/substances that may either gain or lose protons (the hydrogen ion) are called amphipathic or amphiprotic or ampholytes. Examples are shown, below:

\[ \text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{OH}^- \]
\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]

Where **RED** indicates the acid and **BLUE** indicates the base form of each molecule.

\[ \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]
\[ \text{H}_3\text{O}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \]

Where **RED** indicates the acid and **BLUE** indicates the base form of each molecule.
When a reaction is written in the following form,

\[ \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- \]

the nitric acid is the acid and the water is the base. Once they react, a NEW acid and a NEW base are formed. The new acid is the \( \text{H}_3\text{O}^+ \) and the new base is the nitrate ion \( (\text{NO}_3^-) \). The nitric acid and the nitrate ion make up a conjugate acid-base pair, respectively. The water and the hydronium ion \( (\text{H}_3\text{O}^+) \) make up a conjugate base-acid pair, respectively. Two more examples of reactions that produce conjugate acid-base pairs follow:

\[ \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{O}^+ + \text{SO}_4^{2-} \]
\[ \text{HOCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OCl}^- \]

\( \text{H}_2\text{SO}_4 \) and \( \text{SO}_4^{2-} \) are one conjugate acid-base pair in the first reaction. What is the other? \( \text{HOCl} \) and \( \text{OCl}^- \) is one of the conjugate acid-base pairs in the second reaction. What is the other?
The table, below summarizes a few acids with their conjugate bases:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric (HNO₃)</td>
<td>Nitrate ion (NO₃⁻)</td>
</tr>
<tr>
<td>Acetic (HC₂H₃O₂ or HOAc)</td>
<td>Acetate ion (C₂H₃O₂⁻ or OAc⁻)</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>Hydroxide ion (OH⁻)</td>
</tr>
<tr>
<td>Phosphoric (H₃PO₄)</td>
<td>Dihydrogen phosphate ion (H₂PO₄⁻)</td>
</tr>
</tbody>
</table>
In general, a strong acid gives a weak conjugate base; a weak acid gives a strong conjugate base; a strong base gives a weak conjugate acid; a weak base gives a strong conjugate acid.

- Strong acids are those that dissociate 100% in water.
  - Examples include perchloric, sulfuric, hydrochloric and nitric acids.
- Weak acids are those that ionize less than fully in water.
  - Examples include ammonia, water and carbonic acids.

- Strong bases are those that, like the acids, dissociate 100% in water.
  - Examples include sodium hydroxide.
- Weak bases are those that, like the acids, dissociate less than fully in water.
  - Examples include the perchlorate ion, the iodide ion and the bromide ion.
Acid Formation and Dissociation
The formation of protonic acids may occur by 6 different mechanisms. These mechanisms and examples are summarized in the table, below:

<table>
<thead>
<tr>
<th>Acid Formation Mechanism</th>
<th>Representative Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct union of elements</td>
<td>( \text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl} ) &lt;br&gt; ( \text{H}_2 + \text{S} \rightarrow \text{H}_2\text{S} ) &lt;br&gt; ( \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} ) &lt;br&gt; ( \text{H}_2 + \text{F}_2 \rightarrow 2\text{HF} ) &lt;br&gt; ( \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} )</td>
</tr>
<tr>
<td>Action of water on non-metal oxides</td>
<td>( \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 ) &lt;br&gt; ( \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 ) &lt;br&gt; ( \text{P}<em>4\text{O}</em>{10} + 6 \text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4 ) &lt;br&gt; ( \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 )</td>
</tr>
<tr>
<td>Heating salts of volatile acids with NON-volatile or SLIGHTLY volatile acids</td>
<td>( \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl} \uparrow ) &lt;br&gt; ( \text{NaBr} + \text{H}_3\text{PO}_4 \rightarrow \text{NaH}_2\text{PO}_4 + \text{HBr} \uparrow )</td>
</tr>
<tr>
<td>By the action of salts with other acids producing a precipitate</td>
<td>( \text{H}^+ + \text{Cl}^- + \text{Ag}^+ + \text{NO}_3^- \rightarrow \text{AgCl} + \text{H}^+ + \text{NO}_3^- ) &lt;br&gt; ( 2\text{H}^+ + \text{SO}_4^{2-} + \text{Ba}^{2+} + 2\text{ClO}_3^- \rightarrow \text{BaSO}_4 + 2\text{H}^+ + 2\text{ClO}_3^- )</td>
</tr>
<tr>
<td>By hydrolysis</td>
<td>( \text{PBr}_3 + 3 \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3 \text{HBr} ) &lt;br&gt; ( \text{PCl}_5 + 4 \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 5 \text{HCl} )</td>
</tr>
<tr>
<td>By oxidation-reduction reactions</td>
<td>( \text{H}_2\text{S} + \text{I}_2 \rightarrow 2\text{HI} + \text{S} ) &lt;br&gt; ( 2\text{HNO}_3 + 2\text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + \text{NO} \uparrow + \text{NO}_2 \uparrow )</td>
</tr>
</tbody>
</table>
• If the acid has **one ionizable proton**, it is called a mono-protic acid.
  • If it has **2**, a di-protic acid.
• If it has **three ionizable protons**, it is called a triprotic acid.
• The significance has to with eventually using this information in reaction-type calculations.
• Each proton has its own dissociative step, i.e., the protons don't just "fall off" the acids all at once.
  • They are removed a proton at a time.
<table>
<thead>
<tr>
<th>Monoprotic Dissociation -- 1 H⁺</th>
<th>Diprotic Dissociation -- 2 H⁺</th>
<th>Triprotic Dissociation -- 3H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl + H₂O → H₃O⁺ + Cl⁻</td>
<td>H₂CO₃ + H₂O → H₃O⁺ + HCO₃⁻</td>
<td>H₃PO₄ + H₂O → H₃O⁺ + H₂PO₄⁻</td>
</tr>
<tr>
<td></td>
<td>HCO₃⁻ + H₂O → H₃O⁺ + CO₃²⁻</td>
<td>H₂PO₄⁻ + H₂O → H₃O⁺ + HPO₄²⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HPO₄²⁻ + H₂O → H₃O⁺ + PO₄³⁻</td>
</tr>
<tr>
<td>HNO₃ + H₂O → H₃O⁺ + NO₃⁻</td>
<td>H₂SO₄ + H₂O → H₃O⁺ + HSO₄⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HSO₄⁻ + H₂O → H₃O⁺ + SO₄²⁻</td>
<td></td>
</tr>
<tr>
<td>HCN + H₂O → H₃O⁺ + CN⁻</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Hydrogen Halides
• \( \text{CaF}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) + 200\text{-}250^\circ \rightarrow \text{CaSO}_4\downarrow + 2\text{HF} \)

• About \( 8*10^8 \) pounds of HF are used each year to make freons:
  • \( \text{CCl}_4(\text{g}) + \text{HF(}g) + \text{SbCl}_5(\text{l}) + 65\text{-}95^\circ \text{C} \rightarrow \text{CCl}_3\text{F}(\text{g}) + \text{HCl(}g) \)
  • \( \text{CCl}_4(\text{g}) + 2\text{HF(}g) + \text{SbCl}_5(\text{l}) + 65\text{-}95^\circ \text{C} \rightarrow \text{CCl}_2\text{F}_2(\text{g}) + 2\text{HCl(}g) \)

• Freons are used in air conditioners and refrigerators, but they are destructive to the ozone layer (15-30 km layer above the earth).
• Another $8 \times 10^8$ pounds of HF are used per year to produce aluminum:

• $6\text{HF}(g) + \text{Al(OH)}_3(s) + 3\text{NaOH(aq)} \rightarrow \text{Na}_3\text{AlF}_6$ (synthetic cryolite) + $6\text{H}_2\text{O(l)}$

• Bauxite, the ore that contains aluminum ($\text{Al}_2\text{O}_3$) is the subjected to electrolysis in the cryolite solvent to form elemental aluminum.

• HF is used for glass etching and frosting bulbs. The reaction for this is:

  • $\text{SiO}_2(s) + 6\text{HF(aq)} \rightarrow \text{H}_2\text{SiF}_6(aq) + 2\text{H}_2\text{O(l)}$

    • and

  • $\text{CaSiO}_3(s) + 8\text{HF(aq)} \rightarrow \text{H}_2\text{SiF}_6(aq) + \text{CaF}_2(s) + 3\text{H}_2\text{O(l)}$
• HCl is produced in one of three ways and follows:
  • CH$_4$(g) + Cl$_2$(g) + 440 °C → CH$_3$Cl + HCl
  • H$_2$(g) + Cl$_2$(g) + hv → 2HCl(g) ← EXPLOSIVE REACTION!
  • 2NaCl(s) + H$_2$SO$_4$(l) + heat → 2HCl + Na$_2$SO$_4$↓
• The primary use of HCl is to remove oxide scale from rusted steel or metals.
  • Bromides and iodides are formed in the same manners, the ONLY difference is that the reactions with these 2 halogens require H$_3$PO$_4$ instead of H$_2$SO$_4$. 
## Properties of Hydrogen Halides

<table>
<thead>
<tr>
<th>Hydrogen halide</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MW</strong></td>
<td>20</td>
<td>36.5</td>
<td>80.9</td>
<td>127.9</td>
</tr>
<tr>
<td><strong>Solubility in g/100 mL water</strong></td>
<td>∞ @ 0 °C</td>
<td>82.3 @ 0 °C</td>
<td>221 @ 0 °C</td>
<td>234 @ 10 °C</td>
</tr>
<tr>
<td><strong>BP (° C)</strong></td>
<td>120</td>
<td>110</td>
<td>126</td>
<td>127</td>
</tr>
<tr>
<td><strong>MP (° C)</strong></td>
<td>-83.1</td>
<td>-114.2</td>
<td>-86.8</td>
<td>-50.8</td>
</tr>
</tbody>
</table>
Properties of Hydrogen Halides

- **Solubility**
- **BP**
- **MW**
- **MP**

Graph showing properties of HF, HCl, HBr, HI.
The Halogens Form Oxo-Acids

<table>
<thead>
<tr>
<th>Hypohalous acids</th>
<th>HOCI</th>
<th>HOF</th>
<th>HOBr</th>
<th>HOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>halous acids</td>
<td>HClO₂</td>
<td>-----</td>
<td>HBrO₂</td>
<td>HIO₂</td>
</tr>
<tr>
<td>halic acids</td>
<td>HClO₃</td>
<td>-----</td>
<td>HBrO₃</td>
<td>HIO₃</td>
</tr>
<tr>
<td>perhalic acids</td>
<td>HClO₄</td>
<td>-----</td>
<td>HBrO₄</td>
<td>HIO₄</td>
</tr>
</tbody>
</table>

HClO₄ is explosive by shock alone in the pure state.
In terms of acid strengths, the acids with the halogen in the lowest oxidation state are the weakest while those that have the halogen in the highest oxidation state are the strongest oxo-acids:

<table>
<thead>
<tr>
<th>Weakest</th>
<th>Strongest</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO</td>
<td>HClO₄</td>
</tr>
<tr>
<td>Chlorous</td>
<td>Perchloric</td>
</tr>
<tr>
<td>+1 Oxidation state</td>
<td>+7 Oxidation state</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HClO₂</th>
<th>HClO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorous</td>
<td>Chloric</td>
</tr>
<tr>
<td>+3 Oxidation state</td>
<td>+5 Oxidation state</td>
</tr>
</tbody>
</table>
Base Formation
There are 5 mechanisms by which hydroxides are formed. These mechanisms and representative reactions are summarized in the table, below:

<table>
<thead>
<tr>
<th>Base Mechanism</th>
<th>Representative Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkali metals or alkaline earth metals react with water</strong></td>
<td>2 K + 2 H₂O → 2 K⁺ + 2 OH⁻ + H₂↑</td>
</tr>
<tr>
<td></td>
<td>Ca + 2 H₂O → Ca²⁺ + 2 OH⁻ + H₂↑</td>
</tr>
<tr>
<td></td>
<td>2 Na + 2 H₂O → 2 Na⁺ + 2 OH⁻ + H₂↑</td>
</tr>
<tr>
<td><strong>Water reacting with oxides of alkali/alkaline earth metals</strong></td>
<td>Na₂O + H₂O → 2 Na⁺ + 2 OH⁻</td>
</tr>
<tr>
<td></td>
<td>CaO + H₂O → Ca²⁺ + 2 OH⁻</td>
</tr>
<tr>
<td></td>
<td>MgO + H₂O → Mg²⁺ + 2 OH⁻</td>
</tr>
<tr>
<td><strong>Salts with other bases with a resulting precipitate</strong></td>
<td>2 Na⁺ + CO₃²⁻ + Ca²⁺ + 2 OH⁻ → CaCO₃↓ + 2 Na⁺ + 2 OH⁻</td>
</tr>
<tr>
<td><strong>Electrolysis</strong></td>
<td>2 Na⁺ + 2 Cl⁻ + 2 H₂O + Electrolysis → 2 Na⁺ + 2 OH⁻ + H₂↑ + Cl₂↑</td>
</tr>
<tr>
<td><strong>Dissolving NH₃ in water</strong></td>
<td>NH₃ + H₂O → NH₄⁺ + OH⁻</td>
</tr>
</tbody>
</table>
Lewis Definition of Acids and Bases

By this definition, acids are a molecule or ion which can accept a pair of electrons.

\[
\text{H} \cdot \text{O} \cdot \text{H} + \text{H} \cdot \text{Cl} \cdot \text{H} \rightarrow \left[ \text{H} \cdot \text{O} \cdot \text{H} \right]^+ + \left[ \cdot \text{Cl} \cdot \text{H} \right]^{-}
\]

A base is a molecule or ion which can donate a pair of electrons.
Example 2

\[ \text{Coordinate Covalent Bonds} \]
Auto-ionization of Water

Let's for a moment forget about acids and bases and focus on water. Water auto-ionizes in itself:

$$2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$$

The reaction is NOT favored as written, although the ratio of protons to hydroxide ions is unity.

At 25°C, the concentration of both ionic species is $1 \times 10^{-7}$ M.

Now, let's go back to the acids and bases.

**H$_3$O$^+$ is acidic.**

**OH$^-$ is alkaline.**

In ACIDIC solutions, the molar concentration of H$_3$O$^+$ ([H$_3$O$^+$]) is greater than the molar concentration of OH$^-$ ([OH$^-$]).

In NEUTRAL solutions, they are equal to each other.

In ALKALINE solutions, [OH$^-$] is greater than [H$_3$O$^+$].

In any dilute solution of water, the product of the hydronium ion concentration and hydroxide ion concentration is a constant, regardless of the solute. This constant is called the dissociation constant of water and is represented by $K_w$. 

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We can determine the $K_w$ based off of the equilibrium expression for the dissociation of water as follows:

$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Note that the coefficient "2" in the equilibrium reaction became the exponent "2" in the equilibrium expression.
By rearranging, the equation takes on a slightly different look:

$$K [H_2O]^2 = [H_3O^+] * [OH^-]$$

The molar concentration of water is around 55 M -- compared to the small amount that ionizes, it doesn't really change. Since it doesn't really change to any significance, the product of the constant, $K$, and the square of the $[H_2O]$ are equal to the $K_w$ and the equation takes on the following look:

$$K_w = [H_3O^+] * [OH^-]$$

At 25° C, the $K_w$ is equal to the square of $1*10^{-7}$, or $1*10^{-14}$. 
How do we use this information to determine the acidity or alkalinity of a solution?

From:

\[ K_w = [H_3O^+] \times [OH^-] \]

we substitute the numerical values:

\[ 1 \times 10^{-14} = (1 \times 10^{-7}) \times (1 \times 10^{-7}) \]

Next, we take the logs of each side:

\[ \log (1 \times 10^{-14}) = \log[ (1 \times 10^{-7}) \times (1 \times 10^{-7})] \]

which rearranges to:

\[ \log (1 \times 10^{-14}) = \log (1 \times 10^{-7}) + \log (1 \times 10^{-7}) \]

This gives us:

\[ -14 = -7 + -7 \]

Take the negative of both sides and we get:

\[ 14 = 7 + 7 \]
Taking the negative log (-\log) of this equation may be re-written as "p":

\[ p_{Kw} = pH + pOH \]

or:
\[ 14 = pH + pOH, \text{ where } [H^+] = [H_3O^+] \]

Another way to look at this is that:
\[ [H_3O^+] = 1 \times 10^{-pH} \]

At neutrality where the hydronium and hydroxide ion concentrations are equal, the pH is 7 (-\log[1 \times 10^{-7}]).

When the pH is less than 7, the solution is acidic.
When pH equals 7, is neutral.
When the pH is greater than 7, the solution is alkaline or basic.
Acids and Bases Dissociate in Water

Fortunately for us, acids and bases dissociate in water:

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

Where HA is any acid and A\(^-\) is the anion left behind after the proton has separated from the acid.
We may determine the acid dissociation constant (like we did for water) as follows:

\[ K = \frac{[H_3O^+]\cdot[OH^-]}{[HA]\cdot[H_2O]} \]

The water concentration doesn't change as we saw in the \( K_w \) determination, so we'll rearrange the equation as follows:

\[ K\cdot[H_2O] = K_a = \frac{[H_3O^+]\cdot[A^-]}{[HA]} \]

Where \( K_a \) is the acid dissociation constant.
We can do the same for a base:

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \]

The equilibrium expression is as follows:

\[
K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \]

Again, since the water concentration doesn't change, we'll rearrange and manipulate:

\[
K*[\text{H}_2\text{O}] = K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

Where \( K_b \) is the base dissociation constant.

Note that in all cases, these equilibrium expressions are the quotient of the product concentrations and the reactant concentrations.
Would you suspect, then, that there is some sort of relationship between $K_a$, $K_b$ and $K_w$? Let's see. Remember that:

$$K_w = \left[ H_3O^+ \right] \cdot \left[ OH^- \right]$$

and that:

$$K_a = \frac{\left[ H_3O^+ \right] \cdot \left[ OH^- \right]}{[HA]}$$

and that:

$$K_b = \frac{[HA] \cdot \left[ OH^- \right]}{[A^-]}$$
Let's multiply $K_a$ by $K_b$ and see what happens:

$$K_a \times K_b = \frac{[H_3O^+][HA][A^-][OH^-]}{[HA][A^-]}$$

Note that all we're left with after canceling is:

$$[H_3O^+][OH^-] = K_a K_b = K_w$$

So that we now know that the product of the acid and base dissociation constants for the same compound is equal to the $K_w$.

Since $K_a K_b = 1 \times 10^{-14}$, if the $K_a$ or the $K_b$ is in a reference table in a textbook or online, the other can easily be calculated.
Additionally, we can also use this same method with conjugate acid-base pairs, e.g. HF and F\(^{-}\) and NH\(_4\)^{+} and NH\(_3\):

\[
K_w = K_a(HF) \times K_b(F^-) \tag{?}
\]

\[
K_w = \frac{[H_3O^+][HF][F^-][OH^-]}{[HF][F^-]} \tag{?}
\]

\[
K_w^{yes} = [H_3O^+][OH^-] \tag{and:}
\]

\[
K_w = K_a(NH_4^+) \times K_b(NH_3) \tag{?}
\]

\[
K_w = \frac{[H_3O^+][NH_3][NH_4^+][OH^-]}{[NH_3][NH_4^+]} \tag{?}
\]

\[
K_w^{yes} = [H_3O^+][OH^-] \tag{and:}
\]

Why is all of this important? How would you know if a salt solution or any solution from an acid and/or a base will be acidic, alkaline or neutral with both H\(^{+}\) and A\(^{-}\) present?
Method 1:
Eyeball the pH of Solutions of Acids and Bases

A **strong acid** and a **strong base** mixed together yields a neutral solution, e.g., hydrochloric acid with sodium hydroxide.
A **strong acid** and a **weak base** yields an acidic solution, e.g., hydrochloric acid and ammonia.
A **weak acid** plus a **strong base** yields a basic solution, e.g., acetic acid and sodium hydroxide.
A **weak acid** and a **weak base** mixed together can be complex. **BUT**! If they are equal in strength they will yield a neutral solution, e.g., acetic acid and ammonia.
If a solution of 0.3M HOAc dissociates in water by the following reaction:

\[ \text{HOAc} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OAc}^- \]

What is the pH of the solution? \( K_a \) for HOAc is 1.8*10^{-5}

Solution: Always write out the equation, first, in these types of questions as laid out below:

<table>
<thead>
<tr>
<th></th>
<th>HOAc</th>
<th>+</th>
<th>H₂O</th>
<th>→</th>
<th>H₃O⁺</th>
<th>+</th>
<th>OAc⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>[Before reaction]</strong></td>
<td>0.3M</td>
<td></td>
<td></td>
<td></td>
<td>0M</td>
<td></td>
<td>0M</td>
</tr>
<tr>
<td><strong>[After reaction]</strong></td>
<td></td>
<td>- x</td>
<td></td>
<td></td>
<td>+ x</td>
<td></td>
<td>+ x</td>
</tr>
<tr>
<td><strong>Total concentration of species</strong></td>
<td>0.3 - x</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

Note that the concentrations change in proportion to the amount (number of mols) of reactants and products, i.e., 1 mol of HOAc begets 1 mol of hydronium ion and 1 mol of acetate ion.
Write the equilibrium expression, substitute and rearrange and solve:

\[ K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{X \cdot X}{0.3 - X} = \frac{X^2}{0.3 - X} \times \frac{X^2}{0.3} \]

\[ (K_a) \times (0.3) = X^2 \]

\[ \sqrt{(1.8 \times 10^{-5}) \times (0.3)} = X = 0.0023 \text{M} \]

\[ X = 0.0023 \text{M} = [H_3O^+] \]

\[ pH = -\log 0.0023 = 2.64 \]

What is the pOH for this aqueous solution?

Since \( pH + pOH = 14 \), it follows that \( 14 - 2.64 = 11.36 \) is the pOH.
Example #1: What is the pH of a solution that is 0.8M in ammonia? $K_b$ for NH$_3$ = 1.8*10$^{-5}$. 
Solution: Set up as before:

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$</th>
<th>+</th>
<th>H$_2$O</th>
<th>$\rightarrow$</th>
<th>NH$_4^+$</th>
<th>+</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Before reaction]</td>
<td>0.8M</td>
<td></td>
<td></td>
<td>$\rightarrow$</td>
<td>0M</td>
<td></td>
<td>0M</td>
</tr>
<tr>
<td>[After reaction]</td>
<td>- x</td>
<td></td>
<td>+ x</td>
<td>+ x</td>
<td>+ x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total concentration of species</td>
<td>0.8 - x</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{X^2}{0.8 - x} \approx \frac{X^2}{0.8}$$

$$\sqrt{(1.8*10^{-5})*(0.8)} = X = 0.0038 \text{ M}$$

$$pOH = -\log 0.0038 = 2.42$$

$$pH = 14 - 2.42 = 11.58$$
Acid-Base Titrations

Knowing now what we know about acids, how may we apply this information to the lab?
  
  • By studying acid/base titrations.
  
  • Acids and hydroxide bases react to form water and a salt.
  
  • This sort of reaction is called a neutralization reaction.
  
  • Bases that contain bicarbonate or carbonate in them also produce carbon dioxide in addition to the water and the salt.
  
  • Examples of these sorts of [neutralization] reactions are summarized, below, in the table:

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4 + 2 \text{KOH} \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$2\text{HNO}_3 + \text{Ba(OH)}_2 \rightarrow \text{Ba(NO}_3)_2 + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4 + \text{Al(OH)}_3 \rightarrow \text{AlPO}_4 + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$2\text{HCl} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{CO}_2\uparrow + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$6\text{HNO}_3 + \text{Al}_2(\text{CO}_3)_3 \rightarrow 2\text{Al(NO}_3)_3 + 3\text{CO}_2\uparrow + 3 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4 + \text{MgCO}_3 \rightarrow \text{MgSO}_4 + \text{CO}_2\uparrow + \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
Titration ≡ An analytical/quantitative technique where one solution of known concentration (aka standard solution) is slowly added to a known volume but unknown concentration of another solution. Generally, this involves the addition of an unknown amount of base to a known amount of acid. The volume of the base is measured in a buret:
**Indicator** ≡ An organic dye which changes color depending on the pH of the solution, e.g.:

- **Phenolphthalein**: colorless @ pH 8.2 red @ pH 10
- **Bromoethymol blue**: yellow @ pH 6.0 blue @ pH 7.6
- **Methyl red**: red @ pH 4.2 yellow @ pH 6.2
- **Bromocresol purple**: yellow @ pH 5.2 purple @ pH 6.8
- **Congo red**: blue @ pH 3.0 red @ pH 5.2

The pH at which the color of the indicator changes ≡ the titration endpoint.

Indicators are chosen to change color within ± 1 pH unit as close as possible to the equivalence point (the significance of this will be brought out a bit later).

We will discuss at a later time the effects of reacting strong acids/bases, weak acids/bases and other combinations of acids/bases on pH.

If conditions are such that an indicator won't work, e.g., doesn't change close enough to the equivalent point, the analyte is highly colored and interferes with indicator color change, a pH meter can be used to follow the titration.
Titration Technique

• Clean the buret with soap and water; rinse well.
• Rinse buret with 5-10 mL of the standard solution (base) and partially drain through the valve tip. Do NOT allow the buret to empty and put air bubbles in the tip.
• Safely fill the buret with your standard solution (base) and place in buret clamp on the ring stand.
• Drain excess standard out and pour it in the waste container.
• Record the volume on the buret in ink (remember "0" is on the top and "50" is on the bottom of the buret).
• Obtain your unknown acid sample[s]: for a solid, mass it on the balance, then pour into an Erlenmeyer flask and add water as necessary per instructions. For a liquid, pipet the solution into your Erlenmeyer flask.
• Add indicator (phenolphthalein in most CHEM 121/122 titrations) -- 2-4 drops. NOTE: this step is the easiest to forget and the easiest to diagnose.
• Using your WEAK hand, straddle the buret with your index and society fingers on and under the back of the stop-cock and your thumb on the front of the stop-cock.
  • Using your STRONG hand, grasp the outside of the Erlenmeyer flask by the neck, insert the buret tip into the neck and begin swirling the solution vigorously without spilling.
  • Begin adding standard solution (base) to the analyte flask with swirling.
  • In the beginning you may add base fairly rapidly -- as you get closer to the endpoint, add base slower, i.e., drop-by-drop.
  • With phenolphthalein, add enough base with swirling to get the whole solution to turn pink/fuschia for 30 seconds, then back to colorless. This is the ideal end point.
    Record your final volume on the buret in ink in your lab book.
  • NOTE: A crude way in which to see if you've gone WAY over the end point is to swirl the pink solution, take a deep breath and hold it in for approximately 15 seconds, then exhale rapidly into the sample. Do this 3 times. If the solution goes colorless, you're barely over -- if not, you're WAY over. Either way, stop, record your data in ink and go on to the next sample. What's the reaction, here?
    • Dispose of your sample appropriately.
Sample Data Sheet

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Std Volume:</td>
<td>36.34 mL</td>
<td>(why 50 on bottom)</td>
</tr>
<tr>
<td>Initial Std Volume:</td>
<td>1.25 mL</td>
<td>(why 0 on top)</td>
</tr>
<tr>
<td>Volume Std used:</td>
<td>35.09 mL</td>
<td>(how much used)</td>
</tr>
</tbody>
</table>

REMEMBER: read your buret numbers DOWN! See below.

The application of this type of technique and data is discussed later in lecture and lab.

Example of reading a meniscus in a buret. This buret reading is 1.60 mL:
Titrations of acids and bases follow a general sigmoid-shaped curve for a mono-protic acid:

In General:

Lots of OH\(^-\)  
(\(\text{A}^--\))

End Point or Equivalent Point  
\([\text{H}^+] = [\text{OH}^-]\)
Acid-Base Titrations

HA $\leftrightarrow$ H$^+$ + A$^-$
Or
HA + MOH $\leftrightarrow$ HOH + MA
Mono-protic Acid

H$_2$A $\leftrightarrow$ 2H$^+$ + A$^{-2}$
Or
H$_2$A + 2MOH $\leftrightarrow$ 2HOH + M$_2$A
Di-protic Acid

[Graphs showing pH changes with mL 0.1 N NaOH Added]
Tri-Protic Acids have THREE Endpoints

\[ \text{H}_3\text{A} \rightleftharpoons 3\text{H}^+ + \text{A}^{3-} \]

\[ \text{HA}^{2-} \rightleftharpoons \text{A}^{3-} + \text{H}^+ \]

\[ \text{H}_2\text{A}^- \rightleftharpoons \text{HA}^{2-} + \text{H}^+ \]

\[ \text{H}_3\text{A} \rightleftharpoons \text{H}_2\text{A}^- + \text{H}^+ \]
When using a pH meter to keep track of the titration, the equivalent point/end point are not obvious. Typically a technique called "taking the first derivative" of the pH curve (the sigmoid shaped curve) is used to determine these points. Without going into detail, this involves manipulating the sigmoid curve data to take on a sort of "backwards, inside out parabolic shape".

The value of the equivalence point is that it is the pH at which the $[H^+] = [OH^-]$. At that point, divide the volume at the endpoint in half, read from that volume up onto the sigmoid-shaped curve, then over to the pH curve and you will be at the numerical value for the negative log of the acid dissociation constant ($pK_a$).
Amino Acid Titration: 3 Endpoints

Trial 2 Histidine Titration
The $K_a$ is equal to the arithmetic relationship between the undissociated and dissociated acid:

$$HA \Leftrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

and notice that the $K_a$ is directly proportional to $[H^+]$ -- more on this later.
Acids like $H_2A$ and $H_3A$ have multiple dissociation steps.

Each step is represented by its own $K_a$ or $K_b$:

$$H_2A \rightleftharpoons HA^- + H^+$$

$$HA^- \rightleftharpoons A^- + H^+$$

where

$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]}$$

and

$$K_{a2} = \frac{[A^-][H^+]}{[HA^-]}$$
The total $K_a$ for this reaction is equal to the product of the two dissociation constants:

$$K_{a1} \cdot K_{a2} = \frac{[HA^-][H^+][A^-][H^+]}{[H_2A][HA^-]}$$

and

$$K_{a-TOTAL} = \frac{[H^+]^2[A^-]}{[H_2A]}$$

A tri-protic acid has three dissociations, hence the total $K_a$ is equal to the products of the three dissociation constants.
Likewise, the $K_b$'s for bases are calculable in the same manner; an exception for bases is that you are focusing on the OH-'s instead of the protons.
Henderson-Hasselbalch Equation for Calculating the pH of a Weak Acid
The derivation of this equation is a rather lengthy one and is summarized, below.

Note that it starts from the very simple mono-protic acid dissociation that we've pretty much beaten to death.

The salt concentration is equivalent to the anion concentration.

This equation is very useful in biomedical research when making buffers.

\[ HA \leftrightarrow H^+ + A^- \]

\[ K_a = \frac{[H^+][A^-]}{[HA]} \]

Rearranging, sequentially:

\[ \frac{[HA]}{[A^-]} \times K_a = [H^+] \]

\[ - \log \left( \frac{[HA]}{[A^-]} \times K_a \right) = - \log[H^+] \]

\[ - \log \left( \frac{[HA]}{[A^-]} \right) - \log K_a = pH \]

\[ - \log \left( \frac{[HA]}{[A^-]} \right) + pK_a = pH \]

\[ \log \left( \frac{[A^-]}{[HA]} \right) + pK_a = pH \Leftrightarrow pK_a + \log \left( \frac{[salt]}{[acid]} \right) \]
Example #1: Find the pH of a solution that is 0.05M in carbonic acid and 0.025M in bicarbonate ion.

The $K_{a1}$ for carbonic acid is $4.4 \times 10^{-7}$.

Solution: First get the $pK_a$

$$pK_a = -\log(4.4 \times 10^{-7}) = 6.357$$

Secondly, set up, manipulate and plug into the equation:

$$pH = pK_a + \log\left(\frac{[\text{salt}]}{[\text{acid}]}\right) \Rightarrow pK_a + \log\left(\frac{HCO_3^-}{H_2CO_3}\right)$$

$$pH = 6.357 + \log\left(\frac{0.025}{0.05}\right) = 6.357 + \log0.5$$

$$pH = 6.357 - 0.301 = 6.056$$
Example #2: If a solution of carbonic acid was at a pH of 7.35 and was 0.03M in carbonic acid, what molar concentration of bicarbonate ion is present? Use the same $K_{a1}$ as in Example 1, above. Solution: Manipulate the equation right off the bat and substitute right into it:

\[
pH = pK_a + \log \left( \frac{[HCO_3^-]}{[H_2CO_3]} \right)
\]

\[
pH - pK_a = \log \left( \frac{[HCO_3^-]}{H_2CO_3} \right)
\]

\[
pH - pK_a = \log[HCO_3^-] - \log[H_2CO_3]
\]

\[
pH - pK_a + \log[H_2CO_3] = \log[HCO_3^-]
\]

\[
\text{anti log}(pH - pK_a + \log[H_2CO_3]) = [HCO_3^-]
\]

\[
\text{anti log}(7.35 - 6.357 + (\log 0.03)) = [HCO_3^-]
\]

\[
\text{anti log}(-0.530) = [HCO_3^-] = 0.295 \text{M}
\]
Salts are solid crystalline substances at room temperature that contains the cation of a base and the anion of an acid, e.g.:

<table>
<thead>
<tr>
<th>NaCl</th>
<th>Mg₃(PO₄)₂</th>
<th>Al₂(SO₄)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOCl</td>
<td>LiBr</td>
<td>KNO₃</td>
</tr>
</tbody>
</table>
Some common salts are summarized in the table, below:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO$_4$$\cdot$$\frac{1}{2}$H$_2$O</td>
<td>Plaster of Paris</td>
</tr>
<tr>
<td>MgSO$_4$$\cdot$7H$_2$O</td>
<td>Epsom salts</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$$\cdot$10H$_2$O</td>
<td>Borax</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>Baking soda</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>Preservative</td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>Antiseptic/germicide</td>
</tr>
</tbody>
</table>

The formation of salts necessarily depend on their solubility -- or the lack thereof -- in water. Solubility rules that actually help make chemical reactions make sense are tabulated, following slide:
<table>
<thead>
<tr>
<th>Rule</th>
<th>Exceptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali metal and NH$_4^+$ salts are all soluble.</td>
<td>Some cations in analytical group 5 are moderately insoluble.</td>
</tr>
<tr>
<td>Nitrates and acetates are all soluble.</td>
<td>AgOAc is moderately insoluble</td>
</tr>
<tr>
<td>Chlorides, bromides and iodides are all soluble.</td>
<td>Those salts of Pb$^{2+}$, Ag$^+$, Hg$_2$$^{2+}$; BiOCl and SbOCl</td>
</tr>
<tr>
<td>Sulfates are soluble.</td>
<td>Those salts of Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Ag$^+$, Pb$^{2+}$, Hg$_2$$^{2+}$</td>
</tr>
<tr>
<td>Carbonate and sulfite salts are generally insoluble.</td>
<td>Those of the alkali metals and NH$_4^+$</td>
</tr>
<tr>
<td>Sulfides are generally insoluble.</td>
<td>Those of the alkali metals and NH$_4^+$; alkaline earth sulfides and Cr$_2$S$_3$ and Al$_2$S$_3$ are decomposed by water</td>
</tr>
<tr>
<td>Hydroxides are generally insoluble.</td>
<td>Alkali metals and NH$_4^+$; Barium, strontium and calcium hydroxides are moderately soluble.</td>
</tr>
<tr>
<td>All other salts are insoluble.</td>
<td></td>
</tr>
</tbody>
</table>
As a general rule, solubility is defined as being dissolved in aqueous solution to about 3-5%.

Soluble salts are electrolytes, i.e., they will conduct an electrical current. The rules of electrolytes are summarized in the table, below, as well:

<table>
<thead>
<tr>
<th>Rule</th>
<th>Exception</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most acids are weak electrolytes.</td>
<td>The common strong acids: hydrochloric, hydrobromic, hydroiodic, nitric, sulfuric, chloric and perchloric</td>
</tr>
<tr>
<td>Most bases are weak electrolytes.</td>
<td>The strong basic hydroxides: Li, Na, K, Rb, Cs, Ca, Sr, Ba hydroxides</td>
</tr>
<tr>
<td>Most salts are strong electrolytes</td>
<td>The most importantly weakly ionized salt is HgCl$_2$; occasionally, the following are listed without general agreement: Hg(CN)$_2$, CdCl$_2$, CdBr$_2$, CdI$_2$ and Pb(OAc)$_2$</td>
</tr>
</tbody>
</table>
## Preparation of Salts

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Representative Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct union of their elements.</td>
<td>$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe} + \text{S} \rightarrow \text{FeS}$</td>
</tr>
<tr>
<td>Reactions of acids with metals, metal hydroxides or metal oxides.</td>
<td>$\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2 \uparrow$</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe(OH)}_3 + 3\text{HCl} \rightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>$\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Reactions of basic anhydrides with acid anhydrides.</td>
<td>$\text{BaO} + \text{SO}_3 \rightarrow \text{BaSO}_4$</td>
</tr>
<tr>
<td></td>
<td>$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$</td>
</tr>
<tr>
<td>Reaction of acids with salts.</td>
<td>$\text{BaCO}_3 + 2\text{HCl} \rightarrow \text{BaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$</td>
</tr>
<tr>
<td></td>
<td>$\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2\text{HCl}$</td>
</tr>
<tr>
<td>Reaction of salts with other salts.</td>
<td>$\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$</td>
</tr>
<tr>
<td></td>
<td>$\text{ZnCl}_2 + \text{Na}_2\text{S} \rightarrow \text{ZnS} + 2\text{NaCl}$</td>
</tr>
</tbody>
</table>
In reactions, thus far, we've looked at grams and moles. Sometimes, though, we need to express units in terms of protons, hydroxide ions or charges. When we do this we use a unit called EQUIVALENTS.

By definition, an equivalent (Eq) of base is that amount of base that contributes or provides 1 mol of hydroxide ion (OH⁻):

- NaOH → 1 mol OH⁻ which is 1 Eq
- Ba(OH)₂ → 2 mol OH⁻ which is 2 Eq
- Al(OH)₃ → 3 mol OH⁻ which is 3 Eq

By definition, an equivalent (Eq) of acid is that amount of acid that contributes or provides 1 mol of hydronium (H₃O⁺) or hydrogen (H⁺) ion:

- HCl → 1 mol H⁺ which is 1 Eq
- H₂SO₄ → 2 mol H⁺ which is 2 Eq
- H₃PO₄ → 3 mol H⁺ which is 3 Eq

By definition, an equivalent (Eq) of salt is that amount of salt that will contribute or provide 1 mol of positive (OR negative) charges when dissolved or dissociated:

- KCl → K⁺ + Cl⁻ which gives 1 Eq
- CaCl₂ → Ca²⁺ + 2Cl⁻ which gives 2 Eq
- AlCl₃ → Al³⁺ + 3Cl⁻ which gives 3 Eq
Remember that we can calculate Molecular Weight by dividing the mass of $X$ mol of substance (in grams) by the number of mols ("$X$") to get molecular weight in g/mol.

Using equivalents, we can calculate EQUIVALENT WEIGHT, as well:
Let's calculate the equivalent weight of $\text{AlCl}_3$ -- this has a molecular weight of 133.5 g/mol

\[
\frac{133.5 \text{ g}}{\text{mol}} \times \frac{1 \text{ mol AlCl}_3}{3 \text{ Eq}} = \frac{44.5 \text{ g}}{\text{Eq}}
\]

Notice that we used the total number of positive charges (OR negative charges: $3 \times 1 = 3$) for our equivalents.
Let's calculate the equivalent weight of sulfuric acid:

$$\frac{98 \text{ g } H_2SO_4 \times 1 \text{ mol } H_2SO_4}{mol \times 2 \text{ Eq}} = \frac{49 \text{ g}}{Eq}$$

Let's calculate the equivalent weight of LiCl:

$$\frac{42.5 \text{ g } LiCl \times 1 \text{ mol } LiCl}{mol \times 1 \text{ Eq}} = \frac{42.5 \text{ g}}{Eq}$$

Let's calculate the equivalent weight (Eq Wt) of Mg(OH)$_2$

$$\frac{58.3 \text{ g } Mg(OH)_2 \times 1 \text{ mol } Mg(OH)_2}{mol \times 2 \text{ Eq}} = \frac{29.15 \text{ g}}{Eq}$$

Clinically, the unit milli-equivalent is used (mEq) when measuring serum concentrations of electrolytes, e.g., sodium and potassium ions.
When we first learned about the mole, we extended our knowledge by studying a concentration term called molarity (M). This is a unit that expresses how many mols of a substance are dissolved in one liter of solution. We can use equivalents to do a similar concentration term: normality (N). Normality is defined as the number of equivalents of a substance that is dissolved in one liter of solution (Eq/L). Let's begin by calculating the normality of a solution that has 40 g NaOH dissolved in 1 L of water:

\[
(40 \text{ g } \text{NaOH}) \times \frac{1 \text{ mol}}{40 \text{ g } \text{NaOH}} \times \frac{1 \text{ Eq}}{1 \text{ mol}} \times \frac{1}{1 \text{ liter}} = 1 \text{ N} = 1 \frac{\text{Eq}}{\text{L}}
\]

Notice how the units cancel out.
Let's calculate the normality of a solution of 29.15 g Mg(OH)$_2$ that is dissolved in 500 mL of water.

\[
(29.15 \text{ g } \text{Mg(OH)}_2) \times \frac{1 \text{ mol}}{58.3 \text{ g } \text{Mg(OH)}_2} \times \frac{2 \text{ Eq}}{1 \text{ mol}} \times \frac{1}{0.5 \text{ L}} = 2 \text{ N} = 2 \frac{\text{Eq}}{\text{L}}
\]
Buffers

Buffers are solutions of salts that resist changes in pH, i.e., they maintain a relatively constant pH. One example of a buffer pair is the HOAc/OAc⁻ pair:

\[ \text{OAc}^- + H^+ \rightleftharpoons \text{HOAc} \]

\[ \text{HOAc} + \text{OH}^- \rightleftharpoons \text{OAc}^- + \text{H}_2\text{O} \]

Note that BOTH the hydrogen ion and the hydroxide ion react with the acetate ion.
The BUFFER CAPACITY is defined as the amount of hydrogen ion or hydroxide ion "absorbed" by a buffer without causing a significant change in the pH of the system.

One system of significance to all humans is the blood. In the blood, the following reactions occur very rapidly and continuously:

\[ H_2O + CO_2 \rightleftharpoons H_2CO_3 \]
\[ HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \]
\[ H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \]

It is this particular reaction that plays the most significant role in acid-base balance in the human body -- as you will learn in A&P.
Problem Set 15

1. If a solution of 0.5 M HOAc dissociates as follows: \( \text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^- \), what is the final \([\text{H}_3\text{O}^+]\) in the solution? \( K_a \) for HOAc = \( 1.8 \times 10^{-5} \).

2. What is the pH of the above solution?

3. What is the \( K_b \) for HOAc?

4. If a solution of 0.25 M HA dissociates as follows: \( \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \), what is the final \([\text{H}_3\text{O}^+]\) in the solution? \( K_a \) for HA = \( 5.4 \times 10^{-7} \).

5. What is the pH for the above solution (question 4)?

6. What is the \( K_b \) for HA?

7. If a solution of 1.3 M \( \text{H}_2\text{M} \) dissociates as follows:
   \[ \text{H}_2\text{M} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{O}^+ + \text{M}^{2-} \]
   what is the \([\text{H}_3\text{O}^+]\) of the solution? \( K_a \) for \( \text{H}_2\text{M} \) = \( 2 \times 10^{-8} \).

8. What is the pH of the above solution (in question 7)?

9. What is the \( K_b \) for \( \text{H}_2\text{M} \)?

10. Prove that \( K_a K_b = K_w \)
Problem Set 16

1. Mark the pH with “A” for Acidic, “B” for Neutral or “C” for Alkaline or Basic:
   A) 2.5   B) 6.8   C) 10   D) 12
   E) 7.0   F) 9.4
   G) 6   H) 14   I) 3.5   J) 4
   K) 1.5   L) 13.6

2. Calculate the $[\text{H}_3\text{O}^+]$ for all of the above pH’s in Question #1.

3. Which of the following compounds are soluble in water?
   A) PbCl$_2$   B) LiCl   C) (NH$_4$)$_2$SO$_4$
   D) AlF$_3$
   E) SrCl$_2$   F) LiOAc   G) H$_2$SO$_4$
   H) H$_3$PO$_4$

4. Determine the equivalent weight for the following compounds:
   A) HCl   B) Ba(OH)$_2$   C) MgSO$_4$
   D) AlF$_3$
   E) SrCl$_2$   F) LiOAc   G) H$_2$SO$_4$
   H) H$_3$PO$_4$
Problem Set 17

1. 20 g NaOH are dissolved in 1 L H₂O. What is the N of the NaOH solution?

2. 25 g HCl are dissolved in 500 mL of water. What is the N of the HCl solution?

3. 30 g Sr(OH)₂ are dissolved in 750 mL water. What is the N of the Sr(OH)₂ solution?

4. 150 g H₂SO₄ are dissolved in 750 mL water. What is the N of the H₂SO₄ solution?

5. 75 g BaSO₄ are dissolved in 3 L H₂O. What is the N of the BaSO₄ solution?

Problem Set 18

1. A solution of HA and A⁻ is at a pH of 6.4. If the [HA] = 0.4 M and the [A⁻] = 0.25 M, what is the pKₐ for HA?

2. A solution of HB and B⁻ is at a pH of 8.5. If the [HB] = 0.05 M and the [B⁻] = 0.15 M, what is the pKₐ for HB?

3. A solution of HC and C⁻ is at a pH of 7. If the [HC] = 0.5 M and the [C⁻] = 0.5 M, what is the pKₐ for HC?

4. A solution of HA and A⁻ is at a pH of 12. If the [HA] = 0.01 M and the [A⁻] = 0.75 M, what is the pKₐ for HA?

5. A solution of HA and A⁻ is at an unknown pH. The Kₐ for HA is 7.2·10⁻⁸. If [HA] = 0.5 M and [A⁻] = 0.125 M, what is the pH of the solution?
Problem Set 19
1. Define Arrhenius acids and bases.
2. Define Bronsted-Lowry acids and bases.
3. Define Lewis acids and bases.
4. Describe the 5 forms of hydrates and give examples where possible.

Problem Set 20

1. Identify from which acids the following salts were obtained:
   A) K₂SO₄   B) LiCl   C) AlPO₄
   D) MgSO₄   E) Al₂(SO₄)₃   F) BPO₄
   G) SrCl₂   H) NaOCl
   I) Be₃(PO₄)₂   J) Mg(NO₃)₂   K) NaNO₃
   L) KNO₃

2. Define buffers and what the effective range of a buffer is.
3. Design a 3-column table describing unsaturated, saturated and super-saturated solutions.