Acid-base equilibria:

\[ HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq) \]

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

\[ B(aq) + H_2O \rightleftharpoons BH^+(aq) + OH^-(aq) \]

\[ K_b = \frac{[BH^+][OH^-]}{[B]} \]

\[ H_2O(aq) \rightleftharpoons H^+(aq) + OH^- (aq) \]

\[ K_w = [H^+][OH^-] = 1.01 \cdot 10^{-14} \]

\[ pH = -\log[H^+] \quad pOH = -\log[OH^-] \]

\[ pH + pOH = -\log[K_w]=14 \quad @ \quad 25 \, ^\circ C \]
Salts

Salts of weak acid – strong base:
Weak acid HA $\rightarrow$ strong conjugate base A$^-$:
A$^-$ (aq) + H$_2$O(l) $\leftrightarrow$ HA(aq) + OH$^-$ (aq)
– solution will be basic (pH>7)
Examples: NaCH$_3$COO, NaCN, K$_2$CO$_3$, NaHSO$_3$

\[
K_b = \frac{1}{K_a} \cdot K_w
\]

Salts of strong acid – weak base:
Weak base B $\rightarrow$ strong conjugate acid BH$^+$:
BH$^+$ (aq) + H$_2$O(l) $\leftrightarrow$ B(aq) + H$_3$O$^+$ (aq)
– solution will be acidic (pH<7)
Examples: salts of ammonia or amines with HCl

\[
K_a = \frac{1}{K_b} \cdot K_w
\]
The buffer formula:

\[ pH \approx pK_a - \log \frac{[HA]}{[NaA]} \]

\[ pH \approx pK_a - \log \frac{[\text{acid}]}{[\text{base}]} \]

Buffer pH:
- \( pK_a \), and the ratio \([HA]\) and \([NaA]\)

Buffer capacity:
- how large are initial \([HA]\) and \([NaA]\)
Salts of weak organic acid and strong base (NaOH):

e.g., CH$_3$-(CH$_2$)$_n$-COONa
Soaps
How does soap clean:
a soap micelle, from
http://chemistry.about.com/library/weekly/aa081301a.htm?terms=soap

Soap is an excellent cleanser because of its ability to act as an emulsifying agent. An emulsifier is capable of dispersing one liquid into another immiscible liquid. This means that while oil (which attracts dirt) doesn't naturally mix with water, soap can suspend oil/dirt in such a way that it can be removed.
Soaps are produced by saponification, a process by which triglycerides (from fat or oils) are reacted with sodium or potassium hydroxide to produce glycerol and a fatty acid salt, called 'soap':

\[
\begin{align*}
\text{CH}_2\text{O-}\text{C(\text{CH}_2)_{14}\text{CH}_3} \\
\text{CH-O-}\text{C(\text{CH}_2)_{14}\text{CH}_3} \\
\text{CH}_2\text{O-}\text{C(\text{CH}_2)_{14}\text{CH}_3} \\
\text{a fat}
\end{align*}
\]

\[
\begin{align*}
&+ 3 \text{ NaOH} \\
\text{sodium hydroxide} \\
\text{(or KOH, potassium hydroxide)}
\end{align*}
\]

\[
\begin{align*}
\text{saponification} \\
\downarrow
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} \\
\text{CH-OH} \\
\text{CH}_2\text{OH} \\
\text{glycerol}
\end{align*}
\]

\[
\begin{align*}
&+ 3 \text{ CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{Na} \\
\text{a crude soap}
\end{align*}
\]
During the manufacture of commercial soaps, glycerin is produced and is either washed away with the other waste products, or it is separated out and sold on to the cosmetics, food or explosives (think nitro-glycerin!) industries. This is an enormous loss - glycerin is a natural moisturizer for the skin, and the removal of glycerin during the commercial production of soap is one of the reasons why commercial soaps can often be so drying to the skin. In the cold-process soapmaking method the basic mixture of vegetable oils and fats, sodium hydroxide, water, natural nutrients and essential oils is stirred together. No additional heat is supplied apart from the gentle heat needed to melt the oils at the start of the process and the glycerin is stirred back into the soap as the saponification reaction takes place. This means that our handmade soaps retain all the glycerin, making superior and gentle bars of soap.
It is recorded that the Babylonians were making soap around 2800 B.C. and that it was known to the Phoenicians around 600 B.C.
Polyprotic acids: $\text{H}_2\text{SO}_4$, $\text{H}_2\text{SO}_3$, $\text{H}_2\text{CO}_3$, $\text{H}_3\text{PO}_4$, etc

Several equilibria:

\[
\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^- \quad K_{a1} > 100 \\
\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \quad K_{a2} = 1.2 \times 10^{-2}
\]

Note:

hydrogen sulfate ion is amphoteric;
$K_{a1} \gg K_{a2}$, this is very common;

If $K_{a1}$ and $K_{a2}$ are different by a factor 100 or more ->
can treat 2 equilibria sequentially
When a 0.034 M $\text{H}_2\text{CO}_3$ solution is prepared, what are the concentrations of $\text{HCO}_3^-$, $\text{CO}_3^{2-}$ and $\text{H}^+$? $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$.

(1) $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$

$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$

$K_{a1} \approx \frac{x^2}{0.034 - x} = \frac{x^2}{0.034} = 4.3 \times 10^{-7}$

$x = 1.2 \times 10^{-4}$ M = [H$^+$] = [HCO$_3^-$]

(2) $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$

$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$

$K_{a2} \approx \frac{y \cdot (1.2 \cdot 10^{-4} + y)}{1.2 \cdot 10^{-4} - y} \approx \frac{y \cdot 1.2 \cdot 10^{-4}}{1.2 \cdot 10^{-4}} = y = 4.8 \times 10^{-11}$

$y = 4.8 \times 10^{-11}$ = [CO$_3^{2-}$]

Note: [CO$_3^{2-}$] << [HCO$_3^-$] and [H$^+$] from step (1) >> [H$^+$] from step (2) >> [H$^+$] from water ion-n
Superacids
Strength of an acid in water solution:

\[ HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq) \]

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

Strong acids - fully dissociate in water, e.g., \( K_a(HCl) \sim 10^7 \).

Note: the \( K_a \) expression implicitly assumes that solution is dilute and water is present in great excess.

How do we characterize strength of concentrated acids? What is stronger - conc-d HNO\(_3\) or conc-d H\(_2\)SO\(_4\)?
Acids -> proton donors (Bronsted-Lowry)
Stronger acids -> better proton donors -> more efficient protonating agents.

Acid strength:
Use relative scale and quantify how efficient different acids are in protonating some weak base, e.g., nitroanyline:

\[ B + \text{ acid(l)} \leftrightarrow BH^+ \quad K = \frac{[BH^+]}{[B]} \]

Stronger acid -> more BH^+
Weaker base -> less BH^+

Hammet acidity function:

\[ H_0 = pK_{BH^+} - \log\frac{[BH^+]}{[B]} \]
Hammet acidity function:

\[ H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \]

\( H_0 < 0 \): more negative - stronger acids

\( H_0(H_2SO_4) = -12 \)

Acids stronger than sulfuric acid: superacids

First noticed by Gillespie
Described by George Olah in 1960
Professor George Olah (USC): 1994 Nobel Prize Laureate: “for contributions to carbocation chemistry”
## Superacids

\[ H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \]

<table>
<thead>
<tr>
<th>Acid</th>
<th>( H_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% H(_2)SO(_4)</td>
<td>-12</td>
</tr>
<tr>
<td>HClO(_4)</td>
<td>-13</td>
</tr>
<tr>
<td>ClSO(_3)H</td>
<td>-13.8</td>
</tr>
<tr>
<td>FSO(_3)H</td>
<td>-15.1</td>
</tr>
<tr>
<td>CF(_3)SO(_3)H</td>
<td>-14.1</td>
</tr>
</tbody>
</table>
Even stronger superacids:

Combine superacid with strong Lewis acid (e.g., AlCl₃, SbF₅, AsF₅, NbF₅)

The magic acid (invented by George Olah):

\[ \text{FSO}_3\text{H:SbF}_5 \]

\( H_0 = -26.5 \) (10¹⁴ times stronger than 100% H₂SO₄!)

dissolves candle wax!

Transfer protons to even the weakest bases, e.g., protonates methane:

\[
\text{CH}_4 + \text{H}^+ \text{ (super-acid)} \rightarrow [\text{CH}_5^+] \rightarrow \text{CH}_3^+ + \text{H}_2
\]

methonium

\[
\text{CH}_3^+ \text{ reacts further:}
\text{CH}_3^+ + \text{CH}_4 \rightarrow [\text{CH}_3\text{-CH}_4^+] \rightarrow \text{CH}_3\text{CH}_2^+ + \text{H}_2
\]

\[
\text{CH}_3\text{CH}_2^+ + \text{CH}_4 \rightarrow [\text{CH}_3\text{-CH}_2\text{-CH}_4^+] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^+ + \text{H}_2
\]

............................

higher hydrocarbons (e.g., octane - \text{C}_8\text{H}_{18}) - \rightarrow \text{gasoline from methane or coal (through coal gasification: } \text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CH}_4, \text{CO, O}_2, \text{CO}_2...\)

Methonium: \( \text{CH}_5^+ \) - 3-center-2-electron bond
Michael Klein research (University of Pennsylvania): How do superacids work on molecular level?

Getting the Jump on Superacids [PSC]