8. ACID-BASE CHEMISTRY

You know the following seven things from General Chemistry…

1.  pH = -log[H$^+$]
2.  H$_2$O is both an acid and a base.
3.  Bronstead-Lowery Acid is a compound that generates H$^+$ when put in water.
4.  Bronstead-Lowery Base is a compound that generates HO$^-$ when put in water.
5.  Lewis Acids accept an electron pair.
6.  Lewis Bases donate an electron pair.
7.  Lewis Acid/Base and Bronstead-Lowery Acid/Base concepts are COMPLETELY compatible.

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

You are familiar with acids and bases like HCl, H$_2$SO$_4$, HNO$_3$, KOH, NaOH, NH$_3$…maybe even acetic acid. But what about more complex organic systems?

How do we define the acidity of organic compounds, especially given that I have said that organic chemistry is about electrons? Consider the following…

\[
\text{OrgH} + \text{H}_2\text{O} \xleftrightarrow{} \text{Org}^- + \text{H}_3\text{O}^+
\]

…we care about the ability of the OrgH to give up a proton, but we don’t measure pH. We measure the pK$_a$.

\[
\text{AH} + \text{H}_2\text{O} \xleftrightarrow{} \text{A}^- + \text{H}_3\text{O}^+
\]

equilibrium constant,  \[K_{eq} = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{AH}][\text{H}_2\text{O}]\]

acidity constant,  \[K_a = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{AH}]\]

\[pK_a = -\log(K_a)\]
**pKa** is completely analogous to **pH**, but describes the chemistry of an organic molecule rather than a bulk property of a solution.

Lower pKa = more acid  
Higher pKa = less acidic (more basic)

See Tables 4.2, 4.3, 4.4 in Hornback.

At solution pH’s above the pKa of the compound, the compound is more soluble in water…

![Acetosalicylic acid](image)

...is soluble in a water/NaHCO₃ solution (pH ~ 8)

acetylsalicylic acid  
(aspirin), pKa ~ 4.3

**Strong vs. Weak Acids and Bases**

The strength of an acid depends on the stability of the conjugate base. Can a stable anion exist? The more stable the conjugate base (anion) the more acidic the acid. The stability of the conjugate base depends on…

1. Electronegativity (induction)  
2. Solvent  
3. Resonance  
4. s-character at the carbon center

For example:

electronegativity…

![Cl](image)

pKa = 4.8  
pKa = 2.8
resonance…

\[
\text{pKa} = 16 \\
\begin{array}{c}
\text{Cyclohexyl OH} \\
\xrightarrow{\text{resonance}} \\
\text{Cyclohexyl O} \\
+ \text{H}^+
\end{array}
\]

\[
\text{pKa} = 10 \\
\begin{array}{c}
\text{Phenol OH} \\
\xrightarrow{\text{resonance}} \\
\text{Phenolate O} \\
+ \text{H}^+
\end{array}
\]

s-character…

\[
\begin{array}{c}
\text{pKa} \\
50 \\
44 \\
25
\end{array}
\]

Solvents…polar, aprotic solvents are preferred.

e.g., diethylether, DMSO, THF, maybe CH\textsubscript{3}Cl
**BASES**...the exact opposite of acids.

\[
\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{HB}^+ + \text{HO}^-
\]

\[
pK_b = -\log ([\text{HB}^+][\text{HO}^-]/[\text{B}])
\]

What makes a good base...

The more accessible (unstable) the electrons are, the stronger the base.
The less accessible (more stable) the electrons are, the weaker the base.
A negative charged base is more powerful than a neutral base.
The less electronegative the atomic center, the more willing to share electrons,
therefore the stronger the base.

Two main forms of neutral bases (besides water)...O and N.

- $\text{R}_3\text{N}$: amines
- $\text{R}_2\text{C} \equiv \text{O}$: carbonyls
- $\text{R}_3\text{C} \equiv \text{OH}$: alcohols