Introducing Acids and Bases

Recall: \[ \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ \] hydronium ion

in aqueous solution---level of \( \text{H}_3\text{O}^+ \) proportional to \( \text{H}^+ \), so we can either use \([\text{H}^+]\) or \([\text{H}_3\text{O}^+]\) to represent acidity of solution!

**autoprotoysis** of water:  \[ 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

or: \[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

\[ K_w = [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14} \]

at 25\(^\circ\) C

**Bronsted and Lowery Defn:**

Acid---proton donor

Base---proton acid

\[ \text{HA} + \text{B} \rightleftharpoons \text{BH}^+\text{A}^- \text{ (salt)} \]

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

\( \text{A}^- \) is **conjugate base** of \( \text{HA} \)

\[ \text{RNH}_2 + \text{H}^+ \rightleftharpoons \text{RNH}_3^+ \]

\( \text{RNH}_3^+ \) is **conjugate acid** of \( \text{RNH}_2 \)
Acetic acid + Methylamine $\rightleftharpoons$ Acetate ion + Methylammonium ion

Acid $\rightleftharpoons$ Base

Conjugate pair

Conjugate pair
Consequences of Autoprotolysis rxn of Water:

• can always find concentration of H⁺ or OH⁻ if other species is known since in an aqueous solution---the autoprotolysis rxn is always in equilibrium!—-product of [H⁺] [OH⁻] must equal 1 x10⁻¹⁴

e.g.---if you know [H⁺] = 2 x 10⁻³ M; then [OH⁻] = Kw / [H⁺] = 5 x 10⁻¹²

• in pure water---[H⁺] [OH⁻] = x² = 10⁻¹⁴; Hence [H⁺] = [OH⁻] = 1 x 10⁻⁷

pH and [H⁺];

define pH = - log [H⁺] (we will see later that pH = -log aH⁺ ---but in dilute solutions---[H⁺] = aH⁺)

if [H⁺] - 3.8 x 10⁻⁸ ; pH = - log(3.8 x 10⁻⁸) = 7.42
pH Scale

pH = -log [H+] ; therefore: [H+] = 10^{-pH}

(can have pH values < 0 (negative #) and > 14--very strong acids/bases at very high concentrations)

0.1 M HCl

0.001 M HCl

0.00001 M HCl

strong acid--100% dissociation

• What about 1x10^{-8} M HCl? pH=8 ??
  – A dilute acid cannot be basic.
  We shall see--in a minute!
pH for strong acid and strong base determined by moles of H⁺ or OH⁻
generated by complete dissociation of these species;

\[ 10^{-3} \text{M HCl; } \text{HCl}_{(aq)} \rightarrow \text{H}^+ + \text{Cl}^- \]

(arrow in only one direction due to fact that equilibrium is
achieved only when products are present)

pH = -log [10^{-3}] = 3.00  \text{ (report pH to two decimals--usually)}

What is pH of 4.2 \times 10^{-3} \text{M HClO}_4?  \text{pH} = -\log (4.2 \times 10^{-3}) = 2.38

What is pH of 4.2 \times 10^{-3} \text{M NaOH}?  in this case need to use
\( K_w \) expression---and assume all [OH⁻] in water soln is coming from
exogenous base:
\[ [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = 10^{-14} / 4.2 \times 10^{-3} = 2.38 \times 10^{-12} \]

therefore pH = -log (2.38 \times 10^{-12}) = 11.62
Water Auto-dissociation
the “leveling effect”

For strong acids or bases---can neglect 
$[\text{H}^+]$ and $[\text{OH}^-]$ arising from autoprotolysis 
of water----when concentrations of acids 
and bases are $> 10^{-6}$ M----however 
as you use more dilute concentrations---the 
contribution of $\text{H}^+$ and $\text{OH}^-$ are dictated 
by water equilibrium reaction!

pH of $10^{-10}$ M HNO$_3$ = ? = pH 7.00
pH of $10^{-8}$ M HCl = ?

$[\text{H}^+]_{\text{tot}} = [\text{H}^+]_{\text{HCl}} + [\text{H}^+]_{\text{H}_2\text{O}} = 10^{-8} + 10^{-7}$

$= 1.1 \times 10^{-7}$; pH = -log $1.1 \times 10^{-7} = 6.96$

The pH of a very dilute acid can never go above pH=7.0
or the pH of the very dilute base can not go below pH=7.0
Weak Acid Dissociation Constants

any generic acid \text{ conjugate base }  A^-\text{ is weak base--}
\text{A}^- + \text{H}_2\text{O } \rightleftharpoons \text{HA} + \text{OH}^-

HA \rightleftharpoons \text{H}^+ + \text{A}^-

in water, formally--should be written as:  \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-

but we can neglect the water in writing any equilibrium constant

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \text{acid dissociation constant} \]

For diprotic acids:  \text{H}_2\text{A} \rightleftharpoons \text{H}^+ + \text{HA}^- \rightleftharpoons \text{H}^+ + \text{A}^{2-}

(Diprotic acid = two removable protons)

\[ K_{a(1)} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = \text{first acid dissociation constant} \]

\[ K_{a(2)} = \frac{[\text{H}^+][\text{A}^{2-}]}{[\text{HA}^-]} = \text{second acid dissociation constant} \]
Weak Bases:

\[ \text{B} + \text{H}_2\text{O} \leftrightarrow \text{BH}^+ + \text{OH}^- \]

\[ K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \] = base hydrolysis constant

\( K_b \) values are small for weak bases!

\( \text{BH}^+ \) is conjugate acid of B; a salt of \( \text{BH}^+\text{Cl}^- \) dissolved in water would likely yield an acidic pH solution!---

Relationship between \( K_a \) and \( K_b \) of weak acids/bases conjugate pairs:

\[ \frac{\text{B} + \text{H}_2\text{O} \leftrightarrow \text{BH}^+ + \text{OH}^-}{\text{BH}^+ \leftrightarrow \text{H}^+ + \text{B}} \]

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]

Thus (recall from manipulation of K values:

\[ K_w = K_a K_b \]

and \( K_a = K_w / K_b \)
Another example—What is $K_b$ of acetate—the conjugate base of acetic acid?

\[
\text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}^+ \quad \text{K}_a
\]

can write reverse reaction as:

\[
\text{CH}_3\text{CO}_2^- + \text{H}^+ \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} \quad K' = 1/K_a
\]

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad \text{K}_w
\]

\[
\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{OH}^- \quad \text{K}_b
\]

therefore:  $K_b = K_w(1/K_a) = K_w / K_a$

for acetic acid---$K_a = 1.75 \times 10^{-5}$; therefore $K_b$ for acetate =

\[
10^{-14}/ (1.75 \times 10^{-5}) = 5.7 \times 10^{-10}
\]

What is $K_a$ for methylammonium ion (CH$_3$NH$_3^+$)?

if $K_b = 4.4 \times 10^{-4}$ (amine);  $K_a = 1 \times 10^{-14} / 4.4 \times 10^{-4} = 2.3 \times 10^{-11}$
pK\textsubscript{a} and pK\textsubscript{b}:

pK\textsubscript{a} = -\log K\textsubscript{a} \quad \text{and} \quad pK\textsubscript{b} = - \log K\textsubscript{b}

Therefore---the stronger the acid---the lower/smaller its pK\textsubscript{a}
the stronger the base---the lower/smaller its pK\textsubscript{b}
or---the greater the pK\textsubscript{a} of the conjugate acid

<table>
<thead>
<tr>
<th>pK\textsubscript{a}</th>
<th>Group</th>
<th>K\textsubscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>POH\textsubscript{(1)}</td>
<td>0.04</td>
</tr>
<tr>
<td>3.44</td>
<td>OH</td>
<td>3.6 \times 10^{-4}</td>
</tr>
<tr>
<td>6.01</td>
<td>POH\textsubscript{(2)}</td>
<td>9.8 \times 10^{-7}</td>
</tr>
<tr>
<td>8.45</td>
<td>NH</td>
<td>3.5 \times 10^{-9}</td>
</tr>
</tbody>
</table>

pyridoxal phosphate
Comparing Acid/Base Strength

• More convenient to write log(K) values
  \[ pK_A = -\log K_A \]
  \[ pK_B = -\log K_B \]

• Less zeros to write

  Acetic acid    \( pK_A = 4.75 \)
  Chloroacetic acid    \( pK_A = 2.87 \)
  Aminoacetic acid    \( pK_A = 2.35 \)

Complete table in Appendix B

pK\(_A\) scale

Stronger acid

Stronger conjugate base
Calculating pH for Weak Acid Dissociation

• First step, assume \([A^-] \sim [H^+]\)

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

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

\[
\begin{array}{c|c|c|c}
\text{Initial} & \text{F} & 0 & 0 \\
\text{Final} & F-x & x & x \\
\end{array}
\]

• This ignores the small \([H^+] \ (<10^{-7} \text{ M})\) from the dissociation of water

\[
K_a = \frac{x^2}{F-x}
\]
Example--Weak Acid Problem

• What is the pH of a 0.02 M solution of benzoic acid?

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

\[ F = [HA] + [A^-] = 0.02 \text{ M} \]

\[ [H^+] = x ; [A^-] = x \]

• Lookup pK_A from table (appendix B): pK_A = 4.20

\[ K_a = \frac{x^2}{F - x} \]

\[ 6.28 \times 10^{-5} = \frac{x^2}{0.02 - x} \]

\[ 0 = x^2 + 6.28 \times 10^{-5} x - (6.28 \times 10^{-5} \cdot 0.02) \]
Two approaches can be used to solve-----can get rid of quadratic by using successive approximation approach:

• Just in case the programmable calculator is out of reach
• 6.28x10^{-5} is a small number
• What if we neglect the \(-bx\) term

\[ K_a = \frac{x^2}{F - x} \quad 0 = x^2 + 6.28\times10^{-5}x - \left(6.28\times10^{-5} \cdot 0.02\right) \]

1) approximation:

(F-x) \sim F

True if F\gg x

\text{drop}

\[ x^2 = \left(6.28\times10^{-5} \cdot 0.02\right) \]

\[ x = \sqrt{6.28\times10^{-5} \cdot 0.02} \]

\[ \left[H^+\right] = \sqrt{K_A \cdot F_{HA}} \]

\[ x \approx \sqrt{6.28\times10^{-5} \cdot 0.02} \]

\[ x \approx 1.12\times10^{-3} \text{ M} = \left[H^+\right] \]

• Now check assumptions
Checking/Refining the Approximation

- Assumption $F \gg x$  \[ C_6H_5CO_2H \rightarrow C_6H_5CO_2^- + H^+ \]  
  \[ K_a = \frac{x^2}{F - x} \quad F = 0.02M \]

1$^\text{st}$ approximation: $x_1 = [H^+] = 1.12 \times 10^{-3}$

- Now check the approximation--plug back in for $x$ in $F-x$ term---and then solve for $x^2$ and then $x$ as the square root!
  \[ x^2 = 6.28 \times 10^{-5} \cdot (0.02 - x) \]
  \[ x^2 \approx 6.28 \times 10^{-5} \cdot (0.02 - 1.12 \times 10^{-3}) \]
  \[ x \approx 1.09 \times 10^{-3} \] slightly less than initial answer!

- Keep plugging $x_i$, back into the equation until $x_i$ is constant
But what about $[H^+]$ from dissociation of water?

Do we have too worry about this?

- Water also dissociates to give $[H^+]$ and $[OH^-]$

\[ H_2O \rightleftharpoons H^+ + OH^- \]

\[ [OH^-] = K_w/ [H^+] \]

\[ [OH^-] = \frac{10^{-14}}{1.09 \times 10^{-3}} = 9.17 \times 10^{-12} \]

- Water dissociation gives $-[H^+]_{H_2O} = [OH^-]_{H_2O}$
- Final pH of solution is $= -\log [H^+]_{total}$
- $[H^+]_{total} = [H^+]_{H_2O} + [H^+]_{HA}$
- $[H^+]_{total} = 9.17 \times 10^{-12} + 1.09 \times 10^{-3} = 1.09 \times 10^{-3}$ M

\[ C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+ \]

$pK_a = 4.20$

\[ x \approx 1.09 \times 10^{-3} = [H^+] \]

Why so small--? --autoprotoanalysis rxn shifted to left---due to $H^+$ from HA reaction!
Second approach to solve such problems---use formula for solution of quadratic equation!

\[ 0 = x^2 + 6.28 \times 10^{-5} x - \left(6.28 \times 10^{-5} \cdot 0.02\right) \]
\[ 0 = x^2 + 6.28 \times 10^{-5} x - 1.256 \times 10^{-6} \]

\[
    x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = [\text{H}^+] 
\]

\begin{align*}
    a &= 1 \\
    b &= 6.28 \times 10^{-5} \\
    c &= 1.256 \times 10^{-6} \\
    \text{two solutions---} \\
    1.09 \times 10^{-3} \\
    &\quad \quad - 1.09 \times 10^{-3} \quad \text{reject---[H}^+] \text{ cannot be negative!}
\end{align*}
• Fraction of dissociation

\[
\frac{\text{ionic form of acid}}{\text{total acid forms}} = \frac{[A^-]}{[A^-] + [HA]} = \text{fraction dissociated}
\]

\[
[A^-] = 1.09 \times 10^{-3} \quad \text{From our last example}
\]

\[
F = 0.02 \quad M = [HA] + [A^-]
\]

\[
\%D = \text{fraction} \times 100 = \frac{1.09 \times 10^{-3}}{0.02} = 5.4\%
\]

• This is one way to define a weak acid (or base) from a strong one

• A strong acid (or base) is nearly 100% dissociated in dilute solution
at same concentration---fraction of dissociation for stronger acid is greater!!
For weak base-- similar treatment to find pH of solution

\[ B + H_2O \rightarrow BH^+ + OH^- \]

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

again--nearly all the OH\(^-\) in soln comes from the base reaction---not the autoprotolysis of water!

\[ F = [B] + [BH^+] ; \quad [B] = F - [BH^+] = F - x \]

\[ K_b = \frac{x^2}{F - x} \quad \text{this time, } x = [OH^-] \]

however----now when you find x by either successive approx.
or solution of quadratic equation, to find pH you must remember:

\[ [H^+] = K_w / [OH^-] \]
What is pH of 0.0372 M solution of cocaine?

\[
\frac{x^2}{0.0372 - x} = 2.6 \times 10^{-6} = K_b
\]

by method of successive approx; \( x^2 = 9.67_2 \times 10^{-8} \)
\( x = 3.11 \times 10^{-4} \)

plug back into denominator in \( K_b \) expression:
\( x^2 / (0.0372 - 3.11 \times 10^{-4}) = 2.6 \times 10^{-6} \)
\( x^2 / 0.0369 = 2.6 \times 10^{-6} \); \( x = 3.09_7 \times 10^{-4} = 3.10 \times 10^{-4} = [OH^-] \)
therefore--- $[H^+] = K_w / [OH^-] = 10^{-14} / 3.10 \times 10^{-4} = 3.22 \times 10^{-11}$

$$pH = -\log (3.22 \times 10^{-11}) = 10.49$$

fraction reacted?

$$\text{fraction} = \frac{[BH^+]}{([B] + [BH^+])}; \text{ but } [BH^+] = [OH^-]$$

therefore--- fraction $= 3.10 \times 10^{-4} / 0.0372 = 0.0083$

or 0.83 % is reacted with water!

F -total conc. of base initially present!
What is pH of solution of 0.05 M sodium benzoate?

This is a salt---that yields 100% dissociation yielding Na\(^+\) and benzoate ions at equal concentration in solution!

but we know that benzoic acid is the protonated form of benzoate anion----it has $K_a$ of $6.28 \times 10^{-5}$ ;

thus $K_b$ of benzoate--the conjugate base of benzoic acid :

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{6.28 \times 10^{-5}} = 1.5 \times 10^{-10}$$

$$K_b = \frac{x^2}{0.05 - x} = 1.5 \times 10^{-10}$$

solve for $x$- ([OH\(^-\))--by successive approx-- = $2.8 \times 10^{-6}$ M

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2.8 \times 10^{-6}} = 3.5 \times 10^{-9} ;$$

$$\text{pH} = -\log (3.5 \times 10^{-9}) = 8.45$$