Acids and Bases

Chapter 17:
5, 6, 7, 9, 11, 13, 17, 18, 43, 67a-d, 71

Chapter 18:
5-9, 26, 27a-e, 32

Arrhenius Theory of Acids

• an acid-base reaction involves the reaction of hydrogen ions and hydroxide ions to form water. All bases contain OH\(^-\). All acids contain H\(^+\):

\[
\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}
\]

• problem with this theory is that it fails to address the role of the solvent, i.e. H\(_2\)O. Obvious example is NH\(_3\), which does not contain OH\(^-\), but is nonetheless a base.
Bronsted-Lowry Theory

• an acid is a proton donor; a base is a proton acceptor.

• problem with the Arrhenius theory is now taken care of. We now recognize that NH₃ acts as a base because of it’s role as a hydrogen atom acceptor in the reaction:

\[
\begin{align*}
\text{NH}_3 & \quad \text{base(1)} \\
\text{H}_2\text{O} & \quad \text{acid(2)} \\
\text{NH}_4^+ & \quad \text{acid(1)} \\
\text{OH}^- & \quad \text{base(2)}
\end{align*}
\]

Base Ionization Constant

• for the previous reaction, we can write the following equilibrium expression, called the base ionization constant.

• Note that water does not explicitly appear in the equilibrium expression because the reaction is taking place in water

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}
\]

• In the reaction, NH₃ acts as a base (proton acceptor) and H₂O acts as an acid (proton donator). The conjugate acid of NH₃ is NH₄⁺. The conjugate base of water in the reaction is OH⁻. We would refer to NH₄⁺/NH₃ as a conjugate acid/base pair.
A Weak Acid

• water can also act as base (proton acceptor), when it reacts with an acid such as acetic acid, to form the hydronium ion, H₃O⁺

• Acetic acid gives up a proton to form the acetate ion. CH₃CO₂H/CH₃CO₂⁻ form a conjugate acid base pair.

Acid Ionization Constants

• for the acid reaction we can write the acid ionization equilibrium constant, $K_a$

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

• the size of $K_a$ is a measure of the strength of the acid in water. The larger the value of $K_a$, the further the equilibrium lies to the right, the stronger the acid.

• For a base, the larger the value of $K_b$, the stronger the base.

• Regardless of the value of $K_a$ or $K_b$, if the equilibrium for the acid or base reactions do not lie completely to the right, we call them weak acids and weak bases
A Strong Acid

- Hydrochloric acid will react in the following way in water:

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

- We write a single arrow for the reaction since the reaction is “complete”. The \( K_a \) for the reaction is about \( 10^6 \). The large value of \( K_a \) implies that the equilibrium lies completely to the right. Because the acid dissociates completely, we call this a strong acid.

Comparison of Extent of Ionization of Acetic Acid and HCl

- What does complete dissociation mean? To what extent does HCl dissociate in water, and how does this compare to a weak acid such as acetic acid. Let’s calculate the fraction of the acid in the A\(^-\) form after the reaction:

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

<table>
<thead>
<tr>
<th>( I_{\text{initial}} ) (mol/L)</th>
<th>HA</th>
<th>( _ )</th>
<th>H(_3)O(^+)</th>
<th>A(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\text{HA}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{\text{H}_3\text{O}^+} )</td>
<td>-( x )</td>
<td>+( x )</td>
<td></td>
<td>+( x )</td>
</tr>
</tbody>
</table>

\( C_{\text{HA}} \) is the initial “formal” concentration of the acid.
Relative Strength of Acids and Bases

- the stronger an acid, the weaker it’s conjugate base
- e.g. HCl dissociates completely in water. It’s conjugate base, Cl⁻, has virtually no tendency to take a proton from H₃O⁺ (or H₂O).

### Cont’d

\[
K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{x^2}{[C_{HA} - x]} \quad \Rightarrow \quad x^2 + K_a x - K_a C_{HA} = 0
\]

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a C_{HA}}}{2}
\]

fraction of ionized acid = \[
\frac{[A^-]}{[HA] + [A^-]} = \frac{x}{(C_{HA} - x) + x} = \frac{x}{C_{HA}}
\]

<table>
<thead>
<tr>
<th></th>
<th>K_a</th>
<th>x</th>
<th>X/C_{HA}*100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CO₂H</td>
<td>1.8 x 10⁻⁵</td>
<td>4.15 x 10⁻⁴ M</td>
<td>4.15%</td>
</tr>
<tr>
<td>C_{HA} = 0.01 M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>~ 1 x 10⁶</td>
<td>9.99999999 x 10⁻³ M</td>
<td>99.99999999%</td>
</tr>
<tr>
<td>C_{HA} = 0.01 M</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Nonaqueous Solvents

- Note that $\text{HClO}_4$, HI, HBr, HCl, $\text{H}_2\text{SO}_4$ and HNO$_3$ are all strong acids. We cannot tell which acid is stronger because they all dissociate completely in water to yield $\text{H}_3\text{O}^+$.

- Water is said to have a leveling effect on the acids...the strong acids all appear to have the same strength since $\text{H}_3\text{O}^+$ is the strongest acid that can exist in $\text{H}_2\text{O}$.

- To differentiate them, we need use a solvent that is a weaker base than water (acetic acid or diethyl ether).

$$\text{HClO}_4 + \text{C}_2\text{H}_5\text{O} \rightarrow \text{ClO}_4^- + [\text{C}_2\text{H}_5\text{O}]^+$$

$\text{HCl}$ + $\text{C}_2\text{H}_5\text{O} \leftrightarrow \text{Cl}^- + [\text{C}_2\text{H}_5\text{O}]^+$

HCIO$_4$ dissociates completely in diethylether. It is a stronger acid than HCl.

Autoprotolysis of Water

- Electrical conductivity measurements indicate that even the purest water has a finite electrical conductivity.

- Electrical conduction in water requires the presence of ions.

- Finite conductivity remains due to the self ionization of water (autoprotolysis) which stems from its amphiprotic nature (ability to act both as an acid and a base):

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

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \approx 1.0 \times 10^{-14}$ (25 °C)

$K_w$ is referred to as the ion product of water.
Pure water

• What is the [H$_3$O$^+$] in pure water at 25 °C (0 °C, 50 °C, 100 °C)?

\[ 2 \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+ \text{(aq)} + \text{OH}^- \text{(aq)} \]

\[ K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = x^2 \]

\[ x = [\text{H}_3\text{O}^+] = \sqrt{K_w} \]

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$K_w$</th>
<th>$[\text{H}_3\text{O}^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.11 × 10$^{-14}$</td>
<td>0.34 × 10$^{-7}$</td>
</tr>
<tr>
<td>25</td>
<td>1.01 × 10$^{-14}$</td>
<td>1.00 × 10$^{-7}$</td>
</tr>
<tr>
<td>50</td>
<td>5.47 × 10$^{-14}$</td>
<td>2.34 × 10$^{-7}$</td>
</tr>
<tr>
<td>100</td>
<td>4.91 × 10$^{-14}$</td>
<td>7.01 × 10$^{-7}$</td>
</tr>
</tbody>
</table>

Hydronium ion in solution

In solution, the hydronium ion is likely highly solvated. This figure shows a H$_3$O$^+$ surrounded by 4 water molecules, H$_4$O$_4$$^+$. Other hydrated species, such as H$_4$O$_3$$^+$ are also postulated to exist.
**pH**

Soren Sorenson defined pH back in 1909. The potential of hydrogen ion, or pH of a solution is defined to be:

\[
pH = -\log [H_3O^+] \quad (\text{Strictly } pH = -\log a_{H_3O^+})
\]

\[
pOH = -\log [OH^-] \quad (\text{Strictly } pH = -\log a_{H_3O^+})
\]

*How are pH and pOH related?*

\[
K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}
\]

\[-\log K_w = -\log [H_3O^+][OH^-] = -\log 1.0 \times 10^{-14}
\]

\[
pK_w = -\log [H_3O^+] - \log [OH^-] = 14
\]

\[
pH + pOH = 14
\]
Strong Acids and Bases

**TABLE 17.2**
The Common Strong Acids and Strong Bases

<table>
<thead>
<tr>
<th>Acids</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>LiOH</td>
</tr>
<tr>
<td>HBr</td>
<td>NaOH</td>
</tr>
<tr>
<td>HI</td>
<td>KOH</td>
</tr>
<tr>
<td>HClO₄</td>
<td>RbOH</td>
</tr>
<tr>
<td>HNO₃</td>
<td>CsOH</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Mg(OH)₂</td>
</tr>
<tr>
<td></td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td></td>
<td>Sr(OH)₂</td>
</tr>
<tr>
<td></td>
<td>Ba(OH)₂</td>
</tr>
</tbody>
</table>

Strong acids and bases completely dissociate in water.

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

\[
\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} (aq) + 2 \text{OH}^- (aq)
\]

Calculating the pH, pOH, or other quantities is usually trivial in such cases. There are exceptions in dilute solution.

Calculations for Strong Acids & Bases

What is the pH, pOH, \([\text{H}_3\text{O}^+]\), \([\text{OH}^-]\) and \([\text{NO}_3^-]\) for a 0.01 M solution of HNO₃?

<table>
<thead>
<tr>
<th></th>
<th>HNO₃(aq)</th>
<th>(\approx)</th>
<th>(\text{H}_3\text{O}^+)</th>
<th>(\text{NO}_3^-) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (mol/L)</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C (mol/L)</td>
<td>-0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>E (mol/L)</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\([\text{H}_3\text{O}^+]\) = 0.01 M; \([\text{NO}_3^-]\) = 0.01; pH = -\log 0.01 = 2.00

\([\text{OH}^-]\) = \(K_w/\text{H}_3\text{O}^+\) = \(1 \times 10^{-14}/0.01 = 1 \times 10^{-12}\) M

pOH = 14 – pH = 14-2 = 12.0
Dilute Solutions

Q: What is the pH of a 0.001 M solution of HNO₃?
A: pH = -\log [0.001] = 3.00

Q: What is the pH of a 1 \times 10^{-5} M solution of HNO₃?
A: pH = -\log [1 \times 10^{-5}] = 5.0

Q: What is the pH of a 1 \times 10^{-7} M solution of HNO₃?
A: pH = -\log [1 \times 10^{-7}] = 7.0?? Can this be correct?

Q: What is the pH of a 1 \times 10^{-9} M solution of HNO₃?
A: pH = -\log [1 \times 10^{-9}] = 9.0 ?? Definitely incorrect!! A dilute solution of an acid cannot be basic. What’s the problem?

Solution to dilute acid problem

Problem: we ignored the autoprotolysis of H₂O!!

HNO₃(aq) + H₂O \rightarrow H₃O⁺(aq) + NO₃⁻(aq)
2 H₂O = H₃O⁺(aq) + OH⁻(aq)

There are two source of H₃O⁺. Information we can use to solve the problems is as follows:

Cₜ_{HNO₃} = [NO₃⁻] = 1.0 \times 10^{-9} M
K_w = [H₃O⁺][OH⁻] = 1.0 \times 10^{-14} \hspace{1cm} (1)

Charge Balance Equation: for a neutral solution the number of moles of positive charge must be equal to the number of moles of negative charge. In the current case:

[H₃O⁺] = [NO₃⁻] + [OH⁻] \hspace{1cm} (2)
Cont’d

Mass Balance Equation: there is usually a mass balance that can be written in equilibrium problems. In the current case, we could write:

total H₃O⁺ = H₃O⁺ from nitric acid + moles of H₃O⁺ from dissociation of water.

But since water dissociates 1:1 (1 H⁺ for each OH⁻), the amount of H₃O⁺ from water dissociation must be equal to [OH⁻]

\[ [\text{H}_3\text{O}^+] = [\text{HNO}_3] + [\text{OH}^-] \] (3) OR
\[ [\text{H}_3\text{O}^+] = [\text{NO}_3^-] + [\text{OH}^-] \]

Note that in this problem, the charge balance (2) and mass balance equations (3) are identical.

Solution to problem

Substitute (1) into (3):

\[ [\text{H}_3\text{O}^+] = \frac{[\text{HNO}_3] K_w}{[\text{H}_2\text{O}^+]} \]

\[ [\text{H}_3\text{O}^+] = \frac{\sqrt{[\text{HNO}_3]^2 + 4K_w}}{2} \]

If \( [\text{HNO}_3] = 1 \times 10^{-9} \) M, we get

\( [\text{H}_3\text{O}^+] = 1.005 \times 10^{-7} \) M

pH = -log \( [1.005 \times 10^{-7}] \)

pH = 6.998

Exact solutions as a function of \( [\text{HNO}_3] \) are shown on the following graph.
Formulas of Weak Acids

Example: Chloroacetic acid
Empirical Formula: C₂H₃O₂Cl

Molecular Formula: C₂H₃O₂Cl

Acid Formula: HC₂H₂O₂Cl

Condensed Formula: CH₂ClCOOH OR CH₂ClCO₂H

Lewis Structure:

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{O} \\
\text{O} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

\[\text{Ka and Kb}\]

The following are general formulas for the \(K_a\)'s and \(K_b\)'s of monofunctional weak acids and weak bases

\[
\begin{align*}
\text{B} + \text{H}_2\text{O} &\rightleftharpoons \text{BH}^+ + \text{OH}^- & K_b &= \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \\
\text{HA} + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- & K_a &= \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \\
pK_a &= -\log K_a & pK_b &= -\log K_b
\end{align*}
\]

The stronger the weak acid, the larger it’s \(K_a\), and thus the smaller it’s \(pK_a\). Similar argument for strength of bases.
Ka’s of Weak Acids

<table>
<thead>
<tr>
<th>Ionization Equilibrium</th>
<th>Ionization Constant $K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodic acid</td>
<td>HIO$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + IO$_3^-$</td>
<td>$1.6 \times 10^{-1}$</td>
</tr>
<tr>
<td>Chlorous acid</td>
<td>HClO$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + ClO$_2^-$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Chloracetic acid</td>
<td>HC$_2$H$_2$ClO$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + C$_2$H$_2$ClO$_2^-$</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + NO$_2^-$</td>
<td>$7.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + F$^-$</td>
<td>$6.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + CO$_2$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>BC$_6$H$_5$O$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + C$_6$H$_5$O$_2^-$</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hydrazoic acid</td>
<td>NH$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + NH$_2^-$</td>
<td>$1.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>HC$_3$H$_5$O$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + C$_3$H$_5$O$_2^-$</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HOCl + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + OCl$^-$</td>
<td>$2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + CN$^-$</td>
<td>$6.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>Phenol</td>
<td>HOCl$_2$H$_4$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + C$_6$H$_5$O$_2^-$</td>
<td>$1.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H$_2$O$_2$ + H$_2$O $\rightleftharpoons$ H$_2$O$^+$ + HO$_2^-$</td>
<td>$1.8 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

Weak Acid/Weak Base Problems

1. calculate $K_b$ or $K_a$ for a solution of known concentration if pH is measured

2. calculate pH of a solution when amount of dissociation is minimal

3. calculate pH of a solution when amount of dissociation is significant
Finding $K_a$

Hypochlorous acid, HOCl, is used as a disinfectant in pools and water treatment. A 0.150M solution of HOCl has a pH = 4.18. Find $K_a$

Create an ICE table

$$\text{HOCl} + H_2O \rightleftharpoons H_3O^+ + OC1^- \quad K_a = \frac{[H_3O^+][OC1^-]}{[HOCl]}$$

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilib</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>0.15</td>
<td>-x</td>
<td>0.15-x</td>
</tr>
<tr>
<td>H_2O</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>OC1^-</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

But, we should know $[H_3O^+]$

Cont’d

$pH = -\log [H_3O^+] \implies -pH = \log [H_3O^+] \implies [H_3O^+] = 10^{-pH}$

$[H_3O^+] = 10^{-4.18} = 6.61 \times 10^{-5} \text{ M} = x$

$$K_a = \frac{[H_3O^+][OC1^-]}{[HOCl]} = \frac{x^2}{0.15-x} = \frac{(6.61 \times 10^{-5} \text{ M})^2}{(0.15 \text{ M} - 6.61 \times 10^{-5} \text{ M})}$$

$K_a = 2.9 \times 10^{-8}$!
pH of Weak Acid Solution

Boric acid, B(OH)$_3$, is used as a mild antiseptic. What is the pH of a 0.025 $M$ aqueous solution of boric acid? What is the degree of ionization of boric acid in this solution?

Although it’s molecular formula does not imply this to be an acid, the hydrogen ion arises principally from the reaction

$$\text{B(OH)}_3(aq) + 2\text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- + \text{H}_3\text{O}^+ \quad K_a = 5.9 \times 10^{-10}$$

*To solve, create ICE table again.*

*Use HBo as the symbol for boric acid and Bo$^-$ as the symbol for B(OH)$_4^-$.*

Continued

<table>
<thead>
<tr>
<th></th>
<th>HBo</th>
<th>$\leftrightharpoons$</th>
<th>H$^+$</th>
<th>+</th>
<th>Bo$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.025</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.025 - x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$\frac{[\text{H}^+][\text{Bo}^-]}{[\text{HBo}]} = K_a = \frac{[x]^2}{(0.025 - x)} = 5.9 \times 10^{-10}$$

**APPROXIMATION**

Solve the equation for $x$, assuming that $x$ is much smaller than 0.025, so that (0.025 - x) is approximately 0.025.
Boric acid example - continued

\[ x^2 = (5.9 \times 10^{-10})(0.025) = 1.475 \times 10^{-11} \]
\[ x = 3.84 \times 10^{-6} \text{ M} = [H^+] \]

*CHECK ASSUMPTION!*

\[(0.025 - x) = 0.024996\]

Error = \[(0.024996-0.025)/0.025*100\% = -0.015\%\]

When this error is less than 5%, assumption is valid.

\[ \text{pH} = -\log[H^+] = -\log (3.84 \times 10^{-6}) = 5.4156 = 5.42 \]

degree of ionization = \[(3.84 \times 10^{-6})/0.025\]
= 0.000153 = 0.015%

---

Generalization

Go back to previous problem. We had:
\[ x^2 = [H^+]^2 = (5.9 \times 10^{-10})(0.025) \approx (K_a C_{HA}) \]

\[ [H_3O^+] \approx \sqrt{K_a C_{HA}} \]

where:

\[ C_{HA} = \text{formal concentration of weak acid, HA} \]

(i.e. initial concentration before dissociation)

\[ K_a = \text{acid dissociation constant} \]

This approximation only holds if dissociation is insignificant.  
*When would it not be true?*
failure of approximation

1. when acid is relatively strong; (i.e. large $K_a$)
   \[ HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad K_a \uparrow \]

2. when acid is very very dilute

pH of weak acid, significant dissociation

From a weak acid dissociation ICE table, we get:

\[ K_a = \frac{[H_3O^+]^2}{C_{HA} - [H_3O^+]} \]

If dissociation is not insignificant, we CANNOT assume that $[H^+] \ll C_{HA}$. Must solve a quadratic!

The above expression becomes:

\[ [H^+]^2 + K_a[H^+] - K_aC_{HA} = 0 \quad \text{where} \ a = 1, \ b = K_a, \ c = -K_aC_{HA} \]

\[ [H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2} \]
Problem - weak acid, significant dissociation
Find the pH of, and find the concentration of all species in, a 0.015M solution of fluoroacetic acid.
FCH₂COOH. \( K_a = 2.6 \times 10^{-3} \)

Try quick solution. If \([H^+] \ll C_{HA}\) then

\[
[H_3O^+] = \sqrt{C_{HA} K_a} = \sqrt{(0.015)(2.6 \times 10^{-3})} = 0.0062\, M
\]

\[
[H^+] / C_{HA} = 0.0062\, M / 0.015\, M = 0.416 \quad (i.e. \, 42\%)
\]
Approximation is not valid. Use quadratic.

\[
[H_3O^+] = \frac{-2.6 \times 10^{-3} + \sqrt{(2.6 \times 10^{-3})^2 + 4(2.6 \times 10^{-3})(0.015)}}{2}
\]

\[= 0.00508\, M\]

Problem - continued

\[ [H_3O^+] = 0.00508\, M \quad \text{pH} = -\log [H^+] = 2.29 \]

Other species?

\[ [OH^-] = K_w / [H_3O^+] = 1 \times 10^{-14} / 0.00508\, M = 1.97 \times 10^{-12} \, M \]

\[ [CH_2FCOOH] = C_{HA} - [H_3O^+] = 0.015 - 0.0051 = 0.0099\, M \]

\[ [CH_2FCOO^-] = [H_3O^+] = 0.0051\, M \]
Dissociation of Weak Bases

By analogy, create an ICE table for dissociation of a weak base, B.

\[
\begin{align*}
B + H_2O & \rightleftharpoons BH^+ + OH^- \\
\text{K}_b &= \frac{[BH^+][OH^-]}{[B]} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>C_B</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+ x</td>
</tr>
<tr>
<td>Equilib</td>
<td>C_B</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

If \([BH^+] \ll [B]\)

\[
[OH^-] = \sqrt{K_b C_B}
\]

If \([BH^+] \approx [B]\)

\[
[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b C_B}}{2}
\]

Polyprotic Acids (and Bases)

Acids (or bases) that generate more than one H⁺ (OH⁻) upon dissolving in aqueous solution typically undergo a series of acid/base equilibria. Consider H₃PO₄:

\[
\begin{align*}
H_3PO_4 & \rightleftharpoons H^+ + H_2PO_4^- \\
\text{K}_{a1} &= 7.5 \times 10^{-3} \\
H_2PO_4^- & \rightleftharpoons H^+ + HPO_4^{2-} \\
\text{K}_{a2} &= 6.2 \times 10^{-8} \\
HPO_4^{2-} & \rightleftharpoons H^+ + PO_4^{3-} \\
\text{K}_{a3} &= 4.8 \times 10^{-13}
\end{align*}
\]

Intermediate species can act as both an acid and a base. We say they are *amphiprotic*.

\[
\begin{align*}
PO_4^{3-} + H_2O & \rightleftharpoons HPO_4^{2-} + OH^- \\
\text{K}_{b1} &= 2.1 \times 10^{-2} \\
HPO_4^{2-} + H_2O & \rightleftharpoons H_2PO_4^- + OH^- \\
\text{K}_{b2} &= 1.6 \times 10^{-7} \\
H_2PO_4^- + H_2O & \rightleftharpoons H_3PO_4 + OH^- \\
\text{K}_{b3} &= 1.3 \times 10^{-12}
\end{align*}
\]
Other Polyprotic Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Ionization Equilibria</th>
<th>Ionization Constants, $K$</th>
<th>$pK$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrosulfuric$^a$</td>
<td>$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$</td>
<td>$K_a = 1.0 \times 10^{-7}$</td>
<td>$pK_a = 7.00$</td>
</tr>
<tr>
<td></td>
<td>$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$</td>
<td>$K_a = 1 \times 10^{-19}$</td>
<td>$pK_a = 19.0$</td>
</tr>
<tr>
<td>Carbonic$^b$</td>
<td>$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$</td>
<td>$K_a = 4.4 \times 10^{-7}$</td>
<td>$pK_a = 6.36$</td>
</tr>
<tr>
<td></td>
<td>$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_2^{2-}$</td>
<td>$K_a = 4.7 \times 10^{-11}$</td>
<td>$pK_a = 10.33$</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$</td>
<td>$K_a = 7.1 \times 10^{-3}$</td>
<td>$pK_a = 2.15$</td>
</tr>
<tr>
<td></td>
<td>$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$</td>
<td>$K_a = 6.3 \times 10^{-8}$</td>
<td>$pK_a = 7.20$</td>
</tr>
<tr>
<td></td>
<td>$HPO_3^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$</td>
<td>$K_a = 4.2 \times 10^{-13}$</td>
<td>$pK_a = 12.28$</td>
</tr>
<tr>
<td>Sulfurous$^c$</td>
<td>$H_3SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$</td>
<td>$K_a = 1.3 \times 10^{-2}$</td>
<td>$pK_a = 1.89$</td>
</tr>
<tr>
<td></td>
<td>$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$</td>
<td>$K_a = 1.1 \times 10^{-5}$</td>
<td>$pK_a = 7.21$</td>
</tr>
<tr>
<td>Sulfuric$^d$</td>
<td>$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$</td>
<td>$K_a$ = very large</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{3-}$</td>
<td>$K_a = 1.1 \times 10^{-2}$</td>
<td>$pK_a = 1.96$</td>
</tr>
</tbody>
</table>

Relationship between an acid and it’s conjugate base

$$CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO_2^-_{(aq)}$$

$$acetic \ acid \hspace{1cm} acetate$$

$$K_a = \frac{[CH_3CO_2^][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

But let us also consider the hydrolysis reaction of acetate, where acetate acts as a base:

$$CH_3CO_2^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + CH_3CO_2H_{(aq)}$$

$$acetate \hspace{1cm} acetic \ acid$$

$$K_b = \frac{[CH_3CO_2^][OH^-]}{[CH_3CO_2^-]} = 5.6 \times 10^{-10}$$
Acid/Base Relationships-cont’d

\[ K_a K_b = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2]} \times \frac{[CH_3CO_2][OH^-]}{[H_3O^+]} \]

\[ K_a K_b = [H_3O^+][OH^-] \]

\[ K_a K_b = K_w \]

\[ pK_a + pK_b = pK_w \quad \text{OR} \quad pK_a + pK_b = 14 \]

This is a general result, the \( K_a \) of an acid and the \( K_b \) of its conjugate base are related. From this we can write three equivalent statements...

The higher the \( K_a \) of an acid, the lower the \( K_b \) of the base.

The lower the \( pK_a \) of an acid, the higher the \( pK_b \) of the base.

*The stronger an acid is, the weaker is its conjugate base!*

---

**Salts**

Solutions of salts are very common in chemistry, biological systems, environmental matrices, etc. We can now predict in a qualitative sense (and in some cases quantitatively) the \( pH \) of solutions of acids, bases and salts.

**Salts of strong acids/strong bases**

- do not hydrolyze (react with water), \( pH = 7 \)

*Example* – solution of \( \text{MgBr}_2 \), salt of strong acid + strong base

\[ 2\text{HBr} \quad \text{(aq)} \quad + \quad \text{Mg(OH)}_2 \quad \text{(aq)} \quad \rightarrow \quad 2 \quad \text{H}_2\text{O} \quad \text{(l)} \quad + \quad \text{MgBr}_2 \quad \text{(aq)} \quad \text{formation} \]

\[ \text{MgBr}_2 \quad \text{(aq)} \quad \rightarrow \quad \text{Mg}^{2+} \quad \text{(aq)} \quad + \quad 2 \quad \text{Br}^- \quad \text{(aq)} \quad \text{dissolution} \]

\[ \text{Mg}^{2+} \quad \text{(aq)} \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad ?? \quad \text{reaction?} \]

\[ \text{Br}^- \quad \text{(aq)} \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad ?? \quad \text{reaction?} \]
Salt of Strong Acid/Weak Base

Salts of strong acids/weak bases

- conjugate acid of the weak base will hydrolyze, pH < 7

Example – solution of NH$_4$NO$_3$, salt of strong acid + weak base

\[
\text{HNO}_3(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq}) \quad \text{formation}
\]
\[
\text{NH}_4\text{NO}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \quad \text{dissolution}
\]
\[
\text{NO}_3^-(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{?} \quad \text{reaction?}
\]
\[
\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \quad \text{reaction!}
\]

Salt of Weak Acid/Strong Base

Salts of weak acids/strong bases

- conjugate base of the weak acid will hydrolyze, pH > 7

Example – solution of NaF, salt of weak acid + strong base

\[
\text{NaOH}(\text{aq}) + \text{HF}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{NaF}(\text{aq}) \quad \text{formation}
\]
\[
\text{NaF} \rightarrow \text{Na}^+(\text{aq}) + \text{F}^-(\text{aq}) \quad \text{dissolution}
\]
\[
\text{Na}^+(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{?} \quad \text{reaction?}
\]
\[
\text{F}^-\text{(aq)} + \text{H}_2\text{O} \rightarrow \text{HF}(\text{aq}) + \text{OH}^-\text{(aq)} \quad \text{reaction!}
\]
Salt of Weak Acid/Weak Base

Salts of weak acids/weak bases

- conjugate base of the weak acid will hydrolyze, as will the conjugate acid of the weak base. One must look at the $pK_a$ and $pK_b$ to predict the pH of solution.

Example – solution of $C_2H_5NH_3C_7H_5O_2^-$, (ethylammonium benzoate), salt of weak acid + weak base

\[
\begin{align*}
C_7H_5O_2^- (aq) + C_2H_5NH_2 (aq) & \rightarrow C_2H_5NH_3C_7H_5O_2^- (aq) \quad \text{form} \\
C_2H_5NH_3^+C_7H_5O_2^- (aq) & \rightarrow C_2H_5NH_3^+(aq)+C_7H_5O_2^- (aq) \quad \text{dissolution} \\
C_2H_5NH_3^+ (aq) + H_2O & \rightarrow H_3O^+ (aq) + C_2H_5NH_2 (aq) \quad \text{reaction!} \\
C_7H_5O_2^- (aq) + H_2O & \rightarrow C_7H_5O_2H (aq) + OH^- (aq) \quad \text{reaction!}
\end{align*}
\]

How do we predict which wins out in this competition?

Conjugate Acid/Base competition

$pK_a$ of $C_7H_5O_2H = 4.20$; $pK_b$ of $C_7H_5O_2^-$ = 14 – 4.20 = 9.8

$pK_b$ of $C_2H_5NH_2 = 3.37$; $pK_a$ of $C_2H_5NH_3^+$ = 14 – 3.37 = 10.6

Since the $pK_b$ of the basic part of the salt (i.e. benzoate) is lower than the $pK_a$ of the acidic part of the salt (ethylammonium), benzoate’s base strength is stronger than ethylammonium’s acid strength. The base should win out and we predict the final solution will be basic, pH > 7.

(Another way to look at this is to compare the $pK_a$ and $pK_b$ of the acid and base that form the salt. Since ethylamine is a stronger base than benzoic acid is an acid, then in the formation reaction, the base wins out and the resultant solution of the salt must be basic.)
Acid-Base Properties of Salts

Summary

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>Acidic or Basic</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral</td>
<td>neutral</td>
<td>neutral</td>
<td>NaCl</td>
</tr>
<tr>
<td>neutral</td>
<td>conj base of weak acid</td>
<td>basic</td>
<td>NaF</td>
</tr>
<tr>
<td>conj acid of weak base</td>
<td>neutral</td>
<td>acidic</td>
<td>NH₄Cl</td>
</tr>
<tr>
<td>conj acid of weak base</td>
<td>conj base of weak acid</td>
<td>depends on $K_a$ &amp; $K_b$ values</td>
<td>Al₂(SO₄)₃</td>
</tr>
</tbody>
</table>

Structure, Acidity & Basicity

Oxides can be considered to be acid or base anhydrides.

If E has low electronegativity, E-O bond breaks to release OH⁻.
It behaves as base!
Example: KOH, NaOH

If E has high electronegativity, strong covalent E-O bond, but O-H bond is weakened.
It behaves as acid!
Example: $O_n$ClOH, $O_n$SOH
Structure related acidity

\[ K_a = 2.9 \times 10^{-8} \]
Hypochlorous acid

\[ K_a = 1.1 \times 10^{-2} \]
Chlorous acid

\[ K_a = \text{strong?} \]
Chloric acid

\[ K_a = \text{strong!} \]
Perchloric acid

Very strong oxidizing Agent, explosive!

Acidity is not only related to structure of acid, but also to the stability of anion product.

Resonance in acetate ion stabilizes this structure...weak acid.

For ethoxide ion (other alcohols are similar), the charge is localized on –O-, it behaves as relatively strong base. Ethanol is therefore a very weak acid.

Structure Related Basicity of Amines

Lone pair electrons on N are responsible for base behaviour of amines, by binding to H⁺.
Electronegative groups attached to N lower electron density, reducing strength of base.

Hydrocarbon attachments have little electron withdrawing ability. Alkyl amines are stronger base than NH₃.

Aromatic amines have additional electron withdrawing effects due to delocalization on aromatic ring.

The effect is illustrated when comparing base strength of cyclohexylamine (non-aromatic) and aniline (aromatic).

An additional illustration of the effect of an electron withdrawing group on base strength of an aromatic amine.
Lewis Acids & Bases

Lewis Acid: electron pair acceptor
Lewis Base: electron pair donor

To identify Lewis acids, look for species (ions, atoms, etc…) that have valence shells that can accept electron pairs.

To identify Lewis bases, look for species that have lone pair electrons that can be “donated” to form a covalent bond.

\[
\begin{align*}
H^+ & \quad \text{Lewis acid} \\
: \text{NH}_3 & \quad : \text{OH}^- \quad \text{Lewis bases}
\end{align*}
\]

Lewis Acid

Formation of complex ions is an important application of Lewis acid-base theory.

\[
\begin{align*}
\text{Al}^{3+} + 6 : \text{OH} & \rightarrow \text{[Al}^{\text{O}}\text{H}^6\text{]}^{3+} \\
\text{Lewis acid} & \quad \text{Lewis base} \\
\text{Hydrated metal ion in solution}
\end{align*}
\]