Chapter 15

ACIDS, BASES

&

ACID/BASE EQUILIBRIA

Hill, Petrucci, McCreary & Perry 4th Ed.
ACIDS & BASES
The Arrhenius Definition: In Water:

- **Acid** – Substance which increases the concentration of Hydrogen Ion, $[H^+]$.

- **Base** – Substance which increases the concentration of Hydroxide Ion, $[OH^-]$.

- **Strong Acids**: $H_2SO_4$, HI, HBr, HCl, HNO$\text{O}_3$, HClO$\text{O}_4$.

- **Strong Bases**: Hydroxides of $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$. 
ACIDS & BASES

The Bronsted-Lowry Definition: The B-L definition is independent of solvent.

• *Acid* – Substance which donates a Hydrogen Ion, H⁺.

• *Base* – Substance which accepts a Hydrogen Ion, H⁺.

• Conjugate Acid Base Pairs: Species which differ by H⁺. Examples (Acid/Base):
  • HCl/Cl⁻, NH₄⁺/NH₃, H₃O⁺/H₂O, H₂O/OH⁻
• The Lewis Definition: The Lewis definition focuses on electrons and is independent of solvent.

**Acid** – Substance which accepts an electron pair.

**Base** – Substance which donates an electron pair.
Other Lewis Acids

Many Metal Ions:

\[6 \text{H}:\ddot{\text{O}}: + \text{Al}^{3+} \rightarrow \left[ \text{Al} \left( :\ddot{\text{O}}:\dddot{\text{H}} \right)_6 \right]^{3+}\]

Some Acids are not what they seem: \(\text{H}_3\text{BO}_3\)

Boric Acid is not an Oxoacid, but a Lewis Acid:

\[2 \text{H}:\ddot{\text{O}}: + \text{BO}:\dddot{\text{O}}:\text{H} \rightleftharpoons \text{H}:\dddot{\text{O}}:\text{B}(:\ddot{\text{O}}:):\text{H} \hspace{1cm} \Delta \rightarrow \text{H}:\dddot{\text{O}}:\text{B}(:\ddot{\text{O}}:):\text{H} + \text{H}:\ddot{\text{O}}:\dddot{\text{H}}\]
Bronsted Acid/Base Reactions

A competition for Hydrogen Ion (Protons)

Stronger Acid than $\text{H}_3\text{O}^+$

Stronger Base than $\text{Cl}^-$

Weaker Base than $\text{H}_2\text{O}$

Weaker Acid than $\text{HCl}$
B/L Acids/Bases are Named by Function

\[ \text{Strong Base} + \text{Very Weak Acid} \rightarrow \text{Very Weak Acid} + \text{Strong Base} \]

\[ \text{Strong Base (but weaker than NH}_2^-) \]

\[ \text{Strong Base} + \text{Very Weak Acid} \rightarrow \text{Very Weak Acid} + \text{Strong Base} \]

\[ \text{Strong Base (but weaker than O}^{-2}) \]
B/L Acid/Base Strength Relationships

Strongest Acids  <=>  Weakest Conjugate Bases

Strongest Bases  <=>  Weakest Conjugate Acids

Weak Acids  <=>  Weak Conjugate Bases

Weak Acids/Bases have pK_{a/b} between 2 & 12

Weak Acids & Weak Bases

\[ \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]
### pKa & pKb of Conjugate Acid/Base Pairs

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>HCl</td>
<td>H2O</td>
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<tr>
<td>C2H3O2</td>
<td>I-</td>
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<tr>
<td>HF</td>
<td>Cl-</td>
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<tr>
<td>HC2H3O2</td>
<td>Br-</td>
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<tr>
<td>CN-</td>
<td>OH-</td>
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<tr>
<td>NH3</td>
<td>H2O</td>
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**Strong**

**Weak**

**Very Weak**
Competition for Protons

Determining the Direction of Reaction:

\[ H_2S + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2 + HS^- \]

- weaker acid than acetic
- weaker base than \( HS^- \) ion.
- stronger acid than \( H_2S \)
- stronger base than acetate ion

See Table 15.1, p 620, for Relative Acid/Base Strengths

The Hydrogen Sulfide Ion is a stronger base than the acetate ion and will successfully compete for the Hydrogen Ion.
Factors Affecting Acid Strength

1) Polarity of the H-X Bond. The more electronegative X is, the more polar is, more charge separation in, the bond.

\[ \delta^+ H \equiv X \delta^- \]

Where \( \delta^+ \) means not a full positive charge.

2) Strength of the H-X Bond. The stronger the bond the harder it is to ionize.

\[ \delta^+ H \equiv X \delta^- \leftrightarrow H^+ + X^- \]

This Bond must break to form ions!
Trends in Binary Acid Strength

HF  <  HCl  <  HBr  <  HI

Most Polarity Least
Greatest Bond Strength Least

H₂O  <  H₂S  <  H₂Se  <  H₂Te

In Water  HF is a weak acid.

HCl, HBr and HI are strong acids.
Acidity Trends in Oxo-Acids

All Oxo-Acids contain H-O-X Bonds of near equal strength. The H-O Bond is strong!

Electronegativity Trends

H-O-Cl > H-O-Br > H-O-I

Oxygen Substitution is more important!

HClO < HClO₂ < HClO₃ < HClO₄
Acidity Trends in Oxo-Acids

Why Oxygen Substitution is more important!

\[
\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4
\]

The key is the Conjugate Base Strength!

Each added Oxygen reduces the average charge!
POLYPROTIC ACIDS

More Than One Proton Ionizes

Binary Types:

\[ H_2S \rightleftharpoons H^+ + HS^- \]

\[ H_2S > HS^- \]

\[ HS^- \rightleftharpoons H^+ + S^{2-} \]

Oxo-Acid Types:

\[ H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \]

\[ H_2SO_4 > HSO_4^- \]

\[ HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \]

\[ H_3PO_4 > H_2PO_4^- > HPO_4^{2-} \]
The Auto-Ionization of Water

\[
\begin{align*}
\text{H}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \\
K_C & = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = 3.2 \times 10^{-18} \\
\text{In dilute aqueous solution: } [\text{H}_2\text{O}] & \approx \text{constant} \\
[\text{H}_2\text{O}] & = \frac{998 \text{ g/L}}{18.02 \text{ g/mol}} = 55.4 \text{ mol/L} \\
K_C [\text{H}_2\text{O}]^2 & = [\text{H}_3\text{O}^+][\text{OH}^-] \\
& = 3.2 \times 10^{-18} (55.4 \text{ mol/L})^2 \\
K_C [\text{H}_2\text{O}]^2 & \equiv K_W = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}
\end{align*}
\]
Ion Product of Water

For Pure Water at 25° C:

\[ [H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M} \]

For Acid Solution:

\[ [H_3O^+] \equiv [H^+] > 1.0 \times 10^{-7} \text{ M} \]
\[ [OH^-] < 1.0 \times 10^{-7} \text{ M} \]

For Basic (Alkaline) Solution:

\[ [OH^-] > 1.0 \times 10^{-7} \text{ M} \]
\[ [H^+] < 1.0 \times 10^{-7} \text{ M} \]

In all cases the

\[ [OH^-] \times [H^+] = K_w \]
\[
\text{pH: A Convenient Measure of } [\text{H}^+] \\
\]

\[
\begin{array}{cccc}
\text{pH} & \approx & -\log [\text{H}^+] & \text{pH} & [\text{H}^+] & [\text{OH}^-] \\
14 & & 10^{-14} & & 1.0 \\
13 & & 10^{-13} & & 0.1 \\
7 & & 10^{-7} & & 10^{-7} \\
1 & & 0.1 & & 10^{-13} \\
0 & & 1.0 & & 10^{-14} \\
\end{array}
\]

Basic (Alkaline) Solution:

Neutral Solution:

Acidic Solution:

\[
\begin{align*}
p\text{OH} & \equiv -\log [\text{OH}^-] \\
p\text{K}_w & \equiv -\log (\text{K}_w) \\
p\text{K}_w & = 14.00 \\
p\text{K}_a & \equiv -\log (\text{K}_a) \\
p\text{K}_b & \equiv -\log (\text{K}_b)
\end{align*}
\]

Some others we will use later.
Strong Acid Solution

A solution which is 0.080 M HCl:

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

\[
0.080 \text{ M} \quad 0.080 \text{ M} \quad 0.080 \text{ M}
\]

\[
\text{pH} = -\log(0.080) = -(-1.10) = 1.10
\]

\[
[\text{OH}^-] = \frac{K_w}{0.080 \text{ M}} = \frac{1.0 \times 10^{-14}}{0.080 \text{ M}} = 1.25 \times 10^{-13} \text{ M}
\]

\[
\text{pOH} = -\log [\text{OH}^-] = -\log (1.25 \times 10^{-13}) = 12.90
\]
A Strong Base Solution

A solution which is 0.040 M Ca(OH)$_2$:

\[
\text{Ca(OH)}_2(aq) \xrightarrow{100\%} \text{Ca}^{2+}(aq) + 2 \text{OH}^-(aq)
\]

\[
\begin{align*}
-x & \quad +x \\
0.040 \text{ M} & \quad 0.040 \text{ M} \\
\underline{0.080 \text{ M}}
\end{align*}
\]

\[\text{pOH} = -\log(0.080) = -(-1.10) = 1.10\]

\[\left[\text{H}^+\right] = \frac{K_W}{0.080 \text{ M}} = \frac{1.0 \times 10^{-14}}{0.080 \text{ M}} = 1.25 \times 10^{-13} \text{ M}\]

\[\text{pH} = -\log(1.25 \times 10^{-13} \text{ M}) = -(-12.90)\]

\[\text{pH} = 12.90\]
Calculation of $[H^+]$ or $[OH^-]$ from pH

Orange juice has a pH of 3.54. Calculate the $[H^+]$ & $[OH^-]$. Note: $pH + pOH = 14.00$ ($pK_w$).

$pH = 3.54 = -\log[H^+]$

$[H^+] = 10^{-3.54}$

$[H^+] = 2.88 \times 10^{-4}$ M

$pOH = 14.00 - 3.54$

$pOH = 10.46$

$[OH^-] = 10^{-10.46}$

$[OH^-] = 3.47 \times 10^{-11}$ M

Always change the sign of pH or pOH before taking the antilog.
Weak Acid Equilibria

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

\[ K_c = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}] [\text{H}_2\text{O}]} \]

but \([\text{H}_2\text{O}] \approx \text{constant}!\)

\[ K_a \equiv K_c [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]} \]

\[ K_a \equiv \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]} \]
Weak Acid Equilibria: 0.10 M HA in water.

\[
\begin{align*}
\text{HA}_{(aq)} & \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \\
\text{[initial]} & = 0.10 \text{ M} & \text{0 M} & \text{0 M} \\
\Delta & \quad -x & +x & +x \\
\text{[equil]} & = 0.10 - x & +x & +x \\
\end{align*}
\]

\[
K_a = \frac{[H^+][A^-]}{[\text{HA}]} = \frac{(x)(x)}{(0.10 - x)}
\]

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

but \( [H^+] = [A^-] \)

\[
[H^+] = \left( K_a [\text{HA}]_{\text{eq}} \right)^{\frac{1}{2}}
\]

but \([\text{HA}] \gg x\), a weak acid
Calculation of the Ionization Constant, $K_a$, of a weak acid from a pH measurement.

A 0.025 M solution of Lactic Acid, $HLac$, has a pH = 2.75, calculate the $K_a$.

$$K_a = \frac{[H^+] [Lac^-]}{[HLac]}$$
Percent Ionization & Acid Concentration

Any weak acid (or base) dissociates to a greater extent as it becomes more dilute.

LeChatelier’s Principle & the Common Ion Effect

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

\[ K_c = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}] [\text{H}_2\text{O}]} \]

as \([\text{H}_2\text{O}]\) increases and \(K_c\) remains constant the values of \([\text{H}_3\text{O}^+]\) & \([\text{A}^-]\) must increase and \([\text{HA}]\) must decrease!
Example: Weak acid Equilibrium

Calculate the Equilibrium Concentrations for 0.020 M propionic acid, $K_a = 1.3 \times 10^{-5}$

\[
\begin{align*}
[HPr_{aq}] & \quad \leftrightarrow \quad [H^{+}] + [Pr^{-}] \\
\text{[init]} & \quad 0.020 \quad 0 \quad 0 \\
\Delta & \quad -x \quad +x \quad +x \\
\text{[eq]} & \quad 0.020 \quad -x \quad x \quad x
\end{align*}
\]

\[
K_a = \frac{[H^+][Pr^-]}{[HPr]}
\]
Solution:

\[
K_a = \frac{[H^+][Pr^-]}{[HPr]} = \frac{(x)(x)}{(0.020 - x)} = 1.3 \times 10^{-5}
\]

This equation will produce a quadratic unless we approximate. Errors less than 5% are acceptable.

If \(K_a/[HA] < 10^{-2}\)

\(x << [HA]_{eq}\) and 
\([HA]_{eq} \approx [HA]_{initial}\)

\[
K_a = \frac{(x)(x)}{(0.020 - x)} \approx \frac{(x)(x)}{(0.020)}
\]

\(x = 5.0 \times 10^{-4}\)

\(pH = 3.30\)

\(x = 5.1 \times 10^{-4}\)

\(pH = 3.29\)
Ionization Equilibria – Weak Bases

\[ NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \]

\[ K_c = \frac{[NH_4^+] \cdot [OH^-]}{[NH_3] \cdot [H_2O]} \]  

but \([H_2O] \approx \text{constant}!\)

\[ K_b \equiv K_c \cdot [H_2O] = \frac{[NH_4^+] \cdot [OH^-]}{[NH_3]} \]

\[ K_b \cdot [NH_3] = [NH_4^+] \cdot [OH^-] \]  

but: \([NH_4^+] = [OH^-]\)

\[ [OH^-] = \left[ K_b \cdot [NH_3]_{eq} \right]^{\frac{1}{2}} \approx \left[ K_b \cdot [NH_3]_{init} \right]^{\frac{1}{2}} \]
Calculation of $K_b$ from pH Measurements

A 0.0015 M solution of Quinine, $Qn$, has a pH = 9.84. Calculate the $K_b$ for quinine.

\[ Qn_{aq} \rightleftharpoons QnH_{aq}^{+} + OH_{aq}^{-} \]

\[ [\text{eq}] = 0.0015 - x \quad x \quad x \]

\[ [QnH^{+}] = [OH^{-}] = 10^{- (14.00 - 9.84)} = 10^{-4.16} \]

\[ [QnH^{+}] = [OH^{-}] = 6.92 \times 10^{-5} \, \text{M} \]

\[ K_b = \frac{[QnH^{+}][OH^{-}]}{[Qn]} = \frac{(6.92 \times 10^{-5})(6.92 \times 10^{-5})}{(0.0015 - 6.92 \times 10^{-5})} \]

\[ K_b = \frac{(6.92 \times 10^{-5})^2}{(0.0015 - 0.00007)} = 3.2 \times 10^{-6} \]
Acid/Base Properties of Salts

Hydrolysis of Salts

Salts of SA/SB are neutral. Both the conjugate base/acid are very weak neither the conjugate acid or base alter pH = 7.00.

Salts of SA/WB are acidic. The conjugate acid of the weak base makes pH < 7.00.

Salts of WA/SB are basic. The conjugate base of the weak acid makes the pH > 7.00
pK_a \& pK_b of Conjugate Acid/Base Pairs

Weak

Strong

Very Weak

HCl

H_2O

C_2H_3O_2

H_3O^+

HF

HCN

NH_3

OH^-

I^-

HBr

Cl^-

Br^-

F^-

CN^-

NH_4^+

H_2O
Salts of a Strong Acid / Weak Base

Calculate the pH of 0.10 M Ammonium Chloride

\[ \text{NH}_4^{+} + (\text{Cl}^-) \overset{\text{H}_2\text{O}}{\rightleftharpoons} \text{H}^+ + \text{NH}_3 + (\text{Cl}^-) \]

0.10 - x

\[ x \quad x \]

\[ K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \]

rearranging

\[ K_a = \frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]} \cdot \frac{[\text{H}^+][\text{OH}^-]}{[\text{OH}^-]} \]

\[ K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \]

For conjugate pairs

\[ K_a \times K_b = K_w \]
Calculate the pH of 0.10 M Ammonium Chloride

\[
\begin{align*}
\text{NH}_4^{+(aq)} + (\text{Cl}^{-}) & \rightleftharpoons H^{+(aq)} + \text{NH}_3(aq) + (\text{Cl}^{-}) \\
0.10 - x & \quad x \quad x \\
K_a &= \frac{[\text{NH}_3][H^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\
K_a &= 5.6 \times 10^{-10} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10} \\
[H^+] &= x = \left[(5.6 \times 10^{-10})(0.10)\right]^{1/2} = 7.5 \times 10^{-6} \text{ M} \\
\text{pH} &= 5.13 \quad \text{an acidic solution!}
\end{align*}
\]
Salts of a Weak Acid / Strong Base

Calculate the pH of 0.10 M Sodium Cyanide

\[
\text{K}_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{[\text{H}^+]}{[\text{H}^+]}
\]

\[
\text{K}_a = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}
\]

\[
\text{K}_w = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}}
\]
Calculate the pH of 0.10 M Sodium Cyanide

\[(\text{Na}^{+}) + \text{CN}^{-} \rightleftharpoons \text{HCN} + \text{OH}^{-} + \text{Na}^{+}\]

\[\text{K}_b = \frac{[\text{HCN}][\text{OH}^{-}]}{[\text{CN}^{-}]} = 1.6 \times 10^{-5}\]

\[\text{K}_b = 1.6 \times 10^{-5} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}\]

\[\text{[OH}^{-}] = x = \left[(1.6 \times 10^{-5}) (0.10)\right]^{\frac{1}{2}} = 1.3 \times 10^{-3} \text{ M}\]

pOH = 2.9

pH = 14.0 - 2.9 = 11.1 a basic solution!
The Common Ion Effect:

Calculate the pH of a 0.10 M acetic acid solution, then add enough dry sodium acetate to make the solution 0.10 M acetate.

\[
\text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}_2\text{O} + \text{C}_2\text{H}_3\text{O}_2^-(aq)
\]

\[
[\text{HC}_2\text{H}_3\text{O}_2]_{eq} = 0.10 - x
\]

\[
[\text{H}^+] = \sqrt{(1.8 \times 10^{-5})(0.10)} = 1.3 \times 10^{-3} \text{ M}
\]

\[
\text{pH} = 2.89
\]

When we add the base and common ion acetate we will suppress the ionization of acetic acid!

\[
[\text{HC}_2\text{H}_3\text{O}_2]_{eq} = 0.10 - z
\]

The new dissociation z is a lot smaller than x.
Now calculate the pH of a 0.10 M acetic acid solution after adding the dry sodium acetate to make the solution 0.10 M in acetate. 1

\[
\begin{align*}
\text{HC}_2\text{H}_3\text{O}_2^{(aq)} & \rightleftharpoons H^{(aq)} + \text{C}_2\text{H}_3\text{O}_2^{-}\text{(aq)} \\
[ ]_{eq} & \quad 0.10 - z \\
& \quad z \\
& \quad 0.10 + z
\end{align*}
\]

\[
K_a = \frac{[H^+] [C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(z)(0.10 + z)}{(0.10 - z)}
\]

Solving for \([H^+]:\)

\[
[H^+] = \frac{K_a [HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{(1.8 \times 10^{-5})(0.10 - z)}{(0.10 + z)}
\]
Calculate the pH of a 0.10 M acetic acid solution, then add enough dry sodium acetate to make the solution 0.10 M acetate. 2

\[ \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) \]

\[ [\text{H}^+] = \left( \frac{1.8 \times 10^{-5})(0.10 - z)}{0.10 + z} \right) \approx \left( \frac{1.8 \times 10^{-5})(0.10)}{0.10} \right) \]

\[ [\text{H}^+] = 1.8 \times 10^{-5} \text{ M} \]

\[ \text{pH} = 4.75 \]

Compare this to just the weak acid! \[ \text{pH} = 2.89 \]
Buffers the “How” to Control pH

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \]

This amount of acid will absorb a lot of hydroxide ion. This amount of base will not absorb a lot of hydrogen ion.

\[ [\text{eq}] \quad 0.10 - x \]

If we add the conjugate base the solution will absorb both!

\[ [\text{eq}] \quad 0.10 - z \quad z \quad 0.10 + z \]

These amounts of both conjugates will absorb comparable amounts of hydrogen or hydroxide ion.

\[
[H^+] = \frac{K_a (0.10)}{(0.10)} = K_a = 1.8 \times 10^{-5} \text{ M}.
\]

\[ \text{pH} = 4.75 = \text{pK}_a \]
The Henderson Hasselbalch Equation

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

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

or \[ \text{pH} = \text{pK}_a - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right) \]

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

This equation will work for an acid or base buffer!

\[ \text{or} \quad \text{pH} = \text{pK}_a + \log \left( \frac{[\text{CB}]}{[\text{CA}]} \right) \]

But it will only work when \([\text{CB}] \approx [\text{CA}]!!\)
Buffers the “How” to Control pH

\[
\text{NH}_3(aq) + \text{H}_2\text{O}(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]

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

\[
K_a = \frac{K_w}{K_b} = \frac{[\text{OH}^-][\text{H}^+][\text{NH}_3]}{[\text{OH}^-][\text{NH}_4^+]} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}
\]

The Henderson Hasselbalch Equation

\[
pH = pK_a + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right) = pK_a + \log \left( \frac{[\text{CB}]}{[\text{CA}]} \right)
\]

This equation will work for an acid or base buffer!
Buffers Change pH only to the Extent that the Conjugate Ratios Change.

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Buffers Change pH only to the Extent that the Conjugate Ratios Change.

\[
\text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]

Adding acid will cause \( \text{NH}_3 \) to react to form more \( \text{NH}_4^+ \)

Adding base will cause \( \text{NH}_4^+ \) to react to form more \( \text{NH}_3 \)

\[
[H^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]} \Rightarrow \text{pH} = pK_a + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)
\]

Determining the pH of a buffer to which acid or base is added is a problem in stoichiometry and calculating the new conjugate ratio!
15-81: A solution 0.405 M in HCOOH and 0.326 M in HCOO\(^-\) is prepared. What is its pH?

\[
\text{HCOOH}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{HCOO}^-_{(aq)} + \text{Na}^+_{(aq)}
\]

[eq1] 0.405 M \quad \approx 0 \text{ M} \quad 0.326 \text{ M} \quad 0.326 \text{ M}

15-85: To 50.0 mL of the above buffer is added 1.00 mL of 0.250 M HCl. What is the new pH?
Challenging a Buffer

15-81: A solution 0.405 M in HCOOH and 0.326 M in HCOO$^-$ is prepared. What is its pH?

\[
\text{HCOOH}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{HCOO}^-_{(aq)} + \text{Na}^+_{(aq)}
\]

\[
[\text{HCOOH}]_{eq1} = 0.405 \text{ M} \\
[\text{H}^+]_{eq} \approx 0 \text{ M} \\
[\text{HCOO}^-]_{eq} = 0.326 \text{ M} \\
[\text{Na}^+]_{eq} = 0.326 \text{ M}
\]
15-85: To 50.0 mL of the above buffer is added 1.00 mL of 0.250 M HCl. What is the new pH?
Titration of Acids and Bases

• The quantitative addition of an acid solution to a base solution until the equivalence point is reached.

• At the equivalence point the following equation applies:

\[
\text{Moles Acid} = \text{Moles Base}
\]

\[
\text{Vol}_{\text{Acid}} \times M_{\text{Acid}} = \text{Vol}_{\text{Base}} \times M_{\text{Base}}
\]

\[
M_{\text{Acid}} = [H^+] \quad M_{\text{Base}} = [OH^-]
\]
Titrating a Weak Base with Strong Acid

Calculate the volume of 0.052 M HCl required to titrate 32.0 mL of 0.077 M ammonia. Calculate pH at endpoint.

\[ \text{NH}_3(aq) + \text{H}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq) \]

moles acid = moles base (at equivalence point)