

## Unit 6: ACIDS AND BASES AND SOLUTION EQUILIBRIA

### Chapter 14: Acids and Bases

#### 14.1: The Nature of Acids and Bases

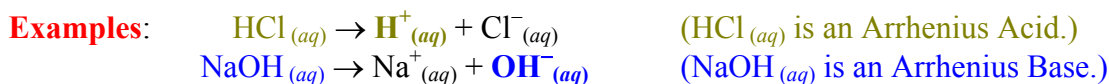
##### Physical and Chemical Properties of Acid and Base

| Acids   | Bases  |
|---|--|
| Taste Sour (Citric Acids).                            | Taste Bitter.                                    |
| Burning Sensation (Stomach Acid).                     | Feels Slippery (Detergent, Degreaser).           |
| Corrosive with Metals (reacts to give off $H_2(g)$ ). | Alkaline in Nature (NaOH, Baking Soda).          |
| Red litmus remains Red; Blue litmus turns Red.        | Red litmus turns Blue; Blue litmus remains Blue. |
| Bromothymol Blue turns Yellow                         | Bromothymol Blue turns Blue.                     |
| Phenolphthalein turns Colourless.                     | Phenolphthalein turns Pink.                      |
| pH < 7  | pH > 7   |



**Conceptual Definition:** - an explanation that attempts to describe why things are the way they are.

**Arrhenius Concept:** - acids are  $H^+$  (proton) producers and bases are  $OH^-$  producers.

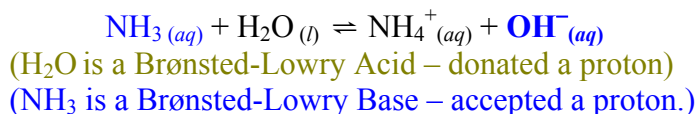
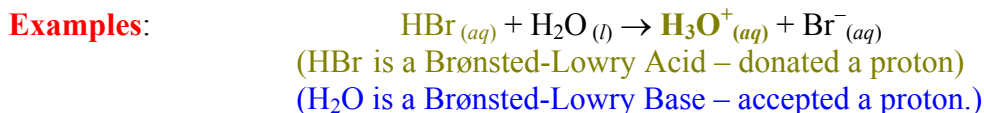


**Brønsted-Lowry Model:** - acids and bases react with water to dissociate where acids are  $H^+$  (proton) donors and bases are  $H^+$  (proton) acceptors.

- first proposed by Johannes Brønsted and Thomas Lowry.

**Hydronium Ion:** - an ion formed when an acid “donated”  $H^+$  ion combined with a  $H_2O$  molecule to form a  $H_3O^+$  ion (hydronium ion).

- essentially has the same function as a  $H^+$  ion, but  $H_3O^+$  denotes that we are using the Brønsted-Lowry model.



**Conjugate Base:** - the product formed after the Acid donated a  $H^+$ . (Acid  $\rightarrow$  Conjugate Base)  
 - behaves like a base when the reaction is looking from reverse.

**Conjugate Acid:** - the product formed after the Base accepted a  $H^+$ . (Base  $\rightarrow$  Conjugate Acid)  
 - behaves like an acid when the reaction is looking from reverse.

**Conjugate Acid-Base Pair:** - the (acid/conjugate base) or (base/conjugate acid) pairs.



Conjugate Acid-Base Pairs: HA/A<sup>-</sup> and H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup>

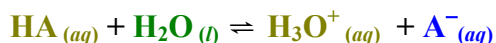


Conjugate Acid-Base Pairs: B/HB<sup>+</sup> and H<sub>2</sub>O/OH<sup>-</sup>

**Acid Dissociation Constant ( $K_a$ ):** - the equilibrium constant of a Brønsted-Lowry Acid Dissociation.

**Base Dissociation Constant ( $K_b$ ):** - the equilibrium constant of a Brønsted-Lowry Base Dissociation.

#### Brønsted-Lowry Acid Dissociation



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

#### Brønsted-Lowry Base Dissociation

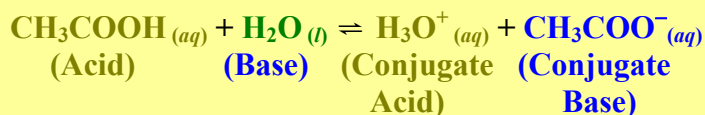


$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

**Example 1:** Write the Brønsted-Lowry dissociation reaction of the following. Identify the Brønsted-Lowry acid and base, along with the conjugate acid and base. Determine the conjugate acid-base pairs. State the equilibrium expression of the dissociation reaction.

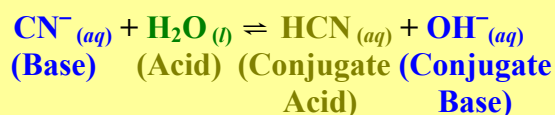
a. Acetic acid ( $\text{CH}_3\text{COOH}_{(aq)}$ )

b. Cyanide Ion ( $\text{CN}^-_{(aq)}$ )



Conjugate Acid-Base Pairs:  
 $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  and  $\text{H}_2\text{O}/\text{H}_3\text{O}^+$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

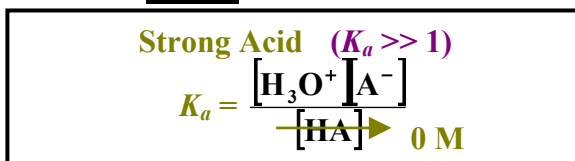


Conjugate Acid-Base Pairs:  
 $\text{CN}^-/\text{HCN}$  and  $\text{H}_2\text{O}/\text{OH}^-$

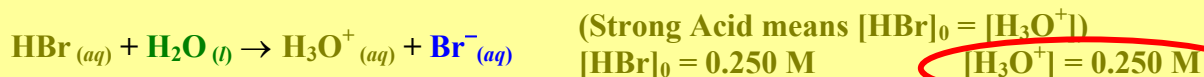
$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

**14.2: Acid Strength****Strong Acids:** - acids that **dissociate completely (100%) in water.**

- when the **acid dissociation constant ( $K_a$ ) is much greater than 1.** ( $K_a \gg 1$ )
- **the equilibrium position strongly favours the products.**
- at equilibrium, the original acid concentration,  $[HA]_{eq} \approx 0$ ;  $[H_3O^+]_{eq} = [A^-]_{eq} = [HA]_0$ .
- the **conjugate base,  $A^-$** , of a strong acid, HA **is itself a weak base** (cannot easily accept protons to do the reverse reaction).
- **Note: Strong Acids DO NOT MEAN that they are VERY CORROSIVE. It is the  $[H_3O^+]$  that defines acidity.**



|                    | [HA] |  | [H <sub>3</sub> O <sup>+</sup> ] | [A <sup>-</sup> ] |
|--------------------|------|--|----------------------------------|-------------------|
| <b>Initial</b>     | $x$  |  | $0$                              | $0$               |
| <b>Change</b>      | $-x$ |  | $+x$                             | $+x$              |
| <b>Equilibrium</b> | $0$  |  | $x$                              | $x$               |

**Examples:** Strong Acids: HClO<sub>4</sub> (aq), HI (aq), HBr (aq), HCl (aq), H<sub>2</sub>SO<sub>4</sub> (aq) and HNO<sub>3</sub> (aq)**Example 2:** Write the dissociation reaction of 0.250 M of HBr (aq) and determine its [H<sub>3</sub>O<sup>+</sup>].**Weak Acids:** - acids that **dissociate LESS than 100% in water.**

- when the **acid dissociation constant ( $K_a$ ) is less than 1.** ( $K_a < 1$ )
- **the equilibrium position strongly favours the reactants.**
- at equilibrium, the hydronium concentration is much less than the original acid concentration,  $[HA]_{eq} > [H_3O^+]_{eq}$  or  $[HA]_0 \approx [HA]_{eq}$ .
- the **conjugate base,  $A^-$** , of a weak acid **is itself a stronger weak base** (can easily accept protons to do the reverse reaction).
- **Note: Weak Acids DO NOT MEAN that they are NOT CORROSIVE. It is the  $[H_3O^+]$  that defines acidity. At a high enough concentration, a weak acid can be corrosive.**



|                    | [HA]                    |  | [H <sub>3</sub> O <sup>+</sup> ] | [A <sup>-</sup> ] |
|--------------------|-------------------------|--|----------------------------------|-------------------|
| <b>Initial</b>     | $x$                     |  | $0$                              | $0$               |
| <b>Change</b>      | $-y$ (where $y \ll x$ ) |  | $+y$                             | $+y$              |
| <b>Equilibrium</b> | $(x - y) \approx x$     |  | $y$                              | $y$               |

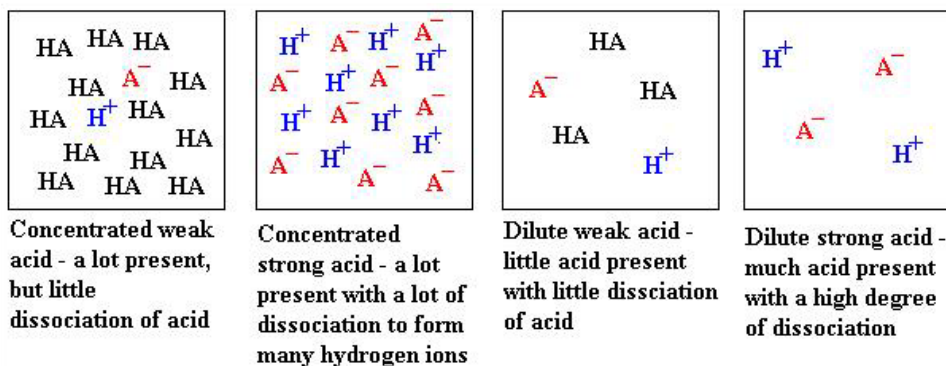
**Examples:** Some Weak Acids: HOCCOOH (aq), H<sub>2</sub>SO<sub>3</sub> (aq), HSO<sub>4</sub><sup>-</sup> (aq), H<sub>3</sub>PO<sub>4</sub> (aq), HNO<sub>2</sub> (aq), H<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> (aq), HF (aq), HCOOH (aq), C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> (aq), C<sub>6</sub>H<sub>5</sub>COOH (aq), CH<sub>3</sub>COOH (aq), H<sub>2</sub>CO<sub>3</sub> (aq), H<sub>2</sub>S (aq), HOCl (aq), HCN (aq), NH<sub>4</sub><sup>+</sup> (aq), and H<sub>3</sub>BO<sub>3</sub> (aq)

$K_a$  and Relative Strength of Some Common Acids and Bases at 25°C

| Acid Name                   | Acid Formula                                      | Conjugate Base Formula                            | $K_a$                       |
|-----------------------------|---|---|-----------------------------|
| perchloric acid             | $\text{HClO}_4 (aq)$                              | $\text{ClO}_4^- (aq)$                             | Very Large                  |
| hydroiodic acid             | $\text{HI} (aq)$                                  | $\text{I}^- (aq)$                                 | Very Large                  |
| hydrobromic acid            | $\text{HBr} (aq)$                                 | $\text{Br}^- (aq)$                                | Very Large                  |
| hydrochloric acid           | $\text{HCl} (aq)$                                 | $\text{Cl}^- (aq)$                                | Very Large                  |
| sulfuric acid               | $\text{H}_2\text{SO}_4 (aq)$                      | $\text{HSO}_4^- (aq)$                             | Very Large                  |
| nitric acid                 | $\text{HNO}_3 (aq)$                               | $\text{NO}_3^- (aq)$                              | Very Large                  |
| hydronium ion               | $\text{H}_3\text{O}^+ (aq)$                       | $\text{H}_2\text{O} (l)$                          | 1                           |
| oxalic acid                 | $\text{HOOC}(\text{COOH}) (aq)$                   | $\text{HOOC}(\text{COO})^- (aq)$                  | $6.5 \times 10^{-2}$        |
| sulfurous acid              | $\text{H}_2\text{SO}_3 (aq)$                      | $\text{HSO}_3^-$                                  | $1.5 \times 10^{-2}$        |
| hydrogen sulfate ion        | $\text{HSO}_4^- (aq)$                             | $\text{SO}_4^{2-}$                                | $1.2 \times 10^{-2}$        |
| chlorous acid               | $\text{HClO}_2 (aq)$                              | $\text{ClO}_2^- (aq)$                             | $1.2 \times 10^{-2}$        |
| phosphoric acid             | $\text{H}_3\text{PO}_4 (aq)$                      | $\text{H}_2\text{PO}_4^- (aq)$                    | $7.5 \times 10^{-3}$        |
| arsenic acid                | $\text{H}_3\text{AsO}_4 (aq)$                     | $\text{H}_2\text{AsO}_4^- (aq)$                   | $5 \times 10^{-3}$          |
| monochloroacetic acid       | $\text{HC}_2\text{H}_2\text{ClO}_2$               | $\text{C}_2\text{H}_2\text{ClO}_2^- (aq)$         | $1.35 \times 10^{-3}$       |
| citric acid                 | $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 (aq)$   | $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^- (aq)$ | $8.4 \times 10^{-4}$        |
| hydrofluoric acid           | $\text{HF} (aq)$                                  | $\text{F}^- (aq)$                                 | $7.2 \times 10^{-4}$        |
| nitrous acid                | $\text{HNO}_2 (aq)$                               | $\text{NO}_2^- (aq)$                              | $4.0 \times 10^{-4}$        |
| methanoic (formic) acid     | $\text{HCOOH} (aq)$                               | $\text{HCOO}^- (aq)$                              | $1.8 \times 10^{-4}$        |
| lactic acid                 | $\text{HC}_3\text{H}_5\text{O}_3 (aq)$            | $\text{C}_3\text{H}_5\text{O}_3^- (aq)$           | $1.38 \times 10^{-4}$       |
| ascorbic acid (vitamin C)   | $\text{H}_2\text{C}_6\text{H}_6\text{O}_6 (aq)$   | $\text{HC}_6\text{H}_6\text{O}_6^- (aq)$          | $7.9 \times 10^{-5}$        |
| benzoic acid                | $\text{C}_6\text{H}_5\text{COOH} (aq)$            | $\text{C}_6\text{H}_5\text{COO}^- (aq)$           | $6.4 \times 10^{-5}$        |
| hydrogen oxalate ion        | $\text{HOOC}(\text{COO})^- (aq)$                  | $\text{OOC}(\text{COO})^{2-} (aq)$                | $6.1 \times 10^{-5}$        |
| ethanoic (acetic) acid      | $\text{CH}_3\text{COOH} (aq)$                     | $\text{CH}_3\text{COO}^- (aq)$                    | $1.8 \times 10^{-5}$        |
| dihydrogen citrate ion      | $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^- (aq)$ | $\text{HC}_6\text{H}_5\text{O}_7^{2-} (aq)$       | $1.8 \times 10^{-5}$        |
| hydrated aluminum (III) ion | $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$          | $[\text{AlOH}(\text{H}_2\text{O})_5]^{2+}$        | $1.4 \times 10^{-5}$        |
| propanoic acid              | $\text{C}_2\text{H}_5\text{COOH} (aq)$            | $\text{C}_2\text{H}_5\text{COO}^- (aq)$           | $1.3 \times 10^{-5}$        |
| hydrogen citrate ion        | $\text{HC}_6\text{H}_5\text{O}_7^{2-} (aq)$       | $\text{C}_6\text{H}_5\text{O}_7^{3-} (aq)$        | $4.0 \times 10^{-6}$        |
| carbonic acid               | $\text{H}_2\text{CO}_3 (aq)$                      | $\text{HCO}_3^- (aq)$                             | $4.3 \times 10^{-7}$        |
| hydrosulfuric acid          | $\text{H}_2\text{S} (aq)$                         | $\text{HS}^- (aq)$                                | $1.0 \times 10^{-7}$        |
| hydrogen sulfite ion        | $\text{HSO}_3^- (aq)$                             | $\text{SO}_3^{2-} (aq)$                           | $1.0 \times 10^{-7}$        |
| dihydrogen arsenate ion     | $\text{H}_2\text{AsO}_4^- (aq)$                   | $\text{HAsO}_4^{2-} (aq)$                         | $8 \times 10^{-8}$          |
| dihydrogen phosphate ion    | $\text{H}_2\text{PO}_4^- (aq)$                    | $\text{HPO}_4^{2-} (aq)$                          | $6.2 \times 10^{-8}$        |
| hypochlorous acid           | $\text{HOCl} (aq)$                                | $\text{OCl}^- (aq)$                               | $3.5 \times 10^{-8}$        |
| hypobromous acid            | $\text{HOBr} (aq)$                                | $\text{OBr}^- (aq)$                               | $2 \times 10^{-9}$          |
| hydrocyanic acid            | $\text{HCN} (aq)$                                 | $\text{CN}^- (aq)$                                | $6.2 \times 10^{-10}$       |
| hydrogen arsenate ion       | $\text{HAsO}_4^{2-} (aq)$                         | $\text{AsO}_4^{3-} (aq)$                          | $6 \times 10^{-10}$         |
| boric acid                  | $\text{H}_3\text{BO}_3 (aq)$                      | $\text{H}_2\text{BO}_3^- (aq)$                    | $5.8 \times 10^{-10}$       |
| ammonium ion                | $\text{NH}_4^+ (aq)$                              | $\text{NH}_3 (aq)$                                | $5.6 \times 10^{-10}$       |
| phenol                      | $\text{C}_6\text{H}_5\text{OH} (aq)$              | $\text{C}_6\text{H}_5\text{O}^- (aq)$             | $1.6 \times 10^{-10}$       |
| hydrogen carbonate ion      | $\text{HCO}_3^- (aq)$                             | $\text{CO}_3^{2-} (aq)$                           | $5.6 \times 10^{-11}$       |
| hypoiodous acid             | $\text{HOI} (aq)$                                 | $\text{OI}^- (aq)$                                | $2 \times 10^{-11}$         |
| hydrogen ascorbate ion      | $\text{HC}_6\text{H}_6\text{O}_6^- (aq)$          | $\text{C}_6\text{H}_6\text{O}_6^{2-} (aq)$        | $1.6 \times 10^{-12}$       |
| hydrogen phosphate ion      | $\text{HPO}_4^{2-} (aq)$                          | $\text{PO}_4^{3-} (aq)$                           | $4.8 \times 10^{-13}$       |
| water (55.49 mol/L)         | $\text{H}_2\text{O} (l)$                          | $\text{OH}^- (aq)$                                | $1.0 \times 10^{-14} = K_w$ |
| hydrogen sulfide ion        | $\text{HS}^- (aq)$                                | $\text{S}^{2-} (aq)$                              | $\sim 10^{-19}$             |

Increasing Acid Strength

Increasing Base Strength

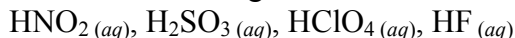


**Check out Strong and Weak Acids Animations at**  
<http://www.sgc.peachnet.edu/users/larnold/WWW/courses/1212/rev1212.html>

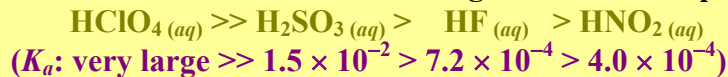
### Relative Strength of Acids and Conjugate Bases:

1. The **stronger the acid** (the bigger the value of  $K_a$ ), the **weaker its conjugate base**.
2. The **weaker the acid** (the smaller the value of  $K_a$ ), the **stronger its conjugate base**.

**Example 2:** Order the following acids from the strongest to the weakest.



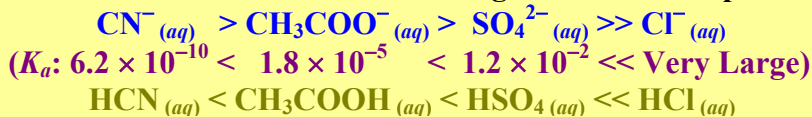
According to the Acid and Bases Relative Strength Table on the previous page:



**Example 3:** Order the following conjugate base from the strongest to the weakest.

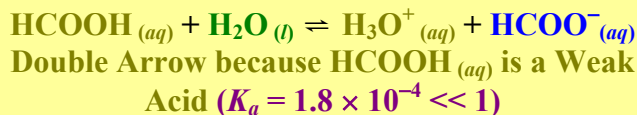
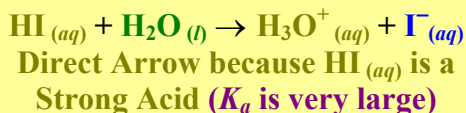


According to the Acids and Bases Relative Strength Table on the previous page:

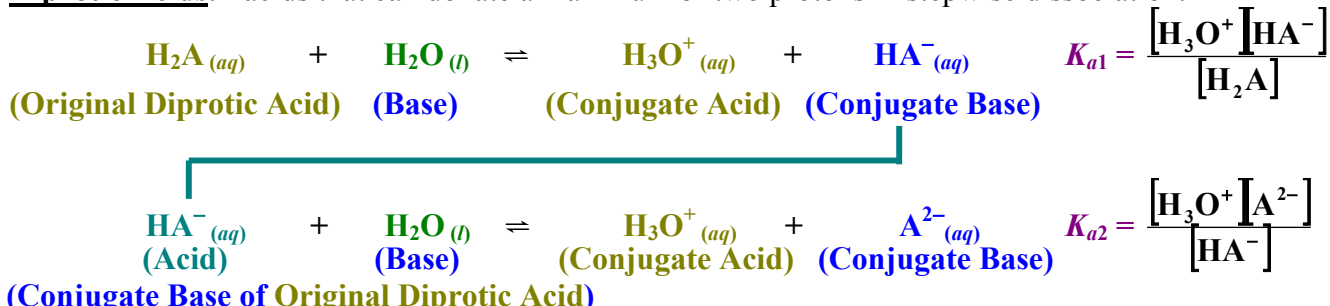


**Monoprotic Acids:** - acids that can donate a maximum of one proton.

**Example 3:** Write the dissociation reaction for the following monoprotic acids.

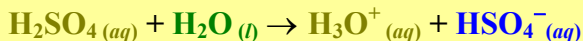


**Diprotic Acids:** - acids that can donate a maximum of two protons in stepwise dissociation.

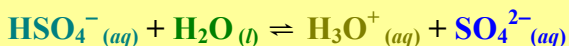


**Example 4:** Write the stepwise dissociation reaction for the following diprotic acids.

a.  $\text{H}_2\text{SO}_4(aq)$

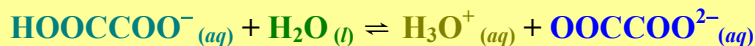
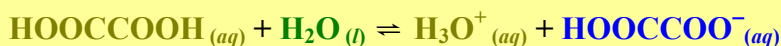


Direct Arrow because  $\text{H}_2\text{SO}_4(aq)$  is a Strong Acid ( $K_{a1}$  is very large)



Double Arrow because  $\text{HCOOH}(aq)$  is a Weak Acid ( $K_{a2} = 1.2 \times 10^{-2} \ll 1$ )

b.  $\text{HOOC}\text{COOH}(aq)$



Double Arrow because both  $\text{HOOC}\text{COOH}(aq)$  and  $\text{HOOC}\text{COO}^-$  are Weak Acids ( $K_{a1}$  and  $K_{a2} \ll 1$ )

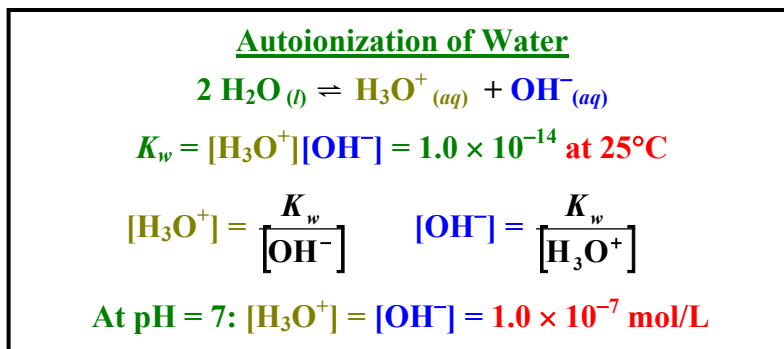
**Amphoteric Substances:** - chemical species that can be an acid or a base.

- all intermediate species of a diprotic acid is an amphoteric substance.

**Examples:** Some Amphoteric Substances:  $\text{HOOC}\text{COO}^-(aq)$ ,  $\text{HSO}_4^-(aq)$ ,  $\text{HSO}_3^-(aq)$ ,  $\text{HCO}_3^-(aq)$ ,  $\text{HS}^-(aq)$ ,  $\text{HC}_6\text{H}_6\text{O}_6^-(aq)$ , and  $\text{H}_2\text{O}(l)$

**Autoionization of Water:** - the process where water dissociates into hydronium and hydroxide ions.

- water's dissociation constant is called ion-product constant ( $K_w = 1.0 \times 10^{-14}$ )  
 - when the solution is neutral (pH = 7),  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol/L}$

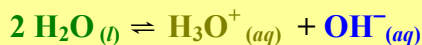


**Example 5:** At  $25^\circ\text{C}$ ,  $K_w = 1.0 \times 10^{-14}$ .

a. Using the ICE box, show that  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol/L}$  for a neutral solution.

b. At  $100^\circ\text{C}$ ,  $K_w = 8.19 \times 10^{-13}$ . What is the  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  for a neutral solution at  $100^\circ\text{C}$ ?

a.



|             | $\text{H}_2\text{O}(l)$ |  | $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$ |
|-------------|-------------------------|--|--------------------------|-----------------|
| Initial     | ----                    |  | 0                        | 0               |
| Change      | ----                    |  | +x                       | +x              |
| Equilibrium | -----                   |  | x                        | x               |

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

$$1.0 \times 10^{-14} = (x)(x)$$

$$x^2 = \sqrt{1.0 \times 10^{-14}}$$

$$x = 1.0 \times 10^{-7}$$

$$x = [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

b. At  $100^\circ\text{C}$ , using  $K_w = 8.19 \times 10^{-13}$

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

$$8.19 \times 10^{-13} = (x)(x)$$

$$x^2 = \sqrt{8.19 \times 10^{-13}}$$

$$x = 2.86 \times 10^{-7}$$

$$x = [\text{H}_3\text{O}^+] = [\text{OH}^-] = 2.86 \times 10^{-7} \text{ M}$$

**Example 6:** Determine the  $[\text{H}_3\text{O}^+]$  and/or  $[\text{OH}^-]$  concentrations of the following solutions at  $25^\circ\text{C}$ .

a.  $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ mol/L}$

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}}$$

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-10} \text{ mol/L}$$

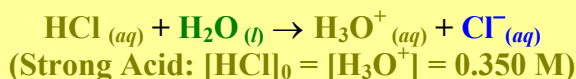
b.  $[\text{H}_3\text{O}^+] = 5.0 \times 10^{-5} \text{ M}$

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

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-5}}$$

$$[\text{OH}^-] = 2.0 \times 10^{-10} \text{ M}$$

c.  $[\text{HCl}] = 0.350 \text{ mol/L}$

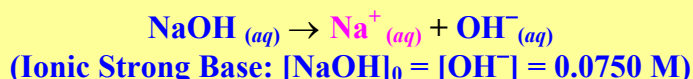


$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.350}$$

$$[\text{OH}^-] = 2.86 \times 10^{-14} \text{ mol/L}$$

d.  $[\text{NaOH}] = 0.0750 \text{ M}$



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

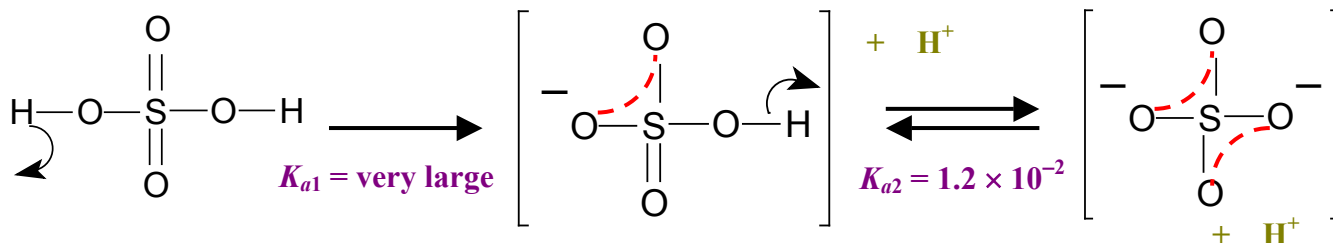
$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0750}$$

$$[\text{H}_3\text{O}^+] = 1.33 \times 10^{-13} \text{ mol/L}$$

**Oxyacids:** - acids where the donating proton is attached to an oxygen atom.

- most acids are oxyacids because of the strong electronegativity of the oxygen atom, the hydrogen atom is more readily to leave as  $\text{H}^+$  ion.

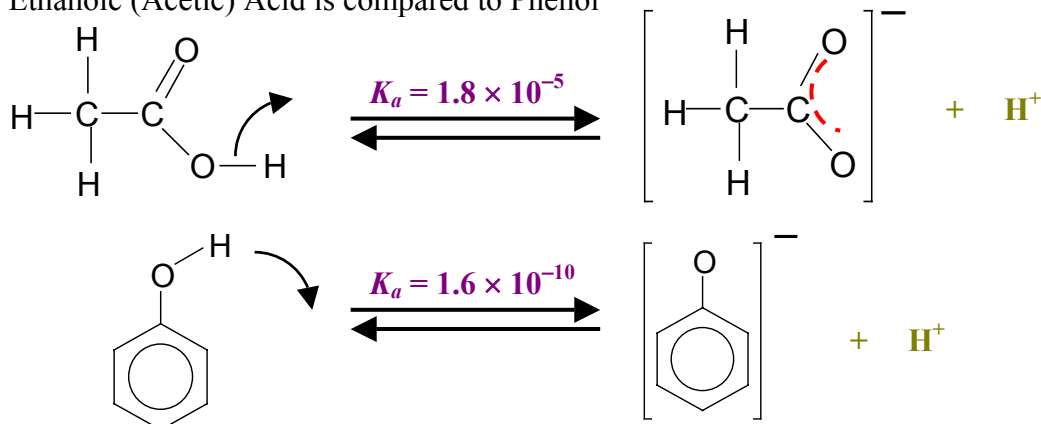
**Example:** Sulfuric Acid ( $\text{H}_2\text{SO}_4_{(aq)}$ ), successively donate protons to finally reach  $\text{SO}_4^{2-}_{(aq)}$



**Organic Acids:** - acids of organic compounds, commonly known as carboxylic acids.

- alcohols can also be considered as organic acids, but they are really weak. This is because carboxylic acids have double-bonded oxygen for resonance to occur, whereas alcohols only contain single-bonded oxygen.

**Example:** Ethanoic (Acetic) Acid is compared to Phenol

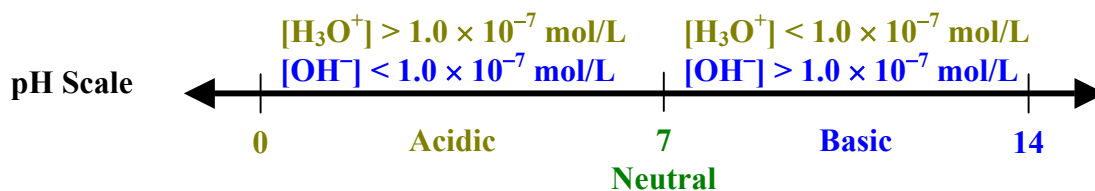




**14.3: The pH Scale**

**pH Scale:** - a logarithmic scale to **measure the acidity (relative  $[\text{H}_3\text{O}^+]$ )** of a solution.

- the **lower the pH, the more acidic** (less basic) is the solution (**more  $[\text{H}_3\text{O}^+]$  and less  $[\text{OH}^-]$** ).
- the **higher the pH, the more basic** (less acidic) is the solution (**less  $[\text{H}_3\text{O}^+]$  and more  $[\text{OH}^-]$** ).
- **acidity is NOT the same as the acid strength**. Just because a solution has a low pH, it does not mean that it is a strong acid. (**Highly Acidic  $\neq$  Strong Acid**)
- it is normally reported between 0 to 14 (**with 7 as neutral**), but it **can be above 14 (very basic) or below 0 (very acidic)**.
- **an increase of 1 on a pH scale means a decrease of  $[\text{H}_3\text{O}^+]$  by a factor of 10; an increase of 2 on a pH scale means a decrease of  $[\text{H}_3\text{O}^+]$  by a factor of 100.**

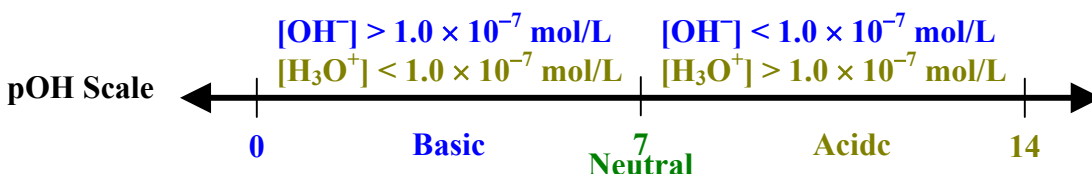


**Example:** pH of Some Common Substances

| Substance    | pH   | Substance  | pH   | Substance                               | pH    |
|--------------|------|------------|------|---|-------|
| 1 M of HCl   | 0.00 | Milk       | 6.30 | 1 M of Baking Soda ( $\text{NaHCO}_3$ ) | 9.68  |
| Stomach Acid | 2.00 | Rain Water | 6.70 | Ammonia as Household Cleaner            | 12.00 |
| Lemon Juice  | 2.50 | Pure Water | 7.00 | 1 M of NaOH                             | 14.00 |
| Vinegar      | 3.00 | Blood      | 7.50 |   |       |

**pOH Scale:** - a logarithmic scale to **measure the basicity (relative  $[\text{OH}^-]$ )** of a solution.

- the **lower the pOH, the more basic** (less acidic) is the solution (**more  $[\text{OH}^-]$  and less  $[\text{H}_3\text{O}^+]$** ).
- the **higher the pOH, the less basic** (more acidic) is the solution (**less  $[\text{OH}^-]$  and more  $[\text{H}_3\text{O}^+]$** ).
- **basicity is NOT the same as the base strength**. Just because a solution has a low pOH, it does not mean that it is a strong base. (**Highly Basic  $\neq$  Strong Base**)
- it is normally reported between 0 to 14 (**with 7 as neutral**), but it **can be above 14 (very acidic) or below 0 (very basic)**.
- **an increase of 1 on a pOH scale means a decrease of  $[\text{OH}^-]$  by a factor of 10; an increase of 2 on a pOH scale means a decrease of  $[\text{OH}^-]$  by a factor of 100.**



**pH and pOH Scales**

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

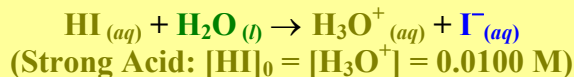
$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14.00$$



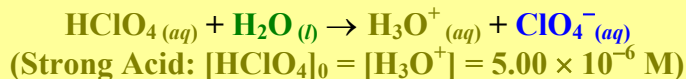
**Example 1:** Calculate the pH and the pOH for the following solutions.

a. 0.0100 mol/L of HI<sub>(aq)</sub>



$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] & \text{pOH} &= 14 - \text{pH} \\ \text{pH} &= -\log(0.0100) & \text{pOH} &= 14 - 2.00 \\ \text{pH} &= \mathbf{2.00} & \text{pOH} &= \mathbf{12.00} \end{aligned}$$

b.  $5.00 \times 10^{-6} \text{ M}$  of HClO<sub>4(aq)</sub>



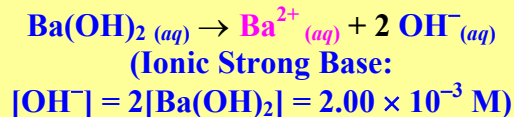
$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] & \text{pOH} &= 14 - \text{pH} \\ \text{pH} &= -\log(5.00 \times 10^{-6}) & \text{pOH} &= 14 - 5.30 \\ \text{pH} &= \mathbf{5.30} & \text{pOH} &= \mathbf{8.70} \end{aligned}$$

c. 1.50 M of KOH<sub>(aq)</sub>



$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] & \text{pH} &= 14 - \text{pOH} \\ \text{pOH} &= -\log(1.50) & \text{pH} &= 14 - (-0.176) \\ \text{pOH} &= \mathbf{-0.176} & \text{pH} &= \mathbf{14.176} \end{aligned}$$

d.  $1.00 \times 10^{-3} \text{ mol/L}$  of Ba(OH)<sub>2(aq)</sub>



$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] & \text{pH} &= 14 - \text{pOH} \\ \text{pOH} &= -\log(2.00 \times 10^{-3}) & \text{pH} &= 14 - (2.70) \\ \text{pOH} &= \mathbf{2.70} & \text{pH} &= \mathbf{11.30} \end{aligned}$$

**Example 2:** Calculate the  $[\text{H}_3\text{O}^+]$  and the  $[\text{OH}^-]$  for the following solutions.

a. pH = 4.00

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-4.00} \\ [\text{H}_3\text{O}^+] &= \mathbf{1.00 \times 10^{-4} \text{ M}} \end{aligned}$$

$$\begin{aligned} \text{pOH} &= 14 - \text{pH} \\ \text{pOH} &= 14 - 4.00 = 10.00 \end{aligned}$$

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ [\text{OH}^-] &= 10^{-\text{pOH}} = 10^{-10.00} \\ [\text{OH}^-] &= \mathbf{1.00 \times 10^{-10} \text{ M}} \end{aligned}$$

b. pOH = 3.00

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ [\text{OH}^-] &= 10^{-\text{pOH}} = 10^{-3.00} \\ [\text{OH}^-] &= \mathbf{1.00 \times 10^{-3} \text{ M}} \end{aligned}$$

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \\ \text{pH} &= 14 - 3 = 11.00 \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-11.00} \\ [\text{H}_3\text{O}^+] &= \mathbf{1.00 \times 10^{-11} \text{ M}} \end{aligned}$$

c. pH = 12.83

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-12.83} \\ [\text{H}_3\text{O}^+] &= \mathbf{1.48 \times 10^{-13} \text{ M}} \end{aligned}$$

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ [\text{OH}^-] &= \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.48 \times 10^{-13}} \end{aligned}$$

$$[\text{OH}^-] = \mathbf{0.0676 \text{ M}}$$

d. pOH = 9.67

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ [\text{OH}^-] &= 10^{-\text{pOH}} = 10^{-9.67} \\ [\text{OH}^-] &= \mathbf{2.14 \times 10^{-10} \text{ M}} \end{aligned}$$

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ [\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.14 \times 10^{-10}} \\ [\text{H}_3\text{O}^+] &= \mathbf{4.68 \times 10^{-5} \text{ mol/L}} \end{aligned}$$

### Assignment

14.1 pg. 704 #29 to 32

14.2 pg. 704–705 #32 to 38

14.3 pg. 705 #39 to 46

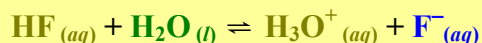


**Example 1:** Determine the  $[\text{H}_3\text{O}^+]$ , and pH of 0.200 mol/L of  $\text{HF}_{(aq)}$  ( $K_a = 7.2 \times 10^{-4}$ ).

**Major Species:**  $\text{HF}_{(aq)}$ ,  $\text{H}_2\text{O}_{(l)}$

**Strongest Acid:**  $\text{HF}$  ( $K_a = 7.2 \times 10^{-4}$ ) ( $K_a$  for  $\text{H}_2\text{O}$  is  $1.0 \times 10^{-14}$ )

**HF is a weak acid and undergoes Brønsted-Lowry Dissociation.**



|                    | [HF]      | [H <sub>3</sub> O <sup>+</sup> ] | [F <sup>-</sup> ] |
|--------------------|-----------|----------------------------------|-------------------|
| <b>Initial</b>     | 0.200 M   | 0                                | 0                 |
| <b>Change</b>      | -x        | +x                               | +x                |
| <b>Equilibrium</b> | (0.2 - x) | x                                | x                 |

**CANNOT use Approximation:**

$$\frac{[\text{HF}]_0}{K_a} = \frac{0.200 \text{ M}}{7.2 \times 10^{-4}} = 277.8 < 1000$$

Have to use (0.2 - x) in the denominator

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \quad 7.2 \times 10^{-4} = \frac{(x)(x)}{(0.2-x)} = \frac{x^2}{(0.2-x)}$$

$$7.2 \times 10^{-4} (0.2 - x) = x^2$$

$$(1.44 \times 10^{-4}) - (7.2 \times 10^{-4})x = x^2$$

$$x^2 + (7.2 \times 10^{-4})x - (1.44 \times 10^{-4}) = 0$$

(Quadratic Equation: Apply the Quadratic Formula!)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 1 \quad b = 7.2 \times 10^{-4} \quad c = -1.44 \times 10^{-4}$$

$$x = \frac{-(7.2 \times 10^{-4}) \pm \sqrt{(7.2 \times 10^{-4})^2 - 4(1)(-1.44 \times 10^{-4})}}{2(1)}$$

$$x = 0.0116453988 \quad x = -0.0247307976 \text{ (omit negative } x)$$

$$[\text{H}_3\text{O}^+] = 0.0116 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0116)$$

$$\text{pH} = 1.93$$

```
solve(X^2/(.2-X)-
7.2E-4,X,0,(0,0.
2))
.0116453988
```

OR

```
solve(X^2+7.2E-4X
-1.44E-4,X,0,(0,
0.2))
.0116453988
```

**Verify that we could NOT use Approximation:**

$$\frac{[\text{H}_3\text{O}^+]}{[\text{HF}]_0} \times 100\% = \frac{0.0116 \text{ M}}{0.200 \text{ M}} \times 100\% = 5.8\% > 5\%$$

Therefore, approximation would NOT be appropriate.

**Percent Dissociation:** - the amount of  $[\text{H}_3\text{O}^+]$  dissociated from the original  $[\text{HA}]_0$  expressed in percentage.  
 - strong acids will have % dissociation = 100%.  
 - weak acids will have % Dissociation < 100%

#### Percent Dissociation of Acids

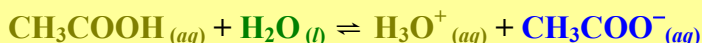
$$\% \text{ Dissociation} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_0} \times 100\%$$

**Example 2:** Determine the  $[\text{H}_3\text{O}^+]$  and pH of an acid mixture of 0.500 mol/L  $\text{HOBr}_{(aq)}$  ( $K_a = 2 \times 10^{-9}$ ) of 0.200 mol/L of  $\text{CH}_3\text{COOH}_{(aq)}$  ( $K_a = 1.8 \times 10^{-5}$ ). Calculate the percent dissociation of this acid mixture.

**Major Species:**  $\text{HOBr}_{(aq)}$ ,  $\text{CH}_3\text{COOH}_{(aq)}$ ,  $\text{H}_2\text{O}_{(l)}$

**Strongest Acid:**  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ) ( $K_a$  for  $\text{HOBr}$  and  $\text{H}_2\text{O}$  are  $2 \times 10^{-9}$  and  $1.0 \times 10^{-14}$ )

**HF is a weak acid and undergoes Brønsted-Lowry Dissociation.**



|                    | $[\text{CH}_3\text{COOH}]$ | $[\text{H}_3\text{O}^+]$ | $[\text{CH}_3\text{COO}^-]$ |
|--------------------|----------------------------|--------------------------|-----------------------------|
| <b>Initial</b>     | 0.200 M                    | 0                        | 0                           |
| <b>Change</b>      | -x                         | +x                       | +x                          |
| <b>Equilibrium</b> | (0.2 - x)                  | x                        | x                           |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.2-x)} \approx \frac{x^2}{(0.2)}$$

$$1.8 \times 10^{-5} (0.2) \approx x^2$$

$$3.6 \times 10^{-6} \approx x^2$$

$$x \approx \sqrt{3.6 \times 10^{-6}}$$

$$x \approx 0.00190$$

**Verify that we could use Approximation:**

$$\frac{[\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]_0} \times 100\% = \frac{0.00190 \text{ M}}{0.200 \text{ M}} \times 100\%$$

$$= 0.95\% \leq 5\%$$

**Therefore, approximation would be appropriate.**

**CAN use Approximation:**

$$\frac{[\text{CH}_3\text{COOH}]_0}{K_a} = \frac{0.200 \text{ M}}{1.8 \times 10^{-5}}$$

$$= 11111 \geq 1000$$

Use 0.2 in the denominator, because  $(0.2 - x) \approx 0.2$  [ $x$  is so small compared to 0.2 M]

$$[\text{H}_3\text{O}^+] = 0.00190 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.00190)$$

$$\text{pH} = 2.72$$

$$\% \text{ Dissociation} = \frac{[\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]_0} \times 100\%$$

$$\% \text{ Dissociation} = \frac{0.00190 \text{ M}}{0.200 \text{ M}} \times 100\%$$

$$\% \text{ Dissociation} = 0.95\%$$

**Example 3:** A 0.0500 mol/L of an unknown acid, HA, has a percent dissociation of 0.38%. What is the acid dissociation constant of this acid?

**Major Species:**  $\text{HA}_{(aq)}$ ,  $\text{H}_2\text{O}_{(l)}$

**Strongest Acid:**  $\text{HA}$  ( $K_a = ?$ ) ( $K_a$  for  $\text{H}_2\text{O}$  is  $1.0 \times 10^{-14}$  and has a 0.000 01 % dissociation)

**HA is a weak acid and undergoes Brønsted-Lowry Dissociation.**



|                    | $[\text{HA}]$         | $[\text{H}_3\text{O}^+]$ | $[\text{A}^-]$         |
|--------------------|-----------------------|--------------------------|------------------------|
| <b>Initial</b>     | 0.0500 M              | 0                        | 0                      |
| <b>Change</b>      | $-1.9 \times 10^{-4}$ | $+1.9 \times 10^{-4}$    | $1.9 \times 10^{-4}$   |
| <b>Equilibrium</b> | 0.04981 M             | $1.9 \times 10^{-4}$ M   | $1.9 \times 10^{-4}$ M |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(1.9 \times 10^{-4})(1.9 \times 10^{-4})}{(0.04981)}$$

$$\% \text{ Dissociation} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_0} \times 100\%$$

$$[\text{H}_3\text{O}^+] = (\% \text{Dissociation})[\text{HA}]_0 / 100\%$$

$$[\text{H}_3\text{O}^+] = (0.38\%)(0.0500 \text{ M}) / 100\%$$

$$[\text{H}_3\text{O}^+] = 1.9 \times 10^{-4} \text{ M} = [\text{A}^-]$$

$$K_a = 7.2 \times 10^{-7}$$

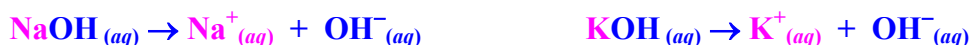
**14.6: Bases**

**Strong Bases:** - bases that dissociate completely (100%) in water.

- all alkali bases (Group IA cations with OH<sup>-</sup>) and some alkaline bases (Group IIA cations with OH<sup>-</sup>) are considered as strong bases because they are ionic compound that dissociates completely.

**Examples:** Strong Ionic Bases:

- a. Alkali Bases: LiOH<sub>(aq)</sub>, NaOH<sub>(aq)</sub>, KOH<sub>(aq)</sub>, RbOH<sub>(aq)</sub>, and CsOH<sub>(aq)</sub>  
(gives off 1 mole of OH<sup>-</sup> when 1 mole of alkali base is dissolved)



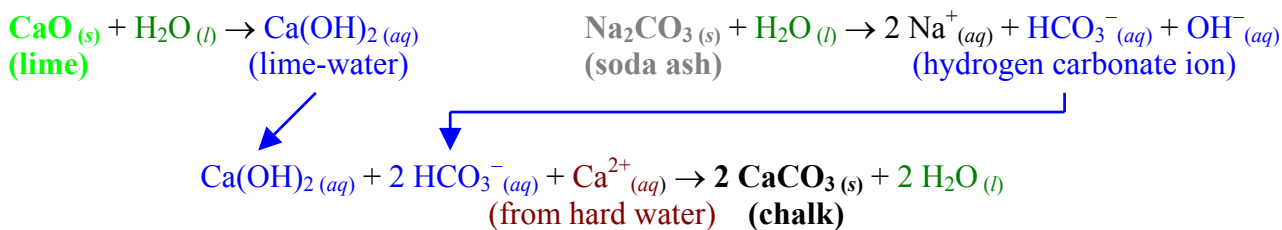
- b. Alkaline Bases: Ca(OH)<sub>2(aq)</sub>, Ba(OH)<sub>2(aq)</sub>, Sr(OH)<sub>2(aq)</sub>  
(gives off 2 moles of OH<sup>-</sup> when 1 mole of alkaline base is dissolved)



**Slaked Lime:** - calcium hydroxide, Ca(OH)<sub>2(s)</sub>; commonly refer to as lime-water when it is dissolved as Ca(OH)<sub>2(aq)</sub>

- in reality, slaked lime do not dissolve that well in water. Its **dissociation constant (solubility product – K<sub>sp</sub>) is 1.3 × 10<sup>-6</sup>** (more on K<sub>sp</sub> in the next chapter). However, it is readily available and as such, it makes good bases in common laboratories.

**Lime-Soda Process:** - a process where lime (CaO) and soda ash (Na<sub>2</sub>CO<sub>3</sub>) are added to water in order to produce chalk (CaCO<sub>3</sub>).



**Major Species of a Strong Base:** - as alkali- and alkaline bases dissociate completely in water, the major species of all strong bases are OH<sup>-</sup> and water.

- special care must be taken with alkaline bases as they generate 2 moles of OH<sup>-</sup> per 1 mole of solid dissolved.



**Example 1:** List the major species  $\text{NaOH}_{(aq)}$ , and calculate its pH, pOH,  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  if it has a concentration of  $1.00 \times 10^{-4} \text{ M}$ .

$$\text{NaOH}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$$

Since NaOH is a strong base, the major species are:  $\text{OH}^-_{(aq)}$  and  $\text{H}_2\text{O}_{(l)}$ .

$$[\text{OH}^-] = [\text{NaOH}]_0 = 1.00 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log (1.00 \times 10^{-4})$$

$$\text{pOH} = 4.00$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - (4.00)$$

$$\text{pH} = 10.00$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10.00}$$

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-10} \text{ M}$$

**Example 2:** List the major species  $\text{Sr}(\text{OH})_2_{(aq)}$ , and calculate its pH, pOH,  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  if it has a concentration of  $1.00 \times 10^{-4} \text{ M}$ .

$$\text{Sr}(\text{OH})_2_{(aq)} \rightarrow \text{Sr}^{2+}_{(aq)} + 2 \text{OH}^-_{(aq)}$$

Since NaOH is a strong base, the major species are:  $\text{OH}^-_{(aq)}$  and  $\text{H}_2\text{O}_{(l)}$ .

$$[\text{OH}^-] = 2 \times [\text{NaOH}]_0 = 2.00 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log (2.00 \times 10^{-4})$$

$$\text{pOH} = 3.70$$

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.00 \times 10^{-4}}$$

$$[\text{H}_3\text{O}^+] = 5.00 \times 10^{-11} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log (5.00 \times 10^{-11})$$

$$\text{pH} = 10.3$$

**Weak Bases:** - bases that dissociate LESS than 100% in water.

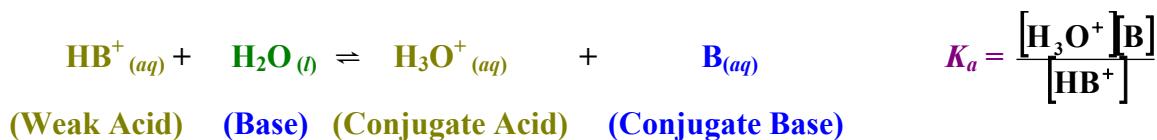
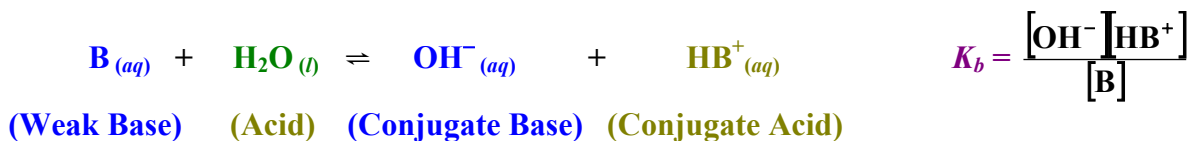
- when the base dissociation constant ( $K_b$ ) is less than 1, ( $K_b < 1$ )
- the equilibrium position strongly favours the reactants.
- at equilibrium, the hydroxide concentration is much less than the original base concentration,  $[\text{OH}^-]_{eq} < [\text{B}]_{eq}$  or  $[\text{B}]_0 \approx [\text{B}]_{eq}$ .
- the conjugate acid,  $\text{HA}^+$ , of a weak base is itself a stronger weak acid (can easily donate protons to do the reverse reaction).



|             | [B]                     |  | $[\text{OH}^-]$ | $[\text{HB}^+]$ |
|-------------|-------------------------|--|-----------------|-----------------|
| Initial     | $x$                     |  | 0               | 0               |
| Change      | $-y$ (where $y \ll x$ ) |  | $+y$            | $+y$            |
| Equilibrium | $(x - y) \approx x$     |  | $y$             | $y$             |

**Examples:** Some Weak Bases:  $\text{HOOC}^-(\text{aq})$ ,  $\text{HSO}_3^-(\text{aq})$ ,  $\text{HSO}_4^-(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\text{NO}_2^-(\text{aq})$ ,  $\text{HCO}_3^-(\text{aq})$ ,  $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-(\text{aq})$ ,  $\text{F}^-(\text{aq})$ ,  $\text{HCOO}^-(\text{aq})$ ,  $\text{C}_6\text{H}_7\text{O}_6^-(\text{aq})$ ,  $\text{C}_6\text{H}_5\text{COO}^-(\text{aq})$ ,  $\text{CO}_3^{2-}(\text{aq})$ ,  $\text{CH}_3\text{COO}^-(\text{aq})$ ,  $\text{HS}^-(\text{aq})$ ,  $\text{OCI}^-(\text{aq})$ ,  $\text{CN}^-(\text{aq})$ ,  $\text{NH}_3(\text{aq})$ , and  $\text{NO}_3^-(\text{aq})$

**Base Dissociation Constant ( $K_b$ ):** - the equilibrium constant of a dissociation of a weak base in water.  
-  $K_b$  of a weak base can be calculated from  $K_a$  of its conjugate acid and  $K_w$ .



$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{B}]}{[\text{HB}^+]} \times \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

**Relationship between Conjugate Acid-Base Pair Dissociation Constants**

$$K_w = K_a \times K_b$$

**Major Species of a Weak Base:** - since weak acid do not dissociate completely ( $K_b < 1$ ) in water, the major species of all weak bases are their original form and water.

**Procedure to calculate pH of Weak Base Solutions:**

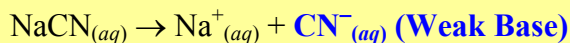
- List all the major species from all weak bases, including water.
- Calculate  $K_b$  from all weak bases using  $K_w = K_a \times K_b$
- Determine which species has the highest  $K_b$ . This is the Strongest Base (SB) of the list.
- Write the Brønsted-Lowry dissociation of this Strongest Base
- Set up the **ICE Box** and the **equilibrium expression**.
- If the original weak base concentration,  $[\text{B}]_0$ , is much larger than  $K_b$ , we can approximate by assuming  $[\text{B}]_{\text{eq}} = ([\text{B}]_0 - x) \approx [\text{B}]_0$ . Thereby, simplifying the calculation. (**A general rule of thumb: if  $[\text{B}]_0 \geq 1000 \times K_b$ , we can use the approximation.**)
- Find the concentration of  $\text{OH}^-$ .
- Verify any approximation made by using the 5% rule.

$$\left( \frac{[\text{OH}^-]}{[\text{B}]_0} \times 100\% \leq 5\% \right)$$



**Example 3:** Determine the  $[\text{OH}^-]$ ,  $[\text{H}_3\text{O}^+]$ , pOH, pH and % dissociation of 0.200 mol/L of  $\text{NaCN}_{(aq)}$ . ( $K_a$  of  $\text{HCN} = 6.2 \times 10^{-10}$ ).

**NaCN dissociates completely in water:**



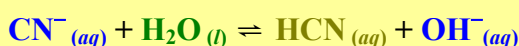
**Major Species:**  $\text{CN}^-_{(aq)}$ ,  $\text{H}_2\text{O}_{(l)}$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} \quad K_b = 1.613 \times 10^{-5}$$

(taking a few more decimal places to avoid round off errors)

**Strongest Base:**  $\text{CN}^-$  ( $K_b = 1.613 \times 10^{-5}$ ) ( $K_b$  for  $\text{H}_2\text{O}$  is  $K_w = 1.0 \times 10^{-14}$ )

$\text{CN}^-$  is a weak base and undergoes Brønsted-Lowry Dissociation.



|                    | $[\text{CN}^-]$  | $[\text{H}_3\text{O}^+]$ | $[\text{OH}^-]$ |
|--------------------|------------------|--------------------------|-----------------|
| <b>Initial</b>     | <b>0.200 M</b>   | <b>0</b>                 | <b>0</b>        |
| <b>Change</b>      | <b>-x</b>        | <b>+x</b>                | <b>+x</b>       |
| <b>Equilibrium</b> | <b>(0.2 - x)</b> | <b>x</b>                 | <b>x</b>        |

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \quad 1.613 \times 10^{-5} = \frac{(x)(x)}{(0.2-x)} \approx \frac{x^2}{(0.2)}$$

$$1.613 \times 10^{-5} (0.2) \approx x^2$$

$$3.226 \times 10^{-6} \approx x^2$$

$$x \approx \sqrt{3.226 \times 10^{-6}}$$

$$x \approx 0.0018$$

**CAN use Approximation:**

$$\frac{[\text{CN}^-]_0}{K_b} = \frac{0.200 \text{ M}}{1.613 \times 10^{-5}}$$

$$= 12399 \geq 1000$$

Use 0.2 in the denominator, because  $(0.2 - x) \approx 0.2$  [ $x$  is so small compared to 0.2 M]

$$[\text{OH}^-] = 0.0018 \text{ mol/L} = 1.8 \text{ mmol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(0.0018)$$

$$\text{pOH} = 2.75$$

$$\% \text{ Dissociation} = \frac{[\text{OH}^-]}{[\text{CN}^-]_0} \times 100\%$$

$$\% \text{ Dissociation} = \frac{0.0018 \text{ M}}{0.200 \text{ M}} \times 100\%$$

$$\% \text{ Dissociation} = 0.90\%$$

Verify that we could use Approximation:

$$\frac{[\text{OH}^-]}{[\text{CN}^-]_0} \times 100\% = \frac{0.0018 \text{ M}}{0.200 \text{ M}} \times 100\%$$

$$= 0.90\% \leq 5\%$$

Therefore, approximation would be appropriate.

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - (2.75)$$

$$\text{pH} = 11.25$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-11.25}$$

$$[\text{H}_3\text{O}^+] = 5.6 \times 10^{-12} \text{ M}$$

### Assignment

14.4 pg. 705 #47 to 52

14.5 pg. 705–706 #53 to 70

14.6 pg. 706–707 #71 to 92

### 14.7: Polyprotic Acids

**Polyprotic Acids:** - acids that can donate more than one protons.

- this includes all diprotic and **triprotic acids** (acids that can **donate three protons**).
- **polyprotic acids dissociate one proton at a time**. Each successive proton donation has its own  $K_a$ , which gets smaller until the last proton is donated. ( $K_{a1} > K_{a2} > K_{a3} > \dots$ ).
- the **intermediates (conjugate bases of each dissociation except the last one) are themselves acids**. Thus, *diprotic acid can generate one amphoteric species*, and *triprotic acid can generate two amphoteric species*.
- **except for sulfuric acid (because  $K_{a1}$  is very large and  $K_{a2}$  is small), all polyprotic acids'  $[\text{H}_3\text{O}^+]$  are calculated from their  $K_{a1}$**  because successive proton donation from smaller subsequent  $K_a$  do not amount to any significant increase in the  $[\text{H}_3\text{O}^+]$ .

**Examples:** Some Polyprotic Acids:

a. Diprotic Acids:  $\text{H}_2\text{SO}_4(aq)$ ,  $\text{HOOC}\text{COOH}(aq)$ ,  $\text{H}_2\text{SO}_3(aq)$ ,  $\text{H}_2\text{C}_6\text{H}_6\text{O}_6(aq)$ ,  $\text{H}_2\text{CO}_3(aq)$ ,  $\text{H}_2\text{S}(aq)$

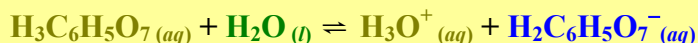
Diprotic Amphoteric Intermediates:  $\text{HSO}_4^-(aq)$ ,  $\text{HOOC}\text{COO}^-(aq)$ ,  $\text{HSO}_3^-(aq)$ ,  $\text{HC}_6\text{H}_6\text{O}_6^-(aq)$ ,  
 $\text{HCO}_3^-(aq)$ ,  $\text{HS}^-(aq)$

b. Triprotic Acids:  $\text{H}_3\text{PO}_4(aq)$ ,  $\text{H}_3\text{AsO}_4(aq)$ ,  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq)$ ,  $\text{H}_3\text{BO}_3(aq)$

Triprotic Amphoteric Intermediates:  $\text{H}_2\text{PO}_4^-(aq)$ ,  $\text{HPO}_4^{2-}(aq)$ ,  $\text{H}_2\text{AsO}_4^-(aq)$ ,  $\text{HASO}_4^{2-}(aq)$ ,  
 $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-(aq)$ ,  $\text{HC}_6\text{H}_5\text{O}_7^{2-}(aq)$ ,  $\text{H}_2\text{BO}_3^-(aq)$ ,  $\text{HBO}_3^{2-}(aq)$

**Example 1:** Determine the pH of 2.00 M of citric acid ( $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq)$ ) and the concentrations of  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq)$ ,  $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-(aq)$ ,  $\text{HC}_6\text{H}_5\text{O}_7^{2-}(aq)$ , and  $\text{C}_6\text{H}_5\text{O}_7^{3-}(aq)$ . The acid dissociation constants are  $K_{a1} = 8.4 \times 10^{-4}$ ,  $K_{a2} = 1.8 \times 10^{-5}$ , and  $K_{a3} = 4.0 \times 10^{-6}$ .

**Major Species:**  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq)$ ,  $\text{H}_2\text{O}(l)$   
**Strongest Acid:**  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq)$  ( $K_{a1} = 8.4 \times 10^{-4}$ )  
 $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$  is a weak acid (Brønsted-Lowry Dissociation).



|                    | $[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]$ | $[\text{H}_3\text{O}^+]$ | $[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]$ |
|--------------------|--|--------------------------|--|
| <b>Initial</b>     | 2.00 M                                       | 0                        | 0  |
| <b>Change</b>      | -x   | +x                       | +x   |
| <b>Equilibrium</b> | (2-x)  | x                        | x  |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]}{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]}$$

$$8.4 \times 10^{-4} = \frac{(x)(x)}{(2-x)} \approx \frac{x^2}{2}$$

$$8.4 \times 10^{-4} (2) \approx x^2$$

$$0.00168 \approx x^2$$

$$x \approx \sqrt{0.00168}$$

$$x \approx 0.0410$$

$$[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]_{eq} = 2.00 \text{ M} - 0.0410 \text{ M}$$

$$[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]_{eq} = 1.96 \text{ M}$$

**Verify that we could use Approximation:**

$$\frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]_0} \times 100\% = \frac{0.0410 \text{ M}}{2.00 \text{ M}} \times 100\%$$

$$= 2.05\% \leq 5\%$$

Therefore, approximation would be appropriate.

**CAN use Approximation:**

$$\frac{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]_0}{K_{a1}} = \frac{2.00 \text{ M}}{8.4 \times 10^{-4}}$$

$$= 2381 \geq 1000$$

Use 2 in the denominator, because  $(2-x) \approx 2$  [x is so small compared to 2.00 M]

$$[\text{H}_3\text{O}^+] = 0.0410 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0410)$$

$$\text{pH} = 1.39$$

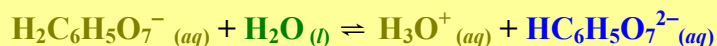
(after 1<sup>st</sup> proton donation)

Next, we have to calculate  $[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]$  after the first proton donation.

Major Species:  $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$  (aq),  $\text{H}_2\text{O}$  (l)

Strongest Acid:  $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$  (aq) ( $K_{a2} = 1.8 \times 10^{-5}$ )

$\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$  is a weak acid (Brønsted-Lowry Dissociation).



|             | $[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]$ | $[\text{H}_3\text{O}^+]$ | $[\text{HC}_6\text{H}_5\text{O}_7^{2-}]$ |
|-------------|--|--------------------------|--|
| Initial     | $x = 0.0410 \text{ M}$                         | $0.0410 \text{ M}$       | $0$                                      |
| Change      | $-y$   | $+y$                     | $+y$                                     |
| Equilibrium | $(0.041 - y)$                                  | $(0.041 + y)$            | $y$                                      |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HC}_6\text{H}_5\text{O}_7^{2-}]}{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]} \quad 1.8 \times 10^{-5} = \frac{(0.041 + y)(y)}{(0.041 - y)} \approx \frac{(0.041)y}{(0.041)}$$

Verify that we could use Approximation:

$$\frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]_0} \times 100\% = \frac{1.8 \times 10^{-5} \text{ M}}{0.0410 \text{ M}} \times 100\% = 0.44\% \leq 5\%$$

$$y \approx 1.8 \times 10^{-5}$$

Therefore, approximation would be appropriate.

$$\text{New } [\text{H}_3\text{O}^+] = 0.0410 \text{ M} + 1.8 \times 10^{-5} \text{ M}$$

$$\text{New pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.041018)$$

$$\text{New } [\text{H}_3\text{O}^+] = 0.041018 \text{ M}$$

$$\text{New pH} = 1.39 \text{ (after second proton donation)}$$

$$[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]_{eq} = 0.041 \text{ M} - 1.8 \times 10^{-5} \text{ M}$$

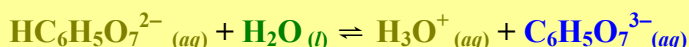
$$[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]_{eq} = 0.040982 \text{ M}$$

Finally, we have to calculate  $[\text{HC}_6\text{H}_5\text{O}_7^{2-}]$  and  $[\text{C}_6\text{H}_5\text{O}_7^{3-}]$  after the last proton donation.

Major Species:  $\text{HC}_6\text{H}_5\text{O}_7^{2-}$  (aq),  $\text{H}_2\text{O}$  (l)

Strongest Acid:  $\text{HC}_6\text{H}_5\text{O}_7^{2-}$  (aq) ( $K_{a3} = 4.0 \times 10^{-6}$ )

$\text{HC}_6\text{H}_5\text{O}_7^{2-}$  is a weak acid (Brønsted-Lowry Dissociation).



|             | $[\text{HC}_6\text{H}_5\text{O}_7^{2-}]$ | $[\text{H}_3\text{O}^+]$ | $[\text{C}_6\text{H}_5\text{O}_7^{3-}]$ |
|-------------|--|--------------------------|---|
| Initial     | $y = 1.8 \times 10^{-5} \text{ M}$       | $0.041018 \text{ M}$     | $0$                                     |
| Change      | $-z$                                     | $+z$                     | $+z$                                    |
| Equilibrium | $(1.8 \times 10^{-5} - z)$               | $(0.041018 + z)$         | $z$                                     |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}_7^{3-}]}{[\text{HC}_6\text{H}_5\text{O}_7^{2-}]} \quad 4.0 \times 10^{-6} = \frac{(0.041018 + z)(z)}{(1.8 \times 10^{-5} - z)}$$

$$0 = \frac{(0.041018 + z)(z)}{(1.8 \times 10^{-5} - z)} - 4.0 \times 10^{-6} \quad z = 1.76 \times 10^{-9}$$

$$\text{Final } [\text{H}_3\text{O}^+] = 0.041018 \text{ M} + 1.76 \times 10^{-9} \text{ M}$$

$$\text{Final pH} = -\log [\text{H}_3\text{O}^+] = -\log(0.0410180018)$$

$$\text{Final } [\text{H}_3\text{O}^+] = 0.0410180018 \text{ M}$$

$$\text{Final pH} = 1.39$$

(no change from the pH at  $K_{a1}$ )

$$[\text{HC}_6\text{H}_5\text{O}_7^{2-}]_{eq} = 1.8 \times 10^{-5} \text{ M} - 1.76 \times 10^{-9} \text{ M}$$

$$[\text{HC}_6\text{H}_5\text{O}_7^{2-}]_{eq} = 1.80 \times 10^{-5} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{O}_7^{3-}]_{eq} = 1.76 \times 10^{-9} \text{ M}$$

CAN use Approximation:

$$\frac{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]}{K_{a2}} = \frac{0.0410 \text{ M}}{1.8 \times 10^{-5}} = 2278 \geq 1000$$

Use 0.041 in the denominator and numerator, because  $(0.041 - y) \approx (0.041 + y) \approx 0.041$  [y is so small compared to 0.041 M]

CANNOT use Approximation:

$$\frac{[\text{HC}_6\text{H}_5\text{O}_7^{2-}]_0}{K_{a3}} = \frac{1.8 \times 10^{-5} \text{ M}}{4.0 \times 10^{-6}} = 4.5 < 1000$$

```
solve((.041018+x)
*x/(1.8e-5-x)-4e-6, x, 0, 1.8e-5)
1.755155695e-9
```

**Example 2:** Determine the pH of 0.0500 M of sulfuric acid ( $\text{H}_2\text{SO}_4(aq)$ ) and the concentrations of  $\text{HSO}_4^-(aq)$ , and  $\text{SO}_4^{2-}(aq)$ . The acid dissociation constant is  $K_{a2} = 1.2 \times 10^{-2}$ .



Since  $\text{H}_2\text{SO}_4$  is a strong acid, the major species are:  $\text{H}_3\text{O}^+(aq)$ ,  $\text{HSO}_4^-(aq)$  and  $\text{H}_2\text{O}(l)$ .

$$[\text{H}_3\text{O}^+] = [\text{H}_2\text{SO}_4]_0 = 0.0500 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log (0.0500)$$

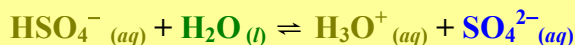
$$\text{pH} = 1.30 \text{ (after } K_{a1}\text{)}$$

Next, we have to calculate  $[\text{HSO}_4^-]$ ,  $[\text{SO}_4^{2-}]$  and the final pH after the last proton donation.

Major Species:  $\text{HSO}_4^-(aq)$ ,  $\text{H}_2\text{O}(l)$

Strongest Acid:  $\text{HSO}_4^-(aq)$  ( $K_{a2} = 1.2 \times 10^{-2}$ )

$\text{HSO}_4^-$  is a weak acid (Brønsted-Lowry Dissociation).



|             | $[\text{HSO}_4^-]$ | $[\text{H}_3\text{O}^+]$ | $[\text{SO}_4^{2-}]$ |
|-------------|--------------------|--------------------------|----------------------|
| Initial     | 0.0500 M           | 0.0500 M                 | 0                    |
| Change      | -x                 | +x                       | +x                   |
| Equilibrium | (0.05 - x)         | (0.05 + x)               | x                    |

CANNOT use Approximation:

$$\frac{[\text{HSO}_4^-]_0}{K_{a2}} = \frac{0.0500 \text{ M}}{1.2 \times 10^{-2}} = 4.167 < 1000$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \quad 1.2 \times 10^{-2} = \frac{(0.05+x)(x)}{(0.05-x)}$$

$$0 = \frac{(0.05+x)(x)}{(0.05-x)} - 1.2 \times 10^{-2}$$

$$x = 0.00851$$

```
solve((0.05+X)*X/
(0.05-X)-1.2E-2,
X,0,(0.05))
.0085094925
```

Final  $[\text{H}_3\text{O}^+] = 0.0500 \text{ M}$  (from  $K_{a1}$ ) +  $0.00851 \text{ M}$  (from  $K_{a2}$ )

Final  $[\text{H}_3\text{O}^+] = 0.0585 \text{ M}$   
(a significant change from before)

$$[\text{HSO}_4^-]_{eq} = 0.0500 \text{ M} - 0.00851 \text{ M}$$

$$\text{Final pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0585)$$

$$[\text{HSO}_4^-]_{eq} = 0.0415 \text{ M}$$

$$[\text{SO}_4^{2-}]_{eq} = 0.00585 \text{ M}$$

Final pH = 1.23  
(different from 1.30 of the pH at  $K_{a1}$ )

From the last two examples, we can see that sulfuric acid ( $\text{H}_2\text{SO}_4(aq)$ ) requires the calculation of  $[\text{H}_3\text{O}^+]$  in both steps of the dissociation. Other polyprotic acids, such as  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq)$  only require the first dissociation step to calculate the  $[\text{H}_3\text{O}^+]$ .

**14.8: Acid-Base Properties of Salts**

**Salts:** - ionic compounds that might dissociate in water.

**Neutral Salts:** - when the **Cation comes from a Strong Base** and the **Anion is the Conjugate-Base of Strong Acid**.

- **no effect on pH; if dissolve in pure water, pH will remain at 7.**

**Examples:** Some Neutral Salts:

- $\text{KNO}_3 (aq)$  ( $\text{K}^+$  can be from a strong base –  $\text{KOH} (aq)$ ;  $\text{NO}_3^-$  is the conjugate-base of a strong acid –  $\text{HNO}_3 (aq)$ )
- $\text{NaCl} (aq)$  ( $\text{Na}^+$  can be from a strong base –  $\text{NaOH} (aq)$ ;  $\text{Cl}^-$  is the conjugate-base a strong acid –  $\text{HCl} (aq)$ )

**Basic Salts:** - when the **Cation comes from a Strong Base** and the **Anion is the Conjugate-Base of a Weak Acid**.

- **pH will increase; if dissolve in pure water, pH > 7 (Basic).**

**Examples:** Some Basic Salts:

- $\text{NaCH}_3\text{COO} (aq)$  ( $\text{Na}^+$  can be from a strong base –  $\text{NaOH} (aq)$ ;  $\text{CH}_3\text{COO}^-$  is the conjugate-base of a weak acid –  $\text{CH}_3\text{COOH} (aq)$ )
- $\text{KF} (aq)$  ( $\text{K}^+$  can be from a strong base –  $\text{KOH} (aq)$ ;  $\text{F}^-$  is the conjugate base of a weak acid –  $\text{HF} (aq)$ )

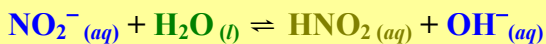
**Example 1:** Determine the pH of 0.235 M of sodium nitrite. The acid dissociation constant for nitrous acid is  $K_a = 4.0 \times 10^{-4}$ .

**Sodium nitrite ( $\text{NaNO}_2$ ) dissociates completely in  $\text{H}_2\text{O}$ :**  $\text{NaNO}_2 (s) \rightarrow \text{Na}^+ (aq) + \text{NO}_2^- (aq)$  (**Weak Base**)

**Major Species:**  $\text{NO}_2^- (aq)$ ,  $\text{H}_2\text{O} (l)$   $K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{4.0 \times 10^{-4}} \quad K_b = 2.5 \times 10^{-11}$

**Strongest Base:**  $\text{NO}_2^-$  ( $K_b = 2.5 \times 10^{-11}$ ) ( $K_b$  for  $\text{H}_2\text{O}$  is  $K_w = 1.0 \times 10^{-14}$ )

$\text{NO}_2^-$  is a weak base and undergoes Brønsted-Lowry Dissociation.



|                    | $[\text{NO}_2^-]$ | $[\text{HNO}_2]$ | $[\text{OH}^-]$ |
|--------------------|-------------------|------------------|-----------------|
| <b>Initial</b>     | 0.235 M           | 0                | 0               |
| <b>Change</b>      | -x                | +x               | +x              |
| <b>Equilibrium</b> | (0.235 - x)       | x                | x               |

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} \quad 2.5 \times 10^{-11} = \frac{(x)(x)}{(0.235 - x)} \approx \frac{x^2}{(0.235)}$$

$$2.5 \times 10^{-11} (0.235) \approx x^2$$

$$5.875 \times 10^{-12} \approx x^2$$

$$x \approx \sqrt{5.875 \times 10^{-12}}$$

$$x = [\text{OH}^-] \approx 2.4 \times 10^{-6} \text{ M}$$

**CAN use Approximation:**

$$\frac{[\text{NO}_2^-]_0}{K_b} = \frac{0.235 \text{ M}}{2.5 \times 10^{-11}} = 9.4 \times 10^9 \geq 1000$$

Use 0.235 in the denominator, because  $(0.235 - x) \approx 0.235$  [x is so small compared to 0.235 M]

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(2.4 \times 10^{-6})$$

$$\text{pOH} = 5.62$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - (5.62)$$

$$\text{pH} = 8.38$$

**Acidic Salts:** - when the Cation is the Conjugate-Acid of a Weak Base and the Anion is the Conjugate-Base of a Strong Acid.

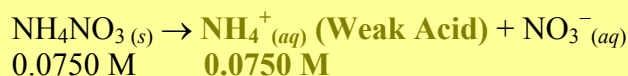
- when the Cation is a Metal Ion that is Highly Charged (Hydrated Complex Cations –  $M(H_2O)_n^{m+}$ ) and the Anion is the Conjugate-Base of a Strong Acid.
- pH will decrease; if dissolve in pure water, pH < 7 (Acidic).

**Examples:** Some Acidic Salts:

- $NH_4ClO_4(aq)$  ( $NH_4^+$  is the conjugate-acid of a weak base –  $NH_3(aq)$ ;  $ClO_4^-$  is the conjugate-base of a strong acid –  $HClO_4(aq)$ )
- $AlCl_3(aq)$  ( $Al^{3+}$  can be form a hydrated complex ion  $[Al(H_2O)_6]^{3+}(aq)$ ;  $Cl^-$  is the conjugate-base of a strong acid –  $HCl(aq)$ )
- $Fe(NO_3)_3(aq)$  ( $Fe^{3+}$  can be form a hydrated complex ion  $[Fe(H_2O)_6]^{3+}(aq)$ ;  $NO_3^-$  is the conjugate-base of a strong acid –  $HNO_3(aq)$ )
- $CoI_3(aq)$  ( $Co^{3+}$  can be form a hydrated complex ion  $[Co(H_2O)_6]^{3+}(aq)$ ;  $I^-$  is the conjugate-base of a strong acid –  $HI(aq)$ )

**Example 2:** Determine the pH of 0.0750 M of ammonium nitrate. The base dissociation constant for  $NH_3(aq)$  is  $K_b = 1.8 \times 10^{-5}$ .

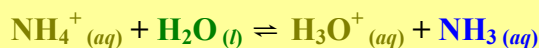
**Ammonium sulfate,  $NH_4NO_3$ , dissociates completely in water:**



**Major Species:**  $NH_4^+(aq)$ ,  $H_2O(l)$                        $K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} \quad K_a = 5.556 \times 10^{-10}$

**Strongest Acid:**  $NH_4^+$  ( $K_a = 5.556 \times 10^{-10}$ ) ( $K_a$  for  $H_2O$  is  $K_w = 1.0 \times 10^{-14}$ )

$NH_4^+$  is a weak acid and undergoes Brønsted-Lowry Dissociation.



|                    | $[NH_4^+]$  | $[H_3O^+]$ | $[NH_3]$ |
|--------------------|-------------|------------|----------|
| <b>Initial</b>     | 0.0750 M    | 0          | 0        |
| <b>Change</b>      | -x          | +x         | +x       |
| <b>Equilibrium</b> | (0.075 - x) | x          | x        |

**CAN use Approximation:**

$$\frac{[NH_4^+]_0}{K_a} = \frac{0.0750 \text{ M}}{5.556 \times 10^{-10}} = 1.35 \times 10^8 \geq 1000$$

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

$$5.556 \times 10^{-10} = \frac{(x)(x)}{(0.075 - x)} \approx \frac{x^2}{(0.075)}$$

$$5.556 \times 10^{-10} (0.075) \approx x^2$$

$$4.167 \times 10^{-11} \approx x^2$$

$$x \approx \sqrt{4.167 \times 10^{-11}}$$

$$x = [H_3O^+] \approx 6.455 \times 10^{-6} \text{ M}$$

Use 0.075 in the denominator, because  $(0.075 - x) \approx 0.075$  [x is so small compared to 0.075 M]

$$pH = -\log [H_3O^+]$$

$$pH = -\log (6.455 \times 10^{-6})$$

$$pH = 5.19$$

Verify that we could use Approximation:

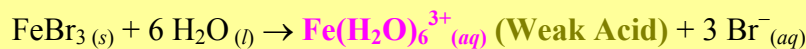
$$\frac{[H_3O^+]}{[NH_4^+]_0} \times 100\% = \frac{6.455 \times 10^{-6} \text{ M}}{0.0750 \text{ M}} \times 100\%$$

$$= 0.0086\% \leq 5\%$$

Therefore, approximation would be appropriate.

**Example 3:** Determine the pH of 44.33 g of iron (III) bromide ( $\text{FeBr}_3$ ) dissolved in 750 mL of water. The acid dissociation constant for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is  $K_a = 8.3 \times 10^{-3}$ .

$\text{FeBr}_3$  dissociates completely in water and form **hydrated complex ion**:



$$n = \frac{44.33 \text{ g}}{295.55 \text{ g/mol}}$$

$$n = 0.1499915412 \text{ mol FeBr}_3$$

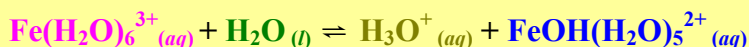
$$[\text{FeBr}_3] = [\text{Fe}(\text{H}_2\text{O})_6^{3+}] = \frac{0.1499915412 \text{ mol}}{0.750 \text{ L}}$$

$$[\text{Fe}(\text{H}_2\text{O})_6^{3+}] = 0.2000 \text{ mol/L}$$

Major Species:  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{H}_2\text{O}$

Strongest Acid:  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  ( $K_a = 8.3 \times 10^{-3}$ )

$\text{Fe}(\text{H}_2\text{O})_6^{3+}$  is a weak acid and undergoes Brønsted-Lowry Dissociation.



|             | $[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$ | $[\text{H}_3\text{O}^+]$ | $[\text{FeOH}(\text{H}_2\text{O})_5^{2+}]$ |
|-------------|--|--------------------------|--|
| Initial     | 0.200 M                                  | 0                        | 0  |
| Change      | -x                                       | +x                       | +x   |
| Equilibrium | (0.2 - x)                                | x                        | x  |

**CANNOT use Approximation:**

$$\frac{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]_0}{K_a} = \frac{0.200 \text{ M}}{8.3 \times 10^{-3}} = 24.1 < 1000$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{FeOH}(\text{H}_2\text{O})_5^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]} \quad 8.3 \times 10^{-3} = \frac{(x)(x)}{(0.2-x)} = \frac{x^2}{(0.2-x)}$$

$$0 = \frac{x^2}{(0.2-x)} - 8.3 \times 10^{-3}$$

$$x = [\text{H}_3\text{O}^+] = 0.037 \text{ M}$$

```
solve(x^2/(.2-x) - 8.3e-3, x, 0, .2)
.036803907
```

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

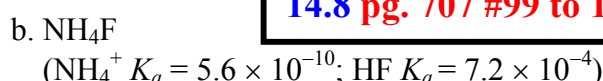
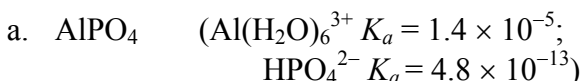
$$\text{pH} = -\log (0.037)$$

$$\text{pH} = 1.43$$

### Salts that Contain both Conjugate-Acid and Conjugate-Base:

- If the **conjugate-acid ion has a greater  $K_a$  than the  $K_b$  of the conjugate-base ion**, then the solution will be **acidic** ( $\text{pH} < 7$  when  $K_a$  of Conj-Acid  $>$   $K_b$  of Conj-Base).
- If the **conjugate-base ion has a greater  $K_b$  than the  $K_a$  of the conjugate-acid ion**, then the solution will be **basic** ( $\text{pH} > 7$  when  $K_b$  of Conj-Base  $>$   $K_a$  of Conj-Acid).
- When **both  $K_a$  from the conjugate-acid ion is equal to the  $K_b$  of the conjugate-base ion**, then the solution will be **neutral** ( $\text{pH} = 7$  when  $K_a$  of Conj-Acid =  $K_b$  of Conj-Base).

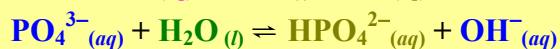
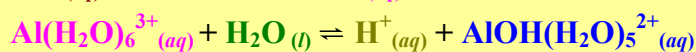
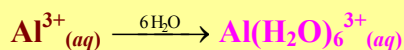
**Example 4:** Classify the following salts as acid, base or neutral.



### Assignment

14.7 pg. 707 #93 to 98

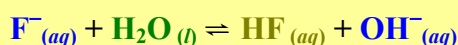
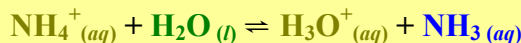
14.8 pg. 707 #99 to 112



$$\text{For } \text{Al}(\text{H}_2\text{O})_6^{3+}: K_a = 1.4 \times 10^{-5}$$

$$\text{For } \text{PO}_4^{3-}: K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.021$$

Since  $K_b$  of  $\text{PO}_4^{3-} >$   $K_a$  of  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  
aluminum phosphate is a Basic Salt.



$$\text{For } \text{NH}_4^+: K_a = 5.6 \times 10^{-10}$$

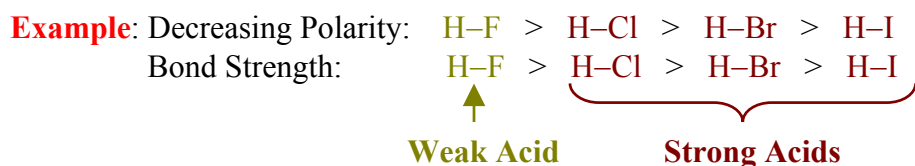
$$\text{For } \text{F}^-: K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

Since  $K_a$  of  $\text{NH}_4^+ >$   $K_b$  of  $\text{F}^-$ ,  
ammonium fluoride is an Acidic Salt.



14.9: The Effect of Structure on Acid-Base PropertiesStructural Factors that affect Acid Properties

- Polarity:** - in general, the **more polar the intramolecular bond between hydrogen and the adjacent atom**, the more likely hydrogen be donated and becoming a **stronger Brønsted-Lowry acid**. (C–H bonds have very little polarity.)
- Bond Strength:** - **the stronger the bond strength** (more exothermic  $\Delta H_f$ ) **means weaker Brønsted-Lowry acid**. This is because the stronger the bond strength, the more energy it will be needed to break the bond between hydrogen and the adjacent atom. Therefore, the proton is less likely to be donated.



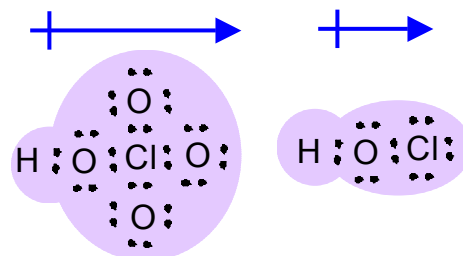
**Despite the high polarity, HF is a weak acid because of its high bond strength. This is also due to the fact that F is in the second orbital and its protons have a more effective “pull” on the bonding electrons. Thereby, keeping the hydrogen atom from donating as a  $\text{H}^+$  ion.**

**Oxyacids ( $\text{H-O-X}$ ):** - any acids that contain an oxygen atom as adjacent atom to the donating hydrogen atom.  
 - the other side of this oxygen atom is bonded by a non-metal atom.

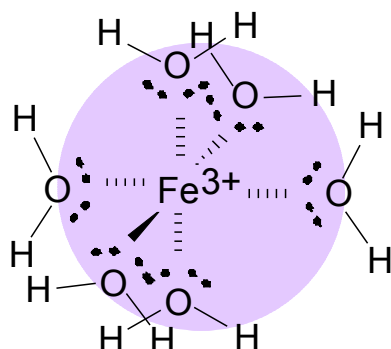
**Examples:** Some oxyacids:  $\text{HClO}_3 (aq)$ ,  $\text{H}_2\text{SO}_4 (aq)$ ,  $\text{HNO}_2 (aq)$

- Electron Density of Oxyacids:** - the **more oxygen atoms that an oxyacid has within a series**, the **stronger the acid**. This is due to the higher electron density for oxyacids with higher number of oxygen (each oxygen atom can provide two lone-pairs).

**Example:** Decreasing Strength of Oxyacid series:



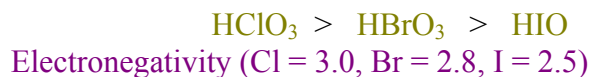
**Higher Electron Density with More Oxygen Atoms in Oxyacids makes Stronger Acids**



- **hydrated metal ions that are highly charged attracts the lone pair of water molecules**, allowing the **electron density to shift towards the metal ion center** and hence, **hydrogen from the exterior water molecules can be donated more readily**. In effect, it makes the hydrated metal ions acidic.

4. **Electronegativity:** - the **higher the electronegativity** of the oxyacid's oxygen attached non-metal atom (H-O-X), the **stronger the acid**. This is because higher electronegativity atom draws bonding electrons closer itself, leaving a weaker bond between the oxygen and the hydrogen. The result is the increasing tendency for the hydrogen to donate (making it a stronger acid).

**Example:** Decreasing Strength of various Oxyacid series with the same number of oxygen atoms:

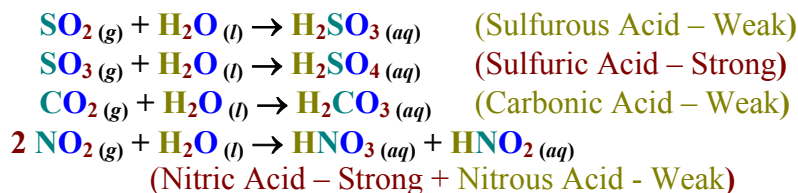


### 14.10: Acid-Base Properties of Oxides

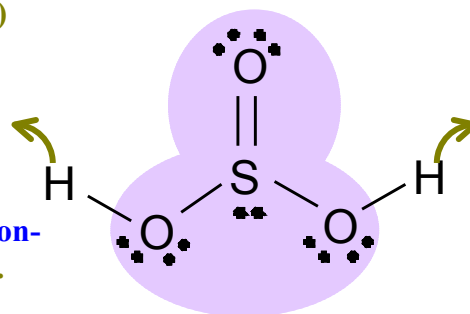
**Acidic Oxides:** - **molecular oxides (XO<sub>n</sub>)** where **X is a non-metal atom** have a **tendency to form acids when dissolved in water**.

- this is due to the fact that the **non-metal atoms have a high electronegativity**. Thereby, they draw the electrons of the adjacent oxygen closer themselves. Hence, the **O-H bond** within X-O-H **becomes so weak** that **hydrogen ion (H<sup>+</sup>) can be easily donated**.

**Example:** The problem of acid rain is created when various molecular oxides from the exhaust of vehicles and fossil-fuel power generator (coal or natural gas) react with water in the atmosphere.



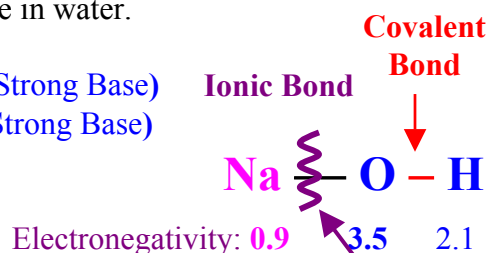
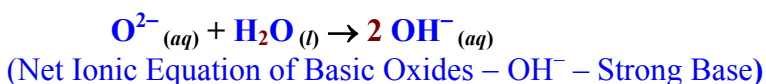
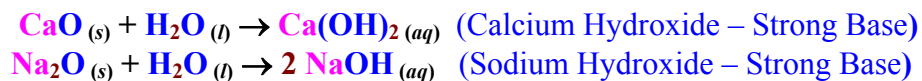
**Higher Electron Density Around the Central Non-Metal Atom makes H<sup>+</sup> more ready to donate.**



**Basic Oxides:** - **ionic oxides (M<sub>m</sub>O<sub>n</sub>)** where **M is a metal atom** have a **tendency to form bases when dissolved in water**.

- this is due to the fact that the metal atoms have small electronegativity. Thereby, the electrons of the adjacent oxygen. Hence, the **O-H bond** within M-O-H **becomes so strong** that **hydroxide ion (OH<sup>-</sup>) can be easily produced** (Arrhenius Base).

**Example:** Some Metal Oxides that can form a base when dissolve in water.



**Bigger Difference in Electronegativities with Ionic Bonds (bond will likely break between the Metal atom and the Oxygen atom) – producing OH<sup>-</sup> ion as a result.**

**14.11: The Lewis Acid-Base Models**

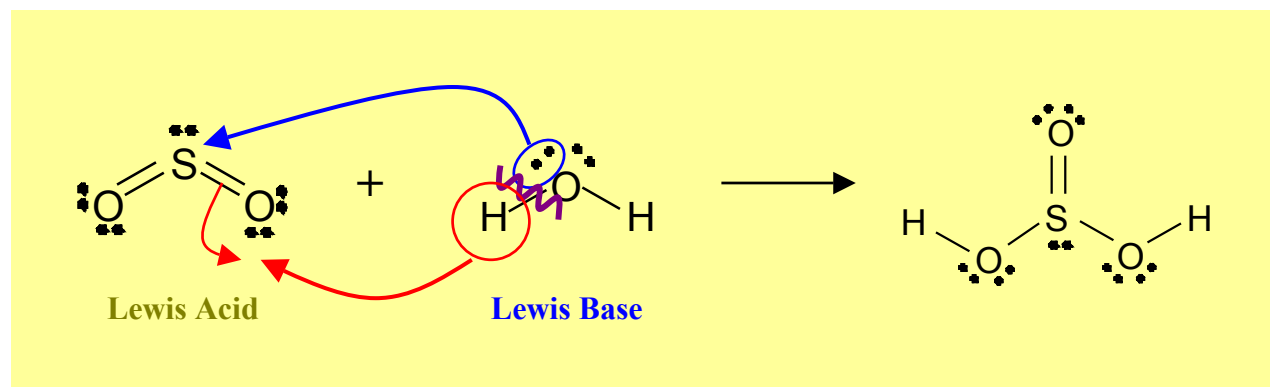
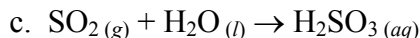
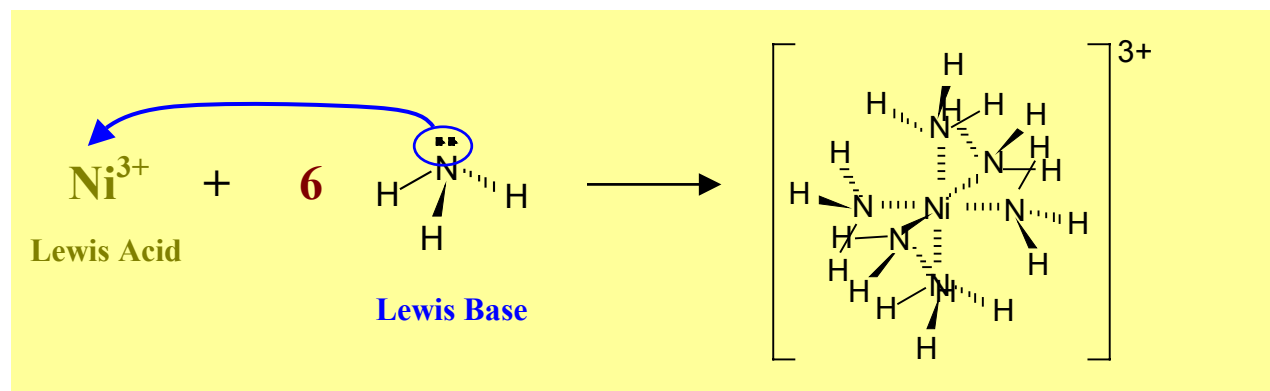
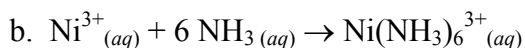
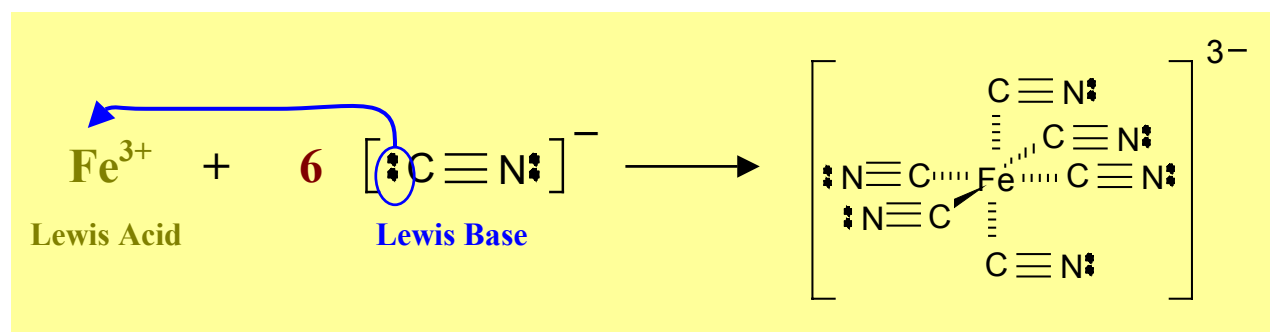
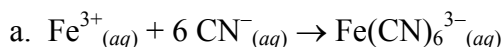
**Lewis Acid-Base Model:** - using **electron pair** instead of **proton**, we can define acids that do not have a proton and bases that do not have a hydroxide ion.

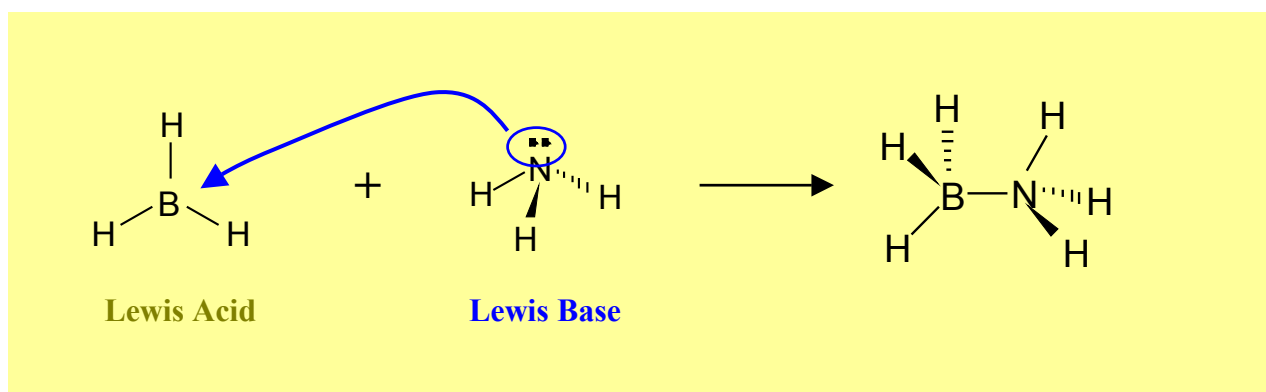
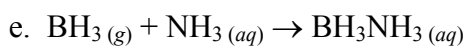
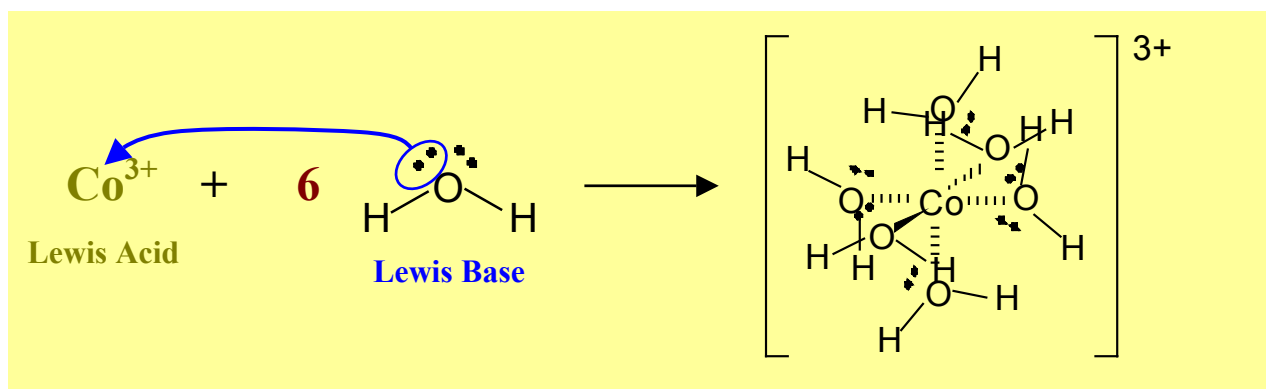
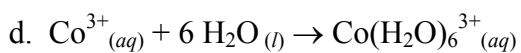
- especially suitable to explain metal hydrated cation as acid, or how metal oxides can turn into a base.

**Lewis Acid:** - a substance that **ACCEPTS an Electron Pair (Lone-Pair)**.

**Lewis Base:** - a substance that **DONATES an Electron Pair (Lone-Pair)**.

**Example 1:** Draw the Lewis diagrams for the reactants and products. Identify the Lewis acids and bases.





**Assignment**

**14.9 pg. 707 #113 to 116**

**14.10 pg. 707–708 #117 and 118**

**14.11 pg. 708 #119 to 124**

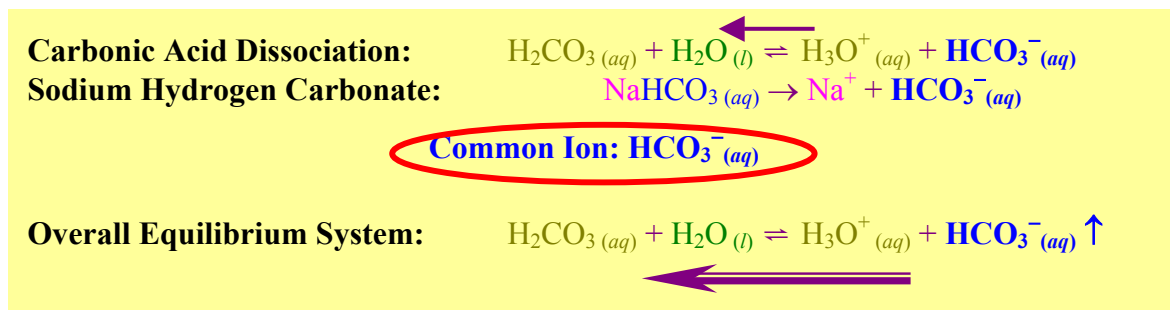
Chapter 15: Applications of Aqueous Equilibria15.1: Solutions of Acids or Bases Containing a Common Ion

**Common Ion:** - the ion that is present in two separate solutions as they are added together.

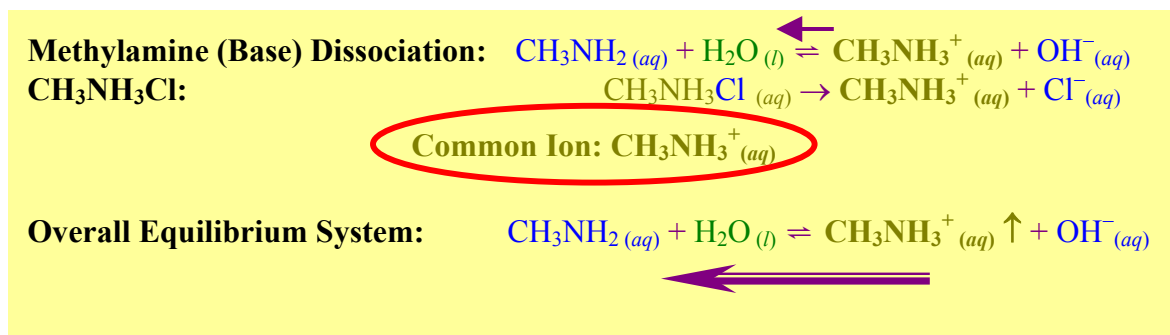
**Common Ion Effect:** - the shifting of the equilibrium, as outlined by Le Châtelier's principle, due to the addition or presence of a common ion in system.

**Example 1:** Identify the common ion in the following solutions.

- a. 0.0250 M of carbonic acid with 0.0300 M of sodium hydrogen carbonate.



- b. 0.500 M of methylamine with 0.450 M of  $\text{CH}_3\text{NH}_3\text{Cl}$

pH Calculation Involving Common Ion:

- Determine the **Initial Concentration of ALL Major Species** in the equilibrium.
- Set up the **ICE Box and the Equilibrium Expression Equating it to the Equilibrium Constant**.
- Calculate the  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  and the **pH**.

**Example 2:** Calculate the pH of the solution that consists of 0.0250 M of carbonic acid ( $K_{a1} = 4.3 \times 10^{-7}$  and  $K_{a2} = 5.6 \times 10^{-11}$ ) with 0.0300 M of sodium hydrogen carbonate.

**Carbonic Acid Dissociation:**  $\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$

**Sodium Hydrogen Carbonate:**  $\text{NaHCO}_3(aq) \rightarrow \text{Na}^+(aq) + \text{HCO}_3^-(aq)$

0.0300 M                      0.0300 M

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

|             | $[\text{H}_2\text{CO}_3]$ | $[\text{H}_3\text{O}^+]$ | $[\text{HCO}_3^-]$ |
|-------------|---------------------------|--------------------------|--------------------|
| Initial     | 0.0250 M                  | 0                        | 0.0300 M           |
| Change      | -x                        | +x                       | +x                 |
| Equilibrium | (0.025 - x)               | x                        | (0.03 + x)         |

**CAN use Approximation:**

$$\frac{[\text{H}_2\text{CO}_3]_0}{K_a} = \frac{0.0250 \text{ M}}{4.3 \times 10^{-7}} = 58140 \geq 1000$$

Use 0.03 in the numerator, because  $(0.03 + x) \approx 0.03$  [x is so small compared to 0.03 M].

Use 0.025 in the denominator, because  $(0.025 - x) \approx 0.025$  [x is so small compared to 0.025 M].

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.3 \times 10^{-7} = \frac{(x)(0.03 + x)}{(0.025 - x)} \approx \frac{x(0.03)}{(0.025)}$$

$$4.3 \times 10^{-7} \frac{(0.025)}{(0.03)} \approx x \quad x \approx 3.58 \times 10^{-7}$$

**Verify that we could use Approximation:**

$$\frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]_0} \times 100\% = \frac{3.58 \times 10^{-7} \text{ M}}{0.0250 \text{ M}} \times 100\% = 0.00143\% \leq 5\% \text{ (Appropriate Approximation)}$$

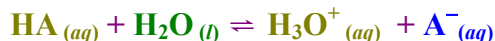
$[\text{H}_3\text{O}^+] = 3.58 \times 10^{-7} \text{ mol/L}$

$\text{pH} = -\log [\text{H}_3\text{O}^+]$   
 $\text{pH} = -\log(3.58 \times 10^{-7})$       **pH = 6.45**

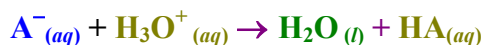
## 15.2: Buffered Solutions

**Buffered Solution:** - a solution that **resists a change in pH** when a small amount of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  is added.  
 - consists of a pair of **weak acid/conjugate base common ion** or a pair of **weak base/conjugate acid common ion**.

### Acidic Buffered Solution:



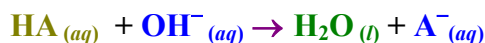
a. Small Amounts of  $\text{H}_3\text{O}^+$  is Added:



( $\text{H}^+$  - Strong Acid reacts **completely** with  $\text{A}^-$ )

(More HA - Weak Acid: pH will only be lowered **SLIGHTLY!**)

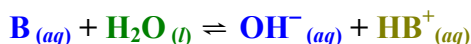
b. Small Amounts of  $\text{OH}^-$  is Added:



( $\text{OH}^-$  - Strong Base reacts **completely** with HA)

(More  $\text{A}^-$  - Weak Base: pH will only be raised **SLIGHTLY!**)

### Basic Buffered Solution:



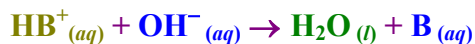
a. Small Amounts of  $\text{H}_3\text{O}^+$  is Added:



( $\text{H}^+$  - Strong Acid reacts **completely** with B)

(More  $\text{HB}^+$  - Weak Acid: pH will only be lowered **SLIGHTLY!**)

b. Small Amounts of  $\text{OH}^-$  is Added:



( $\text{OH}^-$  - Strong Base reacts **completely** with  $\text{HB}^+$ )

(More B - Weak Base: pH will only be raised **SLIGHTLY!**)

pH Calculations Involving Buffered Solutions and any Subsequent Addition of H<sup>+</sup> or OH<sup>-</sup> Amounts:

1. Determine the **initial concentration of all major species** in the equilibrium.
2. Set up the **ICE Box and the Equilibrium Expression Equating it to the Equilibrium Constant**.
3. Calculate the **[H<sub>3</sub>O<sup>+</sup>]** or **[OH<sup>-</sup>]** and the **pH** of the **original buffered solution**.
4. **Write out the Complete Reaction for the ADDITION of H<sup>+</sup> or OH<sup>-</sup> into the system**. Because we are adding a strong acid or a strong base, we will **Treat the Reaction as One-Way**. Hence, we can **Apply Regular Stoichiometric Principle** to calculate the moles of each major species.
5. Again, set up the **ICE Box and the Equilibrium Expression Equating it to the Equilibrium Constant**.
6. Calculate the **[H<sub>3</sub>O<sup>+</sup>]** or **[OH<sup>-</sup>]** and the **pH** of the **revised buffered solution**.

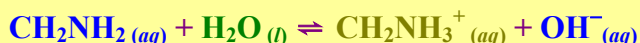
**Example 2:** Calculate the pH of a 1.00 L buffered solution consisting of 0.500 M of methylamine ( $K_b = 4.38 \times 10^{-4}$ ) with 0.450 M of CH<sub>3</sub>NH<sub>3</sub>Cl when:

- 0.0200 mol of KOH is added to it.
- 3.00 mL of 0.750 M of HNO<sub>3</sub> (aq) is added to it.
- Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

First, we have to figure out the [OH<sup>-</sup>] and pH for the buffered solution system.

Methylamine (Base) Dissociation:  $\text{CH}_2\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_2\text{NH}_3^+(aq) + \text{OH}^-(aq)$

CH<sub>3</sub>NH<sub>3</sub>Cl:  $\text{CH}_3\text{NH}_3\text{Cl}(aq) \rightarrow \text{CH}_2\text{NH}_3^+(aq) + \text{Cl}^-(aq)$   
 0.450 M                      0.450 M



|             | [CH <sub>2</sub> NH <sub>2</sub> ] | [CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup> ] | [OH <sup>-</sup> ] |
|-------------|------------------------------------|---|--------------------|
| Initial     | 0.500 M                            | 0.450 M   | 0                  |
| Change      | -x                                 | +x  | +x                 |
| Equilibrium | (0.5 - x)                          | (0.45 + x)                                      | x                  |

CAN use Approximation:

$$\frac{[\text{CH}_2\text{NH}_2]_0}{K_b} = \frac{0.500 \text{ M}}{4.38 \times 10^{-4}} = 1142 \geq 1000$$

$$K_b = \frac{[\text{OH}^-][\text{CH}_2\text{NH}_3^+]}{[\text{CH}_2\text{NH}_2]} \quad 4.38 \times 10^{-4} = \frac{(x)(0.45 + x)}{(0.5 - x)} \approx \frac{x(0.45)}{(0.5)}$$

$$4.38 \times 10^{-4} \frac{(0.5)}{(0.45)} \approx x$$

$$x \approx 4.87 \times 10^{-4}$$

Use 0.45 in the numerator, because (0.45 + x) ≈ 0.45 [x is so small compared to 0.45 M].  
 Use 0.5 in the denominator, because (0.5 - x) ≈ 0.5 [x is so small compared to 0.5 M].

Verify that we could use Approximation:

$$\frac{[\text{OH}^-]}{[\text{CH}_2\text{NH}_2]_0} \times 100\% = \frac{4.87 \times 10^{-4} \text{ M}}{0.500 \text{ M}} \times 100\%$$

$$= 0.0973\% \leq 5\%$$

Therefore, approximation would be appropriate.

$$[\text{OH}^-] = 4.87 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(4.87 \times 10^{-4})$$

$$\text{pOH} = 3.31$$

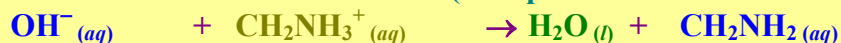
$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 3.31$$

$$\text{pH} = 10.69$$

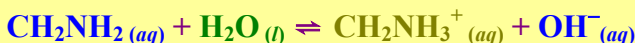


a. 0.0200 mol of KOH is added to the buffered solution (Complete Rxn between  $\text{OH}^-$  &  $\text{CH}_2\text{NH}_3^+$ ).



|        | n of $\text{OH}^-$    | n of $\text{CH}_2\text{NH}_3^+$ | n of $\text{CH}_2\text{NH}_2$ |
|--------|-----------------------|---------------------------------|-------------------------------|
| Before | 0.0200 mol (Limiting) | 0.450 mol                       | 0.500 mol                     |
| Change | -0.0200 mol           | -0.0200 mol                     | +0.0200 mol                   |
| After  | 0                     | 0.430 mol                       | 0.520 mol                     |

Recalculate equilibrium concentrations using NEW  $[\text{CH}_2\text{NH}_3^+]_0$  and  $[\text{CH}_2\text{NH}_2]_0$



|             | $[\text{CH}_2\text{NH}_2]$ | $[\text{CH}_2\text{NH}_3^+]$ | $[\text{OH}^-]$ |
|-------------|----------------------------|------------------------------|-----------------|
| Initial     | 0.520 M                    | 0.430 M                      | 0               |
| Change      | -y                         | +y                           | +y              |
| Equilibrium | (0.52 - y)                 | (0.43 + y)                   | y               |

CAN use Approximation:

$$\frac{[\text{CH}_2\text{NH}_2]_0}{K_b} = \frac{0.520 \text{ M}}{4.38 \times 10^{-4}} = 1187 \geq 1000$$

Use 0.43 in the numerator, because  $(0.43 + y) \approx 0.43$  [y is so small compared to 0.43 M].

Use 0.52 in the denominator, because  $(0.52 - y) \approx 0.52$  [y is so small compared to 0.52 M].

$$K_b = \frac{[\text{OH}^-][\text{CH}_2\text{NH}_3^+]}{[\text{CH}_2\text{NH}_2]} \quad 4.38 \times 10^{-4} \approx \frac{y(0.43)}{(0.52)}$$

$$4.38 \times 10^{-4} = \frac{(y)(0.43 + y)}{(0.52 - y)} \quad 4.38 \times 10^{-4} \frac{(0.52)}{(0.43)} \approx y$$

$$y \approx 5.30 \times 10^{-4}$$

Verify that we could use Approximation:

$$\frac{[\text{OH}^-]}{[\text{CH}_2\text{NH}_2]_0} \times 100\% = \frac{5.30 \times 10^{-4} \text{ M}}{0.520 \text{ M}} \times 100\%$$

$$= 0.102\% \leq 5\% \text{ (Appropriate Approximation)}$$

$$[\text{OH}^-] = 5.30 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(5.30 \times 10^{-4})$$

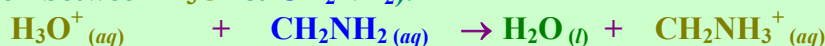
$$\text{pOH} = 3.28$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 3.28$$

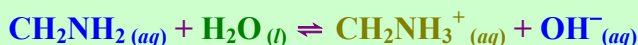
$$\text{pH} = 10.72$$

b. 3.00 mL of 0.750 M (0.00225 mol) of  $\text{HNO}_3_{(aq)}$  is added to the buffered solution (Complete Reaction between  $\text{H}_3\text{O}^+$  &  $\text{CH}_2\text{NH}_2$ ).



|        | n of $\text{H}_3\text{O}^+$ | n of $\text{CH}_2\text{NH}_2$ | n of $\text{CH}_2\text{NH}_3^+$ |
|--------|-----------------------------|-------------------------------|---------------------------------|
| Before | 0.00225 mol (Limiting)      | 0.500 mol                     | 0.450 mol                       |
| Change | -0.00225 mol                | -0.00225 mol                  | +0.00225 mol                    |
| After  | 0                           | 0.49775 mol                   | 0.45225 mol                     |

Recalculate equilibrium concentrations using NEW  $[\text{CH}_2\text{NH}_2]_0$  and  $[\text{CH}_2\text{NH}_3^+]_0$  (neglect  $\Delta$ volume)



CAN use Approximation:

$$\frac{[\text{CH}_2\text{NH}_2]_0}{K_b} = \frac{0.520 \text{ M}}{4.38 \times 10^{-4}} = 1187 \geq 1000$$

Use 0.45225 in the numerator, because  $(0.45225 + z) \approx 0.45225$  [z is so small compared to 0.45225 M].

Use 0.49775 in the denominator, because  $(0.49775 - z) \approx 0.49775$  [z is so small compared to 0.49775 M].

$$K_b = \frac{[\text{OH}^-][\text{CH}_2\text{NH}_3^+]}{[\text{CH}_2\text{NH}_2]} \quad 4.38 \times 10^{-4} \approx \frac{z(0.45225)}{(0.49775)}$$

$$4.38 \times 10^{-4} = \frac{(y)(0.45225 + z)}{(0.49775 - z)} \quad 4.38 \times 10^{-4} \frac{(0.49775)}{(0.45225)} \approx z$$

$$z \approx 4.82 \times 10^{-4}$$

Verify that we could use Approximation:

$$\frac{[\text{OH}^-]}{[\text{CH}_2\text{NH}_2]_0} \times 100\% = \frac{4.82 \times 10^{-4} \text{ M}}{0.49775 \text{ M}} \times 100\%$$

$$= 0.0968\% \leq 5\% \text{ (Appropriate Approximation)}$$

$$[\text{OH}^-] = 4.82 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(4.82 \times 10^{-4})$$

$$\text{pOH} = 3.32$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 3.28$$

$$\text{pH} = 10.68$$

c. Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

i. 0.0200 mol of KOH is added to 1.00 L of water

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(0.0200)$$

$$\text{pOH} = 1.70$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 1.70$$

$$\text{pH} = 12.30$$

Adding the 0.0200 mol of KOH to buffered solution.

pH changes from 10.69 to 10.72

ii. 3.00 mL of 0.750 M (0.00225 mol) of  $\text{HNO}_3(aq)$  is added to 1.00 L of water (neglect  $\Delta$ volume).

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.00225)$$

$$\text{pH} = 2.65$$

Adding the 0.00225 mol of  $\text{HNO}_3$  to buffered solution.

pH changes from 10.69 to 10.68

Acid/Conjugate Base Ratio  $\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$ : together with  $K_a$ , it governs the  $[\text{H}_3\text{O}^+]$  of a buffered solution.

- it can be used to adjust the pH range of the buffered solution.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \implies [\text{H}_3\text{O}^+] = K_a \left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

(Assumes that  $[\text{HA}]_0 \approx ([\text{HA}]_{eq} - x) \approx [\text{HA}]_{eq}$  and  $[\text{A}^-]_0 \approx ([\text{HA}]_{eq} + x) \approx [\text{A}^-]_{eq}$  because  $K_a$  is usually small)

$$[\text{H}_3\text{O}^+] = K_a \left(\frac{[\text{HA}]}{[\text{A}^-]}\right) \quad \text{(Relationship of Conjugate Base/Acid Ratio of Buffered Solution)}$$

$$-\log[\text{H}_3\text{O}^+] = -\log \left[ K_a \left(\frac{[\text{HA}]}{[\text{A}^-]}\right) \right] \quad \text{(Log Both sides)}$$

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \left(\frac{[\text{HA}]}{[\text{A}^-]}\right) \quad \text{(Apply Logarithmic Law: } \log(MN) = \log M + \log N)$$

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \quad \text{(Apply Logarithmic Law: } \log(M^{-1}) = -\log M)$$

### Henderson-Hasselbalch Equation

For a Buffered Solution with small  $K_a$ , assuming  $[\text{HA}]_0 \approx [\text{HA}]_{eq}$  and  $[\text{A}^-]_0 \approx [\text{A}^-]_{eq}$ , it has a pH of:

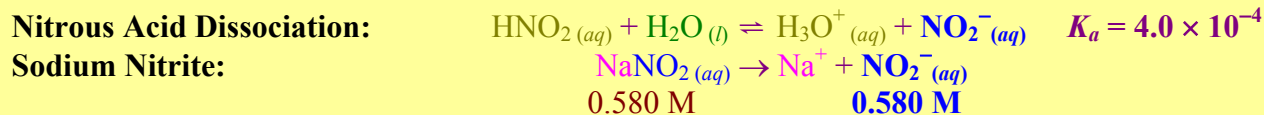
$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \quad \text{(For Basic Buffered Solution } K_a = \frac{K_w}{K_b})$$

$$\text{p}K_a = -\log K_a$$

$[\text{A}^-]$  = initial [Conjugate Base]

$[\text{HA}]$  = initial [Acid]

**Example 3:** Calculate the pH of a 1.00 L buffered solution consisting of 0.650 M of nitrous acid ( $K_a = 4.0 \times 10^{-4}$ ) with 0.580 M of sodium nitrite solution. What is the new pH after 0.125 mol of  $\text{Ba}(\text{OH})_2$  is added to it?



For the buffered solution we can use the Henderson-Hasselbalch Equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right)$$

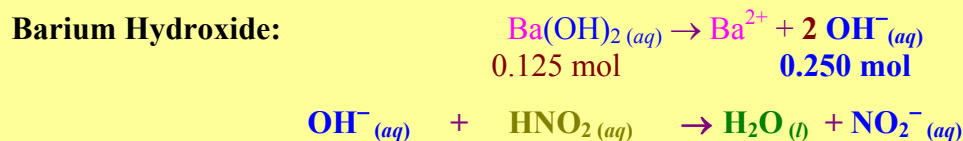
$$\text{pH} = -\log K_a + \log \left( \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right) = -\log(4.0 \times 10^{-4}) + \log \left( \frac{0.580 \text{ M}}{0.650 \text{ M}} \right)$$

**Buffered Solution pH = 3.35**

**CAN use Approximation:**

$$\frac{[\text{HNO}_2]_0}{K_a} = \frac{0.650 \text{ M}}{4.0 \times 10^{-4}} = 1625 \geq 1000$$

Calculate new pH after 0.125 mol of  $\text{Ba}(\text{OH})_2$  is added to the Buffered Solution.  
 (Complete Reaction between  $\text{OH}^-$  &  $\text{HNO}_2$ ).



|               | <i>n</i> of $\text{OH}^-$ | <i>n</i> of $\text{HNO}_2$ | <i>n</i> of $\text{NO}_2^-$ |
|---------------|---------------------------|----------------------------|-----------------------------|
| <b>Before</b> | 0.250 mol (Limiting)      | 0.650 mol                  | 0.580 mol                   |
| <b>Change</b> | -0.250 mol                | -0.250 mol                 | +0.250 mol                  |
| <b>After</b>  | 0                         | 0.400 mol                  | 0.830 mol                   |

**CAN use Approximation:**

$$\frac{[\text{HNO}_2]_0}{K_a} = \frac{0.400 \text{ M}}{4.0 \times 10^{-4}} = 1000 \geq 1000$$

$$[\text{HNO}_2]_{eq} \approx [\text{HNO}_2]_0 = \frac{0.400 \text{ mol}}{1.00 \text{ L}} = 0.400 \text{ M} \quad [\text{NO}_2^-]_{eq} \approx [\text{NO}_2^-]_0 = \frac{0.830 \text{ mol}}{1.00 \text{ L}} = 0.830 \text{ M}$$

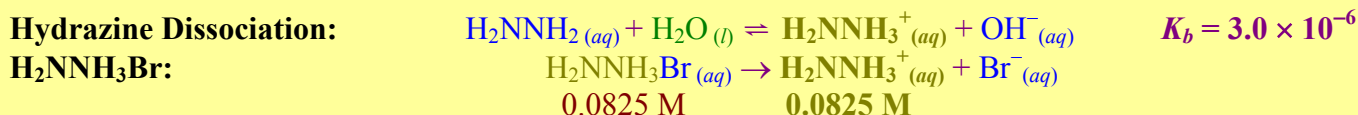
For the buffered solution with  $\text{Ba}(\text{OH})_2$  added, we can again use the Henderson-Hasselbalch Equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right) = -\log K_a + \log \left( \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right)$$

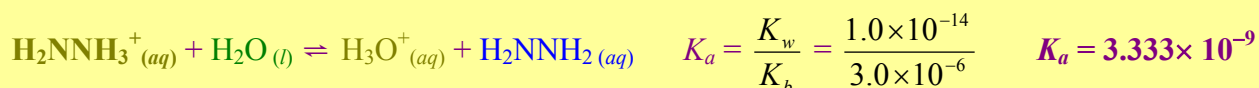
$$\text{pH} = -\log(4.0 \times 10^{-4}) + \log \left( \frac{0.830 \text{ M}}{0.400 \text{ M}} \right)$$

**pH (Buffered Solution with  $\text{Ba}(\text{OH})_2$  added) = 3.71**

**Example 4:** Calculate the pH of a 1.00 L buffered solution consisting of 0.0750 M of hydrazine,  $\text{H}_2\text{NNH}_2$  (aq), ( $K_b = 3.0 \times 10^{-6}$ ) with 0.0825 M of  $\text{H}_2\text{NNH}_3\text{Br}$  solution. What is the new pH after 15.0 mL of 1.00 mol/L HBr is added to it (neglect any volume changes)?



We need to write the acid dissociation reaction and obtain  $K_a$ .



For the buffered solution, we can use the Henderson-Hasselbalch Equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{H}_2\text{NNH}_2]}{[\text{H}_2\text{NNH}_3^+]} \right) = -\log K_a + \log \left( \frac{[\text{H}_2\text{NNH}_2]}{[\text{H}_2\text{NNH}_3^+]} \right)$$

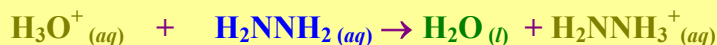
$$\text{pH} = -\log(3.333 \times 10^{-9}) + \log \left( \frac{0.0750 \text{ M}}{0.0825 \text{ M}} \right)$$

**CAN use Approximation:**

$$\frac{[\text{H}_2\text{NNH}_3^+]_0}{K_a} = \frac{0.0825 \text{ M}}{3.333 \times 10^{-9}} = 2.48 \times 10^7 \geq 1000$$

**Buffered Solution pH = 8.44**

Calculate new pH after 15.0 mL of 1.00 mol/L (0.0150 mol) HBr is added to the Buffered Solution. (Complete Reaction between  $\text{H}_3\text{O}^+$  &  $\text{H}_2\text{NNH}_2$ ).



|               | $n$ of $\text{H}_3\text{O}^+$ | $n$ of $\text{H}_2\text{NNH}_2$ | $n$ of $\text{H}_2\text{NNH}_3^+$ |
|---------------|-------------------------------|---------------------------------|-----------------------------------|
| <b>Before</b> | 0.0150 mol (Limiting)         | 0.0750 mol                      | 0.0825 mol                        |
| <b>Change</b> | -0.0150 mol                   | -0.0150 mol                     | +0.0150 mol                       |
| <b>After</b>  | 0                             | 0.0600 mol                      | 0.0975 mol                        |

**CAN use Approximation:**

$$\frac{[\text{HNO}_2]_0}{K_a} = \frac{0.0975 \text{ M}}{3.333 \times 10^{-9}} = 2.93 \times 10^7 \geq 1000$$

$$[\text{H}_2\text{NNH}_3^+]_{eq} \approx [\text{H}_2\text{NNH}_3^+]_0 = \frac{0.0975 \text{ mol}}{1.00 \text{ L}} = 0.0975 \text{ M}$$

$$[\text{H}_2\text{NNH}_2]_{eq} \approx [\text{H}_2\text{NNH}_2]_0 = \frac{0.0600 \text{ mol}}{1.00 \text{ L}} = 0.0600 \text{ M}$$

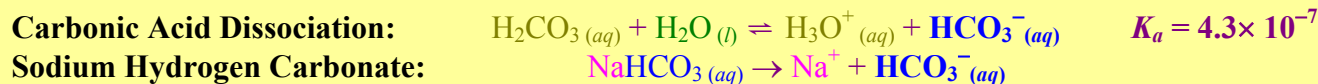
For the buffered solution with HBr added, we can again use the Henderson-Hasselbalch Equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{H}_2\text{NNH}_2]}{[\text{H}_2\text{NNH}_3^+]} \right) = -\log K_a + \log \left( \frac{[\text{H}_2\text{NNH}_2]}{[\text{H}_2\text{NNH}_3^+]} \right)$$

$$\text{pH} = -\log(3.333 \times 10^{-9}) + \log \left( \frac{0.0600 \text{ M}}{0.09750 \text{ M}} \right)$$

**pH (Buffered Solution with HBr added) = 8.27**

**Example 5:** Devise a procedure to make a buffered solution using carbonic acid ( $K_{a1} = 4.3 \times 10^{-7}$  and  $K_{a2} = 5.6 \times 10^{-11}$ ) and sodium hydrogen carbonate that is in the range of  $\text{pH} = 7.50$ .



For the buffered solution, we can use the Henderson-Hasselbalch Equation to find  $\left(\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}\right)$ .

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$\text{pH} - \text{p}K_a = \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$7.50 - [-\log(4.3 \times 10^{-7})] = \log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$\log \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right) = 1.133468456$$

$$10^{1.133468456} = \left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$\left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right) = 13.59779394$$

One way to make this  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$  buffered solution ( $\text{pH} = 7.50$ ) is to use **0.136 M** of  $\text{NaHCO}_3(aq)$  with **0.0100 M** of  $\text{H}_2\text{CO}_3(aq)$ . The conjugate base/acid ratio would be  $\frac{0.136 \text{ M}}{0.0100 \text{ M}} \approx 13.59779394$ .

### Assignment

15.1 pg. 774 #21, 23 to 27, 29 and 31

15.2 pg. 774–775 #33 to 38

## 15.3: Buffering Capacity

**Buffering Capacity:** - the amounts of  $\text{H}^+$  or  $\text{OH}^-$  a buffered solution can handle before there is a significant change in pH.

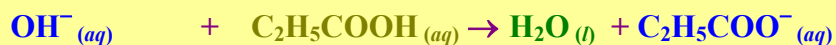
- a large buffering capacity means it can absorb large amount of  $\text{H}^+$  or  $\text{OH}^-$  before there is a notable change in pH.

- depends very much on the conjugate base/acid ratio  $\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ .

- the optimal buffering occurs when  $[\text{A}^-] = [\text{HA}]$  and they are relatively large compared to the amounts of  $\text{H}^+$  or  $\text{OH}^-$  added.



Calculate new pH after 0.0150 mol of NaOH is added to the 0.0300 M of  $\text{NaC}_2\text{H}_5\text{COO}_{(aq)}/\text{C}_2\text{H}_5\text{COOH}_{(aq)}$  Buffered Solution. (Complete Reaction between  $\text{OH}^-$  &  $\text{C}_2\text{H}_5\text{COOH}$ ).



|        | $n$ of $\text{OH}^-$  | $n$ of $\text{C}_2\text{H}_5\text{COOH}$ | $n$ of $\text{C}_2\text{H}_5\text{COO}^-$ |
|--------|-----------------------|--|---|
| Before | 0.0150 mol (Limiting) | 0.0300 mol                               | 0.0300 mol                                |
| Change | -0.0150 mol           | -0.0150 mol                              | +0.0150 mol                               |
| After  | 0                     | 0.0150 mol                               | 0.0450 mol                                |

$$[\text{C}_2\text{H}_5\text{COOH}]_{eq} \approx [\text{C}_2\text{H}_5\text{COOH}]_0 = \frac{0.0150 \text{ mol}}{1.00 \text{ L}} = 0.0150 \text{ M}$$

$$[\text{C}_2\text{H}_5\text{COO}^-]_{eq} \approx [\text{C}_2\text{H}_5\text{COO}^-]_0 = \frac{0.0450 \text{ mol}}{1.00 \text{ L}} = 0.0450 \text{ M}$$

CAN use Approximation:

$$\frac{[\text{C}_2\text{H}_5\text{COOH}]_0}{K_a} = \frac{0.0150 \text{ M}}{1.3 \times 10^{-5}} = 1154 \geq 1000$$

For the buffered solution with NaOH added, we can again use the Henderson-Hasselbalch Equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} \right) = -\log K_a + \log \left( \frac{[\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} \right)$$

$$\text{pH} = -\log(1.3 \times 10^{-5}) + \log \left( \frac{0.0450 \text{ M}}{0.0150 \text{ M}} \right)$$

pH changed from 4.89 to 5.36

↓

**pH (0.0300 M Buffered Solution with NaOH added) = 5.36**

Calculate new pH after 0.0150 mol of NaOH is added to the 3.00 M of  $\text{NaC}_2\text{H}_5\text{COO}_{(aq)}/\text{C}_2\text{H}_5\text{COOH}_{(aq)}$  Buffered Solution. (Complete Reaction between  $\text{OH}^-$  &  $\text{C}_2\text{H}_5\text{COOH}$ ).



|        | $n$ of $\text{OH}^-$  | $n$ of $\text{C}_2\text{H}_5\text{COOH}$ | $n$ of $\text{C}_2\text{H}_5\text{COO}^-$ |
|--------|-----------------------|--|---|
| Before | 0.0150 mol (Limiting) | 3.00 mol                                 | 3.00 mol                                  |
| Change | -0.0150 mol           | -0.0150 mol                              | +0.0150 mol                               |
| After  | 0                     | 2.985 mol                                | 3.015 mol                                 |

$$[\text{C}_2\text{H}_5\text{COOH}]_{eq} \approx [\text{C}_2\text{H}_5\text{COOH}]_0 = \frac{2.985 \text{ mol}}{1.00 \text{ L}} = 2.985 \text{ M}$$

$$[\text{C}_2\text{H}_5\text{COO}^-]_{eq} \approx [\text{C}_2\text{H}_5\text{COO}^-]_0 = \frac{3.015 \text{ mol}}{1.00 \text{ L}} = 3.015 \text{ M}$$

CAN use Approximation:

$$\frac{[\text{C}_2\text{H}_5\text{COOH}]_0}{K_a} = \frac{2.985 \text{ M}}{1.3 \times 10^{-5}} = 229615 \geq 1000$$

For the buffered solution with NaOH added, we can again use the Henderson-Hasselbalch Equation.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} \right) = -\log K_a + \log \left( \frac{[\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} \right)$$

$$\text{pH} = -\log(1.3 \times 10^{-5}) + \log \left( \frac{3.015 \text{ M}}{2.985 \text{ M}} \right)$$

pH stayed at 4.89 from before

↓

**pH (3.00 M Buffered Solution with NaOH added) = 4.89**

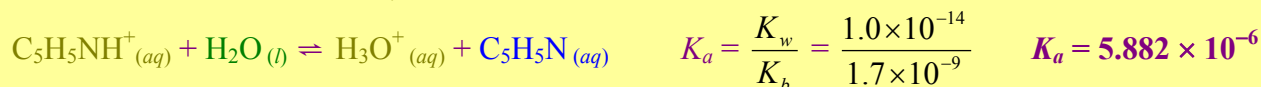
Hence, when  $[\text{A}^-] = [\text{HA}]$  and if both concentrations are large, then we achieve optimal buffering capacity.



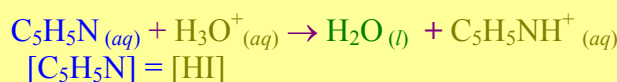
**Example 2:** Calculate the number of moles of HI<sub>(aq)</sub> that must be added to 0.500 L of 2.00 mol/L of C<sub>5</sub>H<sub>5</sub>NHI<sub>(aq)</sub> ( $K_b$  of C<sub>5</sub>H<sub>5</sub>N =  $1.7 \times 10^{-9}$ ) to produce a solution buffered at pH = 4.75.



C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup> is a weak acid. Hence, we need to write the acid dissociation reaction and obtain  $K_a$ .



Adding HI (or H<sub>3</sub>O<sup>+</sup>) will **react completely** with the base C<sub>5</sub>H<sub>5</sub>N:



For the buffered solution, we can use the Henderson-Hasselbalch Equation to find  $\left( \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} \right)$ .

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} \right) \qquad \text{pH} - \text{p}K_a = \log \left( \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} \right)$$

$$4.75 - [-\log(5.882 \times 10^{-6})] = \log \left( \frac{[\text{C}_5\text{H}_5\text{N}]}{2.00 \text{ M}} \right)$$

$$\log \left( \frac{[\text{C}_5\text{H}_5\text{N}]}{2.00 \text{ M}} \right) = -0.4804749798$$

$$10^{-0.4804749798} = \left( \frac{[\text{C}_5\text{H}_5\text{N}]}{2.00 \text{ M}} \right)$$

$$\text{Since } [\text{C}_5\text{H}_5\text{N}] = [\text{HI}] \qquad [\text{C}_5\text{H}_5\text{N}] = (2.00 \text{ M})(10^{-0.4804749798})$$

$$[\text{HI}] = 0.662 \text{ M} \qquad \qquad \qquad [\text{C}_5\text{H}_5\text{N}] = 0.662 \text{ M}$$

$$n_{\text{HI}} = [\text{HI}]V = (0.662 \text{ mol/L})(0.500 \text{ L})$$

$$n_{\text{HI}} = 0.331 \text{ mol}$$

**Example 3:** From a list of the  $K_a$  below, select the buffered solution that has a pH of around 3.20. Write up a procedure that makes 1.00 L of this particular buffered solution.

|  |                             |
|--|-----------------------------|
| Monochloroacetic Acid (HC <sub>2</sub> H <sub>2</sub> ClO <sub>2</sub> <sub>(aq)</sub> ) | $K_a = 1.35 \times 10^{-3}$ |
| Hydrofluoric Acid (HF <sub>(aq)</sub> )  | $K_a = 7.2 \times 10^{-4}$  |
| Nitrous Acid (HNO <sub>2</sub> <sub>(aq)</sub> )   | $K_a = 4.0 \times 10^{-4}$  |
| Methanoic Acid (HCOOH <sub>(aq)</sub> )  | $K_a = 1.8 \times 10^{-4}$  |

For Optimal Buffering Capacity, [HA] = [A<sup>-</sup>], which means pH = p $K_a$ .

$$\text{p}K_a = -\log K_a$$

$$K_a = 10^{-\text{p}K_a} = 10^{-(3.20)} \qquad K_a = 6.31 \times 10^{-4} \text{ (Closest Weak Acid to this } K_a \text{ is HF}_{(aq)})$$

**Possible Procedure to Make 2.00 M of F<sup>-</sup>/HF Buffered Solution.**

(Large concentrations are needed for good buffering capacity.)

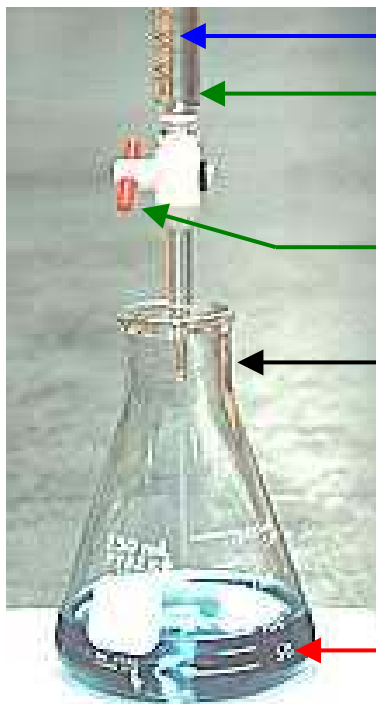
- Obtain 1.00 L of 2.00 M of HF. (May entail dilution from stock solution.)
- Dissolve 83.98 g of NaF ( $m = nM = 2.00 \text{ mol/L} \times 1.00 \text{ L} \times 41.99 \text{ g/mol}$ ) into the 1.00 L of 2.00 M HF<sub>(aq)</sub>

### 15.4: Titrations and pH Curve

**pH Curve:** - a graph that shows the how the pH changes as the titration proceeds (as titrant is to the analyzed).

**Titration:** - a volumetric analysis that involves measuring the volume of known concentration solution to measure a given volume of an unknown concentration solution.

#### Titration Set-up



**Titrant:** - the solution of known concentration.

**Buret:** - a precise apparatus to deliver the titrant.  
- the volume of the titrant added is read by subtracting the final volume and the initial volume.

**Buret Valve:** - can be adjusted to let one drop out at a time.

**Erlenmeyer Flask:** - a container commonly uses to hold the analyte. (Narrow mouth prevents splash and spillage.)

**Analyte:** - the solution of an unknown concentration.  
- the exact volume is usually delivered by a pipet.

**Acid-Base Titration:** - volumetric analysis that assist in determining the unknown concentration in an acid and base neutralization.

**Equivalent Point (Stoichiometric Point):** - a point where the number of moles of  $H^+$  is equivalent to the number of moles of  $OH^-$ . ( $n_{H^+} = n_{OH^-}$ )

**Endpoint:** - a point where the indicator actually changes colour to indicate neutralization is completed.

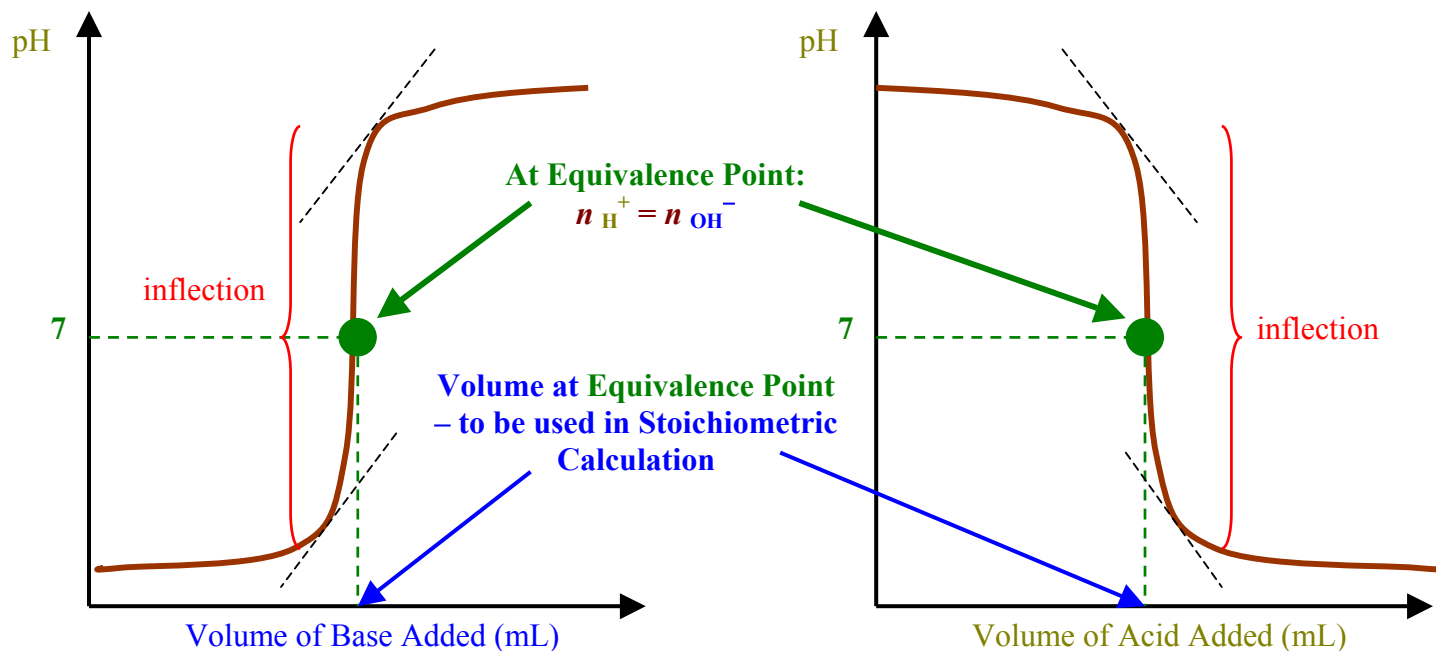
**Indicator:** - a chemical that changes colour due to the pH of the solution (more in the next section).

**Inflection:** - the part of the curve where there is a sudden rise or drop in pH.  
- the midpoint of the inflection marks the equivalence point.

1. Titration Between Strong Acids and Strong Base: - **Equivalence Point** always occur at **pH = 7**.

**Strong Acid (unknown concentration with known volume - analyte) titrated with Strong Base (known concentration - titrant)**

**Strong Base (unknown concentration and known volume - analyte) titrated with Strong Acid (known concentration - titrant)**



**Example 1:** Calculate the pH when 30.0 mL of 0.100 M of  $HCl_{(aq)}$  is titrated with 0.200 M of  $KOH_{(aq)}$  at:

- 0 mL of  $KOH_{(aq)}$  added.
- 5.00 mL of  $KOH_{(aq)}$  added.
- 15.00 mL of  $KOH_{(aq)}$  added.
- 20.00 mL of  $KOH_{(aq)}$  added.

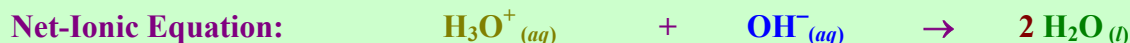
a. At 0 mL of  $KOH_{(aq)}$  added, the pH will be solely based on the  $[HCl]$  in the flask:



$$pH = -\log [H_3O^+] = -\log(0.100)$$

$$pH = 1.00$$

b. At 5.00 mL of  $KOH_{(aq)}$  added: (Before Stoichiometric Point)



|               | $n$ of $H_3O^+$                     | $n$ of $OH^-$                           |
|---------------|-------------------------------------|---|
| <b>Before</b> | (0.100 mol/L)(30.00 mL) = 3.00 mmol | (0.200 mol/L)(5.00 mL) = 1.00 mmol (LR) |
| <b>Change</b> | - 1.00 mmol                         | - 1.00 mmol                             |
| <b>After</b>  | <b>2.00 mmol</b>                    | <b>0.00 mmol</b>                        |

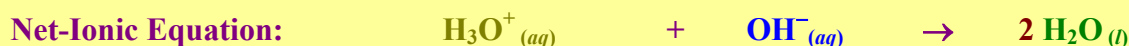
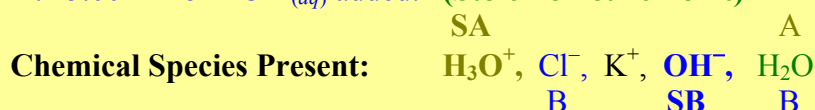
$$[H_3O^+] = \frac{n_{H_3O^+}}{\text{Total Volume}} = \frac{2.00 \text{ mmol}}{(30.00 \text{ mL} + 5.00 \text{ mL})} = 0.05714 \text{ mol/L}$$

$$pH = -\log [H_3O^+] = -\log(0.05714)$$

$$pH = 1.24$$

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on the next page.)

c. At 15.00 mL of KOH<sub>(aq)</sub> added: **(Stoichiometric Point)**



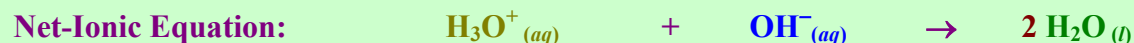
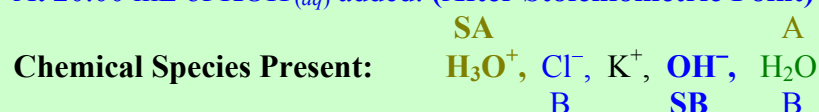
|        | $n$ of $\text{H}_3\text{O}^+$       | $n$ of $\text{OH}^-$                |
|--------|-------------------------------------|-------------------------------------|
| Before | (0.100 mol/L)(30.00 mL) = 3.00 mmol | (0.200 mol/L)(15.00 mL) = 3.00 mmol |
| Change | - 3.00 mmol                         | - 3.00 mmol                         |
| After  | 0.00 mmol                           | 0.00 mmol                           |

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-7})$$

$$\text{pH} = 7.00$$

d. At 20.00 mL of KOH<sub>(aq)</sub> added: **(After Stoichiometric Point)**



|        | $n$ of $\text{H}_3\text{O}^+$                             | $n$ of $\text{OH}^-$                |
|--------|---|-------------------------------------|
| Before | (0.100 mol/L)(30.00 mL) = 3.00 mmol<br>(Limiting Reagent) | (0.200 mol/L)(20.00 mL) = 4.00 mmol |
| Change | - 3.00 mmol   | - 3.00 mmol                         |
| After  | 0.00 mmol   | 1.00 mmol                           |

$$[\text{OH}^-] = \frac{n_{\text{OH}^-}}{\text{Total Volume}} = \frac{1.00 \text{ mmol}}{(30.00 \text{ mL} + 20.00 \text{ mL})} = 0.0200 \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(0.0200)$$

$$\text{pH} = 14 - \text{pOH}$$

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)

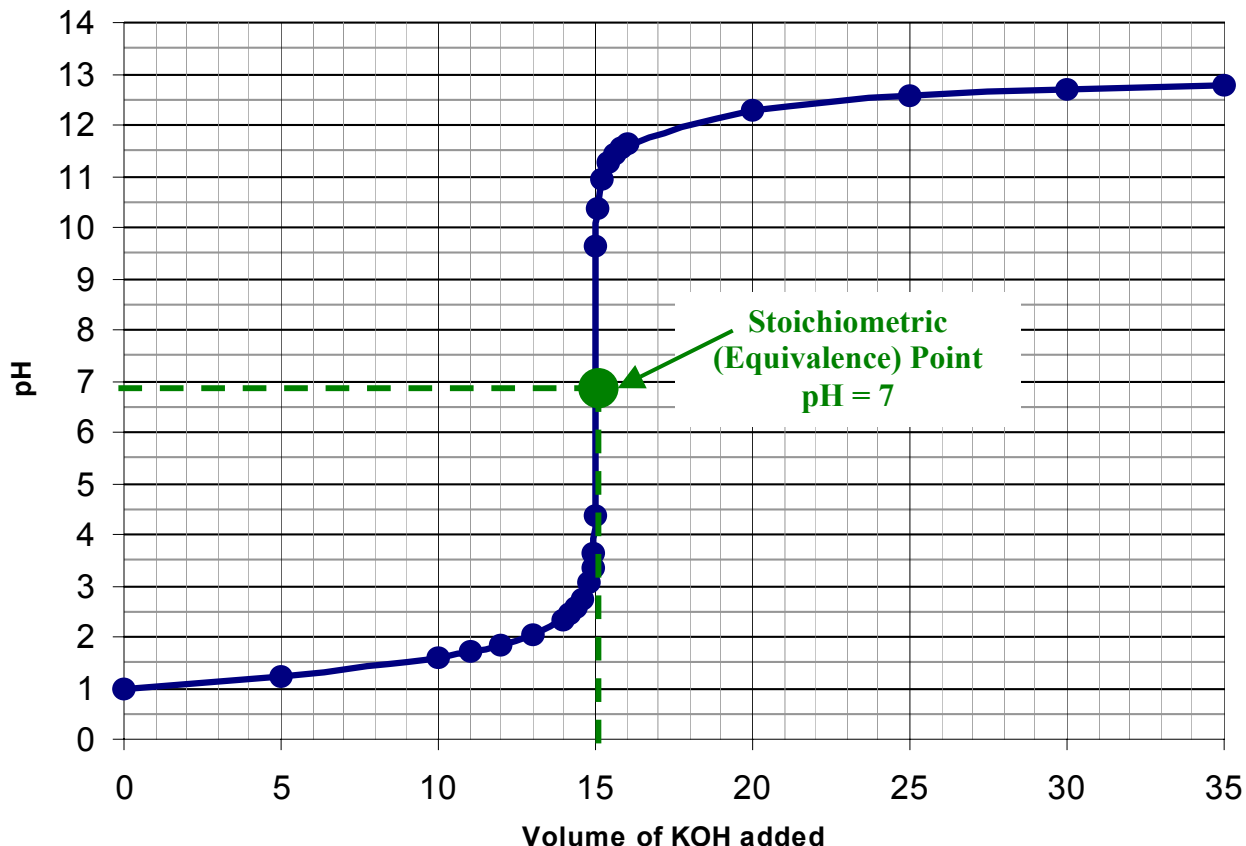
$$\text{pOH} = 1.70$$

$$\text{pH} = 12.30$$

**pH of 30.0 mL of 0.100 M HCl<sub>(aq)</sub> titrated by 0.200 M of KOH<sub>(aq)</sub>**

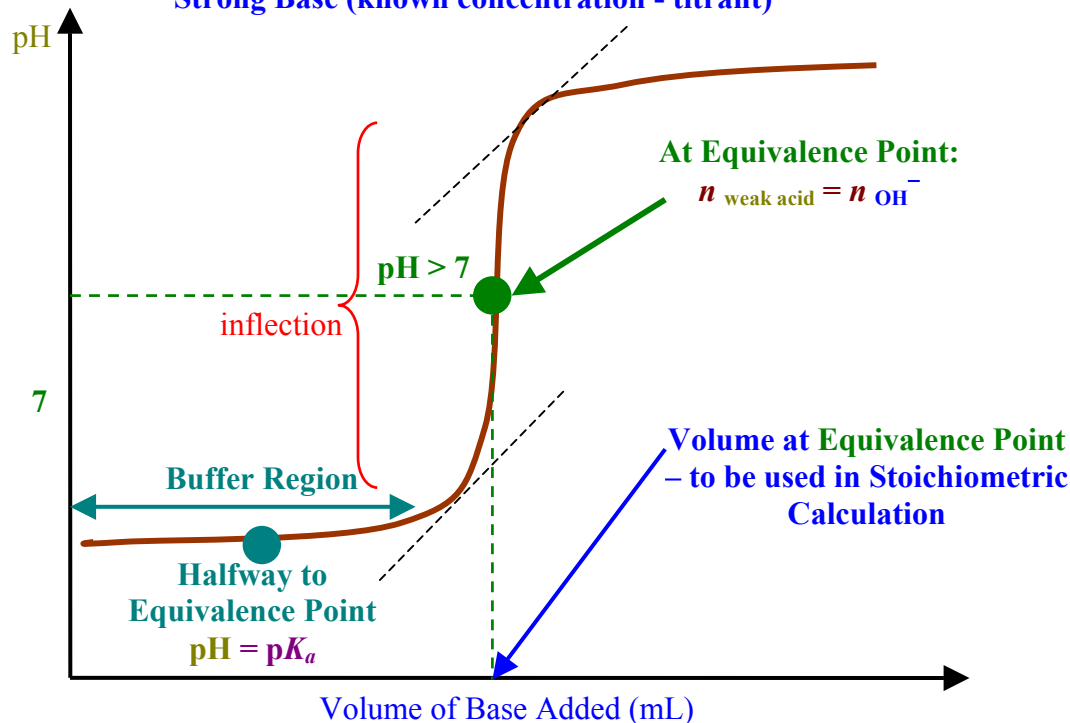
| Volume of KOH added | pH   | Volume of KOH added           | pH          | Volume of KOH added | pH    |
|---------------------|------|-------------------------------|-------------|---------------------|-------|
| 0.00 mL             | 1.00 | 14.60 mL                      | 2.75        | 15.40 mL            | 11.25 |
| 5.00 mL             | 1.24 | 14.80 mL                      | 3.05        | 15.60 mL            | 11.42 |
| 10.00 mL            | 1.60 | 14.90 mL                      | 3.35        | 15.80 mL            | 11.54 |
| 11.00 mL            | 1.71 | 14.95 mL                      | 3.65        | 16.00 mL            | 11.64 |
| 12.00 mL            | 1.85 | 14.99 mL                      | 4.35        | 20.00 mL            | 12.30 |
| 13.00 mL            | 2.03 | <b>15.00 mL (Equivalence)</b> | <b>7.00</b> | 25.00 mL            | 12.56 |
| 14.00 mL            | 2.34 | 15.01 mL                      | 9.65        | 30.00 mL            | 12.70 |
| 14.20 mL            | 2.44 | 15.05 mL                      | 10.35       | 35.00 mL            | 12.79 |
| 14.40 mL            | 2.57 | 15.20 mL                      | 10.95       |                     |       |

**pH of 30.0 mL of 0.100 M HCl titrated by 0.200 M of KOH**



2. **Titration Between Weak Acids and Strong Base:** - Equivalence Point always occur at  $\text{pH} > 7$ .

Weak Acid (unknown concentration with known volume - analyte) titrated with Strong Base (known concentration - titrant)



- Example 2:** Calculate the pH when 30.0 mL of 0.100 M of  $\text{HCOOH}_{(aq)}$  ( $K_a = 1.8 \times 10^{-4}$ ) is titrated with 0.200 mol/L of  $\text{KOH}_{(aq)}$  at:
- 0 mL of  $\text{KOH}_{(aq)}$  added.
  - 7.50 mL of  $\text{KOH}_{(aq)}$  added.
  - 15.00 mL of  $\text{KOH}_{(aq)}$  added.
  - 20.00 mL of  $\text{KOH}_{(aq)}$  added.

a. At 0 mL of  $\text{KOH}_{(aq)}$  added, the pH will be calculated the weak acid dissociation in the flask:



|             | [HCOOH]   | [H <sub>3</sub> O <sup>+</sup> ] | [HCOO <sup>-</sup> ] |
|-------------|-----------|----------------------------------|----------------------|
| Initial     | 0.100 M   | 0                                | 0 M                  |
| Change      | -x        | +x                               | +x                   |
| Equilibrium | (0.1 - x) | x                                | x                    |

**CANNOT use Approximation:**

$$\frac{[\text{HCOOH}]_0}{K_a} = \frac{0.100 \text{ M}}{1.8 \times 10^{-4}} = 555.6 < 1000$$

```
solve(X^2/(0.1-X)-1.8E-4,X,0,(0,0.1))
.0041535952
```

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \quad 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.1-x)} = \frac{x^2}{(0.1-x)}$$

$$[\text{H}_3\text{O}^+] = x = 0.0042 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(0.042)$$

$$\text{pH} = 2.38$$

b. At 7.50 mL of  $\text{KOH}_{(aq)}$  added: (Before Stoichiometric Point: at Halfway to Equivalence Point)

Chemical Species Present:  $\text{HCOOH}$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$

SA                      SB      A/B

Net-Ionic Equation:  $\text{HCOOH}_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{HCOO}^-_{(aq)}$

|        | n of HCOOH                             | n of OH <sup>-</sup>                       | n of HCOO <sup>-</sup> |
|--------|--|--|------------------------|
| Before | (0.100 mol/L)(30.00 mL)<br>= 3.00 mmol | (0.200 mol/L)(7.50 mL)<br>= 1.50 mmol (LR) | 0 mmol                 |
| Change | - 1.50 mmol                            | - 1.50 mmol                                | + 1.50 mmol            |
| After  | 1.50 mmol                              | 0 mmol                                     | 1.50 mmol              |

$$[\text{HCOOH}] = \frac{n_{\text{HCOOH}}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$$[\text{HCOO}^-] = \frac{n_{\text{HCOO}^-}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$$\left. \begin{aligned} [\text{HCOOH}] = [\text{HCOO}^-] \\ \text{pH} \approx \text{p}K_a \\ \text{(Max Buffer Capacity)} \end{aligned} \right\}$$

After all the  $\text{OH}^-$  is used up, the resulting solution follows the regular weak acid dissociation.



|             | [HCOOH]    | [H <sub>3</sub> O <sup>+</sup> ] | [HCOO <sup>-</sup> ] |
|-------------|------------|----------------------------------|----------------------|
| Initial     | 0.0400 M   | 0                                | 0.0400 M             |
| Change      | -x         | +x                               | +x                   |
| Equilibrium | (0.04 - x) | x                                | (0.04 + x)           |

**CANNOT use Approximation:**

$$\frac{[\text{HCOOH}]_0}{K_a} = \frac{0.0400 \text{ M}}{1.8 \times 10^{-4}} = 222.22 < 1000$$

```
solve(X(0.04+X)/(0.04-X)-1.8E-4,X,0,(0,0.04))
1.784015157E-4
```

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \quad 1.8 \times 10^{-4} = \frac{(x)(0.04+x)}{(0.04-x)}$$

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-4} \text{ mol/L} \quad \text{pH} = \text{p}K_a = -\log(1.8 \times 10^{-4})$$

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on page 306.)

$$\text{pH} = 3.75$$

c. At 15.00 mL of KOH<sub>(aq)</sub> added: (Stoichiometric Point)

Chemical Species Present: HCOOH, K<sup>+</sup>, OH<sup>-</sup>, H<sub>2</sub>O  
 SA SB A/B

Net-Ionic Equation: HCOOH<sub>(aq)</sub> + OH<sup>-</sup><sub>(aq)</sub> → H<sub>2</sub>O<sub>(l)</sub> + HCOO<sup>-</sup><sub>(aq)</sub>

|        | n of HCOOH                             | n of OH <sup>-</sup>                   | n of HCOO <sup>-</sup> |
|--------|--|--|------------------------|
| Before | (0.100 mol/L)(30.00 mL)<br>= 3.00 mmol | (0.200 mol/L)(15.00 mL)<br>= 3.00 mmol | 0 mmol                 |
| Change | - 3.00 mmol                            | - 3.00 mmol                            | + 3.00 mmol            |
| After  | 0 mmol                                 | 0 mmol                                 | 3.00 mmol              |

$$[\text{HCOO}^-] = \frac{n_{\text{HCOO}^-}}{\text{Total Volume}} = \frac{3.00 \text{ mmol}}{(30.00 \text{ mL} + 15.00 \text{ mL})} = 0.0667 \text{ mol/L}$$

At Stoichiometric Point, after all the OH<sup>-</sup> and HCOOH are used up, the resulting solution follows the regular weak base dissociation.

|             | HCOO <sup>-</sup> <sub>(aq)</sub> | H <sub>2</sub> O <sub>(l)</sub> | HCOOH <sub>(aq)</sub> | OH <sup>-</sup> <sub>(aq)</sub> |
|-------------|-----------------------------------|---------------------------------|-----------------------|---------------------------------|
| Initial     | 0.0667 M                          |                                 | 0                     | 0 M                             |
| Change      | -x                                |                                 | +x                    | +x                              |
| Equilibrium | (0.0667 - x)                      |                                 | x                     | x                               |

CAN use Approximation:

$$\frac{[\text{HCOO}^-]}{K_b} = \frac{0.0667 \text{ M}}{5.556 \times 10^{-11}} = 1.2 \times 10^9 \geq 1000$$

Use 0.0667 in the denominator, because (0.0667 - x) ≈ 0.03667 [x is so small compared to 0.0667 M].

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} \quad K_b = 5.556 \times 10^{-11} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]}$$

$$5.556 \times 10^{-11} = \frac{(x)(x)}{(0.0667 - x)} \approx \frac{x^2}{0.0667}$$

$$[\text{OH}^-] = x = 1.92 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} = -\log(1.92 \times 10^{-6}) = 5.72$$

$$\text{pH} = 14 - \text{pOH} = 14 - 5.72$$

$$\text{pH} = 8.28$$

d. At 20.00 mL of KOH<sub>(aq)</sub> added: (After Stoichiometric Point)

Chemical Species Present: HCOOH, K<sup>+</sup>, OH<sup>-</sup>, H<sub>2</sub>O  
 SA SB A/B

Net-Ionic Equation: HCOOH<sub>(aq)</sub> + OH<sup>-</sup><sub>(aq)</sub> → H<sub>2</sub>O<sub>(l)</sub> + HCOO<sup>-</sup><sub>(aq)</sub>

|        | n of HCOOH                                  | n of OH <sup>-</sup>                   |
|--------|---|--|
| Before | (0.100 mol/L)(30.00 mL)<br>= 3.00 mmol (LR) | (0.200 mol/L)(20.00 mL)<br>= 4.00 mmol |
| Change | - 3.00 mmol                                 | - 3.00 mmol                            |
| After  | 0 mmol                                      | 1.00 mmol                              |

After all the HCOOH is used up, the resulting solution has the following major species.

Chemical Species Present: K<sup>+</sup>, OH<sup>-</sup>, H<sub>2</sub>O  
 SB A/B

$$[\text{OH}^-] = \frac{n_{\text{OH}^-}}{\text{Total Volume}} = \frac{1.00 \text{ mmol}}{(30.00 \text{ mL} + 20.00 \text{ mL})} = 0.0200 \text{ mol/L} \quad \text{pOH} = -\log(0.0200) = 1.70$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.70$$

$$\text{pH} = 12.30$$

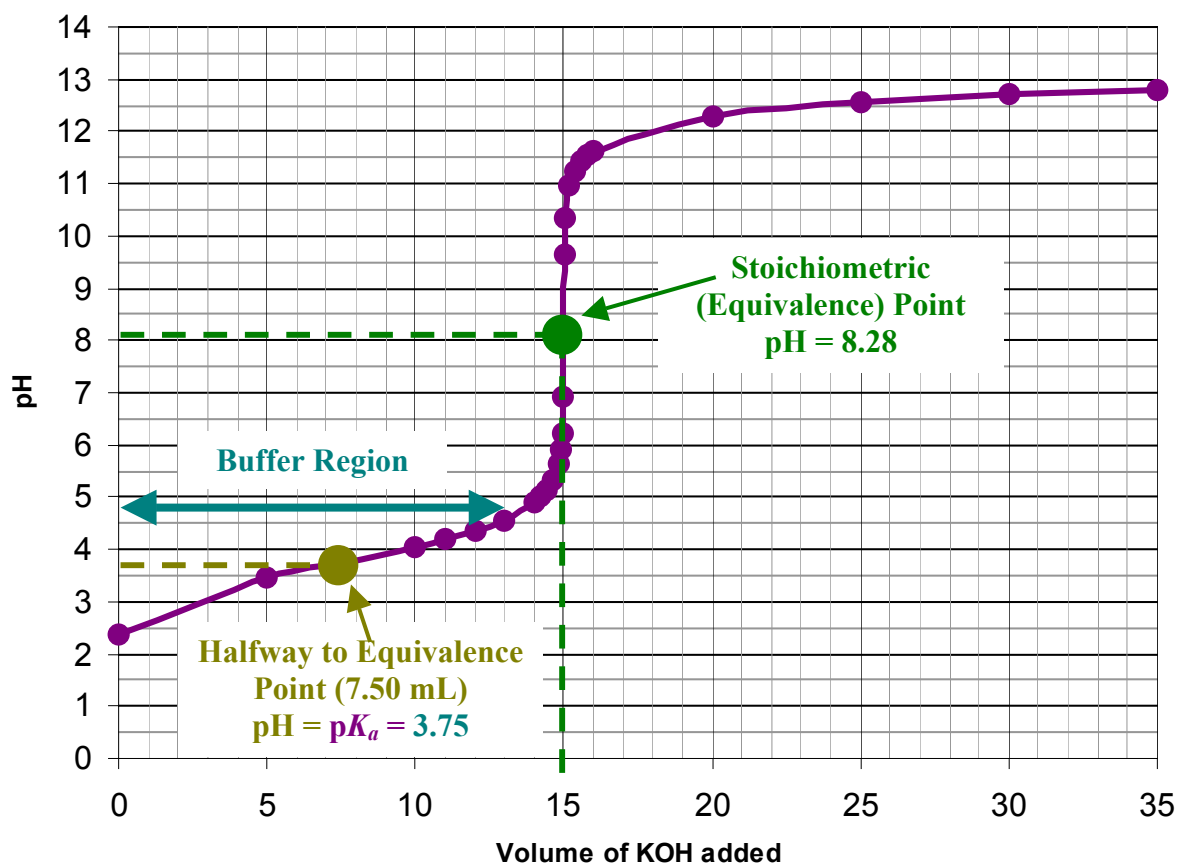
(pH's results from similar Calculations with other volumes after the stoichiometric point is listed on the next page.)



**pH of 30.0 mL of 0.100 M HCOOH<sub>(aq)</sub> titrated by 0.200 M of KOH<sub>(aq)</sub>**

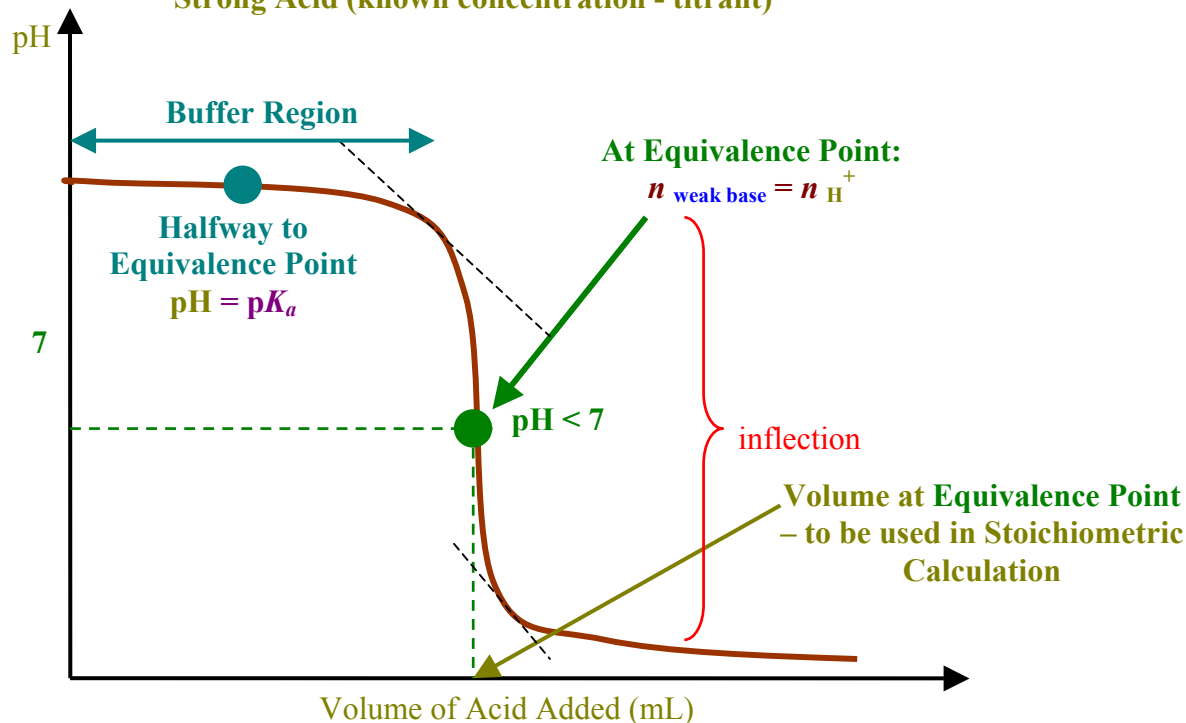
| Volume of KOH added              | pH   | Volume of KOH added    | pH    | Volume of KOH added | pH    |
|----------------------------------|------|------------------------|-------|---------------------|-------|
| 0.00 mL                          | 2.38 | 14.40 mL               | 5.13  | 15.20 mL            | 10.95 |
| 5.00 mL                          | 3.45 | 14.60 mL               | 5.31  | 15.40 mL            | 11.25 |
| 7.50 mL (Halfway to Equivalence) | 3.75 | 14.80 mL               | 5.62  | 15.60 mL            | 11.42 |
| 10.00 mL                         | 4.05 | 14.90 mL               | 5.91  | 15.80 mL            | 11.54 |
| 11.00 mL                         | 4.19 | 14.95 mL               | 6.22  | 16.00 mL            | 11.64 |
| 12.00 mL                         | 4.35 | 14.99 mL               | 6.92  | 20.00 mL            | 12.30 |
| 13.00 mL                         | 4.56 | 15.00 mL (Equivalence) | 8.28  | 25.00 mL            | 12.56 |
| 14.00 mL                         | 4.89 | 15.01 mL               | 9.65  | 30.00 mL            | 12.70 |
| 14.20 mL                         | 5.00 | 15.05 mL               | 10.35 | 35.00 mL            | 12.79 |

**pH of 30.0 mL of 0.100 M HCOOH titrated by 0.200 M of KOH**



### 3. Titration Between Weak Bases and Strong Acid: - Equivalence Point always occur at $\text{pH} < 7$ .

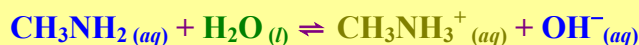
Weak Base (unknown concentration with known volume - analyte) titrated with Strong Acid (known concentration - titrant)



**Example 3:** Calculate the pH when 30.0 mL of 0.100 M of  $\text{CH}_3\text{NH}_2(aq)$  ( $K_b = 4.38 \times 10^{-4}$ ) is titrated with 0.200 mol/L of  $\text{HCl}(aq)$  at:

- 0 mL of  $\text{HCl}(aq)$  added.
- 7.50 mL of  $\text{HCl}(aq)$  added.
- 15.00 mL of  $\text{HCl}(aq)$  added.
- 20.00 mL of  $\text{HCl}(aq)$  added.

a. At 0 mL of  $\text{HCl}(aq)$  added, the pH will be calculated the weak base dissociation in the flask:



|             | $[\text{CH}_3\text{NH}_2]$ | $[\text{CH}_3\text{NH}_3^+]$ | $[\text{OH}^-]$ |
|-------------|----------------------------|------------------------------|-----------------|
| Initial     | 0.100 M                    | 0                            | 0 M             |
| Change      | -x                         | +x                           | +x              |
| Equilibrium | (0.1 - x)                  | x                            | x               |

**CANNOT use Approximation:**

$$\frac{[\text{CH}_3\text{NH}_2]_0}{K_b} = \frac{0.100 \text{ M}}{4.38 \times 10^{-4}} = 228.3 < 1000$$

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

$$4.38 \times 10^{-4} = \frac{(x)(x)}{(0.1-x)} = \frac{x^2}{(0.1-x)}$$

$$[\text{OH}^-] = x = 0.00640 \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(0.00640) = 2.19$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.19$$

```
solve(X^2/(0.1-X)
-4.38E-4,X,0,0,
0.1)
.0064027793
```

$$\text{pH} = 11.81$$

b. At 7.50 mL of  $\text{HCl}_{(aq)}$  added: (Before Stoichiometric Point: at Halfway to Equivalence Point)

Chemical Species Present:  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_3\text{O}^+$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$   
 SB SA A/B

Net-Ionic Equation:  $\text{CH}_3\text{NH}_2_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{CH}_3\text{NH}_3^+_{(aq)}$

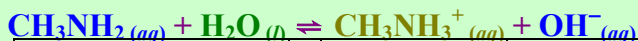
|        | $n$ of $\text{CH}_3\text{NH}_2$        | $n$ of $\text{H}_3\text{O}^+$              | $n$ of $\text{CH}_3\text{NH}_3^+$ |
|--------|--|--|-----------------------------------|
| Before | (0.100 mol/L)(30.00 mL)<br>= 3.00 mmol | (0.200 mol/L)(7.50 mL)<br>= 1.50 mmol (LR) | 0 mmol                            |
| Change | - 1.50 mmol                            | - 1.50 mmol                                | + 1.50 mmol                       |
| After  | 1.50 mmol                              | 0 mmol                                     | 1.50 mmol                         |

$$[\text{CH}_3\text{NH}_2] = \frac{n_{\text{CH}_3\text{NH}_2}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$$[\text{CH}_3\text{NH}_3^+] = \frac{n_{\text{CH}_3\text{NH}_3^+}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

}  $[\text{CH}_3\text{NH}_3^+] = [\text{CH}_3\text{NH}_2]$   
 $\text{pH} \approx \text{p}K_a$   
 (Max Buffer Capacity)

After all the  $\text{H}_3\text{O}^+$  is used up, the resulting solution follows the regular weak base dissociation.



|             | $[\text{CH}_3\text{NH}_2]$ | $[\text{CH}_3\text{NH}_3^+]$ | $[\text{OH}^-]$ |
|-------------|----------------------------|------------------------------|-----------------|
| Initial     | 0.0400 M                   | 0                            | 0.0400 M        |
| Change      | -x                         | +x                           | +x              |
| Equilibrium | (0.04 - x)                 | x                            | (0.04 + x)      |

CANNOT use Approximation:

$$\frac{[\text{CH}_3\text{NH}_2]_0}{K_b} = \frac{0.0400 \text{ M}}{4.38 \times 10^{-4}} = 91.3 < 1000$$

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} \quad 4.38 \times 10^{-4} = \frac{(x)(0.04 + x)}{(0.04 - x)}$$

$$[\text{OH}^-] = x = 4.29 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(4.29 \times 10^{-4}) = 3.37$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.37$$

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on the next page.)

$\text{pH} = 10.63$

c. At 15.00 mL of  $\text{HCl}_{(aq)}$  added: (Stoichiometric Point)

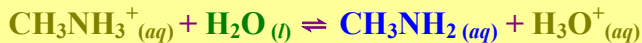
Chemical Species Present:  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_3\text{O}^+$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$   
 SB SA A/B

Net-Ionic Equation:  $\text{CH}_3\text{NH}_2_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{CH}_3\text{NH}_3^+_{(aq)}$

|        | $n$ of $\text{CH}_3\text{NH}_2$        | $n$ of $\text{H}_3\text{O}^+$          | $n$ of $\text{CH}_3\text{NH}_3^+$ |
|--------|--|--|-----------------------------------|
| Before | (0.100 mol/L)(30.00 mL)<br>= 3.00 mmol | (0.200 mol/L)(15.00 mL)<br>= 3.00 mmol | 0 mmol                            |
| Change | - 3.00 mmol                            | - 3.00 mmol                            | + 3.00 mmol                       |
| After  | 0 mmol                                 | 0 mmol                                 | 3.00 mmol                         |

$$[\text{CH}_3\text{NH}_3^+] = \frac{n_{\text{CH}_3\text{NH}_3^+}}{\text{Total Volume}} = \frac{3.00 \text{ mmol}}{(30.00 \text{ mL} + 15.00 \text{ mL})} = 0.0667 \text{ mol/L}$$

At Stoichiometric Point, after all the  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{NH}_2$  are used up, the resulting solution follows the regular weak acid dissociation.



|                    |                              |                            |                          |
|--------------------|------------------------------|----------------------------|--------------------------|
|                    | $[\text{CH}_3\text{NH}_3^+]$ | $[\text{CH}_3\text{NH}_2]$ | $[\text{H}_3\text{O}^+]$ |
| <b>Initial</b>     | 0.0667 M                     | 0                          | 0 M                      |
| <b>Change</b>      | -x                           | +x                         | +x                       |
| <b>Equilibrium</b> | (0.0667 - x)                 | x                          | x                        |

CAN use Approximation:

$$\frac{[\text{CH}_3\text{NH}_3^+]_0}{K_a} = \frac{0.0667 \text{ M}}{2.28 \times 10^{-11}} = 2.9 \times 10^9 \geq 1000$$

Use 0.0667 in the denominator, because  $(0.0667 - x) \approx 0.03667$  [x is so small compared to 0.0667 M].

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.38 \times 10^{-4}} \quad K_a = 2.28 \times 10^{-11} = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$2.28 \times 10^{-11} = \frac{(x)(x)}{(0.0667 - x)} \approx \frac{x^2}{0.0667}$$

$$[\text{H}_3\text{O}^+] = x = 1.23 \times 10^{-6} \text{ mol/L} \quad \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.23 \times 10^{-6})$$

**pH = 5.91**

e. At 20.00 mL of  $\text{HCl} (aq)$  added: (After Stoichiometric Point)

Chemical Species Present:  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_3\text{O}^+$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$   
   SB          SA          A/B



|               |   |   |
|---------------|---|---|
|               | <b>n of <math>\text{CH}_3\text{NH}_2</math></b> | <b>n of <math>\text{H}_3\text{O}^+</math></b> |
| <b>Before</b> | (0.100 mol/L)(30.00 mL)<br>= 3.00 mmol (LR)     | (0.200 mol/L)(20.00 mL)<br>= 4.00 mmol        |
| <b>Change</b> | - 3.00 mmol                                     | - 3.00 mmol                                   |
| <b>After</b>  | 0 mmol  | 1.00 mmol                                     |

After all the  $\text{CH}_3\text{NH}_2$  is used up, the resulting solution has the following major species.

Chemical Species Present:  $\text{Cl}^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}$   
   SA          A/B

$$[\text{H}_3\text{O}^+] = \frac{n_{\text{H}_3\text{O}^+}}{\text{Total Volume}} = \frac{1.00 \text{ mmol}}{(30.00 \text{ mL} + 20.00 \text{ mL})} = 0.0200 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(0.0200)$$

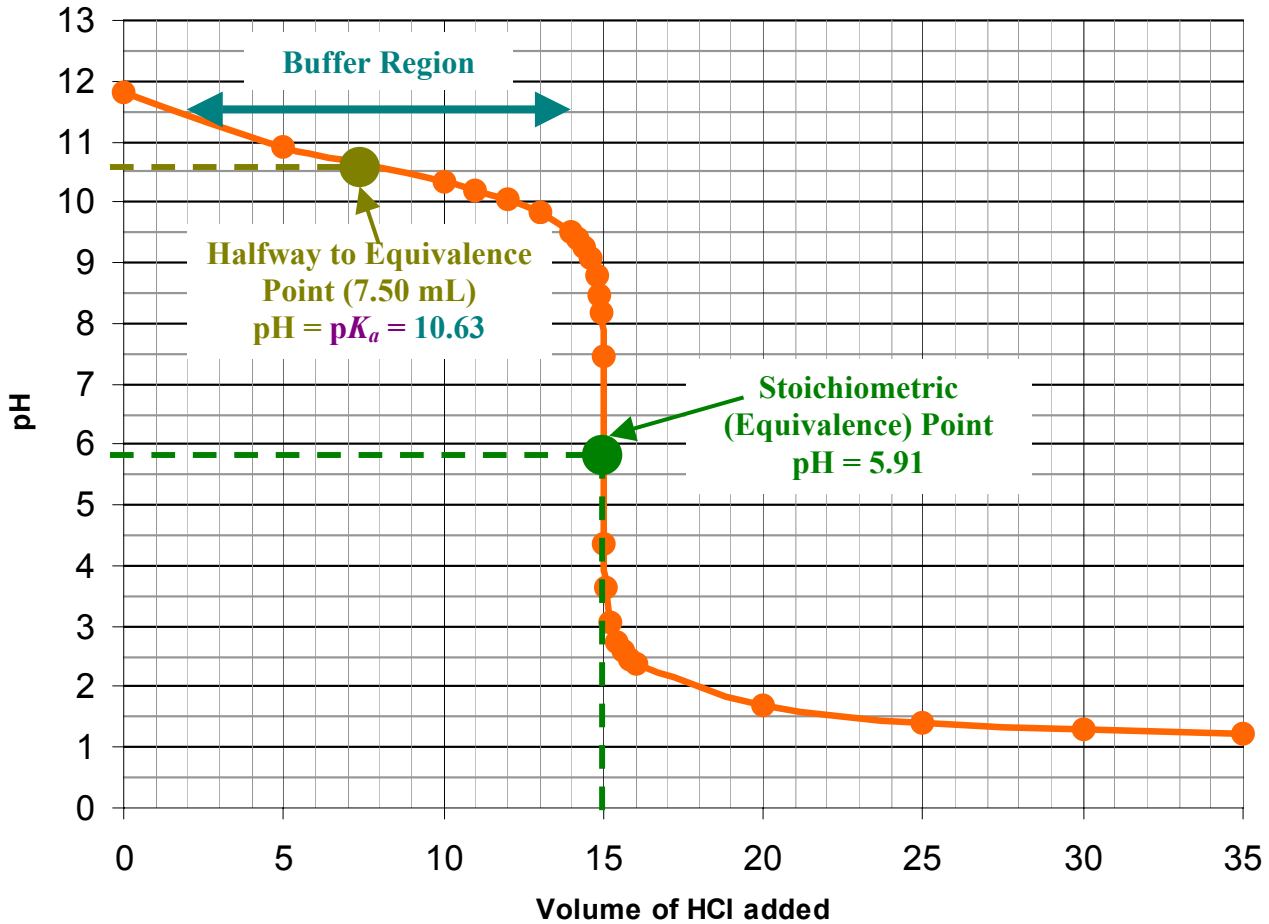
**pH = 1.70**

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)

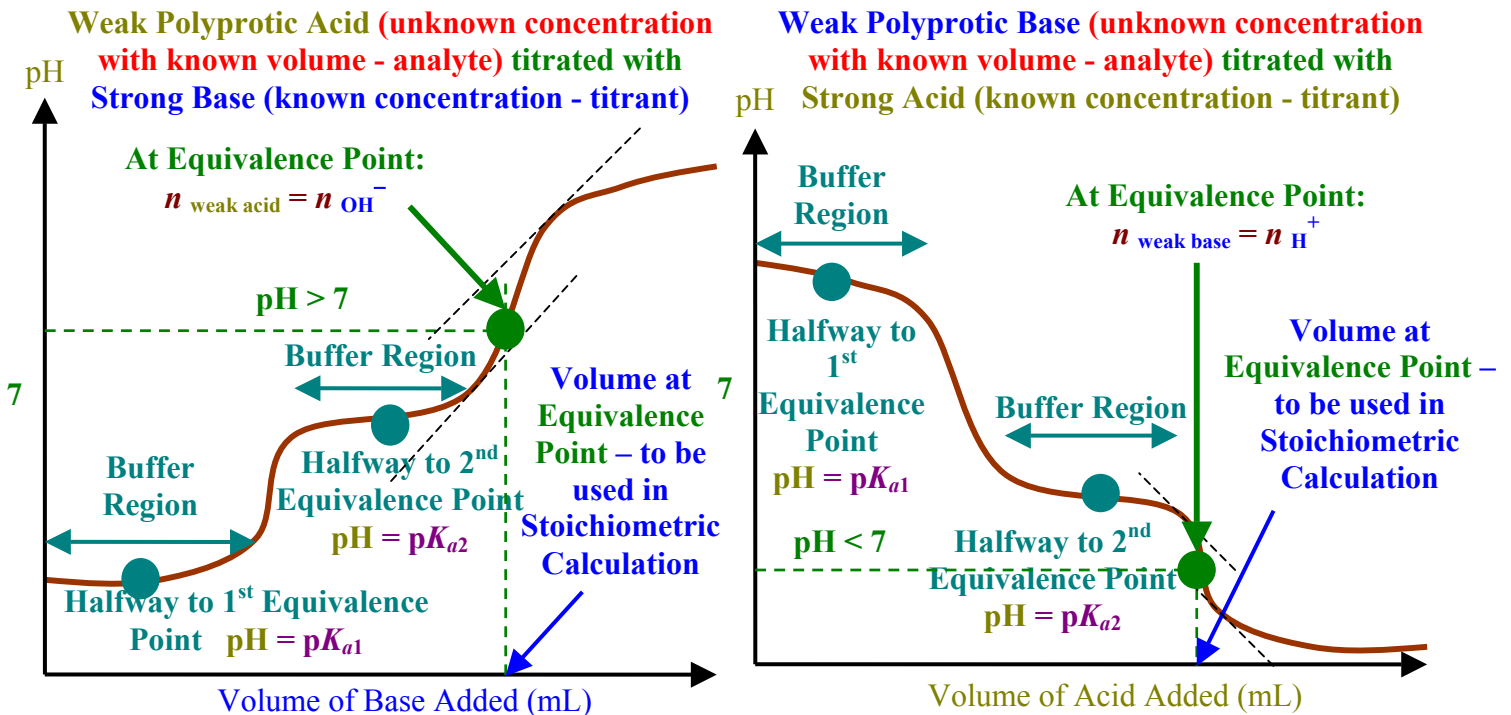
**pH of 30.0 mL of 0.100 M  $\text{CH}_3\text{NH}_2 (aq)$  titrated by 0.200 M of  $\text{HCl} (aq)$**

| Volume of HCl added              | pH    | Volume of HCl added    | pH   | Volume of HCl added | pH   |
|----------------------------------|-------|------------------------|------|---------------------|------|
| 0.00 mL                          | 11.81 | 14.40 mL               | 9.26 | 15.20 mL            | 3.05 |
| 5.00 mL                          | 10.92 | 14.60 mL               | 9.08 | 15.40 mL            | 2.75 |
| 7.50 mL (Halfway to Equivalence) | 10.63 | 14.80 mL               | 8.77 | 15.60 mL            | 2.58 |
| 10.00 mL                         | 10.33 | 14.90 mL               | 8.47 | 15.80 mL            | 2.46 |
| 11.00 mL                         | 10.20 | 14.95 mL               | 8.16 | 16.00 mL            | 2.36 |
| 12.00 mL                         | 10.03 | 14.99 mL               | 7.46 | 20.00 mL            | 1.70 |
| 13.00 mL                         | 9.82  | 15.00 mL (Equivalence) | 5.91 | 25.00 mL            | 1.40 |
| 14.00 mL                         | 9.49  | 15.01 mL               | 4.35 | 30.00 mL            | 1.30 |
| 14.20 mL                         | 9.39  | 15.05 mL               | 3.65 | 35.00 mL            | 1.21 |

**pH of 30.0 mL of 0.100 M Methylamine titrated by 0.200 M of HCl**



4. **Titration Between Strong Acid/Bases and Polyprotic Acid/Base:** - there are multiple equivalence points.  
 - the last equivalence point indicates the stoichiometric volume.



**Example 4:** Calculate the concentration of 10.00 mL of  $\text{Na}_2\text{S}_{(aq)}$  is titrated with 0.0350 M of  $\text{HBr}_{(aq)}$  when the first and second equivalence points are at 13.34 mL and 27.88 mL respectively.

**For Acid-Base Stoichiometry, do NOT write the Net-Ionic Equation. Write the Molecular Equation to do Stoichiometry. We use the second equivalence point because  $\text{Na}_2\text{S}$  can accept two protons.**



$$\textcircled{1} n_{\text{HBr}} = CV = (0.0350 \text{ mol/L}) (27.88 \text{ mL}) = 0.9758 \text{ mmol}$$

$$\textcircled{2} n_{\text{Na}_2\text{S}} = 0.9758 \text{ mmol HBr} \times \frac{1 \text{ mol Na}_2\text{S}}{2 \text{ mol HBr}} = 0.4879 \text{ mmol Na}_2\text{S}$$

$$\textcircled{3} [\text{Na}_2\text{S}] = \frac{n}{V} = \frac{0.4879 \text{ mmol}}{10.0 \text{ mL}} = 0.04879 \text{ mol/L}$$

$$[\text{Na}_2\text{S}] = 0.0488 \text{ mol/L}$$

### 15.5: Acid-Base Indicators

**Acid-Base Indicators:** - chemicals that change colours at a specific pH range.

- they are themselves organic acids. Since they are usually very big structurally, we usually use abbreviations to describe them in chemical equations.
- this is due to the acidic form of the indicator ( $\text{HIn}$ ) has a different colour than its basic form ( $\text{In}^-$ ).

- the colour change occurs when  $\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$  (titrating an acid with a base) or when

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{10}{1} \text{ (titrating a base with an acid).}$$

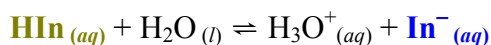
**Using the Henderson-Hasselbach Equation to determine pH Range for Indicators to Change Colour:**

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) \quad \text{(Substitute observable Colour Change Ratio } \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10} \text{ or } \frac{10}{1}\text{)}$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{1}{10}\right) \quad \text{or} \quad \text{pH} = \text{p}K_a + \log\left(\frac{10}{1}\right)$$

$$\text{pH} = \text{p}K_a - 1 \quad \text{or} \quad \text{pH} = \text{p}K_a + 1$$

#### pH Range for Indicators to Change Colour



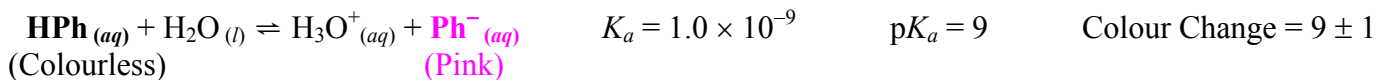
$$\text{pH} = \text{p}K_a \pm 1$$

$$\text{pH} \leq (\text{p}K_a - 1) \rightarrow \text{Colour of HIn}_{(aq)}$$

$$\text{pH} \geq (\text{p}K_a + 1) \rightarrow \text{Colour of In}^-_{(aq)}$$

$$\text{pH} = \text{p}K_a \rightarrow \text{Mixed Colours of HIn}_{(aq)} + \text{In}^-_{(aq)}$$

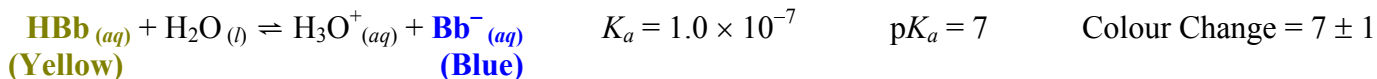
**Example:** Phenolphthalein ( $\text{HPh}_{(aq)}/\text{Ph}^-_{(aq)}$ ) changes colours from colourless to pink at a pH range of 8.0 to 10.0. At its **mid-range (9.0 – average of 8.0 and 10.0)**, the colour would be **light pink (colourless + pink)**.



At  $\text{pH} \leq 9$ , phenolphthalein is colourless.

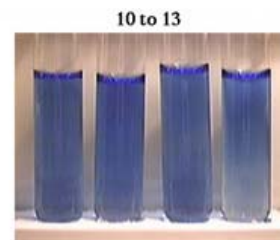
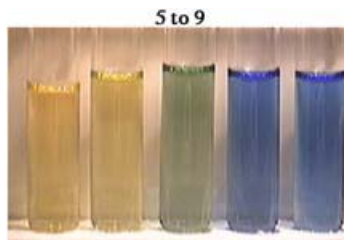
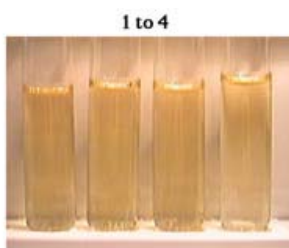
At  $\text{pH} \geq 10$ , phenolphthalein is pink.

**Example:** Bromothymol Blue ( $\text{HBb}_{(aq)}/\text{Bb}^-_{(aq)}$ ) changes colours from yellow to blue at a pH range of 6.0 to 8.0. At its **mid-range (7.0 – average of 6.0 and 8.0)**, the colour would be **green (yellow + blue)**.



At  $\text{pH} \leq 6$ , bromothymol blue is yellow.

At  $\text{pH} \geq 8$ , bromothymol blue is blue.



**Example 1:** Using the pH curve of methylamine with HCl on page 310 (equivalence point at  $\text{pH} = 5.91$ ), and the following information below, decide on an indicator to use in this titration and state what colour change the experimenter should be looking for.

| Indicators       | Colour Change  | $K_a$                |
|------------------|----------------|----------------------|
| methyl orange    | red to yellow  | $3.5 \times 10^{-4}$ |
| methyl red       | red to yellow  | $1.0 \times 10^{-5}$ |
| chlorophenol red | yellow to red  | $5.6 \times 10^{-7}$ |
| bromothymol blue | yellow to blue | $1.0 \times 10^{-7}$ |

First, we need to decide on the pH range that these indicators will change colors.

| Indicators         | Colour Change    | $K_a$                | pH range ( $\text{p}K_a \pm 1$ ) |
|--------------------|------------------|----------------------|----------------------------------|
| methyl orange      | red to yellow    | $1.6 \times 10^{-4}$ | $3.8 \pm 1$ (2.8 to 4.8)         |
| methyl red         | red to yellow    | $1.0 \times 10^{-5}$ | $5.0 \pm 1$ (4.0 to 6.0)         |
| bromocresol purple | yellow to purple | $2.0 \times 10^{-6}$ | $5.7 \pm 1$ (4.7 to 6.7)         |
| bromothymol blue   | yellow to blue   | $1.0 \times 10^{-7}$ | $7.0 \pm 1$ (6.0 to 8.0)         |

We can see that  $\text{pH} = 5.91$  is well within the color change of **bromocresol purple** (for methyl red, it is too close to the boundary point). **The color where the experimenter will stop is brown (yellow + purple) with the  $\text{pH} = 5.7$  (end-point).**

### Assignment

**15.3 pg. 775 #39 to 50**

**15.4 pg. 775–776 #51 to 61 and 63**

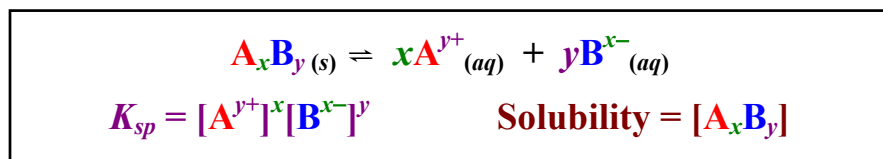
**15.5 pg. 776–777 #65 to 72**



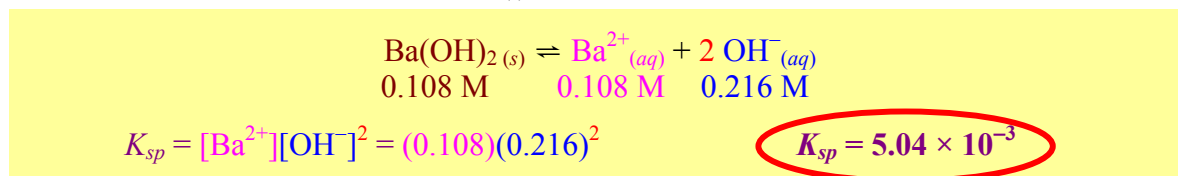
**15.6: Solubility Equilibria and the Solubility Product**

**Solubility Product ( $K_{sp}$ ):** - the equilibrium constant as a salt dissolves into its aqueous ions.  
 - sometimes refer to as **solubility product constant**.  
 - like equilibrium constant,  **$K_{sp}$  is unitless**.

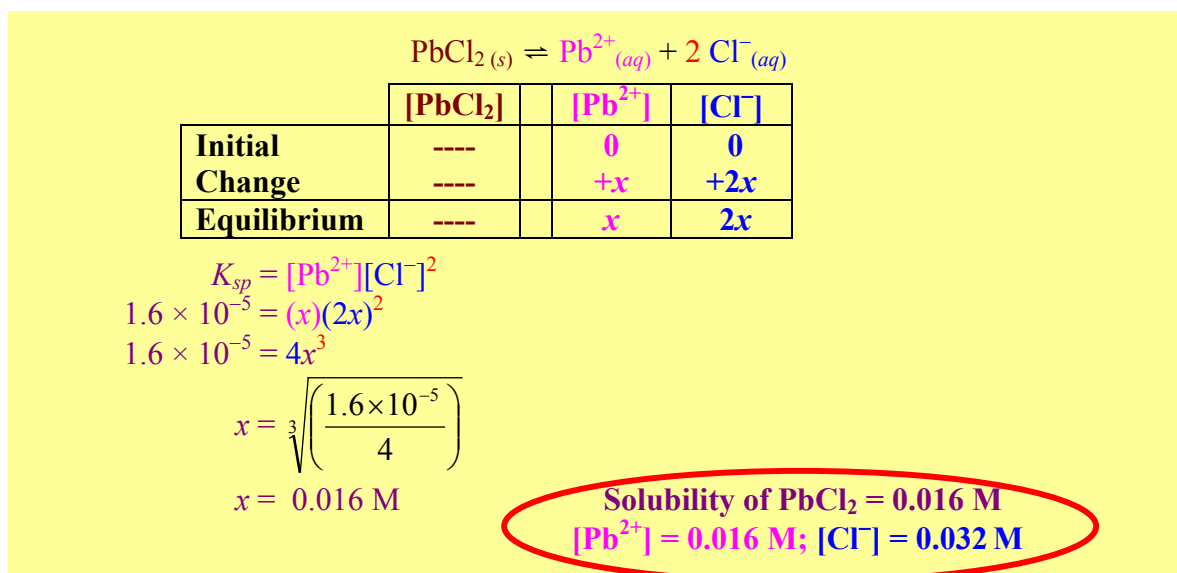
**Solubility:** - the equilibrium position of the solvation equilibrium.  
 - the maximum amount of salts in moles dissolved per Litre of solvent.



**Example 1:** The solubility of  $Ba(OH)_2 (s)$  is 0.108 mol/L. Determine the molar concentration of each ion and the solubility product of  $Ba(OH)_2 (s)$ .



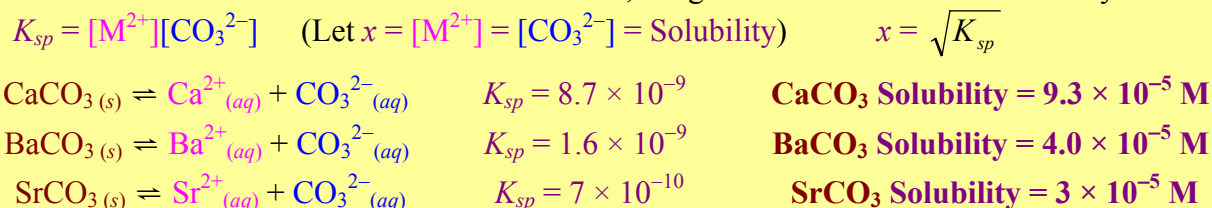
**Example 2:** The  $K_{sp}$  for lead (II) chloride is  $1.6 \times 10^{-5}$ . Calculate the molar concentrations of each ion and the solubility of solid lead (II) chloride.



**Relative Solubility:** - how the solubilities of various salts compare.  
 - **the solubilities of salts can only be compared directly from  $K_{sp}$  values when the salts produce the same number of ions.** (In general, the bigger the  $K_{sp}$ , the higher the solubility.)  
 - **the solubilities of salts that produce Different Number of Ions CANNOT be compared directly from  $K_{sp}$ .** They must be calculated individually before comparison can be made.

**Example 3:** Compare the solubilities of  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and  $\text{SrCO}_3$  with the  $K_{sp}$  values as  $8.7 \times 10^{-9}$ ,  $1.6 \times 10^{-9}$ , and  $7 \times 10^{-10}$  respectively.

Since all salts listed here have the same number of ions, the general solution for the solubility is as follows:



**The Solubility increases from  $\text{SrCO}_3 < \text{BaCO}_3 < \text{CaCO}_3$ .** (Since  $\text{CaCO}_3$  has the largest  $K_{sp}$  and all salts have the same number of ions dissociated,  $\text{CaCO}_3$  has the highest solubility.)

**Example 4:** Compare the solubilities of  $\text{AgCl}$ ,  $\text{Ag}_2\text{CO}_3$ , and  $\text{Ag}_3\text{PO}_4$  with the  $K_{sp}$  values as  $1.6 \times 10^{-10}$ ,  $8.1 \times 10^{-12}$ ,  $1.8 \times 10^{-18}$  respectively.

Since all salts listed here have different number of ions, the solubility of each salt has to be calculated separately.



|             | [AgCl] | [Ag <sup>+</sup> ] | [Cl <sup>-</sup> ] |
|-------------|--------|--------------------|--------------------|
| Initial     | ----   | 0                  | 0                  |
| Change      | ----   | +x                 | +x                 |
| Equilibrium | ----   | x                  | x                  |

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.6 \times 10^{-10} = (x)(x)$$

$$1.6 \times 10^{-10} = x^2$$

$$x = \sqrt{1.6 \times 10^{-10}}$$

$$x = 1.3 \times 10^{-5} \text{ M}$$

**Solubility of  $\text{AgCl} = 1.3 \times 10^{-5} \text{ M}$**



|             | [Ag <sub>2</sub> CO <sub>3</sub> ] | [Ag <sup>+</sup> ] | [CO <sub>3</sub> <sup>2-</sup> ] |
|-------------|------------------------------------|--------------------|----------------------------------|
| Initial     | ----                               | 0                  | 0                                |
| Change      | ----                               | +2x                | +x                               |
| Equilibrium | ----                               | 2x                 | x                                |

$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$

$$8.1 \times 10^{-12} = (2x)^2(x)$$

$$8.1 \times 10^{-12} = 4x^3$$

$$x = \sqrt[3]{\left(\frac{8.1 \times 10^{-12}}{4}\right)} = 1.3 \times 10^{-4} \text{ M}$$

**Solubility of  $\text{Ag}_2\text{CO}_3 = 1.3 \times 10^{-4} \text{ M}$**



|             | [Ag <sub>3</sub> PO <sub>4</sub> ] | [Ag <sup>+</sup> ] | [PO <sub>4</sub> <sup>3-</sup> ] |
|-------------|------------------------------------|--------------------|----------------------------------|
| Initial     | ----                               | 0                  | 0                                |
| Change      | ----                               | +3x                | +x                               |
| Equilibrium | ----                               | 3x                 | x                                |

$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

$$1.8 \times 10^{-18} = (3x)^3(x)$$

$$1.8 \times 10^{-18} = 27x^4$$

$$x = \sqrt[4]{\left(\frac{1.8 \times 10^{-18}}{27}\right)} = 1.6 \times 10^{-5} \text{ M}$$

**Solubility of  $\text{Ag}_3\text{PO}_4 = 1.6 \times 10^{-5} \text{ M}$**

**The Solubility increases from  $\text{AgCl} < \text{Ag}_3\text{PO}_4 < \text{Ag}_2\text{CO}_3$ .** Again we can see here because these salts do not dissociate the same number of ions, we cannot compare their solubilities directly from their  $K_{sp}$  values.

**Common-Ion Effect and Solubility:** - when a solution containing a common ion of a salt is used as a solvent, the **solubility of the salt will lower** as a result.  
- set up equilibrium ICE Box to assist in calculation.

**Example 5:** A solution of 0.0150 M of KBr is used as a solvent for solid  $\text{PbBr}_2$ . Calculate the final concentrations for both ions and the solubility of  $\text{PbBr}_2(s)$  given that  $K_{sp}$  for  $\text{PbBr}_2$  is  $4.6 \times 10^{-6}$ .

KBr dissociates completely in water.



|             | $\text{PbBr}_2(s)$   | $\rightleftharpoons$ | $\text{Pb}^{2+}_{(aq)}$ | $+ 2 \text{Br}^-_{(aq)}$ |
|-------------|----------------------|----------------------|-------------------------|--------------------------|
|             | [PbBr <sub>2</sub> ] |                      | [Pb <sup>2+</sup> ]     | [Br <sup>-</sup> ]       |
| Initial     | ----                 |                      | 0                       | 0.0150 M                 |
| Change      | ----                 |                      | +x                      | +2x                      |
| Equilibrium | ----                 |                      | x                       | 0.0150 + 2x              |

**CANNOT use Approximation:**

$$\frac{[\text{Br}^-]_0^2}{K_{sp}} = \frac{(0.0150 \text{ M})^2}{4.6 \times 10^{-6}} = 48.9 < 1000$$

Because in the  $K_{sp}$  expression,  $\text{Br}^-$  is squared, the rule of thumb must reflect this operation.

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

$$4.6 \times 10^{-6} = (x)(0.0150 + 2x)^2$$

$$x = 0.0062 \text{ M}$$

```
solve(X(0.0150+2
X)^2-4.6E-6,X,0,(
0,.0150/2))
.006161609
```

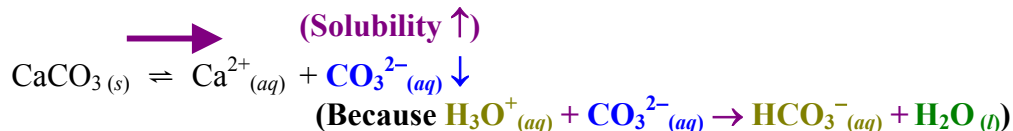
$$[\text{Br}^-] = 0.0150 \text{ M} + 2(0.0062 \text{ M})$$

**Solubility of  $\text{PbBr}_2$  in 0.0150 M of  $\text{KBr}_{(aq)}$  = 0.0062 M**  
 **$[\text{Pb}^{2+}] = 0.0062 \text{ M}$ ;  $[\text{Br}^-] = 0.027 \text{ M}$**

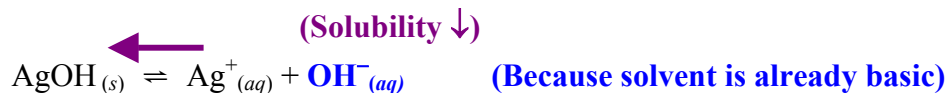
Note: If there was no common ion, the solubility of  $\text{PbBr}_2$  would be 0.010 M. Hence, **with the presence of a common ion, the solubility of a salt is lowered.**

**pH and Solubility:** - when salts containing effective bases of weak acids ( $\text{OH}^-$ ,  $\text{S}^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{CrO}_4^{2-}$ ) are dissolved in acids, their solubilities increases.  
- conversely, if these effective bases salts are dissolved in bases, their solubilities decreases.

**Example:** Calcium carbonate is dissolved in acidic solution.



**Example:** Silver hydroxide is dissolved in basic solution.



**15.7: Precipitation and Qualitative Analysis**

**Ion Product ( $Q$ ):** - similar to reaction quotient, it measures the initial ion concentrations and compares it with  $K_{sp}$ .

$$Q = [A^{j+}]_0^x [B^{x-}]_0^y$$

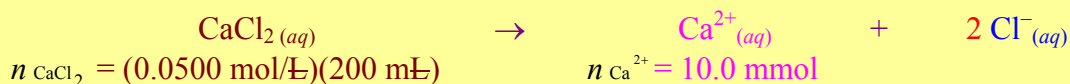
- a. **When  $Q > K_{sp}$ , the system will shift to the solid salt (reactant).** In this condition,  $Q$  indicates that **there are too much ions (products)**. Therefore, the system has to **Shift back to the Left and Precipitation occurs**.
- b. **When  $Q < K_{sp}$ , the system will shift to the ions (product).** In this condition,  $Q$  indicates that **there are too little ions (products)**. Therefore, the system has to **Shift to the Right and there will be NO Precipitation**.

**Calculations involving Ion Product and Final Ion Concentrations:**

- Determine the **Initial Concentrations** of the ions that will likely form a precipitate. (Remember to divide the moles by the total volume.)
- Calculate the **Ion product**.
- Compare it to the  $K_{sp}$  value** of the solid and decide whether precipitation will form.
- If precipitation occurs ( $Q > K_{sp}$ ), then **write the net ionic equation for the precipitation**.
- Using regular stoichiometry**, run the reaction to completion and **determine the concentration of the excess ion**.
- Redo the equilibrium for dissolving**. Using  $K_{sp}$  and the excess ion concentration as initial concentration to find the **final concentrations of both ions**.

**Example 1:** 200 mL of 0.0500 M of calcium chloride is reacted with 150 mL of 0.0600 M of ammonium phosphate. Determine whether  $\text{Ca}_3(\text{PO}_4)_2$  will precipitate and calculate the concentrations of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  in the final solution. The  $K_{sp}$  value of  $\text{Ca}_3(\text{PO}_4)_2$  is  $1.3 \times 10^{-32}$ .

Both  $\text{CaCl}_2$  and  $(\text{NH}_4)_3\text{PO}_4$  dissociates completely in water.

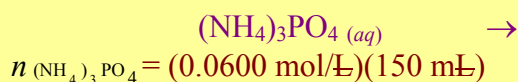


$$n_{\text{CaCl}_2} = (0.0500 \text{ mol/L})(200 \text{ mL})$$

$$n_{\text{Ca}^{2+}} = 10.0 \text{ mmol}$$

$$n_{\text{CaCl}_2} = 10.0 \text{ mmol}$$

$$[\text{Ca}^{2+}]_0 = \frac{10.0 \text{ mmol}}{350 \text{ mL}} = 0.0285714286 \text{ M}$$



$$n_{(\text{NH}_4)_3\text{PO}_4} = (0.0600 \text{ mol/L})(150 \text{ mL})$$

$$n_{\text{PO}_4^{3-}} = 9.00 \text{ mmol}$$

$$n_{(\text{NH}_4)_3\text{PO}_4} = 9.00 \text{ mmol}$$

$$[\text{PO}_4^{3-}]_0 = \frac{9.00 \text{ mmol}}{350 \text{ mL}} = 0.0257142857 \text{ M}$$



Calculating Ion Product:  $Q = [\text{Ca}^{2+}]_0^3 [\text{PO}_4^{3-}]_0^2 = (0.0285714286)^3 (0.0257142857)^2$   
 $Q = 1.5 \times 10^{-8}$

$Q (1.5 \times 10^{-8}) > K_{sp} (1.3 \times 10^{-32})$  **Precipitation Occurs**

Running the precipitation reaction to completion and using regular stoichiometry,

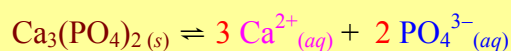


|        | $n$ of $\text{Ca}^{2+}$ | $n$ of $\text{PO}_4^{3-}$                      |
|--------|-------------------------|--|
| Before | 10.0 mmol (LR)          | 9.00 mmol                                      |
| Change | -10.00 mmol             | $-\left(\frac{2}{3}\right)(10.0 \text{ mmol})$ |
| After  | 0 mmol                  | 2.33333333 mmol                                |

$$\text{New } [\text{PO}_4^{3-}]_0 = \frac{2.33333333 \text{ mmol}}{350 \text{ mL}}$$

$$\text{New } [\text{PO}_4^{3-}]_0 = 0.019047619 \text{ M}$$

Finally, using  $K_{sp}$  and the new  $[\text{PO}_4^{3-}]_0$ ,



|             | $[\text{Ca}_3(\text{PO}_4)_2]$ | $[\text{Ca}^{2+}]$ | $[\text{PO}_4^{3-}]$ |
|-------------|--------------------------------|--------------------|----------------------|
| Initial     | ----                           | 0                  | 0.019047619 M        |
| Change      | ----                           | +3x                | +2x                  |
| Equilibrium | ----                           | 3x                 | 0.019047619 + 2x     |

$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

$$1.3 \times 10^{-32} = (3x)^3 (0.019047619 + 2x)^2$$

$$1.3 \times 10^{-32} \approx (3x)^3 (0.019047619)^2$$

$$x^3 \approx \frac{1.3 \times 10^{-32}}{(3)^3 (0.019047619)^2}$$

$$x \approx \sqrt[3]{\frac{1.3 \times 10^{-32}}{(3)^3 (0.019047619)^2}} \approx 1.0989 \times 10^{-10}$$

$$[\text{Ca}^{2+}] = 3(1.0989 \times 10^{-10} \text{ M})$$

$$[\text{Ca}^{2+}] = 3.3 \times 10^{-10} \text{ M}$$

$$[\text{PO}_4^{3-}] = 0.019047619 \text{ M} + 2(1.0989 \times 10^{-10} \text{ M})$$

$$[\text{PO}_4^{3-}] = 0.019 \text{ M}$$

CAN use Approximation:

$$\frac{[\text{PO}_4^{3-}]_0^2}{K_{sp}} = \frac{(0.019047619 \text{ M})^2}{1.3 \times 10^{-32}}$$

$$= 2.8 \times 10^{28} \gg 1000$$

Because in the  $K_{sp}$  expression,  $\text{PO}_4^{3-}$  is squared, the rule of thumb must reflect this operation.

Use 0.019047619 in the denominator, because  $(0.019047619 + 2x) \approx 0.019047619$  [ $2x$  is so small compared to 0.019047619 M].

- Selective Precipitation:** - by using a chemical reagent with an anion that will form precipitates with metal ions in a solution, the salts of each of these metal ions can be separated because one will precipitate first.
- when two or more precipitates is likely to form, **the solid with the lowest anion concentration at its  $K_{sp}$  will precipitate first.**
  - recall that **we can only use  $K_{sp}$  to compare solubilities if and only if the solids can produce the same number of ions.** Otherwise, we have to calculate the anion concentration needed of each salt individually.

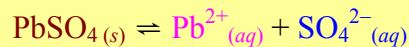
**Example 2:** A chemical reagent consisting of  $\text{SO}_4^{2-}(\text{aq})$  is slowly poured into a solution containing  $3.00 \times 10^{-3} \text{ mol/L}$  of  $\text{Ag}^+(\text{aq})$  and  $1.50 \times 10^{-4} \text{ mol/L}$  of  $\text{Pb}^{2+}(\text{aq})$ . The  $K_{sp}$  values of  $\text{Ag}_2\text{SO}_4$  and  $\text{PbSO}_4$  are  $1.2 \times 10^{-5}$  and  $1.3 \times 10^{-8}$  respectively. Determine which of the above solids will precipitate first by calculating the  $[\text{SO}_4^{2-}]$  require for each solid.



$$K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$$

$$1.2 \times 10^{-5} = (3.00 \times 10^{-3})^2[\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = \frac{1.2 \times 10^{-5}}{(3.00 \times 10^{-3})^2}$$



$$K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$1.3 \times 10^{-8} = (1.50 \times 10^{-3})[\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = \frac{1.3 \times 10^{-8}}{1.50 \times 10^{-3}}$$

$[\text{SO}_4^{2-}] = 1.3 \text{ M}$  is needed for  $\text{Ag}_2\text{SO}_4(\text{s})$  to form     $[\text{SO}_4^{2-}] = 8.7 \times 10^{-5} \text{ M}$  is needed for  $\text{PbSO}_4(\text{s})$  to form

Since  $[\text{SO}_4^{2-}]$  is less for  $\text{PbSO}_4(\text{s})$  to form, lead (II) sulfate will precipitate first as  $\text{SO}_4^{2-}(\text{aq})$  is slowly added to the solution.  $\text{PbSO}_4$  can then be separated leaving the  $\text{Ag}^+(\text{aq})$  in the filtrate.

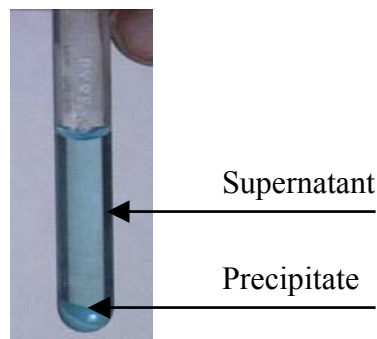
**Centrifuge:** - a device that speeds up the precipitation process by the use of centrifugal force (spinning the test tubes really fast).

**Supernatant:** - the liquid that remained after the precipitate is collected at the bottom of a test tube from the centrifuge process.

test tube wells

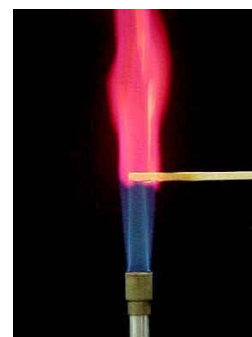
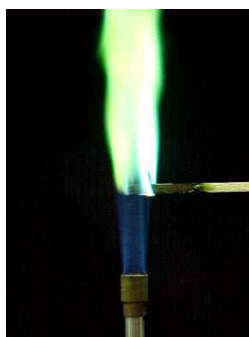
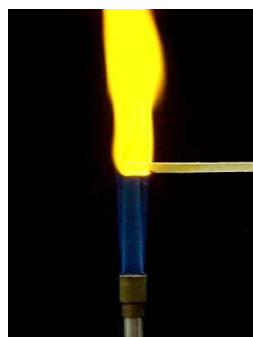


A typical laboratory centrifuge. Test tubes are placed inside the wells and the spinning will pull the precipitate down to the bottom.



**Flame Test:** - a test performed on a salt to detect the identity of a metal ion by the colour of the flame emitted as it is placed over a lighted Bunsen-burner.

- the principle of a metal ion emitting a certain visible colour is due to the electrons are excited to jump into higher orbitals as it is placed in a flame. As they come down to the lower orbital, a unique frequency is given in the visible spectrum producing a specific colour.



From left to right:  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{CuCl}_2$ , and  $\text{SrCl}_2$  produce different colors during the flame tests

**Qualitative Analysis:** - testing for the identities of metal ions by using selective precipitation or flame tests.  
- usually both tests are used to identify the exact metal ions in the solution.

**Developing a Qualitative Analysis Scheme:**

- HCl is used to precipitate with  $\text{Pb}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ , and  $\text{Cu}^+$**  because their  $K_{sp}$  with  $\text{Cl}^-$  are small.
- Sulfide ion ( $\text{S}^{2-}$ ) in acidic solution such as  $\text{H}_2\text{S}_{(aq)}$  is commonly used to precipitate out the most insoluble salts such as ( $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ , and  $\text{SnS}_2$ ).** At low pH (high  $[\text{H}^+]$ ), the concentration of  $\text{S}^{2-}$  is small. ( $\text{H}_2\text{S}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{HS}^-_{(aq)}$  and  $\text{HS}^-_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{S}^{2-}_{(aq)}$ ) Therefore, metal-sulfide salts with higher  $K_{sp}$  values will remain in the solution as metal ions.
- Increasing the pH by adding NaOH will make the metal-sulfide salts with higher  $K_{sp}$  values to precipitate out ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cr}^{3+}$ ).** This is because a decrease in the  $[\text{H}^+]$  will drive both acid dissociation reactions forward, increasing the  $[\text{S}^{2-}]$ .
- Finally,  **$\text{CO}_3^{2-}$  is added to precipitate the alkaline-earth ions such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ .**
- At each stage of the analysis, the residual (precipitate) can be filtered out and be subject to a flame test** for more accurate identification. Since alkali-metal ions are soluble with all anions, we will run a flame test on the filtrate or supernatant from step 4 to determine the identity of the remaining metal ions.

**A Common Qualitative Analysis Scheme for most Metal Ions**

| Group Number | Solution Tested                      | Precipitating Reagent             | Solids Precipitated  | Metal Ions Detected   | Flame Tests   |
|--------------|--------------------------------------|-----------------------------------|--|---|---|
| 1            | Unknown                              | 0.1 M HCl                         | $\text{PbCl}_2$ ,<br>$\text{Hg}_2\text{Cl}_2$ ,<br>$\text{AgCl}$ , $\text{TlCl}$ ,<br>and $\text{CuCl}$  | $\text{Pb}^{2+}$ , $\text{Hg}^+$ ,<br>$\text{Ag}^+$ , $\text{Tl}^+$ ,<br>and $\text{Cu}^+$  | $\text{Pb}^{2+}$ - light blue; $\text{Hg}^+$ - white;<br>$\text{Ag}^+$ - gray; $\text{Tl}^+$ - green;<br>$\text{Cu}^+$ - blue green   |
| 2            | Filtrate or Supernatant from Group 1 | $\text{H}_2\text{S}$ at pH 1      | $\text{HgS}$ , $\text{CuS}$ ,<br>$\text{CdS}$ , $\text{Bi}_2\text{S}_3$ ,<br>$\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ ,<br>$\text{SnS}_2$                       | $\text{Hg}^{2+}$ , $\text{Cu}^{2+}$ ,<br>$\text{Cd}^{2+}$ , $\text{Bi}^{3+}$ ,<br>$\text{As}^{3+}$ , $\text{Sb}^{3+}$ ,<br>and $\text{Sn}^{4+}$                       | $\text{Hg}^+$ - white; $\text{Cu}^{2+}$ - blue green<br>$\text{Cd}^{2+}$ - colourless;<br>$\text{As}^{3+}$ - light blue;<br>$\text{Bi}^{3+}$ - yellow brownish;<br>$\text{Sb}^{3+}$ - green; $\text{Sn}^{4+}$ - colourless                  |
| 3            | Filtrate or Supernatant from Group 2 | NaOH at pH 10                     | $\text{MnS}$ , $\text{FeS}$ ,<br>$\text{NiS}$ , $\text{CoS}$ ,<br>$\text{ZnS}$ ,<br>$\text{Fe}(\text{OH})_3$ ,<br>$\text{Al}(\text{OH})_3$ ,<br>$\text{Cr}(\text{OH})_3$ | $\text{Mn}^{2+}$ , $\text{Fe}^{2+}$ ,<br>$\text{Ni}^{2+}$ , $\text{Co}^{2+}$ ,<br>$\text{Zn}^{2+}$ , $\text{Fe}^{3+}$ ,<br>$\text{Al}^{3+}$ , and<br>$\text{Cr}^{3+}$ | $\text{Mn}^{2+}$ - violet<br>$\text{Fe}^{2+}$ & $\text{Fe}^{3+}$ - yellow brownish red<br>$\text{Ni}^{2+}$ - brown; $\text{Co}^{2+}$ - blue<br>$\text{Zn}^{2+}$ - whitish green;<br>$\text{Al}^{3+}$ - colourless; $\text{Cr}^{3+}$ - green |
| 4            | Filtrate or Supernatant from Group 3 | $\text{Na}_2\text{CO}_3$ at pH 10 | $\text{MgCO}_3$ ,<br>$\text{CaCO}_3$ ,<br>$\text{SrCO}_3$ ,<br>$\text{BaCO}_3$   | $\text{Mg}^{2+}$ ,<br>$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$<br>and $\text{Ba}^{2+}$   | $\text{Mg}^{2+}$ - white; $\text{Ca}^{2+}$ - yellowish red<br>$\text{Sr}^{2+}$ - scarlet red;<br>$\text{Ba}^{2+}$ - yellow green  |
| 5            | Filtrate or Supernatant from Group 4 | None                              | Soluble Ions   | $\text{Li}$ , $\text{Na}^+$ ,<br>$\text{K}^+$ , and<br>$\text{NH}_4^+$  | $\text{Li}^+$ - red; $\text{Na}^+$ - yellow;<br>$\text{K}^+$ - violet; $\text{NH}_4^+$ - green  |



**15.8: Equilibria Involving Complex Ion**

**Complex Ion:** - metal ion that is surrounded by Lewis Base (species with electron lone-pairs to donate).  
 - the resulting bonds between the metal ion and these Lewis Bases are called **ligands**.

**Coordination Number:** - the number of ligands that is attached to the metal ion.

**Metal Ions and Coordination Numbers**

| Coordination Number | Metal Ions  | Complex Ion Geometry         |
|---------------------|---|------------------------------|
| 2                   | Cu <sup>+</sup> , Ag <sup>+</sup> , and Au <sup>+</sup>   | Linear                       |
| 4                   | Cu <sup>+</sup> , Au <sup>+</sup> , Mn <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> ,<br>Cu <sup>2+</sup> , Zn <sup>2+</sup> and Au <sup>3+</sup>                        | Tetrahedral or Square Planar |
| 6                   | Mn <sup>2+</sup> , Fe <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Cu <sup>2+</sup> ,<br>Zn <sup>2+</sup> , Sc <sup>3+</sup> , Cr <sup>3+</sup> , and Co <sup>3+</sup> | Octahedral                   |

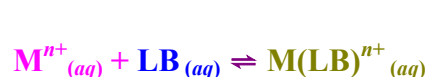
**Formation Constants (K):** - the equilibrium constant of the formation of complex ions from the metal ions and their Lewis bases.

- also refer to as **Stability Constants**.

- for a particular coordination number of a complex ion, there are equal number of formation constants.

- the values of most formation constants are relatively large ( $K_n \gg 1$ ).

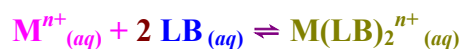
Therefore, we can **assume the formation of complex ions goes to completion**.



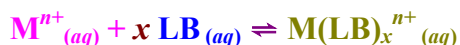
$$K_1 = \frac{[M(LB)^{n+}]}{[M^{n+}][LB]}$$



$$K_2 = \frac{[M(LB)_2^{n+}]}{[M(LB)^{n+}][LB]}$$



$$K = \frac{[M(LB)_2^{n+}]}{[M^{n+}][LB]^2} = K_1 \times K_2 = \frac{\cancel{[M(LB)^{n+}]}}{[M^{n+}][LB]} \times \frac{[M(LB)_2^{n+}]}{\cancel{[M(LB)^{n+}][LB]}}$$

**Overall Formation Constant**

$$K = K_1 \times K_2 \times K_3 \times \dots \times K_x$$

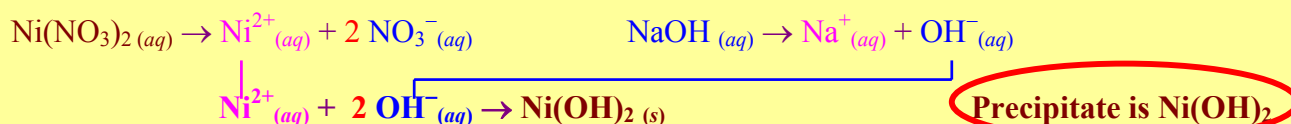


**Complex Ion and Solubility:** - solubility of insoluble salts can be **“re-dissolved”** when mixed with sufficient Lewis base.

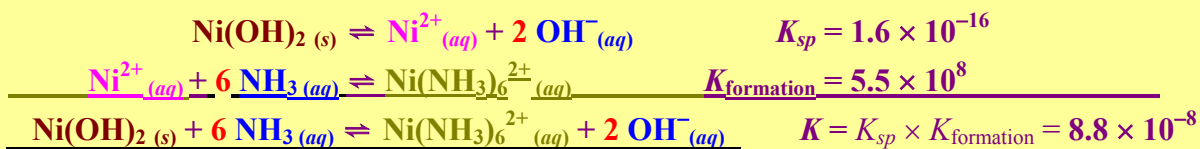
**Example 2:** A NaOH solution is added to  $\text{Ni}(\text{NO}_3)_2(aq)$  and a precipitate forms ( $K_{sp} = 1.6 \times 10^{-16}$ ). Addition of 6.00 M of  $\text{NH}_3(aq)$  redissolved the precipitate into a complex ion with 6 as its coordination number.

- Identify the precipitate and the resulting complex ion.
- Calculate the solubility of the precipitate in  $\text{NH}_3(aq)$  if the overall formation constant is  $5.5 \times 10^8$ . Neglect the volume of the NaOH and  $\text{Ni}(\text{NO}_3)_2$  solutions.

a. Both  $\text{Ni}(\text{NO}_3)_2$  and NaOH dissociates completely in water.



b. We need to calculate the overall formation constant for the complex ion from  $\text{Ni}(\text{OH})_2(s)$ .



|                    | $[\text{Ni}(\text{OH})_2]$ | $[\text{NH}_3]$ | $[\text{Ni}(\text{NH}_3)_6^{2+}]$ | $[\text{OH}^-]$       |
|--------------------|----------------------------|-----------------|-----------------------------------|-----------------------|
| <b>Initial</b>     | ----                       | 6.00 M          | 0 M                               | $\approx 0 \text{ M}$ |
| <b>Change</b>      | ----                       | -6x             | +x                                | +2x                   |
| <b>Equilibrium</b> | ----                       | 6-6x            | x                                 | $\approx 2x$          |

We can assume  $[\text{OH}]_0 \approx 0 \text{ M}$  because of the small value of  $K_{sp}$

$$K = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}][\text{OH}^-]^2}{[\text{NH}_3]^6}$$

$$8.8 \times 10^{-8} = \frac{(x)(2x)^2}{(6-6x)^6} = \frac{4x^3}{(6-6x)^6}$$

$$x = 0.085$$

```
solve(4x^3/(6-6x)^6-8.8E-8,x,0,(0,1))
.0845388877
```

**Solubility of  $\text{Ni}(\text{OH})_2$  in 6.00 M of  $\text{NH}_3(aq)$  = 0.085 M**

### Assignment

15.6 pg. 777–778 #73 to 90

15.7 pg. 778 #91 to 96

15.8 pg. 778–779 #97 to 106