Acids, Bases and Salts

م.م زينب يحيى كاظم

1-THE ARRHENIUS THEORY

❖ **Arrhenius acid**: Any substance that, when dissolved in water, increases the concentration of hydronium ion (H_3O^+)

$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$ **Acid**

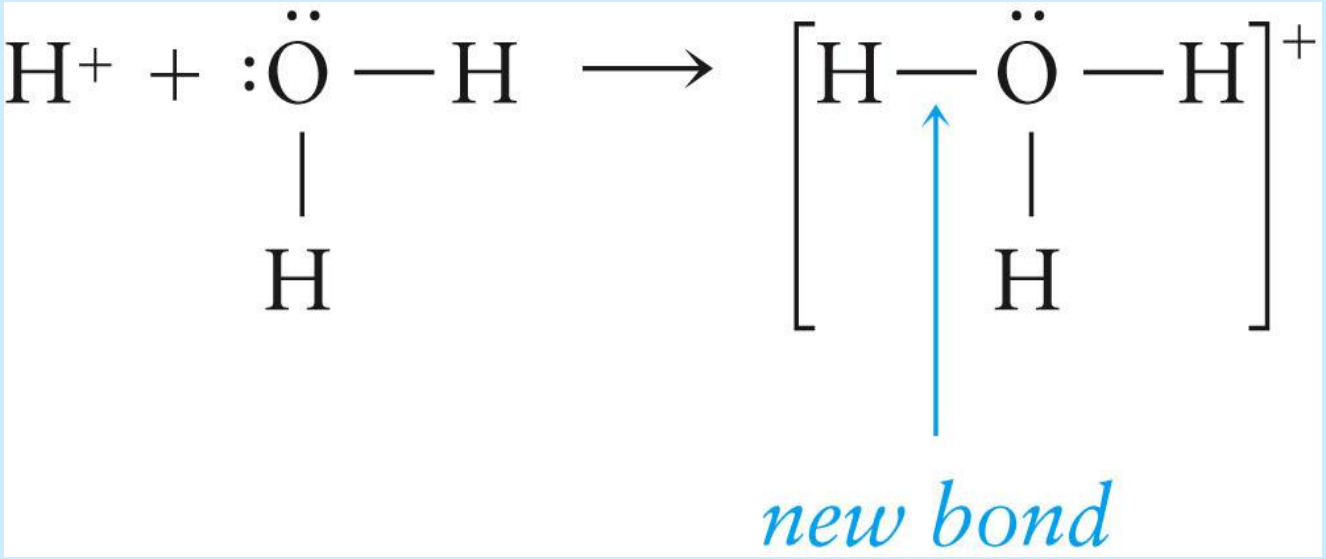
Svante Arrhenius

❖ **Arrhenius base**: Any substance that, when dissolved in water, increases the concentration of hydroxide ion (OH^-)

$NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)$ **Base**

Hydronium Ion

Unknown to Arrhenius **free H^+** ions **do not** exist in water. They **covalently** react with water to produce **hydronium ions**, H_3O^+.



or:

$$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$$

This new bond is called a **coordinate covalent** bond since both new bonding electrons come from the same atom

2-THE BRONSTED-LOERY THEORY

An acid: is a hydrogen containing species that donates a proton.

Bronsted Lowry

$$HClO_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + ClO^-_{(aq)}$$

$$K_a = \frac{[H_3O^+]\,[ClO^-]}{[HClO]}$$

A base: is any substance that accepts a proton"

$$NH_{3\,(aq)} + H_2O_{(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

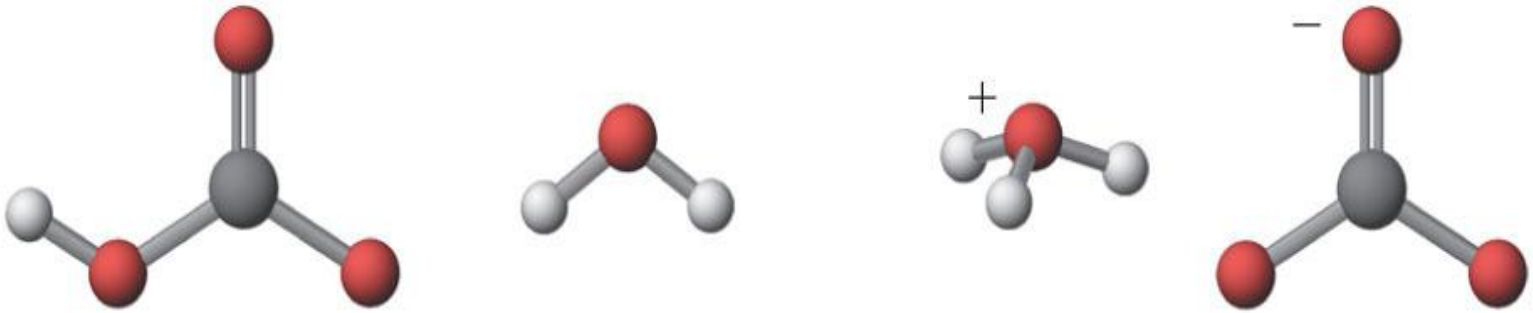
$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

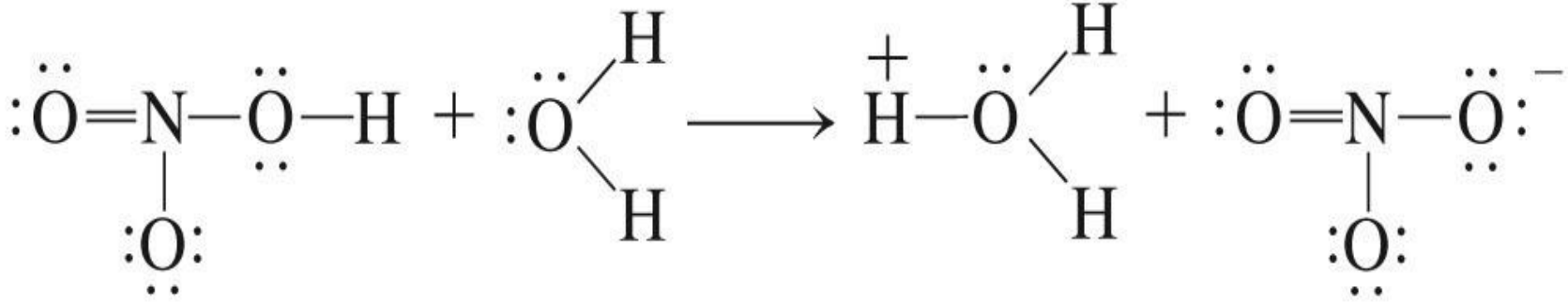
Brønsted-Lowry Theory of Acids & Bases

Acid: H^+ source

Base: H^+ remover

$$HNO_3(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$





Brønsted-Lowry Theory of Acids & Bases

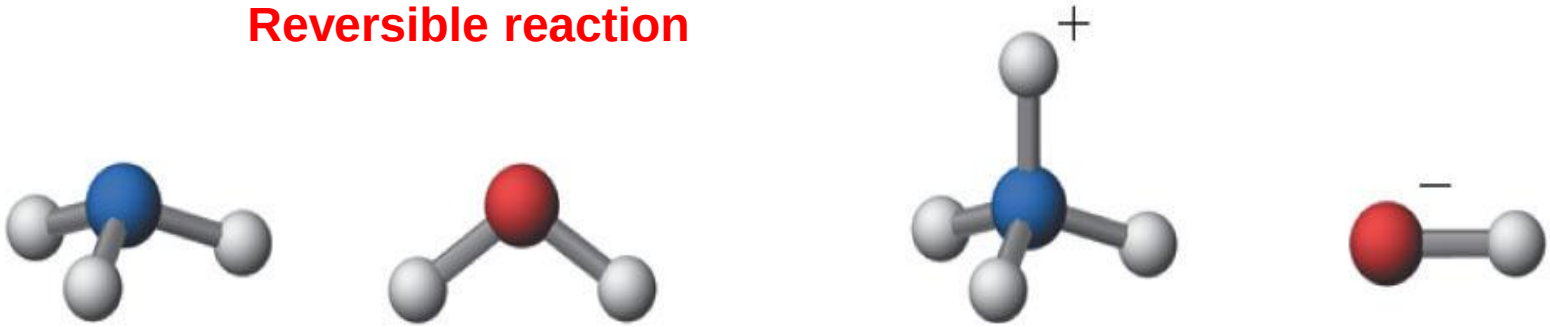
Base: H^+ remover

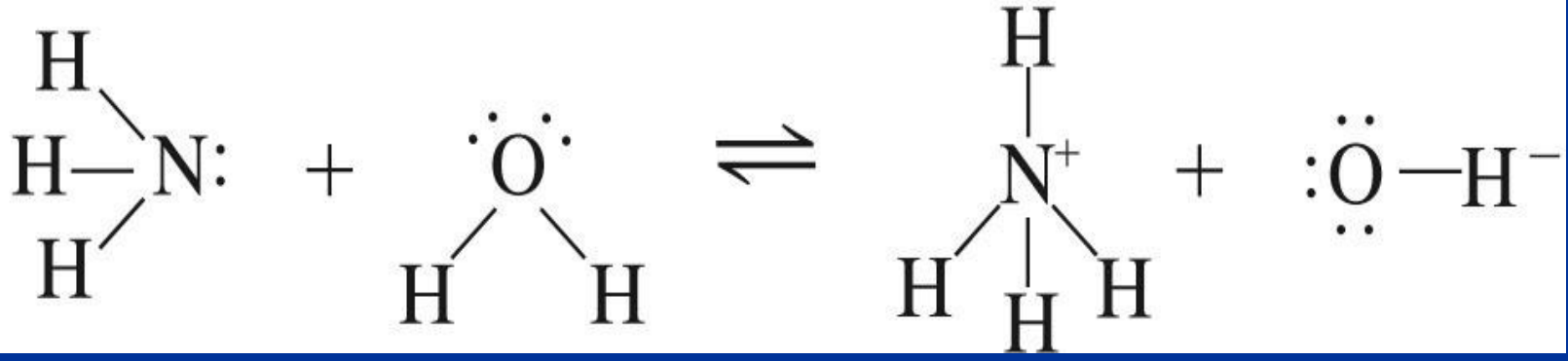
Acid: H^+ source

Notice that water is both an acid & a base = amphoteric

$$NH_3(g) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

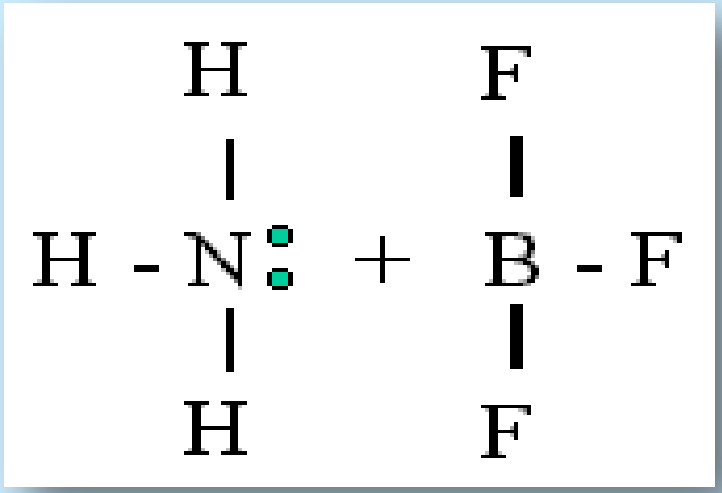
Reversible reaction





3-THE Lewis THEORY

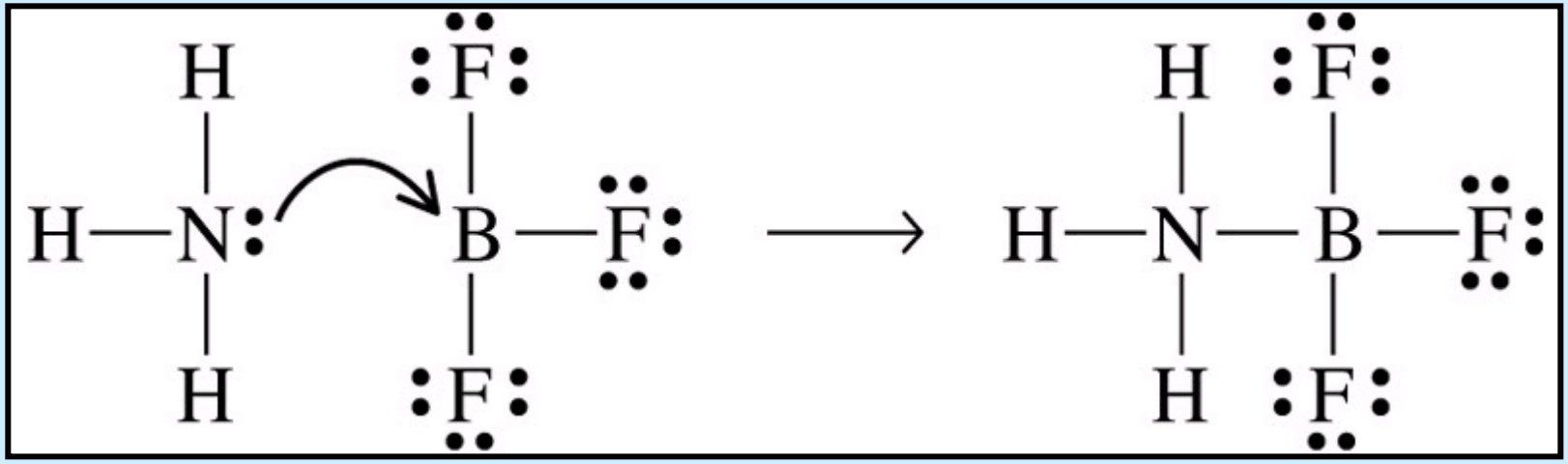
- **Lewis acid**: An electron acceptor
- **Lewis bases:** An electron donor



Lewis

Lewis acids are electrophils: H^+, Na^+, BF_3,

Lewis bases are nucleophils: NH_3, H_2O, PH_3



Lewis bases Lewis acid

Autoionization of Water

- Auto-ionization of water:

$$2H_2O \rightarrow H_3O^+(aq) + OH^-(aq)$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^oC$$

- Water ionizes to produce both H_3O^+ and OH^-, thus it has both acid and base properties. K_w is called *water ionization constant.*
- Pure water at 25°C: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ *M*

Autoionization of Water

- $pH = -\log[H^+]$ (note: $[H^+] = [H_3O^+]$)
- $pOH = -\log[OH^-]$
- $pK_w = -\log(K_w)$; $pK_a = -\log(K_a)$; $pK_b = -\log(K_b)$
- For water, $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$
- $-\log(K_w) = -\log[H_3O^+] + (-\log[OH^-])$
- $pK_w = pH + pOH = 14.00$
- At 25°C, $pOH = 14 - pH$

Autoionization of Water

Acidic solutions:

$[H_3O^+] > 1.0 \times 10^{-7}$ *M*;

pH < 7;

Basic solutions:

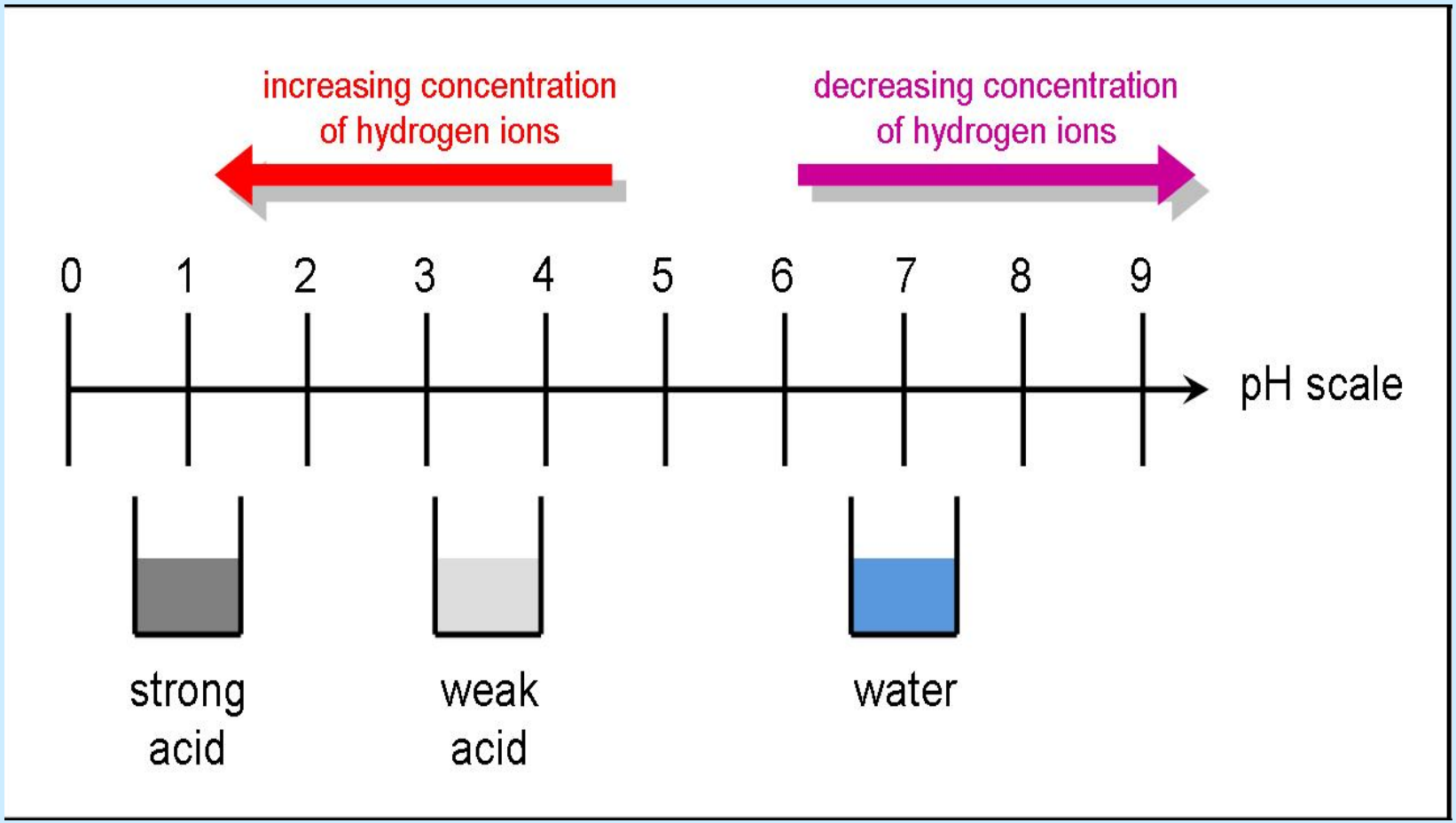
$[OH^-] > 1.0 \times 10^{-7}$ *M* or $[H_3O^+] < 1.0 \times 10^{-7}$ M

pH > 7;

Neutral solutions:

$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ *M*; pH = 7.00

Relationship between acidity of solution and pH



Autoionization of Water

The value of this constant in pure water at 25 °C as1 X 10^{-14}.In pure water. which is denoted as a neutral solution, $[H+] = [OH-] = \sqrt{1.0 \times 10^{-14}} = 1 \times 10^{-7}$. Therefore, an acidic solution will have a [H+] greater than 1 X 10^{-7}, and a [OH"] less than 1 X 10^{-7}. The opposite is true in a basic solution.

We define an **aqueous solution** as being **neutral** when the

$[H^+] = [OH^-]$.

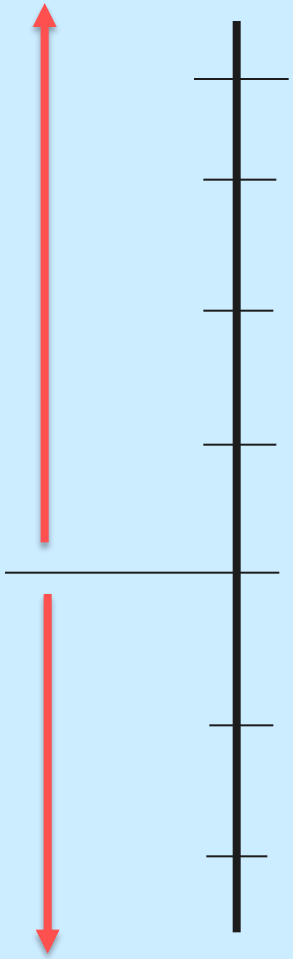
We define an **aqueous solution** as being **acidic** when

$[H^+] > [OH^-]$.

We define an **aqueous solution** as being **basic** when

$[H^+] < [OH^-]$.

Autoionization of Water



basic

acidic

pH = 16

$[H^+] = 10^{-16}$

$[OH^-] = 10^{2}$

$[H^+] < [OH^-]$

basic

pH = 12

$[H^+] = 10^{-12}$

$[OH^-] = 10^{-2}$

$[H^+] < [OH^-]$

basic

pH = 7

$[H^+] = 10^{-7}$

$[OH^-] = 10^{-7}$

$[H^+] = [OH^-]$

neutral

pH = 2

$[H^+] = 10^{-2}$

$[OH^-] = 10^{-12}$

$[H^+] > [OH^-]$

acidic

ACIDS AND BASES: STRONG VERSUS WEAK

Strong acids. There are two types of strong acids:

1. The hydrohalic acids HCl, HBr, and HI
2. Oxoacids in which the number of O atoms exceeds the number of ionizable H atoms by two or more, such as HNO_3, H_2SO_4, $HClO_4$

Weak acids. There are many more weak acids than strong ones. Four types, with examples, are:

1. The hydrohalic acid HF
2. Those acids in which H is bounded to O or to halogen, such as HCN and H_2S
3. Oxoacids in which the number of O atoms equals or exceeds by one the number of ionizable H atoms, such as HClO, HNO_2, and H_3PO_4
4. Organic acids (general formula RCOOH), such as CH_3COOH and C_6H_5COOH

ACIDS AND BASES: STRONG VERSUS WEAK

Strong bases. Soluble compounds containing O^{2-} or OH^- ions are strong bases. The cations are usually those of the most active metals:

1) M_2O or MOH, where M= Group 1A(1) metals (Li, Na, K, Rb, Cs)
2) MO or $M(OH)_2$, where M = Group 2A(2) metals (Ca, Sr, Ba) [MgO and $Mg(OH)_2$ are only slightly soluble, but the soluble portion dissociates completely.]

Weak bases. Many compounds with an electron-rich nitrogen are weak bases (none are Arrhenius bases). The common structural feature is an N atom that has a lone electron pair in its Lewis structure.

1) Ammonia ($:NH_3$)
2) Amines (general formula RNH_2, R_2NH, R_3N), such as $CH_3CH_2NH_2$, $(CH_3)_2NH$, $(C_3H_7)_3N$, and C_5H_5N

Calculate the pH of a 1.00 M HNO_2 Solution

Problem: Calculate the pH of a 1.00 M Solution of Nitrous acid HNO_2.

Solution:

$$HNO_{2\,(aq)} \rightleftharpoons H^+_{(aq)} + NO_2^-{}_{(aq)} \qquad K_a = 4.0 \times 10^{-4}$$

$$K_a = \frac{[H^+]\,[NO_2^-]}{[HNO_2]} = 4.0 \times 10^{-4} = \frac{(x)\,(x)}{1.00 - x}$$

Assume 1.00 – x = 1.00 to simplify the problem.

$$\frac{x^2}{1.00} = 4.0 \times 10^{-4} \qquad \text{or} \quad x^2 = 4.0 \times 10^{-4}$$

$$x = 2.0 \times 10^{-2} = 0.02\ M = [H^+] = [NO_2^-]$$

$$pH = -\log[H^+] = -\log(2.0 \times 10^{-2}) = 2.00$$

Calculate the pH of a 2.0×10^{-3} M solution of NaOH.

Since NaOH is a strong base, it will dissociate 100% in water.

$$NaOH_{(aq)} \longrightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

Since [NaOH] = 2.0×10^{-3} M , $[OH^-] = 2.0 \times 10^{-3}$ M
The concentration of $[H^+]$ can be calculated from K_w:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ M}$$

$$pH = -\log [H^+] = -\log(5.0 \times 10^{-12}) = 12.00$$

Problem: Ammonia is commonly used cleaning agent in households and is a weak base, with a K_b of 1.8×10^{-5}. What is the pH of a 1.5 *M* NH_3 solution?

Plan: Ammonia reacts with water to form $[OH^-]$ and then calculate $[H_3O^+]$ and the pH. The balanced equation and K_b expression are:

$$NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

Concentration (*M*)	**NH_3**	**H_2O**	**NH_4^+**	**OH^-**
Initial	1.5	----	0	0
Change	-x	----	+x	+x
Equilibrium	1.5 - x	----	x	x

making the assumption: since K_b is small: 1.5 M - x = 1.5 *M*

Substituting into the K_b expression and solving for x:

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = \frac{(x)(x)}{1.5} = 1.8 \times 10^{-5}$$

$$x^2 = 2.7 \times 10^{-5} = 27 \times 10^{-6}$$

$$x = 5.20 \times 10^{-3} = [OH^-] = [NH_4^+]$$

Calculating pH:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.20 \times 10^{-3}} = 1.92 \times 10^{-12}$$

$$pH = -\log[H_3O^+] = -\log(1.92 \times 10^{-12}) = 12.000$$

pH =

$[H_3O^+]$ and pH of Strong Acids

- Strong acids like HCl and $HClO_4$ ionize completely in aqueous solution:

  $HCl_{(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$;

  $HClO_{4(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + ClO_4^-{}_{(aq)}$;

- In solutions of strong *monoprotic* acids HA, such as HCl and $HClO_4$,

  $[H_3O^+] = [HA]_0$

- For example, in 0.10 M HCl, $[H_3O^+]$ = 0.10 M, and pH = -log(0.10) = 1.00

$[OH^-]$ and pH of Strong Bases

- Like strong acids, strong bases also ionize completely in aqueous solution.
- Examples: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$;

  $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$;
- In a base solution such as 0.050 M NaOH,

  $[OH^-] = [NaOH]_0 = 0.050$ M;

  pOH = -log(0.050 M) = 1.30; pH = 14.00 - 1.30 = 12.70
- In a base solution such as 0.050 M $Ba(OH)_2$,

  $[OH^-] = 2 \times [Ba(OH)_2]_0 = 0.10$ M;

  pOH = -log(0.10) = 1.00; pH = 14.00 - 1.00 = 13.00

$[H_3O^+]$ and pH of Weak Acids

- In weak acid solutions, $[H_3O^+] < [HA]_0$;
- $[H_3O^+]$ and pH can be calculated from the initial concentration of the acid and its K_a value.

- For example, in 0.100 *M* acetic acid, CH_3COOH, with $K_a = 1.8 \times 10^{-5}$, $[H_3O^+]$ and pH can be calculated using the "ICE" table.

ICE Table for Acetic Acid

Ionization: $CH_3CO_2H + H_2O \rightarrow H_3O^+ + CH_3CO_2^-$

Initial [M]	0.100	0.00	0.00
Change [M]	$-x$	$+x$	$+x$
Equilm. [M]	$(0.100 - x)$	x	x

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]} = \frac{x^2}{(0.100 - x)} = 1.8 \times 10^{-5}$$

Calculating $[H_3O^+]$ from initial concentration and K_a by approximation method.

- Solving for x in the expression for K_a:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{x^2}{(0.100 - x)} = 1.8 \times 10^{-5}$$

$$K_a << [HA]_0 \; (1.8 \times 10^{-5} << 0.100) \Rightarrow \; x << 0.100,$$

$$\text{and } (0.10 - x) \sim 0.10. \text{ This makes } \frac{x^2}{(0.100 - x)} \sim \frac{x^2}{0.100} = 1.8 \times 10^{-5};$$

$$x^2 = (0.100)(1.8 \times 10^{-5}) = 1.8 \times 10^{-6}; \text{ and } x = \sqrt{1.8 \times 10^{-6}} = 1.34 \times 10^{-3};$$

$$[H_3O^+] = x = 1.34 \times 10^{-3} \text{ M}; \quad pH = -\log(1.34 \times 10^{-3}) = 2.873$$

$[OH^-]$ and pH of a Weak Base

- In a weak base, $[OH^-] < [Base]_0$;
- $[OH^-]$ and pH can be calculated from the initial concentration of the base and its K_b value.

- For example, in 0.100 *M* ammonia, NH_3, with $K_b = 1.8 \times 10^{-5}$, $[OH^-]$ and pH can be calculated using the following "ICE" table.

ICE Table for the Ionization of Ammonia

Ionization:	NH_3	+ H_2O →	NH_4^+	+ OH^-
Initial [M]	0.100		0.00	0.00
Change [M]	$-x$		$+x$	$+x$
Equilm. [M]	$(0.100 - x)$		x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{(0.100 - x)} = 1.8 \times 10^{-5}$$

Calculate $[OH^-]$ from initial concentration and K_b by approximation method.

- Solving for x in the expression for K_b:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{(0.100 - x)} = 1.8 \times 10^{-5}$$

$K_b \ll [B]_0$ $(1.8 \times 10^{-5} \ll 0.100) \Rightarrow$ $x \ll 0.100$, and

$(0.100 - x) \sim 0.100$, which makes $\frac{x^2}{(0.100 - x)} \sim \frac{x^2}{0.100} = 1.8 \times 10^{-5}$;

$x^2 = (0.100)(1.8 \times 10^{-5}) = 1.8 \times 10^{-6}$, which yields $x = 1.34 \times 10^{-3}$;

$[OH^-] = 1.34 \times 10^{-3}$ M $\Rightarrow$ pOH = 2.873, and pH = 11.127

Strong Acids:

$HClO_4$

H_2SO_4

HI

HBr

HCl

HNO_3

Strong Bases:

LiOH

NaOH

KOH

$Ca(OH)_2$

$Sr(OH)_2$

$Ba(OH)_2$

Polyprotic Acids

- Polyprotic acids have more than one ionizable proton, such as H_2SO_3.
- These acids have acid-dissociation constants that decrease in magnitude in the order $K_{a1} > K_{a2} > K_{a3}$.
- Because nearly all the $H^+(aq)$ in a polyprotic solution comes from the first dissociation, the pH can usually be estimated using only K_{a1}.

Polyprotic Acids

A polyprotic acid can donate more than one H^+

Carbonic acid: $H_2CO_3(aq)$; dissolved CO_2 in water

Sulfuric acid: $H_2SO_4(aq)$

Phosphoric acid: $H_3PO_4(aq)$

A polyprotic base: can accept more than one proton

Carbonate ion: $CO_3^{2-}(aq)$

Sulfate ion: $SO_4^{2-}(aq)$

Phophate ion: $PO_4^{3-}(aq)$

Treat each step of protonation or deprotonation sequentially

Polyprotic Acids

$H_2CO_3(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + HCO_3^-(aq)$ $K_{a1} = 4.3 \times 10^{-7}$

$HCO_3^-(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CO_3^{2-}(aq)$ $K_{a2} = 4.8 \times 10^{-11}$

Typically:

$K_{a1} >> K_{a2} >> K_{a3} >> \ldots$

Harder to loose a positively charged proton from a negatively charged ion, because of attraction between opposite charges.

Polyprotic Acids

TABLE 10.9 Acidity Constants of Polyprotic Acids

Acid	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}
sulfuric acid, H_2SO_4	strong		1.2×10^{-2}	1.92		
oxalic acid, $(COOH)_2$	5.9×10^{-2}	1.23	6.5×10^{-5}	4.19		
sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81	1.2×10^{-7}	6.91		
phosphorous acid, H_3PO_3	1.0×10^{-2}	2.00	2.6×10^{-7}	6.59		
phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12	6.2×10^{-8}	7.21	2.1×10^{-13}	12.68
tartaric acid, $C_2H_4O_2(COOH)_2$	6.0×10^{-4}	3.22	1.5×10^{-5}	4.82		
carbonic acid, H_2CO_3	4.3×10^{-7}	6.37	5.6×10^{-11}	10.25		
hydrosulfuric acid, H_2S	1.3×10^{-7}	6.89	7.1×10^{-15}	14.15		

Calculate the pH of 0.010 M $H_2SO_4(aq)$ at 25°C.

Sulfuric acid is the only common polyprotic acid where the first deprotonation step is complete. The second deprotonation step is much weaker and adds slightly to the $H_3O^+(aq)$ concentration.

For the first step assume all $H_2SO_4(aq)$ deprotonates

$$H_2SO_4\,(aq) + H_2O(l) \rightarrow H_3O^+\,(aq) + HSO_4^-(aq)$$

From the first step $[H_3O^+(aq)] = 0.010$ M

Second deprotonation

HSO_4^- (aq) + H_2O(l) ⇔ H_3O^+ (aq) + SO_4^{2-} (aq) $K_{a2} = 0.012$

	HSO_4^- (aq)	SO_4^{2-} (aq)	H_3O^+ (aq)
Initial	0.010	0	0.010
Change	-x	+ x	0.010 + x
Equilibrium	0.010-x	x	0.010 + x

$K_{a2} = ([H_3O^+ (aq)])([SO_4^{2-} (aq)]) / ([HSO_4^- (aq)])$

$0.012 = (0.010+x)(x) / (0.010-x)$

Solve the quadratic equation for x. K_{a2} is large; cannot assume that $x << 0.010$

$[H_3O^+ (aq)] = 1.4 \times 10^{-2}$ M

pH = 1.9

Determine the pH of 0.20 M $H_2S(aq)$ at 25°C

$H_2S\ (aq) + H_2O(l) \Leftrightarrow H_3O^+\ (aq) + HS^-\ (aq)$ $\quad K_{a1} = 1.3 \times 10^{-7}$

$HS^-\ (aq) + H_2O(l) \Leftrightarrow H_3O^+\ (aq) + S^{2-}\ (aq)$ $\quad K_{a2} = 7.1 \times 10^{-15}$

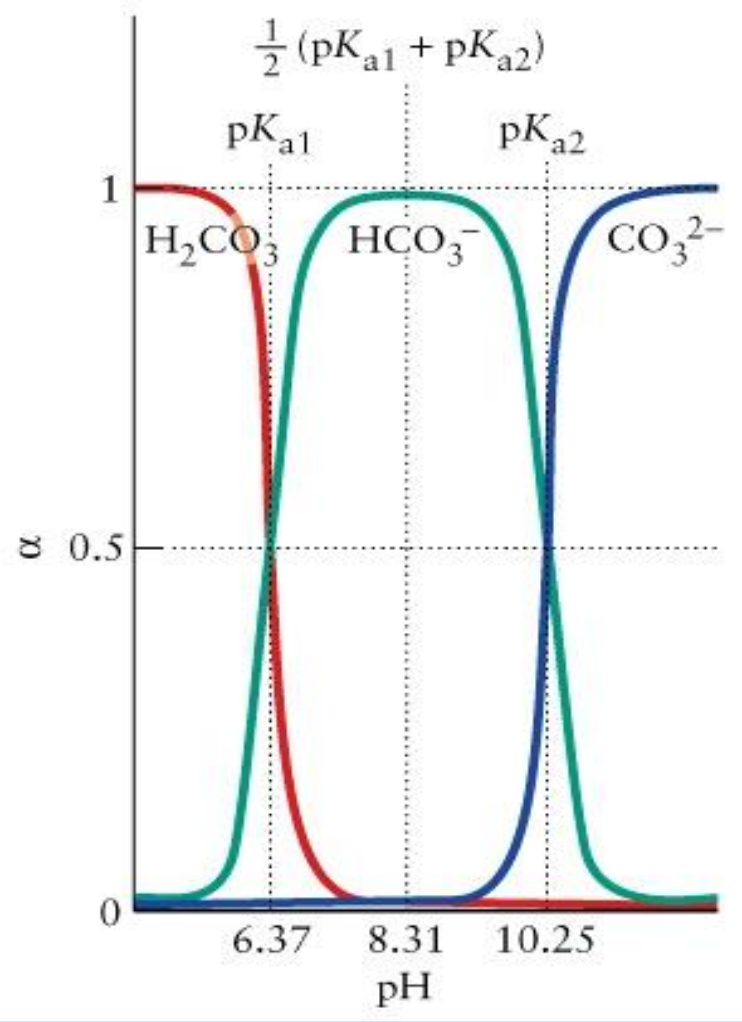
For the first deprotonation step determine $[H_3O^+(aq)]$ using equilibrium tables. $[H_3O^+(aq)] = 1.6 \times 10^{-4}$ M

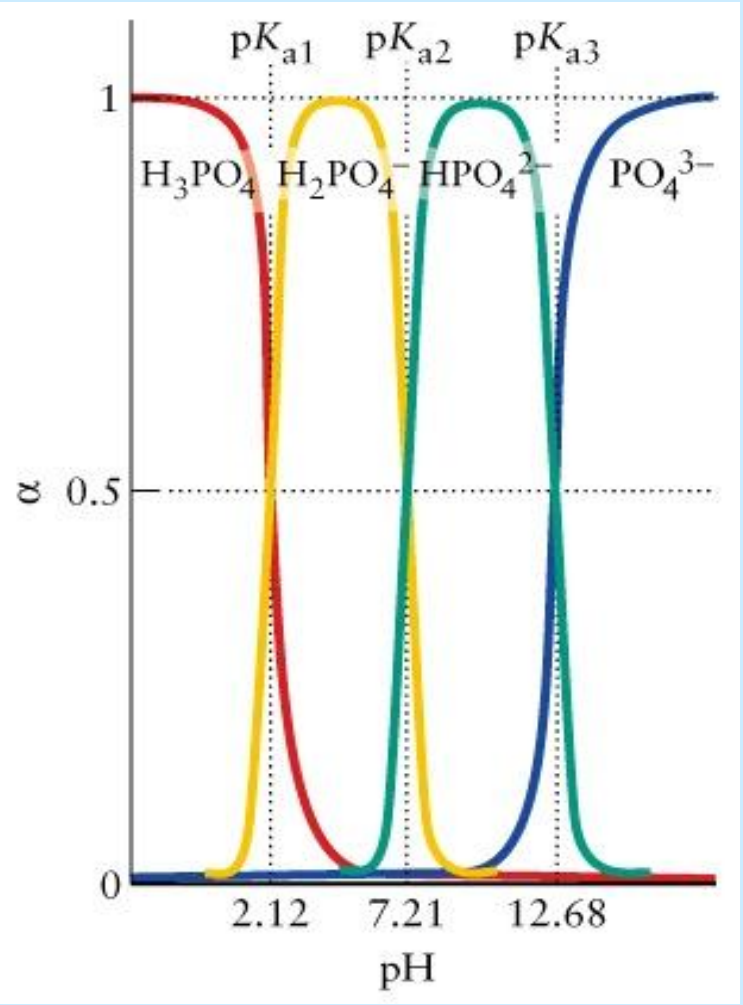
Can assume that $x << 0.20$ since K_{a1} is small

Second deprotonation constant is very small, so ignore addition of $H_3O^+(aq)$ due to second step.

pH determined by first step alone. pH = 3.8

Polyprotic Acids





SALTS AND HYDROLYSIS

1. **No hydrolysis:** Salts of *strong acids and strong bases* are **neutral** in solution.

   (NaCl, K_2SO_4, $CaCl_2$….)

2. **Anion-hydrolysis: Salts of weak acids and strong bases are basic in solution.**

   Dissolution: $KCN \rightarrow K^+ + CN^-$

   Hydrolysis: $CN^- + H_2O \Leftrightarrow HCN + OH^-$

SALTS AND HYDROLYSIS

3. **Cation-hydrolysis:** Salts of strong acids and weak bases are **acidic** in solution.

   Dissolution: $NH_4Cl \rightarrow NH_4^+ + Cl^-$

   Hydrolysis: $NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+$

4. **Cation-anion hydrolysis:** Salts of weak acids and weak bases can be acidic, basic or neutral in solution, owing to the hydrolysis of both ions. The reaction depends on relative acid-base strengths.

   Dissolution: $NH_4CN \rightarrow NH_4^+ + CN^-$

   Cation-Hydrolysis: $NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+$

   Anion-hydrolysis: $CN^- + H_2O \Leftrightarrow HCN + OH^-$

SALTS AND HYDROLYSIS

Salts are the ionic product of an acid base neutralization reaction.

Acidic Salts are formed from a strong acid and a weak base.

Neutral salts are formed from a strong acid and strong base.

Basic salts are formed from a strong base and a weak acid.

Give the acid and base the following salts were formed from and label the salts as acidic, basic, or neutral.

1. $NaCl$

neutral salt

$$\underset{\text{s.a.}}{HCl} + \underset{\text{s.b.}}{NaOH} \longrightarrow NaCl + HOH$$

2. $NaC_2H_3O_2$

basic salt

$$\underset{\text{w.a.}}{HC_2H_3O_2} + \underset{\text{s.b.}}{NaOH} \longrightarrow NaC_2H_3O_2 + HOH$$

3. NH_4Cl

acidic salt

$$\underset{\text{s.a.}}{HCl} + \underset{\text{w.b.}}{NH_4OH} \longrightarrow NH_4Cl + HOH$$

THANK YOU