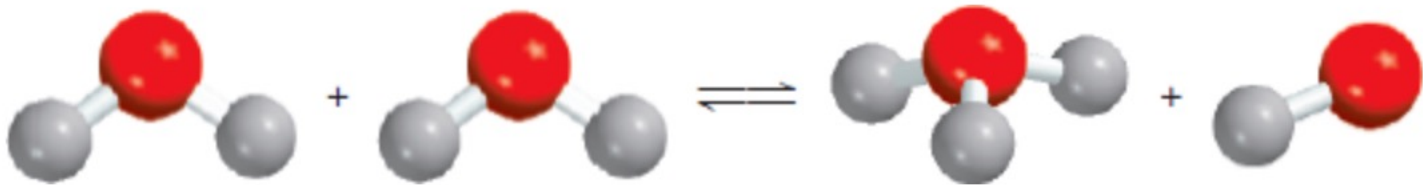
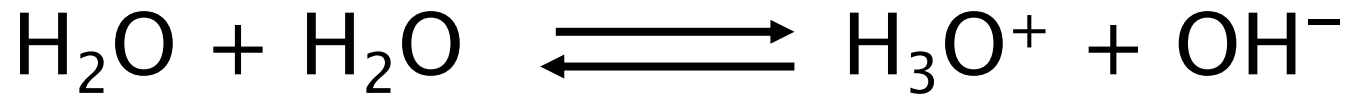


Chapter 17

Acids & Bases



Some Polyatomic Ions that are Important for Acids & Bases

Ammonium	NH_4^+	Nitrate	NO_3^-
Hydronium	H_3O^+	Nitrite	NO_2^-
Acetate	CH_3COO^-	Phosphate	PO_4^{3-}
Carbonate	CO_3^{2-}	Perchlorate	ClO_4^-
Hydroxide	OH^-	Sulfate	SO_4^{2-}
Cyanide	CN^-		

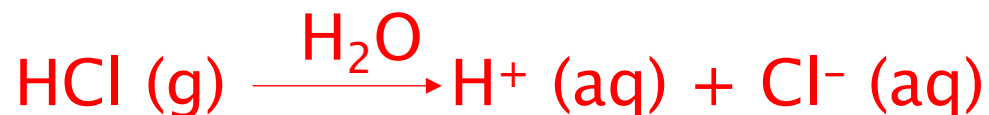
You should know these ions

What are Acids & Bases?

Arrhenius Definition

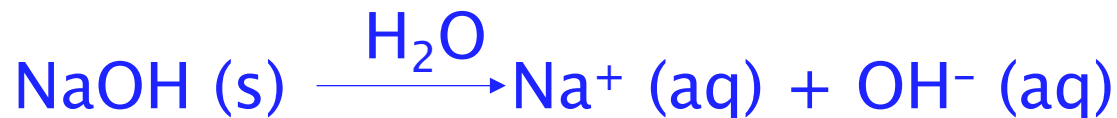
Acid:

A substance that, when dissolved in water, increases the concentration of hydrogen (H^+) ions (aka protons).



Base:

A substance that, when dissolved in water, increases the concentration of hydroxide ions (OH^-).



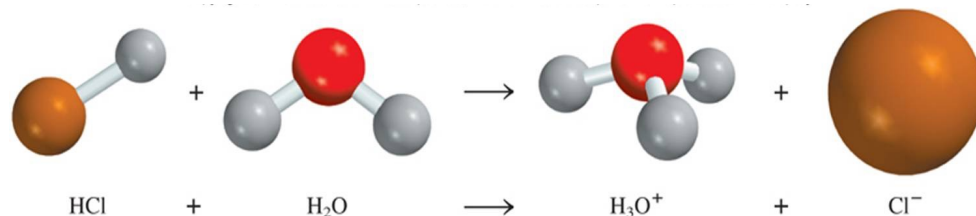
What are Acids & Bases?

Brønsted–Lowry Definition

Acid:

A proton (H^+) donor

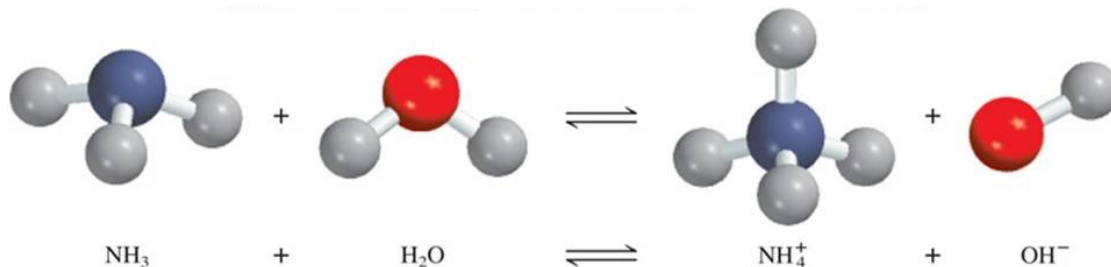
- Must have a removable proton
- Proton goes to a base



Base:

A proton (H^+) acceptor

- Must have a pair of non-bonding electrons



Lewis Acids & Bases

Acid:

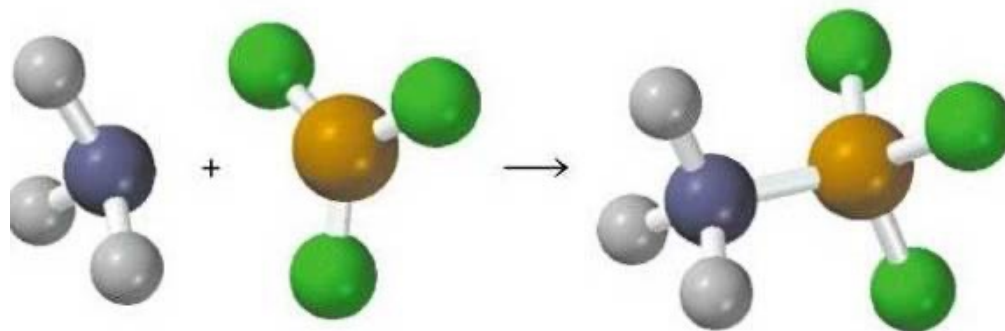
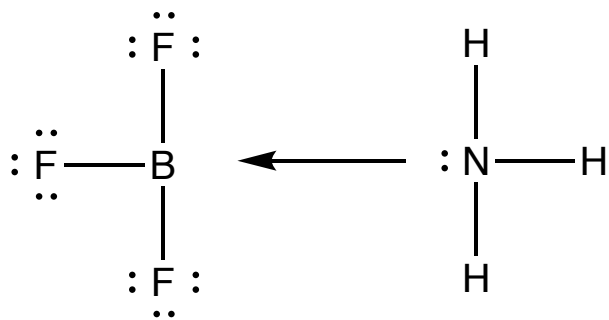
An electron pair acceptor

- Do not need to have a removable proton
- Must have an empty orbital to put electrons in

Base:

An electron pair donor

- Must have a pair of non-bonding electrons



Strength of Acids & Bases

Strong Acids & Bases: Complete dissociation

- Non H^+ / OH^- ions form spectator ions
- Can use basic stoichiometry (CHM 101) in calculations
- No undissociated reactant left in solution

Weak Acids & Bases: Incomplete dissociation

- Equilibrium process
- Equilibrium constants are K_a or K_b
- Titrations involve stoichiometry and equilibrium calcs.

Aqueous Solutions

- Acid or Base reacts with water
 - Water acts as a weak acid or base in the reaction

Factors impacting acid strength

Basic concept: easier to lose H, stronger acid

Charge:

- Higher charge = stronger bond to H^+ = weaker acid
- Ex: $HAsO_4^{2-}$ weaker than $H_2AsO_4^-$ weaker than H_3AsO_4

Bond length:

- Shorter bonds are stronger so H^+ harder to remove
- Ex: HF weaker than HCl weaker than HBr

Electronegativity:

- Less electronegative, share e^- more equally, stronger bond
- Ex: P less electronegative than S, H_3PO_4 weaker than H_2SO_4

For Oxoacids

- If all else is equal, fewer double bonds = weaker acid
- Ex: H_2SO_3 weaker than H_2SO_4
- More double bonds = more resonance = more stability with H^+ removed

Stability of conjugate base: more stable anion = more acidic

Binary Acid Trends in the Periodic Table

4A	5A	6A	7A
CH₄ Neither acid nor base	NH₃ Weak base $K_b = 1.8 \times 10^{-5}$	H₂O	HF Weak acid $K_a = 6.8 \times 10^{-4}$
SiH₄ Neither acid nor base	PH₃ Very weak base $K_b = 4 \times 10^{-28}$	H₂S Weak acid $K_a = 9.5 \times 10^{-8}$	HCl Strong acid
		H₂Se Weak acid $K_a = 1.3 \times 10^{-4}$	HBr Strong acid

Increasing acid strength

Increasing acid strength

For binary acids:

Acidity increases left to right across a row

- Electronegativity increases left to right

Acidity increases top to bottom down a group

- Atomic size increases down a group

Common Acids & Bases You Will Need to Know

Strong Acids:

Hydrochloric Acid	HCl
Sulfuric Acid	H ₂ SO ₄
Nitric Acid	HNO ₃
Perchloric Acid	HClO ₄
Hydrobromic Acid	HBr
Hydroiodic Acid	HI

Strong Bases:

Soluble Hydroxides:	
Sodium	NaOH
Potassium	KOH
Lithium	LiOH
Barium	Ba(OH) ₂
etc.	

Weak Acids:

Carbonic Acid	H ₂ CO ₃
Phosphoric Acid	H ₃ PO ₄
Acetic Acid	CH ₃ COOH
Hydrofluoric Acid	HF
Nitrous Acid	HNO ₂
Hydrocyanic acid	HCN
Carboxylic Acids	R-COOH

Weak Bases:

Ammonia	NH ₃
Amines	R-NH ₂ , R ₂ NH
Insoluble/slightly soluble hydroxides	

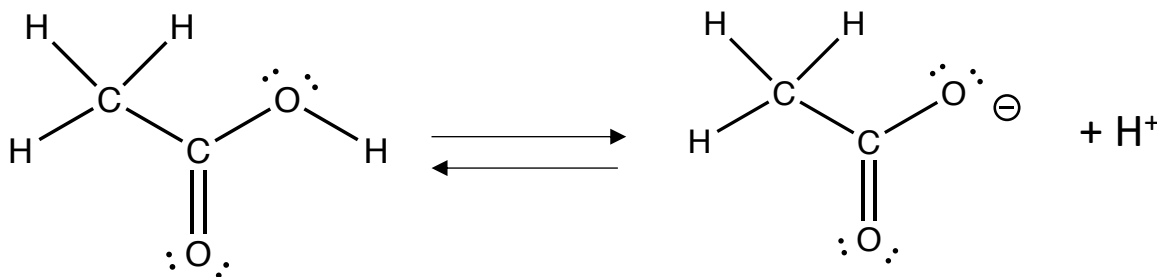
Organic Acids: Carboxylic Acids (-COOH)

Weak organic acids

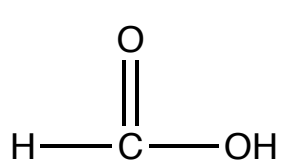
- -COOH group on molecule is acidic
- Removal of proton (H⁺) creates resonance structure
- Stabilizes anion

Never fully dissociate in water

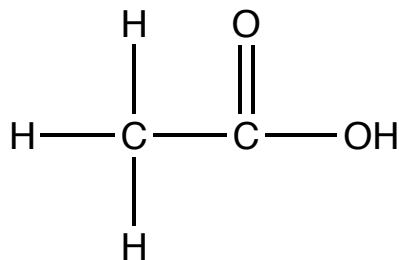
- Equilibrium process



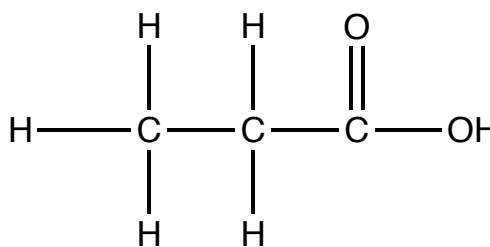
Examples:



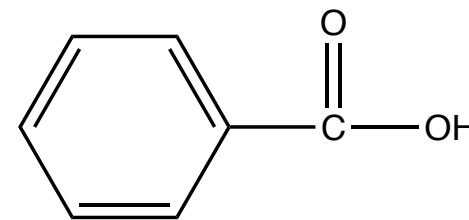
Formic Acid



Acetic Acid



Butyric Acid



Benzoic Acid

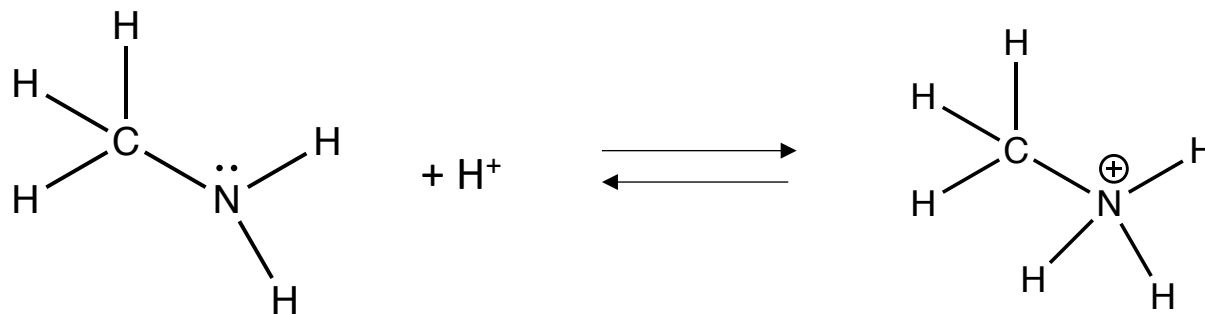
Organic Bases: Amines (contain N)

Weak organic bases

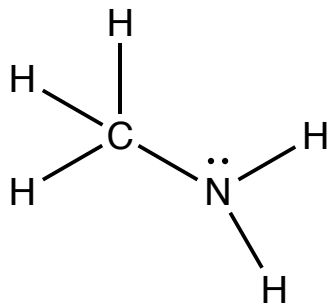
- Derivatives of ammonia
- N has lone pair of electrons to accept a proton

Also do not fully dissociate in water

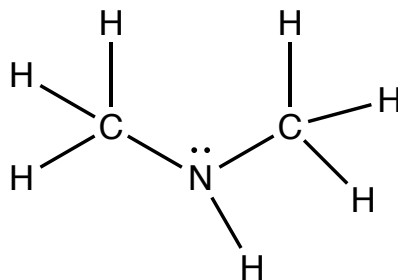
- Equilibrium process



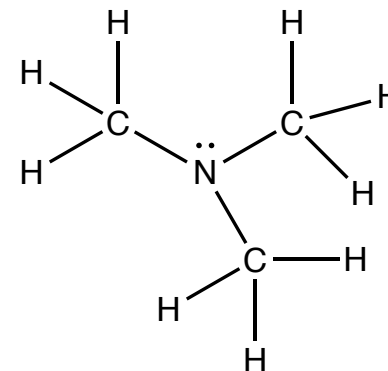
Examples:



Methyl amine



Dimethyl amine



Trimethyl amine

Organic Acids & Bases: Things to keep in mind

Organic Acids & Bases:

Only acidic proton

Acid: CH_3COOH Becomes CH_3COO^-

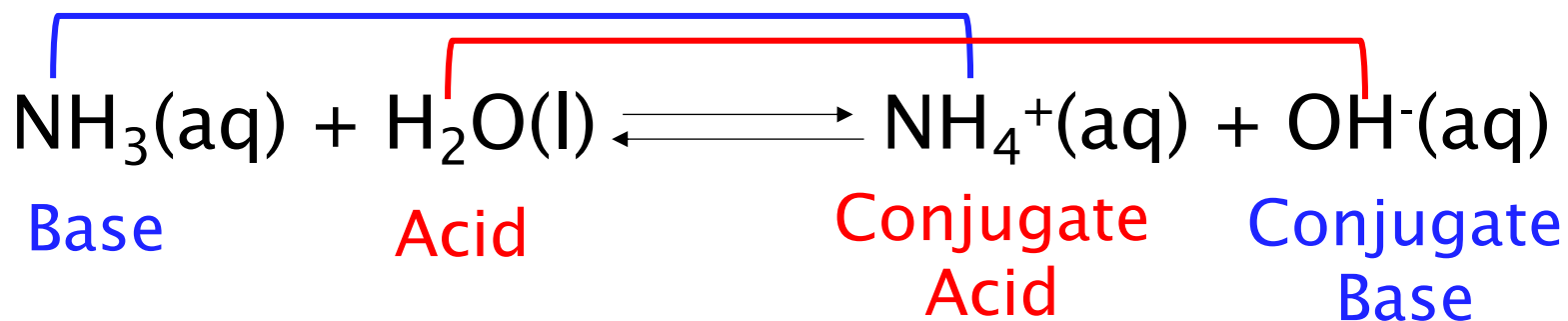
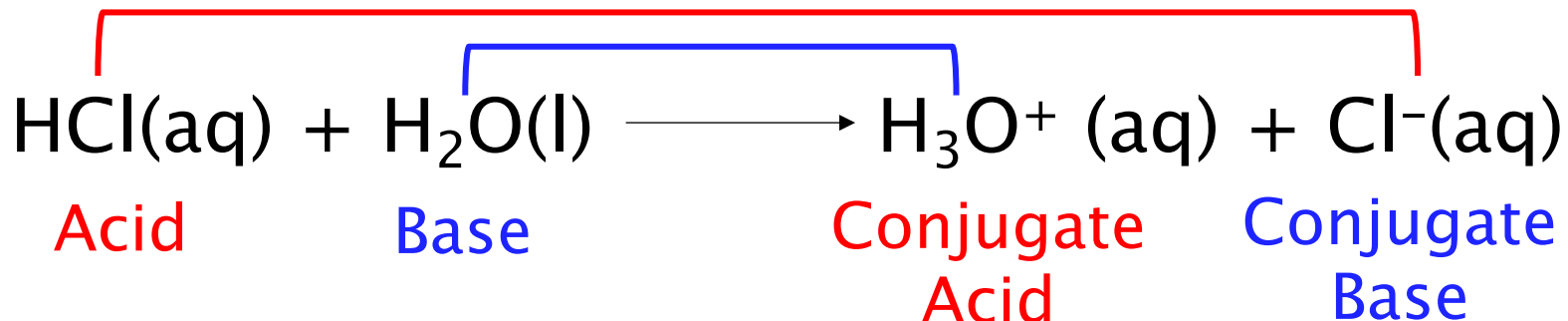
Amine: CH_3NH_2 Becomes CH_3NH_3^+

Carbon: no lone pairs

- Cannot accept extra protons
- Protons bonded to carbon are not acidic

Added proton bonds via lone pair on N

Conjugate Acid–Base Pairs



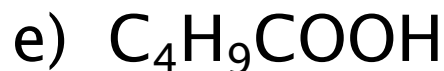
Conjugate Acid: Formed from the **base** after H^+ is added

Conjugate Base: Formed from the **acid** after H^+ is lost

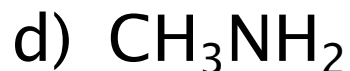
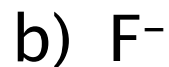
Each acid has a conjugate base, each base has a conjugate acid. For substances that can both gain or lose a proton, whether they act as an acid or base depends on the system.

Conjugate Acid–Base Pair Examples

1. Give the conjugate base of each of the following acids:



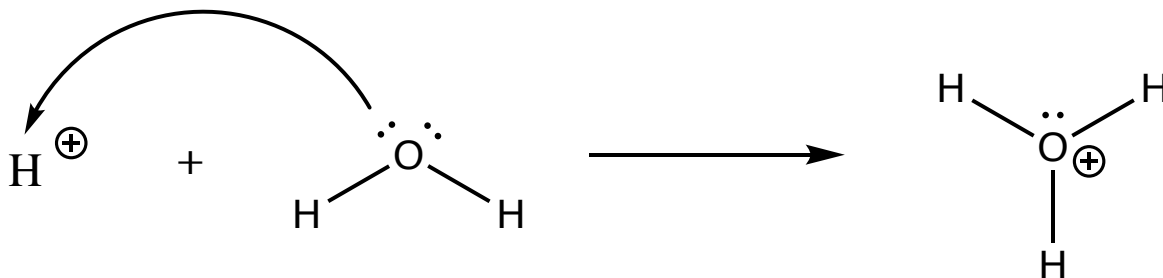
2. Write the formula for the conjugate acid of each of the following bases:



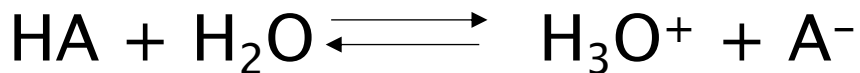
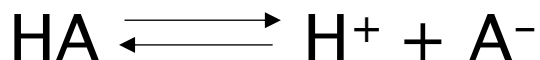
H⁺ Ion in Water

H⁺ is simply a proton – an H atom with no electron

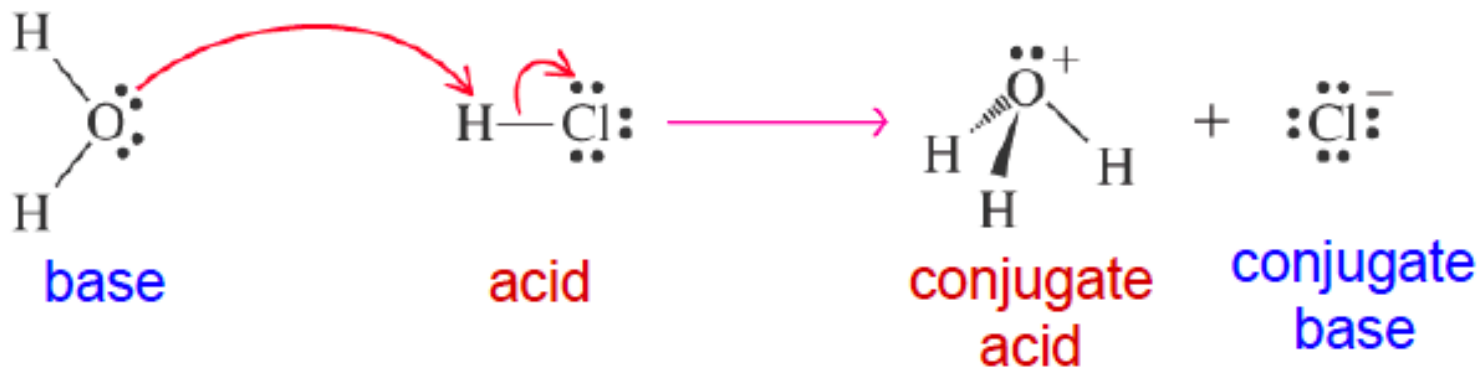
- In water, clusters of hydrated H⁺ form
- Simplest cluster is the hydronium ion: H₃O⁺



- H⁺ (aq) & H₃O⁺(aq) are used interchangeably

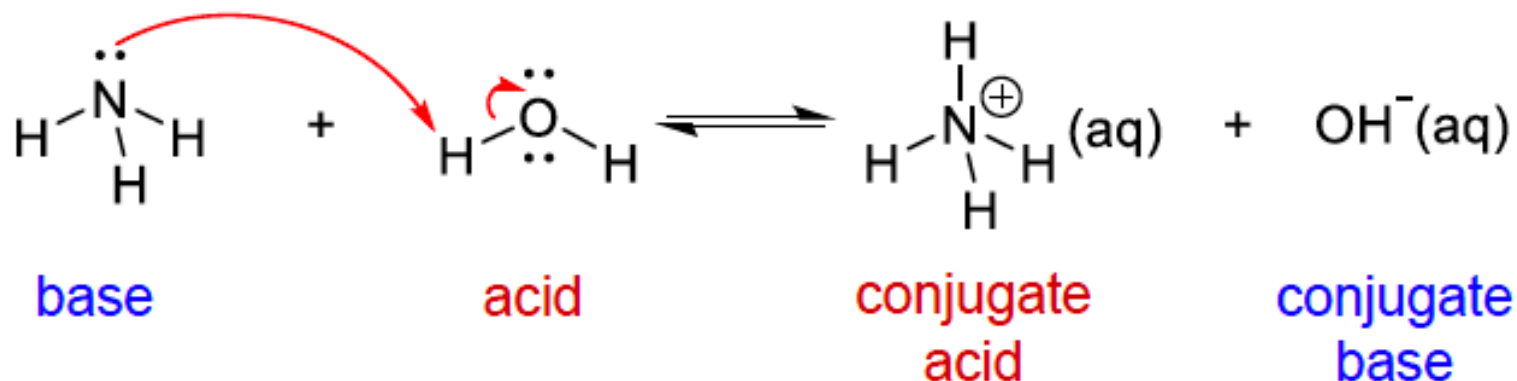


Proton Transfer Reactions: Aqueous Acid



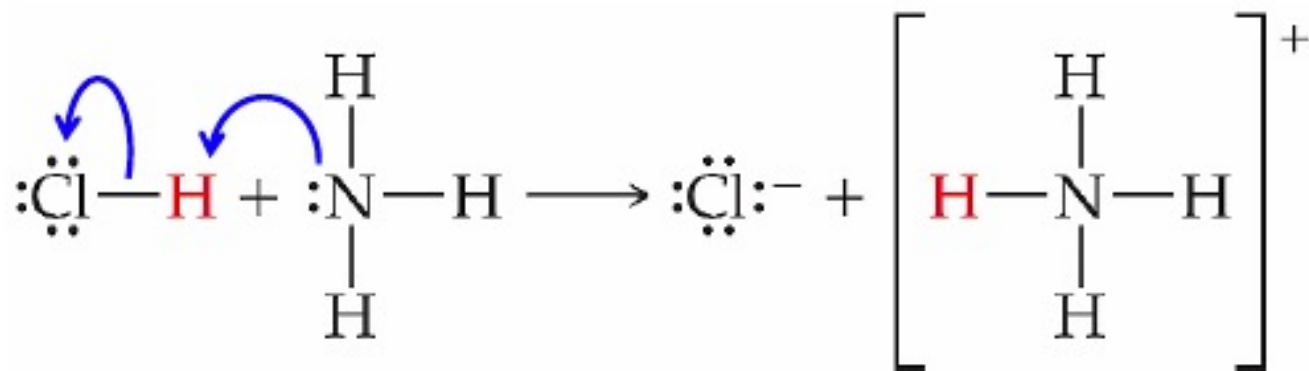
- **HCl** (the acid) donates a proton (H⁺)
- **Water** (the base) accepts the proton
- The conjugate base of the acid (Cl⁻) and the conjugate acid of the base (H₃O⁺) are formed

Proton Transfer Reactions: Aqueous Base



- **Water** (the acid) donates a proton (H⁺)
- **Ammonia** (the base) accepts the proton
- Water is **AMPHIPROTIC** – it can act as either an acid or a base (donate or accept a proton)

Proton Transfer Reactions: Non-Aqueous

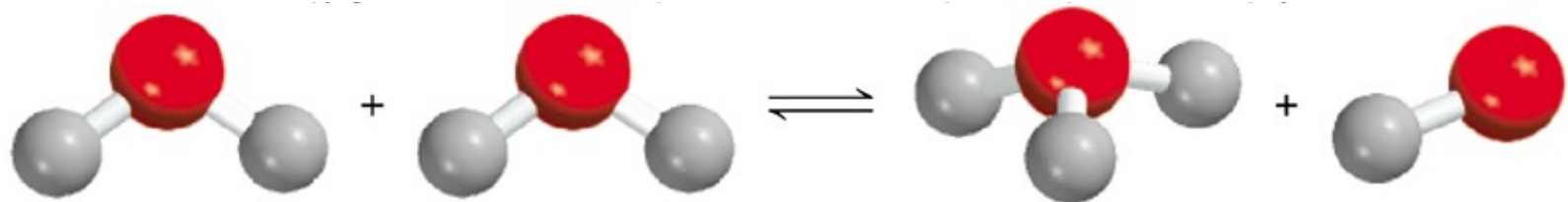
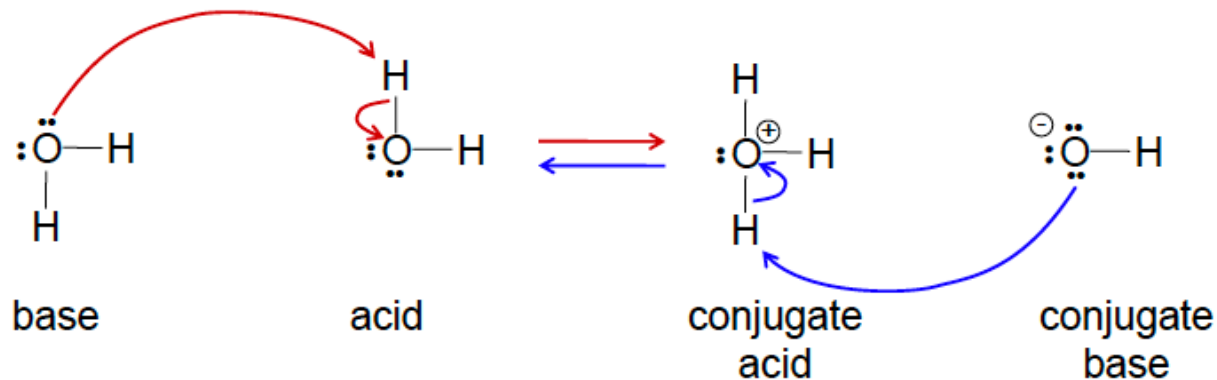


- **HCl** (the acid) donates a proton (H^+)
- **Ammonia** (the base) accepts the proton
- Can occur in the gas phase – water not needed
- Advantage of Brønsted–Lowry definition over Arrhenius definition
- Lewis definition even more broad (electron pair donor/acceptor)

Acid-Base Properties of Water: Autoionization

Autoionization: In pure water, one water molecule can donate a proton to another water molecule

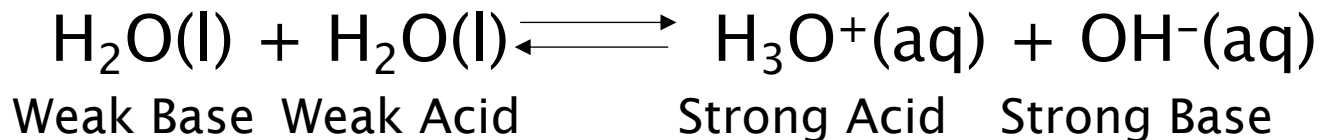
- Essentially the water ionizes itself (“auto”)



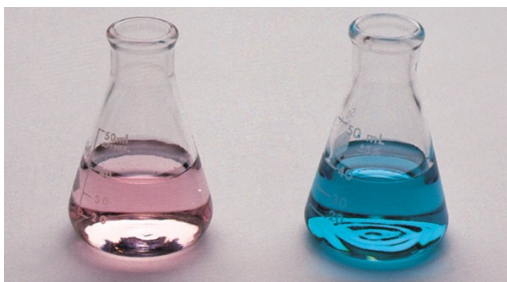
This is why pure water can conduct electricity

Autoionization: An Equilibrium Process

Consider the autoionization of water at 25°C



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



This H_3O^+ & OH^- concentration is where the pH of 7 for pure water comes from

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (ion-product constant)}$$

K_w is very small = favors reactants (H_2O)

K_w applies to both pure water and aqueous solutions

- If know acid concentration, can use K_w to find the base concentration & vice versa

pH & pOH

Method of Measuring Acidity

- Power of the Hydrogen Ion

Formulas:

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
- $[\text{H}_3\text{O}^+] = 10^{(-\text{pH})}$
- $\text{pOH} = -\log[\text{OH}^-]$
- $[\text{OH}^-] = 10^{(-\text{pOH})}$
- $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{M}$
- $\text{p}K_w = \text{pH} + \text{pOH} = 14$

Neutral: $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ $\text{pH} = 7$

Acidic: $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ $\text{pH} < 7$

Basic: $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ $\text{pH} > 7$

Sample	pH Value
Gastric juice in the stomach	1.0–2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8–7.5
Water exposed to air*	5.5
Saliva	6.4–6.9
Milk	6.5
Pure water	7.0
Blood	7.35–7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

Sig Figs: # sig figs in concentration = # sig figs after decimal point in pH/pOH

What is log?

Consider the number 1.0×10^{-3}

- Log refers to base 10
- Essentially, log refers to the exponent in a number written in scientific notation
- It tells you the magnitude (size) of the number
- The log of 1.0×10^{-3} is -3
- The formula for pH is $-\log$ to eliminate the negative sign in the answer

Consider the number 2.8×10^{-3}

- Log still refers primarily to the exponent, but the actual value is impacted by the rest of the number
- The log of 2.8×10^{-3} will be close to, but not exactly, -3
- $\text{Log}(2.8 \times 10^{-3}) = -2.6$

Low pH values are acidic because concentrations generally have negative exponents. $1 \times 10^{-3} \text{M} > 1 \times 10^{-10} \text{M}$

Measuring pH

Most Accurate: pH meter

- Measures the voltage in a solution to determine concentration & pH



	pH range for color change													
	0	2	4	6	8	10	12	14						
Methyl violet	Yellow													Violet
Thymol blue		Red			Yellow					Yellow				Blue
Methyl orange			Red			Yellow								
Methyl red				Red			Yellow							
Bromthymol blue					Yellow									Blue
Phenolphthalein								Colorless						Pink
Alizarin yellow R												Yellow		Red

Other methods:

- Litmus paper
 - Red litmus paper turns blue above ~ pH 8
 - Blue litmus paper turns red below ~ pH 5
- Indicators
 - In solution or on pH indicator paper

Concentrated vs. Dilute Solutions

Do we need to take the autoionization of water into account when determining pH?

Example 1: Concentrated Solutions

Consider an aqueous 0.010M solution of nitric acid.

Two reactions are occurring:



The $[\text{H}_3\text{O}^+]$ from ionization of water is negligible:

$$0.010\text{M} + 0.0000001\text{M} = 0.0100001\text{M}$$

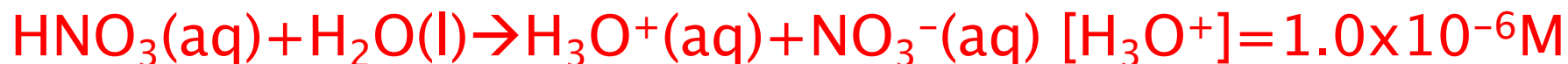
It can be ignored

Concentrated vs. Dilute Solutions

Example 2: Dilute Solutions

Consider an aqueous $1.0 \times 10^{-6} \text{M}$ solution of nitric acid.

Two reactions are again occurring:



*Likely somewhat less due to Le Châtelier's Principle

The $[\text{H}_3\text{O}^+]$ from ionization of water is 10% of the amount contributed by the acid:

$$1.0 \times 10^{-6} \text{M} + 0.1 \times 10^{-6} \text{M} = 1.1 \times 10^{-6} \text{M}$$

It CANNOT be ignored

Contribution from autoionization of water must be taken into account if acid/base provides $< 10^{-6} \text{M}$ $\text{H}_3\text{O}^+/\text{OH}^-$

pH Calculations for Strong Acids/Bases

1. Calculate $[H^+]$ at $25^\circ C$ for an aqueous solution in which $[OH^-] = 0.00045M$. Indicate whether it is acidic, basic, or neutral. **A: $2.2 \times 10^{-11}M$; basic**
2. Find the pH and pOH of a $0.0050M$ HBr solution at $25^\circ C$
pH: 2.30; pOH: 11.70
3. Calculate the H_3O^+ and OH^- concentrations at $25^\circ C$ of an aqueous $0.010M$ solution of nitric acid. **$[H_3O^+]: 0.010M$
 $[OH^-]: 1.0 \times 10^{-12}$**

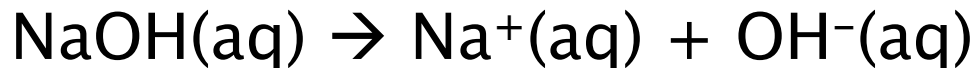
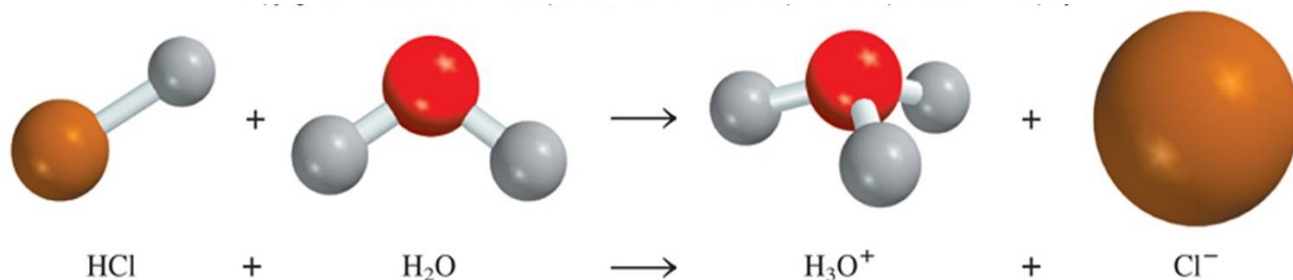
4. Calculate the pH made from 15.00mL of 1.00M HCl diluted to 0.500L. A:1.523

5. What is the concentration of a solution of Ba(OH)₂ for which the pH is 10.05? A: 5.6x10⁻⁵M

Strength of Acids & Bases

Strong Acids & Bases: Complete dissociation

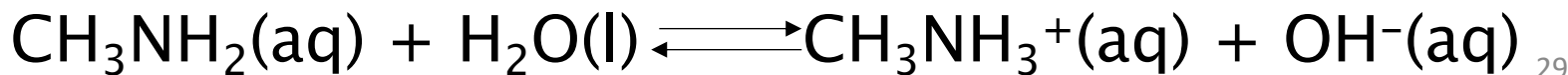
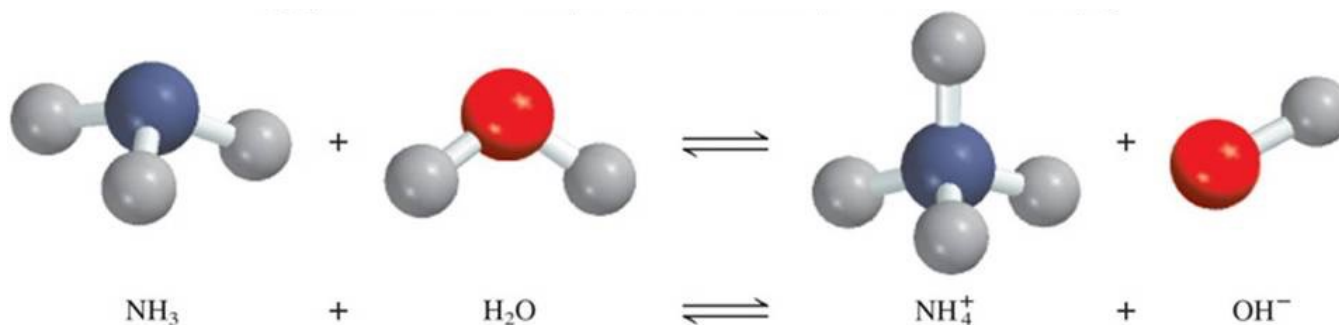
- Strong electrolytes
- Good conductors of electricity
- Completely ionized in aqueous solution; no original compound remains
- Conjugate has no measurable strength
- Single arrow – not equilibrium



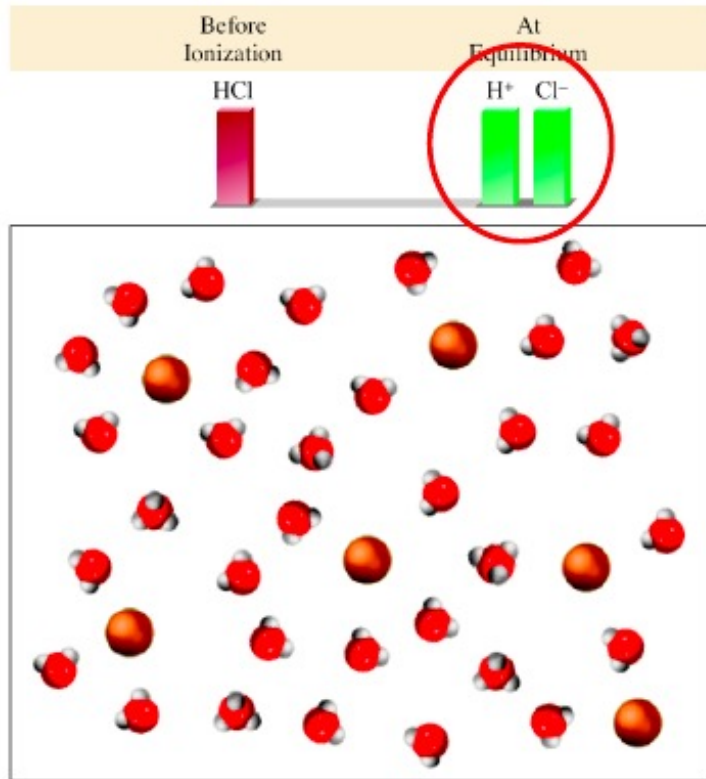
Strength of Acids & Bases

Weak Acids & Bases: Incomplete dissociation

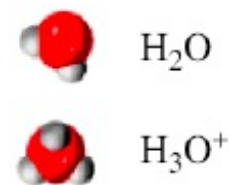
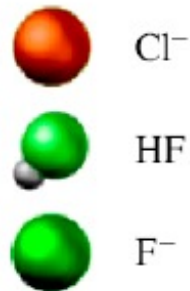
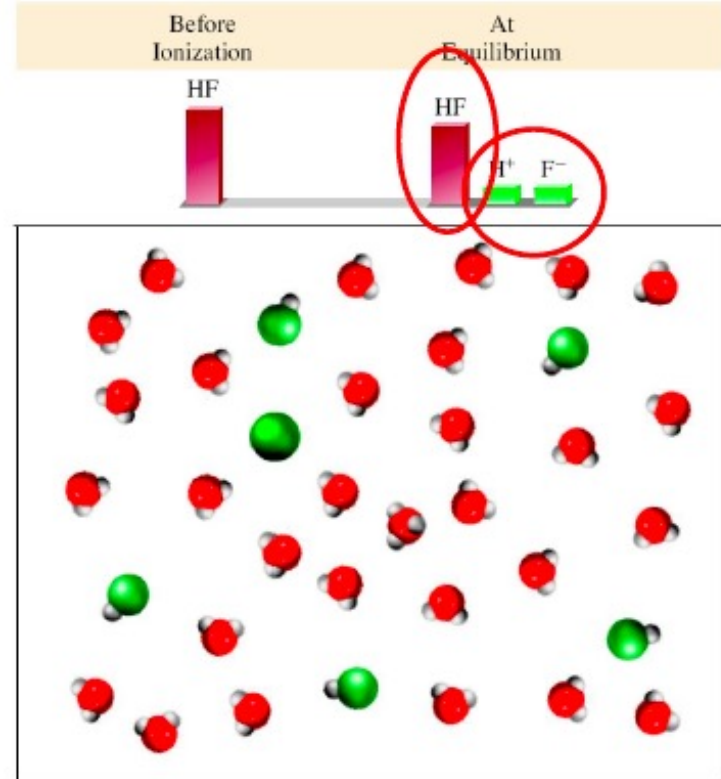
- Some of original compound remains along with ions
- Equilibrium process; represented by double arrow
- Dissociation is governed by an equilibrium constant
 - K_a or K_b
- Poor conductors of electricity
- Conjugates can act as acids/bases



Strong Acid (HCl)



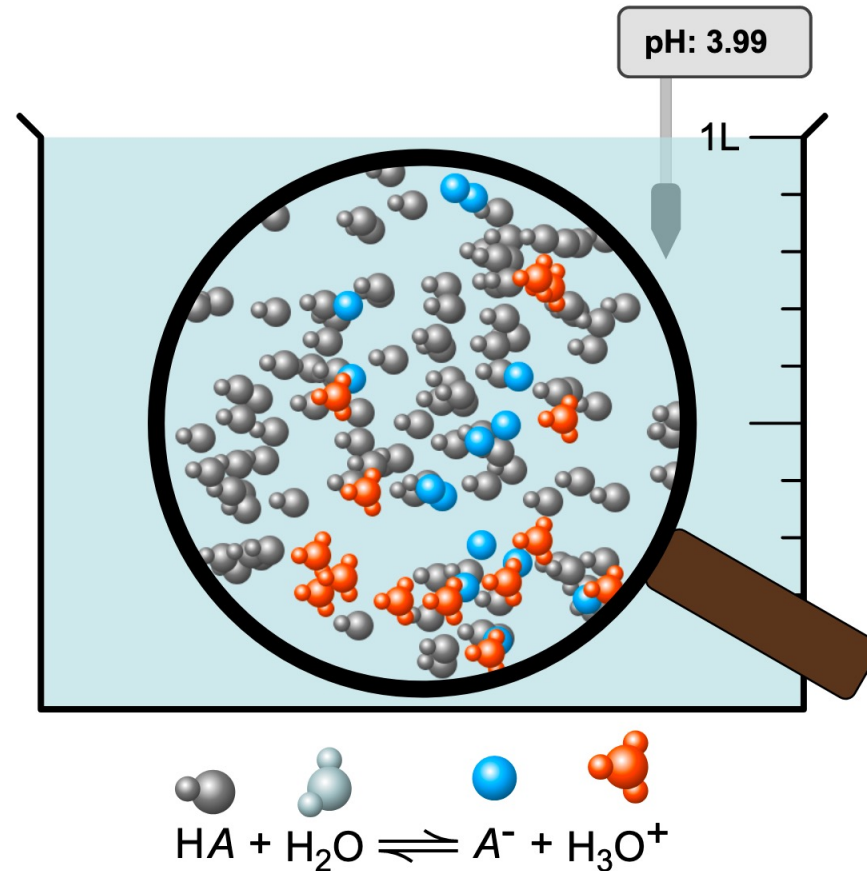
Weak Acid (HF)



Strong vs. weak
simulation

2 Factors affect pH of solution:

- nature of acid/base
- concentration



Relative Strengths of Conjugate Acid-Base Pairs

Strong Acids/Bases give weak conjugates and vice versa

Table 16.2 Relative Strengths of Conjugate Acid-Base Pairs

Acid	Conjugate Base
HClO ₄ (perchloric acid)	ClO ₄ ⁻ (perchlorate ion)
HI (hydroiodic acid)	I ⁻ (iodide ion)
HBr (hydrobromic acid)	Br ⁻ (bromide ion)
HCl (hydrochloric acid)	Cl ⁻ (chloride ion)
H ₂ SO ₄ (sulfuric acid)	HSO ₄ ⁻ (hydrogen sulfate ion)
HNO ₃ (nitric acid)	NO ₃ ⁻ (nitrate ion)
H ₃ O ⁺ (hydronium ion)	H ₂ O (water)
HSO ₄ ⁻ (hydrogen sulfate ion)	SO ₄ ²⁻ (sulfate ion)
HF (hydrofluoric acid)	F ⁻ (fluoride ion)
HNO ₂ (nitrous acid)	NO ₂ ⁻ (nitrite ion)
HCOOH (formic acid)	HCOO ⁻ (formate ion)
CH ₃ COOH (acetic acid)	CH ₃ COO ⁻ (acetate ion)
NH ₄ ⁺ (ammonium ion)	NH ₃ (ammonia)
HCN (hydrocyanic acid)	CN ⁻ (cyanide ion)
H ₂ O (water)	OH ⁻ (hydroxide ion)
NH ₃ (ammonia)	NH ₂ ⁻ (amide ion)

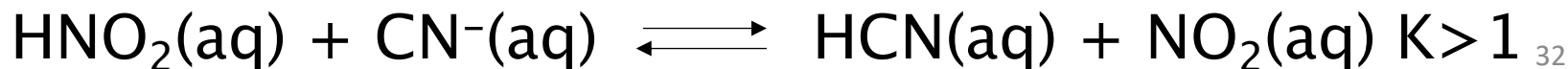
Acid strength increases ↑

Strong acids

Weak acids

Base strength increases ↓

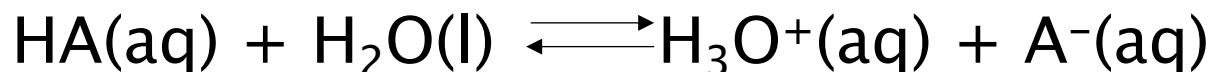
Stronger acids will dominate over weaker acids



Acid Ionization Constant: K_a

Equilibrium constant for acid dissociation

Dissociation of acid in water:



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

K_a is the acid ionization (aka acid dissociation) constant

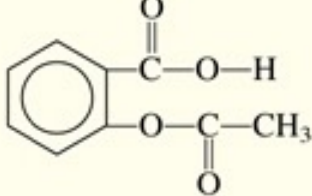
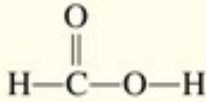
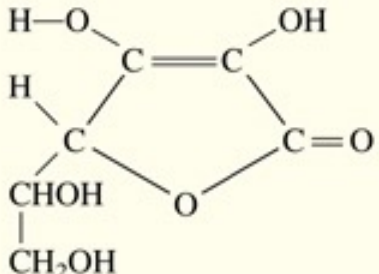
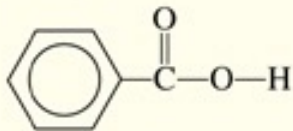
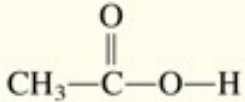
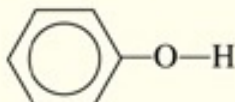
- Quantitative measure of acid strength
- Higher K_a = stronger acid
- Sometimes discussed in terms of $\text{p}K_a$

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

K_a ↑ Weak acid strength ↑

$\text{p}K_a$ ↑ Weak acid strength ↓

K_a Values for Some Common Weak Acids

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Hydrofluoric acid	HF	H—F	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	O=N—O—H	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	HCOOH		1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH		1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

Calculations Using K_a

1.) 0.100mol of HF is dissolved in 1.00L of water at 25°C. The pH at equilibrium was found to be 2.08. Calculate K_a and pKa.

Note: Do not use approximation method if you have the value of X!

$$\begin{aligned} \text{A: } K_a &= 7.5 \times 10^{-4} \\ \text{p}K_a &= 3.12 \end{aligned}$$

2.) What is the pH of a weak 0.122M monoprotic acid whose K_a is 5.7×10^{-6} ?

A: pH = 3.08

3.) Find the pH of a 0.20M solution of Formic Acid (HCHO_2)

Look up K_a in table:

Determining Relative Acidity

1.) Which is the stronger acid, HF or HNO₂?

Look up K_a in table:

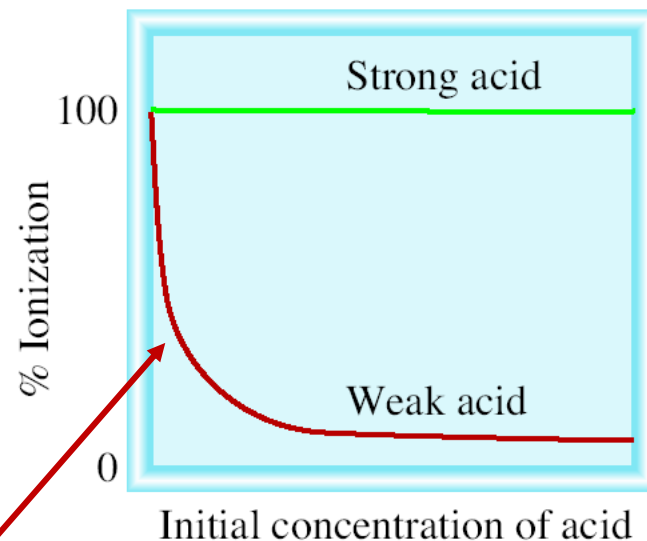
HF: 7.5×10^{-4}

HNO₂: 4.6×10^{-4}

Percent Ionization and K_a

- Indicates the extent to which an acid is ionized
- Only matters for weak acids (100% for strong)
- Higher percent ionization = more ions = stronger acid
 - Ex: 0.1M HCl, pH = 1.00
 - 0.1M HCOOH, pH = 2.38

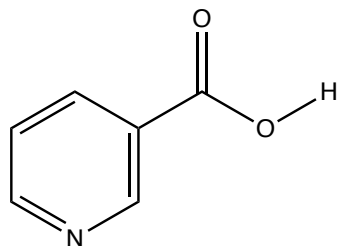
$$\text{Percent Ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_{\text{initial}}} \times 100$$



% ionization of a weak acid decreases as the initial concentration of the acid increases

Calculations Involving Percent Ionization

1.) Niacin, one of the B vitamins, has the following structure:



a.) If a 0.020M solution has a pH of 3.26, what is the K_a for niacin?
A: 1.6×10^{-5}

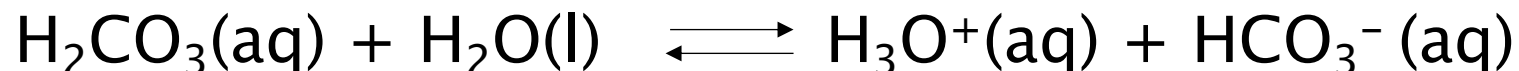
b.) What is the percent ionization of the 0.020M solution?

2.) A 0.0100M solution of HNO_2 is 19% ionized at equilibrium. What is the K_a ?

Polyprotic Acids

Acids that have more than one ionizable proton

- Ionize in successive steps



- Each step has its own K_a
- Easier to remove the first proton than the second, etc.
 - $K_{a1} > K_{a2} > K_{a3} \dots$
- Successive equilibrium constants have less and less impact on pH
 - May not need to use all K values to solve a problem

Polyprotic Acids

If the difference between the K_a values for the first and 2nd, 3rd, etc. K_a values is 10^3 or more, the pH generally depends on only the first dissociation.

If the difference is smaller, additional dissociating protons may impact pH.

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-3}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	1.0×10^{-3}	4.6×10^{-5}	

Polyprotic Acid Calculations

Calculate the pH of a 1.5M solution of tartaric acid.

$$K_{a1} = 1.0 \times 10^{-3} \quad K_{a2} = 4.6 \times 10^{-5}$$

1st ionizable proton:



1.5	0	0	$K_{a1} = \frac{X^2}{1.5} = 1.0 \times 10^{-3}$ $X^2 = 1.5 \times 10^{-3}$ $X = 3.873 \times 10^{-2} \text{ M} = [\text{H}_3\text{O}^+]$
-X	+X	+X	
<u>1.5-X</u>	<u>X</u>	<u>X</u>	
1.5-X ignore			

2nd ionizable proton:



3.873x10 ⁻²	3.873x10 ⁻²	0	Total [H ₃ O ⁺] $H_1 = 3.873 \times 10^{-2} \text{ M}$ $H_2 = 4.6 \times 10^{-5} \text{ M}$ <hr style="width: 100%;"/> $3.8776 \times 10^{-2} \text{ M}$ $\text{pH} = -\log(3.8776 \times 10^{-2})$ $= 1.4114 \rightarrow 1.41$
-X	+X	+X	
<u>3.873x10⁻²</u>	<u>3.873x10⁻²</u>	<u>X</u>	
3.873x10⁻² ignore	3.873x10⁻² ignore		

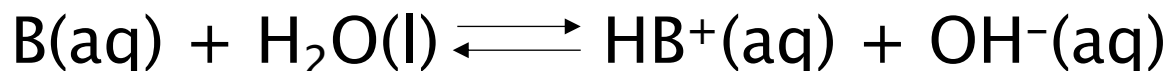
$$K_{a2} = \frac{[3.873 \times 10^{-2}][X]}{[3.873 \times 10^{-2}]} = 4.6 \times 10^{-5}$$

$$X = 4.6 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

Base Ionization Constant: K_b

Equilibrium constant for base dissociation

Weak bases react with water to produce hydroxide ions:



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

K_b is the base ionization constant

- Quantitative measure of base strength
- Higher K_b = stronger base
- Sometimes discussed in terms of pK_b

$$pK_b = -\log K_b$$

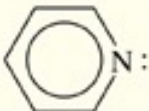
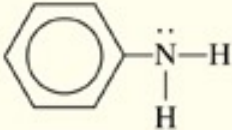
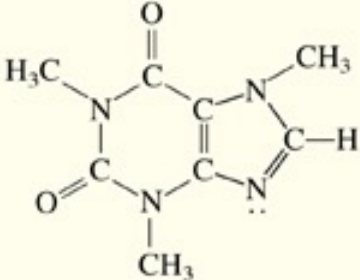
K_b ↑ Weak base strength ↑

pK_b ↑ Weak base strength ↓

Types of Weak Bases

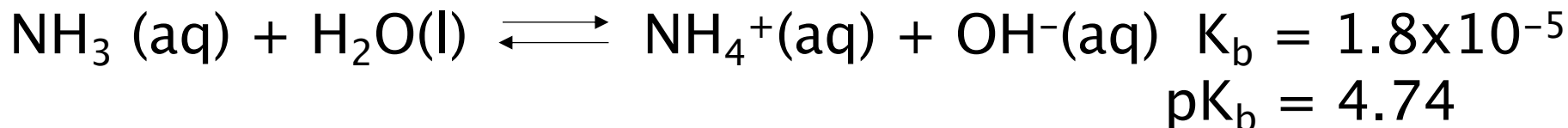
- Neutral substances that have an atom with a non-bonding pair of electrons
 - Examples include ammonia (NH_3) & amines
 - Amines described earlier in the chapter (slide 11)
- Anions (conjugate bases) of weak acids
 - Examples include HCO_3^- , ClO^- , HS^-
 - Act as H^+ acceptors in water
 - Anions of strong acids do not act as bases – not an equilibrium process
- Insoluble/slightly soluble hydroxides
 - Soluble hydroxides are strong bases
 - $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$
 - Solubility equilibria (K_{sp}) will be discussed in the next chapter

K_b Values for Some Common Weak Bases

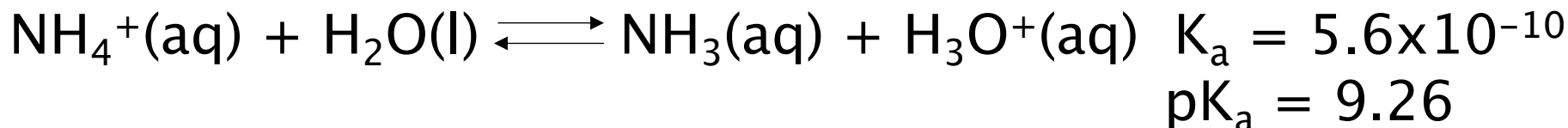
Name of Base	Formula	Structure	K_b^*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\ddot{N}-H$ H	5.6×10^{-4}	$C_2H_5\overset{+}{N}H_3$	1.8×10^{-11}
Methylamine	CH_3NH_2	$CH_3-\ddot{N}-H$ H	4.4×10^{-4}	$CH_3\overset{+}{N}H_3$	2.3×10^{-11}
Ammonia	NH_3	$H-\ddot{N}-H$ H	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5\overset{+}{N}H$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5\overset{+}{N}H_3$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}\overset{+}{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$	$H-\ddot{N}-\overset{O}{\parallel}C-\ddot{N}-H$ H H	1.5×10^{-14}	$H_2N\overset{+}{C}ONH_3$	0.67

K_a & K_b Relationship for Conjugate Acid/Base Pairs in Water

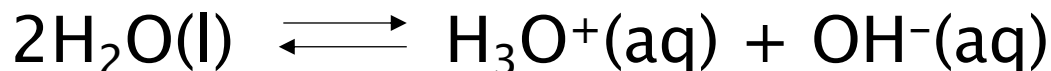
Base & water



Conjugate acid & water



Add the two reactions together: multiply K values (Ch15)



$$K_w = K_a \times K_b = 1.0 \times 10^{-14}$$

$$1.8 \times 10^{-5} \times 5.6 \times 10^{-10} = 1.0 \times 10^{-14}$$

$$\text{p}K_a + \text{p}K_b = 14$$
$$9.26 + 4.74 = 14$$

High K_a must have Low K_b & vice versa

Calculations Using K_b

1.) What is the pH of a 0.15M solution of NH_3 ? $K_b = 1.8 \times 10^{-5}$

A: pH = 11.22 49

2.) Codeine is a weak organic base. A $5.0 \times 10^{-3} \text{M}$ solution of codeine has a pH of 9.95. Calculate the pK_b and the value of K_b for this base.

Reminder: Do not use approximation method if you have the value of X!

$$\begin{aligned} \text{A: } K_b &= 1.62 \times 10^{-6} \\ \text{pK}_b &= 5.79 \end{aligned}$$

3.) A solution of ammonia in water has a pH of 11.17.
What is the molarity of the solution? $K_b = 1.8 \times 10^{-5}$

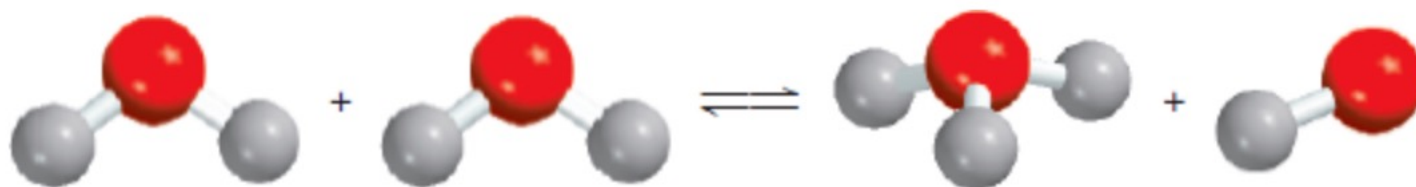
Acid–Base Properties of Salts

Salts are ionic compounds – contain cation (+) & anion (–)

- Can be formed from acid/base neutralization
- Dissociate (separate into ions) when dissolve in water
- Can sometimes impact pH through hydrolysis

Hydrolysis:

- Hydro = water
- lysis = to cut
- Reactions that break water into H^+ (H_3O^+) & OH^-



Extent to which a salt causes hydrolysis determines extent of its acid–base properties (if any)

Reminders: Strong vs. Weak No Equilibrium vs. Equilibrium



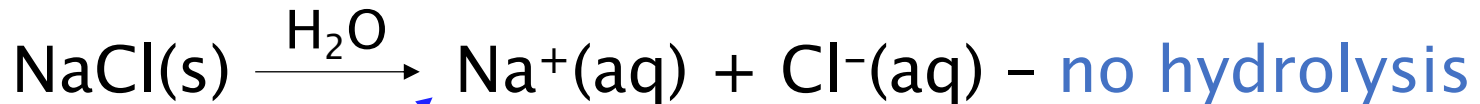
Acid-Base Properties of Salts

Hydrolysis can be caused by both cations & anions, but does not happen in every situation

Salts formed from conjugates of a strong acid + a strong base do not cause hydrolysis

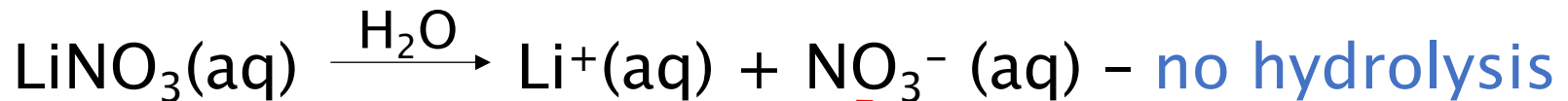
No equilibrium = no desire to reform parent acid/base

For salt solutions: no hydrolysis = neutral (no OH^- or H_3O^+)



From NaOH
strong base

From HCl
strong acid



From LiOH
strong base

From HNO_3
strong acid

Acid–Base Properties of Salts

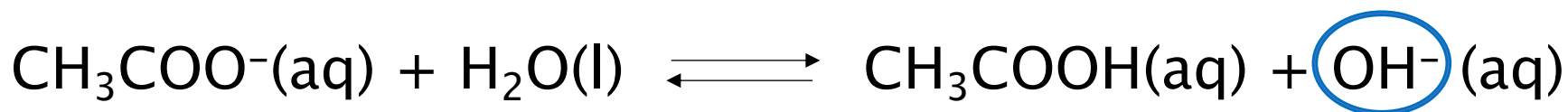
Soluble ions derived from a weak base or a weak acid will cause hydrolysis

Ex 1: **NaOH: strong base**

CH₃COOH: weak acid



Weak base

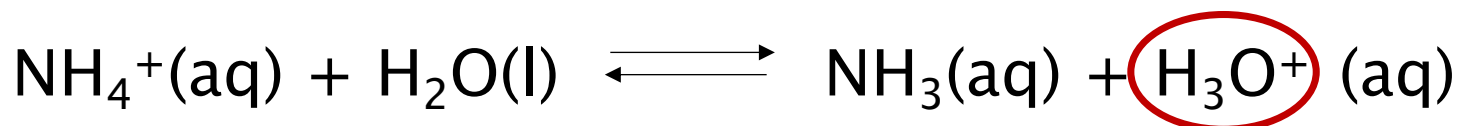


Ex 2: **NH₃: weak base**

HCl: strong acid



Weak acid



Equilibrium = Must have both acid/base AND its conjugate

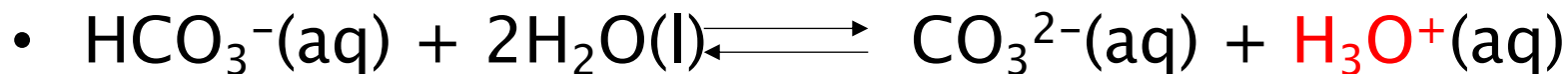
What if an ion can act as either an acid or a base?

Occurs with salts from polyprotic acids such as H_2CO_3 , H_3PO_4 , H_2SO_4 .

Need to compare K_a and K_b values

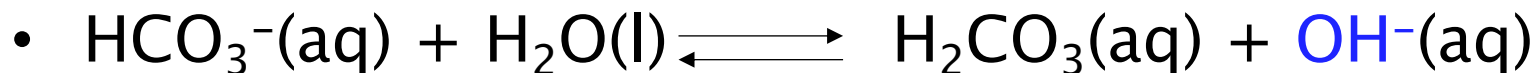
- Example: NaHCO_3

Acting
as acid



$$K_a = 4.8 \times 10^{-11}$$

Acting
as base



$$K_b = K_w / K_a = 2.4 \times 10^{-8}$$

- $K_b > K_a$ so solution will be basic!

Determining if a Salt Solution is Acidic, Basic, or Neutral

Look at the ions that the salt dissociates into:

- Negative ion* is the potential base; ex: Cl^- , NO_2^- , CH_3COO^-
 - Write the anion as an acid: HCl , HNO_2 , CH_3COOH
 - If the ion would be part of a strong acid, it does not act as a base; ex: Cl^-
 - If the ion would be part of a weak acid, it acts as a base when in a salt solution; ex: NO_2^- , CH_3COO^-
- Positive ion* is the potential acid: ex: Na^+ , NH_4^+ , Fe^{2+}
 - Write the cation as a base: NaOH , NH_3 , $\text{Fe}(\text{OH})_2$
 - If the ion would be part of a strong base, it does not act as an acidic; ex: Na^+
 - If the ion would be part of a weak base, it acts as an acid when in a salt solution; ex: NH_4^+ , Fe^{2+}

*Unless the ion is amphiprotic

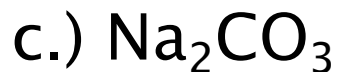
Determining if a Salt Solution is Acidic, Basic, or Neutral

Look at the ions that the salt dissociates into:

- If both cation & anion have a strong parent, neither acts as an acid or base and the solution is neutral; ex: NaCl
- If both cation & anion have a weak parent; ex: NH_4NO_2
 - Acidity/basicity depends on relative strength
 - Math can be complicated
 - Qualitatively:
 - $K_a < K_b$ basic solution
 - $K_a > K_b$ acidic solution
 - $K_a \approx K_b$ pretty close to neutral

Determining if a Salt Solution is Acidic, Basic, or Neutral

1.) Predict whether aqueous solutions of the following compounds are acidic, basic, or neutral.



2.) For each of the following pairs, indicate which salt would form the more acidic (i.e. less basic) 0.010M solution.

a.) NaNO_3 or $\text{Fe}(\text{NO}_3)_3$

b.) $\text{CH}_3\text{NH}_3\text{Cl}$ or BaCl_2

c.) KNO_2 or KNO_3

d.) $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{SO}_3$

3.) Calculate the $[\text{OH}^-]$ and pH of a 0.10M NaCN solution. K_a for HCN is 4.9×10^{-10} .

A: $[\text{OH}^-] = 1.4 \times 10^{-3}\text{M}$
pH = 11.16

4.) Calculate the pH of a 0.42M NH_4Cl solution.
 K_b for NH_3 is 1.8×10^{-5}

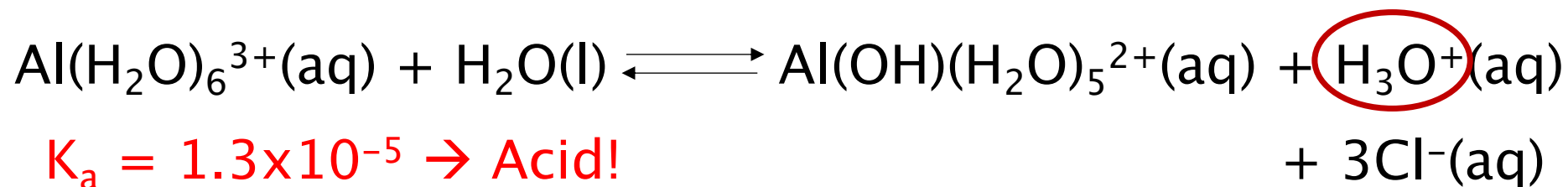
A: pH = 4.82

Hydration of Metal Ions

Salts with small, highly charged metal cations (e.g. Al^{3+} , Fe^{3+} , Cr^{3+} , Be^{2+}) and the conjugate base of a strong acid can also have acidic properties

Example:

AlCl_3 dissolved in water produces:



- e^- in water molecules are pulled toward metal ion
- O–H bonds in attached waters become more polarized
- H^+ dissociates from water molecule forming H_3O^+

Hydration of Metal Ions



Higher charge & smaller size make cations more acidic

Less acidic



More acidic

Hydration of Metal Ions

Which member of each pair would produce a more acidic solution & why?

1.) CuCl or $\text{Cu}(\text{NO}_3)_2$

2.) CrCl_3 or NiCl_3