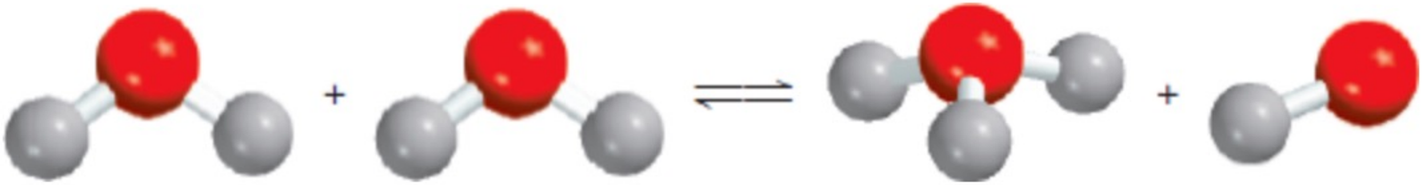
Chapter 17

Acids & Bases

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$



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).

$$HCl\ (g) \xrightarrow{H_2O} H^+\ (aq) + Cl^-\ (aq)$$

Base:

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

$$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$$

What are Acids & Bases?

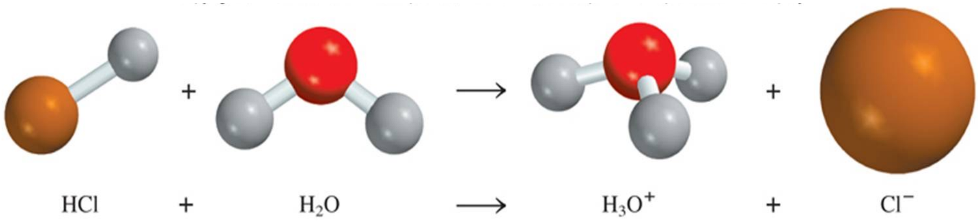
Brønsted-Lowry Definition

Acid:

A proton (H^+) donor

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

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+ (aq) + Cl^-(aq)$$

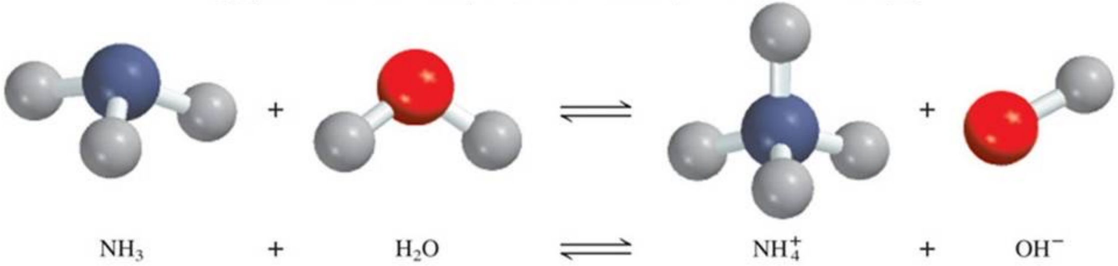


Base:

A proton (H^+) acceptor

- Must have a pair of non-bonding electrons

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



Lewis Acids & Bases

Acid:

An electron pair acceptor

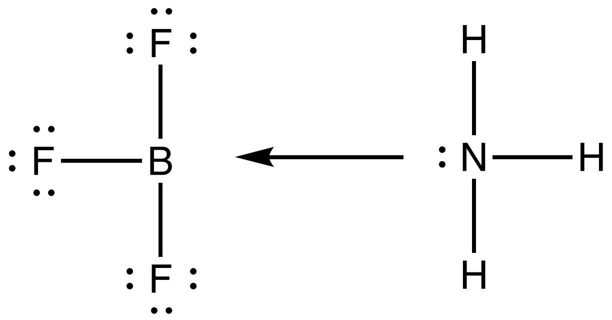
- Do not need to have a removable proton
- Must have an empty orbital to put electrons in

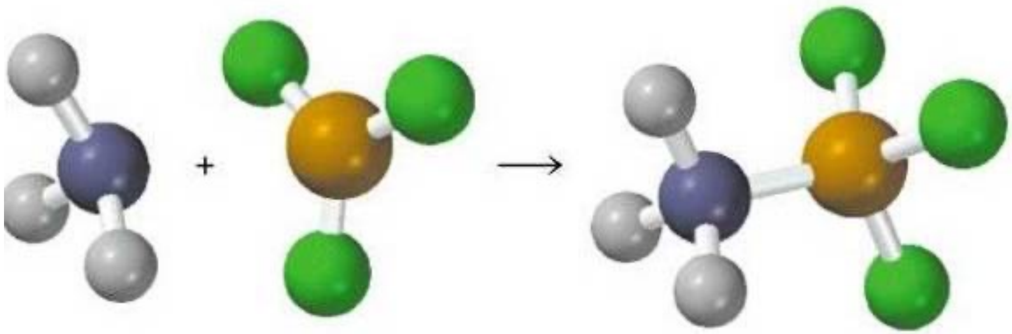
Base:

An electron pair donor

- Must have a pair of non-bonding electrons

Ex: $BF_3(g) + NH_3(g) \rightarrow F_3B\text{–}NH_3(g)$





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:

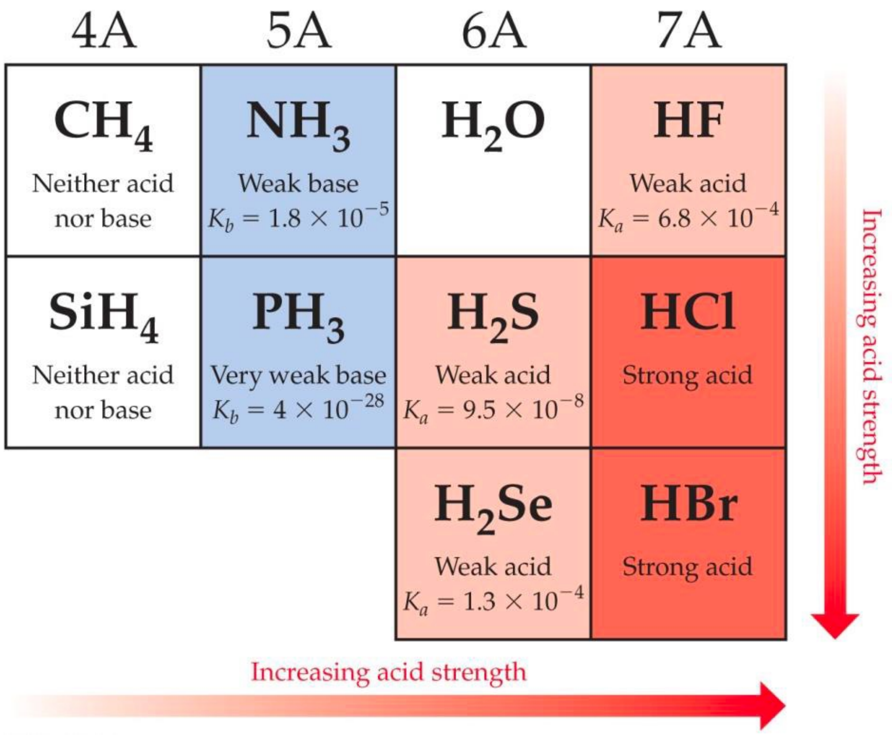
- Less electronegative, share e^- more equally, stronger bond
- Ex: P less electronegative than S, H_3PO_4 weaker than H_2SO_4

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
CH_4 Neither acid nor base	**NH_3** Weak base $K_b = 1.8 \times 10^{-5}$	**H_2O**	**HF** Weak acid $K_a = 6.8 \times 10^{-4}$
SiH_4 Neither acid nor base	**PH_3** Very weak base $K_b = 4 \times 10^{-28}$	**H_2S** Weak acid $K_a = 9.5 \times 10^{-8}$	**HCl** Strong acid
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	**HBr** Strong acid

For <u>binary</u> acids:

Acidity increases left to right across a row

- Electrongativity 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:		**Strong Bases:**	
Hydrochloric Acid	HCl	Soluble Hydroxides:	
Sulfuric Acid	H_2SO_4	Sodium	$NaOH$
Nitric Acid	HNO_3	Potassium	KOH
Perchloric Acid	$HClO_4$	Lithium	$LiOH$
Hydrobromic Acid	HBr	Barium	$Ba(OH)_2$
Hydroiodic Acid	HI	etc.	

Weak Acids:		**Weak Bases:**	
Carbonic Acid	H_2CO_3	Ammonia	NH_3
Phosphoric Acid	H_3PO_4	Amines	$R-NH_2, R_2NH$
Acetic Acid	CH_3COOH	Insoluble/slightly soluble hydroxides	
Hydrofluoric Acid	HF		
Nitrous Acid	HNO_2		
Hydrocyanic acid	HCN		
Carboxylic Acids	$R-COOH$		

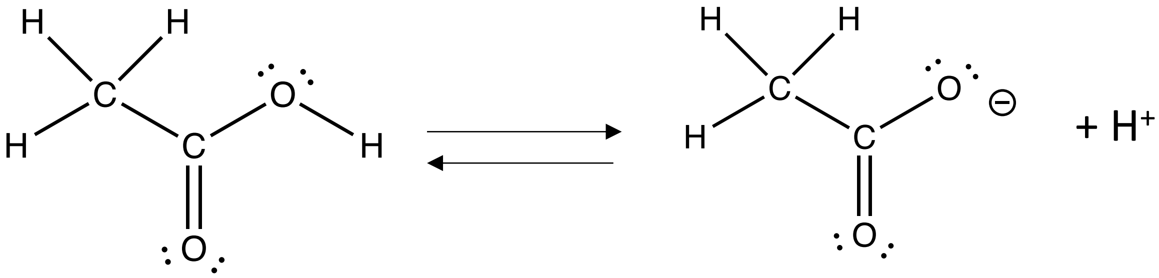
Organic Acids: Carboxylic Acids (–COOH)

Weak organic acids

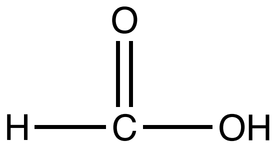
- –COOH group on molecule is acidic
- Removal of proton (H^+) creates resonance structure
- Stabilizes anion

Never fully dissociate in water

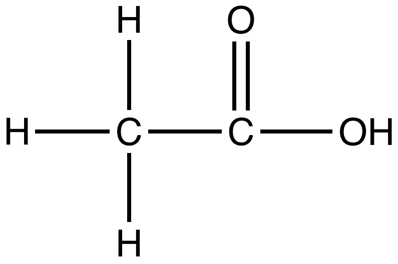
- Equilibrium process



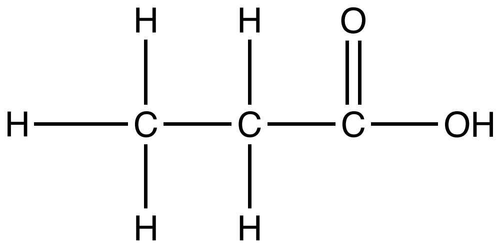
Examples:



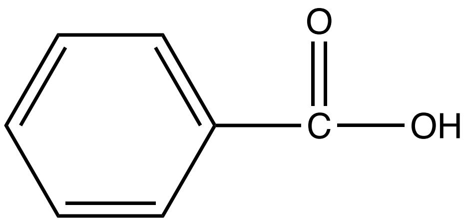
Formic Acid



Acetic Acid



Butyric Acid



Benzoic Acid

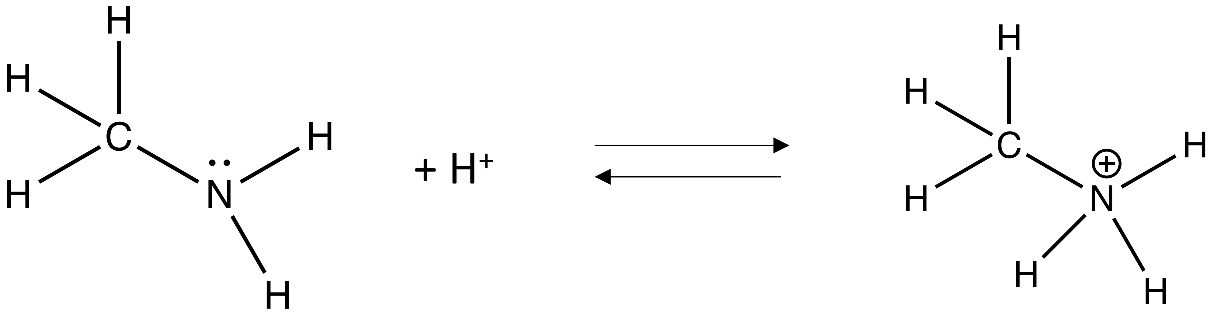
Organic Bases: Amines (contain N)

Weak organic bases

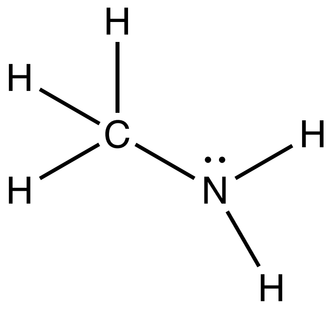
- Derivatives of ammonia
- N has lone pair of electrons to accept a proton

Also do not fully dissociate in water

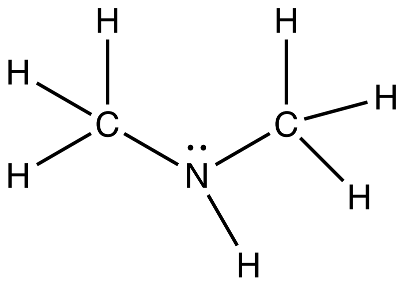
- Equilibrium process



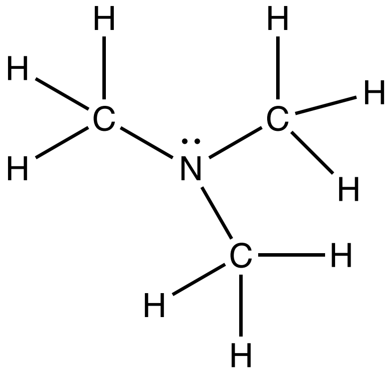
Examples:



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^-

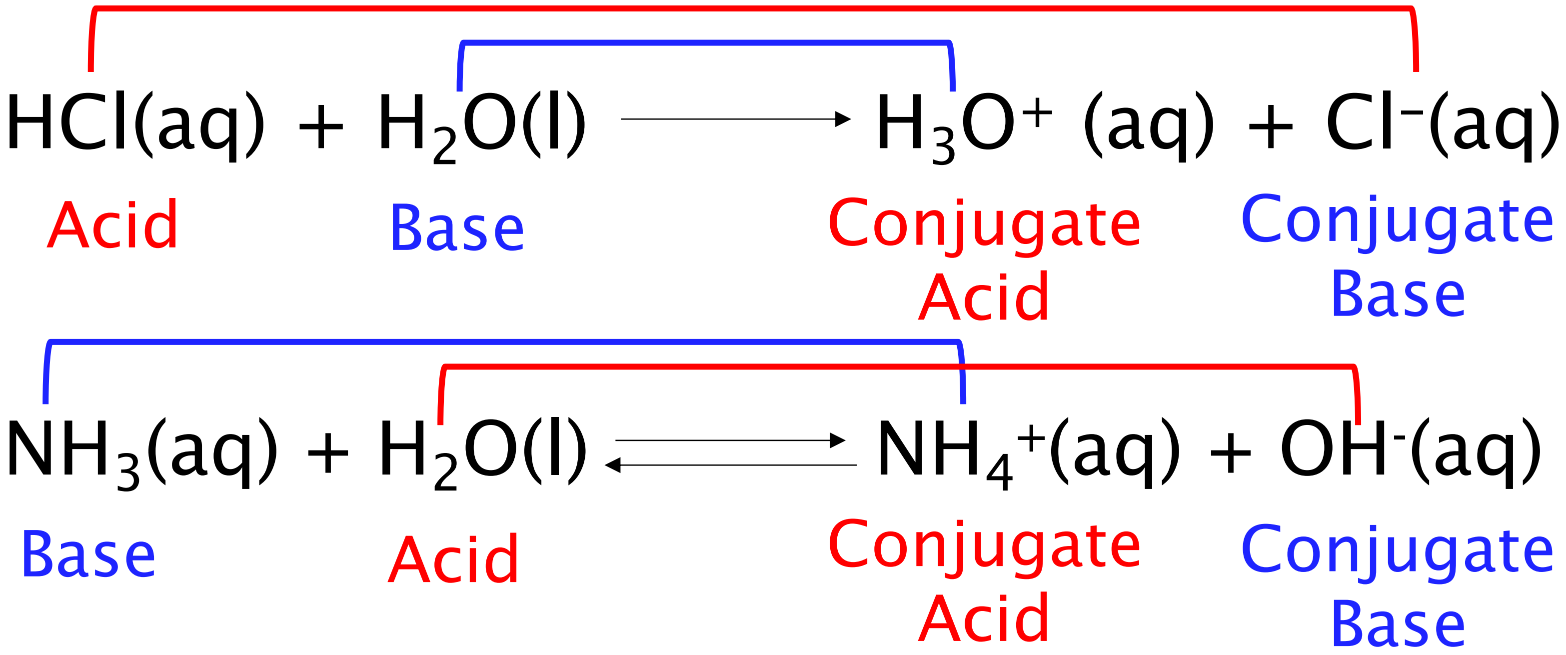
Amine: CH_3NH_2 Becomes $CH_3NH_3^+$

Added proton bonds via lone pair on N

Carbon: no lone pairs

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

Conjugate Acid–Base Pairs



$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Acid

Base

Conjugate Acid

Conjugate Base

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

Base

Acid

Conjugate Acid

Conjugate Base

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

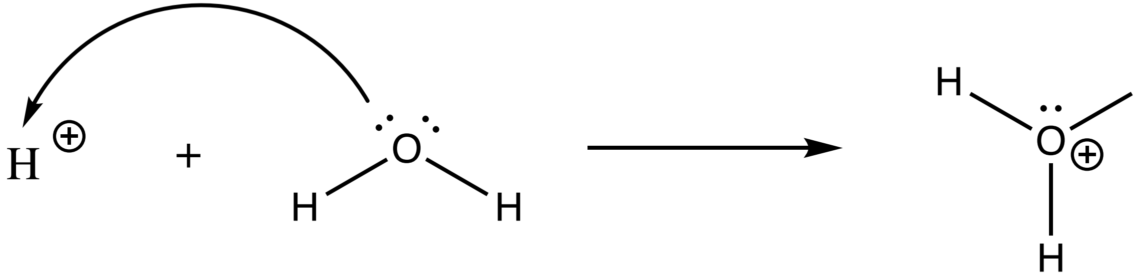
1. Give the conjugate base of each of the following acids:
   - a) HIO_3
   - b) NH_4^+
   - c) H_2S
   - d) HPO_4^{2-}
   - e) C_4H_9COOH

2. Write the formula for the conjugate acid of each of the following bases:
   - a) HSO_3^-
   - b) F^-
   - c) CO_3^{2-}
   - d) CH_3NH_2

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: H_3O^+

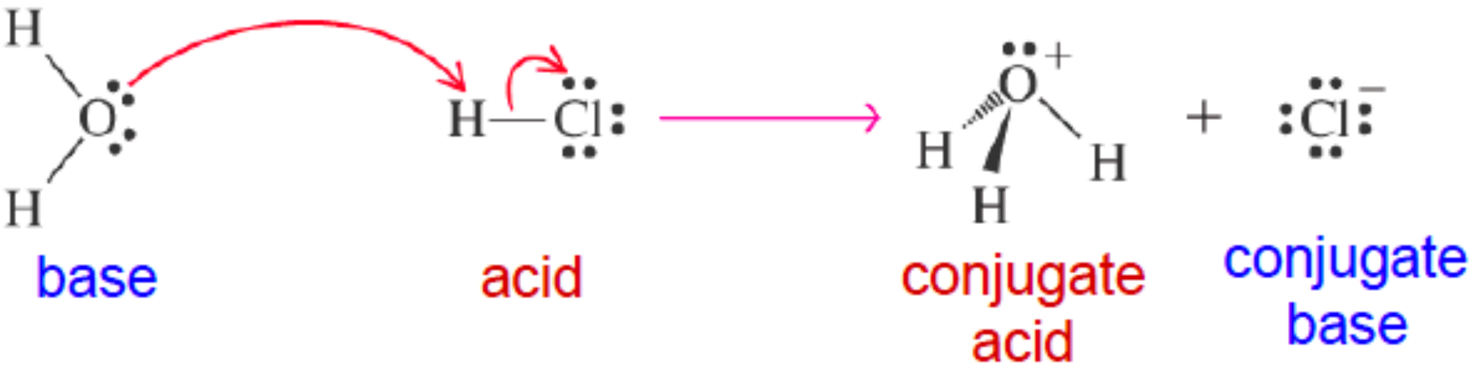


- H^+ (aq) & H_3O^+(aq) are used interchangeably

$$HA \rightleftharpoons H^+ + A^-$$

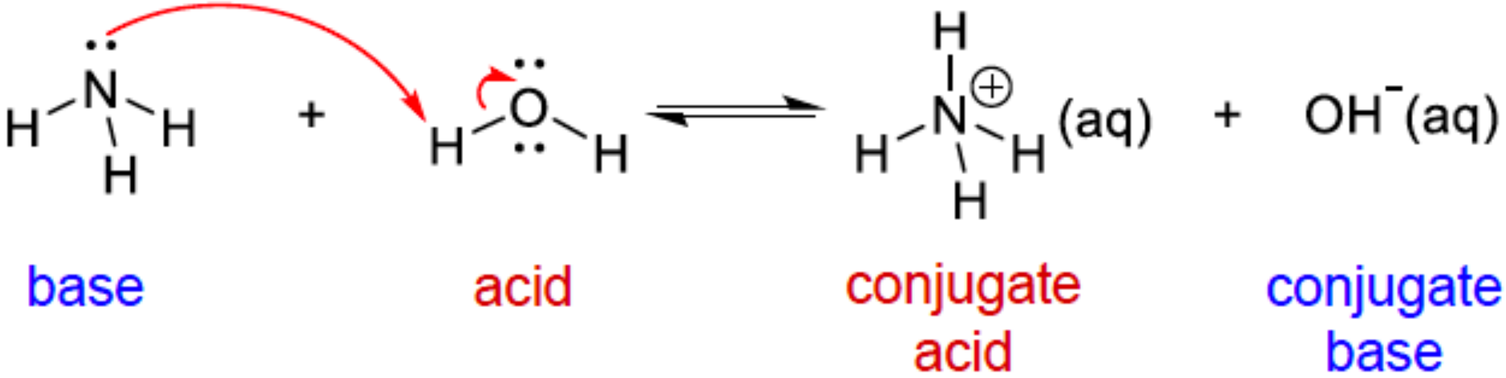
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Proton Transfer Reactions: Aqueous Acid



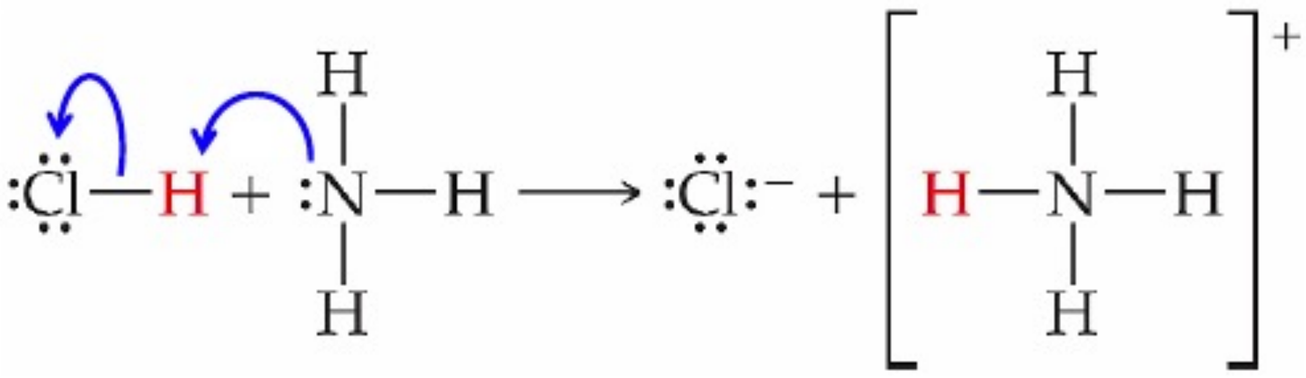
- HCl (the acid) donates a proton (H^+)
- Water (the base) accepts the proton
- The conjugate base of the acid (Cl^-) and the conjugate acid of the base (H_3O^+) are formed

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



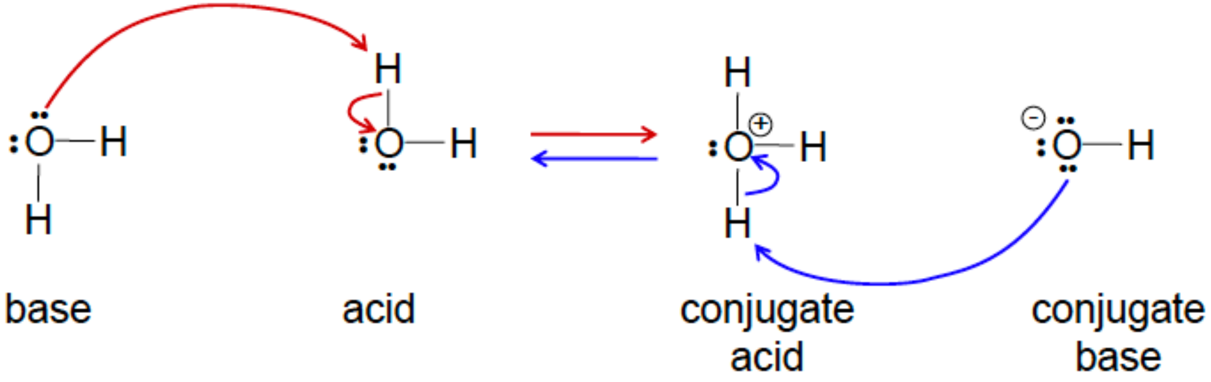
- HCl (the acid) donates a proton (H^+)
- Ammonia (the base) accepts the proton
- Can occur in the gas phase – water not needed
- Advantage of Brønsted-Lowry definition over Arrhenius definition
- Lewis definition even more broad (electron pair donor/acceptor)

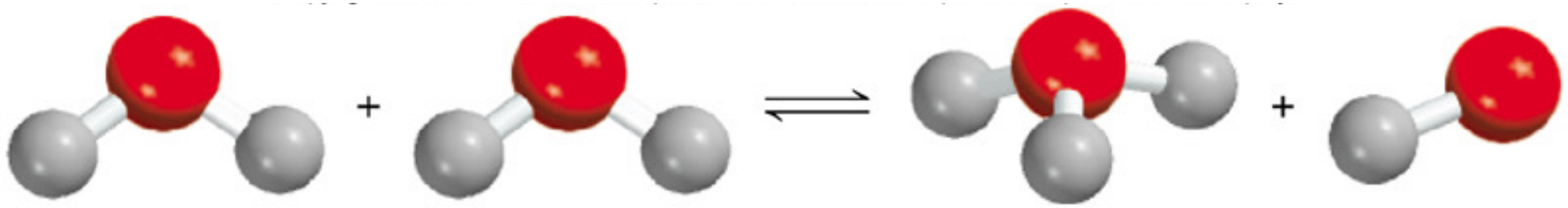
Acid–Base Properties of Water: Autoionization

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

- Essentially the water ionizes itself (“auto”)

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





This is why pure water can conduct electricity

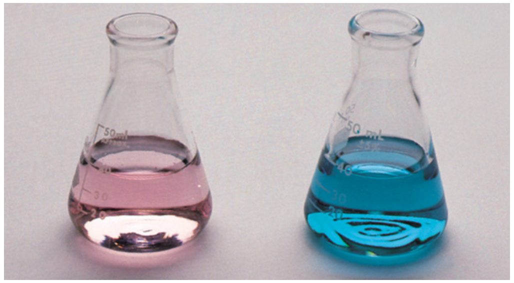
Autoionization: An Equilibrium Process

Consider the autoionization of water at 25°C

$$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

Weak Base Weak Acid Strong Acid Strong Base

$[H_3O^+] = [OH^-] = 1.0x10^{-7}M$



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

$K_w = [H_3O^+][OH^-] =$ 1.0x10^{-14} (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

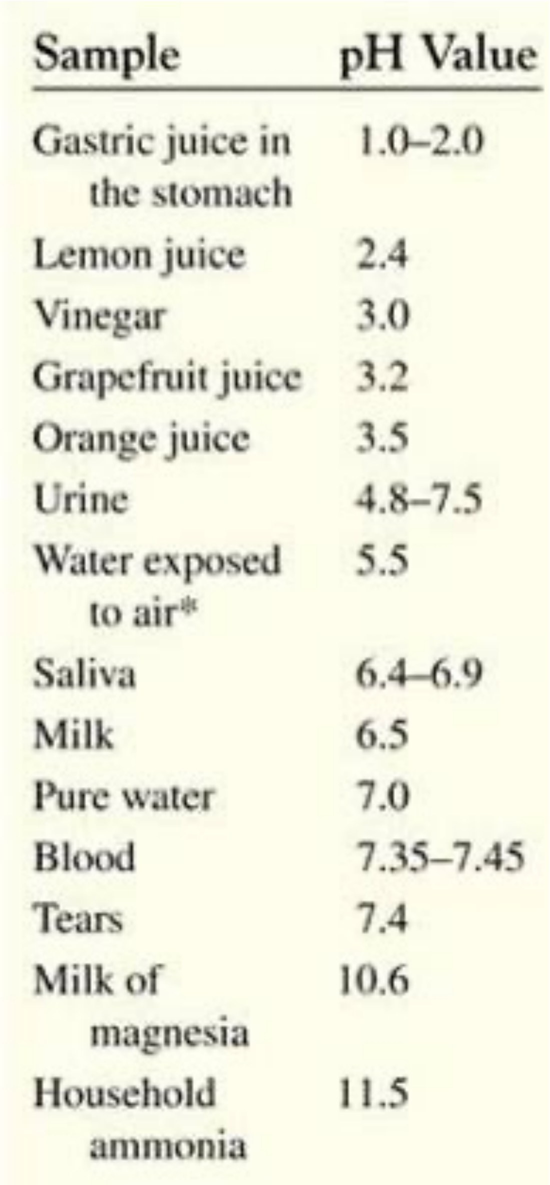
Formulas:

- $pH = -\log[H_3O^+]$
- $[H_3O^+] = 10^{(-pH)}$
- $pOH = -\log[OH^-]$
- $[OH^-] = 10^{(-pOH)}$
- $K_w = [H_3O^+][OH^-] = 1.0\times10^{-14}M$
- $pK_w = pH + pOH = 14$

Neutral: $[H_3O^+] = [OH^-]$ $pH = 7$

Acidic: $[H_3O^+] > [OH^-]$ $pH < 7$

Basic: $[H_3O^+] < [OH^-]$ $pH > 7$



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 x 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 x 10^{-3} is –3
- The formula for pH is –log to eliminate the negative sign in the answer

Consider the number 2.8 x 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 x 10^{-3} will be close to, but not exactly, –3
- $\log(2.8\times10^{-3}) = -2.6$

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

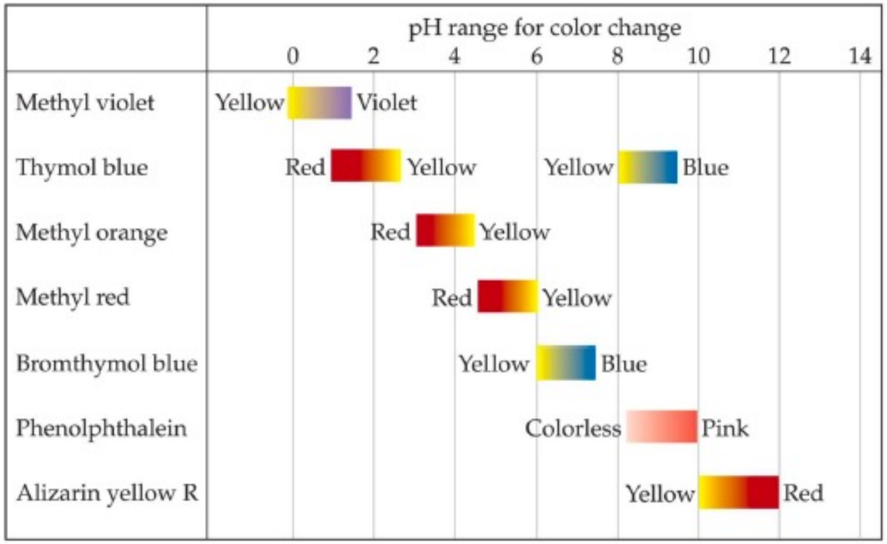
Measuring pH

Most Accurate: pH meter

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

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 pHydrion 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:

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$ $[H_3O^+]=0.010M$

$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $[H_3O^+] = 1.0x10^{-7}M$

The $[H_3O^+]$ from ionization of water is negligible:

0.010M + 0.0000001M = 0.0100001M

<u>It can be ignored</u>

Concentrated vs. Dilute Solutions

Example 2: **Dilute Solutions**

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

Two reactions are again occurring:

$HNO_3(aq)+H_2O(l) \rightarrow H_3O^+(aq)+NO_3^-(aq)$ $[H_3O^+]=1.0\text{x}10^{-6}M$

$2H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$ $[H_3O^+] = 1.0\text{x}10^{-7}M^*$

*Likely somewhat less due to Le Châtelier’s Principle

The $[H_3O^+]$ from ionization of water is 10% of the amount contributed by the acid:

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

<u>It CANNOT be ignored</u>

Contribution from autoionization of water must be taken into account if acid/base provides < $10^{-6}M$ H_3O^+/OH^-

pH Calculations for Strong Acids/Bases

1. Calculate $[H^+]$ at 25°C for an aqueous solution in which $[OH^-] = 0.00045M$. Indicate whether it is acidic, basic, or neutral. A: 2.2×10^{-11}M; basic

2. Find the pH and pOH of a 0.0050M HBr solution at 25°C

   pH: 2.30; pOH: 11.70

3. Calculate the H_3O^+ and OH^- concentrations at 25°C of an aqueous 0.010M solution of nitric acid. $[H_3O^+]$: 0.010M
   $[OH^-]$: 1.0×10^{-12}

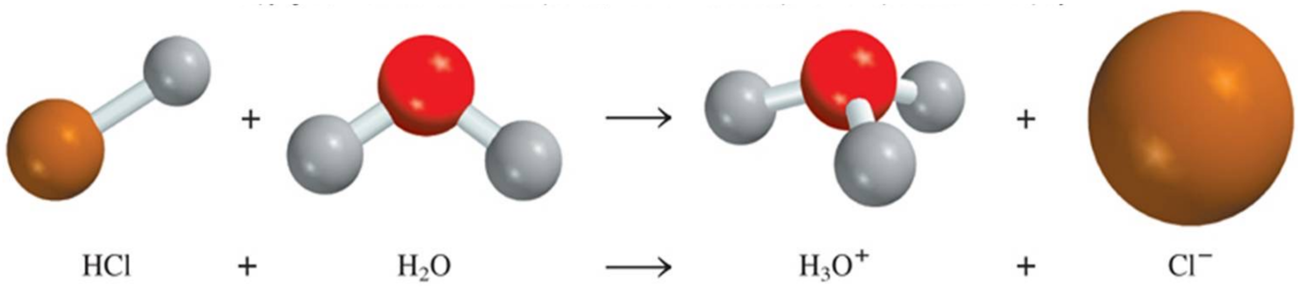
4. Calculate the pH made from 15.00mL of 1.00M HCl diluted to 0.500L. A:1.523

5. What is the concentration of a solution of $Ba(OH)_2$ for which the pH is 10.05? A: 5.6×10^{-5}M

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



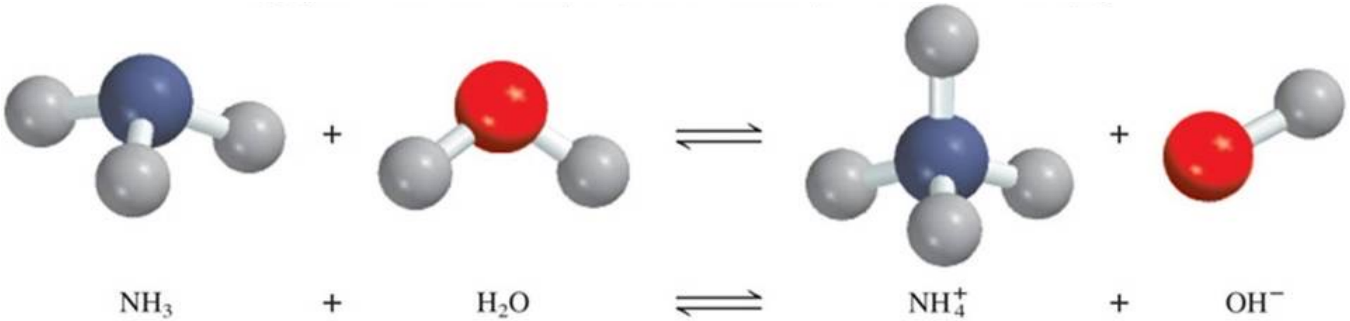
$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

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

Strength of Acids & Bases

Weak Acids & Bases: Incomplete dissociation

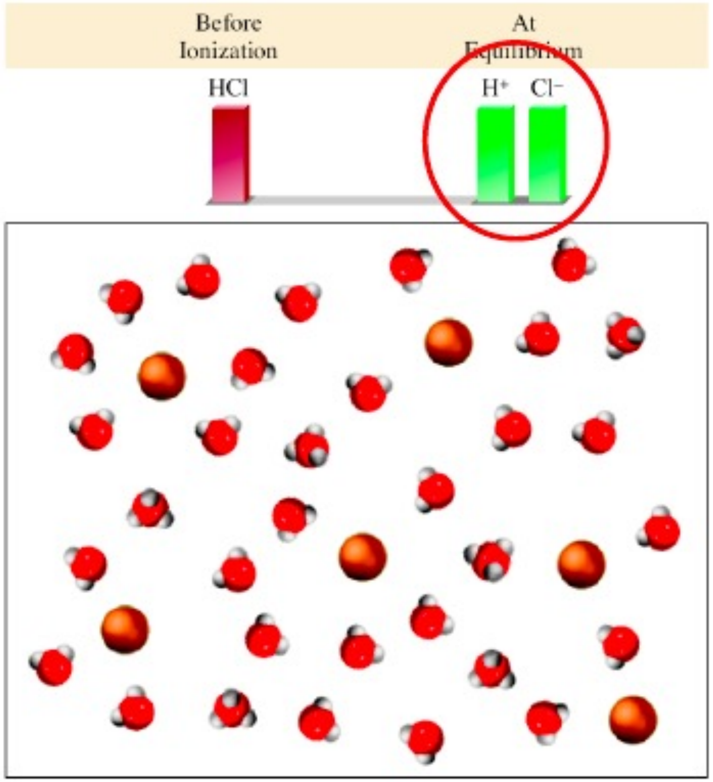
- Some of original compound remains along with ions
- Equilibrium process; represented by double arrow
- Dissociation is governed by an equilibrium constant
  - K_a or K_b
- Poor conductors of electricity
- Conjugates can act as acids/bases



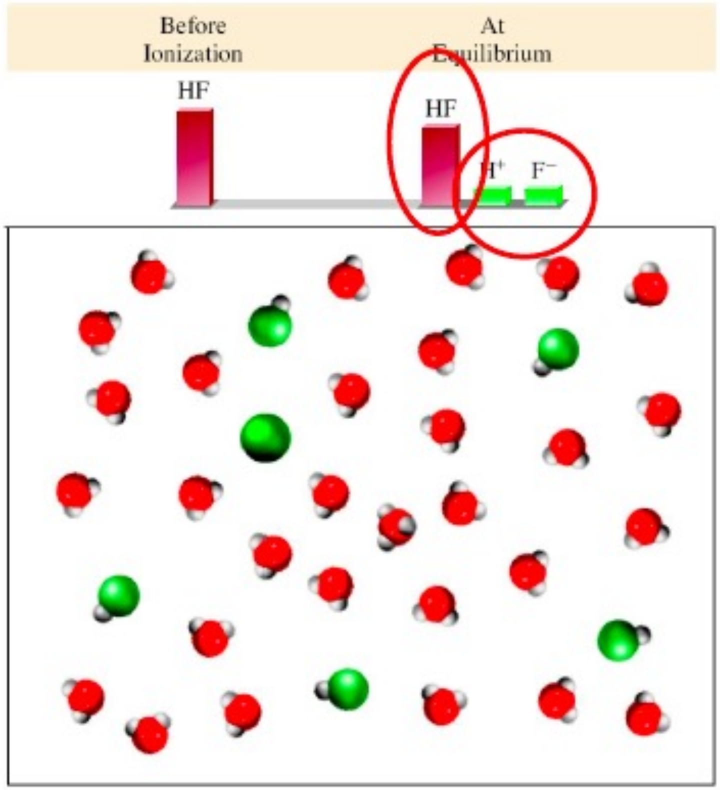
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Strong Acid (HCl)



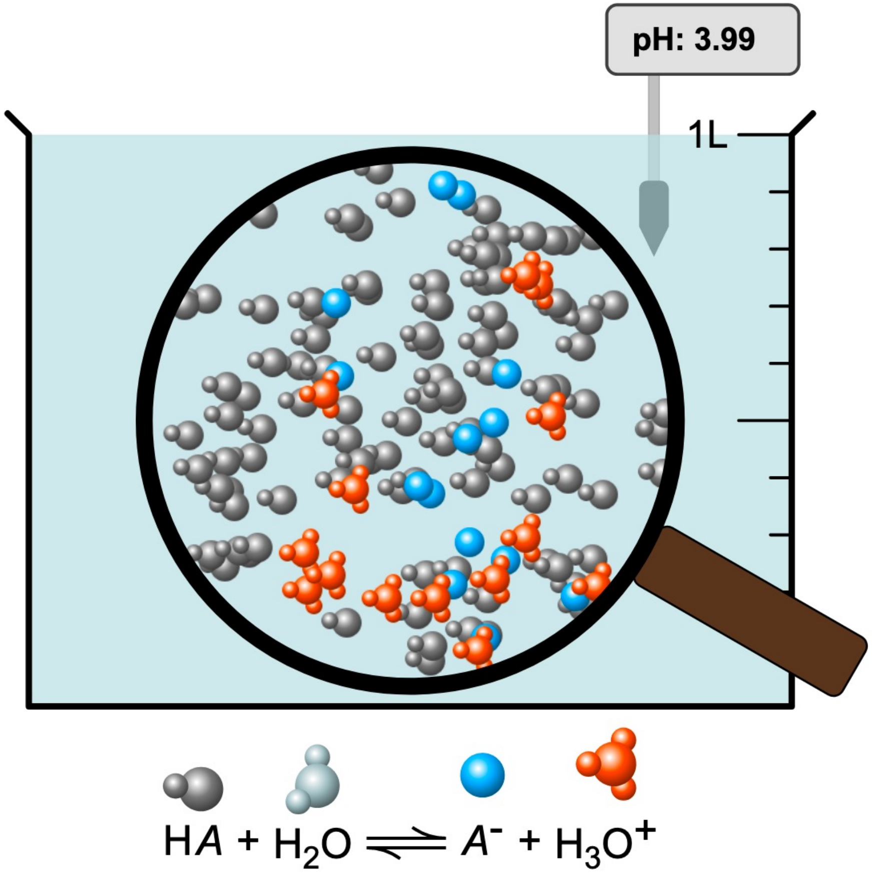
Weak Acid (HF)



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

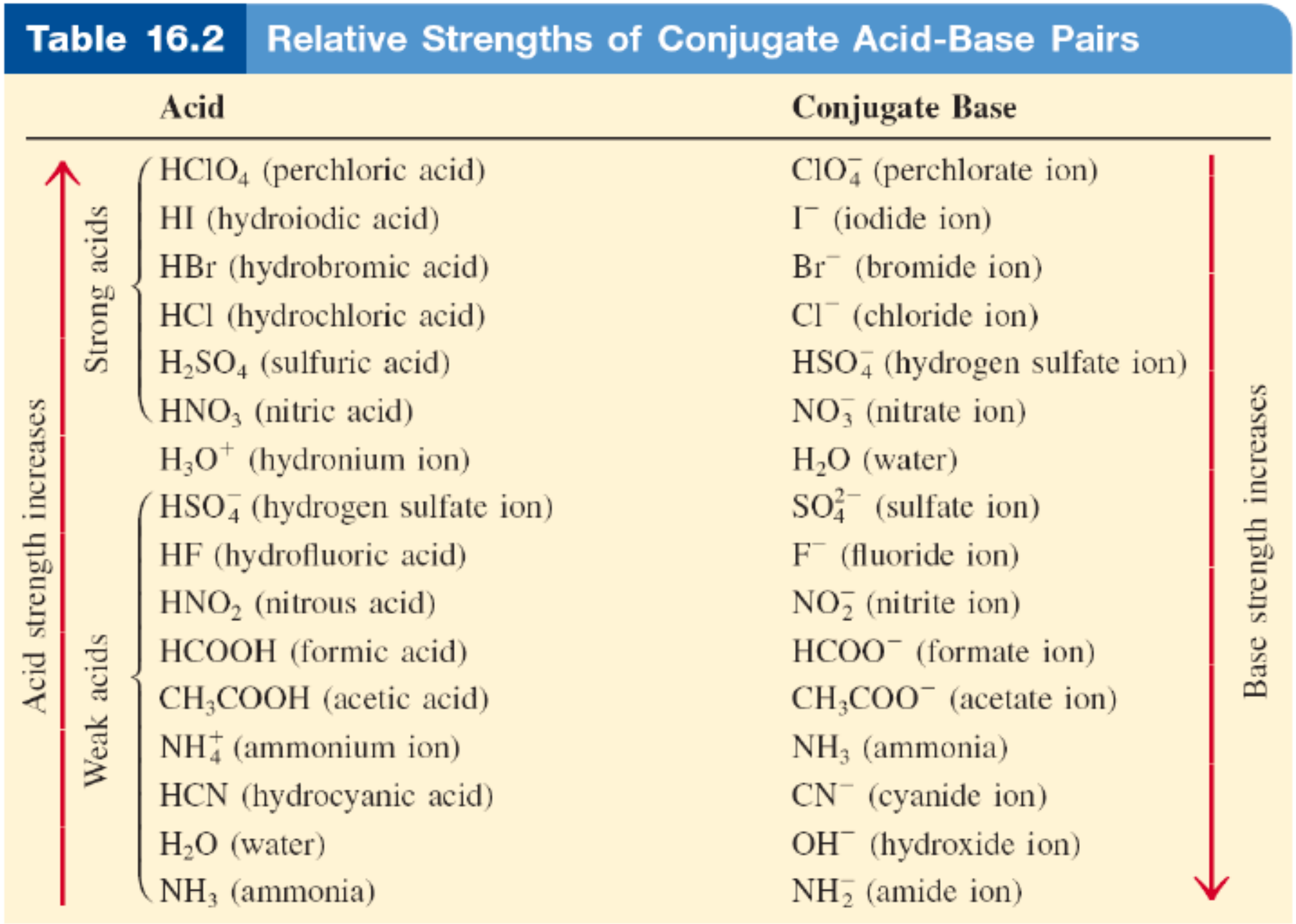


Table 16.2 Relative Strengths of Conjugate Acid-Base Pairs

Acid strength increases ↑ · Base strength increases ↓

	Acid	Conjugate Base
Strong acids	$HClO_4$ (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_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
	HNO_3 (nitric acid)	NO_3^- (nitrate ion)
	H_3O^+ (hydronium ion)	H_2O (water)
Weak acids	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_3COOH (acetic acid)	CH_3COO^- (acetate ion)
	NH_4^+ (ammonium ion)	NH_3 (ammonia)
	HCN (hydrocyanic acid)	CN^- (cyanide ion)
	H_2O (water)	OH^- (hydroxide ion)
	NH_3 (ammonia)	NH_2^- (amide ion)

Stronger acids will dominate over weaker acids

$HNO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NO_2(aq)$ K>1

Acid Ionization Constant: K_a

Equilibrium constant for acid dissociation

Dissociation of acid in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA]} = K_a$$

K_a is the acid ionization (aka acid dissociation) constant

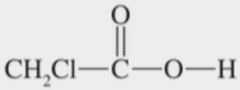
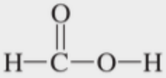
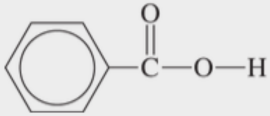
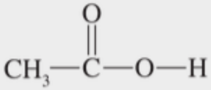
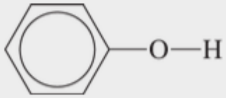
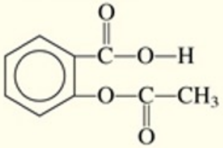
- Quantitative measure of acid strength
- Higher K_a = stronger acid
- Sometimes discussed in terms of pK_a

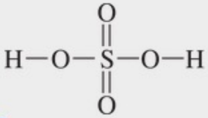
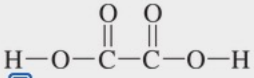
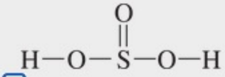
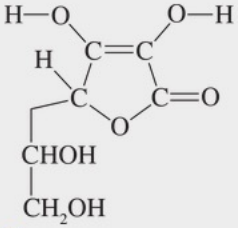
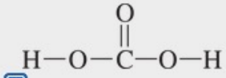
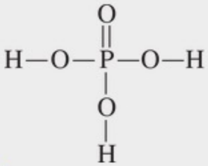
$$pK_a = -\log K_a$$

K_a ↑ Weak acid strength ↑

pK_a ↑ Weak acid strength ↓

K_a Values for Some Common Weak Acids

Name of Acid	Formula	Structure	K_a
Chloroacetic acid	$CH_2ClCOOH$	 $CH_2Cl-\overset{O}{\overset{\|}{C}}-O-H$	1.4×10^{-3}
Hydrofluoric acid	HF	$H-F$	6.1×10^{-4}
Nitrous acid	HNO_2	$O=N-O-H$	5.6×10^{-4}
Formic acid	$HCOOH$	 $H-\overset{O}{\overset{\|}{C}}-O-H$	1.8×10^{-4}
Benzoic acid	C_6H_5COOH		6.3×10^{-5}
Acetic acid	CH_3COOH	 $CH_3-\overset{O}{\overset{\|}{C}}-O-H$	1.8×10^{-5}
Hydrocyanic acid	HCN	$H-C\equiv N$	6.2×10^{-10}
Phenol	C_6H_5OH		1.0×10^{-10}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}

Name of Acid	Formula	Structure	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric acid *	H_2SO_4	 $H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$	Very large	1.3×10^{-2}	
Oxalic acid	$H_2C_2O_4$	 $H-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-H$	5.0×10^{-2}	1.6×10^{-5}	
Sulfurous acid	H_2SO_3	 $H-O-\overset{O}{\overset{\|}{S}}-O-H$	1.3×10^{-2}	6.3×10^{-8}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$		9.1×10^{-5}	1.6×10^{-12}	
Carbonic acid	H_2CO_3	 $H-O-\overset{O}{\overset{\|}{C}}-O-H$	4.0×10^{-7}	5.0×10^{-11}	
Hydrosulfuric acid*	H_2S	$H-S-H$	7.9×10^{-8}	1×10^{-19}	
Phosphoric acid	H_3PO_4	 $H-O-\underset{\underset{\underset{H}{\|}}{O}}{\overset{\overset{O}{\|}}{P}}-O-H$	6.3×10^{-3}	6.3×10^{-8}	5.0×10^{-13}

* Only the second proton in H_2SO_4 is weak

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!

A: $K_a = 7.5x10^{-4}$
$pK_a = 3.12$

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: 1.8×10^{-4}

A: pH=2.22

Determining Relative Acidity

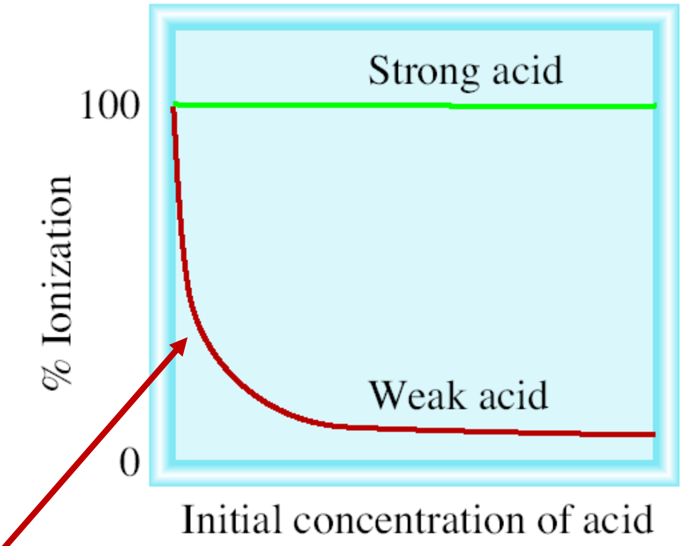
1.) Which is the stronger acid, HF or HNO_2?

Look up K_a in table:
HF: 6.1×10^{-4}
HNO_2: 5.6×10^{-4}

A: HF

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

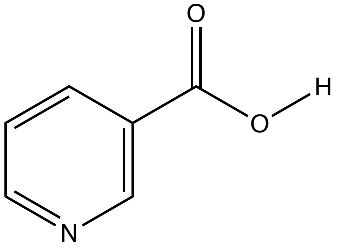


Percent Ionization $= \frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$

% 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:$1.6x10^{-5}$

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

A: 2.7%

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

A:$4.46x10^{-4}$

Polyprotic Acids

Acids that have more than one ionizable proton

- Ionize in successive steps

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

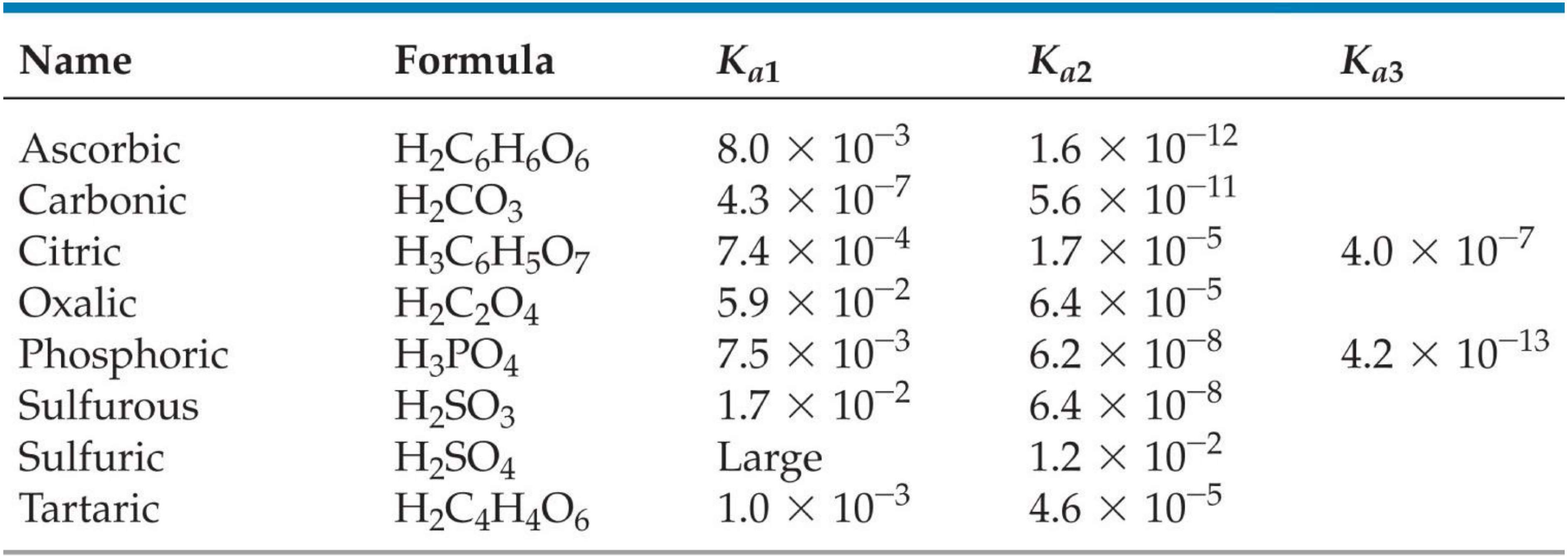
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

- Each step has its own K_a
- Easier to remove the first proton than the second, etc.
  - $K_{a1} > K_{a2} > K_{a3}$.....
- 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	$H_2C_6H_6O_6$	8.0×10^{-3}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	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	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Polyprotic Acid Calculations

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

$K_{a1} = 1.0x10^{-3}$ $K_{a2} = 4.6x10^{-5}$

1st ionizable proton:

$H_2A(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + HA^-(aq)$

H_2A	H_3O^+	HA^-
1.5	0	0
–X	+X	+X
$1.5\cancel{-X}$ ignore	X	X

$$K_{a1} = \frac{X^2}{1.5} = 1.0x10^{-3}$$

$X^2 = 1.5x10^{-3}$

$X = 3.873x10^{-2}\ M = [H_3O^+]$

2nd ionizable proton:

$HA^-(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^{2-}(aq)$

HA^-	H_3O^+	A^{2-}
$3.873x10^{-2}$	$3.873x10^{-2}$	0
–X	+X	+X
$3.873x10^{-2}\cancel{-X}$ ignore	$3.873x10^{-2}\cancel{+X}$ ignore	X

$$K_{a2} = \frac{[\cancel{3.873x10^{-2}}][X]}{]\cancel{3.873x10^{-2}}]} = 4.6x10^{-5}$$

$X = 4.6x10^{-5}\ M = [H_3O^+]$

Total $[H_3O^+]$

$H_1 = 3.873x10^{-2}M$

$\underline{H_2 = 4.6x10^{-5}\ M}$

$3.8776x10^{-2}\ M$

$pH = -\log(3.8776x10^{-2})$

$= 1.4114 \rightarrow 1.41$

A: pH= 1.41

Base Ionization Constant: K_b

Equilibrium constant for base dissociation

Weak bases react with water to produce hydroxide ions:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

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

K_b is the base ionization constant

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

$$pK_b = -\log K_b$$

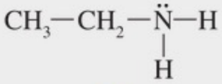
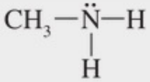
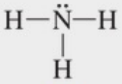
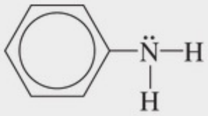
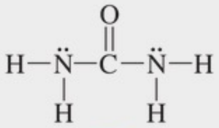
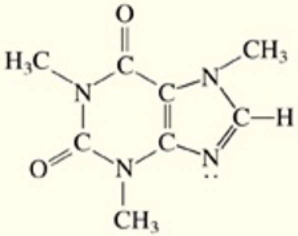
K_b ↑ Weak base strength ↑

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
  - $Ca(OH)_2$, $Fe(OH)_3$
  - Solubility equilibriums (K_{sp}) will be discussed in the next chapter

K_b Values for Some Common Weak Bases

Name of Base	Formula	Structure	K_b
Ethylamine	$C_2H_5NH_2$	 $CH_3-CH_2-\underset{H}{\underset{\vert}{\ddot{N}}}-H$	4.5×10^{-4}
Methylamine	CH_3NH_2	 $CH_3-\underset{H}{\underset{\vert}{\ddot{N}}}-H$	4.6×10^{-4}
Ammonia	NH_3	 $H-\underset{H}{\underset{\vert}{\ddot{N}}}-H$	1.8×10^{-5}
Pyridine	C_5H_5N		1.7×10^{-9}
Aniline	$C_6H_5NH_2$		7.4×10^{-10}
Urea	H_2NCONH_2	 $H-\underset{H}{\underset{\vert}{\ddot{N}}}-\overset{O}{\overset{\Vert}{C}}-\underset{H}{\underset{\vert}{\ddot{N}}}-H$	1.3×10^{-14}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}

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

Base & water

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $K_b = 1.8\text{x}10^{-5}$

$pK_b = 4.74$

Conjugate acid & water

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ $K_a = 5.6\text{x}10^{-10}$

$pK_a = 9.26$

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

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

$$\mathbf{K_w = K_a x K_b = 1.0x10^{-14}}$$

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

$$\mathbf{pK_a + pK_b = 14}$$

$$9.26 + 4.74 = 14$$

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? $K_b=1.8x10^{-5}$

A: pH = 11.22

2.) Codeine is a weak organic base. A 5.0×10^{-3}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!

A: $K_b = 1.62\times10^{-6}$
pK_b = 5.79

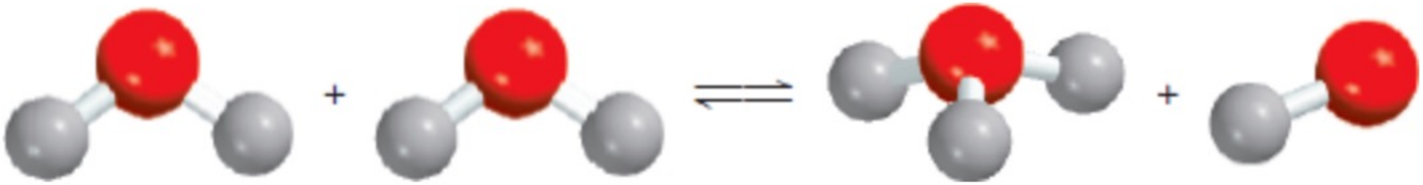
3.) A solution of ammonia in water has a pH of 11.17. What is the molarity of the solution? $K_b = 1.8 \times 10^{-5}$

A: 0.123M

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

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

$$NH_3\,(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Acid–Base Properties of Salts

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

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^+)

$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$ – no hydrolysis

From NaOH strong base

From HCl strong acid

$LiNO_3(aq) \xrightarrow{H_2O} Li^+(aq) + NO_3^-\ (aq)$ – no hydrolysis

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

CH_3COOH: weak acid

Weak base

$$NaCH_3COO(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \boxed{OH^-}(aq)$$

Ex 2: NH_3: weak base

HCl: strong acid

Weak acid

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + \boxed{H_3O^+}(aq)$$

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

- $HCO_3^-(aq) + 2H_2O(l) \rightleftarrows CO_3^{2-}(aq) + H_3O^+(aq)$

$K_a = 4.8x10^{-11}$

Acting as base

- $HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$

$K_b = K_w/K_a = 2.4x10^{-8}$

- $K_b > K_a$ 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, $Fe(OH)_2$
    - 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.

a.) NH_4NO_3

b.) $FeCl_3$

c.) Na_2CO_3

d.) $KClO_4$

e.) ZnF_2

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 $Fe(NO_3)_3$

b.) CH_3NH_3Cl or $BaCl_2$

c.) KNO_2 or KNO_3

d.) $(NH_4)_2SO_4$ or $(NH_4)_2SO_3$

3.) Calculate the $[OH^-]$ and pH of a 0.10M NaCN solution. K_a for HCN is 6.2×10^{-10}.

A: $[OH^-] = 1.3 \times 10^{-3}$M
pH = 11.10

4.) Calculate the pH of a 0.42M NH_4Cl solution.
K_b for NH_3 is $1.8x10^{-5}$

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:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + \boxed{H_3O^+}(aq) + 3Cl^-(aq)$$

$K_a = 1.3 \times 10^{-5}$ → Acid!

- 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 $Na^+ < Ca^{2+} < Zn^{2+} < Al^{3+}$ More acidic

Hydration of Metal Ions

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

1.) $CuCl$ or $Cu(NO_3)_2$

2.) $CrCl_3$ or $NiCl_3$