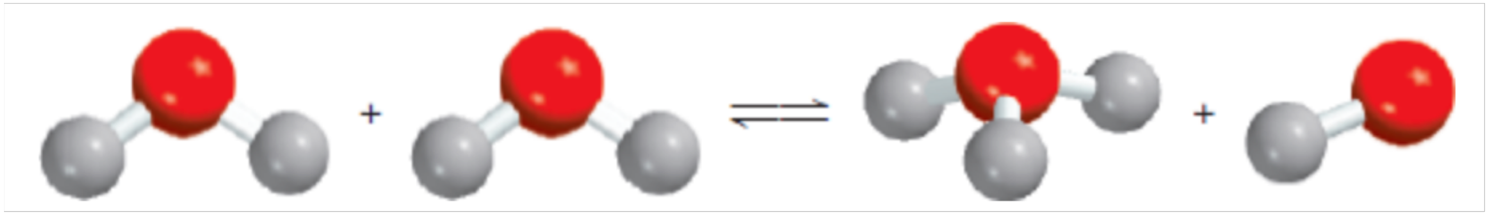
Chapter 16

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-}

You should know these ions

Common Acids & Bases You Will Need to Know

Strong Acids:

Hydrochloric Acid	HCl
Sulfuric Acid	H_2SO_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_2CO_3
Phosphoric Acid	H_3PO_4
Acetic Acid	CH_3COOH
Hydrofluoric Acid	HF
Carboxylic Acids	

Weak Bases:

Ammonia	NH_3
Amines	
Insoluble/slightly soluble hydroxides	

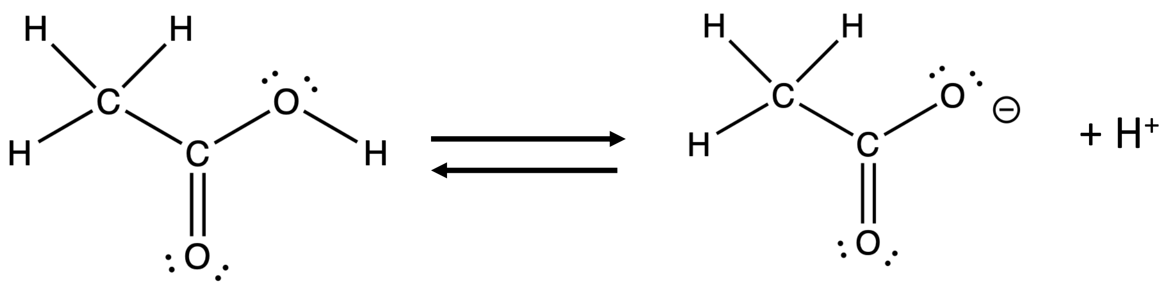
Organic Acids: Carboxylic Acids (-COOH)

Weak organic acids

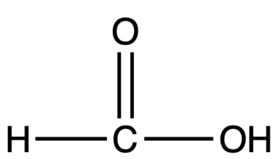
- COOH group on molecule is acidic
- Removal of proton (H^+) creates resonance structure
- Stabilizes anion

Never fully dissociate in water

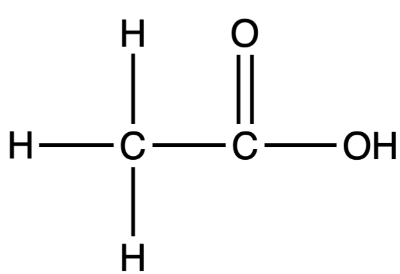
- Equilibrium process



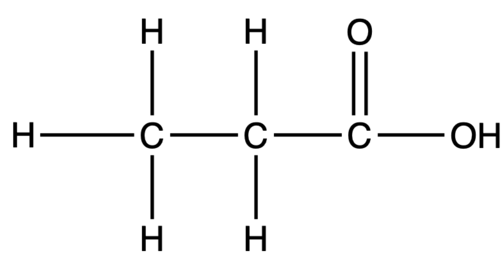
Examples:



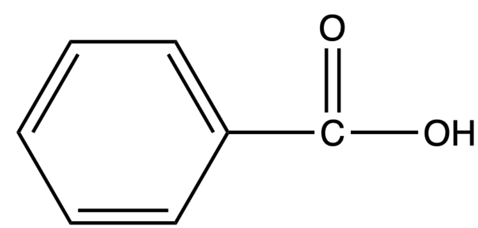
Formic Acid



Acetic Acid



Butyric Acid



Benzoic Acid

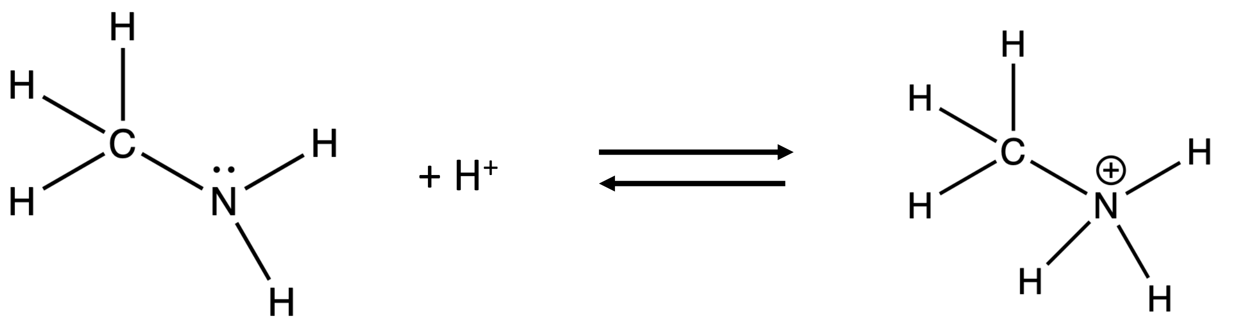
Organic Bases: Amines (contain N)

Weak organic bases

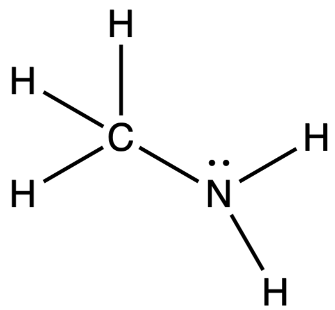
- Derivatives of ammonia
- N has lone pair of electrons to accept a proton

Also do not fully dissociate in water

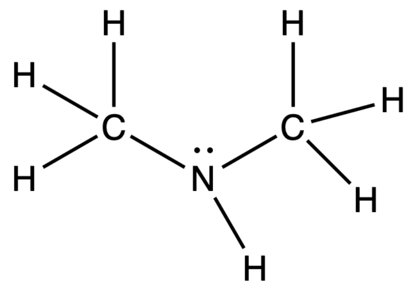
- Equilibrium process



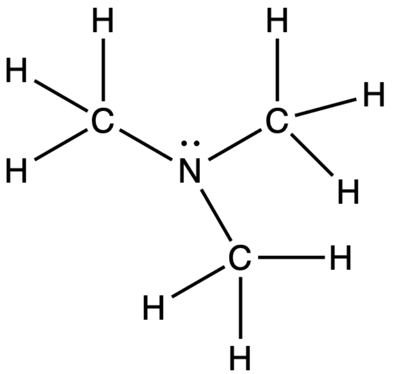
Examples:



Methyl amine



Dimethyl amine



Trimethyl amine

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^-).

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

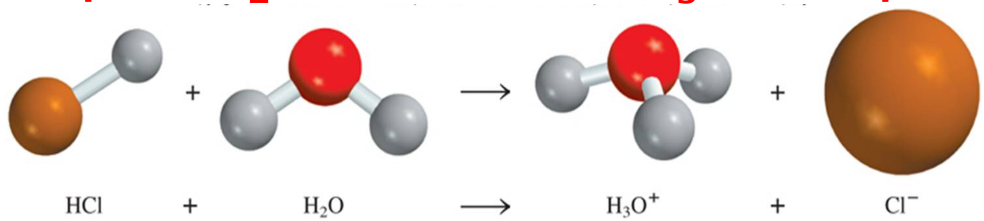
What are Acids & Bases?
Brønsted-Lowry Definition

Acid:

A proton (H^+) donor

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

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

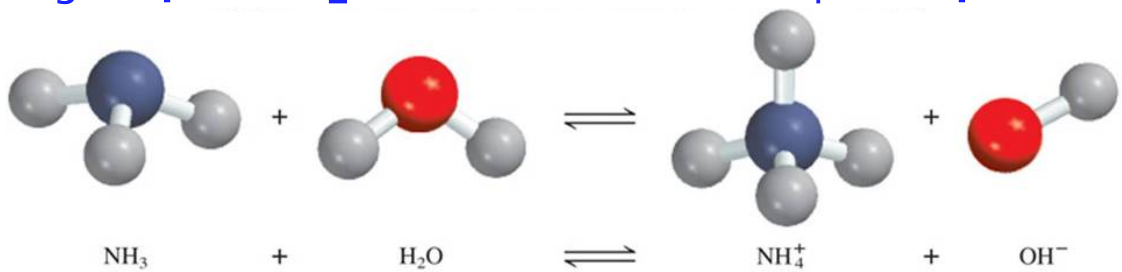


Base:

A proton (H^+) acceptor

- Must have a pair of non-bonding electrons

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



Strength of Acids & Bases

Strong Acids & Bases: Complete dissociation

- Conjugate acids & bases form spectator ions
- Can use basic stoichiometry (CHM 101) in calculations
- No original reactant or product left in solution

Weak Acids & Bases: Incomplete dissociation

- Equilibrium process
- Equilibrium constants are K_a or K_b

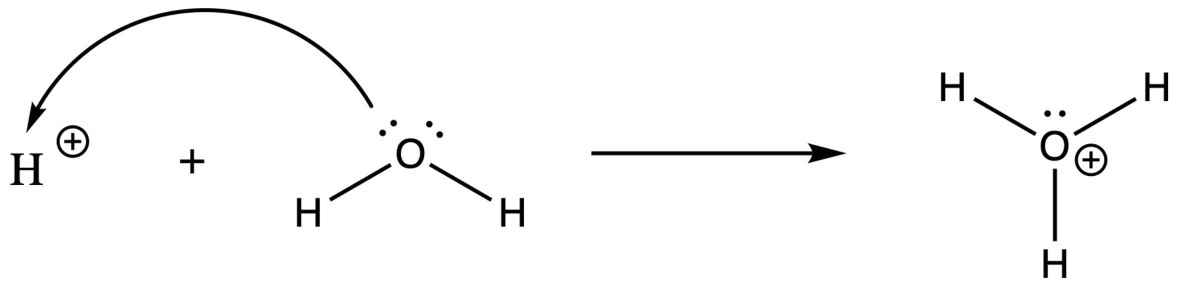
Acid/Base Strength in Aqueous Solutions

- H_3O^+ is the strongest acid
- OH^- is the strongest base
- Acid or Base reacts with water
  - Water acts as a weak acid or base in the reaction

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^+

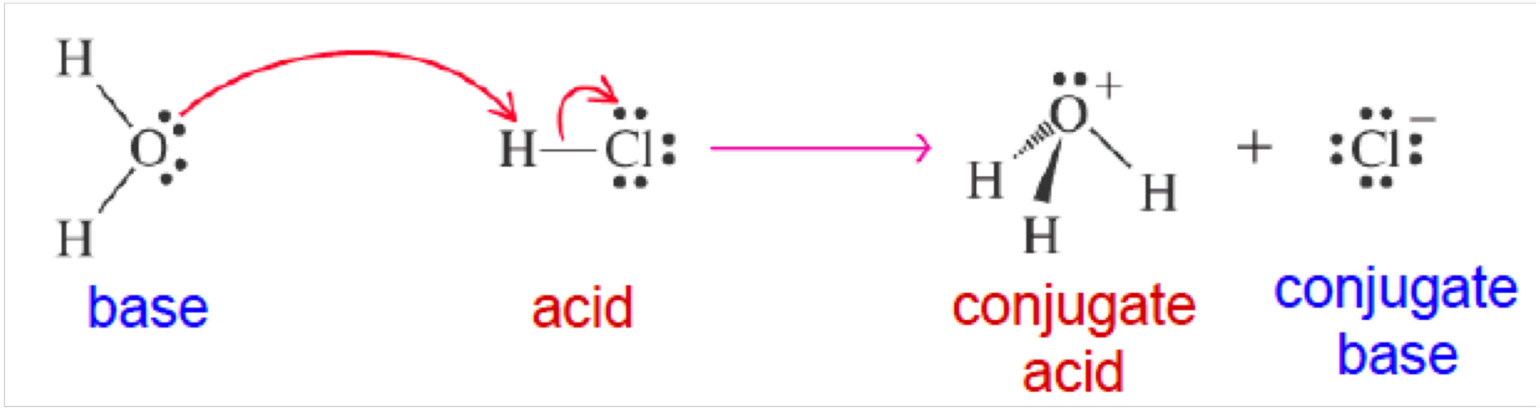


- H^+ (aq) & H_3O^+(aq) are used interchangeably

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

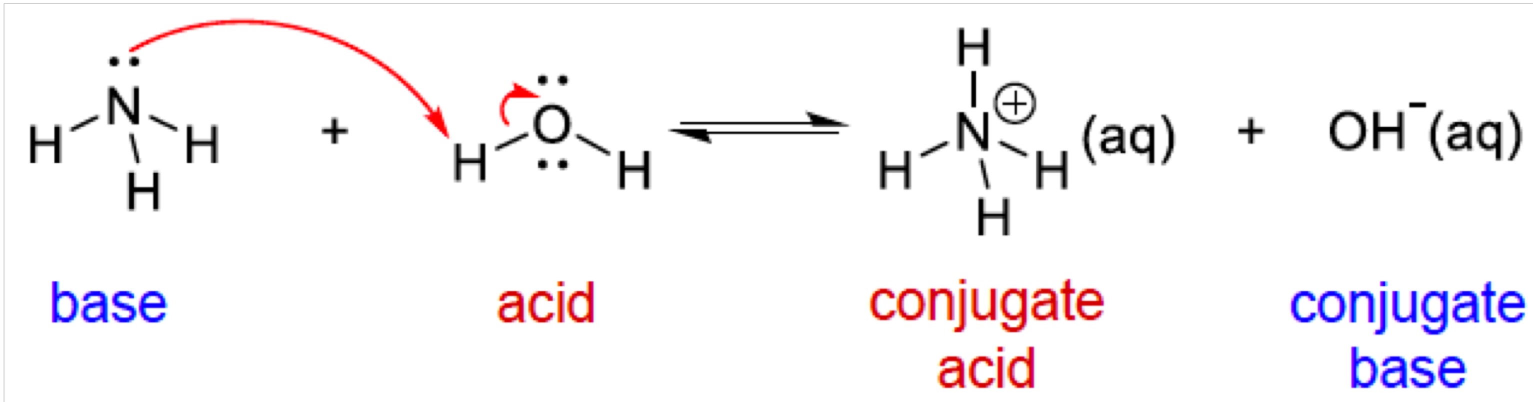
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Proton Transfer Reactions: Aqueous Acid



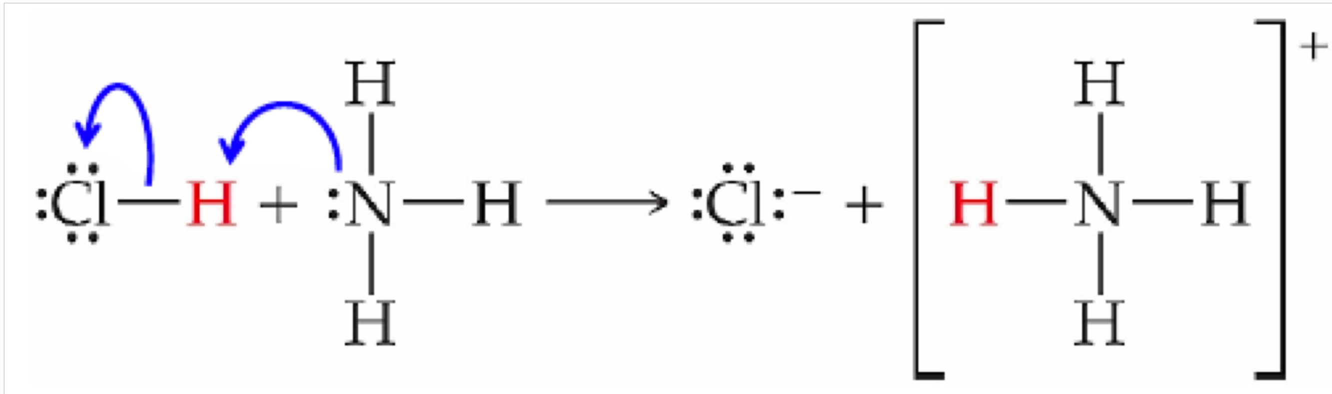
- HCl (the BL acid) donates a proton (H^+)
- Water (the BL base) accepts the proton
- The conjugate base of the acid (Cl^-) and the conjugate acid of the base (H_3O^+) are formed

Proton Transfer Reactions: Aqueous Base



- Water (the BL acid) donates a proton (H^+)
- Ammonia (the BL 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 BL acid) donates a proton (H^+)
- Ammonia (the BL 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)

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. Whether something is 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-}

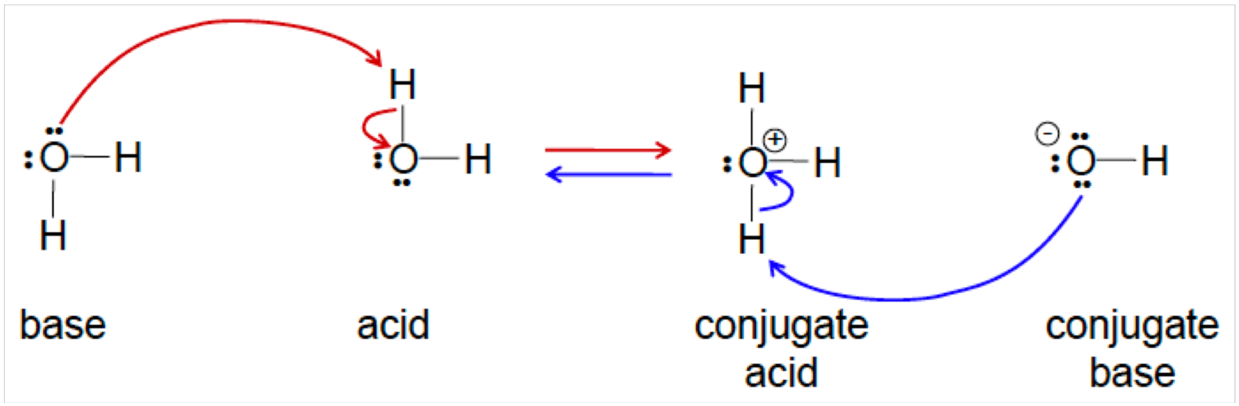
2. Write the formula for the conjugate acid of each of the following bases:
    a) HSO_3^-
    b) F^-
    c) CO_3^{2-}
    d) CH_3NH_2

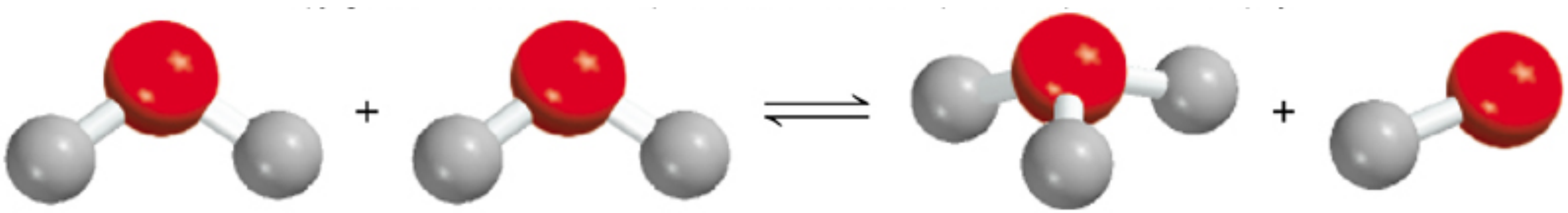
Acid-Base Properties of Water: Autoionization

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

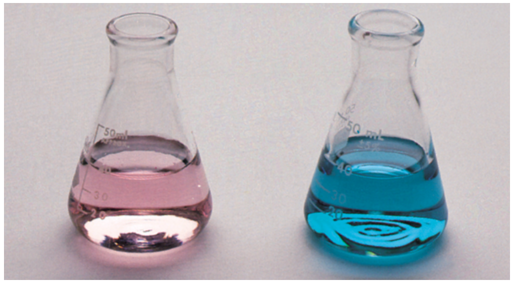
Autoionization: An Equilibrium Process

Consider the autoionization of water at 25˚C

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

Weak Base Weak Acid Strong Acid Strong Base

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



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

$K_w = [H_3O^+][OH^-] = 1.0\text{x}10^{-14}$ (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

What is log?

Consider the number 1.0×10^{-3}

- Log refers to base 10
- Essentially, it 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. $1 \times 10^{-3}M > 1 \times 10^{-10}M$

pH & pOH

Method of Measuring Acidity

- Power of the Hydrogen Ion

Formulas:

- $pH = -\log[H_3O^+]$
- $[H_3O^+] = 10^{(-pH)}$
- $pOH = -\log[OH^-]$
- $[OH^-] = 10^{(-pOH)}$
- $K_w = [H_3O^+][OH^-] = 1.0x10^{-14}M$
- $pK_w = pH + pOH = 14$

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

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

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

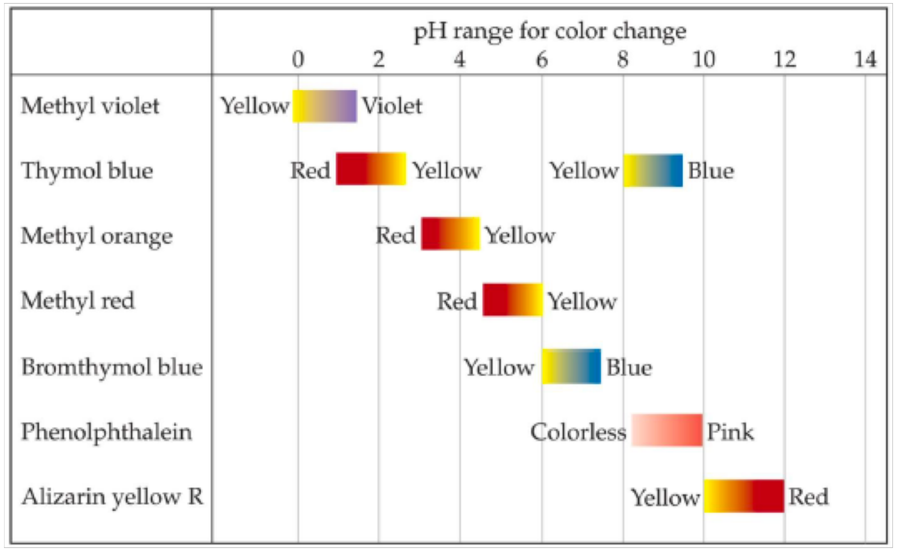
Sample	pH Value
Gastric juice in the stomach	1.0–2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8–7.5
Water exposed to air*	5.5
Saliva	6.4–6.9
Milk	6.5
Pure water	7.0
Blood	7.35–7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

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

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

Example 1: **Concentrated Solutions**

Consider an aqueous 0.010M solution of nitric acid.

Two reactions are occurring:

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

$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $[H_3O^+] = 1.0 \times 10^{-7}M$

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 1.0×10^{-6}M solution of nitric acid.

Two reactions are again occurring:

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

$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $[H_3O^+] = 1.0 \times 10^{-7}$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:

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

<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: $2.2x10^{-11}$M; basic

2. Find the pH and pOH of a 0.0050M HBr solution at 25˚C
pH: 2.30; pOH: 11.7

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}M

4. Find the pH of a 0.035 M aqueous solution of sulfuric acid. A:1.15

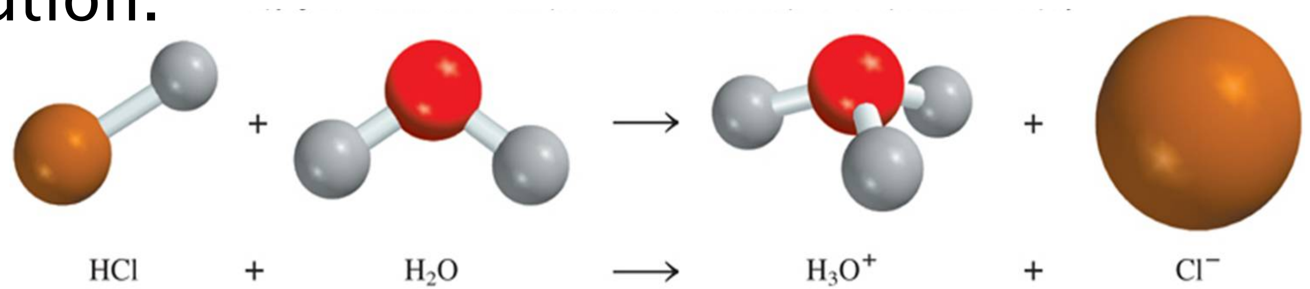
5. Calculate the pH made from 15.00mL of 1.00M HCl diluted to 0.500L. A:1.523

6. 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
- H_3O^+ is the strongest acid that can exist in aqueous solution.



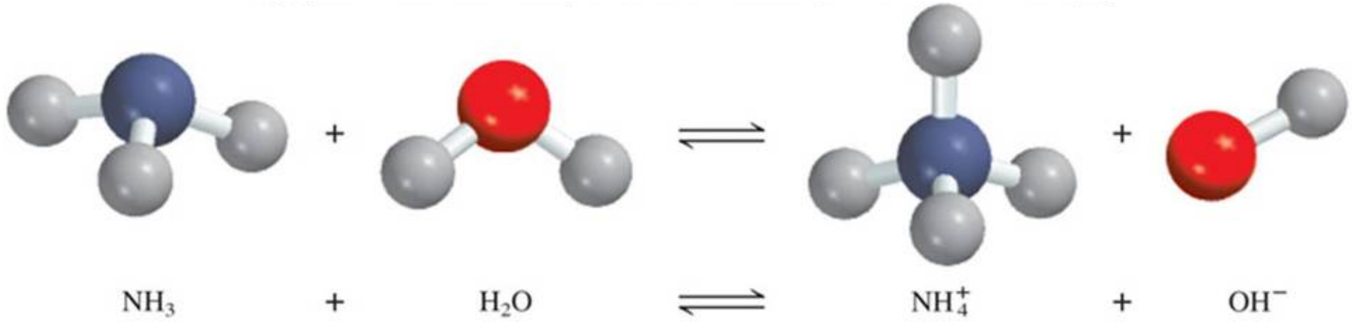
$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

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

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

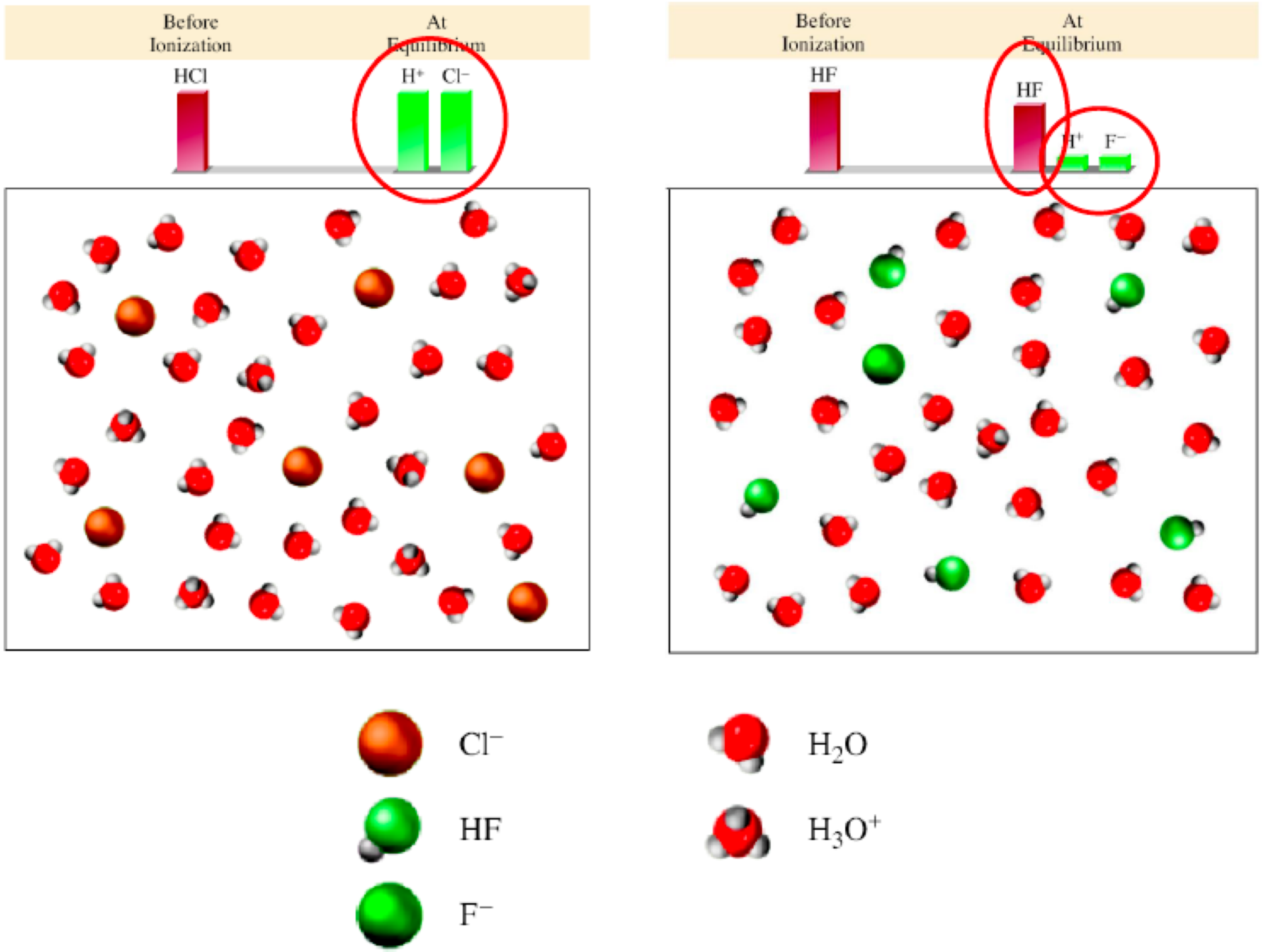


$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$$

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

Strong Acid (HCl)

Weak Acid (HF)



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
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)

Acid strength increases ↑

Base strength increases ↓

Stronger acids will dominate over weaker acids

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