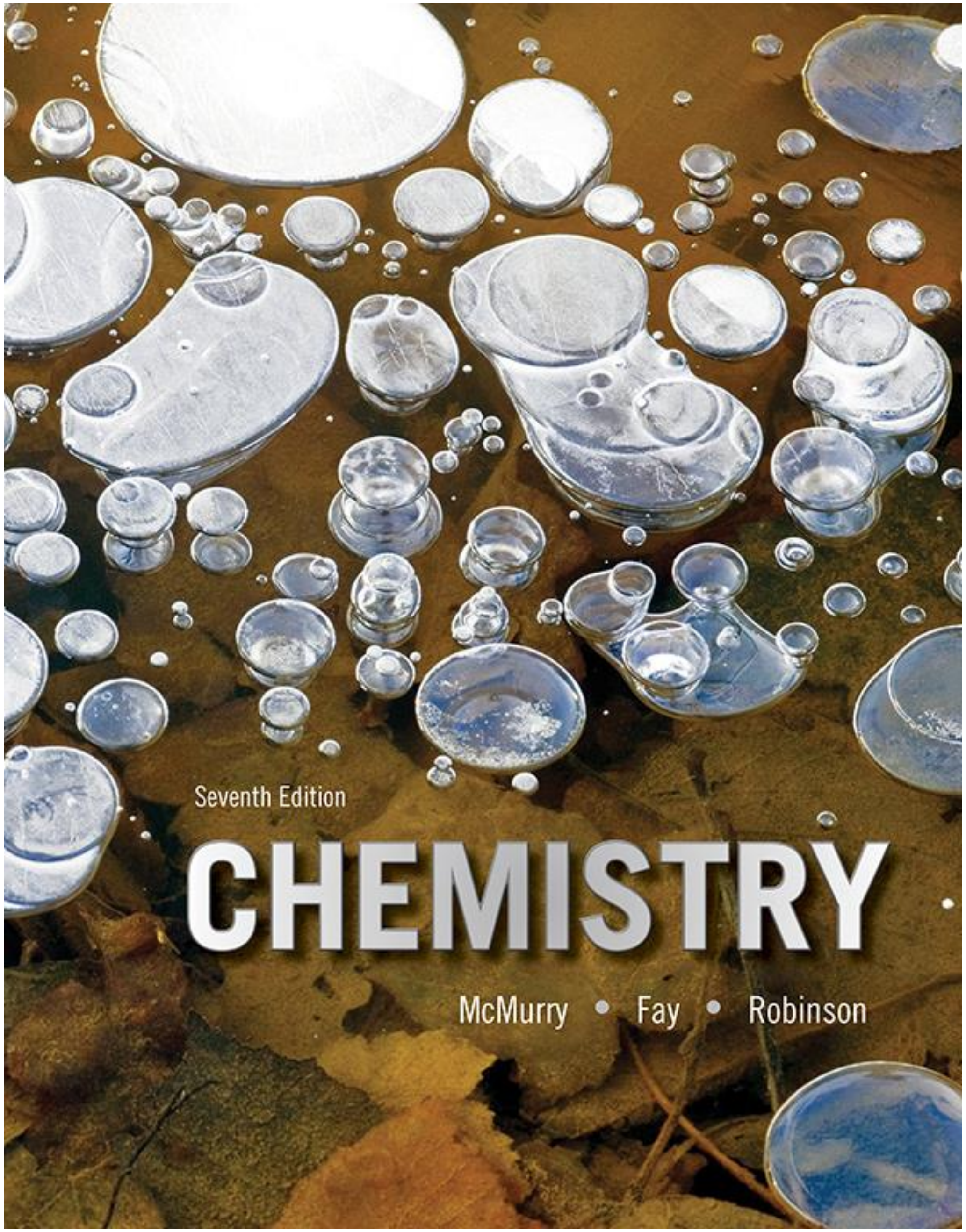


Lecture Presentation

Chapter 15

Aqueous Equilibria: Acids and Bases

John E. McMurry
Robert C. Fay

Instructor's Resource Materials (Download only) for *Chemistry,* 7e
John E. McMurry, Robert C. Fay, Jill Robinson

Acid-Base Concepts: The Brønsted-Lowry Theory

Arrhenius Acid: A substance that dissociates in water to produce hydrogen ions, H^+

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

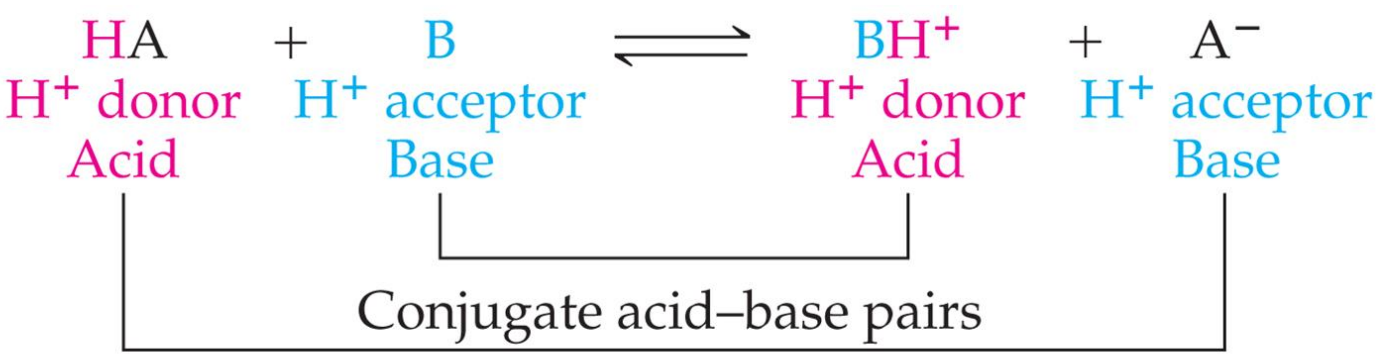
Arrhenius Base: A substance that dissociates in water to produce hydroxide ions, OH^-

$$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$$

Acid-Base Concepts: The Brønsted-Lowry Theory

Brønsted-Lowry Acid: A substance that can transfer hydrogen ions, H^+. In other words, a proton donor

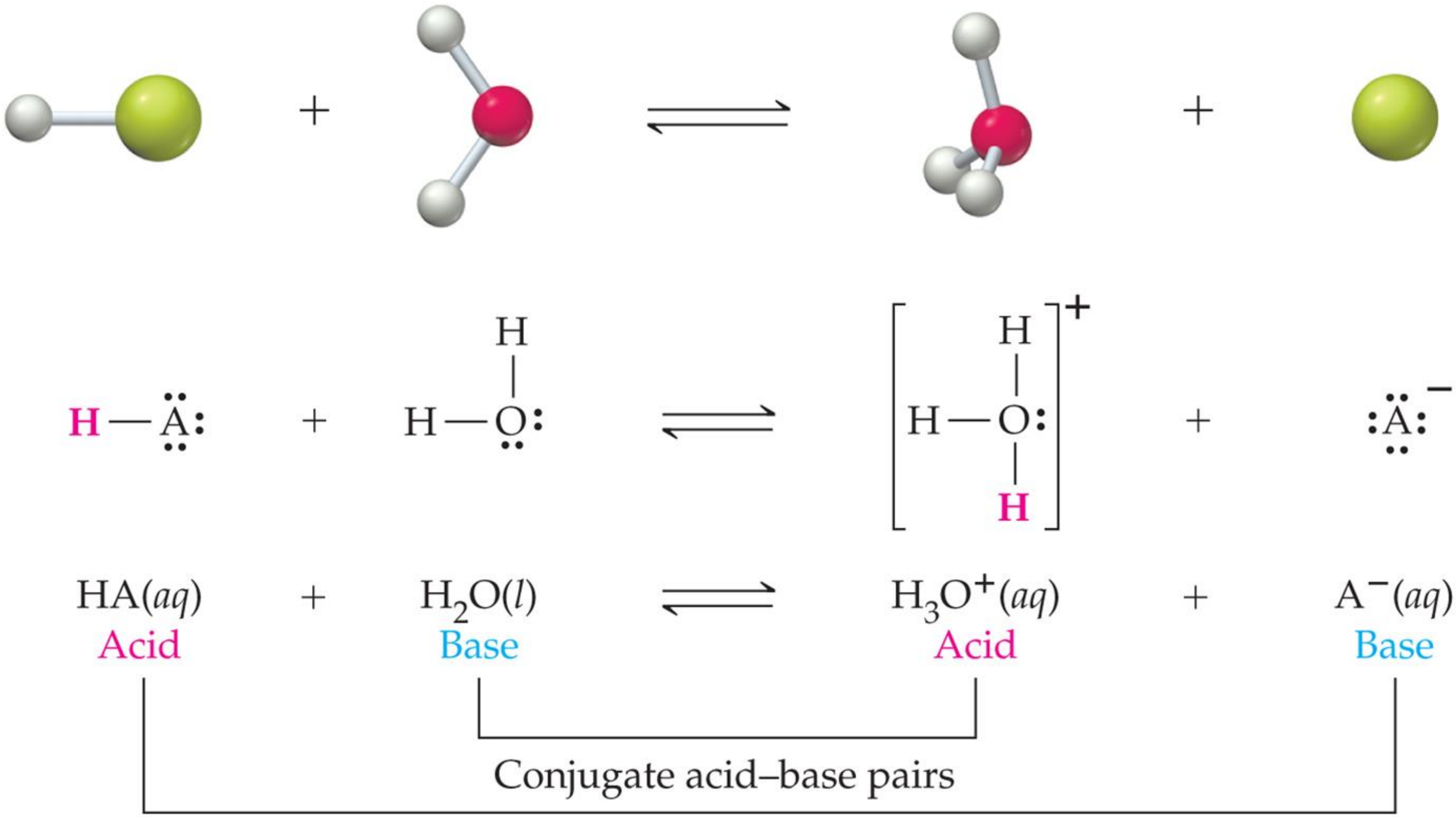
Brønsted-Lowry Base: A substance that can accept hydrogen ions, H^+. In other words, a proton acceptor



Conjugate Acid-Base Pairs: Chemical species whose formulas differ only by one hydrogen ion, H^+

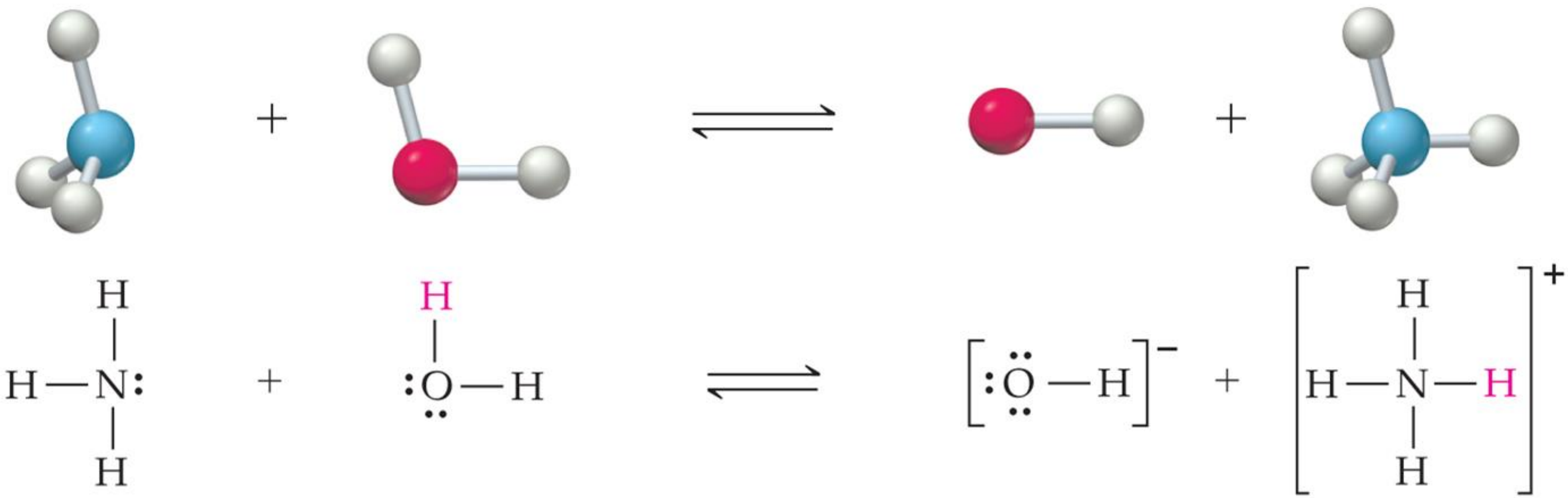
Acid-Base Concepts: The Brønsted-Lowry Theory

Acid-Dissociation Equilibrium



Acid-Base Concepts: The Brønsted-Lowry Theory

Base-Dissociation Equilibrium



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

Base | Acid | Base | Acid

Conjugate acid–base pairs

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Acid Strength and Base Strength

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

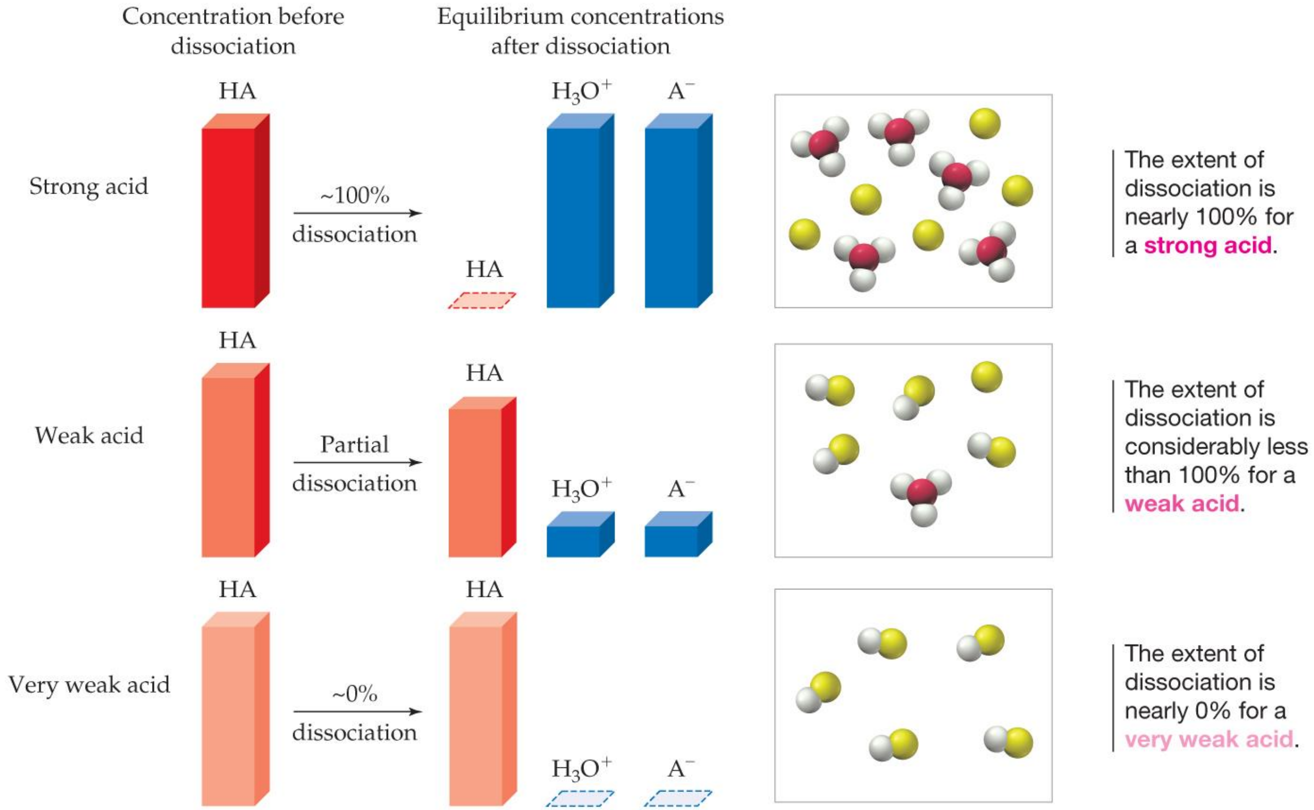
Acid Base Acid Base

With equal concentrations of reactants and products, what will be the direction of reaction?

Stronger acid + Stronger base $\longrightarrow$ Weaker acid + Weaker base

Acid Strength and Base Strength

Weak Acid: An acid that is only partially dissociated in water and is thus a weak electrolyte



Acid Strength and Base Strength

TABLE 15.1 Relative Strengths of Conjugate Acid–Base Pairs

	Acid, HA		Base, A^-		
Stronger acid	$HClO_4$	**Strong acids:** 100% dissociated in aqueous solution.	ClO_4^-	**Very weak bases:** Negligible tendency to be protonated in aqueous solution.	Weaker base
	HCl		Cl^-		
	H_2SO_4		HSO_4^-		
	HNO_3		NO_3^-		
	H_3O^+		H_2O		
	HSO_4^-	**Weak acids:** Exist in solution as a mixture of HA, A^-, and H_3O^+.	SO_4^{2-}	**Weak bases:** Moderate tendency to be protonated in aqueous solution.	
	H_3PO_4		$H_2PO_4^-$		
	HNO_2		NO_2^-		
	HF		F^-		
	CH_3CO_2H		$CH_3CO_2^-$		
	H_2CO_3		HCO_3^-		
	H_2S		HS^-		
	NH_4^+		NH_3		
	HCN		CN^-		
	HCO_3^-		CO_3^{2-}		
	H_2O		OH^-		
Weaker acid	NH_3	**Very weak acids:** Negligible tendency to dissociate.	NH_2^-	**Strong bases:** 100% protonated in aqueous solution.	Stronger base
	OH^-		O^{2-}		
	H_2		H^-		

Hydrated Protons and Hydronium Ions

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

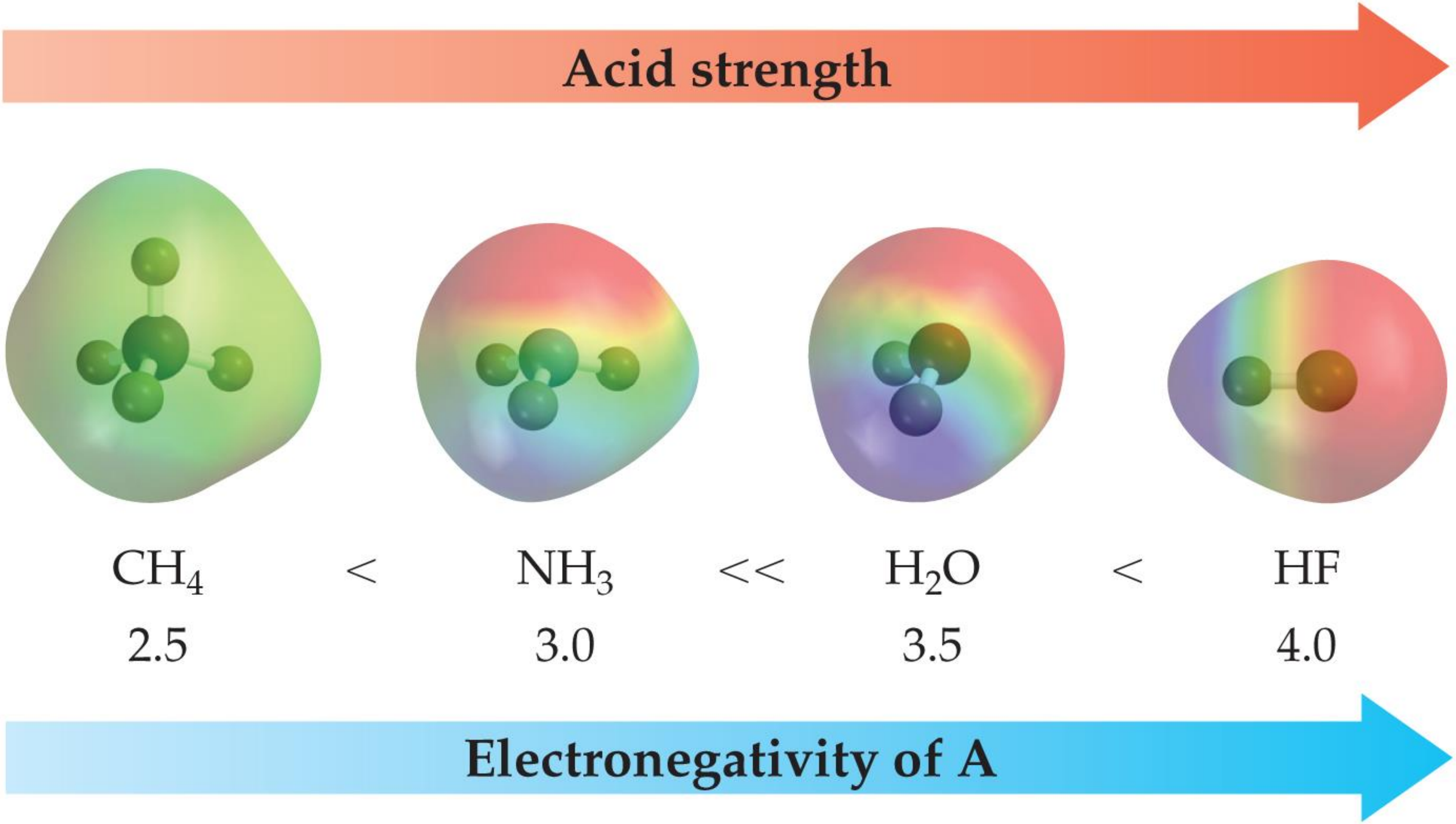
Due to high reactivity of the hydrogen ion, it is actually hydrated by one or more water molecules.

$$[H(H_2O)_n]^+ \begin{cases} n = 1 & H_3O^+ \\ n = 2 & H_5O_2^+ \\ n = 3 & H_7O_3^+ \\ n = 4 & H_9O_4^+ \end{cases}$$

For our purposes, H^+ is equivalent to H_3O^+.

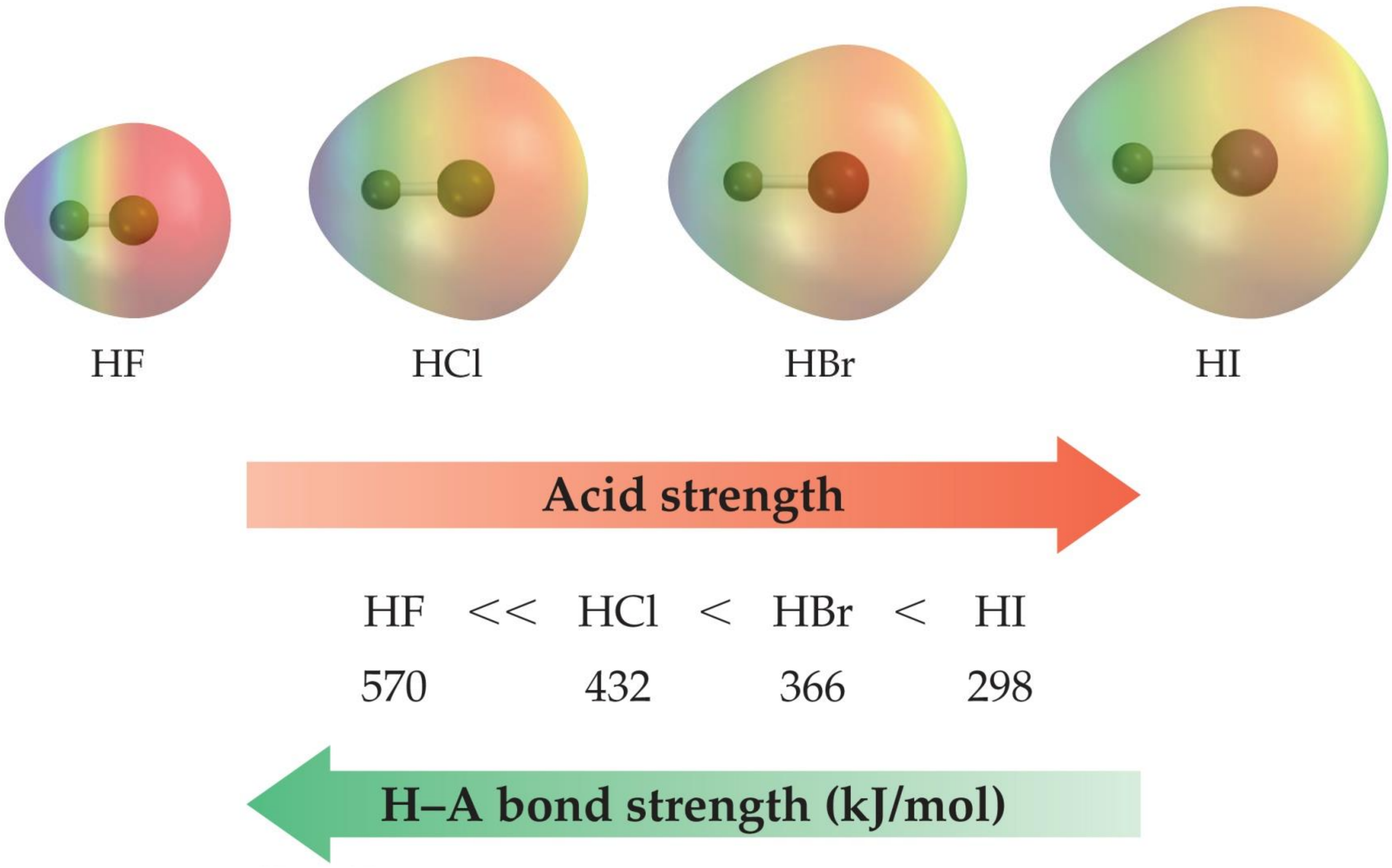
Factors That Affect Acid Strength

Bond Polarity



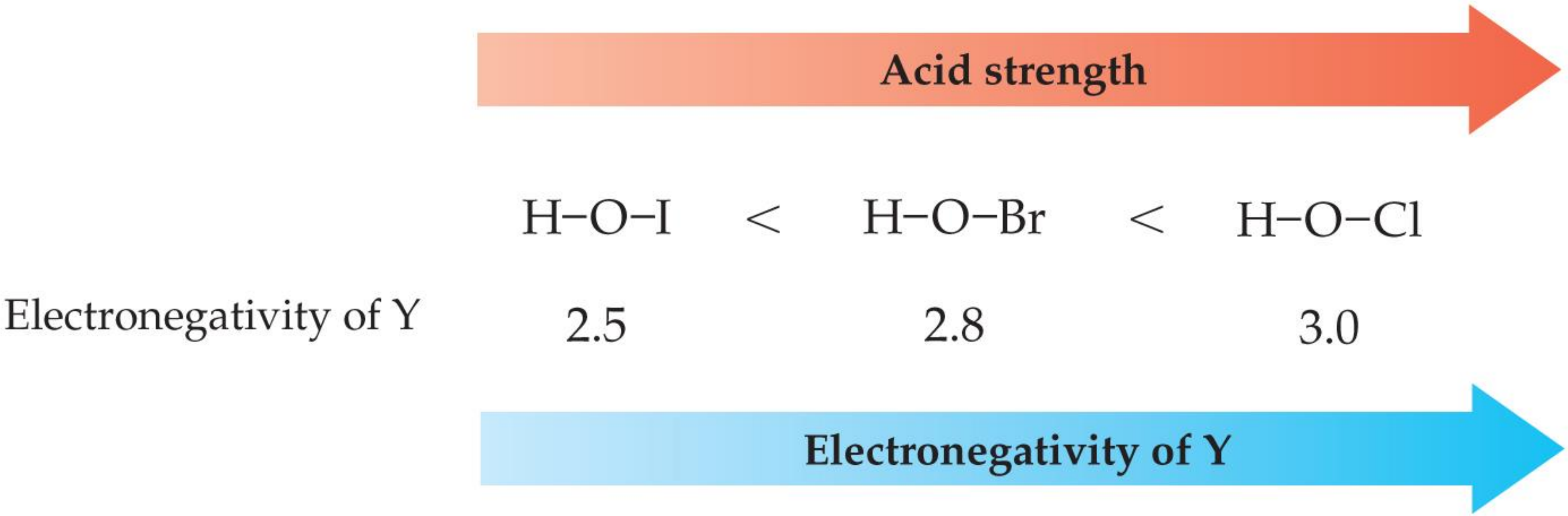
Factors That Affect Acid Strength

Bond Strength



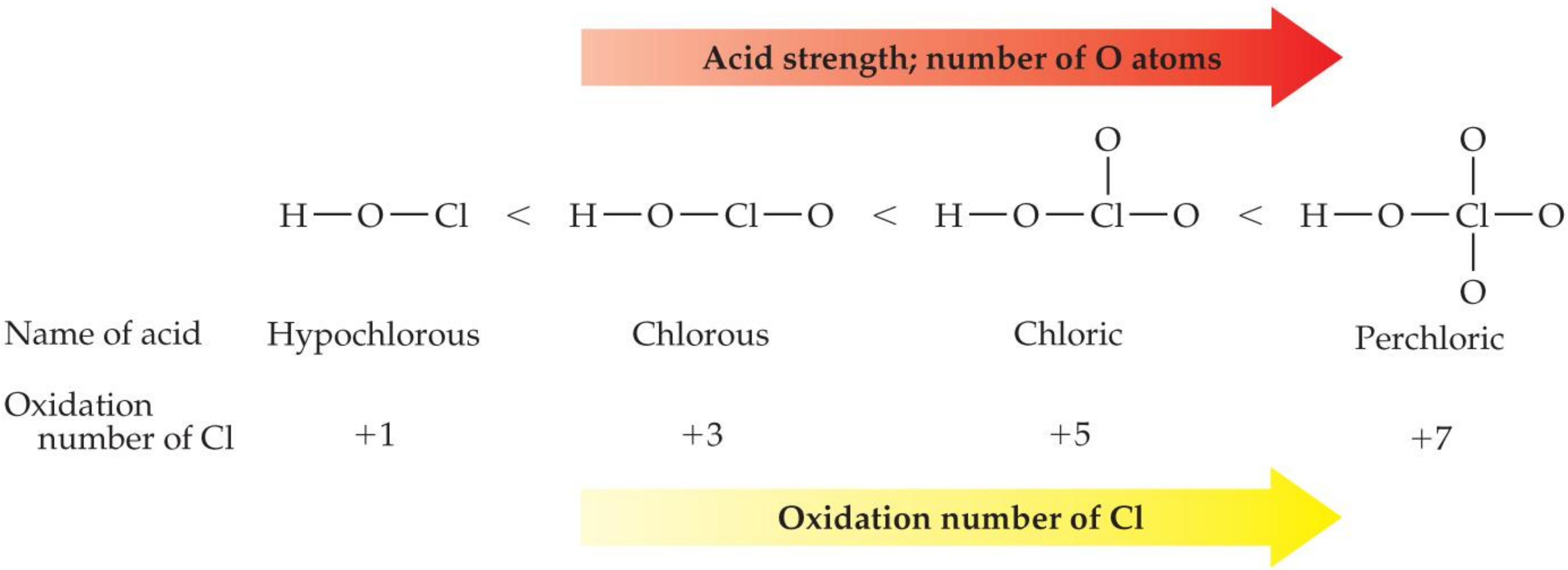
Factors That Affect Acid Strength

Oxoacids

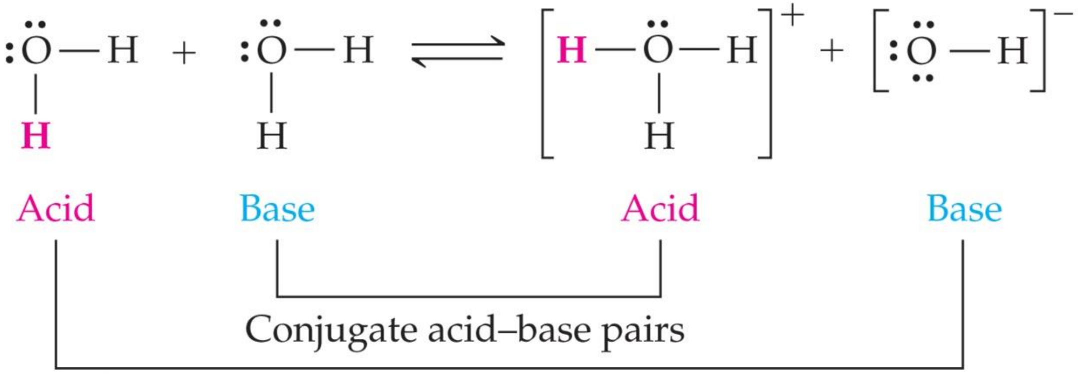


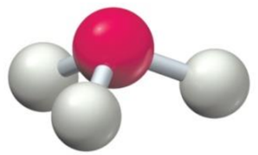
Factors That Affect Acid Strength

Oxoacids



Dissociation of Water




The hydronium ion, H_3O^+

Dissociation of Water: $2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

Ion-Product Constant for Water: $K_w = [H_3O^+][OH^-]$

at 25 °C: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M

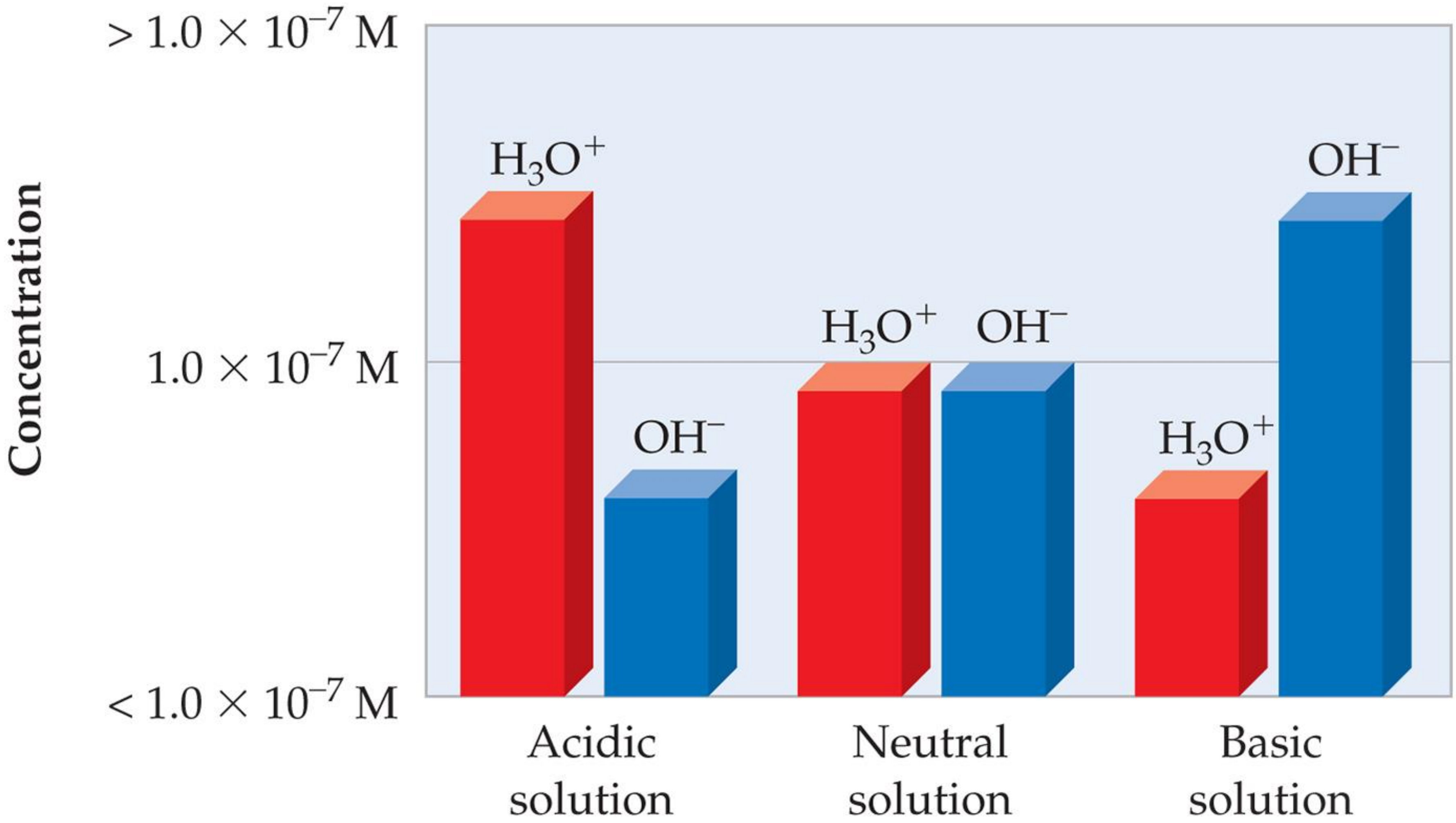
$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = \mathbf{1.0 \times 10^{-14}}$

Dissociation of Water

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

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} \qquad [OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$

Dissociation of Water



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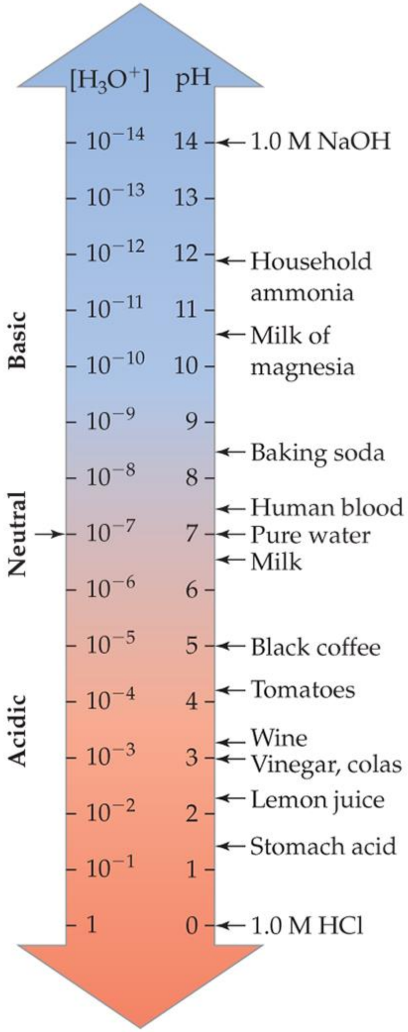
Dissociation of Water

Acidic: $[H_3O^+] > [OH^-]$

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

Basic: $[H_3O^+] < [OH^-]$

The pH Scale



$$pH = -\log[H_3O^+] \qquad [H_3O^+] = 10^{-pH}$$

Acidic: $pH < 7$

Neutral: $pH = 7$

Basic: $pH > 7$

The pH Scale

The hydronium ion concentration for lemon juice is approximately 0.0025 M. What is the pH when $[H_3O^+]$ = 0.0025 M?

2 significant figures

$$pH = -\log(0.0025) = 2.60$$

2 decimal places

The pH Scale

Calculate the pH of an aqueous ammonia solution that has an OH^- concentration of 0.0019 M.

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^{1-}]} = \frac{1.0 \times 10^{-14}}{0.0019} = 5.3 \times 10^{-12}\ M$$

$$pH = -\log(5.3 \times 10^{-12}) = 11.28$$

The pH Scale

Acid rain is a matter of serious concern because most species of fish die in waters having a pH lower than 4.5–5.0. Calculate $[H_3O^+]$ in a lake that has a pH of 4.5.

$$[H_3O^+] = 10^{-4.5} = 3 \times 10^{-5}\ M$$

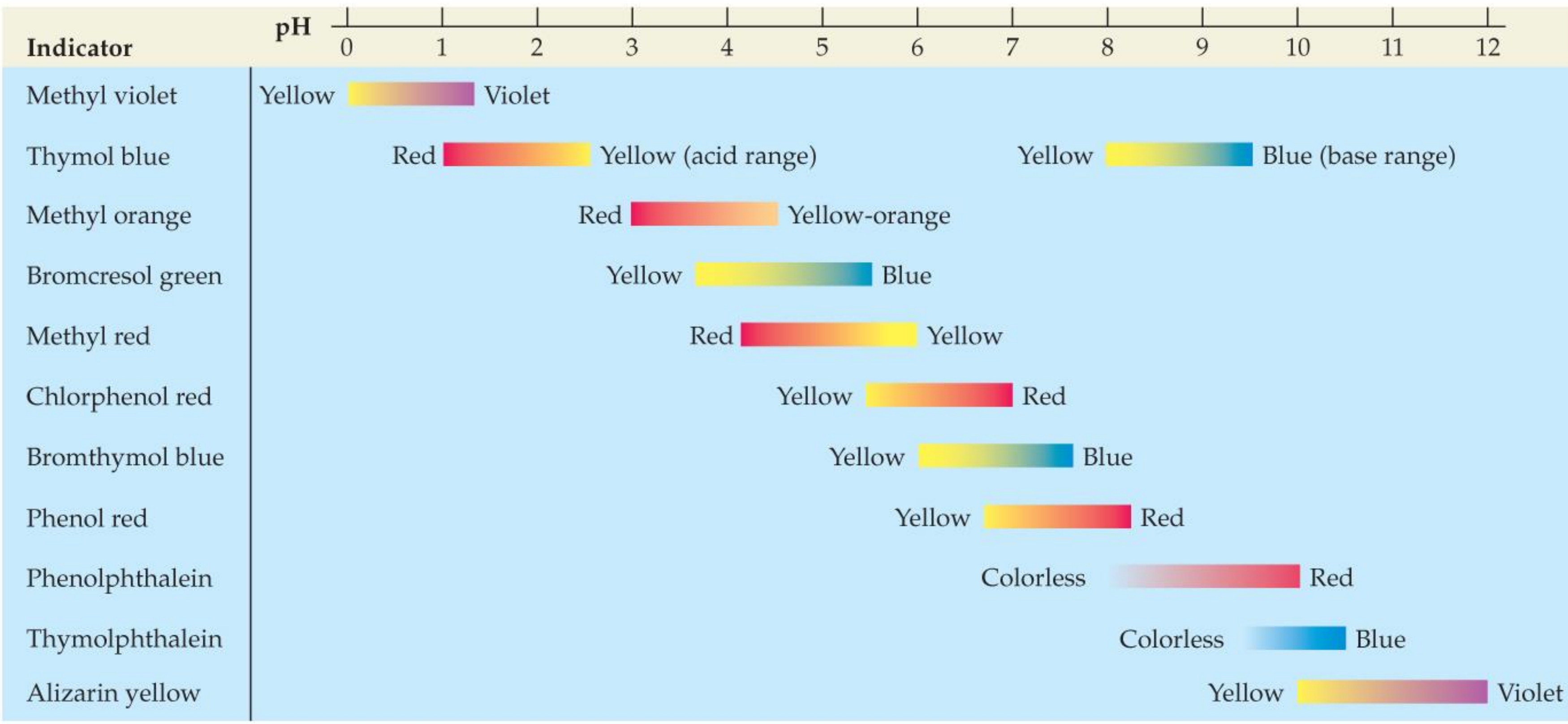
Measuring pH

Acid–Base Indicator: A substance that changes color in a specific pH range. Indicators exhibit pH-dependent color changes because they are weak acids and have different colors in their acid (HIn) and conjugate base (In^-) forms.

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

Color A　　　　　　　　Color B

Measuring pH



The pH in Solutions of Strong Acids and Strong Bases

What is the pH of a 0.025 M solution of HNO_3?

$$HNO_3(aq) + H_2O(l) \xrightarrow{100\%} H_3O^+(aq) + NO_3^-(aq)$$

Since HNO_3 is a strong acid, $[H_3O^+] = [HNO_3]$.

$$pH = -\log([H_3O^+]) = -\log(0.025) = \boxed{1.60}$$

The pH in Solutions of Strong Acids and Strong Bases

What is the pH of a 0.025 M solution of NaOH?

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

Since NaOH is a strong base, $[OH^{-}] = [NaOH]$.

$$[H_3O^{+}] = \frac{1.0 \times 10^{-14}}{[OH^{-}]} = \frac{1.0 \times 10^{-14}}{0.025} = 4.0 \times 10^{-13}\ M$$

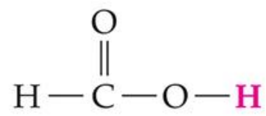
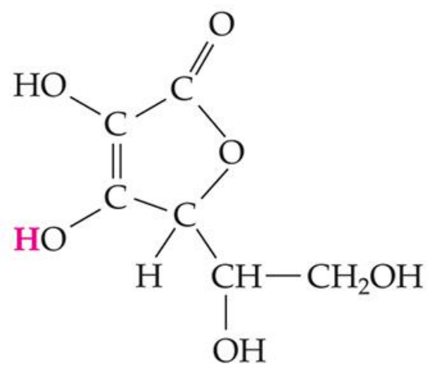
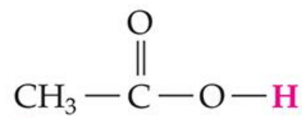
$$pH = -\log([H_3O^{+}]) = -\log(4.0 \times 10^{-13}) = \boxed{12.40}$$

Equilibria in Solutions of Weak Acids

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

Acid-Dissociation Constant: $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

TABLE 15.2 Acid-Dissociation Constants at 25 °C

	Acid	Molecular Formula	Structural Formula*	K_a	pK_a†
Stronger acid	Hydrochloric	HCl	**H**—Cl	2×10^{6}	−6.3
	Nitrous	HNO_2	**H**—O—N=O	4.5×10^{-4}	3.35
	Hydrofluoric	HF	**H**—F	3.5×10^{-4}	3.46
	Formic	HCO_2H		1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$C_6H_8O_6$		8.0×10^{-5}	4.10
	Acetic	CH_3CO_2H		1.8×10^{-5}	4.74
	Hypochlorous	$HOCl$	**H**—O—Cl	3.5×10^{-8}	7.46
Weaker acid	Hydrocyanic	HCN	**H**—C≡N	4.9×10^{-10}	9.31
	Methanol	CH_3OH	CH_3—O—**H**	2.9×10^{-16}	15.54

* The proton that is transferred to water when the acid dissociates is shown in red.
† $pK_a = -\log K_a$.

Equilibria in Solutions of Weak Acids

The pH of 0.250 M HF is 2.036. What are the values of K_a and pK_a for hydrofluoric acid?

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

0.250		≈0	0
$-x$		$+x$	$+x$
$0.250 - x$		x	x

$$x = [H_3O^+] = 10^{-2.036} = 0.00920 \text{ M}$$

Equilibria in Solutions of Weak Acids

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$[F^-] = [H_3O^+] = 0.00920\ M$$

$$[HF] = 0.250 - x = 0.250 - 0.00920 = 0.241\ M$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(0.00920)(0.00920)}{0.241} = \boxed{3.51 \times 10^{-4}}$$

$$pK_a = -\log(K_a) = -\log(3.51 \times 10^{-4}) = \boxed{3.455}$$

Calculating Equilibrium Concentrations of Weak Acids

Calculate the pH of a 0.10 M HCN solution. At 25 ^{o}C, K_a = 1.4 × 10^{-9}.

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

0.10		≈0	0
$-x$		$+x$	$+x$
$0.10 - x$		x	x

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

Calculating Equilibrium Concentrations of Weak Acids

$$4.9 \times 10^{-10} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{x^2}{0.10}$$

$$x = [H_3O^+] = 7.0 \times 10^{-6}\ M$$

$$pH = -\log([H_3O^+]) = -\log(7.0 \times 10^{-6}) = \boxed{5.15}$$

Step 1. List the species present before dissociation and identify them as Brønsted–Lowry acids or bases.

↓

Step 2. Write balanced equations for all possible proton-transfer reactions.

↓

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

↓

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:

- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

↓

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

↓

Step 6. Calculate the "big" concentrations—the concentrations of the species involved in the principal reaction.

↓

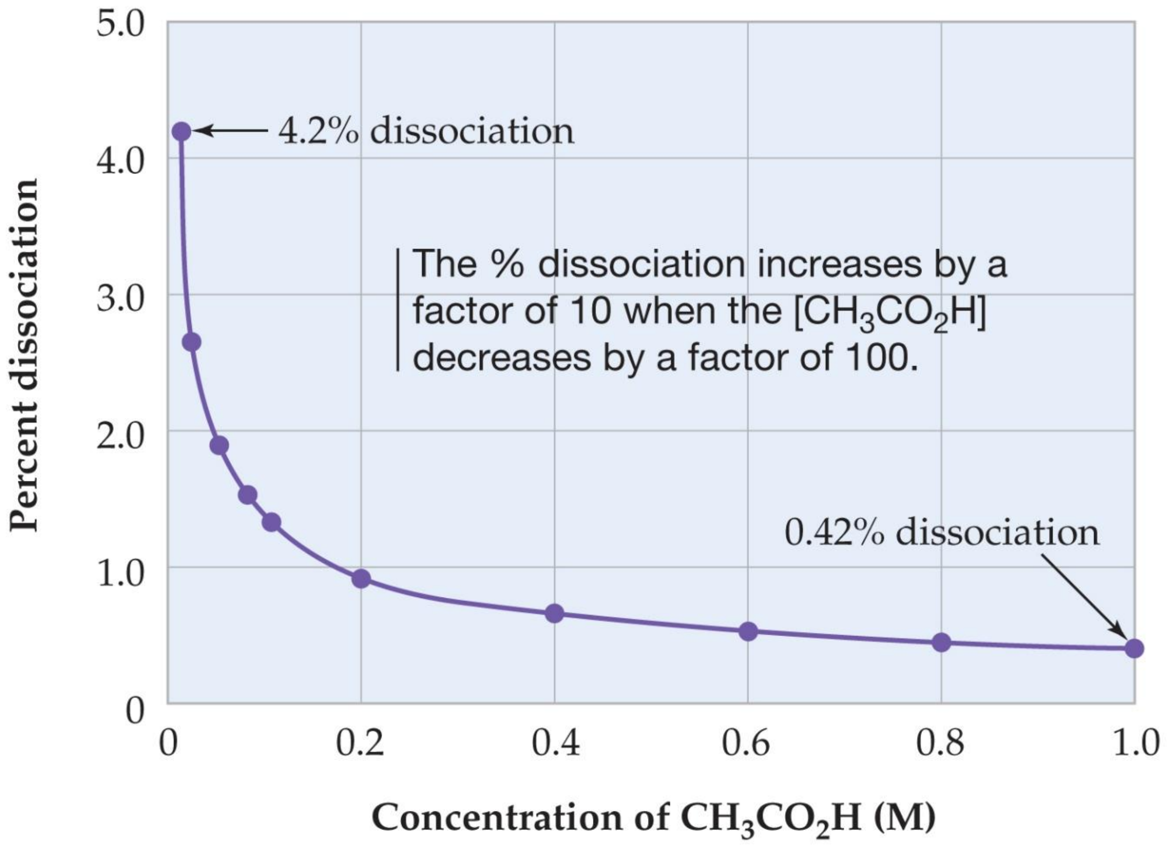
Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

↓

Step 8. Calculate the pH = $-\log [H_3O^+]$.

Percent Dissociation in Solutions of Weak Acids

$$\text{Percent dissociation} = \frac{[HA]_{dissociated}}{[HA]_{initial}} \times 100\%$$



Polyprotic Acids

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

$$K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

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

$$K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

Polyprotic Acids

TABLE 15.3 Stepwise Dissociation Constants for Polyprotic Acids at 25 °C

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Hydrogen sulfide[a]	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Sulfuric acid	H_2SO_4	Very large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	6.3×10^{-8}	

[a] Because of its very small size, K_{a2} for H_2S is difficult to measure and its value is uncertain.

Polyprotic Acids

Calculate the pH of a 0.020 M H_2CO_3 solution. At 25 ^oC, K_{a1} = 4.3×10^{-7}.

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

0.020		≈0	0
$-x$		$+x$	$+x$
$0.\ 20 - x$		x	x

$$K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]}$$

Polyprotic Acids

$$4.3 \times 10^{-7} = \frac{(x)(x)}{(0.020 - x)} \approx \frac{x^2}{0.020}$$

$$x = [H_3O^{1+}] = 9.3 \times 10^{-5}\ M$$

$$pH = -\log([H_3O^{+}]) = -\log(9.3 \times 10^{-5}) = \boxed{4.03}$$

Equilibria in Solutions of Weak Bases

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

Base Acid Acid Base

Base-Dissociation Constant: $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

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

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

Equilibria in Solutions of Weak Bases

TABLE 15.4 K_b Values for Some Weak Bases and K_a Values for Their Conjugate Acids at 25 °C

Base	Formula, B	K_b	Conjugate Acid, BH^+	K_a
Ammonia	NH_3	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Aniline	$C_6H_5NH_2$	4.3×10^{-10}	$C_6H_5NH_3^+$	2.3×10^{-5}
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	$(CH_3)_2NH_2^+$	1.9×10^{-11}
Hydrazine	N_2H_4	8.9×10^{-7}	$N_2H_5^+$	1.1×10^{-8}
Hydroxylamine	NH_2OH	9.1×10^{-9}	NH_3OH^+	1.1×10^{-6}
Methylamine	CH_3NH_2	3.7×10^{-4}	$CH_3NH_3^+$	2.7×10^{-11}

Equilibria in Solutions of Weak Bases

Calculate the pH of a 0.40 M NH_3 solution. At 25 °C, $K_b = 1.8 \times 10^{-5}$.

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

0.40		0	≈0
$-x$		$+x$	$+x$
$0.40 - x$		x	x

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

Equilibria in Solutions of Weak Bases

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.40 - x)} \approx \frac{x^2}{0.40}$$

$$x = [OH^-] = 0.0027\ M$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.0027} = 3.7 \times 10^{-12}\ M$$

$$pH = -\log([H_3O^+]) = -\log(3.7 \times 10^{-12}) = \boxed{11.43}$$

Relation Between K_a and K_b

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_a$$

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

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

$$K_a \times K_b = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-] = K_w$$

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

Relation Between K_a and K_b

$$\underbrace{K_a \times K_b}_{\text{conjugate acid-base pair}} = K_w$$

conjugate acid-base pair

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

$$pK_a + pK_b = pK_w = 14.00$$

Acid–Base Properties of Salts

Salts That Yield Neutral Solutions

The following ions do not react appreciably with water to produce either H_3O^+ or OH^- ions:

- **Cations from strong bases**:
  - Alkali metal cations of group 1a (Li^+, Na^+, K^+)
  - Alkaline earth metal cations of group 2a (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), except for Be^{2+}

- **Anions from strong monoprotic acids**:
  - Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-

Acid–Base Properties of Salts

Salts That Yield Acidic Solutions

Salts such as NH_4Cl that are derived from a weak base (NH_3) and a strong acid (HCl) yield acidic solutions.

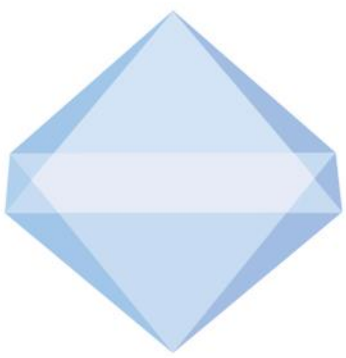
$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

Ammonium ion (NH_4^+) is the conjugate acid of the weak base ammonia (NH_3) while chloride ion (Cl^-) is neither acidic nor basic.

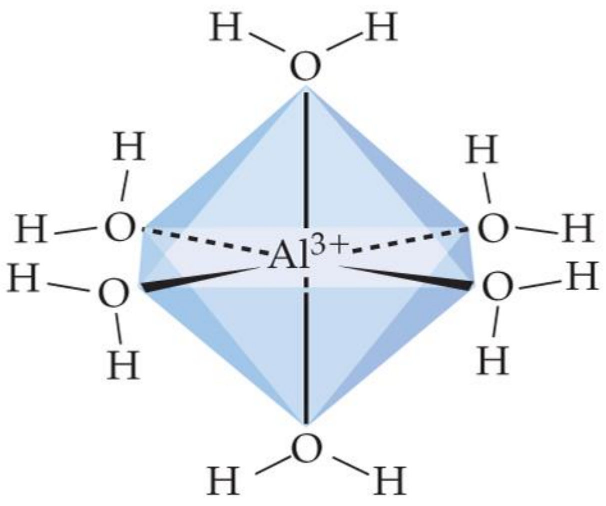
Acid–Base Properties of Salts

Salts That Yield Acidic Solutions

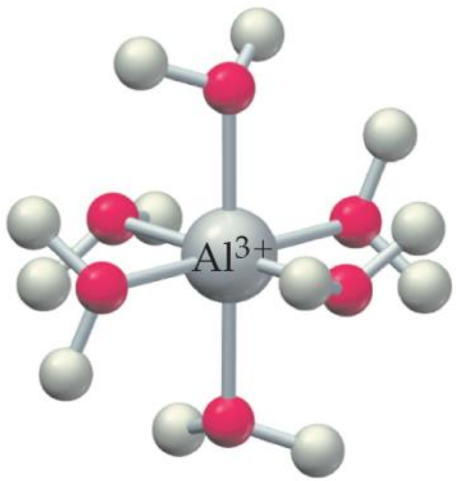
Hydrated cations of small, highly charged metal ions, such as Al^{3+}.



A regular octahedron has eight equilateral triangular faces and six vertices.



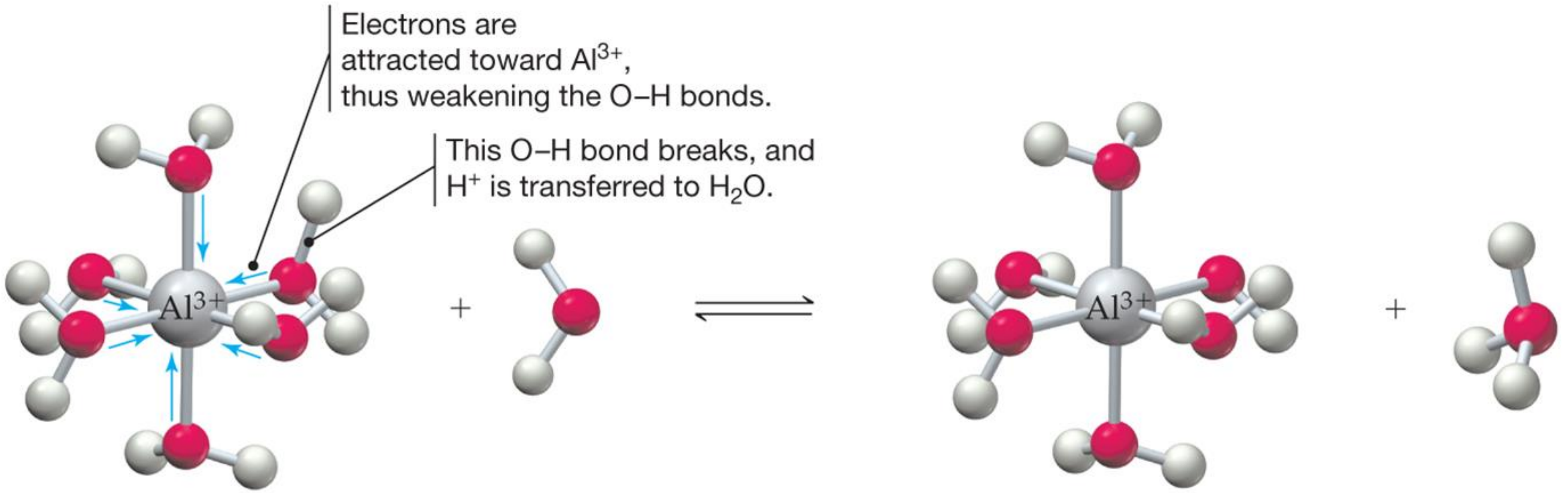
The six Al–O bonds point toward the six vertices of the octahedron.



A model of the $Al(H_2O)_6^{3+}$ cation, showing the octahedral arrangement of bonds to the six H_2O molecules.

Acid–Base Properties of Salts

Salts That Yield Acidic Solutions



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

Acid–Base Properties of Salts

Salts That Yield Basic Solutions

Salts such as NaCN that are derived from a strong base (NaOH) and a weak acid (HCN) yield basic solutions.

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

Cyanide ion (CN^-) is the conjugate base of the weak acid hydrocyanic acid (HCN) while sodium ion (Na^+) is neither acidic nor basic.

Acid–Base Properties of Salts

Salts That Contain Acidic Cations and Basic Anions

The pH of an ammonium carbonate solution, $(NH_4)_2CO_3$, depends on the relative acid strength of the cation and the relative base strength of the anion.

Is it *acidic* or *basic*?

Acid–Base Properties of Salts

Salts That Contain Acidic Cations and Basic Anions

$(NH_4)_2CO_3$:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_a$$

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

Three possibilities:

- $\boldsymbol{K_a > K_b}$: The solution will contain an excess of H_3O^+ ions (pH < 7).
- $\boldsymbol{K_a < K_b}$: The solution will contain an excess of OH^- ions (pH > 7).
- $\boldsymbol{K_a \approx K_b}$: The solution will contain approximately equal concentrations of H_3O^+ and OH^- ions (pH ≈ 7).

Acid–Base Properties of Salts

Salts That Contain Acidic Cations and Basic Anions

$(NH_4)_2CO_3$:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_a$$

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

$$K_a \text{ for } NH_4^+ = \frac{K_w}{K_b \text{ for } NH_3} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b \text{ for } CO_3^{2-} = \frac{K_w}{K_a \text{ for } HCO_3^-} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = \boxed{1.8 \times 10^{-4}}$$

Basic, $K_a < K_b$

Acid–Base Properties of Salts

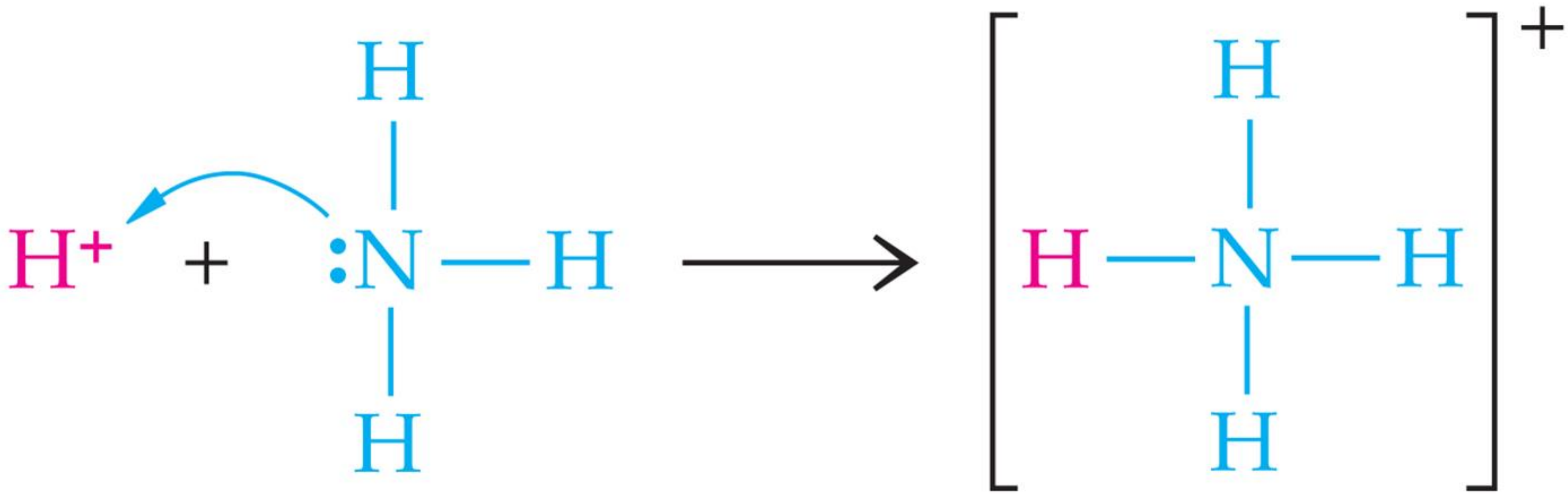
TABLE 15.5 Acid–Base Properties of Salts

Type of Salt	Examples	Ions That React with Water	pH of Solution
Cation from strong base; anion from strong acid	$NaCl$, KNO_3, BaI_2	None	~7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3, $[(CH_3)_3NH]Cl$	Cation	<7
Small, highly charged, cation; anion from strong acid	$AlCl_3$, $Cr(NO_3)_3$, $Fe(ClO_4)_3$	Hydrated cation	<7
Cation from strong base; anion from weak acid	$NaCN$, KF, Na_2CO_3	Anion	>7
Cation from weak base; anion from weak acid	NH_4CN, NH_4F, $(NH_4)_2CO_3$	Cation and anion	<7 if $K_a > K_b$ >7 if $K_a < K_b$ ~ 7 if $K_a \approx K_b$

Lewis Acids and Bases

Lewis Acid: An electron-pair acceptor

Lewis Base: An electron-pair donor



Lewis Acids and Bases

$$Cu^{2+} + 4\,{:}NH_3 \longrightarrow Cu(NH_3)_4^{2+}$$

Lewis acid   Lewis base

(a) Light blue Cu^{2+}(*aq*)

(b) Addition of NH_3(*aq*) to **(a)** gives a light blue precipitate of $Cu(OH)_2$.

(c) Addition of excess NH_3(*aq*) to **(a)** or **(b)** yields the deep blue $Cu(NH_3)_4^{2+}$ ion.

Lewis Acids and Bases