

Acids and Bases

Chapter 15

Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

React with certain metals to produce hydrogen gas.

React with carbonates and bicarbonates to produce carbon dioxide gas

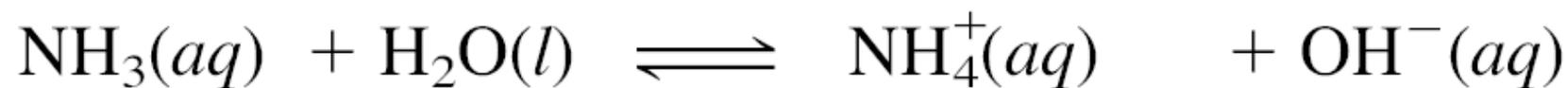
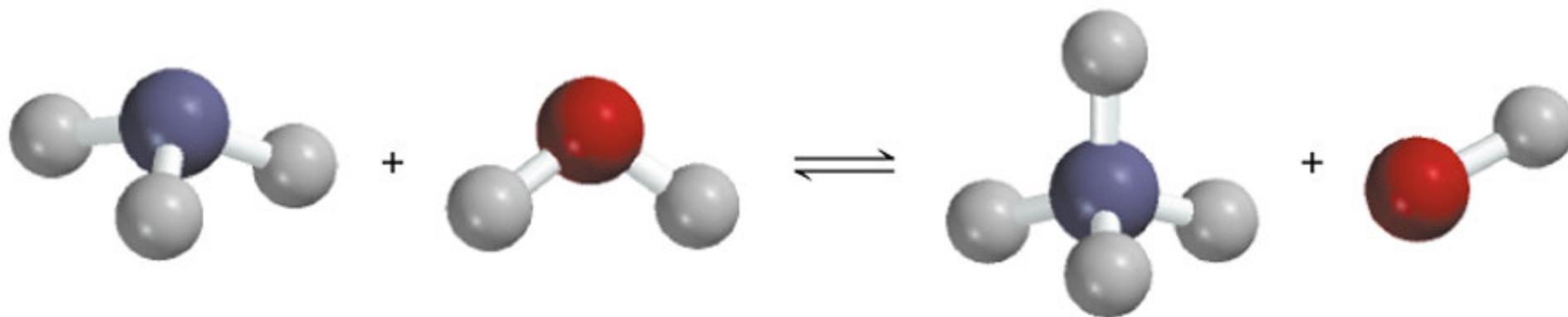
Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

A Brønsted **acid** is a proton donor

A Brønsted **base** is a proton acceptor



base

acid



acid

base

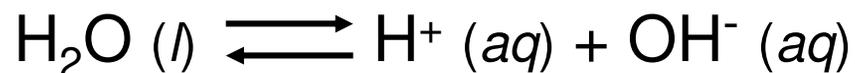
base

acid

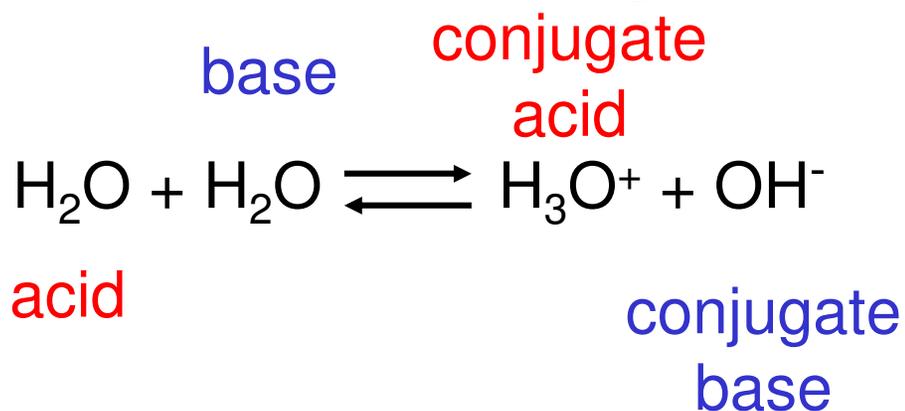
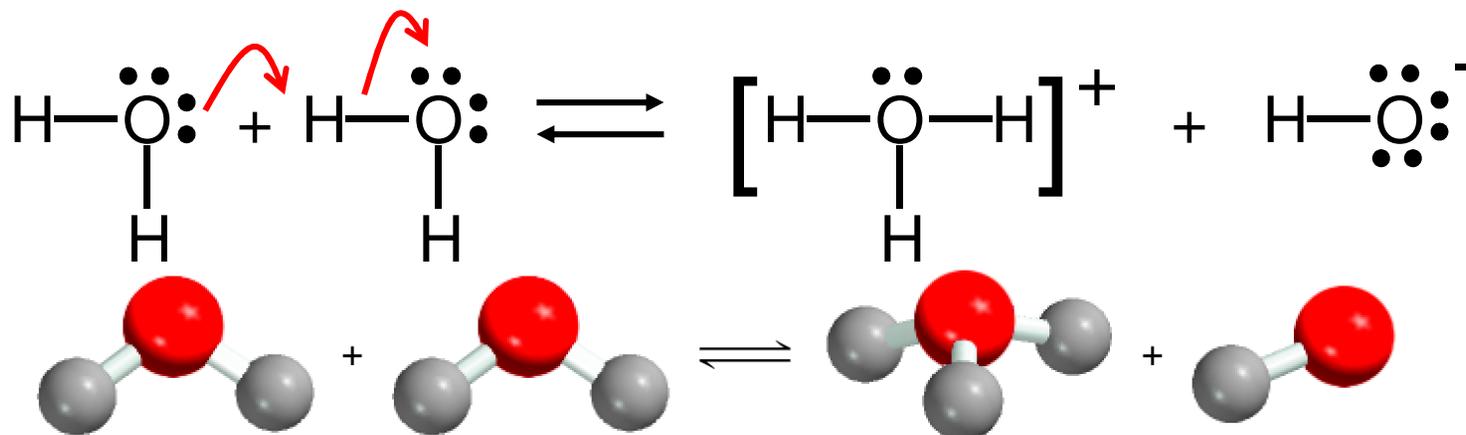
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conjugate
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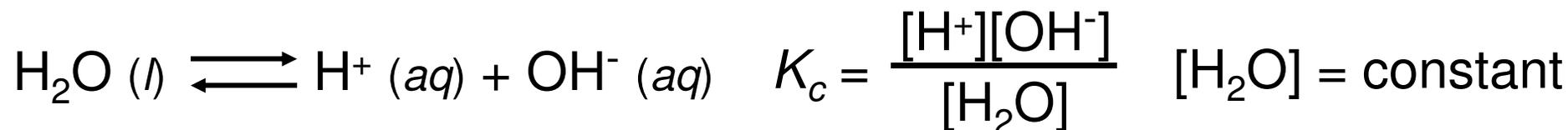
Acid-Base Properties of Water



autoionization of water



The Ion Product of Water



$$K_c[\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-]$$

The ***ion-product constant*** (K_w) is the product of the molar concentrations of H^+ and OH^- ions **at a particular temperature.**

<p>At 25°C</p> $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

$$[\text{H}^+] = [\text{OH}^-]$$

$$[\text{H}^+] > [\text{OH}^-]$$

$$[\text{H}^+] < [\text{OH}^-]$$

Solution Is

neutral

acidic

basic

What is the concentration of OH⁻ ions in a HCl solution whose hydrogen ion concentration is 1.3 M?

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

$$[\text{H}^+] = 1.3 \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{1.3} = 7.7 \times 10^{-15} \text{ M}$$

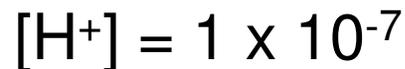
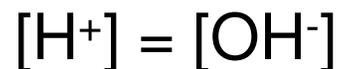
pH – A Measure of Acidity

$$\text{pH} = -\log [\text{H}^+]$$

Solution Is

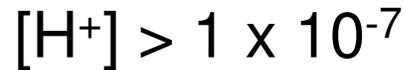
At 25°C

neutral



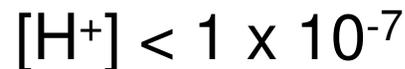
$$\text{pH} = 7$$

acidic



$$\text{pH} < 7$$

basic



$$\text{pH} > 7$$

pH ↑

[H⁺] ↓

TABLE 15.1**The pHs of Some Common Fluids**

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

*Water exposed to air for a long period of time absorbs atmospheric CO_2 to form carbonic acid, H_2CO_3 .

Other important relationships

$$\text{pOH} = -\log [\text{OH}^-]$$

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

$$-\log [\text{H}^+] - \log [\text{OH}^-] = 14.00$$

$$\text{pH} + \text{pOH} = 14.00$$



pH Meter

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the H⁺ ion concentration of the rainwater?

$$\text{pH} = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.82} = 1.5 \times 10^{-5} \text{ M}$$

The OH⁻ ion concentration of a blood sample is $2.5 \times 10^{-7} \text{ M}$. What is the pH of the blood?

$$\text{pH} + \text{pOH} = 14.00$$

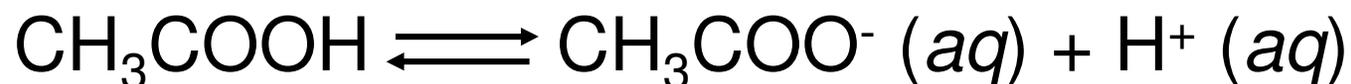
$$\text{pOH} = -\log [\text{OH}^-] = -\log (2.5 \times 10^{-7}) = 6.60$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 6.60 = 7.40$$

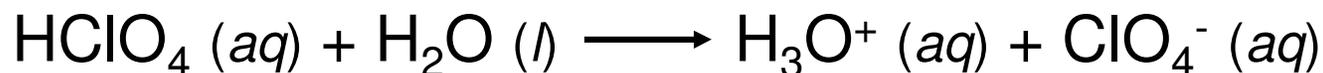
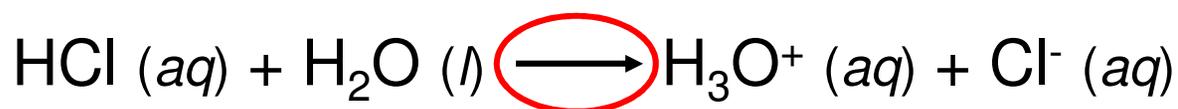
Strong Electrolyte – 100% dissociation



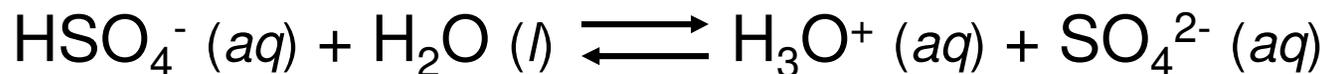
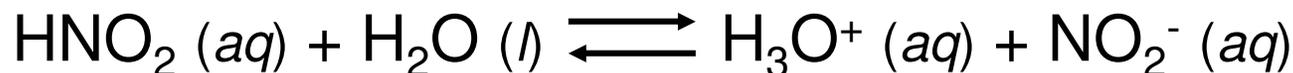
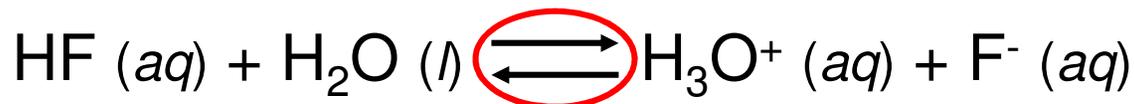
Weak Electrolyte – not completely dissociated



Strong Acids are strong electrolytes



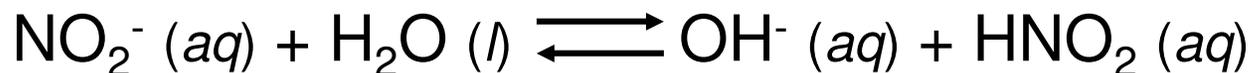
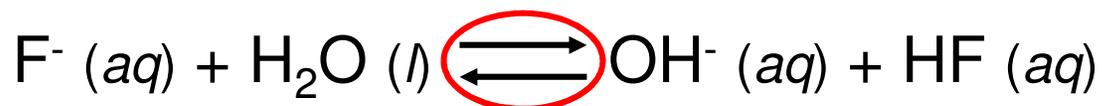
Weak Acids are weak electrolytes



Strong Bases are strong electrolytes



Weak Bases are weak electrolytes



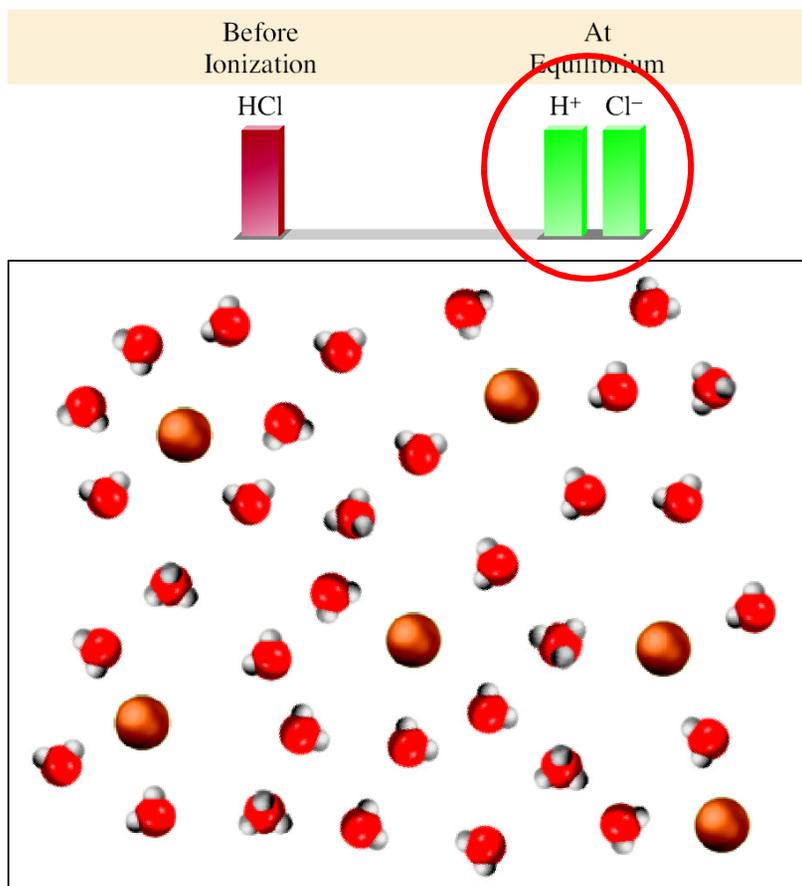
Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqueous solution.

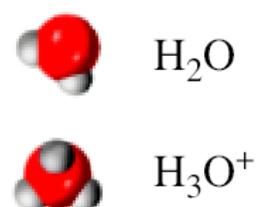
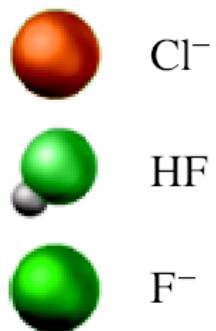
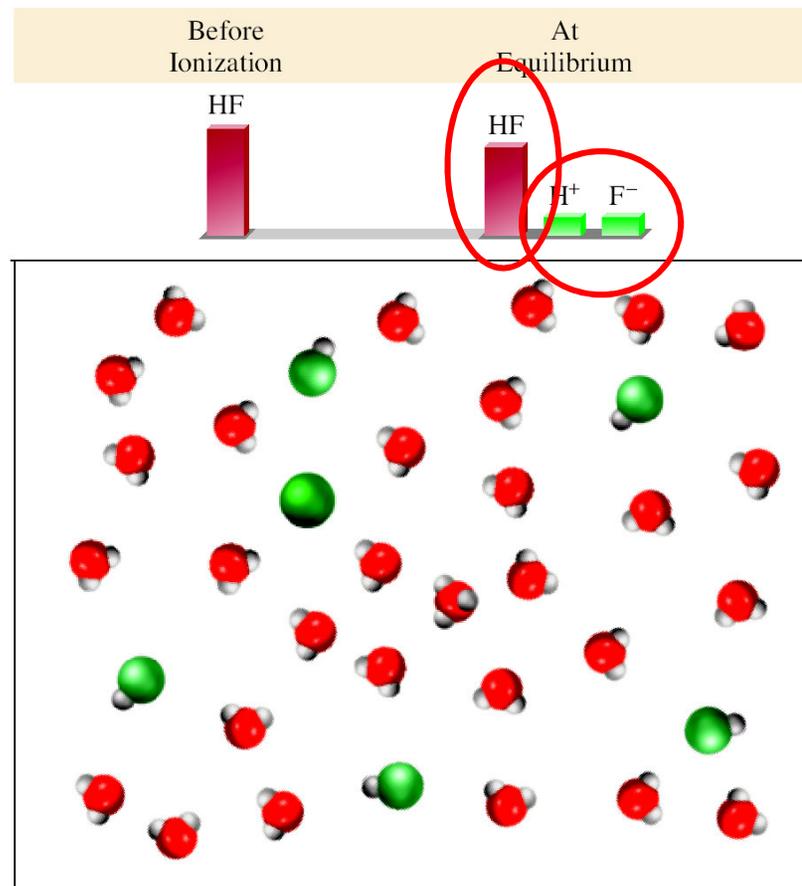
TABLE 15.2 Relative Strengths of Conjugate Acid-Base Pairs

	Acid	Conjugate Base	
Acid strength increases ↑	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 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)
	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 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)		
		↓ Base strength increases	

Strong Acid (HCl)

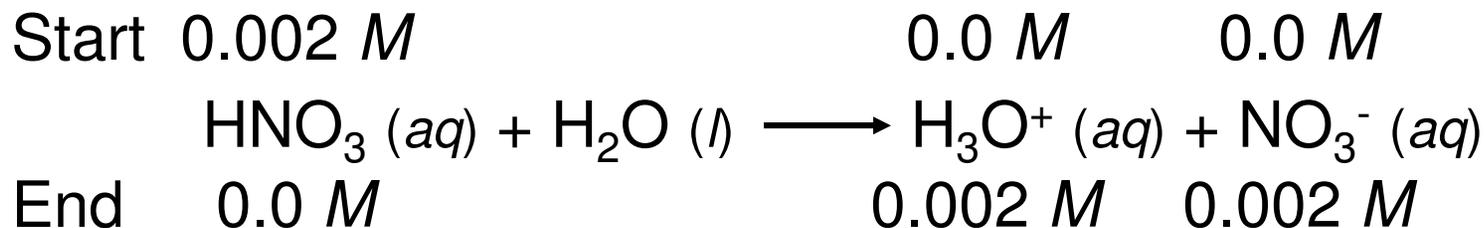


Weak Acid (HF)



What is the pH of a $2 \times 10^{-3} \text{ M HNO}_3$ solution?

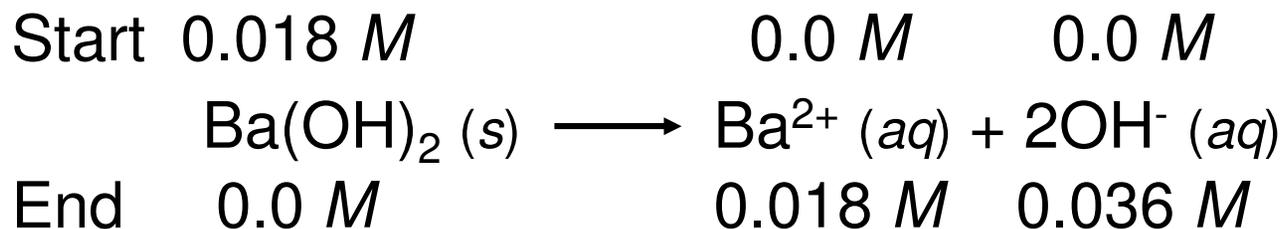
HNO_3 is a strong acid – 100% dissociation.



$$\text{pH} = -\log [\text{H}^+] = -\log [\text{H}_3\text{O}^+] = -\log(0.002) = 2.7$$

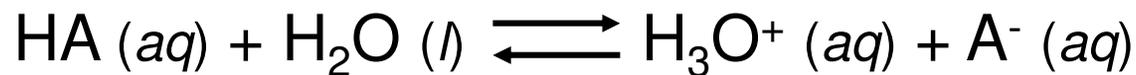
What is the pH of a $1.8 \times 10^{-2} \text{ M Ba(OH)}_2$ solution?

Ba(OH)_2 is a strong base – 100% dissociation.



$$\text{pH} = 14.00 - \text{pOH} = 14.00 + \log(0.036) = 12.6$$

Weak Acids (HA) and Acid Ionization Constants



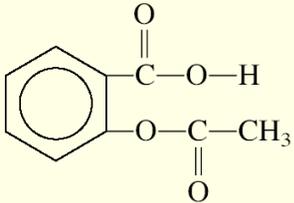
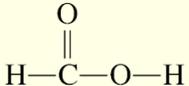
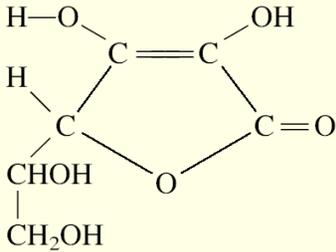
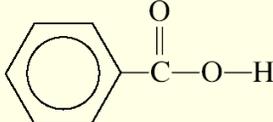
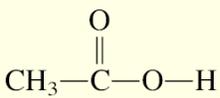
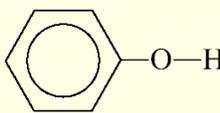
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is the ***acid ionization constant***

K_a ↑

weak acid
strength ↑

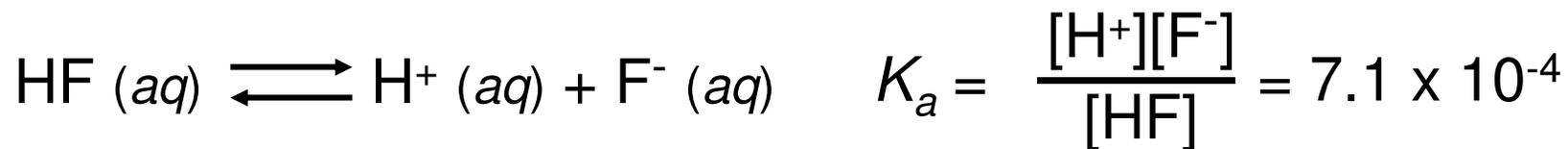
TABLE 15.3 Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b^\dagger
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 ₉ H ₈ O ₄		3.0×10^{-4}	C ₉ H ₇ O ₄ ⁻	3.3×10^{-11}
Formic acid	HCOOH		1.7×10^{-4}	HCOO ⁻	5.9×10^{-11}
Ascorbic acid*	C ₆ H ₈ O ₆		8.0×10^{-5}	C ₆ H ₇ O ₆ ⁻	1.3×10^{-10}
Benzoic acid	C ₆ H ₅ COOH		6.5×10^{-5}	C ₆ H ₅ COO ⁻	1.5×10^{-10}
Acetic acid	CH ₃ COOH		1.8×10^{-5}	CH ₃ COO ⁻	5.6×10^{-10}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}	CN ⁻	2.0×10^{-5}
Phenol	C ₆ H ₅ OH		1.3×10^{-10}	C ₆ H ₅ O ⁻	7.7×10^{-5}

*For ascorbic acid it is the upper left hydroxyl group that is associated with this ionization constant.

†The base ionization constant K_b is discussed in Section 15.6.

What is the pH of a 0.5 M HF solution (at 25°C)?



Initial (M) 0.50 0.00 0.00

Change (M) -x +x +x

Equilibrium (M) 0.50 - x x x

$$K_a = \frac{x^2}{0.50 - x} = 7.1 \times 10^{-4} \quad K_a \ll 1 \quad 0.50 - x \approx 0.50$$

$$K_a \approx \frac{x^2}{0.50} = 7.1 \times 10^{-4} \quad x^2 = 3.55 \times 10^{-4} \quad x = 0.019 \text{ M}$$

$$[\text{H}^+] = [\text{F}^-] = 0.019 \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = 1.72$$

$$[\text{HF}] = 0.50 - x = 0.48 \text{ M}$$

When can I use the approximation?

$$K_a \ll 1 \quad 0.50 - x \approx 0.50$$

When x is less than 5% of the value from which it is subtracted.

$$x = 0.019 \quad \frac{0.019 \text{ M}}{0.50 \text{ M}} \times 100\% = 3.8\% \quad \begin{array}{l} \text{Less than 5\%} \\ \text{Approximation ok.} \end{array}$$

What is the pH of a 0.05 M HF solution (at 25°C)?

$$K_a \approx \frac{x^2}{0.05} = 7.1 \times 10^{-4} \quad x = 0.006 \text{ M}$$

$$\frac{0.006 \text{ M}}{0.05 \text{ M}} \times 100\% = 12\% \quad \begin{array}{l} \text{More than 5\%} \\ \text{Approximation **not** ok.} \end{array}$$

Must solve for x exactly using quadratic equation or method of successive approximations.

Solving **weak acid** ionization problems:

1. Identify the major species that can affect the pH.
 - In most cases, you can ignore the autoionization of water.
 - Ignore $[\text{OH}^-]$ because it is determined by $[\text{H}^+]$.
2. Use ICE to express the equilibrium concentrations in terms of single unknown x .
3. Write K_a in terms of equilibrium concentrations. Solve for x by the approximation method. If approximation is not valid, solve for x exactly.
4. Calculate concentrations of all species and/or pH of the solution.

What is the pH of a 0.122 M monoprotic acid whose K_a is 5.7×10^{-4} ?



Initial (M)	0.122	0.00	0.00
Change (M)	-x	+x	+x
Equilibrium (M)	0.122 - x	x	x

$$K_a = \frac{x^2}{0.122 - x} = 5.7 \times 10^{-4}$$

$$K_a \ll 1 \quad 0.122 - x \approx 0.122$$

$$K_a \approx \frac{x^2}{0.122} = 5.7 \times 10^{-4}$$

$$x^2 = 6.95 \times 10^{-5} \quad x = 0.0083 \text{ M}$$

$$\frac{0.0083 \text{ M}}{0.122 \text{ M}} \times 100\% = 6.8\%$$

More than 5%
Approximation **not** ok.

$$K_a = \frac{x^2}{0.122 - x} = 5.7 \times 10^{-4} \quad x^2 + 0.00057x - 6.95 \times 10^{-5} = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 0.0081$$

~~$$x = -0.0081$$~~



Initial (M)	0.122	0.00	0.00
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Change (M)	-x	+x	+x
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Equilibrium (M)	0.122 - x	x	x
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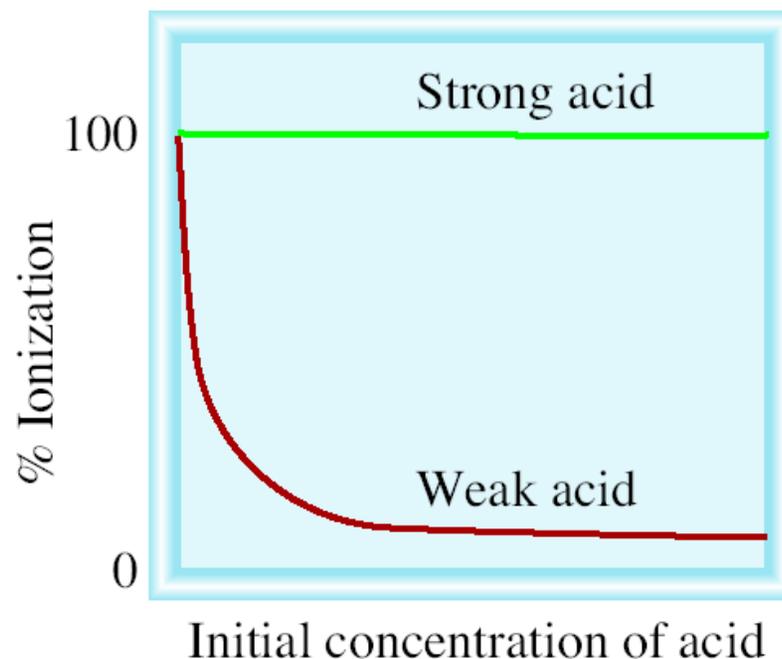
$$[\text{H}^+] = x = 0.0081 \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = 2.09$$

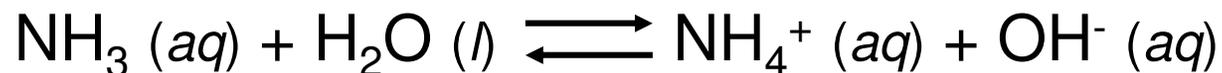
$$\textit{percent ionization} = \frac{\text{Ionized acid concentration at equilibrium}}{\text{Initial concentration of acid}} \times 100\%$$

For a monoprotic acid HA

$$\text{Percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\% \quad [\text{HA}]_0 = \text{initial concentration}$$



Weak Bases and Base Ionization Constants



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

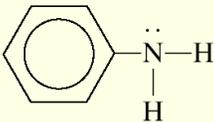
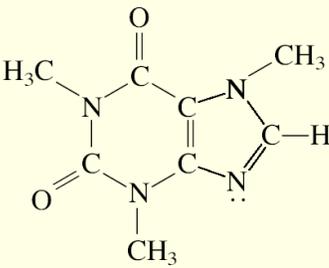
K_b is the **base ionization constant**

$K_b \uparrow$

weak base strength \uparrow

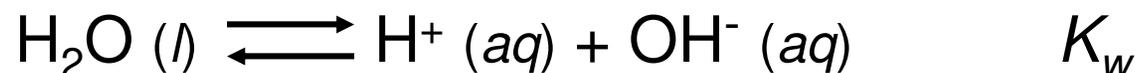
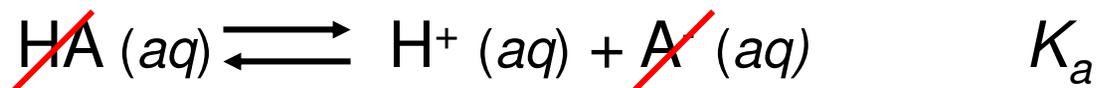
Solve weak base problems like weak acids **except** solve for $[\text{OH}^-]$ instead of $[\text{H}^+]$.

TABLE 15.4 Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C

Name of Base	Formula	Structure	K_b^*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\overset{\cdot\cdot}{N}-H$ H	5.6×10^{-4}	$C_2H_5NH_3^+$	1.8×10^{-11}
Methylamine	CH_3NH_2	$CH_3-\overset{\cdot\cdot}{N}-H$ H	4.4×10^{-4}	$CH_3NH_3^+$	2.3×10^{-11}
Ammonia	NH_3	$H-\overset{\cdot\cdot}{N}-H$ H	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5NH^+$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5NH_3^+$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}N_4O_2^+$	0.19
Urea	$(NH_2)_2CO$	$H-\overset{\cdot\cdot}{N}-\overset{O}{\parallel}C-\overset{\cdot\cdot}{N}-H$ H H	1.5×10^{-14}	$H_2NCONH_3^+$	0.67

*The nitrogen atom with the lone pair accounts for each compound's basicity. In the case of urea, K_b can be associated with either nitrogen atom.

Ionization Constants of Conjugate Acid-Base Pairs



$$K_a K_b = K_w$$

Weak Acid and Its Conjugate Base

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

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

Diprotic and Triprotic Acids

- May yield more than one hydrogen ion per molecule.
- Ionize in a stepwise manner; that is, they lose one proton at a time.
- An ionization constant expression can be written for each ionization stage.
- Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution.

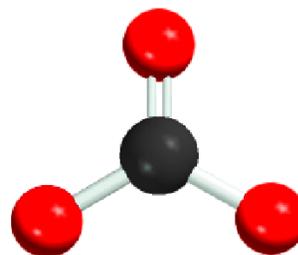
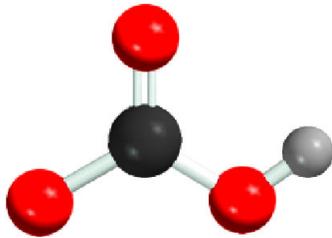
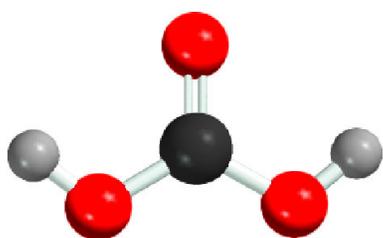
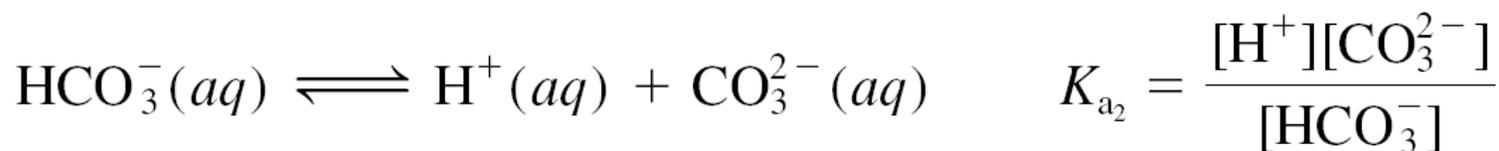


TABLE 15.5 Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Sulfuric acid	H_2SO_4	$\begin{array}{c} O \\ \\ H-O-S-O-H \\ \\ O \end{array}$	very large	HSO_4^-	very small
Hydrogen sulfate ion	HSO_4^-	$\begin{array}{c} O \\ \\ H-O-S-O^- \\ \\ O \end{array}$	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Oxalic acid	$H_2C_2O_4$	$\begin{array}{c} O \quad O \\ \quad \\ H-O-C-C-O-H \end{array}$	6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
Hydrogen oxalate ion	$HC_2O_4^-$	$\begin{array}{c} O \quad O \\ \quad \\ H-O-C-C-O^- \end{array}$	6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Sulfurous acid*	H_2SO_3	$\begin{array}{c} O \\ \\ H-O-S-O-H \end{array}$	1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
Hydrogen sulfite ion	HSO_3^-	$\begin{array}{c} O \\ \\ H-O-S-O^- \end{array}$	6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Carbonic acid	H_2CO_3	$\begin{array}{c} O \\ \\ H-O-C-O-H \end{array}$	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
Hydrogen carbonate ion	HCO_3^-	$\begin{array}{c} O \\ \\ H-O-C-O^- \end{array}$	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrosulfuric acid	H_2S	$H-S-H$	9.5×10^{-8}	HS^-	1.1×10^{-7}
Hydrogen sulfide ion†	HS^-	$H-S^-$	1×10^{-19}	S^{2-}	1×10^5
Phosphoric acid	H_3PO_4	$\begin{array}{c} O \\ \\ H-O-P-O-H \\ \\ O \\ \\ H \end{array}$	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
Dihydrogen phosphate ion	$H_2PO_4^-$	$\begin{array}{c} O \\ \\ H-O-P-O^- \\ \\ O \\ \\ H \end{array}$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen phosphate ion	HPO_4^{2-}	$\begin{array}{c} O \\ \\ H-O-P-O^- \\ \\ O^- \end{array}$	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}

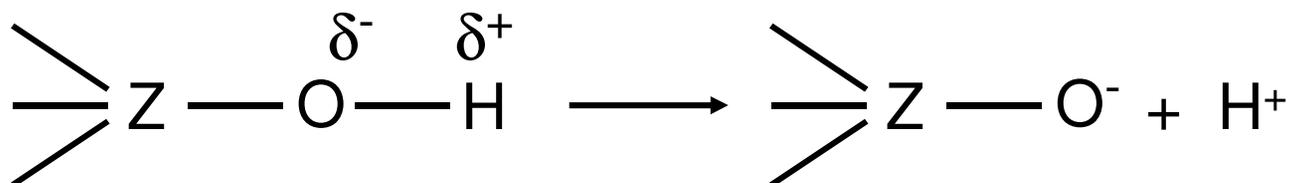
* H_2SO_3 has never been isolated and exists in only minute concentration in aqueous solution of SO_2 . The K_a value here refers to the process $SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$.

†The ionization constant of HS^- is very low and difficult to measure. The value listed here is only an estimate.

TABLE 15.6**Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids**

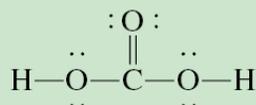
Bond	Bond Enthalpy (kJ/mol)	Acid Strength
H—F	568.2	weak
H—Cl	431.9	strong
H—Br	366.1	strong
H—I	298.3	strong

Molecular Structure and Oxoacid Strength

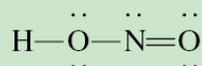


The O-H bond will be more polar and easier to break if:

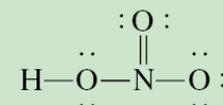
- Z is very electronegative or
- Z is in a high oxidation state



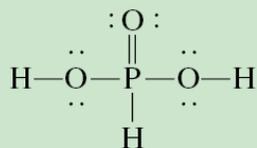
Carbonic acid



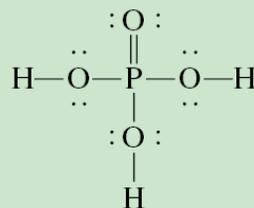
Nitrous acid



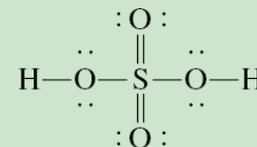
Nitric acid



Phosphorous acid



Phosphoric acid

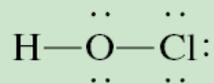


Sulfuric acid

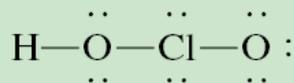
Molecular Structure and Acid Strength

2. Oxoacids having the same central atom (Z) but different numbers of attached groups.

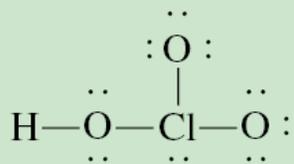
Acid strength increases as the oxidation number of Z increases.



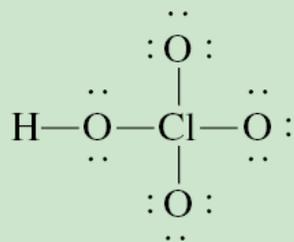
Hypochlorous acid (+1)



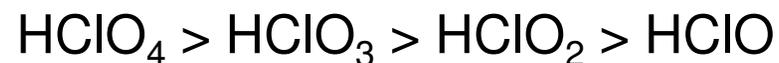
Chlorous acid (+3)



Chloric acid (+5)



Perchloric acid (+7)



Acid-Base Properties of Salts

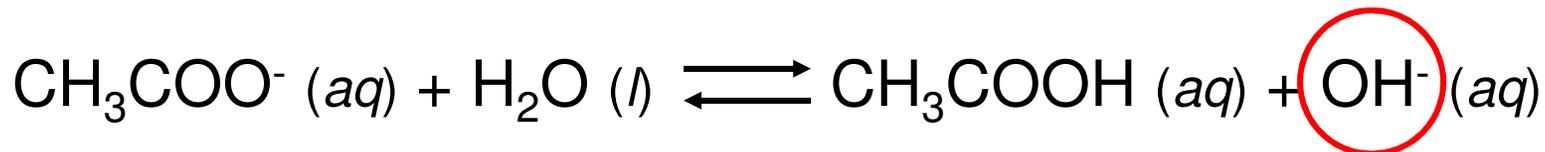
Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^- , Br^- , and NO_3^-).



Basic Solutions:

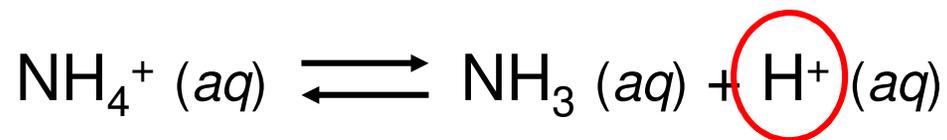
Salts derived from a strong base **and** a **weak** acid.



Acid-Base Properties of Salts

Acid Solutions:

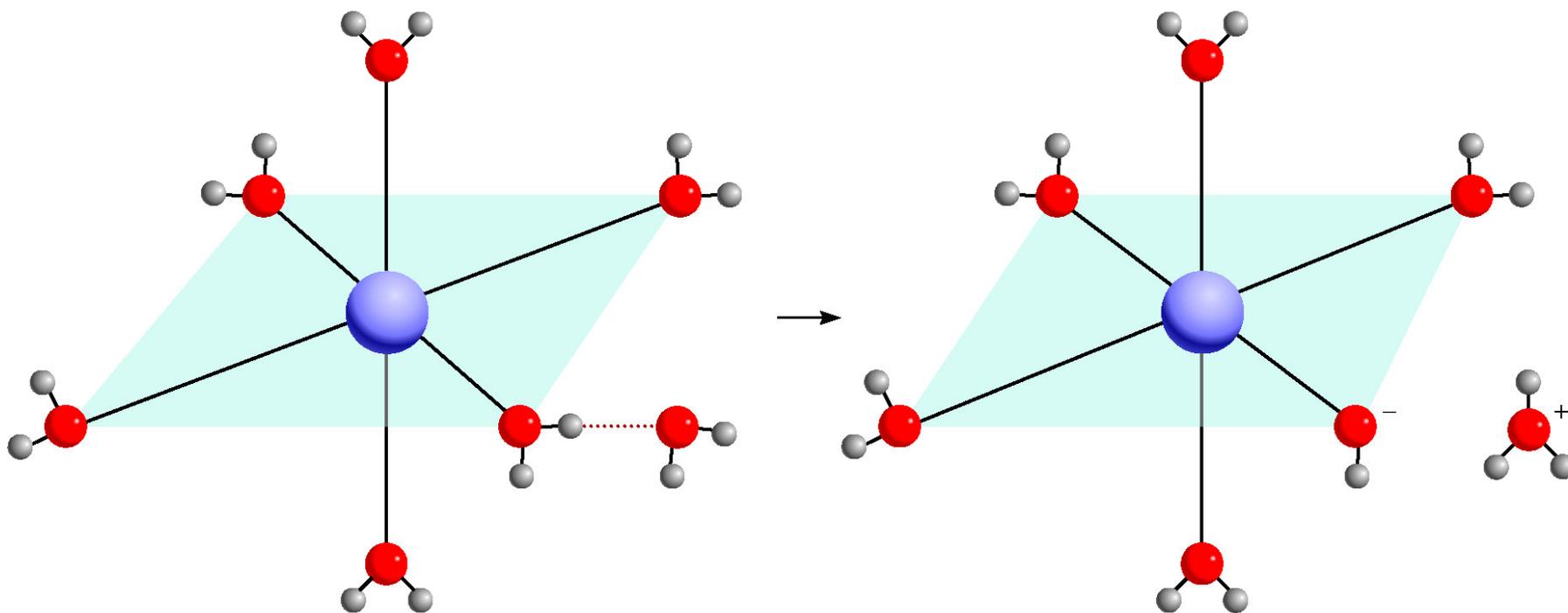
Salts derived from a strong acid and a weak base.



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



Acid Hydrolysis of Al^{3+}



Acid-Base Properties of Salts

Solutions in which both the cation and the anion hydrolyze:

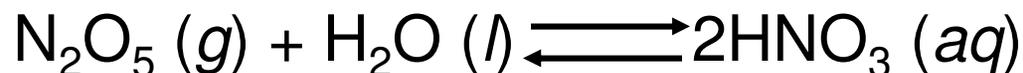
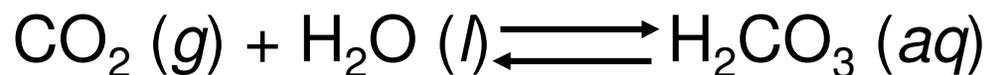
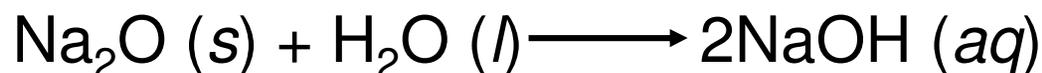
- K_b for the anion $>$ K_a for the cation, solution will be basic
- K_b for the anion $<$ K_a for the cation, solution will be acidic
- K_b for the anion \approx K_a for the cation, solution will be neutral

TABLE 15.7 Acid-Base Properties of Salts

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO ₃ , RbBr, BaCl ₂	None	≈ 7
Cation from strong base; anion from weak acid	CH ₃ COONa, KNO ₂	Anion	> 7
Cation from weak base; anion from strong acid	NH ₄ Cl, NH ₄ NO ₃	Cation	< 7
Cation from weak base; anion from weak acid	NH ₄ NO ₂ , CH ₃ COONH ₄ , NH ₄ CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	AlCl ₃ , Fe(NO ₃) ₃	Hydrated cation	< 7

Oxides of the Representative Elements In Their Highest Oxidation States

1 1A	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	18 8A	
Li ₂ O	BeO											B ₂ O ₃	CO ₂	N ₂ O ₅		OF ₂		
Na ₂ O	MgO	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B		9	10	11 1B	12 2B	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇	
K ₂ O	CaO												Ga ₂ O ₃	GeO ₂	As ₂ O ₅	SeO ₃	Br ₂ O ₇	
Rb ₂ O	SrO												In ₂ O ₃	SnO ₂	Sb ₂ O ₅	TeO ₃	I ₂ O ₇	
Cs ₂ O	BaO												Tl ₂ O ₃	PbO ₂	Bi ₂ O ₅	PoO ₃	At ₂ O ₇	



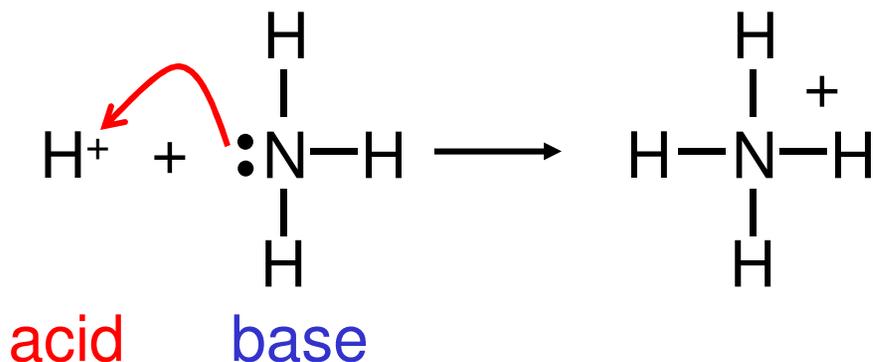
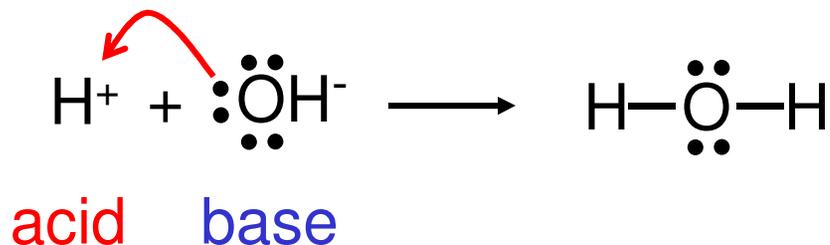
Definition of An Acid

Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

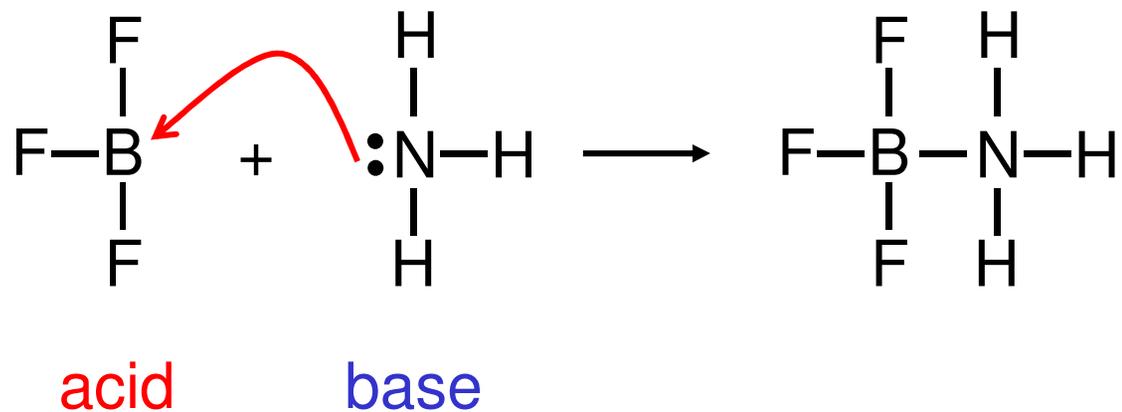
A **Brønsted acid** is a proton donor

A **Lewis acid** is a substance that can accept a pair of electrons

A **Lewis base** is a substance that can donate a pair of electrons



Lewis Acids and Bases



No protons donated or accepted!

Chemistry In Action: Antacids and the Stomach pH Balance

Some Common Commercial Antacid Preparations

Commercial Name	Active Ingredients
Alka-2	Calcium carbonate
Alka-Seltzer	Aspirin, sodium bicarbonate, citric acid
Bufferin	Aspirin, magnesium carbonate, aluminum glycinate
Buffered aspirin	Aspirin, magnesium carbonate, aluminum hydroxide-glycine
Milk of magnesia	Magnesium hydroxide
Rolaids	Dihydroxy aluminum sodium carbonate
Tums	Calcium carbonate

