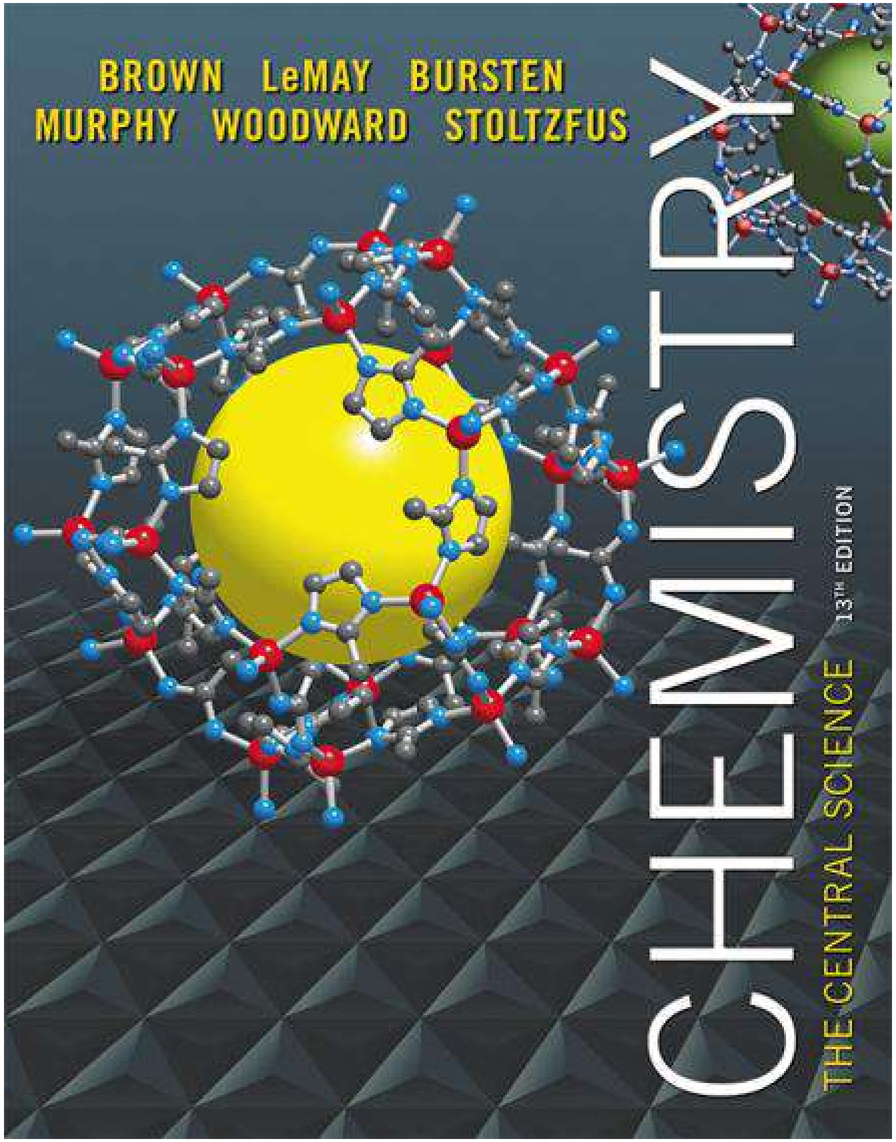

Lecture Presentation

Chapter 16

Acid–Base Equilibria

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Some Definitions

- Arrhenius
    - An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.
    - A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.
- Brønsted–Lowry
    - An acid is a proton donor.
    - A base is a proton acceptor.

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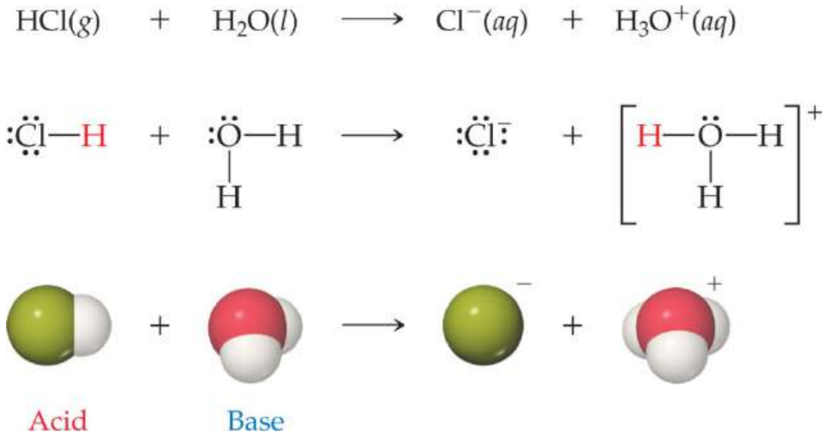
Brønsted–Lowry Acid and Base

A Brønsted–Lowry **acid** must have at least one removable (acidic) proton (H^+) to donate.

A Brønsted–Lowry base must have at least one nonbonding pair of electrons to accept a proton (H^+).



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

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What Is Different about Water?

- Water can act as a Brønsted–Lowry base and accept a proton (H^+) from an acid, as on the previous slide.
- It can also donate a proton and act as an acid, as is seen below.
- This makes water **amphiprotic**.

$$\underset{\text{Base}}{\mathrm{NH_3}(aq)} + \underset{\text{Acid}}{\mathrm{H_2O}(l)} \rightleftharpoons \mathrm{NH_4}^{+}(aq) + \mathrm{OH}^{-}(aq)$$

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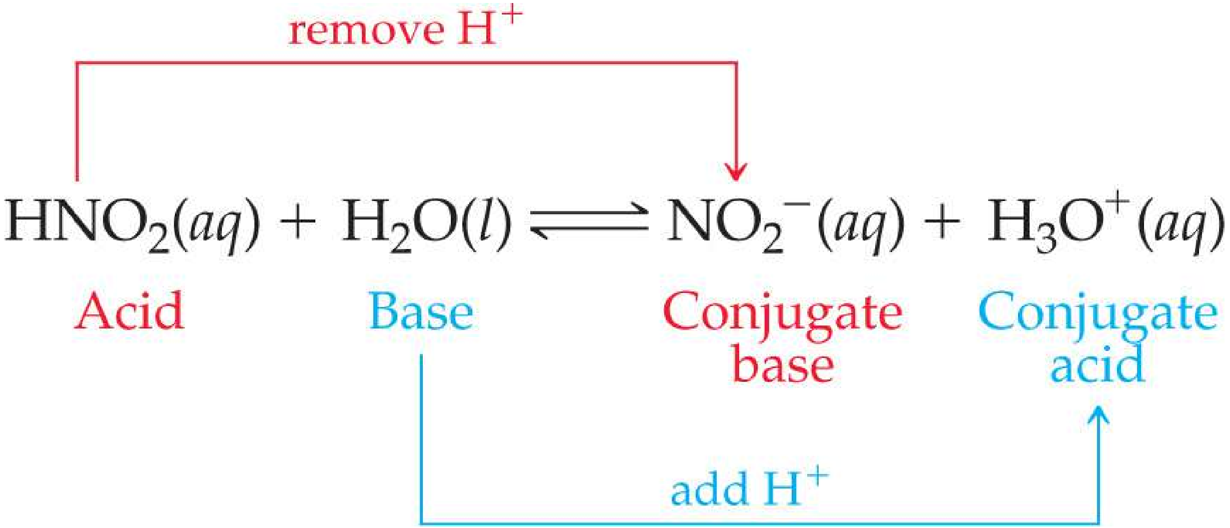
Conjugate Acids and Bases

- The term **conjugate** means “joined together as a pair.”
- Reactions between acids and bases always yield their conjugate bases and acids.



remove H^+

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

Acid

Base

Conjugate base

Conjugate acid

add H^+

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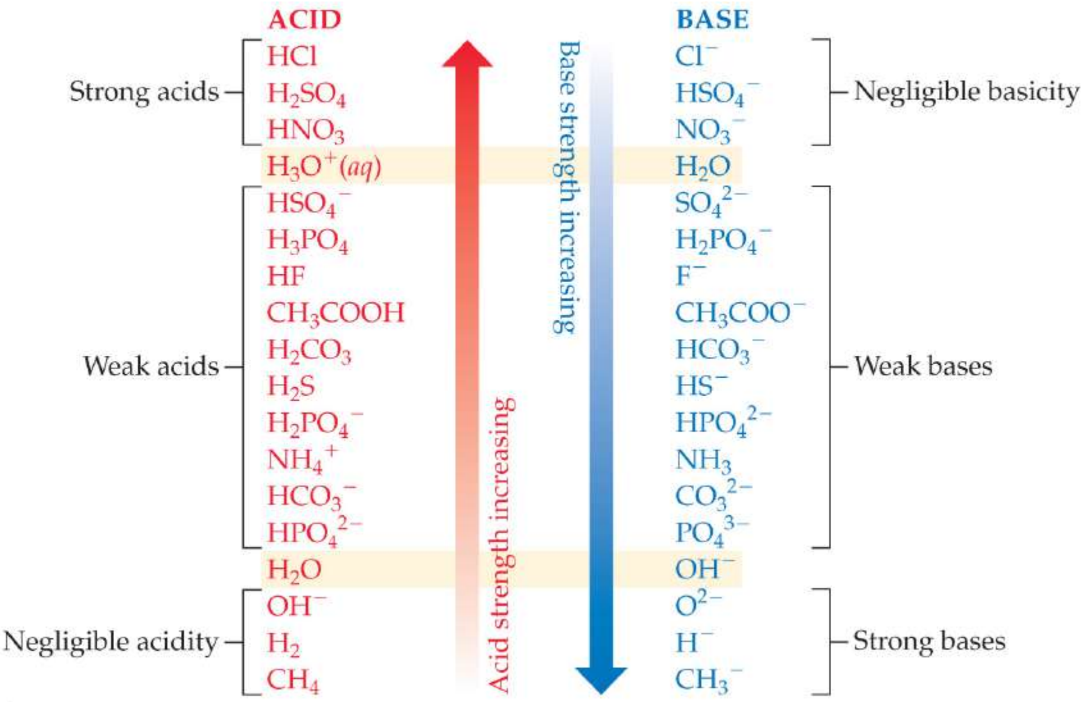
Relative Strengths of Acids and Bases

- Acids above the line with H_2O as a base are *strong acids*; their conjugate bases do *not* act as acids in water.
- Bases below the line with H_2O as an acid are *strong bases*; their conjugate acids do *not* act as acids in water.



	ACID	BASE	
Strong acids	HCl	Cl^-	Negligible basicity
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak acids	HSO_4^-	SO_4^{2-}	Weak bases
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible acidity	OH^-	O^{2-}	Strong bases
	H_2	H^-	
	CH_4	CH_3^-	

- The substances between the lines with H_2O are conjugate acid–base pairs in water.

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Acid and Base Strength

- *In every acid–base reaction, equilibrium favors transfer of the proton from the stronger acid to the stronger base to form the weaker acid and the weaker base.*

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

➢ H_2O is a much stronger base than Cl^-, so the equilibrium lies far to the right ($K >> 1$).

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

❖ Acetate is a stronger base than H_2O, so the equilibrium favors the left side ($K < 1$).

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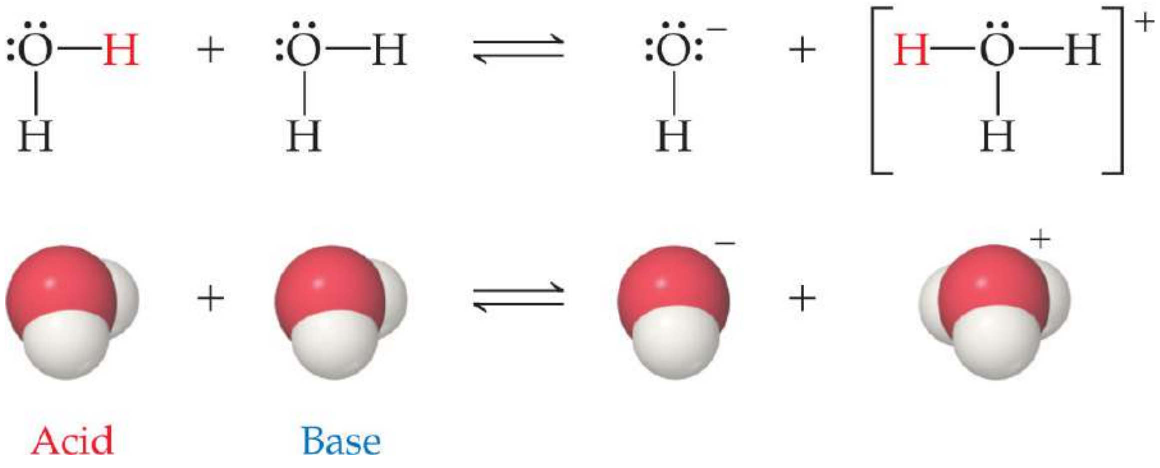
Autoionization of Water

- Water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.
- This is referred to as **autoionization**.

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



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Ion Product Constant

- The equilibrium expression for this process is

$$K_c = [H_3O^+][OH^-]$$

- This special equilibrium constant is referred to as the **ion product constant** for water, K_w.
- At 25 °C, $K_w = 1.0 \times 10^{-14}$

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Aqueous Solutions Can Be Acidic, Basic, or Neutral

- If a solution is neutral, $[H^+] = [OH^–]$.
- If a solution is acidic, $[H^+] > [OH^–]$.
- If a solution is basic, $[H^+] < [OH^–]$.

Acidic solution

$[H^+] > [OH^-]$

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

Neutral solution

$[H^+] = [OH^-]$

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

Basic solution

$[H^+] < [OH^-]$

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

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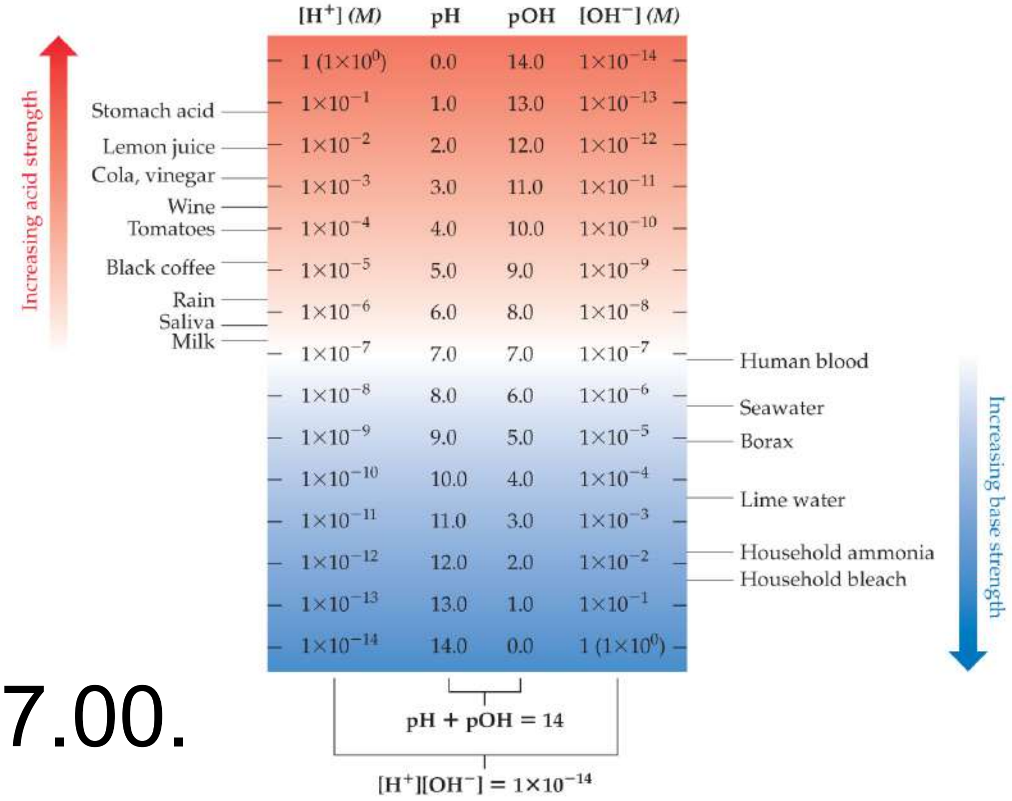
pH

- pH is a method of reporting hydrogen ion concentration.
- $\mathrm{pH} = -\log[\mathrm{H}^+]$
- Neutral pH is 7.00.
- Acidic pH is below 7.00.
- Basic pH is above 7.00.



$[\mathrm{H}^+]$ (*M*)	pH	pOH	$[\mathrm{OH}^-]$ (*M*)
$1\ (1\times10^{0})$	0.0	14.0	1×10^{-14}
1×10^{-1}	1.0	13.0	1×10^{-13}
1×10^{-2}	2.0	12.0	1×10^{-12}
1×10^{-3}	3.0	11.0	1×10^{-11}
1×10^{-4}	4.0	10.0	1×10^{-10}
1×10^{-5}	5.0	9.0	1×10^{-9}
1×10^{-6}	6.0	8.0	1×10^{-8}
1×10^{-7}	7.0	7.0	1×10^{-7}
1×10^{-8}	8.0	6.0	1×10^{-6}
1×10^{-9}	9.0	5.0	1×10^{-5}
1×10^{-10}	10.0	4.0	1×10^{-4}
1×10^{-11}	11.0	3.0	1×10^{-3}
1×10^{-12}	12.0	2.0	1×10^{-2}
1×10^{-13}	13.0	1.0	1×10^{-1}
1×10^{-14}	14.0	0.0	$1\ (1\times10^{0})$

$\mathrm{pH} + \mathrm{pOH} = 14$

$[\mathrm{H}^+][\mathrm{OH}^-] = 1\times10^{-14}$

Acids and Bases

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Other “p” Scales

- The “p” in pH tells us to take the –log of a quantity (in this case, hydrogen ions).
- Some other “p” systems are
  - pOH: $-\log[\mathrm{OH}^-]$
  - pK_w: $-\log K_w$

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Relating pH and pOH

Because

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

we can take the –log of the equation

$$-\log[H_3O^+] + -\log[OH^-] = -\log K_w = 14.00$$

which results in

$$pH + pOH = pK_w = 14.00$$

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How Do We Measure pH?

- Indicators, including litmus paper, are used for less accurate measurements; an indicator is one color in its acid form and another color in its basic form.
- pH meters are used for accurate measurement of pH; electrodes indicate small changes in voltage to detect pH.

Methyl red

Bromthymol blue

Phenolphthalein

Acids
and
Bases

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Strong Acids

- You will recall that the seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution; e.g.,

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

- So, for the monoprotic strong acids,

$$[H_3O^+] = [acid]$$

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Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}).
- Again, these substances dissociate completely in aqueous solution; e.g.,

$$\mathrm{MOH}(aq) \rightarrow \mathrm{M}^{+}(aq) + \mathrm{OH}^{-}(aq) \qquad \textit{or}$$

$$\mathrm{M(OH)_2}(aq) \rightarrow \mathrm{M}^{2+}(aq) + 2\ \mathrm{OH}^{-}(aq)$$

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Weak Acids

- For a weak acid, the equation for its dissociation is

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

- Since it is an equilibrium, there is an equilibrium constant related to it, called the **acid-dissociation constant**, K_a:$K_a = [H_3O^+][A^-] / [HA]$

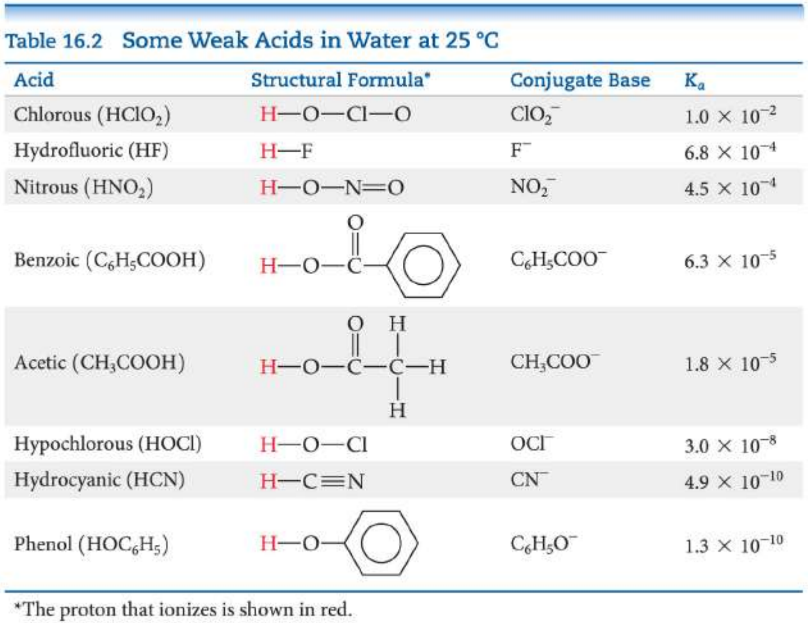

Table 16.2 Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	H—O—Cl—O	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	H—F	F^-	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N═O	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)	$\mathrm{H{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}}$	$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)	$\mathrm{H{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}\underset{H}{\overset{H}{C}}{-}H}$	CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	H—O—Cl	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)	H—O—	$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

- The greater the value of K_a, the stronger is the acid.

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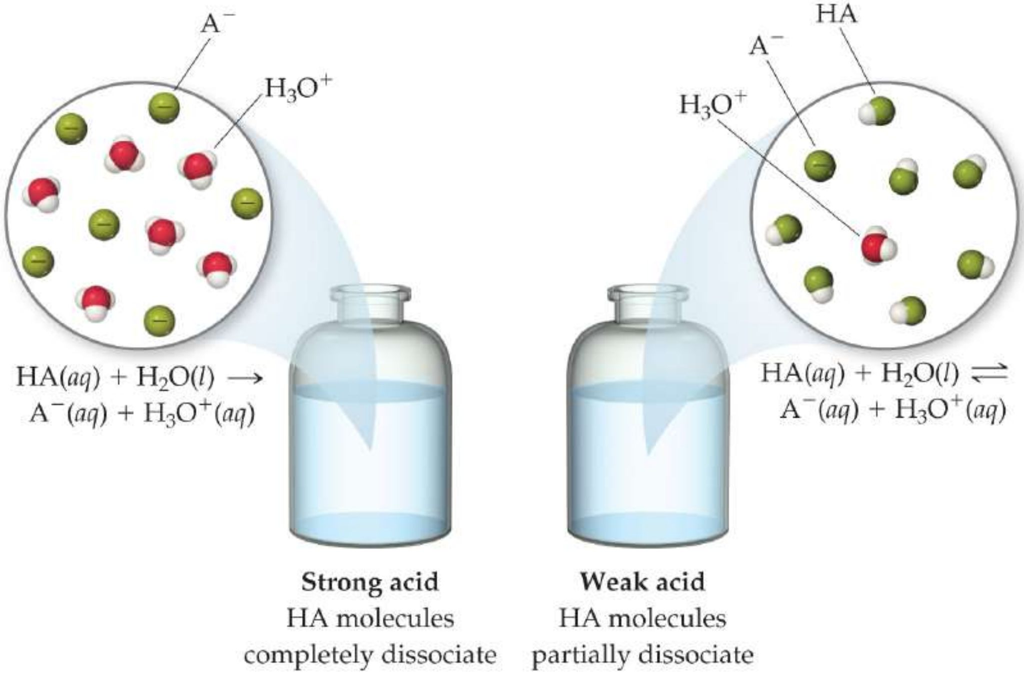
Comparing Strong and Weak Acids

- What is present in solution for a strong acid versus a weak acid?
- Strong acids *completely* dissociate to ions.
- Weak acids only *partially* dissociate to ions.



Strong acid
HA molecules
completely dissociate

Weak acid
HA molecules
partially dissociate

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Calculating K_a from the pH

- The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25 °C is 2.38. Calculate K_a for formic acid at this temperature.

➢ We know that

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

➢ To calculate K_a, we need the equilibrium concentrations of all three things.

➢ We can find $[H_3O^+]$, which is the same as $[HCOO^-]$, from the pH.

➢ $[H_3O^+] = [HCOO^-] = 10^{-2.38} = 4.2 \times 10^{-3}$

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Calculating K_a from pH

Now we can set up a table for equilibrium concentrations. We know initial HCOOH (0.10 *M*) and ion concentrations (0 *M*); we found equilibrium ion concentrations (4.2×10^{-3} *M*); so we calculate the change, then the equilibrium HCOOH concentration.

	[HCOOH], *M*	$[H_3O^+]$, *M*	$[HCOO^-]$, *M*
Initially	0.10	0	0
Change	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
At equilibrium	$0.10 - 4.2 \times 10^{-3}$ $= 0.0958 = 0.10$	4.2×10^{-3}	4.2×10^{-3}

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Calculating K_a from pH

- This allows us to calculate K_a by putting in the equilibrium concentrations.

$$K_a = \frac{[4.2 \times 10^{-3}][4.2 \times 10^{-3}]}{[0.10]}$$

$$= 1.8 \times 10^{-4}$$

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Calculating Percent Ionization

- Percent ionization = $\dfrac{[\mathrm{H_3O^+}]_{\mathrm{eq}}}{[\mathrm{HA}]_{\mathrm{initial}}} \times 100$
- In this example,

$$[\mathrm{H_3O^+}]_{\mathrm{eq}} = 4.2 \times 10^{-3}\ M$$

$$[\mathrm{HCOOH}]_{\mathrm{initial}} = 0.10\ M$$

$$\text{Percent ionization} = \frac{4.2 \times 10^{-3}}{0.10} \times 100$$

$$= 4.2\%$$

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Method to Follow to Calculate pH Using K_a

1) Write the chemical equation for the ionization equilibrium.
2) Write the equilibrium constant expression.
3) Set up a table for Initial/Change in/Equilibrium Concentration to determine equilibrium concentrations as a function of change (*x*).
4) Substitute equilibrium concentrations into the equilibrium constant expression and solve for *x*. (Make assumptions if you can!)

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Example

- Calculate the pH of a 0.30 *M* solution of acetic acid, $HC_2H_3O_2$, at 25 °C.

1) $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$
2) $K_a = [H_3O^+][C_2H_3O_2^-] / [HC_2H_3O_2]$
3)

	CH_3COOH (*M*)	H_3O^+ (*M*)	CH_3COO^- (*M*)
Initial Concentration (*M*)	0.30	0	0
Change in Concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium Concentration (*M*)	$0.30 - x$	x	x

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Example (concluded)

4) $K_a = [H_3O^+][C_2H_3O_2^-] / [HC_2H_3O_2]$

$= (x)(x) / (0.30 - x)$

If we assume that $x << 0.30$, then $0.30 - x$ becomes 0.30. The problem becomes easier, since we don't have to use the quadratic formula to solve it.

$K_a = 1.8 \times 10^{-5} = x^2 / 0.30$, so $x = 2.3 \times 10^{-3}$

$x = [H_3O^+]$, so $\text{pH} = -\log(2.3 \times 10^{-3}) = 2.64$

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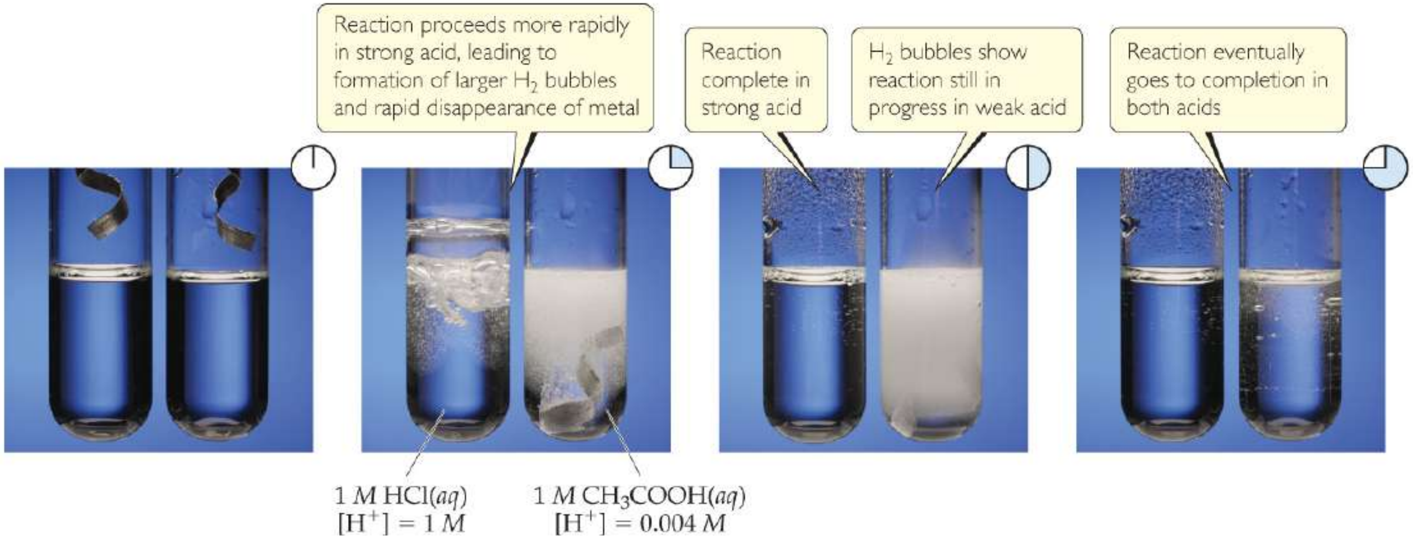
Strong vs. Weak Acids—Another Comparison

- Strong Acid: $[H^+]_{eq} = [HA]_{init}$
- Weak Acid: $[H^+]_{eq} < [HA]_{init}$
- This creates a difference in conductivity and in rates of chemical reactions.



Reaction proceeds more rapidly in strong acid, leading to formation of larger H_2 bubbles and rapid disappearance of metal

Reaction complete in strong acid

H_2 bubbles show reaction still in progress in weak acid

Reaction eventually goes to completion in both acids

1 *M* HCl(*aq*)
$[H^+] = 1\ M$

1 *M* CH_3COOH(*aq*)
$[H^+] = 0.004\ M$

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Polyprotic Acids

- Polyprotic acids have more than one acidic proton.
- It is always easier to remove the first proton than any successive proton.
- If the factor in the K_a values for the first and second dissociation has a difference of 3 or greater, the pH generally depends *only* on the first dissociation.

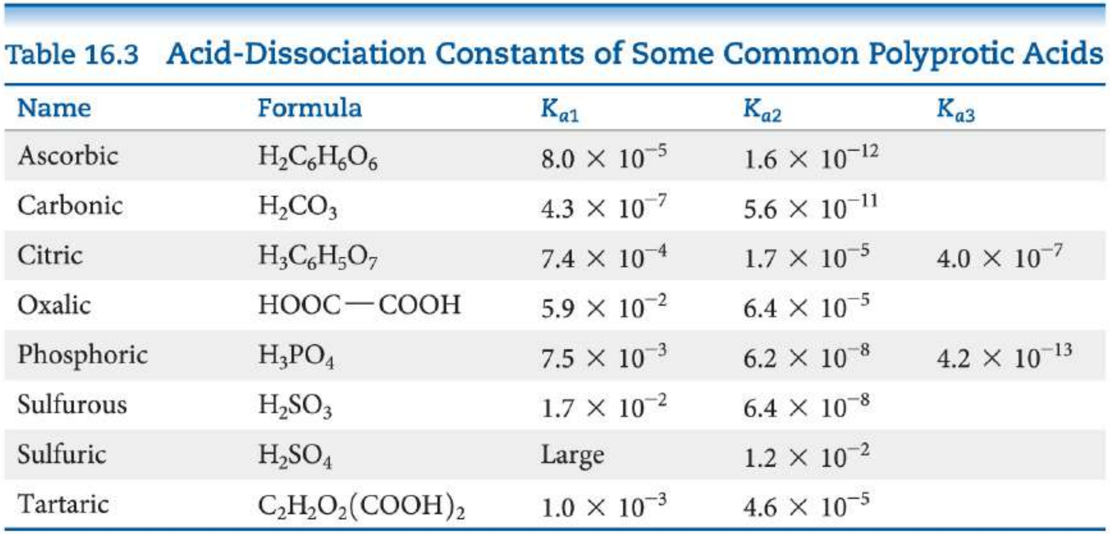

Table 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	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	$HOOC{-}COOH$	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	$C_2H_2O_2(COOH)_2$	1.0×10^{-3}	4.6×10^{-5}	

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Weak Bases

- Ammonia, NH_3, is a weak base.
- Like weak acids, weak bases have an equilibrium constant called the **base dissociation constant**.
- Equilibrium calculations work the *same* as for acids, using the base dissociation constant instead.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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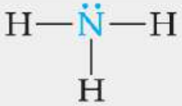
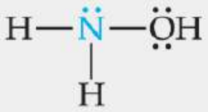
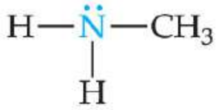
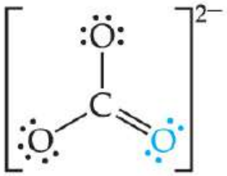
Base Dissociation Constants

Table 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)		$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)		$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		$HClO$	3.3×10^{-7}

*The atom that accepts the proton is shown in blue.

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Example

- What is the pH of 0.15 *M* NH_3?

1) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

2) $K_b = [NH_4^+][OH^-] / [NH_3] = 1.8 \times 10^{-5}$

3)

	NH_3 (*M*)	NH_4^+ (*M*)	OH^- (*M*)
Initial Concentration (*M*)	0.15	0	0
Change in Concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium Concentration (*M*)	$0.15 - x$	x	x

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Example (completed)

4) $1.8 \times 10 - 5 = x^2 / (0.15 - x)$

If we assume that $x << 0.15$, $0.15 - x = 0.15$.

Then: $1.8 \times 10^{-5} = x^2 / 0.15$

and: $x = 1.6 \times 10^{-3}$

Note: x is the molarity of OH^-, so $-\log(x)$ will be the pOH (pOH = 2.80) and [14.00 – pOH] is pH (pH = 11.20).

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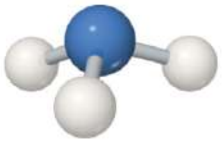
Types of Weak Bases

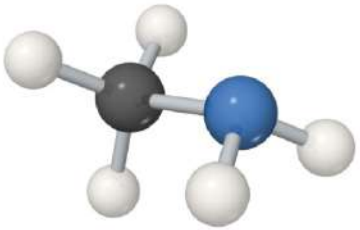
- Two main categories

1) Neutral substances with an Atom that has a nonbonding pair of electrons that can accept H^+ (like ammonia and the **amines**)

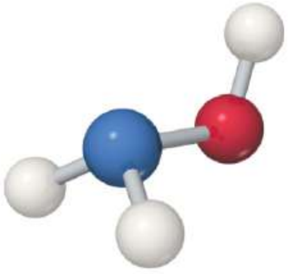
2) Anions of weak acids



Ammonia
NH_3



Methylamine
CH_3NH_2



Hydroxylamine
NH_2OH

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Relationship between K_a and K_b

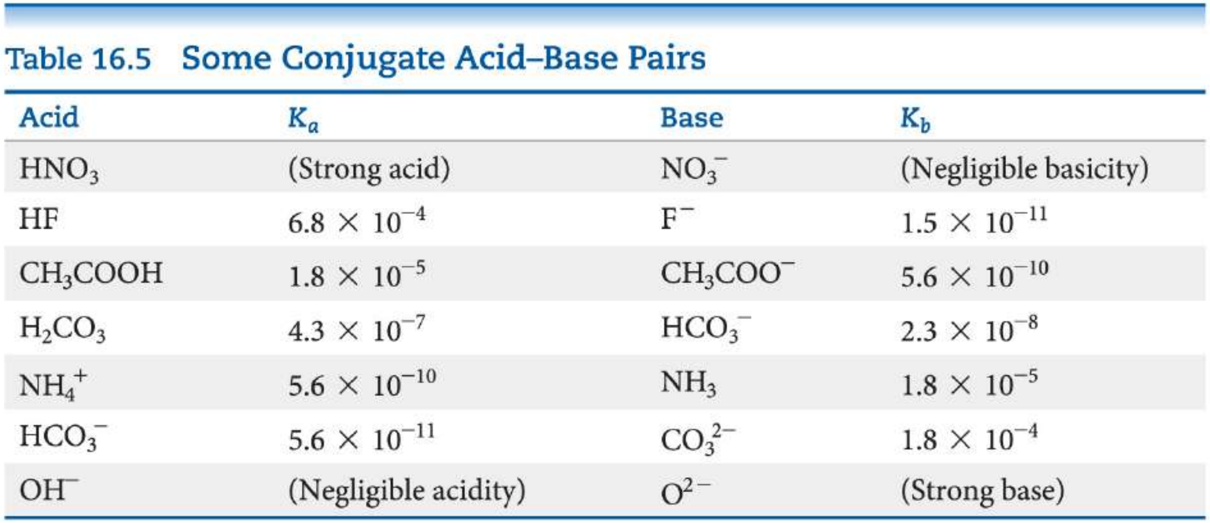

Table 16.5 Some Conjugate Acid–Base Pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

For a conjugate acid–base pair, K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

Therefore, if you know one of them, you can calculate the other.

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Acid–Base Properties of Salts

- Many ions react with water to create H^+ or OH^-. The reaction with water is often called **hydrolysis**.
- To determine whether a salt is an acid or a base, you need to look at the cation and anion separately.
- The cation can be acidic or neutral.
- The anion can be acidic, basic, or neutral.

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Anions

- Anions of strong acids are neutral. For example, Cl^- will *not* react with water, so OH^- can't be formed.
- Anions of weak acids are conjugate bases, so they create OH^- in water; e.g., $C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$
- Protonated anions from polyprotic acids can be acids or bases: If $K_a > K_b$, the anion will be acidic; if $K_b > K_a$, the anion will be basic.

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Cations

- Group I or Group II (Ca^{2+}, Sr^{2+}, or Ba^{2+}) metal cations are neutral.
- Polyatomic cations are typically the conjugate acids of a weak base; e.g., NH_4^+.
- Transition and post-transition metal cations are acidic. Why? (There are no H atoms in these cations!)

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Hydrated Cations

- Transition and post-transition metals form hydrated cations.
- The water attached to the metal is more acidic than free water molecules, making the hydrated ions acidic.

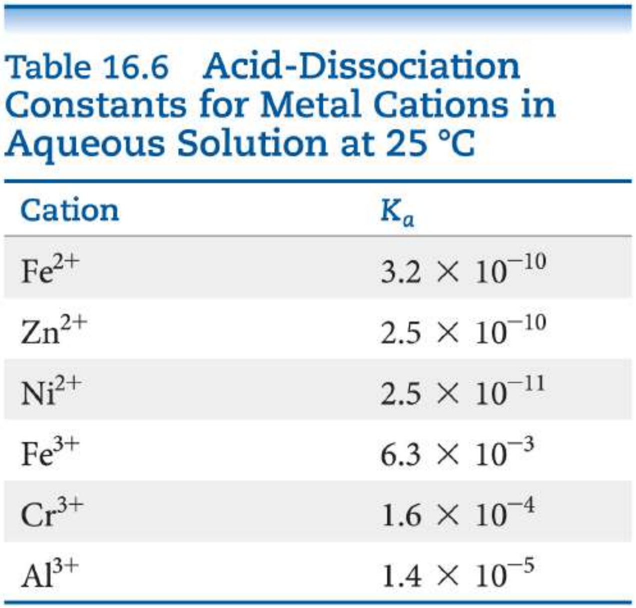
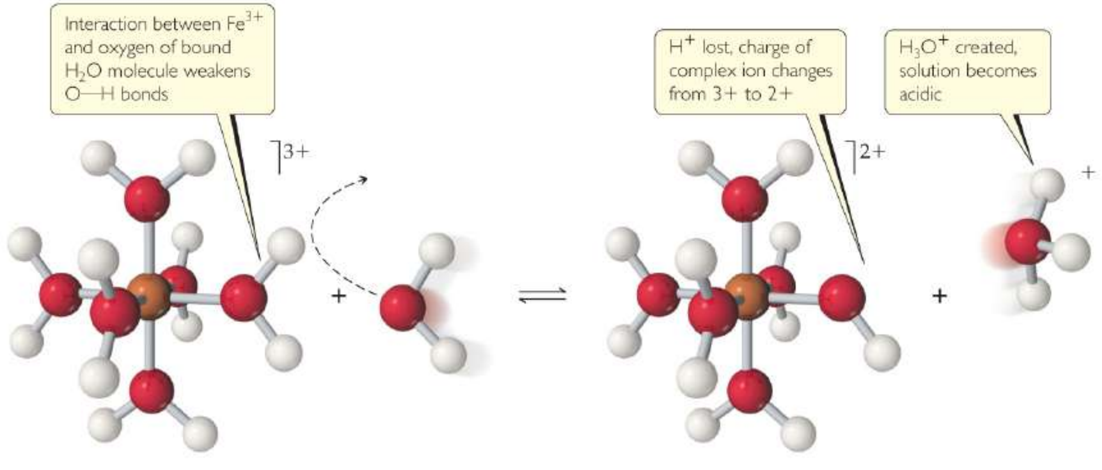


Table 16.6 Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

Cation	K_a
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}



Interaction between Fe^{3+} and oxygen of bound H_2O molecule weakens O—H bonds

H^+ lost, charge of complex ion changes from 3+ to 2+

H_3O^+ created, solution becomes acidic

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

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Salt Solutions—Acidic, Basic, or Neutral?

1) Group I/II metal cation with anion of a strong acid: neutral
2) Group I/II metal cation with anion of a weak acid: basic (like the anion)
3) Transition/Post-transition metal cation or polyatomic cation with anion of a strong acid: acidic (like the cation)
4) Transition/Post-transition metal cation or polyatomic cation with anion of a weak acid: compare K_a and K_b; whichever is greater dictates what the salt is.

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Factors that Affect Acid Strength

1) H—A bond must be polarized with $\delta+$ on the H atom and $\delta-$ on the A atom
2) Bond strength: Weaker bonds can be broken more easily, making the acid stronger.
3) Stability of A^-: More stable anion means stronger acid.

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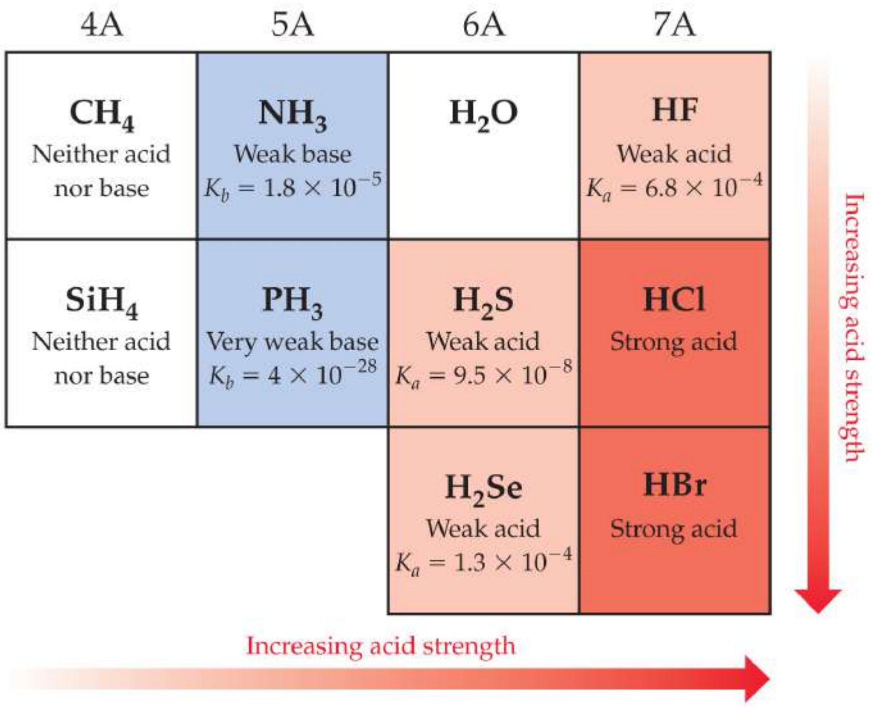
Binary Acids

- Binary acids consist of H and one other element.
- Within a group, H—A bond strength is generally the most important factor.
- Within a period, bond polarity is the most important factor to determine acid strength.



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

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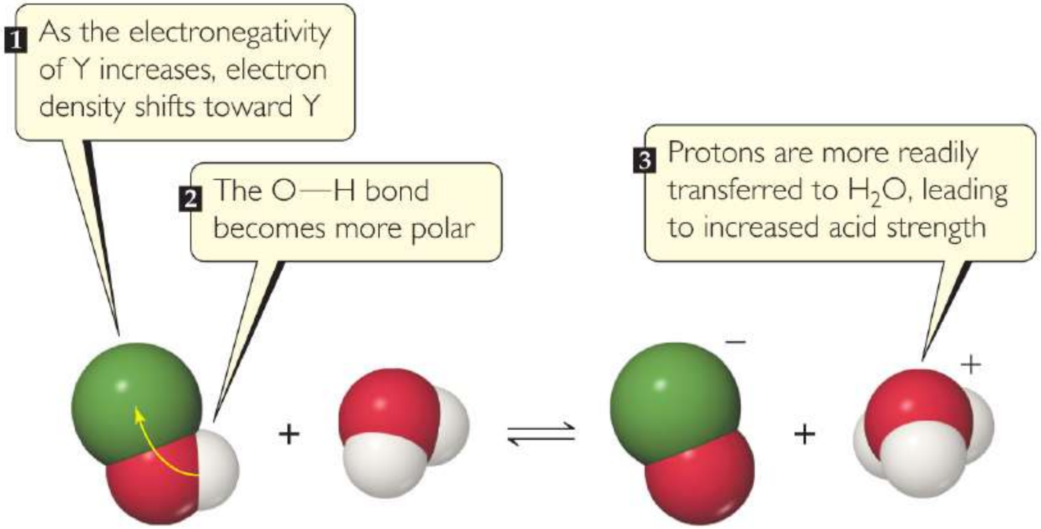
Oxyacids

- **Oxyacids** consist of H, O, and one other element, which is a nonmetal.
- Generally, as the electronegativity of the nonmetal increases, the acidity increases for acids with the same structure.


1 As the electronegativity of Y increases, electron density shifts toward Y

2 The O—H bond becomes more polar

3 Protons are more readily transferred to H_2O, leading to increased acid strength

Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

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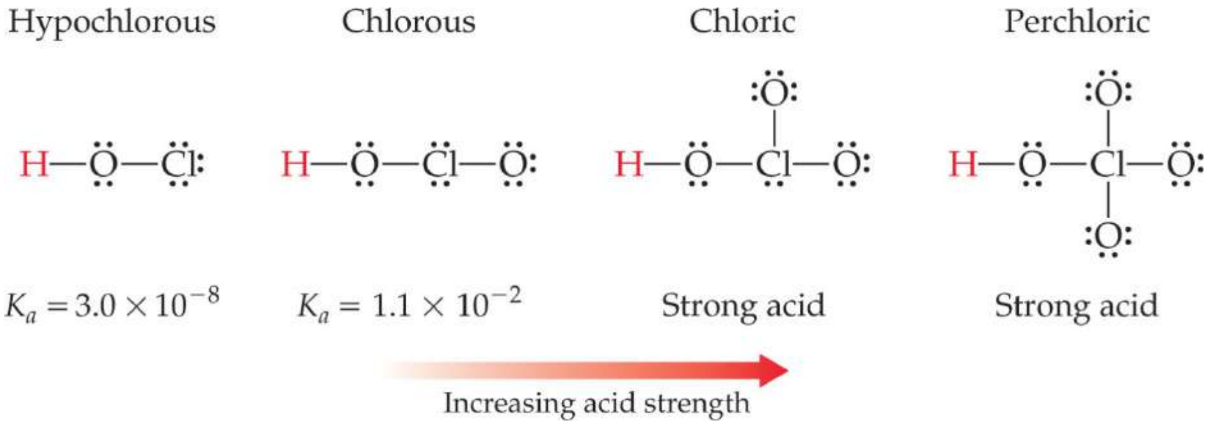
Oxyacids with Same “Other” Element

- If an element can form more than one oxyacid, the oxyacid with more O atoms is more acidic; e.g., sulfuric acid versus sulfurous acid.
- Another way of saying it: If the oxidation number increases, the acidity increases.



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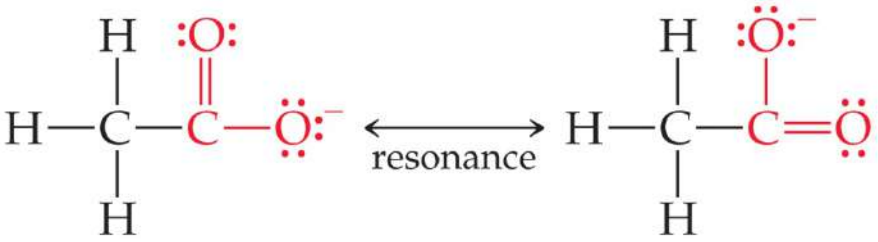
Carboxylic Acids

- **Carboxylic acids** are organic acids containing the —COOH group.
- Factors contributing to their acidic behavior:
  - ➢ Other O attached to C draws electron density from O—H bond, increasing polarity.
  - ➢ Its conjugate base (carboxylate anion) has resonance forms to stabilize the anion.



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Lewis Acid/Base Chemistry

- Lewis acids are electron pair acceptors.
- Lewis bases are electron pair donors.
- All Brønsted–Lowry acids and bases are also called Lewis acids and bases.
- There are compounds which do *not* meet the Brønsted–Lowry definition which meet the Lewis definition.

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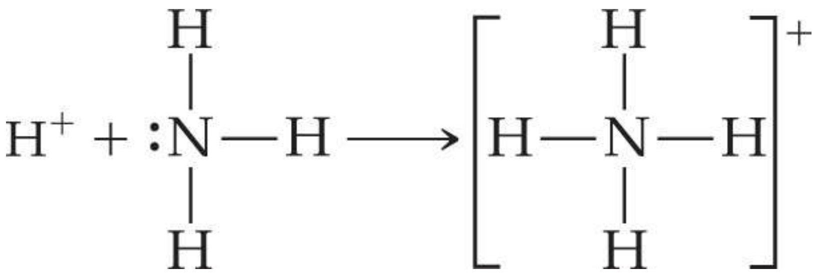
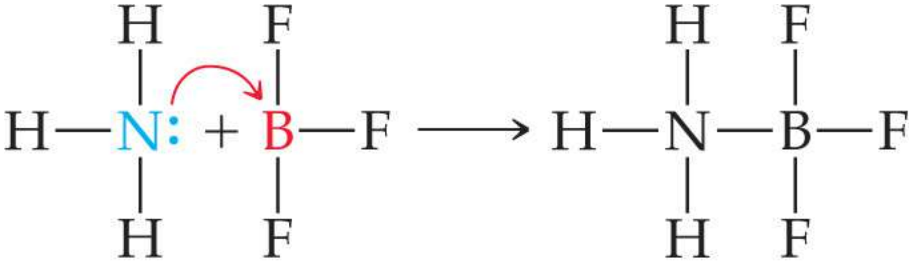
Comparing Ammonia's Reaction with H^+ and BF_3



$$H^+ + NH_3 \longrightarrow [NH_4]^+$$



$$NH_3 + BF_3 \longrightarrow H_3N{-}BF_3$$

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