Petrucci's General Chemistry

PRINCIPLES AND MODERN APPLICATIONS

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Acids and Bases

17

KAIST CHEMISTRY

Acids and Bases

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CONTENTS

17-1 Acids, Bases, and Conjugate Acid-Base Pairs

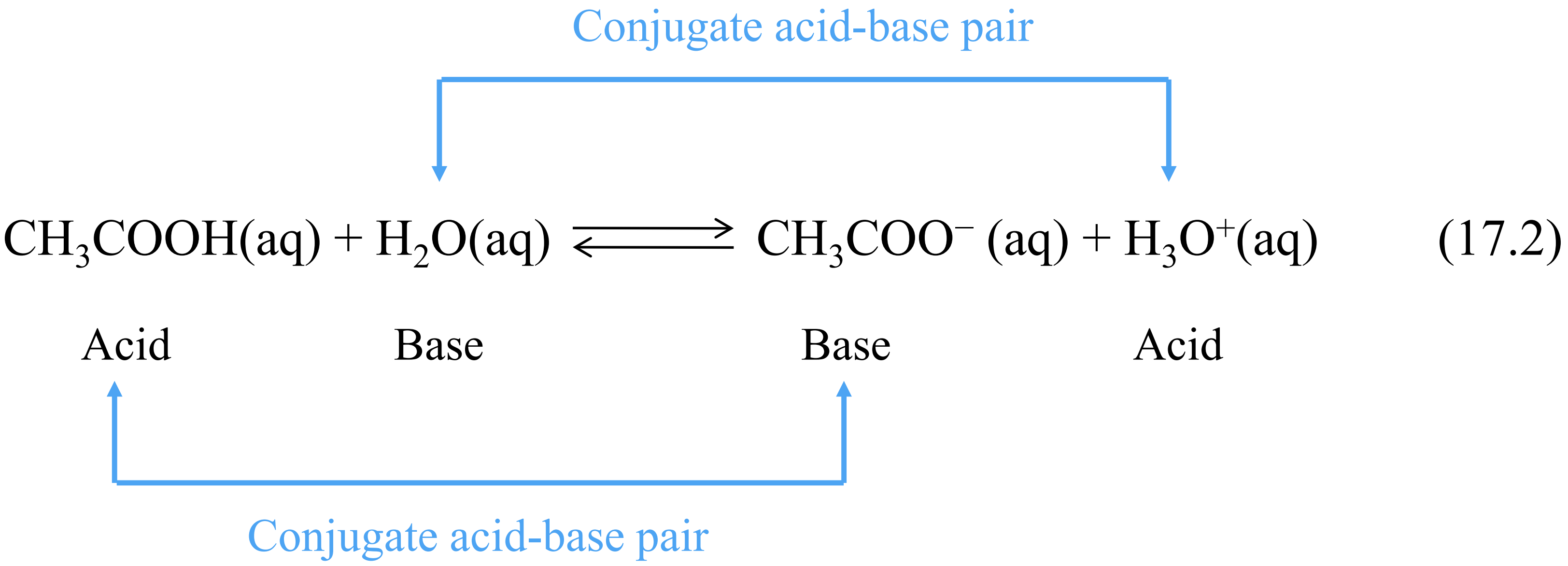
Brønsted-Lowry theory

An acid is a **proton donor**.

A base is a **proton acceptor**.

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad (17.1)$$

Acid	Base	Base	Acid



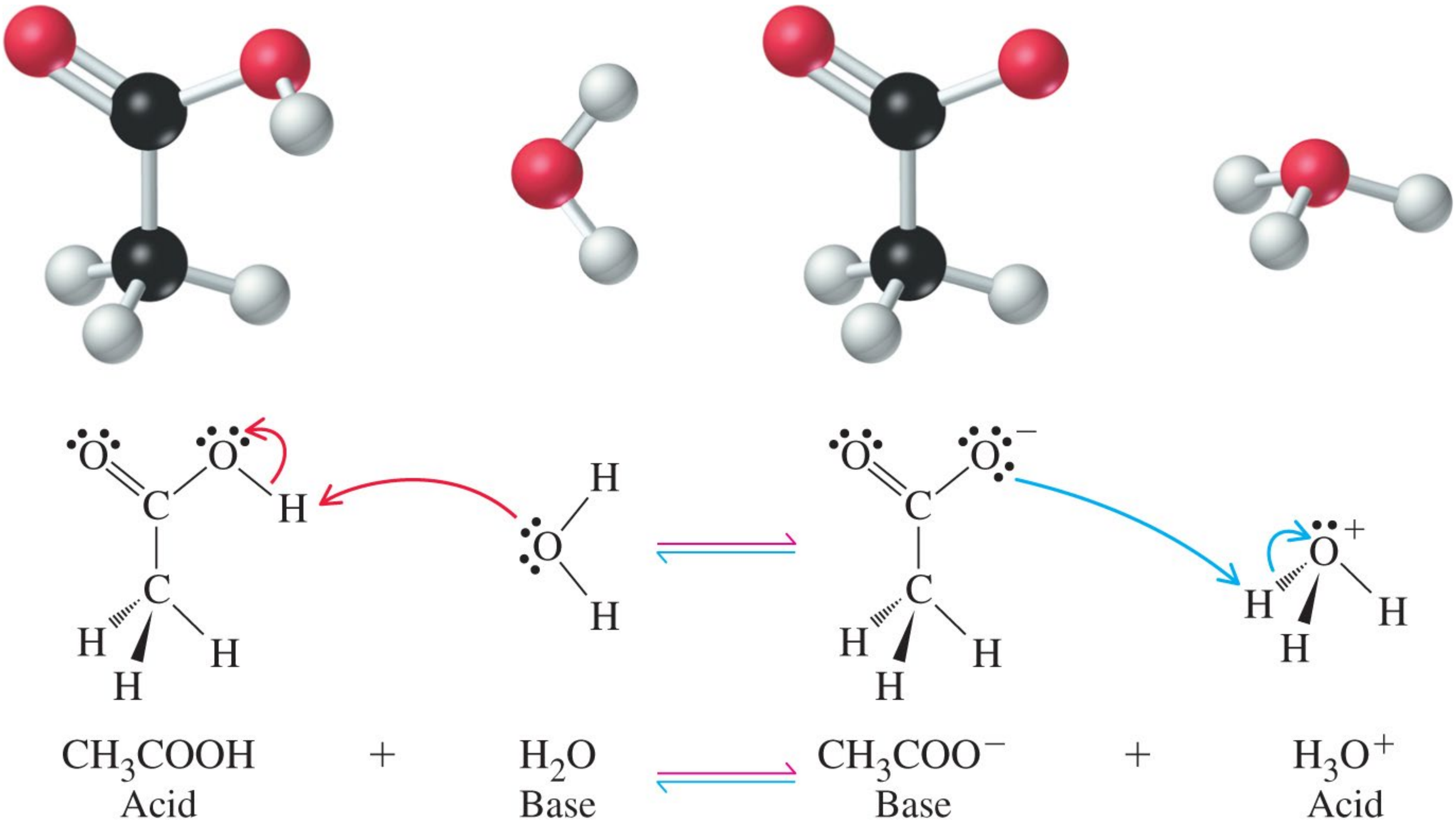
Conjugate acid-base pair

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad (17.2)$$

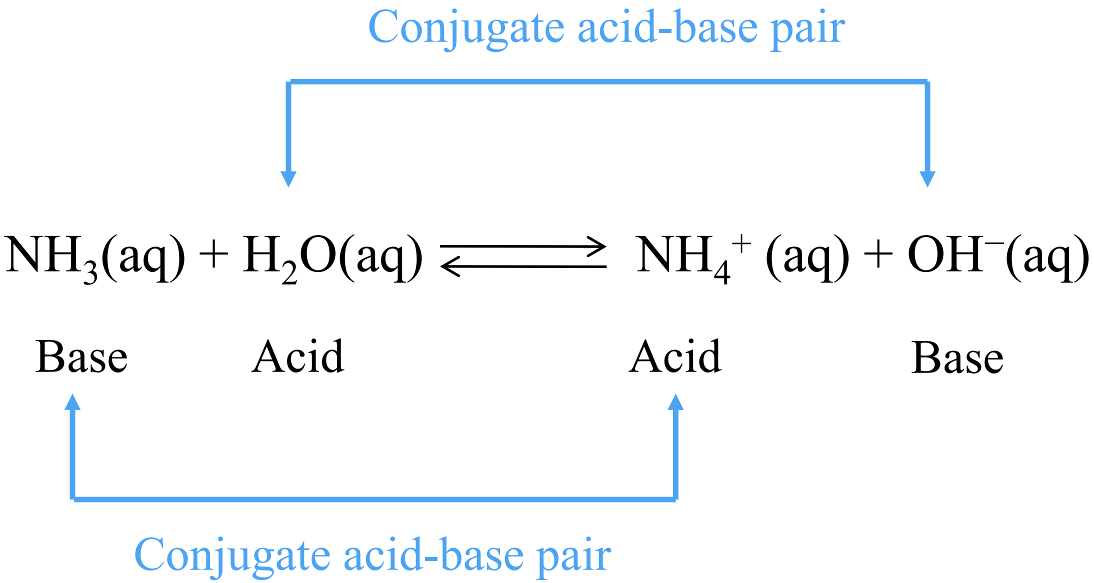
Acid Base Base Acid

Conjugate acid-base pair

An acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind.



▲ FIGURE 17-1
The ionization of CH_3COOH in water

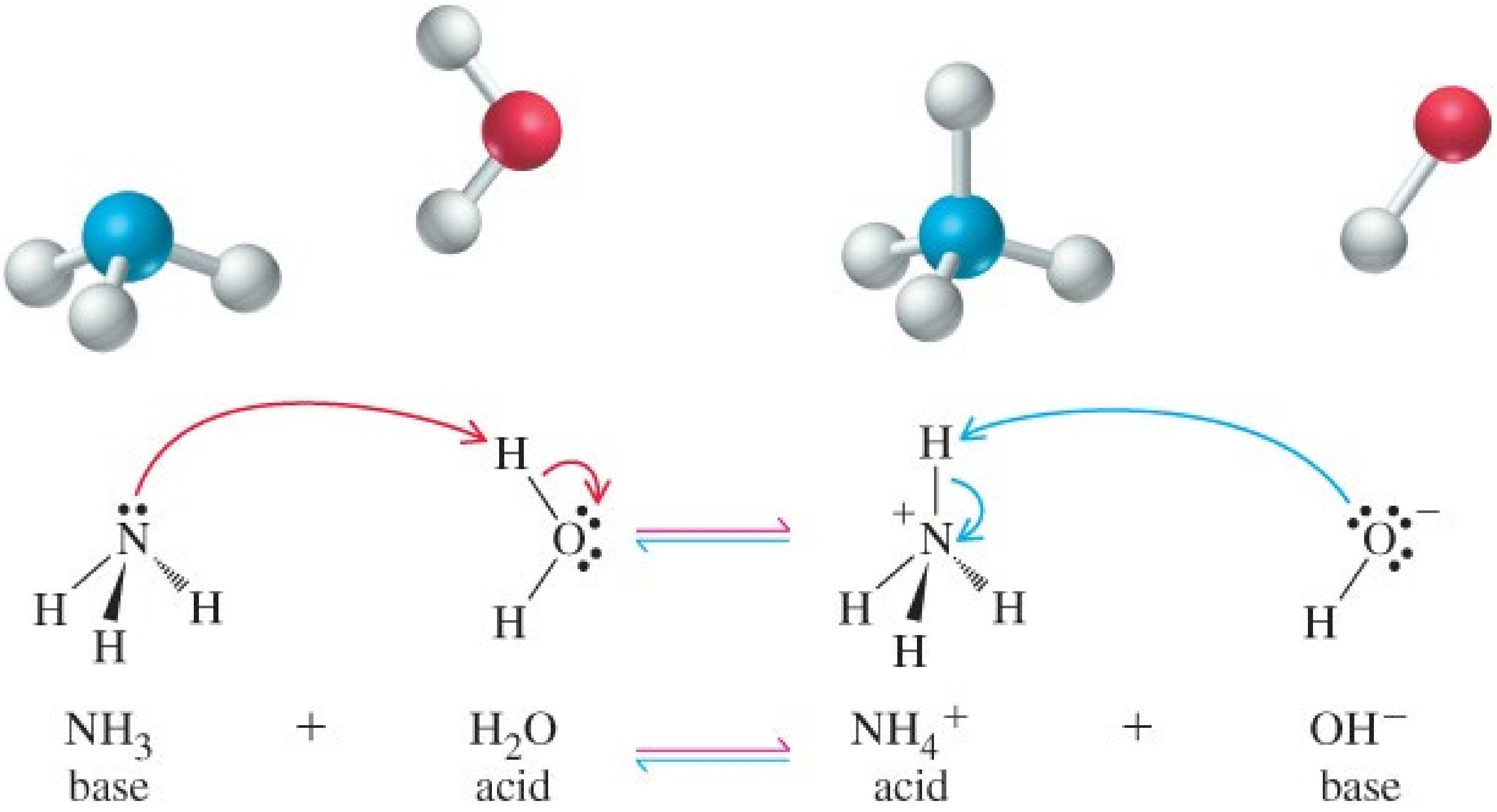


Conjugate acid-base pair

$$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad (17.2)$$

Base Acid Acid Base

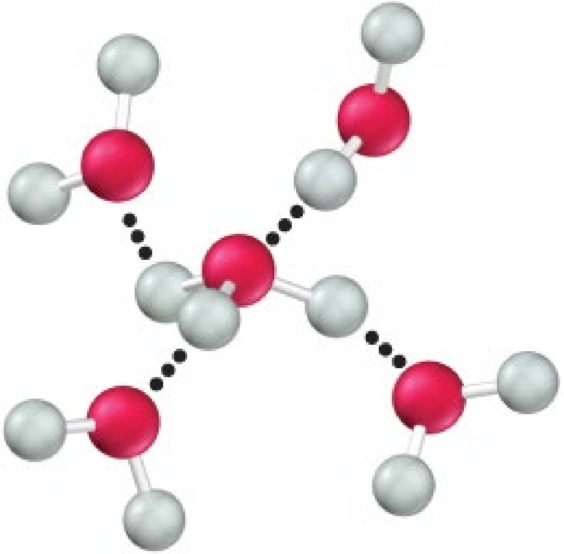
Conjugate acid-base pair



▲ FIGURE 17-2

The ionization of NH_3 in water

- An acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind.
- For a conjugate acid–base pair, the molecular formulas for the acid and base differ by a single proton (H^+)
- When added to water, acids protonate water molecules to form hydronium (H_3O^+) ions and bases deprotonate water molecules to form hydroxide (OH^-) ions.



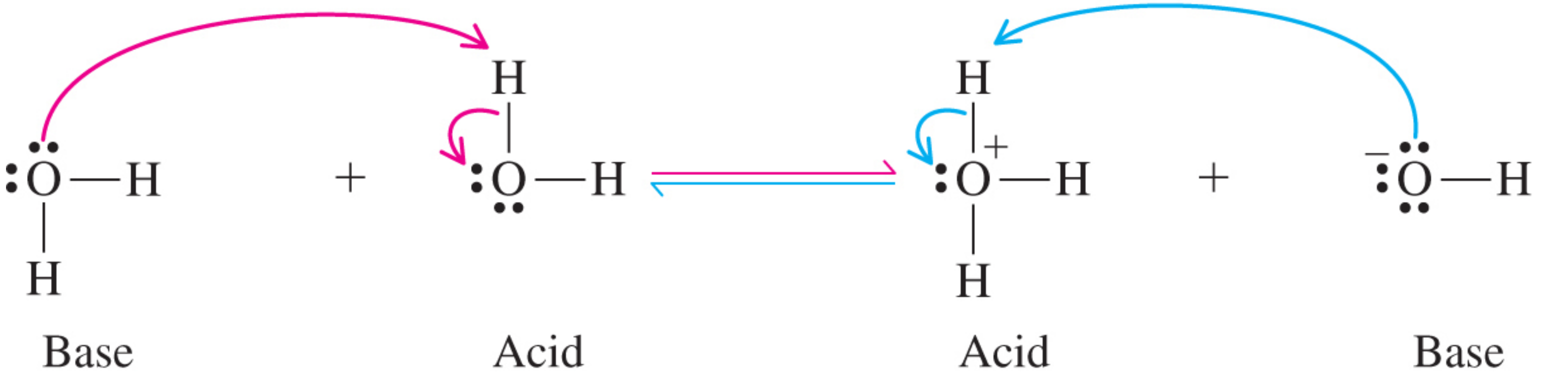
▶ FIGURE 17-3

The hydrated hydronium ion

17-2 Self-Ionization of Water and the pH Scale

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad (17.3)$$

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



ion product of water

$$K_w = \frac{a_{H_3O^+(aq)} a_{OH^-(aq)}}{a^2_{H_2O(l)}} = \frac{([H_3O^+]/c°)\ ([OH^-]/c°)}{(1)^2} = \left(\frac{[H_3O^+]}{1\,M}\right)\left(\frac{[OH^-]}{1\,M}\right)$$

$$K = [H_3O^+][OH^-] = 1.0 \times 10^{-14} (\text{at } 25^{o}\text{C}) \qquad (17.4)$$

In pure water:

$$[H_3O^+]/(1\,M) = [OH^-]/(1\,M) = 1.0 \times 10^{-7} (\text{at } 25^{o}\text{C}) \qquad (17.5)$$

In all aqueous solutions at 25ºC, the product of $[H_3O^+]$ and $[OH^-]$ always equals 1.0×10^{-14}.

The self-ionization of water is partially suppressed by the addition of acid or base to water.

pH and pOH

The "potential of the hydrogen ion" was defined in 1909 as ***the negative of the logarithm of* [H$^+$]**.

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

$[\mathrm{H_3O^+}] = 2.5 \times 10^{-3}$ M

$\mathrm{pH} = -\log(2.5 \times 10^{-3}) = 2.60$

$\mathrm{pH} = 4.5$

$\log\,[\mathrm{H_3O^+}] = -4.5$

$[\mathrm{H_3O^+}] = 10^{-4.5} = 3.2 \times 10^{-5}$

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

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

$$-\log K_W = -(\log[H_3O^+] + \log[OH^-])$$

$$pK_W = -(\log[H_3O^+] + \log[OH^-])$$

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

$$= pH + pOH$$

$$K_W = 1.0 \times 10^{-14} \qquad pK_W = 14$$

$$pH + pOH = 14 \text{ (at 25ºC)} \qquad (17.8)$$

Acidic, Basic, and Neutral Solutions

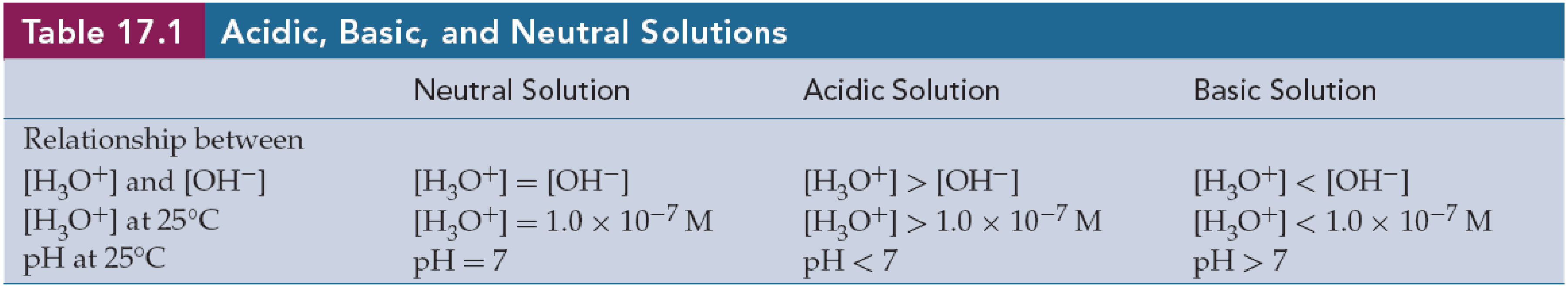
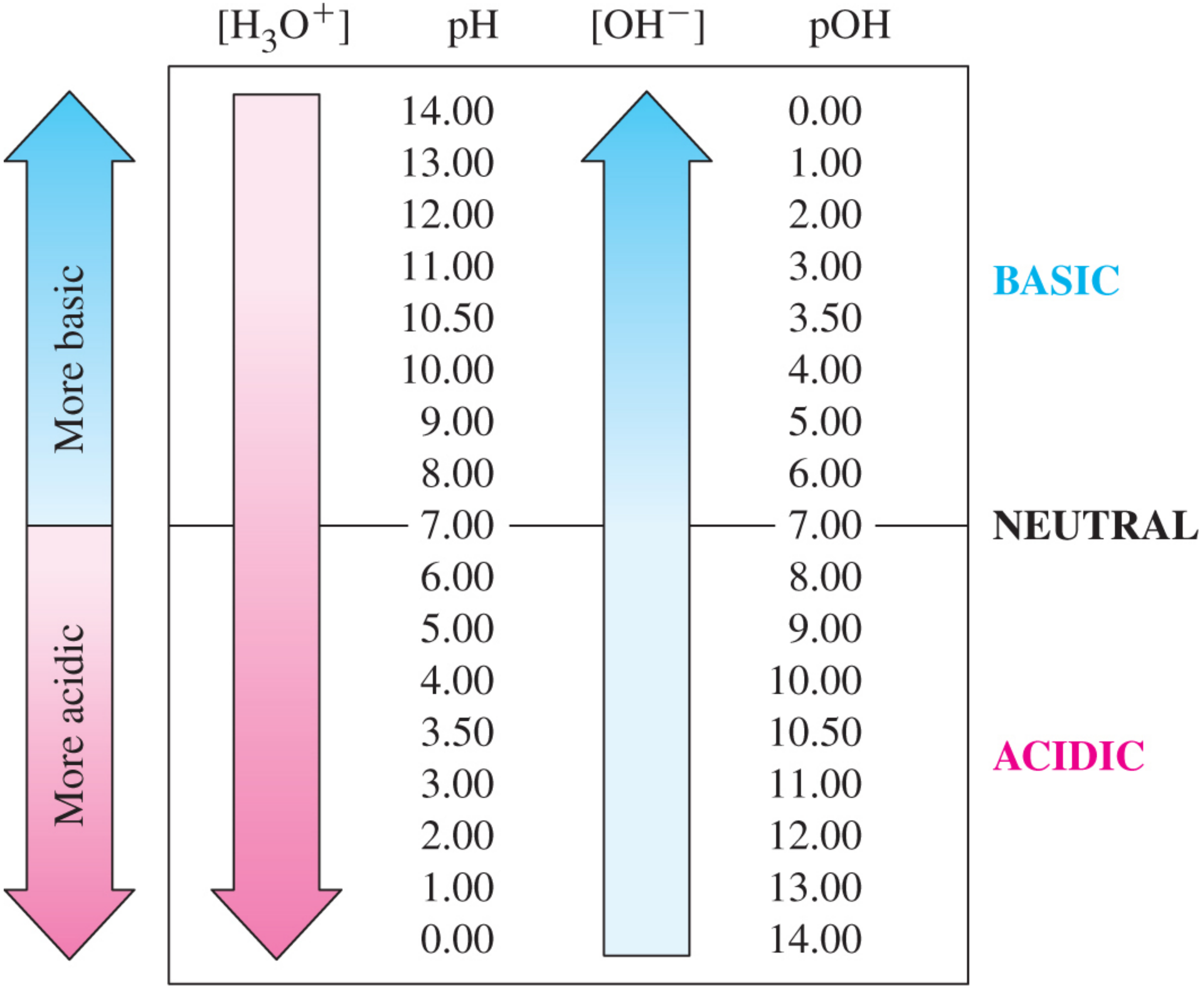


Table 17.1 Acidic, Basic, and Neutral Solutions

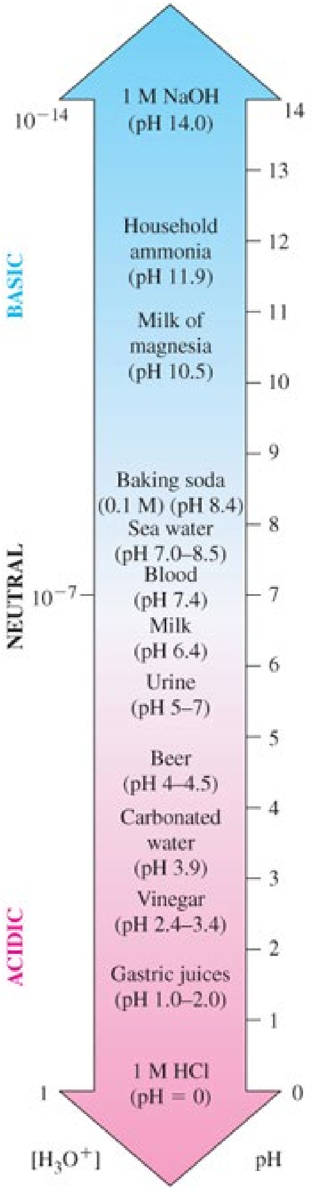
	Neutral Solution	Acidic Solution	Basic Solution
Relationship between $[H_3O^+]$ and $[OH^-]$	$[H_3O^+] = [OH^-]$	$[H_3O^+] > [OH^-]$	$[H_3O^+] < [OH^-]$
$[H_3O^+]$ at 25°C	$[H_3O^+] = 1.0 \times 10^{-7}$ M	$[H_3O^+] > 1.0 \times 10^{-7}$ M	$[H_3O^+] < 1.0 \times 10^{-7}$ M
pH at 25°C	$pH = 7$	$pH < 7$	$pH > 7$



pH	pOH
14.00	0.00
13.00	1.00
12.00	2.00
11.00	3.00
10.50	3.50
10.00	4.00
9.00	5.00
8.00	6.00
7.00	7.00
6.00	8.00
5.00	9.00
4.00	10.00
3.50	10.50
3.00	11.00
2.00	12.00
1.00	13.00
0.00	14.00

▲ FIGURE 17-4

Relating $[H_3O^+]$, pH, $[OH^-]$, and pOH



▲ FIGURE 17-5

The pH scale and pH values of some common materials

17-3 Ionization of Acids and Bases in Water

▲ FIGURE 17-6

Strong and weak acids compared

Thymol Blue Indicator

pH < 1.2 < pH < 2.8 < pH

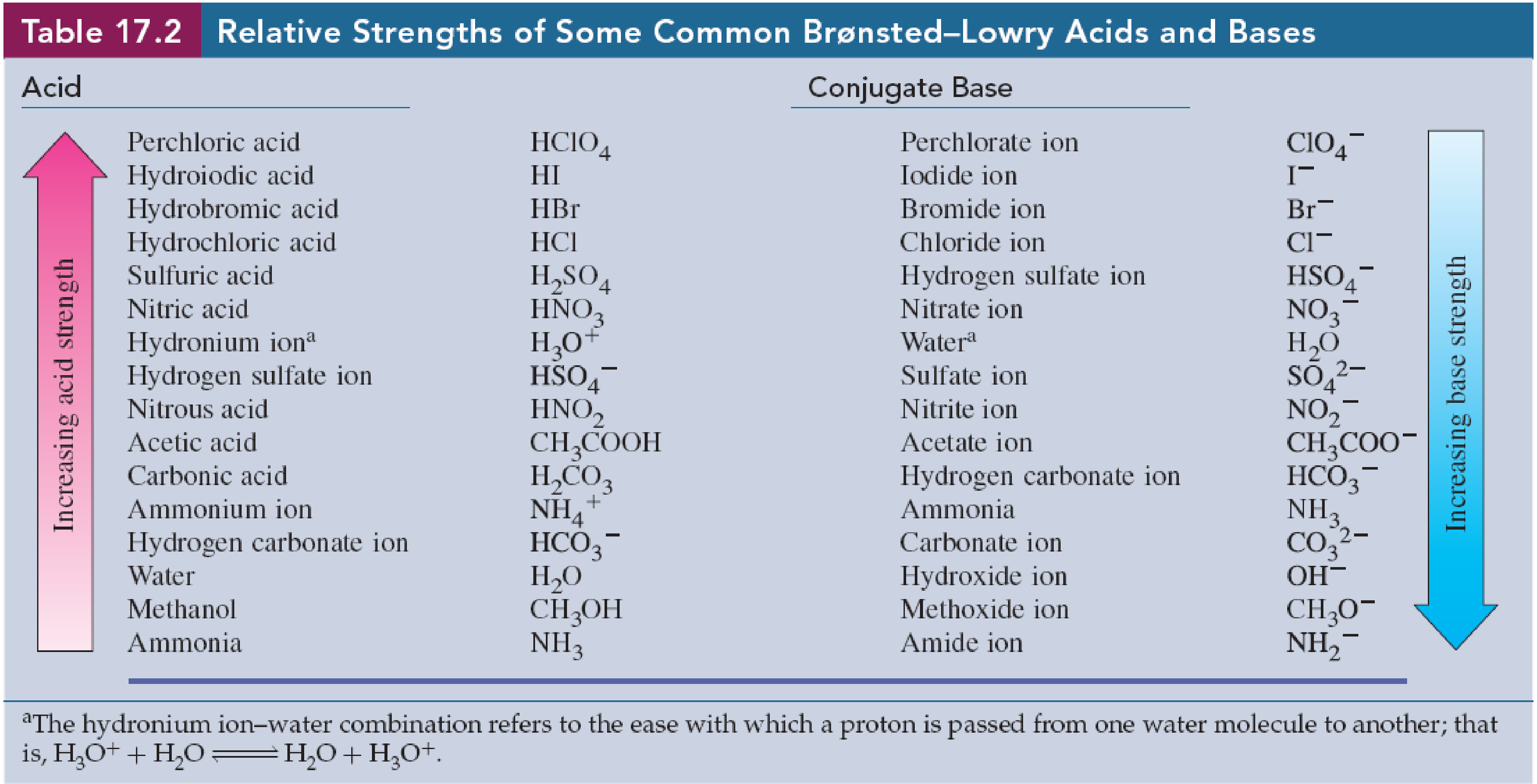


Table 17.2 Relative Strengths of Some Common Brønsted–Lowry Acids and Bases

Increasing acid strength

Acid		Conjugate Base	
Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
Hydroiodic acid	HI	Iodide ion	I^-
Hydrobromic acid	HBr	Bromide ion	Br^-
Hydrochloric acid	HCl	Chloride ion	Cl^-
Sulfuric acid	H_2SO_4	Hydrogen sulfate ion	HSO_4^-
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Hydronium ion[a]	H_3O^+	Water[a]	H_2O
Hydrogen sulfate ion	HSO_4^-	Sulfate ion	SO_4^{2-}
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Acetic acid	CH_3COOH	Acetate ion	CH_3COO^-
Carbonic acid	H_2CO_3	Hydrogen carbonate ion	HCO_3^-
Ammonium ion	NH_4^+	Ammonia	NH_3
Hydrogen carbonate ion	HCO_3^-	Carbonate ion	CO_3^{2-}
Water	H_2O	Hydroxide ion	OH^-
Methanol	CH_3OH	Methoxide ion	CH_3O^-
Ammonia	NH_3	Amide ion	NH_2^-

Increasing base strength

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[a] The hydronium ion–water combination refers to the ease with which a proton is passed from one water molecule to another; that is, $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$.

$$\mathrm{HA(aq) + H_2O(aq) \rightleftharpoons A^- (aq) + H_3O^+(aq)} \qquad (17.9)$$

$$K = \frac{a_{\mathrm{H_3O^+}(aq)}a_{\mathrm{A^-}(aq)}}{a_{\mathrm{HA}(aq)}a_{\mathrm{H_2O}(l)}} = \frac{([\mathrm{H_3O^+}]/c°)\ ([\mathrm{OH^-}]/c°)}{([\mathrm{HA}]/c°)\ (1)} = \left(\frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}\right) \times \left(\frac{1}{c°}\right)$$

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad (17.10)$$

$$pK_a = -\log K_a \ or \ K_a = 10^{-pK_a} \qquad (17.11)$$

$$\mathrm{B(aq) + H_2O(aq) \rightleftharpoons BH^+ (aq) + OH^-(aq)} \qquad (17.12)$$

$$K_b = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}]} \qquad (17.13)$$

$$pK_b = -\log K_b \; or \; K_b = 10^{-pK_b} \qquad (17.14)$$

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

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

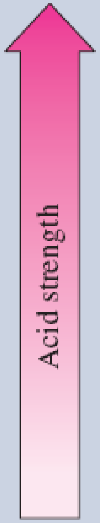
- A strong acid or base has a large ionization constant: K_a or K_b is much greater than 1.
- A weak acid or base has a small ionization constant: K_a or K_b is much less than 1.

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

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Table 17.4 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25°C

	Ionization Equilibrium	Ionization Constant K	pK
Acid		K_a =	pK_a =
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$ClCH_2COOH + H_2O \rightleftharpoons H_3O^+ + ClCH_2COO^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$	1.8×10^{-4}	3.74
Benzoic acid	$C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		K_b =	pK_b =
Diethylamine	$(CH_3CH_2)_2NH + H_2O \rightleftharpoons (CH_3CH_2)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13



17-4 Strong Acids and Strong Bases

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

unless the solution of HCl is extremely dilute we can ignore the self-ionization of water. Even when [HCl] is as low as 1×10^{-6} M, the ionization of H_2O only contributes 1%.

With strong bases, the contribution from the self-ionization of water is also negligible.

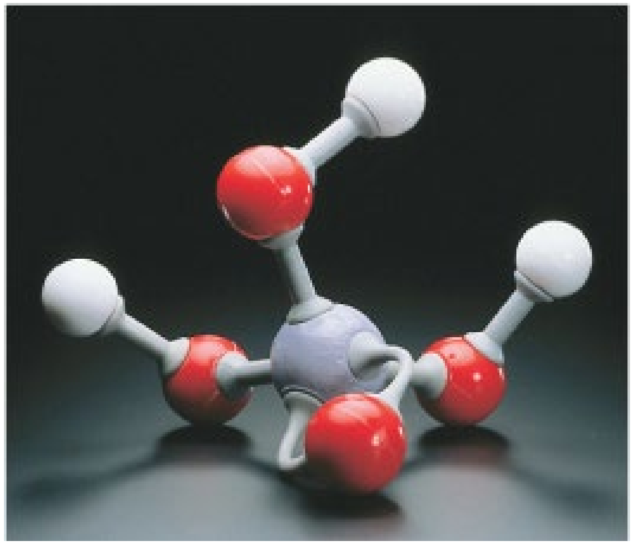
$$Ca(OH)_2(aq) + H_2O(aq) \longrightarrow Ca^+\,(aq) + OH^-(aq)$$

17-5 Weak Acids and Weak Bases

The key to solving equilibrium problems is to be able to imagine what is going on. Ask yourself:

- Which are the principal species in solution?
- What are the chemical reactions that produce them?
- Can some reactions (for example, the self-ionization of water) be ignored?
- Can you make any assumptions that allow you to simplify the equilibrium calculations?
- What is a reasonable answer to the problem? For instance, should the final solution be acidic ($pH < 7$) or basic ($pH > 7$).

17-6 Polyprotic Acids



▶ Phosphoric acid, H_3PO_4

A *triprotic acid.*

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.1\times10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3\times10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2\times10^{-13}$$

H_3PO_4

$K_{a1} >> K_{a2}$

All H_3O^+ is formed in the first ionization step.

$H_2PO_4^-$ essentially does not ionize further.

Assume $[H_2PO_4^-] = [H_3O^+]$.

$[HPO_4^{2-}] \approx K_{a2}$ regardless of solution molarity.

$$\frac{\cancel{[H_3O^+]}[HPO_4^{2-}]}{\cancel{[H_2PO_4^-]}} = K_{a2}$$

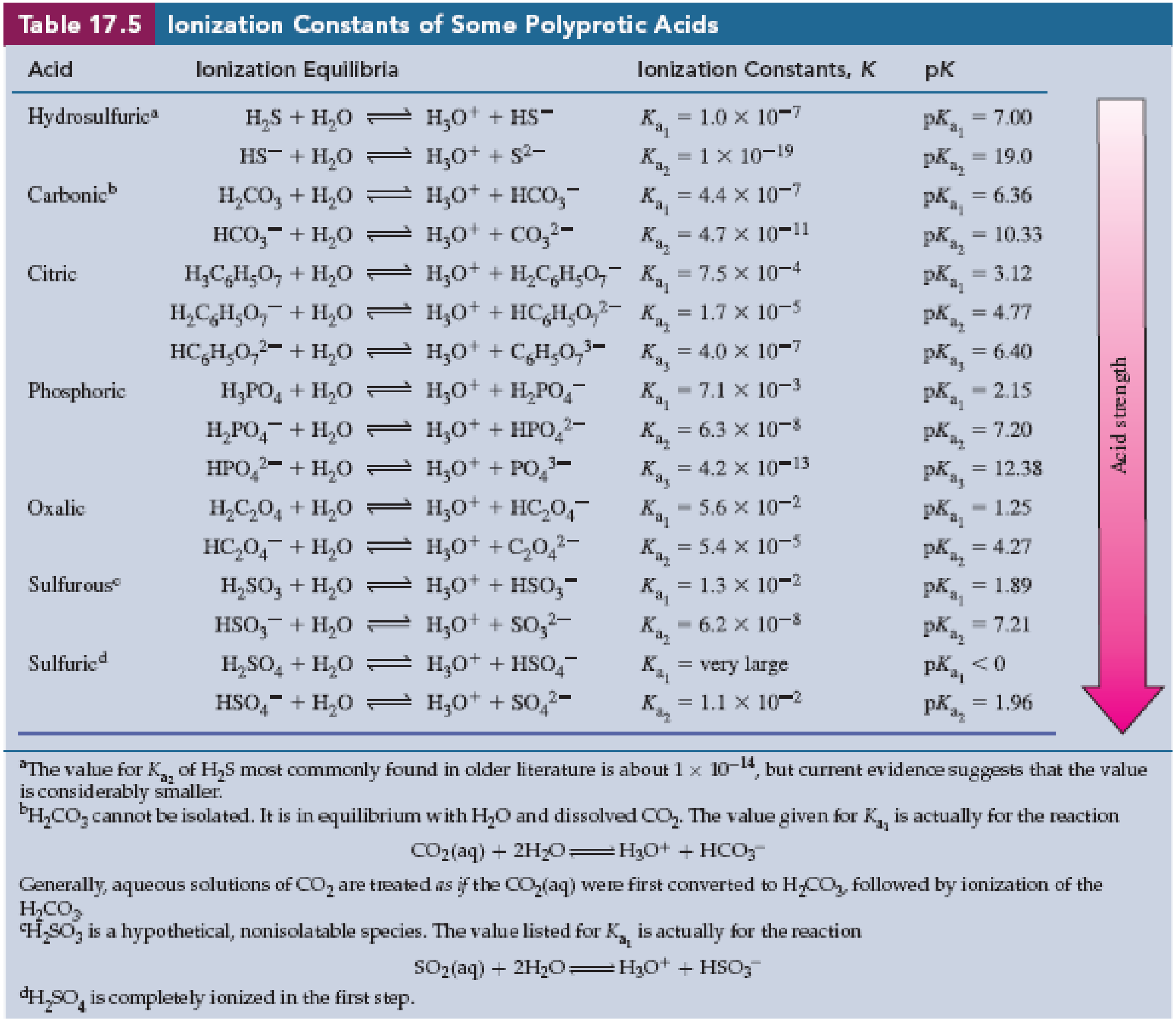


Table 17.5 Ionization Constants of Some Polyprotic Acids

Acid	Ionization Equilibria	Ionization Constants, K	pK
Hydrosulfuric[a]	$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	$K_{a_1} = 1.0 \times 10^{-7}$	$pK_{a_1} = 7.00$
	$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$	$K_{a_2} = 1 \times 10^{-19}$	$pK_{a_2} = 19.0$
Carbonic[b]	$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	$K_{a_1} = 4.4 \times 10^{-7}$	$pK_{a_1} = 6.36$
	$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	$K_{a_2} = 4.7 \times 10^{-11}$	$pK_{a_2} = 10.33$
Citric	$H_3C_6H_5O_7 + H_2O \rightleftharpoons H_3O^+ + H_2C_6H_5O_7^-$	$K_{a_1} = 7.5 \times 10^{-4}$	$pK_{a_1} = 3.12$
	$H_2C_6H_5O_7^- + H_2O \rightleftharpoons H_3O^+ + HC_6H_5O_7^{2-}$	$K_{a_2} = 1.7 \times 10^{-5}$	$pK_{a_2} = 4.77$
	$HC_6H_5O_7^{2-} + H_2O \rightleftharpoons H_3O^+ + C_6H_5O_7^{3-}$	$K_{a_3} = 4.0 \times 10^{-7}$	$pK_{a_3} = 6.40$
Phosphoric	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	$K_{a_1} = 7.1 \times 10^{-3}$	$pK_{a_1} = 2.15$
	$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$	$K_{a_2} = 6.3 \times 10^{-8}$	$pK_{a_2} = 7.20$
	$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$	$K_{a_3} = 4.2 \times 10^{-13}$	$pK_{a_3} = 12.38$
Oxalic	$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$	$K_{a_1} = 5.6 \times 10^{-2}$	$pK_{a_1} = 1.25$
	$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$	$K_{a_2} = 5.4 \times 10^{-5}$	$pK_{a_2} = 4.27$
Sulfurous[c]	$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$	$K_{a_1} = 1.3 \times 10^{-2}$	$pK_{a_1} = 1.89$
	$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$	$K_{a_2} = 6.2 \times 10^{-8}$	$pK_{a_2} = 7.21$
Sulfuric[d]	$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$	K_{a_1} = very large	$pK_{a_1} < 0$
	$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	$K_{a_2} = 1.1 \times 10^{-2}$	$pK_{a_2} = 1.96$

[a] The value for K_{a_2} of H_2S most commonly found in older literature is about 1×10^{-14}, but current evidence suggests that the value is considerably smaller.

[b] H_2CO_3 cannot be isolated. It is in equilibrium with H_2O and dissolved CO_2. The value given for K_{a_1} is actually for the reaction

$$CO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

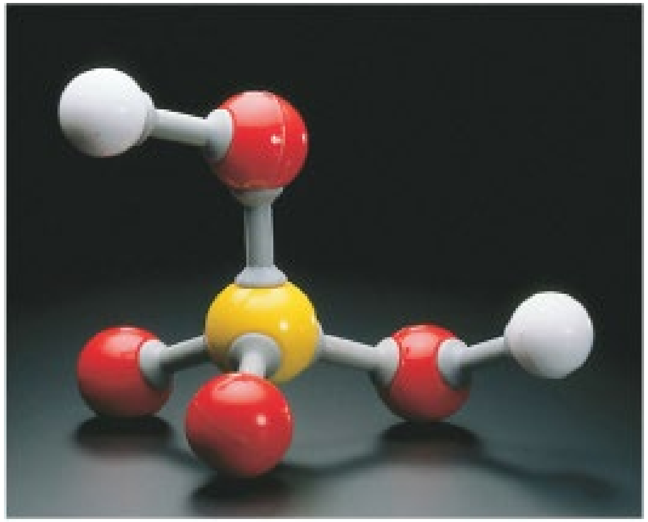
Generally, aqueous solutions of CO_2 are treated *as if* the $CO_2(aq)$ were first converted to H_2CO_3, followed by ionization of the H_2CO_3.

[c] H_2SO_3 is a hypothetical, nonisolatable species. The value listed for K_{a_1} is actually for the reaction

$$SO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HSO_3^-$$

[d] H_2SO_4 is completely ionized in the first step.

A Somewhat Different Case: H_2SO_4



▶ Sulfuric acid, H_2SO_4

A *diprotic acid*.

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^- \qquad K_a = \text{very large}$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \qquad K_a = 1.1 \times 10^{-2}$$

the small second ionization can be treated as in EXAMPLE 17-11

17-7 Simultaneous or Consecutive Acid-Base Reactions: A General Approach

1. Identify species present in solution (excluding H_2O).
2. Write equations that include these species.

   Number of equations = number of unknowns.

   a) equilibrium constant expressions.
   b) material balance equations.
   c) electroneutrality condition.
3. Solve the system of equations for the unknowns.

Consider 0.10 M H_3PO_4

Species in solution

H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3O^+, OH^-

Reactions and equilibrium constants

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.1\times10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3\times10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2\times10^{-13}$$

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

Consider 0.10 M H_3PO_4

Species in solution

H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3O^+, OH^-

Reactions and equilibrium constants

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.1 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13}$$

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

We have four equations and six unknowns. Need two equations.

Material balance equation (MBE)

$$0.1\ \mathrm{M} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

Charge balance equation (CBE)

$$[H_3O^+] = [H_2PO_4^-] + 2 \times [HPO_4^{2-}] + 3 \times [PO_4^{3-}] + [OH^-]$$

In principle, the system of six equations can be used to solve for six unknowns, either by making appropriate simplifying approximations or by computerized calculation.

17-8 Ions as Acids and Bases

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad (17.17)$$

Acid (1) Base (2) Base (1) Acid (2)

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^- \qquad (17.18)$$

Base (2) Acid (1) Acid (2) Base (1)

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = ? \qquad (17.19)$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

Acid (1) Base (2) Base (1) Acid (2)

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = ?$$

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

Base (2) Acid (1) Acid (2) Base (1)

$$K_a = \frac{[NH_3]\,[H_3O^+]\,[OH^-]}{[NH_4^+]\,[OH^-]} = \frac{K_W}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

The product of the ionization constants of an acid and its conjugate base equals the ion product of water.

$$K_a \text{ (acid)} \times K_b \text{ (its conjugate base)} = K_w$$

$$K_b \text{ (base)} \times K_a \text{ (its conjugate acid)} = K_w \qquad (17.20)$$

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^- \qquad (17.18)$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a(CH_3COOH)} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5\times10^{-10}$$

The conjugate of weak is weak.

$$K_b(\mathrm{I}^-) = K_w / K_b = 10^{-14} / 10^9 = 10^{-23}$$

The conjugate of strong is *extremely* weak.

17-10 Molecular Structure and Acid-Base Behavior

Why is HCl a strong acid, but HF is a weak one?

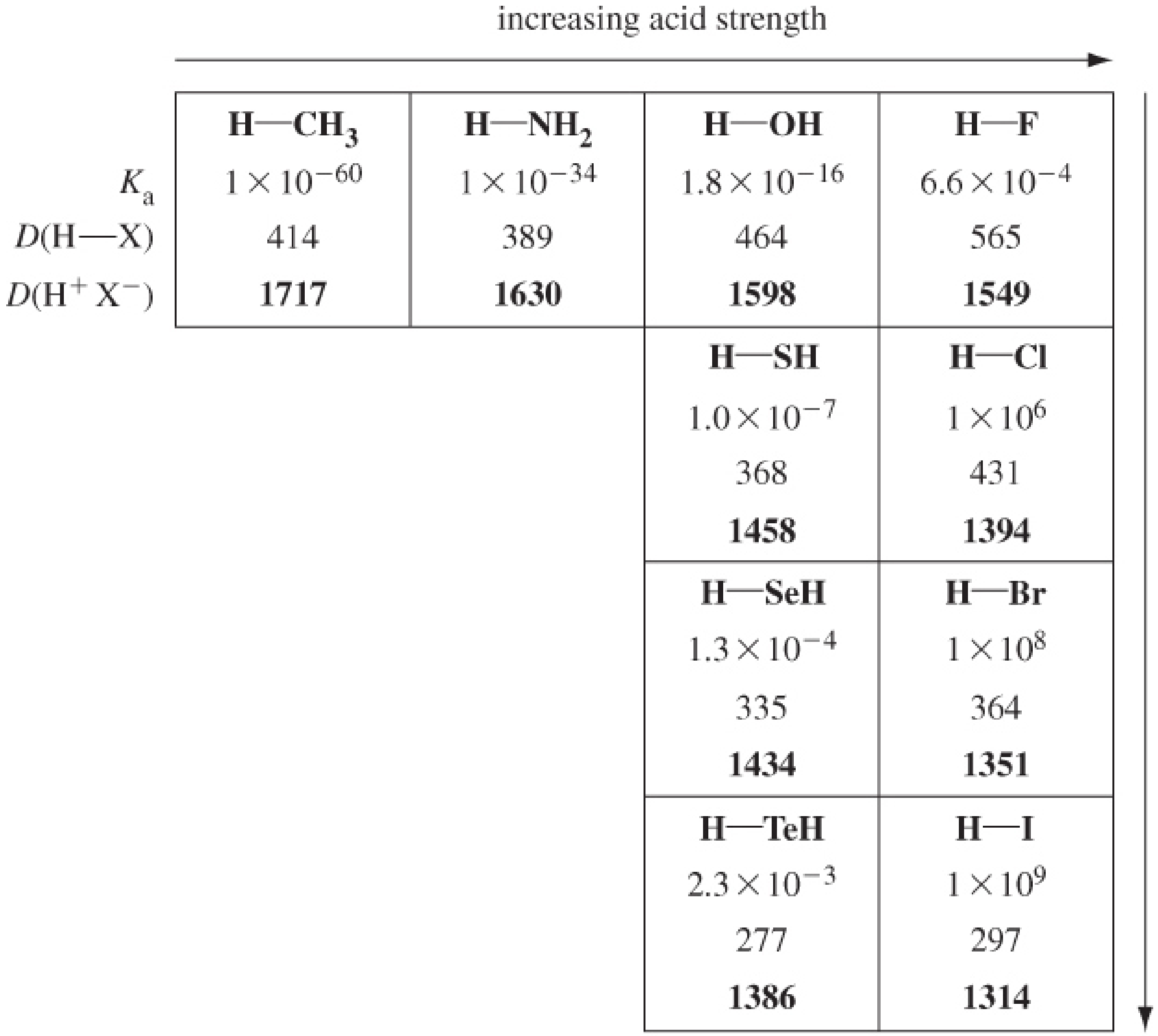
Why is CH_3CO_2H a stronger acid than CH_3CH_2OH?

Molecular structure and acid strength are related.

Strengths of Binary Acids

$$HX(g) \longrightarrow H^{+}(g) + X^{-}(g) \qquad (17.23)$$

$$\begin{tikzcd}
HX(g) \arrow[r, "D(H\text{—}X)"] \arrow[dr, swap, "D(H^{+}X^{-})"] & H(g) \arrow[d, swap, "E_i(H)"] \arrow[d, "-e^{-}"] & + & X(g) \arrow[d, swap, "\Delta_{ea}H"] \arrow[d, "+e^{-}"] \\
 & H^{+}(g) & + & X^{-}(g)
\end{tikzcd}$$



	H—CH$_3$	**H—NH$_2$**	**H—OH**	**H—F**
K_a	1×10^{-60}	1×10^{-34}	1.8×10^{-16}	6.6×10^{-4}
D(H—X)	414	389	464	565
$D(H^+X^-)$	**1717**	**1630**	**1598**	**1549**
			H—SH	**H—Cl**
			1.0×10^{-7}	1×10^{6}
			368	431
			1458	**1394**
			H—SeH	**H—Br**
			1.3×10^{-4}	1×10^{8}
			335	364
			1434	**1351**
			H—TeH	**H—I**
			2.3×10^{-3}	1×10^{9}
			277	297
			1386	**1314**

▲ FIGURE 17-10

Bond dissociation energies (kJ mol^{-1}) and K_a values for some binary acids

When comparing binary acids of elements in the same row of the periodic table, acid strength increases as the polarity of the bond increases.

When comparing binary acids of elements in the same group of the periodic table, acid strength increases as the length of the bond increases.

HF is even weaker than expected based on periodic trends.

$$\mathrm{HF} + \mathrm{H_2O} \longrightarrow \underset{\text{Ion pair}}{(\mathrm{F^-\cdots H_3O^+})} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{F^-}$$

Strengths of Oxoacids

Factors promoting electron withdrawal from the OH bond to the oxygen atom:

- High electronegativity (*EN*) of the central atom.
- A large number of terminal O atoms in the molecule.

H−O−Cl

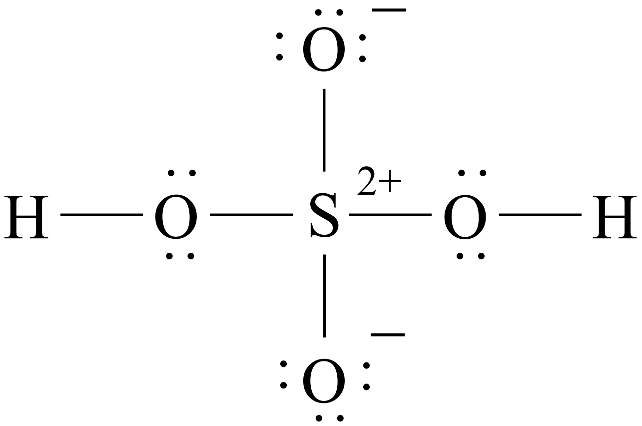
$EN_{\mathrm{Cl}} = 3.0$

$K_a = 2.9 \times 10^{-8}$

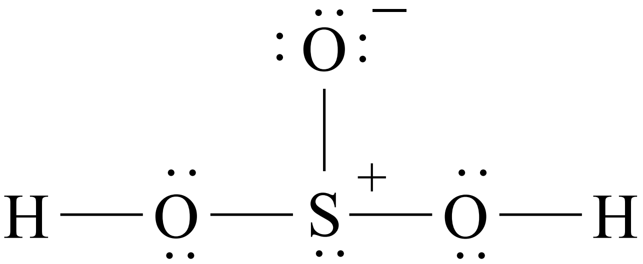
H−O−Br

$EN_{\mathrm{Br}} = 2.8$

$K_a = 2.1 \times 10^{-9}$

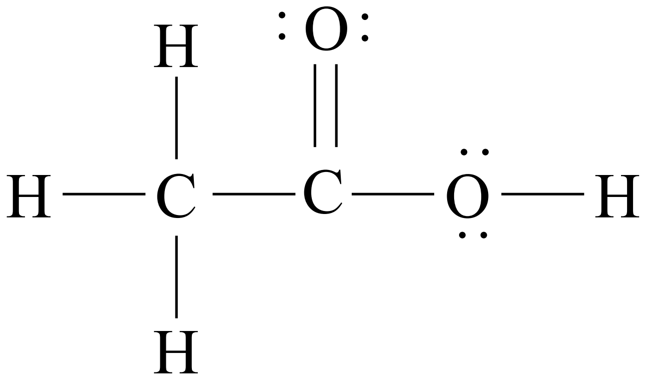


$K_a \approx 10^3$



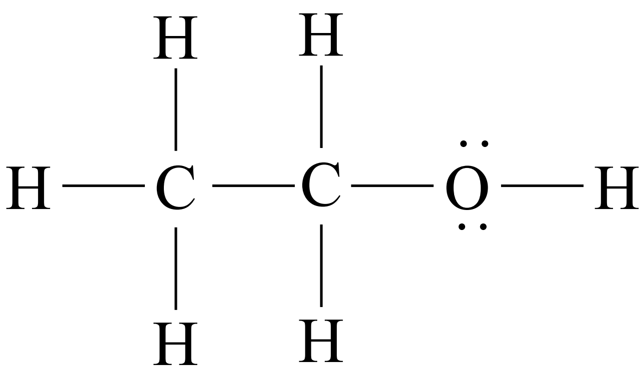
$K_a = 1.3 \times 10^{-2}$

Strengths of Organic Acids



Acetic acid

$K_a = 1.8 \times 10^{-5}$

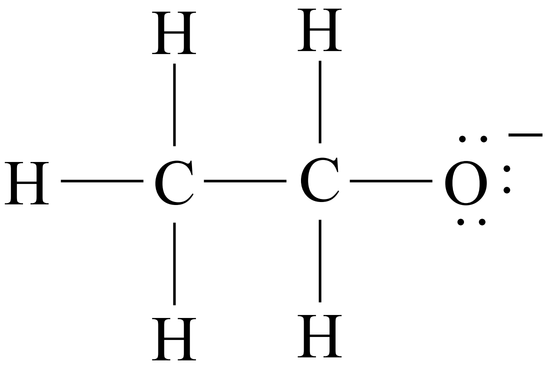


Ethanol

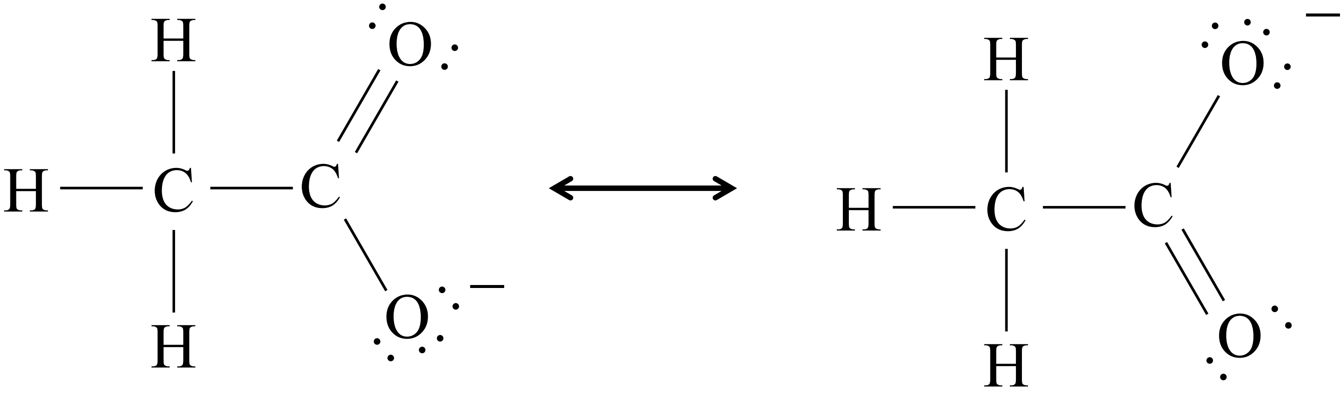
$K_a = 1.3 \times 10^{-16}$

Focus on the anions formed in the ionization.

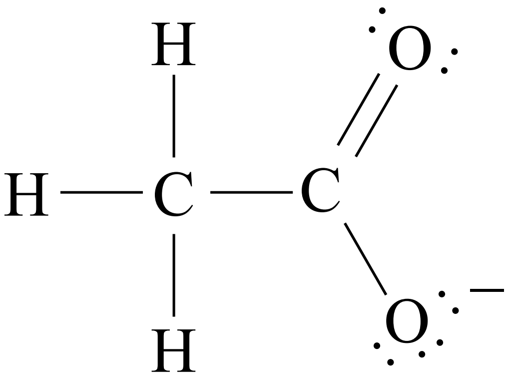
Ethoxide ion



Acetate ion



Chain length has little effect on the acid strength.

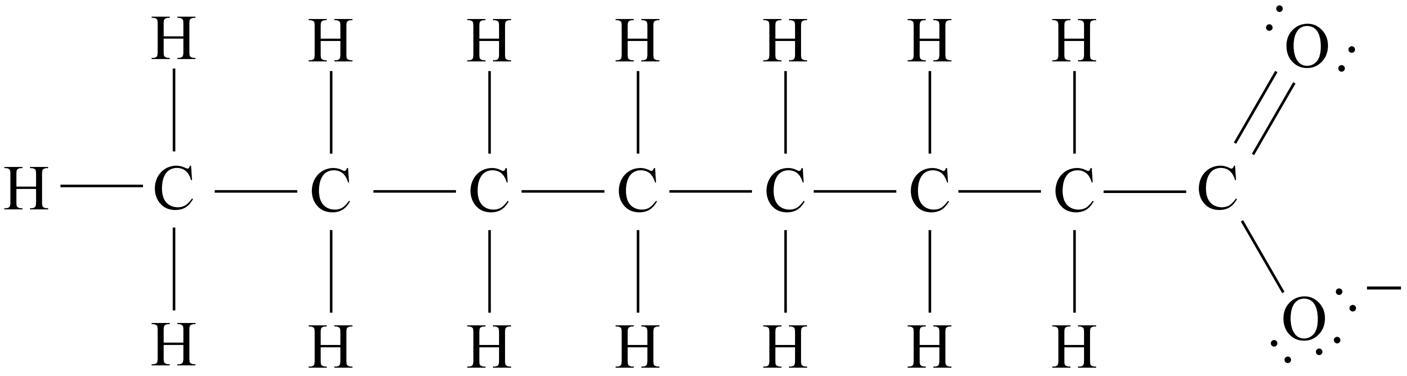


acetic acid

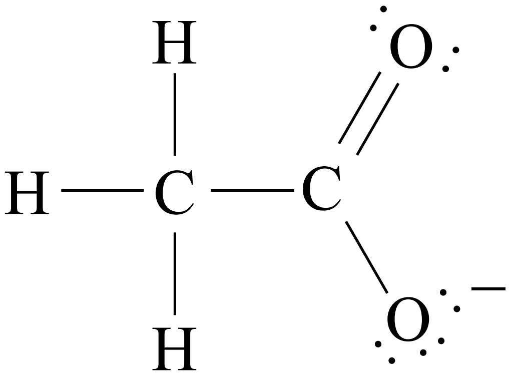
$K_a = 1.8 \times 10^{-5}$

octanoic acid

$K_a = 1.3 \times 10^{-5}$



Substitution may strongly affect acid strength.

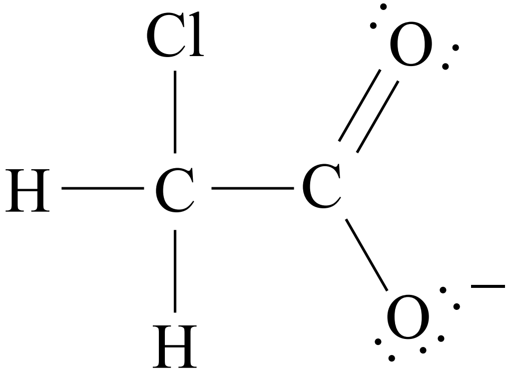


acetic acid

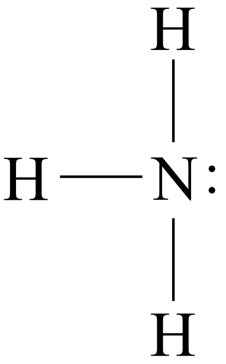
$K_a = 1.8 \times 10^{-5}$

chloroacetic acid

$K_a = 1.4 \times 10^{-3}$

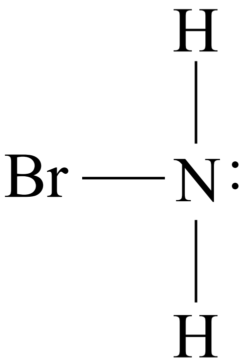


Strengths of Amines as Bases



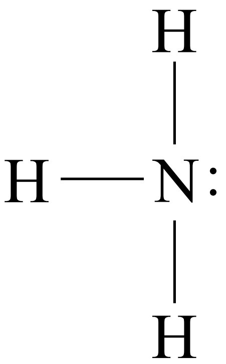
ammonia

NH_3, pK_b = 4.74



bromamine

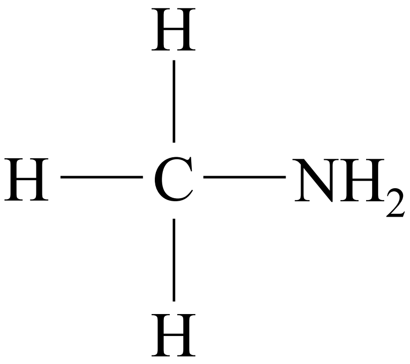
NH_2Br, pK_b = 7.61



$H-\overset{H}{\underset{H}{N}}:$

ammonia

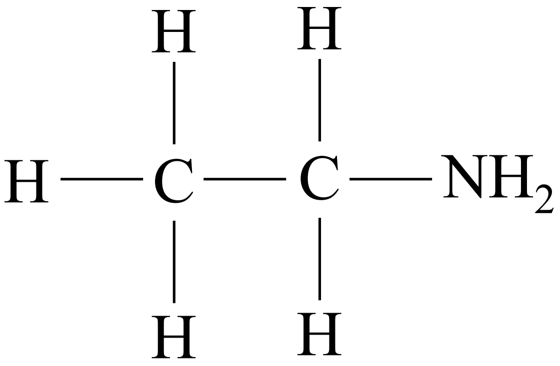
NH_3, pK_b = 4.74



$H-\overset{H}{\underset{H}{C}}-NH_2$

methylamine

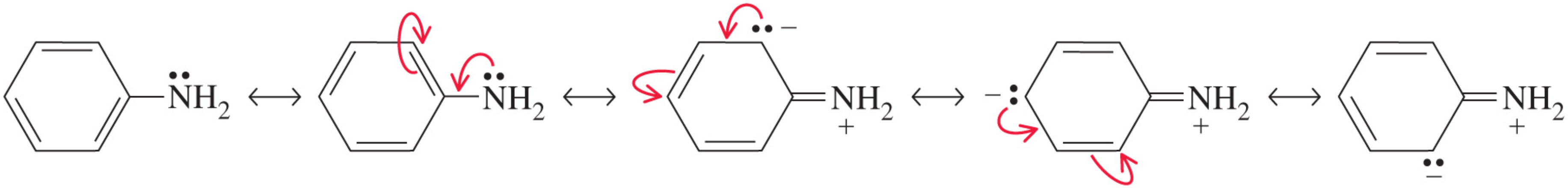
CH_3NH_3, pK_b = 4.74

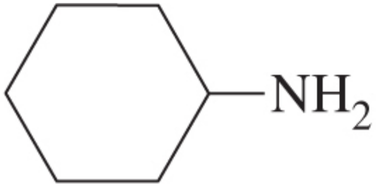


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-NH_2$

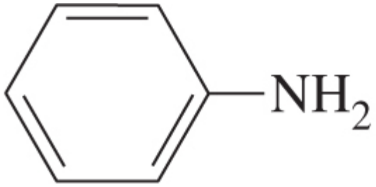
ethylamine

$CH_3CH_2NH_3$, pK_b = 3.38

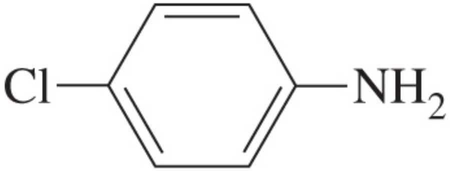




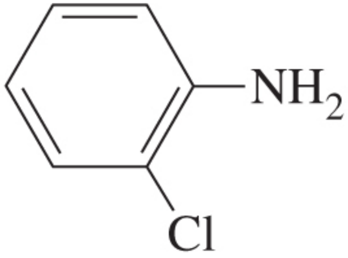
Cyclohexylamine, pK_b = 3.36



Aniline, pK_b = 9.13



para-Chloroaniline, pK_b = 10.01

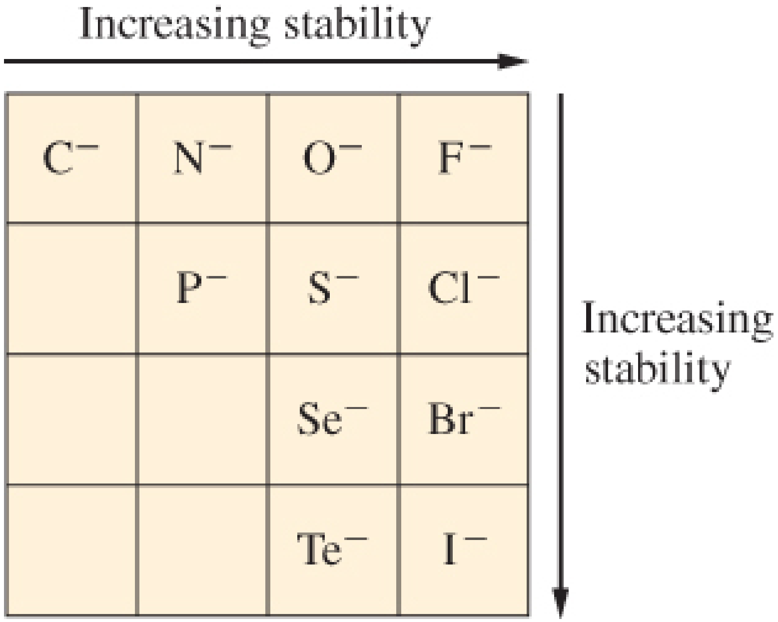


ortho-Chloroaniline, pK_b = 11.36

Rationalization of Acid Strengths: An Alternative Approach

Two approaches to rationalize the strength of an acid, HA.

- factors that cause electron density to be drawn away from the H atom
- factors that make A^- stable with respect to protonation



Increasing stability

C^-	N^-	O^-	F^-
	P^-	S^-	Cl^-
		Se^-	Br^-
		Te^-	I^-

Increasing stability

- the more electronegative the atom is, the better it is able to bear a negative charge. (CH_3O^- is more stable than NH_2^-)
- the larger the atom, the greater its ability to bear a negative charge. (HS^- is more stable than HO^-)
- the stability of the anion increases as the number of electron-withdrawing groups increases.
- the stability of the anion increases as the number of atoms sharing the charge increases

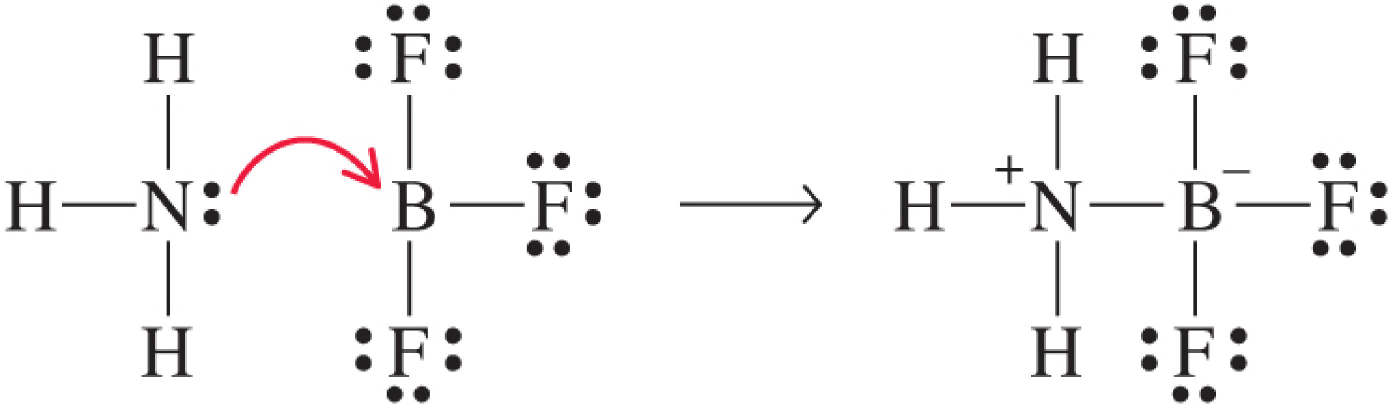
17-9 Lewis Acids and Bases

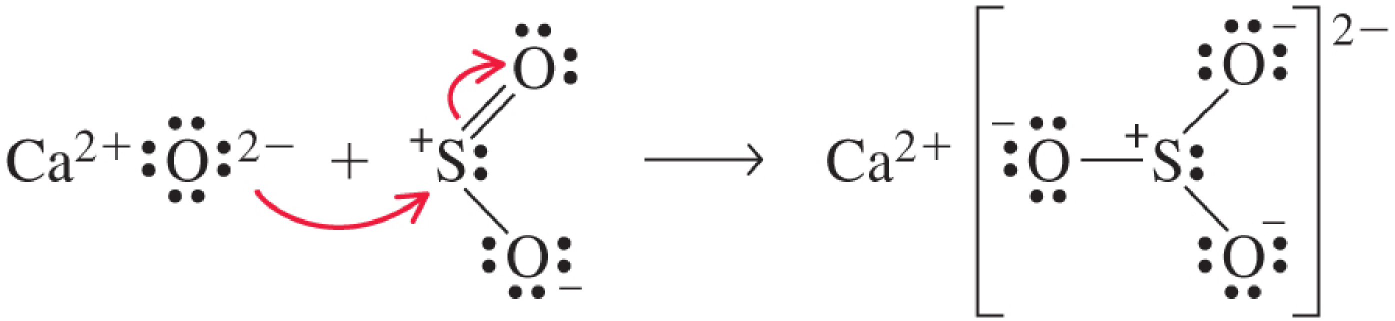
Lewis acid

A species (atom, ion or molecule) that is an electron pair *acceptor*.

Lewis base

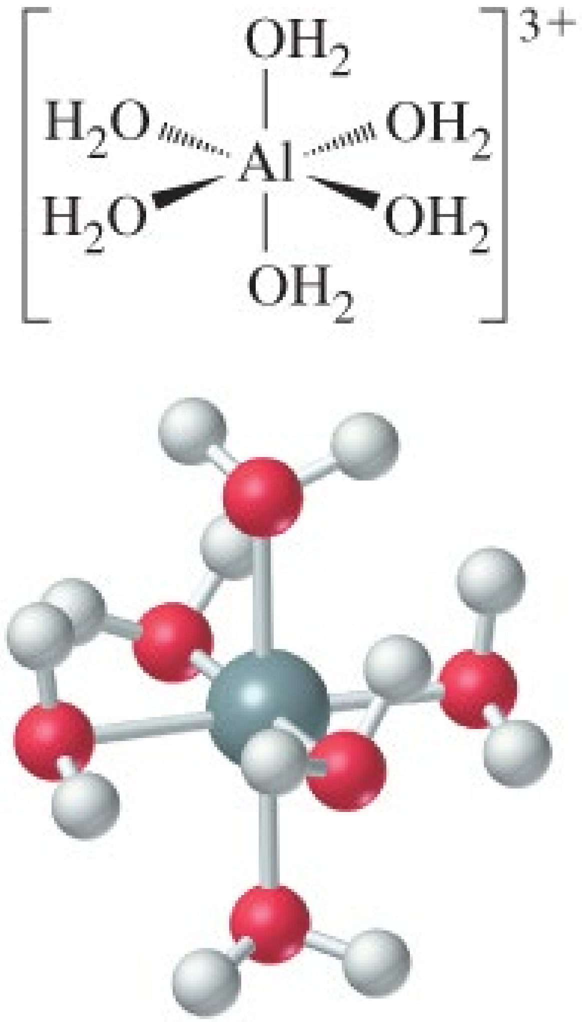
A species that is an electron pair *donor*.





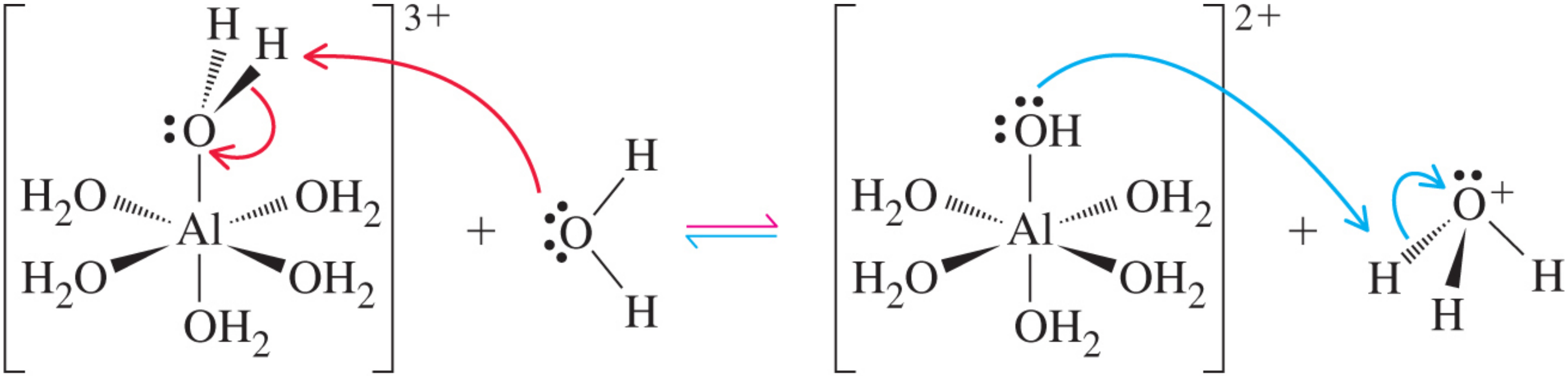
(17.24)

Complex ions



▲ FIGURE 17-11

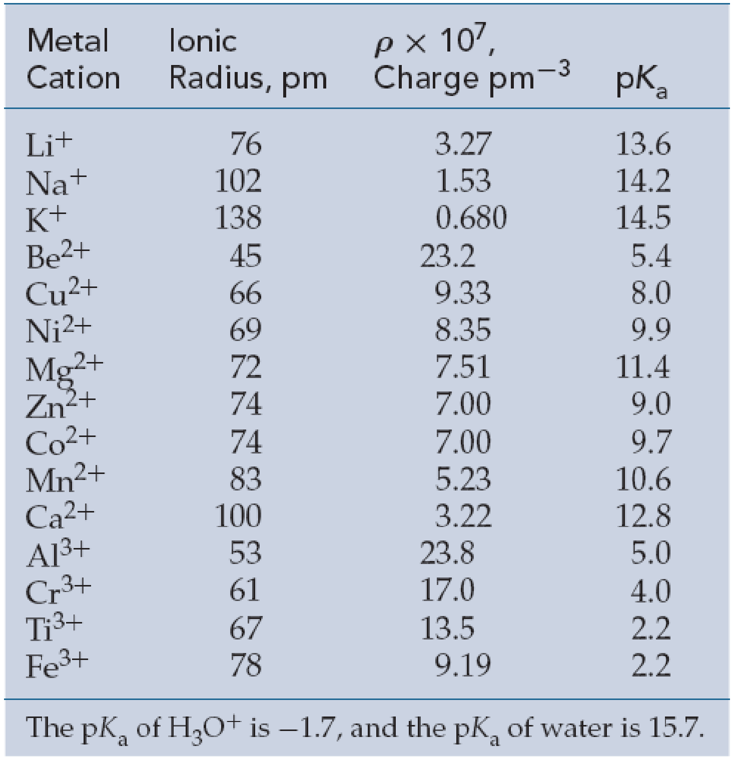
The Lewis structure of $[Al(H_2O)_6]^{3+}$ and a ball-and-stick representation



▲ FIGURE 17-12

Hydrolysis of $[Al(H_2O)_6]^{3+}$ to produce H_3O^+

$$\rho = \text{charge density} = \frac{\text{ionic charge}}{\text{ionic volume}}$$



Metal Cation	Ionic Radius, pm	$\rho \times 10^7$, Charge pm^{-3}	pK_a
Li^+	76	3.27	13.6
Na^+	102	1.53	14.2
K^+	138	0.680	14.5
Be^{2+}	45	23.2	5.4
Cu^{2+}	66	9.33	8.0
Ni^{2+}	69	8.35	9.9
Mg^{2+}	72	7.51	11.4
Zn^{2+}	74	7.00	9.0
Co^{2+}	74	7.00	9.7
Mn^{2+}	83	5.23	10.6
Ca^{2+}	100	3.22	12.8
Al^{3+}	53	23.8	5.0
Cr^{3+}	61	17.0	4.0
Ti^{3+}	67	13.5	2.2
Fe^{3+}	78	9.19	2.2

The pK_a of H_3O^+ is –1.7, and the pK_a of water is 15.7.