GENERAL CHEMISTRY

Chapter 16

Acid-Base Equilibria

Contents

16-1 Acids and Bases: A Brief Review

- **Arrhenius**
  - An **acid** is a substance that, when dissolved inwater, increases the concentration of **hydrogen** ions, **H^+**.

$$\mathrm{HCl\ (g)} \xrightarrow{H_2O} \mathrm{H^+\ (aq) + Cl^-\ (aq)}$$

  - A **base** is a substance that, when dissolved in water, increases the concentration of **hydroxide** ions, **OH^-**.

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

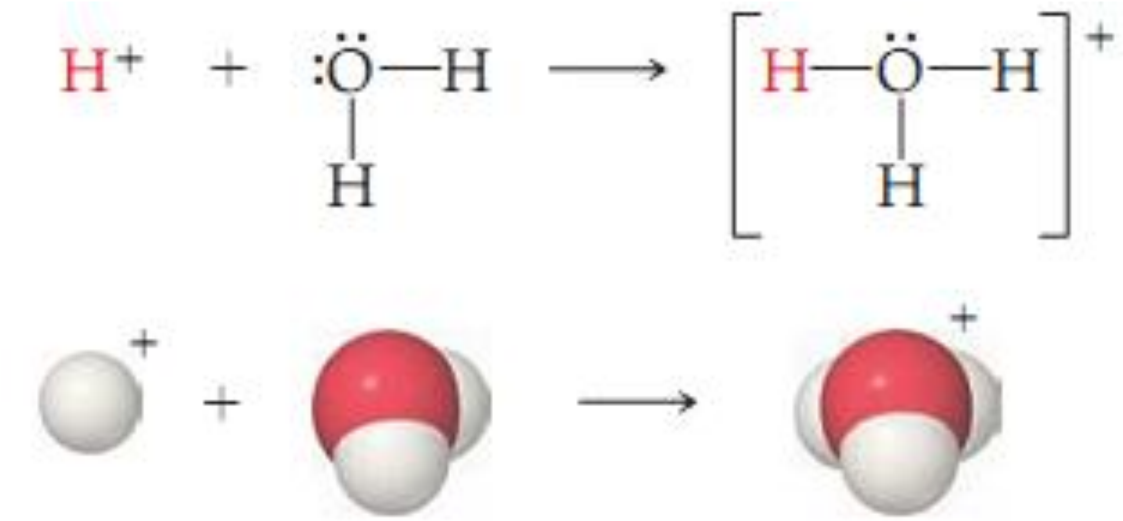
16-2 Brønsted–Lowry Acids and Bases

- **Brønsted–Lowry :** *Acid–base reactions involve the transfer of* H^+ *ions from one substance to another*
  - An acid is a proton donor.
    - … must have a removable proton
  - A base is a proton acceptor.
    - …must have a pair of nonbonding electrons

The H^+ Ion in Water

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

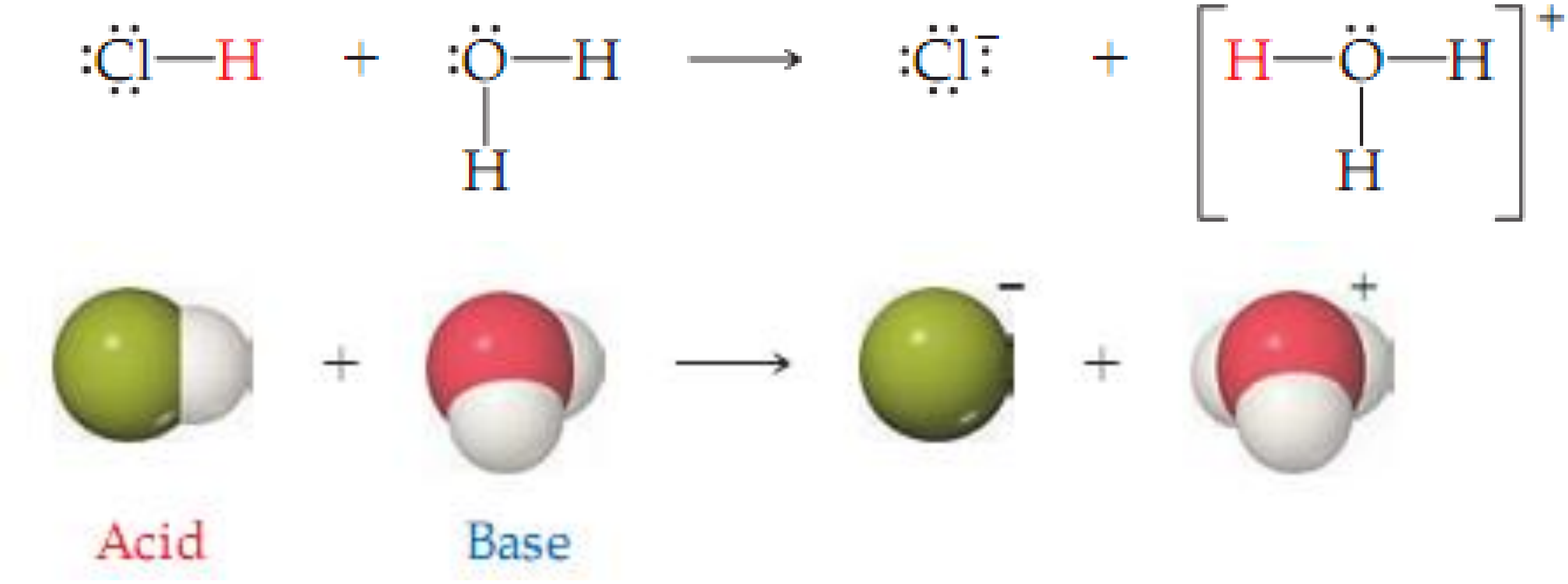
The H^+ ion interacts strongly with any source of electron density, such as the nonbonding electron pairs on the oxygen atoms of water molecules



Chemists use the notations H^+ and H_3O^+ interchangeably

Proton-Transfer Reactions

What Happens When an Acid Dissolves in Water?

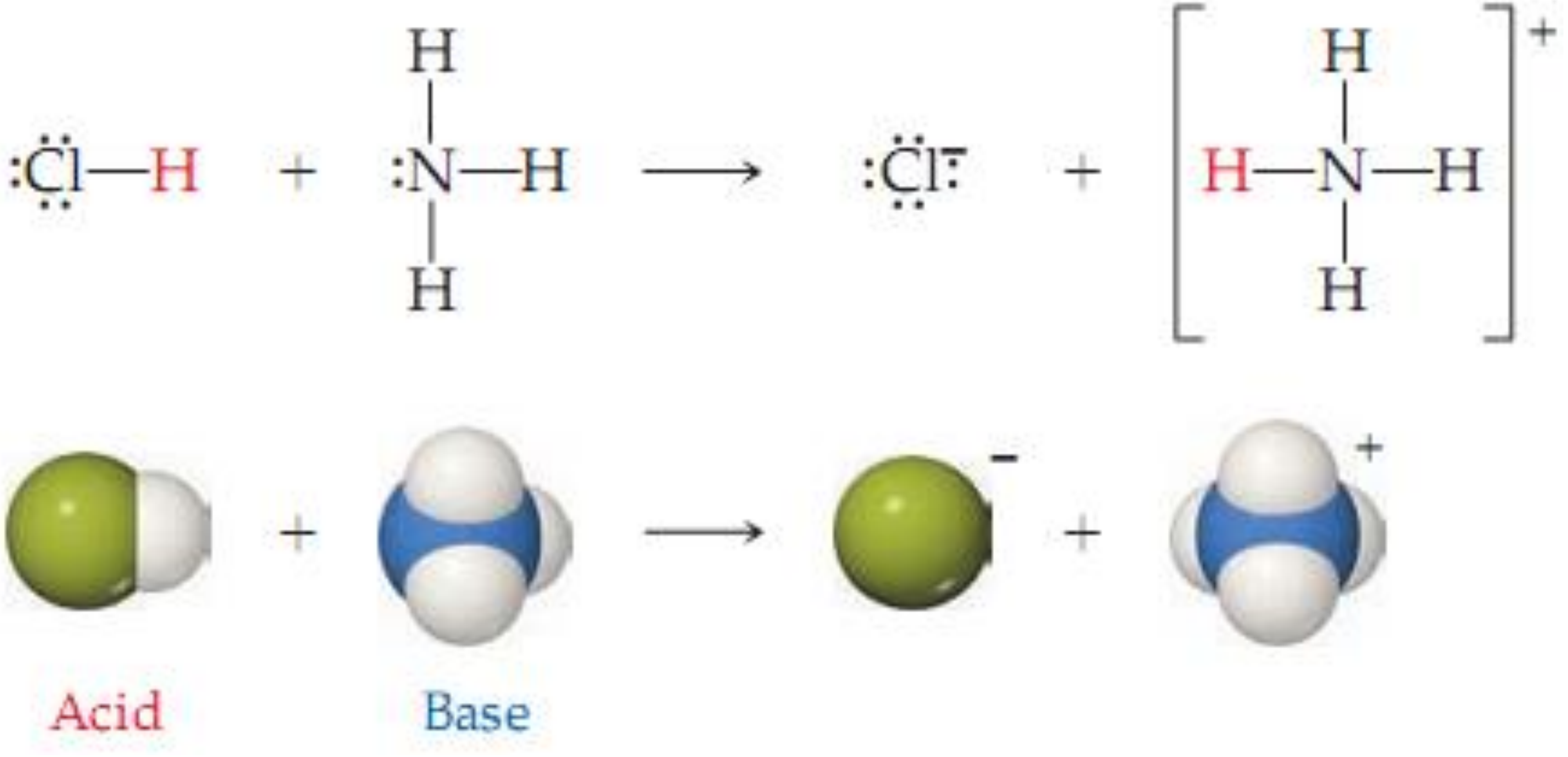


proton donor *proton acceptor* *conjugate base* *hydronium ion*

- Water acts as a Brønsted–Lowry base and abstracts a proton from the acid.
- The **conjugate base** of the acid and a **hydronium ion** are formed.

Proton-Transfer Reactions

The Brønsted–Lowry concept also applies to reactions that do not occur in aqueous solutions



Proton-Transfer Reactions

H_2O and HCO_3^- can be either acid or base

$\mathbf{HCO_3^-} + H_20 \rightarrow CO_3^{--} + \mathbf{H_3O^+}$

(HCO_3^- as an acid,
water as a base)

$\mathbf{HCO_3^-} + H_20 \rightarrow H_2CO_3 + \mathbf{OH^-}$

(HCO_3^- as a base,
water as an acid)

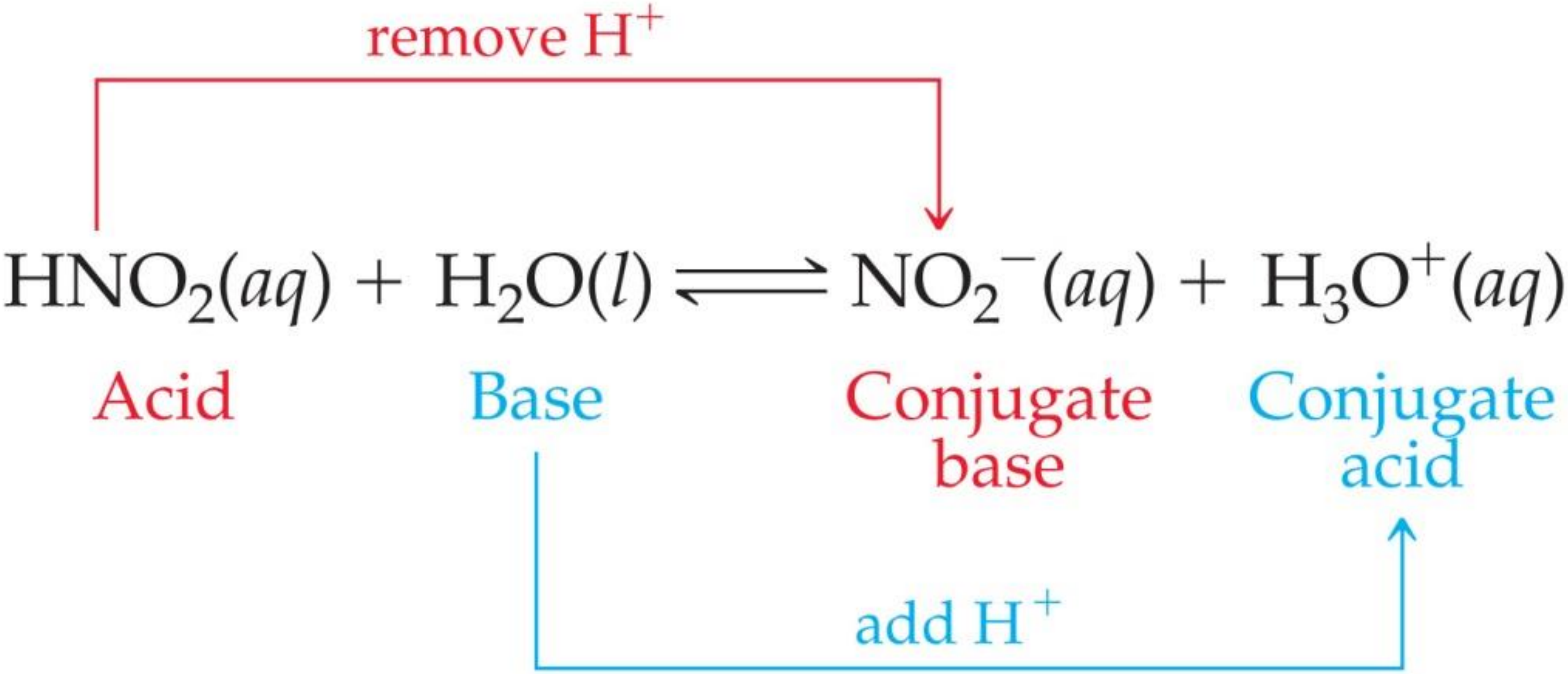
$NH_3 + \mathbf{H_20} \rightarrow NH_4^+ + \mathbf{OH^-}$ (water as an acid)

$HNO_2 + \mathbf{H_20} \rightarrow NO_2^- + \mathbf{H_3O^+}$ (water as a base)

They are **amphiprotic**

Conjugate Acids and Bases

- The term **conjugate** comes from the Latin word "conjugare," meaning "to join together."
- 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^+

EXAMPLE

(a) What is the conjugate base of

$HClO_4$	ClO_4^+
H_2S	HS^+
PH_4^+	PH_3
HCO_3^-	CO_3^{2-}

(b) What is the conjugate acid of

CN^-	HCN
SO_4^{2-}	HSO_4^-
H_2O	H_3O^+
HCO_3	H_2CO_3

EXAMPLE

The hydrogen sulfite ion (HSO_3^-) is amphiprotic. Write an equation for the reaction of HSO_3^- with water

(a) in which the ion acts as an acid

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$$

acid conjugate base

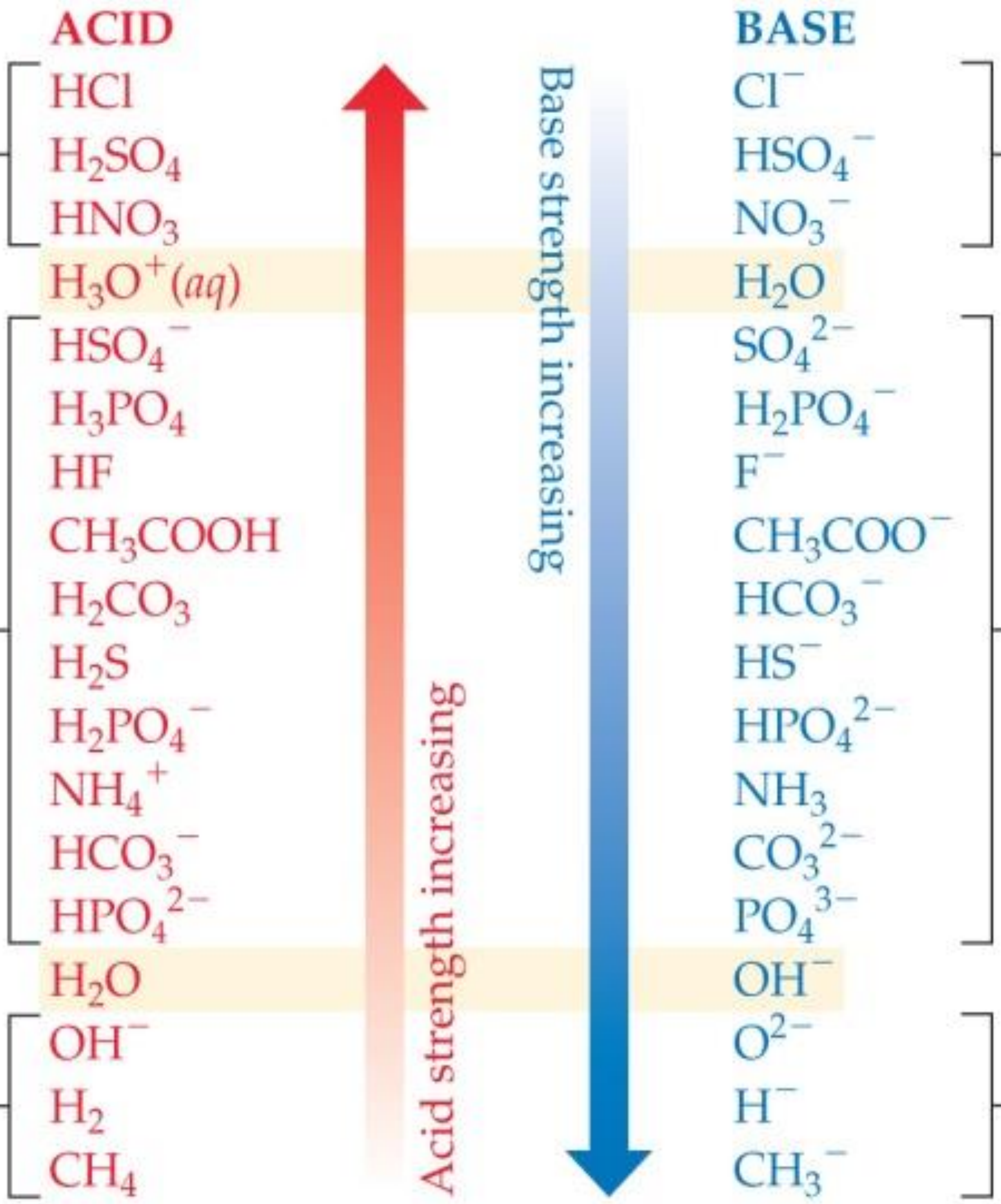
(b) in which the ion acts as a base.

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$$

base conjugate acid

In both cases identify the conjugate acid–base pairs.

Relative Strengths of Acids and Bases



	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^-	

Strong acids are completely dissociated in water

Substances with negligible acidity do not dissociate in water

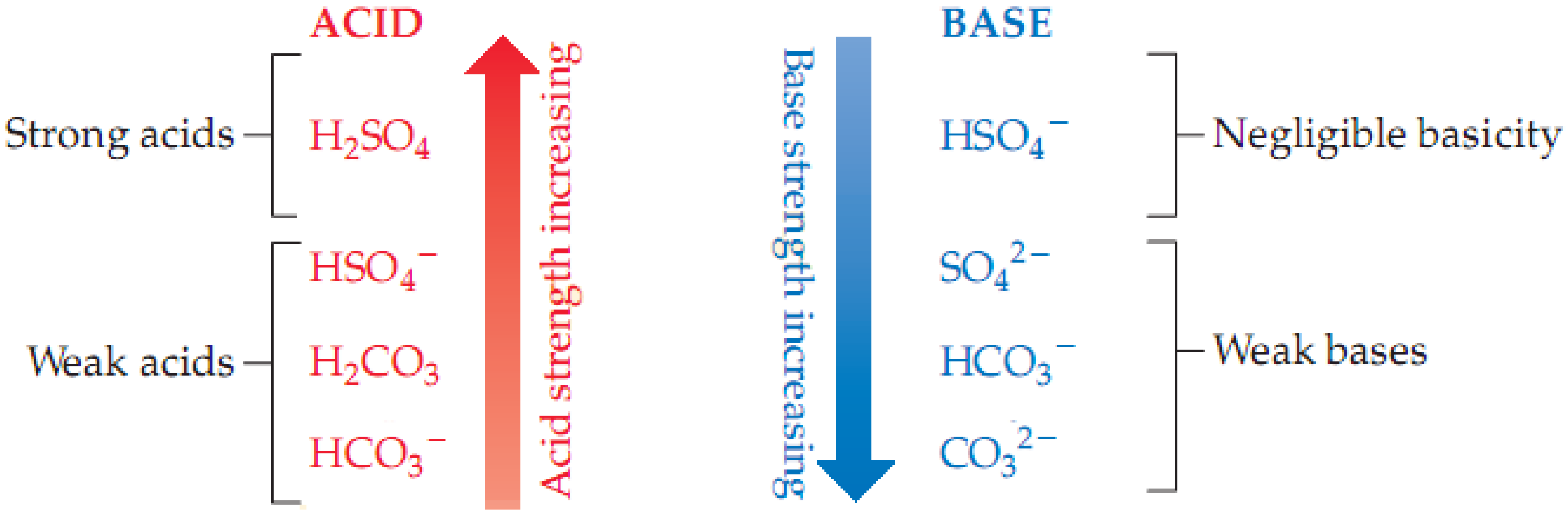
(The conjugate base of a strong acid shows negligible basicity

Conjugate bases of substances with negligible acidity are exceedingly strong

EXAMPLE

Predict whether the equilibrium of the following proton-transfer reaction lies to the left ($K_c<1$) or to the right ($K_c > 1$)?

$$\underset{\text{Acid}}{HSO_4^-(aq)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons \underset{\text{Conjugate base}}{SO_4^{2-}(aq)} + \underset{\text{Conjugate acid}}{HCO_3^-(aq)}$$



	ACID	BASE	
Strong acids	H_2SO_4	HSO_4^-	Negligible basicity
Weak acids	HSO_4^-	SO_4^{2-}	Weak bases
	H_2CO_3	HCO_3^-	
	HCO_3^-	CO_3^{2-}	

Acid strength increasing

Base strength increasing

CO_3^{2-} is the stronger base, therefore it will get the proton preferentially

➔ The reaction lies to the right ($K_c > 1$)?

Acid and Base Strength

- In any acid–base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base to form the weaker acid and the weaker base.

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

H_2O is a much stronger base than Cl^-, so the equilibrium lies **completely to the right**

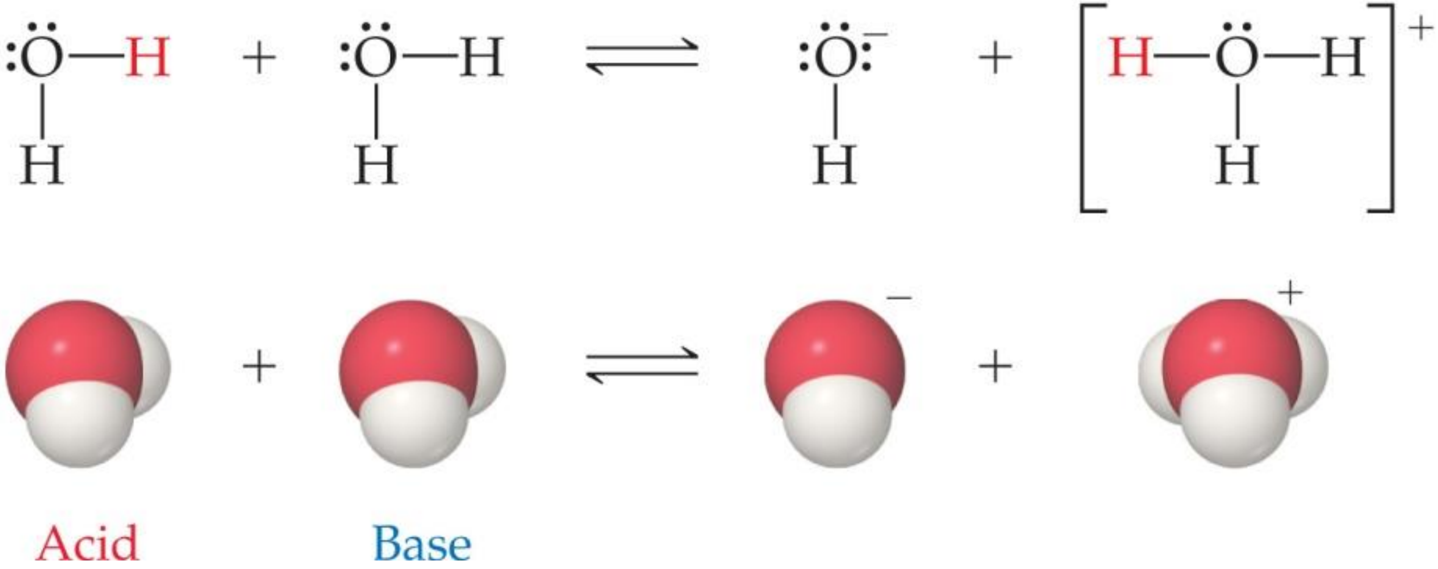
$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

Acetate is a stronger base than H_2O, so **the reverse reaction is favored** more than the forward reaction

16-3 The Autoionization of Water

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

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



The Ion Product of Water

- The equilibrium expression for the autoionization of water 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, $K_w = 1.0 \times 10^{-14}$

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

$$x^2 = 1.0 \times 10^{-14}$$

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

The relative concentrations of H^+ and OH^- in aqueous solutions at 25 °C

Acidic solution

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

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

Neutral solution

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

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

Basic solution

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

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

EXAMPLE

Calculate the concentration of H+(aq) in

(a) a solution in which [OH$^-$] is 0.010 M,

(b) a solution in which [OH$^-$] is 1.8 x 10^{-9}

The temperature of these solutions is 25 °C

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

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

a) $$[\mathrm{H^+}] = \frac{(1.0 \times 10^{-14})}{[\mathrm{OH^-}]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\,M$$

b) $$[\mathrm{H^+}] = \frac{(1.0 \times 10^{-14})}{[\mathrm{OH^-}]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}\,M$$

16-4 The pH scale

pH is the negative logarithm in base 10 of the concentration of hydronium ion:

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

- **For pure water at 25ºC**,

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

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

Thus,

$$[H_3O^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

$$\mathbf{pH = -\log\,(1.0 \times 10^{-7}) = 7.00}$$

pH of Acids and Bases

- An **acid** has a higher [H_3O^+] than pure water, so its **pH < 7**.
- A **base** has a lower [H_3O^+] than pure water, so its **pH > 7**.

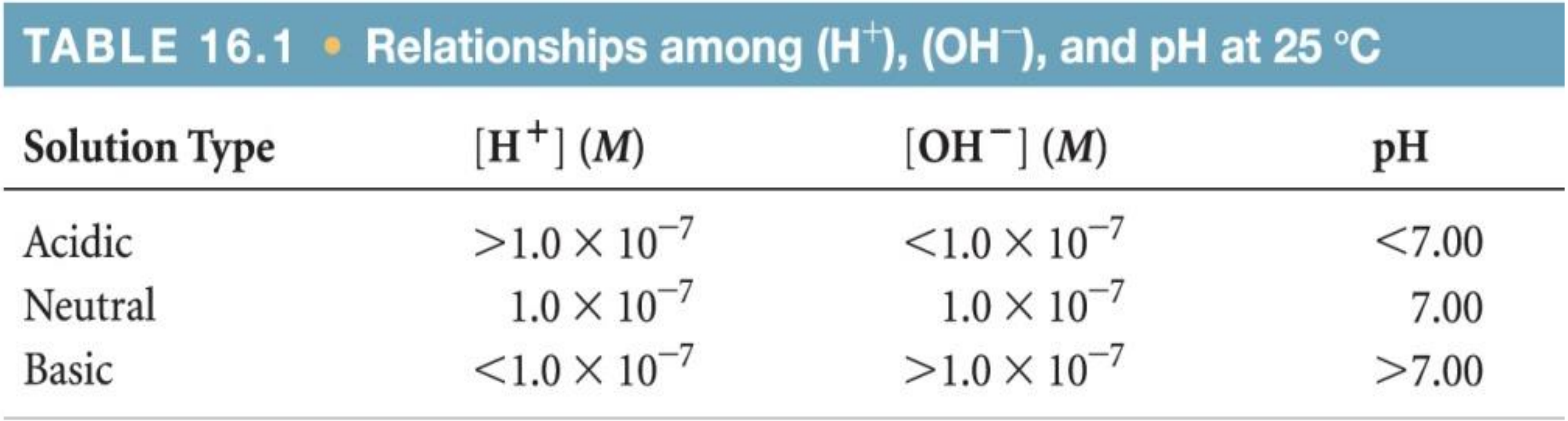
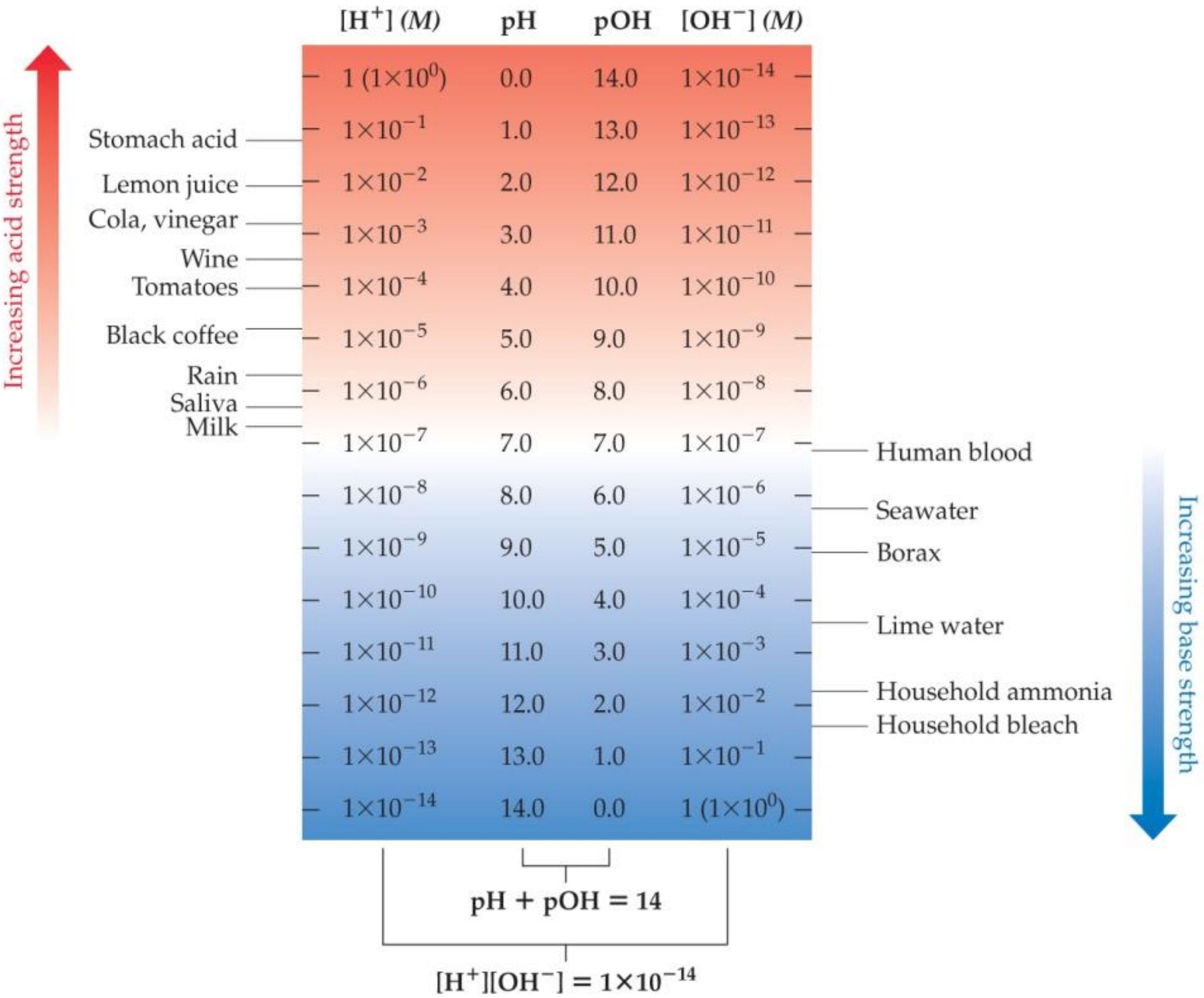


TABLE 16.1 • Relationships among (H^+), (OH^-), and pH at 25 °C

Solution Type	[H^+] (*M*)	[OH^-] (*M*)	pH
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	1.0×10^{-7}	1.0×10^{-7}	7.00
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

pH of Acids and Bases

These are the pH values for several common substances



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*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	$1\ (1\times10^{0})$

pH + pOH = 14

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

pOH and Other "p" Scales

- The "p" in pH tells us to take the negative logarithm in base 10 of a quantity (in this case, concentration of hydronium ions).
- Some similar examples are
  - pOH: $-\log [OH^-]$
  - pK_w: $-\log K_w$

pOH and Other “p” Scales

Because

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

we know that

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

or, in other words,

$$pH + pOH = pK_w = 14.00$$

EXAMPLE

A sample of freshly pressed apple juice has a pOH of 10.24. Calculate [H^+].

$$\mathrm{pH} = 14.00 - \mathrm{pOH}$$

$$\mathrm{pH} = 14.00 - 10.24 = 3.76$$

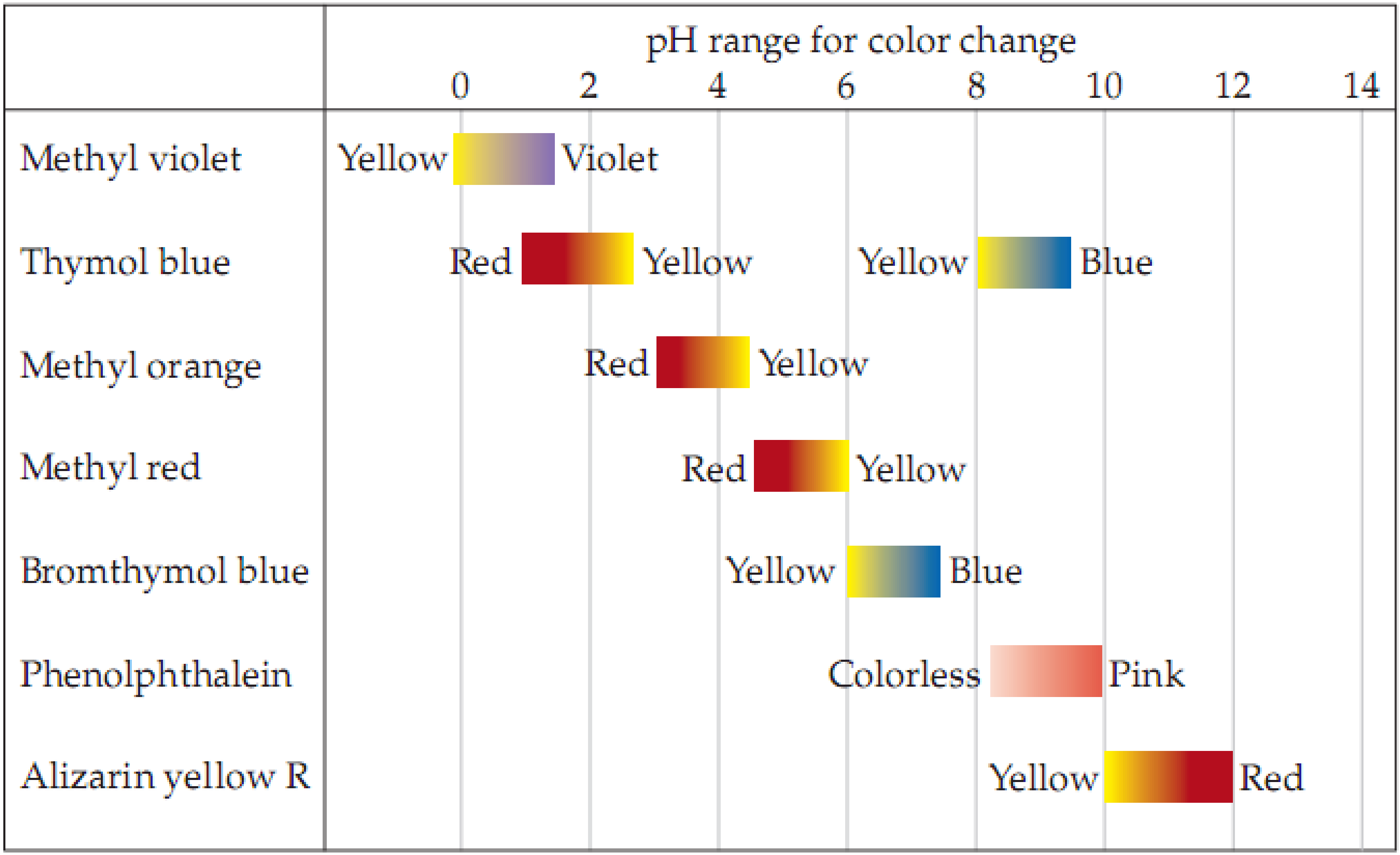
$$\mathrm{pH} = -\log[H^+] = 3.76$$

$$\log[H^+] = -3.76$$

$$[H^+] = \mathrm{antilog}(-3.76) = 10^{-3.76} = 1.7 \times 10^{-4}\,M$$

Measuring pH

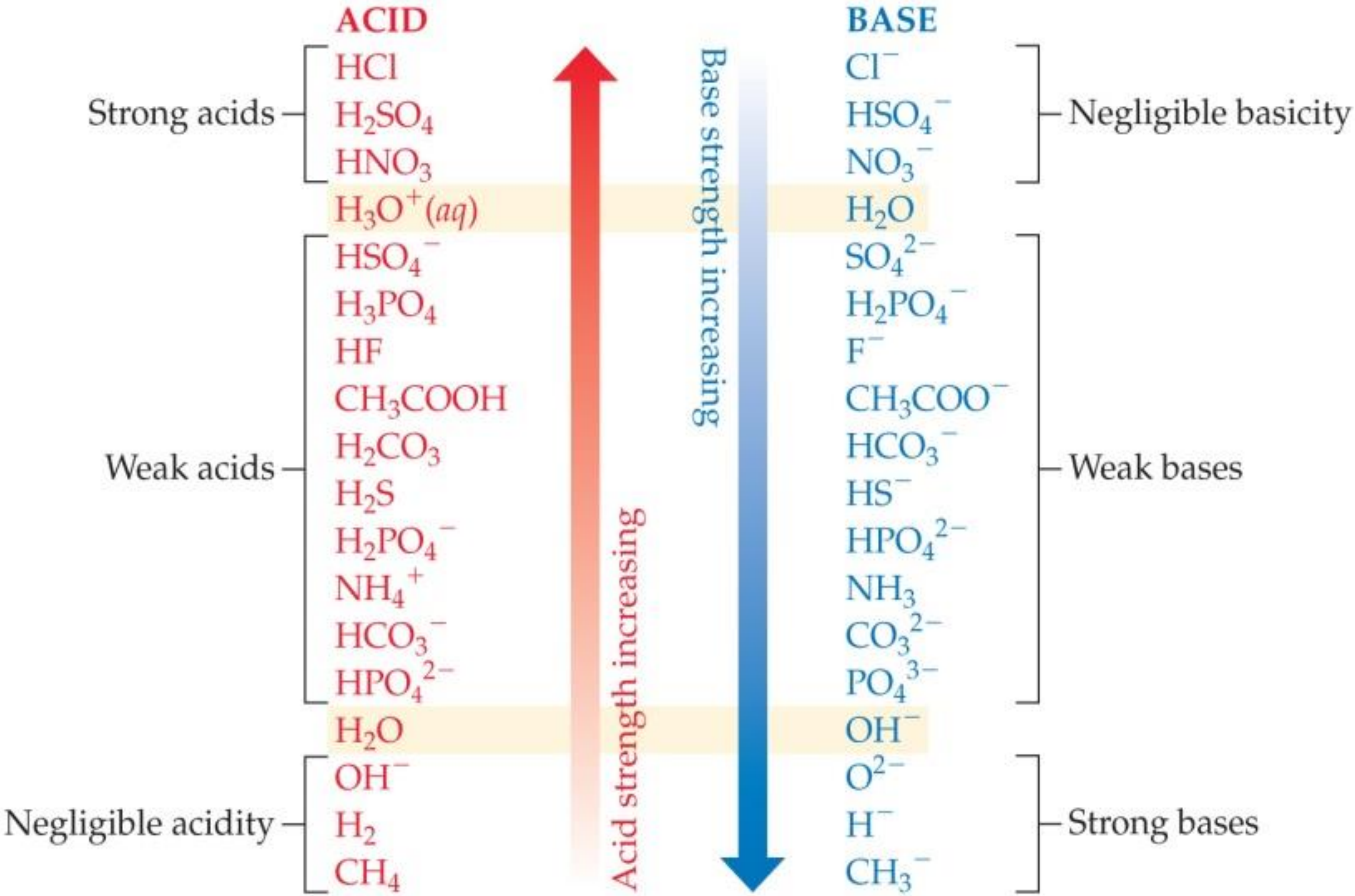
- For less accurate measurements, one can use litmus paper or an indicator



Measuring pH

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.

16.5 Strong Acids and Bases



	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^-	

Strong Acids

- The seven most common strong acids include
  - six monoprotic acids HCl, HBr, HI, HNO_3, , $HClO_3$, $HClO_4$ and
  - one diprotic acid H_2SO_4.

- They are strong electrolytes and exist totally as ions in aqueous solution.
- For the **monoprotic strong acids**,

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

Example: In a 0.20 M solution of HNO_3(aq), $[H^+] = [NO_3^-] = 0.20$ M

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+}).
- These substances dissociate completely in aqueous solution.

EXAMPLE

What is the pH of

(a) a 0.040 M solution of $HClO_4$

Because $HClO_4$ is a strong acid, it is completely ionized in water, giving $[H^+] = [ClO_4^-] = 0.040$ M

$$\mathrm{pH} = -\log(0.040) = 1.40$$

(b) a 0.0011 M solution of $Ca(OH_2)$

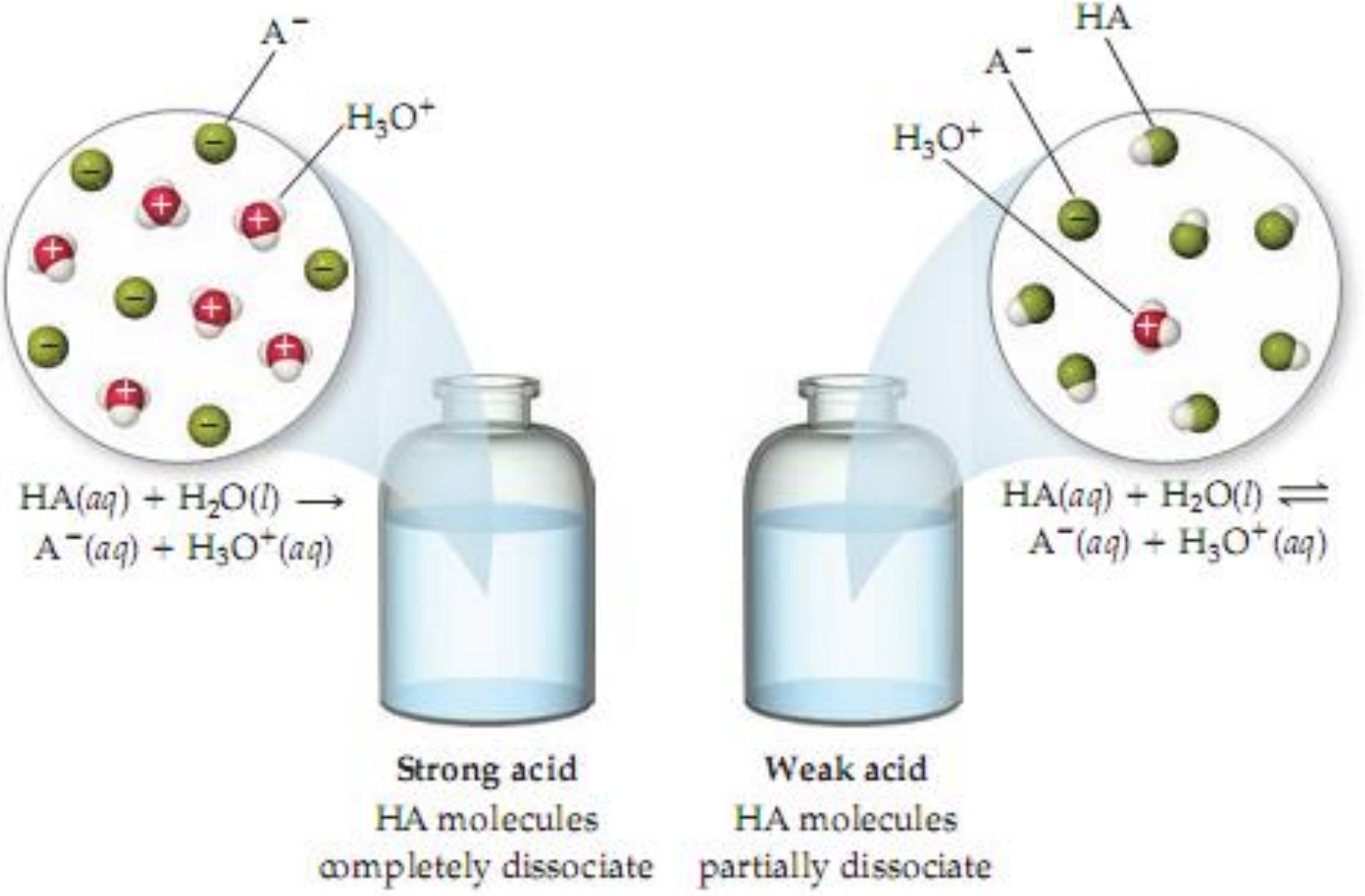
$Ca(OH_2)$ is a strong base that dissociates in water to give two OH^- ions per formula unit, giving $[OH^-] = 2 \times 0.0011 = 0.0022$ M

$$\mathrm{pOH} = -\log(0.0022) = 2.66$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 11.34$$

16-6 Weak Acids

- Most acidic substances are weak acids and therefore only partially ionized in aqueous solution



Dissociation Constants

- For a generalized acid dissociation,

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

the equilibrium expression would be

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

- This equilibrium constant is called the **acid-dissociation constant**, K_a.

Dissociation Constants

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

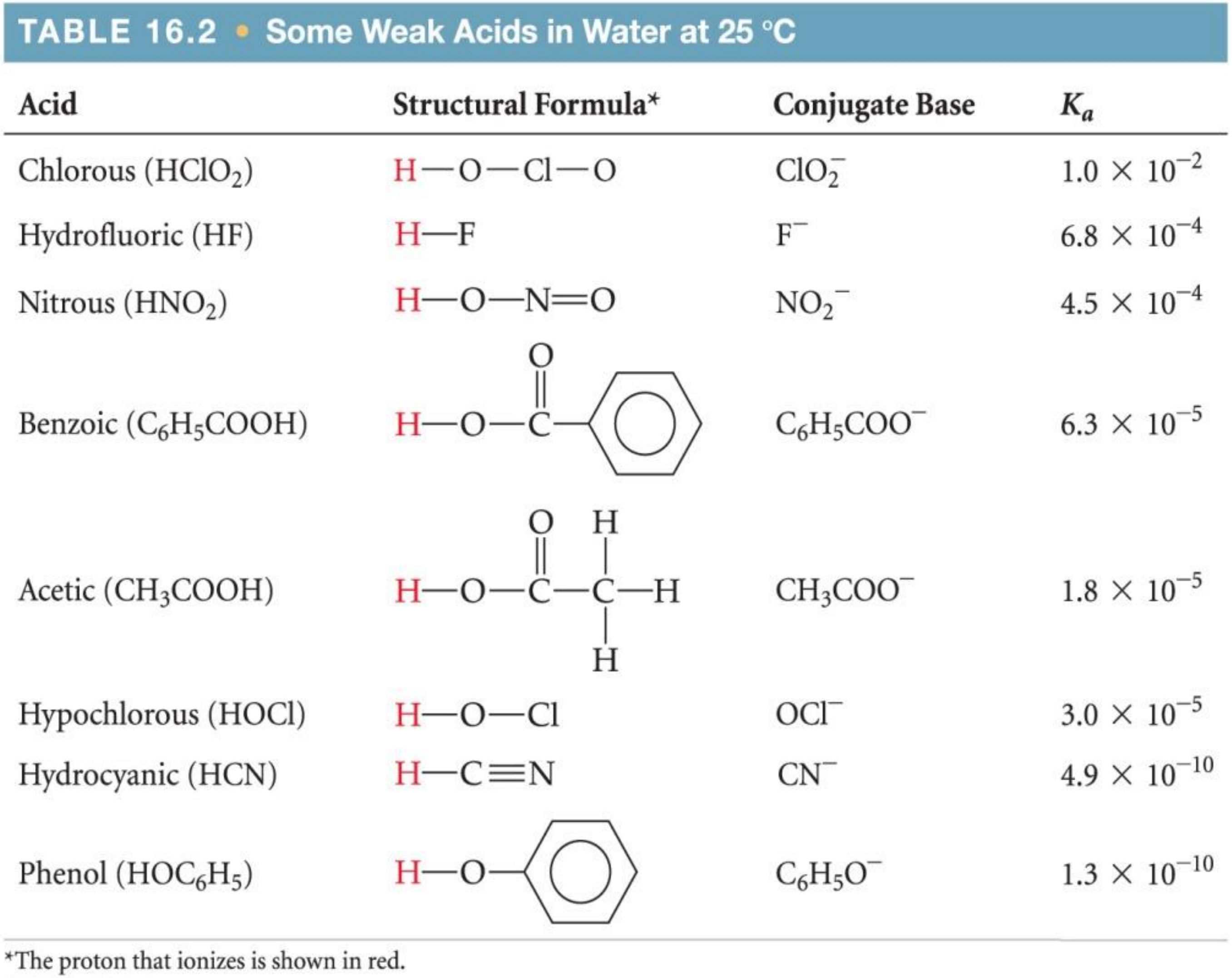


TABLE 16.2 • Some Weak Acids in Water at 25 °C

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)	$H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}$	$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)	$H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}H$	CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$H{-}O{-}Cl$	OCl^-	3.0×10^{-5}
Hydrocyanic (HCN)	$H{-}C{\equiv}N$	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.

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

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

$$pH = -\log[H^+] = 2.38$$

$$\log[H^+] = -2.38$$

$$[H^+] = 10^{-2.38} = 4.2 \times 10^{-3}\ M$$

The dissociation equation: $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$

Using the ICE chart

I	0.10	0	0
C			
E			

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{(0.10 - 4.2 \times 10^{-3})} = 1.8 \times 10^{-4}$$

Percent Ionization

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

- In this example,

I	0.10	0	0
C	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
E	$0.10 - 4.2 \times 10^{-3}$	4.2×10^{-3}	4.2×10^{-3}

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

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

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

Calculating pH from K_a

1. Write the ionization equilibrium
2. Write the equilibrium-constant expression and the value for the equilibrium constant
3. Express the concentrations involved in the equilibrium reaction using ICE chart
4. Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for change in concentration
5. Calculate pH

Calculating pH from K_a

Calculate the pH of a 0.30 M solution of acetic acid, $HC_2H_3O_2$, at 25°C. K_a for acetic acid at 25°C is 1.8×10^{-5}.

1. $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

2. $$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

3. $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

I	0.30	0	0
C	-x	+x	+x
E	0.30-x	x	x

4. $$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5}$$

$$x = 2.3 \times 10^{-3}\,M \quad = [H^+]$$

5. $$pH = -\log(2.3 \times 10^{-3}) = 2.64$$

EXAMPLE

Calculate the pH of a 0.20 M solution of HCN. Ka for HCN is 4.9 x 10^{-10}

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = 4.9 \times 10^{-10}$$

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

I	0.20	0	0
C	-x	+x	+x
E	0.20-x	x	x

$$K_a = \frac{(x)(x)}{0.20 - x} = 4.9 \times 10^{-10}$$

$$x = \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6}\,M = [H^+]$$

$$pH = -\log[H^+] = -\log(9.9 \times 10^{-6}) = 5.00$$

Polyprotic Acids

Polyprotic acids have more than one acidic proton.

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8}$$

- It is always easier to remove the first proton from a polyprotic acid than to remove the second. Therefore **$K_{a1} > K_{a2}$**
- For an acid with three ionizable protons, it is easier to remove the second proton than the third. Therefore, **$K_{a2} > K_{a3}$**
- If the difference between the K_a for the first dissociation and subsequent K_a values is 10^3 or more, the pH generally depends *only* on the first dissociation.

Polyprotic Acids

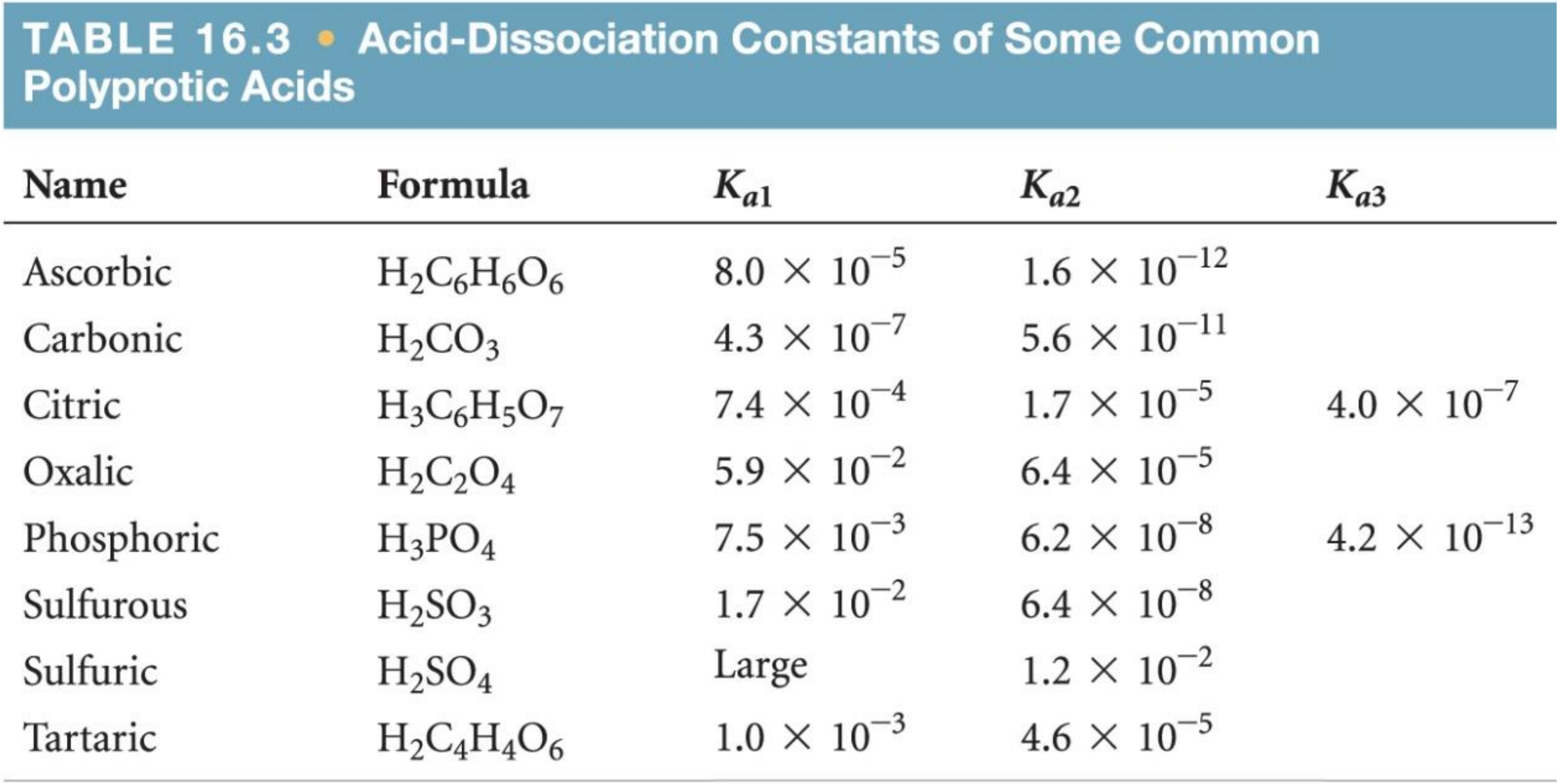


TABLE 16.3 • Acid-Dissociation Constants of Some Common Polyprotic Acids

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	$H_2C_2O_4$	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	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

EXAMPLE

The solubility of CO_2 in water at 25 °C and 0.1 atm is 0.0037 M. The common practice is to assume that all the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced in the reaction:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

(a) What is the pH of a 0.0037 M solution of H_2CO_3?

(b) What is the concentration of CO_3^{2-}

For H_2CO_3, $K_{a1} = 4.3\ x10^{-7}$, $K_{a2} = 5.6 \text{ x } 10^{-11}$

K_{a1} and K_{a2} differ by more than a factor of 10^3 the pH can be determined by considering only K_{a1}

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

I	0.0037	0	0
C	-x	+x	+x
E	0.0037-x	x	x

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

$$x = 4.0 \times 10^{-5}\ M$$

$$pH = -\log(4.0 \times 10^{-5}) = 4.40$$

EXAMPLE

	$HCO_3^-(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CO_3^{2-}(aq)$
I	4.0×10^{-5}	4.0×10^{-5}	0
C	$-y$	$+y$	$+y$
E	$4.0 \times 10^{-5} - y$	y	y

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\ M = [CO_3^{2-}]$$

16-7 Weak Bases

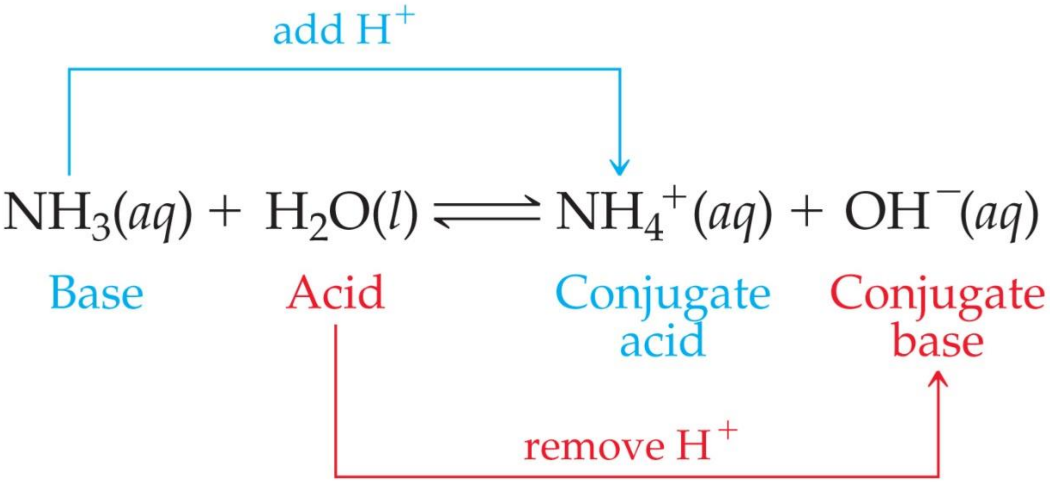
Bases react with water to produce hydroxide ion.

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

The equilibrium constant expression for this reaction is

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

K_b is the base-dissociation constant



add H^+

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

Base

Acid

Conjugate acid

Conjugate base

remove H^+

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

K_b can be used to find $[OH^-]$ and, through it, pH.

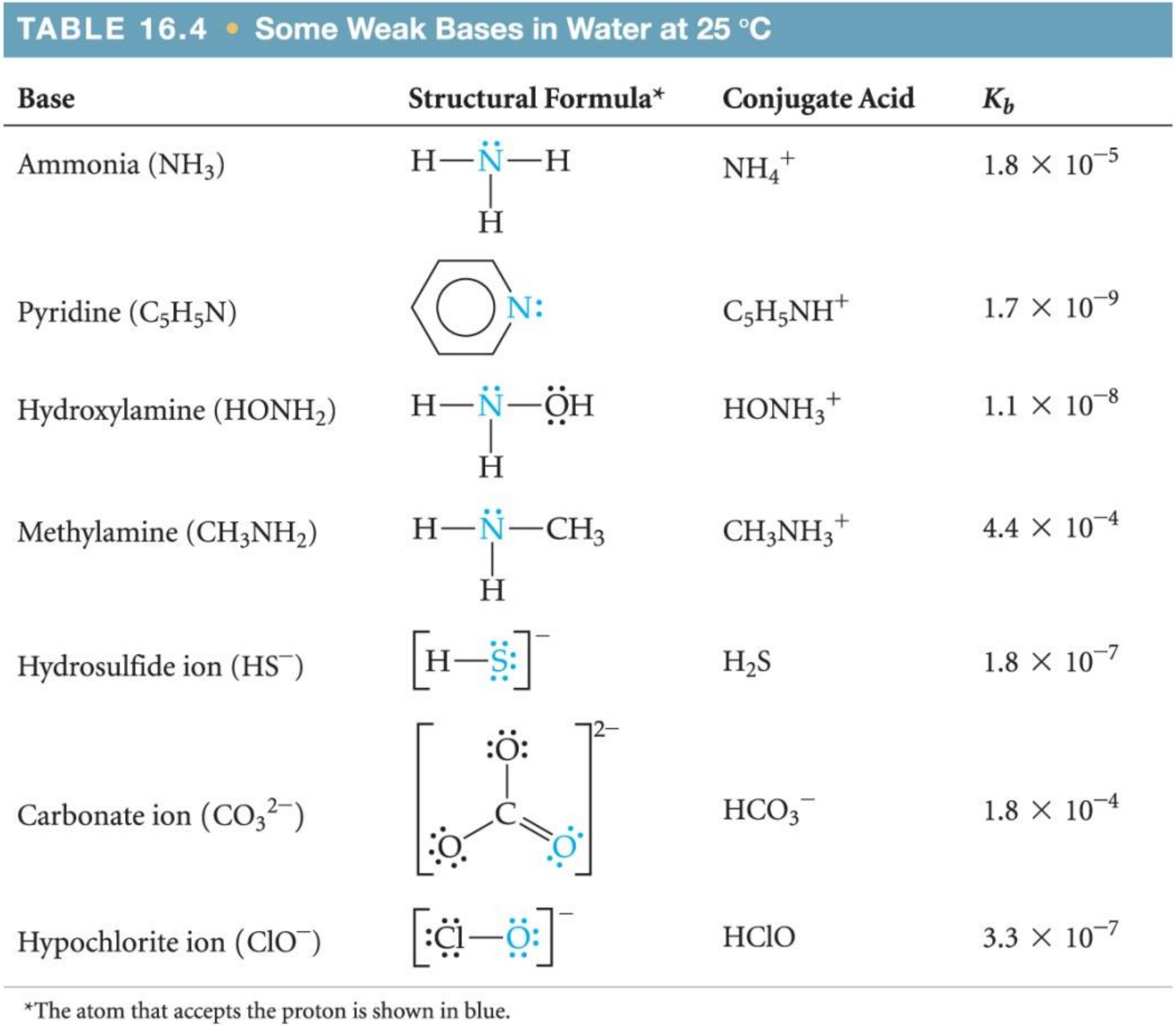


TABLE 16.4 • Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)	$\mathrm{H{-}\ddot{N}{-}H}$ H	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)	N:	$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)	$\mathrm{H{-}\ddot{N}{-}\ddot{O}H}$ H	$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)	$\mathrm{H{-}\ddot{N}{-}CH_3}$ H	$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$[\mathrm{H{-}\ddot{S}:}]^-$	H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})	$\left[\begin{array}{c} :\ddot{O}: \\ \mid \\ C \\ :\ddot{O}\quad \ddot{O} \end{array}\right]^{2-}$	HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$[:\ddot{Cl}{-}\ddot{O}:]^-$	HClO	3.3×10^{-7}

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

EXAMPLE

What is the pH of a 0.15 *M* solution of NH_3? For NH_3, $K_b = 1.8 \text{ x } 10^{-5}$

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

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

	$NH_3(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$NH_4^+(aq)$ +	OH^-
I	0.15		0	0
C	-x		+x	+x
E	0.15-x		x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.15 - x} = 1.8 \times 10^{-5}$$

$$x = [NH_4^+] = [OH^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3}\ M$$

$$pOH = -\log(1.6 \times 10^{-3}) = 2.80$$

$$pH = 14.00 - 2.80 = 11.20.$$

16-8 Relationship Between K_a and K_b

The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water:

$$K_a \text{ x } K_b = K_w$$

$$pK_a + pK_b = pK_w = 14 \text{ at } 25^{o}C$$

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

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

$$\begin{array}{rcl} NH_4^+(aq) & \rightleftharpoons & NH_3(aq) + H^+(aq) \\ NH_3(aq) + H_2O(l) & \rightleftharpoons & NH_4^+(aq) + OH^-(aq) \\ \hline H_2O(l) & \rightleftharpoons & H^+(aq) + OH^-(aq) \end{array}$$

$$K_a \times K_b = \left(\frac{[NH_3][H^+]}{[NH_4^+]}\right)\left(\frac{[NH_4^+][OH^-]}{[NH_3]}\right)$$

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

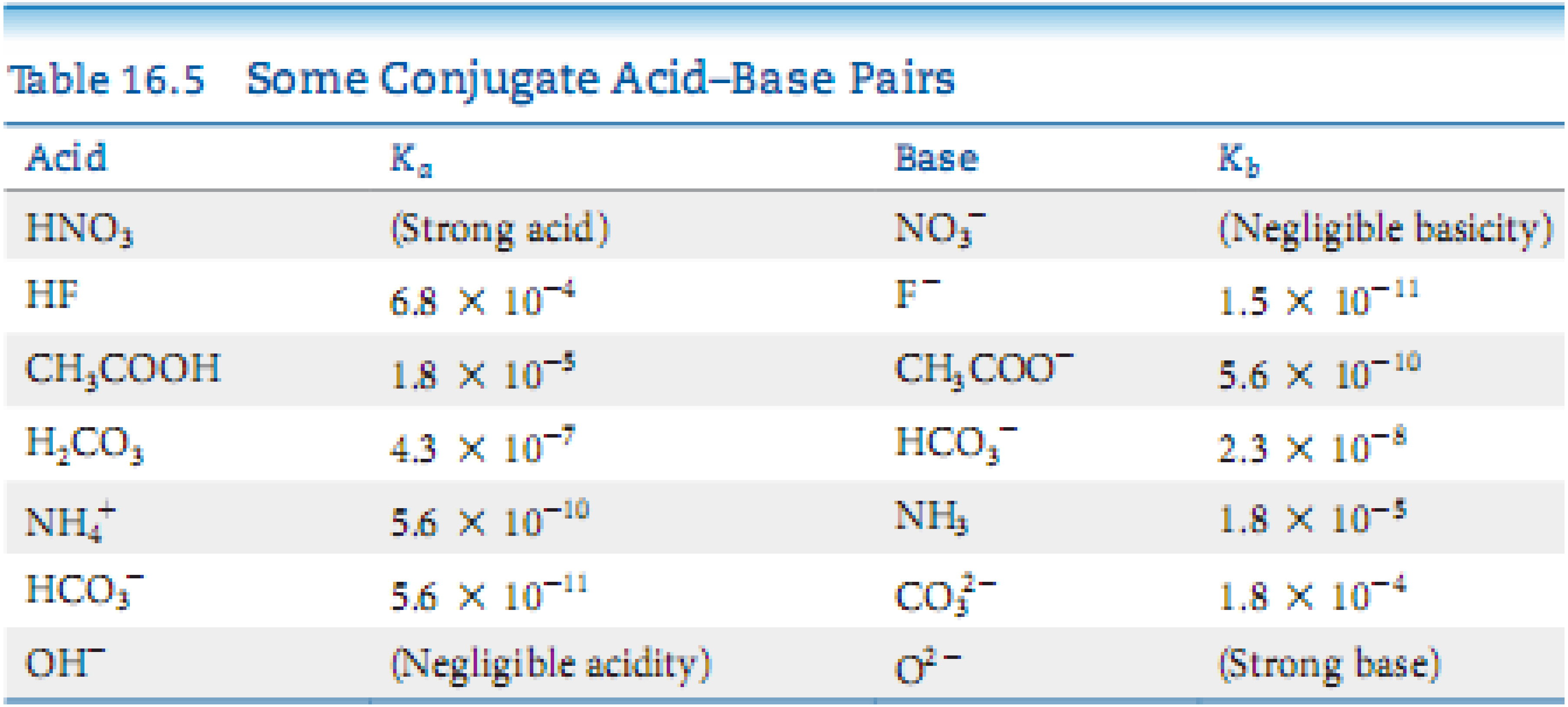


Table 16.5 Some Conjugate Acid–Base Pairs

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)

16-9 Acid–Base Properties of Salt Solutions

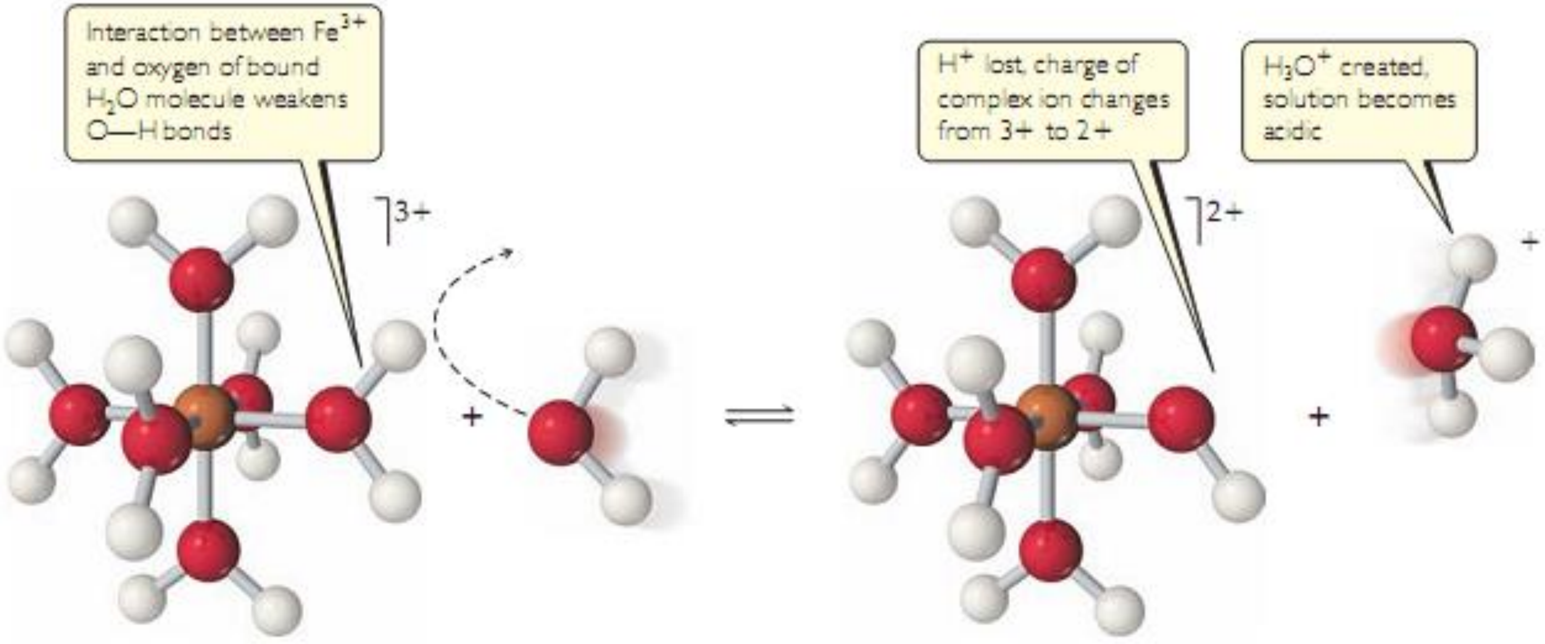
- Anions can be considered the conjugate bases of acids.
  - As such, they can react with water in a **hydrolysis reaction** to form OH$^-$ and the conjugate acid:

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

- Polyatomic cations containing one or more protons can be considered the conjugate acids of weak bases.
  - As such, they can **donate a proton to water**, producing hydronium ions and thereby lowering the pH

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

Reactions of Cations with Water



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

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

- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O–H bond more polar and the water more acidic.

Reactions of Cations with Water

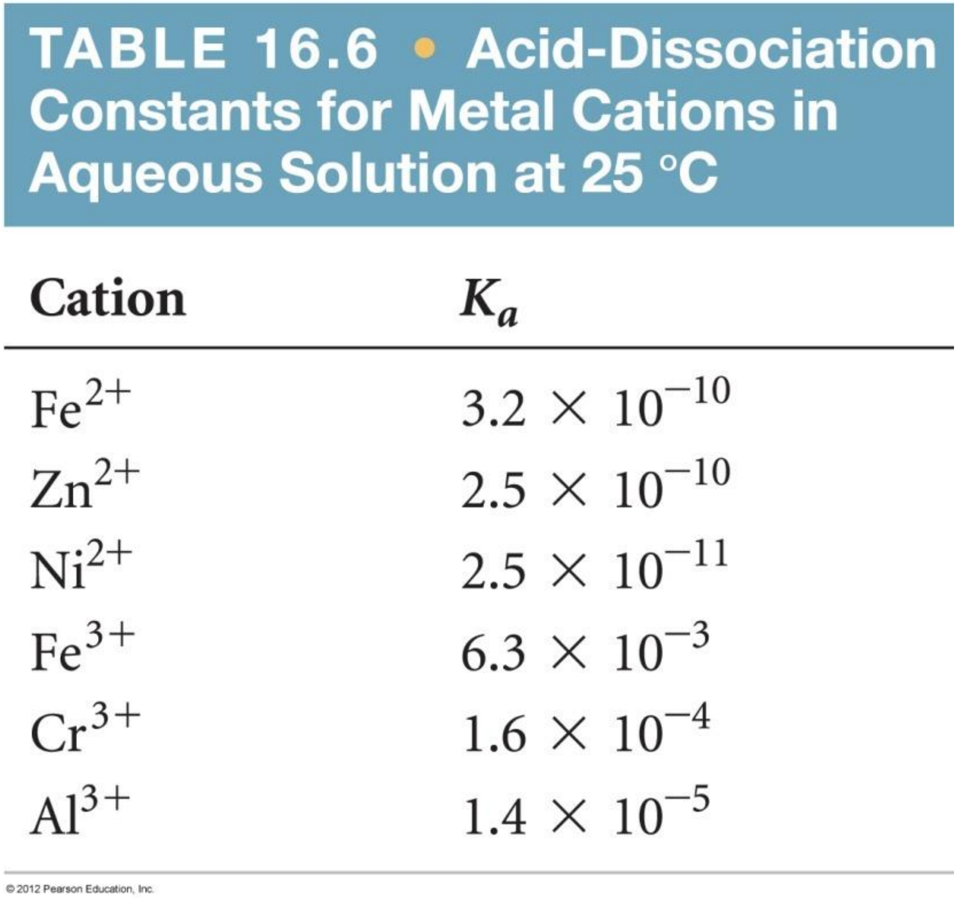


TABLE 16.6 • Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

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}

- Most metal cations that are hydrated in solution also lower the pH of the solution
- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O–H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic

Combined Effect of Cation and Anion in Solution

1. An anion that is the conjugate base of a strong acid will not affect the pH.
2. An anion that is the conjugate base of a weak acid will increase the pH.
3. A cation that is the conjugate acid of a weak base will decrease the pH.
4. Cations of the strong Arrhenius bases will not affect the pH.
5. Other metal ions will cause a decrease in pH.
6. When a solution contains both a weak acid and a weak base, the affect on pH depends on the K_a and K_b values.

EXAMPLE

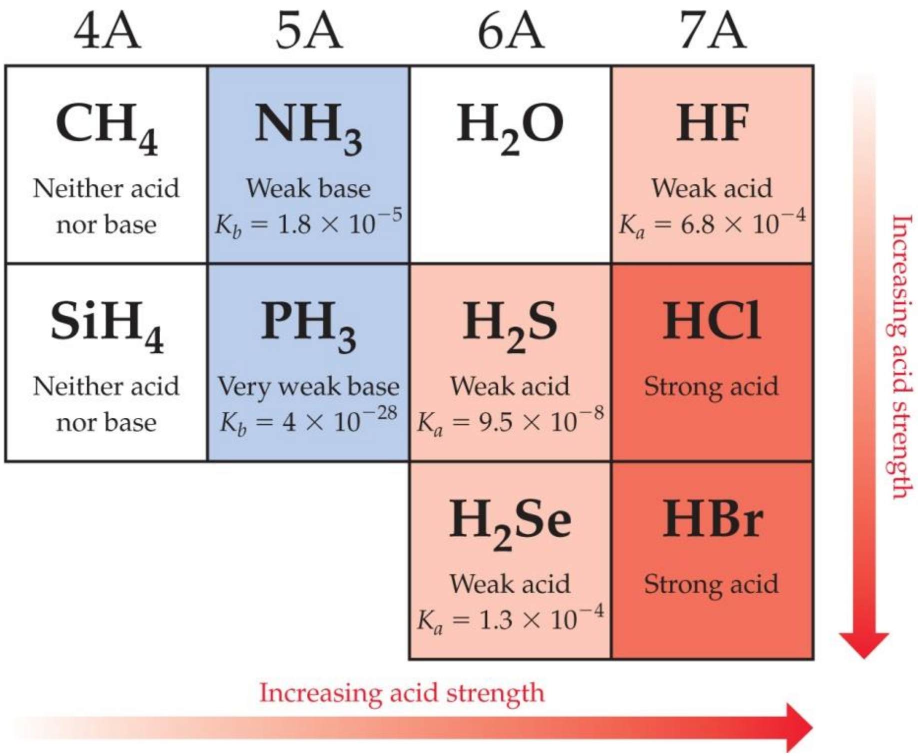
Determine whether aqueous solutions of each of these salts are acidic, basic, or neutral:

(a) $Ba(CH_3COO)_2$	**Basic**
(b) NH_4Cl	**Acidic**
(c) CH_3NH_3Br,	**Acidic**
(d) KNO_3,	**Neutral**
(e) $Al(ClO_4)_3$	**Acidic**

16-10 Acid–Base Behavior and Chemical Structure

Factors Affecting Acid Strength

- The more polar the H–X bond the more acidic the compound
- The weaker the H–X bond, the more acidic the compound.
- The greater the stability of the conjugate base, the stronger the acid.



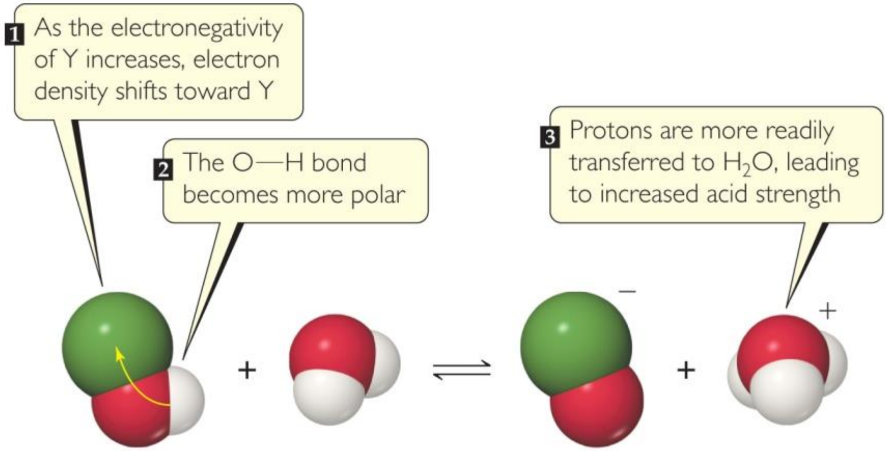
4A	5A	6A	7A
CH_4 Neither acid nor base	**NH_3** Weak base $K_b = 1.8 \times 10^{-5}$	**H_2O**	**HF** Weak acid $K_a = 6.8 \times 10^{-4}$
SiH_4 Neither acid nor base	**PH_3** Very weak base $K_b = 4 \times 10^{-28}$	**H_2S** Weak acid $K_a = 9.5 \times 10^{-8}$	**HCl** Strong acid
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	**HBr** Strong acid

Binary Acids

- As the element A increases in size ➔ The strength of an H – A bond tends to decrease ➔ The acidity **increases down a group**
  - HCl is a stronger acid than HF
  - H_2S is a stronger acid than H_2O
- Bond polarity is the major factor determining acidity: acidity increases as the electronegativity of the element A increases
  - C – H bond is essentially nonpolar, CH_4 shows no tendency to form H^+ and CH_3^- ions.
  - N – H bond is polar, but NH_3 has a lone pair of electrons on the nitrogen atom that dominates its chemistry, so NH_3 acts as a base rather than an acid

Oxyacids

In oxyacids, in which an –OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.



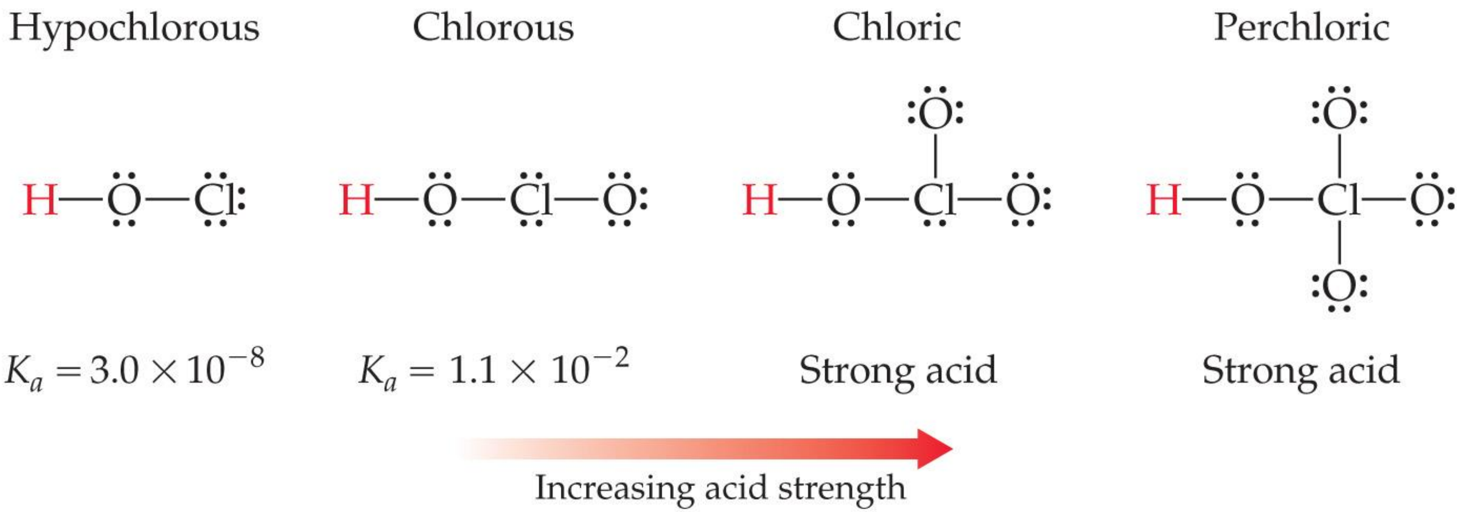
1 As the electronegativity of Y increases, electron density shifts toward Y

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	$K_w = 1.0 \times 10^{-14}$

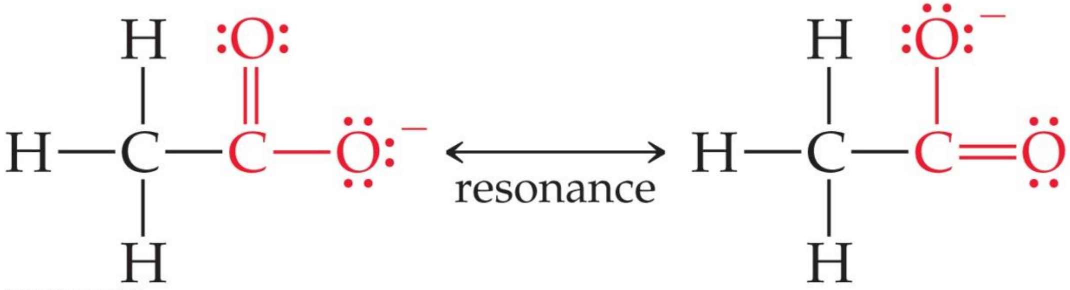
Oxyacids



For a series of oxyacids, acidity increases with the number of oxygens.

Carboxylic Acids

Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.



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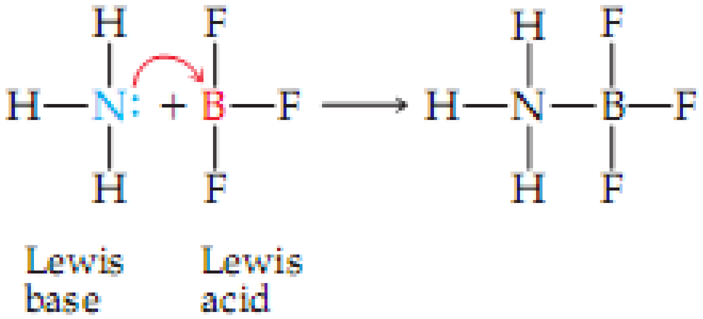
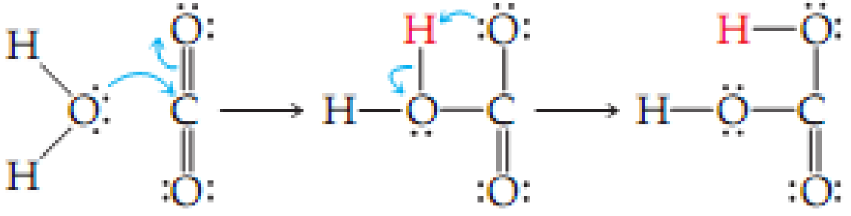
16.11 | Lewis Acids and Bases

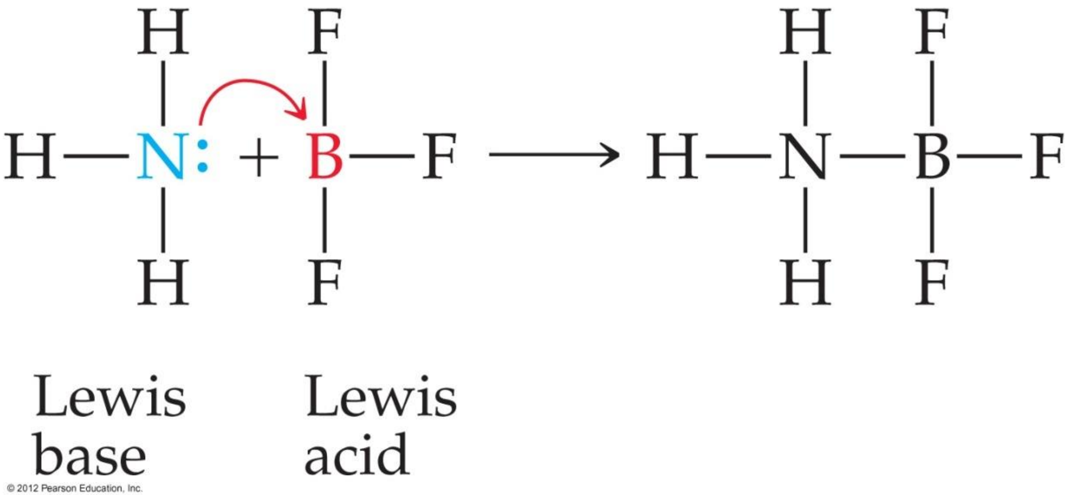


- **Lewis acids** are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.

$$Fe^{3+} + 6[:C\equiv N:]^{-} \longrightarrow [Fe(C\equiv N:)_6]^{3-}$$



Lewis Bases



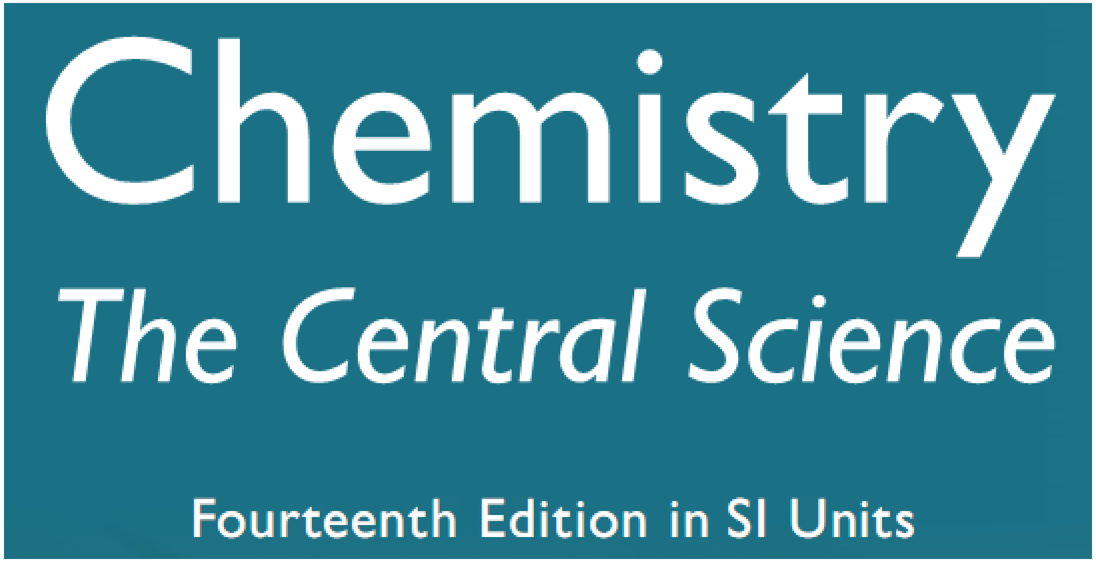
- **Lewis bases** are defined as electron-pair donors.
- Anything that could be a Brønsted–Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.

Homeworks

16.119

16.126

Due: August 14th 2019



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It's a quick reminder that Group 1 and Group 2 will present their research topics on Wednesday August 14th 2019