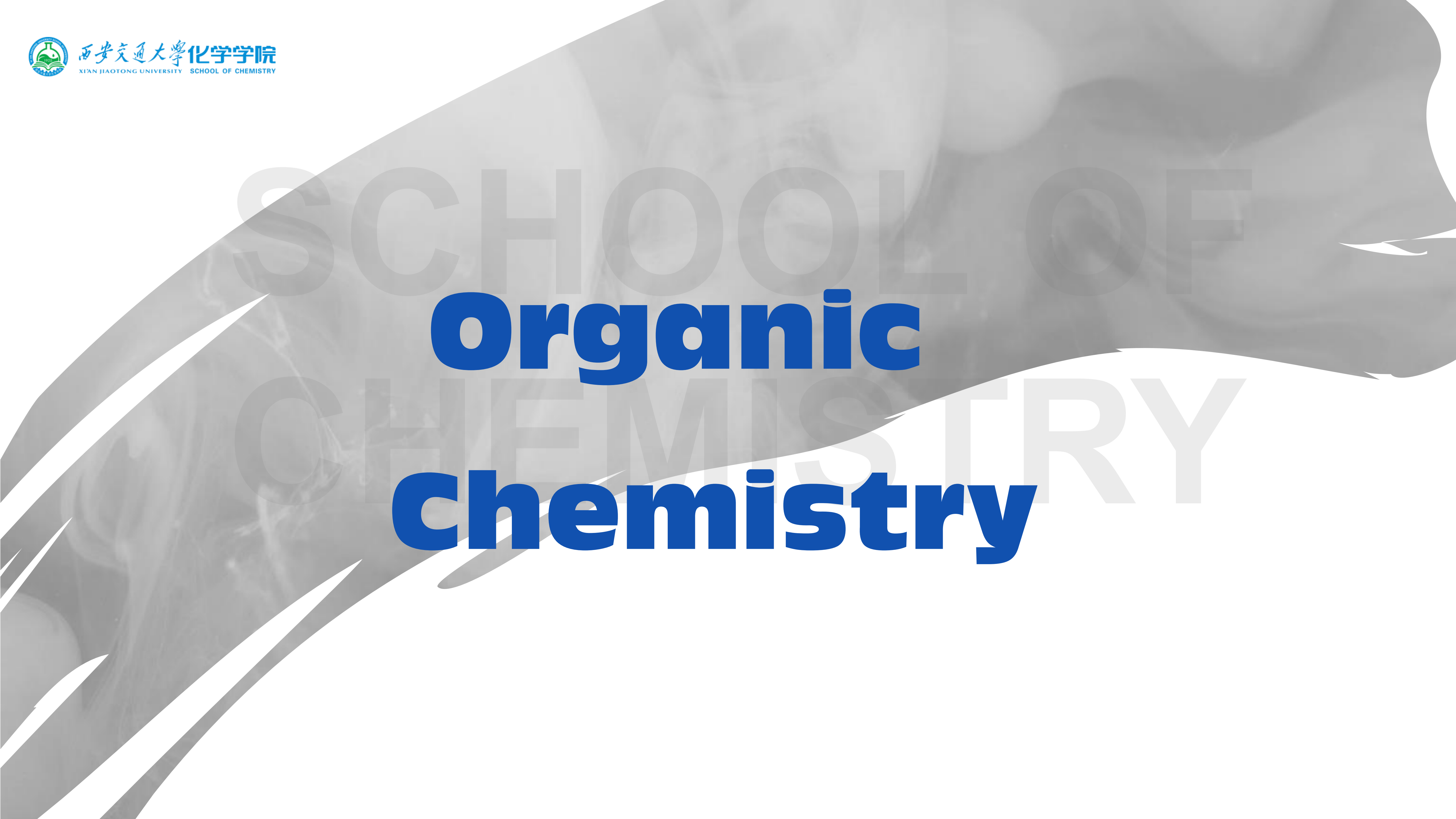
西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY



SCHOOL OF CHEMISTRY

Organic Chemistry

Chapter 2

Basic theory(4)

Acids and Bases

1.What Are Arrhenius Acids and Bases?

2. What Are Brønsted–Lowry Acids and Bases?

3. How Do We Measure the Strength of an Acid or Base?

4. How Do We Determine the Position of Equilibriumin an Acid–Base Reaction?

5. What Are the Relationships between Acidity and Molecular Structure?

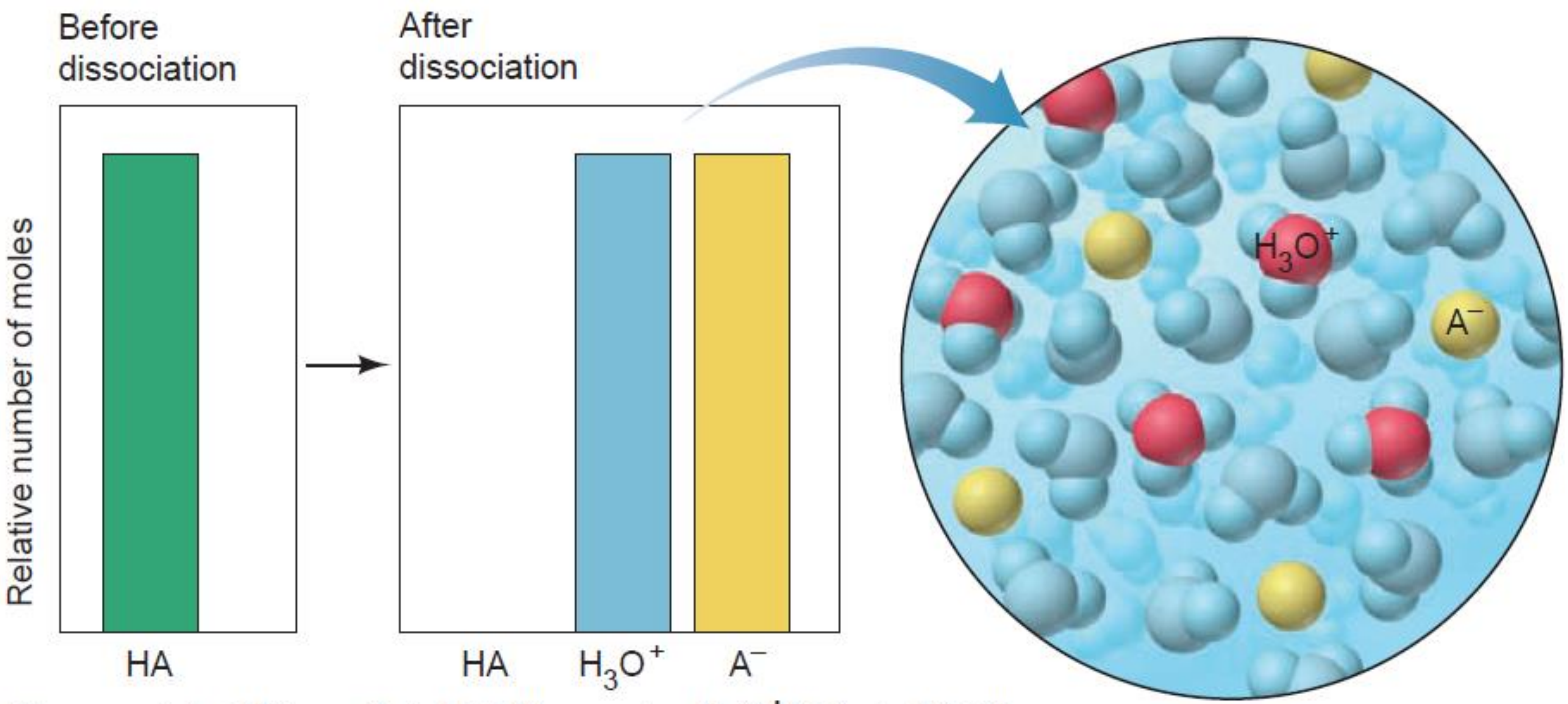
6. What Are Lewis Acids and Bases?

2.1 What are arrhenius acids and Bases?（酸碱电离理论）

- ✓ The first useful definitions of an acid and a base were put forward by Svante Arrhenius(1859–1927) in 1884; Nobel Prize in Chemistry 1903.
- ✓ According to the original Arrhenius definitions, an acid is asubstance that dissolves in water to produce H^+ , and a base is a substance that dissolves in water to produce OH^-.

$$H^+(aq) + H_2O(l) \longrightarrow \underset{\text{Hydronium ion}}{H_3O^+(aq)}$$

S. A. Arrhenius
(1859~1927)，瑞典，1903
年诺贝尔化学奖

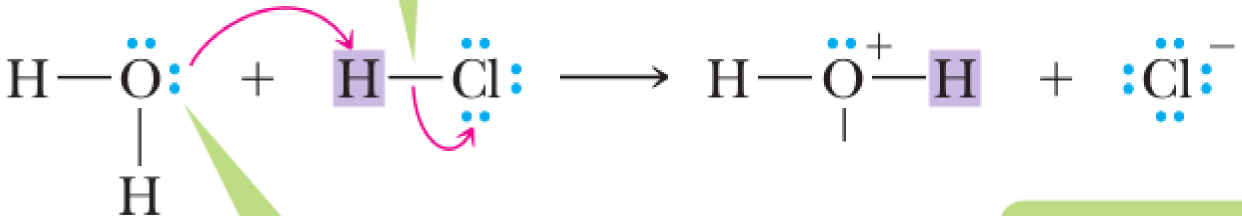


Strong acid: $HA(g \text{ or } l) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$

FIGURE 18.2 The extent of dissociation for strong acids. The bar graphs show the relative numbers of moles of species before *(left)* and after *(right)* acid dissociation occurs. When a strong acid dissolves in water, it dissociates completely, yielding $H_3O^+(aq)$ and $A^-(aq)$ ions; virtually no HA molecules are present.

Use Curved arrows to Show the transfer of a proton from an acid to a Base

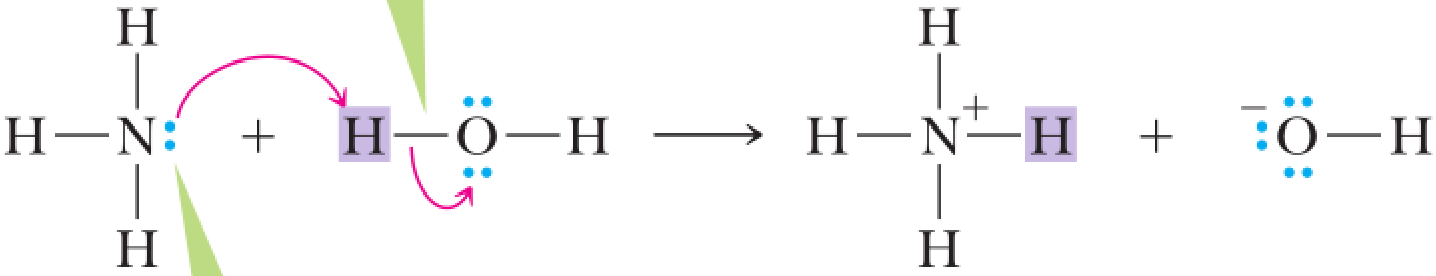
this pair of electrons is given to chlorine to form chloride ion



$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

this electron pair is used to form a new O—H bond

this curved arrow orginates at a bonding pair of electrons and points to an atom. The result is a new lone pair of electrons



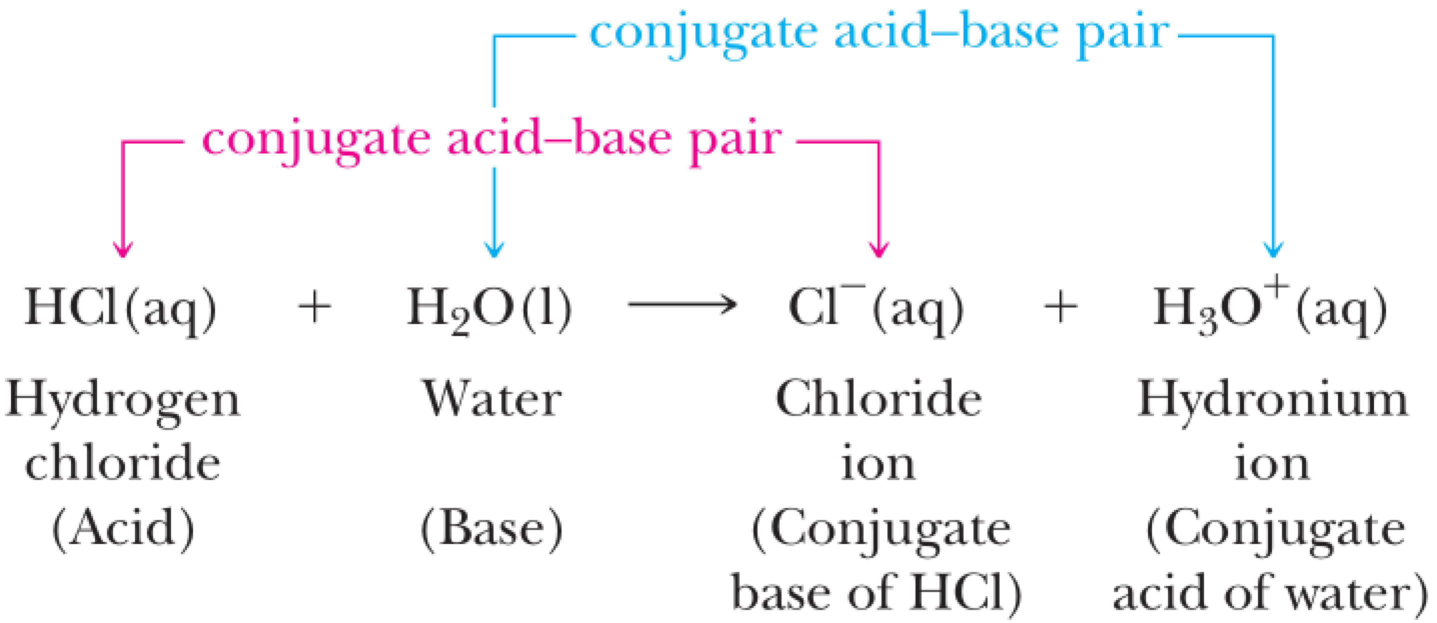
$$NH_3 + H_2O \longrightarrow NH_4^+ + {}^-OH$$

this curved arrow orginates at a lone pair and results in the formation of a new bond

2.2 What Are Brønsted–Lowry Acids and Bases?（酸碱质子理论）

In 1923, chemist Johannes Brønsted Thomas Lowry independently proposed the following definitions:

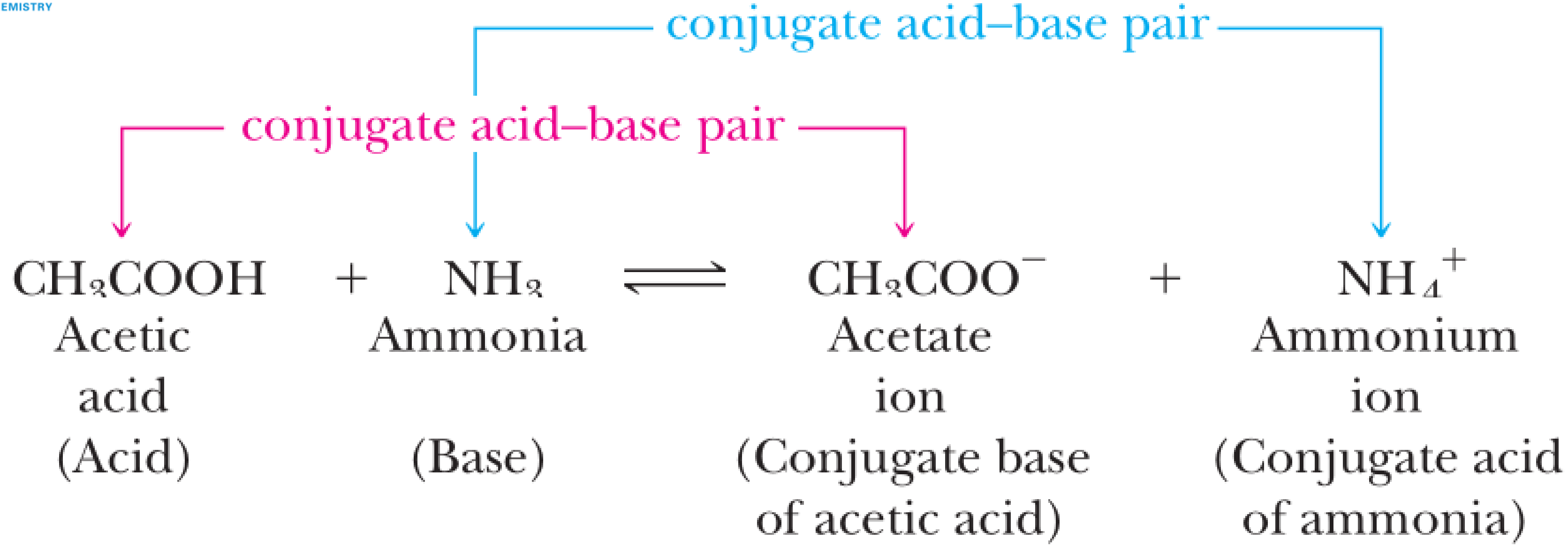
- ✓ **An acid is a proton donor, a base is a proton acceptor, and an acid–base reaction is a proton-transfer reaction.**
- ✓ any pair of molecules or ions that can be interconverted by the transfer of a proton is called **a conjugate acid–base pair.**


conjugate acid–base pair
conjugate acid–base pair

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

Hydrogen chloride (Acid)	Water (Base)	Chloride ion (Conjugate base of HCl)	Hydronium ion (Conjugate acid of water)


布朗斯特,丹,1879~1947

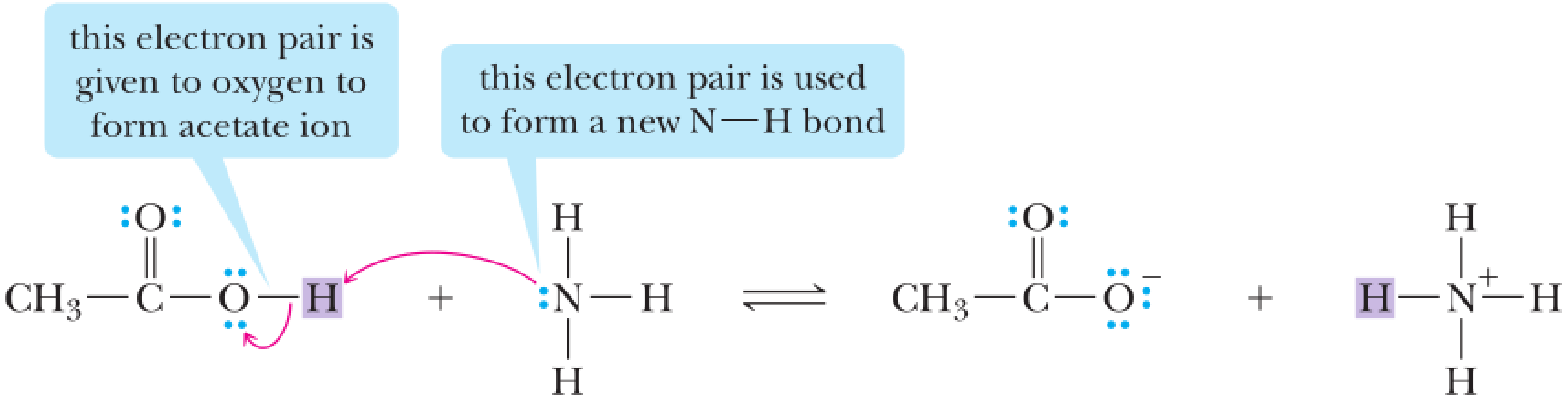


conjugate acid–base pair

conjugate acid–base pair

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

CH_3COOH	NH_3	CH_3COO^-	NH_4^+
Acetic acid	Ammonia	Acetate ion	Ammonium ion
(Acid)	(Base)	(Conjugate base of acetic acid)	(Conjugate acid of ammonia)



this electron pair is given to oxygen to form acetate ion

this electron pair is used to form a new N—H bond

Acetic acid (proton donor) + Ammonia (proton acceptor) ⇌ Acetate ion + Ammonium ion

2.3 how Do We Measure the Strength of an acid or Base?

The equation for the ionization of a weak acid, HA, in water and the acid ionization constant K_a for this equilibrium are, respectively,

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^-} + \mathrm{H_3O^+}$$

$$K_a = K_{eq}[\mathrm{H_2O}] = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$pK_a = -\log_{10} K_a$$

Ethanol, $K_a = 1.3 \times 10^{-16}$
Carbonic acid, $K_a = 4.4 \times 10^{-7}$

Ethanol, $pK_a = 15.9$
Carbonic acid, $pK_a = 6.36$

the weaker the acid, the stronger is its conjugate base

the stronger the acid, the weaker is its conjugate base

TABLE 2.2 pK_a Values for Some Organic and Inorganic Acids

	Acid	Formula	pK_a	Conjugate Base	
Weaker acid	ethane	CH_3CH_3	51	$CH_3CH_2^-$	Stronger base
	ammonia	NH_3	38	NH_2^-	
	ethanol	CH_3CH_2OH	15.9	$CH_3CH_2O^-$	
	water	H_2O	15.7	HO^-	
	methylammonium ion	$CH_3NH_3^+$	10.64	CH_3NH_2	
	bicarbonate ion	HCO_3^-	10.33	CO_3^{2-}	
	phenol	C_6H_5OH	9.95	$C_6H_5O^-$	
	ammonium ion	NH_4^+	9.24	NH_3	
	carbonic acid	H_2CO_3	6.36	HCO_3^-	
	acetic acid	CH_3COOH	4.76	CH_3COO^-	
	benzoic acid	C_6H_5COOH	4.19	$C_6H_5COO^-$	
	phosphoric acid	H_3PO_4	2.1	$H_2PO_4^-$	
	hydronium ion	H_3O^+	−1.74	H_2O	
	sulfuric acid	H_2SO_4	−5.2	HSO_4^-	
	hydrogen chloride	HCl	−7	Cl^-	
	hydrogen bromide	HBr	−8	Br^-	
Stronger acid	hydrogen iodide	HI	−9	I^-	Weaker base

2.4 How Do We Determine the Position of Equilibrium in an Acid–Base Reaction?

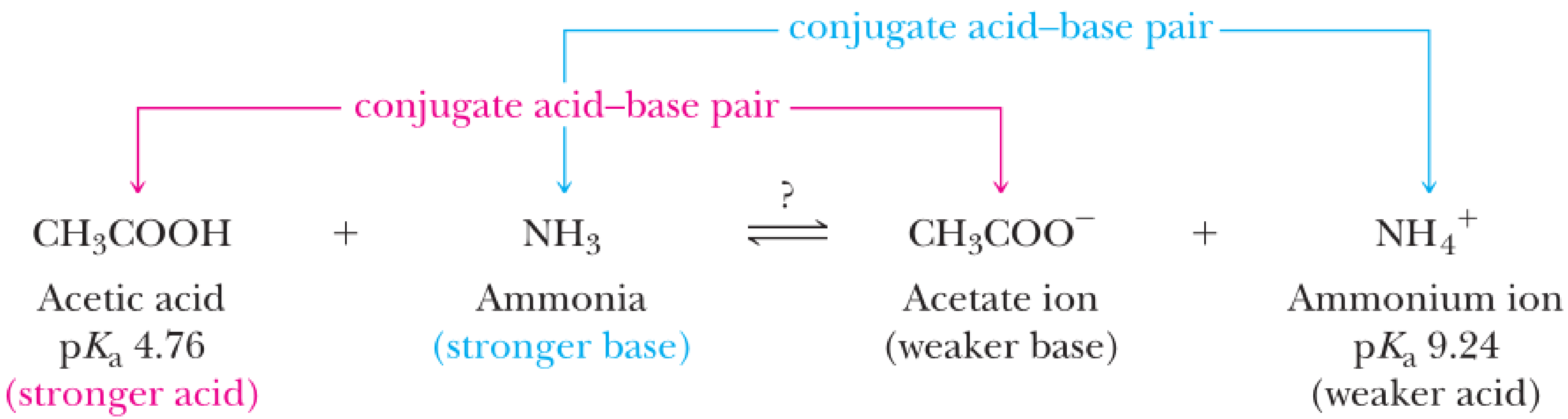
Strong acid $HCl + H_2O \longrightarrow Cl^- + H_3O^+$

Weak acid $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Acetic acid		Acetate ion

$$CH_3COOH + NH_3 \overset{?}{\rightleftharpoons} CH_3COO^- + NH_4^+$$

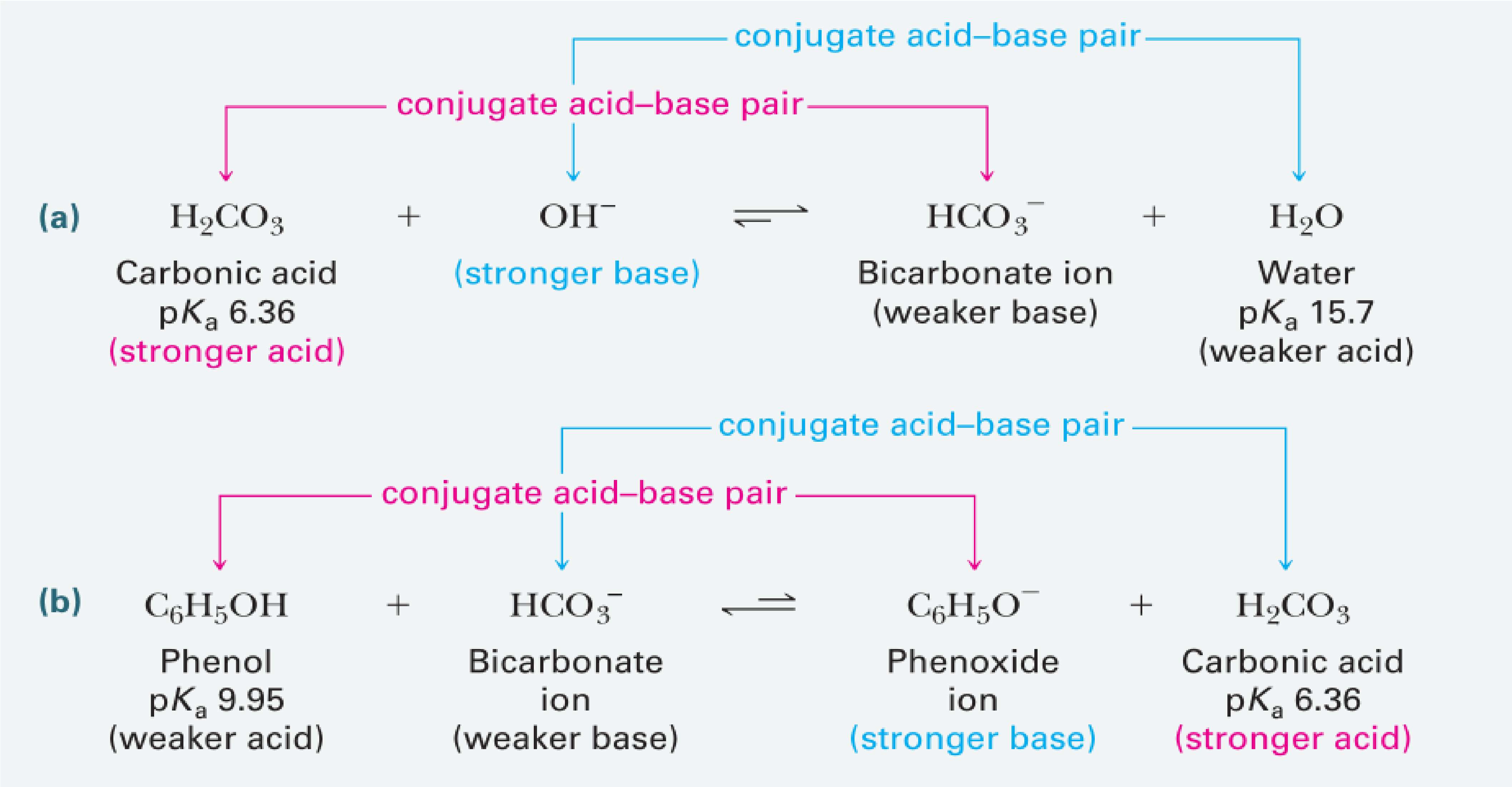
CH_3COOH	NH_3	CH_3COO^-	NH_4^+
Acetic acid (Acid)	Ammonia (Base)	Acetate ion (Conjugate base of CH_3COOH)	Ammonium ion (Conjugate acid of NH_3)



$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

In an acid–base reaction, the position of equilibrium always favors reaction of the stronger acid and stronger base to form the weaker acid and weaker base. Thus, at equilibrium, the major species present are the weaker acid and weaker base. In the reaction between acetic acid and ammonia, therefore, the equilibrium lies to the right, and the major species present are acetate ion and ammonium ion:

Arrows over each equilibrium show the conjugate acid–base pairs. The position of equilibrium in (a) lies toward the right. In (b) it lies toward the left.



(a) $H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O$

H_2CO_3: Carbonic acid, pK_a 6.36 (stronger acid)

OH^-: (stronger base)

HCO_3^-: Bicarbonate ion (weaker base)

H_2O: Water, pK_a 15.7 (weaker acid)

(b) $C_6H_5OH + HCO_3^- \rightleftharpoons C_6H_5O^- + H_2CO_3$

C_6H_5OH: Phenol, pK_a 9.95 (weaker acid)

HCO_3^-: Bicarbonate ion (weaker base)

$C_6H_5O^-$: Phenoxide ion (stronger base)

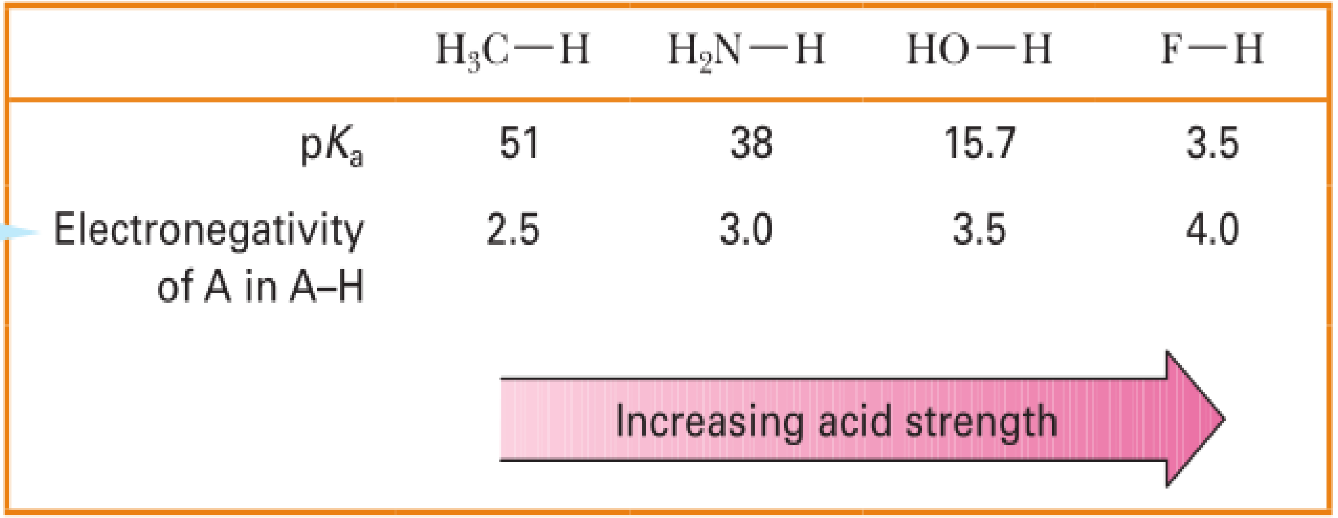
H_2CO_3: Carbonic acid, pK_a 6.36 (stronger acid)

2.5 What Are the Relationships between Acidity and Molecular Structure?

A. Electronegativity: Acidity of HA within a Period of the Periodic Table

when comparing negatively charged *atoms in the same period* of the Periodic Table, **the more electronegative the atom, the better it is at sustaining the negative charge**

电负性越强，容纳电荷能力越强



	H_3C-H	H_2N-H	$HO-H$	$F-H$
pK_a	51	38	15.7	3.5
Electronegativity of A in A–H	2.5	3.0	3.5	4.0

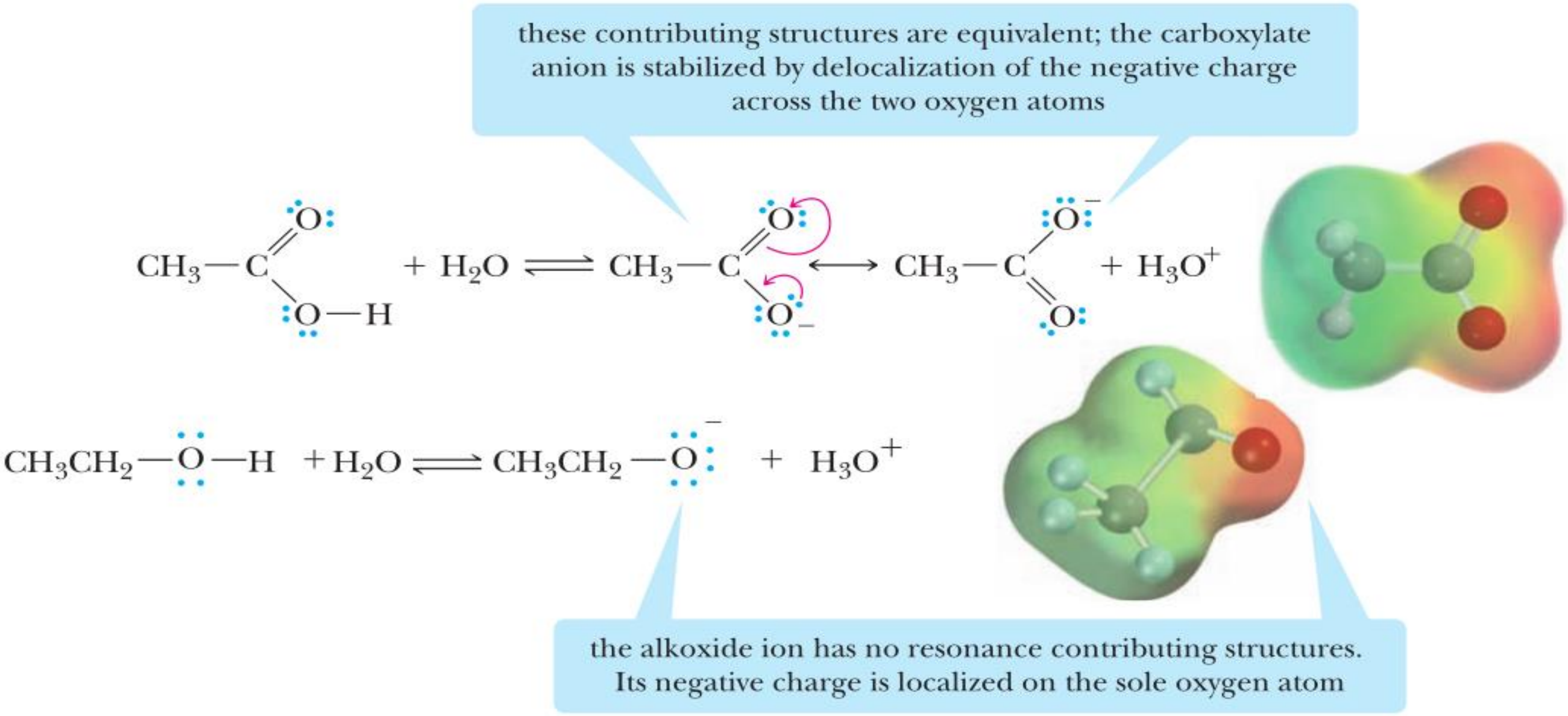
B. Resonance Effect: Delocalization of the Charge in A

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \quad pK_a = 4.76$$

A carboxylic acid — A carboxylate anion

$$CH_3CH_2O{-}H + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+ \quad pK_a = 15.9$$

An alcohol — An alkoxide ion

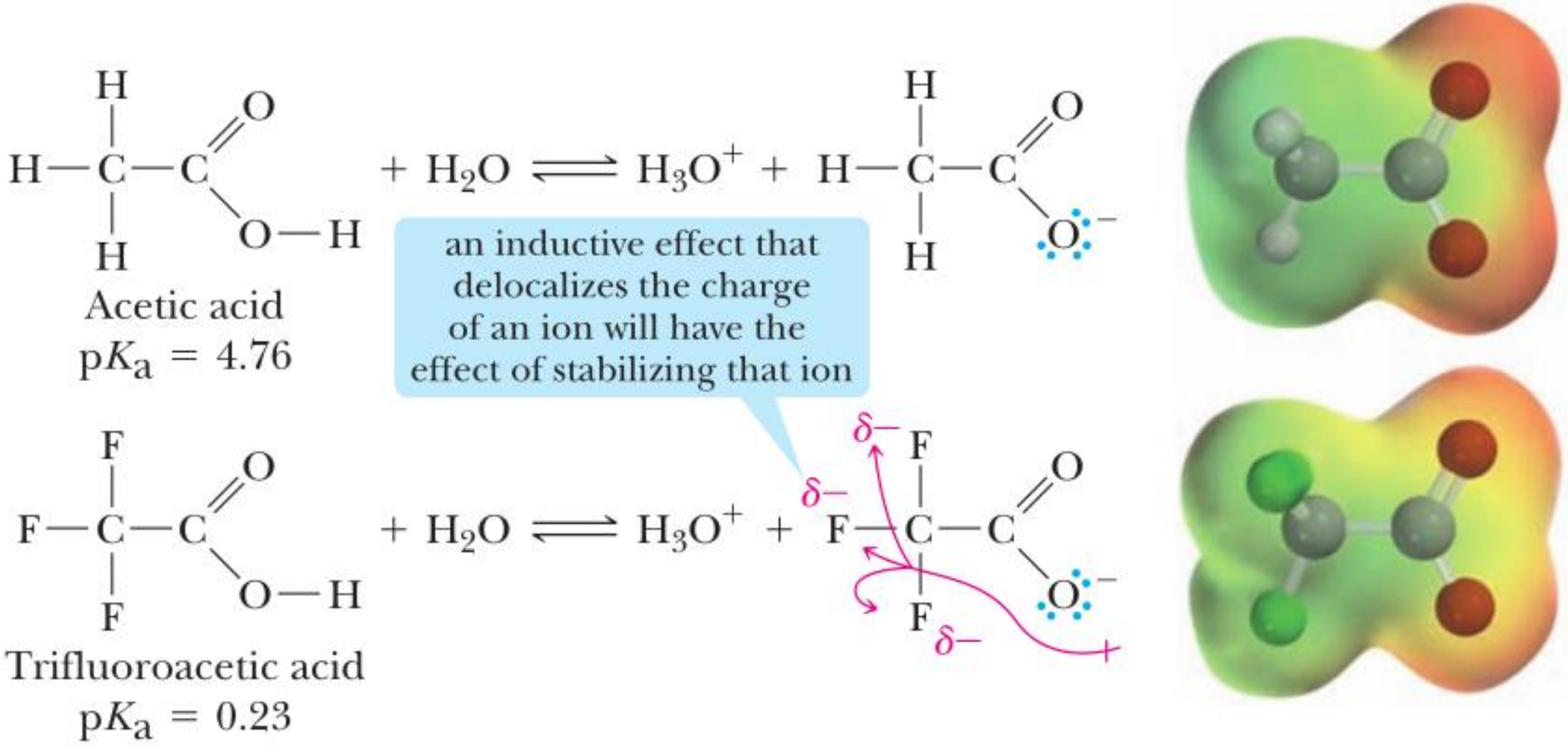


these contributing structures are equivalent; the carboxylate anion is stabilized by delocalization of the negative charge across the two oxygen atoms

the alkoxide ion has no resonance contributing structures. Its negative charge is localized on the sole oxygen atom

C. The inductive Effect: Withdrawal of Electron Density from the HA Bond

inductive effect: **（诱导效应）** The polarization of electrondensity transmitted through covalent bonds caused by a nearby atom of higher electronegativity.



$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Acetic acid
pK_a = 4.76

$$CF_3COOH + H_2O \rightleftharpoons H_3O^+ + CF_3COO^-$$

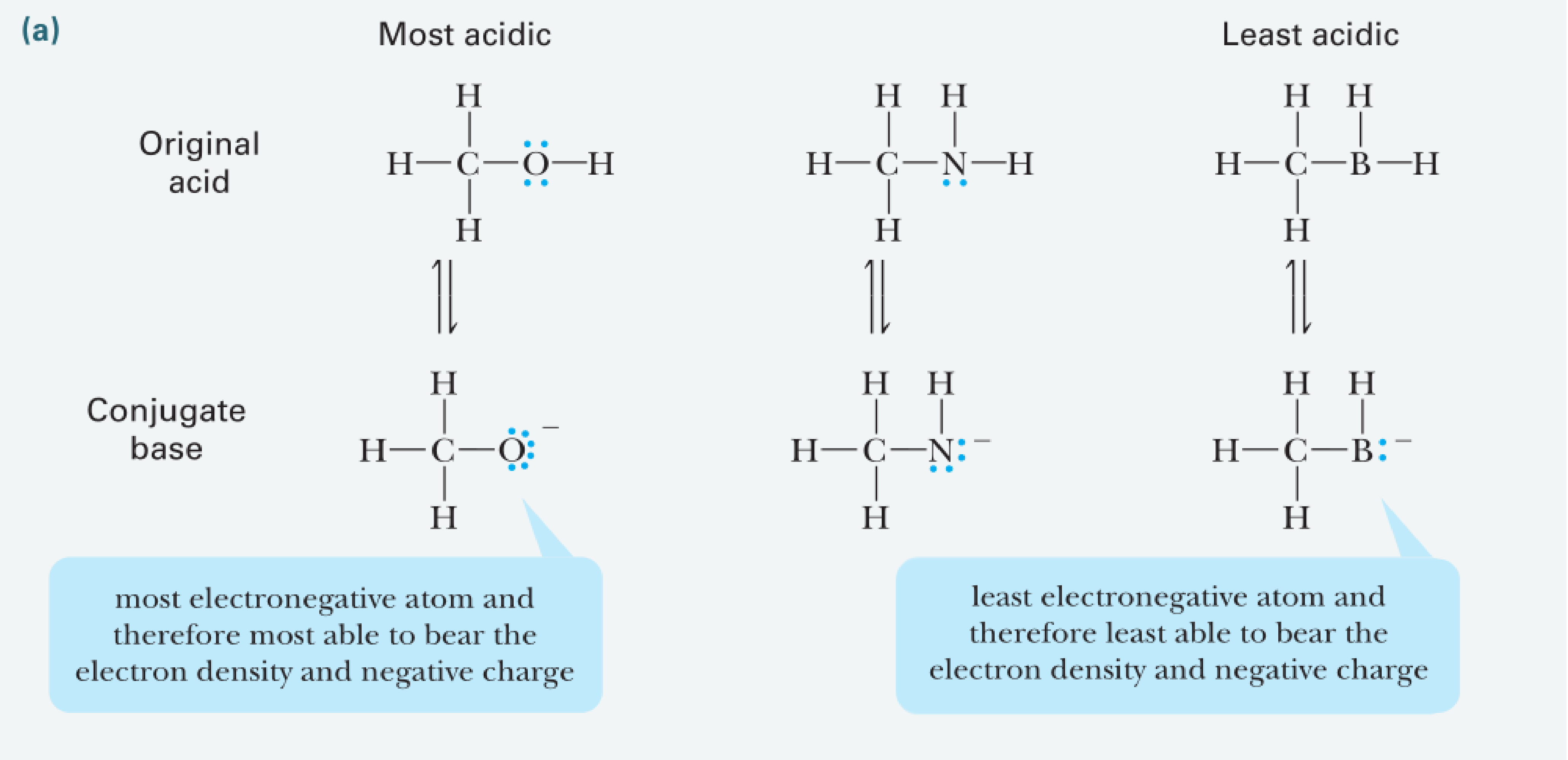
Trifluoroacetic acid
pK_a = 0.23

an inductive effect that delocalizes the charge of an ion will have the effect of stabilizing that ion

D. Size and the Delocalization of Charge in A

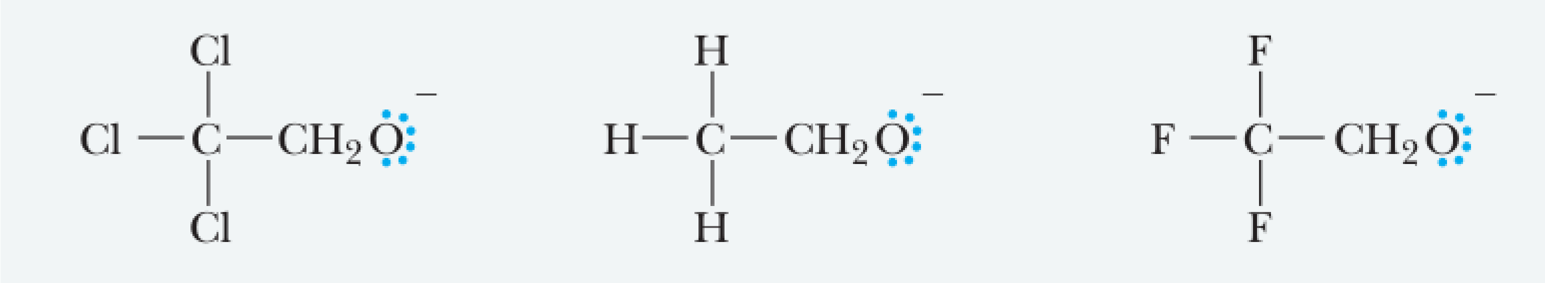
1. For main group elements, atomic radii increase going down a group in the Periodic Table and increase going across a period. $(I > Br > Cl > F)$

2. Anions are always larger than the atoms from which they are derived. $(I^- > Br^- > Cl^- > F^-)$

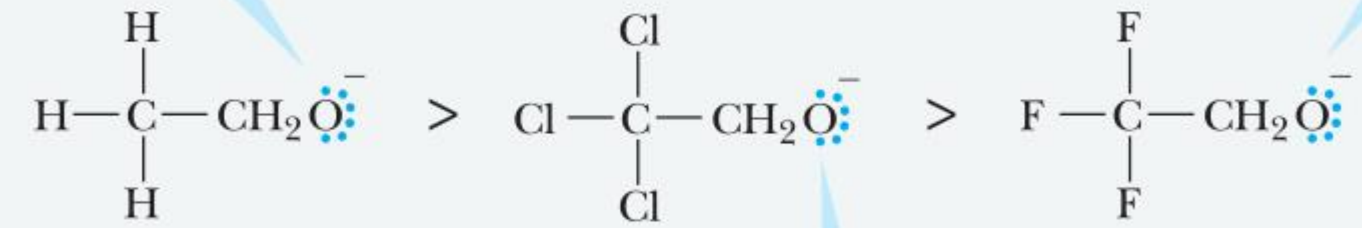


most electronegative atom and therefore most able to bear the electron density and negative charge

least electronegative atom and therefore least able to bear the electron density and negative charge



$Cl_3C{-}CH_2\ddot{O}{:}^-$ $\quad H_3C{-}CH_2\ddot{O}{:}^-$ $\quad F_3C{-}CH_2\ddot{O}{:}^-$



$H_3C{-}CH_2\ddot{O}{:}^- > Cl_3C{-}CH_2\ddot{O}{:}^- > F_3C{-}CH_2\ddot{O}{:}^-$

Most basic

Least basic

this oxygen atom has no charge delocalization

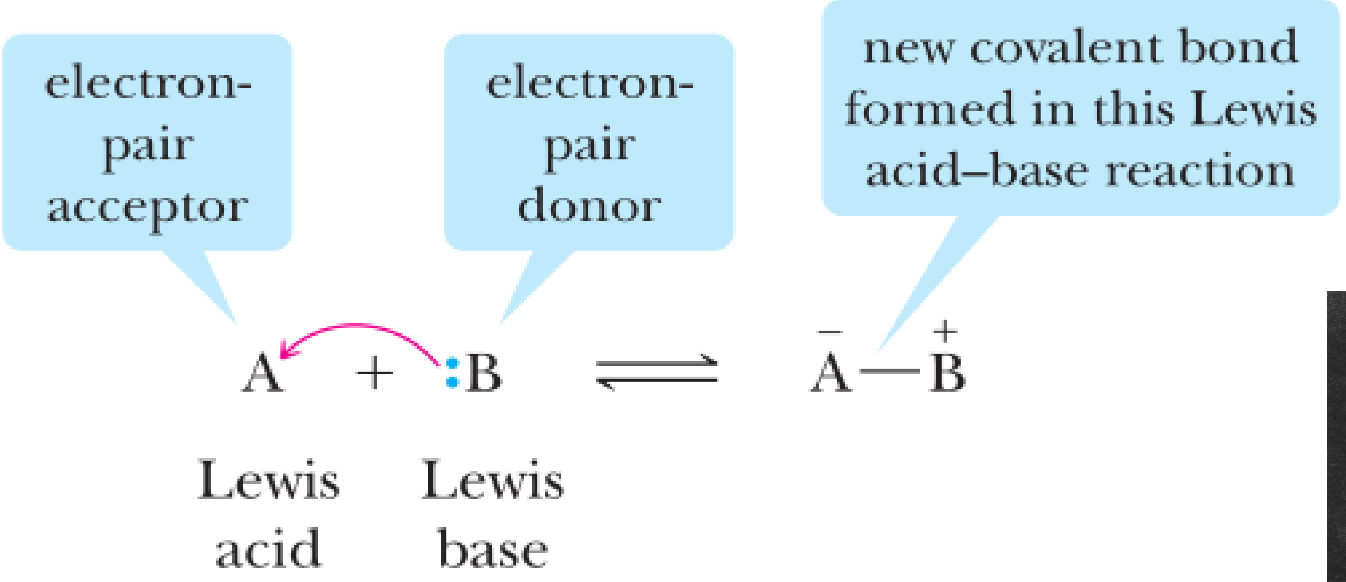
this oxygen atom has some charge delocalization from the electronegative chlorine atoms

this oxygen atom has the most charge delocalization from the highly electronegative fluorine atoms, and therefore it is the most stable ion and least reactive

2.6 What Are Lewis Acids and Bases?

Lewis acid Any molecule or ion that can form a new covalent bond by accepting a pair of electrons.

Lewis base Any molecule or ion that can form a new covalent bond by donating a pair of electrons.



electron-pair acceptor

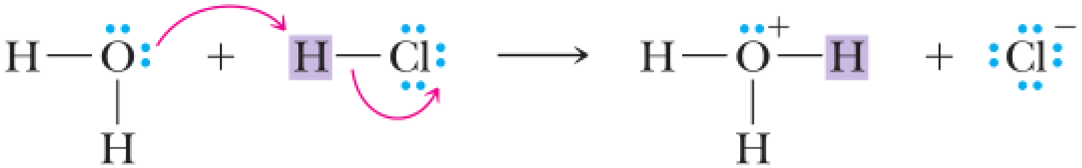
electron-pair donor

new covalent bond formed in this Lewis acid–base reaction

$$A + :B \rightleftharpoons \overset{-}{A}-\overset{+}{B}$$

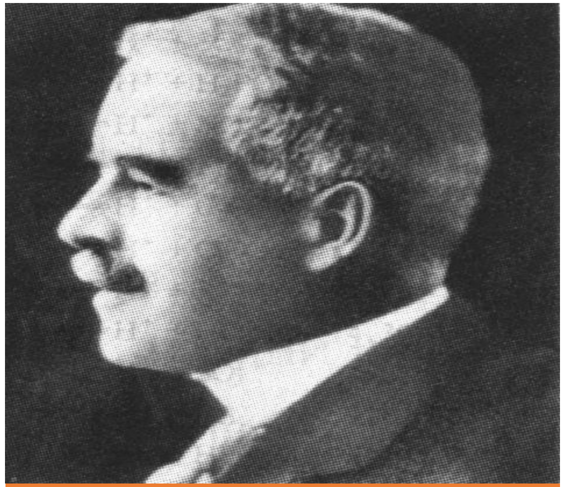
Lewis acid

Lewis base

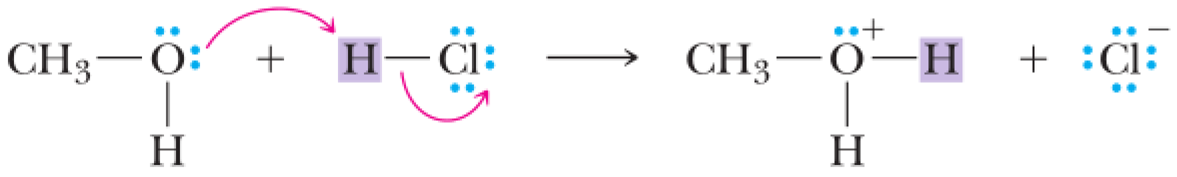


$$\underset{\displaystyle H}{H-\ddot{O}:} + H-\ddot{Cl}: \longrightarrow \underset{\displaystyle H}{H-\overset{+}{\ddot{O}}-H} + :\ddot{Cl}:^{-}$$

Hydronium ion



路易斯
(1875-1946)美



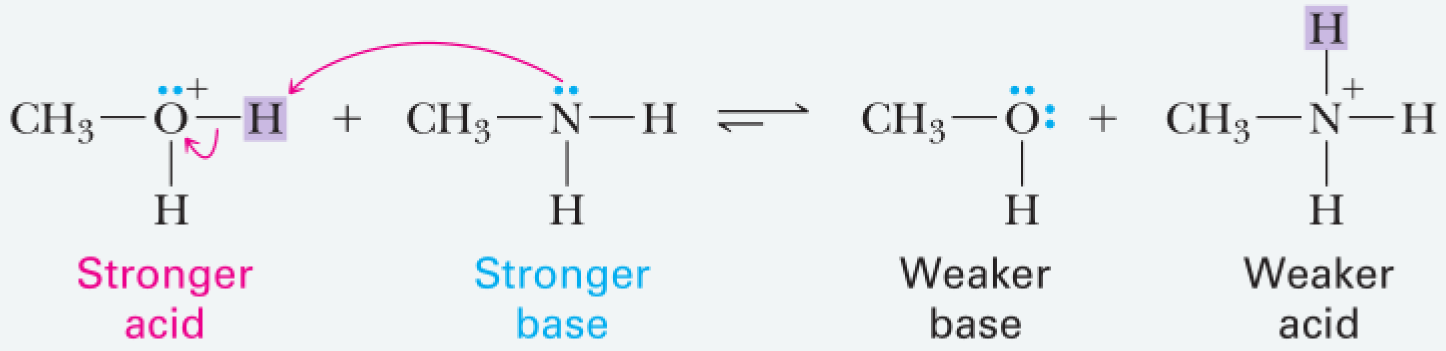
$$\text{CH}_3-\ddot{\text{O}}\text{(H)}: + \text{H}-\ddot{\text{Cl}}: \longrightarrow \text{CH}_3-\ddot{\text{O}}^{+}\text{(H)}-\text{H} + :\ddot{\text{Cl}}:^{-}$$

Methanol
(a Lewis base)

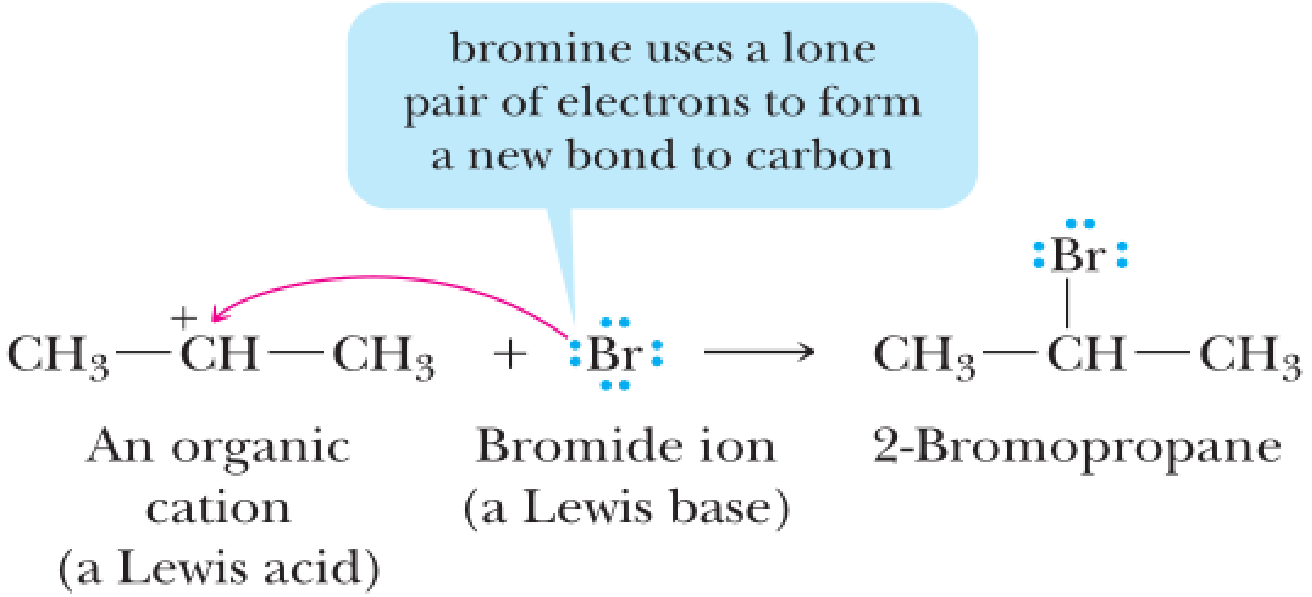
An oxonium
ion

TABLE 2.3 Some Organic Lewis Bases and Their Relative Strengths in Proton-Transfer Reactions

Halide Ions	Water, Alcohols, and Ethers	Ammonia and Amines	Hydroxide Ion and Alkoxide Ions	Amide Ions
$:\ddot{\text{Cl}}:^{-}$	$\text{H}-\ddot{\text{O}}-\text{H}$	$\text{H}-\ddot{\text{N}}(\text{H})-\text{H}$	$\text{H}-\ddot{\text{O}}:^{-}$	$\text{H}-\ddot{\text{N}}(\text{H}):^{-}$
$:\ddot{\text{Br}}:^{-}$	$\text{CH}_3-\ddot{\text{O}}-\text{H}$	$\text{CH}_3-\ddot{\text{N}}(\text{H})-\text{H}$	$\text{CH}_3-\ddot{\text{O}}:^{-}$	$\text{CH}_3-\ddot{\text{N}}(\text{H}):^{-}$
$:\ddot{\text{I}}:^{-}$	$\text{CH}_3-\ddot{\text{O}}-\text{CH}_3$	$\text{CH}_3-\ddot{\text{N}}(\text{CH}_3)-\text{H}$		$\text{CH}_3-\ddot{\text{N}}(\text{CH}_3):^{-}$
		$\text{CH}_3-\ddot{\text{N}}(\text{CH}_3)-\text{CH}_3$		
Very weak	Weak	Strong	Stronger	Very strong



$$\mathrm{CH_3{-}\overset{+}{\ddot{O}}(H){-}H} + \mathrm{CH_3{-}\ddot{N}(H){-}H} \rightleftharpoons \mathrm{CH_3{-}\ddot{O}\!:\!(H)} + \mathrm{CH_3{-}\overset{+}{N}H_2{-}H}$$



bromine uses a lone pair of electrons to form a new bond to carbon

$$\mathrm{CH_3{-}\overset{+}{C}H{-}CH_3} + :\ddot{\underset{..}{Br}}:^{-} \longrightarrow \mathrm{CH_3{-}\underset{}{CH}(Br){-}CH_3}$$

作 业

2.11、 2.13、 2.16 、 2.18 、 2.19
2.25 2.28（a、b、c）
2.30（b） 2.31（a、b、c）

选做

2.34、2.35、2.36