Structure and Bonding; Acids and Bases

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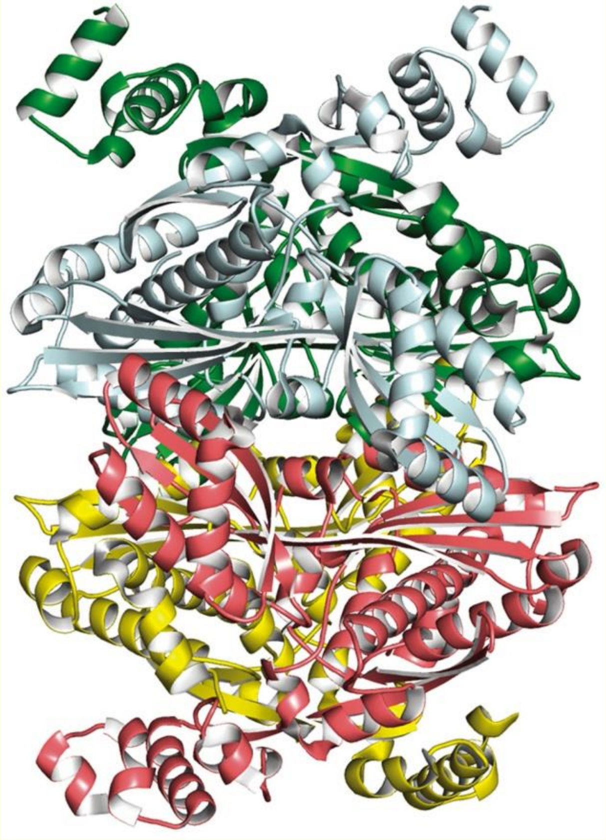
1. Structure and Bonding; Acids and Bases



Bond Polarity and Electronegativity

- **Electronegativity (EN):** intrinsic ability of an atom to attract the shared electrons in a covalent bond
- **Differences in EN** produce **bond polarity**
- Arbitrary scale. Electronegativities are based on an arbitrary scale
- F is most electronegative (EN = 4.0), Cs is least (EN = 0.7)
- Metals on left side of periodic table attract electrons weakly, lower EN
- Halogens (Fluorine, Chlorine, Bromine) and other reactive nonmetals on right side of periodic table attract electrons strongly, higher electronegativities
- EN of C = 2.5

H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

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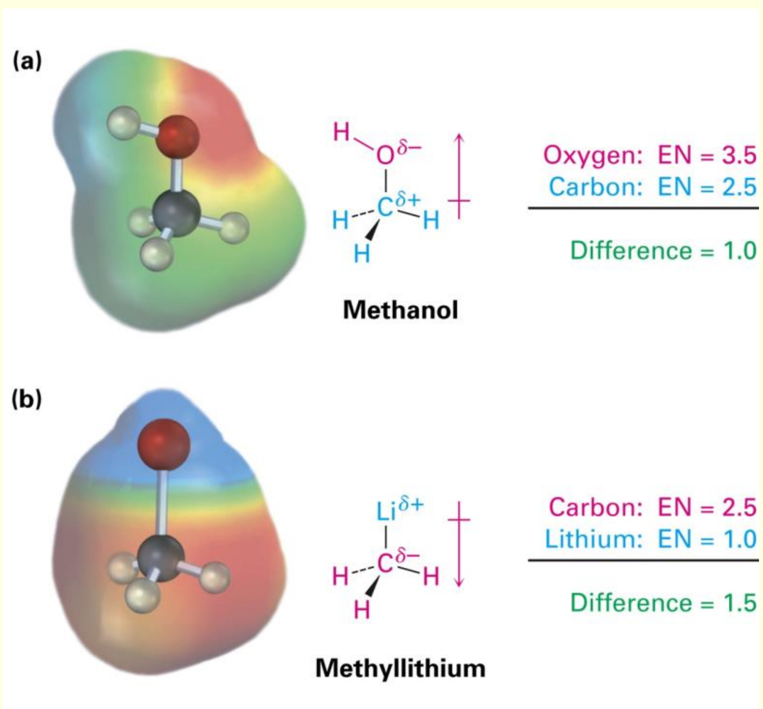
The Periodic Table and Electronegativity

Bond Polarity and Inductive Effect

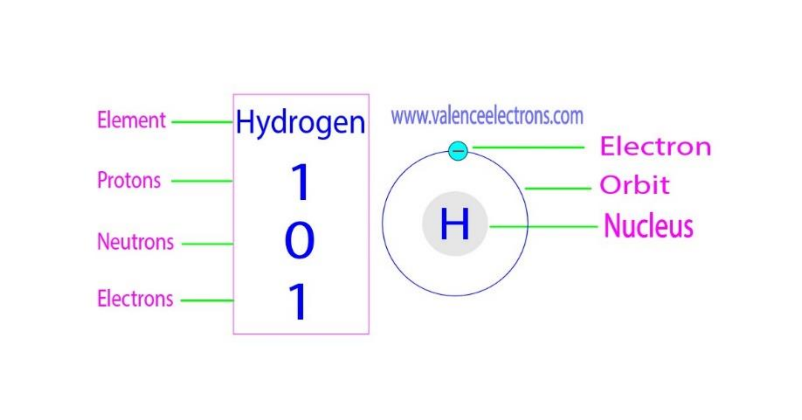
- Bonding electrons toward electronegative atom
  - C acquires partial positive charge, $\delta+$
  - Electronegative atom acquires partial negative charge, $\delta-$
- **Inductive effect:** shifting of electrons in a bond in response to EN of nearby atoms



- **Electrostatic potential maps** show calculated charge distributions: Colors indicate **electron-rich (red)** and **electron-poor (blue) regions**
- **Arrows** indicate direction of bond polarity

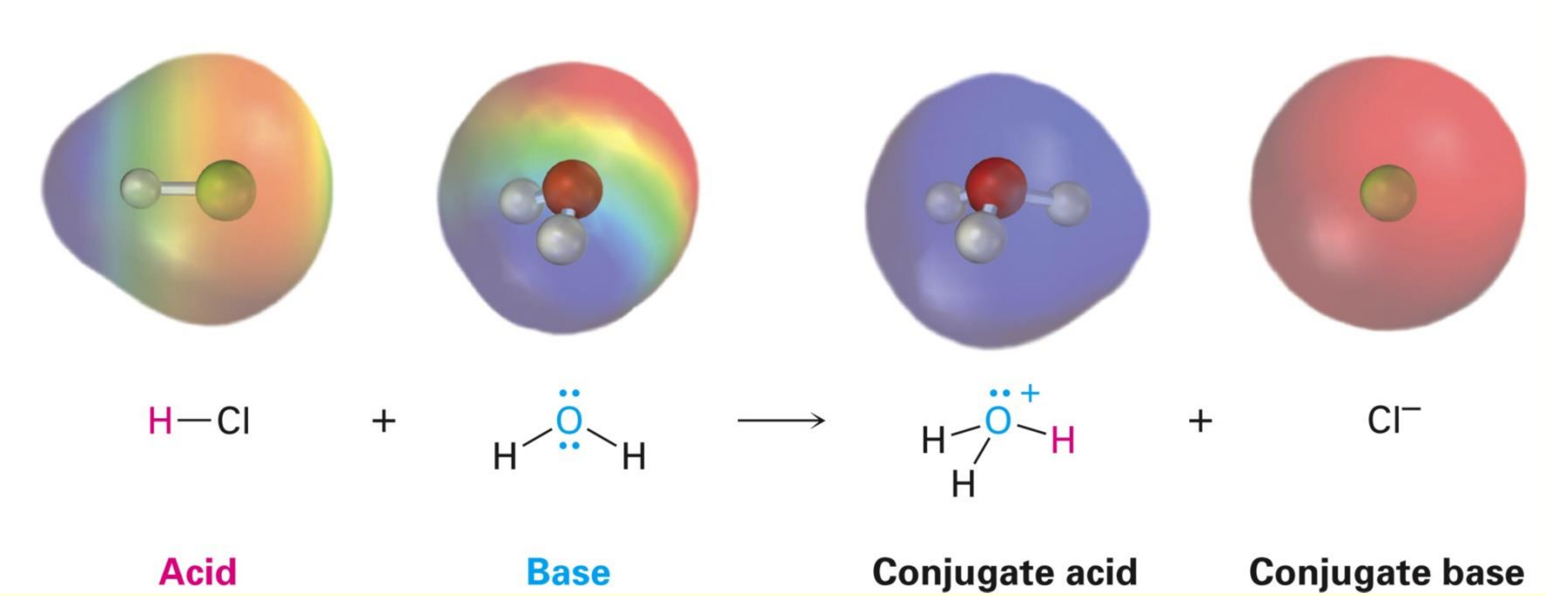
1.10 Acids and Bases: The Brønsted–Lowry Definition

- A **Brønsted acid** is a substance **that donates a hydrogen ion (H^+)**
- A **Brønsted base** is a substance that **accepts the H^+**
  - "proton" is a synonym for H^+ - loss of an electron from H leaving the bare nucleus—a proton



The Reaction of Acid with Base

- Hydronium ion **(H_3O^+)**, product when base H_2O gains a proton
- HCl donates a proton to water molecule, yielding **hydronium ion (H_3O^+) [conjugate acid] and $Cl^–$ [conjugate base]**
- The reverse is also a Brønsted acid–base reaction of the conjugate acid and conjugate base



Hydronium ion (H_3O^+)

Acid Strength

- The strength of a given acid HA in water solution can be expressed by its **acidity constant, K_a** .
- K_a ranges from 10^{15} for the strongest acids to very small values (10^{-60}) for the weakest

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

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

pK_a – the Acid Strength Scale

- pK_a = -log K_a
- A smaller value of pK_a indicates a stronger acid and is proportional to the energy difference between products and reactants
- The pK_a of water is 15.74

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

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

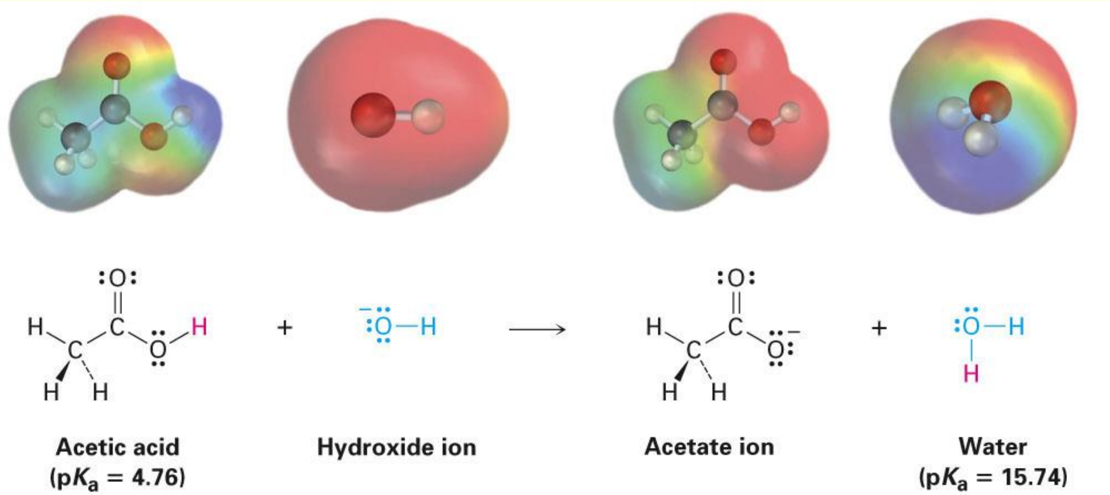
$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad \text{and} \quad K_a = K_{eq} \times [H_2O] = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

Table 1.2 Relative Strengths of Some Common Acids and Their Conjugate Bases

	Acid	Name	pK_a	Conjugate base	Name	
Weaker acid	CH_3CH_2OH	Ethanol	16.00	$CH_3CH_2O^-$	Ethoxide ion	Stronger base
	H_2O	Water	15.74	HO^-	Hydroxide ion	
	HCN	Hydrocyanic acid	9.31	CN^-	Cyanide ion	
	$H_2PO_4^-$	Dihydrogen phosphate ion	7.21	HPO_4^{2-}	Hydrogen phosphate ion	
	CH_3CO_2H	Acetic acid	4.76	$CH_3CO_2^-$	Acetate ion	
	H_3PO_4	Phosphoric acid	2.16	$H_2PO_4^-$	Dihydrogen phosphate ion	
	HNO_3	Nitric acid	−1.3	NO_3^-	Nitrate ion	
Stronger acid	HCl	Hydrochloric acid	−7.0	Cl^-	Chloride ion	Weaker base

- pK_a values are related as logarithms to equilibrium constants
- Useful for predicting whether a given acid-base reaction will take place
- The difference in two pK_a values is the log of the ratio of equilibrium constants, and can be used to calculate the extent of transfer
- The stronger base holds the proton more tightly
- **A strong acid yields a weak conjugate base, and a weak acid yields a strong conjugate base.**



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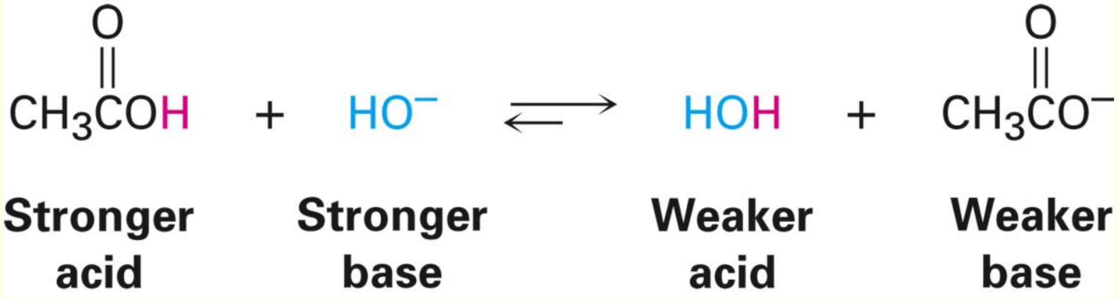
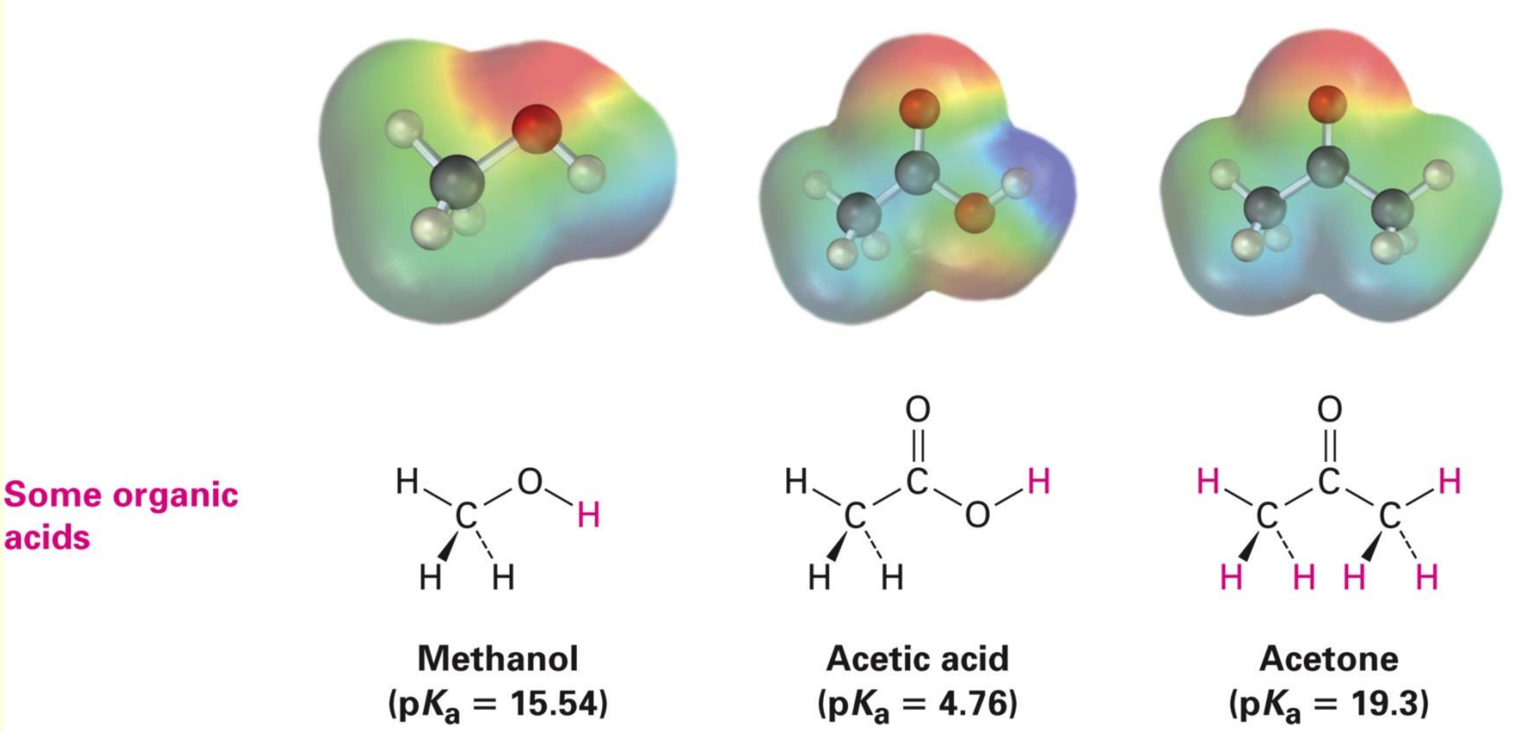
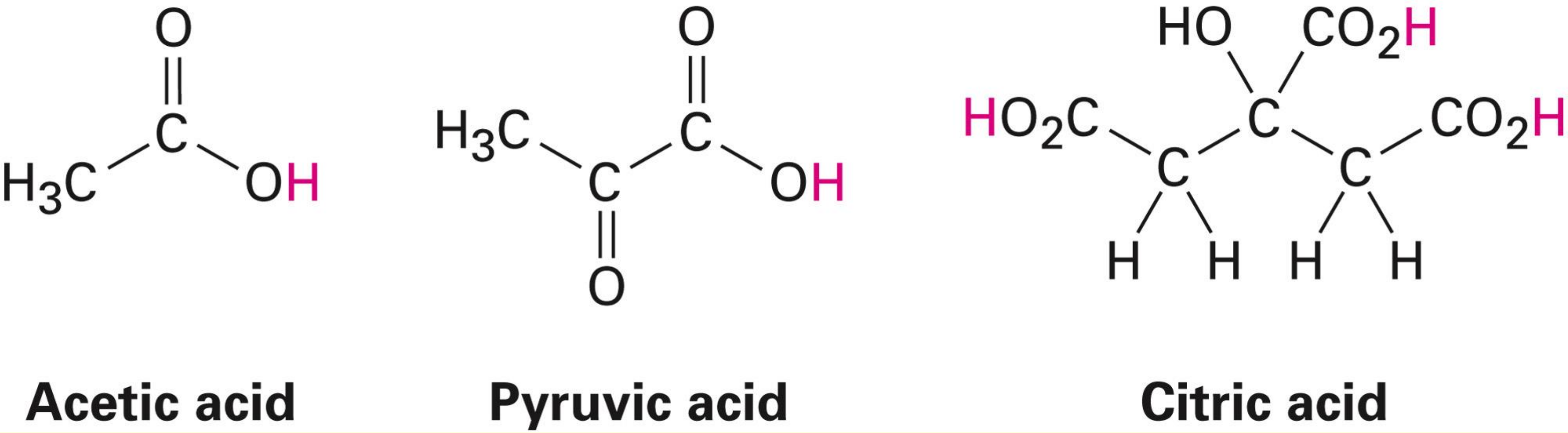


1.11 Organic Acids and Organic Bases

- **Organic Acids**
- Those that lose a proton from O–H, such as methanol and acetic acid
- Those that lose a proton from C–H, usually from a carbon atom next to a C=O double bond (O=C–C–H)

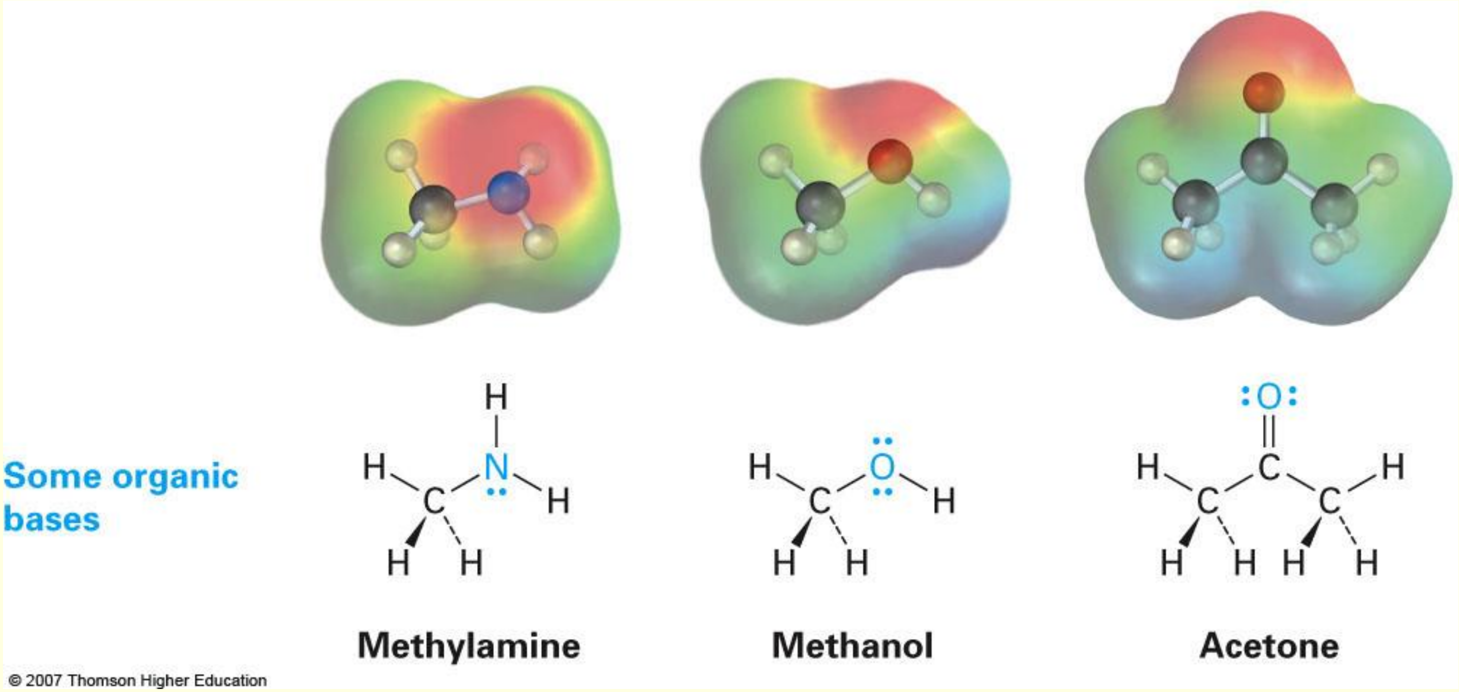


Carboxylic acids

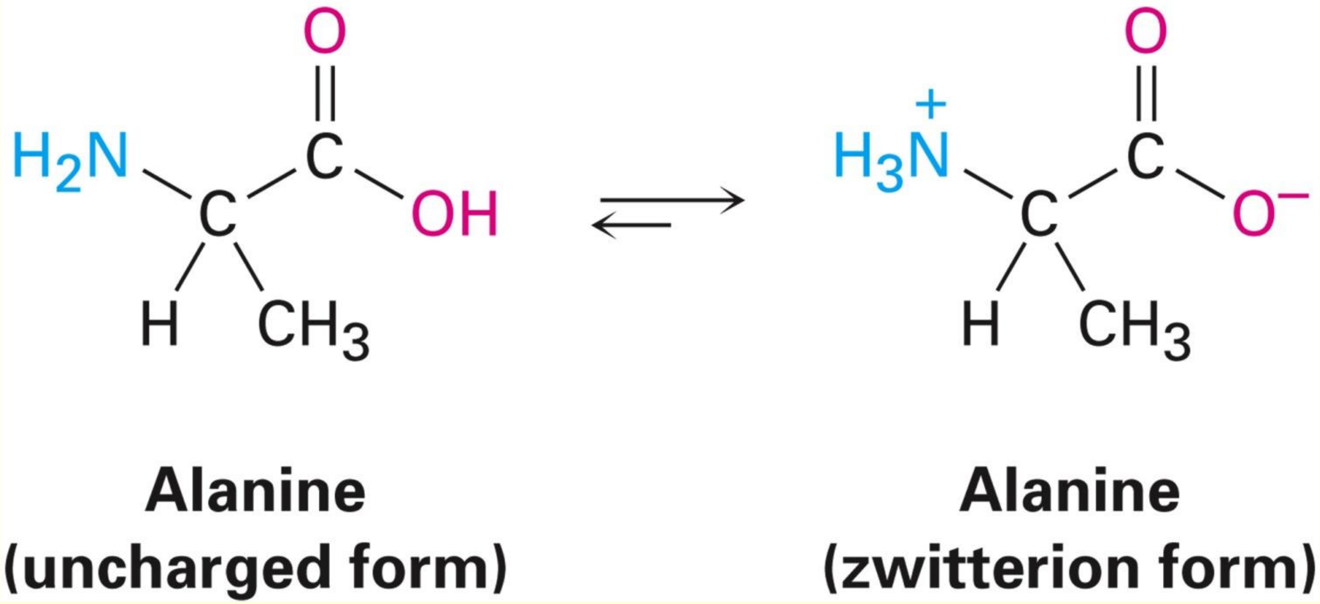


Organic Bases

- Have an **atom with a lone pair of electrons** that can bond to H^+
- **Nitrogen-containing compounds** derived from ammonia are the most common organic bases
- **Oxygen-containing compounds** can react as bases when with a strong acid or as acids with strong bases

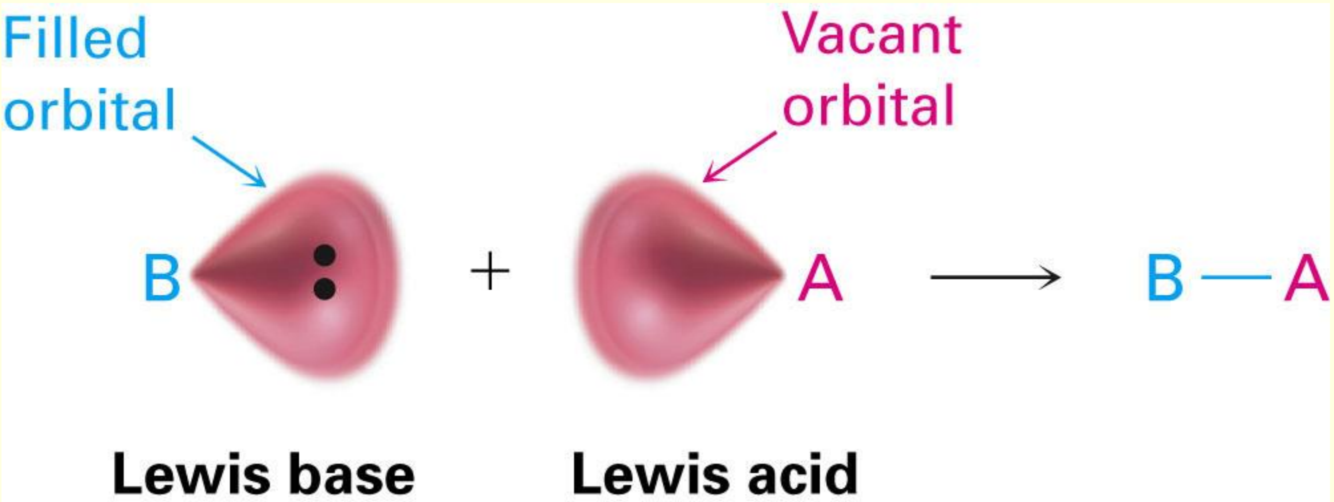


Amino acids


O
H_2N
C
C
OH
H
CH_3
Alanine
(uncharged form)
O
$H_3\overset{+}{N}$
C
C
O^-
H
CH_3
Alanine
(zwitterion form)

1.12 Acids and Bases: The Lewis Definition

- Lewis acids are electron pair acceptors and Lewis bases are electron pair donors
- The Lewis definition leads to a general description of many reaction patterns but there is no scale of strengths as in the Brønsted definition of pK_a



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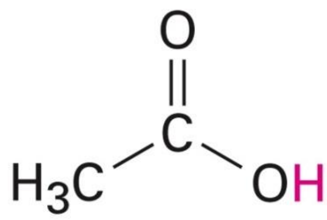
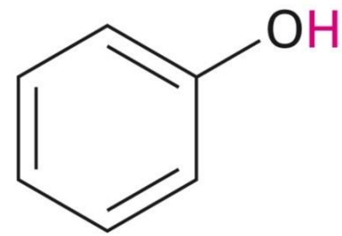
Some Lewis acids

Some neutral proton donors:

H_2O HCl HBr HNO_3 H_2SO_4



A carboxylic acid



A phenol

CH_3CH_2OH

An alcohol

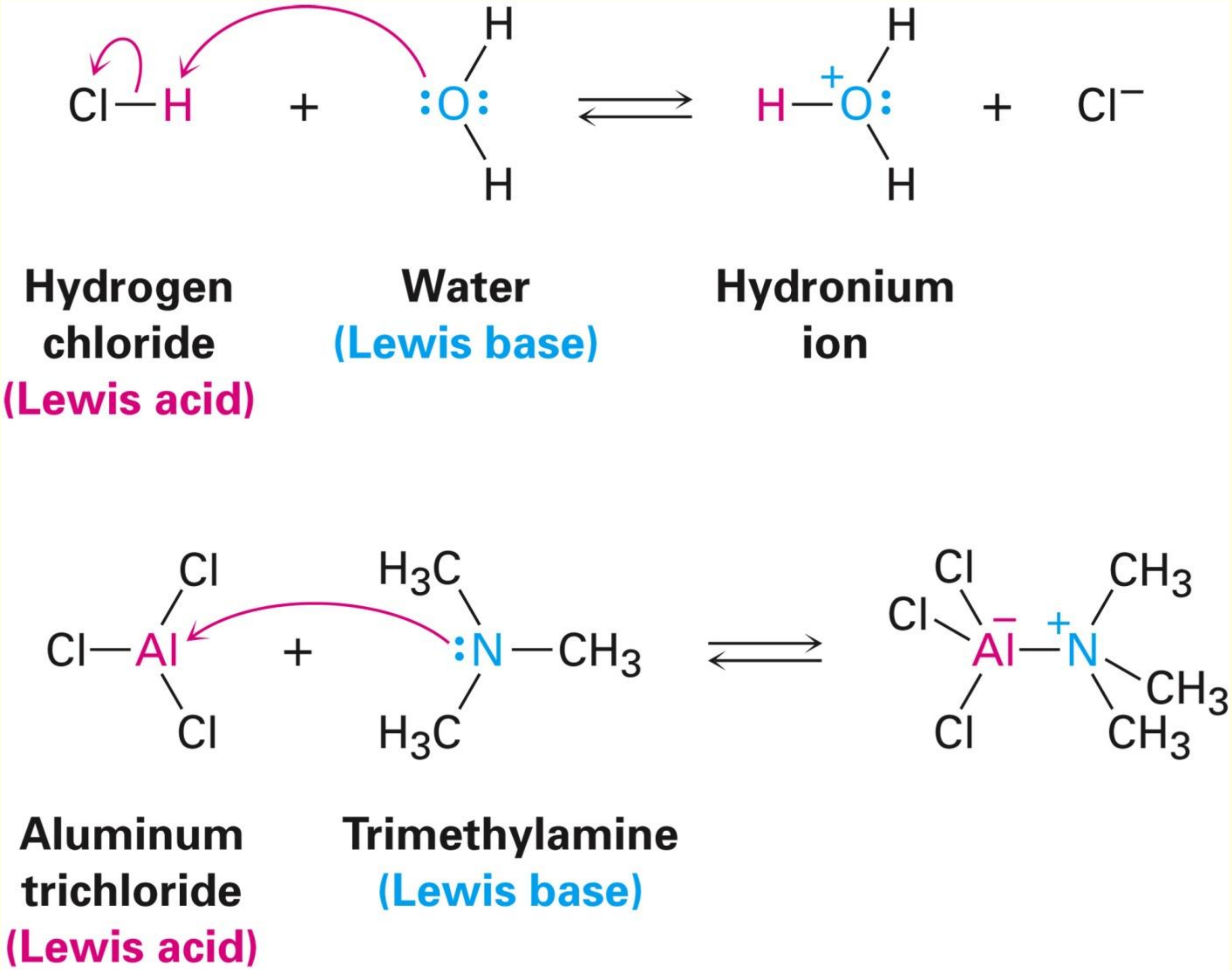
Some cations:

Li^+ Mg^{2+}

Some metal compounds:

$AlCl_3$ $TiCl_4$ $FeCl_3$ $ZnCl_2$

- The combination of a Lewis acid and a Lewis base can shown with a **curved arrow** from base to acid



Worked Example 1.6

Predicting Acid–Base Reactions

Water has $\mathrm{p}K_a = 15.74$, and acetylene has $\mathrm{p}K_a = 25$. Which of the two is more acidic? Will hydroxide ion react with acetylene?

$$\underset{\textbf{Acetylene}}{H{-}C{\equiv}C{-}H} \;+\; OH^- \xrightarrow{?} H{-}C{\equiv}C{:}^- \;+\; H_2O$$

Strategy In comparing two acids, the one with the smaller $\mathrm{p}K_a$ is stronger. Thus, water is a stronger acid than acetylene.

Solution Because water loses a proton more easily than acetylene, the HO^- ion has less affinity for a proton than the $HC{\equiv}C{:}^-$ ion. In other words, the anion of acetylene is a stronger base than hydroxide ion, and the reaction will not proceed as written.

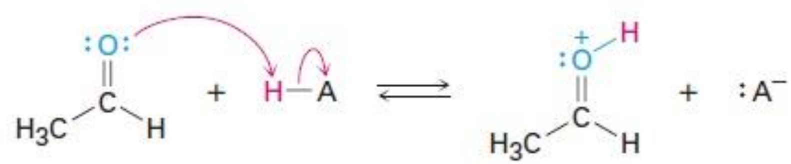
Worked Example 1.8

Using Curved Arrows to Show Electron Flow

Using curved arrows, show how acetaldehyde, CH_3CHO, can act as a Lewis base in a reaction with a strong acid, H^+.

Strategy A Lewis base donates an electron pair to a Lewis acid. We therefore need to locate the electron lone pairs on acetaldehyde and use a curved arrow to show the movement of an electron pair from the oxygen toward a strong acid.

Solution



Acetaldehyde