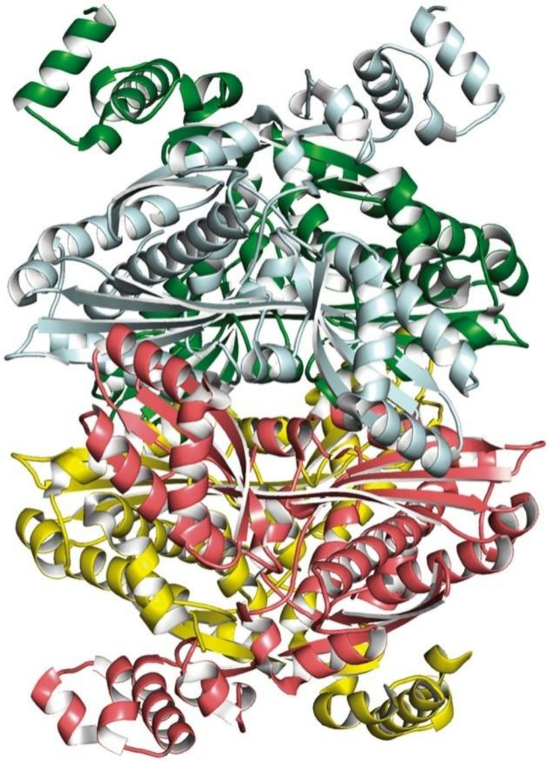
Structure and Bonding; Acids and Bases



McMurry, ‘Fundamentals of Organic Chemistry’, 7th Ed.

Chapter 1

Origins of Organic Chemistry

Foundations of organic chemistry from mid-1700's.

Compounds obtained from plants, animals hard to isolate, and purify.

Compounds also decomposed more easily.

Torben Bergman (1770) first to make distinction between organic and inorganic chemistry.

It was thought that organic compounds must contain some "vital force" because they were from living sources.

- **Organic chemistry is study of carbon compounds**
- **Why is it so special?**
  - **99% of more than 37 million chemical compounds contain carbon.**
  - **Examination of carbon in periodic chart answers some of these questions.**

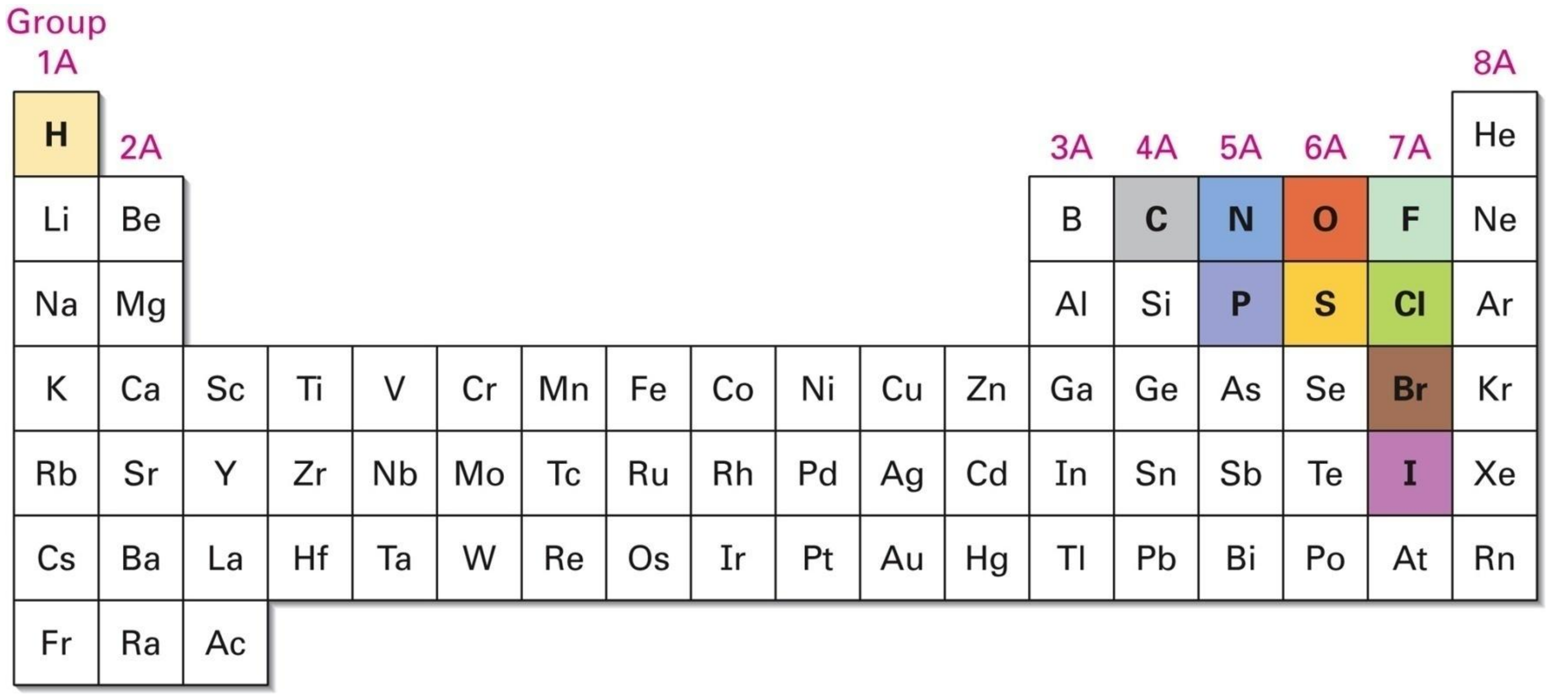


Figure 1.1 The position of carbon in the periodic table.

Carbon is group 4A element, it can share 4 valence electrons and form 4 covalent bonds.

1.1 Atomic Structure

- **Structure of an atom**
  - **Positively charged *nucleus* (very dense, protons and neutrons) and small (10^{-15} m)**
  - **Negatively charged electrons are in a cloud (10^{-10} m) around nucleus**
- **Diameter is about 2×10^{-10} m (200 *picometers* (pm)) [the unit *angstrom* (Å) is 10^{-10} m = 100 pm]**

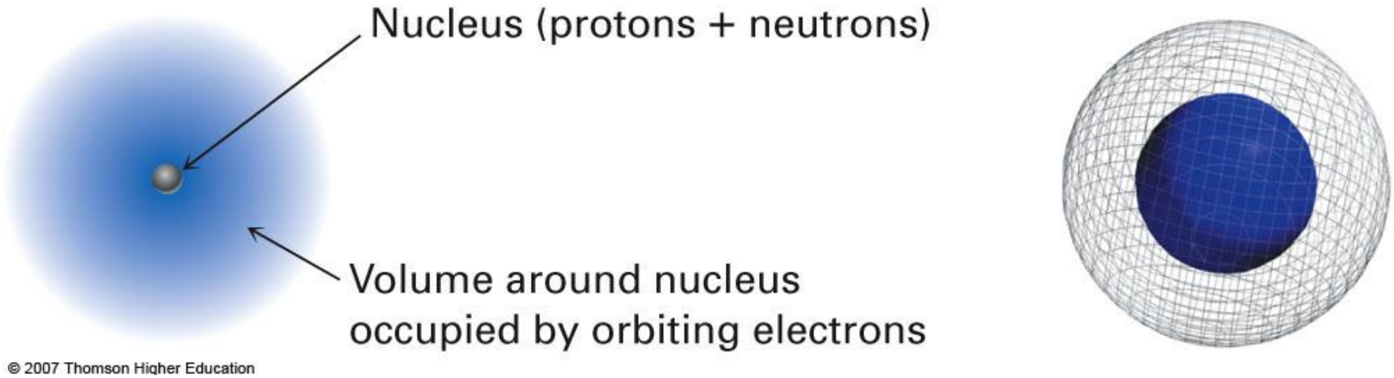


Figure 1.2 A schematic view of an atom.

Atomic Number and Atomic Mass

- **The *atomic number* (*Z*) is the number of protons in the atom's nucleus**
- **The *mass number* (*A*) is the number of protons plus neutrons**
- **All the atoms of a given element have the same atomic number**
- **Isotopes are atoms of the same element that have different numbers of neutrons and therefore different mass numbers**
- **The atomic mass (*atomic weight*) of an element is the weighted average mass in atomic mass units (amu) of an element's naturally occurring isotopes**

Atomic Structure: Orbitals

- **Quantum mechanics**: describes electron energies and locations by a *wave equation*
  - *Wave function* solution of wave equation
  - Each wave function is an **orbital**, ψ

- Electron cloud has no specific boundary so we show most probable area

Shapes of Atomic Orbitals for Electrons

- Four different kinds of orbitals for electrons based on those derived for a hydrogen atom
- Denoted *s*, *p*, *d*, and *f*
- *s* and *p* orbitals most important in organic and biological chemistry
- *s* orbitals: spherical, nucleus at center
- *p* orbitals: dumbbell-shaped, nucleus at middle

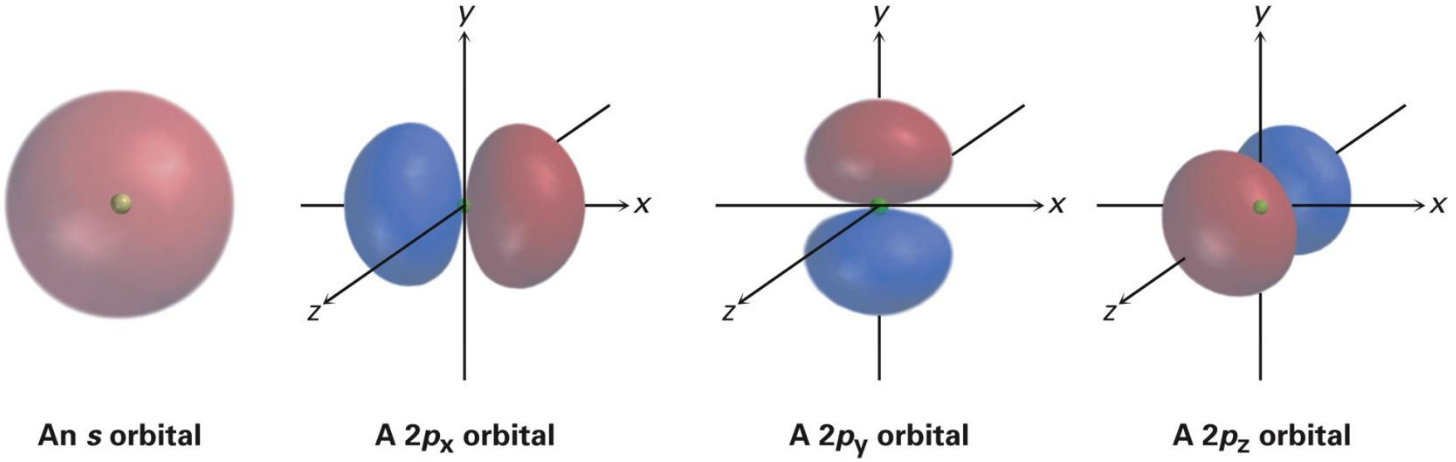


Figure 1.3 Representations of *s* and *p* orbitals.

Orbitals and Shells

- Orbitals are grouped in **shells** of increasing size and energy
- Different shells contain different numbers and kinds of orbitals
- Each orbital can be occupied by two electrons
- First shell contains one *s* orbital, denoted 1*s*, holds only two electrons
- Second shell contains one *s* orbital (2*s*) and three *p* orbitals (2*p*), eight electrons
- Third shell contains an *s* orbital (3*s*), three *p* orbitals (3*p*), and five *d* orbitals (3*d*), 18 electrons

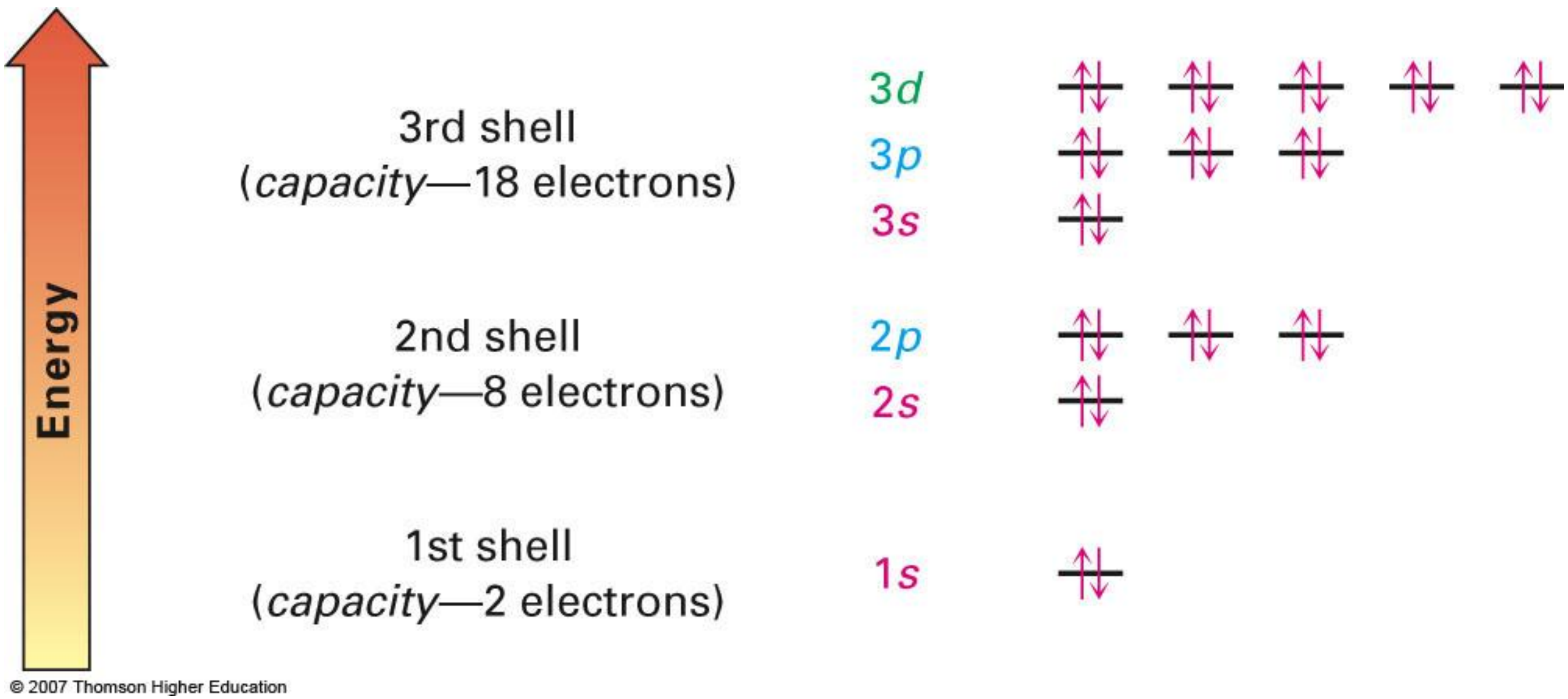


Figure 1.4 The energy levels of electrons in an atom.

1.2 Atomic Structure: Electron Configurations

Ground-state electron configuration (lowest energy arrangement) of an atom lists orbitals occupied by its electrons. **Rules**:

1. Lowest-energy orbitals fill first: $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$ (*Aufbau* (“build-up”) principle)
2. Electrons act as if they were spinning around an axis. Electron spin can have only two orientations, up $\uparrow$ and down $\downarrow$. Only two electrons can occupy an orbital, and they must be of opposite spin (*Pauli exclusion principle*) to have unique wave equations.
3. If two or more empty orbitals of equal energy are available, electrons occupy each with spins parallel until all orbitals have one electron (*Hund's rule*).

Table 1.1 Ground-State Electron Configuration of Some Elements

Element	Atomic number	Configuration		Element	Atomic number	Configuration	
Hydrogen	1	1*s*	↑	Phosphorus	15	3*p*	↑ ↑ ↑
Carbon	6	2*p*	↑ ↑ —			3*s*	↑↓
		2*s*	↑↓			2*p*	↑↓ ↑↓ ↑↓
		1*s*	↑↓			2*s*	↑↓
						1*s*	↑↓

1.3 Development of Chemical Bonding Theory

- **Kekulé and Couper independently observed that carbon always has four bonds**
- **Van't Hoff and Le Bel proposed that the four bonds of carbon have specific spatial directions**
- **Atoms surround carbon as corners of a tetrahedron**

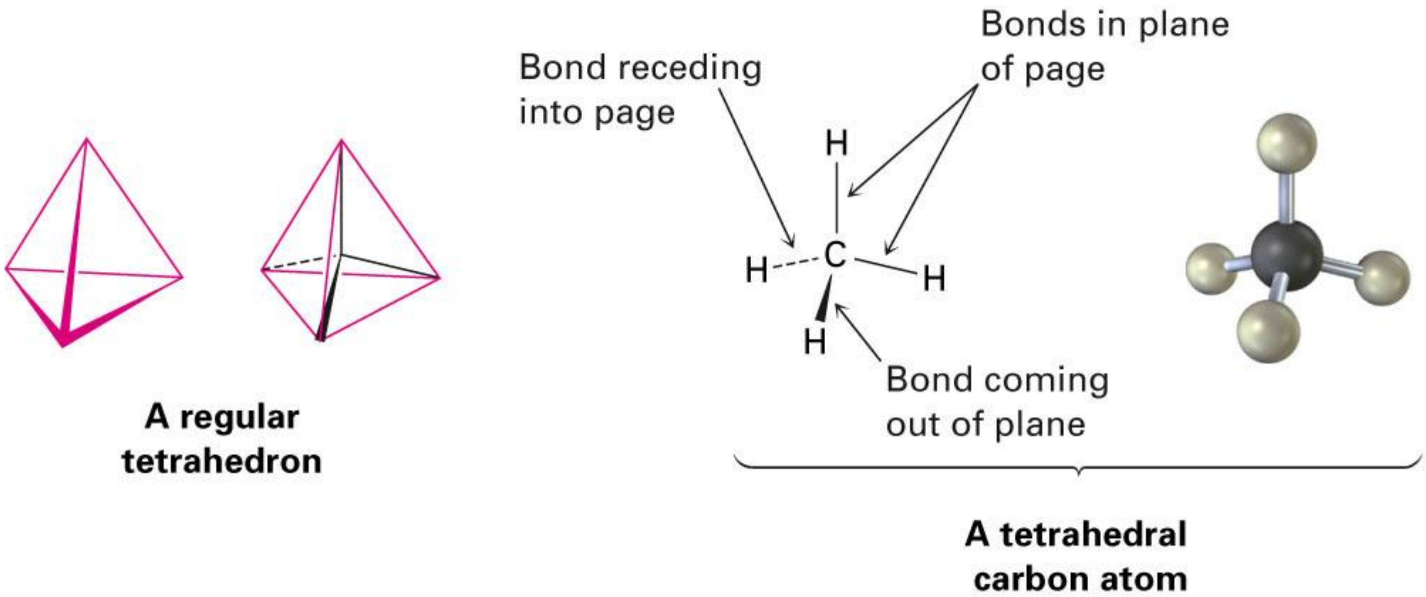


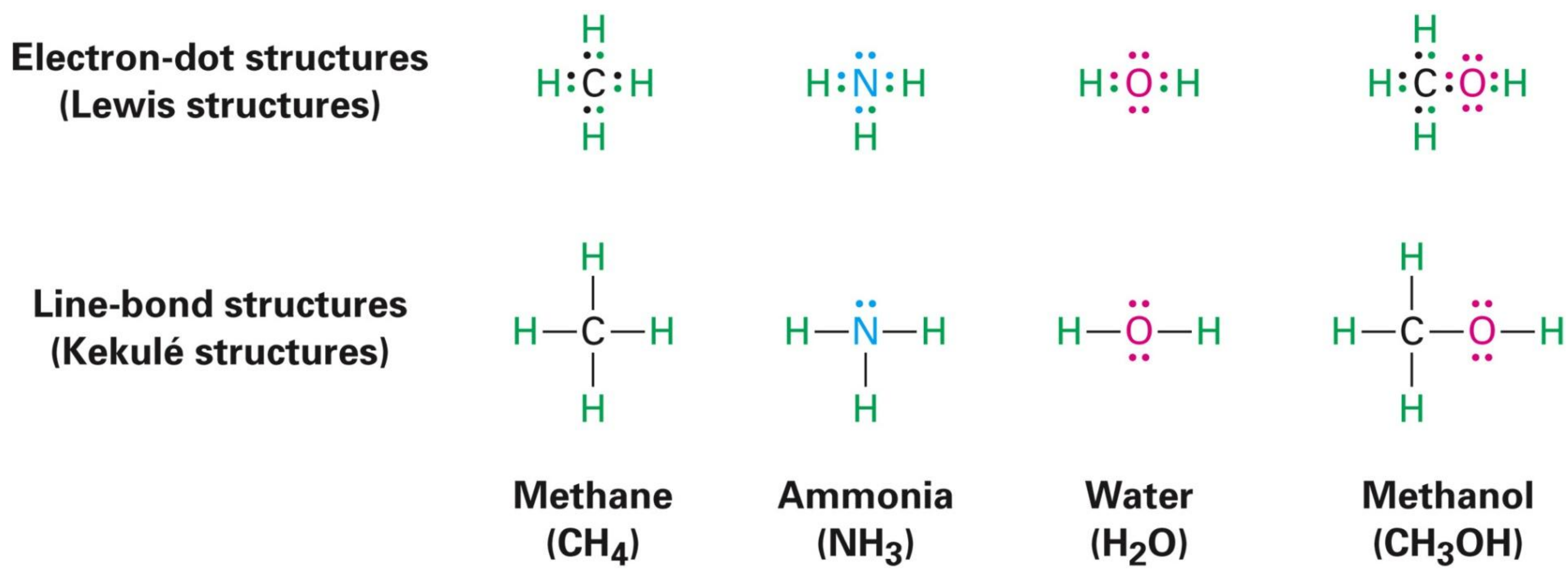
Figure 1.5 A representation of van't Hoff's tetrahedral carbon atom.

1.4 The Nature of Chemical Bonds

- Atoms form bonds because the compound that results is more stable than the separate atoms
- Ionic bonds in salts form as a result of electron transfers
- Organic compounds have covalent bonds from sharing electrons (G. N. Lewis, 1916)
- Stable molecule results at completed shell, octet (eight dots) for main-group atoms

  (cf. two for hydrogen)

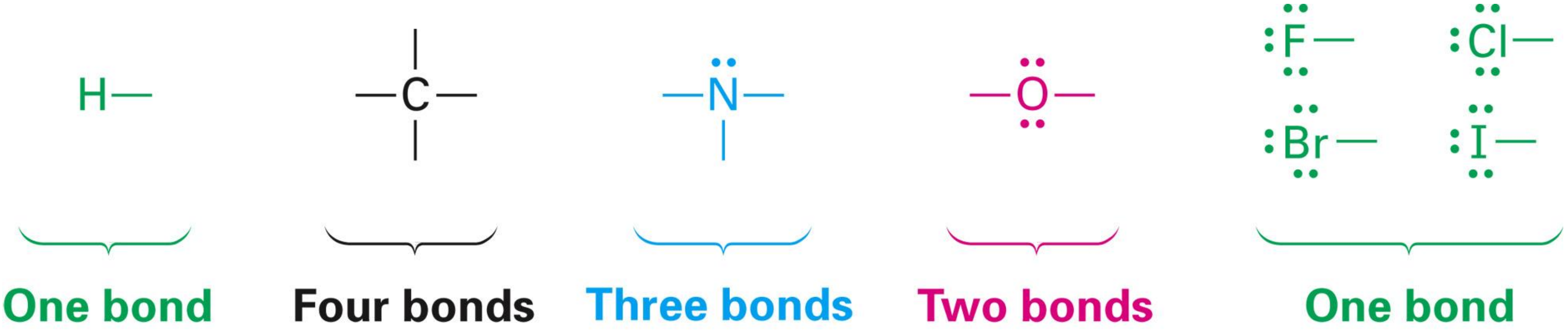
- **Lewis structures** (electron dot) show valence electrons of an atom as dots
  - Hydrogen has one dot, representing its 1*s* electron
  - Carbon has four dots ($2s^2\ 2p^2$)
- **Kekule structures** (line-bond structures) have a line drawn between two atoms indicating a 2 electron covalent bond



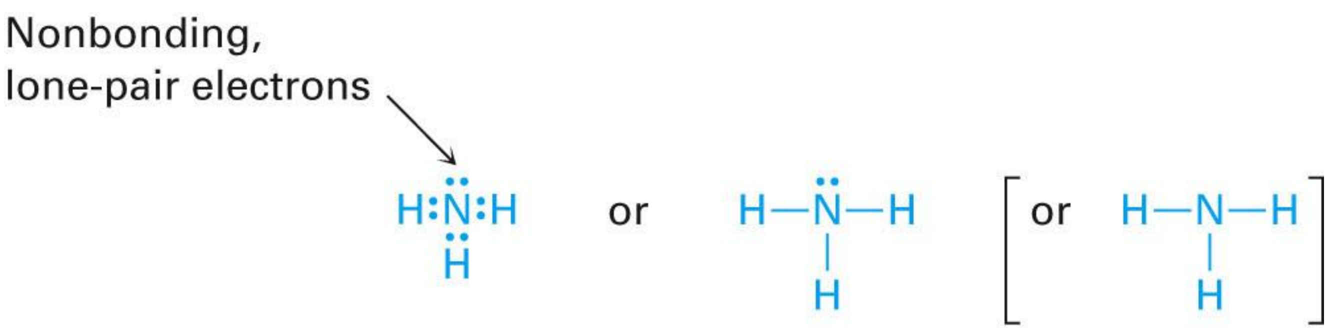
- **Atoms with one, two, or three valence electrons form one, two, or three bonds**

- **Atoms with four or more valence electrons form as many bonds as they need electrons to fill the *s* and *p* levels of their valence shells to reach a stable octet**

  - **Carbon has four valence electrons ($2s^2$ $2p^2$), forming four bonds (CH_4)**
  - **Nitrogen has five valence electrons ($2s^2$ $2p^3$) and forms three bonds (NH_3)**
  - **Oxygen has six valence electrons ($2s^2$ $2p^4$) and forms two bonds (H_2O)**



- Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons**
  - Nitrogen atom in ammonia (NH_3)

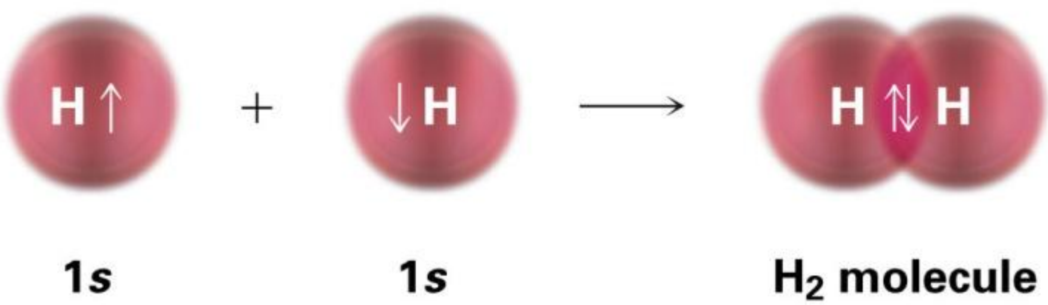


Ammonia

1.5 Forming Covalent Bonds: Valence Bond Theory

- Covalent bond forms when two atoms approach each other closely so that a singly occupied orbital on one atom *overlaps* a singly occupied orbital on the other atom
- **Valence Bond Theory**:

  Electrons are paired in the overlapping orbitals and are attracted to nuclei of both atoms
  - H–H bond results from the overlap of two singly occupied hydrogen 1*s* orbitals



- Reaction 2 H· → H_2 releases 436 kJ/mol
- Product has 436 kJ/mol less energy than two atoms: H–H has **bond strength** of 436 kJ/mol. (1 kJ = 0.2390 kcal; 1 kcal = 4.184 kJ)
- Bond Length: Distance between nuclei that leads to maximum stability

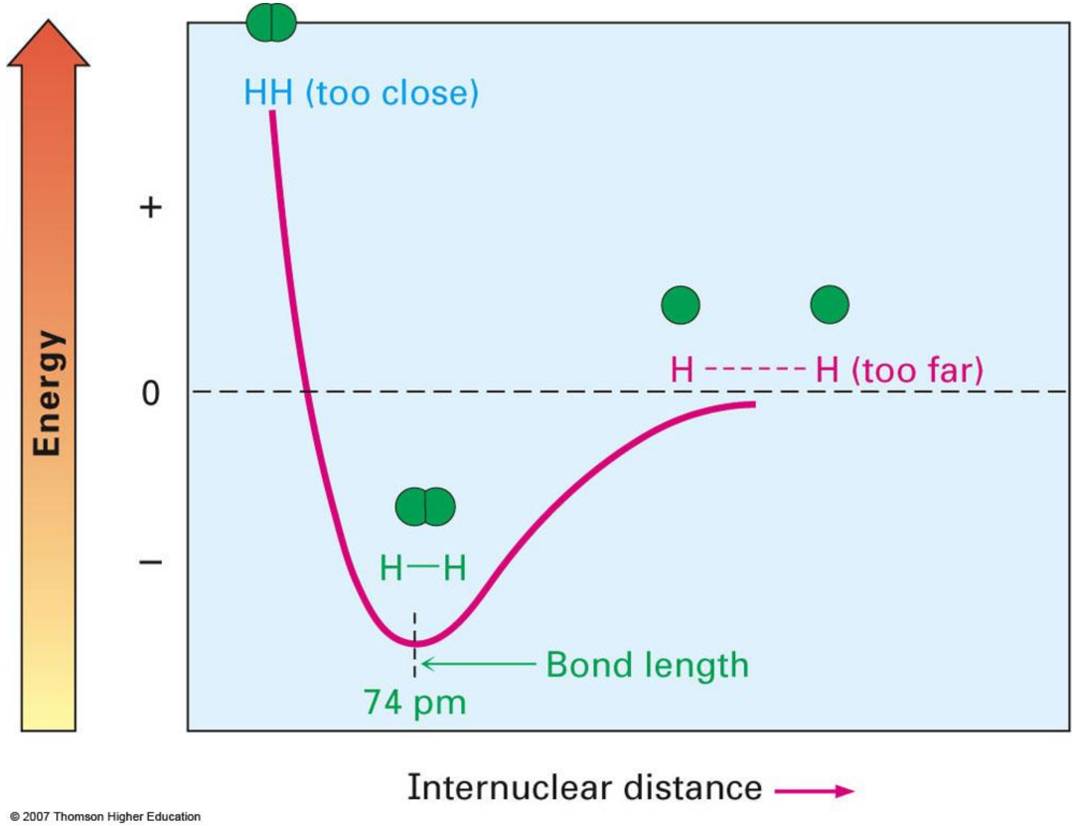
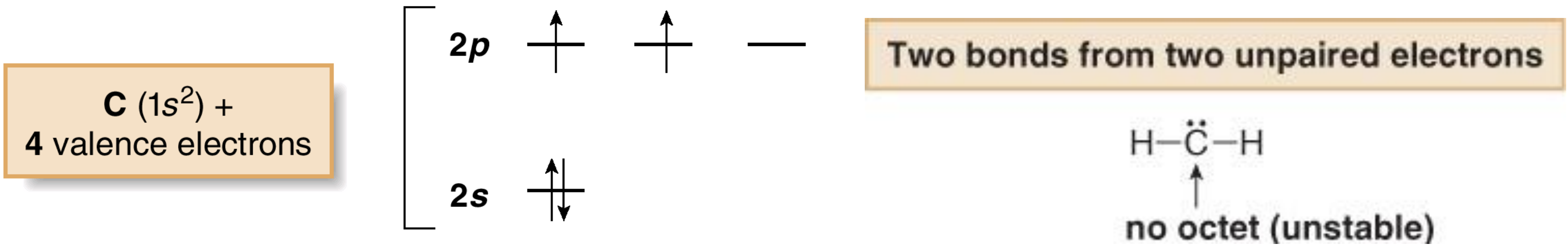
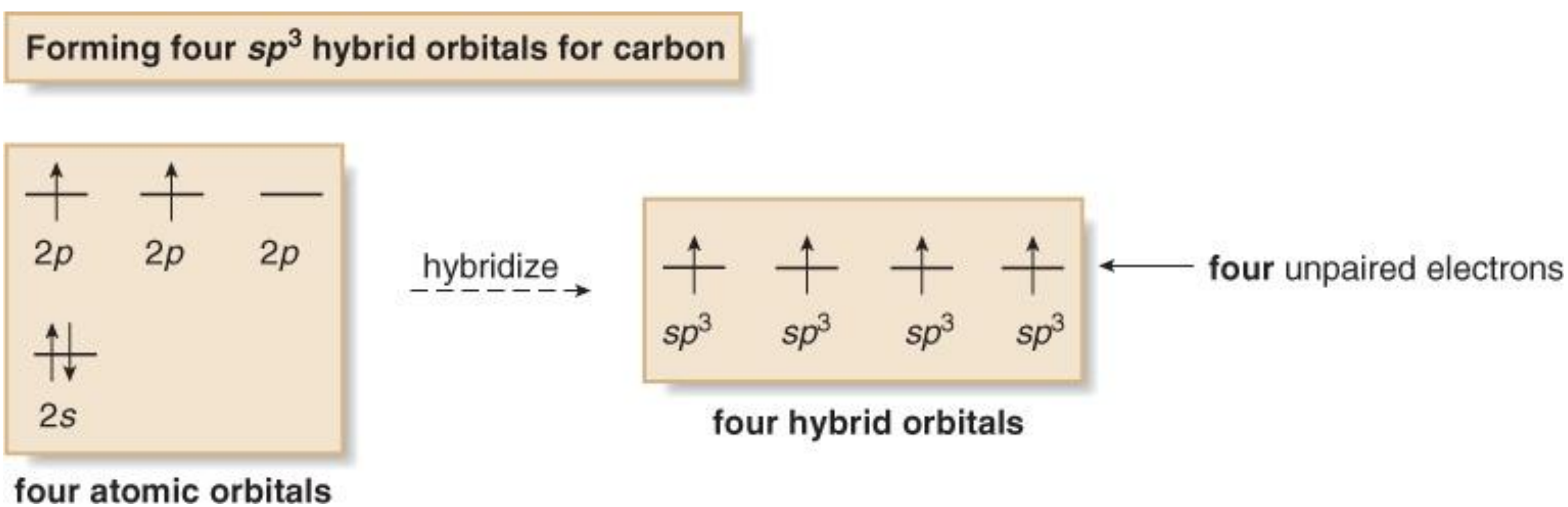


Figure 1.6 A plot of energy versus internuclear distance for two hydrogen atoms.

1.6 *sp³* Orbitals and the Structure of Methane

- **Carbon has 4 valence electrons ($2s^2\ 2p^2$)**





1.6 *sp³* Orbitals and the Structure of Methane

- **In CH_4, all C–H bonds are identical (tetrahedral)**
- ***sp³* hybrid orbitals: *s* orbital and three *p* orbitals combine to form four equivalent, unsymmetrical, tetrahedral orbitals (sppp = *sp³*), Pauling (1931)**

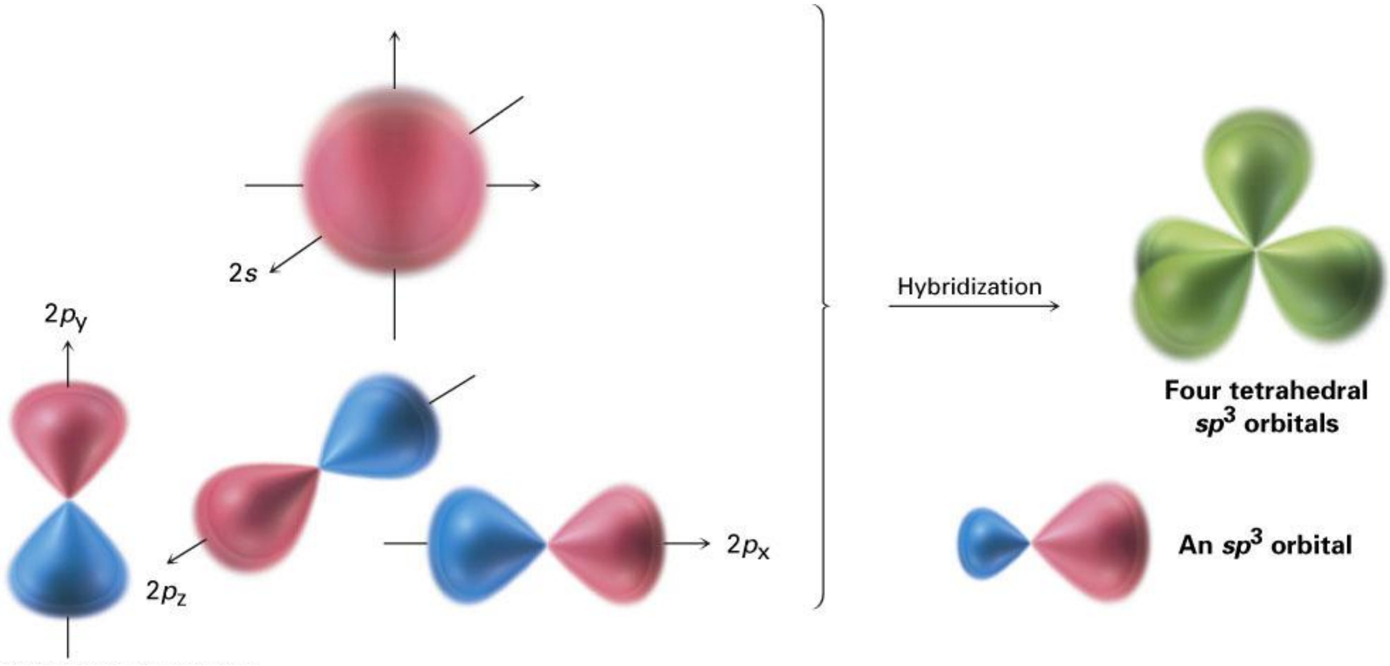


Figure 1.7 Four sp^3 hybrid orbitals (green), orientated to the corners of a regular tetrahedron, are formed by combination of an atomic *s* orbital (red), and three atomic *p* orbitals (red/blue).

The Structure of Methane

- *sp^3* orbitals on C overlap with 1*s* orbitals on 4 H atoms to form four identical C-H bonds
- Each C–H bond has a strength of 439kJ/mol and length of 109 pm
- **Bond angle**: each H–C–H is 109.5°, the *tetrahedral angle*

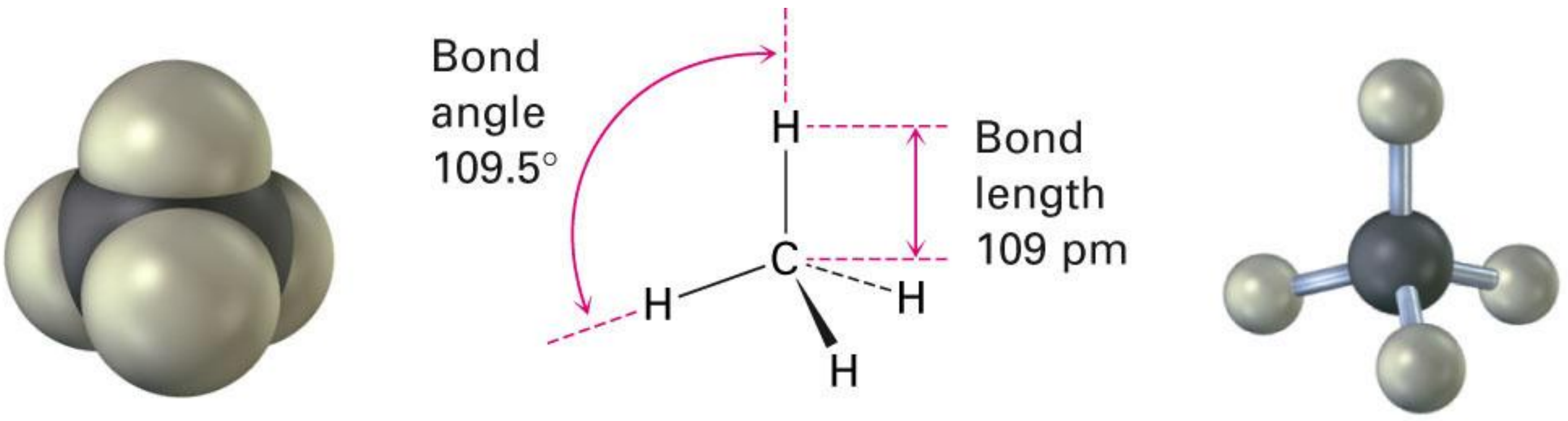
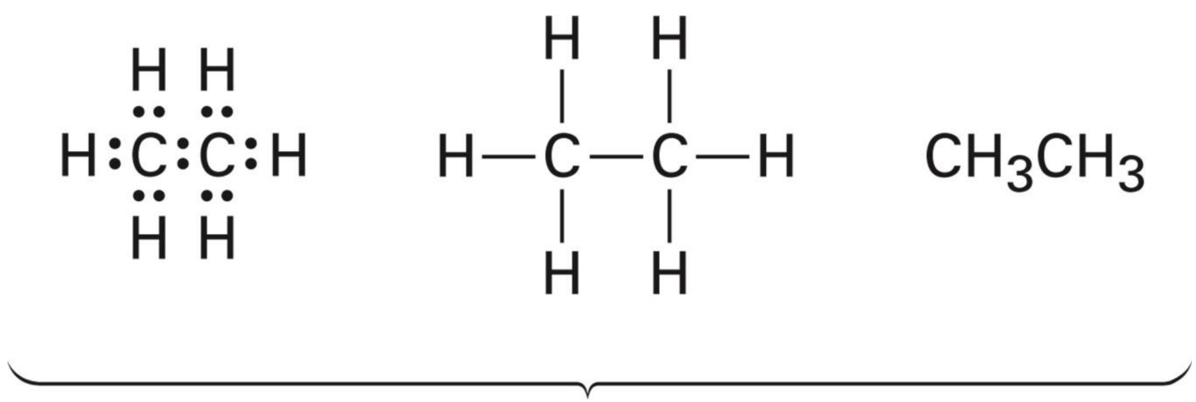


Figure 1.8 The structure of methane, showing its 109.5° bond angles.

1.7 *sp*^{3} Orbitals and the Structure of Ethane

- Two C's bond to each other by σ overlap of an *sp*^{3} orbital from each
- Three *sp*^{3} orbitals on each C overlap with H 1*s* orbitals to form six C–H bonds
- C–H bond strength in ethane is 421 kJ/mol
- C–C bond is 154 pm long and strength is 376 kJ/mol
- All bond angles of ethane are tetrahedral



Some representations of ethane

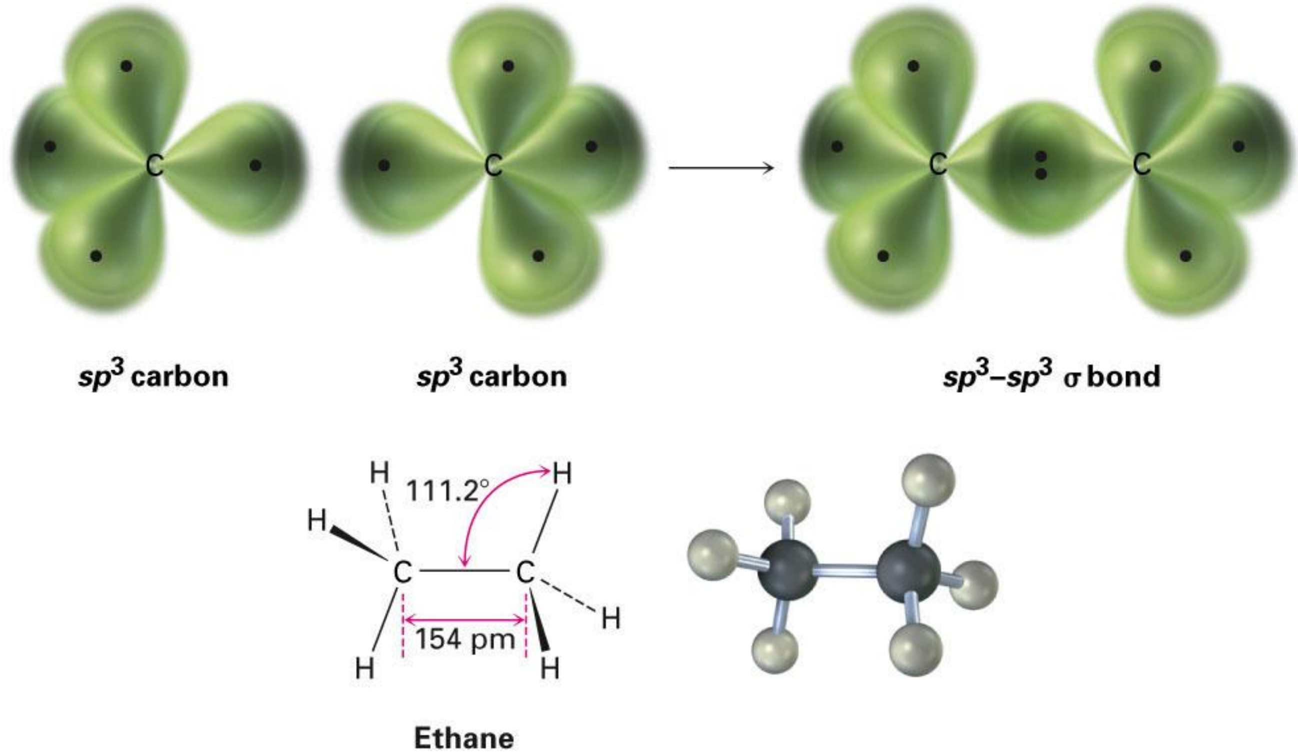
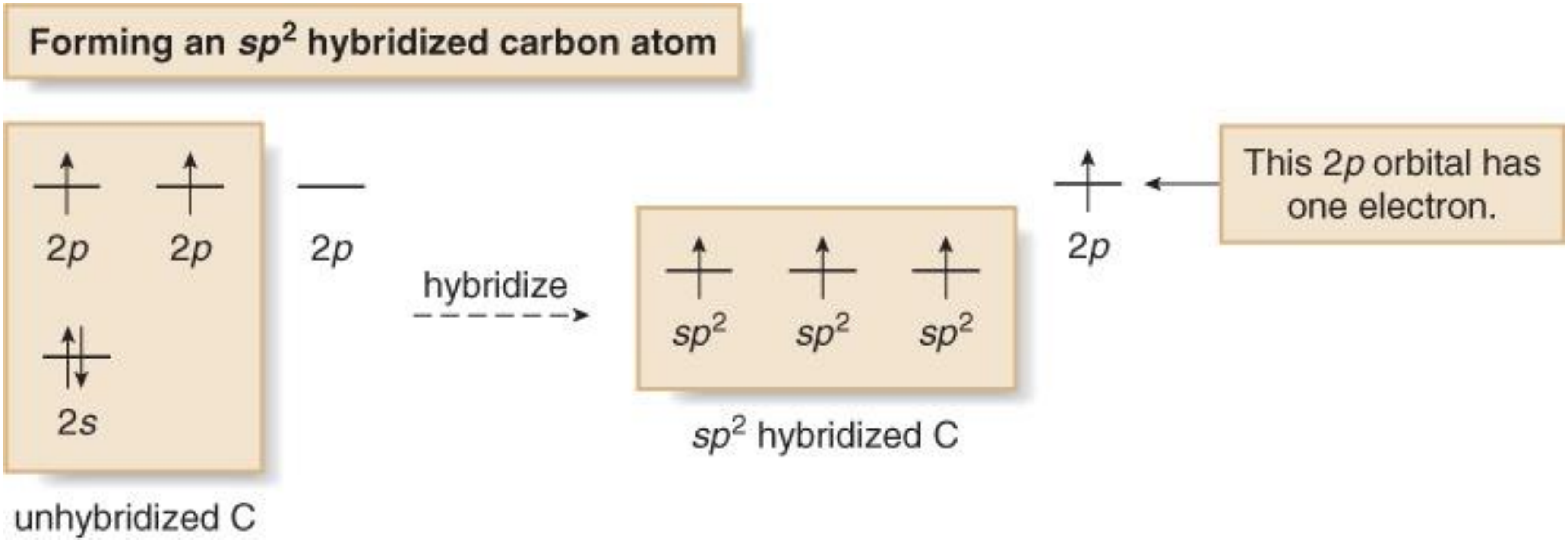


Figure 1.9 The structure of ethane.

1.8 Other Kinds of Hybrid Orbitals: *sp*^{2} and *sp*

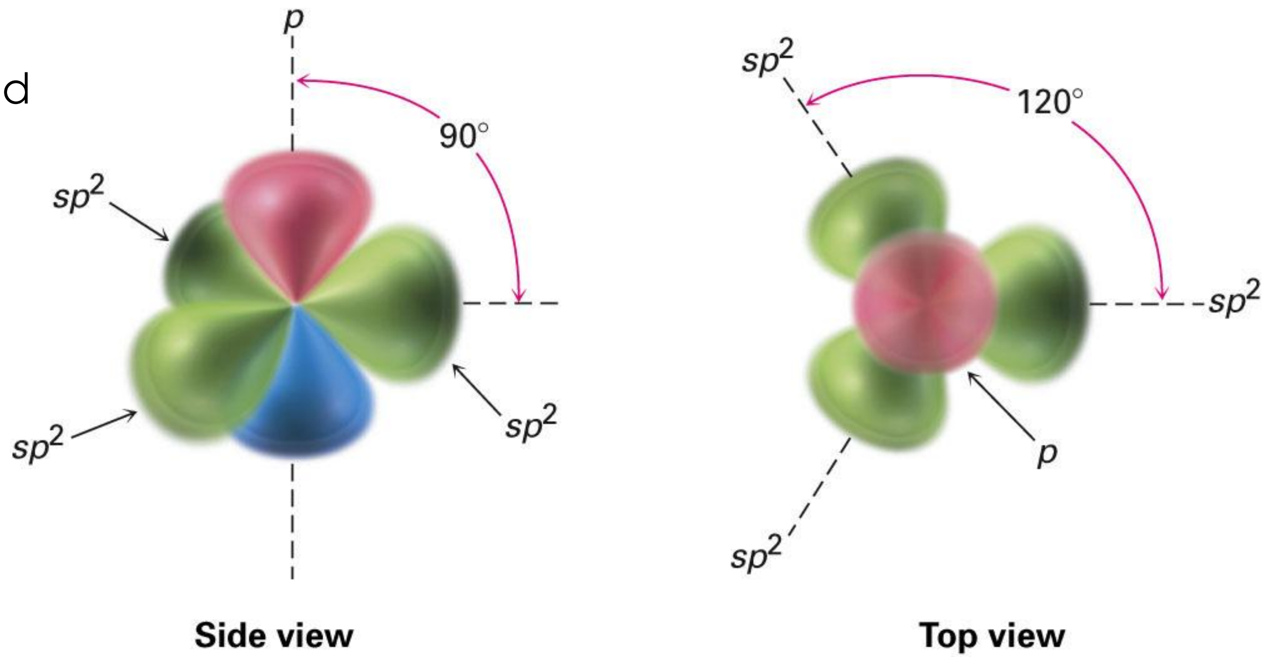
sp^2 Hybrid Orbitals

- **2*s* orbital combines with *two* 2*p* orbitals, giving 3 orbitals (spp = *sp*^{2}). This results in a *double* bond.**



- sp^2 **orbitals are in a plane with 120° angles**
- **Remaining *p* orbital is perpendicular to the plane**

Figure 1.10
(a) An sp^2-hybridized carbon.



Bonds from sp^2 Hybrid Orbitals

- Two sp^2-hybridized orbitals overlap to form a **sigma (σ) bond**
- p orbitals overlap *side-to-side* to formation a **pi (π) bond**
- sp^2–sp^2 σ bond and $2p$–$2p$ π bond result in sharing four electrons and formation of C-C double bond
- Electrons in the σ bond are centered between nuclei
- Electrons in the π bond occupy regions are on either side of a line between nuclei

Structure of Ethylene

- 4 H atoms form σ bonds with four sp^2 orbitals
- H–C–H and H–C–C bond angles of about 120°
- C–C double bond in ethylene shorter and stronger than single bond in ethane
- Ethylene C=C bond length 134 pm (C–C 154 pm)

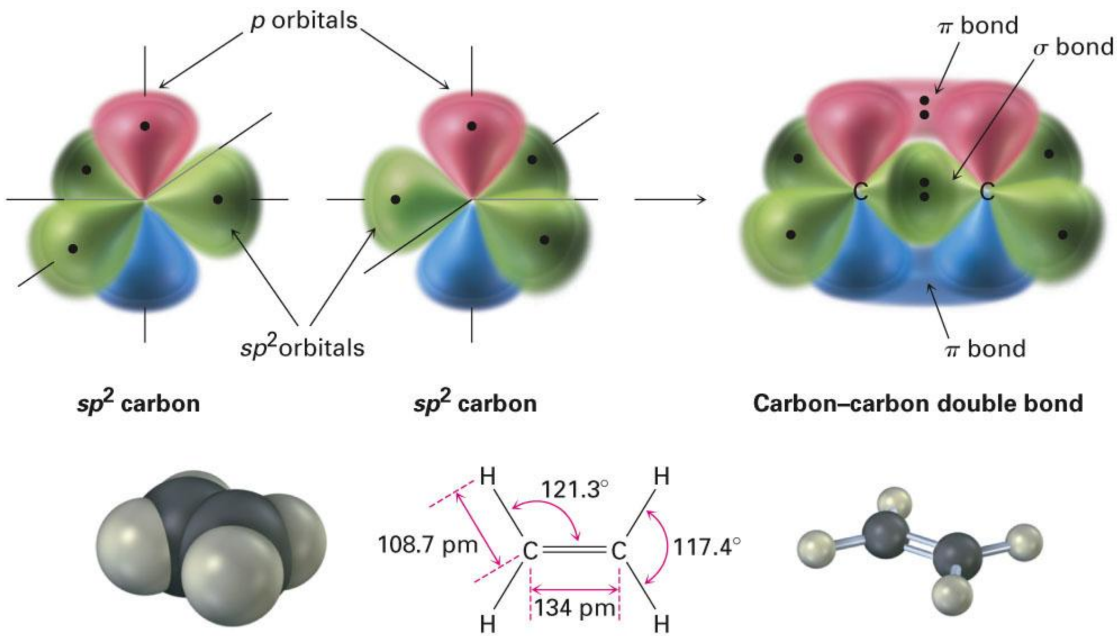
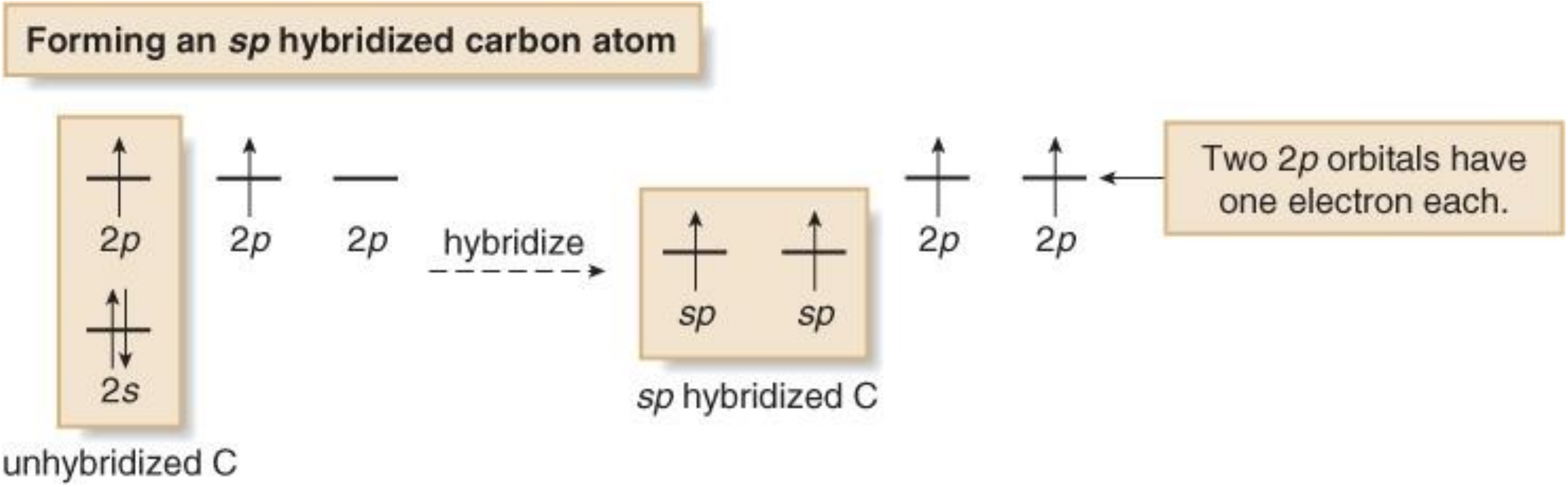


Figure 1.11 The structure of ethylene.

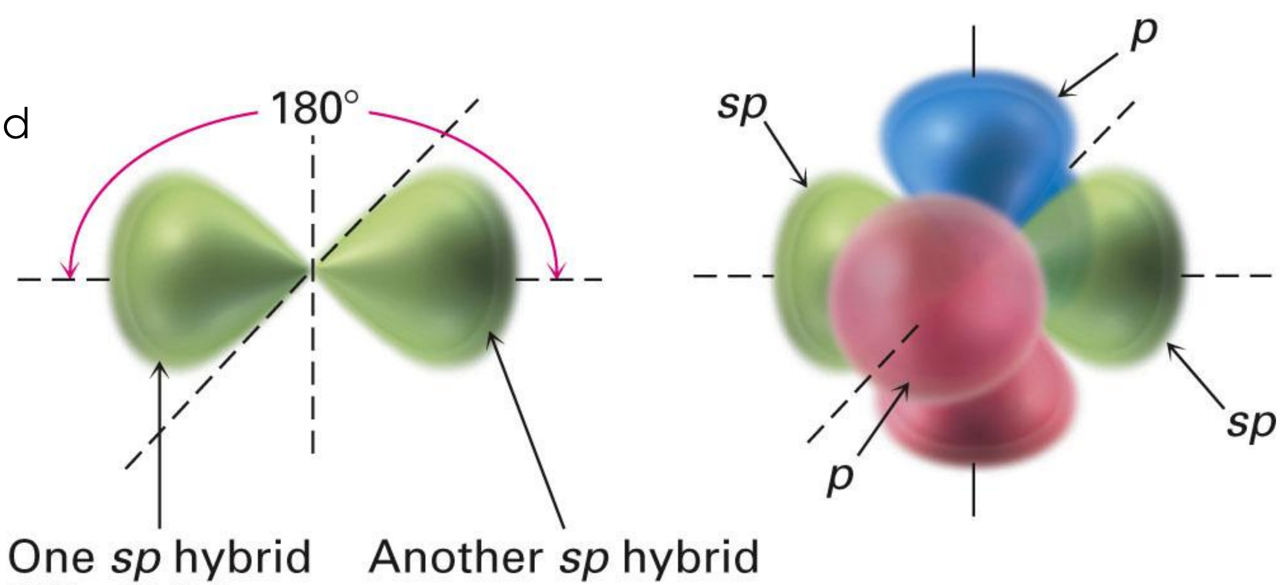
sp Hybrid Orbitals

- C-C a *triple* bond sharing six electrons
- Carbon 2*s* orbital hybridizes with a single *p* orbital giving two *sp* hybrids
  - two *p* orbitals remain unchanged



- *sp* orbitals are linear, 180° apart on *x*-axis
- Two *p* orbitals are perpendicular on the *y*-axis and the *z*-axis

Figure 10
(b) An *sp*-hybridized carbon.



Structure of Acetylene

- Two *sp* hybrid orbitals from each C form *sp–sp* σ bond
- p_z orbitals from each C form a p_z–p_z π bond by sideways overlap and p_y orbitals overlap similarly

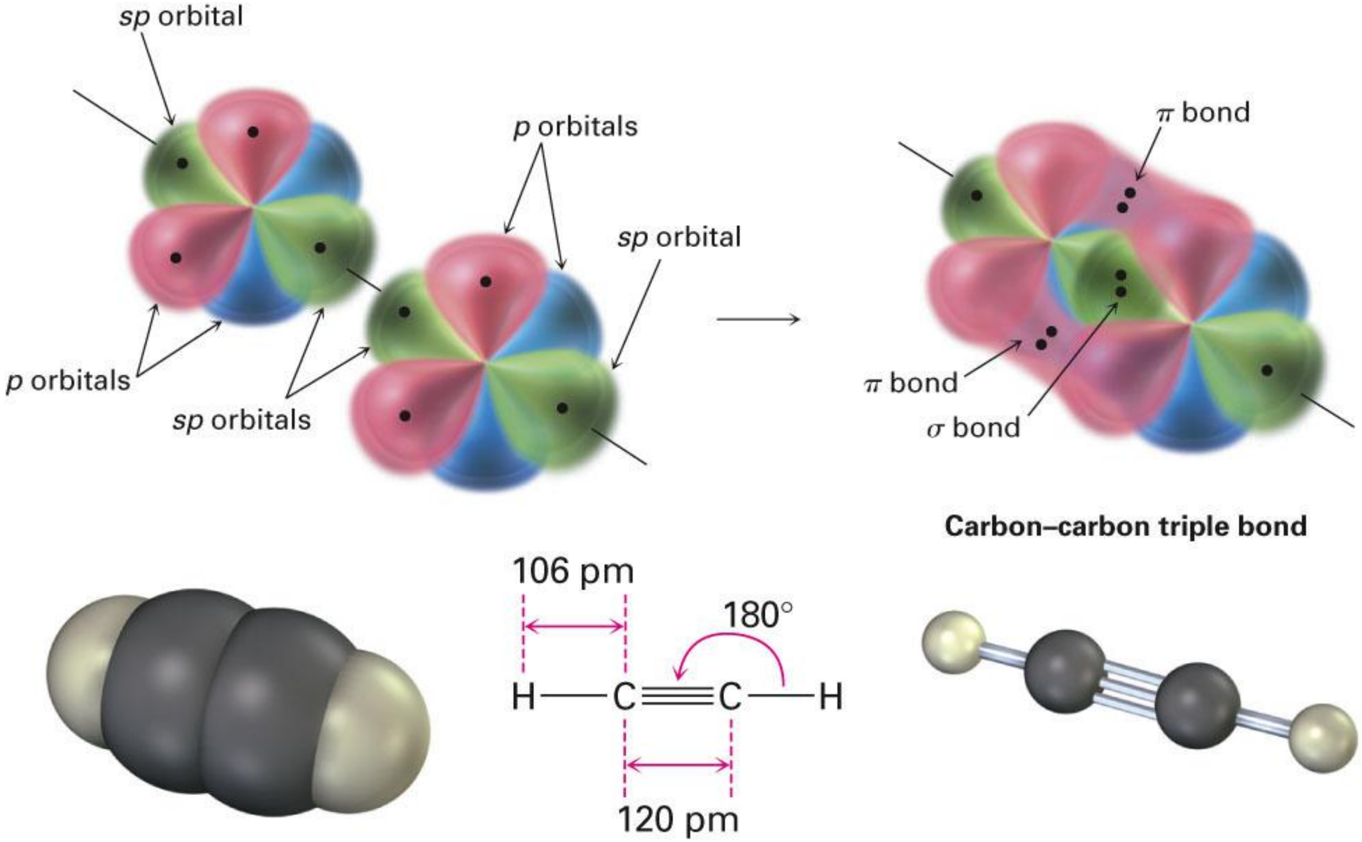
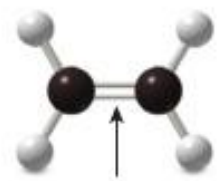
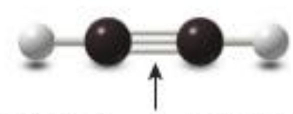


Figure 1.12 The structure of acetylene.

Summary of Covalent Bonding Seen in Carbon Compounds

Number of groups bonded to C	Hybridization	Bond angle	Example	Observed bonding
4	*sp*^{3}	109.5°	CH_3CH_3 ethane	 one σ bond $C_{sp^3}–C_{sp^3}$
3	*sp*^{2}	120°	$CH_2{=}CH_2$ ethylene	 one σ bond + one π bond $C_{sp^2}–C_{sp^2}$ $C_{2p}–C_{2p}$
2	*sp*	180°	$HC{\equiv}CH$ acetylene	 one σ bond + two π bonds $C_{sp}–C_{sp}$ $C_{2p}–C_{2p}$ $C_{2p}–C_{2p}$

1.9 Polar Covalent Bonds: Electronegativity

- Covalent bonds can have ionic character
- These are **polar covalent bonds**
  - Bonding electrons attracted more strongly by one atom than by the other
  - Electron distribution between atoms is not symmetrical

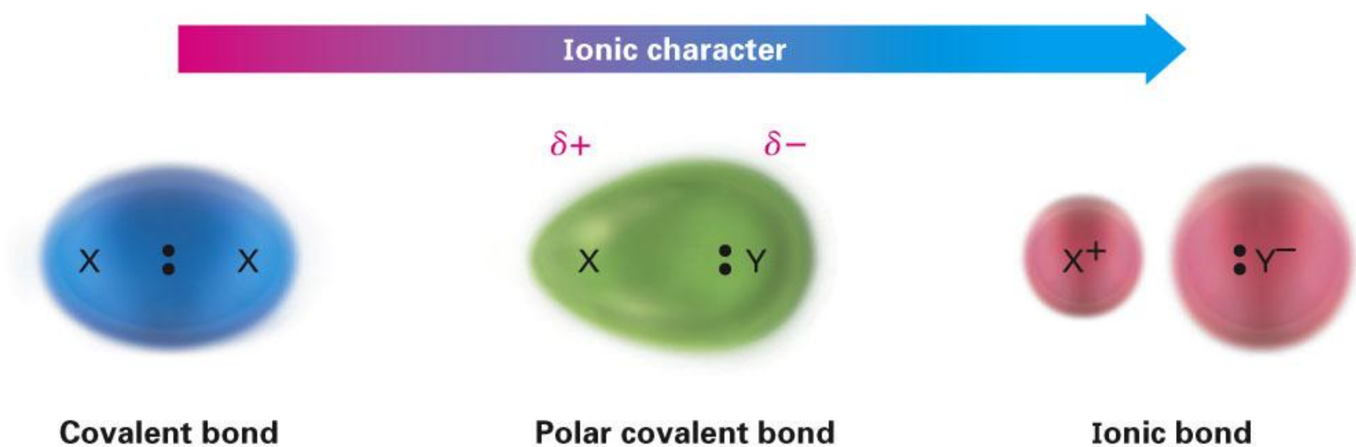


Figure 1.13 The continuum in bonding from covalent to ionic is a result of an unequal distribution of bonding electrons between atoms.

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 and other reactive nonmetals on right side of periodic table attract electrons strongly, higher EN
- EN of C = 2.5

The Periodic Table and Electronegativity

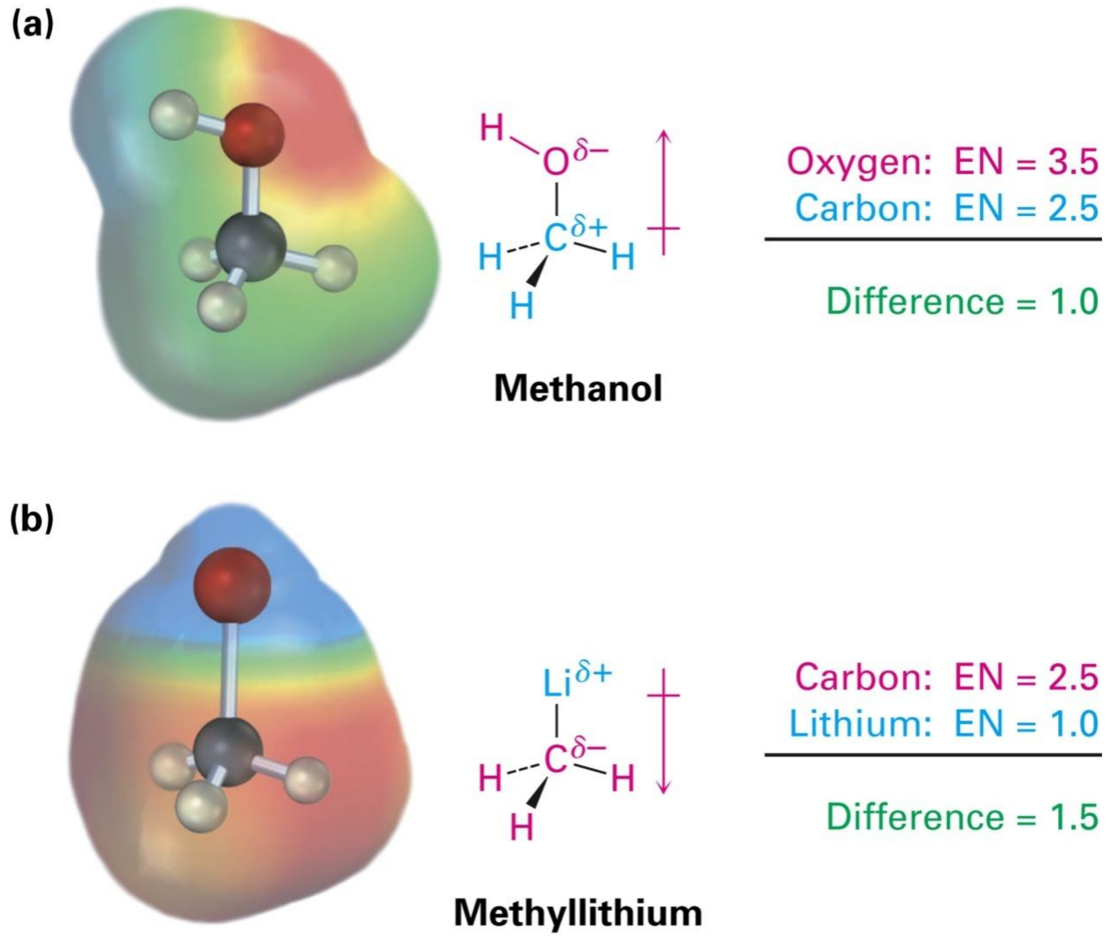
H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	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

Figure 1.14 Electronegativity values and trends.

Bond Polarity and Inductive Effect

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

Figure 1.15
(a) Methanol, CH_3OH, has a polar covalent C-O bond, and
(b) methyllithium, CH_3Li, has a polar covalent C-Li bond.



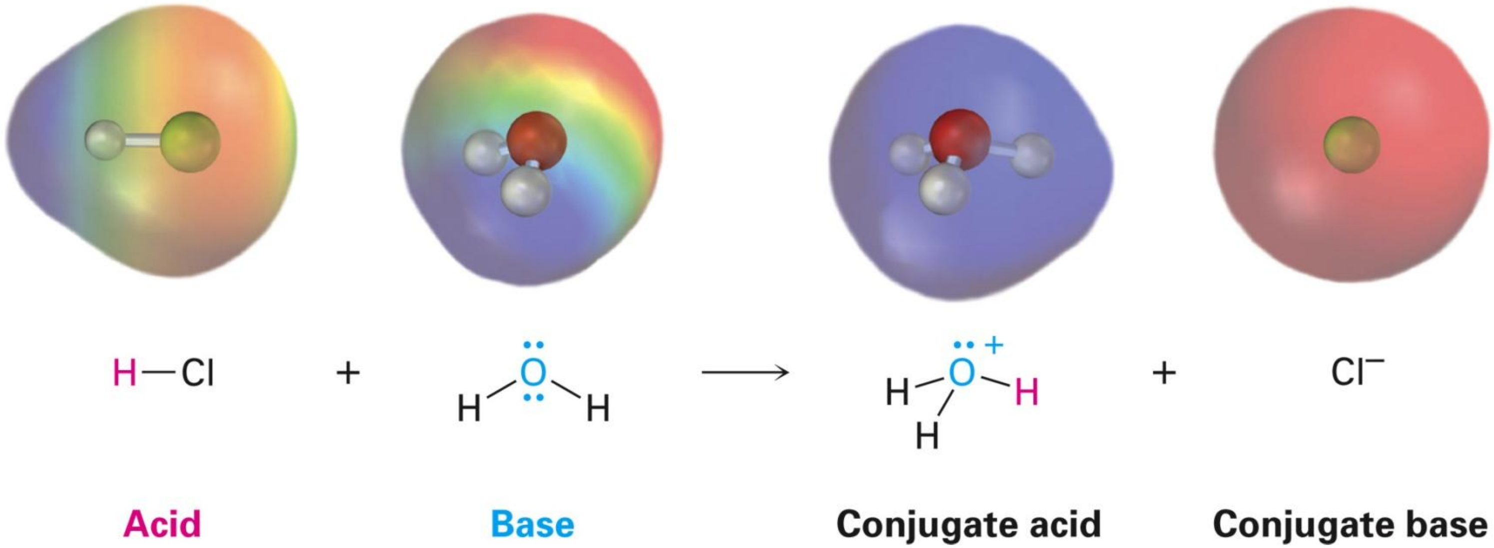
- **Electrostatic potential maps** show calculated charge distributions: Colors indicate electron-rich (red) and electron-poor (blue) regions
- **Arrows** indicate direction of bond polarity

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, 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



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

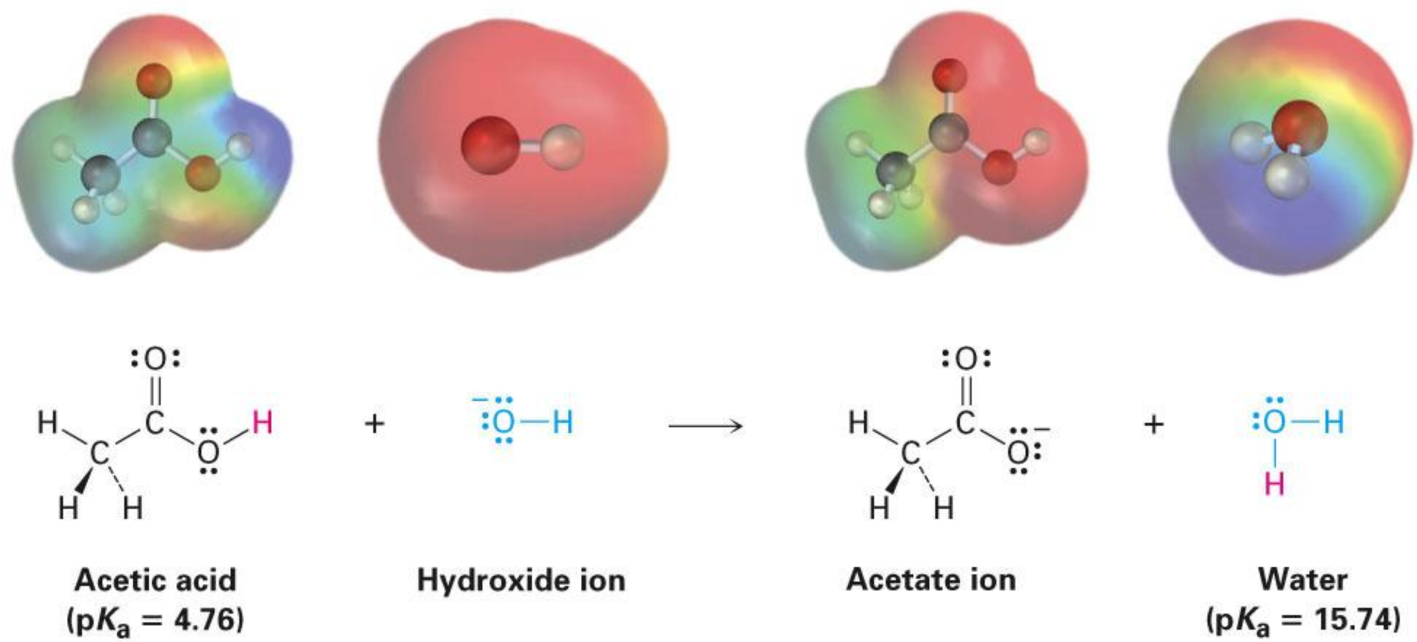
$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

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

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



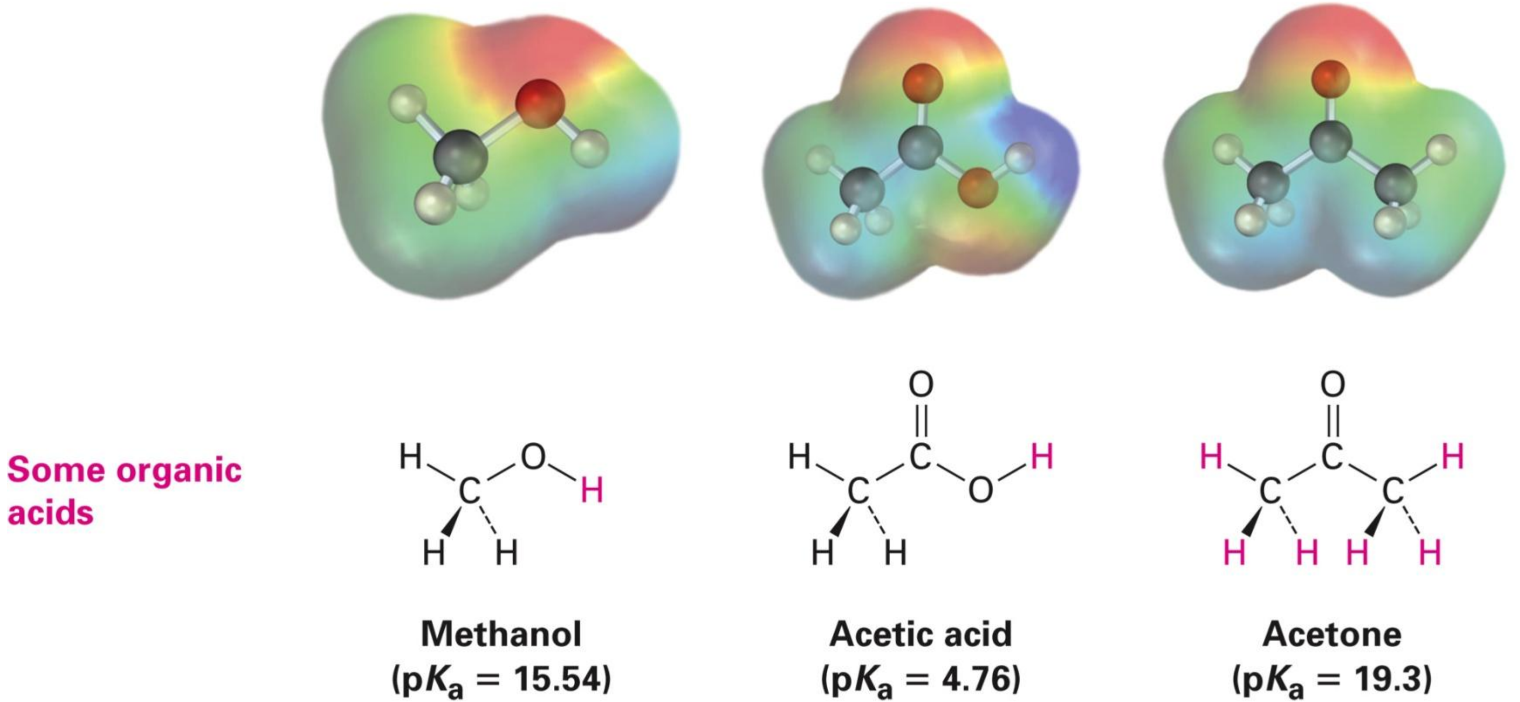
- The stronger base holds the proton more tightly
- The product conjugate acid in an acid-base reaction must be weaker and less reactive than the starting acid that that the product conjugate base must be weaker and less reactive than the starting base

$$\underset{\textbf{Stronger acid}}{CH_3\overset{\overset{O}{\|}}{C}OH} \quad + \quad \underset{\textbf{Stronger base}}{HO^-} \quad \rightleftharpoons \quad \underset{\textbf{Weaker acid}}{HOH} \quad + \quad \underset{\textbf{Weaker base}}{CH_3\overset{\overset{O}{\|}}{C}O^-}$$

1.11 Organic Acids and Organic Bases

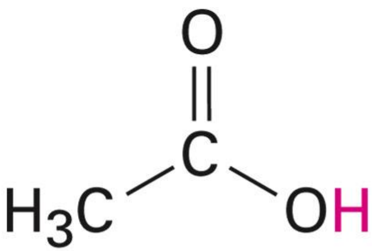
Organic Acids

- 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)

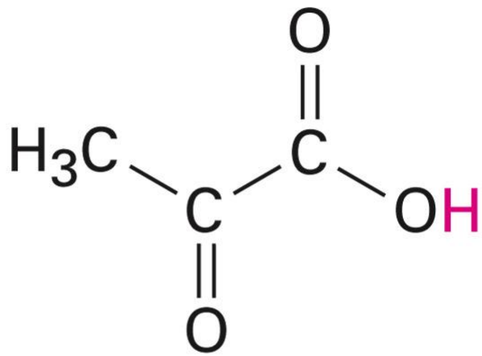


Carboxylic acids (-CO_2H)

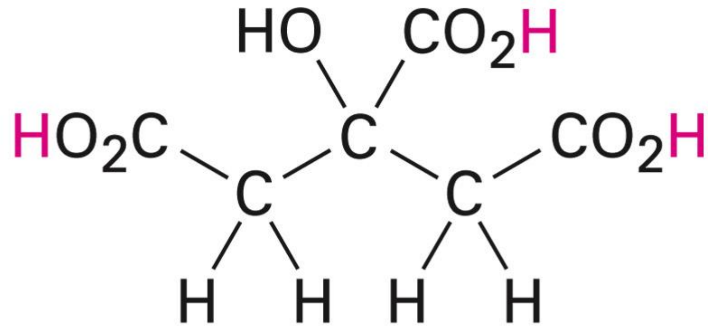
- **They occur abundantly in all living organisms and are involved in almost all metabolic pathway**



Acetic acid



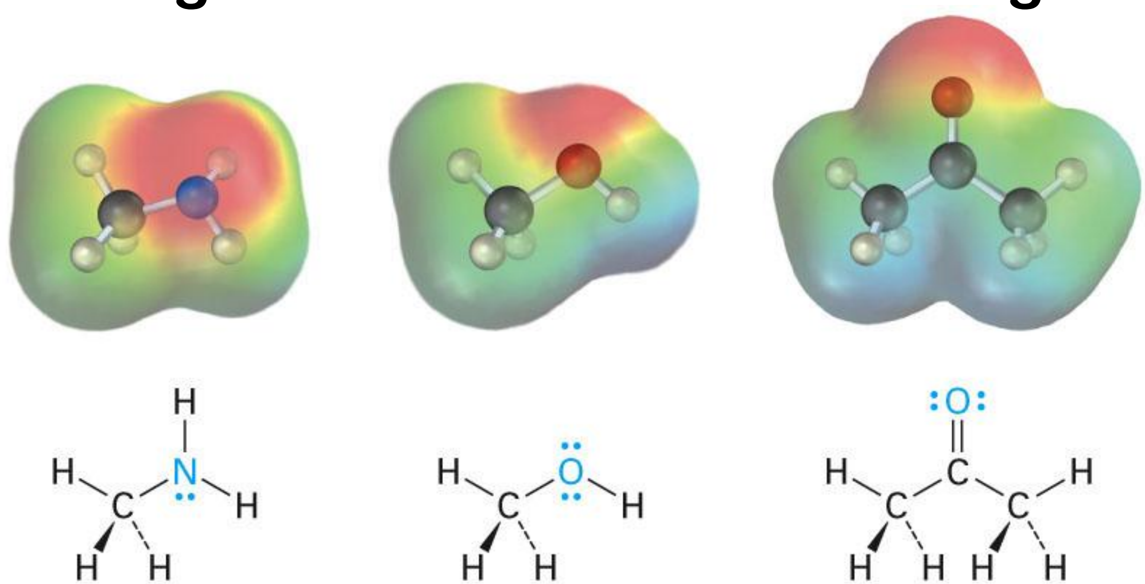
Pyruvic acid



Citric acid

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

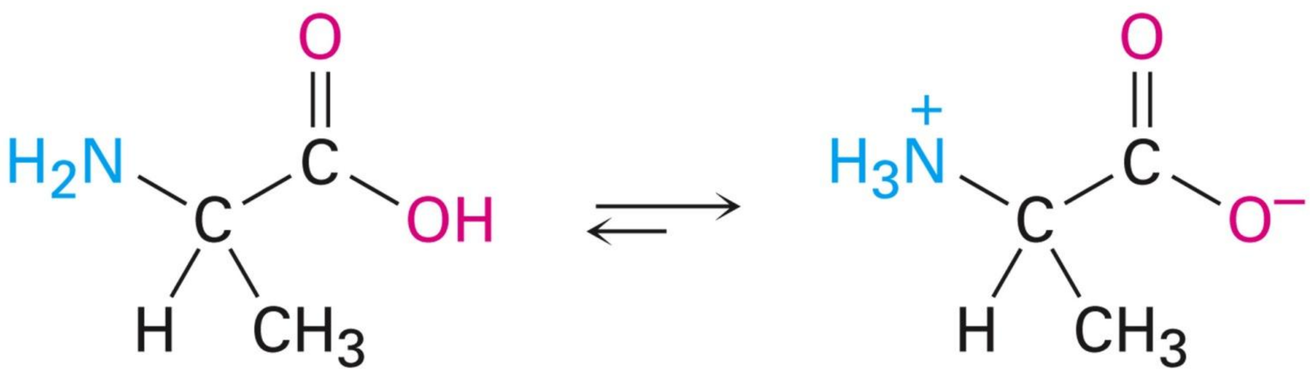


Some organic bases

Methylamine Methanol Acetone

Amino acids

- They are the building blocks from which the proteins present in all living organisms are made
- Twenty different amino acids go into making up proteins; alanine is an example

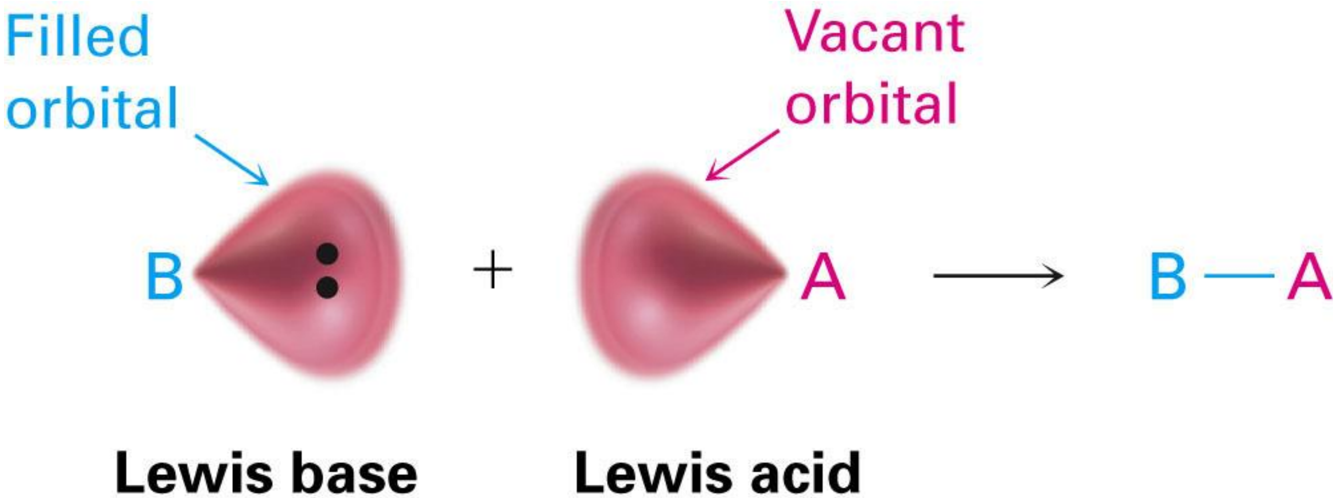


Alanine (uncharged form)

Alanine (zwitterion form)

1.12 Acids and Bases: The Lewis Definition

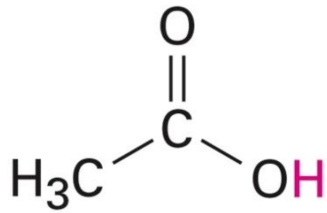
- **Lewis acids** are electron pair acceptors
- **Lewis bases** are electron pair donors
- The Lewis definition leads to a general description of many reaction patterns but there is no scale of strengths as in the Brønsted definition of pK_a

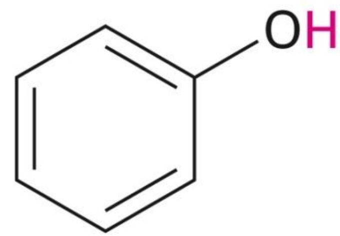


Some Lewis acids

Some neutral proton donors:

H_2O HCl HBr HNO_3 H_2SO_4





CH_3CH_2OH

A carboxylic acid **A phenol** **An alcohol**

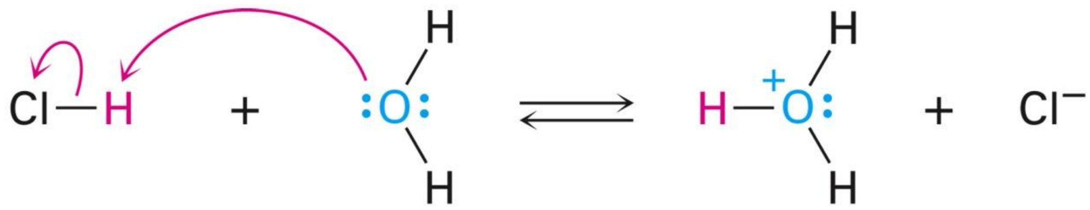
Some cations:

Li^+ Mg^{2+}

Some metal compounds:

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

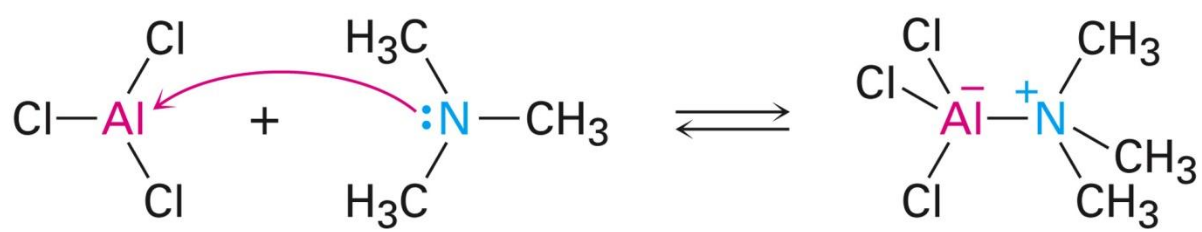
- **The combination of a Lewis acid and a Lewis base can shown with a curved arrow from base to acid**



Hydrogen chloride (Lewis acid)

Water (Lewis base)

Hydronium ion



Aluminum trichloride (Lewis acid)

Trimethylamine (Lewis base)

- **A number of types of arrows are used in describing organic reactions.**

A Summary of Arrow Types in Chemical Reactions

Arrow	Name	Use
$\longrightarrow$	Reaction arrow	Drawn between the starting materials and products in an equation
$\rightleftharpoons$	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation
$\longleftrightarrow$	Double-headed arrow	Drawn between resonance structures
$\curvearrowright$	Full-headed curved arrow	Shows movement of an electron pair
$\curvearrowright$	Half-headed curved arrow (fishhook)	Shows movement of a single electron

Organic Foods: Risk versus Benefit

Table 1.3 Some LD_{50} Values

Substance	LD_{50} (g/kg)	Substance	LD_{50} (g/kg)
Strychnine	0.005	Chloroform	1.2
Arsenic trioxide	0.015	Iron(II) sulfate	1.5
DDT	0.115	Ethyl alcohol	10.6
Aspirin	1.1	Sodium cyclamate	17