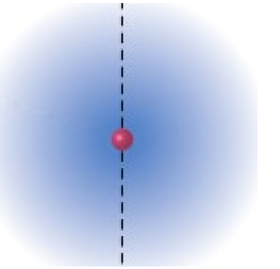

Organic Chemistry, 7th Edition

L. G. Wade, Jr.

Chapter 1

Introduction and Review

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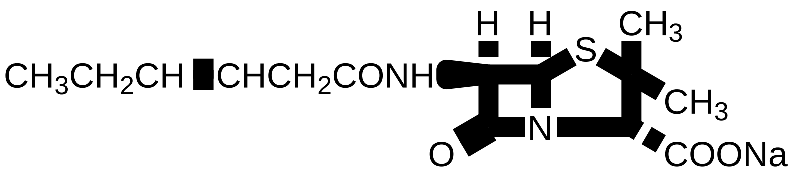
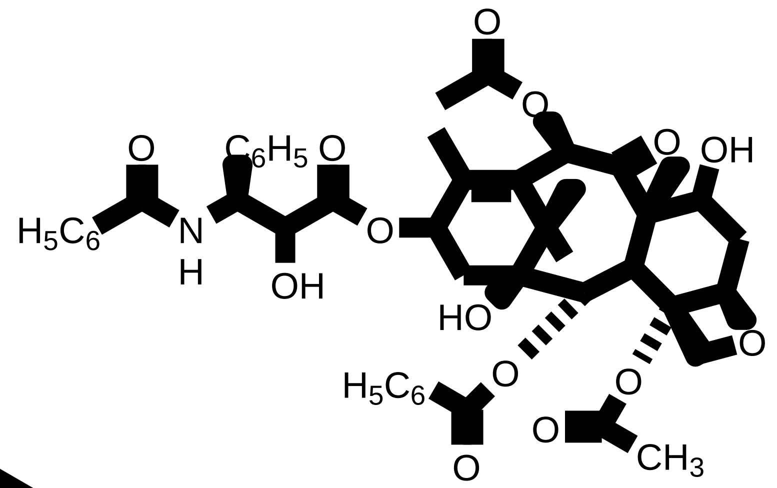
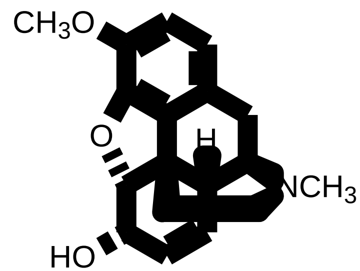
Organic Chemistry



2-Pentenylpenicillin



Taxol

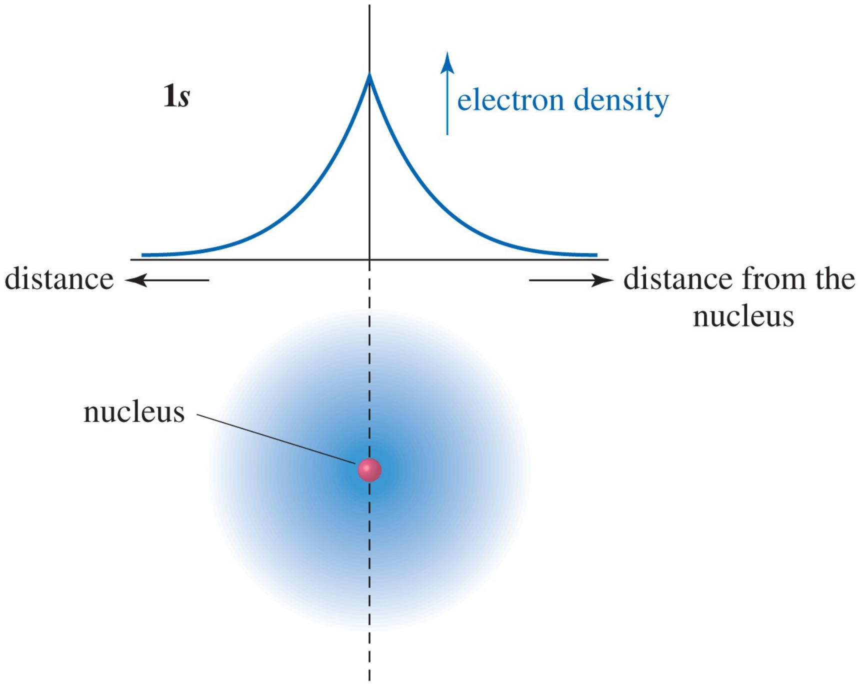


Codeine

- Organic chemistry is the chemistry of carbon compounds.

Electronic Structure of the Atom

- An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.
- The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.



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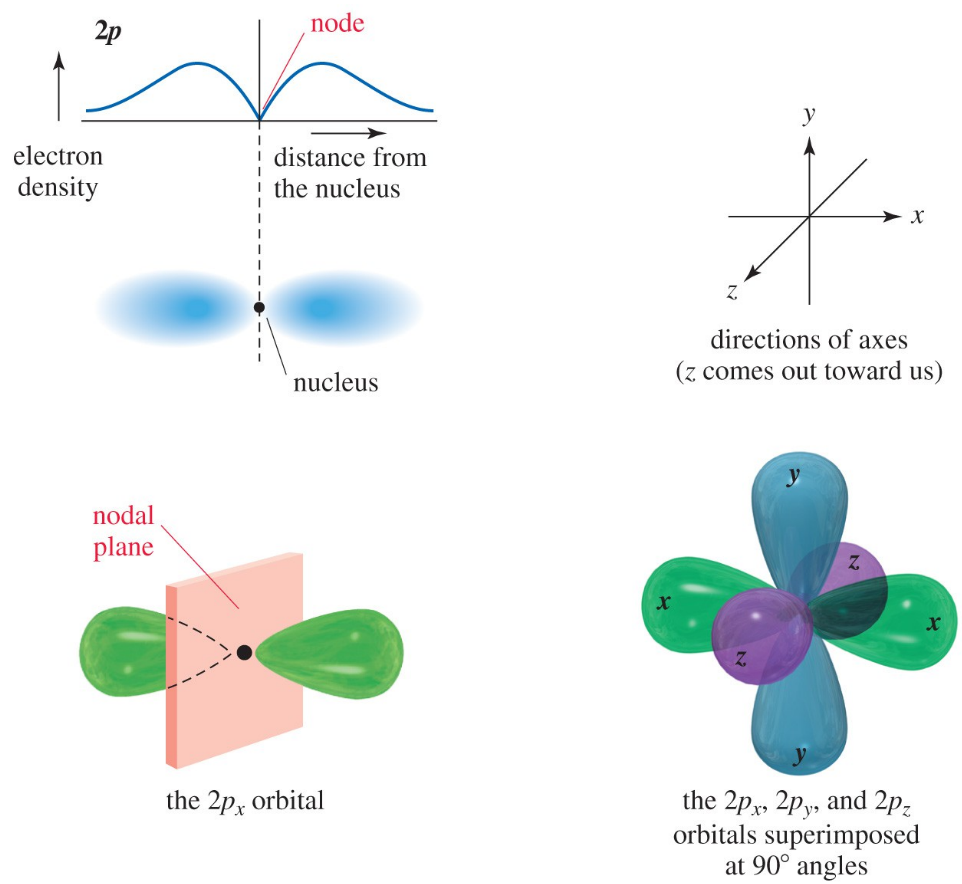
The 2*p* Orbitals

- There are three 2*p* orbitals, oriented at right angles to each other.
- Each *p* orbital consists of two lobes.
- Each is labeled according to its orientation along the *x*, *y*, or *z* axis.



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Isotopes

$$^{12}_{6}\mathrm{C} \qquad ^{14}_{6}\mathrm{C}$$

- ***Isotopes*** are atoms with the same number of protons but different number of neutrons.
- ***Mass number*** is the sum of the protons and neutrons in an atom.

Electronic Configurations of Atoms

- ***Valence electrons*** are electrons on the outermost shell of the atom.

TABLE 1-1

Electronic Configurations of the Elements of the First and Second Rows

Element	Configuration	Valence Electrons
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8

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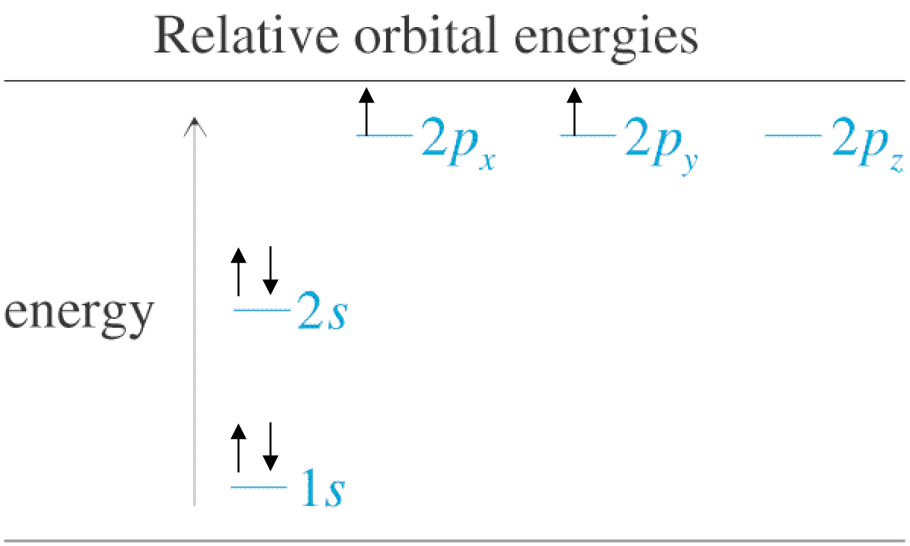
Electronic Configurations

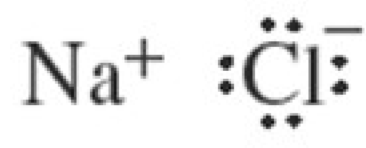


Electronic configuration of carbon

- The ***aufbau principle*** states to fill the lowest energy orbitals first.
- ***Hund's rule*** states that when there are two or more orbitals of the same energy (degenerate), electrons will go into different orbitals rather than pairing up in the same orbital.

Ionic Bonding

- To obtain a noble gas configuration (a full valence shell), atoms may transfer electrons from one atom to another.
- The atoms, now bearing opposite charges, stay together by electrostatic attraction.



ionic bond

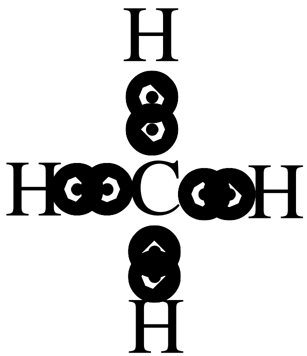
Covalent Bonding

- Electrons are shared between the atoms to complete the octet.
- When the electrons are shared evenly the bond is said to be ***nonpolar*** or pure covalent.
- When electrons are not shared evenly between the atoms, the resulting bond will be ***polar***.

Lewis Structures

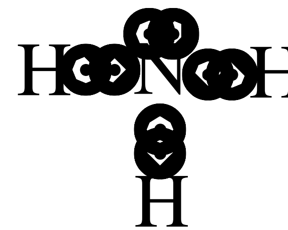
CH_4

Carbon: 4 *e*
4 H@1 *e* ea: <u>4 *e*</u>
8 *e*



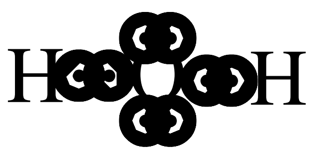
NH_3

Nitrogen: 5 *e*
3 H@1 *e* ea: <u>3 *e*</u>
8 *e*



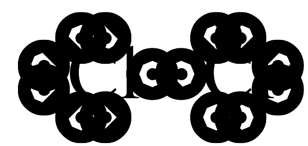
H_2O

Oxygen: 6 *e*
2 H@1 *e* ea: <u>2 *e*</u>
8 *e*

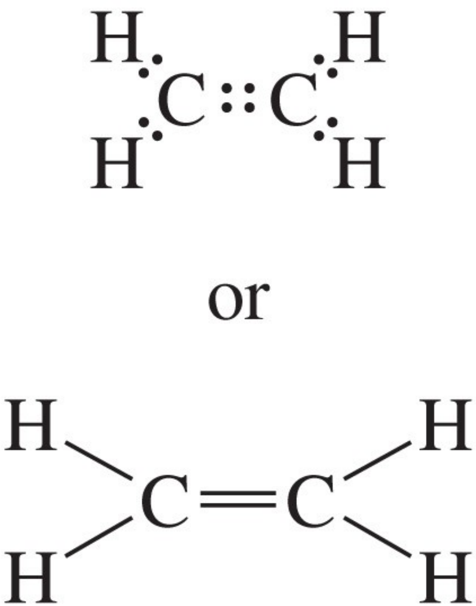


Cl_2

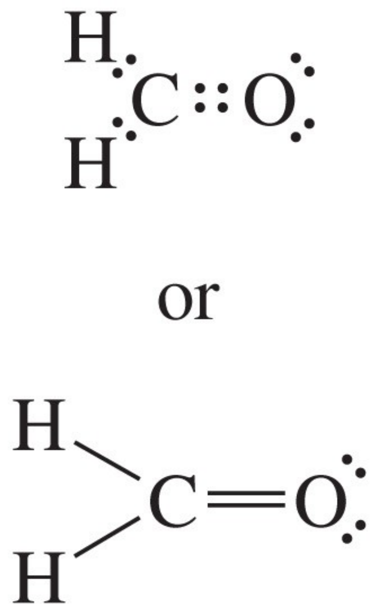
2 Cl @7 *e* ea: 14 *e*



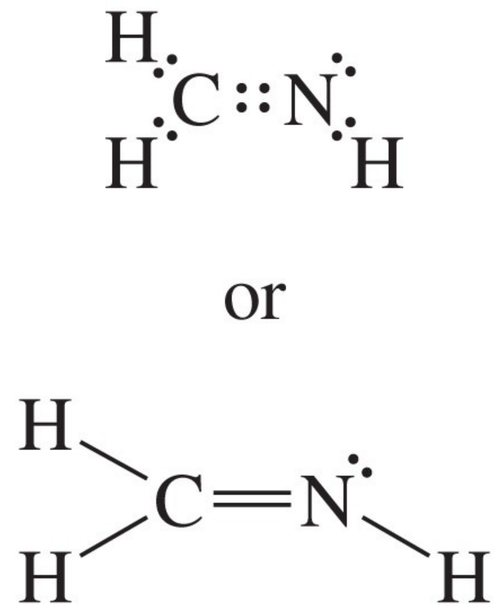
Double and Triple Bonds



ethylene



formaldehyde



formaldimine

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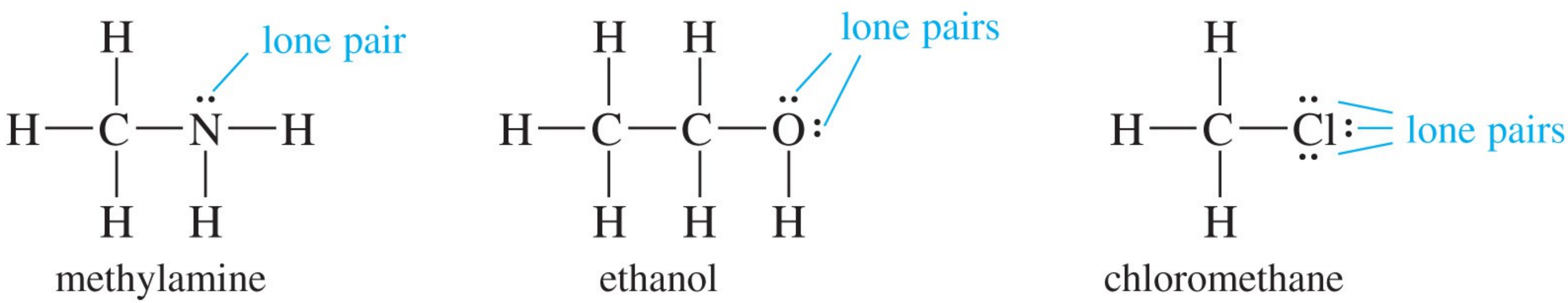
Bonding Patterns

	Valence electrons	# Bonds	# Lone Pair Electrons
C	**4**	**4**	**0**
N	**5**	**3**	**1**
O	**6**	**2**	**2**
Halides (F, Cl, Br, I)	**7**	**1**	**3**

Lone Pairs



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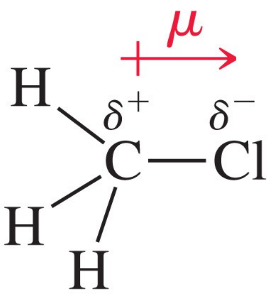
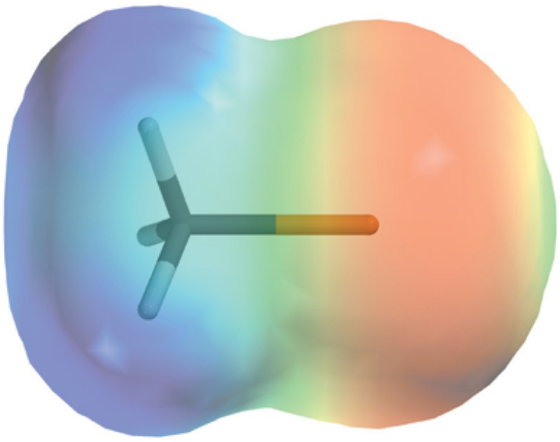
Dipole Moment



chloromethane



chloromethane

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- Amount of electrical charge x bond length.
- Charge separation shown by electrostatic potential map (EPM).
- Red indicates a partially negative region and blue indicates a partially positive region.

Electronegativity and Bond Polarity

- Electronegativities can be used to predict whether a bond will be polar.
- Since the electronegativity of carbon and hydrogen are similar, C—H bonds are considered to be nonpolar.

H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8						Br 3.0
						I 2.7

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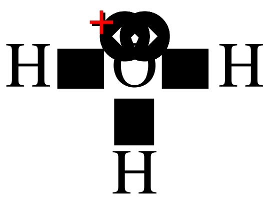
Charged Species

Formal charge = number of valence electrons – (*e* in lone pairs + # bonds)

H_3O^+

6 – (2 + 3) = +1



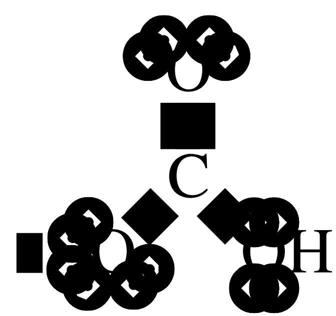
NO^+

6 – (2 + 3) = +1

5 – (2 + 3) = 0

HCO_3^-

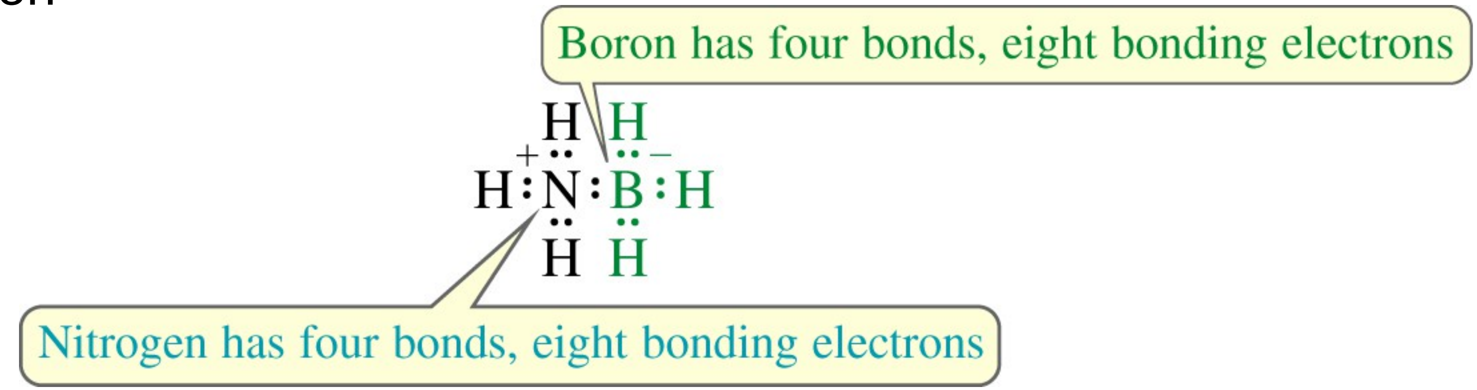
6 – (6 + 1) = -1



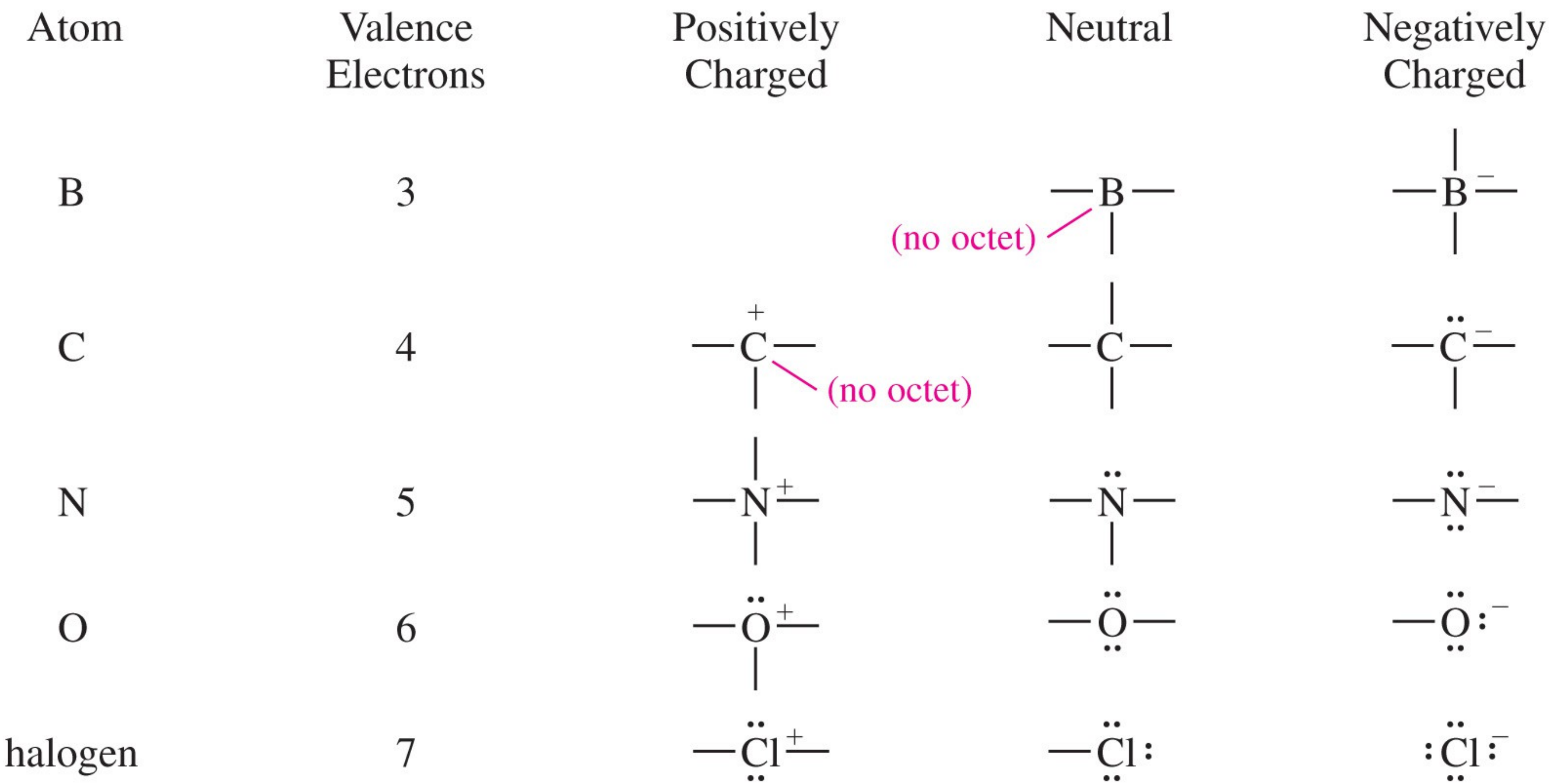
Solved Problem 1

Compute the formal charge (FC) on each atom in $H_3N - BH_3$.

Solution



Common Bonding Patterns



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Resonance Forms

- In a resonance form, only the electrons are moved. Connectivity between atoms stay the same.
- The real structure is a hybrid of the different resonance forms.
- Arrows connecting resonance forms are double headed.
- Spreading the charges over two or more atoms stabilize the ion.

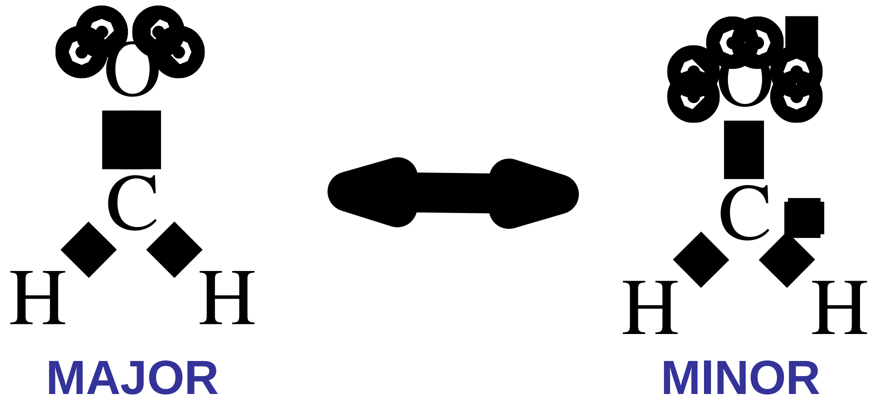
Resonance Forms

Resonance Forms can be compared using the following criteria, beginning with the most important:

- Has as many octets as possible.
- Has as many bonds as possible.
- Has the negative charge on the most electronegative atom.
- Has as little charge separation as possible.

Major and Minor Contributors

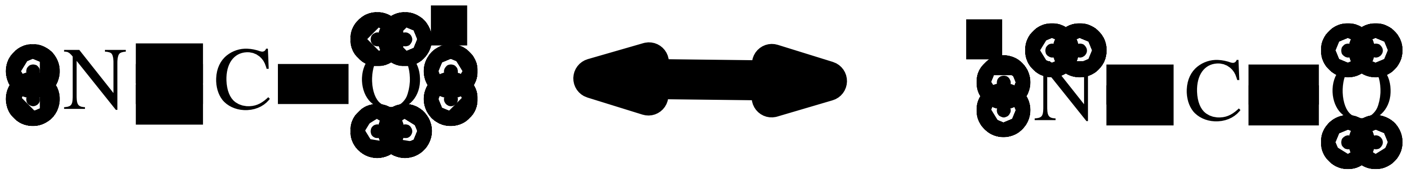
- The major contributor is the one in which all the atoms have a complete octet of electrons.



The carbon atom does not have a complete octet of electrons.

Major and Minor Contributors (Continued)

- When both resonance forms obey the octet rule, the major contributor is the one with the negative charge on the most electronegative atom.

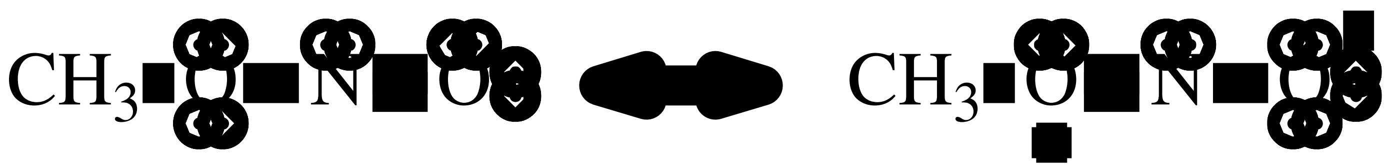


MAJOR **MINOR**

The oxygen is more electronegative, so it should have the negative charge.

Non-Equivalent Resonance

- Opposite charges should be on adjacent atoms.



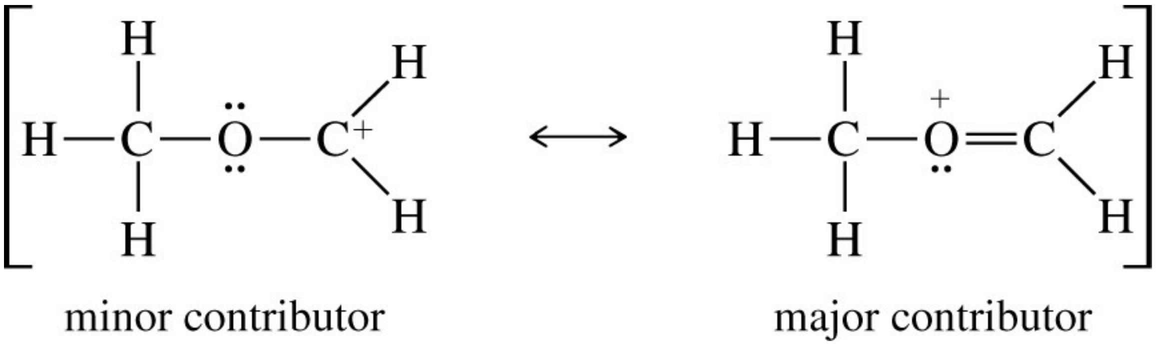
MAJOR **MINOR**

The most stable one is the one with the smallest separation of oppositely charged atoms.

Solved Problem 2

Draw the important resonance forms for $[CH_3OCH_2]^+$. Indicate which structure is major and minor contributor or whether they would have the same energy.

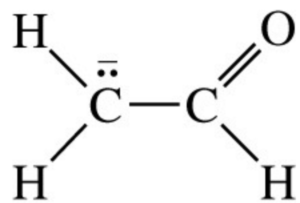
Solution



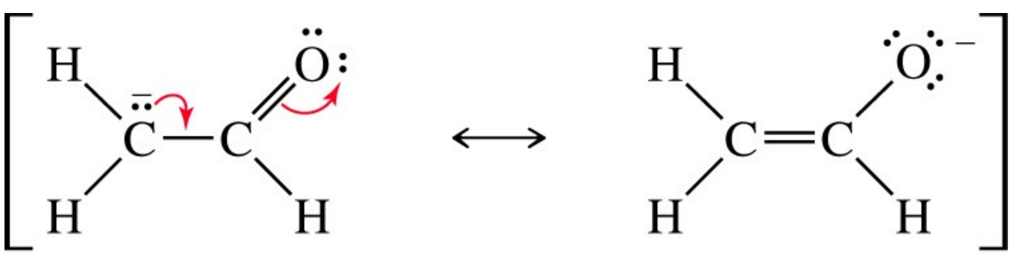
The first (minor) structure has a carbon atom with only six electrons around it. The second (major) structure has octets on all atoms and an additional bond.

Solved Problem 3

Draw the resonance structure the compound below. Indicate which structure is major and minor contributor or whether they would have the same energy.



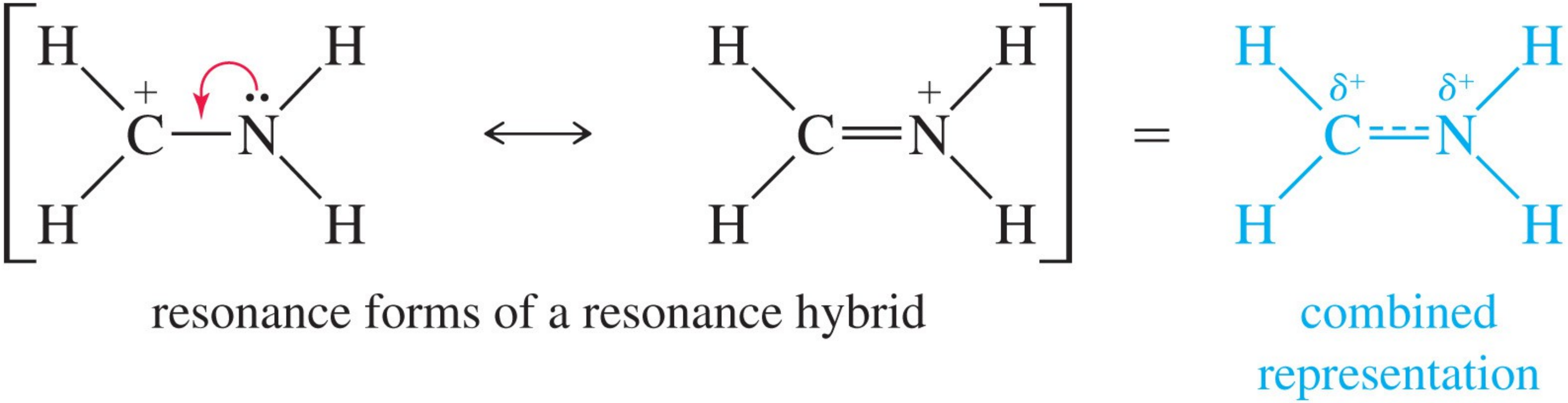
Solution



minor contributor major contributor

Both of these structures have octets on oxygen and both carbon atoms, and they have the same number of bonds. The first structure has the negative charge on carbon; the second has it on oxygen. Oxygen is the more electronegative element, so the second structure is the major contributor.

Resonance Forms



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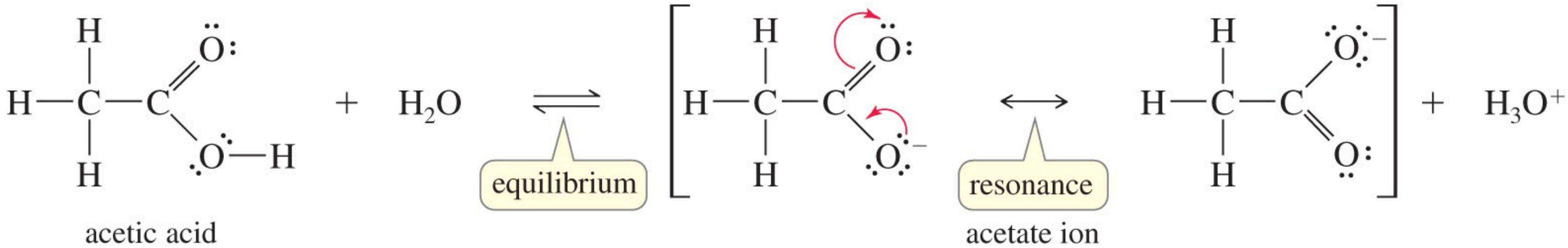
- The structure of some compounds are not adequately represented by a single Lewis structure.
- Resonance forms are Lewis structures that can be interconverted by moving electrons only.
- The true structure will be a hybrid between the contributing resonance forms.

Resonance Forms for the Acetate Ion



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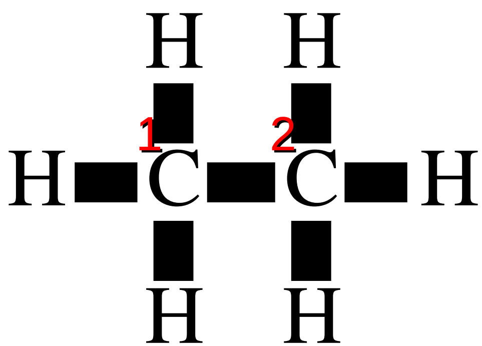
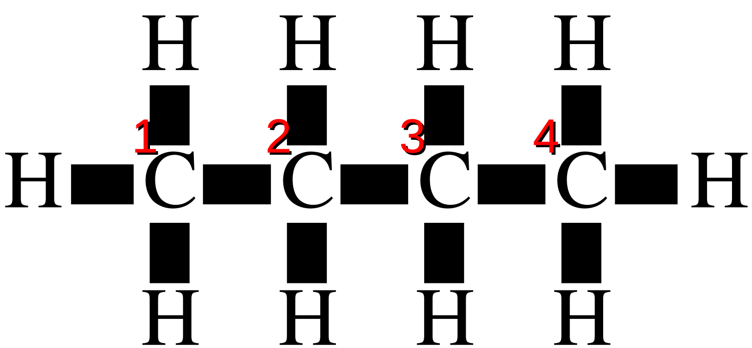
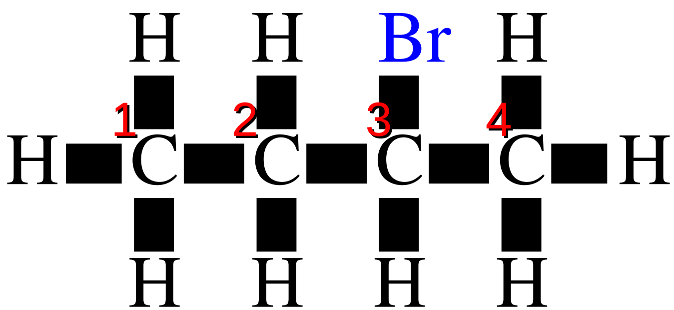
- When acetic acid loses a proton, the resulting acetate ion has a negative charge delocalized over both of the oxygen atoms.
- Each oxygen atom bears half of the negative charge, and this delocalization stabilizes the ion.
- Each of the carbon–oxygen bonds is halfway between a single bond and a double bond, and they are said to have a ***bond order*** of 1½.

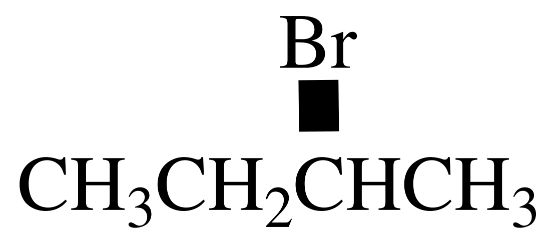
Structures and Formulas

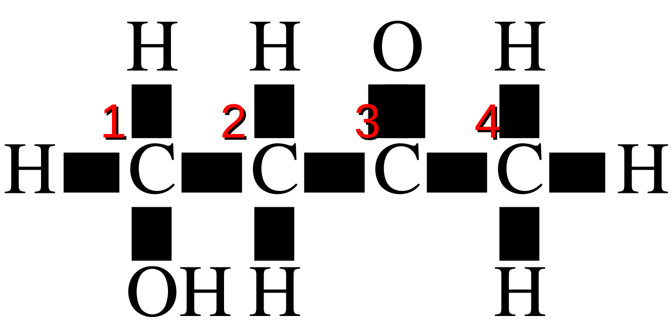
Extended	Condensed
	CH_3CH_3
	$CH_3CH_2CH_2CH_3$

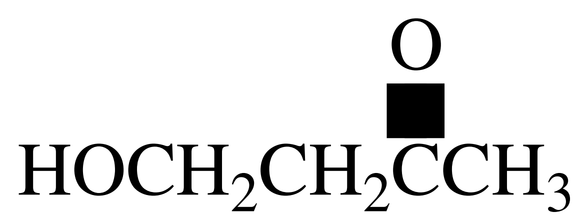
Structures and Formulas

Extended	Condensed

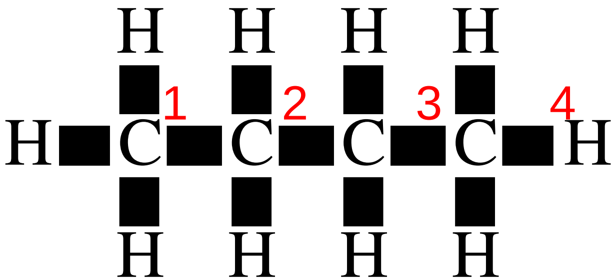


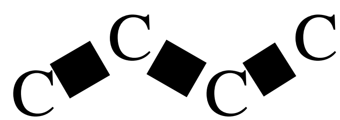


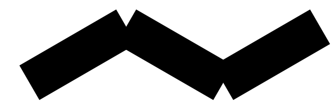


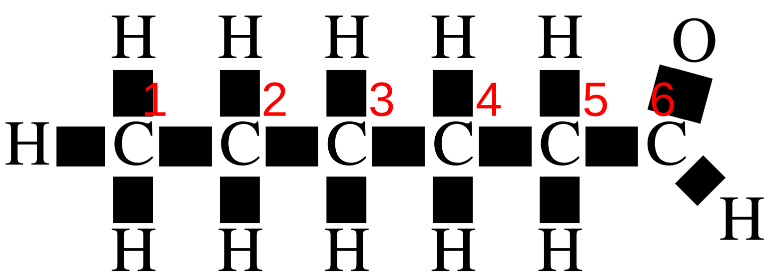


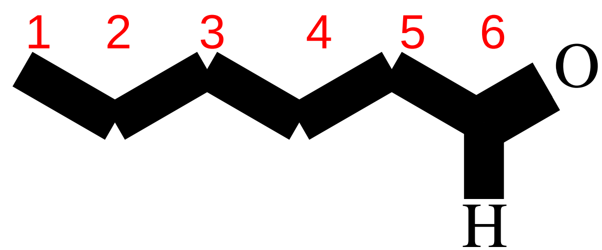
Line-Angle Formulas





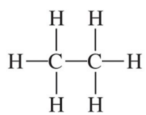
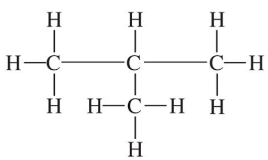
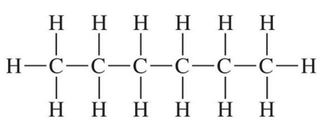






Line-Angle Formulas (Continued)

TABLE 1-2
Examples of Condensed Structural Formulas

Compound	Lewis Structure	Condensed Structural Formula
ethane		CH_3CH_3
isobutane		$(CH_3)_3CH$
n-hexane		$CH_3(CH_2)_4CH_3$

(*Continued*)

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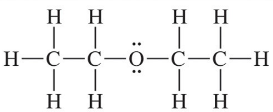
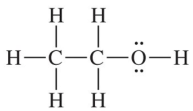
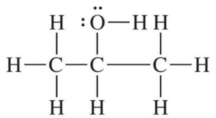
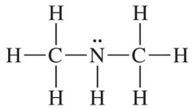
TABLE 1-2
Continued

Compound	Lewis Structure	Condensed Structural Formula
diethyl ether		$CH_3CH_2OCH_2CH_3$ or $CH_3CH_2—O—CH_2CH_3$ or $(CH_3CH_2)_2O$
ethanol		CH_3CH_2OH
isopropyl alcohol		$(CH_3)_2CHOH$
dimethylamine		$(CH_3)_2NH$

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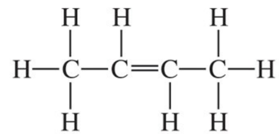
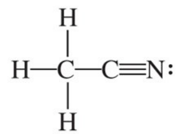
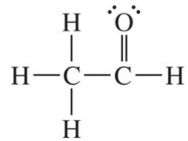
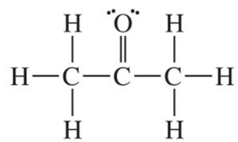
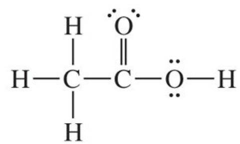
Line-Angle Formulas (Continued)

TABLE 1-3

Condensed Structural Formulas for Double and Triple Bonds

Compound	Lewis Structure	Condensed Structural Formula
2-butene		$CH_3CHCHCH_3$ or $CH_3CH{=}CHCH_3$
acetonitrile		CH_3CN or $CH_3C{\equiv}N$
acetaldehyde		CH_3CHO or $CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$
acetone		CH_3COCH_3 or $CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$
acetic acid		CH_3COOH or $CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$ or CH_3CO_2H

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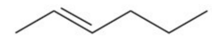
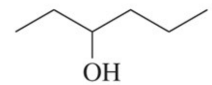
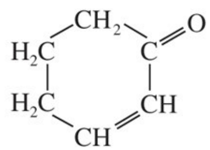
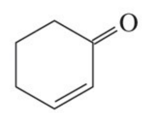
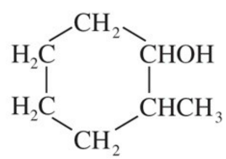
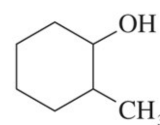
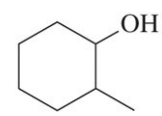
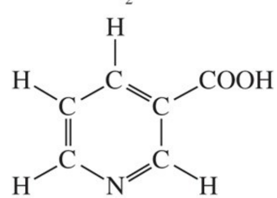
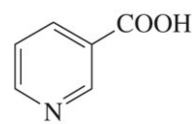
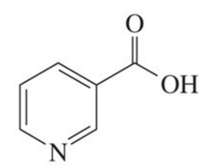
Line-Angle Formulas (Continued)

TABLE 1-4

Examples of Line–Angle Drawings

Compound	Condensed Structure	Line–Angle Formula
hexane	$CH_3(CH_2)_4CH_3$	
2-hexene	$CH_3CH{=}CHCH_2CH_2CH_3$	
3-hexanol	$CH_3CH_2CH(OH)CH_2CH_2CH_3$	
2-cyclohexenone		
2-methylcyclohexanol		 or 
nicotinic acid (a vitamin, also called niacin)		 or 

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Calculating Empirical Formulas

The following are items that need to be considered when calculating empirical formulas:

- Given % composition for each element, assume 100 grams.
- Convert the grams of each element to moles.
- Divide by the smallest moles to get ratio.
- Molecular formula may be a multiple of the empirical formula.

Arrhenius Acids

- Arrhenius acids are substances that dissociate in water to give H_3O^+ ions.

$$\underset{\text{sulfuric acid}}{H_2SO_4} + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

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Arrhenius Bases

- Arrhenius bases are substances that dissociate in water to give hydroxide ions.

$$NaOH \rightleftharpoons Na^{+} + {}^{-}OH$$

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2\ {}^{-}OH$$

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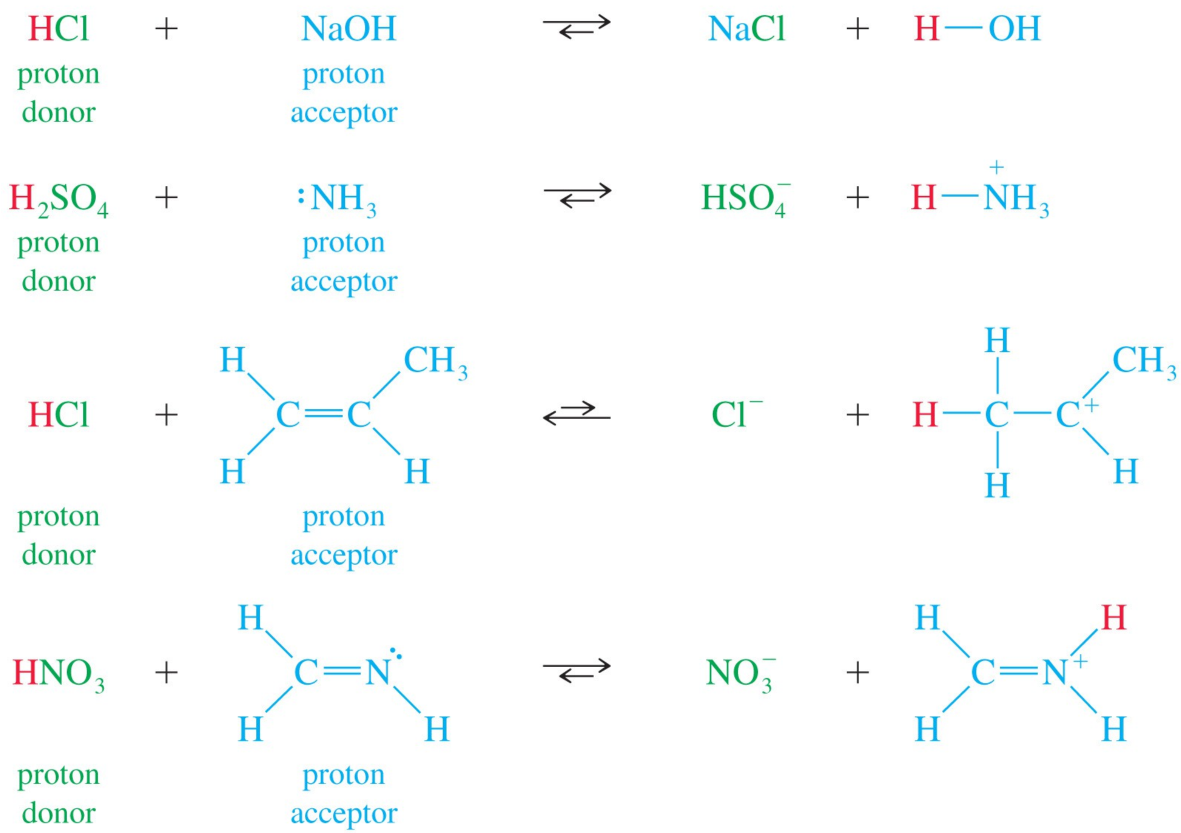
Brønsted-Lowry Acids and Bases

Brønsted-Lowry acids are any species that donate a proton.
Brønsted-Lowry bases are any species that can accept a proton.



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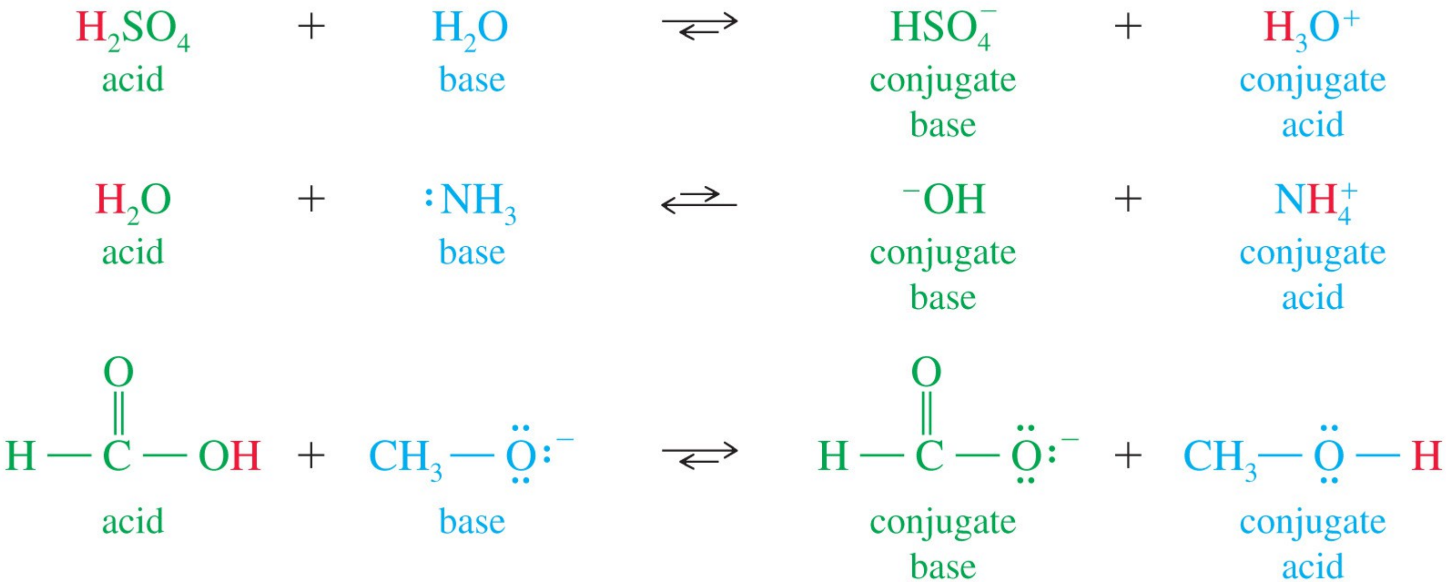
Conjugate Acids and Bases



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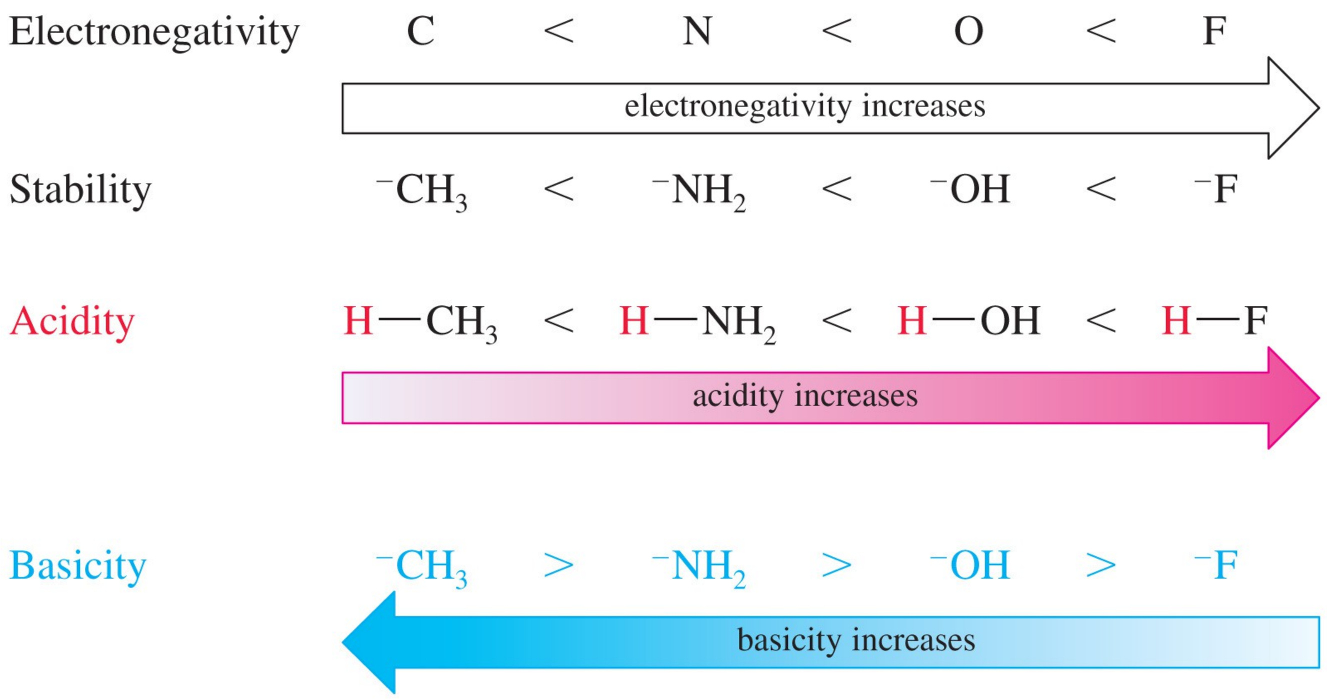
- ***Conjugate acid***: when a base accepts a proton, it becomes an acid capable of returning that proton.
- ***Conjugate base***: when an acid donates its proton, it becomes capable of accepting that proton back.

Effect of Electronegativity on pK_a

- As the bond to H becomes more polarized, H becomes more positive and the bond is easier to break.



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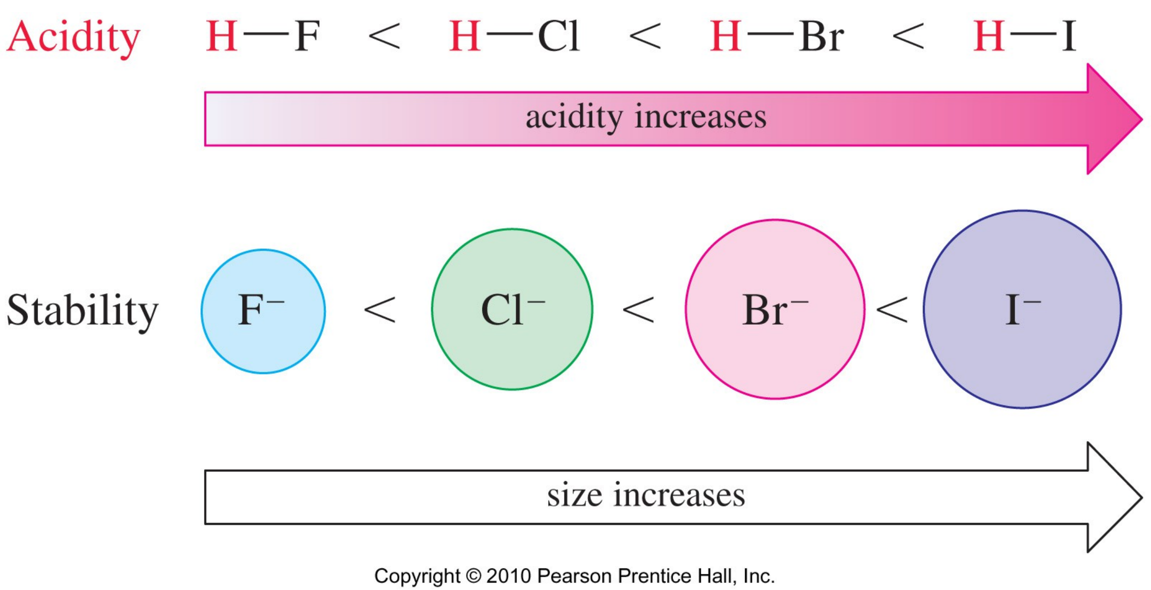
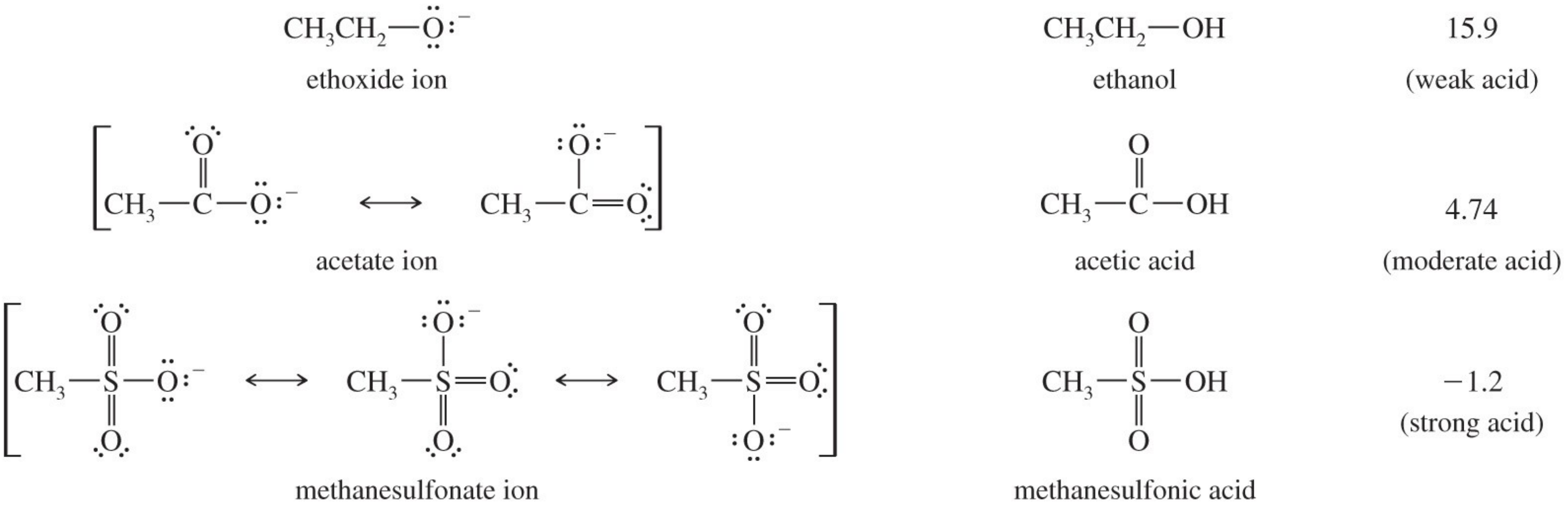
Effect of Size on pK_a



- As size increases, the H is more loosely held and the bond is easier to break.
- A larger size also stabilizes the anion.

Effect of Resonance on pK_a



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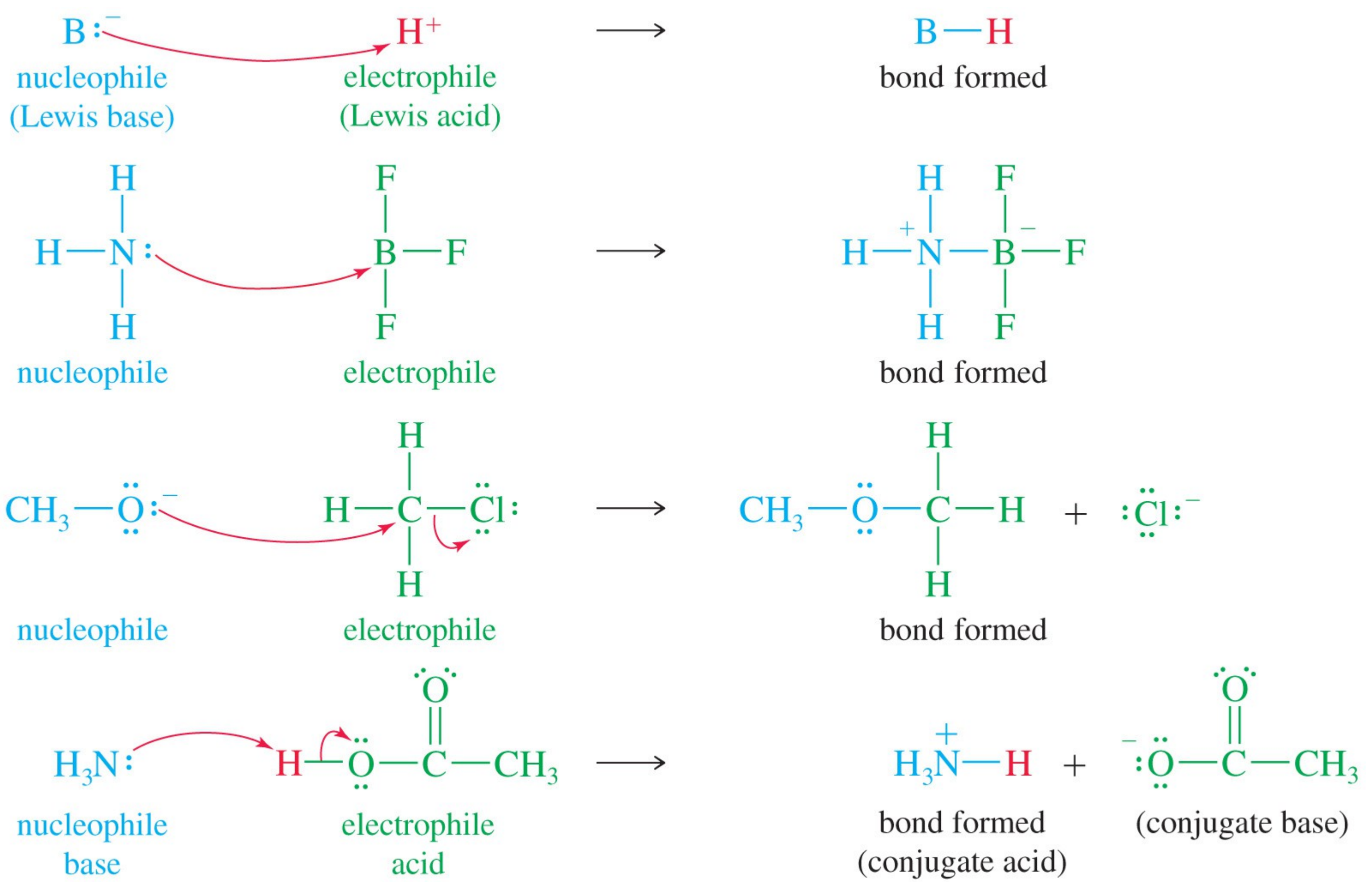
- If the negative charge on an atom can be delocalized over two or more atoms, the acidity of that compound will be greater than when the negative charge cannot be delocalized.
- The ethoxide anion is less acidic than the acetate ion simply because the acetate ion can delocalize the negative charge.
- Methanesulfonic acid can delocalize the charge in three different resonance forms, making it more acidic than the acetate ion.

Nucleophiles and Electrophiles

- ***Nucleophile***: Donates electrons to a nucleus with an empty orbital.
- ***Electrophile***: Accepts a pair of electrons.
- When forming a bond, the nucleophile attacks the electrophile, so the arrow goes from negative to positive.
- When breaking a bond, the more electronegative atom receives the electrons.

Nucleophiles and Electrophiles (Continued)



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