Structure & Shape of Organic Molecules

Organic (living things, chemistry of carbon) **Inorganic** (rocks, minerals, metals, glass)

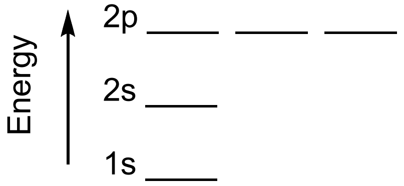
Examples of Organic Compounds:

Products	Materials	in Nature
medicine	paper	hormones/steroids
pesticides	cotton	DNA
dye/paint/ink	tires/rubber	protein/fats/sugars
gasoline/fuels	nylon/polyester	flavors/fragrances
cosmetics	plastic/vinyl	molecular bio. = organic rxns

Review Some Chemistry Basics (B&P 1.1, 1.2)

electronic configurations and the Periodic Table

- electrons (e-) are held in atomic orbitals around the nucleus (s, p, d, f), and s orbitals are more stable (lower Energy) than p orbitals



- fluorine is the most <u>electronegative</u> element (pulls electron density toward itself) C ≈ H, Cl = N

Periodic trends:

F

Which is more electronegative, C or N?

- all elements want to "look like" the Noble gases (have same electronic configuration) atom is <u>stable</u> if it has a filled valence shell (octet rule)

Ex: Na^+ Ca^{2+} Br^-
8 e^- = s^2p^6 (or $1s^2$ for He)

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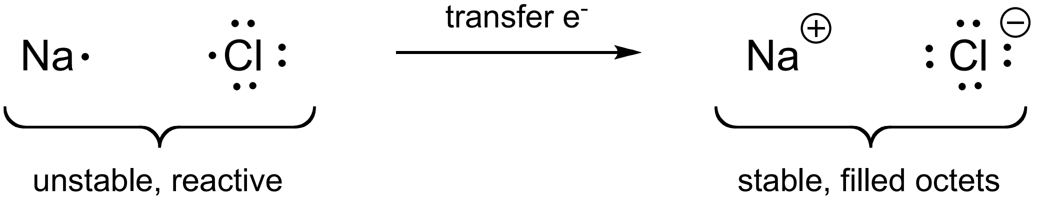
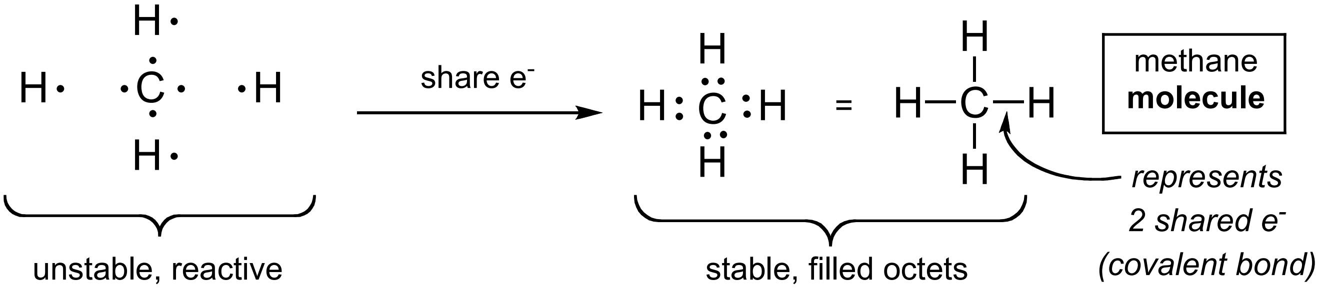
ionic bonds are formed between atoms if they have a large difference in electronegativities



a **salt** (network structure)

covalent bonds are formed between atoms if they have similar electronegativities



methane **molecule**

represents 2 shared e⁻ (covalent bond)

<u>polar covalent bonds</u> arise if there is a difference in electronegativities between atoms

$C-O$

polar bond
(O is more elcgtronegative than C)

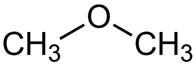
$C-H$

nonpolar bond
(there is no significant difference
in electronegativities)

polarity of molecule depends on geometry (B&P 1.4)

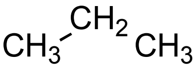
$O=C=O$
nonpolar

linear molecule: equal and opposite polar bonds, so no net dipole moment



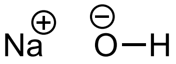
polar

bent molecule: has a net dipole moment



nonpolar

no polar bonds: no net dipole possible
(regardless of geometry)



$\overset{\oplus}{Na}\quad \overset{\ominus}{O}-H$

(NaOH)
ionic

ionic: full charges are the ultimate in polarity
hydroxide (OH^-) is called a covalent ion
NaOH has both ionic and covalent bonds

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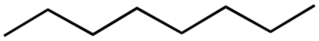
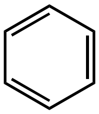
line drawings (B&P 3.1) are a short-hand way to draw carbon structures

- end points and intersections represent C atoms
- omit H's attached to C's



≡ $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Octane
(gasoline component)



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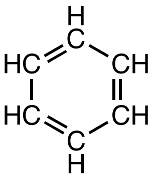
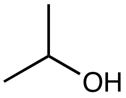


Benzene



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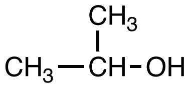
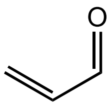
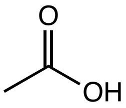


$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-OH$

Isopropyl Alcohol
(rubbing alcohol)

CH_2CHCHO ≡





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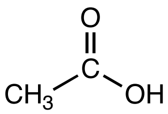
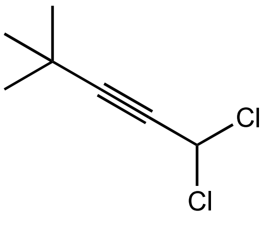


CH_3CO_2H

Acetic acid
(vinegar)

$(CH_3)_3CCCCHCl_2$ ≡



Drawing Lewis Structures (B&P 1.2)

example $ClCH_2CN$

Drawing Lewis Structures

1) draw skeleton - connectivity

2) count total # of valence electrons (valence e^- = group no.)

3) subtract charge (if any)

4) fill in missing electrons (fill octets)

5) determine formal charges (if any)

example $CH_3OH_2^+$

Formal Charges

- calculate for each atom
- determine "electron count"
  = all nonbonded + 1/2 bonded/shared
- compare "electron count" with valence

missing an electron → + charge
extra electron → – charge

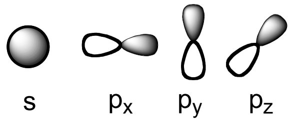
Typical, stable bonding (know by inspection)

Atom	example	# bonds	# lone pairs	"e^- count"
H				
C				
N				
O				
X				

X = halogen
(F, Cl, Br, I)

Orbitals and Covalent Bonding (B&P 1.6)

carbon's AOs



How are the bonds in methane, CH_4, formed?

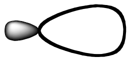
carbon's atomic orbitals (AOs) contain _________ valence electrons

2p ____ ____ ____ $\xrightarrow[\text{promote electron}]{\text{add Energy}}$ 2p ____ ____ ____

2s ____ 2s ____

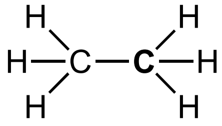
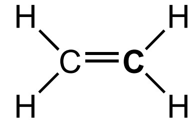
But CH_4 has 4 identical bonds. How can that be?

mixing of AOs to give new hybrid orbitals

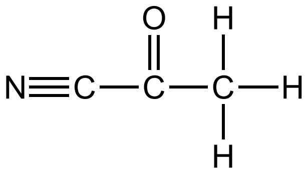


type of hybridization (sp, sp^2, sp^3) depends on the number of groups around the carbon "regions of electron density"

Determining Hybridization

Example molecule	Regions of e⁻ density	Hybrid-ization	s p p p	Result	Geometry (VSEPR)
					
					
$H-C\equiv \mathbf{C}-H$					

practice: assign hybridizations on given molecule


$N\equiv C-\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{H}{C}}-H$

1) complete Lewis structure
2) hybridization is for each atom
3) count "regions" on each atom

a "region of electron density" is a lone pair or single bond or double bond or triple bond

3-D Sketches of Molecules (B&P 1.3, 1.6)

$CH_3—CH_3$

note: can rotate about σ bond
(many drawings are possible)

$CH_2=CH_2$

note: CANNOT rotate
about π bond
(aligned p orbitals)

$HC\equiv CH$

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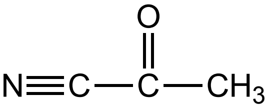
practice: provide
3D sketch of
given molecule



$N\equiv C—C(=O)—CH_3$

1) complete Lewis structure

2) assign atom hybridizations

3) sketch with maximum number of atoms in the plane of the page

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practice: Draw the Lewis structure of nitric acid, HNO_3

Understanding Resonance (B&P 1.5)

1. Any compound for which more than one Lewis structure may be written is accurately described by no single structure. The actual structure is a resonance hybrid of them all (NOT "flipping back and forth" between resonance forms). The various structures are called contributing structures or resonance forms.

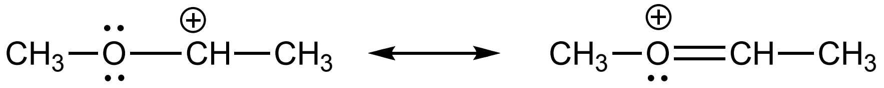
2. The stability of a resonance hybrid is greater than that which would be expected of any of the contributing structures. The hybrid is therefore said to be stabilized by resonance or resonance stabilized (by an amount of energy called the resonance energy).

3. The greater the stability (the lower the energy) of a contributing structure, the greater will be its contribution to the total structure of the hybrid.

4. Resonance is the interaction of electrons in p orbitals. Only pi and nonbonded electron density is reorganized in resonance (no σ bonds break). No atoms move (no change in bond length, angles). Since electrons are not being added or removed, there is no change in overall charge.

Rules for Estimating Stability of Resonance Structures

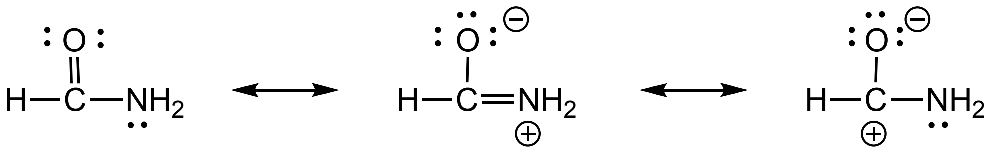
1. The greater the number of **filled octets**, the greater the stability. You might notice that a structure with more covalent bonds is more stable (since more atoms will have complete octets).



$\mathrm{CH_3{-}\underset{\cdot\cdot}{\ddot{O}}{-}\overset{\oplus}{C}H{-}CH_3 \longleftrightarrow CH_3{-}\underset{\cdot\cdot}{\overset{\oplus}{O}}{=}CH{-}CH_3}$

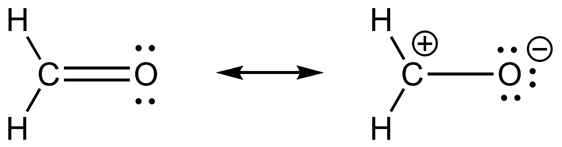
less important more important

2. The structure with **fewer formal charges** is more stable. If the species already has a net charge, creation of new charges is not favorable. For such charged compounds, the goal in drawing resonance forms is to *delocalize the charge* – relocate it to as many different positions as possible.

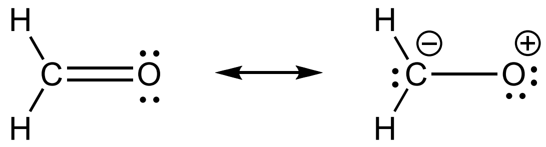


more important (best Lewis structure) less important least important

3. Other things being equal, a structure with a **negative charge on the more electronegative element** will be more stable. Similarly, a positive charge on a less electronegative element is more stable.

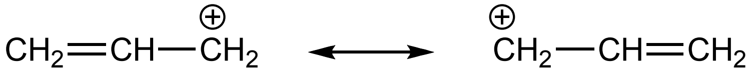


important resonance



not important resonance (unlikely)

4. Resonance forms that are **equivalent** have no difference in stability and contribute equally.

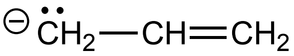


$\mathrm{CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2}$

"allyl" carbocation both forms are equal in energy

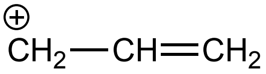
Looking for Resonance Delocalization of Electrons (3 main types/patterns*)

1. lone pair next to a pi bond (**allylic lone pair**)



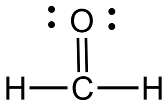
$^{\ominus}\ddot{C}H_2-CH=CH_2$

2. vacancy (missing octet) next to a pi bond (**allylic carbocation**)



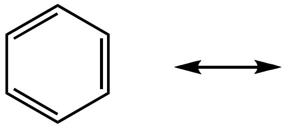
$\overset{\oplus}{C}H_2-CH=CH_2$

3. pi bond between two different elements (**carbonyl-like** resonance)
   electrons move toward the more electronegative element



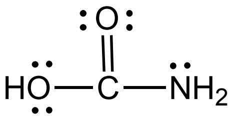
$H-\overset{\overset{:O:}{\|}}{C}-H$

Note: we will encounter a fourth important type of resonance later, called **aromatic resonance, that is found in molecules like benzene*



benzene

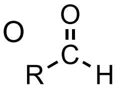
practice: <u>draw</u> and <u>rank</u> all possible resonance forms (explain rankings)

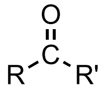


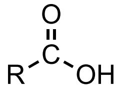
$H\underset{..}{\ddot{O}}-\overset{\overset{:O:}{\|}}{C}-\ddot{N}H_2$

Chapter 1 Summary (Brown & Poon textbook)

I. Review of General Chemistry concepts (1.1 – 1.2)
  A. atomic structure; energy of atomic orbitals (s, p)
  B. electronegativity - ability of an atom to attract electron density
    i. fluorine is most electronegative element (oxygen is second-most!)
    ii. periodic trends; CÅH, N=Cl electronegativity
  C. a filled valence shell (full octet) imparts stability
  D. covalent vs. ionic bonds
  E. bond and molecule polarity (δ+ and δ–) (1.4)
II. Line Drawings (3.1)
III. Lewis Structures (1.2)
  A. structures show sigma (s), pi (p) and nonbonded electrons
  B. how to determine formal charges
  C. recognize "typical" configurations for common atoms: H, C, N, O, halogens (X)
IV. Hybrid Orbitals (1.6)
  A. sp^3 hybridization
    i) 4 regions of electron density
    ii) tetrahedral geometry
  B. sp^2 hybridization
    i) regions of electron density
    ii) trigonal planar geometry
    iii) contains an unhybridized p orbital
  C. sp hybridization
    i) 2 regions of electron density
    ii) linear geometry
    iii) contains two unhybridized p orbitals
V. 3-D sketches (1.3, 1.6)
  A. determine hybridization to learn geometry about each atom
  B. draw aligned p orbitals to show pi bonds
VI. Resonance (1.5)
  a. moves (delocalizes) pi and nonbonded electrons in p orbitals to stabilize a molecule
  b. three general types (things to look for):
    i. lone pair next to pi bond (allylic lone pair)
    ii. vacancy next to a pi bond (allylic empty p orbital)
    iii. pi bond between two different atoms (carbonyl-like)
  c. curved arrows show the redistribution of electron density
  d. resonance forms can be ranked (find most important contributor, etc.)
VII. Intro to Functional Groups (FG) (1.7)
  A. alcohols, ROH (R = a carbon chain)
  B. amines RNH_2 (primary), R_2NH (secondary) or R_3N (tertiary)

  C. aldehydes, RCHO 

  D. ketones, RCOR' 

  E. carboxylic acids, RCO_2H 

Suggested Problems *(the answers to these problems can be found at the back of the book)*:
1–12, Quick Quiz (skip FG questions), 17–51 (odd only), 63, 65, 67.