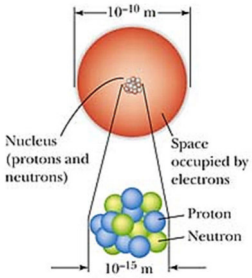
Chapter 1: Covalent Bonding and Shapes of Molecules

1.1 Atomic Structure



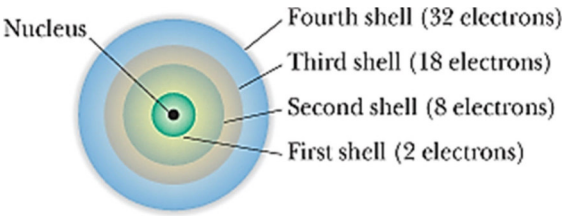
Atoms

Nucleus
- small, dense core of protons and neutrons
- Atomic number (Z)
- positively charged

Orbitals
Regions around the nucleus where an electron is most likely to be found
- Each orbital may hold only 2 electrons
- Orbital types – s, p, d, f

- In organic chemistry we can focus on *s and p orbitals* as organic molecules often only contain carbon, hydrogen, nitrogen, and oxygen

Shells



- Organization of orbitals by size and energy
- Different numbers and kinds of orbitals in each shell
- Correspond to rows in the periodic table
- Electrons nearest to the positively charged nucleus are held more tightly and have the lowest energy

Valence shell
- outermost shell of an atom's electronic configuration
- Valence electrons are important for chemical bonding and are responsible for atomic properties

Example: How many electrons does oxygen have in total and how many of these are valence electrons?

Elements
- differ by the number of protons (atomic number Z)

Isotopes
- atoms of the same element (Z stays the same)
- differ by the number of neutrons

Example: How many protons, electrons, and neutrons does each of the following carbon isotopes have?

	protons	*electrons*	*neutrons*
^{12}**C**	6	6	6
^{13}**C**	6	6	7
^{14}**C**	6	6	8

Ground-state electron configuration of atoms
Lowest-energy arrangement of electrons in the available orbitals
- Fill the orbitals in order of energy
  (1s → 2s → 2p → 3s → 3p → 4s → 3d)
- An orbital may contain a maximum of two electrons which must have opposite spins
- If two or more of the same orbital type is present, place one electron in each orbital then go back and pair up the electrons.

Example: **Sulfur**
$1s^2\ 2s^2 2p^6\ 3s^2 3p^4$

1.2 Chemical Bonds and the Octet Rule

How many electrons are required in the valence shell for a given atom to reach a stable electron configuration?

Octet Rule
- In organic molecules, most atoms (e.g. C, N, O, F) except H desire an octet
- Atoms tend to react in such a way that allows them to achieve 8 valence electrons.

Example: **Mg**

Ion formation by a) gaining 6 electrons or b) losing 2 electrons
- Losing 2 electrons is more favorable

Valence (not valence electrons) is the number of electrons needed to achieve a full octet (or the number of bonds the atom in question can form to other atoms)

C	**N**	**O**	**F**
tetravalent	trivalent	divalent	monovalent

Types of bonds

- Covalent or ionic bonds
- Depends on electronegativity (EN) difference between atoms
- Electronegativity is a measure of how much an atom wants electrons
- An atom's attraction for electrons shared in a chemical bond

Pauling Electronegativity

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
								H 2.1								
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
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 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
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
Cs 0.7	Ba 0.9	La 1.1	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 1.8	Bi 1.9	Po 2.0	At 2.2

<1.0 | 1.0 – 1.4 | 1.5 – 1.9 | 2.0 – 2.4 | 2.5 – 2.9 | 3.0 – 4.0

s

Ionic Bonds: one electron (or more) is completely transferred from one atom to another atom

- Ionic bonds are the result of reactions between atoms with an electronegativity difference of more than 1.9
- Usually the type of bond between a (low-valent) metal and a halide
- When dissolved in a polar solvent, the ions separate

Example of salt formation:

Na ($1s^2 2s^2 2p^6 3s^1$) + Cl ($1s^2 2s^2 2p^6 3s^2 3p^5$) →

Anion – atom that becomes a negatively (-)-charged ion
Cation – atom that becomes a positively (+)-charged ion

***Nonpolar Covalent Bonds**:* a pair of electrons is shared mutually between the bonded atoms

- Stable bond type that requires a lot of energy to be broken
- Electronegativity difference less than 0.5

Example: **C-H**

***Polar Covalent Bonds**:* an unequal sharing of a bonding electron pair

- The more electronegative atom draws the bonding electrons more strongly to itself, resulting in an unequal electron distribution between the atoms
- δ^- indicates the more electronegative atom
- δ^+ indicates the more electropositive atom
- Electronegativity difference of 0.5-1.9

Example: **C-F**

Review: Count the valence electrons and determine the number of bonds and lone pairs these atoms have after achieving their octet.

Atom	# of valence electrons	# of bonds	# of lone pairs
H	1	1	0
C	4	4	0
O	6	2	2
N	5	3	1
Cl	7	1	3

1.3 Covalent Bonds and Lewis Structures

Covalent bonds: When two or more atoms of the same or similar electronegativities react, these atoms achieve noble gas configurations by sharing electrons.

Molecules: neutral collection of atoms held together by covalent bonds

Ions: (+) or (-) charged species

Lewis structures – representations of atoms used to determine bonding and shape

- *Electron-dot structures* show valence electrons as dots around a central elemental symbol
- Useful but chemists simplify them by representing bonds as lines and nonbonding electron as dots in so-called dash structural formulae
- Paired non-bonding electrons (two dots) can also be represented as lines
- *Nonbonding electrons (lone-pair electrons)* play an important part in reactions: *Don't forget to draw these in if they are crucial to your reaction!*

Organic chemists generally represent molecules as dash formulae when asked to draw a Lewis structure.

Guidelines to Drawing Lewis Structures of Molecules and Ions:

1. Determine the number of valence electrons in the molecule or ion (for anions, add one electron; for cations subtract one electron)

2. Determine arrangement of atoms
   (H and halogens are monovalent and only form one single bond)

3. Connect the atoms with single bonds (a dash represents 2 electrons)

4. Arrange the remaining electrons in pairs to give each atom a full valence shell (Tip: start with most electronegative atom; assign 8 electrons to all elements except hydrogen which gets 2 electrons)

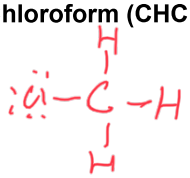
5. Lone pair electrons (non-bonding electrons) are shown as (:)

6. Multiple covalent bonds: More than one pair of bonding electrons may be shared to give all atoms an octet.
   Single bond:
   Double bond:
   Triple bond:

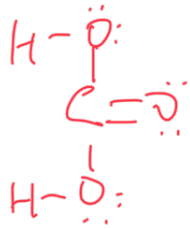
7. Exception to the octet rule: Elements of the third row and below can accommodate more than 8 electrons in their valence shell and may form more that 4 bonds. Most commonly this is encountered with sulfur (e.g. SF_6, H_2SO_4) and phosphorus (e.g. PCl_5, $POCl_3$)

Draw the Lewis structures of the following molecules:

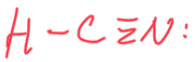
Chloroform ($CHCl_3$)



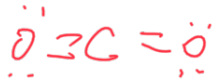
H_2CO_3



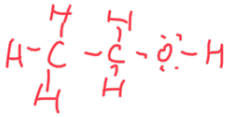
HCN



CO_2

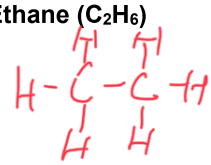


Ethanol (C_2H_6O)

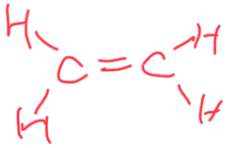


NH_2^-

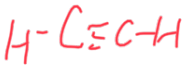
Ethane (C_2H_6)



Ethene (Ethylene, C_2H_4)



Ethyne (Acetylene, C_2H_2)



1.4 Formal Charges and How to Calculate Them

Formal Charge: charge on each atom in a molecule or ion

- Used to determine which atom(s) in a polyatomic ion or molecule possess the charge
- Must have a valid Lewis structure first

Formal Charge = valence electrons - ½ of the shared electrons- lone pair electrons

$$F = Z - (1/2)S - U$$

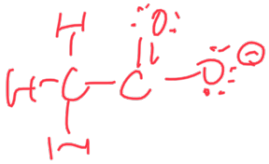
With F = formal charge
Z = group number of the element
S = the number of shared electrons
U = the number of unshared electrons

- **The arithmetic sum of all the formal charges in a molecule or ion will equal the overall charge on the molecule or ion**.

Assign formal charges to all atoms of the following molecules. What is the overall charge?

Nitric Acid (HNO_3)

Acetate ($CH_3CO_2^-$)

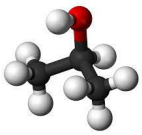


1.5. Structural Formulae (Summary)

There are many different ways to draw organic molecules. Chemists chose often the one requiring the least time to draw but which has all the essential information for that particular application.

For example, 2-propanol can be represented many different ways:

a) Ball-and stick model (molecular model kit)



b) Electron-dot formula

c) Dash formula

d) Condensed formula

Organic chemists use the following:

e) Bond-line formula

f) Three-dimensional formula (for showing three-dimensional geometry)

1.6 VSEPR (valence shell electron-pair repulsion) Theory

- Angles are predicted by all electron pairs (bonds and lone pairs)
- Shapes of molecules are predicted by bonds only

Atomic and molecular shape based on Lewis structure and hybridization

linear	trigonal planar	tetrahedral
180°	120°	109.5°

TABLE 1.3 SHAPES OF MOLECULES AND IONS FROM VSEPR THEORY

Number of Electron Pairs at Central Atom			Hybridization State of Central Atom	Shape of Molecule or Ion[a]	Examples
Bonding	Nonbonding	Total			
2	0	2	sp	Linear	BeH_2
3	0	3	sp^2	Trigonal planar	BF_3, $\overset{+}{C}H_3$
4	0	4	sp^3	Tetrahedral	CH_4, $\overset{+}{N}H_4$
3	1	4	$\sim sp^3$	Trigonal pyramidal	NH_3, $\overset{-}{C}H_3$
2	2	4	$\sim sp^3$	Angular	H_2O

Exercise: Complete the following table

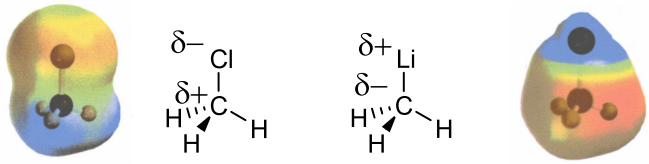
Molecule	# of VE at central atom	Lewis structure and angles between bonds	Shape of molecule
CH_4			tetrahedral
NH_3			trigonal pyramidal
BH_3			trigonal plannar
H_2O			bent (angular)

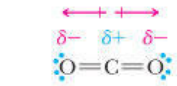
Exercise: Complete the following table (continued

Molecule	# of VE at central atom	Lewis structure and angles between bonds	Shape of molecule
H_2CO			trigonal plannar
HCCH			linear
CO_2			linear

1.7 Polar and Nonpolar Molecules

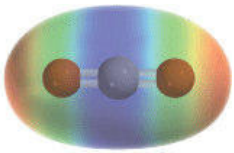
How can we predict whether a molecule is overall polar or nonpolar?
By knowing its shape and the electronegativity of the atoms





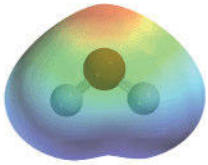
Carbon dioxide
(a nonpolar molecule)

$\mu = 0$

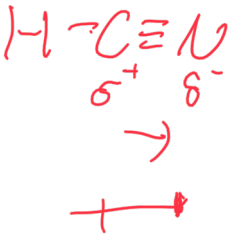


Center of partial positive charge is midway between the two hydrogen atoms

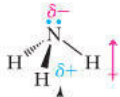
Water
(a polar molecule)



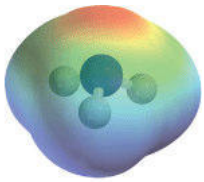
Question: Is HCN a polar molecule?



Center of partial positive charge is midway between the three hydrogen atoms



Ammonia
(a polar molecule)



1.8 Resonance Structures

Resonance Structures exist only on paper. They are representations of a molecule or ion that differs only in the distribution of its valence electrons which all contribute to the real (hybrid) structure of a compound

Rules for Drawing Resonance Structure

1. All structures have same number of valence electrons
2. The connectivity of the atoms does not change; however, bond orders can differ in the individual resonance structures. Do not move atoms!
3. All structures must be proper Lewis structures, e.g. no atom may have more than a full valence shell. (H: max 2 electrons, row 2 elements: max 8 electrons, and row 3 elements: max 12 electrons)

Example 1: **$CH_3CO_2^-$**

Valence electrons:

Lewis structure:

Resonance structures:

Example 2: **HNO_3**

Valence electrons:

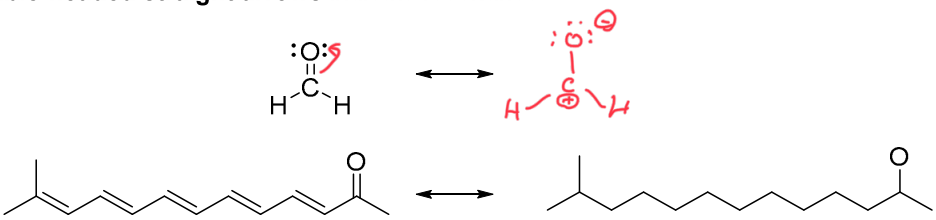
Lewis structure:

Resonance structures:

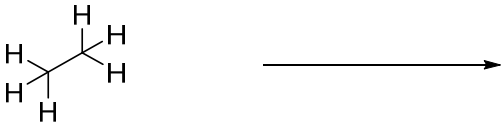
Arrows move from (-) to (+)
Not all structures carry the same weight
Fewer charged atoms is better
If (+) and (-) formal charges appear in same structure, closer together is better

1.9 Summary of Different Types of Arrows

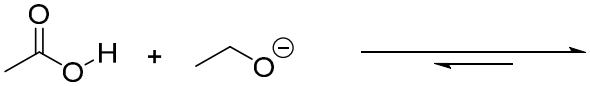
- **Curved arrows** ("Curly arrows") always show that *a pair of electrons* is moving from the atom at the tail of the arrow to the atom at the head of the arrow
- **Double-headed straight arrows** indicate resonance



- **Fishhook arrows** show movement of *one electron*
- **Straight arrows** (reaction arrows) point from reactants to products



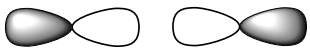
- **Straight arrows with half heads** (equilibrium arrows) indicate that a reaction is reversible



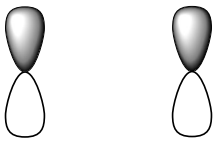
1.10 From Atomic Orbitals to Molecular Orbitals

Bonding: Atoms approach each other which allows their atomic orbitals to overlap either in-phase (resulting in a bonding molecular orbital) or out-of-phase (giving rise to antibonding orbitals).

σ bonds: have spherical symmetry about the bond and may be formed by overlap of any of the following orbitals

	atomic orbitals	bonding molecular orbital	antibonding molecular orbital
s-s overlap			
s-p overlap			
p-p overlap (end-on)			

π bonds: result from side-on overlap of p orbitals and are rigid

	atomic orbitals	bonding molecular orbital	antibonding molecular orbital
p-p overlap (π bond)			

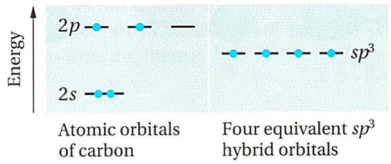
1.11 Hybridization

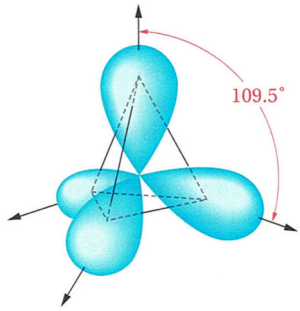
Hybridization: mixing of orbitals to give identical hybrid orbitals

- Four orbitals are available on C for bonding – s, p_x, p_y, p_z
- Carbon atoms occur in three different hybridizations: sp^3, sp^2, and sp

sp^3 – Single bonds, tetrahedral shape

Formation of four sp^3 hybrid orbitals:





Overlap of sp^3 orbitals with s orbitals leads to single bonds:

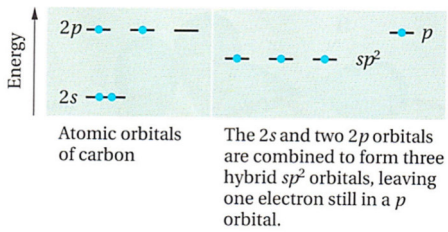
Example: Methane

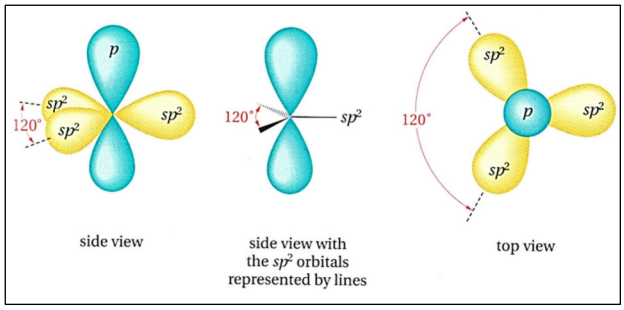
Overlap of two sp^3 orbitals leads to single bonds:

Example: Ethane

sp^2 – Double bonds, trigonal planar shape

Formation of three sp^2 hybrid orbitals:





Formation of a C=C double bond:

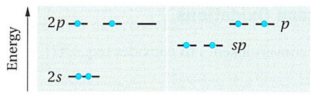
Example: Ethylene (Ethene)

Cis-Trans Isomerism (a type of stereoisomerism)
Due to the restricted rotation about double bonds, cis-trans isomerism can be observed:

cis-1,2-Dichloroethene

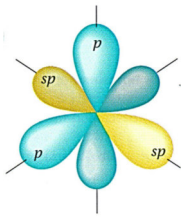
trans-1,2-Dichloroethene

sp – Triple bonds, linear shape



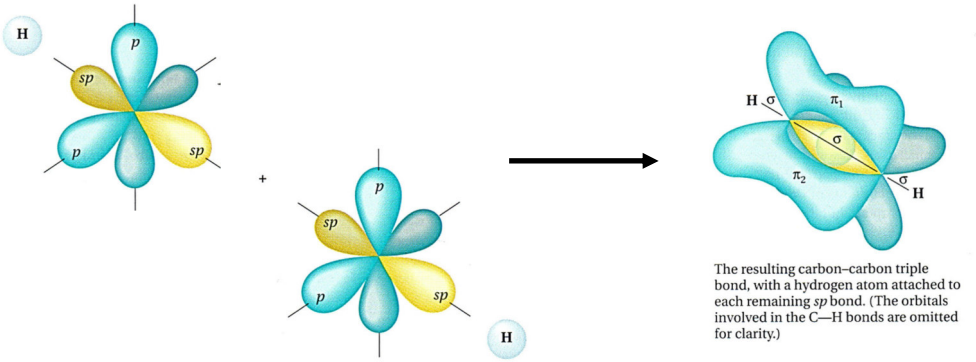
Atomic orbitals of carbon

The 2*s* and one 2*p* orbital are combined to form two hybrid *sp* orbitals, leaving one electron in each of two *p* orbitals.



Formation of C≡C triple bond:

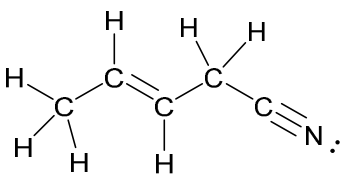
Example: Acetylene (Ethyne)



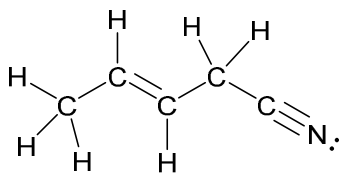
The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

Exercise: Provide type of bonds, hybridization, and bond angles for the following compound.

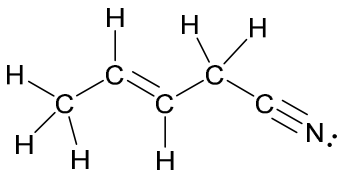
Types of bonds?



Hybridization?



Bond angles?



1.12 Functional Groups

Functional groups are common and specific arrangements of atoms that govern reactivity and properties of (organic) molecules.

At this point you are expected to know the following functional groups:

a) Alcohols

-OH (hydroxyl) group bonded to a tetrahedral carbon

Primary alcohol Secondary alcohol Tertiary alcohol

b) Amines

$-NR_2$ (amino) group: Nitrogen atom bonded to 1, 2, or 3 carbon atoms

Primary amine Secondary amine Tertiary amine

c) Aldehydes and Ketones

C=O (carbonyl) group

Aldehydes Ketones

d) Carboxylic Acids, Esters, and Amides

Carboxyl group Carboxylate Carbamide

Carboxylic acid Ester Amide