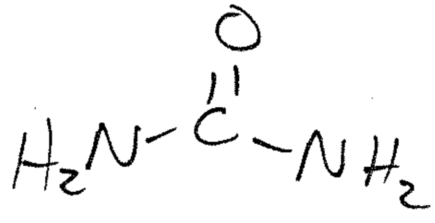
Chapter 1: An Introduction to Structure and Bonding in Organic Chemistry

Organic Chemistry: the chemistry of carbon compounds

→ These compounds are essential to all living things
- energy and metabolism
- enzymes and proteins
- DNA, RNA
- lipids

→ Main elements found in organic compounds:
C, H, N, O, S, P, halogens
- There are <u>millions</u> of known organic cmpds!

→ At one time people thought that organic cmpds were special and possessed a "vital force" responsible for their formation and breakdown. This vitalism theory was debunked when an organic compound, urea, was created in the lab.



$$H_2N-\overset{\overset{\large O}{\|}}{C}-NH_2$$

<u>urea</u>

→ Chemists can synthesize virtually any organic compound:

- vitamins
- drugs
- food additives (Nutrasweet) etc

To do this requires an understanding of:

- type of reactive group (functional group)
- chemistry of these reactive groups
- atomic and molecular structure
- stereochemistry of atomic arrangements
- knowledge of synthetic procedures

COMPOUNDS

Ionic Cmpds

- Composed of cations and anions
- ions form from electron transfer
- opposite charge attraction holds cations + anions together in the solid state

Covalent Cmpds

- Composed of molecules whose atoms are held together by covalent bonds
- covalent bonds result from the sharing of e⁻ pairs between atoms

What makes some compounds ionic while others are covalent?

→ Depends on the difference in electronegativity between the bonding atoms.

ELECTRONEGATIVITIES

H 2.1	He																He
Li 1.0	Be 1.5											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 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	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 1.1	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	Rn
Fr 0.7	Ra 0.9	Ac 1.1															

- Elements with a <u>low</u> electronegativity tend to <u>lose</u> electrons easily
- Highly electronegative elements tend to <u>gain</u> electrons easily

electron transfer occurs

Forms ionic compounds with ionic bonds

Both have noble gas config.; full outer shell

Ex.

$$Na\cdot + \cdot\underset{..}{\ddot{Cl}}: \longrightarrow Na^+[:\underset{..}{\ddot{Cl}}:]^-$$

1 valence e^-

7 valence e^-

alence
e^- → $3s^1$
onfiguration

$3s^2 3p^5$

Remember: valence e^-'s are electrons in the outermost shell

→ For nonmetallic + metalloid elements with similar electronegativities too much energy is required to either gain or lose electrons to complete their valence shell octets

⇓

These elements fill their shell by **sharing** electrons to form covalent bonds

☆ Write the Lewis Electron Dot Structure to show covalent bonding in CH_3F

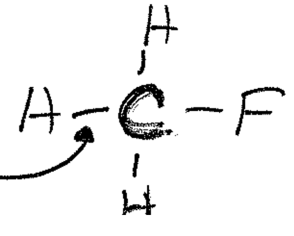
(1st) – Find the total # of valence e^-
(# of valence e^- equal to the group #)

C	3H	F	
4	3(1)	7	$= 14e^-$

(if the structure is a polyatomic ion, we add or subtract electrons)

(2nd) – Write the central atom (usually element with the lowest electronegativity – except H) Then attach outer atoms with a pair of electrons

never the central atom

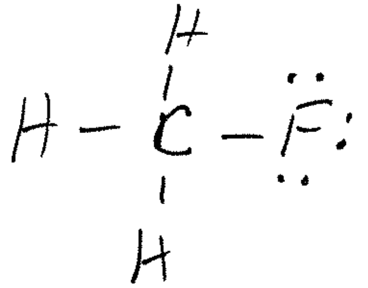


$$H-\overset{H}{\underset{H}{C}}-F$$

• represents one covalent bond; 2e⁻ per bond

$8e^-$ used in bond pairs

3rd - Add the remaining valence electrons to the outer atoms first (to complete the octets) then to the inner atoms. (H-atoms only need 2e⁻ to be filled)



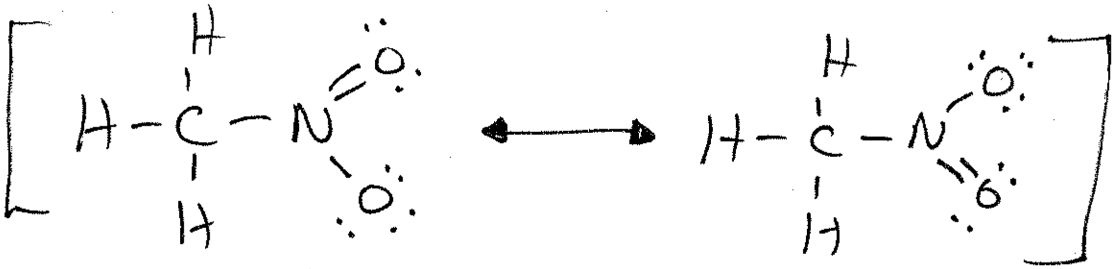
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & \ddot{\underset{..}{F}}: \\ & & | & & \\ & & H & & \end{array}$$

14 valence e^-
$-8e$ used in bonds
$6e^-$ left

→ C, N, O, F <u>always</u> have an octet of electrons

Write the Lewis Structure for CH_3NO_2

↑ (Condensed molecular formula) → tells about connectivity of atoms



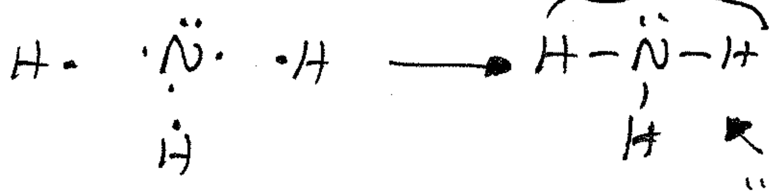
RESONANCE STRUCTURES

- The overall electronic structure of nitromethane is best described by both resonance structures → is a 50/50 hybrid of the two.

FORMAL CHARGE

→ An atom will possess a formal charge if it "possesses" fewer or more electrons than the neutral atom

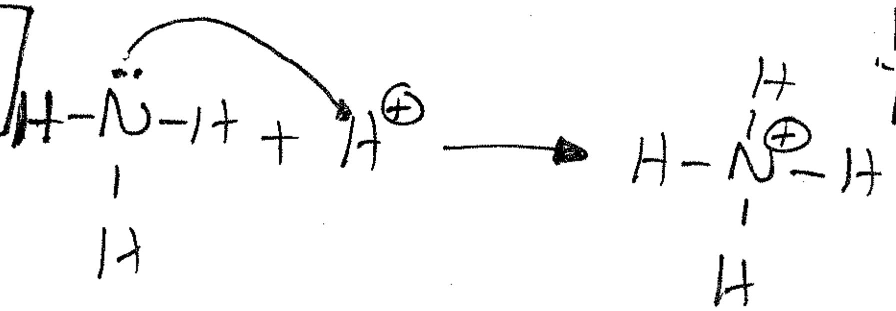
ex: $\boxed{NH_3}$



Formal charges on each atom is zero

each H "possesses" 1e⁻ + nitrogen "possesses" 5e⁻

ex: $\boxed{NH_4^+}$



- In NH_4^+, each H "possesses" 1 electron (formal charge = zero) but nitrogen only "possesses" 4 electrons, 1 less electron than the 5 valence e⁻'s found in a neutral atom of N → so N has a $\boxed{+1}$ Formal charge

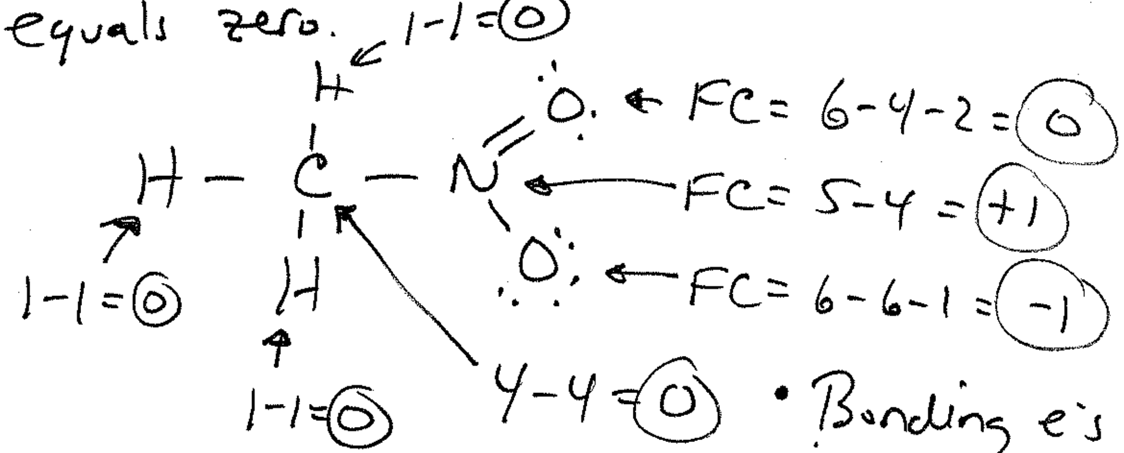
- The sum of the formal charges of the atoms in a structure MUST equal the net charge of the molecule or ion.

$$\boxed{\text{Formal Charge (FC)} = (\text{Group \#}) - (\text{\# of Nonbonding Electrons}) - \tfrac{1}{2}(\text{shared } e^-\text{'s})}$$

↑ lone pair electrons

↑ bonding electrons

- CH_3NO_2 doesn't have a net charge so the sum of it's atoms formal charges equals zero.



- Bonding e⁻'s in N-O single bond both come from N.

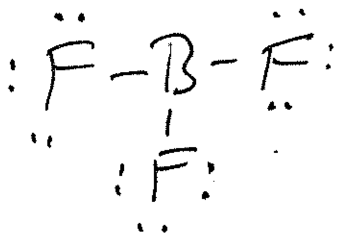
→ With some compounds, more than one non equivalent Lewis structure can be drawn (that follows all the rules). In these cmpds, formal charges can be used to determine which structure is most important.

☆☆ **Structure with Formal Charges closest to zero is most important**

★ Write the Lewis structure for CH_3NCO.
(connectivity of the molecule is CH_3 N–C–O)

- Some atoms, B and elements of the 3rd period and higher, can be exceptions to the octet rule.

ex: BF_3 valence e^-'s → $3 + 3(7) = 24e^-$



doesn't have an octet around B → OK

★ Draw the best Lewis structure for H_2SO_4 (note: both H's attached to oxygen)

→ Not all molecules can be described well by only one Lewis's structure. For some molecules or ions, more than one equivalent Lewis's structure can be drawn.

✯ Write the Lewis structure(s) for the carbonate ion, CO_3^{2-}.

RESONANCE STRUCTURE RULES

1. Resonance only involves a change in <u>electron</u> organization. (<u>NOT</u> moving atoms or nuclei)

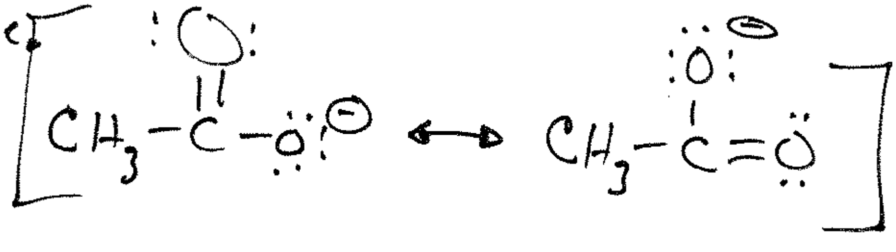
$$CH_2=C=CH_2 \quad \text{and} \quad CH_3-C\equiv C-H$$

are <u>not</u> resonance structures. Why?

Because an H-atom moves.

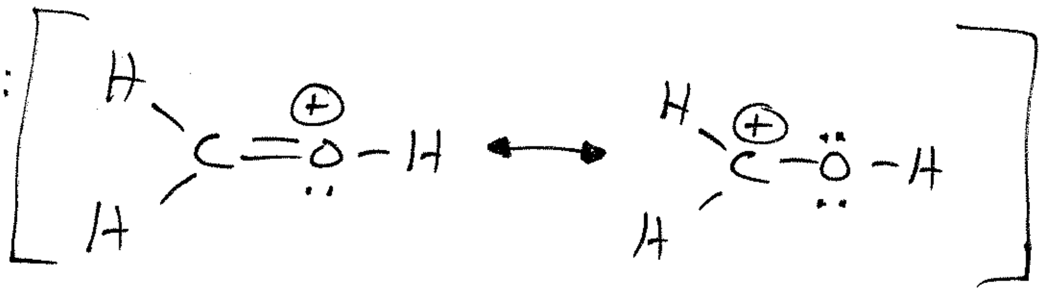
2. Identical electronic arrangements are of equal importance.

Acetate Ion



$$\left[CH_3-\overset{\overset{:\ddot{O}:}{\parallel}}{C}-\ddot{O}:^{\ominus} \longleftrightarrow CH_3-\overset{\overset{:\ddot{O}:^{\ominus}}{|}}{C}=\ddot{O}\right]$$

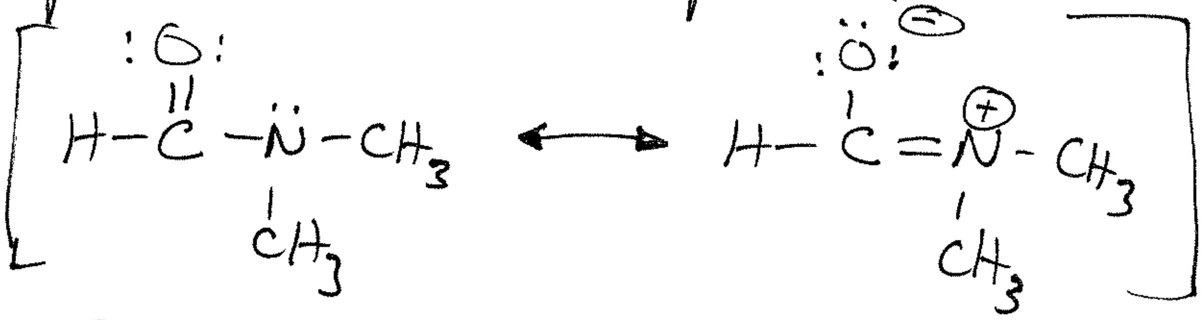
3. Structures containing the greater # of covalent bonds are more important. Structures with filled octets are more important

ex:


oxonium ion (more imp)

carbocation (less imp)

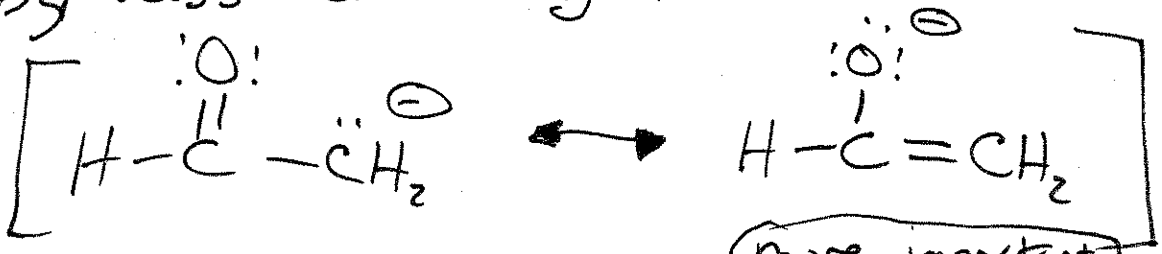
4. Structures involving a minimum of charge separation are more important.



(more imp.)

(less imp.)

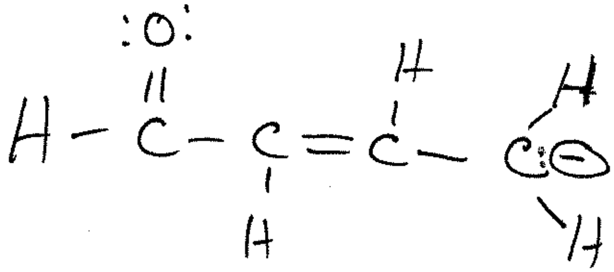
5. Negative charges are most stable by more electronegative elements and positive charges by less electronegative elements.



more important

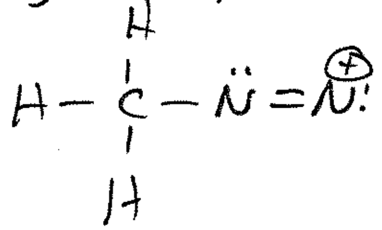
"O" more electronegative than "C"

☆ Draw The important resonance structures for The following ion. Which structure is most important?

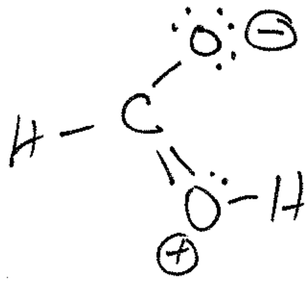


☆ Moving only electrons, write a more important Lewis structure for The following compounds. (specify formal charges) Why is your structure more important?

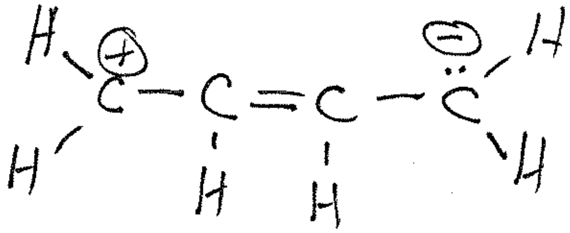
a)



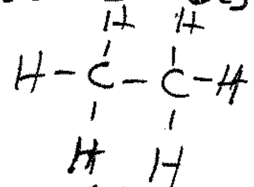
b)



c)



CHEMICAL FORMULAS

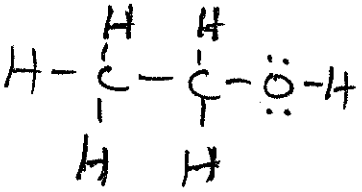
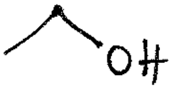
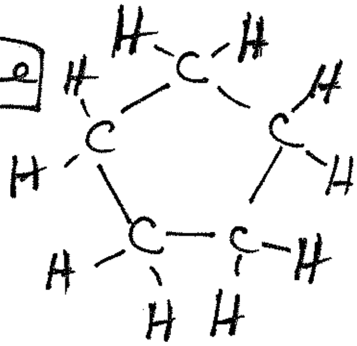
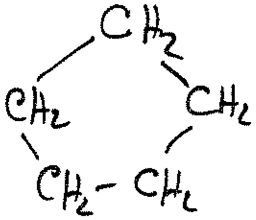
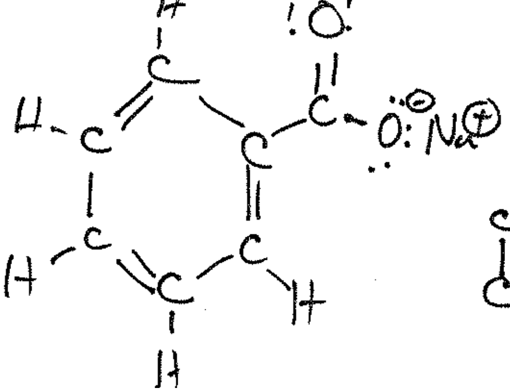
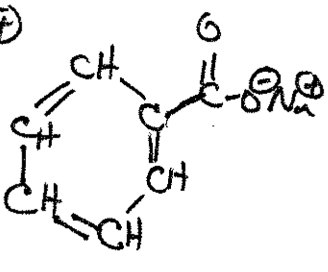
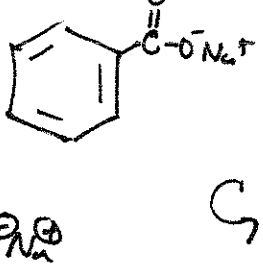
Condensed structural formulas: individual bonds are not shown, but implied CH_3CH_3 = 
$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

line angle formulas: bonds represented by lines, carbons assumed present where lines intersect, show heteroatoms

empirical formula: ratio of elements present in a compound

molecular formula: actual # of each element in a compound

Ex.

	Lewis	Condensed	line angle	mol.	emp.
ethanol	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\ddot{\underset{..}{O}}-H$	CH_3CH_2OH		C_2H_6O	C_2H_6O
cyclopentane				C_5H_{10}	CH_2
odium benzoate				$C_7H_5O_2Na$	$C_7H_5O_2Na$

Unit of Unsaturation: when 2 Hydrogen atoms are missing because of a double or triple bond or a ring

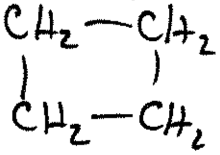
- Saturated hydrocarbon (no units of unsat.) $CH_3CH_2CH_2CH_3$ (butane) C_4H_{10}

  $\boxed{C_nH_{2n+2}}$ ← general Formula for Sat. HC

- 1-UNIT of Unsaturation $CH_3CH_2CH=CH_2$ (1-butene) C_4H_8

  $\boxed{C_nH_{2n}}$

  also



(cyclobutane)

- 2-UNITS OF Unsaturation $CH_3CH_2C\equiv CH$ (1-butyne) C_4H_6

  $\boxed{C_nH_{2n-2}}$

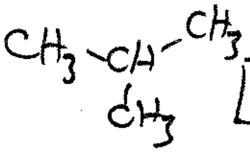
  also

  $CH_2=CH-CH=CH_2$ (1,3-butadiene)

ISOMERS

→ Constitutional (Configurational): have different connectivitie

ex $CH_3CH_2CH_2CH_3$ and



$CH_3-CH(CH_3)-CH_3$

$\boxed{\text{butane}}$ $\boxed{\text{isobutane}}$ (2-methylpropane)

→ Stereoisomers: same connectivity; different arrangement of atoms in space (Chap. 6)

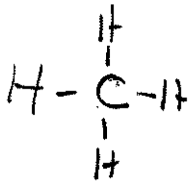
SHAPES OF COVALENT MOLECULES

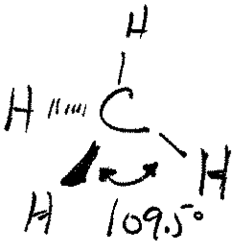
VSEPR Theory

- Valence Shell Electron Pair Repulsion

Tetrahedral Electronic Geometry

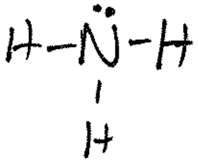
→ Four regions of electron density around the central atom

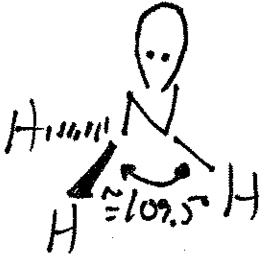

methane



tetrahedral electronic geometry

tetrahedral molecular geometry

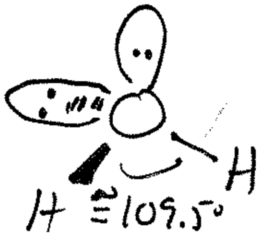

ammonia



tetrahedral electronic geometry

trigonal pyramidal molecular geometry


water



tetrahedral electronic geometry

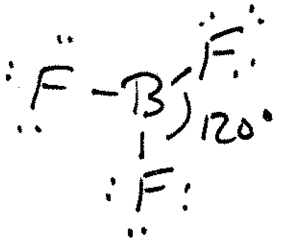
bent molecular geometry

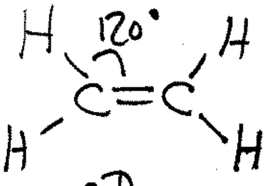
- Lone Pairs count as one region of electron density.

- Multiple Bonds count as one region of electron density.

Trigonal Planar Electronic Geometry

→ 3 regions of electron density around the central atom





ethene

Trigonal planar electronic and molecular geometry

Linear Electronic Geometry

→ 2 regions of electron density around the central atom

(each double bond counts as 1-region)

$:\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$

carbon dioxide

H-C≡C-H

ethyne

BOND POLARITY

- When bonding electrons are <u>NOT</u> equally shared by the atoms due to electronegativity differences of the bonded atoms → yields a **POLAR BOND**

→ Two ways to illustrate a polar bond

ex: $\overset{+\!\!\!\longrightarrow}{\text{H}—\text{Cl}}$ or $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{Cl}}$

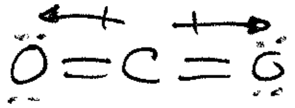
electron cloud is distorted

The more electronegative atom has a greater share of the shared electron density

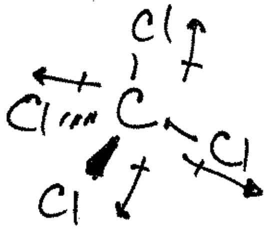
Overall Dipole Moment (μ) = vector sum of the individual bond dipoles

↑ symbol "mu"

ex:



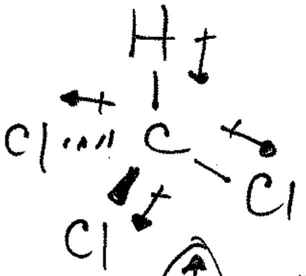
$\mu = 0$



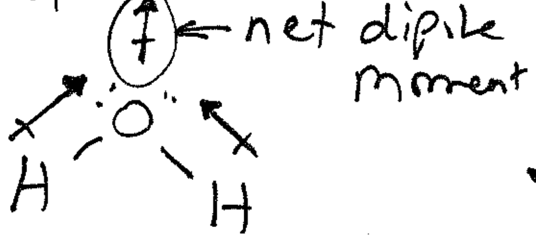
$\mu = 0$

bond dipoles cancel

- non polar molecules
- no net dipole moment even though there are polar bonds



μ = vector sum along the H−C bond



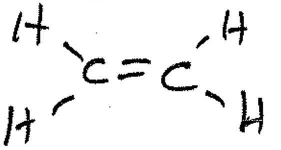
- vector sum of bond dipoles bisects the molecule

Bond Lengths

- Higher Bond Order = shorter bond length

Bond Order = # of bonds between two nuclei (angstrom (Å) = 10^{-14} m)

CH_3-CH_3 1 bond 1.53 Å



2 bonds 1.34 Å

H−C≡C−H 3 bonds 1.20 Å

Non-Bonding Interactions Between Molecules

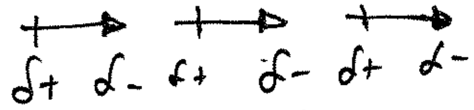
Three Types of Intermolecular Forces

1. Dipole-Dipole
2. Hydrogen Bonding (subset of Dipole-dipole)
3. Van der Waals (London Forces)

Dipole-Dipole Interactions

→ forces that act between polar molecules

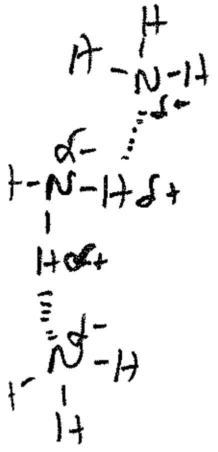
- in solution, polar molecules tend to allign themselves such that thier dipoles are head-to-tail

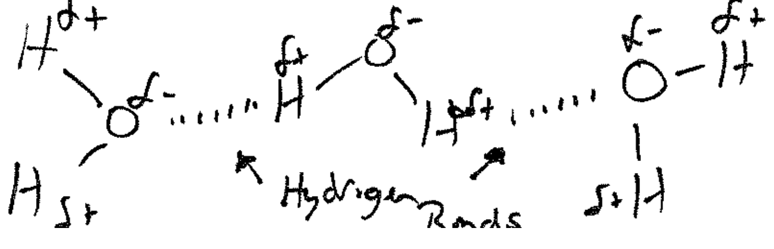


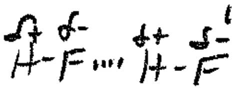
(electrostatic interactions between regions of opposite charge)

Hydrogen Bonding

→ Hydrogen covalently bonded to a very electronegative atom (such as O, N or F) gives rise to molecules with dipoles which interact in solution with special strength called <u>HYDROGEN BONDS</u> ← (just a particularly strong dipole-dipole interaction)



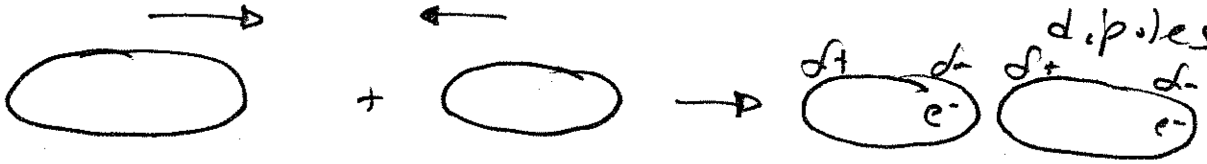




$\overset{\delta+}{H}-\overset{\delta-}{F}\cdots\overset{\delta+}{H}-\overset{\delta-}{F}$

Van der Waals Interactions ← also called London Forces

- important in nonpolar molecules
- a relatively weak interaction That arises from a MOMENTARY dipole That is induced when two nonpolar molecules approach one another
  - → A temporary dipole occurs because of Constant electron motion. This motion creates small, momentary distortions = momentary dipoles



Net Result: A slight attraction between molecules which is, in general, proportional to molecular surface area

Larger Surface Area = Stronger Van der Waals Interactions

- Intermolecular Interactions have a pronounced effect on physical properties of organic molecules i.e. boiling pt, melting pt, solubilities etc.

rder of Strength
Hydrogen
Dipole
Van der Waals

→ more hydrogen bonding = higher boiling pt

→ Stronger Van der Waals = higher boiling pt