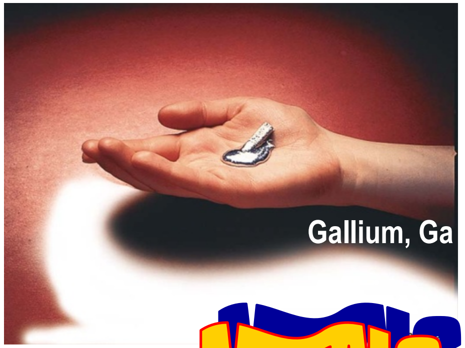
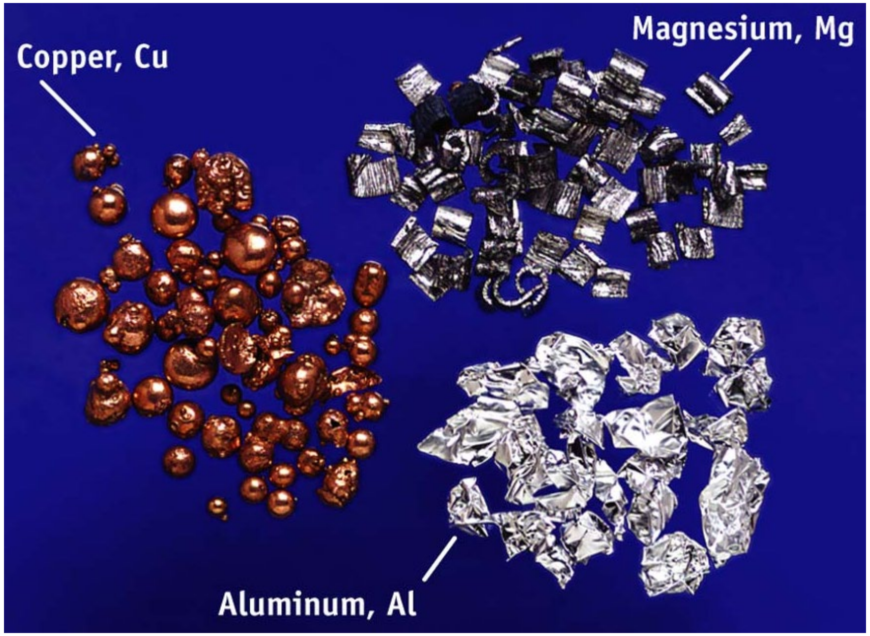


METALS



CHEMISTRY 1000

NONMETALS

Topic #2: The Chemical Alphabet

Fall 2020

Dr. Susan Findlay

See Exercises 8.1 to 8.7 and 9.1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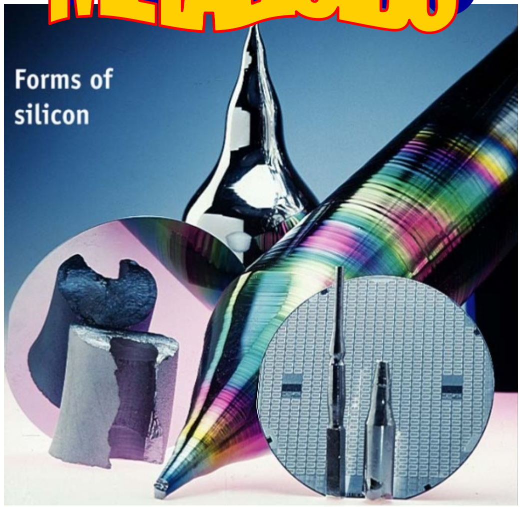
Forms of Carbon

METALLOIDS



Molecules and Covalent Bonds

- Stable compounds and elements tend to contain atoms with a noble gas *(or pseudo noble gas)* electron configuration. Depending on the element, this may be most easily achieved by gaining electrons, losing electrons or sharing electrons. You may have heard this tendency referred to as the **octet rule**:

- There are three main types of bonding:
  - Ionic

  - Covalent

  - Metallic

Molecules and Covalent Bonds

- To find the optimum bond length, we can plot energy versus internuclear distance:

The lowest energy point on the graph is at the **average bond length**. Bonds are not rigid. At any temperature above 0 K, they vibrate around the equilibrium bond length.

Molecules and Covalent Bonds

- In a covalent bond, valence electrons are shared between two or more atoms. These bonding electrons are literally “co-valent”.

- Covalent bonds form if heat is released when atoms bond:

  $$\mathrm{H}\cdot \quad + \quad \cdot\mathrm{H} \longrightarrow \mathrm{H{-}H} \qquad \Delta H = -435\ \mathrm{kJ/mol}$$

  The negative enthalpy of reaction means that the product (H_2) is more stable than the reactants (2 × H) at constant pressure.

- By convention, chemists typically write the reverse reaction equation and list the **bond dissociation enthalpy** (i.e. how much heat is required to break the bond and move the atoms far enough away from each other that they don’t interact):

  $$\mathrm{H{-}H} \longrightarrow \mathrm{H}\cdot \quad + \quad \cdot\mathrm{H} \qquad \Delta_{BD}H = +435\ \mathrm{kJ/mol}$$

Properties of Covalent Bonds

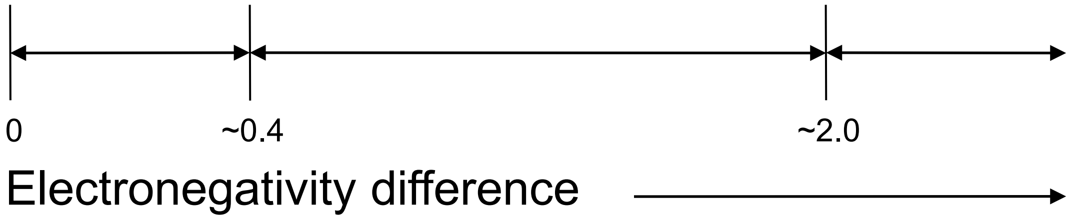
- Estimate the enthalpy change that accompanies the reaction below.

$$2\ CH_{4(g)} + O_{2(g)} \rightarrow 2\ CH_3OH_{(g)}$$

	$\Delta_{BD}H$ (kJ/mol)
H-H	436
H-C	414
H-O	464
C-C	347
C-O	360
O-O	142
O=O	498

Properties of Covalent Bonds

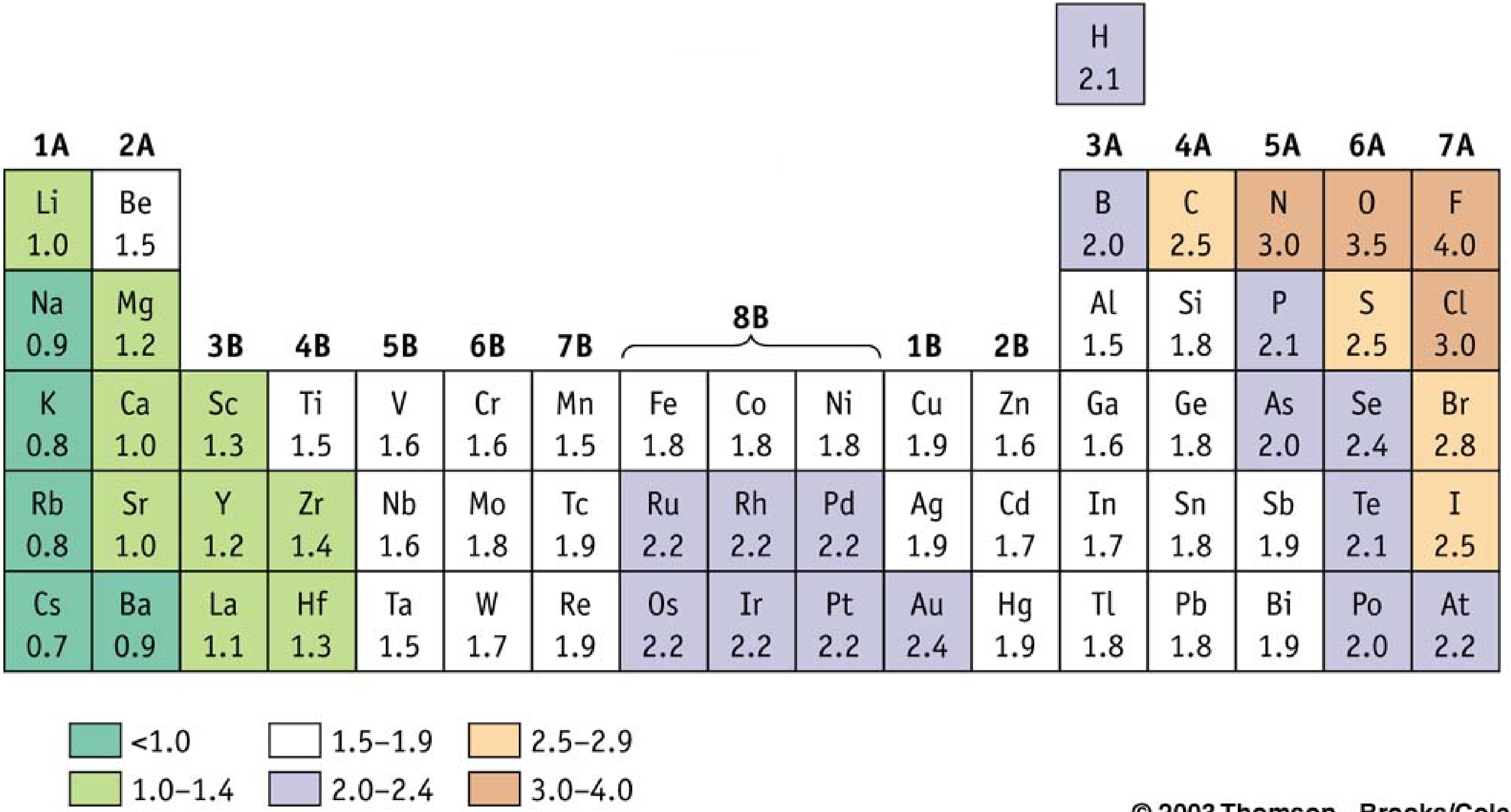
- Bond Polarity
  - Not all bonds are 100% ionic or 100% covalent.
  - Think of a bond as the rope in a tug-of-war:
    - Both atoms want to keep the electrons in the bond so that they can have a complete octet.
    - Sometimes, the two competitors have equal strengths (atoms with equal electronegativity) so the electrons are shared equally in a **nonpolar bond**.
    - Sometimes, one competitor is stronger (one atom has higher electronegativity) so the electrons are pulled toward it and are shared unequally in a **polar bond**.
  - Thus, polarity of a bond depends on the relative ability of each atom to attract electrons to itself (i.e. its **electronegativity,** χ):



0 ~0.4 ~2.0

Electronegativity difference →

Table of Electronegativities



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

Properties of Covalent Bonds

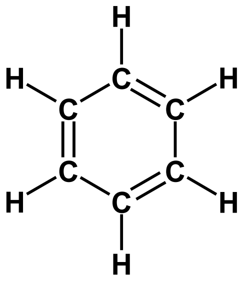
- Bond Polarity
  - Recall that electronegativity is conceptually a combination of electron affinity and ionization energy. As such, it:
    - ___________________ left to right across a period
    - ___________________ top to bottom down a group

    See p. 318 in Silberberg text for a table of electronegativity values.
  - It is not sufficient to simply know if a bond is ionic, polar covalent or covalent. We use **dipole vectors** to show the direction in which the electrons are pulled in **polar bonds**. The IUPAC convention for drawing dipole vectors is an arrow pointing toward the positive end of the molecule:
  - We can also use the symbols δ+ and δ- to indicate partial charges:

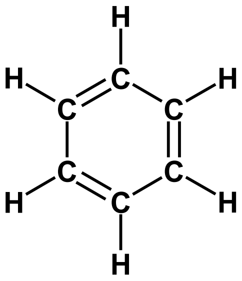
Properties of Covalent Bonds

- Bond Order
  - Bond order indicates how many electrons are involved in holding a pair/group of atoms together.
  - A single bond has a bond order of ____, a double bond has a bond order of ____, and a triple bond has a bond order of ____.
  - Fractional bond orders are also possible. If a molecule can be drawn using two different (but equally valid) structures, it exists as an average of those two structures.

    e.g. Benzene can be drawn as either structure below:



or



Each carbon-carbon bond has a bond order of 1.5 since 9 pairs of electrons are holding 6 atoms together. Thus, each is halfway between a single and a double bond.

Properties of Covalent Bonds

- Bond Length
  - Bond length is primarily determined by atomic radii. A bond between two larger atoms must be longer than one between two smaller atoms:
  - Also, the more strongly two atoms are held together, the shorter the bond. As such, a bond with a _____________ bond order will have a _________________ bond length and vice versa:

Drawing Molecules (Lewis Diagrams)

Steps for Drawing Lewis Diagrams

1. Determine the **connectivity**. *(i.e. identify the central atom(s) and the terminal atoms)*
2. Determine the total number of valence electrons.
3. Use one pair of electrons to make a single bond between each pair of bonded atoms.
4. Use any remaining electrons as lone pairs around each terminal atom (except H) so that each terminal atom has a complete octet, if possible.
5. Place any excess electrons around the central atom.
6. Check the central atom to see if it has a complete **octet**.
7. If the central atom has too few electrons, increase the **bond order** of one or more bonds by sharing non-bonded electrons.
   (i.e. make double or triple bonds as necessary)
8. Calculate **formal charge** for all atoms, and indicate any which are not zero.

Drawing Molecules (Lewis Diagrams)

Notes:

- Once you have finished drawing a Lewis diagram, always review it to check that that it has the correct number of atoms/electrons and that the **octet rule** is obeyed (only 2 electrons for hydrogen).
- If more than one valid Lewis diagram can be drawn for a molecule, the true electron distribution is a hybrid of the possible distributions. This is called **resonance**.
- If it is impossible to avoid having one atom with too few or too many electrons, it is usually the central atom. Elements in the 2nd period can **never** have more than eight electrons **under any circumstance**.
- Molecules with odd numbers of electrons form **free radicals** and cannot fully obey the rules as they must have one unpaired electron.
- **Lewis diagrams do not show a molecule's shape.**

Drawing Molecules (Lewis Diagrams)

Guidelines for Determining Connectivity

1. If you have many atoms of one element and one atom of another, the lone atom is usually the central one.
2. Hydrogen and fluorine rarely form more than one bond *(except under unusual circumstances like B_2H_6)*.
3. Carbon is rarely a terminal atom.
4. Oxygen is usually a terminal atom (or between the central atom and a hydrogen atom).
5. When writing a Lewis diagram for an oxoacid (e.g. H_2SO_4, HNO_3), draw a valid Lewis structure for the fully deprotonated form (e.g. SO_4^{2-}, NO_3^-) then attach protons (H^+) to the negatively charged oxygen atoms.

Drawing Molecules (Lewis Diagrams)

- Draw a valid Lewis diagram for each of the following molecules:

NH_3 C_2H_6

CH_3Cl C_2H_4

CH_2O C_2H_2

Formal Charges (Lewis Diagrams)

- Draw a Lewis diagram for ClO^-.

  Which atom has the charge?

- The **formal charge** (Q_f) of an atom is the charge that atom would bear if its molecule was blown apart such that each atom kept one electron from each of its bonds (and its lone pair electrons). It can be calculated using the following formula:

$$Q_f(X) = e_{\text{valence}} - \left[e_{\text{nonbonding}} + \frac{1}{2} e_{\text{bonding}} \right]$$

Formal Charges (Lewis Diagrams)

- As a general rule, we want to keep the formal charge on each atom as close to 0 as possible (without giving any atom more than a complete octet).

- Draw the best Lewis diagram for BF_3.

Resonance Structures (Lewis Diagrams)

- Draw the best Lewis diagram for nitrate (NO_3^-).

  Note that there are actually _____ equally correct answers.

- When you can draw different valid Lewis diagrams by moving electrons *<u>but not atoms</u>*, they are called **resonance structures**.
- What is the average bond order for a $N - O$ bond in nitrate?

Resonance Structures (Lewis Diagrams)

- How many resonance diagrams can you draw for ozone?
  (O_3 with a central oxygen atom and two terminal oxygen atoms)

- What is the average bond order for an $O - O$ bond in ozone?

Shapes of Molecules (VSEPR)

- Much of a molecule's chemistry is influenced by its shape. Lewis diagrams are drawn in two dimensions but molecules exist in three dimensions. As such, a Lewis diagram does not necessarily show the real shape of a molecule.

- VSEPR
  - VSEPR theory allows us to predict a molecule's overall shape:

    Valence Shell Electron Pair Repulsion

  - The best shape for a molecule has the atoms arranged to minimize electron repulsion. In other words, all of the electrons surrounding an atom (either as part of a bond or as a "lone pair") have pushed each other as far apart as possible.

Shapes of Molecules (VSEPR)

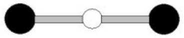
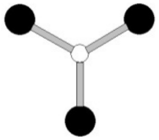
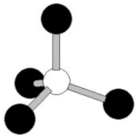
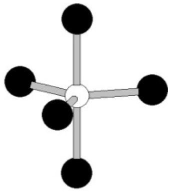
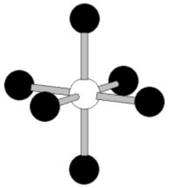
- To determine the best shape around an atom, first count the number of atoms bonded to it and the number of lone pairs on it. These are the **electron groups**. The number of electron groups is often referred to as the **steric number**.

  e.g. NH_3 BH_3 CH_2O

- Based on the number of electron groups, we can define five general shape families, or **electron group geometries,** for the central atom. Each electron group geometry derives from the need to keep the electrons (both bonding and nonbonding) around the central atom as far apart as possible.

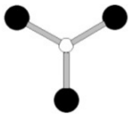
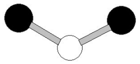
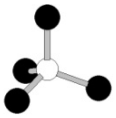
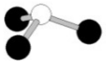
  See Figure 9.2 in Silberberg (or Table 6.2 in Olmsted or Table 10.1 in Petrucci) for a summary of all five electron group geometries and the corresponding shapes.

Shapes of Molecules (VSEPR)

Steric Number	Electron Group Geometry	Approximate Bond Angle(s)	Shape
2	linear	180°	
3	trigonal planar	120°	
4	tetrahedral	109.47°	
5	trigonal bipyramidal	90°, 120°, 180°	
6	octahedral	90° , 180°	

Shapes of Molecules (VSEPR)

- Lone pairs help to determine the electron group geometry but ‘disappear’ in the final shape of the molecule. As such, each electron group geometry can give rise to several different **molecular geometries**:

Steric Number	**Electron Group Geometry**	**# Bonded Atoms**	**# Lone Pairs**	**Molecular Geometry**
3	trigonal planar	3	0	 trigonal planar
		2	1	 bent
4	tetrahedral	4	0	 tetrahedral
		3	1	 trigonal pyramidal
		2	2	 bent

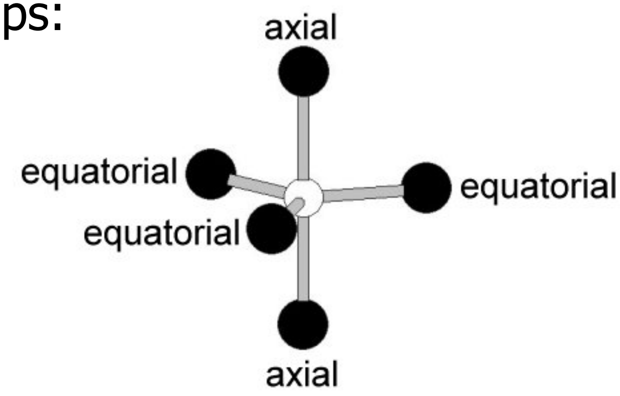
Shapes of Molecules (VSEPR)

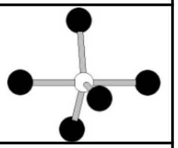
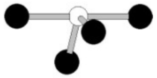
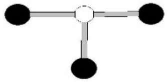
- It is also worth noting that a lone pair of electrons acts as if it is ‘bigger’ than a group of bonding electrons when determining bond angle:

- CH_4, NH_3 and H_2O all have _____ electron groups but a different number of lone pairs about the central atom:
  - CH_4 is tetrahedral with $H-C-H$ bond angles of _______
  - NH_3 is trigonal pyramidal with $H-N-H$ bond angles of ______
  - H_2O is bent with $H-O-H$ bond angle of _________

Shapes of Molecules (VSEPR)

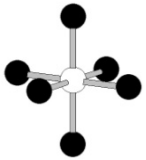
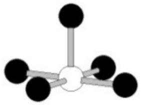
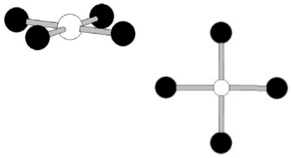
- For the trigonal bipyramidal electron group geometry, there are two different types of 'site' for electron groups:
  - Each **axial site** is _______ away from all three equatorial sites.
  - Each **equatorial site** is _______ away from the other two equatorial sites and _______ away from the two axial sites.
  - Lone pairs are always found in the 'larger' _______________ sites:



Steric Number	Electron Group Geometry	# Bonded Atoms	# Lone Pairs	Molecular Geometry
5	trigonal bipyramidal	5	0	trigonal bipyramidal 
		4	1	seesaw 
		3	2	T-shaped 

Shapes of Molecules (VSEPR)

- For the octahedral electron group geometry, all sites are initially equivalent and the first lone pair can be put anywhere. If a second lone pair is to be added, however, it must be put *opposite* the first one. Both sites with lone pairs are called ________ sites

Steric Number	**Electron Group Geometry**	**# Bonded Atoms**	**# Lone Pairs**	**Molecular Geometry**
6	octahedral	6	0	 octahedral
		5	1	 square pyramidal
		4	2	 square planar

Shapes of Molecules (VSEPR)

- What is the molecular geometry of each of the following molecules?

CO_2

SiF_4

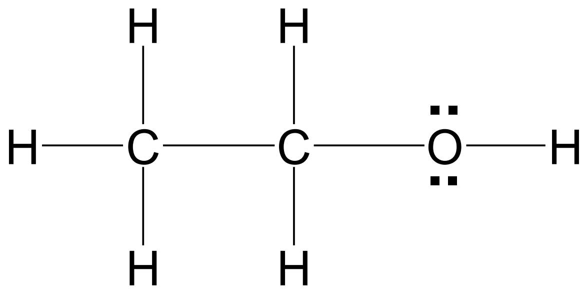
XeF_2

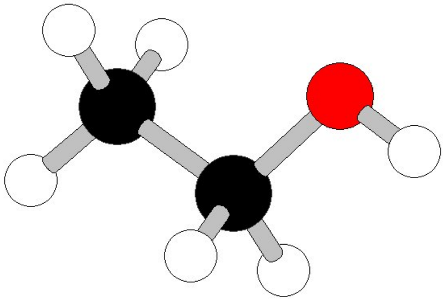
SCl_4

Shapes of Molecules (VSEPR)

- VSEPR theory can also be used to predict the shapes of larger molecules by treating each ‘central’ atom separately.

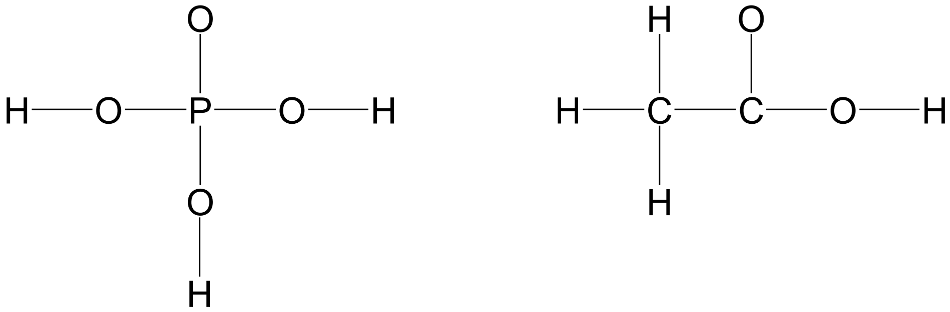
- A Lewis diagram for ethanol is shown below (next to a 3-dimensional picture of what it actually looks like).
  - What is the geometry at each central atom?
  - What are the approximate bond angles?





Shapes of Molecules (VSEPR)

- The connectivities for phosphoric acid (H_3PO_4) and acetic acid (CH_3CO_2H) are shown below. Draw Lewis diagrams for each acid, and identify the geometry at each ‘central’ atom.



Polarity of Molecules

- Many of a compound's properties are determined by how polar (or nonpolar) it is.
  - To determine whether a molecule is polar or nonpolar, we need to look at two things:
    - ____
    - ____
  - If a molecule has **no dipoles** *or* all of the **dipoles cancel** out due to symmetry, it is ___________________.
  - If a molecule has **dipoles that don't cancel** out, it has a permanent **dipole moment (μ)** and is __________________.
  - Dipoles have direction! They must be added as *vectors*:

Polarity of Molecules

- Determine whether or not each of the following molecules is polar. If it's polar, show the direction of its dipole moment.

CO_2

BHF_2

$AlBr_3$

SO_3

H_2O

CH_3CH_2OH (ethanol)