



AP* Chemistry

CHEMICAL BONDING & MOLECULAR STRUCTURE

WHAT IS A CHEMICAL BOND? It will take us the next two chapters to answer this question! Bonds are attractive forces that hold groups of atoms together and make them function as a unit. [Defined in 25 words or less, but leaves out LOTS of details!] Bonding relates to physical properties such as melting point, hardness and electrical and thermal conductivity as well as solubility characteristics. *The system is achieving the lowest possible energy state by bonding.* If you think about it, most of the chemical substances you can name or identify are NOT elements. They are compounds. That means being bound requires less energy than existing in the elemental form. It also means that energy *was released* from the system. This is a HUGE misconception most students have—it takes energy to break a bond, not make a bond! Energy is RELEASED when a bond is formed, therefore, it REQUIRES energy to break a bond.

Bond energy—energy required to break the bond

TYPES OF CHEMICAL BONDS

- **ionic bonds**—an electrostatic attraction between ions; usually produced by the reaction between a metal and nonmetal. Cause very high melting points and usually a solid state since the attraction is SO strong that the ions are VERY close together in a crystal formation.
- **covalent bonds**—electrons are shared by nuclei [careful, sharing is hardly ever 50-50!]
- **Coulomb's Law**--used to calculate the Energy of an ionic bond.

$$E = 2.31 \times 10^{-19} \text{ J} \cdot \text{nm} \left(\frac{Q_1 Q_2}{r} \right)$$

r is the distance between the ion centers in nanometers [size matters!]

J is the energy in Joules

Q_1 and Q_2 are the numerical ion charges; don't neglect their signs

There will be a negative sign on the Energy once calculated—it indicates an attractive force so that the *ion pair has lower energy than the separated ions.*

You can also use Coulomb's Law to calculate the repulsive forces between like charges. What sign will that calculation have?

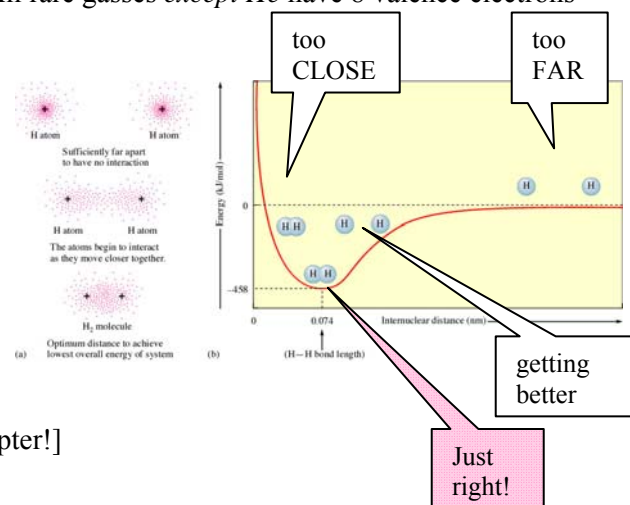
VALENCE ELECTRONS

- valence electrons--outermost electrons; focus on ns , np and d electrons of transition elements.
- Lewis dot structures--(usually main group elements) G.N. Lewis, 1916
- Emphasizes rare gas configurations, s^2p^6 , as a stable state. All rare gasses *except He* have 8 valence electrons and follow the octet rule.

CHEMICAL BOND FORMATION

Level 1—When 2 hydrogen atoms approach each other 2 “bad” E things happen: electron/electron repulsion and proton/proton repulsion. One “good” E thing happens: proton/electron attraction. When the attractive forces offset the repulsive forces, the energy of the two atoms decreases and a *bond* is formed. Remember, nature is always striving for a **LOWER ENERGY STATE**.

- **bond length**—the *distance* between the 2 nuclei where the *energy is minimum* between the two nuclei.
- energy decrease is small--*van der Waals* IMFs [another chapter!]
- energy decrease is larger--*chemical bonds*



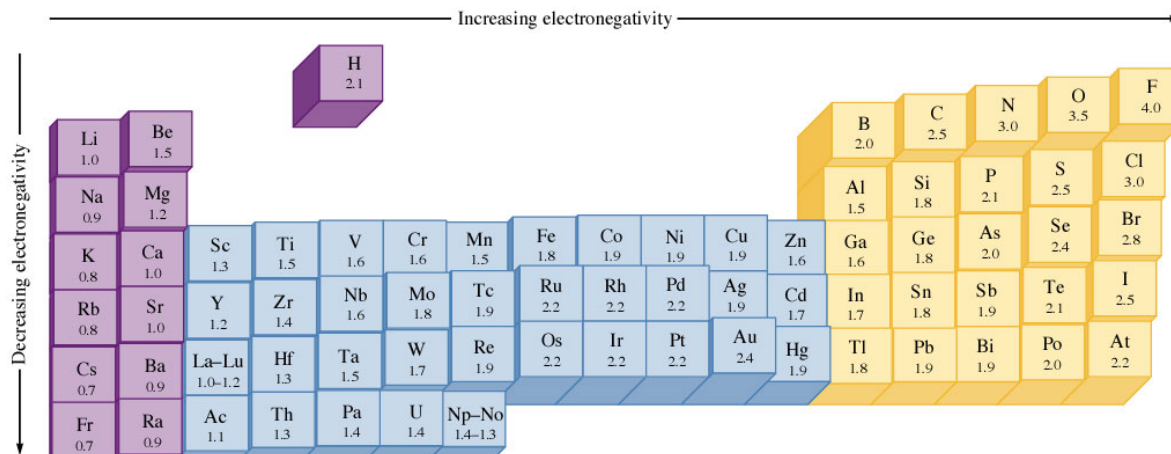
Level 2--Orbital Theory – electrons and + nucleus of one atom strongly perturb or change the spatial distribution of the *other* atom’s valence electrons. A new orbital (wave function) is needed to describe the distribution of the bonding electrons **bond orbital**

- **bond orbital**--describes the motion of the 2 electrons of *opposite spin*
- **lone pair orbital**--the orbitals of electrons on a bonded atom that are distorted *away* from the bond region also have new descriptions (wave functions)
- The new bond orbital is “built” from the atomic orbitals of the two bonded atoms. Looks a lot like the original BUT, the bond orbital is concentrated in the region *between* the bonded nuclei.
- The energy of the electrons in a bond orbital, where the electrons are attracted by **two** nuclei, is lower than their energy in valence electron orbitals where the electrons are attracted to *only one* nucleus. [ZAPPED!!]
- **ionic bond**--the bonding orbital is strongly displaced toward one nuclei (metal from the left side of table + nonmetal from right side of the periodic table)
- **covalent bond**--bond orbital is more or less (polar or non-polar) evenly distributed and the electrons are *shared* by two nuclei. (elements lie close to one another on the periodic table)
- *Most chemical bonds are in fact somewhere between purely ionic and purely covalent.*

Recall the information you’ve already learned about electronegativity:

ELECTRONEGATIVITY (En)—The ability of an atom IN A MOLECULE [meaning it’s participating in a BOND] to attract shared electrons to itself. Think “tug of war”. Now you know why they teach you such games in elementary school!

- o Linus Pauling’s scale—Nobel Prize for Chemistry & Peace
- o Fluorine is the most En and Francium is the least En



- o Why is F the most? Highest Z_{eff} and smallest radius so that the nucleus is closest to the “action”.
- o Why is Fr the least? Lowest Z_{eff} and largest radius so that the nucleus is farthest from the “action”.
- o We’ll use this concept a great deal in our discussions about bonding since this atomic trend is **only used when atoms form molecules.**

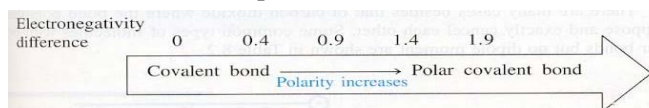
Table 8.1 The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic

Covalent character decreases; Ionic character increases

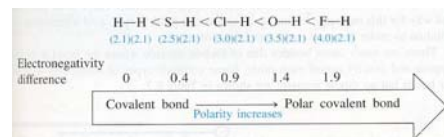
Use the difference in En to determine the type of bond formed.

- o ionic--Electronegativity difference > 1.67
- o covalent--Electronegativity difference < 1.67
- o NONpolar En difference < 0.4

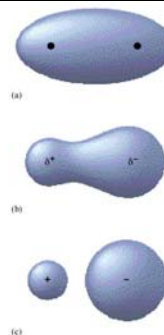


Exercise 1 Relative Bond Polarities

Order the following bonds according to polarity: H—H, O—H, Cl—H, S—H, and F—H.



- **bond polarity and electronegativity**--En (χ) determines polarity since it measures a nucleus' attraction or "pull" on the bonded electron pair. En ranges from 0--4.0. When 2 nuclei are the same, the sharing is equal \therefore the bond is described as NONPOLAR (a). When the 2 nuclei are different the electrons are not shared equally, setting up slight +/- poles \therefore POLAR (b). When the electrons are shared unequally to a greater extent \therefore IONIC (c).



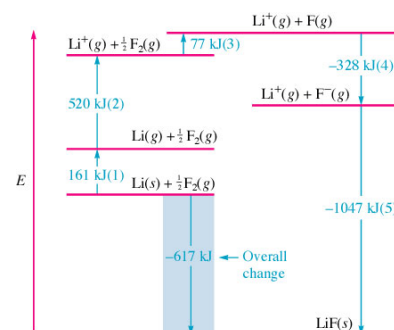
- The polarity of a bond can be estimated from $\Delta\chi/\Sigma\chi$. Range is 0 for pure covalent bonds to 1 for completely ionic bonds.

IONIC BONDING

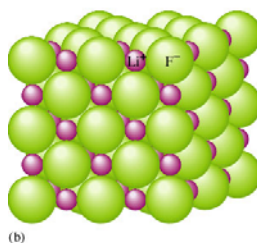
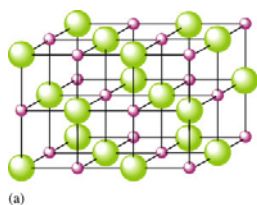
The final result of ionic bonding is a solid, regular array of cations and anions called a *crystal lattice*. At right, you can see the energy changes involved in forming LiF from the elements Li and F₂

- Enthalpy of dissociation--energy required to decompose an ion pair (from a lattice) into ions \therefore a measure of the strength of the ionic bond
- from Coulomb's law:

$$E = \Delta H_{\text{dissociation}} \propto \frac{q_+ q_-}{r}$$



where q_+ is the charge on the positive ion and q_- is the charge on the negative ion and r is the distance between the ion centers in the crystal lattice.



- energy of attraction depends directly on the magnitude of the charges (higher the charges the greater the attractive energy) and inversely on the distance between them (greater the distance, the smaller the attractive energy).
- the larger the ion the smaller the $\Delta H_{\text{dissociation}}$ (it's a distance thing)
 - ion-ion attractions have a profound effect on *melting points* and solubilities.
- Water must overcome the ion-ion attractions to dissolve an ionic substance. Size affects this as does charge HOW??
- The crystal lattice for LiF is shown at the left.
- Lattice energy can be represented by a modified form of Coulomb's Law: k is a proportionality constant that depends on the structure of the solid and the electron configurations of the ions.

$$\text{Lattice Energy} = k \left(\frac{Q_1 Q_2}{r} \right)$$

COVALENT BONDING

Most compounds are covalently bonded, especially carbon compounds.

We have 3 major bonding theories to discuss. Only one for this chapter though!

- **Localized Electron [LE] Bonding Model**—assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the *atomic* orbitals of the bound atoms. Electron pairs are assumed to be localized *on* a particular atom [**lone pairs**] or in the space *between* two atoms [**bonding pairs**].
 1. Lewis Structures describe the valence electron arrangement
 2. Geometry of the molecule is predicted with VSEPR
 3. Description of the type of atomic orbitals “blended” by the atoms to share electrons or hold lone pairs [hybrids—next chapter].
- **Number of Bond Pairs: The Octet Rule**—“noble is good”
 - predict # of bonds by counting the number of unpaired electrons in a Lewis structure
 - a dash is used to represent a **pair** of shared electrons, : is used to represent a **lone pair**

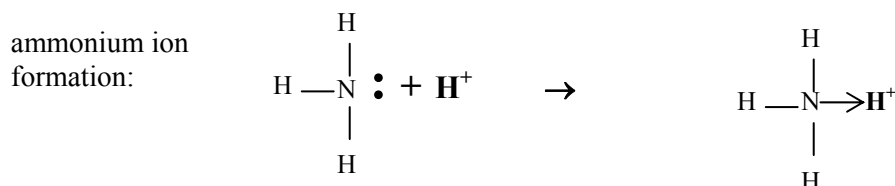
SINGLE AND MULTIPLE BONDS:

- **single bond**--one pair of electrons shared \rightleftharpoons sigma (σ) bond
- MULTIPLE BONDS ARE MOST OFTEN FORMED by C,N,O,P and S ATOMS—say “C-NOPS”
- **double bond**--two pairs of electrons shared \rightleftharpoons one σ bond and one π bond
- **triple bond**--three pairs of electrons shared \rightleftharpoons one σ bond and two π bonds
- obviously, combinations of σ and π are stronger than σ alone. Pi bonds are weaker than sigma but never exist alone
- Multiple bonds increase the electron density between two nuclei and therefore decrease the nuclear repulsions while enhancing the nucleus to electron density attractions—either way, the nuclei move closer together and the bond length is shorter for a double than a single and triple is shortest of all!

HUGE
concept

COORDINATE COVALENT BONDS:

Some atoms such as N and P, tend to share a **lone pair** with another atom that is short of electrons, leading to the formation of a coordinate covalent bond: These bonds are in all coordination compounds and Lewis Acids/Bases



We show that N is sharing the lone PAIR of electrons by drawing an arrow from it to the H^+ , remember H^+ has NO electrons to contribute to the bond. Note that all four bonds are actually identical in length and strength.

EXCEPTIONS TO THE OCTET RULE:

CRITICAL stuff!

- **Fewer than eight**--H at most only 2 electrons (one bond)! BeH_2 , only 4 valence electrons around Be (only two bonds)! Boron compounds, only 6 valence electrons (three bonds)! ammonia + boron trifluoride is a classic Lewis A/B reaction.
- **Expanded Valence**—can only happen if the central element has *d*-orbitals which means it is from the 3rd period or greater [periods 4, 5, 6...] and can thus be surrounded by more than four valence pairs in certain compounds. The number of bonds depends on the balance between the ability of the nucleus to attract electrons and the repulsion between the pairs.
- **odd-electron compounds**--A few stable cmpds. contain an odd number of valence electrons and thus cannot obey the octet rule. NO, NO_2 , and ClO_2 .

Drawing Lewis Structures: (VERY USEFUL when predicting molecular shape)

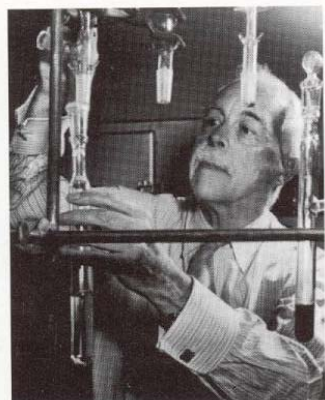


Figure 8.13
G. N. Lewis (1875–1946).

To predict arrangement of atoms within the molecule use the following rules:

1. H is always a terminal atom. ALWAYS connected to only one other atom!!
2. LOWEST En is central atom in molecule [not just the oddball element]
3. Find the total # of valence electrons by adding up group #'s of the elements. FOR IONS **add** for *negative* and **subtract** for *positive* charge.
Divide by two to get the number of electron PAIRS.
4. Place one pair of electrons, a σ bond, between each pair of bonded atoms.
5. Subtract from the total the number of bonds you just used.
6. Place lone pairs about each terminal atom (EXCEPT H) to satisfy the octet rule. Left over pairs are assigned to the central atom. If the central atom is from the 3rd or higher period, it can accommodate more than four electron pairs, up to six pairs.
7. If the central atom is not yet surrounded by four electron pairs, convert one or more terminal atom lone pairs to pi bonds pairs. NOT ALL ELEMENTS FORM pi BONDS!! **only C, N, O, P, and S!!**

Exercise 6 Writing Lewis Structures

Give the Lewis structure for each of the following:

- | | |
|--------------------|--------------------|
| a. HF | d. CH ₄ |
| b. N ₂ | e. CF ₄ |
| c. NH ₃ | f. NO ⁺ |

Exercise 7 Lewis Structures for Molecules That Violate the Octet Rule I

Write the Lewis structure for PCl₅.

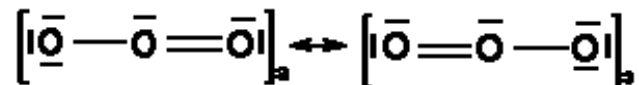
Exercise 8 Lewis Structures for Molecules That Violate the Octet Rule II

Write the Lewis structure for each molecule or ion.

- | | | | | |
|---------------------|---------------------|----------------------|----------------------|----------------------------------|
| a. ClF ₃ | b. XeO ₃ | c. RnCl ₂ | d. BeCl ₂ | e. ICl ₄ ⁻ |
|---------------------|---------------------|----------------------|----------------------|----------------------------------|

RESONANCE STRUCTURES:

Experiments show that ozone, O_3 has equal bond lengths and equal bond strengths, implying that there is an equal number of bond pairs on each side of the central O atom. When you draw the Lewis structure, that situation is NOT what you draw! So, we draw a **resonance structure**:



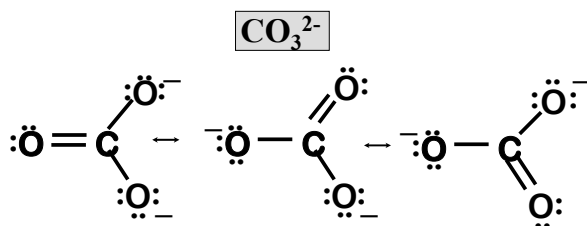
We draw it as having a double bond and a single bond [the dashes are another way of representing lone pairs] BUT since there are equal bond lengths and strengths, they are clearly NOT as pictured above. The bonds are more equivalent to a “bond and $\frac{1}{2}$ ” in terms of length and strength. We use the double edged arrows to indicate resonance. We also bracket the structures just as we do for polyatomic ions.

In an attempt to improve the drawing, we sometimes use a single composite picture. The drawing at right better shows the bond angle. Focus on the central atom in either of the resonance structures above. The central atom is surrounded by three sites of electron density: a lone pair, a single σ bond and a double bond (consisting of one σ bond and one π bond). Three electron-dense sites surrounding a central point in a 3-dimensional space will orient themselves at 120° so that electron/electron repulsions are minimized.

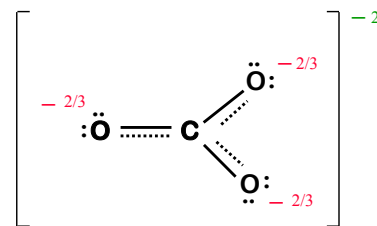


Carbonate ion:

NOTE: These all 3 need brackets and the charge shown in the upper right corner [like the composite at right] to gain full credit on the AP Exam!!!!



THREE EQUIVALENT STRUCTURES
RESONANCE HYBRID



Notice: 1) resonance structures differ only in the assignment of electron pair positions, NEVER atom positions.
2) resonance structures differ in the number of bond pairs between a given pair of atoms

Exercise 9

Resonance Structures

Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model.

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	1 + 7 = 8	H—F	6	H—F̣:	H, 2 F, 8
b. N ₂	5 + 5 = 10	N—N	8	:N≡N:	N, 8
c. NH ₃	5 + 3(1) = 8	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$	2	$\begin{array}{c} \text{H} \\ \\ \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$	H, 2 N, 8
d. CH ₄	4 + 4(1) = 8	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	0	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	H, 2 C, 8
e. CF ₄	4 + 4(7) = 32	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-\text{F} \\ \\ \text{F} \end{array}$	24	$\begin{array}{c} \text{:F:} \\ \\ \text{:F}-\text{C}-\text{F:} \\ \\ \text{:F:} \end{array}$	F, 8 C, 8
f. NO ⁺	5 + 6 - 1 = 10	N—O	8	[:N≡O:] ⁺	N, 8 O, 8

BOND PROPERTIES

- **bond order**—simply the number of bonding electron pairs shared by two atoms in a molecule.
 - 1--only a sigma bond between the 2 bonded atoms
 - 2--2 shared pairs between two atoms; one sigma and one pi (CO₂ and ethylene)
 - 3--3 shared pairs between two atoms; one sigma and two pi (acetylene and CO and cyanide)
 - fractional--resonance; ozone 3/2; carbonate 2/3

$$\text{bond order} = \frac{\# \text{ of shared pairs linking X and Y}}{\text{number of X-Y links}}$$

- **bond length**--distance between the nuclei of two bonded atoms C—N < C=C < C—P
The effect of bond order is evident when you compare bonds between the *same* two atoms

Bond	C—O	C=O	C≡O
Bond order	1	2	3
Bond length (pm)	143	122	113

Table 8.5 Bond Lengths for Selected Bonds

Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	Single	154	347
C=C	Double	134	614
C≡C	Triple	120	839
C—O	Single	143	358
C=O	Double	123	745
C—N	Single	143	305
C=N	Double	138	615
C≡N	Triple	116	891

The bond length is reduced by adding multiple bonds since it increases the electron density between the two nuclei. Variations in neighboring parts of a molecule can affect the length of a particular bond as much as 10%

- **bond energy**—the greater the number of electron pairs between a pair of atoms, the shorter the bond. This implies that atoms are held together more tightly when there are multiple bonds, so there is a relation between bond order and the energy required to separate them.
- **bond dissociation energy(D)**--gaseous atom; E supplied to break a chemical bond (bond energy for short!)
 - D is + and breaking bonds is *endothermic*. The converse is also true.
 - D in table 10.4 is +
 - D is an average with a +/- 10%
 - Gaseous atoms
 - What is the connection between bond energy and bond order???
- Calculating reaction energies from bond energies: Bonds in reactants are broken while bonds in products are formed. Energy released is greater than energy absorbed in EXOthermic reactions. The converse is also true.

$$\Delta H^{\circ}_{\text{reaction}} = \sum mD (\text{bonds broken}) - \sum nD (\text{bonds made})$$

$$\Delta H^{\circ}_{\text{reaction}} = \text{reactants}_{(E \text{ cost})} - \text{products}_{(E \text{ payoff})}$$

NOTE THIS IS “BACKWARDS” FROM THE THERMODYNAMICS “BIG MAMMA” EQUATION. We’re back to that misconception if you are confused by this. It takes energy to break bonds NOT make bonds! First we must break the bonds of the reactants [costs energy] then subtract the energy gained by forming new bonds in the products.

Table 8.4 Average Bond Energies (kJ/mol)

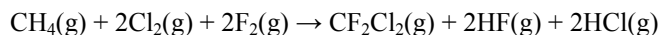
Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO₂) = 799

Exercise 5

ΔH from Bond Energies

Using the bond energies listed in Table 8.4, calculate ΔH° for the reaction of methane with chlorine and fluorine to give Freon-12 (CF₂Cl₂).



$$\Delta H = -1194 \text{ kJ/mol}$$

FORMAL CHARGE

Often, many nonequivalent Lewis structures may be obtained which all follow the rules. Use the idea of formal charge to determine the most favored structure. Physicists tell us that oxidation states of more than +/- two are pure fantasy and that formal charges are much more realistic.

- **formal** charge--The difference between the number of valence electrons on the free element and the number of electrons assigned to the atom in the molecule.

$$\text{Atom's formal charge} = \text{group number} - [\# \text{ of lone electrons} - 2 (\# \text{ of bonding electrons})]$$

THE SUM OF THE FORMAL CHARGES MUST EQUAL AN ION'S CHARGE!!

- Use formal charges along with the following to determine resonance structure
 - Atoms in molecules (or ions) should have formal charges as small as possible—as close to zero as possible [**principle of electroneutrality**]
 - A molecule (or ion) is most stable when any negative formal charge resides on the most electronegative atom.

Example: Draw all possible structures for the sulfate ion. Decide which is the most plausible using formal charges.

**** Caution**** Although formal charges are considered closer to the atomic charges than the oxidation states, they are still only *estimates* and should not be taken as the actual atomic charges. Second, using formal charges can often lead to erroneous structures, so tests based on experiments must be used to make the final decisions on the correct description of bonding.

Exercise 10

Formal Charges

Give possible Lewis structures for XeO_3 , an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

Structures with the lower values of formal charge would be most appropriate

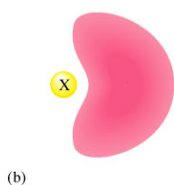
MOLECULAR SHAPE—MINIMIZE ELECTRON PAIR REPULSIONS!!!

VSEPR--valence shell electron pair repulsion theory

- Molecular shape changes with the numbers of σ bonds plus lone pairs about the central atom

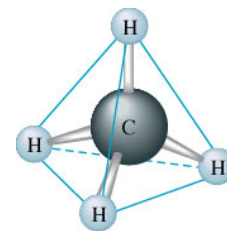
σ bonds + lone pairs on central atom	STRUCTURAL PAIR or ELECTRONIC GEOMETRY (NOT to be confused with molecular geometry!)
2	Linear
3	Trigonal planar
4	Tetrahedral (or pyramidal)
5	Trigonal bipyramidal
6	Octahedral

THE VSEPR MODEL AND MOLECULAR SHAPE

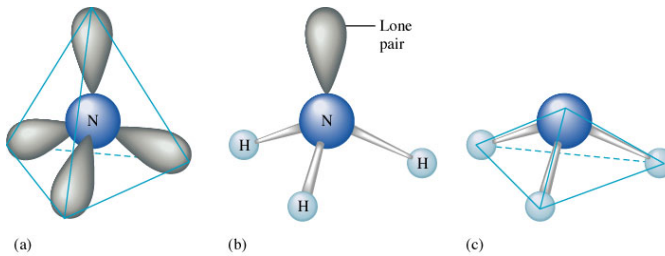


- **molecular geometry**--the arrangement in space of the atoms bonded to a central atom *not necessarily the same as the structural pair geometry* ☞ lone pairs have a different repulsion since they are experiencing an attraction or “pull” from only one nucleus as opposed to two nuclei. They also take up more space around an atom as you can see on the left.
- Each lone pair or bond pair repels all other lone pairs and bond pairs--they try to avoid each other making as wide an angle as possible.
 - works well for elements of the *s* and *p*-blocks
 - VSEPR does *not* apply to transition element compounds (exceptions)

- **MOLECULAR SHAPES FOR CENTRAL ATOMS WITH NORMAL VALENCE:** no more than 4 structural pairs if the atom obeys the octet rule. Since no lone pairs are present, the molecular and structural pair [or *electronic*] geometry is the same. 109.5° bond angle.

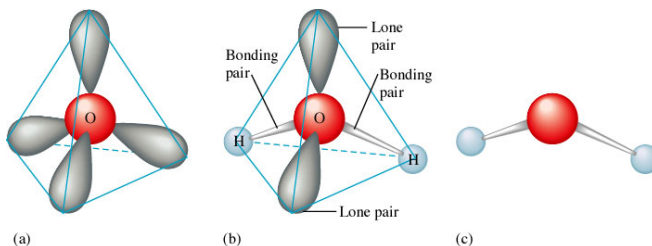


- Ignore lone pairs **AFTER** you've determined the angles \therefore only the relative positions of the atoms are important in *molecular* geometry
- Below is ammonia—3 sigma bonds and one lone pair—when lone pairs are present, the structural pair or electronic geometry are ***different!!***
- “electronic geometry”—tetrahedral while molecular geometry—trigonal pyramidal, 107.5° bond angle

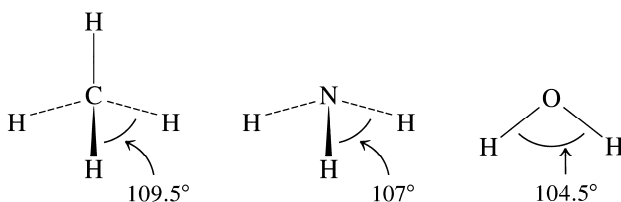


ANY time lone pairs are present, the electronic and molecular geometries will be different.

- Water has 2 lone pairs and still obeys the octet rule. Again, the electronic and molecular geometries will be ***different***. The electronic is still tetrahedral since the octet rule is obeyed BUT the molecular geometry is described as “bent” or V-shaped, 104.5° bond angle.



Now, let's discuss the warping of the 109.5° bond angle. The lone pairs have more repulsive

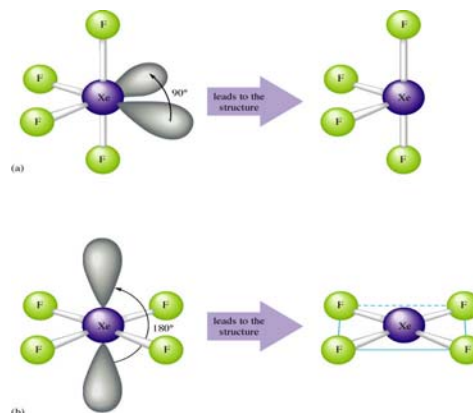


force than shared pairs and are “space hogs”. They force the shared pairs to squeeze together.

- To determine the geometry:
 1. Sketch the Lewis dot structure [DO NOT SKIP THIS STEP.]
 2. Describe the structural pair or *electronic* geometry
 3. Focus on the bond locations (ignore lone pairs) and assign a molecular geometry based on their locations

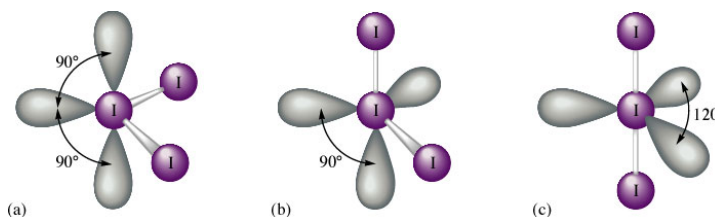
- **MOLECULAR SHAPES FOR CENTRAL ATOMS WITH EXPANDED VALENCE**—only elements with a principal energy level of 3 or higher can expand their valence and violate the octet rule on the high side. Why?
 d orbitals are needed for the expansion to a 5th or 6th bonding location—the combination of 1 s and 3 p 's provides the four bonding sites that make up the octet rule.

- seems to be a limit of 3 lone pairs about the central atom
- XeF_4 ; There are 2 lone pairs and 4 shared pairs. Two possible arrangements exist for this situation.
- *equatorial*—shared pairs surround Xe. In both molecular arrangements the electronic geometry is octahedral with 90° angles. (a) has a molecular geometry known as “see saw”. This puts the lone pairs only 90° apart.
- *axial*—lone pairs are located “top and bottom” This is preferred for this molecule since the lone pairs are 180° apart which minimizes their repulsion. Lone pairs prefer maximum separation—use this in your determinations! (b at upper right) has a molecular geometry that is more stable—square planar



Which of these arrangements do you predict to be the most stable for I_3^- ?

Remember to look at the lone pair-lone pair angles to make your determination.



Exercise 11 Prediction of Molecular Structure I

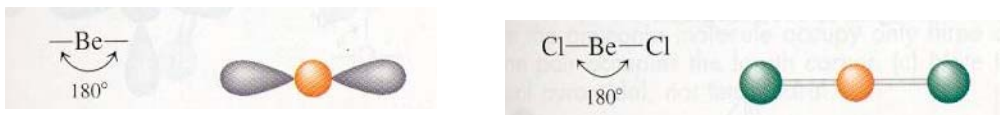
Describe the molecular structure of the water molecule.

**Two bonding and two non-bonding pairs of electrons
Forming a V shape molecule**

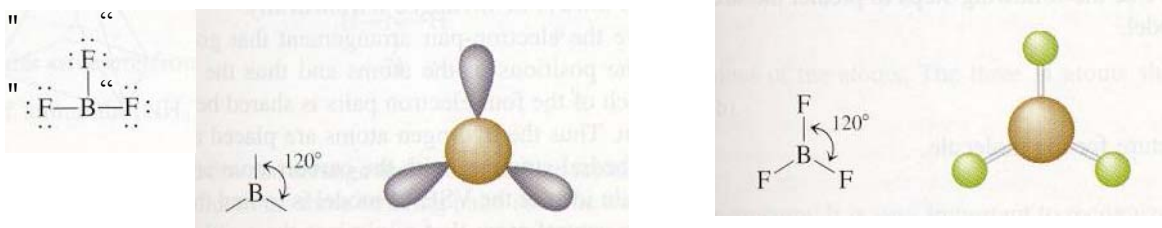
Exercise 12 Prediction of Molecular Structure II

When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl_5) is formed. In the gaseous and liquid states, this substance consists of PCl_5 molecules, but in the solid state it consists of a 1:1 mixture of PCl_4^+ and PCl_6^- ions. Predict the geometric structures of PCl_5 , PCl_4^+ , and PCl_6^- .

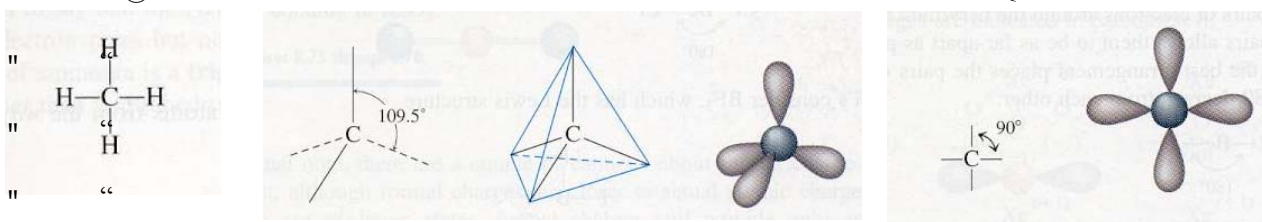
- RECAP including bond angles for all
- **structural pairs**-- σ bond (π bond pairs occupy the same space) pairs about an atom
 - 2 @ 180° \therefore linear [and of course, planar]



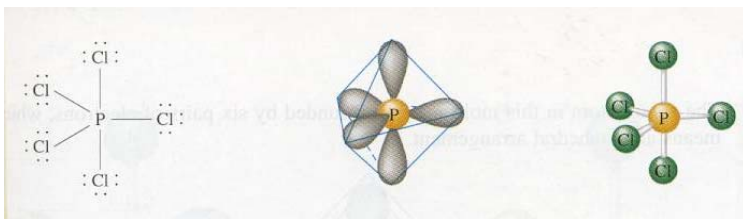
- 3 @ 120° \therefore trigonal planar



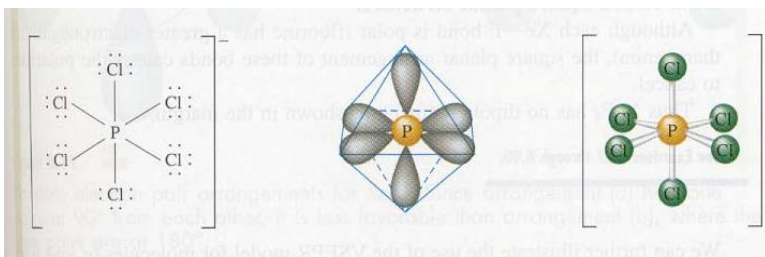
- 4 @ 109.5° \therefore tetrahedral



- 3 @ 120 & 2 @ 90° with each other through central atom \therefore trigonal bipyramidal



- 6 @ 90° \therefore octahedral



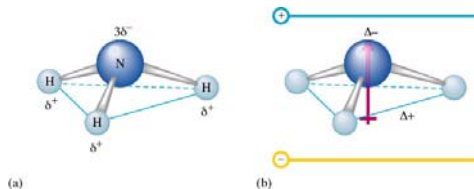
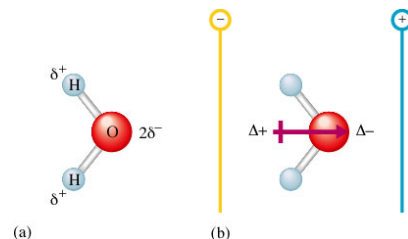
The presence of lone pairs alters the six basic MOLECULAR geometries, but the *electronic or structural pair* geometry remains one of these six basic types.

MOLECULAR POLARITY

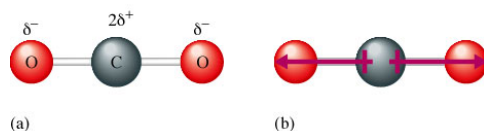
polar--bonds can be polar while the entire molecule isn't and vice versa.

dipole moment--separation of the charge in a molecule; product of the size of the charge and the distance of separation

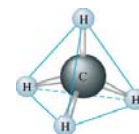
- align themselves with an electric field (figure b at right)
- align with each other as well in the absence of an electric field
- water—2 lone pairs establish a strong negative pole
- ammonia—has a lone pair which establishes a neg. pole
- note that the direction of the “arrow” indicating the dipole moment always points to the negative pole with the cross hatch on the arrow (looks sort of like we're trying to make a + sign) is at the positive pole. Logical?



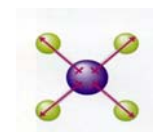
- IF octet rule is obeyed [which it is in both water and ammonia] AND all the surrounding bonds are the same [even if very polar] then the molecule is NONpolar since all the dipole moments cancel each other out.



- carbon dioxide, above is nonpolar since the dipole moments cancel. For those of you in physics, the dipole moments are vector quantities.
- Methane is a great example. Replace one H with a halogen and it becomes polar. Replace all and it's nonpolar again!



Draw CH₄, CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄ Indicate dipole moment(s) where necessary.



Exercise 2 **Bond Polarity and Dipole Moment**

For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HCL, Cl₂, SO₃ (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH₄ [tetrahedral (see Table 8.2) with the carbon atom at the center], and H₂S (V-shaped with the sulfur atom at the point).

Exercise 13 **Prediction of Molecular Structure III**

Because the noble gases have filled *s* and *p* valence orbitals, they were not expected to be chemically reactive. In fact, for many years these elements were called inert gases because of this supposed inability to form any compounds. However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized. For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF₄). Predict its structure and whether it has a dipole moment.

Exercise 14 **Structures of Molecules with Multiple Bonds**

Predict the molecular structure of the sulfur dioxide molecule. Is this molecule expected to have a dipole moment?

ONCE MORE WITH FEELING...

CHEMICAL BONDS—Forces of attraction that hold groups of atoms together *within* a molecule or crystal lattice and make them function as a unit.

IONIC

Characteristics of ionic substances usually include:

- electrons that are transferred between atoms having high differences in electronegativity (greater than 1.67)
- compounds containing a metal and a nonmetal (Remember that metals are located on the left side of the periodic table and nonmetals are to the right of the “stairs”.)
- strong electrostatic attractions between positive and negative ions
- formulas given in the simplest ratio of elements (empirical formula; NaCl, MgCl₂)
- crystalline structures that are solids at room temperature
- ions that form a crystal lattice structure as pictured in Figure 1
- compounds that melt at high temperatures
- substances that are good conductors of electricity in the molten or dissolved state

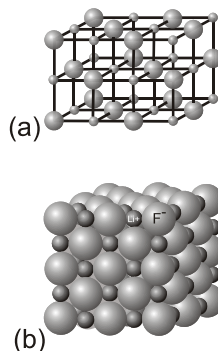


Fig. 1

COVALENT

Characteristics of covalent substances usually include:

- the sharing of electrons between atoms having small differences in electronegativities (less than 1.67)
- nonmetals attracted to other nonmetals
- formulas that are given in the true ratios of atoms (molecular formulas; C₆H₁₂O₆)
- substances that may exist in any state of matter at room temperature (solid, liquid, or gas)
- compounds that melt at low temperatures
- substances that are nonconductors of electricity

METALLIC

Characteristics of metallic substances usually include:

- substances that are metals
- a “sea” of mobile or delocalized electrons surrounding a positively charged metal center
- an attraction between metal ions and surrounding electrons
- formulas written as a neutral atom (Mg, Pb)
- solids with a crystalline structure at room temperature
- a range of melting points—usually depending on the number of valence electrons
- substances that are excellent conductors of electricity since the electrons in the “sea” are free to move

Most chemical bonds are in fact somewhere between purely ionic and purely covalent.

DRAW THE DANG LEWIS STRUCTURE

when answering bonding multiple choice or free-response questions.