More Chemical Bonding

Reading:	Ch 10: section 1 - 8 Ch 9: section 4, 6, 10	Homework:	Chapter 10: .31, 33, 35*, 39*, 43, 47, 49* Chapter 9: 43, 45, 55*, 57, 75*, 77, 79

* = ‘important’ homework question

Molecular Geometry – VSEPR Theory

The shape of most molecules in 3D can be determined by applying the Valence Shell Electron Pair Repulsion (VSEPR) Theory to a Lewis structure of the respective molecule

Electron pairs in the valence shell of a *center* atom (as drawn in a Lewis structure) *repel* one another as they have the same *negative* charge

The 3-D shape of a molecule is directly correlated to how the valence electron pairs are arranged in (3-D) *in order to be as greatly separated from one another as possible.*

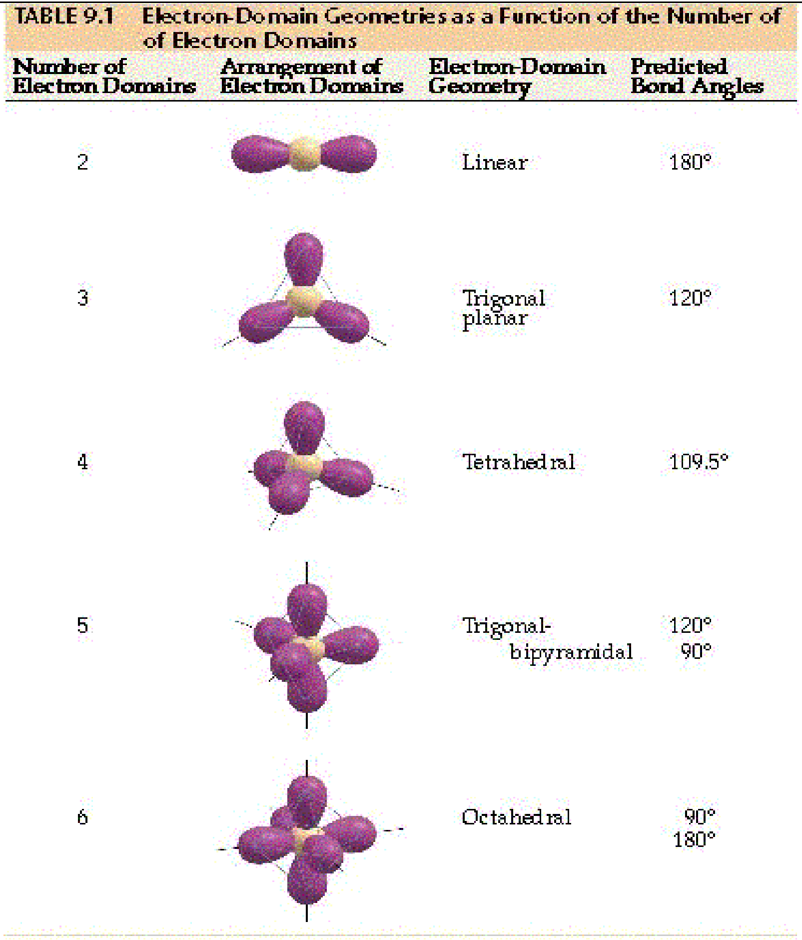
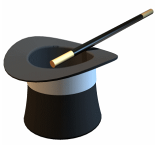


TABLE 9.1 Electron-Domain Geometries as a Function of the Number of of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles	**Hybridization (later)**	**Bond Types (later)**
2		Linear	180°		
3		Trigonal planar	120°		
4		Tetrahedral	109.5°		
5		Trigonal-bipyramidal	120° 90°		
6		Octahedral	90° 180°		



Consider each electron pair (*bonded* or *lone*) as 'clumps' of negative charge. These clumps adopt the above 3-D shapes in order to obey the VSEPR effect (see appendix and slide)

<u>Examples of AX_n structures</u>: Draw Lewis structures and determine the 3-D molecular shapes of carbon dioxide (CO_2), methanal (CH_2O) and the sulfate anion (SO_4^{2-}). Recall that you have previously completed Lewis structures for these species.

Molecular shape vs Electronic shape

The *molecular* (where the atoms are) and *electronic* (where the 'clumps' of electrons are) shapes of molecules are often different

Recall: The valence electron pairs' (bonded (X) *and* lone (E)) determine the overall *electronic shape* of the molecule

But: The positions of the molecule's atoms *relative to one another* (after the electronic shape has been fixed) determine the *molecular shape*

Examples: Draw Lewis structures and determine the 3-D molecular and electronic shapes of methane (CH_4), water (H_2O) and ammonia (NH_3)

The relationship between *molecular shape*, *electronic shape* and numbers of *bonding* (X) and/or *lone* (E) pairs of valence electrons. See appendix.

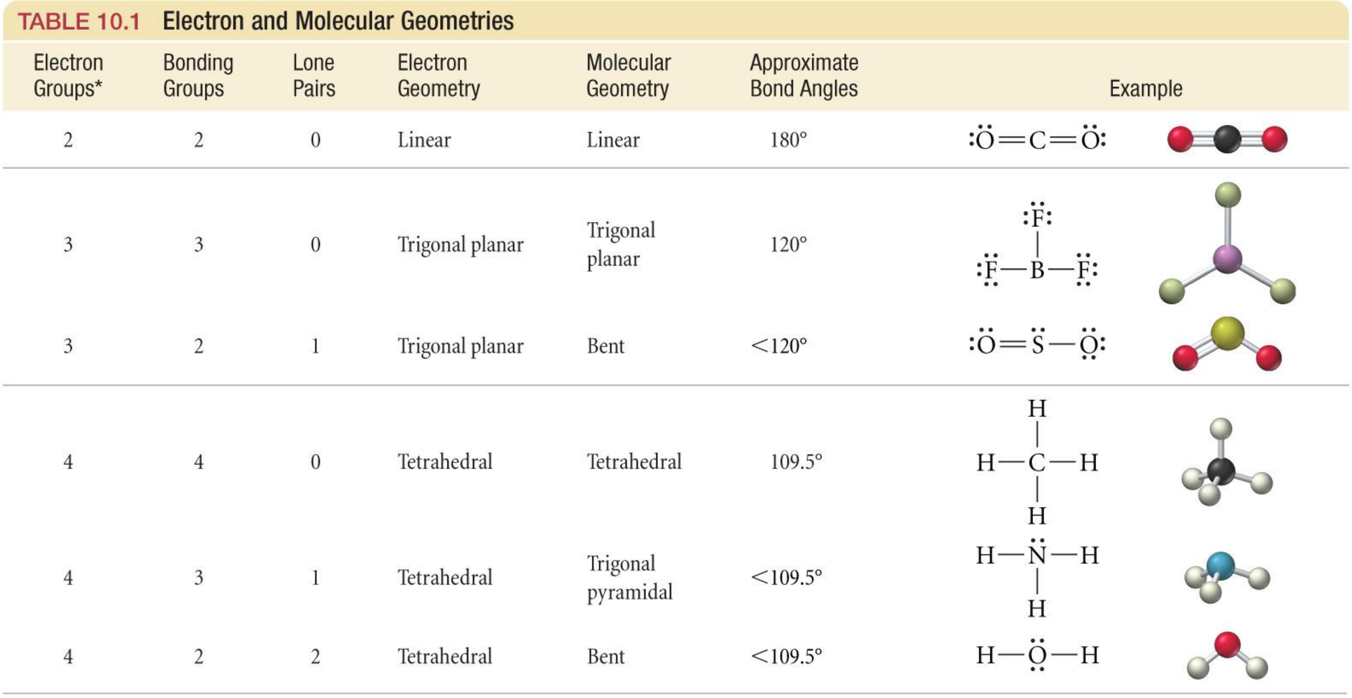
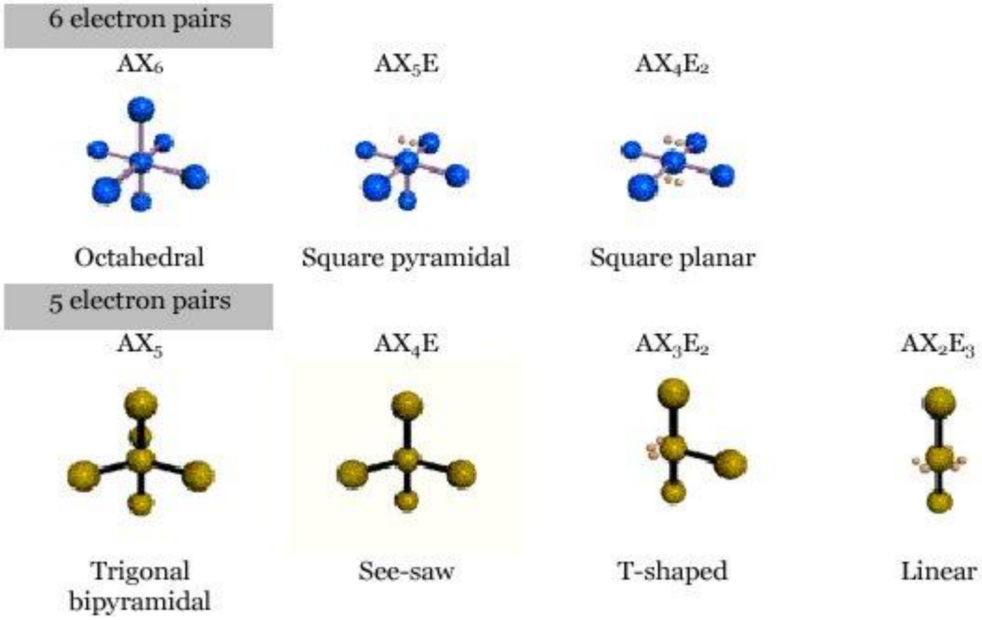


TABLE 10.1 Electron and Molecular Geometries

Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles	Example
2	2	0	Linear	Linear	180°	
3	3	0	Trigonal planar	Trigonal planar	120°	
3	2	1	Trigonal planar	Bent	<120°	
4	4	0	Tetrahedral	Tetrahedral	109.5°	
4	3	1	Tetrahedral	Trigonal pyramidal	<109.5°	
4	2	2	Tetrahedral	Bent	<109.5°	

Examples of 5 and 6 electron domain systems. See appendix and slides



Examples of AX_mE_n structures: Draw Lewis structures and determine the 3D molecular and electronic shapes of water XeF_4 and NO_2. Recall that you have previously completed Lewis structures for these species.

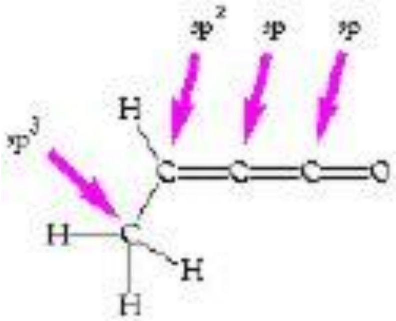
Question of the week: Draw Lewis structures for the Chlorate ion (ClO_4^-). Determine their respective molecular ***and*** electronic shapes using VSEPR theory. Assume a completely expanded octet (valencey = 7) for chlorine.

Hybridization and Molecular Orbital (MO) Theory

Task: Read sections 10.6 - 10.8 of your text. Make *brief* notes on hybridization and MO theory. Reference the below diagrams in your notes

Hybridization Overview

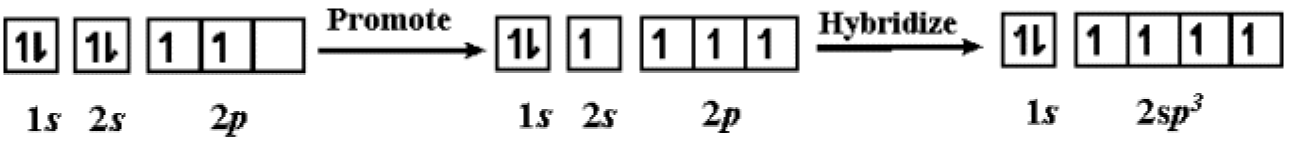
***The Organic Chemist's Trick*: An easy way to determine the hybridization of an atom is to simply count the number of *electron domains* ('clumps') it has - seen as *either* single, double, triple bonds and/or lone pairs. This relates directly to its respective orbital box diagram (hybridization).**

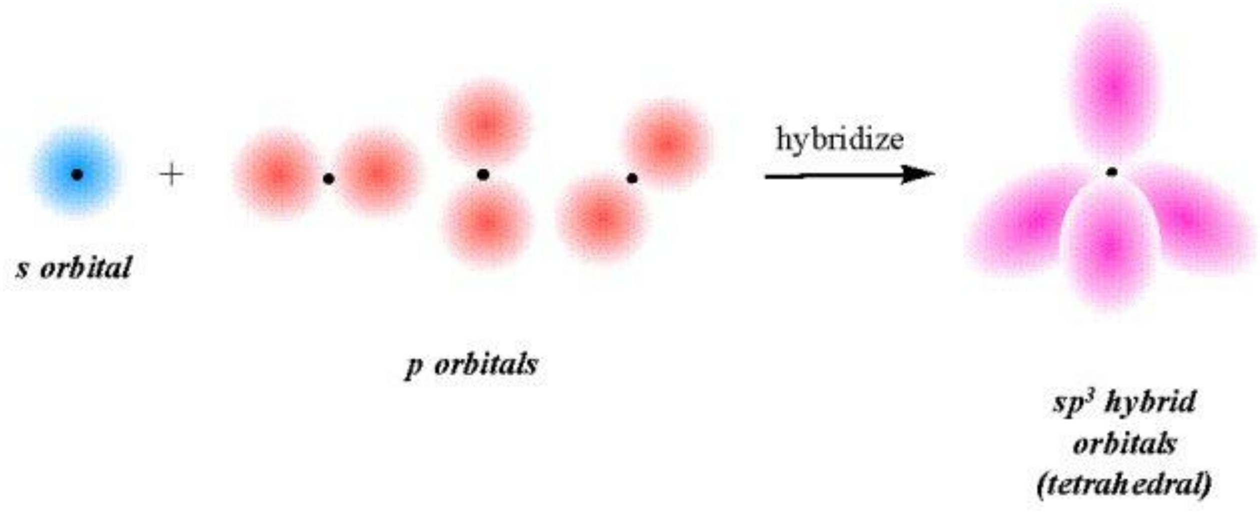
Hybridization (Carbon)	Number and Types of Bond (**σ , π**)	Example
sp^3	4 x σ bonds (or 3 x σ bonds + 1 l.p. for N) (4 single bonds)	
sp^2	3 x σ bonds, 1 x π bond (2 single bonds, 1 double bond)	
sp	2 x σ bonds, 2 x π bond (2 double, *or* 1 triple and 1 single bonds)	

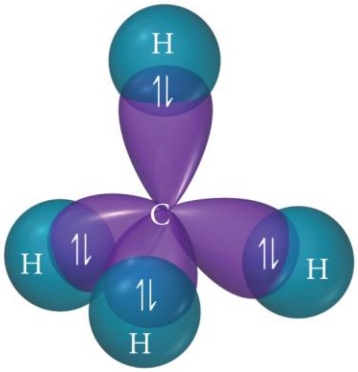
'EZ' Lewis	**Hybridization**	**#Domains**	**Shape**	**Orbital box Diagrams**	
				Ground	**Hybridized (bound)**
	sp^3	**4**	Td	X: ☐ ☐☐☐ 2s 2p	X: ☐☐☐☐ sp^3
	sp^2	**3**	Trig. Planar	X: ☐ ☐☐☐ 2s 2p	X: ☐☐☐ ☐ sp^2 p^z

***See appendix for sp^2 hybridization example**

Case Study: sp^3 hybridization





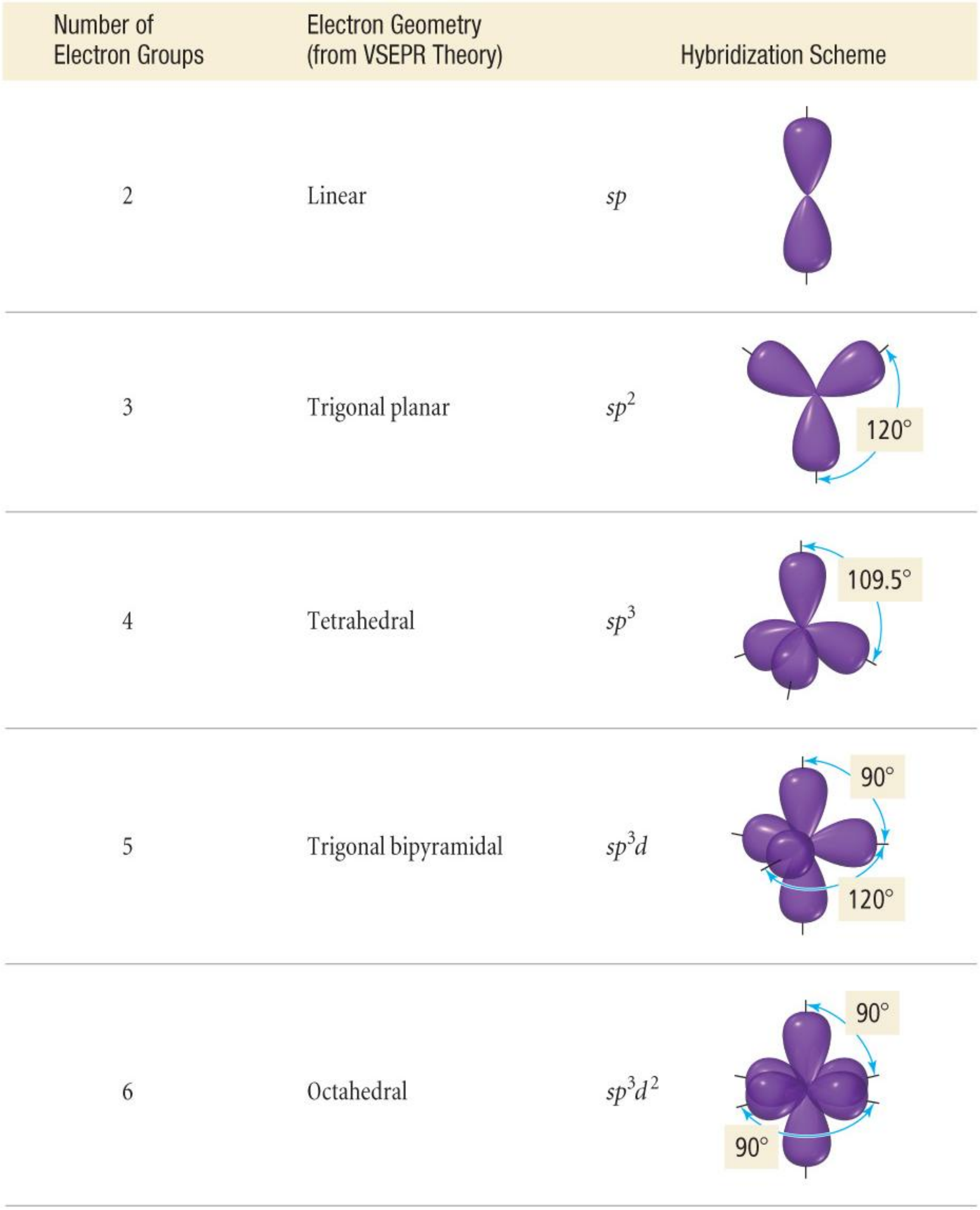


Methane (CH_4) possesses 4 identical 'single' bonds.

Hybridization center atom: sp^3

Bond Type(s): 4 x σ

Summary

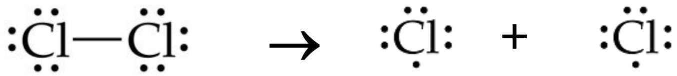


Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme
2	Linear	*sp*
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

<u>Use the above information to complete the table on page 1 of this packet!</u>

The Strength of Covalent Bonds (Bond Enthalpy)

Background: Enthalpy the *energy* (in kJ) required to break one *mole* of a specified type of bond. Units are kJ/mole. For Cl_2:



$\text{:}\underset{\cdot\cdot}{\ddot{\text{Cl}}}\text{—}\underset{\cdot\cdot}{\ddot{\text{Cl}}}\text{:} \rightarrow \text{:}\underset{\cdot}{\ddot{\text{Cl}}}\text{:} + \text{:}\underset{\cdot}{\ddot{\text{Cl}}}\text{:}$; ΔH = 242 kJ/mol

i.e. it takes 242 kJ of energy to break one mole of Cl-Cl bonds (see appendix)

Question: Which do you think are the stronger bonds? Why?

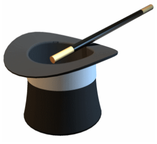
1. C-C (carbon–carbon single bond) *or* C=C (carbon–carbon double bond)

2. C-O (carbon–oxygen single bond) *or* C-C (carbon–carbon single bond)

Task: Work out the bond enthalpy for the C-H bond in methane (CH_4), given the following *thermochemical equation*:

$$CH_4(g) \rightarrow C(g) + 4\,H(g)\ ;\ \Delta H = 1660\ kJ/mol$$

Hint: Draw a Lewis style bond breaking equation.



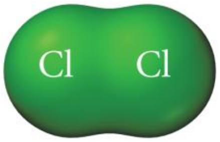
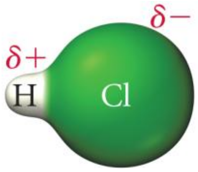
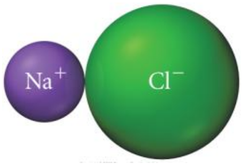
Recall the Thermochemistry packet – the DIFFERENCE in bond strengths (enthalpies) between reactants and products is ΔH for that process. If the bonds formed in the products are 'stronger' than those in the reactants the process is exothermic, i.e a –ve sign for ΔH.

Remember: *A thermochemical equation* assumes *the same # moles of actual reactant and product* are involved in the chemical process *as indicated by their respective stoichiometric constants* (balancing numbers)

Task: Use the bond enthalpy data in the appendix to determine **ΔH** for the combustion of methane

Bond Enthalpy Trends

Describe the type of bonding in Cl_2, HCl and NaCl. Use this information to complete the following table:

Compound	Cl-Cl	H-Cl	$[Na]^+[Cl]^-$
Model			
Bonding Type			
Bond Enthalpy (kJ/mole)	243	431	787*

Discussion: What trend do you notice with regard to the type of bonding and bond enthalpy?

Bond Length / Strength Trends: Complete the following table using the bond length and bond enthalpy tables (see appendix). **What correlation do you notice regarding the length and strength of chemical bonds?**

Bond Coordinate	C-C	C-O	C=C	C=O
Bond Length (pm)				
Bond Enthalpy (kJ/mole)				

Notes:

Typical Question: Arrange the following bond coordinates in order of *increasing bond enthalpy* and *increasing bond length*

1. C-N, C≡N, C=N

Bond Enthalpy:

Bond Length:

2. C-C, C-O, C-F

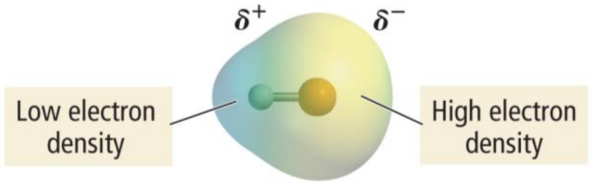
Bond Enthalpy:

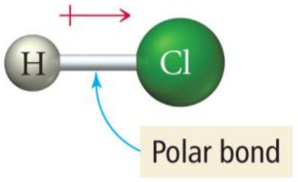
Bond Length:

Molecular Shape and Polarity

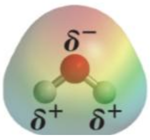
Discussion: Would you expect the following molecules to have *net dipole moments*?

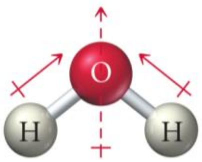
HCl





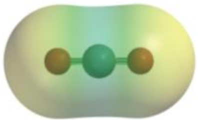
H_2O

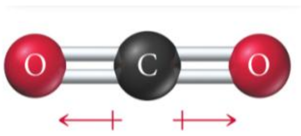




Net dipole moment

CO_2



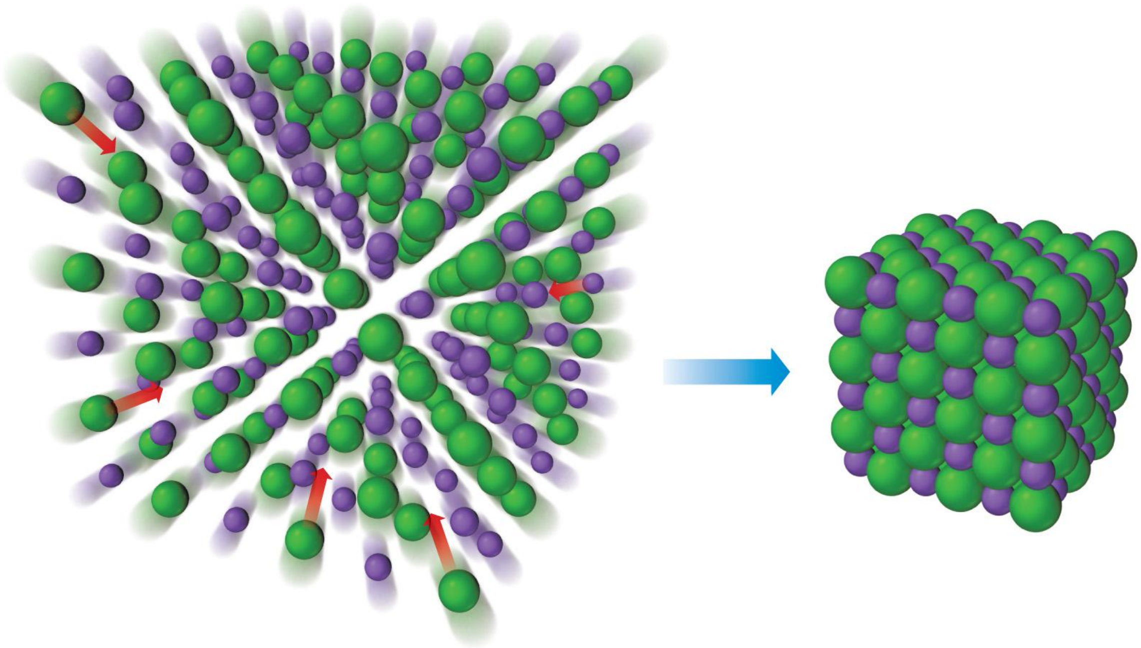


No net dipole moment

The Strength of Ionic Bonds (Lattice Energy)

Definition: The energy associated with forming a crystalline lattice from gaseous ions (see 9.4 and figure immediately below)

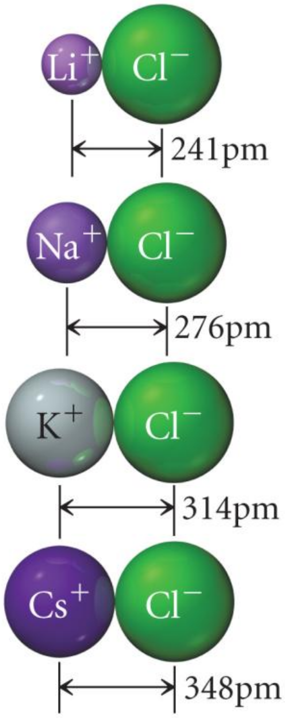
Lattice Energy of an Ionic Compound



$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s)$ $\Delta H^{\circ} = \text{lattice energy}$

Since ionic bonds are electrostatic in nature and, by definition, omni-directional, *all* the respective +ve and –ve charges in the lattice will be attracted to one another. *Think of the lattice energy as the average of this force for a single pair of ions in the lattice*

Trends in Lattice Energy: Ion Size

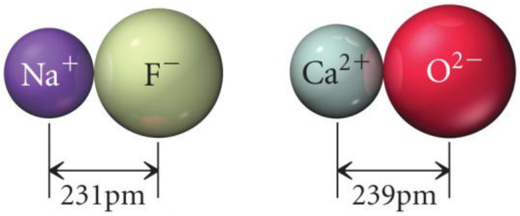


Discussion: Using the accompanying figure as a guide, describe how relative size differences among ion pairs effect bond distance. How will this effect bond strength (lattice energy)?

*Check the lattice energy values on page 371of Tro

Trends in Lattice Energy: Ion Charge

Discussion: Describe how relative charge differences among the respective ion pairs, see figure below, effect bond strength (lattice energy). How would you expect the magnitude of this effect to compare with the above ion size trend?



*Check the lattice energy values on page 366 of Tro (***charge beats size!!***)

“Lewis”

The following question was taken from your 3rd practice midterm (you can now answer the second part also):

Question 2a (20 points) Draw Lewis structure(s) for the PO_4^{3-} ion, *include all possible resonance forms* ***and*** *include formal charge labels on one of your structures*. Assume a completely expanded octet for phosphorus.

Question 2b (5 points) Use VSEPR theory to determine the electronic and molecular geometry of the phosphate ion:

Electronic geometry:

Molecular geometry:

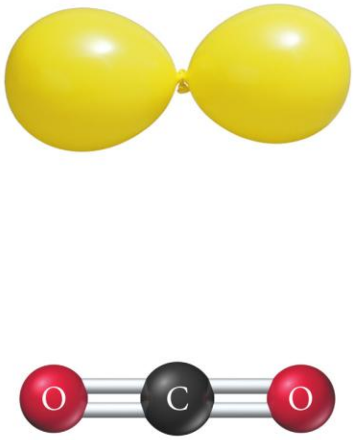
"Trends"

The following question was taken from your 3rd practice midterm:

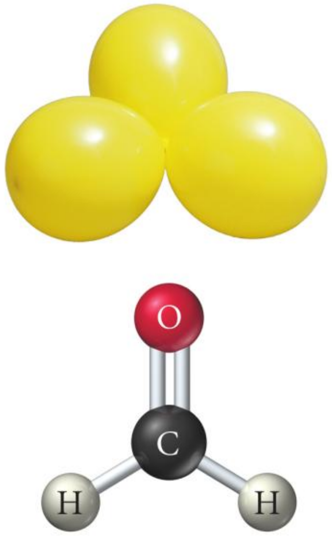
State whether the following bonds are considered to be covalent, polar covalent or ionic:

Bond coordinate	Type of bond (covalent, polar covalent or ionic)
O=O	
O-H	
Na-Cl	
K-F	
S-F	

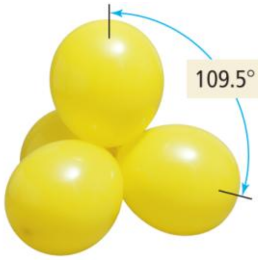
Appendix



(a) Linear geometry

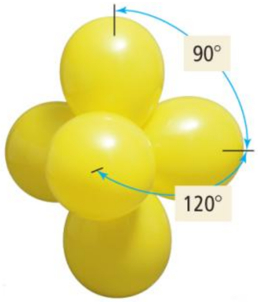


(b) Trigonal planar geometry



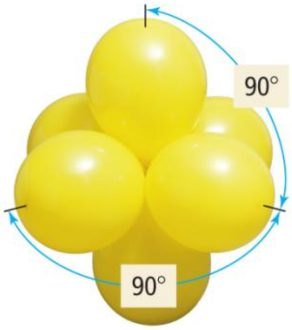
Tetrahedral geometry

Tetrahedron



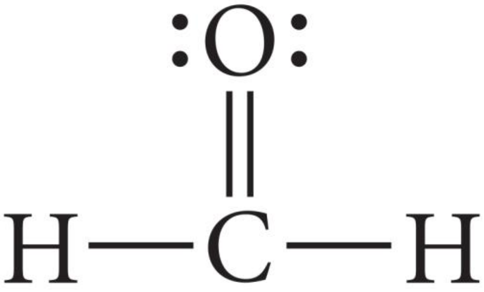
Trigonal bipyramidal geometry

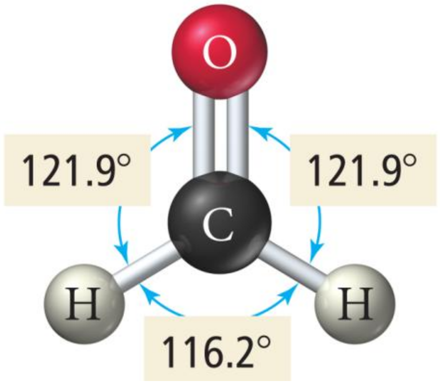
Trigonal bipyramid

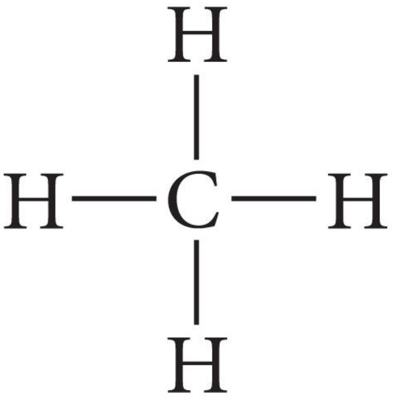


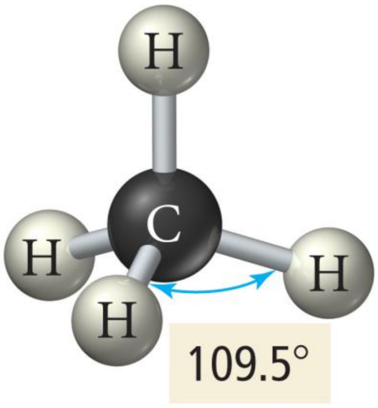
Octahedral geometry

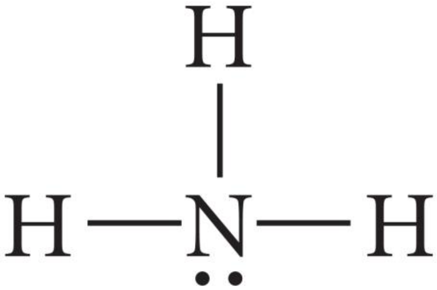
Octahedron

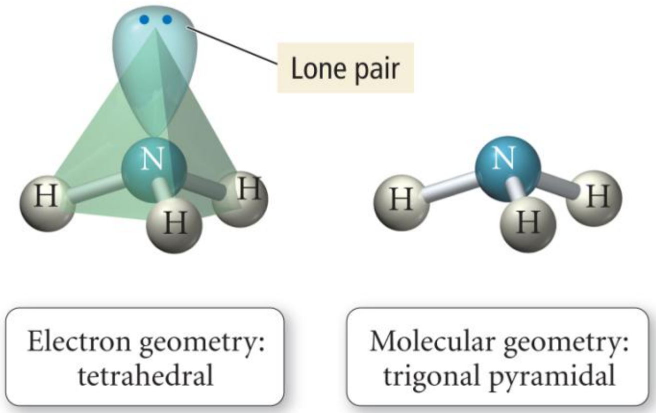


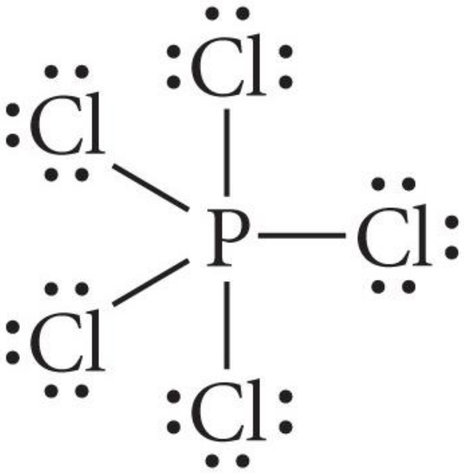

O
121.9°
121.9°
C
H
H
116.2°

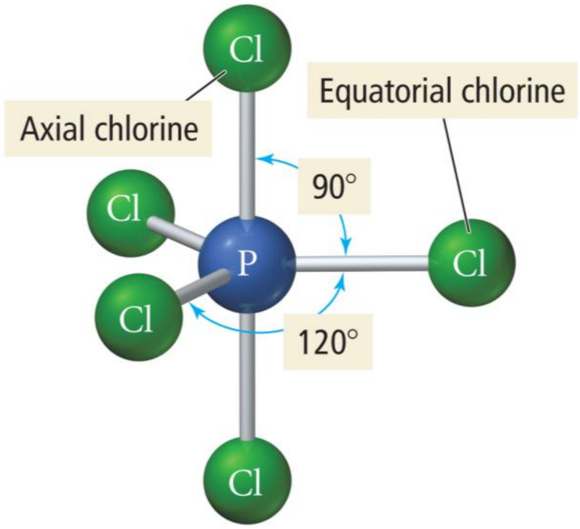


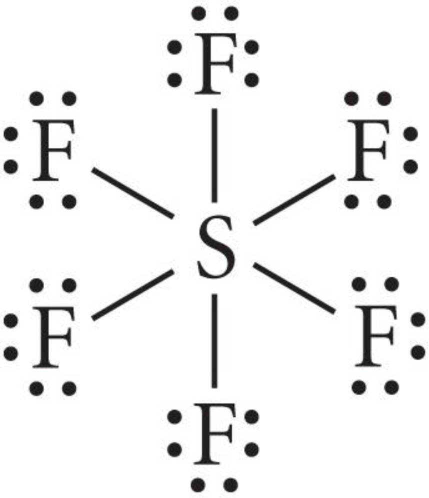

H
C
H
H
H
109.5°

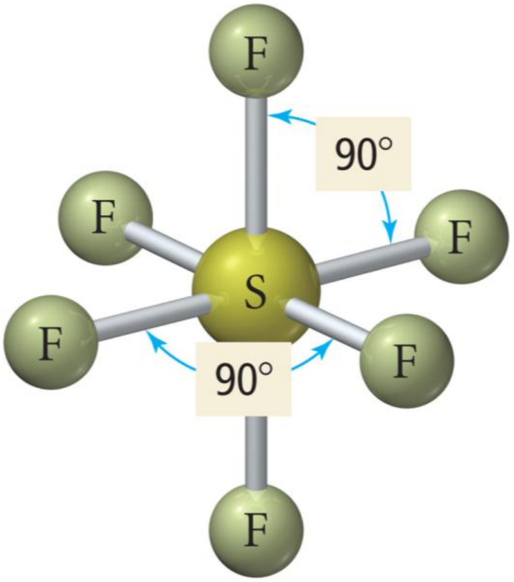



Lone pair
N
H
H
H
N
H
H
H
Electron geometry: tetrahedral
Molecular geometry: trigonal pyramidal

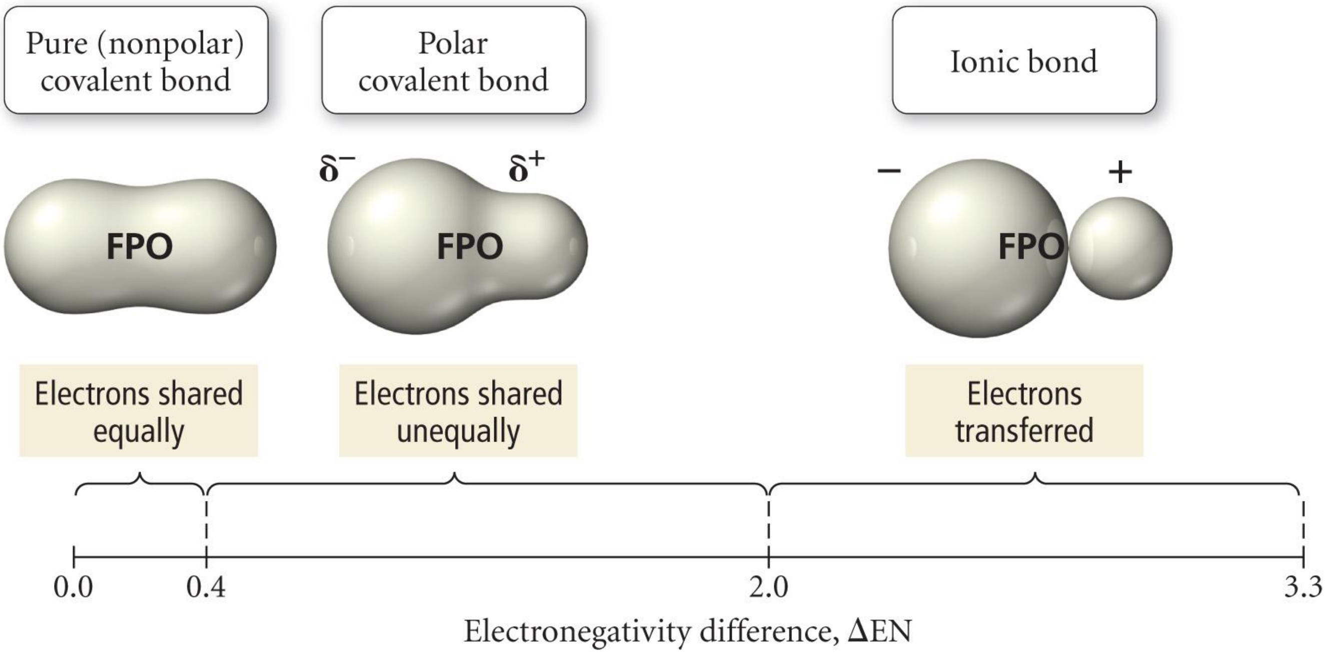

Cl
Cl
P
Cl
Cl
Cl
Cl


Cl
Axial chlorine
Equatorial chlorine
90°
Cl
P
Cl
Cl
120°
Cl


F
F
F
S
F
F
F


F
90°
F
F
S
F
F
90°
F

The Continuum of Bond Types



Some Average Single- and Multiple-Bond Energies*

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	414	389	464	569	293	318	339	431	368	297
C		347	293	351	439	289	264	259	330	276	238
N			159	201	272		209		201	243?	
O				138	184	368	351		205		201
F					159	540	490	285	255	197?	
Si						176	213	226	360	289	
P							213	230	331	272	213
S								213	251	213	
Cl									243	218	209
Br										192	180
I											151

Multiple Bonds

N=N	418	C=C	611
N≡N	946	C≡C	837
N=O	590	C=O (in O=C=O)	803
C≡N	891	C=O (as in $H_2C=O$)	745
O=O (in O_2)	498	C≡O	1075

*In kilojoules per mole.

Some Approximate Single and Multiple Bond Lengths*

Single Bond Lengths

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	74	110	98	94	92	145	138	132	127	142	161
C		154	147	143	141	194	187	181	176	191	210
N			140	136	134	187	180	174	169	184	203
O				132	130	183	176	170	165	180	199
F					128	181	174	168	163	178	197
Si						234	227	221	216	231	250
P							220	214	209	224	243
S								208	203	218	237
Cl									200	213	232
Br										228	247
I											266

Multiple Bond Lengths

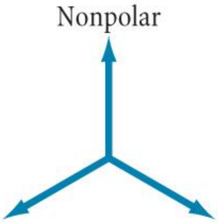
C=C	134	C≡C	121
C=N	127	C≡N	115
C=O	122	C≡O	113
N=O	115	N≡O	108

*In picometers (pm); 1 pm = 10^{-12} m.

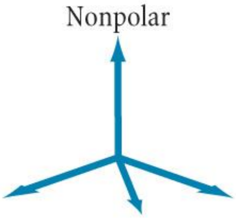
TABLE 10.2 Common Cases of Adding Dipole Moments to Determine whether a Molecule Is Polar

The dipole moments of two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.

The dipole moments of two polar bonds with an angle of less than 180° between them will not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.



The dipole moments of three identical polar bonds at 120° from each other will cancel. The molecule is nonpolar.



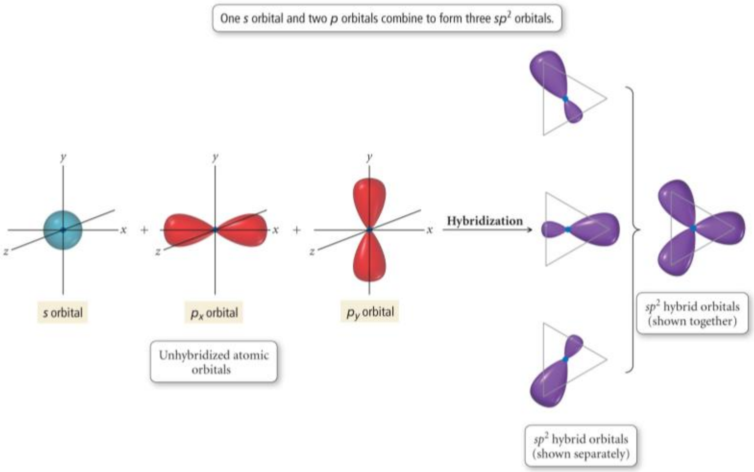
The dipole moments of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) will cancel. The molecule is nonpolar.

The dipole moments of three polar bonds in a trigonal pyramidal arrangement (109.5° from each other) will not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.

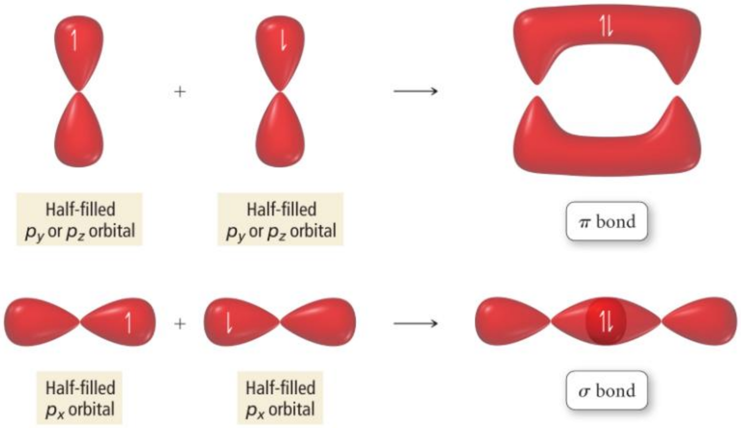
Note: In all cases where the dipoles of two or more polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.

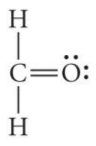
σ and π bonds (sp^2 hybridization) – CH_2O

3 x sp^2 hybridized orbitals → 3 x σ bonds

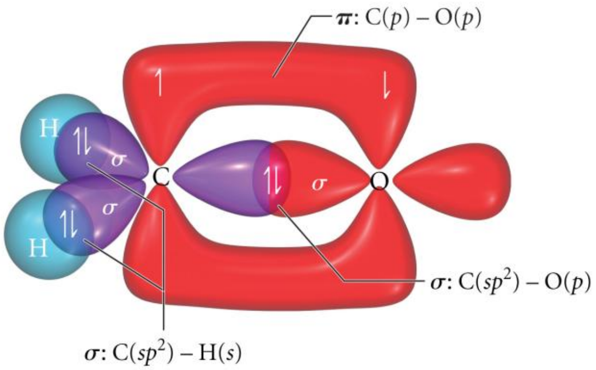


1 x p orbital → 1 x π bond





Lewis structure



Valence bond model