Chemical Bonding

Chemistry, Zumdahl & Zumdahl – Chapter 8

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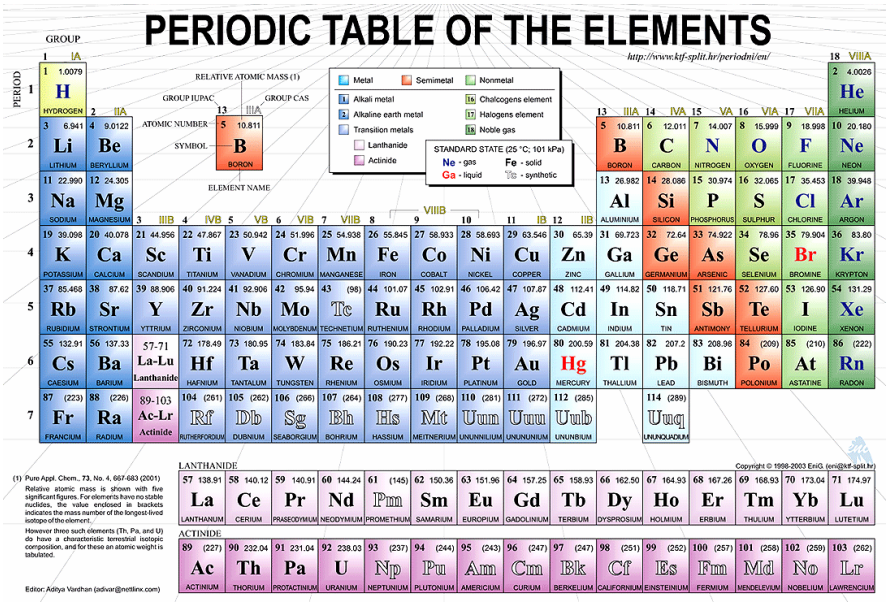
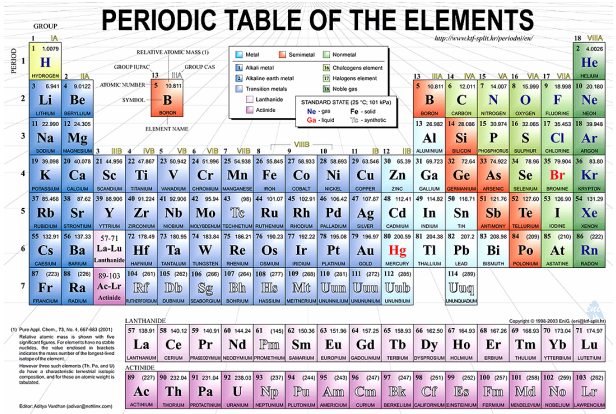
June 28, 2011 American University of Beirut

Periodic Table of Elements



Types of Chemical Bonds

- Types of Bonding:
  - Metal to non-metal (Ionic bonding)
  - Non-metal to non-metal (Covalent bonding)
  - Metal to metal (Metallic bonding)



Ionic Bonding

Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons. An **ionic compound** results when a metal reacts with a nonmetal.

The energy of interaction between a pair of ions can be calculated using **Coulomb's law**.

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

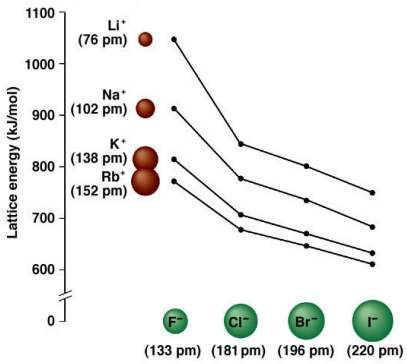
r is the distance between the ion centers in nm, and Q_1 and Q_2 are the numerical ion charges.

Ionic Bonding

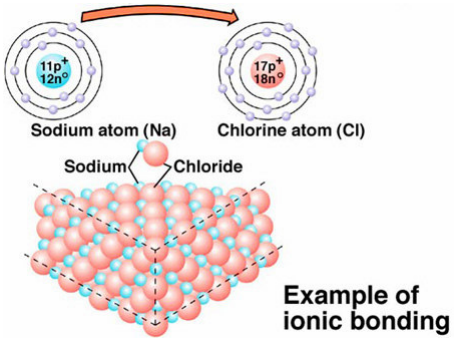
Lattice energy ($\Delta H^0_{Lattice}$) is the energy required to completely separate one mole of a solid ionic compound into gaseous ions.

Therefore, *Lattice energy* ($\Delta H^0_{Lattice}$) increases as Charge of the cation and anion increases and/or as radii of cation and anion decreases.

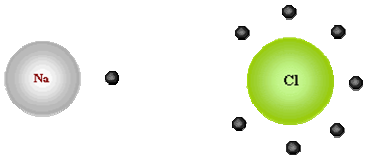
$$\Delta H^0_{Lattice} \propto \frac{\text{Cation charge x Anion charge}}{r_{cation} + r_{anion}}$$

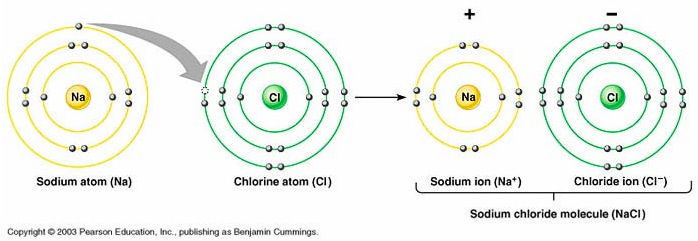


Ionic Bonding



Example of ionic bonding





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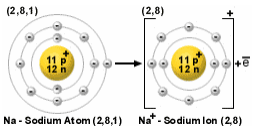
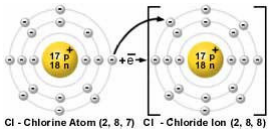
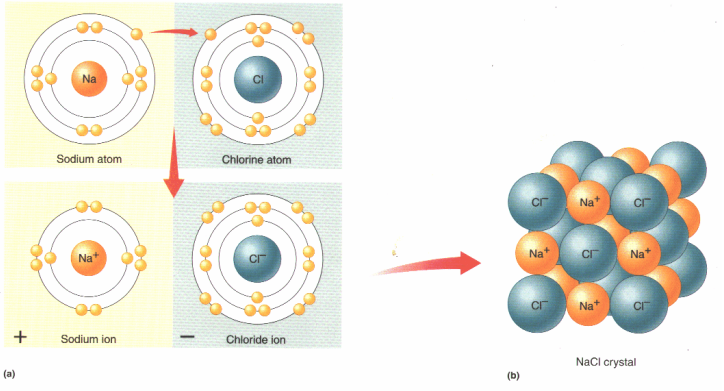
Ionic Bonding

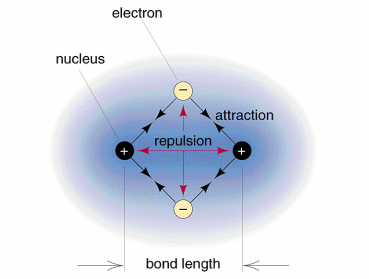


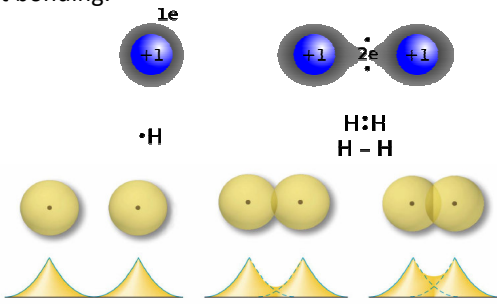




Covalent Bonding

A covalent bond is a form of chemical bonding that is characterized by the sharing of pairs of electrons between atoms, and other covalent bonds. In short, the stable balance of attractive and repulsive forces between atoms when they share electrons is known as covalent bonding.



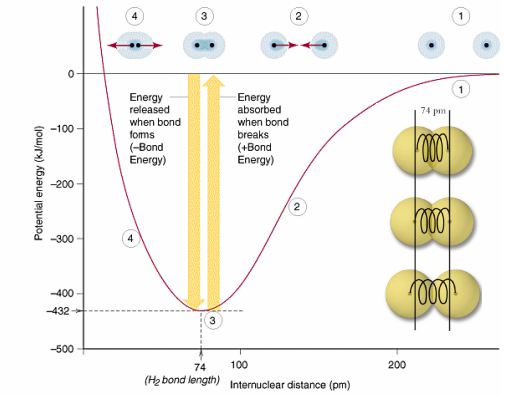


As two hydrogen atoms approach each other, constructive interference between the two valence orbitals leads to a new wave, a new orbital containing both electrons. This new orbital is called a *covalent bond.*

The energy of interaction between the atoms changes with distance between the nucleii.

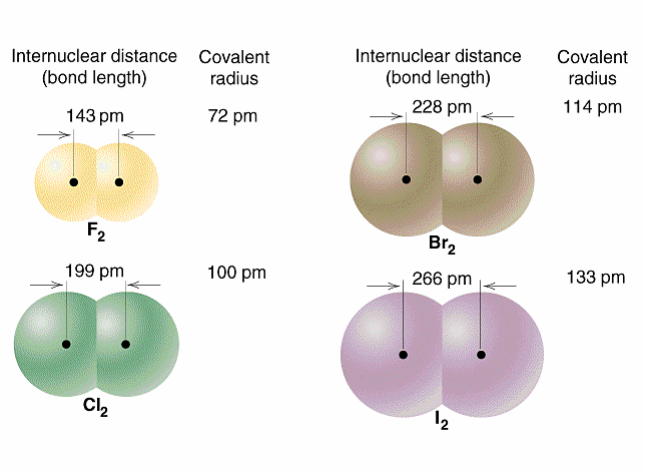
There is an optimal distance for the chemical bond which is where this energy is at a minimum.

The minimum energy with respect to the energy of dissociated fragments (r -> infinity) is called the **bond energy**.



AUB
Covalent Bonding

The bond between two atoms acts like a spring. The average distance between the atoms is the **bond length**.



Ionic Bonding vs. Covalent Bonding

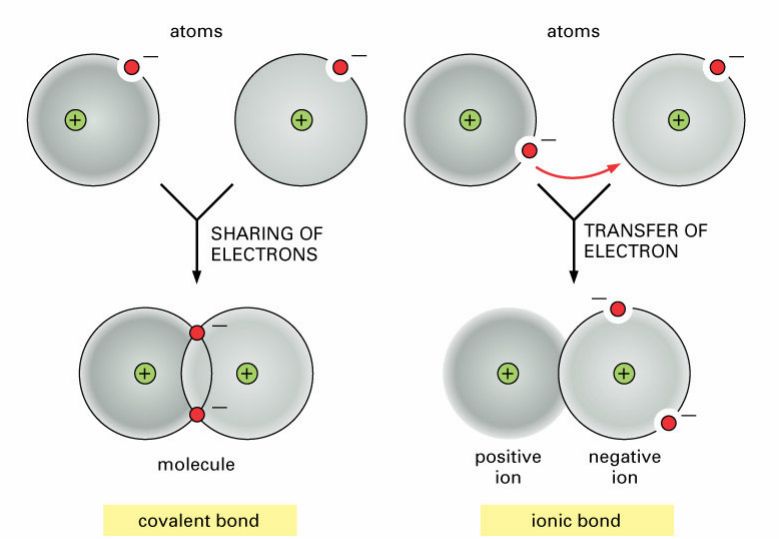
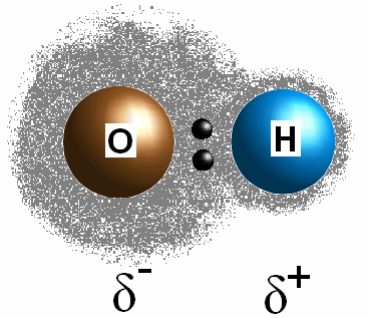


Figure 2.6 Essential Cell Biology, 2/e. (© 2004 Garland Science)

Electronegativity

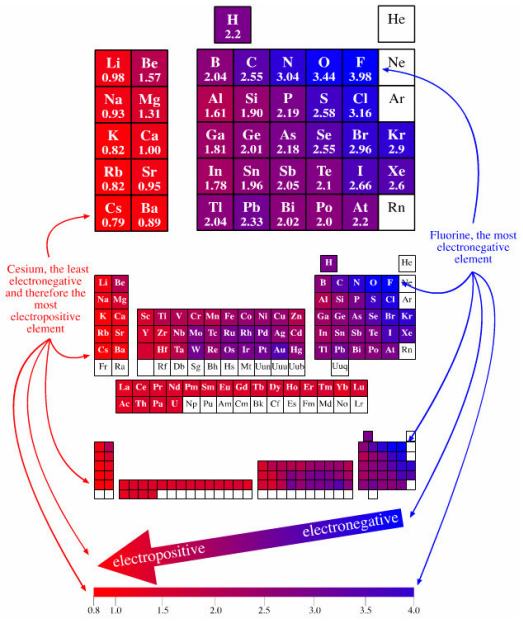
The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity**.

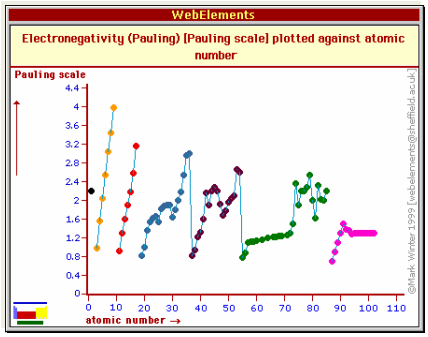
Electronegativity is the ability of atom in a molecule to attract shared electrons to itself.



Linus Pauling
(1901 – 1994)
Nobel Prize in Chemistry 1955
Nobel Peace Prize 1962

Electronegativity & Periodicity





Electronegativity & Bond Polarity

Pauling reasoned that the dissociation energy of a purely covalent bond A-B $\{D_{(A-B)}\}$should be the mean of the dissociation energies for the homonuclear bonds A-A$\{D_{(A-A)}\}$, and B-B $\{D_{(B-B)}\}$:

$$D_{(A-B),theory} = \tfrac{1}{2} (D_{(A-A)} + D_{(B-B)})$$

Any additional energy must be caused by electrostatic attraction between A and B (attributed to ionic character in a bond). If $\Delta'_{(A-B)}$ is the *ionic resonance energy* in kJ/mol ($\Delta_{(A-B)}$ is in eV) then:

$$\Delta'_{(A-B)} = D_{(A-B),experimental} - D_{(A-B),theory}$$

The ionic character, Δ', must be related to the difference in the electronegativities of A and B. Pauling calculated this difference as follows:

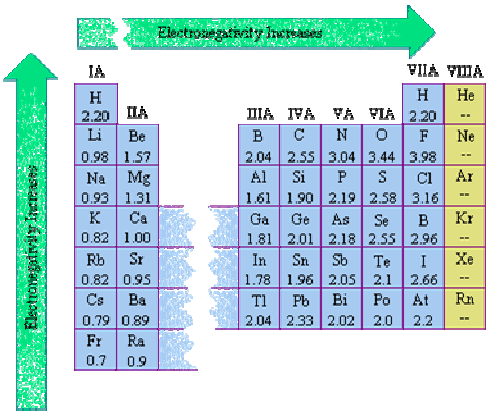
$$X_A - X_B = 0.102\,(\Delta'_{(A\text{-}B)})^{½}$$

Electronegativities of A & B

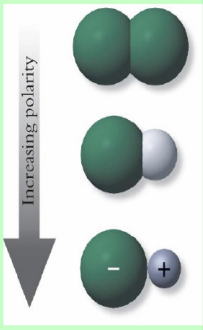
$X_A - X_B < 0.5$ → Covalent or Slightly Polar

$0.5 < X_A - X_B < 2$ → Polar

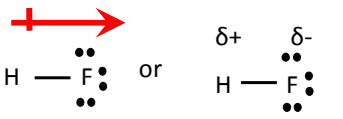
$X_A - X_B > 2$ → Ionic

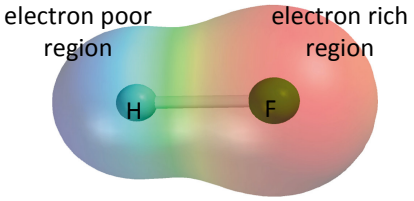


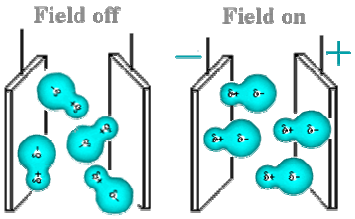
Compound	Δχ	Bond Type
Cl_2	3.5 - 3.5 = 0	Nonpolar
IBr	2.8 - 2.5 = 0.3	Slightly polar
NO	3.5 - 3.0 = 0.5	Slightly polar
CO	3.5 - 2.5 = 1.0	Polar
HCl	3.5 - 2.1 = 1.4	Polar
HF	4.0 - 2.1 = 1.9	Highly polar
KI	2.5 - 0.9 = 1.6	Ionic
CaO	3.5 - 1.0 = 2.5	Ionic
LiF	4.0 - 1.0 = 3.0	Ionic

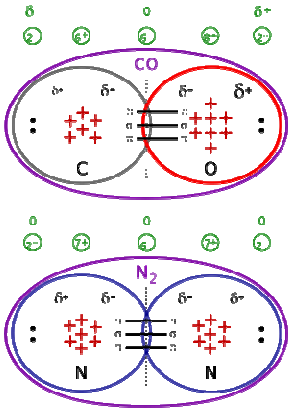


Electronegativity & Bond Polarity









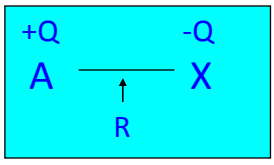
A molecule such as HF that has a center of positive charge and a center of negative charge is said to be **dipolar** or have a **dipole moment**.

Dipole Moments and Ionic Character

It is useful to have some measure of ionic character when considering a series of molecules such as

H_2 (covalent) HF (polar covalent) K^+F^- (ionic)

The *dipole moment* of a molecule (μ) can be determined by spectroscopic measurements. For a diatomic molecule AX:



$\mu = QR$
(R = distance in m)

the SI unit for μ is the Coulomb meter (Cm).

the Debye is commonly used: $1\ D = 3.336 \times 10^{-30}$ Cm.

Dipole Moments and Ionic Character

Consider the polar covalent molecule HF. If HF were totally ionic (H^+F^-), we would expect:

μ (Calc) = (1 electronic charge) (1 HF distance)

= $(1.60 \times 10^{-19}$ C) (9.17×10^{-11})

= 1.47×10^{-29} Cm = 4.40 D

However the measured μ for HF is only 1.83 D !!

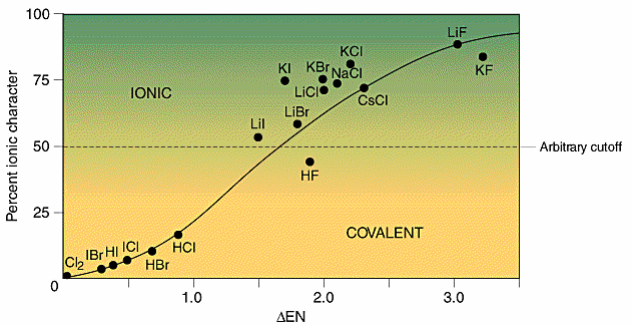
Using this result we can express the percentage ionic character in HF as:

δ^+ H-F δ^- $\qquad \delta = \frac{1.83}{4.40} = 0.42\ (42\%)$

Dipole Moments and Ionic Character

Molecule	μ(D)	% ionic character
H_2	0	0
CO	0.112	2
HCl	1.109	18
NaCl	9.001	79
NaF	8.156	88

We now have two measures of ionic character:
-the *electronegativity*
-the *dipole moment*



Dipole Moments and Ionic Character

Place the following bonds in increasing ionic character (decreasing covalent character):

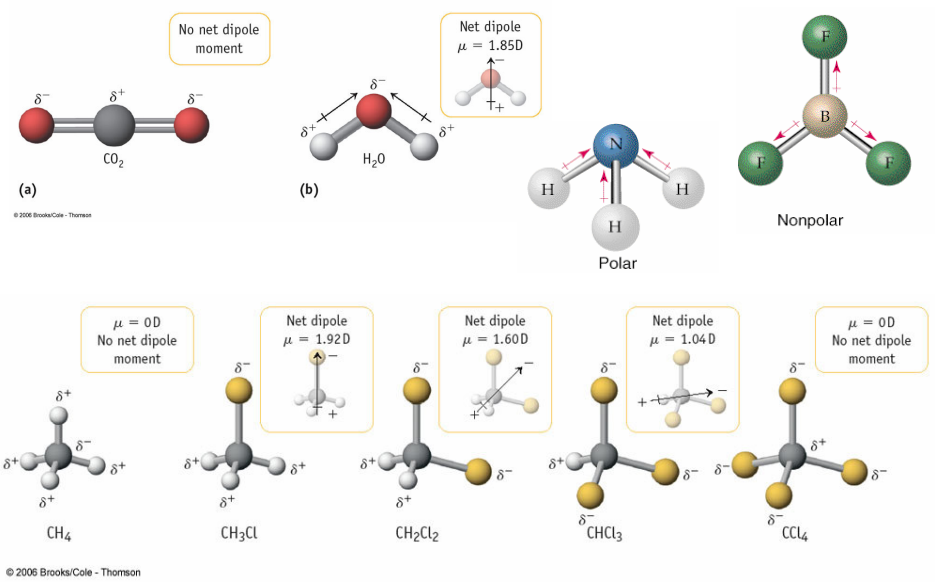
O—H, P—N, As—O, C—H, C—Br, C—P

EN of O = 3.5 and of H = 2.1: ΔEN = 1.4
EN of C = 2.5 and of P = 2.1 : ΔEN = 0.4
EN of P = 2.1 and of N = 3.0: ΔEN = 0.9
EN of C = 2.5 and of Br = 2.8: ΔEN = 0.3
EN of As = 2.0 and of O = 3.5: ΔEN = 1.5

C—Br < C—P < P—N< O—H < C—H < As—O

ΔEN: 0.3 < 0.4 < 0.9 < 1.4 < 1.4 < 1.5

Molecular Shape & Polarity



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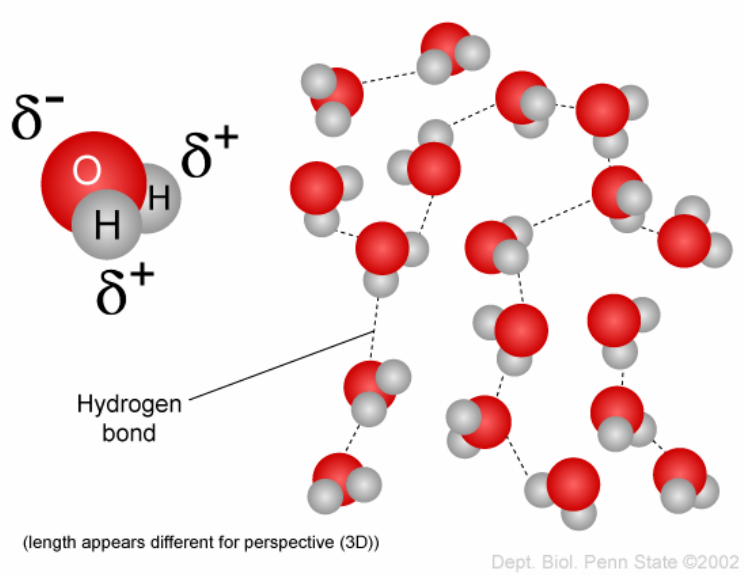
Water Molecules

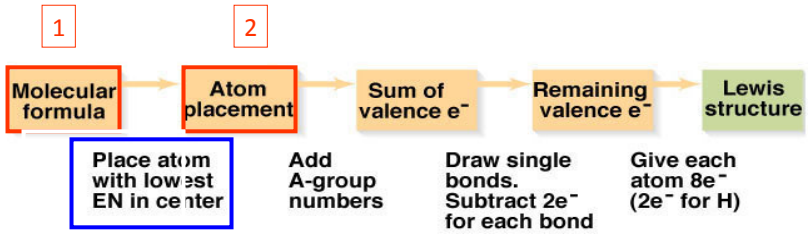


Lewis Structures

The Octet Rule: When atoms bond, they lose, gain or share electrons to attain a filled outer shell of 8 (or 2) electrons.

1) Only the *valence* electrons appear in a Lewis structure.
2) The line joining two atoms represents a pair of electrons shared between two atoms.
   - single bond - two shared electrons, one line
   - double bond - four shared electrons, two lines
   - triple bond - six shared electrons, three lines
3) Dots placed next to an atom represent non-bonding electrons.

Lewis Structures



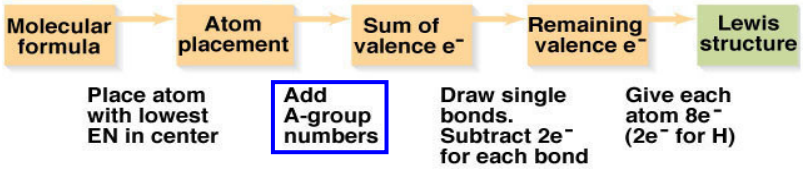
Example: Formula NF_3

EN (F) > EN (N), N is central atom

F

F N F

Lewis Structures

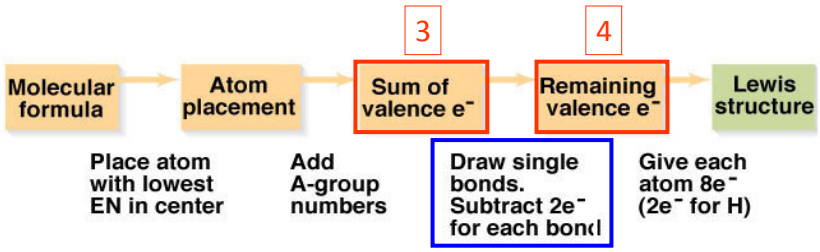


F

F N F

PERIODIC TABLE ELEMENTS 1–20

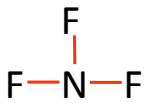
HYDROGEN 1 H·							HELIUM 2 He·
LITHIUM 3 Li·	BERRYLLIUM 4 ·Be·	BORON 5 ·B·	CARBON 6 ·C·	NITROGEN 7 ·N:	OXYGEN 8 ·O:	FLOURINE 9 :F:	NEON 10 :Ne:
SODIUM 11 Na·	MAGNESIUM 12 Mg·	ALUMINUM 13 ·Al·	SILICON 14 ·Si·	PHOSPHORUS 15 ·P:	SULFUR 16 ·S:	CHLORINE 17 :Cl:	ARGON 18 :Ar:
POTASSIUM 19 K·	CALCIUM 20 Ca·						



1 x N (Gp 5) = 5 e

3 x F (Gp 7) = 21 e

26 e



26 e - 6 e = 20 e

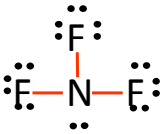
Molecular formula → Atom placement → Sum of valence e⁻ → Remaining valence e⁻ → Lewis structure

Place atom with lowest EN in center

Add A-group numbers

Draw single bonds. Subtract 2e⁻ for each bond

Give each atom 8e⁻ (2e⁻ for H)



Does each atom have full octet?

AUB Lewis Structures

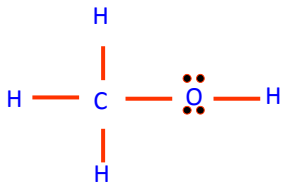
Molecules with more than one central atom

Methanol, CH_4O or CH_3OH

- H can only have one bond, C often has 4 and O 2, therefore:

1 x C (Gp 4) = 4 e
1 x O (Gp 6) = 6 e
4 x H (Gp 1) = 4 e
14 e

14 e - 10 e = 4 e remaining



CHECK:
Octet on O and C,
2 e on each H

Lewis Structures

Molecules with multiple bonds

Nitrogen gas, N_2

2 x N (Gp 5) = 10 e

10 e

10 e - 2 e = 8 e remaining

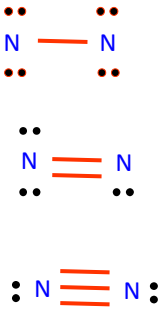
CHECK: No Octet on either N.

Change 1 lone pair to a bond

CHECK: Octet on only one N.

Change 1 lone pair to a bond

CHECK: Octet on both N's. OK



The Covalent Bonding Model

Relationship between Bond Order, Length & Energy

Bond	Order	Length (pm)	Av BE (kJ/mol)
C — O	1	143	358
C = O	2	123	745
C ≡ O	3	113	1070
C — C	1	154	347
C = C	2	134	614
C ≡ C	3	121	839
N — N	1	146	160
N = N	2	122	418
N ≡ N	3	110	945

Exceptions to the Octet Rule

- Be compounds ⇒ BeH_2, $BeCl_2$

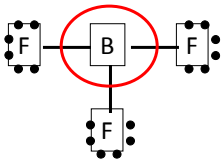
BeH_2

Be – $2e^-$
2H – 2x$1e^-$
$4e^-$

- Boron and Al compounds ⇒ BF_3, $AlCl_3$, BCl_3

BF_3

B – $3e^-$
3F – 3x$7e^-$
$24e^-$

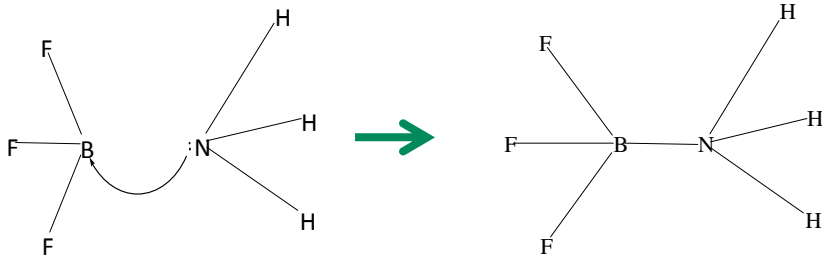


3 single bonds (3x2) = 6
9 lone pairs (9x2) = 18
Total = 24

Exceptions to the Octet Rule

BF_3 is stable Þ The B central atom has a tendency to pick up an unshared e- pair from another compound

$$BF_3 + NH_3 \rightarrow BF_3NH_3$$

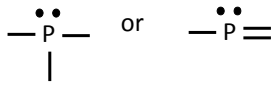


the B-N bond is an example of a coordinate covalent bond, or a "dative" bond → i.e. a bond in which one of the atoms donates both bonding electrons.

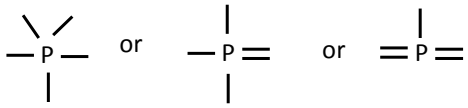
Exceptions to the Octet Rule

"An exception to the Octet Rule occurs for Expanded valence shells…."

- Occurs because of atoms with vacant d-orbitals can expand their valence shells to form > 4 bonds (lowers energy), i.e for non-metals from P onwards.
- P is $3s^2\ 3p^3\ 3d^0$
- If we treat it just as $3s^2\ 3p^3$, then must apply Octet rule, ie.

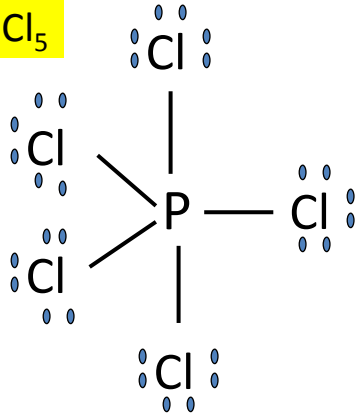


- But if we consider it as $3s^2\ 3p^3\ 3d^0$, then there is room to accommodate extra bonding pairs, ie. Up to 5 bonding pairs



Exceptions to the Octet Rule

PCl_5



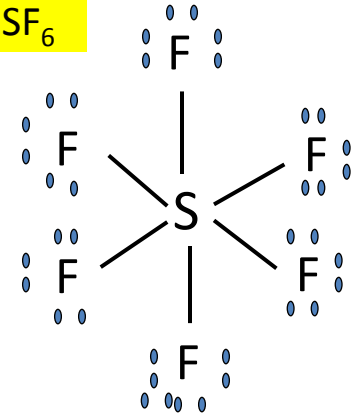
P = 5

Cl = 5 x 7

40 valence electrons

10 ve on P

SF_6



S = 6

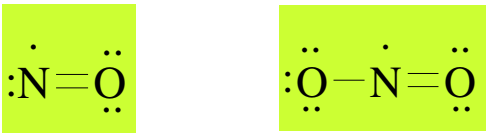
F = 6 x 7

48 valence electrons

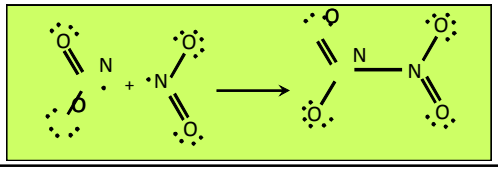
12 ve on S

Odd e- molecules (Free radicals)

- These molecules have uneven numbers of electrons therefore no way that they can form octets.
- Examples: NO and NO_2. These species have an odd number of electrons.



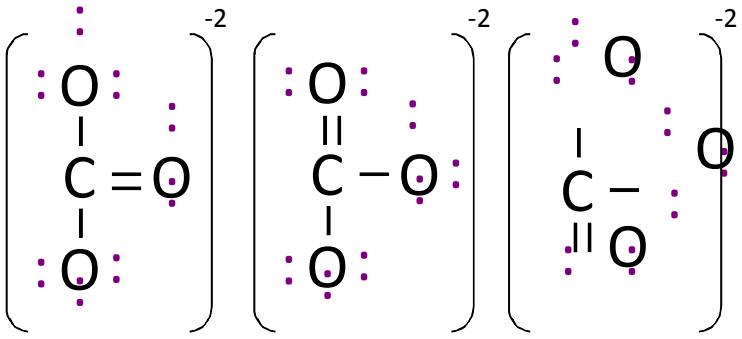
- NO_2 (present in smog from photochemical reaction of NO with O_3).
- Radicals react to form dimeric N_2O_4 obeys Octet rule.



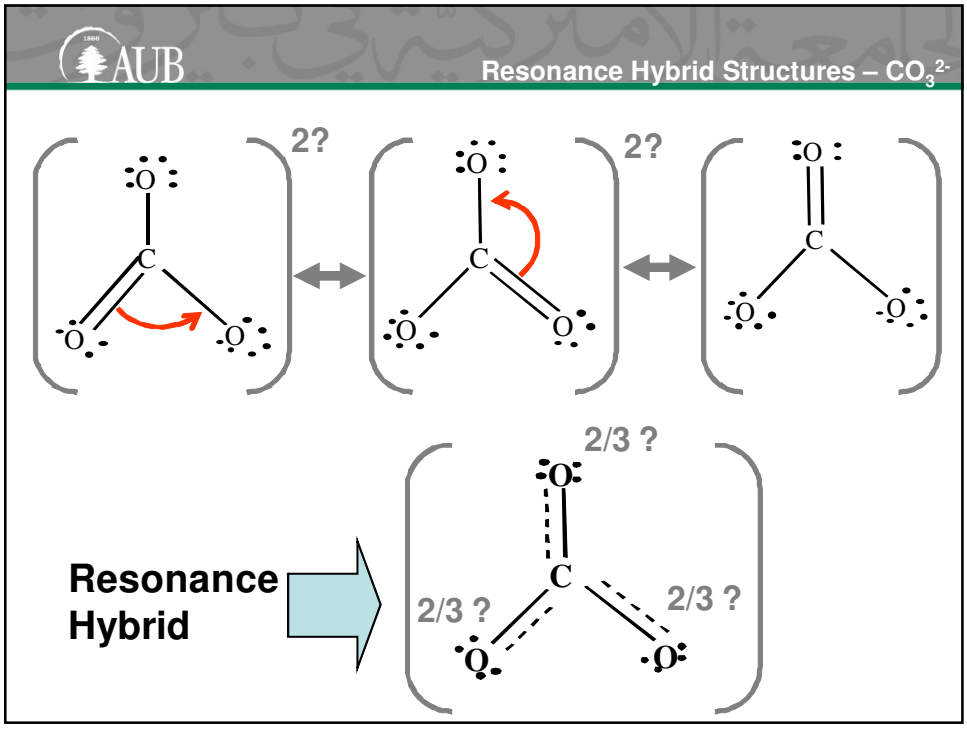
Resonance Hybrid Structures – CO_3^{2-}

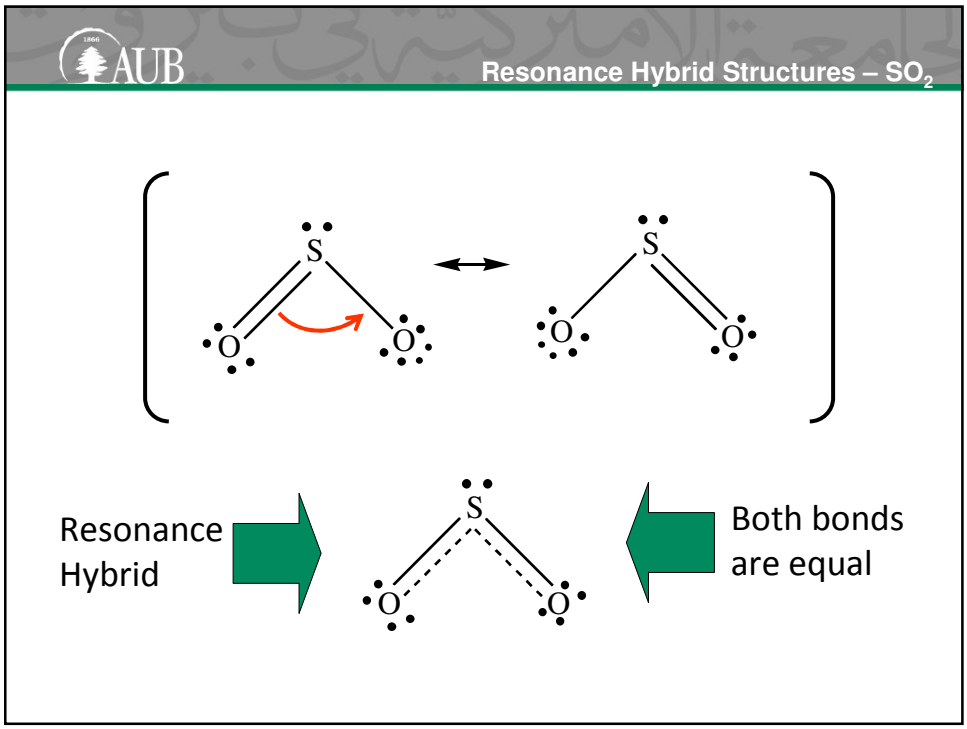
When two or more different Lewis structures are possible for a molecule, they are termed resonance hybrids.

The *actual* electronic structure of such a molecule should be viewed as an *average* of the different possible resonance hybrids.

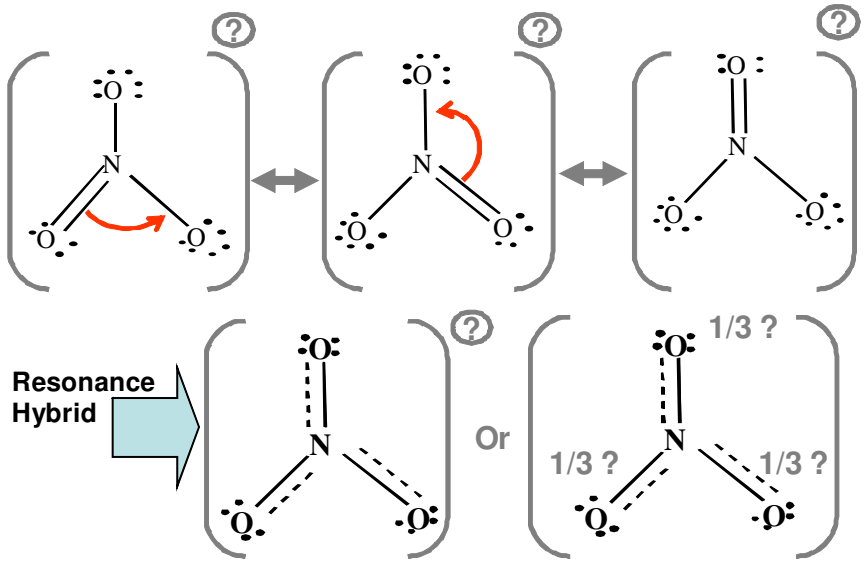


I II III


AUB
Resonance Hybrid Structures – CO_3^{2-}
2?
2?
2/3 ?
2/3 ?
2/3 ?
Resonance
Hybrid


AUB
Resonance Hybrid Structures – SO_2
Resonance
Hybrid
Both bonds
are equal

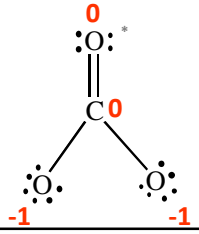
Resonance Hybrid Structures – NO_3^-



Formal Charges

Formal charge = [Number of valence electrons in free atom] − [Number of valence electrons in bonded atom]

= [Number of valence electrons in free atom] − ½ [Number of bonding electrons] − [Number of nonbonding electrons]



FC on C: 4 – 1/2 (8) = 0

FC on O*: 6 – 1/2 (4) – 4 = 0

FC on O: 6 – 1/2 (2) – 6 = – 1

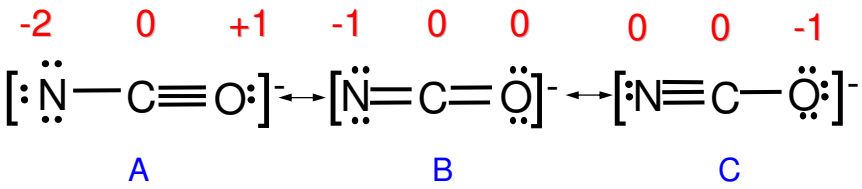
Sum of formal charges = -2 = charge of the carbonate anion

Most Stable Structure

Q: Which are the *most likely* contributors to the resonance hybrid?

A: Resonance structures with:

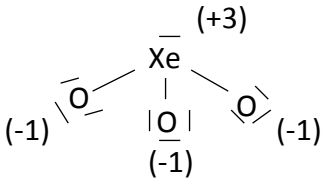
- lowest formal charges
- unlike charges on adjacent atoms
- a more negative formal charge on more EN atom

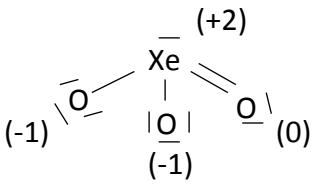


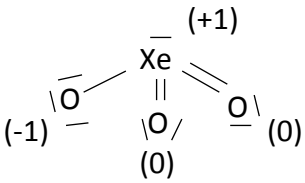
A is excluded (largest formal charge)
B has -1 on N (less EN than O)
C has -1 on O (more EN than N

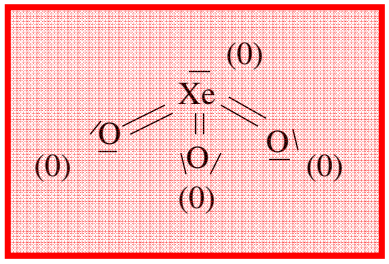
C most favoured

Most Stable Structure – XO_3





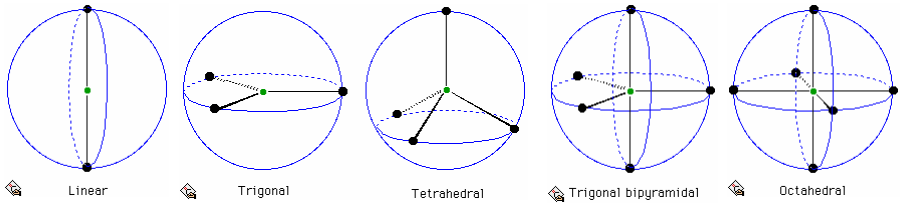




Valence Shell Electron Pair Repulsion (VSEPR)

Five basic molecular shapes based on electron group repulsion:

- Linear
- Trigonal Planar
- Tetrahedral
- Trigonal Bipyramidal
- Octahedral



Actual molecular shape depends on whether electron groups are bonding or lone pairs.

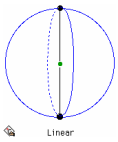
Valence Shell Electron Pair Repulsion (VSEPR)

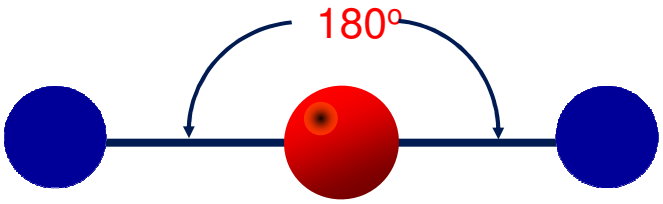
= Central Atom (A)

= Peripheral Atom (X)

= Electron Pair (E)

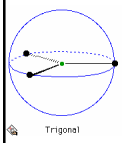
AX_2 - linear



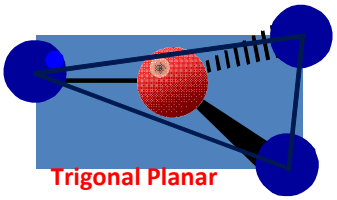


H — Be — H

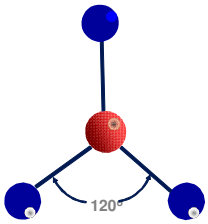
Shapes With 3 Electron Groups



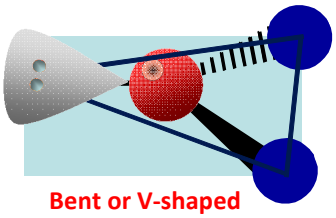
AX_3



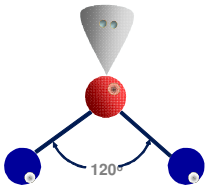
Trigonal Planar



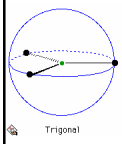
AX_2E



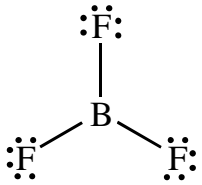
Bent or V-shaped



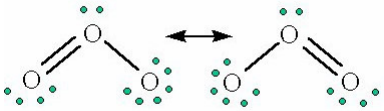
Shapes With 3 Electron Groups



AX_3



AX_2E

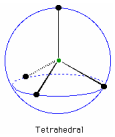


SO_2

$PbCl_2$

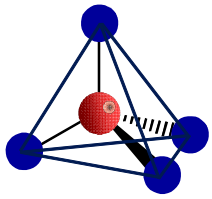
$SnBr_2$

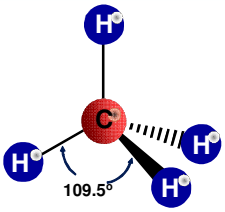
Shapes With 4 Electron Groups



AX_4

Tetrahedral





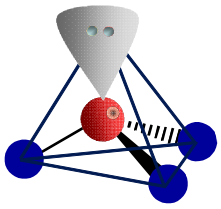
$SiCl_4$

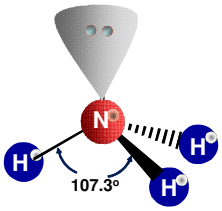
$SO_4^{2?}$

$ClO_4^?$

AX_3E

Trigonal Pyramidal





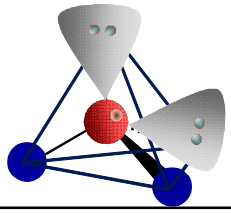
PF_3

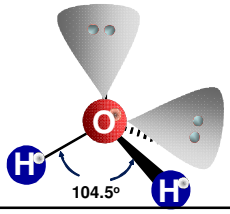
H_3O^+

ClO_3

AX_2E_2

Bent or V-shaped

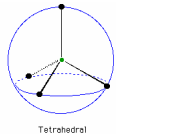


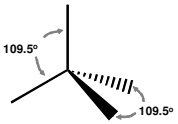


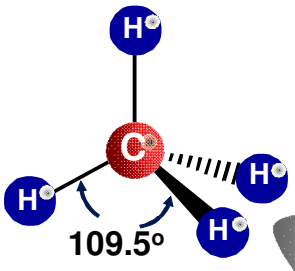
OF_2

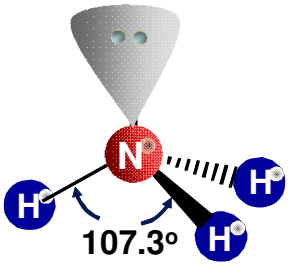
SCl_2

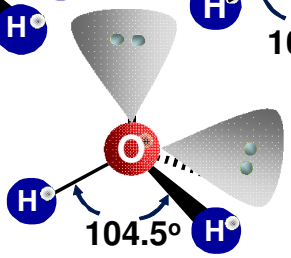
Effect of Lone Pairs on Bond Angles



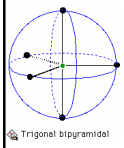




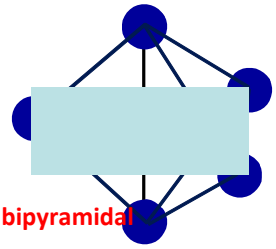




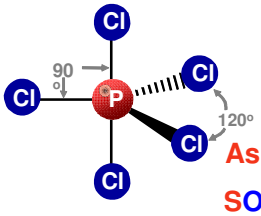
Shapes With 5 Electron Groups



AX_5



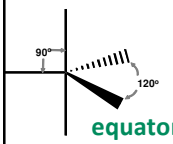
Trigonal bipyramidal



AsF_5

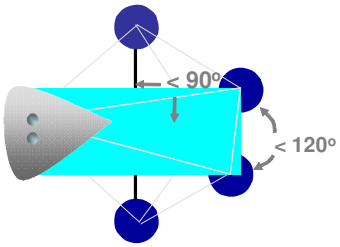
SOF_4

axial

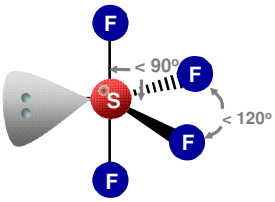


equatorial

AX_4E



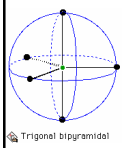
See-saw



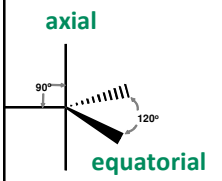
IF_4^+ $PCl_4^?$

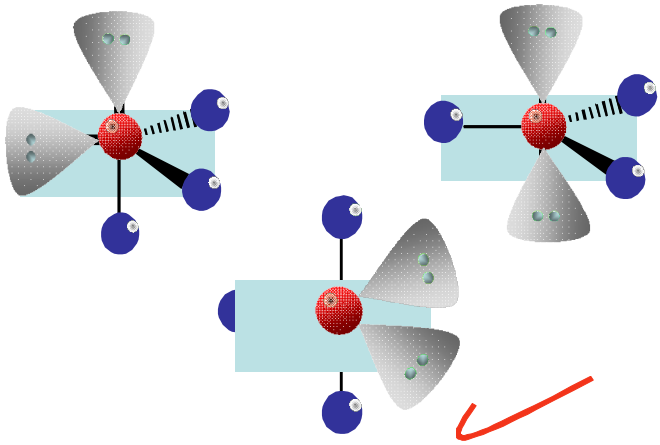
XeO_2F_2 $IO_2F_2^?$

Shapes With 5 Electron Groups

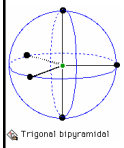


AX_3E_2

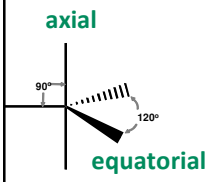


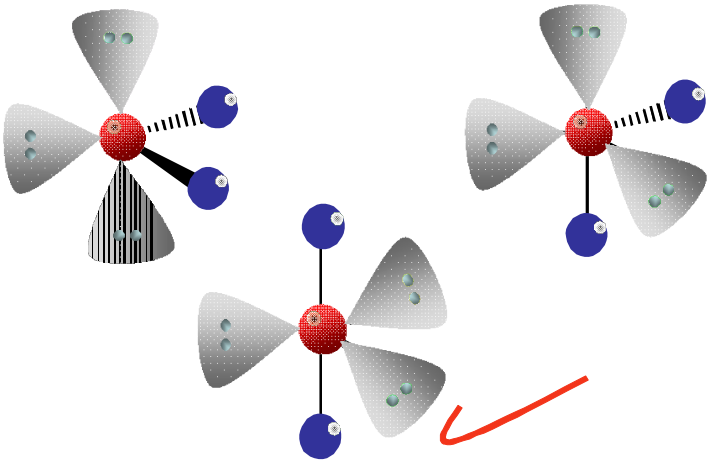


Shapes With 5 Electron Groups

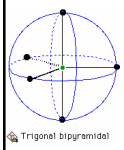


AX_2E_3



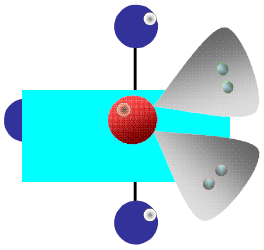


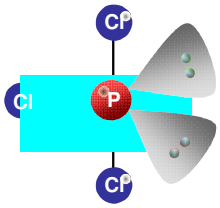
Shapes With 5 Electron Groups



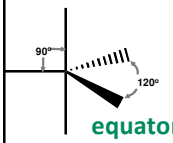
AX_3E_2

T-shaped





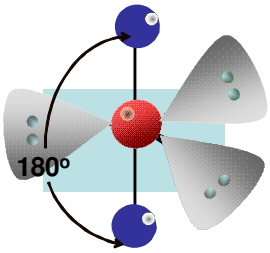
axial

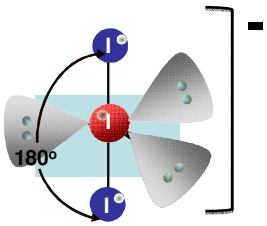


equatorial

AX_2E_3

Linear

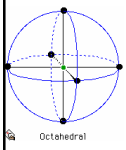




XeF_2

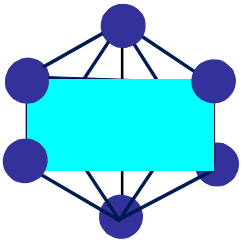
$IF_2^?$

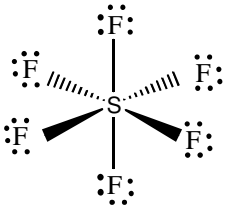
Shapes With 6 Electron Groups

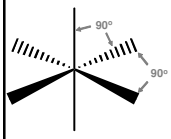


AX_6

Octahedral

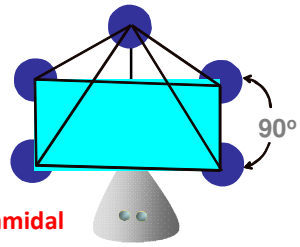


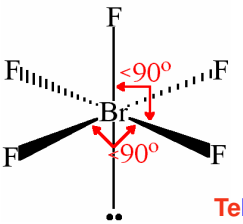




AX_5E

Square pyramidal

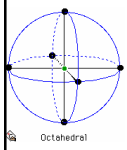




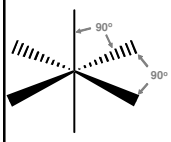
$TeF_5^?$

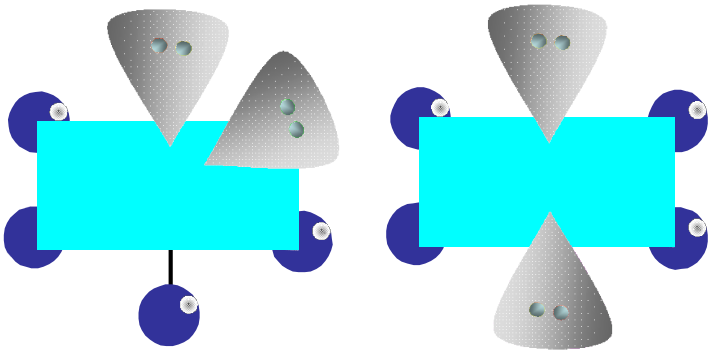
$XeOF_4$

Shapes With 6 Electron Groups

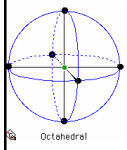


AX_4E_2





Shapes With 6 Electron Groups



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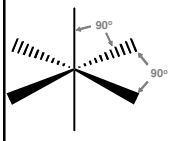
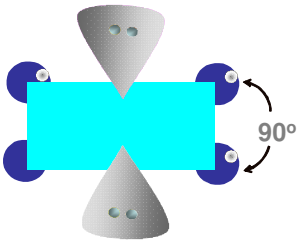
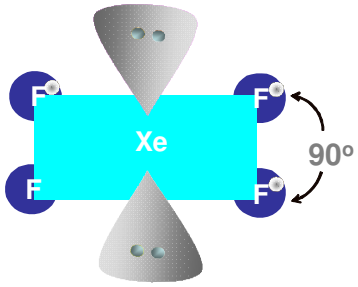


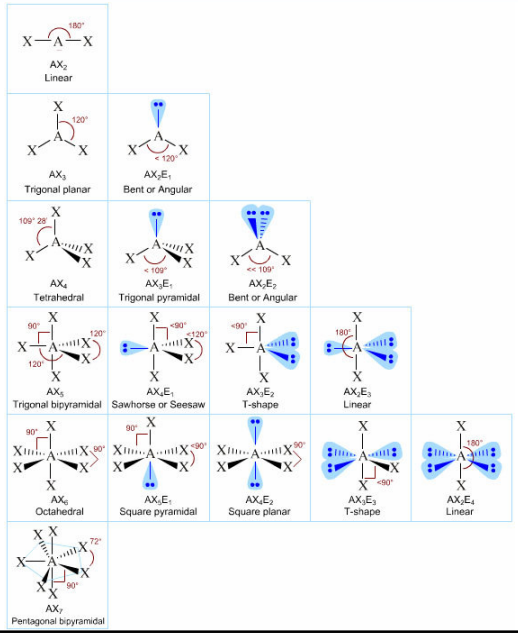
Square planar



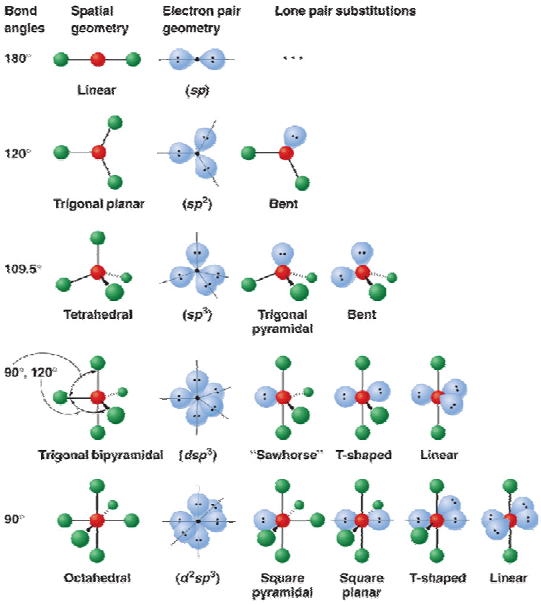


ICl_4^-

VSEPR - Summary



VSEPR - Summary



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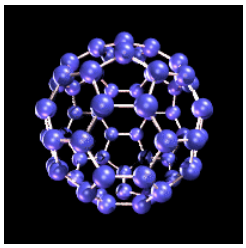
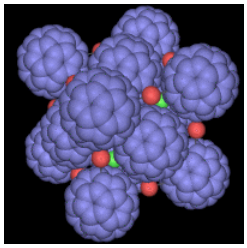
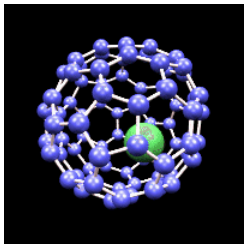
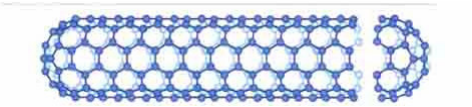
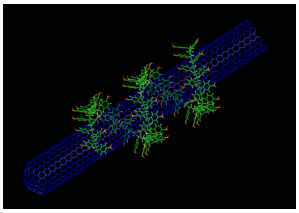
Odd Shaped Molecules for the Third Millennium

Fullerenes

- Buckminsterfullerene, C_{60}, was the first reported in soot in 1985 - prepared in 1990. A third form of crystalline carbon? Electron delocalisation.
- By atomic insertion, and bonding different groups, a whole new range of materials for lubricants, superconductors, batteries, cancer and AIDS drugs is being developed.
- See http://www.physik.uni-stuttgart.de/ExPhys/2.Phys.Inst./member/k.thier/fullerenes/fullerene_gallery.html

Odd Shaped Molecules for the Third Millennium

Nanotubes

- Discovered in 1991, these long carbon tubes have fullerene ends.
- Have highly delocalized electrons, are very conductive, and many times stronger than steel.
- Suggested applications include manufacture of nanoscale electronics and wires made by inserting metal atoms inside the tubes.
  - See: http://www.rdg.ac.uk/~scsharip/tubes.htm
  - http://cnst.rice.edu/pics.html

Molecular Shape and Reactivity - Enzymes

Enzymes

–Protein molecules that catalyse rates of certain chemical reactions on a particular *substrate* (reactants) by factors of 10^8 - 10^{11} compared to the uncatalysed processes.

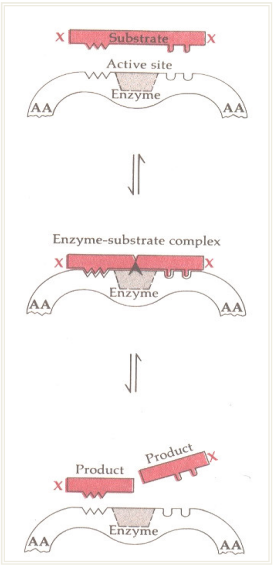
–Enzymes have an *active site* into which a substrate fits

–Active site must provide a perfect fit for the substrate ("lock and key" concept).

–Active site offers some mild attractive binding for the substrate

- capture substrate,
- hold substrate in right position.

–Product molecule must be able to leave enzyme after reaction.



Molecular Shape and Reactivity - Enzymes

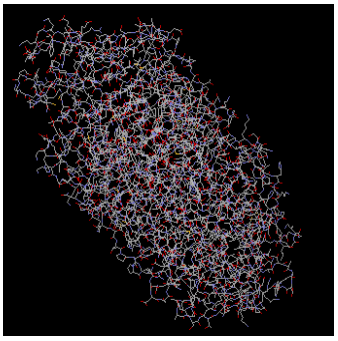
Example: Alkaline phosphatase

–Catalyses the hydrolysis of phosphate ester molecules

$R\text{-}O\text{-}PO_3 + H_2O \rightarrow R\text{-}OH + PO_4^{3-}$ at pH 8-10.

–Metalloenzyme

- requires Zn^{2+} or Mg^{2+} (or both) as cofactors (coenzymes) for catalysis to occur.

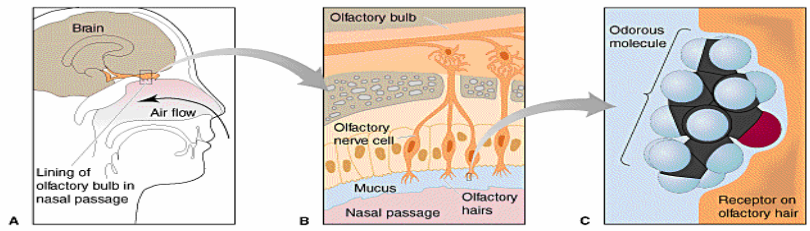


Molecular structure of *E. coli* alkaline phosphatase (MW ≈ 75,000 Dalton)

Molecular Shape and the Sense of Smell

Nature of odorous molecules

- –Capable of travelling through air-must be a gas, or from a volatile solid or liquid.
- –Must have a shape that will fit into an olfactory sensor *(receptor sites)* of nerve endings in the nasal passage.

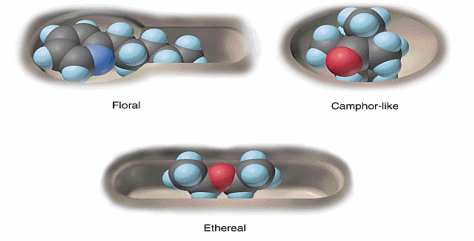


The Location of Olfactory Receptors within the Nose

Molecular Shape and the Sense of Smell

Seven Primary Odors or Olfactory Receptor Sites

- *– Camphor-like, Musky, Floral, Peppermint, Etheral, Pungent, Putrid.*
- – Molecules with parts that fit more than one type of receptor site will have a mixture of odors, eg. Benzaldehyde fits floral, musky and minty receptors, and the combined odor is almond-like.



Molecular Shape and the Sense of Smell

– Different molecules that fit the same receptor sites smell the same, eg. for the camphor receptor: