Chapter 9: Bonding & Molecular Structure: Fundamentals

Recall: Valence electrons are the outermost s+p electrons = Group No.
- determine chemical properties of atom
- loss or gain or rearrangement of these e^- caused by reactions

Lewis dot symbols for main group atoms (use valence electrons

1A	2A	3A	4A	5A	6A	7A	8A
Li·	·Be·	·B̈·	·C·	·N·	:O·	:F·	:Ne:

Chemical bonds: attractive forces that hold atoms together in compounds

(1) Ionic bonds: electrostatic interaction between ions $F \propto \frac{q^+ q^-}{d^2}$

(bonding force F is proportional to $q^+ q^-$, charge on ions; d = distance between ions)

- involves transfer of 1 or more electrons from one atom or group of atoms to another
- occurs between metals (low EN) and non metals (high EN)

Mg and N combine together to form what simple binary compound?

$Mg + N \rightarrow$? (ans. Mg_3N_2)

First ask how do Mg and N both gain noble gas configuration?

·Mg· (2A, must lose $2e^-$) + ·N· (5A, must gain $3e^-$) $\longrightarrow$ Mg^{2+} (isoelectronic with Ne) and N^{3-} (isoelectronic with Ne) in compound

But total number of e^- lost by Mg = total number of e^- gained by N

∴ need 3 Mg atoms (lose $6e^-$) to react with 2 N atoms (gain $6e^-$)

$Mg\ [Ne]3s^2 \xrightarrow{-2e^-} Mg^{2+}\ [Ne]$

$N\ 1s^2 2s^2 2p^3 \xrightarrow{+3e^-} N^{3-}\ 1s^2 2s^2 2p^6 \equiv [Ne]$

So $3Mg + 2N \rightarrow \overset{+2}{Mg_3}\overset{-3}{N_2}$

(2) covalent bonds : involve sharing of one or more electron pairs
occurs between nonmetals only (similar EN)

1 pair shared electrons ($2e^-$) : single bond A–B or A:B
2 pairs shared electrons ($4e^-$) : double bond A=B or A::B
3 pairs shared electrons ($6e^-$) : triple bond A≡B or A⋮⋮B

Examples: Lewis dot formula : each electron expressed by dot
dash formula : each electron pair is expressed by dash

H_2 H:H H–H HF H:F̤̈: H–F̤̈: ← lone pair of electrons

The electrons in bond may not be shared equally. If the electronegativities of the 2 elements are different, the more EN element will pull electrons closer to itself, creating polar bond. If they are the same, the bond is non polar.

Polar Bond: $+\delta \longleftrightarrow -\delta$ H – F̤̈: EN 2.1 4.0

$+\delta$ small + charge
$-\delta$ small - charge
⟷ represents a dipole with separation of charge

∴ H–F̤̈: is a polar covalent bond. $\Delta EN = 1.9$

Non Polar Bonds :C̤̈l – C̤̈l: P – As (EN 2.1 2.1) C–S (2.5 2.5)

How do we tell if a molecule is polar? By its geometry!

Step 1 : Lewis dot formula for molecules and polyatomic ions

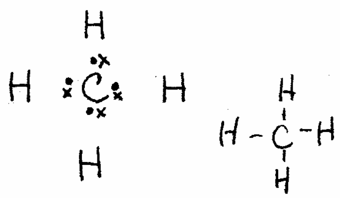
Representative ("A") elements usually achieve noble gas configuration in most compounds. Since all noble gases (but He) have $8e^-$ in outer shell, this is called "octet rule" – a guideline for determining structure.

Example N_2 (N is a 5A – has $5e^-$ in outer shell; each N wants $8e^-$
* we have $10e^-$ to play with

:N⋮⋮N:
:N≡N: triple bond

Note: Octet Rule: $S = N - A$ where S = # shared e^- in bonds
N = # needed e^-
A = # available e^- (valence e^-)

Example 2. CH_4 (C is IVA: has 4 e^- in outer shell
each C wants 8e^-
each H wants 2e^- } they will share electrons in such a way so that they will get them.

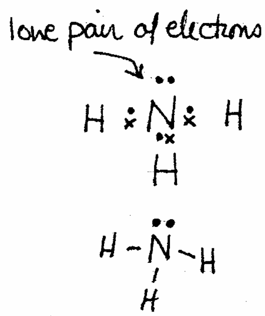


$S = N - A$
$= (\overset{C}{1} \times \overset{C}{8} + 4 \times \overset{H}{2}) - (4 + (\overset{H}{4} \times 1)) = 16 - 8$
$= 8$ electrons shared.

Arrangement of elements:

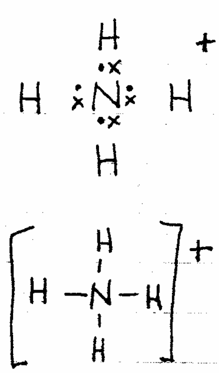
Rules of thumb:
(1) the element needing the most electrons to fill its octet is usually the central atom.
(2) the most symmetrical skeleton is usually correct.
(3) oxygen atoms are usually bonded to another nonmetal — not to each other
(4) in ternary acids, eg H_2SO_4, H are bonded to O. (A ternary acid contains H, O and another nonmetal) Always obeys octet rule.

Example 3. NH_3 (N is VA: has 5 e^- in outer shell
each N wants 8e
each H wants 2e



$S = N - A$
$= [(\overset{N}{1} \times 8) + (\overset{H}{3} \times 2)] - [\overset{N}{1} \times 5 + \overset{H}{3} \times 1]$
$= 14 - 8$
$= 6$ electrons shared.

Example 4. NH_4^+ (N is VA BUT lost 1 electron
∴ has 4 e^- only in outer shell.

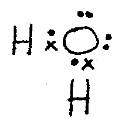


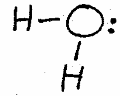
$S = N - A$
$= [(\overset{N}{1} \times 8) + (\overset{H}{4} \times 2)] - [\overset{N}{1} \times 5 + \overset{H}{4} \times 1 - 1]$
$= 16 - 8$
$= 8$ electrons shared

More Rules of Thumb:

(1) Halogens and H <u>always</u> share one electron to complete outer shell.
(2) oxygen can do several things depending on the molecule
(a) single bond by sharing an electron

H_2O water

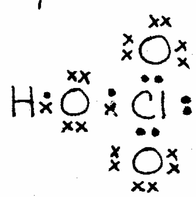


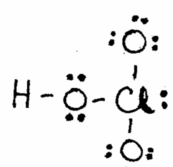


$S = N - A$
$= (8 + 4) - (6 + 2)$
$= 12 - 8 = 4$

(b) single bond by accepting 2 electrons from another atom and not sharing at all.

$HClO_3$



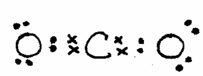


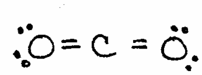
$S = N - A$
$= (4\times8 + 2) - (7 + 3\times6 + 1)$
$= 34 - 26$
$= 8$ electrons shared.

Recall: in a ternary acid, H must be bonded to an oxygen atom

(c) double bond by sharing 2 of its electrons.

CO_2



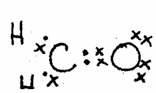


$S = N - A$
$= (3\times8) - (4 + 2\times6)$
$= 24 - 16$
$= 8$ electrons shared

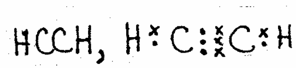
when C is physically at end of molecule or ion eg CN^- CO it has a lone pair :C≡N-Ö:⁻ Otherwise, there are never any lone pairs on C.

(3) there are ~~never~~ rarely any lone pairs of electrons on a carbon atom. exceptions CO CN^- + similar compounds. C always obeys octet rule
(4) when forming multiple bonds between atoms (ie double + triple bonds), both atoms donate the <u>same</u> number of electrons.

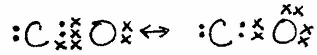
double bond H_2CO,

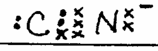


triple bond HCCH,

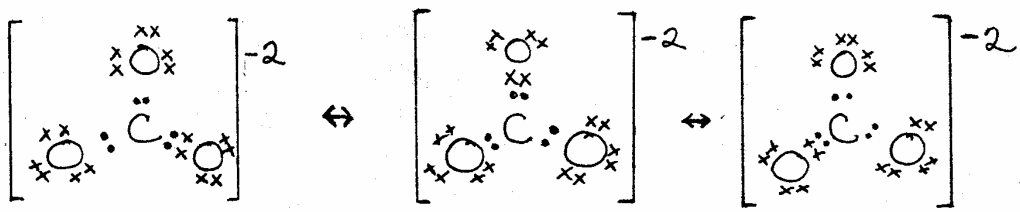


Note: two notable exceptions to these rules are the heteronuclear diatomic species

CO 

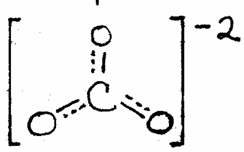
CN^- 

Example: CO_3^{2-} carbonate ion — C is IVA but gained 2 extra electrons ∴ has 6 electrons total



$$S = N - A$$
$$= (4 \times 8) - (\overset{O}{3} \times 6 + \overset{C}{1} \times 4 + \overset{e^-}{2})$$
$$= 32 - 24$$
$$= 8$$

The "↔" means that the true structure is somewhere in between the three structures.
These 3 structures are called RESONANCE structures.
A molecule or ion for which 2 or more equally acceptable dot formulas are available to describe the bonding is said to exhibit resonance.
We can represent CO_3^{-2} ion as



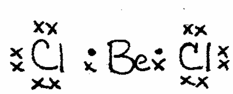
delocalized structure

the C–O bonds are neither double nor single bonds but somewhere in between.

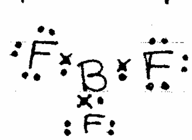
C–O single bond length is ~ 1.43 Å
C=O double bond length is ~ 1.22 Å (shorter) (stronger)
C–O in carbonate ion is 1.29 Å

<u>Exceptions to OCTET Rule</u>: (where S=N-A does NOT apply).

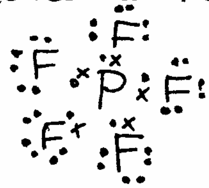
1. most covalent compounds of Be (IIA)

$BeCl_2$  Cl atoms have octet, Be only has 4 e^-

2. most covalent compounds of Group IIIA

BF_3  F atoms have octet, B only has 6e^-

3. Compounds in which the central element must have a share in more than 8 valence electrons to accomodate all attached atoms.

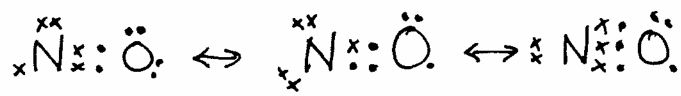
PF_5  P has $10e^-$ around it since each F atom had to have 1 extra e^- to complete its octet.

Note: In compounds + ions, outside atoms ALWAYS obey octet rule. Central atoms may or may not obey octet rule.

4. Compounds containing d- or f- transition elements.
5. species containing odd number of electrons. – free radicals
   very reactive

NO
nitrogen oxide

need resonance to explain



N   5 valence e^-
O   6 valence e^-
total   11 valence e^-

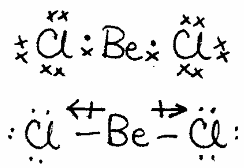
Now that we can figure out Lewis dot structures, next: <u>Molecular Shapes</u>

Valence Shell Electron Pair Repulsion Theory (VSEPR) is based on idea that bonding and lone pairs of electrons in the valence shell of an atom want to be as far apart as possible to gain maximum stability. This results in electron pair geometry. If we are concerned with actual shape of the molecule or ion, the lone pairs of e^-s are invisible, but their presence is still felt. In fact lone pairs of e^- take up more space than electrons in bonds. In this class, we are only concerned with "ideal" bond angles.

Let us go through examples, in order

I. Two (2) regions of high electron density around central atom.
sp hybridization (180°)
electronic geometry : linear

example : $BeCl_2$



EN 3.0 1.5 3.0

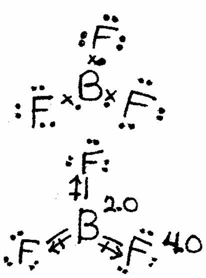
NONPOLAR

Be-Cl bond is polar but the bond polarities CANCEL!

molecular geometry : linear

II Three (3) regions of high electron density around central atom.
sp^2 hybridization (120° ideal)
electronic geometry : trigonal planar

example : BF_3

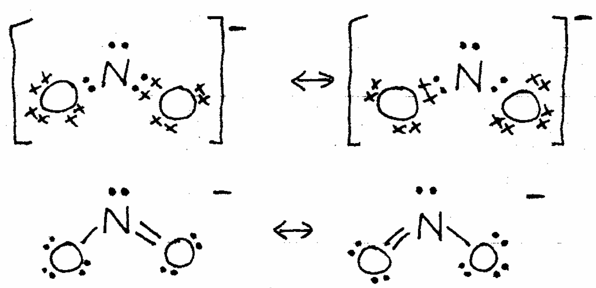


NONPOLAR

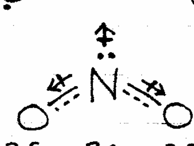
B-F bond is polar but ~~the~~ bond polarities CANCEL!

molecular geometry : trigonal planar.

NO_2^-



molecular geometry : angular



EN 3.5 3.0 3.5

POLAR

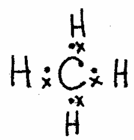
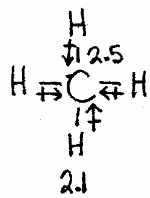
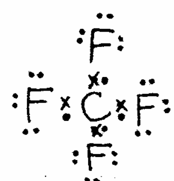
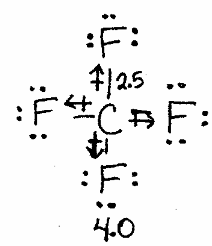
Bond polarities do NOT cancel

III Four (4) regions of high electron density

sp^3 hybridization

electronic geometry: tetrahedral (109° 28′ ideal)

Examples: CH_4 and CF_4

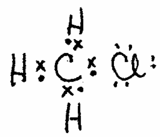
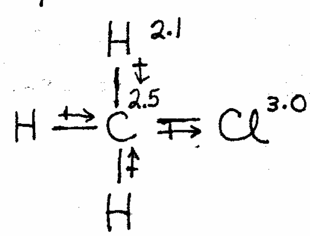





C–H bonds is polar but CH_4 is nonpolar since polarities cancel

C–F bond is polar but CF_4 is nonpolar.

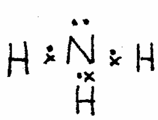
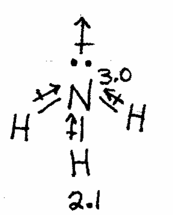
molecular geometry = electronic geometry = tetrahedral for CH_4, CF_4, CH_3Cl

CH_3Cl

POLAR

Examples: NH_3

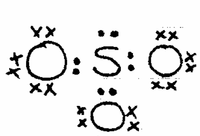
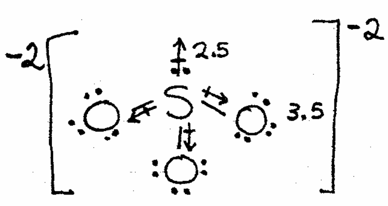
POLAR

electronic geometry: tetrahedral

molecular geometry: pyramidal

pyramidal

SO_3^{2-}

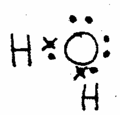



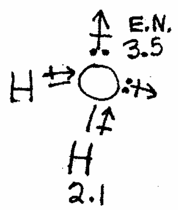
electronic geometry: tetrahedral

molecular geometry: pyramidal

POLAR

Examples: H_2O



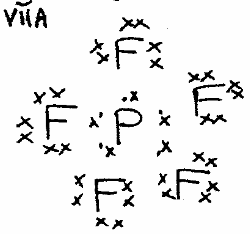


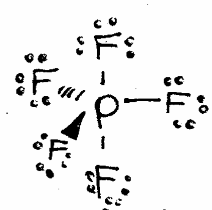
POLAR

electronic geometry: tetrahedral
molecular geometry: angular

IV Five (5) regions of high electron density (does not obey octet rule)
sp^3d hybridization
electronic geometry: trigonal bipyramidal 90° 120° 180°

Example:
PF_5 (does not obey octet rule)
VA VIIA

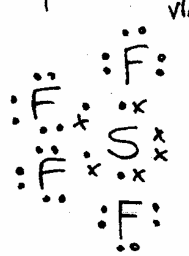


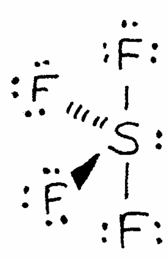


NONPOLAR

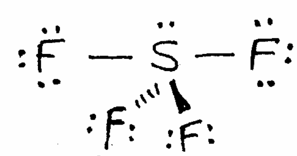
molecular geometry = electronic geometry = trigonal bipyramidal

Example: SF_4 (1 lone pair of electrons on central atom)
VIA VIIA





or

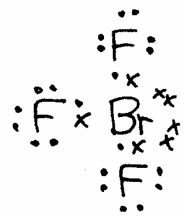


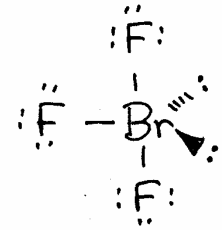
"see saw"

electronic geometry: trigonal bipyramidal
molecular geometry: see saw
molecule is polar

Example: 2 lone pairs of electrons on central atom

BrF_3
VIIA VIIA



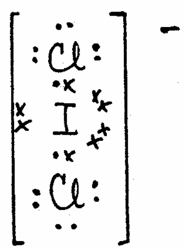


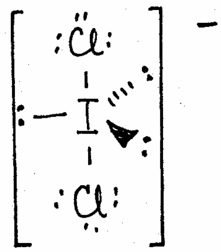
T-shaped

electronic geometry: trigonal bipyramidal
molecular geometry: T-shaped and molecule is polar

Example: 3 lone pairs of electrons on central atom

ICl_2^-
VIIA VIIA
with 1 extra electron



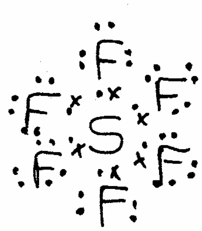


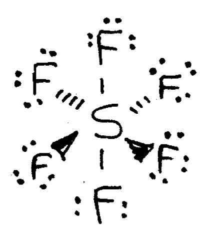
electronic geometry: trigonal bipyramidal
ionic geometry (since this is an ion): linear + NONPOLAR

V Six (6) Regions of High Electron Density (does not obey octet rule)
sp^3d^2 hybridization
electronic geometry: octahedral (90°, 180° bond angle)

Example: No (Ø) lone pairs of electrons on central atom

SF_6

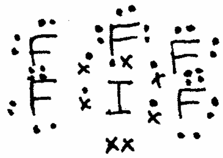


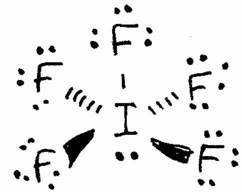


molecular geometry = electronic geometry = octahedral
molecule is nonpolar

Example: 1 lone pair of electrons on central atom

IF_5
VIIA VIIA



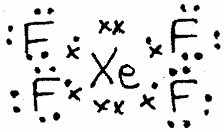


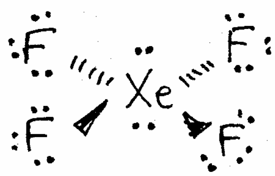
square pyramidal

electronic geometry: octahedral
molecular geometry: square pyramidal; molecule is polar.

Example: 2 lone pairs of electrons on central atom

XeF_4

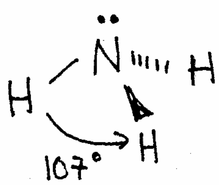


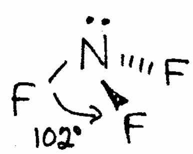


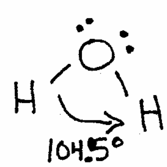
electronic geometry: octahedral
molecular geometry: square planar; molecule is <u>non</u>polar.

Note: In discussing bond angles, we have only considered IDEAL bond angles eg. in a molecule with tetrahedral electronic geometry, the bond angle is 109°28' ideally.

In reality, lone pairs of electrons occupy more space than bonding pairs with the following result: a decrease in the angles between bonding pairs.







Review

Regions of High Electron Density Around Center Atom	Hybridization (Ch 10)	Electron Pair (Electronic) Geometry	No. of Lone Pairs of Electrons Around Central Atom	Molecular (Ionic) Geometry	Examples
2	sp	linear	0	linear	$BeCl_2$, CO_2
3	sp^2	trigonal planar	0	trig. planar	BF_3, CO_3^{2-}
			1	bent or angular	NO_2^-
4	sp^3	tetrahedral	0	tetrahedral	$HClO_4$, CH_4, CH_3Cl, NH_4^+
			1	pyramidal	NH_3, SO_3^{2-}, H_3O^+
			2	bent or angular	H_2O
5	sp^3d or dsp^3	trigonal bipyramidal	0	trig. bipyr.	PF_5
			1	see saw	SF_4
			2	T-shaped	BrF_3, ClF_3
			3	linear	I_3^-, XeF_2
6	sp^3d^2 or d^2sp^3	octahedral	0	octahedral	SF_6
			1	square pyramidal	IF_5, BrF_5
			2	square planar	IF_4^-, XeF_4

Formal Charges

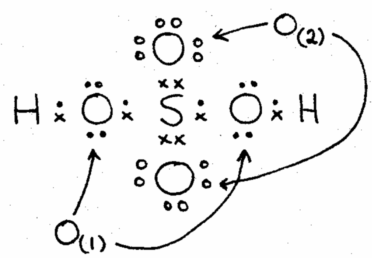
The concept of formal charges helps us choose the correct Lewis structure for a molecule.

Rules for assigning formal charges to Group A elements:

1. For a molecule, the sum of the formal charges for all elements is zero
   For an ion, the sum of the formal charges for all the elements equals charge on ion.
2. Formal charge, FC = Group No. − (no. of bonds + no. unshared e^-)
   Note: Group Number of noble gases = $\overline{\text{VIII}}$; double bond counts as 2 bonds.
3. A good Lewis dot structure has
   - low (near zero) or zero values of FC for all elements
   - adjacent atoms are <u>not</u> given FC values of the same sign
   - the more electronegative atom in a bond is given the more negative FC.

Consider two Lewis dot structures for sulfuric acid, H_2SO_4.

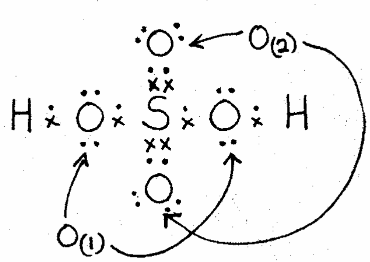
(a)



FC $H = 1-(1+0) = 0$
$O_{(1)} = 6-(2+4) = 0$
$O_{(2)} = 6-(1+6) = -1$
$S = 6-(4+0) = +2$

This is an OK dot structure, but there might be a better one where FC of S is closer to zero. Consider

(b)



Note: sulfur does not obey the octet rule

FC $H = 1-(1+0) = 0$
$O_{(1)} = 6-(2+4) = 0$
$O_{(2)} = 6-(2+4) = 0$
$S = 6-(6-0) = 0$

Structure is a little strange, but all elements have zero FC. Good!!
There is data to support this structure for H_2SO_4.

Bond properties

bond order – number of bonding electron pairs shared by 2 atoms

Bond Order	bond
1	single
2	double
3	triple

Note: can be fractional eg 1.5 (between single + double bond)

bond length – distance between nuclei of 2 bonded atoms

units: Å 1×10^{-10} m

nm 1×10^{-9} m

pm 1×10^{-12} m

in general single bonds > double bonds > triple bonds

single bonds: longest, weakest bond (smallest bond energy)

triple bonds: shortest, strongest bond (largest bond energy)

bond energy –

- Bond dissociation energy, D, is enthalpy change (ΔH) for breaking a bond in a gaseous molecule; process is endothermic
- you can use information to estimate ΔH_{rxn}.

Example: Calculate ΔH_{rxn} for $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ using bond energies:

H–H 436 kJ/mol

H–Cl 432 kJ/mol

Cl–Cl 242 kJ/mol

Note: it takes energy to break bonds; energy is released when making bonds.

Reaction $H{-}H(g) + Cl{-}Cl(g) \rightarrow H{-}Cl(g) + H{-}Cl(g)$

+436 +242 +432 +432

$\Delta H_{rxn} = D_{H_2} + D_{Cl_2} - 2D_{HCl}$

$= +436$ kJ/mol $+ 242$ kJ/mol $- 2\times432$ kJ/mol

$= -186$ kJ

Note $\Delta H_{rxn} = 2\Delta H_f^\circ\ HCl(g) = -184.6$ kJ – VERY CLOSE!!