CHAPTER 8

Chemical Bonding

Atoms of *elements* (*except Gp.8A*) exist in some form of aggregation.

All *compounds* made (by chemical combination) of different elements exist in some form of aggregation of elements.

The 'force' or the bond which makes these aggregations possible is termed a chemical bond.

All matter in it's "core" is electrical in nature.

Matter, made up of atoms, that contain electrons, neutrons and protons, two of which are electrically charged.

The basis for *bondage* between 'atomic' species is <u>*electrical*</u> in nature.

Starting point - constitution of the electrons in of the atom.

Nucleus: positively charged entity that does not change during chemical/physical changes.

Extra nuclear particles - electrons.

Electronic constitution of atoms changes during chemical reactions in some manner.

Electronic configuration: [core] valence ; electrons.

Core, is very stable; does not change under reaction conditions.

Valence electrons, at the edge of the atom are the least strongly held, easily moved out if it leads to stability.

Valence shell may also accommodate electrons with least difficulty if it leads to stability.

Classification matter by type of chemical bonds (3 distinct types, ionic, covalent, metallic):

<u>Ionic</u>	<u>Covalent</u>
Electrolytes (ions)	Non-electrolytes (molecules)
Solutions conduct electricity	Solutions do not conduct electricity
Metals-nonmetals	Nonmetals-nonmetals
High b.p., m.p.	Lower b.p., m.p.
Solids - always	Solids, liquids, gases

What makes a material ionic or covalent?

The drive of (atoms of) elements to reach stability.

One major 'driving force' to reach stability is the attainment of stable electronic environment.

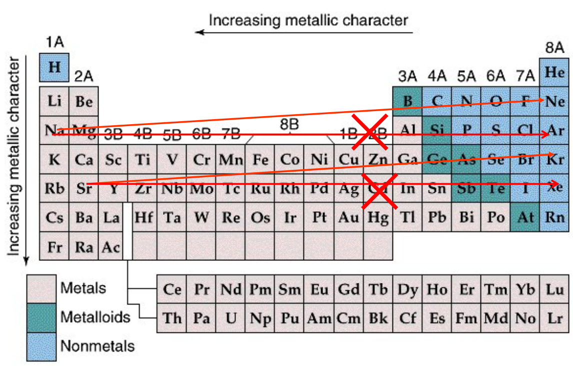
Stable electron environment = inert gas environment, mostly ns^2np^6 outer most shell - STABLE OCTET. (representative elements)

Lewis Theory

Gilbert Lewis (1916): Proposed that atoms tend to lose, gain, or share electrons to achieve an electron configuration of a noble gas (filled shell).

Octet: Set of 8 electrons in valence shell (ns^2np^6) inert gas configuration.

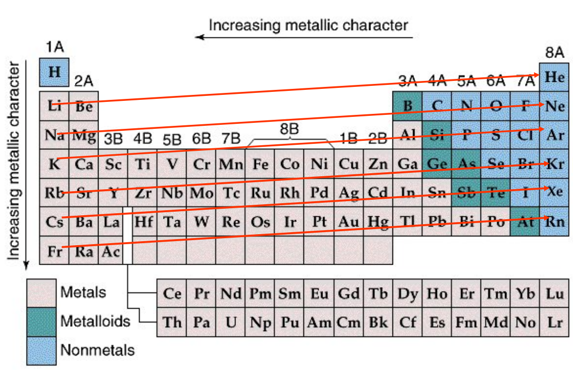
Note: Hydrogen contains a maximum of 2 electrons (duet) in the 1*s* orbital to obtain a filled $n = 1$ shell.



The *energetically least demanding* 'path' that allows the 'attainment' of an 'inert gas electronic *environment*' by 'atoms' leads to ionic/covalent bonds between them.

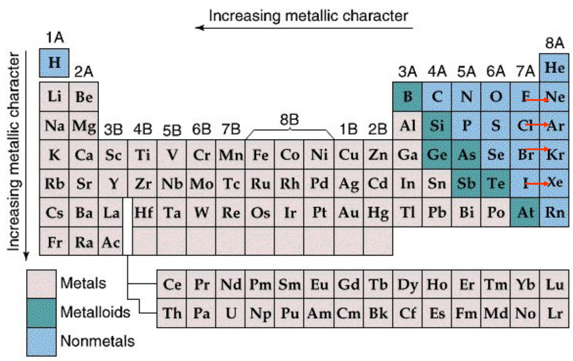
Atoms most likely to form +ve ions are metals; low IE.

alkali metals +1
alkaline earths +2
transition metals *variable*



Atoms most likely to form negative ions are non-metals (in p-groups); larger EA.

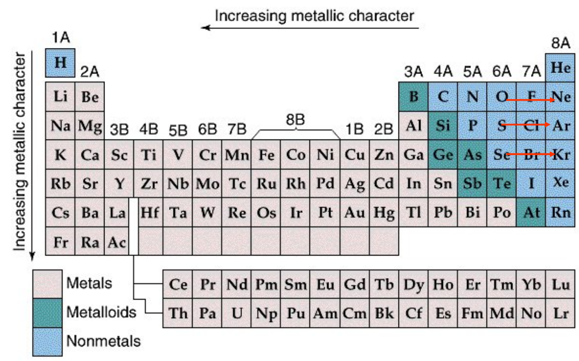
halogens -1
oxygen group -2
nitrogen -3 (lower likelihood, but does occur)
carbon group -4 (even lower likelihood)



Especially in *s* and high *p* groups, the drive of atomic species is to form the stable octet.

Ionization (formation of ions) is one way to achieve this octet.

Some chemical reactions involve the electron transfers that yields the stable octets.



Ionic bond:

The type of bond existing in electrolytes (*s*).
Electrolytes are made of ions of opposite charges.

Ion formation involve loss/gain of electrons by atoms

Such a loss/gain occurs if it leads to the attainment of stable electronic environment.

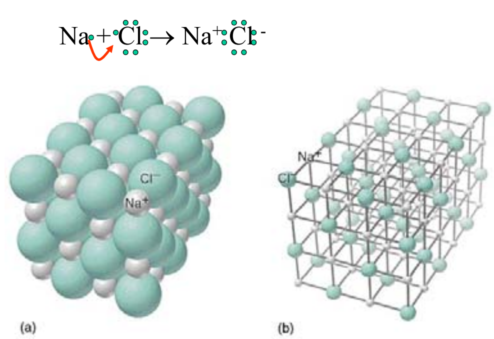
Ions are formed will attract (loss of energy, favoring the process) to form a lattice of ions.

The attraction between the opposite charged species are very strong, thus large b.p.s and m.p.s, in ionic compounds.

In the topic of chemical bonding the electron 'exchanges' occur only in the valence shells.

A simpler method to show the valence electrons in atomic/ionic/molecular species is the Lewis structure.

where valence electron = •



Note: well ordered ions in crystal lattices strongly held.

Electrostatic attraction of closely packed, oppositely charged ions.

Cation (positively charged particle):

Loss of electron(s) by an atom with low ionization energy (metals).

Anion (negatively charged particle):

Gain of electron(s) by an atom with high electron affinity (non-metals).

TABLE 8.1 Electron-Dot Symbols

Element	Electron Configuration	Electron-Dot Symbol
Li	$[He]2s^1$	Li•
Be	$[He]2s^2$	•Be•
B	$[He]2s^22p^1$	•B̈•
C	$[He]2s^22p^2$	•Ċ•
N	$[He]2s^22p^3$	•N:
O	$[He]2s^22p^4$	:O:
F	$[He]2s^22p^5$	•F:
Ne	$[He]2s^22p^6$	:Ne:

Lewis structure of atoms and ions: Atoms

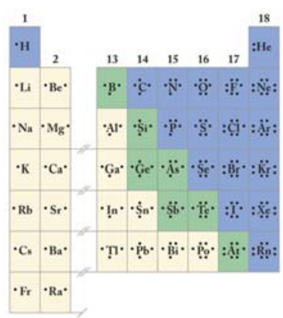
H• :He

Li• Be •B• •C• :N• :O: :F: :Ne:

The # of valence electrons on an atom = group #.

THE INERT GAS ELEMENT ARRANGEMENT
STABLE OCTET (duet for He)

Lewis symbols of atoms



Unpaired dots = bonding capacity= Valency.

Main Group Elements: Members of same family have same number of valence electrons, similar bonding capacities.

Lewis structure of ions:

H :He

Li Be •B• •C• :N: :O: :F: :Ne:

↑ ↑ ↑ ↑ ↑

+1 +2 -3 -2 -1

each of these the ion has the inert gas/8-electron environment. STABLE OCTET

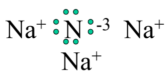
The strong attraction between oppositely charged ions leads to the ionic bonding.

Electrostatic attractions holds the ions together.

Li^+ :F:$^-$

note: Lewis notation shows the electrons in the valence shell only!

Na_3N: ionic (*metal-nonmetal*)



The force of attraction between ions;

$$F = \frac{z_+ z_-}{d}$$

$$F = \frac{z_+ z_-}{r_+ + r_-}$$ charge z_i and ion radius r_i

Related directly with charges on the ions and inversely with inter ionic distance.

The force of attraction between ions;

LiCl > NaCl

NaCl < $MgCl_2$

Covalent Bond (between non-metals):

Nonmetals are very reluctant to give up electrons.

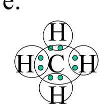
The elements in the middle of the s/p groups (e.g. 4A) require removal of many electrons or addition of many electrons - energetically expensive.

Such situations do not favor ion formation. Alternate path to achieve stable octet is followed; leads to the formation of ***covalent bonds***.

Alternate path - sharing electrons among atoms.

Methane - CH_4

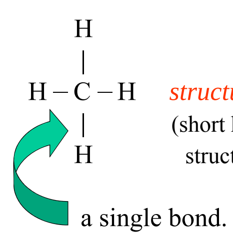
Lewis structure:



four covalent bonds
each carry two e's

the # valence electrons taking part in bonding;
4 from C; 4 from(1 per atom) hydrogen.

A covalent bond carrying 2 electrons - *single bond*.

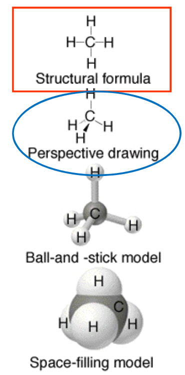


structural formula
(short hand Lewis structure)

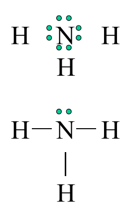
Octet Rule:

To form bonds, main group elements lose, gain or share electrons to achieve a *stable electron configuration* characterized by 8 *outer shell* electrons.

Sharing of electrons make covalent bonds, the type of bond encountered in ***molecular species*** (predominantly) containing nonmetals.



Ammonia: NH_3 (*nonmetal - nonmetal*)



structural formula
(short hand Lewis structure)

Lewis structure shows the electron distribution among atoms.

Covalent bonds: H_2

Atoms achieve octet by sharing of electrons, (H duet).

H• + •H → (H:H) = H - H

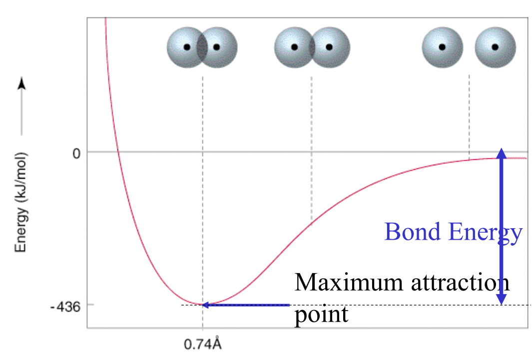
both atoms share the 2 e's
single bond, bond order =1

What makes a covalent bond possible, energetically?

Bond form because in doing so the atomic system attain stability.

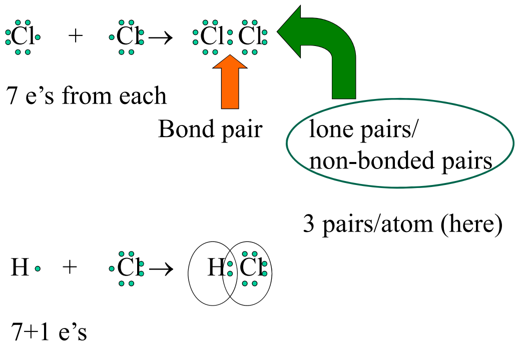
There should exist a process that leads to lowering of energy.

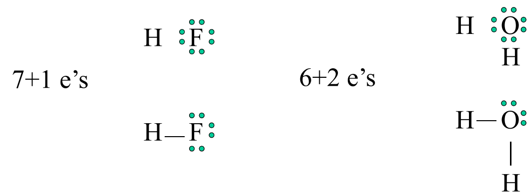
Valence orbital view. (Note: electrons reside in orbitals)



Attraction of the shared electrons that exist between to two nuclei of atoms is a driving force for the formation of covalent bonds.

Cl_2





<u>Single bond:</u>

Two atoms sharing one pair of electrons.

<u>Lone pair of electrons</u>:

Unshared pair of electrons associated with one atom.

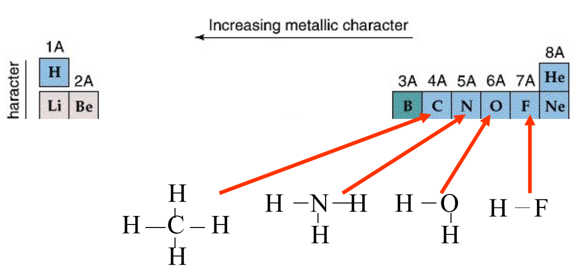
<u>Bonding pair of electrons:</u>

Pair of electrons shared between two atoms in a covalent bond.

<u>Concept of Valency</u>:

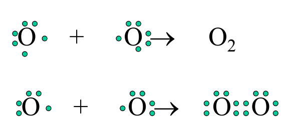
The number of electrons needed to the complete octet (for H, a duet).

Happens to be equal to the # of covalent bonds the atom make to achieve the octet – bonding capacity.



Elements in the same group has the same *normal* valency.

<u>Multiple Bonds</u>:



Double bond , bond order =2

O=O

Note: two bonds on O atom; (valency of O = 2)

:N· + ·N: → N_2

:N· + ·N: → :N⋮N:

Triple bond, bond order =3

N≡N

Note: two bonds on N atom; (valency of N = 3)

Try CO_2

Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

As the bond order increases between two bonded atoms, bond length decreases *and* bond energy (strength) increases.

Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

<u>Polyatomic ions</u>:

Two or more atoms covalently linked atoms, yet the entity carry a charge.

OH^-, NH_4^+, CO_3^{-2}, NO_3^-

Is the sharing of electrons in a given covalent bond equal?

Only in *homo-nuclear* bonds.

<u>Electronegativity</u>: The ability of a covalently bonded atom to draw the 'shared' electrons towards an atom.

<u>Pauling Electronegativity Scale</u>

H 2.1																H 2.1	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9										Hg 1.9						

Non-homo nuclear bonds

H :Ö:
H

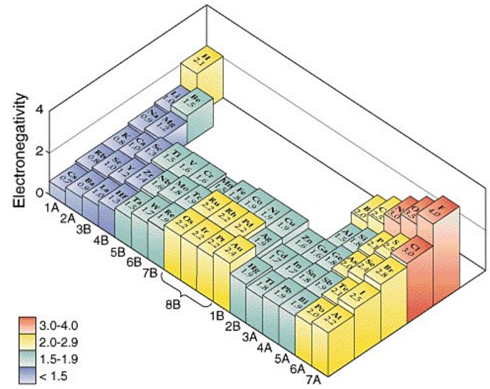
O has a higher affinity of electrons

+δ H→ O: -δ
↑
H
+δ

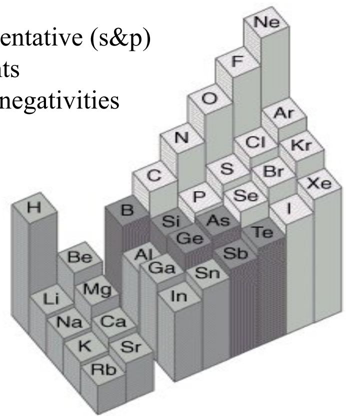
Note: two bonds on O atom; (valency of O =2)

polarization of covalent bonds.

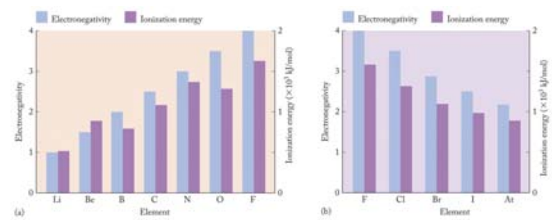
Polar covalent bond.



Representative (s&p) elements electronegativities



Electronegativies and Ionization Energies



EN increases across a row.

EN decreases down a column.

The difference in electronegativity of atoms, ΔEN, of a bond determines the degree of polarization of the bond.

|ΔEN|	>2.0 ionic
	0.5 – 1.9 polar covalent
	< 0.5 non polar covalent

B-Cl	3.0 - 2.0 = 1.0	polar
C-Cl	3.0 - 2.5 = 0.5	polar to a lesser degree
P-F	4.0 - 2.1 = 1.9	polar to a high degree
P-Cl	3.0 - 2.1 = 0.9	polar
NaBr	2.8 - 0.9 = 1.9	highly polar
LiF	4.0 - 1.0 = 3.0	fully ionic

polar = polar (covalent)

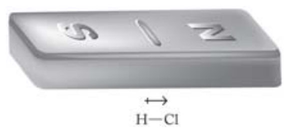
Polar Covalent Bonds

Polar Covalent Bond:

Unequal sharing of electrons in covalent bond resulting in uneven distribution of charge.

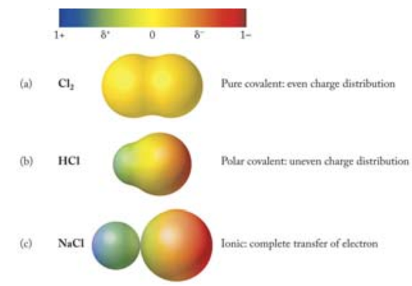
Results from differences in "electronegativity".

Polarity indicated by arrow pointing to more negative end, "+" at more positive end.



Bond Types

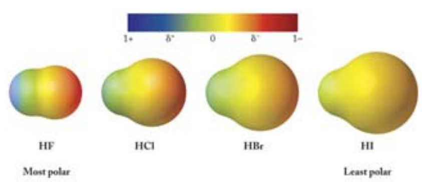
Ionic Polar covalent Covalent



Bond Polarity Trends

Electronegativity increases moving up, to the right in periodic table. (Noble gases not included.)

Bond polarity increases as ΔEN increases.



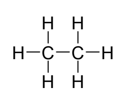
ΔEN = 1.9 0.9 0.7 0.4

Drawing Lewis Structures:

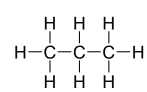
1. Count all available valence e's; charge add for-ve ions, subtract for +ve ions (pool)
2. Calculate # valence electron pairs
3. Find the 'central atom'; high valency atom/low EN
4. Join central atom to 'peripheral atoms' (skeletal structure)
5. Subtract "bonded" pairs from total # of pairs
6. Distribute the *remaining* pairs on peripherals to satisfy their octets
7. Place any left over pairs on central atom
8. If center octet not satisfied, try multiple bonds

CCl_4
CO_2
NH_3
PCl_3
CH_2Cl_2

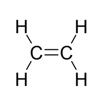
OH^-, NH_4^+, CO_3^{-2}, NO_3^- , PO_4^{-3}



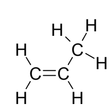
C_2H_6



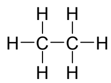
C_3H_8

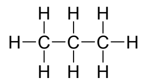


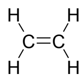
C_2H_4

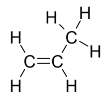


C_3H_6

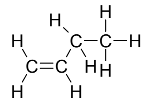

C_2H_6

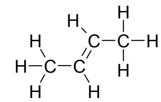

C_3H_8


C_2H_4

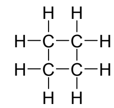

C_3H_6

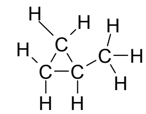
All C are ‘central atoms’.



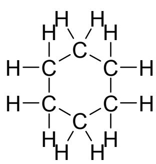


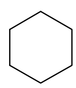
C_4H_8

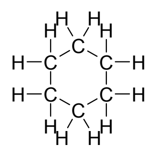


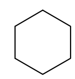


Structural isomers (some) *cycles*





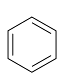


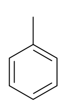


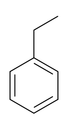
In carbon compounds C are abbreviated as vertexes and junctions; H on them are implied.

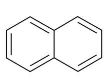
What is the molecular Formula?

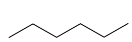

C_5H_{10}

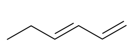

C_6H_6

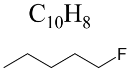

C_7H_8


C_8H_{10}

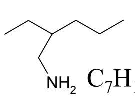

$C_{10}H_8$


C_6H_{14}

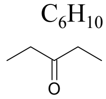

C_6H_{10}



$C_6H_{13}F$



$C_7H_{15}N$



$C_5H_{10}O$

The above method however does not generate a unique Lewis structure, always.

NCS^{-1}

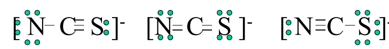
$[N-C\equiv S]^-$ $[N=C=S]^-$ $[N\equiv C-S]^-$

which?

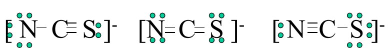
Formal Charge:

Distribute shared electrons equally among the bonded atoms; compare # electrons with the # electrons neutral atom; find '*charge*' that the atom would acquire because of equal sharing; (= formal charge).

Lewis Structure with *smallest* formal charges, with (-) on more EN and (+) on less EN atom of the bond is the correct Lewis structure.



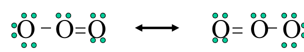
-2 0 +1   -1 0 0   0 0 -1



-2 0 +1   -1 0 0   0 0 -1

Note: sum of all formal charges = actual charge

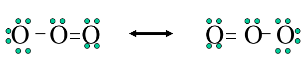
Resonance Structures:

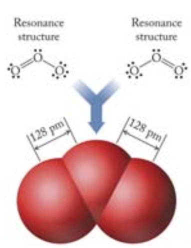


More than one *acceptable* Lewis structures.

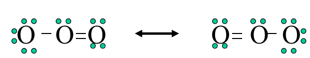
Actual structure is neither one but a hybrid of them; but an "average" of two resonance structures.

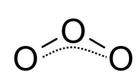
Resonance structures differ in *electron pair assignments* but *never in their atom positions.*





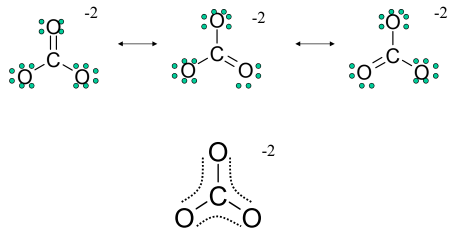
Resonance structures differ in *electron pair assignments* but *never in their atom positions*.



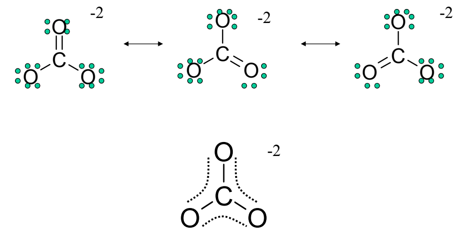


B.O. of actual structure = 1.5

CO_3^{-2}

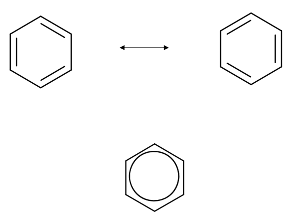


CO_3^{-2}



B.O.= (1/3)2+(2/3)1 = 1.33

C_6H_6

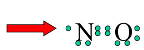


<u>Exceptions to octet rule</u>:

a. Molecules with odd # electrons, <u>free radicals</u>
b. Molecules with insufficient electrons to satisfy all octets, <u>electron deficient</u>
c. Molecules with <u>expanded octet</u>; > 8 e's on central atom
period 3 (row 3) and above
(involvement of empty d orbitals)

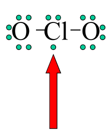
a. NO

5+6 e's



ClO_2

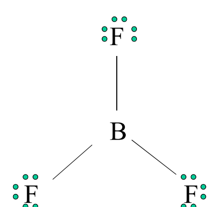
7+12



Free radicals

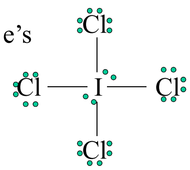
b. BF_3

24 e's



c. ICl_4^-

(35+1) e's



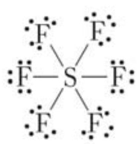
Always try to satisfy the valency of the atoms.

Elements above period 3 *can* have more than 8 electrons (*expanded octet*) in the valence shell.

Expanded valence shells occur:

- In molecules having strongly electronegative elements (F, O, Cl).
- When expanded shell decreases formal charge on central atom (for elements Z >12)

Example: SF_6



Sulfur (S) in SF_6:

- Has $Z > 12$ ($Z = 16$)
- Is bonded to strongly electronegative element (F)
- Has formal charge = 0

Strength of Covalent bonds

Bond Enthalpy/Energy (bond dissociation energy)

Heat absorbed in breaking a particular bond of a molecule in gas phase.

Average bond enthalpy

Mean value of bond dissociation energies of a given type of bond between two specific atoms.

Strength of Covalent bonds

Bond Enthalpy (bond association energy)

Heat absorbed in breaking a particular bond of a molecule in gas phase.

—Si - H → —Si• + •H   ΔH = + 323 kJ/mol

D(Si-H) ↑

note: endothermic

Bond enthalpy larger for stronger bonds.

Strength of Covalent bonds

Other view;

—Si - H ← —Si• + •H   ΔH = - 323 kJ/mol

⇑

note: exothermic

Note the inverse relationship as anticipated.

Average bond enthalpy

Mean value of bond dissociation energies of a given type of bond between two specific atoms.

Use of bond enthalpies to calculate ΔH of reactions:

$$\Delta H_{rxn} = \sum D_{bondbreaks} - \sum D_{bondmakes}$$

$$H-CH_3(g) + Cl-Cl(g) \rightarrow Cl-CH_3(g) + H-Cl(g)$$

break break make make

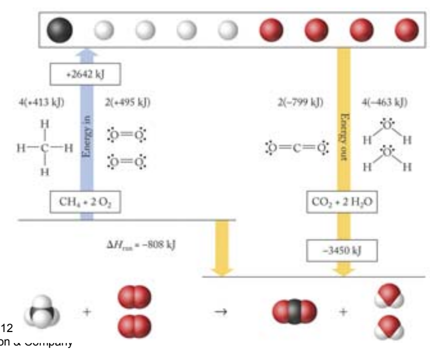
$$\Delta H_{rxn} = \sum D_{bondbreaks} - \sum D_{bondmakes}$$

$$H-CH_3(g) + Cl-Cl(g) \rightarrow Cl-CH_3(g) + H-Cl(g)$$

break break make make

$$\Delta H = [D(CH) + D(ClCl)] - [D(HCl) + D(HCl)]$$
$$= [413 + 242] - [328 + 341] = -104 kJ/mol$$

Example: ΔH_{rxn}



The unequal sharing of ‘shared’ pairs of electrons in ‘covalently bonded’ species,

or

the total transfer of electrons in ionic compounds,

amounts to an oxidation/reduction process; from the point of view from the atoms.