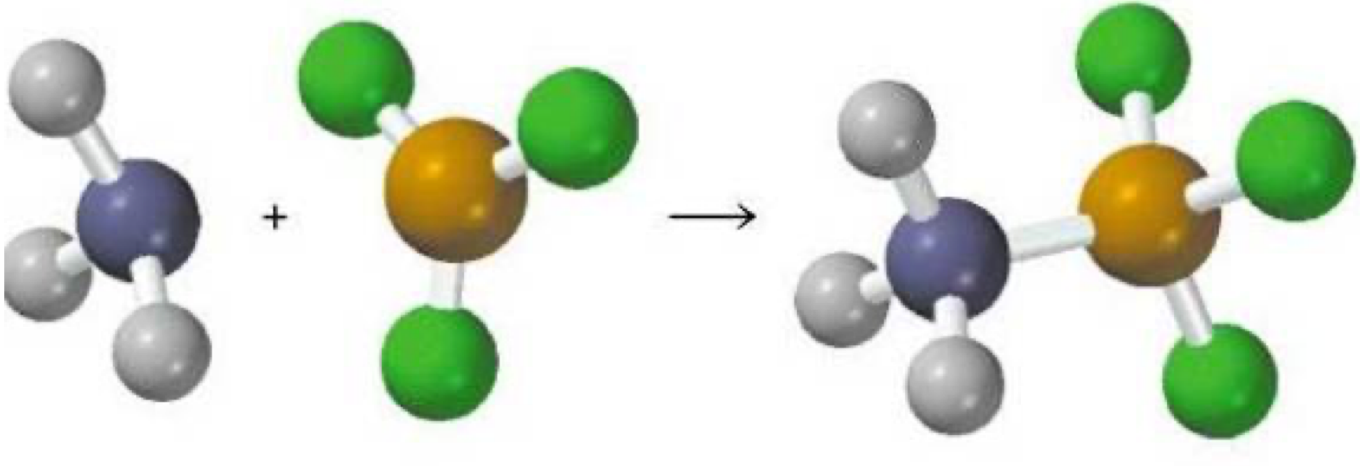
Chapter Nine

Chemical Bonding I

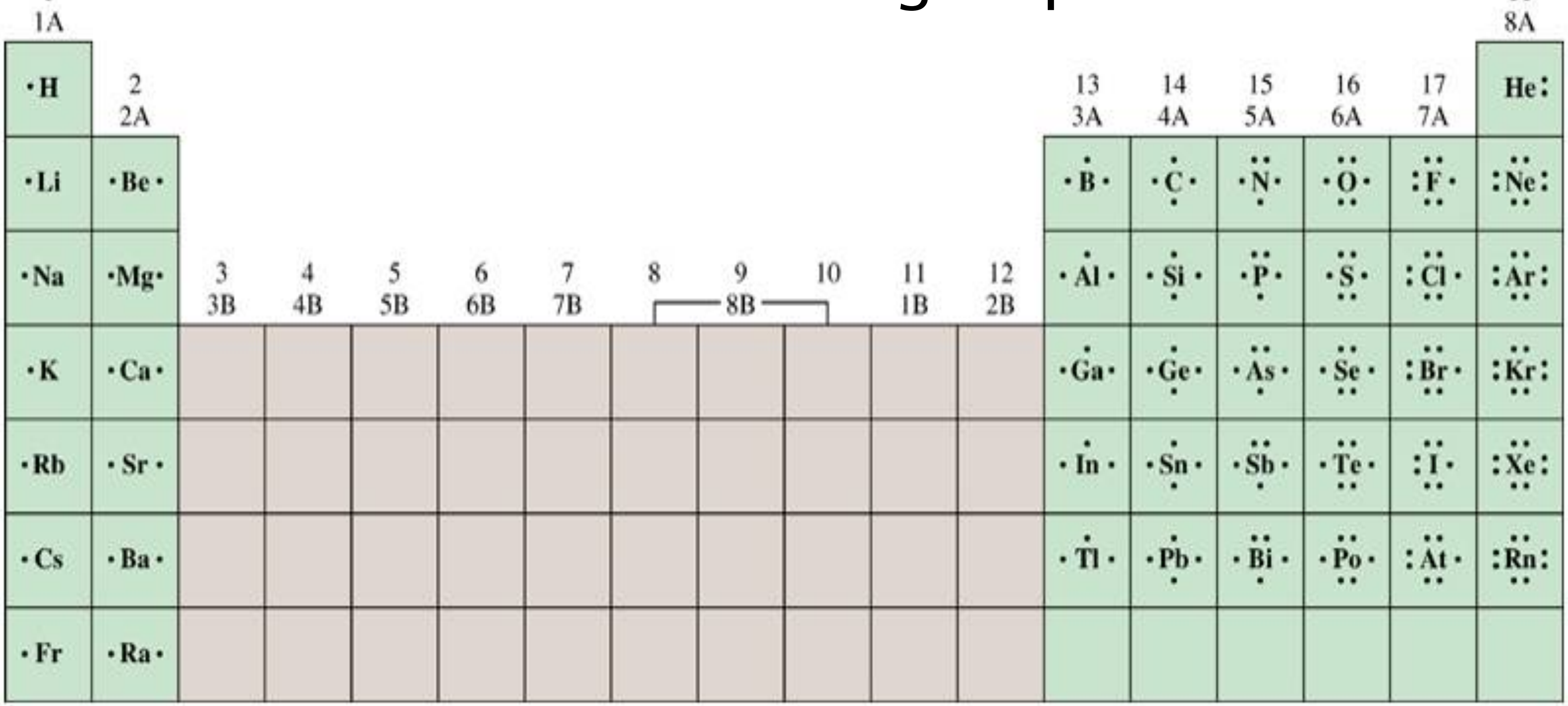


Lewis Dot Symbols

Consists of atomic symbol surrounded by 1 dot for each valence electron in the atom

Only used for main group elements

valence electrons = group number



Drawing Lewis Dot Symbols

Mg

S

Cl

Ar

Ionic Bonding

Electrons are transferred from 1 atom to another

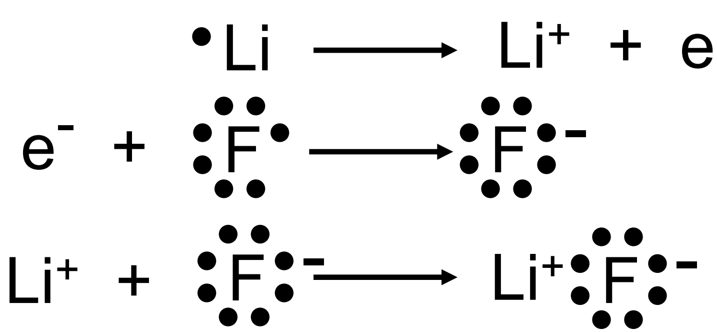
- Metal atoms: Lose electrons to form cations
- Nonmetal atoms: Gain electrons to form anions

Electrostatic force (+ & - attraction) bonds ions into an ionic compound

- Form an ionic salt with repeating structure: NaCl, LiF

Ionic Bonds follow the octet rule

- Atoms lose or gain valence e- to make an octet (8e-)
- 8 valence e- = Noble gas configuration



$1s^2 2s^1 \rightarrow 1s^2$

$1s^2 2s^2 2p^5 \rightarrow 1s^2 2s^2 2p^6$

Ionic Bonding:
Ca & Cl

Lattice Energy – energy released when ions come together to form a crystal

Crystal Formation is an <u>Exothermic Process</u>

Lattice energies are negative for crystal formation, positive when breaking the crystal apart.

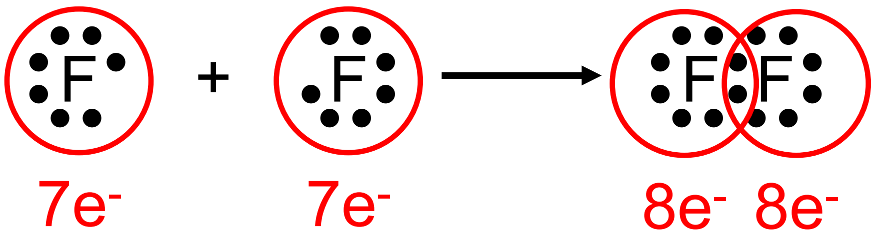
TABLE 9.1 Lattice Energies and Melting Points of Some Alkali Metal and Alkaline Earth Metal Halides and Oxides

Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
LiBr	787	550
LiI	732	450
NaCl	788	801
NaBr	736	750
NaI	686	662
KCl	699	772
KBr	689	735
KI	632	680
$MgCl_2$	2527	714
Na_2O	2570	Sub*
MgO	3890	2800

*Na_2O sublimes at 1275°C.

Lewis Structures

Lewis structures represent covalent bond formation



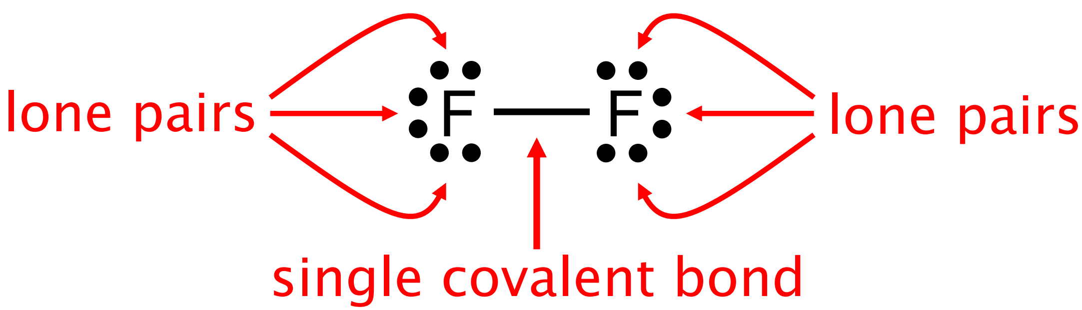
$1s^2 2s^2 2p^5 \rightarrow 1s^2 2s^2 2p^6$

Bonding Pairs: Electrons shared by both atoms

- Represented by a dash (-) between bonded atoms

Lone Pairs: Non-shared electrons count for 1 atom

- Represented by a pair of dots (••) around atom

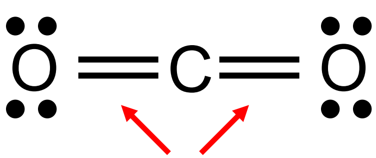


Multiple Bonds

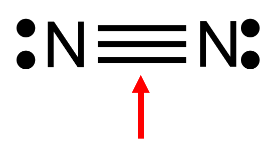
More than one pair of electrons is shared between atoms so each atom can form an octet.

Single Bond:	1 shared pair:	1 dash (-)
Double bonds:	2 shared pairs:	2 dashes (=)
Triple bonds:	3 shared pairs:	3 dashes (≡)

Allows atoms in a molecule to share extra e^- if there are not enough for the central atom



double bonds



triple bond

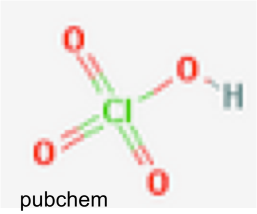
Writing Lewis Structures: Hints & Tips

Electronegativity

- Central atom usually has the **lowest** electronegativity
  (atom lower or to the left in periodic table)
- Terminal atoms (except H) have **higher** electronegativities

Terminal Atoms

- Bonded to only one other atom
- Hydrogen atoms are terminal atoms
- Halogens (col 17) are often terminal atoms



Oxoacids

- Hydrogen atoms are bonded to oxygen atoms in oxoacids

Hints & Tips for Drawing Lewis Structures Con't

- Final structure must include same number of valance e^- as sum of valance e^- from all atoms in the molecule
- Final structure must satisfy octet rule (unless it is an exception)
- Start with single bonds, try double then triple if necessary
- **Hydrogen** only wants one more e^-
  - forms ONE SINGLE BOND
  - will not be between two atoms
- **Carbon** usually does not have lone pairs
  - all 8 e^- must come from single, double, or triple bonds
- **Halogens** only want one more e^-
  - generally only form <u>one single bond</u>
- Molecules are often symmetrical
  - try single atom in middle with other atoms around it

Example: Write the Lewis Structure of HNO

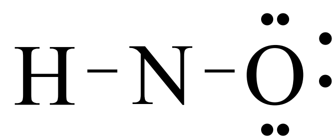
1. Add up the valence electrons in the structure

   1(H) + 5(N) + 6(O) = 12 valence electrons

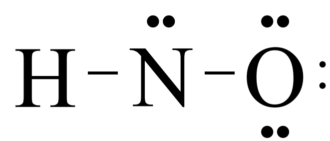
2. Arrange the atoms & place bonding electrons

   H–N–O nitrogen less electronegative, put in center

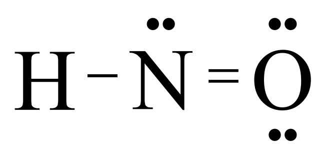
3. Place e- pairs around terminal atoms to get 8



4. Place remaining electron pairs on central atom



5. Add double bond to finish nitrogen octet (8)



Drawing Lewis Structures:

CH_4

N_2

CO_2

NF_3

Drawing Lewis Structures: Polyatomic ions & simple organic molecules

CO_3^{2-}

C_2H_6

$C_2H_2I_2$

C_2H_6O

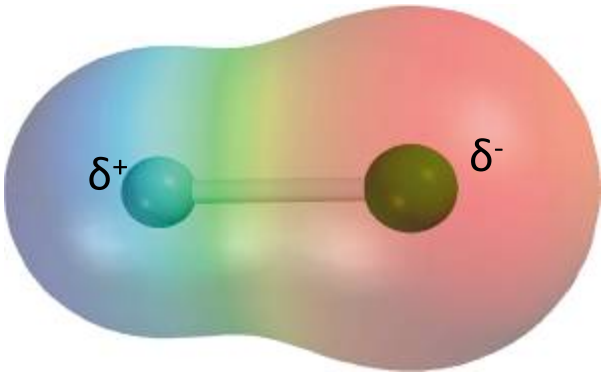
C_3H_6O

Orgo – degrees of unsaturation:
C_nH_{2n+2} – all single bonds
C_nH_{2n} – one double bond (or ring)
C_nH_{2n-2} – 1 triple bond, 2 double bonds, 2 rings, double bond + ring

– 2 for each double bond/ring
– 4 for each triple bond

Electronegativity & Polar Covalent Bonds

Electronegativity



- The ability of an atom to attract e^-
- F is the most electronegative atom
- Nonmetals - high electronegativities

Polar Covalent Bonds

- Differences in electronegativity result in unequal sharing of electrons between atoms
- More electronegative atom has a partial neg. charge (δ^-)
- More electropositive atoms has a partial pos. charge (δ^+)

Percent Ionic Character

- Measure of polarity of bond
  - 100% ionic is full transfer of electron, no sharing
  - 100% covalent is equal sharing, H_2, Cl_2, etc.

Electronegativities of Common Elements

Increasing electronegativity →

Increasing electronegativity ↑

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	
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** 3.0
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** 2.6
Cs 0.7	**Ba** 0.9	**La-Lu** 1.0-1.2	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.9	**Bi** 1.9	**Po** 2.0	**At** 2.2	
Fr 0.7	**Ra** 0.9																

Electronegativity Difference determines bond type

0 – 0.4	0.4 – 1.7	1.7 – 4
Nonpolar	Polar	Ionic

F & Na: 4.0 – 0.9 = 3.1 = ionic

C & H: 2.5 – 2.1 = 0.4 = nonpolar covalent

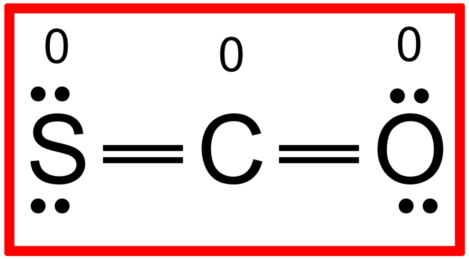
Formal Charge

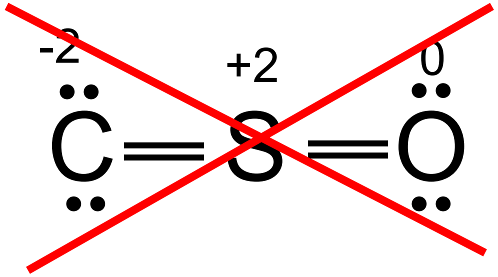
Difference between the # of valence e⁻ in a free atom & the # of e⁻ assigned to that atom in a Lewis structure.

F.C. = # ve⁻ - (# of lone e- + # bonds)

Get #ve⁻ from group #

Molecule is most stable if formal charge is 0 for each atom.





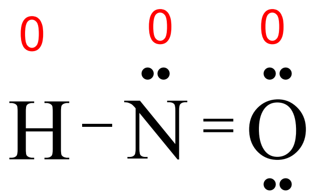
- Most likely Lewis structure has lowest formal charges
- Negative F.C. must be on more electroneg. atom
- Sum of formal charges:

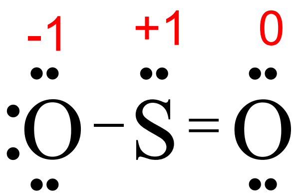
    Molecules = 0

    Polyatomic ions = charge

Calculating formal charge

F.C. = # ve$^-$ - (# of lone e- + # bonds)

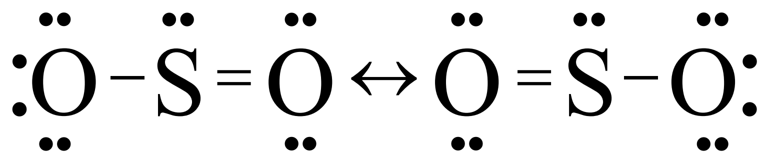




Resonance Theory

If a molecule or ion can be represented by 2 or more Lewis structures that differ only in electron location, the true structure is a blend of those structures.

- Electrons are moving around the molecule
- Neither bond is completely single or double (1.5)



-1 +1 0 0 +1 -1

Resonance Structures

- Equivalent Lewis structures for a single molecule
- Formal charges will usually be present

Delocalization

- Electrons are shared by more than two atoms
- Stabilizes the molecule

Exceptions to the Octet Rule: Incomplete Octet

Not enough electrons for central atom to have 8

BeH_2

$$\begin{array}{r} \text{Be} - 2e^- \\ \text{2H} - 2\text{x}1e^- \\ \hline 4e^- \end{array}$$

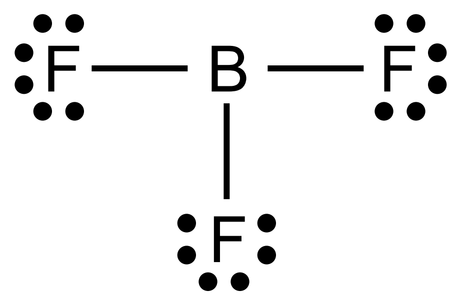
H—Be—H

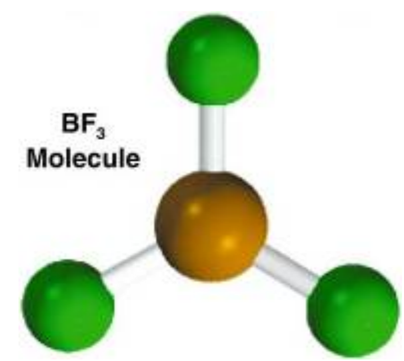
Terminal atoms unwilling to donate more electrons

- Would destabilize terminal atoms & create formal charge

BF_3

$$\begin{array}{r} \text{B} - 3e^- \\ \text{3F} - 3\text{x}7e^- \\ \hline 24e^- \end{array}$$

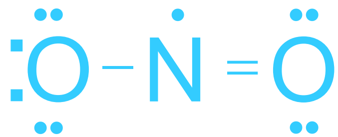




Free Radicals and Expanded Octets

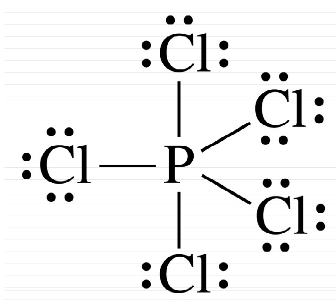
Free Radicals:

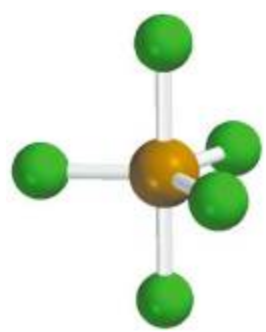
- Molecules with an odd number of valence electrons (N)
- Extremely reactive, odd electron wants to be part of a pair

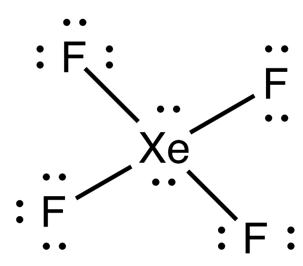


Compounds with expanded valence shells

- Central atom has more than eight electrons
- May have lone pair electrons as well as bonding pairs
- Must be in column 3 or above to have an expanded octet







Drawing Lewis Structures: Exceptions to the Octet Rule

$XeCl_2$

H_2SO_4

PI_5

BeF_2

Coordinate Covalent Bonds

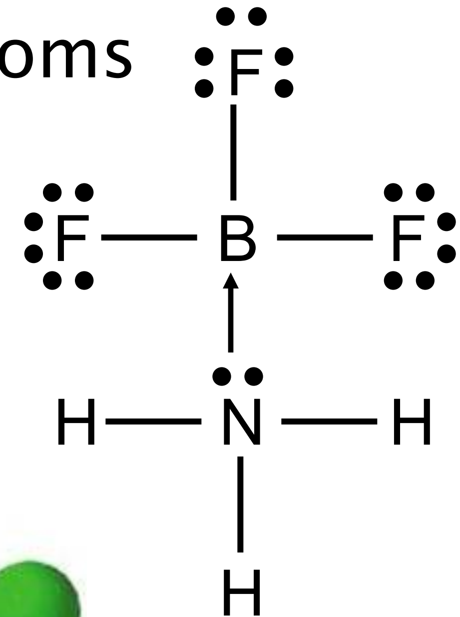
1 atom provides both electrons

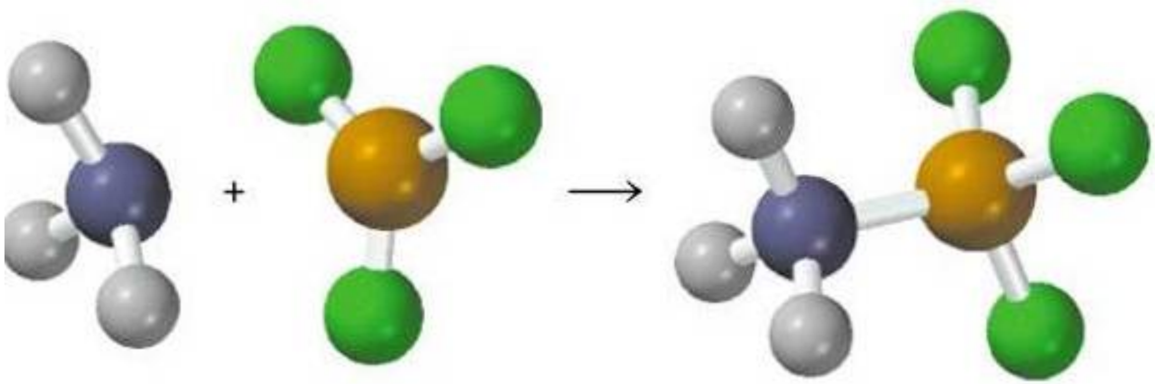
Electrons are then shared between 2 atoms

Ex: BF_3 and NH_3

B needs 2 electrons to fill octet

N has a lone pair to share



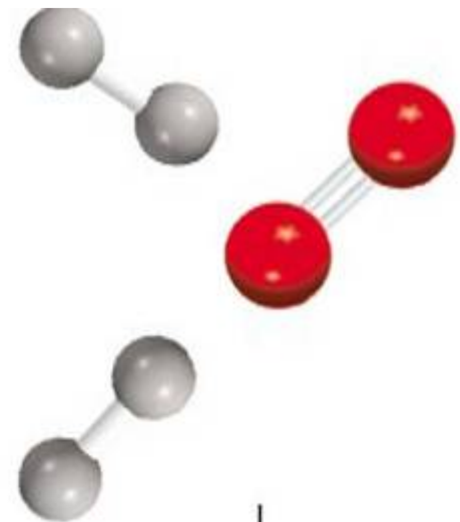


Seen often with transition metals – can accept electrons into empty d-orbitals

Bond Enthalpy

Bond Enthalpy

- Energy required to break a particular bond in a molecule in the **gas** phase.

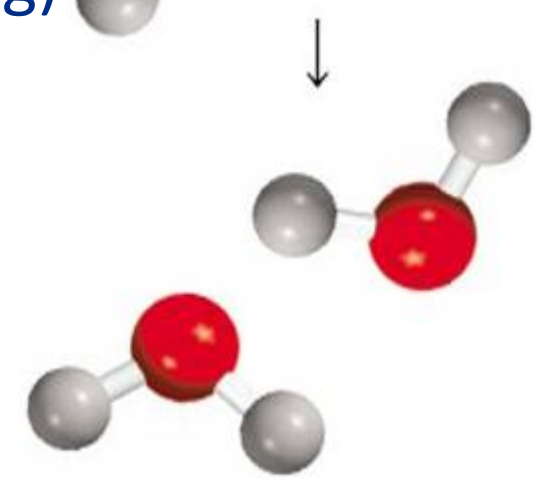


Enthalpy change for the Reaction (ΔH)

$\Delta H = \Delta H_{\text{bond breaking}} + \Delta H_{\text{bond formation}}$ Hess' Law!

(Note that bond formation is <u>**negative**</u>)

Enthalpy change: $2H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$



$\Delta H_{\text{bond breaking}} = 2\Delta H_{\text{H-H}} + \Delta H_{\text{O=O}}$

$= 2(436\text{kJ}) + 499\text{kJ}$

$= 1371\text{kJ}$ (endothermic)

$\Delta H_{\text{formation}} = 4\Delta H_{\text{H-O}} \quad = 4(460\text{kJ})$

$= 1840\text{kJ}$ (exothermic)

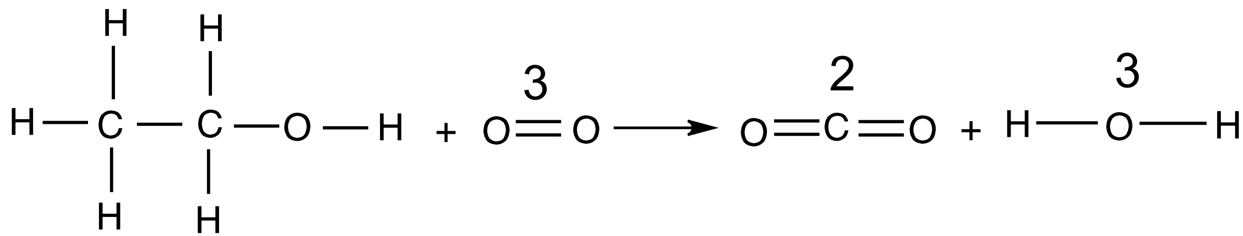
$\Delta H_{\text{reaction}} = \Delta H_{\text{bond breaking}} + \Delta H_{\text{bond formation}}$

$\Delta H_{\text{reaction}} = 1371\text{kJ} - 1840\text{kJ} = -469\text{kJ}$

Theoretical Calculation of ΔH

$$\Delta H = \Delta H_{\text{bond breaking}} + \Delta H_{\text{bond formation}}$$

$$CH_3CH_2OH + 3\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$$



C-C Bond = 80 kcal/mole

C-H Bond = 100 kcal/mole

C-O Bond = 90 kcal/mole

O=O Bond = 120 kcal/mole

O-H Bond = 110 kcal/mole

C=O Bond = 180 kcal/mole

$\Delta H_{\text{bond breaking}}$

1 C-C bond x 80 kcal/mol = 80 kcal/mol
5 C-H bonds x 100 kcal/mol = 500 kcal/mol
1 C-O bond x 90 kcal/mol = 90 kcal/mol
1 O-H bond x 110 kcal/mol = 110 kcal/mol
3 O=O bond x 120 kcal/mol = 360 kcal/mol

1140 kcal/mol

$\Delta H_{\text{bond formation}}$

2x2 C=O bonds x 180 kcal/mol = 720 kcal/mol
3x2 O-H bonds x 110 kcal/mol = 660 kcal/mol

1380 kcal/mol

$$\Delta H = \Delta H_{BB} + \Delta H_{BF}$$
$$= 1140 \text{ kcal/mol} - 1380 \text{ kcal/mol}$$
$$= -240 \text{ kcal/mol}$$

Estimate the enthalpy change for the combustion of 1 mole of methane

1. Write the reaction: $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

2. Calculate energy needed to break the bonds in reactants (ΔH_{BB}) and energy produced when the bonds of products form (ΔH_{BF}).

Bonds broken	ΔH	Bonds formed	ΔH

3. Calculate ΔH for the reaction ($\Delta H = \Delta H_{BB} + \Delta H_{BF}$) & divide by coefficient of CH_4.

$\Delta H_{approx} =$

A = – 785 kJ/mol methane

Representative Bond Enthalpies

TABLE 9.3 Some Bond Enthalpies of Diatomic Molecules* and Average Bond Enthalpies for Bonds in Polyatomic Molecules

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615	S=S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C=O†	745	Br—Br	192.5
C—P	263	I—I	151.0

C=O in CO_2: 799 kJ/mol