Chapter 8

Basic Concepts of Chemical Bonding

Chemical Bonds

forces of attraction which hold atoms or ions together

3 fundamental types of bonding

Ionic - metals & nonmetals

Covalent - nonmetals (semimetals)

Metallic - metals

B) Lewis Symbols & Octet Rule

Valence e^- involved in chem. bonding

For representative elements:

e^- in highest energy s & p subshells

val. e^- **=** group **#**

1) Lewis Symbols

Represent e^- in the s & p orb. of the valence shell as dots arranged around the symbol of the element.

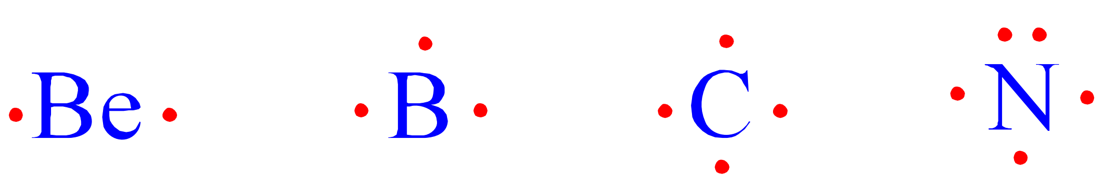
s
p E p
p

a) Separate Atoms

Show e⁻ as they appear in the orbital diagram

b) For Bonding

Place e⁻ around symbol singly before pairing



2) "OCTET" Rule

Atoms tend to gain, lose or share e^- to achieve noble gas configuration.

$$ns^2\ np^6 \qquad (\text{or } 1s^2)$$

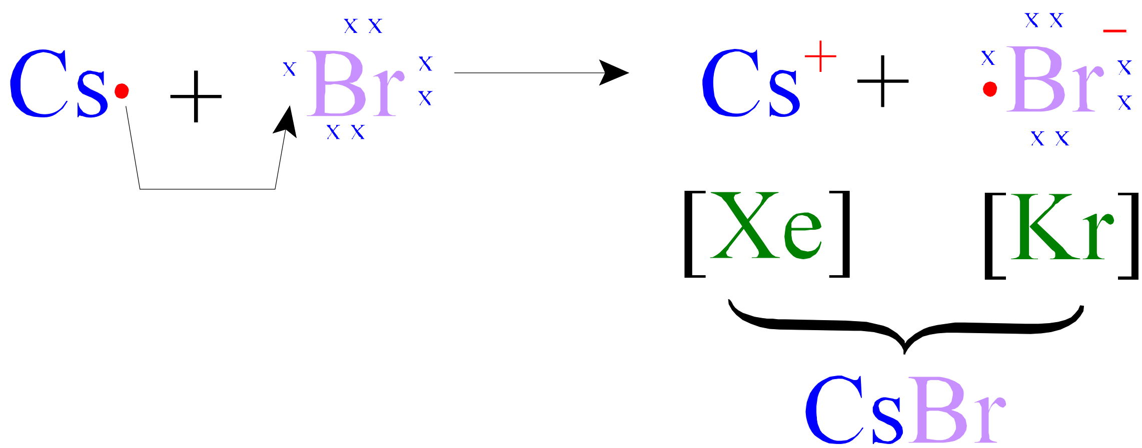
Full s & p subshells

II) Ionic Bonding

electrostatic attraction between
(+) & (−) ions resulting from
complete e^- transfer

- Cations & Anions formed

Show using e^- dot or Lewis Structures

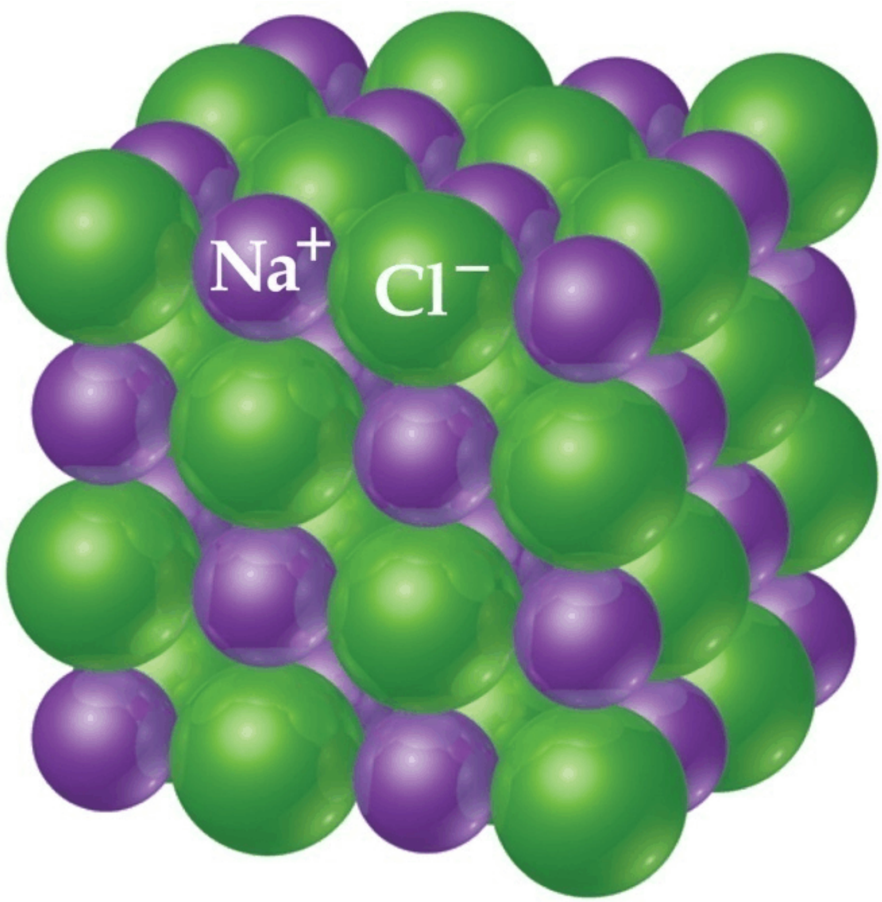


Cs: metal, low I.E.

Br: nonmetal, large neg. EA

A) Energetics

Ionic cmpd. is an array (lattice or crystal structure) of (+) & (–) ions, packed so attractive forces between ions of opposite charges are maximized & repulsive forces between ions of same charge are minimized.



1) Lattice Energy

Measure of the strength of attraction between (+) & (−) ions

Energy required to separate 1 mole of ionic solid to gaseous ions

$$NaCl\,(s) \rightarrow Na^{+}\,(g) + Cl^{-}\,(g)$$

$$LE \propto \frac{Q_1\,Q_2}{d}$$

Q_1, Q_2 : charges on ions

d : distance between ions
- sum of ionic radii

For a given arrangement of ions:

LE inc. as charges on ions inc. & as their radii dec.

i.e. Greater charges and smaller ions => greater LE

a) Charge is more impt. factor

$CaS > (CaBr_2, K_2S) > KBr$

b) Same charges, consider size

$LiF > KF > KBr > CsBr$

			Sum of radii (Å)	LE (kJ/mol)
KF	K^+	F^-	2.71	808
CaO	Ca^{2+}	O^{2-}	2.40	3414
ScN	Sc^{3+}	N^{3-}	2.44	7547

Ionic bonds are very strong resulting in very high melting points (m.p.) but solids are brittle as they cleave along planes of ions.

2) Born-Haber Cycle

$$NaCl\,(s) \rightarrow Na^{+}\,(g) + Cl^{-}\,(g)$$

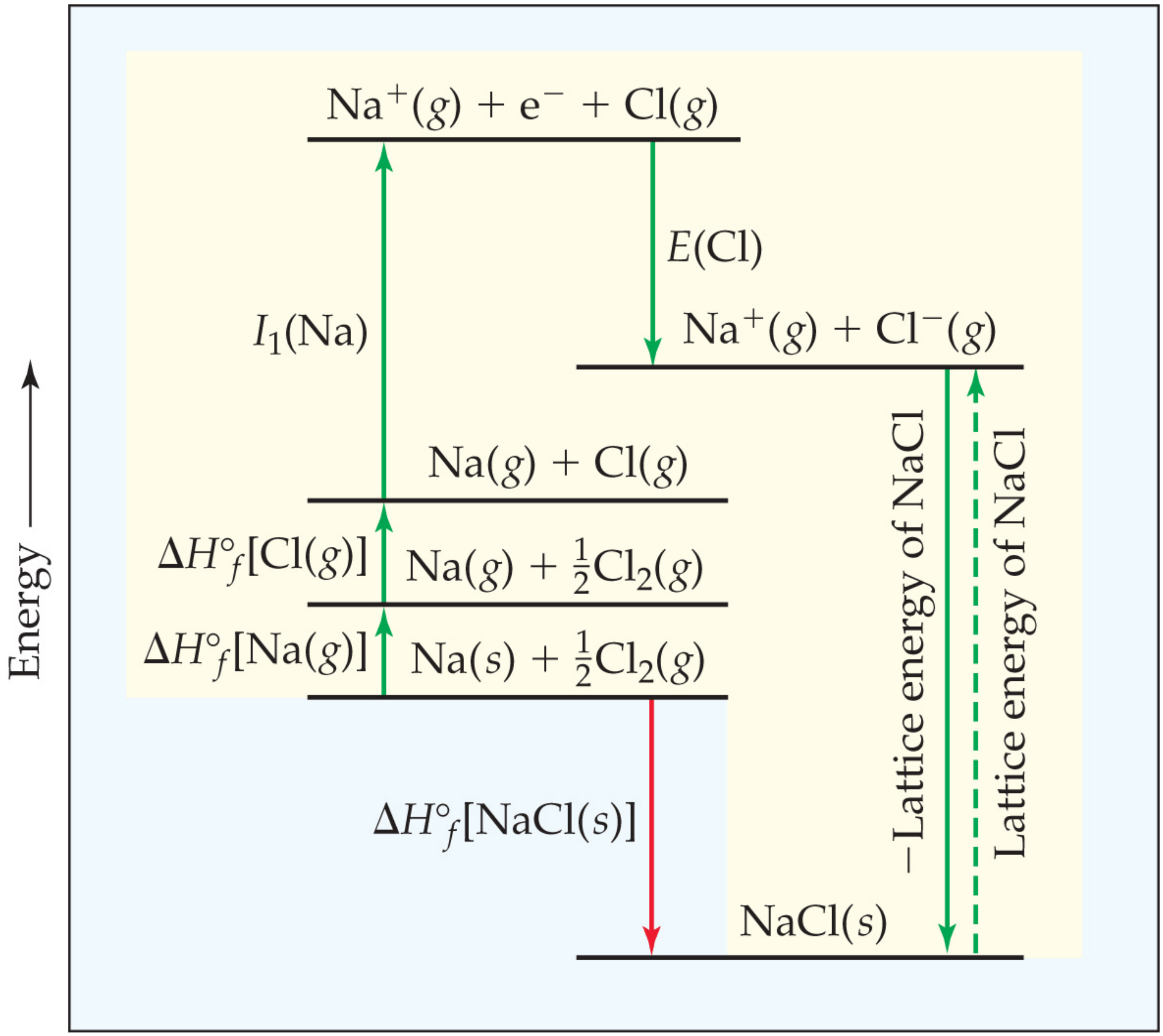
LE = ?

Born-Haber Cycle

- analyze the formation rxn. for ionic solid as a series of steps

(based on Hess's Law)

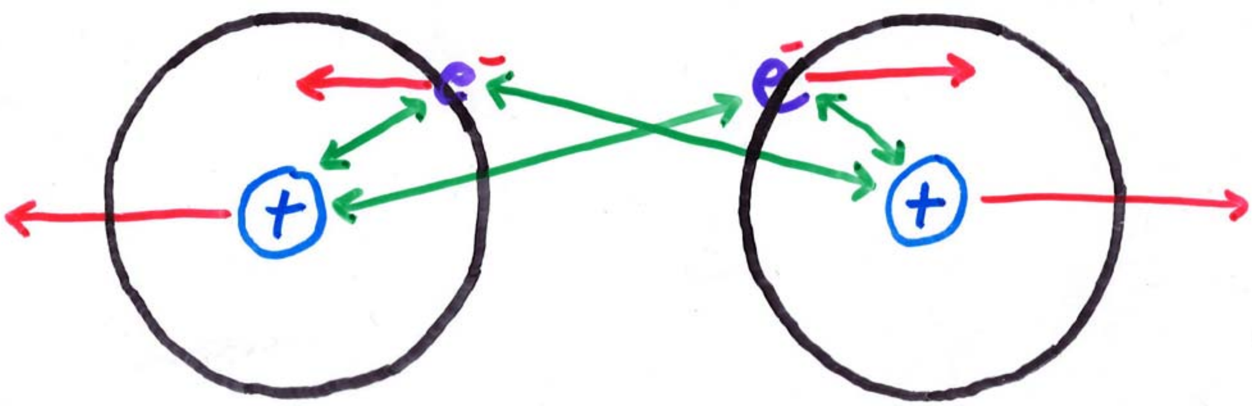
Born-Haber Cycle for formation of NaCl(s)



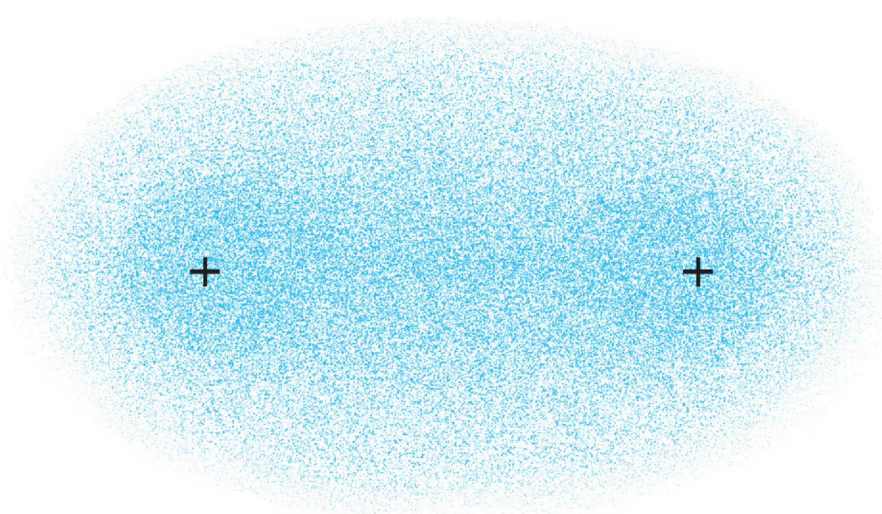
III) Covalent Bonds

Not complete e^- transfer

Covalent Bond: pair of e^- are shared



H H



A) Single Bond

2 e^- shared by 2 atoms

$$H\bullet \quad + \quad \bullet H \longrightarrow H\bullet\ \bullet H$$

Attraction of e^- for both nuclei that holds molecules together

Lewis Structure

replace bonding e^- pair w. line

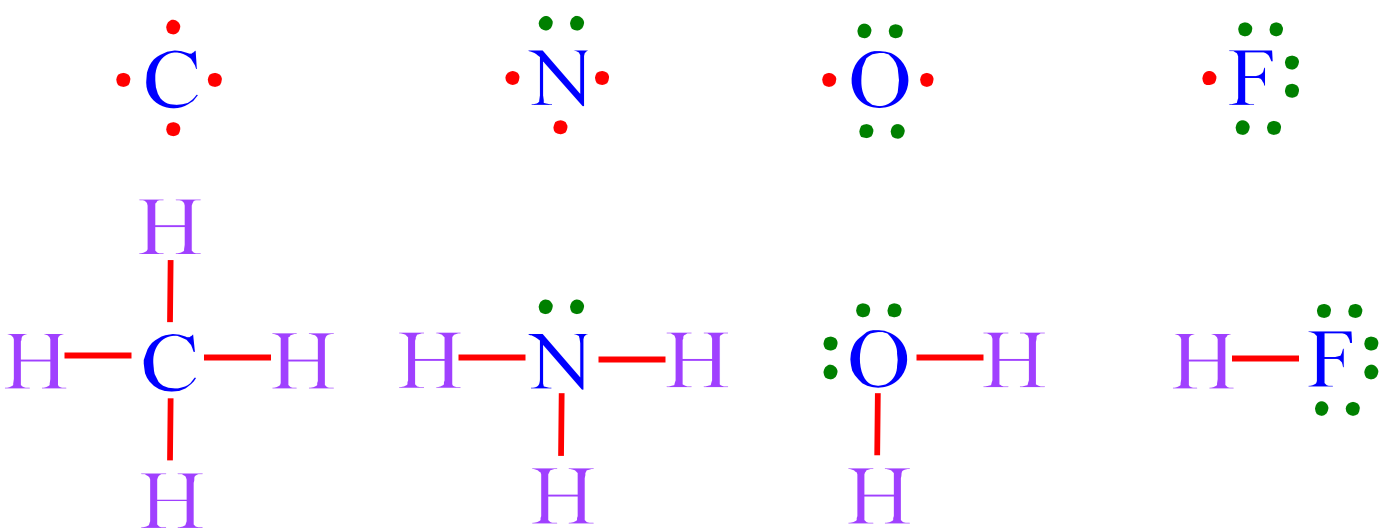
$$H\text{—}H$$

- single bond

B) Group No. & Number of Bonds Formed

Atoms combine to achieve noble gas config., $1s^2$ or ns^2np^6, an OCTET

4A	5A	6A	7A



4	3	2	1

Unshared e^- pairs shown as dots :

nonbonding or lone pair e^-

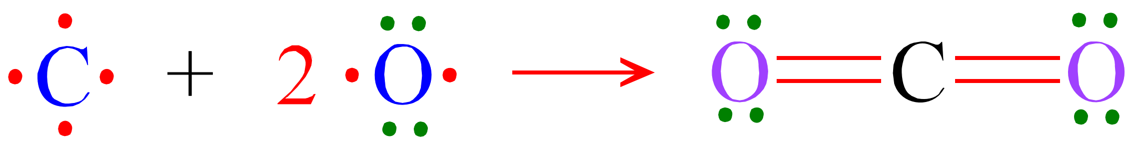
C) Multiple Bonds

Complete octet by forming more than one bond between same 2 atoms

1) Double Bond

Sharing of 2 pairs of e^- ($4\ e^-$)

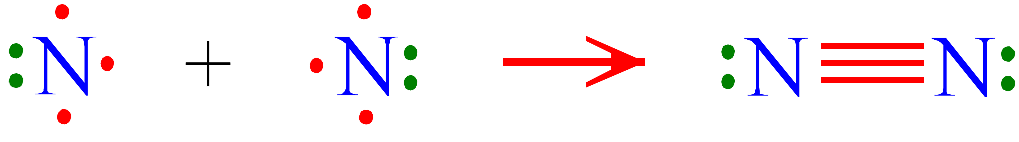
CO_2



2) Triple Bond

Sharing of 3 pairs of e^- ($6\ e^-$)

N_2



IV) Bond Polarity & Electronegativity

A) Bond Polarity

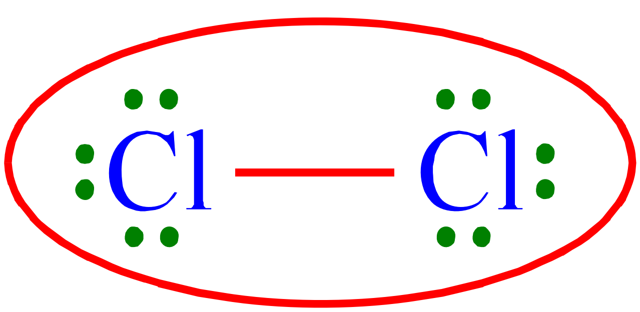
1) Ionic Bond

complete e^- transfer

Cs^+ Cl^- e^- from Cs^+ spends most of its time in vicinity of Cl^-.

2) Pure Covalent Bond:

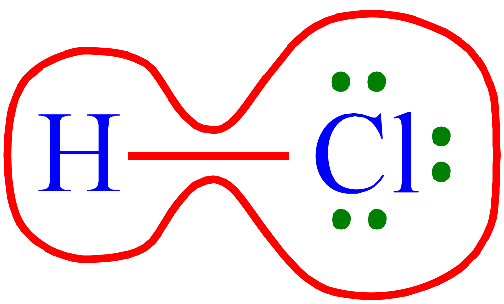
e^- pair shared equally by 2 identical atoms



3) Polar Covalent Bond:

e⁻ pair shared unequally between 2 diff. atoms

- Somewhere between ionic & covalent bonds



Dipole : (+) & (−) charges separated by a distance

Extent of polarity depends on IE and EA of 2 atoms involved

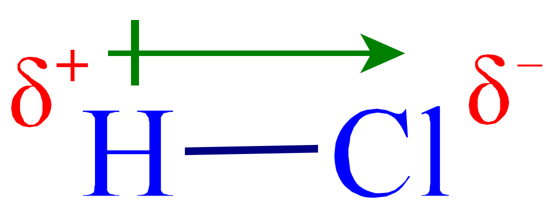


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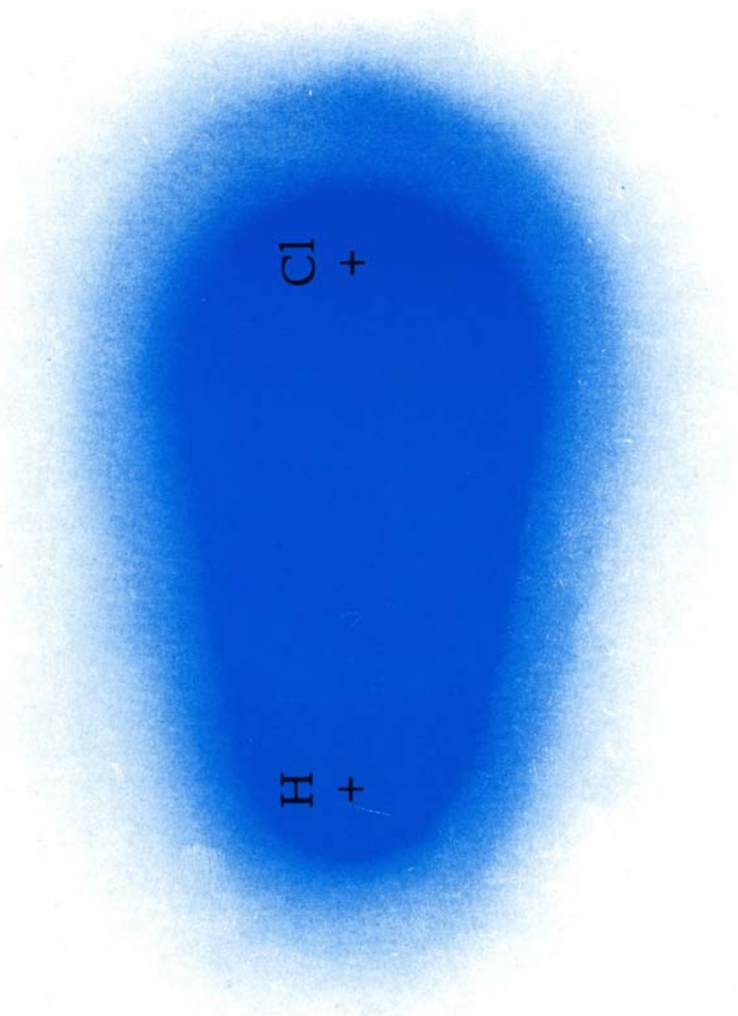
Figure 7.4 Distribution of bonding electrons in HCl



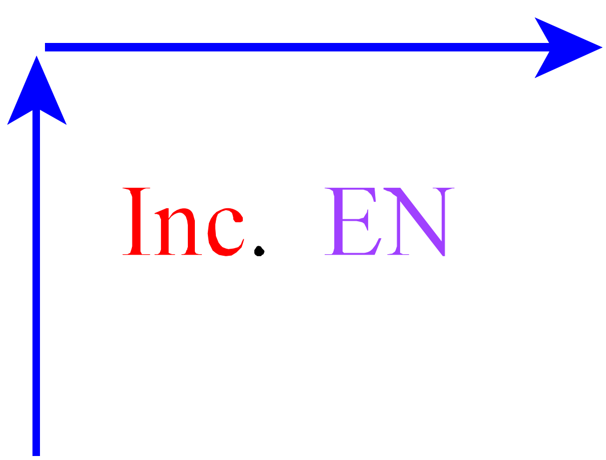
B) Electronegativity

Reflects the ability of an atom in a molecule to attract bonding e^- to itself.

- depends somewhat on bonds formed & rest of molecule

Relative Scale:

F is most EN element and has a value of 4.0 (Pauling Scale)



increasing electronegativity →

IA	IIA	IIIA	IVA	VA	VIA	VIIA
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	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9					

↑ increasing electronegativity

C) EN & Bond Polarity

Generally, use diff. between E.N. to predict the type of bond formed.

$\Delta EN > 2.0$ ionic

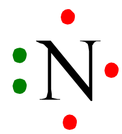
$0.5 \leq \Delta EN < 2.0$ polar covalent

$\Delta EN < 0.5$ nonpolar covalent

$\Delta EN = 0$ pure covalent

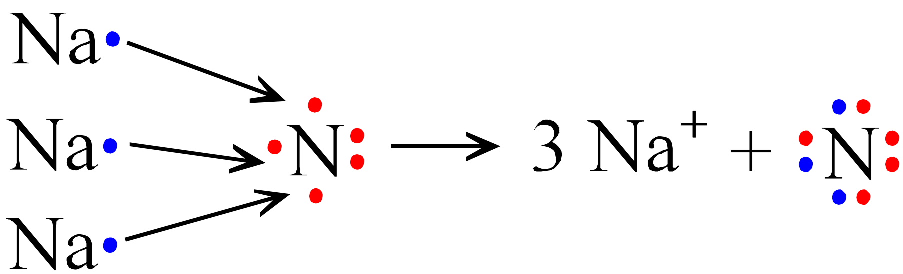
Nitrogen Can Acheive the Noble Gas Configuration of Neon in Three Ways

Lewis structure of nitrogen atom, Group 5A



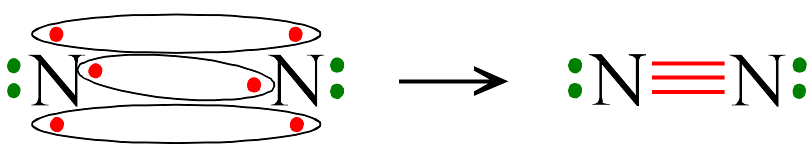
three electrons short of neon configuration

1. electron transfer ⟶ ionic bond



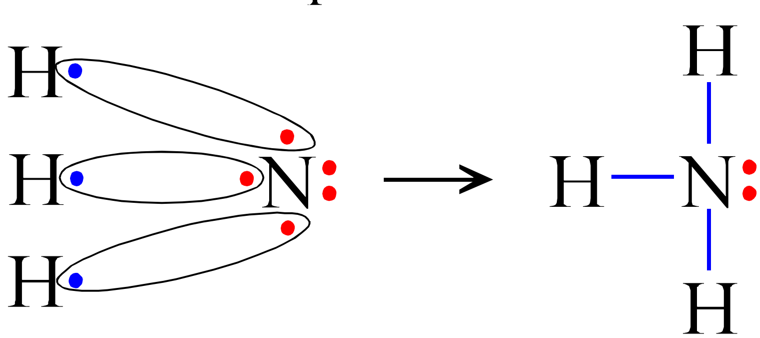
or Na_3N

2. equal sharing of electron pairs ⟶ pure covalent bond



or N_2

3. unequal sharing of electron pairs ⟶ polar-covalent bond



or NH_3

D) Dipole Moment

A polar molecule has opposite charges separated by a distance,

it has a dipole moment

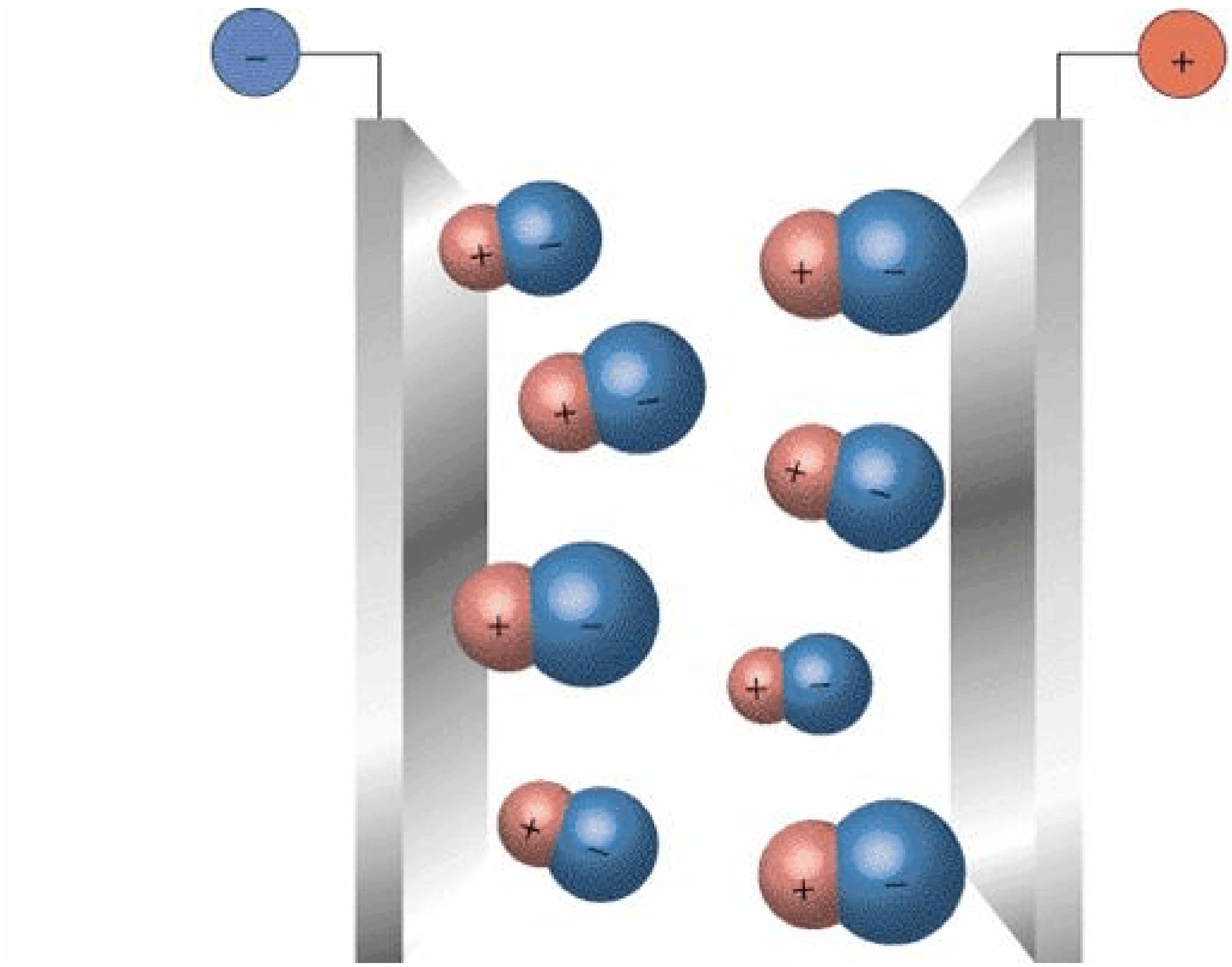
magnitude of charge × distance between charges

$\mu = Q \bullet r$ (Debye, D)

1 D = 3.34×10^{-30} coulomb-meters

The magnitude of the charge is indicated by the difference in EN & the distance which is the bond length

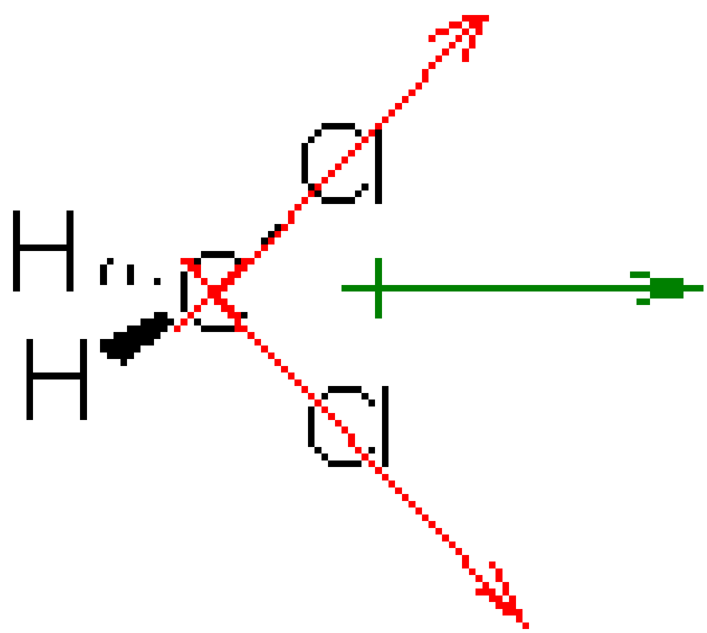
Polar molecules interact w. electric fields



Experimentally the dipole moment is determined by how the molecule behaves in an electric field.

The more polar the molecule, the larger the dipole moment.

The molecular dipole moment is the vector sum of the bond moments, i.e.



1) Ex: Calculate dipole moment and partial charges on the atoms for HF. The bond length is 0.92 Å.

a) Calc. dipole moment assuming charges of +1 and −1

$$\mu = Q \bullet r$$

$$r = 0.92\ \text{Å} \times (10^{-10}\ \text{m}/1\ \text{Å})$$

$$\mu = (1.60 \times 10^{-19}\ \text{C})(9.2 \times 10^{-11}\ \text{m})\left(\frac{1\ \text{D}}{3.34 \times 10^{-30}\ \text{C}\bullet\text{m}}\right)$$

$$\mu = 4.\mathbf{4}07\ \text{D}$$

b) Calc. partial charges in *e*

Experimentally, $\mu = 1.82$ D

$$Q = \frac{\mu}{r}$$

$$= \frac{(1.82\ D)\ (3.34 \times 10^{-30}\ C \bullet m / 1\ D)}{(0.92 \times 10^{-10}\ m)}$$

$$= 6.\underline{\mathbf{6}}07 \times 10^{-20}\ C$$

Q in *e*:

$$= (6.607 \times 10^{-20}\ C) \times \frac{1\ e}{1.60 \times 10^{-19}\ C}$$

$$= 0.4\underline{\mathbf{1}}2\ e$$

$$\overset{0.412+}{H} \text{———} \overset{0.412-}{F}$$

TABLE 8.3 ■ Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

V) Lewis Structures, (LS)

Very simple model of chemical bonding and the structure of molecules.

deals with valence shell e^-

- generally think octet rule

Do not provide information about the observed geometry (shape) of molecules, explain how or why bonds form, or how the e^- are shared in bonds.

A) <u>2 General Requirements</u>

1) All val. e^- must be shown

2) All atoms generally have octet of e^-

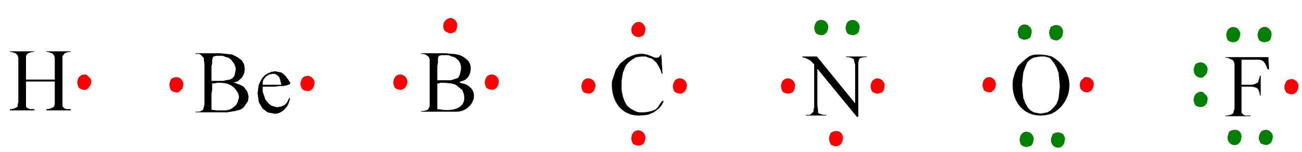
a) <u>Exceptions</u>

H Li Be B (Al) less than octet

Periods 3-6 greater than octet

B) <u>Number Bonds Atoms Generally form?</u>

- determined by possible # unpaired e^- in valence shell



1 2 3 4 3 2 1

B) Procedure for Drawing Lewis Struc.

1) Number val. e^- Available, A

Determine total # val. e^-

val. e^- = group

a) adjust for charge

1) subtract for (+) chg.

H_3O^+

$A = 3(1) + 1(6) - 1 = 8$ e^- avail.

2) add for (−) chg.

CO_3^{2-}

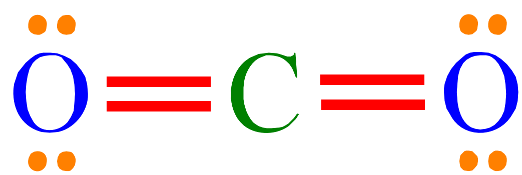
$A = 1(4) + 3(6) + 2 = 24$ e^- avail.

2) Draw Skeleton Structure

Connect atoms w. single bond

a) least E.N. element is usually central element (except H)

CO_2



b) Multiple O-atoms usually bonded to central atom (not to each other)

3) Complete octets on terminal atoms

4) Place remaining e^- on central atom

$$\frac{\#\, e^-}{\text{remaining}} = \frac{\#\, e^-}{\text{available}} - \frac{\#\, e^-}{\text{used}}$$

distribute on central atom

- for every 2 e^- short form 1 more bond to central atom

(form multiple bonds)

5) Check Formal Charges

C) Examples

1) H_3O^+

a) How many e^- do we have ?

O H +1 chg

$6\ e^- + 3(1\ e^-) - 1\ e^- = 8\ e^-$

b) Draw skeleton struct. &
distribute e^-

c) Complete octet on central atom

2) ClO_2^-

a) How many e^- do we have ?

Cl O -1 chg

$7\ e^- + 2(6\ e^-) + 1\ e^- = 20\ e^-$

b) Draw skeleton struct. &

distribute e^-

c) Complete octet on central atom

3) Cl_2CO

a) How many e^- do we have ?

Cl		C		O		
$2(7\ e^-)$	+	$4\ e^-$	+	$6\ e^-$	=	$24\ e^-$

b) Draw skeleton struct. &

distribute e^-

c) Complete octet on central atom

D) Formal Charges

Decide which alternative Lewis structures are most important

1) Bonding e^- divided equally between atoms forming the bond

- homolytic bond cleavage

2) Nonbonding e^- assigned entirely to atom on which they reside

FC = # val. e^- – (½ # bond e^- + # n.b.e.)

3) Should add to give actual charge on molecule

Note:

do NOT represent real charges (not same as ox. numbers.)

3) Rules

a) Choose LS with lowest magnitudes of FC's

- lowest sum of absolute values of FC's

b) Choose LS w. (−) FC on more EN atom whenever possible

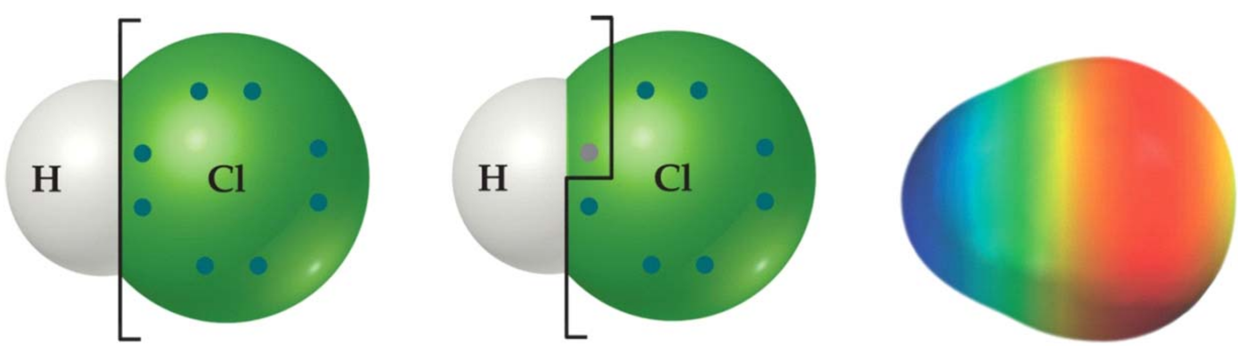
c) Adjacent Charge Rule

LS w. FC of same sign on adjacent atoms are NOT likely

Note: Oxidation numbers and FC are NOT the same thing.

a) Ox. #'s are calculated by assigning ALL electrons in a bond to the more EN atom - heterolytic bond cleavage

b) FC are calculated by assigning the electrons in a bond equally to both atoms - homolytic bond cleavage



(a) (b) (c)

4) Ex: N_2O, nitrous oxide

a) Valence e^-

2 N O

b) Skeleton Structure

N N O

c) Complete octets

\# e^- left

Middle N 4 e^- short

N N O N N O

Why not the following:

N N O

N O N

N O N

VI) Resonance Structures

Sometimes can draw more than one acceptable Lewis Structure

Resonance Structures

Differ only in the placement of the e^-

Actual structure is an "average" or "combination" of ALL the resonance forms

e^- are delocalized over several atoms

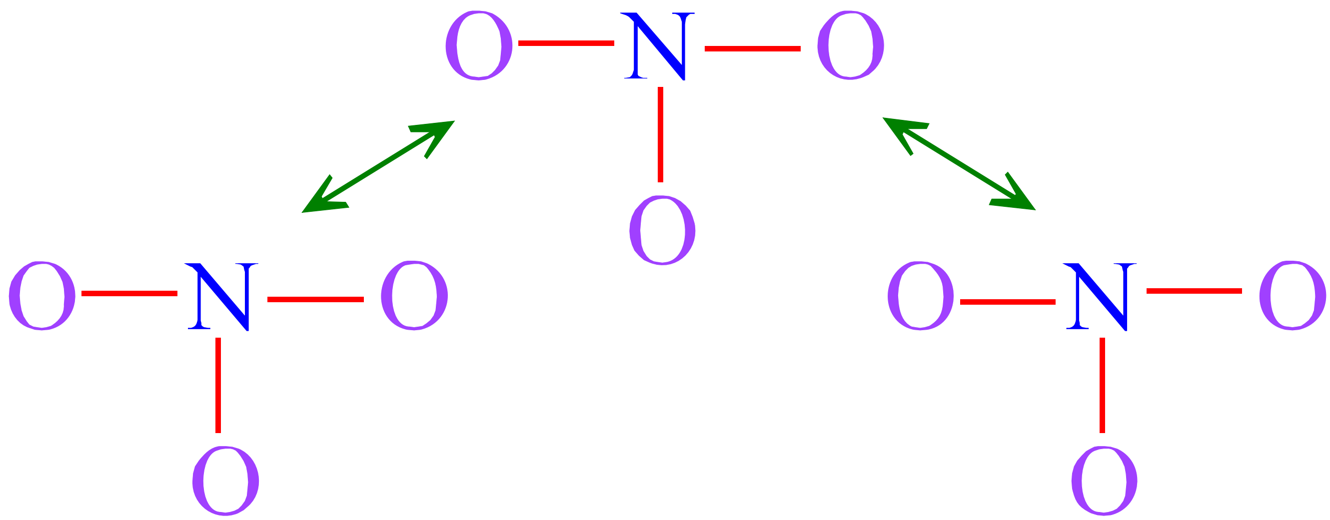
A) NO_3^-, nitrate ion

a) How many e^- do we have ?

N 3 O chg

b) Draw skeleton struct. & distribute e^-

c) <u>Structure</u>



Bonds are somewhere between single & double bonds

"extra" e^- pair is Delocalized

- spread out over all 3 bonding regions

B) Benzene molecule

C_6H_6

VII) Exceptions to Octet Rule

A) Odd Number of Electrons - Radicals

NO NO_2 ClO_2

1) Ex: NO_2

a) How many e^- do we have ?

N 2 O

b) Draw skeleton struct. & distribute e^-

O N O

c) Structure

O N O

O N O

O N O

O N O

B) Central Atom w. Less than Octet

Central atom is e^- deficient

- Do NOT follow Octet Rule

Be	B (Al)
·Be·	·$\dot{B}$·
2	3 bonds

- Do NOT form multiple bonds

$BeCl_2$ BF_3

C) Central Atom w. More than Octet

More than 8 e^- on central atom

"expanded" valence shell

S, P, Cl, Se, As, Br, etc.

occurs only for elements
in 3rd period & below

- larger size (most impt. factor)

- have empty d-orbitals
  in valence shell
  (minor factor)

1) Ex: ClF_4^+

a) How many e^- do we have ?

Cl		F		+1 chg		
$7\ e^-$	+	$4(7\ e^-)$	−	$1\ e^-$	=	$34\ e^-$

b) Draw skeleton struct. &

distribute e^- on outer atoms

c) Structure

D) Summary of LS

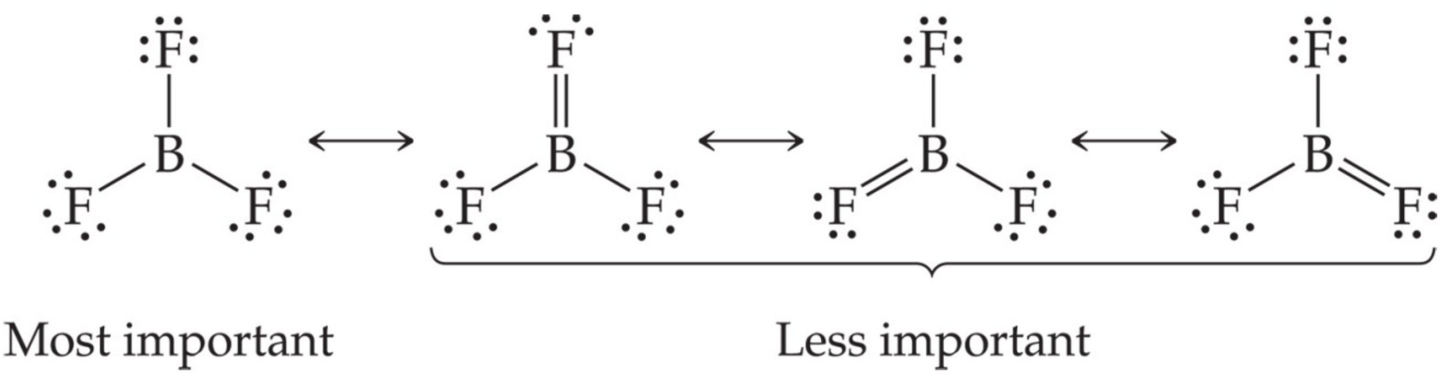
Good LS should:

1) obey octet rule if possible

2) have fewest number of FC's

3) have (−) charges on more EN atoms

4) Not have same charge adjacent



VIII) Strengths of Covalent Bonds

For ionic compounds LE is an indication of the strength of attraction of the ions.

For covalent bonds the strength is measured as the bond dissociation energy (BDE) or bond enthalpy (BE).

Energy required to dissociate one mole of bonds in the gas phase (kJ/mol)

A) Homonuclear Molecules

$H_2(g) \rightarrow 2\ H(g) \qquad \Delta H = D(H\text{-}H) = 436$

$Cl_2(g) \rightarrow 2\ Cl(g) \qquad \Delta H = D(Cl\text{-}Cl) = 242$

H-H bond is stronger than Cl-Cl bond

$H_2(g)$ is more stable and less reactive

B) Polyatomic Molecules

Average BE values for a particular bond from several molecules

1) Atomization

H-O-H(g) → 2 H(g) + O(g)

$\Delta H = 926$ kJ/mol

Avg. for an O-H bond:

D(O-H) = 926/2 = 463 kJ/mol

Not same as individual ΔH's:

H-O-H(g) → H(g) + O-H(g)

ΔH = 501 kJ/mol

O-H(g) → H(g) + O(g)

ΔH = 425 kJ/mol

Due to H_2O and OH having diff. e^- config. (arrangement of e^-)

Not same in all molecules w. OH bond

- variation is slight and get BE by taking an average from several molecules

C) Estimating ΔH_{rxn} from BE

$$\Delta H_{rxn} = \Sigma\, BE(\text{bonds broken}) - \Sigma\, BE(\text{bonds formed})$$

1) Ex: Determine ΔH_{rxn}

$$2\,NH_3(g) + 3\,Cl_2(g) \rightarrow N_2(g) + 6\,HCl(g)$$

D(N-H) = 391 kJ/mol
D(Cl-Cl) = 242 kJ/mol
D(N≡N) = 941 kJ/mol
D(H-Cl) = 431 kJ/mol

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D) Bond Length & Bond Energy

Diff. between single, double & triple bonds are seen in bond lengths & energies

Bond Length: Distance between nuclei of the 2 atoms bonded

Bond Energy: Energy required to break a mole of a particular bond

	N—N		N=N		N≡N
length (nm)	0.145	>	0.123	>	0.109
energy (kJ/mol)	163	<	418	<	941
Bond Order	1		2		3