

# 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

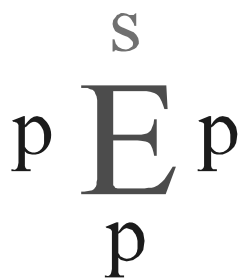
For representative elements:

$e^-$  in highest energy s & p subshells

$$\text{val. } e^- = \text{group \#}$$

### 1) Lewis Symbols

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



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.



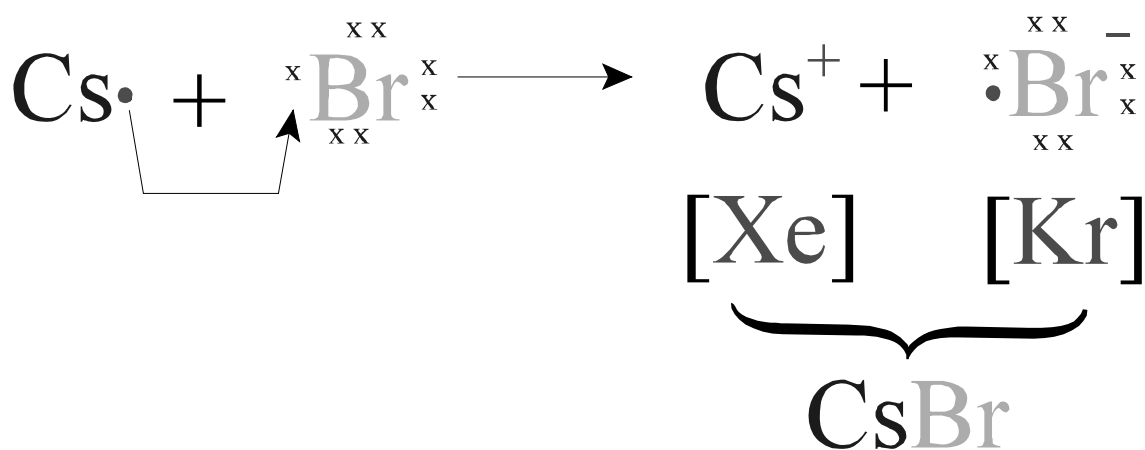
Full s & p subshells

## II) Ionic Bonding

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

- Cations & Anions formed

Show using  $e^-$  dot or Lewis Structures

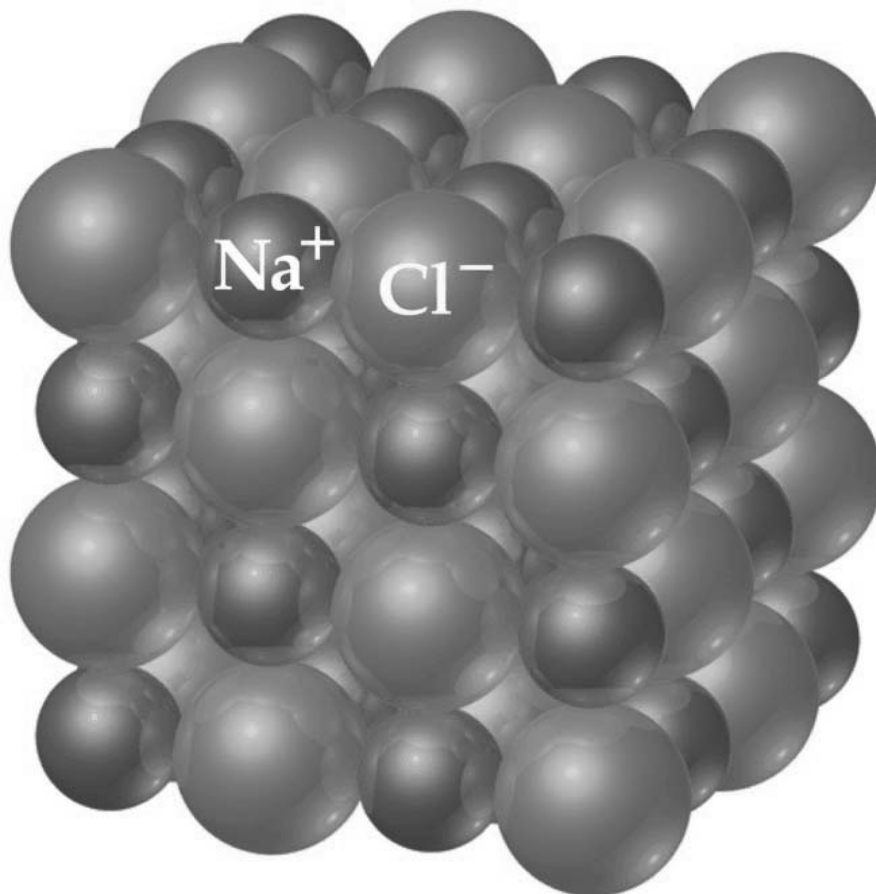


Cs: metal, low I.E.

Br: nonmetal, large neg. EA

## A) Energetics

Ionic compd. 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.

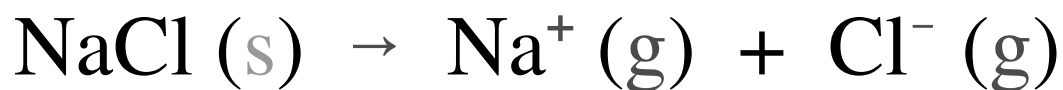


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# 1) Lattice Energy

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

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



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

$Q_1, Q_2$  : 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



b) Same charges, consider size





			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



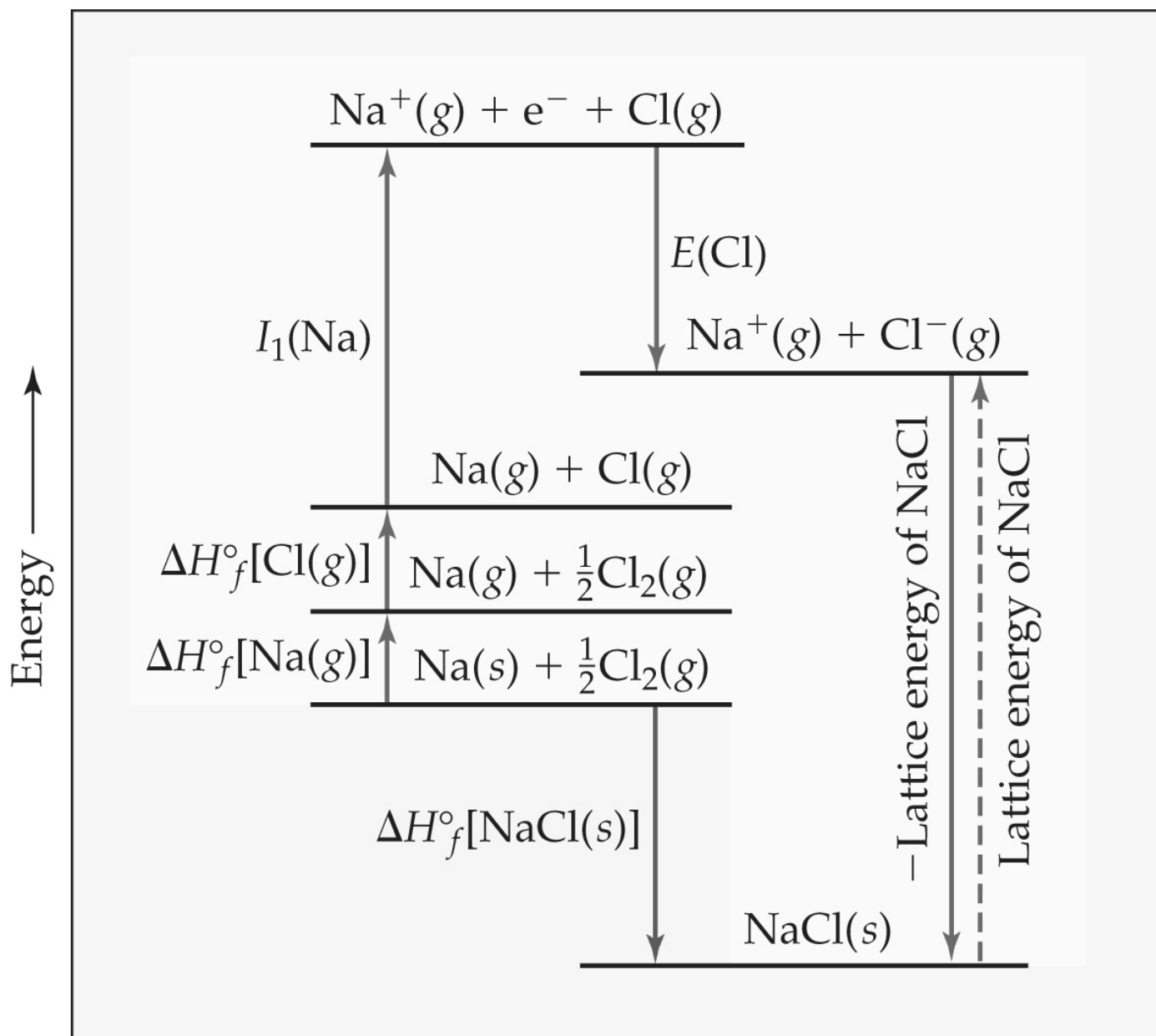
$$\text{LE} = ?$$

### 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)

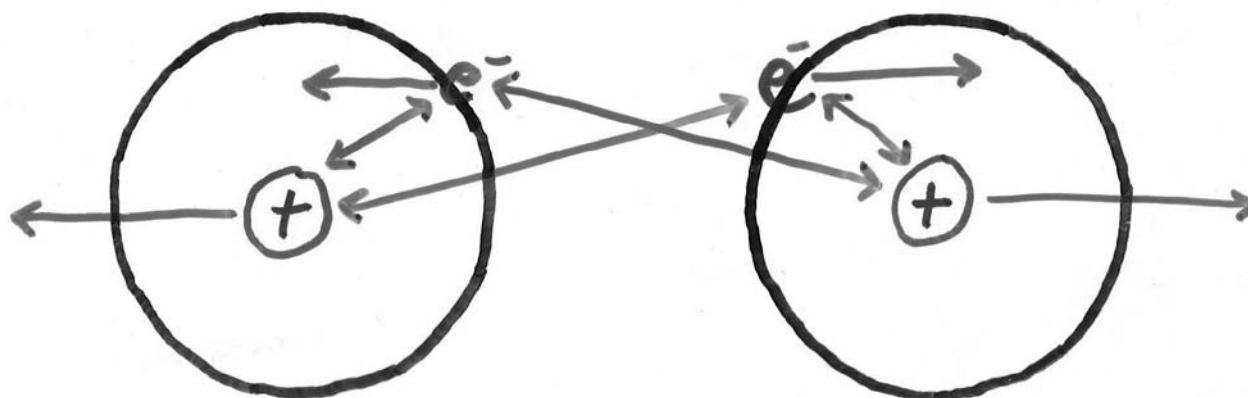


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### III) Covalent Bonds

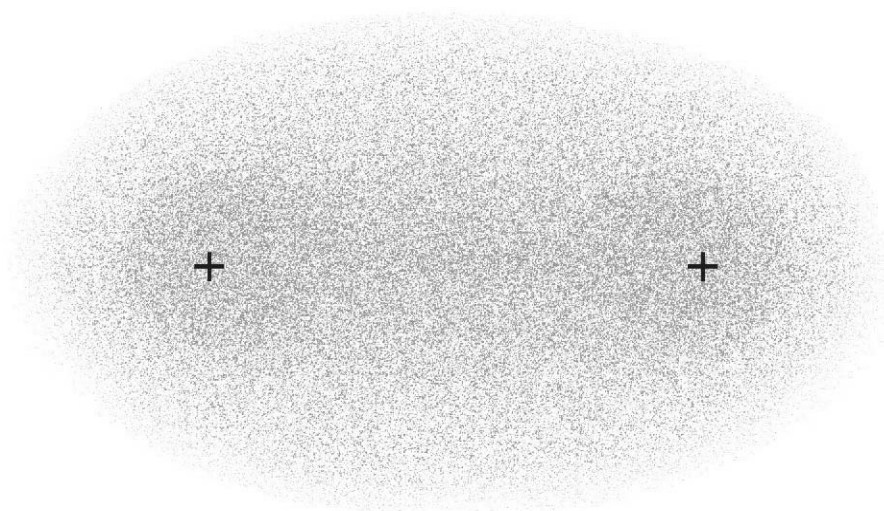
Not complete  $e^-$  transfer

Covalent Bond: pair of  $e^-$  are shared



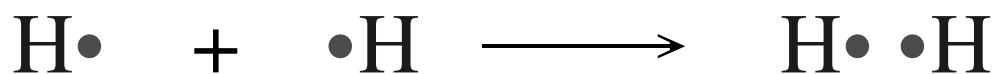
H

H



## A) Single Bond

2 e<sup>-</sup> shared by 2 atoms



Attraction of e<sup>-</sup> for both nuclei  
that holds molecules together

## Lewis Structure

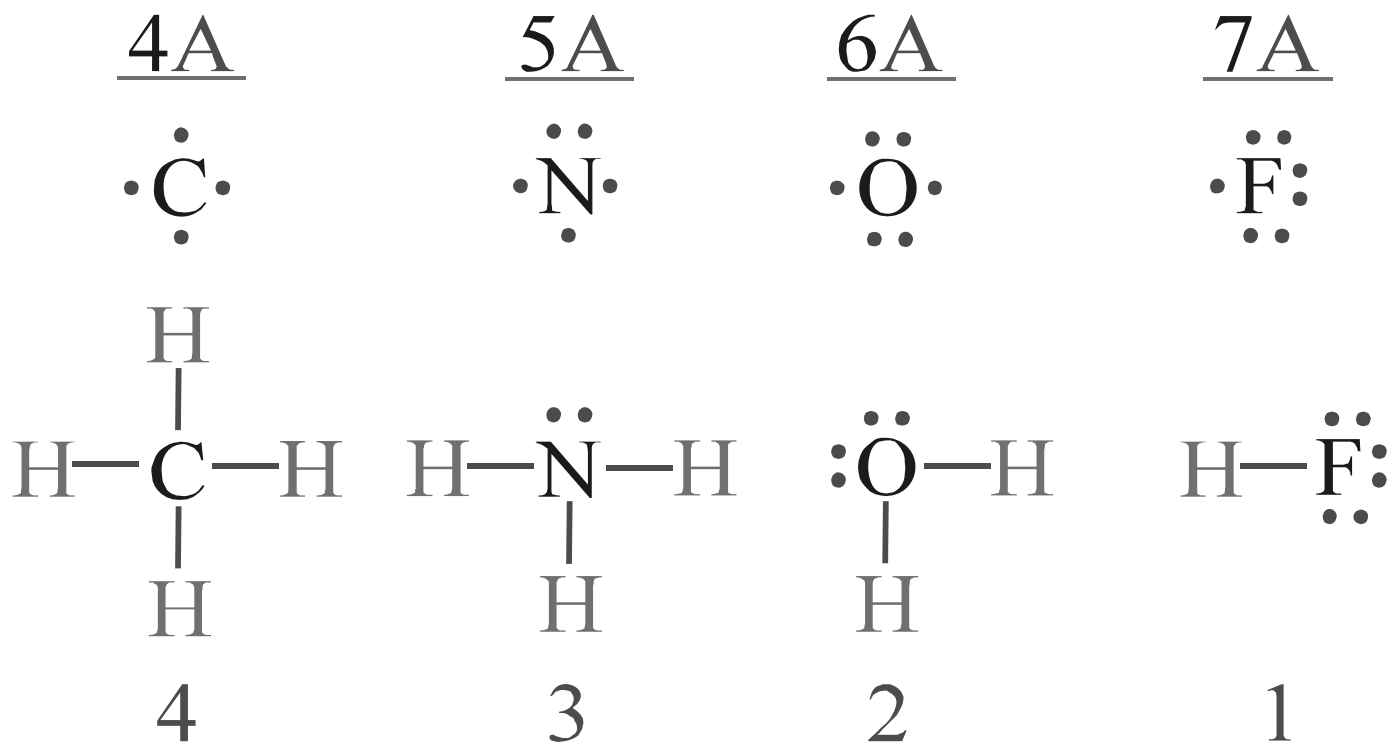
replace bonding e<sup>-</sup> pair w. line



- single bond

## B) Group No. & Number of Bonds Formed

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



Unshared  $e^-$  pairs shown as dots :

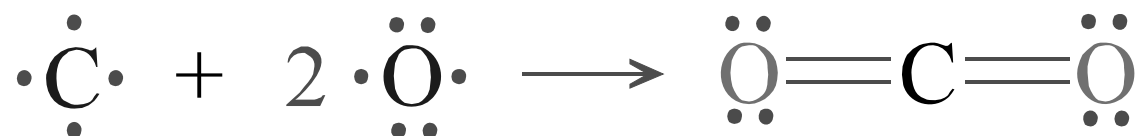
nonbonding or lone pair  $e^-$

## C) Multiple Bonds

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

### 1) Double Bond

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



### 2) Triple Bond

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



## IV) Bond Polarity & Electronegativity

### A) Bond Polarity

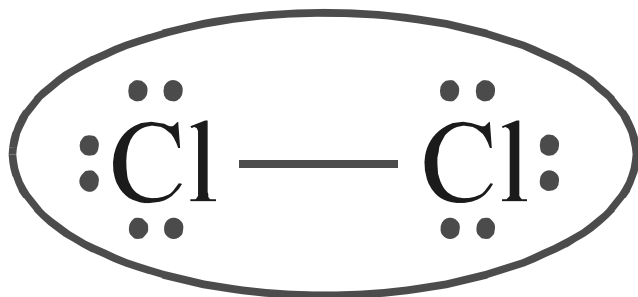
#### 1) Ionic Bond

complete  $e^-$  transfer

$\text{Cs}^+ \quad \text{Cl}^-$        $e^-$  from  $\text{Cs}^+$  spends  
most of its time in  
vicinity of  $\text{Cl}^-$ .

#### 2) Pure Covalent Bond:

$e^-$  pair shared equally  
by 2 identical atoms

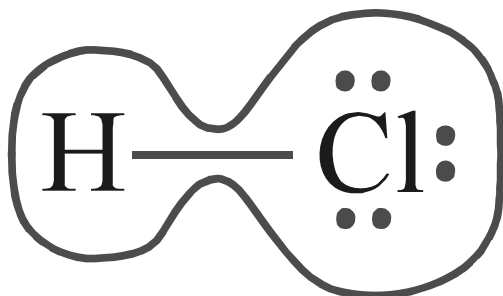




### 3) Polar Covalent Bond:

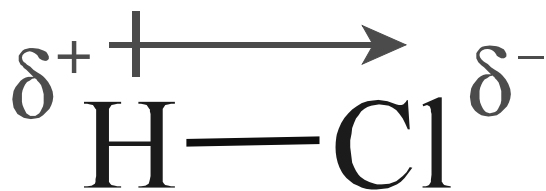
$e^-$  pair shared unequally  
between 2 diff. atoms

- Somewhere between ionic  
& covalent bonds



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

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



Ebbing, GENERAL CHEMISTRY  
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)



IA      increasing electronegativity  $\longrightarrow$

IA		IIA	IIIA	IVA	VA	VIA	VIIA	
<b>H</b> <b>2.1</b>								
<b>Li</b> <b>1.0</b>	<b>Be</b> <b>1.5</b>	<b>B</b> <b>2.0</b>	<b>C</b> <b>2.5</b>	<b>N</b> <b>3.0</b>	<b>O</b> <b>3.5</b>	<b>F</b> <b>4.0</b>		
<b>Na</b> <b>0.9</b>	<b>Mg</b> <b>1.2</b>	<b>Al</b> <b>1.5</b>	<b>Si</b> <b>1.8</b>	<b>P</b> <b>2.1</b>	<b>S</b> <b>2.5</b>	<b>Cl</b> <b>3.0</b>		
<b>K</b> <b>0.8</b>	<b>Ca</b> <b>1.0</b>	<b>Ga</b> <b>1.6</b>	<b>Ge</b> <b>1.8</b>	<b>As</b> <b>2.0</b>	<b>Se</b> <b>2.4</b>	<b>Br</b> <b>2.8</b>		
<b>Rb</b> <b>0.8</b>	<b>Sr</b> <b>1.0</b>	<b>In</b> <b>1.7</b>	<b>Sn</b> <b>1.8</b>	<b>Sb</b> <b>1.9</b>	<b>Te</b> <b>2.1</b>	<b>I</b> <b>2.5</b>		
<b>Cs</b> <b>0.7</b>	<b>Ba</b> <b>0.9</b>	<b>Tl</b> <b>1.8</b>	<b>Pb</b> <b>1.8</b>	<b>Bi</b> <b>1.9</b>	<b>Po</b> <b>2.0</b>	<b>At</b> <b>2.2</b>		
<b>Fr</b> <b>0.7</b>	<b>Ra</b> <b>0.9</b>							

$\uparrow$  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

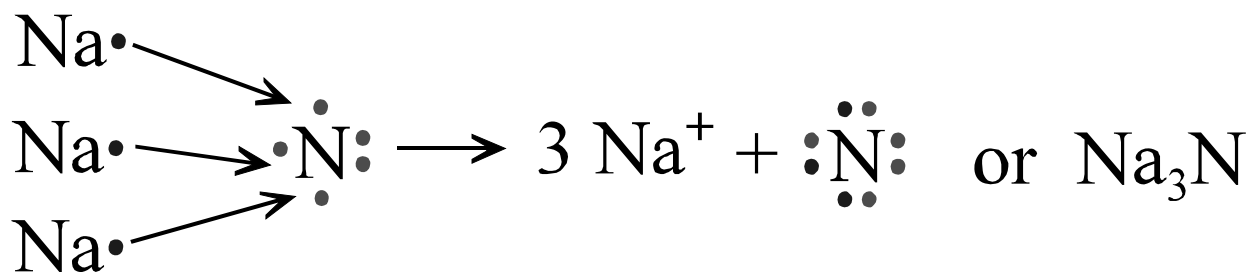
$\Delta EN < 0.5$  nonpolar covalent

$\Delta EN = 0$  pure covalent

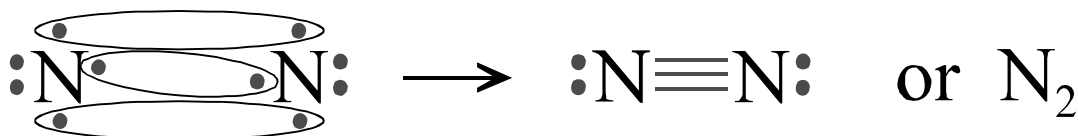
## Nitrogen Can Achieve the Noble Gas Configuration of Neon in Three Ways

Lewis structure of nitrogen atom, Group 5A  $\begin{array}{c} \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \end{array} \text{N} \cdot$  three electrons short of neon configuration

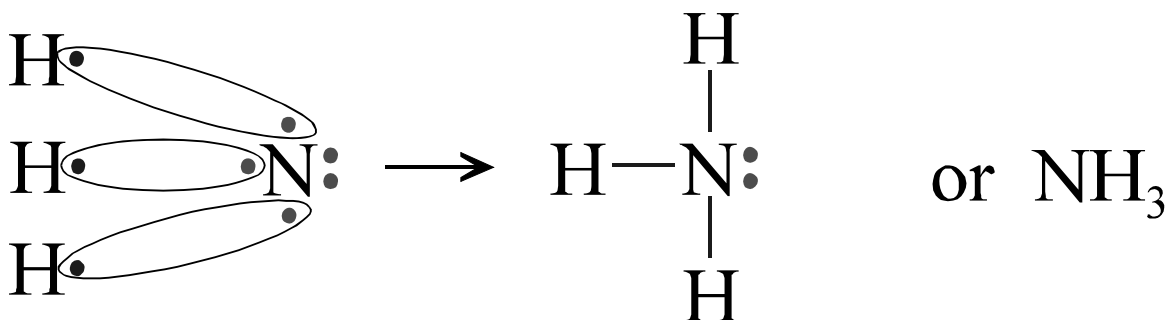
1. electron transfer  $\longrightarrow$  ionic bond



2. equal sharing of electron pairs  $\longrightarrow$  pure covalent bond



3. unequal sharing of electron pairs  $\longrightarrow$  polar-covalent bond



## D) Dipole Moment

A polar molecule has opposite charges separated by a distance,

it has a dipole moment

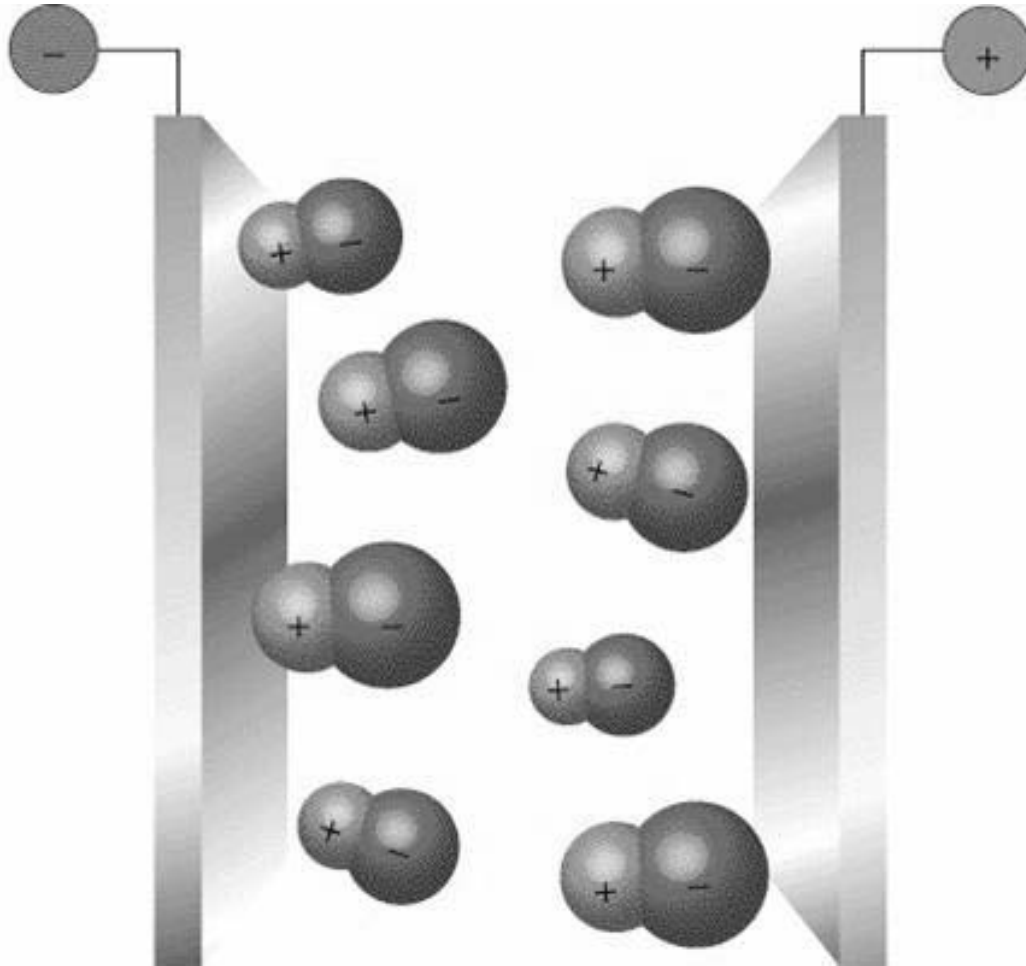
magnitude of charge  $\times$  distance between charges

$$\mu = Q \cdot r \quad (\text{Debye, D})$$

$$1 \text{ D} = 3.34 \times 10^{-30} \text{ coulomb-meters}$$

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

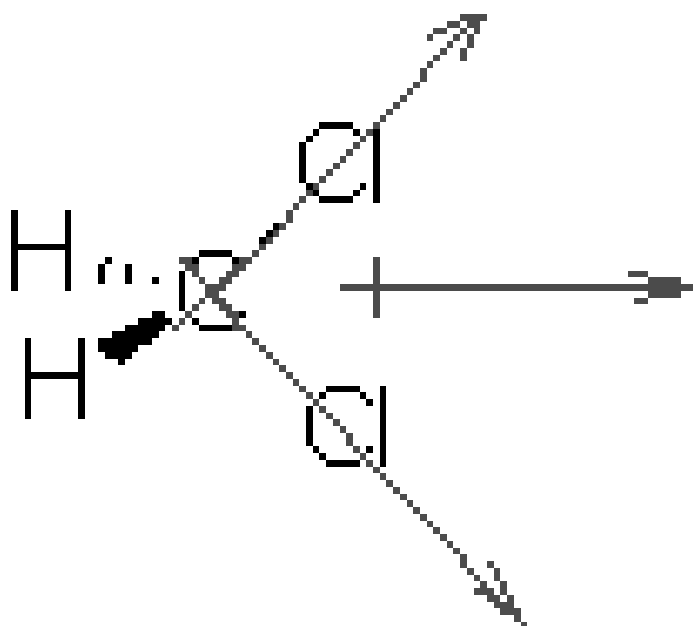




Experimentally the dipole moment is determined by how the molecule behaves in an electric field.

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

$$\mu = Q \cdot r$$

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

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

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

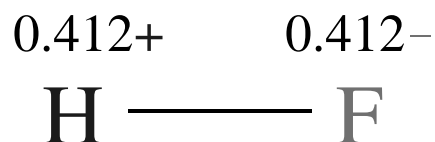
b) Calc. partial charges in  $e$

Experimentally,  $\mu = 1.82 \text{ D}$

$$Q = \frac{\mu}{r}$$
$$= \frac{(1.82 \text{ D}) (3.34 \times 10^{-30} \text{ C}\cdot\text{m}/1 \text{ D})}{(0.92 \times 10^{-10} \text{ m})}$$
$$= 6.607 \times 10^{-20} \text{ C}$$

Q in  $e$ :

$$= (6.607 \times 10^{-20} \text{ C}) \times \frac{1 e}{1.60 \times 10^{-19} \text{ C}}$$
$$= 0.412 e$$



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

<b>Compound</b>	<b>Bond Length (Å)</b>	<b>Electronegativity Difference</b>	<b>Dipole Moment (D)</b>
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

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## 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) 2 General Requirements

- 1) All val.  $e^-$  must be shown
- 2) All atoms generally have octet of  $e^-$

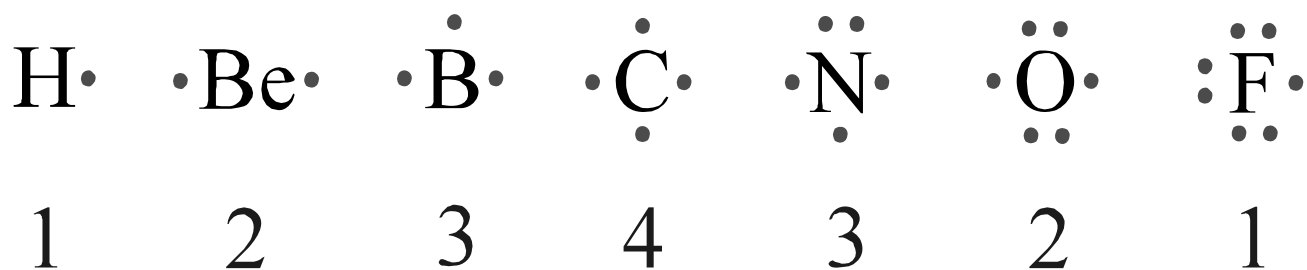
### a) Exceptions

H Li Be B (Al)    less than octet

Periods 3-6    greater than octet

## B) Number Bonds Atoms Generally form?

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



## B) Procedure for Drawing Lewis Struc.

### 1) Number val. e<sup>-</sup> Available, A

Determine total # val. e<sup>-</sup>

$$\# \text{ val. e}^{-} = \text{group } \#$$

#### a) adjust for charge

##### 1) subtract for (+) chg.



$$A = 3(1) + 1(6) - 1 = 8 \text{ e}^{-} \text{ avail.}$$

##### 2) add for (-) chg.

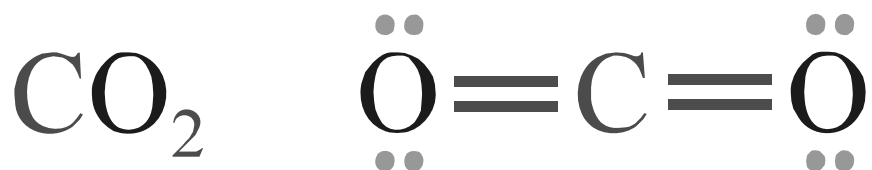


$$A = 1(4) + 3(6) + 2 = 24 \text{ e}^{-} \text{ avail.}$$

## 2) Draw Skeleton Structure

Connect atoms w. single bond

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



- 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

$$\begin{array}{ccc} \# e^- & & \# e^- \\ \text{remaining} & = & \text{available} - \# e^- \\ & & \text{used} \end{array}$$

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<sub>3</sub>O<sup>+</sup>

a) How many e<sup>-</sup> do we have ?

$$\begin{array}{ccccccc} \text{O} & & \text{H} & & +1 \text{ chg} & & \\ 6 \text{ e}^- & + & 3(1 \text{ e}^-) & - & 1 \text{ e}^- & = & 8 \text{ e}^- \end{array}$$

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

c) Complete octet on central atom

## 2) ClO<sub>2</sub><sup>-</sup>

a) How many e<sup>-</sup> do we have ?

$$\begin{array}{rccccccc} \text{Cl} & & \text{O} & & -1 \text{ chg} & & \\ 7 e^- & + & 2(6 e^-) & + & 1 e^- & = & 20 e^- \end{array}$$

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

c) Complete octet on central atom

### 3) Cl<sub>2</sub>CO

a) How many e<sup>-</sup> do we have ?

$$\begin{array}{ccccc} \text{Cl} & & \text{C} & & \text{O} \\ 2(7 e^-) & + & 4 e^- & + & 6 e^- = 24 e^- \end{array}$$

b) Draw skeleton struct. &  
distribute e<sup>-</sup>

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

$$FC = \# \text{ val. } e^- - (\frac{1}{2} \# \text{ bond } e^- + \# \text{ n.b.e.})$$

- 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

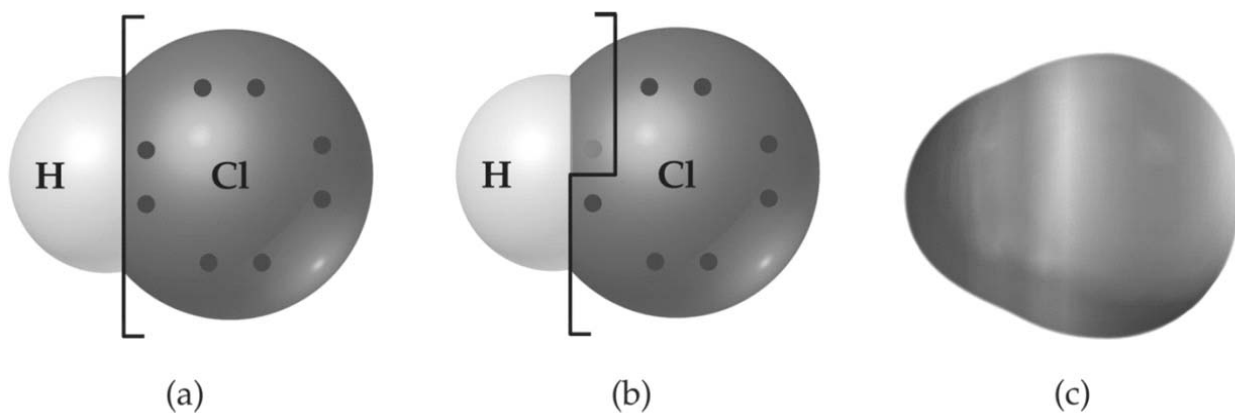
c) Adjacent Charge Rule

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



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4) Ex:  $\text{N}_2\text{O}$ , 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

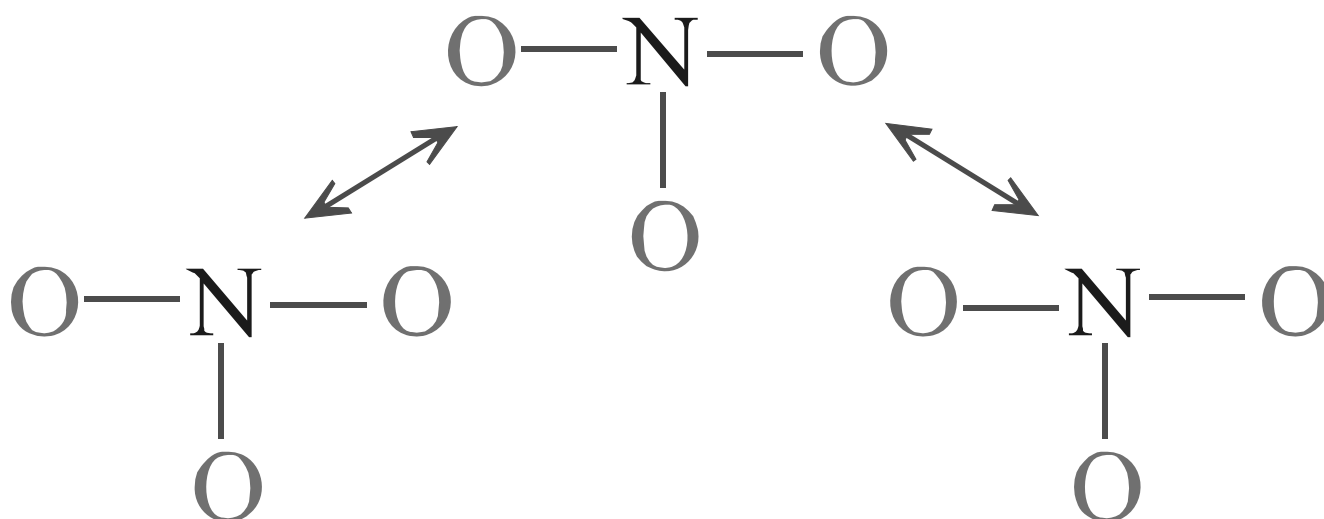
A)  $\text{NO}_3^-$ , nitrate ion

a) How many  $e^-$  do we have ?

N      3 O      chg

b) Draw skeleton struct. &  
distribute  $e^-$

### c) Structure

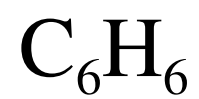


Bonds are somewhere between  
single & double bonds

“extra”  $e^-$  pair is Delocalized

- spread out over all  
3 bonding regions

## B) Benzene molecule



## VII) Exceptions to Octet Rule

### A) Odd Number of Electrons - Radicals



1) Ex: NO<sub>2</sub>

a) How many e<sup>-</sup> do we have ?



b) Draw skeleton struct. &  
distribute e<sup>-</sup>



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)

$\cdot\text{Be}\cdot$

$\cdot\overset{\cdot}{\text{B}}\cdot$

2

3

bonds

- Do NOT form multiple bonds

$\text{BeCl}_2$

$\text{BF}_3$

$\text{Cl}-\text{Be}-\text{Cl}$

$\begin{array}{c} \text{F}-\text{B}-\text{F} \\ | \\ \text{F} \end{array}$



## C) Central Atom w. More than Octet

More than 8 e<sup>-</sup> on central atom

“expanded” valence shell

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

occurs only for elements  
in 3<sup>rd</sup> period & below

- larger size (most impt. factor)

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

1) Ex:  $\text{ClF}_4^+$

a) How many  $e^-$  do we have ?

$$\begin{array}{r} \text{Cl} \qquad \qquad \text{F} \qquad \qquad +1 \text{ chg} \\ 7 e^- + 4(7 e^-) - 1 e^- = 34 e^- \end{array}$$

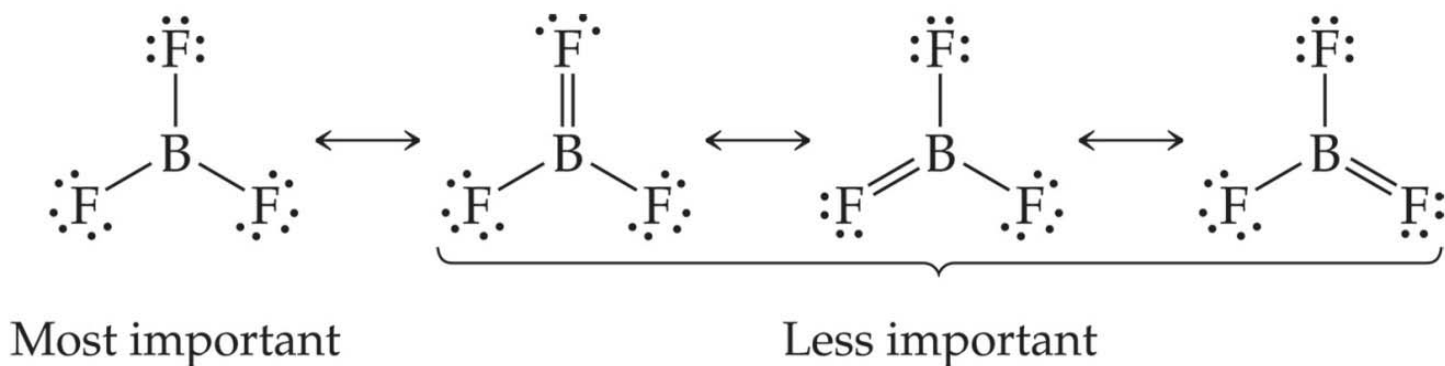
b) Draw skeleton struct. &  
distribute  $e^-$  on outer atoms

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



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## 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-H bond is stronger than Cl-Cl bond

H<sub>2</sub>(g) is more stable and less reactive

## B) Polyatomic Molecules

Average BE values for a particular bond from several molecules

### 1) Atomization



$$\Delta H = 926 \text{ kJ/mol}$$

Avg. for an O-H bond:

$$D(\text{O-H}) = 926/2 = 463 \text{ kJ/mol}$$

Not same as individual  $\Delta H$ 's:



$$\Delta H = 501 \text{ kJ/mol}$$



$$\Delta H = 425 \text{ kJ/mol}$$

Due to  $\text{H}_2\text{O}$  and  $\text{OH}$  having diff.  
 $e^-$  config. (arrangement of  $e^-$ )

Not same in all molecules w.  $\text{OH}$  bond

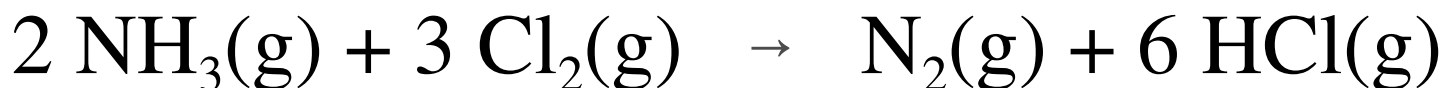
- variation is slight and get BE  
by taking an average from  
several molecules

## C) Estimating $\Delta H_{\text{rxn}}$ from BE

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

$$\Sigma \text{BE}(\text{bonds formed})$$

1) Ex: Determine  $\Delta H_{\text{rxn}}$



$$D(\text{N-H}) = 391 \text{ kJ/mol}$$

$$D(\text{Cl-Cl}) = 242 \text{ kJ/mol}$$

$$D(\text{N}\equiv\text{N}) = 941 \text{ kJ/mol}$$

$$D(\text{H-Cl}) = 431 \text{ kJ/mol}$$

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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

	$\text{N}-\text{N}$		$\text{N}=\text{N}$		$\text{N}\equiv\text{N}$
length (nm)	0.145	>	0.123	>	0.109
energy (kJ/mol)	163	<	418	<	941
Bond Order	1		2		3