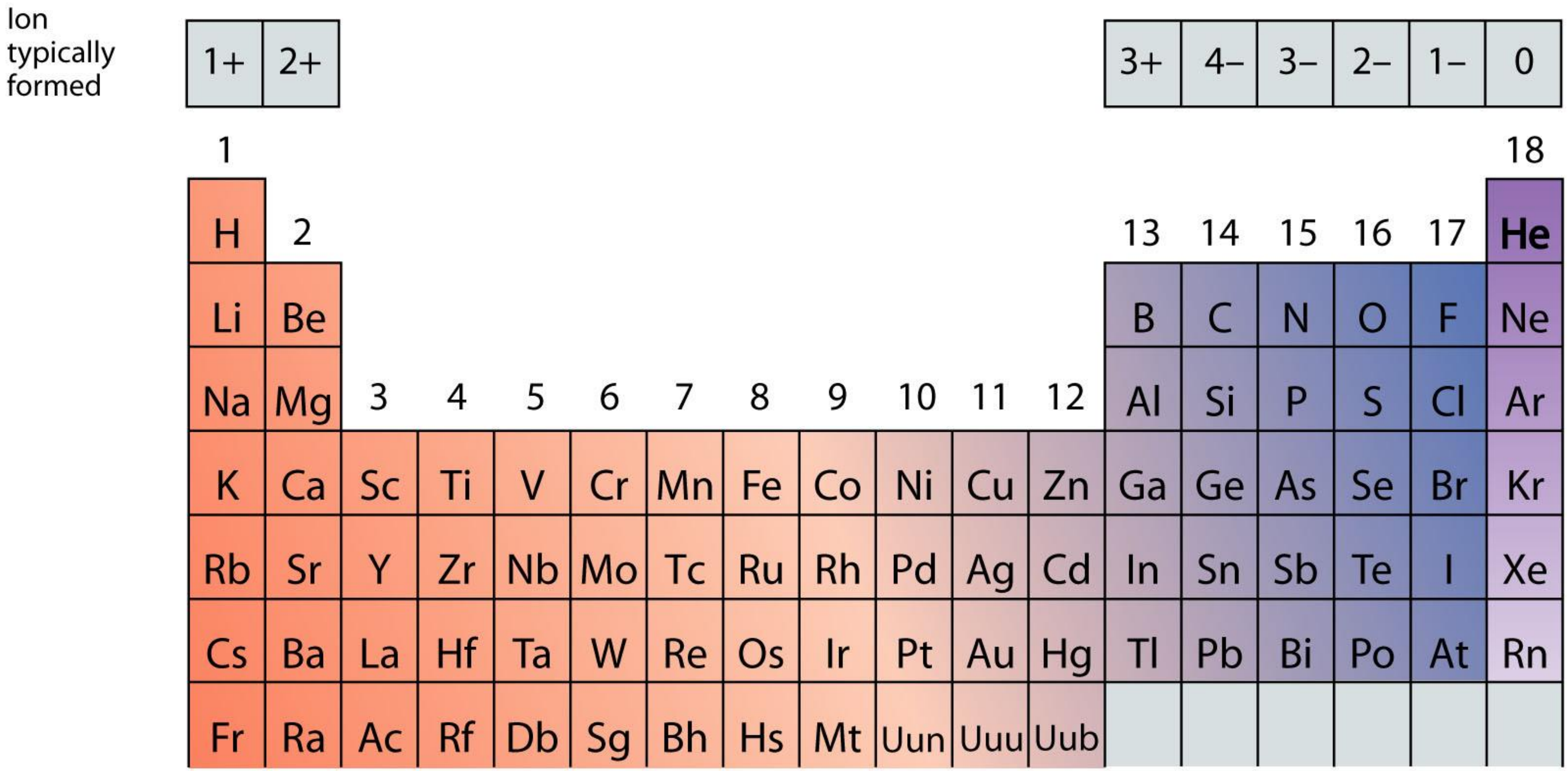
Ionic and Covalent Bonding



= Weak nuclear attraction for valence electrons; tendency to form positive ions

= Strong nuclear attraction for valence electrons; tendency to form negative ions

= Strong nuclear attraction for valence electrons but valence shell is already filled; no tendency to form ions of either type

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Lewis Structures

- The availability of electrons and needs of atoms in a molecule are tracked
- Show how available valence e^- are shared between atoms in a molecule
- Can indicate either ionic and covalent bonding
- The element symbol is imagined to have a box around it. The valence e- are distributed around the four sides of the box.
- For the “a” group elements, the group number is the number of valence e-.
- For, Al, a group IIIa element, there are 3 valence e^-. Its Lewis structure is

Electron Configurations and Lewis Symbols

TABLE 8.1 Lewis Symbols

Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
Li	[He]$2s^1$	Li·	Na	[Ne]$3s^1$	Na·
Be	[He]$2s^2$	·Be·	Mg	[Ne]$3s^2$	·Mg·
B	[He]$2s^2 2p^1$	·Ḃ·	Al	[Ne]$3s^2 3p^1$	·Ȧl·
C	[He]$2s^2 2p^2$	·Ċ̣·	Si	[Ne]$3s^2 3p^2$	·Ṩi·
N	[He]$2s^2 2p^3$	·Ṇ̇:	P	[Ne]$3s^2 3p^3$	·Ṗ̣:
O	[He]$2s^2 2p^4$	:Ọ̇:	S	[Ne]$3s^2 3p^4$	:Ṩ:
F	[He]$2s^2 2p^5$	·F̤̈:	Cl	[Ne]$3s^2 3p^5$	·C̤̈l:
Ne	[He]$2s^2 2p^6$	:N̤̈e:	Ar	[Ne]$3s^2 3p^6$	:Ä̤r:

The Octet Rule

- Stable atoms tend to have full or exactly half-full sublevels.
- Special stability is achieved in the noble gases, which have full sublevels.
- The "***octet rule***"- atoms will lose or gain e- in order to have 8 e- surrounding them as have the noble gases.
- H and He will need only 2 e-, thus follow the "duet rule".

The Octet Rule – Rephrased

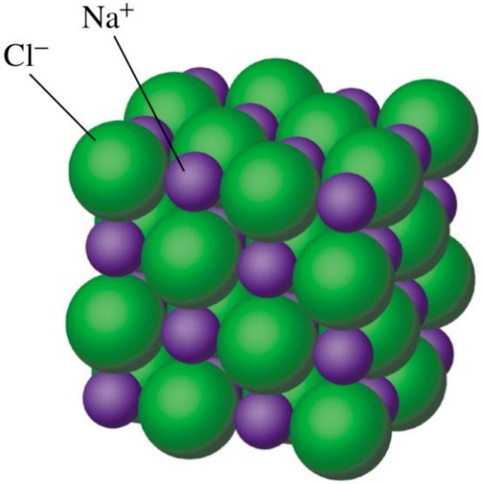
- Atoms tend to gain, lose and/or share electrons in order to obtain a stable noble gas configuration in their valence electrons.
- For elements 1-5 “duet” rule
- For the rest of the elements “Octet” rule

Ionic Compounds

Ionic compounds form when oppositely charged ions are attracted to each other

NaCl

Resulting compound is electrically neutral



Na^+		**Cl^-**		
(+1)	+	**(–1)**	=	**0**

Sodium chloride

EOS

Chemical Bonds - Ionic

Ionic bonds form when atoms transfer valence electrons in the forming ions that are then attracted to each other.

Metal - nonmetal bonds are ionic because:

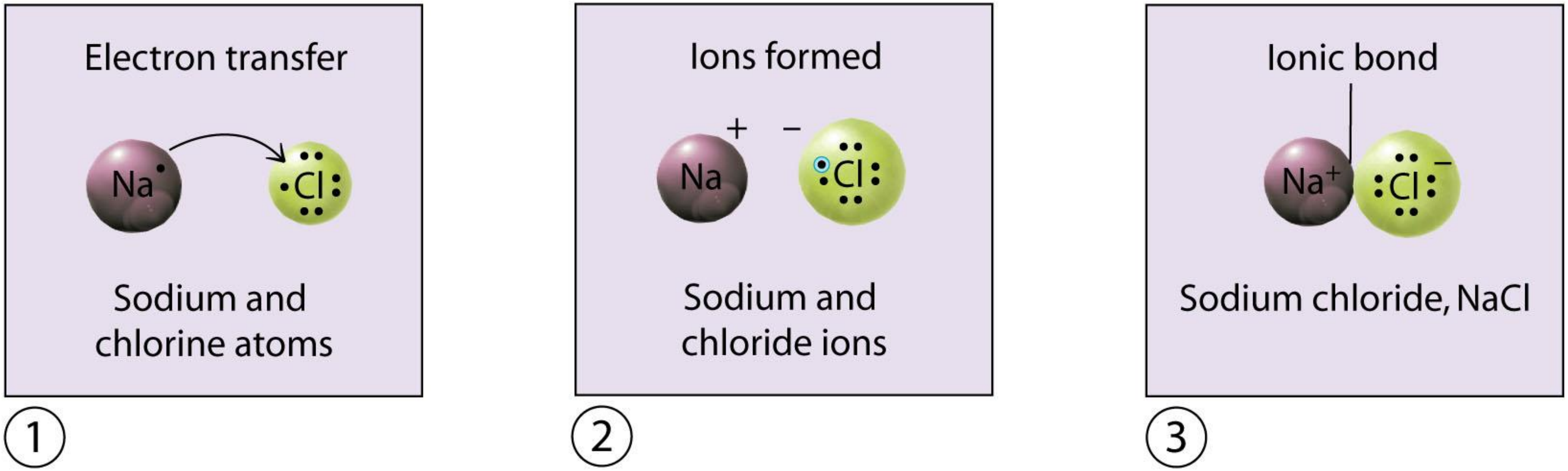
- metals have low ionization energies and easily lose e^- to be stable
- non-metals have higher electron affinities
- the formation of the lattice stabilizes the ions.

- ***Ionic crystals:*** exist in a 3-dimensional array of cations and anions called a ***lattice structure***

- ***Ionic chemical formulas***: always written as empirical formula (smallest whole number ratio of cation to anion)

- "***Formula Unit***" is the term used to describe the empirical formula of ionic compounds

Ionic Bonding is the TRANSFER of electrons from one element to another.



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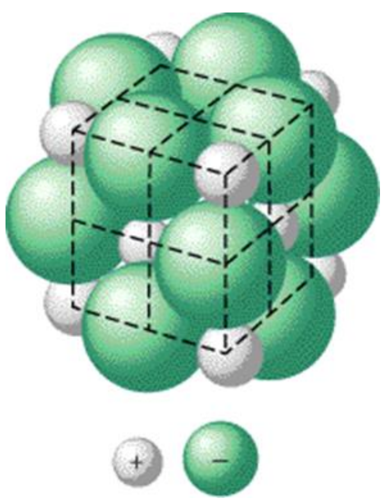
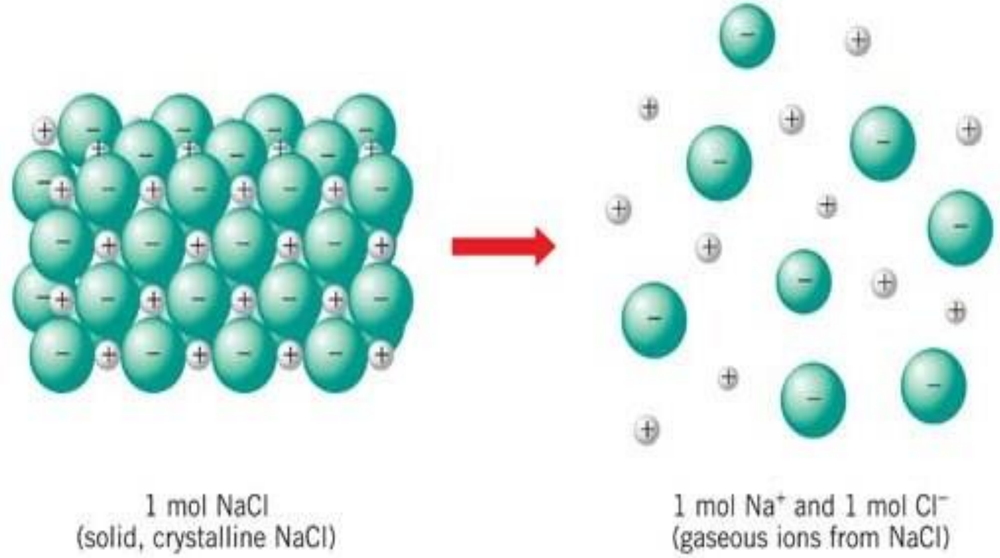


Lattice Energy, U

- Formation of gaseous ions from an ionic solid
- $A_xB_{y(s)} \rightarrow xA^{y+}_{(g)} + yB^{x-}_{(g)}$



Compound	Ions	Lattice Energy (kJ mol^{-1})
LiCl	Li^+ and Cl^-	845
NaCl	Na^+ and Cl^-	778
KCl	K^+ and Cl^-	709
LiF	Li^+ and F^-	1033
$CaCl_2$	Ca^{2+} and Cl^-	2258
$AlCl_3$	Al^{3+} and Cl^-	5492
CaO	Ca^{2+} and O^{2-}	3401
Al_2O_3	Al^{3+} and O^{2-}	15,916

U vs. Bond Formation Energy

- The formation of one mole of solid from gaseous ions (***ionic bond formation***) is numerically the same as the lattice energy
- $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ + 787 kJ
- Since this is energy released, the value for this process would be –U
- Smaller ions have greater attractive forces, as have those with higher charges

$$U = \frac{q_1 q_2}{kr}$$

Electron Configurations Ions

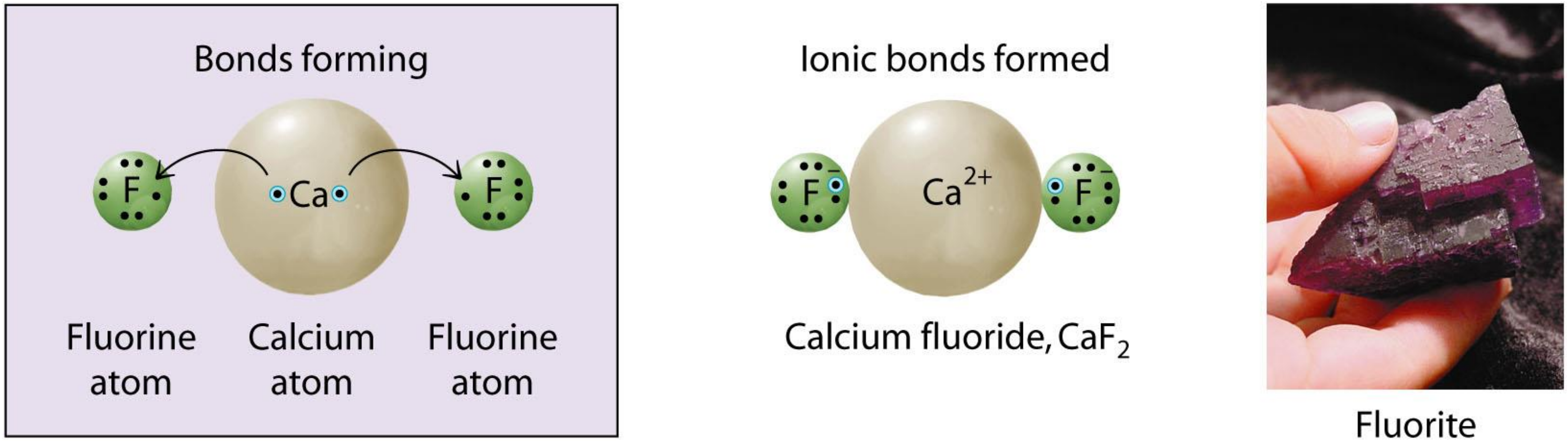
1. The first electrons to be lost by an atom or ion are always those from the shell with the largest value of *n*
2. As electrons are removed from a given shell, they come from the highest-energy occupied subshell first before any are removed from a lower-energy subshell.
3. Within a given shell, the energies of the subshells vary as follows: *s p d f*.

Electron Configurations Of Cations

- Main Group metals lose the electrons in their highest energy *subshell* first to achieve the previously filled noble gas (the ***octet rule***)
- Group Ia: [Noble gas core]ns^1
  - Form 1+ ions to be ***isoelectronic*** with noble gas core element
- Group IIa: [n.g.c.]ns^2
  - Forms 2+ ions
- Group IIIa: [n.g.c.]ns^2np^1
  - Forms 3+ ions

Electron Configuration of Cations

- Main Group metals lose the electrons in their highest energy subshell first. Elements in group IIIa below Al also form 1+ ions.
- Ga : $[Ar]\ 4s^2\ 3d^{10} 4p^1$ - 1 e- →
- Ga^+ : $[Ar]\ 4s^2\ 3d^{10}$ - 2 more e- →
- Ga^{3+} : $[Ar]\ 3d^{10}$



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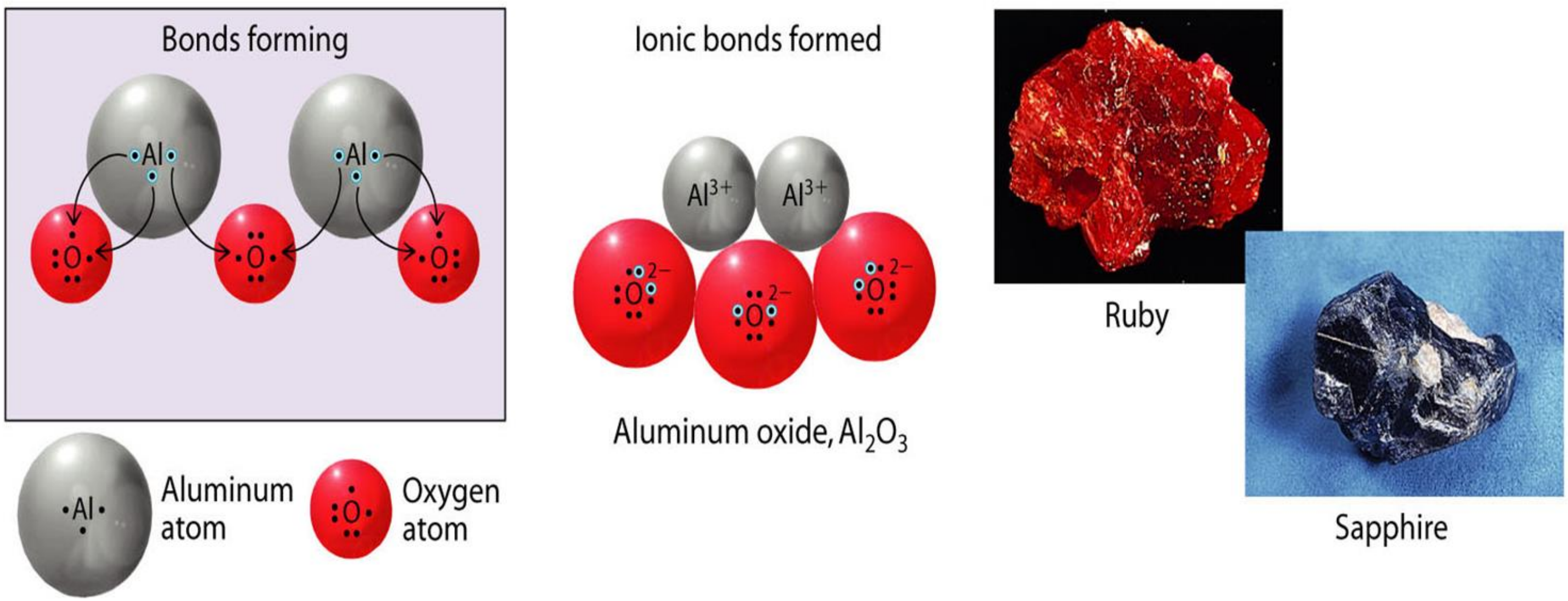

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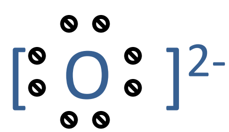
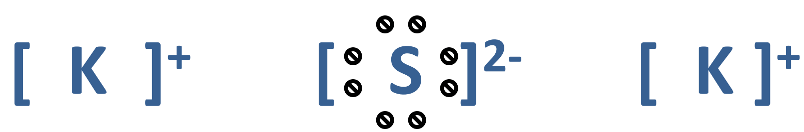
Lewis Structures For Monatomic Ions

- We subtract the charge on the ion from the number of valence e- and show these around the element symbol
- We enclose the symbol in brackets and indicate the charge
- for Na^+ ion 1-1=0 $[\ Na\ ]^+$
- for O^{2-} ion, 6-(-2)=8 

Ionic Compounds – Lewis Structures

Ionic compounds are formed by the attraction between oppositely charged ions

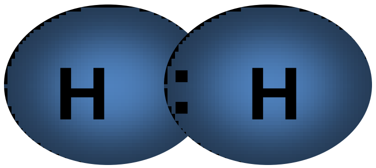
- show each ion, separately, alternating charges
- for the ionic compound K_2S:



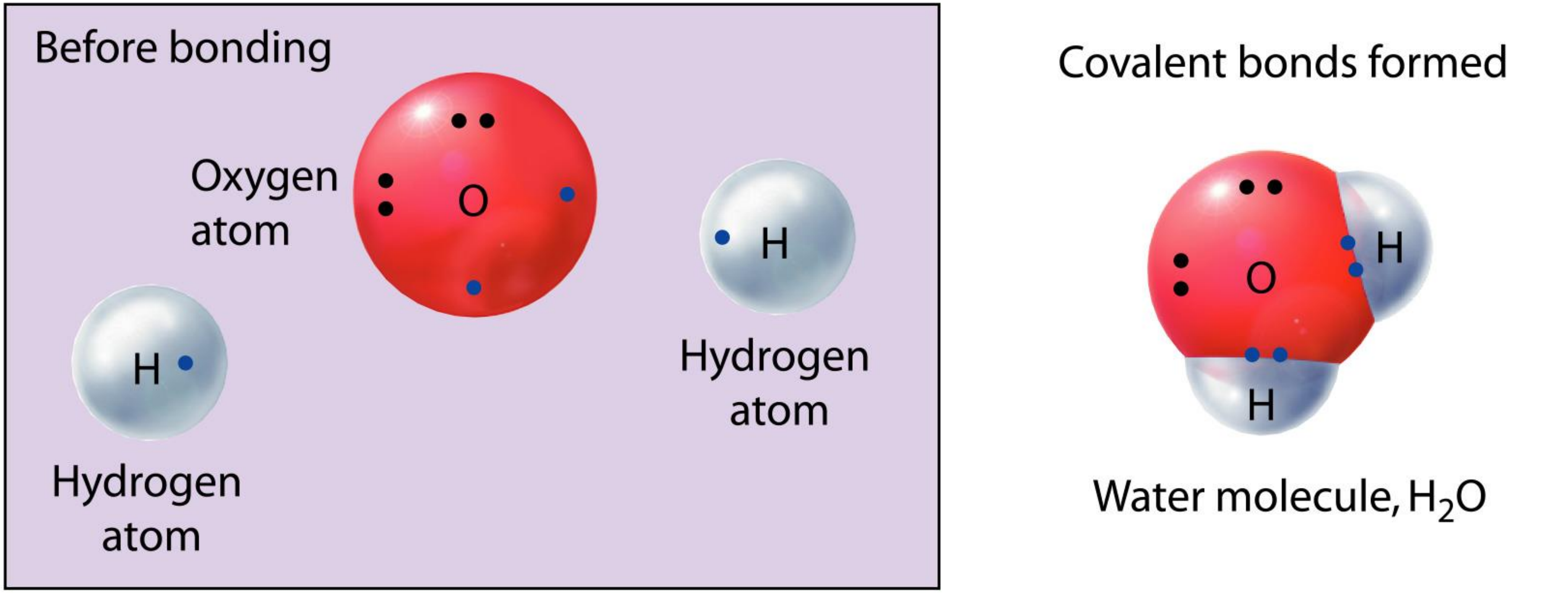
Chemical Bonds - Covalent

- ***Covalent bonds*** form when atoms share valence electrons in the region of space created by orbital overlap

Nonmetal - nonmetal bonds are shared or covalent bonds because neither element easily loses e^-



In a *Covalent Bond*, atoms SHARE electrons to form stable pairs.



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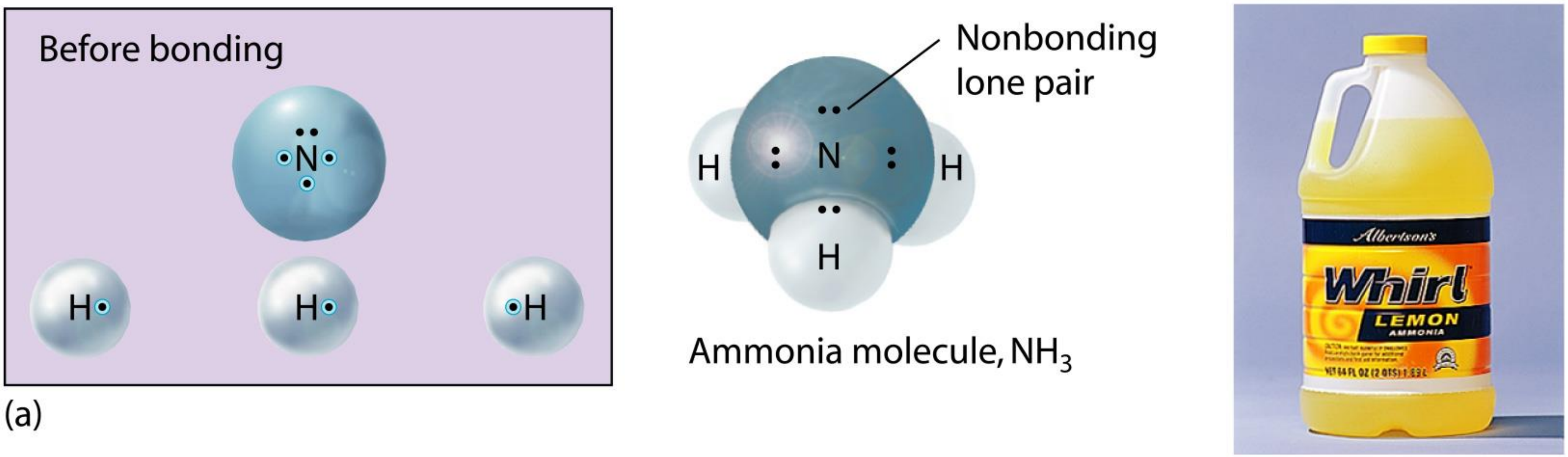
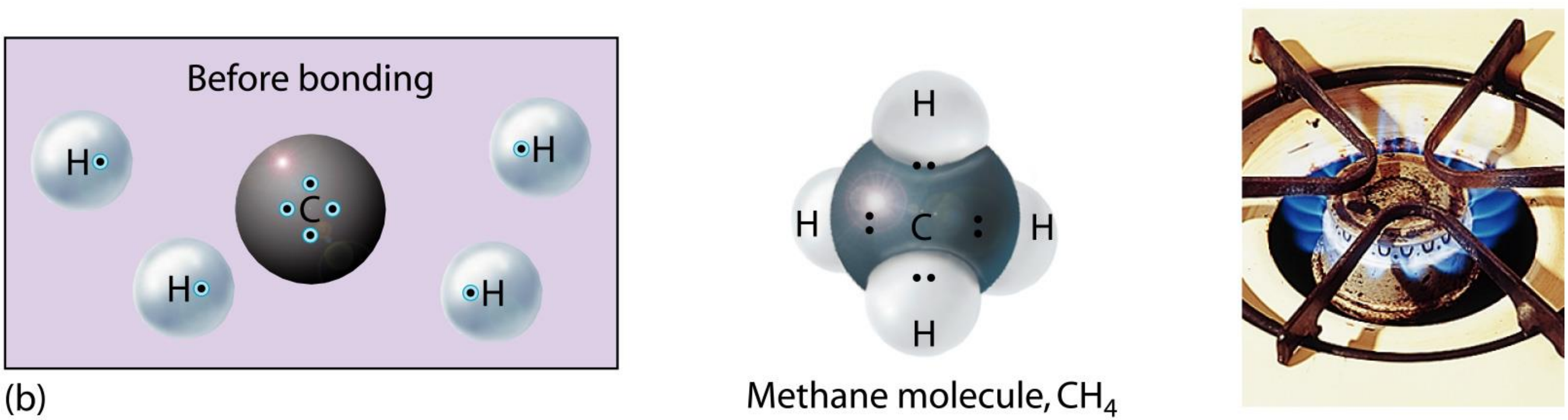


(a)



(b)

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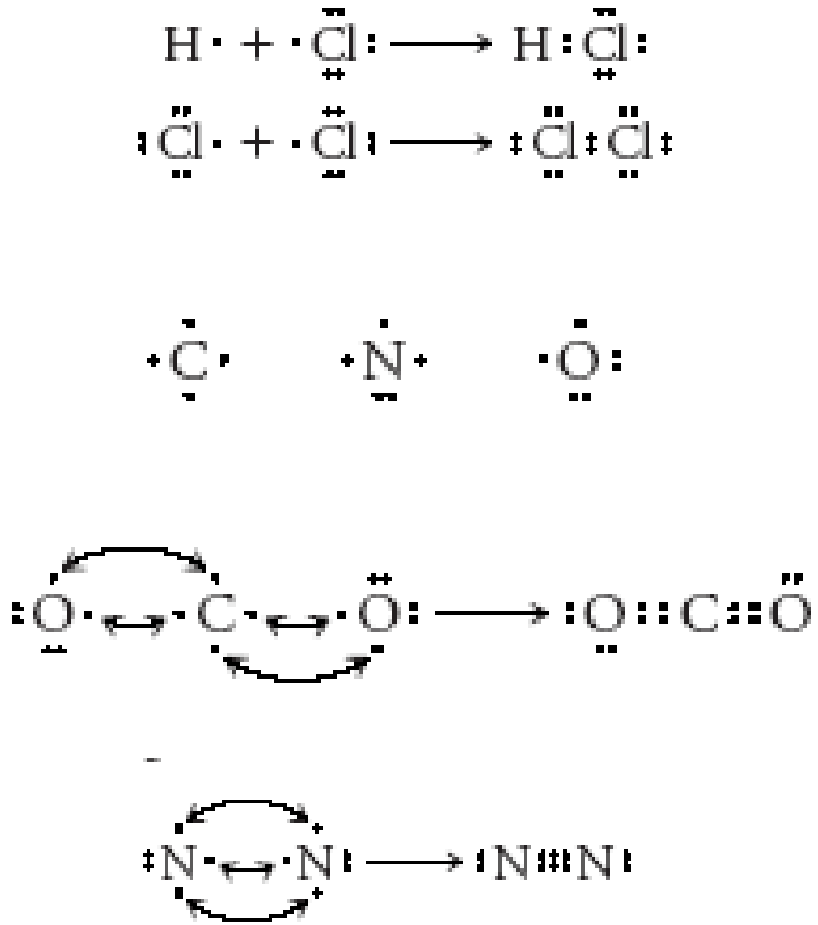
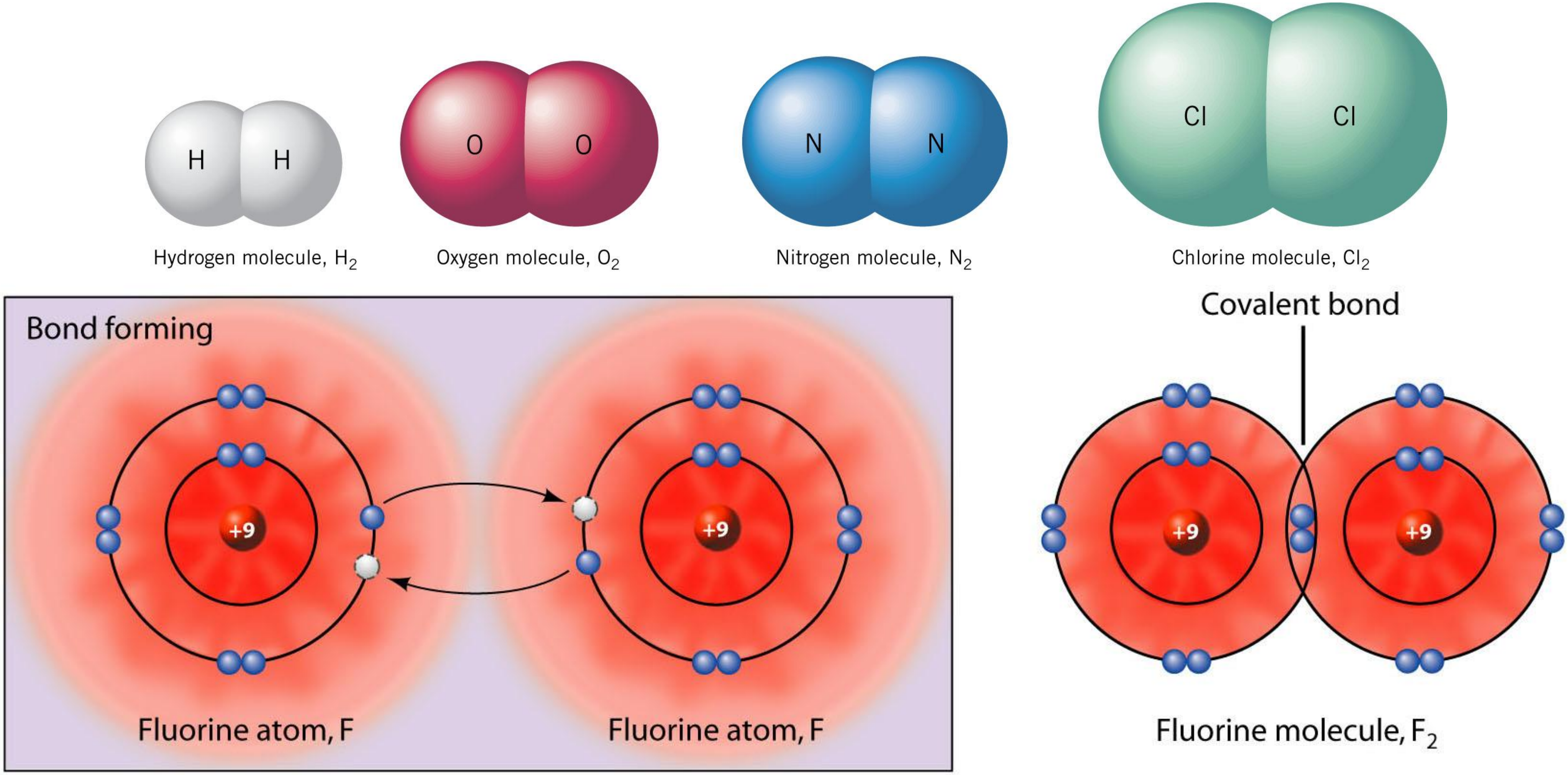
Molecules Often Obey The Octet Rule

- Share e^- to gain octet
- May form single, double or triple bonds
- Each atom has 8 e^- surrounding it



Many nonmetals occur as **diatomic molecules**



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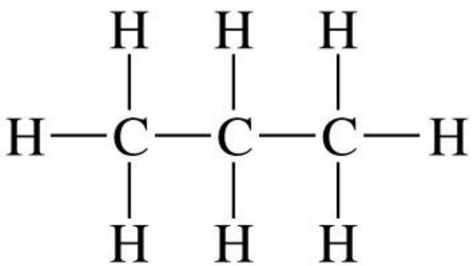
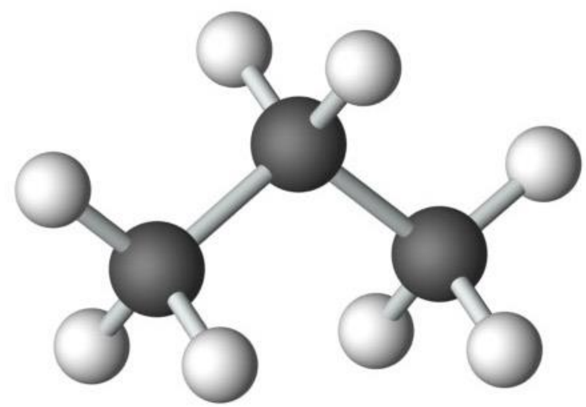
Representations of Molecules



Structural Formula

Ball and Stick



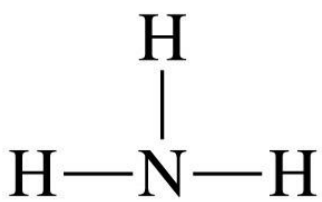
Condensed Structural Formula

$CH_3CH_2CH_3$

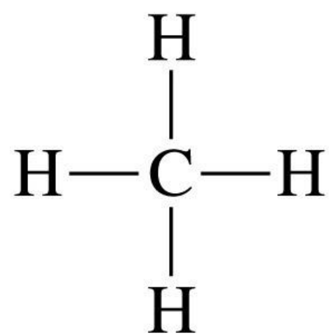
EOS

Structural Formulas – Derived from Lewis Structures

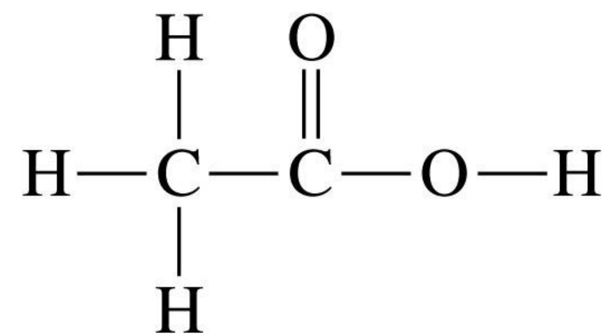
Show how atoms are attached to one another.



Ammonia (NH_3)



Methane (CH_4)



Acetic acid (CH_3COOH)

Electron Pairs in Lewis Symbols

- Symbolized by a line between the atoms

- May include up to three pairs of e^-:

  *One pair forms a **single bond*** *X-Y*

  *Two pairs form a **double bond*** *X=Y*

  *Three pairs form a **triple bond*** *X≡Y*

Not All Atoms Share Electrons Equally

- While electrons in a covalent bond are shared, the electrons are not evenly distributed between the two nuclei
- ***Electronegativity*** is a measure of the attractive force that one atom in a covalent bond has for the electrons of the bond

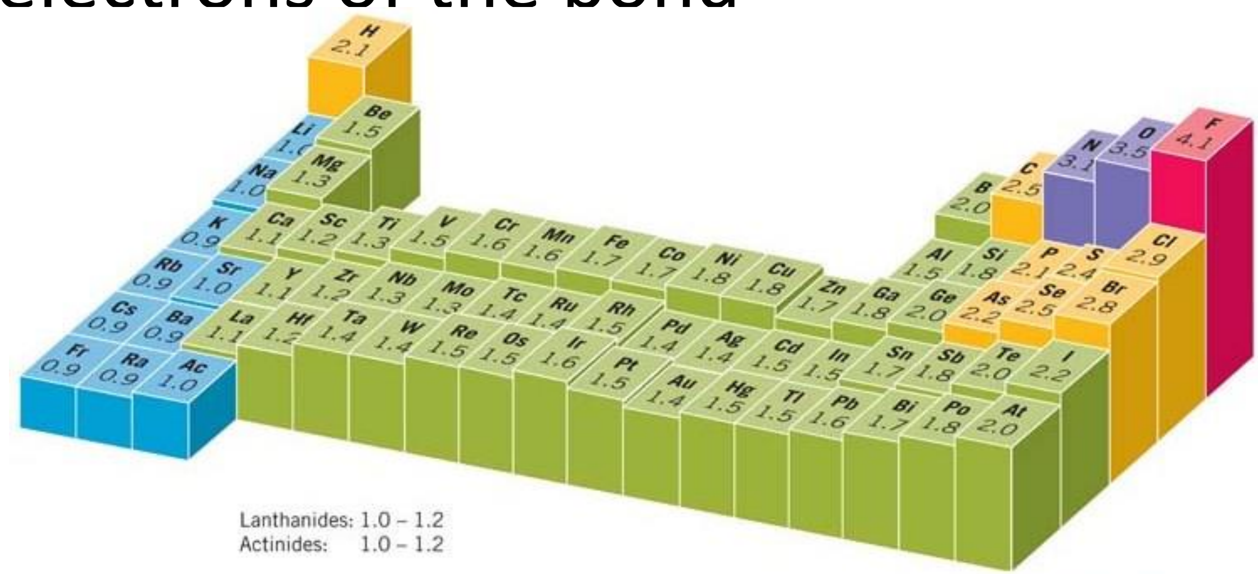
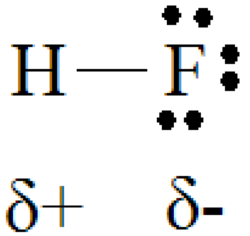


FIG. 8.6 The electronegativities of the elements.

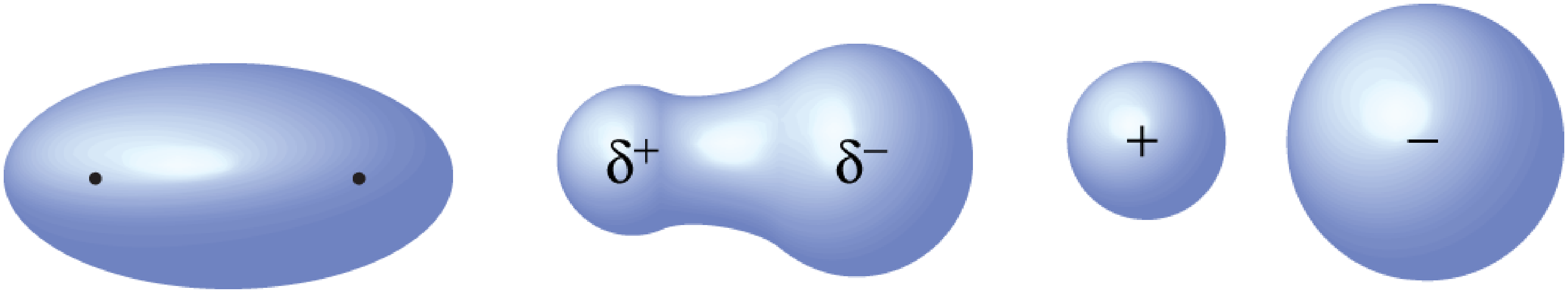
Bond Dipoles

- Atoms with different electronegativity values will share electrons unequally
- Electron density is uneven, with a higher charge concentration around the more electronegative atom
- ***Bond dipoles*** indicate with delta (δ) notation that a partial charge has arisen
- Partial negative (δ-) charge is assigned to the more electronegative element
- Such a bond is termed a ***polar bond***



Electronegativity

- The polarity of a bond depends on the difference between the electronegativity values of the atoms forming the bond



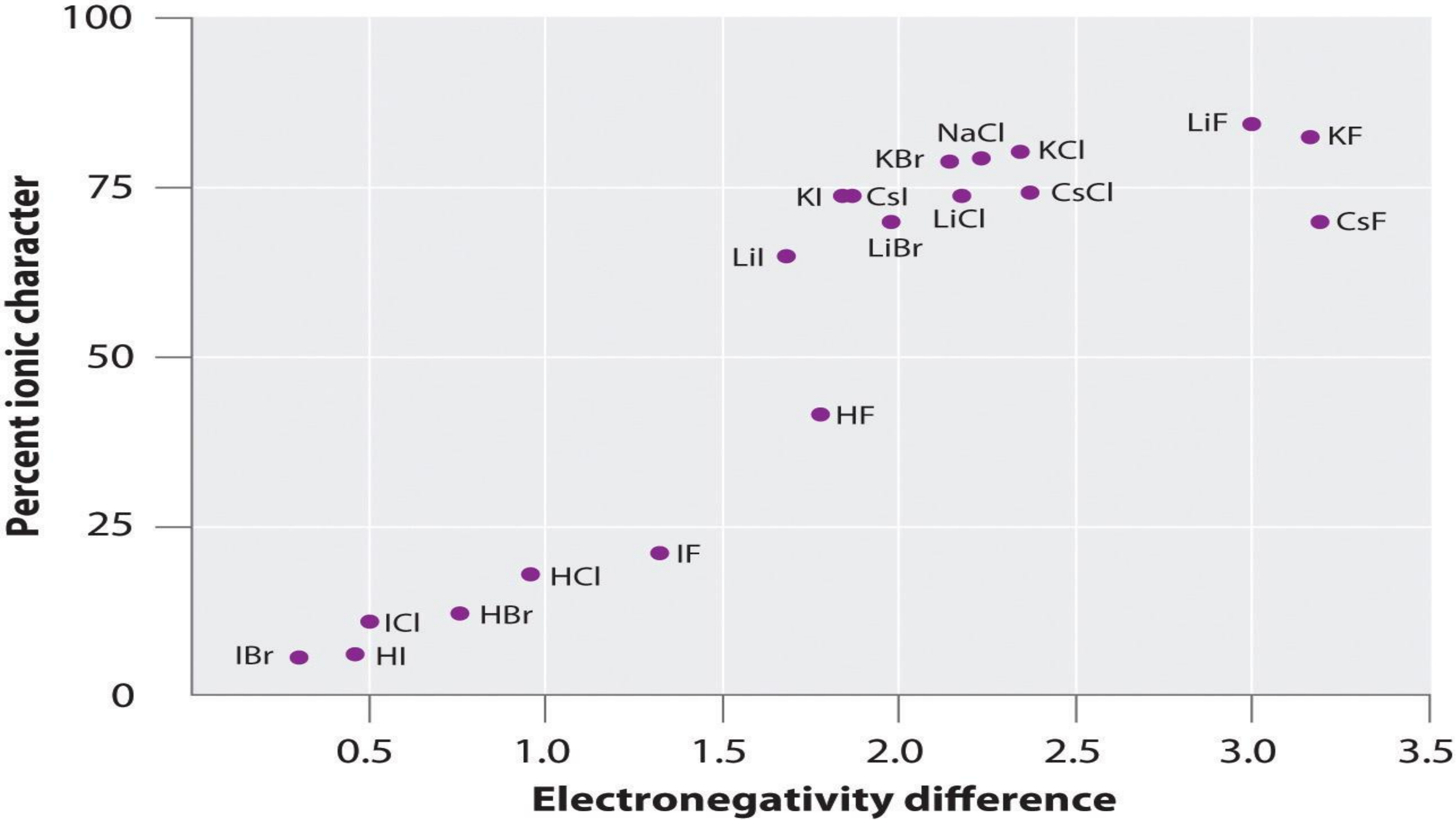
(a) (b) (c)

Differences in Electronegativity Indicate Bond Polarity

Type of Bond	Difference in Electronegativity
Non-Polar Covalent	less than 0.5
Polar Covalent	between 0.5 and 2.1
Ionic	greater than 2.1

http://chemsite.lsrhs.net/ChemicalBonds/electronegativity.html

Partial Ionic Character of Bonds



Compare differences in electronegativity.

None of the bonds reach 100% ionic character –

(measured dipole moment/ calculated dipole moment x 100 %)

An Example:

Using the electronegativity values given in Figure 12.4, arrange the following bonds in order of increasing polarity: H—H, O—H, Cl—H, S—H, and F—H.

Bond	Electronegativity Value	Difference in Electronegativity Values	Bond Type	Polarity
H—H	(2.1) (2.1)	2.1 − 2.1 = 0	Covalent	Increasing ↓
S—H	(2.5) (2.1)	2.5 − 2.1 = 0.4	Polar covalent	
Cl—H	(3.0) (2.1)	3.0 − 2.1 = 0.9	Polar covalent	
O—H	(3.5) (2.1)	3.5 − 2.1 = 1.4	Polar covalent	
F—H	(4.0) (2.1)	4.0 − 2.1 = 1.9	Polar covalent	

Therefore, in order of increasing polarity, we have

H—H S—H Cl—H O—H F—H

Dipole Moment

- $\mu = q \times r$
  - q= charge in coulombs, C
  - r= distance separating charges, m
  - 1 D=3.34×10^{30} C m

TABLE 8.2 **Dipole Moments and Bond Lengths for Some Diatomic Molecules[a]**

Compound	Dipole Moment (D)	Bond Length (pm)
HF	1.83	91.7
HCl	1.09	127
HBr	0.82	141
HI	0.45	161
CO	0.11	113
NO	0.16	115

[a]*Source*: National Institute of Standards and Technology.

Lewis Structures For Covalent Structures

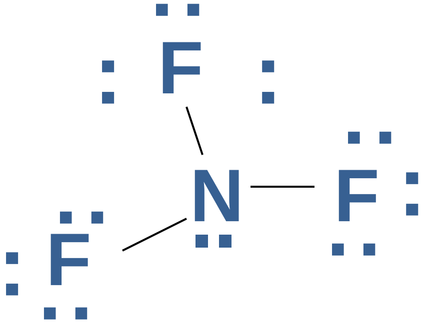
- Arrange atoms around central atom
- Sum valence electrons; divide by 2 to find pairs
- Bond atoms to central atom with a single bond
  - bond pairs are shown as a line; non-bonding e- are shown as dots

Lewis Structures For Covalent Structures

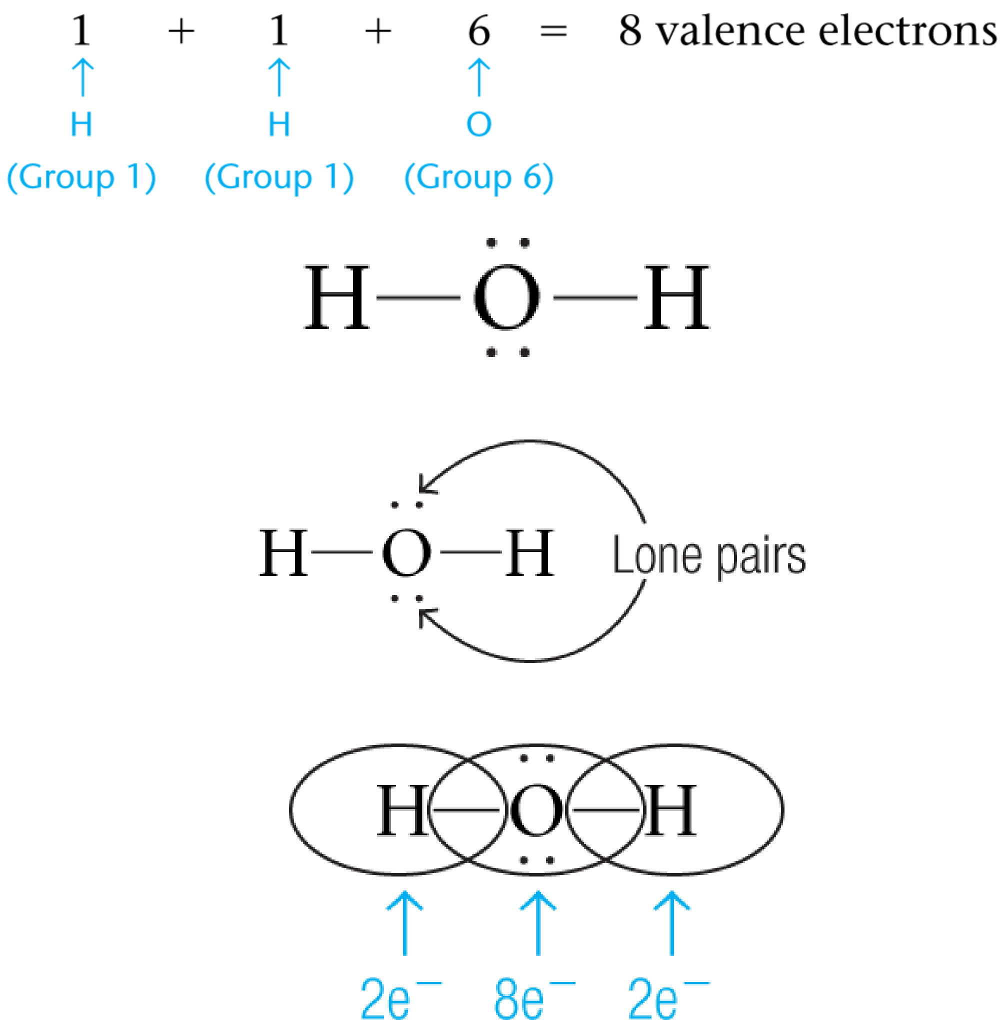
- Complete the octet for central atom
- Distribute e- to complete the octet for any attached atoms
  - place extra electrons on central atom
  - form double/triple bonds if necessary to complete octet atoms and/or reduce formal charges
- Central atom is the unique atom
- If there is more than one element contributing only one atom, the element farther left on the periodic table is the central atom
- H is always terminal
- Halogens are usually terminal
- C is always central

Draw the Lewis Structure for NF_3

- Which atom is the central atom?
- How many valence e- does NF_3 have? **$5 + 3(7) = 26\ e^-$**
- Bond N to F
- Satisfy the N octet
- How many e^- remain? Distribute them on F to complete octet.
- Does each atom have an octet? If not, multiple bond.



Writing Lewis Structures



Lewis Structures of Molecules with Multiple Bonds

- Single bond – covalent bond in which 1 pair of electrons is shared by 2 atoms
- Double bond – covalent bond in which 2 pairs of electrons are shared by 2 atoms
- Triple bond – covalent bond in which 3 pairs of electrons are shared by 2 atoms
- Atoms that often form multiple bonds are C, O, N, P, and S
- Because of their flexibility in bonding types, these often form the backbone of large (more than 5 atoms) molecules
- Carbon Hates Lone Pairs of Electrons!
  - After you have drawn your structure, check to see if carbon has any lone (unshared) e- pairs
  - if it does, check to see if there is any other arrangement
  - Two common species exist with lone pairs on C: CN-, and CO. What are their Lewis structures?

Exceptions To Octet Rule

- H and He follow the duet rule
- B usually has only 6 surrounding electrons
- Be bonds with just 4 surrounding electrons
- Elements in the 3rd period and higher contain “d” orbitals, so may accommodate more than 8. This is not the most likely situation, but can occur.
- The result is an “expanded octet”

Bond Length And Bond Order

- ***Bond length*** is the distance between the nuclei of the two atoms in a bond
- ***Bond order*** is the number of electron pairs shared between the atoms
- As bond order increases, the bond length decreases and the ***bond energy*** increases, provided we are comparing bonds between the same elements

Bond	Bond Length (pm)	Bond Energy (kJ/mol)
C–C	154	348
C═C	134	615
C≡C	120	812

Isomerism and Resonance: Variations on a Theme

- Structures with the same formula in which the atoms are in different arrangement are termed ***isomers***
- If the atoms are in the same geometric configuration but the electrons are arranged differently, the structures are termed_***resonance structures***
- How do you know if your structure is reasonable? Check the ***formal charges***!

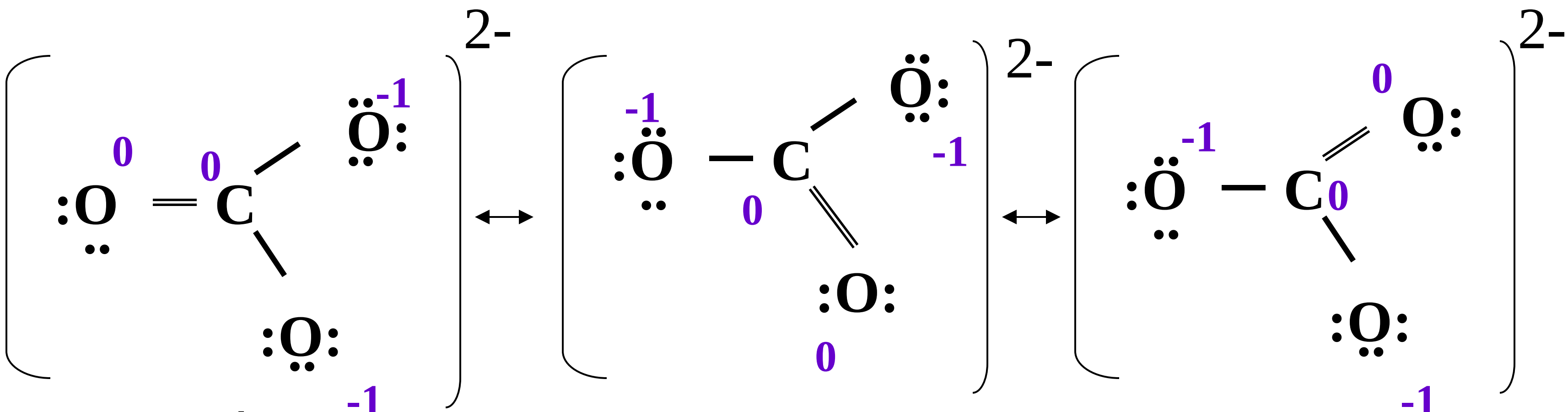
Formal Charges

FC = [# Valence e^-] –[# bonds + # unshared e^-]

- Sum of FC = charge on particle
- Calculated for all atoms in the structure
- A good structure should have :
  - small formal charge values (0 is best)
  - few atoms with a non-zero formal charge
  - most electronegative element is 0 or negative
  - no adjacent positive or negative formal charges

Evidence of Resonance: Carbonate, CO_3^{2-}

- Three possible ways of writing the Lewis structure
- Structures have equally good formal charge distribution
- Experimental bond lengths are the same
- Actual molecule must be a blend



Resonance Structures: The Nitrate Ion, NO_3^-