Chem 1045 — **General Chemistry by Ebbing and Gammon, 8th Edition**

Prof George W.J. Kenney, Jr — **Last Update: 06-April-2009**

Chapter 9 Ionic and Covalent Bonding

These Notes are to SUPPLIMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

The author is providing these notes as an addition to the students reading the text book and listening to the lecture. Although the author tries to keep errors to a minimum, the student is responsible for correcting any errors in these notes.

Chemical Bond is a strong attractive force that exists between certain atoms in a substance.

Ionic Bonds result from the attractive force of oppositely charged ions. e.g. NaCl = Na^+ + Cl^-

Na looses one electron to become Na^+. Build up for Sodium, atomic number 11:

1s	2s	2p (-1)	2p (0)	2p (+1)	3s
↑↓	↑↓	↑↓	↑↓	↑↓	↑

Cl takes on one electron to become Cl^- Build up for Chlorine, atomic number 17:

1s	2s	2p (-1)	2p (0)	2p (+1)	3s	3p (-1)	3p (0)	3p (+1)
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑

Salts are crystalline solids with high MP's.

Covalent Bonds result where two atoms share valence electrons. e.g. Cl_2 Cl : Cl

Metalic Bonds in a crystal where the valence electrons move throughout the crystal and are attracted to the positive cores of the metal positive ion.

9.1 Ionic Bond

9.1 Ionic Bond is a chemical bond formed by the electrostatic attraction between positive and negative ions.

The **Cation +**. Is the atom that loses electrons becomes **positively** charged.

The **Anion -** is the atom that gains the electron and is **negatively** charged.

Ionic bonded compounds usually form a crystalline ionic solid.

Na + Cl → NaCl → Na^+ + Cl^-

And showing the electron transfer based on a Noble Gas Configuration [produce stable compounds]:

REACTANT — **PRODUCTS**

Na = [Ne] $3s^1$ + Cl = [Ne] $3s^2$ $3s^5$ → Na+ [Ne] + Cl- [Ne] $3s^2$ $3p^6$

Na· + :Cl· (with two dots above and two below Cl) → Na^+ + [: Cl :]$^-$ (with two dots above and two below Cl)

Build up for Sodium, atomic number 11:

1s	2s	2p -1	2p 0	2p +1	3s	
↑↓	↑↓	↑↓	↑↓	↑↓	↑	Can loose this electron

Build up for Chlorine, atomic number 17:

1s	2s	2p -1	2p 0	2p +1	3s	3p -1	3p 0	3p +1	
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	Gains and electron

Each of the products now has a noble gas configuration for the outer electron shell. This forms a very stable ionic solid with a high melting point.

<u>Lewis electron-dot symbol:</u> the electrons in the valence shell of the atom or ion are represented by dots which are placed around the letter symbol of the element.

Na· + ·Cl: → Na+ + :Cl:

Writing the Lewis Electron Dot Formulae

Bonding electron pairs are shown by either two dots ":" or a dash "-".

1. Calculate the total number of valence electrons for the molecule

   \# of valence electrons = the group number

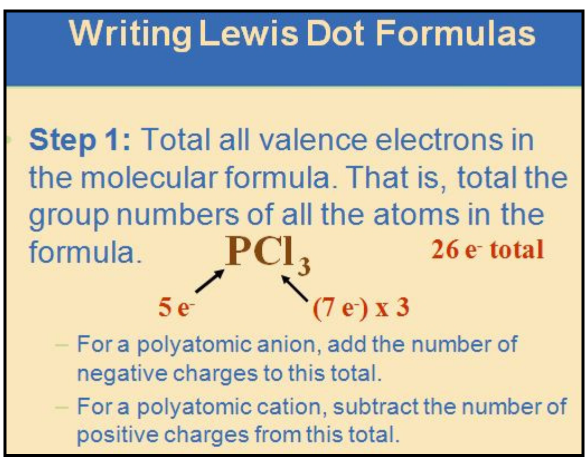
   For an anion [CO_3^{-2}] add 2 electrons for the negative charges

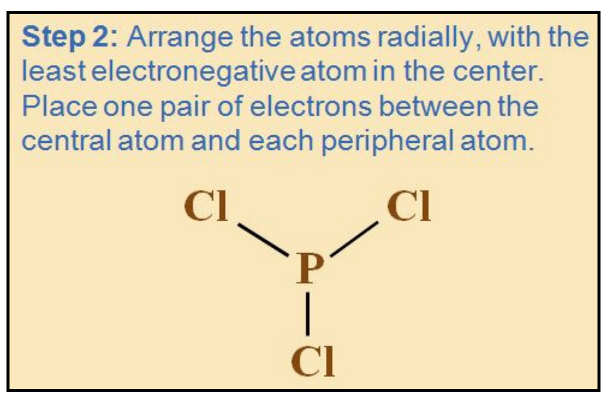
   For a cation [NH_4^+] subtract the number of positive charges

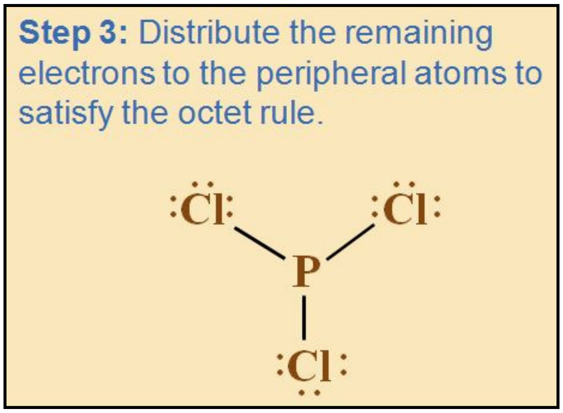
2. Write the skeleton structure of the molecule connecting the bonded pair of atoms with dots or dash

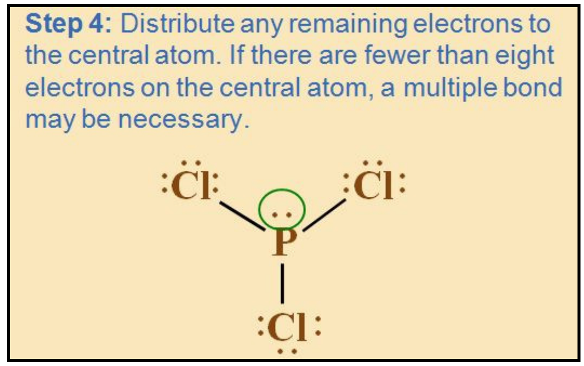
3. Distribute the electrons to the atoms surrounding the central atom to satisfy the octet rule

4. Distribute the remaining electrons as pairs to the central atom









Lewis Electron Dot Symbols for Atoms of the 2nd and 3rd Period

Period	1A ns^1	IIA ns^2	IIIA $ns^2\ np^1$	IVA $ns^2\ np^2$	VA $ns^2\ np^3$	VIA $ns^2\ np^4$	VIIA $ns^2\ np^5$	VIIIA $ns^2\ np^6$
2nd	Li·	·Be·	·B·	·C·	: N·	: O·	: F·	: Ne :
3rd	Na·	·Mg·	·Al·	· Si ·	: P ·	: S ·	: Cl ·	: Ar :

Example 9.1 Use the Lewis Symbols for Magnesium to Fluorine electron transfer in MgF_2.

: F· + ·Mg· + ·F : → [: F :]$^-$ + Mg $+^2$ + [: F :]$^-$

Exercise 9.1 Use the Lewis Symbols for Magnesium to Oxygen electron transfer in MgO.

Transition Metals form several ions

They lose the ns electrons before the (n-1)d electrons

Fe Z=26 X $d^6\ 4s^2$ Loosing the $4s^2 = Fe^{+2}$

Mn Z=25 *$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$* *$M^{+2}$ loose the $4s^2$*

Ionic Bonding Energy: when atoms come together and bond, there should be a decrease in energy. This is due to the attraction of the oppositely charged ions.

You can estimate the oppositely charge ion attraction using Coulombs Law!

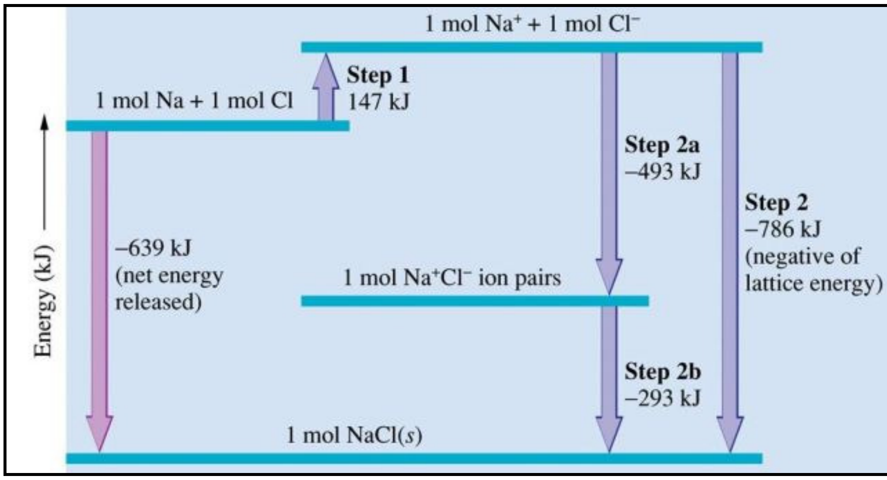
$$\mathbf{E = k\ Q_1\ Q_2 / r_2}$$

E = energy obtained in bringing two ions together, **Q** charges, **r** = distance apart

NaCl vs MgO. Q1/2 is larger for MgO, +1 for NaCl, +2 for MgO. The distance between the molecules is closer together for MgO. Therefore MgO will be held together with more energy than NaCl.
NaCl melts at 801 °C. MgO melts at 2800 °C.

Lattice Energy is the change in energy that occurs when an ionic solid is separated into its isolated ions in the gas phase:

$NaCl_{solid} \rightarrow Na^+_{gas} + Cl^-_{gas}$ 639 kJ / mol [must put energy into it]



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Born-Haber Cycle is used to indirectly determine the lattice energy of an ionic solid from an experiment using a theromchemical cycle:

1. Sodium sublimes [metal to vapour] $Na_s \rightarrow Na_g$ $\Delta H = 108$ kJ
2. Dissociation of Chlorine $\frac{1}{2} Cl_{2g} \rightarrow Cl_g$ $\Delta H = 120$ kJ
3. Ionization of the Sodium $Na_g \rightarrow Na^+_g + e^-$ $\Delta H = 496$ kJ
4. Formation of the Chloride $Cl_g + e^- \rightarrow Cl^-_g$ $\Delta H = -349$ kJ
5. Formation of NaCl $\underline{Na^+_g + Cl^-_g \rightarrow NaCl}$ $\Delta H =$ - Lattice Energy

$Na_s + \frac{1}{2} Cl_{2g} \rightarrow NaCl$ $\Delta H = 375$ kJ - Lattice Energy

The Enthalpy of formation , ΔH_f has been determined to be – 411 kJ.
So the **Lattice Energy** is 365 kJ + 411 kJ = 786 kJ.

Properties of Ionic Substances
High melting point solids due to the strong bonding interaction between the small spherical cations and anions. Melting involves the ions vibrating apart through larger and larger distances.

Electron Configuration of Ions

Ionization Energies of	Element	1st	2nd	3rd	4th
In kJ / mol	**Na**	**496**	*4,562*	*6,912*	*9,543*
	Mg	**738**	**1,451**	*7,733*	*10,540*
	Al	**578**	**1,817**	**2,745**	*11,577*

These ions have the noble or pseudo-noble gas configurations:
$Na \rightarrow Na^+ + 1\,e^-$ $Mg \rightarrow Mg+^2 + 2\,e^-$ $Al \rightarrow Al^{+3} + 3\,e^-$

Tin = Sn Element # 50. Forms $SnCl_2$ using ionic bonds
Forms $SnCl_4$ using covalent bonds **Class Project**
Z = 50 = Sn Period 5, Group Iva

Summary of Monoatomic ions:
1. Group IA to IIIA Cations have noble or pseudo-noble gas config, the ion charge equals the group number.
2. Group IIIA to VA Cations with ns^2 electrons, the ion charge equals the group number minus 2.
   Z = 81 Ti+ IIIA, Z = 50 Sn2+ IVA, Z = 82 Pb2+ IVA, Z = 82 Bi3+ VA.
3. Groups VA to VIIA Anions having noble or pseudo-noble gas configs, the ion charge equals the group number minus 8.

\

Example 9.2 Write the Lewis Symbol for N^{-3} [He] $2s^2$ $2p^3$ $\left[\ :\underset{..}{N}:\ \right]^{-3}$

Exercise 9.2 Write the electron configuration and Lewis Symbol for Ca^{2+} and S^{2-} **Class Project**
The electron configuration of the Ca atom is $[Ar]4s^2$.
By losing two electrons, the atom assumes a 2+ charge and the argon configuration, [Ar].
The Lewis symbol is Ca^{2+}.

The S atom has the configuration $[Ne]3s^23p^4$.
By gaining two electrons, the atom assumes a 2- charge and the argon configuration $[Ne]3s^23p^6$ and is the same as [Ar]. The Lewis symbol is $\left[\ :\ddot{\underset{..}{S}}:\ \right]^{2-}$

Exercise 9.3 Write the electron configuration and Lewis Symbol for Pb and Pb2+ **Class Project**

The electron configuration of lead (Pb) is $\mathbf{[Xe]4f^{14}5d^{10}6s^26p^2}$.

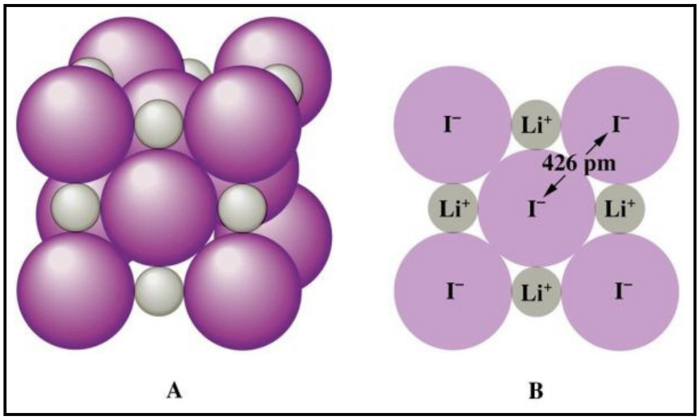
The electron configuration of Pb^{2+} is $\mathbf{[Xe]4\mathit{f}^{14}5\mathit{d}^{10}6\mathit{s}^2}$.

Polyatomic Ions The polyatomic ions are held together by covalent bonds [discussed later] and these covalently bonded polyatomics form ions!

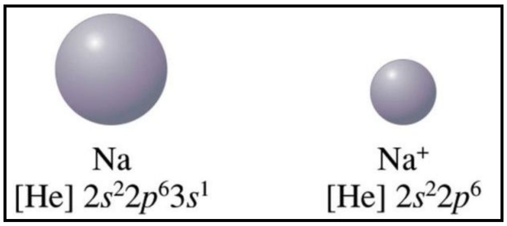
Name	Formula	Name	Formula
Mercury(I) or mercurous	Hg_2^{2+}	Nitrite	NO_2^-
Ammonium	NH_4^+	Nitrate	NO_3^-
Cyanide	CN^-	Hydroxide	OH^-
Carbonate	CO_3^{2-}	Peroxide	O_2^{2-}
Hydrogen carbonate (or bicarbonate)	HCO_3^-	Phosphate	PO_4^{3-}
		Monohydrogen phosphate	HPO_4^{2-}
Acetate	$C_2H_3O_2^-$	Dihydrogen phosphate	$H_2PO_4^-$
Oxalate	$C_2O_4^{2-}$	Sulfite	SO_3^{2-}
Hypochlorite	ClO^-	Sulfate	SO_4^{2-}
Chlorite	ClO_2^-	Hydrogen sulfite (or bisulfite)	HSO_3^-
Chlorate	ClO_3^-		
Perchlorate	ClO_4^-	Hydrogen sulfate (or bisulfate)	HSO_4^-
Chromate	CrO_4^{2-}		
Dichromate	$Cr_2O_7^{2-}$	Thiosulfate	$S_2O_3^{2-}$
Permanganate	MnO_4^-		

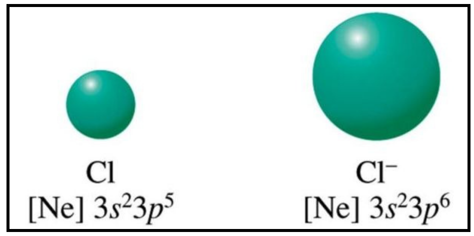
Transition-Metal Ions form several cations. Iron forms Fe^{2+} and Fe^{3+}.
They usually loose the outer s^2 electrons first and then some d electrons.
The +2 results from the loss of the s^2 electrons.

Ionic Radius is a measure of the size of a spherical region around the nucleus of an ion within which the electrons are most likely to be found.



LiI crystal. ½ the distance between two iodine nuclei [426 pm]is the ionic radius [213 pm].





Sodium looses the one 3s1 electron, so Na^+ ionic radius is smaller
Chlorine gains a 3p electron so the Cl^- ionic radius is larger.

Exercise 9.5 Which has the larger radius, S or S^{2-}? **Class Project**

S^{2-} has a larger radius than S.

The anion has more electrons than the atom.
The electron-electron repulsion is greater; hence, the valence orbitals expand.
The anion radius is larger than the atomic radius.

A Cation is always smaller than its neutral atom Na^+ is smaller than Na

Ionic Radii in pm

Period	**IA**	**IIA**	**IIIA**	**VIA**	**VIIA**
2	Li^+ 60	Be^{+2} 31		O^{-2} 140	F^- 136
3	Na^+ 95	Mg^{+2} 65	Al^{+3} 50	S^{-2} 184	Cl^- 181
4	K^+ 133	Ca^{+2} 99	Ga^{+3} 62	Se^{-2} 198	Br^- 195
5	Rb^+ 148	Sr^{+2} 113	In^{+3} 81	Te^{-2} 221	I^- 216

Ionic radii increase going down a column because of the addition of electrons
Ionic radii decrease going partially across due to the increase in positive nuclear charge

Isoelectronic refers to different species having the same number and configuration of electrons:
Na^+ and Mg^{+2} and Al^{+3} all have the same outer electron configuration.
But number of positive charges in the nucleus increases, so there is a greater attractive force with Al^{+3} over Na^+.

Example 9.4 Order the following in decreasing ionic size and explain? F^-, Mg^{2+}, O^{2-}.
Answer: All have the same outer electron configuration: $1s^2$ $2s^2$ $3p^6$.
So the size will decrease as Z increases – more protons in the center pulling in on the electron cloud.

Exercise 9.7 Order the following in decreasing ionic size and explain? Cl^-, Ca^{2+}, P^{3-}. **Class Project**

Cl^-, Ca^{2+}, and P^{3-} are isoelectronic with an electronic configuration equivalent to [Ar].
In an isoelectronic sequence, the ionic radius decreases with increasing nuclear charge.
Therefore, in order of increasing ionic radius, we have Ca^{2+}, Cl^-, and P^{3-}.

COVALENT BONDS are a chemical bond formed by sharing of a pair of electrons between atoms.

Hydrogen = H_2 = H· + ·H = H : H

The electrons are attracted simultaneously by the positive charges of the two hydrogen nuclei.
The attraction bonds the electrons to both nuclei and is the **binding force** holding the atoms together.

Bond Length is the distance between the nuclei at the minimum energy

Bond Dissociation Energy is the energy that must be added to separate the atoms n the molecule.

Lone Pair are the bonding pair of electrons, they are shared between the atoms.

Lone Pair are the electron pair that remain on one atom, they are not shared between atoms.

Usually, the **number of bonds** formed by an atom in Grp IVA to VIIA equals the number of unpaired electrons in the atom [or 8 – Group Number].

```
                    . .          . .
Lewis Formula:  H· + ·Cl :  →  H : Cl :     Note which e- are the lone pair and bonding pair
                    ..           ..

                                 H
                     .          . .
        3 H· + ·N :  →  H : N :
                                 ..
                                 H
```

Coordinate Covalent Bonds are bonds formed when both electrons of the bond are donated by one atom:

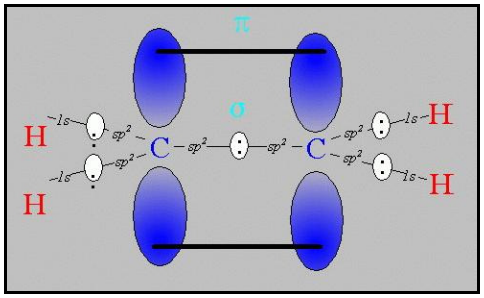
```
                              H
                              . .
H⁺  +  : NH₃  →  [ H : N :  H ]⁺
                              ..
                              H
```

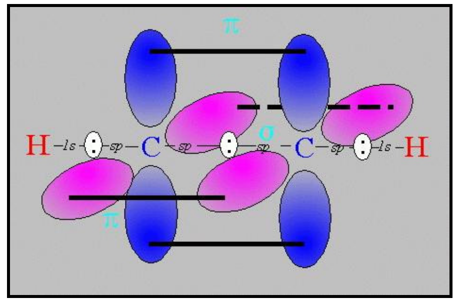
Octet Rule is the tendency of atoms in molecules to have eight electrons in their valence shells.

Multiple Bonds: **Single Bond** is a covalent bond in which a single pair of electrons is shared by two atoms
Double Bond is a covalent bond in which two pairs of electrons is shared
Triple Bond is a covalent bond is which three pairs of electrons is shared

Double bonds occur with C, N and O. Triple bonds with C and N.

$H_3C - CH_3$	$H_2C = CH_2$	HC = CH
Ethane	Ethylene	Acetylene





- The **bond order**, determined by the Lewis structure, is the number of pairs of electrons in a bond.
  - Bond length depends on bond order.
  - As the bond order increases, the bond gets shorter and stronger.

	Bond length	Bond energy
C—C	154 pm	346 kJ/mol
C═C	134 pm	602 kJ/mol
C≡C	120 pm	835 kJ/mol

Polar Covalent Bonds is a covalent bond is which the bonding electrons spend more time near one atom than the other.

H : H	H : Cl :	Na^+ : Cl :$^-$
Non Polar Covalent	Polar Covalent	Ionic

Electronegativity is a measure of the ability of an atom in a molecule to draw bonding electrons to itself

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	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	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
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
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	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 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7														

Left side of the periodic table slight Electronegativity. Right side has strong electronegativity. Electronegativity increases going from left to right and decreases going from top to bottom

Fluorine attracts one electron easily to complete its p orbital.

<u>DRAW THE ELECTRON CONFIGURATION OF F and F^-</u>

Nonpolar bonds form when the difference in electronegativity is less than 0.5

Polar bonds form when the difference in electronegativity is greater than 0.5

Ionic bonds form when the difference in electronegativity is greater than 1.8

Ionic Bonds form between a metal and non metal because the **electronegativity differences are the largest**

Covalent Bonds form between two nonmetals because the **electronegativity differences are small**

The large differences in electronegativity between metals and non-metals explain why they form Ionic Bonds.
The small difference in electronegativity between two non-metals explain why they form Covalent Bonds

Example 9.5 Arrange the following according the order of increasing polarity

P — H	H — O	C — Cl
2.1 2.1	2.1 3.5	2.5 3.0
1st	**3rd**	**2nd**

Exercise 9.8 Which bonds are most polar:

C — O	C — S	H — Br
2.5 3.4	2.5 2.5	2.1 2.8

The absolute value of the electronegativity differences are C-O, 1.0; C-S, 0.0; and H-Br, 0.7.
Therefore, C-O is the most polar bond.

HCl is a polar molecule – **why & show the relative charges?**

Example 9.6 Sulfur dichloride is SCl_2, write the Lewis Formulae?

S is element 16 in Group VI. So it has 6 valence electrons [$1s^2$ $2s^2$ $2p^6$ $\underline{\mathbf{3s^2\ 3p^4}}$]

Cl is element 17 in Group VII, so it has 7 electrons [$1s^2$ $2s^2$ $2p^6$ $\underline{\mathbf{3s^2\ 3p^5}}$]

S = 6, 2 Cl = 2 * 7 = Total of 20 electrons

```
  ..    ..                             ..  ..  ..
: Cl : S : Cl :   is 16 electrons.  Then  : Cl : S : Cl :
  ..    ..                             ..  ..  ..
```

Exercise 9.9 Write the Lewis Formulae? $C\ Cl_2\ F_2$

First, calculate the total number of valence electrons.

C has four, Cl has seven, and F has seven.

The total number is 4 + (2 x 7) + (2 x 7) = 32.

The expected skeleton consists of a carbon atom surrounded by Cl and F atoms.

Distribute the electron pairs to the surrounding atoms to satisfy the octet rule.

All 32 electrons (16 pairs) are accounted for.

```
      ..
     : Cl
  ..   ..
: F :  C  : F
  ..   ..
     : Cl :
      ..
```

Example 9.7 Write the electron dot formulae for: C O Cl_2

C is element 6 in Group IVA. So it has 4 valence electrons [$1s^2$ **$2s^1$ $2p^3$**]
O is element 8 in Group VI. So it has 6 valence electrons [$1s^2$ **$2s^2$ $2p^4$**]
Cl is element 17 in Group VII, so it has 7 electrons [$1s^2$ $2s^2$ $2p^6$ **$3s^2$ $3p^5$**]

The total number of valence electrons is 4 + 6 + (2 * 7) = 24. Assume the Carbon is the central atom.

```
  ..       ..                      ..         ..
: Cl : C  : O :                  : Cl -- C -- O :
  ..   ..   ..         or          ..    |    ..
    : Cl :                             : Cl :
      ..                                 ..
```

This takes care of all 24 electrons, but the Carbon only has 6 instead of 8, so we move two of the oxygen electrons:

```
  ..       ..                      ..         ..
: Cl : C :: O                    : Cl -- C == O
  ..   ..   ..         or          ..    |    ..
    : Cl :                              : Cl :
      ..                                  ..
```

Exercise 9.10 Write the electron dot formulae for CO_2

The total number of electrons in CO_2 is 4 + (2 x 6) = 16.
Because carbon is more electropositive than oxygen, it is expected to be the central atom.
Distribute the electrons to the surrounding atoms to satisfy the octet rule.

```
   ..
:  O : C : O
   ..
```

All sixteen electrons have been used, but notice there are only four electrons on carbon.
This is four electrons short of a complete octet, which suggests the existence of double bonds.
Move a pair of electrons from each oxygen to the carbon-oxygen bonds.

```
..                ..
O : : C : :   or  O == C == O
..                ..
```

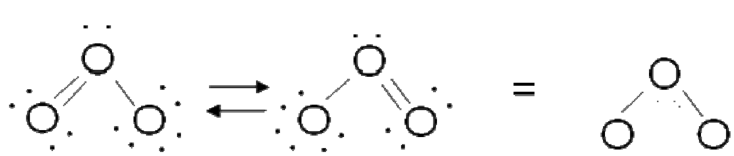
Exercise 9.11 Write the electron dot formulae for BF_4^- SEE BOOK PAGE 350

Exercise 9.11 Write the electron dot formulae for the Hydronium Ion – H_3O^+

There are (3 x 1) + 6 = 9 valence electrons in H_3O.
The H_3O^+ ion has one less electron than is provided by the neutral atoms because the charge on the ion is +1. Hence, there are eight valence electrons in H_3O^+. The electron-dot formula is

```
 _        _  +
|    H     |
|    ..    |
| H : O :  |
|_   ..   _|
```

Delocalization Bonding is a type of bonding in which a bonding pair of electrons is spread over a number of atoms rather then localized between two.
Resonance Description describes the electron structure of a molecule having delocalized bonding by writing all possible electron dot formulae.



Resonance Description **Delocalization Bonding**

Example 9.9 Write the electron structure for the carbonate ion, CO^{2-}

C is element 6 in Group IVA. So it has 4 valence electrons [$1s^2$ $\underline{\mathbf{2s^1\ 2p^3}}$]

O is element 8 in Group VI. So it has 6 valence electrons [$1s^2$ $\underline{\mathbf{2s^2\ 2p^4}}$]

So we have 4 + (3 * 6) electrons = 22 electrons + $2e^-$ = 24 electrons

See picture on 352

Exceptions to the Octet Rule: Will not be covered in this class.

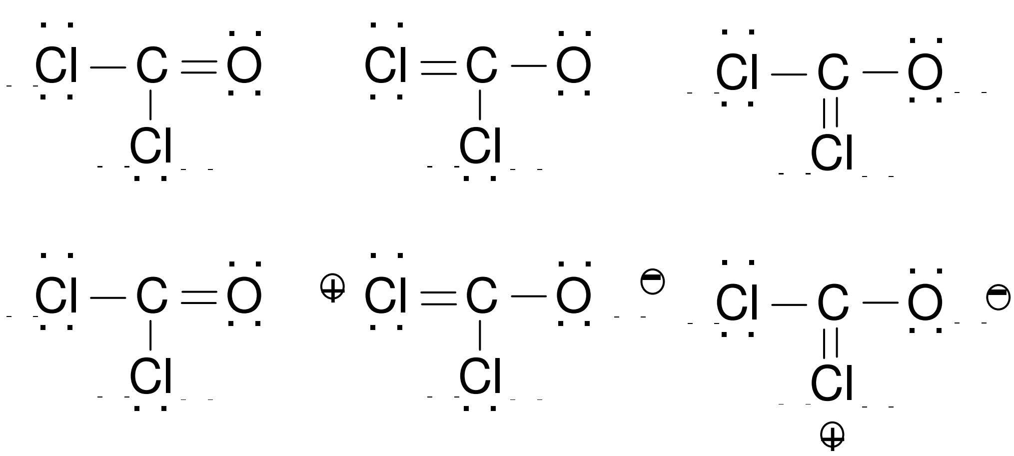
Formal Charges and the Lewis Formulae: Will not be covered in this class.

A Formal charge of an atom in a Lewis Formulae is the hypothetical charge obtained by assuming that bonding electrons are equally shared between bonded atoms and that the electrons of each lone pair belong completely to one atom.

1. Write the possible Lewis Formulae

2. Apply these rules for determining the formal charge on each atom
   A. ½ of the electrons of a bond are assigned to each atom in the bond
   B. Both electrons of a lone pair are assigned to that atom

Calculate the formal charge by taking the number of valence electrons in the free atom and subtracting the number determined above. Then:
Rule A: When you can write several Lewis Structures, the one having the lowest formal charges wins!
Rule B: When 2 structures have the same formal charge, the one having the negative formal charge on the more electronegative atom wins!



Bond Length is the distance between the nuclei in a bond.

Covalent radii are the values assigned to the atoms in such a way that the sum of the covalent radii of atoms A and B predicts and approximate A-B bond length.

Bond Order is the number of pairs of electrons in a bond. C-C is bond order 1, C=C is bond order 2.

Bond Energy is the average enthalpy change for the breaking of an A-B bond in a molecule in the gas phase

A reaction is exothermic if the weak bonds are replaced by strong bonds

Infrared Spectroscopy and Vibrations of Chemical Bonds