

# **Chapter 9**

## **Ionic and Covalent Bonding**

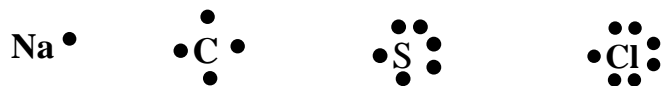
## Lewis Dot Symbol for Elements

Recall: valance  $e^-$  which are  $e^-$  residing in the outermost shell of the atom.

Note: number of valance  $e^-$  in an element is the same as the group number for the main group elements

### Lewis Dot Symbol

is used to represent valance  $e^-$  in an element



Atoms gain, lose or share  $e^-$  to achieve Noble gas  $e^-$  configurations

Nobel gases are stable due to

- 1) high ionization energies
- 2) low  $e^-$  affinities
- 3) low reactivity

How many  $e^-$  are lost or gained?

### Octet Rule ("Rule of 8")

Atoms gain, lose or share  $e^-$  until they are surrounded by 8 valance  $e^-$

(except H, He which has a maximum of 2  $e^-$ . The first shell of  $e^-$  can hold a maximum of two electrons.)

This rule works will for most main group elements. There are exceptions which will be covered later in the section of the Expanded Octet.

## Ionic Bonds

### Ionic Bond

w electrostatic attraction between cations and anions

w involves transfer of  $e^-$

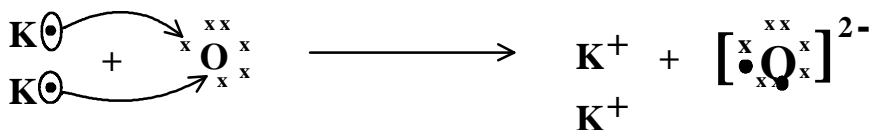
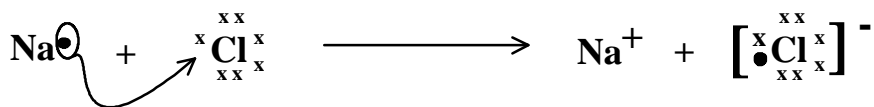
w metal and nonmetal (or polyatomic ions)

recall: anions gain  $e^-$  (form negative ions)

cations lose  $e^-$  (form positive ions)

## Lewis Dot Formula

Show transfer of  $e^-$  Lewis Dot Formula



Do the ions obtain an  $e^-$  configuration of a Noble gas? (yes)

## Energy in Ionic bonds

When a bond forms

- 1)  $e^-$  is transferred between 2 atoms
- 2) ions are attracted to each other

Formation of Ionic Bond involves the release of energy

## Coulomb's Law

used to determine amount of energy released  
includes attraction of oppositely charged ions

E has a negative sign if  
 $Q_1$  and  $Q_2$  have opposite signs

$Q_1$  and  $Q_2$  - charges on the ions  
r - distance between ion charges  
k -  $8.99 \times 10^9 \text{ J/mC}^2$  (physical constant)  
C - coulombs

## Lattice Energy

Energy required to separate a solid ionic substance completely into gaseous ions.



## Why do atoms (metals) lose all their valence $e^-$ ?

Once the Noble gas configuration is achieved Ionization Energy sky rockets.

### Main Group Metals

#### 1) Cations

Group IA to IIIA tend to lose all the valence  $e^-$

#### 2) Cations

Group IIIA to VA (period 4 and greater)

tend to lose the  $p$  subshell  $e^-$  and keep the  $s e^-$

#### 3) Anions

Groups VA and VIIA nonmetals tend to gain  $e^-$

### Transition Metals

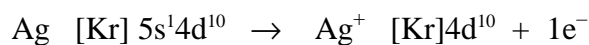
will form ions

a) by losing  $ns 2e^-$  first

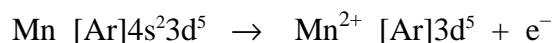
b) after which they will then lose  $(n - 1)d e^-$



Achieve a completely filled shell of  $e^-$  (including  $d$  orbitals)



or half filled  $d$  subshell



## Ionic Radii (sizes of the ions)

The **size of the ion** depends on

- w nuclear charge
- w number of  $e^-$  it possesses
- w orbital in which the outer-shell  $e^-$  reside

### Positive ions (cations)

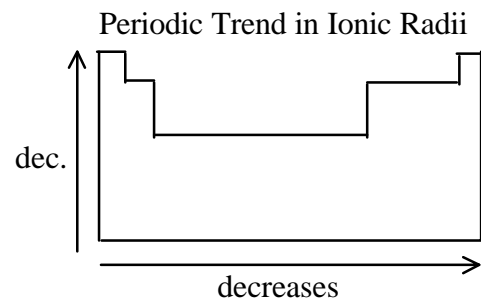
- w formed by removing  $e^-$  from the outermost shell vacates most spatially extended orbital, decreasing the total  $e^- - e^-$  repulsion
- w are smaller than the parent atoms

### Negative ions (anions)

- w formed by adding  $e^-$  to outermost shell, which increases  $e^- - e^-$  repulsions, causing  $e^-$  to spread out more in space
- w are larger than parent atoms

### Periodic trend in ionic radii

- Ions of the same charge (within same column)
  - w decrease in size going up a group
  - because shell of  $e^-$  is decreased going up a column
- Ions within the same row
  - w decrease in size going across a period
  - because the effective nuclear charge increases going across a period



**Isoelectronic series:** ions possess the same number of electrons

- w The radius of an ion in an isoelectronic series decreases with an increase in positive nuclear charge

w series  $O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}$  all have  $10 e^-$ ,  $1s^2 2s^2 2p^6$  or [Ne]

$\xrightarrow{\text{radius decreases}}$

# Covalent Bond

## Covalent bond

involve sharing of a pair of  $e^-$  between atoms  
 nonmetal bonded with another nonmetal

overlapping orbitals

refer to figure 9.9 in Ebbing

This figure shows the potential energy of atoms as they approach one another and then bond

Minimum energy is reached when the repulsion of (+) charge becomes larger than the attraction of  $e^-$  of the nuclei

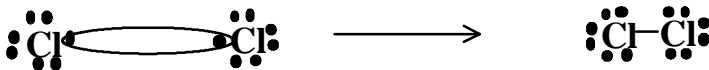
## Lewis Formulas (Lewis Structures)

1) Diatomic molecules:  $H_2$ ,  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $O_2$ ,  $N_2$

a) Single bonds between atoms

Keep in mind the octet rule ('rule of 8')

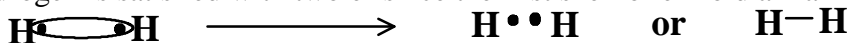
$Cl_2$  each atom has seven valence electrons



$F_2$ ,  $Br_2$ ,  $I_2$  will have the same basic Lewis Formula as  $Cl_2$

$H_2$  hydrogen atoms follows the exception to the 'rule of 8' (the 'rule of 2')

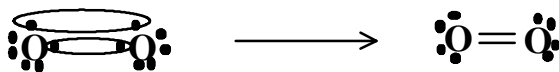
hydrogen is satisfied with two  $e^-$  since the first shell of  $e^-$  hold a maximum of two  $e^-$



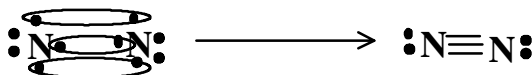
b) Multiple bonds between atoms

need to use the octet rule again to pair up electrons until both atoms have eight  $e^-$  around them

$O_2$



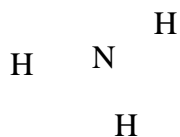
$N_2$



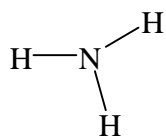


**Example:**ammonia,  $\text{NH}_3$ 

- 1) add up val  $e^-$  : 5 val  $e^-$  from N + 3 \* (1 val  $e^-$ ) from H = 8 val  $e^-$
- 2) determine number of  $e^-$  pairs: 8 val  $e^-$  / 2 = 4  $e^-$  pairs
- 3) arrange atoms: one central atom and the remaining atoms surround the central atom

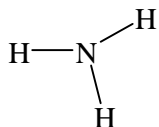


- 4a) connect the central atom to the peripheral atoms with a shared pair of  $e^-$



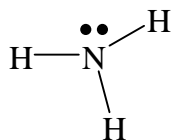
so far 3  $e^-$  pairs have been distributed out of 4  $e^-$  pairs

- 4b) put lone pairs of  $e^-$  on peripheral atoms until the octet rule is satisfied. In the case of hydrogen, the H atom is satisfied with 2  $e^-$  since the first shell of electrons has a maximum capacity of 2  $e^-$ .



so far 3  $e^-$  pairs have been distributed out of 4  $e^-$  pairs

- 4ci) The central atom does not obey the octet rule, N only has 6  $e^-$  or 3  $e^-$  pairs and one  $e^-$  pair still has to be distributed. Put a lone pair of  $e^-$  on N.



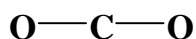
The central atom and the peripheral atoms all obey the octet rule (or 'rule of 2' for H) and all the  $e^-$  pairs have been distributed. Therefore the above structure is the Lewis Structure for  $\text{NH}_3$

**Example:**ammonia,  $\text{CO}_2$ 

- 1) add up val  $e^-$  : 4 val  $e^-$  from C + 2 \* (6 val  $e^-$ ) from O = 16 val  $e^-$
- 2) determine number of  $e^-$  pairs: 16 val  $e^-$  / 2 = 8  $e^-$  pairs
- 3) arrange atoms: one central atom and the remaining atoms surround the central atom

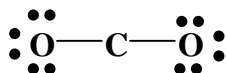


- 4a) connect the central atom to the peripheral atoms with a shared pair of  $e^-$



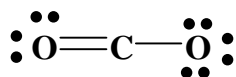
so far 2  $e^-$  pairs have been distributed out of 8  $e^-$  pairs

- 4b) put lone pairs of  $e^-$  on peripheral atoms until the octet rule is satisfied.

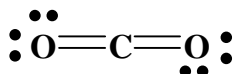


so far 8  $e^-$  pairs have been distributed out of 8  $e^-$  pairs

- 4ci) The central atom does not obey the octet rule, C only has 4  $e^-$  or 2  $e^-$  pairs and all the  $e^-$  pairs have been distributed. Need to form a multiple bond between C and O to help C obtain 8  $e^-$  around it.



Now C has 6  $e^-$  or 3  $e^-$  pairs and still does not satisfy the octet rule. An additional multiple bond is needed.



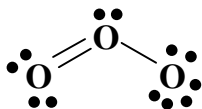
The central atom and the peripheral atoms all obey the octet rule and all the  $e^-$  pairs have been distributed. The above structure is the Lewis Structure for  $\text{CO}_2$

## Resonance in a covalent molecule

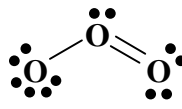
Draw the Lewis structure for ozone,  $O_3$ .

It is possible to draw two structures.

a)

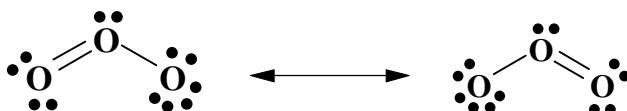


b)



Neither structure is correct. Experiments have shown that two bonds are of equal length, not one longer than the other as one would expect with a single and double bond. It has been theorized that one of the bonding pair of electrons is delocalized over all three oxygen atoms instead of just between two atoms. This delocalization of an electron pair over several atoms is known as **resonance**. To give a better representation of resonance using Lewis structures since two or more structures represent the molecule, a resonance structure is drawn with a double headed arrow written in between them. Resonance structures have the same sequence of atoms but differ in the location of the bonding and lone pairs.

The resonance structure of ozone is



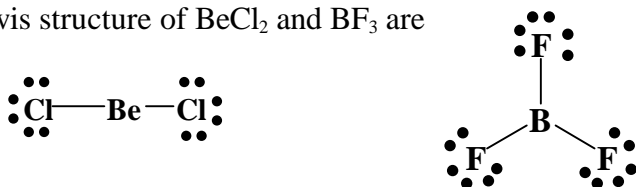
## Exceptions to the Octet Rule

These exceptions usually involve more than or less than an octet of  $e^-$  around the central atom.

### 1) Less than an octet of $e^-$ around the central atom

Molecules containing beryllium and boron often form with fewer than eight  $e^-$  around the Be or B atom.

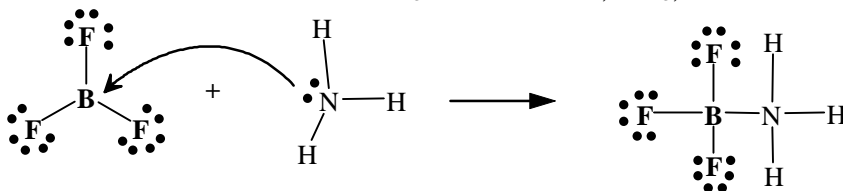
The Lewis structure of  $BeCl_2$  and  $BF_3$  are



Why do multiple bond not form between the Be or B and the halogen to satisfy the octet rule?

Halogen atoms are much more electronegative than Be or B, so the F and Cl will hold on to their lone pairs instead of sharing them. Also, experimental evidence has shown the Lewis structure for  $BF_3$  is correct.

This evidence is the reaction between  $BF_3$  and ammonia,  $NH_3$ , in which B obtains an octet of electrons.



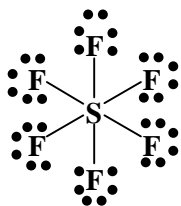
Nitrogen will share both of the electrons in the lone pair when forming a bond with boron. The bond formed when one atom donates both electrons between two atoms is known as a **coordinate covalent bond**.

## 2) More than an octet of $e^-$ around the central atom

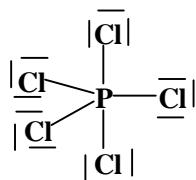
A central atom with an empty outer d subshell can use this subshell to accommodate extra electrons. Therefore elements in period 3 or higher can form an **expanded octet**, which can hold up to 12  $e^-$ .

### Examples:

sulfur hexafluoride,  $SF_6$

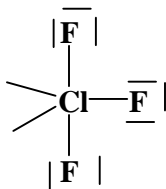


phosphorus pentachloride,  $PCl_5$



A dash represents a pair of electrons

chlorine trifluoride,  $ClF_3$



## Formal Charges

Formal charges are

used to determine best Lewis Formula

w hypothetical charge

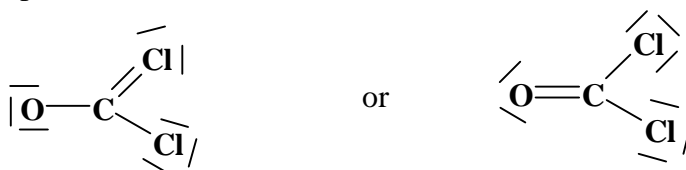
Each atom in the Lewis structure will have a formal charge and it is calculated using the following equation.

$$\text{Formal Charge} = \text{valence } e^- - [\text{lone pair of } e^- + 1/2 \text{ shared pair of } e^-]$$

Note: the lone pair e and the shared pair of e are only those surrounding the element for which the formal charge is being calculated.

What is the Lewis structure for  $\text{COCl}_2$ ?

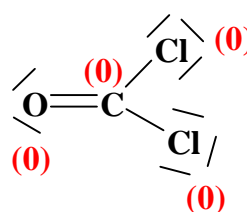
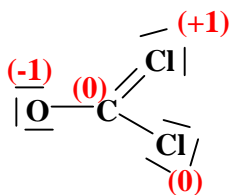
Two structures are possible.



Calculate the formal charges on each element to determine which is the better structure.

The better Lewis Structure will have

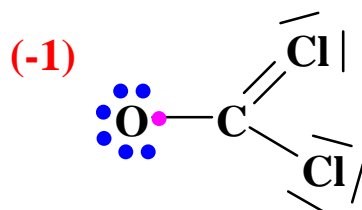
- 1) the lowest magnitude of formal charges (containing mostly zeros for formal charges)
- 2) a negative formal charge on the more electronegative atom.



Since this Lewis structure has all zeros for formal charges, this is the better Lewis structure of the two.

How was the formal charge calculated on the O atom in the first structure?

$$\begin{aligned} \text{Formal Charge} &= \text{valence } e^- - [\text{lone pair of } e^- + 1/2 \text{ shared pair of } e^-] \\ -1 &= 6 - [6 + 1] \end{aligned}$$



## Bond Energy and Strength of a Bond

Bond energy increases with the strength of the chemical bond.

	Bond energy (kJ/mol)	bond length (pm)	Bond length decreases	Strength of bond increases
C—C	346	154	↓	↓
C=C	602	134		
C≡C	835	120		

**Bond order** is equal to the number of pairs of electrons in a bond.

Bond	Order
C—C	1
C=C	2
C≡C	3

## Bond energy (BE)

is the average enthalpy change for breaking a bond between two atoms in a molecule in the gas phase.

Bond energies are used to estimate the heats of reaction,  $\Delta H_{\text{rxn}}$ , for gaseous reactions.

A table of bond energies are found in most General Chemistry textbooks.

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