Chapter 9 - Chemical Bonding

Section 1 - Introduction to Bonding

Dr. Sapna Gupta

Introduction

There are very few elements that occur naturally in the world. Most elements are found in combination with other elements. Even the most common element we can think of, oxygen, is found as a diatomic (O_2) gas and not as just O.

This indicates that there must be more stability in forming a compound with other elements. To understand this stability, we need to review at least two concepts before going forward.

1. Classify the element as metal or nonmetal.
2. Know the number of valence electrons of any element.

Bonding is a valence shell property. The core electrons do not get involved until they become valence electrons.

Why Bonding Occurs

Bonding occurs to make elements more stable. We learn this lesson from the noble gases. Group VIII gases (noble gases) are stable and non-reactive. This must have something to do with their electron configuration. Noble gases have eight electrons in their valence shell. After filling the last electron of noble gases, the next electron is filled in a new shell. A full valence shell must be a stable shell.

We can conclude that all elements try to have the noble gas configuration, which is 8 e- in the valence shell.

This is called the **OCTET RULE.**

Bonding

Ionic
- Transfer of electrons
- Between metals and nonmetals
- Cations and Anions
- High melting points

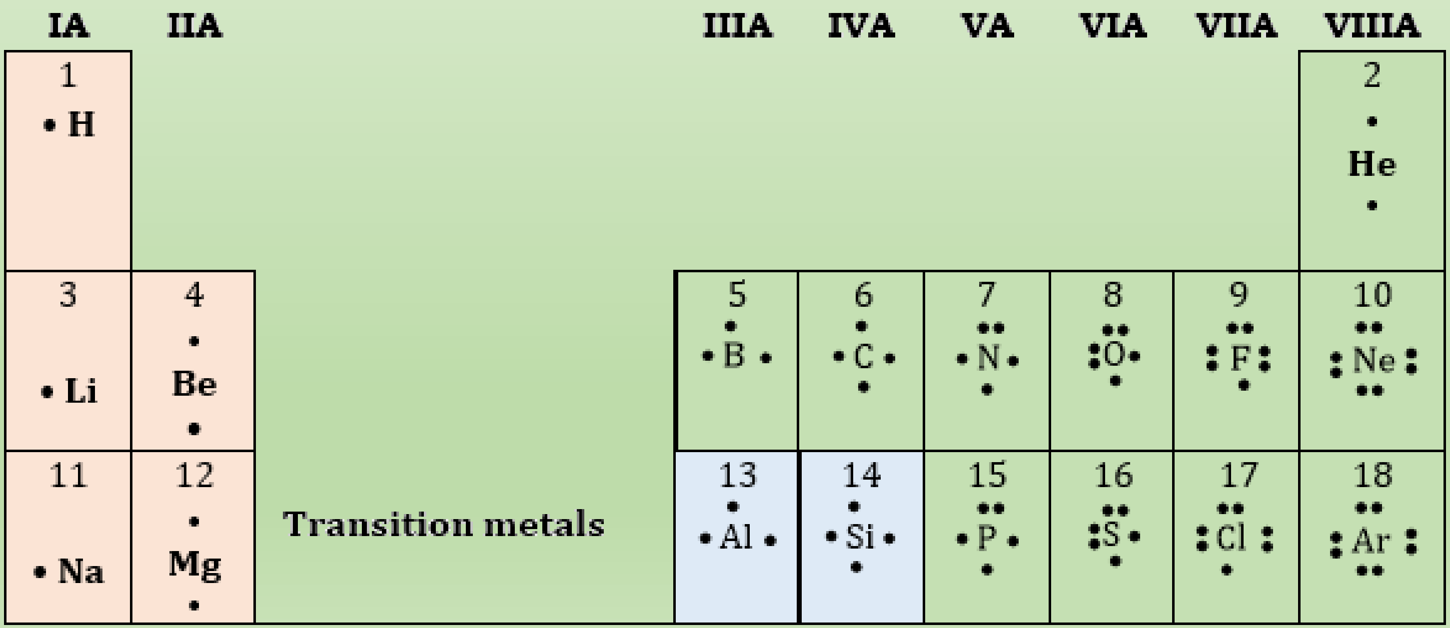
Covalent
- Sharing of electrons
- Between nonmetals only
- No ions
- Low melting points

Lewis Dot Symbol

Lewis dot symbols is a notation where valence electrons are shown as dots. The maximum valence electrons possible are 8, so this is easy to do for all elements.

Electrons are drawn symmetrically around the sides (top, bottom, left and right).

The table below shows some examples of Lewis dot structures. Note that the elements in the same group have the same Lewis structures since they have the same number of valence electrons.



Lewis Structure of Cations

When an element, metal, gives electrons, it becomes a cation. This results in the next shell becoming the valence shell which now has 8 electrons (a noble gas configuration)

The number electrons given by metals can be determined by their group: Group I has 1 VE and gives 1 electron thus forming a monocation.

Group II has 2 VE and gives 2 electron thus forming a dication.

Group III can give 3 electrons.

Group IV can accept or give 4 electrons.

We will not be covering transition metals even though they also give electrons to form cations.

When a cation forms there are no electrons left in the valence shell, the Lewis structure will show no dots to reflect it.

$\dot{\mathrm{Na}}$ $\quad \mathrm{Na^+}$ $\quad \cdot\dot{\mathrm{Al}}\cdot$ $\quad \mathrm{Al^{3+}}$

Lewis Structure of Anions

When an element, nonmetal, accepts electrons, it becomes an anion. This results in the shell having 8 electrons (a noble gas configuration)

The number electrons accepted by nonmetals can be determined by their group:

Group VII has 7 VE and can accept 1 electron thus forming a monoanion.

Group VI has 6 VE and accepts 2 electrons forming a dianion.

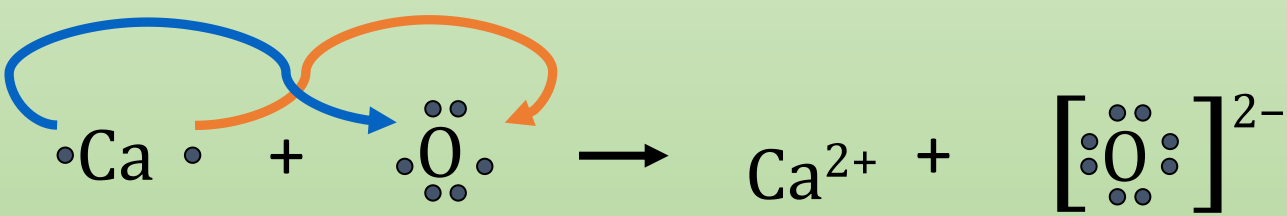
Group V has 5 VE and accepts 3 electrons forming a trianion.

Group IV can accept or give 4 electrons.

When an anion forms there are 8 electrons in the valence shell and thus the Lewis structure will show 8 dots. Square brackets and the charge on the anion are drawn as shown below. Note: when we write this many electrons sometimes it is easier to show a pair of electrons as a line as shown in the structures on the right. You might want to start drawing these lines as it will become easier later.

Ionic Bond

- Ionic bonds are formed by transfer of electrons from metals to nonmetals.
- Metals lose electrons and become cations (metals have low ionization energy so lose electrons easily).
- Nonmetals gain electrons and become anions (nonmetals have high electron affinity so they gain electrons)
- Below is a representation of transfer of electrons, where the two electrons from calcium are transferred to oxygen, making them both a stable octet structure.



<u>Solved Problem: Writing Lewis structure of ionic compounds</u>

Write the Lewis structures of the compounds formed between

a) sodium and chlorine

b) calcium and fluorine

c) aluminum and oxygen

a) <u>Sodium and Chlorine</u>

Na – needs to give one electron becomes Na^+

Cl – needs to gain one electrons becomes Cl^-, so each Na needs one Cl atom.

$Na\cdot \; + |\overline{\underline{Cl}}\cdot \qquad\qquad Na^+ [\,|\overline{\underline{Cl}}|\,]^-$

b) <u>Calcium and Fluorine</u>

Ca – needs to give two electron becomes Ca^{2+}

F – needs to gain one electrons becomes F^-, so each Ca needs two F atoms.

$Ca{:} \; + |\overline{\underline{F}}\cdot \; + \; |\overline{\underline{F}}\cdot \qquad\qquad Ca^{2+}\, 2[\,|\overline{\underline{F}}|\,]^-$

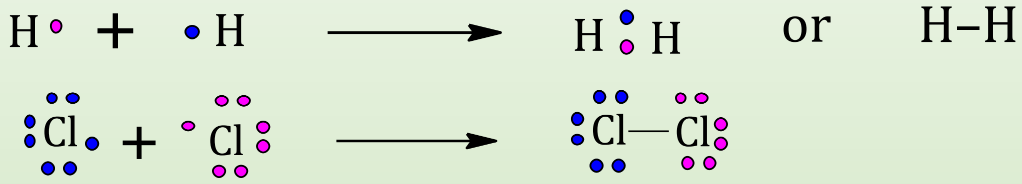
c) <u>Aluminum and Oxygen</u> – a simple way to do this is the criss-cross method.

$2Al^{3+}\, 3\, [\,|\overline{\underline{O}}|\,]^{2-}$

Valency $\qquad Al^{3+} \qquad O^{-2}$

Covalent Compounds – Lewis Structures

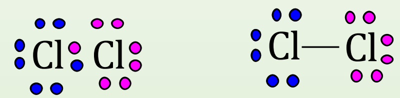
Nonmetal atoms share electrons to form covalent bonds.



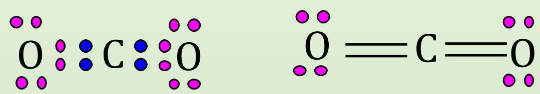
The bond between H and Cl can be shown as below. The two Lewis structures shown on the right are correct. It is cleaner to draw the lines.

Types of Covalent Bonds

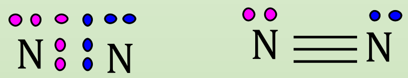
A **single bond** is a covalent bond in which one pair of electrons is shared by two atoms.



A **double bond** is a covalent bond in which two pairs of electrons are shared by two atoms.



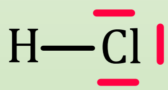
A **triple bond** is a covalent bond in which three pairs of electrons are shared by two atoms.



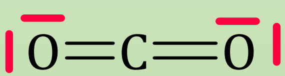
Double bonds form primarily with C, N, and O.
Triple bonds form primarily with C and N.

Types of Electrons

When covalent bonding occurs, the electrons in the structure can be classified as **bonding** and **nonbonding electrons**. The bonding electrons are involved in formation of the bond while nonbonding are the left on the atoms. These are also sometimes referred to as lone pair of electrons.



In the covalent structure of HCl, the black electrons are the bonding electrons – 2 electrons or one pair.
The red electrons on chlorine are the nonbonding electrons – 6 electrons or 3 lone pair electrons.

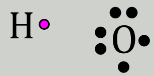
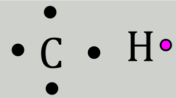
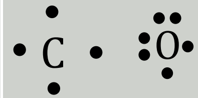
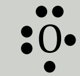
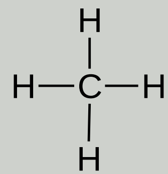
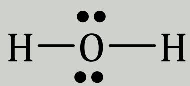
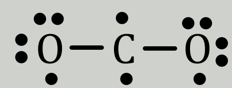
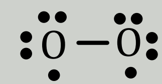
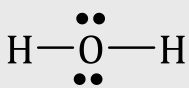
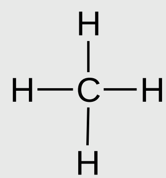
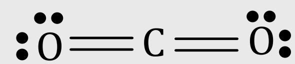
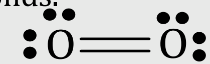


In the covalent structure of CO_2, the black electrons are the bonding electrons – 8 electrons, 4 pairs in the two double bonds.
The red electrons on oxygen are the nonbonding electrons – 8 electrons or 4 lone pair electrons.

Writing Lewis Structures

1. Write the Lewis structure of the individual atoms.
2. Add all the valence electrons of ALL the atoms.
3. Draw the skeleton structure of the molecule or ion by placing the element on the left of the periodic table in the center. Highest valency (*charge*) element should be in the middle. Share one pair of electrons between each atom.
4. Subtract those from the total number of electrons (from step 2).
5. Distribute electrons to the atoms surrounding the central atom.
6. Redistribute the electrons to form multiple bonds, if needed, to satisfy the octet rule.
7. Add all electrons in the end to make sure the total is the same as in step 2.

Steps for Writing Lewis Structure

Step	H_2O	CH_4	CO_2	O_2
1				
2	(2 x 1) + 6 = 8	(1 x 4) + 4 = 8	(2 x 6) + 4 = 16	6 + 6 = 12
3	H – O –H		O – C – O	O – O
4	8 - 4 = 4	8 - 8 = 0	16 – 4 = 12	12 – 2 = 10
5				
5			Use the single electrons on each atom to form double bonds. 	Use the single electrons on each atom to form double bonds. 
6	4 bonding e + 4 nonbonding e = **8**	**8** bonding e	8 bonding e + 8 nonbonding e = **18**	4 bonding e + 8 nonbonding e = **12**

Quick Steps for Writing Lewis Structure

A simpler way of writing structures quickly is to follow the rules below.

- H and halogens have single bonds (unless halogen is in the center).
- O and S have two bonds (two single or one double).
- N and P have three bonds (three single, one double one single or triple).
- C has four bonds (different combinations).

Solved Problem: Writing Lewis structure of covalent compounds

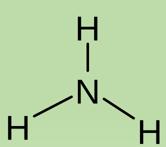
Write the Lewis structures of a) NH_3 b) HCN

NH_3

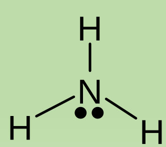
1. N will go in the middle.
2. Symmetrically write the 3 H around N and draw bonds between them.
3. Remember N can have only three bonds.
4. At this time add the remaining electrons on N.

HCN

1. C will go in the middle since its on the left of N.
2. Symmetrically write the H and N around C and draw single bonds between them.
3. Remember C should have 4 bonds and N can have three bonds.
4. At this time add the remaining electrons on N.



Step 2



Step 4

Step 2 $H-C-N$

Step 3 $H-C\equiv N$

Step 4 $H-C\equiv \ddot{N}$

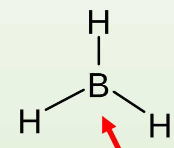
Exceptions to the Octet Rule

Exceptions to the octet rule fall into three categories:

- Molecules with an incomplete octet.
- Molecules with an expanded octet.
- Molecules with an odd number of electrons.

Incomplete Octet

Example: BH_3 (boron hydride)
$BH_3 \Rightarrow (1 \times 3) + (3 \times 1) = 6$ valence e^-

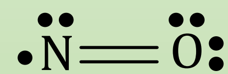


no octet

Common with Be, B and Al compounds as they have 2 or 3 electrons in the valence shell for bonding.

Odd Numbers of Electrons

Example: NO (nitrogen monoxide).
$NO \Rightarrow (1 \times 5) + (1 \times 6) = 11$ valence e^-



Unpaired electron

Common with N and P since they have odd number of electrons.

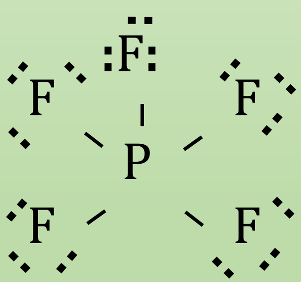
Expanded Octet

Elements of the 3rd period and below can form more than the 4 bond (8 electron octet). Valence shells can have a maximum of 8 electrons only, the extra electrons are accommodated in the *d*-orbitals in the penultimate shell.

Phosphorous can form up to 5 bonds, using all the 5 valence electrons for bonding, giving it a total of 10 electrons in its valence shell.

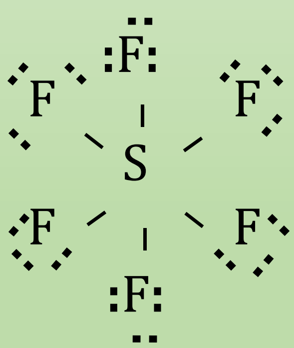
Sulfur can bond all its 6 valence electrons to have a total of 12 valence electrons after bonding.

PF_5



P has 10 valence electrons (count the number of bonds on P and multiply by 2)

SF_6



S has 12 valence electrons (count the number of bonds on S and multiply by 2)

Covalent Bond – Equal Sharing?

In a covalent bond it should be that electrons are shared equally. However sometimes that does not happen because atoms have a property called electronegativity which causes an element to attract electrons more towards themselves in a covalent bond.

Note that ionic bonds are inherently polar because they have a cation and anion.

Covalent bonds are thus classified into two types:

- ***Nonpolar covalent bond*** is when electrons are shared *equally* by two bonded atoms.
- ***Polar covalent bond*** is when electrons are shared *unequally* by two bonded atoms.

M:X	$M^{\delta+}X^{\delta-}$	$M^{+}X^{-}$
Covalent bond	Polar covalent bond	Ionic bond
Equal sharing of electrons of the same electronegativity	Partially charged atoms held by unequally sharing electrons	Cations and anions held by electrostatic forces

Electronegativity

Electronegativity, *X*, is a measure of the ability of an atom in a molecule to attract bonding electrons to itself. Electronegativity increases across the group and decreases down a group.

Increasing Electronegativity

Decreasing Electronegativity

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
1 **H** 2.1																
3 **Li** 1.0	4 **Be** 1.5											5 **B** 2.0	6 **C** 2.5	7 **N** 3.0	8 **O** 3.5	9 **F** 4.0
11 **Na** 0.9	12 **Mg** 1.2											13 **Al** 1.5	14 **Si** 1.8	15 **P** 2.1	16 **S** 2.5	17 **Cl** 3.0
19 **K** 0.8	20 **Ca** 1..0	21 **Sc** 1.3	22 **Ti** 1.5	23 **V** 1.6	24 **Cr** 1.6	25 **Mn** 1.5	26 **Fe** 1.8	27 **Co** 1.9	28 **Ni** 1.9	29 **Cu** 1.9	30 **Zn** 1.6	31 **Ga** 1.6	32 **Ge** 1.8	33 **As** 2.0	34 **Se** 2.4	35 **Br** 2.8
37 **Rb** 0.8	38 **Sr** 1.0	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In** 1.7	50 **Sn** 1.8	51 **Sb** 1.9	52 **Te** 2.1	53 **I** 2.1
55 **Cs** 0.7	56 **Ba** 0.9	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl** 1.9	82 **Pb** 1.8	83 **Bi** 1.9	84 **Po** 2.0	85 **At** 2.2

Polar Bond, Contd…

The difference in electronegativity between the two atoms in a bond is a rough measure of bond polarity. You generally don't have these numbers during test taking, so it is better to remember the trend. When the difference is large (*more than 0.5 on subtraction of the electronegativity values*), the bond is polar. When the difference is small (< 0.5), the bond is nonpolar.

Polar covalent bonds are represented by δ- and δ+ to show the small charges that the atoms will have because of unequal sharing of electrons. An arrow with crosshair can be drawn to show where there is more concentration of negative charge.

$$\overset{\delta+}{H} - \overset{\delta-}{F}$$

$$H - F$$

This polarity can lead to the molecule being polar which in turn affects the physical properties of molecule such as boiling point, surface tension etc.

Solved Problem: Determining polarity in a bond

Using electronegativities, arrange the following bonds in order by increasing polarity: C—N, Na—F, O—H.

For C—N, the difference is 3.0 (N) – 2.5 (C) = 0.5.

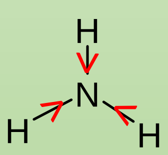
For Na—F, the difference is 4.0 (F) – 0.9 (Na) = 3.1.

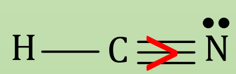
For O—H, the difference is 3.5 (O) – 2.1 (H) = 1.4.

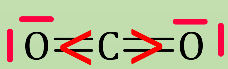
Bond Polarities: C-N < O-H < Na - F

Solved Problem: Polar bonds in Lewis structures

Using electronegativity identify polar bonds in the following three structures. Show the arrow on the bond to show polarity.







Solved Problem: Determining polarity in a bond

Using the trend of electronegativity, identify which bonds are polar. Write the partial positive and negative on the proper atom.

C-H, H-Cl, H-H, H-O

C-H – almost nonpolar bond since both have very low electronegativity.

H-Cl – polar bond: $H^{\delta+}$-$Cl^{\delta-}$

H-H - nonpolar bond since both have the same electronegativity.

H-O – polar bond: $H^{\delta+}$-$O^{\delta-}$

Key Points

- Lewis dot symbols
- Ionic bonding
- Covalent bonding
- Octet rule
- Lewis structures
- Exceptions to the Octet Rule
    - Incomplete octets
    - Expanded octets
    - Odd numbers of electrons
- Bond polarity